Sadhan Kumar Ghosh *Editor*

Waste Valorisation and Recycling

7th IconSWM—ISWMAW 2017, Volume 2

Springer

Waste Valorisation and Recycling

Sadhan Kumar Ghosh
Editor

Waste Valorisation and Recycling

7th IconSWM—ISWMAW 2017, Volume 2

Springer

Editor
Sadhan Kumar Ghosh
Department of Mechanical Engineering
Jadavpur University, President, International
Society of Waste Management,
Air and Water (ISWMAW)
Kolkata, West Bengal, India

ISBN 978-981-13-2783-4 ISBN 978-981-13-2784-1 (eBook)
https://doi.org/10.1007/978-981-13-2784-1

Library of Congress Control Number: 2018957052

© Springer Nature Singapore Pte Ltd. 2019
This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.
The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.
The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, express or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Singapore Pte Ltd.
The registered company address is: 152 Beach Road, #21-01/04 Gateway East, Singapore 189721, Singapore

Preface

The global amounts of waste generated are estimated to be between 7 and 10 billion tons per year. The amount of solid waste recorded in official statistics is around 3.2 billion tons. It is estimated that from this amount 47% is landfilled, 31% recycled and 22% incinerated. At present, nearly 70% of waste is not reused or recycled worldwide which represents a big loss of opportunities of recovering resources. These cause environmental impacts from uncontrolled disposal of waste into the environment accumulating micro- plastics in the oceans threatening the marine fauna and many other daunting issues in the society. Valorisation practices of different types of wastes have attracted a significant amount of attention in recent years with the aim of managing waste in the most sustainable way.

Waste valorisation is an attractive approach of increasing popularity which can offer a range of potentially useful alternatives for dealing with residues other than disposal and/or landfilling. The valorisation technologies or processes being looked upon are flow chemical technology, pyrolysis, bioconversion, composting, regenerated animal feed and bedding, incineration, anaerobic digestion, gasification, co-processing, etc., and converting them into more useful products including materials, chemicals, fuels, other sources of energy and some other products that society currently does not appreciate in case of valorising food waste components. Waste-to-energy aspects are becoming more prominent due to the rapid depletion of natural resources and an increase in waste generation. Basic valorisation strategies are known and largely accepted practices which, however, are able to recover/convert less than 50 wt.% of the waste into useful products. Advanced valorisation strategies based on green chemical technologies are more appealing from the practical, economic and sustainability viewpoints in that these can diversify the generation of multiple products from a single feedstock using environmentally sound technologies which combine bio-/chemo-technological protocols. These include (but are not restricted to) microwave-assisted extraction of useful components, biological (e.g. fermentation) and combined chemo-enzymatic approaches for the production of useful bio-derived products, flow technologies able to provide cascade-type separation/isolation of valuable chemicals, etc. Food waste constitutes a largely under-exploited residue from which a variety of valuable chemicals can be derived. This contribution is aimed to set the scene for further development and promotion of sustainable food waste valorisation practices to different end products using green chemical technologies.

Waste management regulations become tighter, and the demand for resource recovery is pushing the stakeholders to look upon emerging technology for waste valorisation for environmental sustainability. Waste valorisation as a source or through symbiosis approach is associated with resource efficiency and circular economy. Various valorisation techniques are currently showing promise in meeting sustainable development goals. Some of the technique comes as a last resort basis on the consideration of 3Rs methodology. There is a huge potential for improvement and an increase in waste valorisation for environmental protection. Waste valorisation leads to recycling and reuse of resources locked in waste and leads to environmental sustainability reducing the carbon footprint.

The International Society of Waste Management, Air and Water (ISWMAW) has been working and committed for sustainable waste management and environmental protection by reducing air and water pollution. It encourages and promotes the resource circulation through different processes including the valorisation techniques and the implementation of circular economy concepts. IconSWM movement was initiated for better waste management and environmental protection in the year 2009 through generating awareness and bringing all the stakeholders together from all over the world in a bracket for discussion under the aegis of the International Society of Waste Management, Air and Water (ISWMAW). It establishes research projects across the country and in collaboration with the Consortium of Researchers in International Collaboration (CRIC) across the world. IconSWM has become significantly one of the biggest international platforms in India for knowledge sharing, awareness generation and encouraging the urban local bodies (ULBs), government departments, researchers, industries, NGOs, communities and other stakeholders in the area of sustainable waste management towards circular economy encouraging business out of wastes generated by its recirculation. The conference, IconSWM, attracted huge interest from academics, practitioners and policy makers around the world.

The seventh IconSWM received more than 340 abstracts and 260 full papers from 42 countries based on waste management, policy and strategies, circular economy, recycling, treatment technologies, nanotechnology, modelling, biomass, biofuels and bio-energy and covered them in several tracks. All the papers were separated in three volumes, e.g. Volume 1—Sustainable Waste Management: Policies and Case Studies, Volume 2—Waste Valorisation and Recycling Technologies, and Volume 3—Waste Water Recycling and Management. Each full paper was put to the review process by at least two experts. This book, Volume 2—Waste Valorisation and Recycling Technologies, includes 58 accepted full papers those are organised in 13 parts as follows. The conference offered both the academics and practitioners the opportunity to share knowledge and experience relevant to the waste management and resource circulation. The overarching question was how we collaborate to facilitate further development in these emerging areas. This book represents the selected papers from the conference.

Volume 2 : Waste Valorisation and Recycling Technologies

Part 1: Energy from Waste = 10 Papers
Part 2: Waste Utilization and Valorisation = 3 Papers
Part 3: Landfill and Leachate Management = 3 Papers
Part 4: Hazardous Waste, Industrial Waste and Biomedical Waste = 4 Papers
Part 5: Fly Ash Utilisation = 4 Papers
Part 6: Composting = 4 Papers
Part 7: Waste Biomass valorisation and Biomethanation = 8 Papers
Part 8: WEEE Recycling = 7 Papers
Part 9: Applied Biotechnology = 5 Papers
Part 10: Applied Nanotechnology = 3 Papers
Part 11: Chemical Engineering in Waste Management = 7 Papers

Kolkata, India
December 2018

Sadhan Kumar Ghosh

7th IconSWM 2017 Editorial Board

Editor : Prof. Sadhan Kumar Ghosh

Members

Prof. Agamuthu Pariatamby
University of Malaya, Malaysia

Mr C. R. C. Mohanty
Advisor, UNCRD, Japan

Prof. Francesco Di Maria
University of Perugia, Italy

Prof. JinhuiLi
Tsinghua University, R.P. China

Prof. Mont Michael Nelles
Universität Rostock, Germany

Dr. Ronald L. Mersky
Widener University, USA

Dr. H. N. Chanakya
Indian Institute of Science, India

Prof. Shinichi Sakai,
Kyoto University, Japan

Prof. Seung-Whee Rhee,
Kyonggi Univ., Rep. of
Korea

Acknowledgements

ISWMAW and IconSWM express gratitude to all the organisations who helped in organising the seventh IconSWM 2017 at PJTSAU, Hyderabad, Telangana, India. The editor on behalf of the members of the editorial board and ISWMAW-IconSWM expresses gratitude to Springer Nature India Private Limited for publishing the book and to the following persons who helped in bringing the volume.

Authors of articles in the book.
Mr. Aninda Bose,
Director, NAARM, Hyderabad
Dr. B. Janardhan Reddy, Commissioner, GHMC
Dr. N . Visal, IAS, DMA, Government of Karnataka,
Dr. V. Kirubakaran, GGRI, Chennai,
Mr. G. Anjanyelu,
IconSWM Editorial Board Members
IconSWM Local Working Group Members, Hyderabad
IconSWM National Organizing Committee
IconSWM Technical Committee Members and International Scientific Committee
Mr Praveen Prakash, IAS, JS(W), UDD, GOI
Dr. Ramakant, UDD, GOI;
Mr. Manjunath Prasad, IAS, Commissioner, BBMP
Mrs. Pranati Ghosh
Ms. Kamiya Khatter
Ms. Sheetal Singh
My PhD researchers: Biswajit Debnath, Rahul Baidhya, Ipsita Saha
Reviewers
Sannidhya Kumar Ghosh, University of Boulder, USA
Secretariat members: Suresh Mondal, Bisweswar Ghosh, Gobinda Debnath.
Vice Chancellor, PJTSAU, Hyderabad

Contents

Editor and Contributors

About the Editor

Prof. Sadhan Kumar Ghosh Professor & Former Head of the Mechanical Engineering Department and Founder Coordinator of the Centre for QMS at Jadavpur University, Kolkata, India, is a prominent figure in the field on Waste Management, Green Manufacturing & Green Factories. He served as the Director, CBWE, Ministry of Labour and Employment, Govt. of India and L&T Ltd. Prof. Ghosh is also the founder and Chairman of the IconSWM; President of the International Society of Waste Management, Air and Water; and chairman of the Indian Congress on Quality, Environment, Energy and Safety Management Systems (ICQESMS). In 2012 he was awarded a Distinguished Visiting Fellowship by the Royal Academy of Engineering, UK to work on 'Energy Recovery from Municipal Solid Waste'. More recently, he was tasked with the Horizon 2020 research project entitled "Bio-mimetic and phyto-technologies designed for low-cost purification and recycling of water - India H2O" (2018–22), which is funded by the European Union.

Prof. Ghosh is also an international expert affiliated with a) the United Nations Centre for Regional Development under the UN in 3R Forum (Adelaide, 2016); b) the Asian Productivity Organization (APO), Japan and China Productivity Council (CPC) on Green Manufacturing and Green Factories (Taiwan 2014, 2015, 2016); and c) a Research Project for GP for the BoP business in APO member countries in Asia (May 2016–June 2017). His papers on waste management, namely on bio-waste, e-wastes and MSW have received Excellence Awards in many countries.

In addition to holding two Indian patents and serving as a member of the editorial boards of several journals, he initiated the movement for worldwide Sustainable Waste Management with partners in many countries through the "Consortium of Researchers in International Collaboration" (CRIC). Prof. Ghosh has been Principal Investigator of more than 25 research projects, and has written nine books and more than 180 national and international articles and book chapters. He can be reached at: sadhankghosh9@gmail.com.

Contributors

M. F. Abadir Chemical Engineering Department, Faculty of Engineering, Cairo University, Giza, Egypt

H. H. Abo-Almaged Inorganic Chemical Industries and Mineral Resources Division, Ceramic and Building Materials Department, Refractories, National Research Centre (NRC), Dokki, Giza, Egypt

Gaffer Ahmed Department of Energy, Tezpur University, Napaam, Tezpur, Assam, India

M. Alamgir Department of Civil Engineering, Khulna University of Engineering and Technology, Khulna, Bangladesh

M. Alamin Department of Civil Engineering, Khulna University of Engineering & Technology (KUET), Khulna, Bangladesh

Babu J. Alappat Department of Civil Engineering, IIT Delhi, New Delhi, India

Afreen Aman Centre for Sustainable Technologies, Indian Institute of Science, Bengaluru, India

Sh. K. Amin Engineering Research Division, Chemical Engineering and Pilot Plant Department, National Research Centre (NRC), Dokki, Giza, Egypt

K. Annapurna Academy of Scientific and Innovative Research (AcSIR), CSIR-Central Glass and Ceramic Research Institute, Kolkata, India; Glass Science and Technology Section, CSIR-Central Glass and Ceramic Research Institute, Kolkata, India

Roopa Ashwath Centre for Sustainable Technologies (Formerly ASTRA), Indian Institute of Science, Bengaluru, India

Seung Ki Back Yonsei University, Wonju, South Korea

Rahul Baidya Department of Mechanical Engineering, Jadavpur University, Kolkata, India; Centre for Research and Innovation, Department of Mechanical Engineering, Institute of Engineering & Management, Kolkata, India

R. Balaji Department of Environmental Engineering, Government College of Technology, Coimbatore, Tamil Nadu, India

Priyabrata Banerjee CSIR-Central Mechanical Engineering Research Institute (CMERI), Durgapur, West Bengal, India; Academy of Scientific and Innovative Research, CSIR-Central Mechanical Engineering Research Institute (CMERI), Durgapur, West Bengal, India

Bivek Baral Department of Mechanical Engineering, Kathmandu University, Dhulikhel, Nepal

Jyul Bardoliwala CSIR-Structural Engineering Research Centre, Chennai, India

Q. H. Bari Department of Civil Engineering, Khulna University of Engineering & Technology (KUET), Khulna, Bangladesh

D. C. Baruah Department of Energy, Tezpur University, Napaam, Tezpur, Assam, India

D. Bhagawan Centre for Alternative Energy Options, Centre for Environment, Jawaharlal Nehru Technological University Hyderabad, Kukatpally, Telangana, India

B. Bhaskara Rao Former General Manager (R&D) and Corporate Planning, SCCL, Kothagudem, Andhra Pradesh, India

Tapobrata Bhattacharya Centre for Research and Innovation, Department of Mechanical Engineering, Institute of Engineering & Management, Kolkata, India

Pinaki Bhattacharya Department of Chemical Engineering, Heritage Institute of Technology, Kolkata, India

Suparna Bhattacharyya Department of Chemical Engineering, Jadavpur University, Kolkata, India; International Society of Waste Management, Air and Water (ISWMAW), Kolkata, India

Khushbu K. Birawat Department of Civil Engineering, Global Academy of Technology, Bengaluru, India

Moumita Bose Chemical Engineering Department, Jadavpur University, Kolkata, India

Margaret Brennan-Tonetta Rutgers University, The State University of New Jersey, New Brunswick, USA

Anup D. Chahande Department of Biotechnology, Priyadarshini Institute of Engineering and Technology, Nagpur, India

B. Chakradhar Environmental Consultancy, Ramky Enviro Services Private Limited, Gachibowli, Hyderabad, India

H. N. Chanakya Centre for Sustainable Technologies (Formerly ASTRA), Indian Institute of Science, Bengaluru, India

P. K. Chatterjee CSIR-Central Mechanical Engineering Research Institute (CMERI), Durgapur, West Bengal, India

Ranjana Chowdhury Department of Chemical Engineering, Jadavpur University, Kolkata, India

Bimal Das Department of Chemical Engineering, National Institute of Technology, Durgapur, India

P. Das Jadavpur University, Kolkata, India; CSIR-Central Mechanical Engineering Research Institute (CMERI), Durgapur, West Bengal, India

S. Das CSIR-Central Mechanical Engineering Research Institute (CMERI), Durgapur, West Bengal, India

Venkata D. B. C. Dasireddy School of Chemistry and Physics, University of KwaZulu-Natal, Durban, South Africa

S. Dasappa Centre for Sustainable Technologies (Formerly ASTRA), Indian Institute of Science, Bengaluru, India

S. Datta Chemical Engineering Department, Jadavpur University, Kolkata, India

Biswajit Debnath Department of Chemical Engineering, Jadavpur University, Kolkata, India

Naveen N. Desai Department of Civil Engineering, B.L.D.E.A's V.P. Dr. P.G.H. College of Engineering & Technology, Vijayapur, Karnataka, India

N. Dhivya Priya Department of Environmental Engineering, Government College of Technology, Coimbatore, Tamil Nadu, India

C. V. Dinesh Kumar Rural Energy Centre, The Gandhigram Rural Institute-Deemed University, Dindigul, India

Isabell Eickhoff Department of Waste Management and Material Flow, University of Rostock, Rostock, Germany

Mervat El-Hoz University of Balamand, El-Koura, Lebanon

S. A. El-Sherbiny Chemical Engineering Department, Faculty of Engineering, Cairo University, Giza, Egypt

Anna-Sabina Emmerich Department of Waste Management and Material Flow, University of Rostock, Rostock, Germany

A. Ganguly CSIR-Central Mechanical Engineering Research Institute (CMERI), Durgapur, West Bengal, India

Vidyadhar V. Gedam Environmental Engineering and Management, National Institute of Industrial Engineering (NITIE), Mumbai, India

A. Ghimire Soil Water and Air Testing Laboratories Pvt. Ltd., Kathmandu, Nepal

Anaya Ghosh Department of Chemical Engineering, National Institute of Technology, Durgapur, India

S. Ghosh Academy of Scientific and Innovative Research (AcSIR), CSIR-Central Glass and Ceramic Research Institute, Kolkata, India; Ceramic Membrane Division, CSIR-Central Glass and Ceramic Research Institute, Kolkata, India

Sadhan Kumar Ghosh Department of Mechanical Engineering, Jadavpur University, Kolkata, India

Parveen Gill Chaudhary Charan Singh Haryana Agricultural University, Hisar, Haryana, India

N. Gunaseelan Rural Energy Centre, The Gandhigram Rural Institute-Deemed University, Dindigul, India

Mayank Gupta Environmental Consultancy, Ramky Enviro Services Private Limited, Gachibowli, Hyderabad, India

R. K. Gupta Chaudhary Charan Singh Haryana Agricultural University, Hisar, Haryana, India

Serpil Guran Rutgers Eco Complex “Clean Energy Innovation Center”, Rutgers, The State University of New Jersey, Bordentown, USA

S. M. Haque Urban and Rural Planning Discipline, Khulna University, Khulna, Bangladesh

A. Hazra CSIR-Central Mechanical Engineering Research Institute (CMERI), Durgapur, West Bengal, India; Academy of Scientific and Innovative Research, CSIR-Central Mechanical Engineering Research Institute (CMERI), Durgapur, West Bengal, India

T. Hemalatha CSIR-Structural Engineering Research Centre, Chennai, India

V. Himabindu Centre for Alternative Energy Options, Centre for Environment, Jawaharlal Nehru Technological University Hyderabad, Kukatpally, Telangana, India

Raaginii Jaain Swachh Bharat National Expert, Mumbai, India

Naveen Janardhana Centre for Sustainable Technologies (Formerly ASTRA), Indian Institute of Science, Bengaluru, India

S. B. Jonnalagadda School of Chemistry and Physics, University of KwaZulu-Natal, Durban, South Africa

A. K. KC Oxfam, Kathmandu, Nepal

R. Karmakar Thapar University, Ludhiana, India

Kåre Helge Karstensen SINTEF, Oslo, Norway; Asian Institute of Technology, Khlong Luang, Thailand

V. Madhan Karthik Rural Energy Centre, The Gandhigram Rural Institute-Deemed University, Dindigul, Tamil Nadu, India

N. R. Khatiwada Department of Environmental Science and Engineering, Kathmandu University, Dhulikhel, Nepal

Himanshu Kumar Khuntia Centre for Sustainable Technologies (Formerly ASTRA), Indian Institute of Science, Bengaluru, India

Jung Hoon Kim Yonsei University, Wonju, South Korea

V. Kirubakaran Rural Energy Centre, The Gandhigram Rural Institute-Deemed University, Dindigul, India

Dinesh Kumar North Delhi Municipal Corporation, New Delhi, India

Vimal Kumar C-FARM and Former Mission Director & Head, Fly Ash Unit, DST, GOI, New Delhi, India

K. Kundu CSIR CMERI CoEFM, Patiala, India

G. N. Lalith Pankaj Raj Nadimuthu Rural Energy Centre, The Gandhigram Rural Institute-Deemed University, Dindigul, Tamil Nadu, India

Hem Lata Chaudhary Charan Singh Haryana Agricultural University, Hisar, Haryana, India

Eun Song Lee Yonsei University, Wonju, South Korea

Joo Chan Lee Yonsei University, Wonju, South Korea

R. Loganath Department of Civil Engineering, Indian Institute of Engineering Science and Technology, Shibpur, Howrah, West Bengal, India

Suresh Maddila School of Chemistry and Physics, University of KwaZulu-Natal, Durban, South Africa

S. Majumdar Ceramic Membrane Division, CSIR-Central Glass and Ceramic Research Institute, Kolkata, India

Sreesha Malayil Centre for Sustainable Technologies (Formerly ASTRA), Indian Institute of Science, Bengaluru, India

Maitri Mapa CSIR-Structural Engineering Research Centre, Chennai, India

S. Mathiyazhagan Rural Energy Centre, The Gandhigram Rural Institute-Deemed University, Dindigul, India

T. Meenambal Department of Civil Engineering, Madanapalli Institute of Technology, Madanapalli, Chittor, Andhra Pradesh, India

Ronald MersÝky Widener University, Chester, PA, USA

M. Mohanraj Rural Energy Centre, The Gandhigram Rural Institute-Deemed University, Dindigul, Tamil Nadu, India

AHM Mojammal Yonsei University, Wonju, South Korea

G. Morscheck Department Waste and Resource Management, University of Rostock, Rostock, Germany

D. Mukherjee Academy of Scientific and Innovative Research (AcSIR), CSIR-Central Glass and Ceramic Research Institute, Kolkata, India

N. C. Murmu CSIR-Central Mechanical Engineering Research Institute (CMERI), Durgapur, West Bengal, India; Academy of Scientific and Innovative Research, CSIR-Central Mechanical Engineering Research Institute (CMERI), Durgapur, West Bengal, India

S. Murugan Department of Environmental Engineering, Government College of Technology, Coimbatore, Tamil Nadu, India

Milind Murumkar Alternate Fuels & Raw Materials, Vicat in India, Hyderabad, India

Sunny Natekar Centre for Sustainable Technologies (Formerly ASTRA), Indian Institute of Science, Bengaluru, India

D. Neela Priya Environmental Consultancy, Ramky Enviro Services Private Limited, Gachibowli, Hyderabad, India

Michael Nelles Department Waste and Resource Management, University of Rostock, Rostock, Germany; German Biomass Research Centre gGmbH (DBFZ), Leipzig, Germany

Aastha Paliwal Centre for Sustainable Technologies (Formerly ASTRA), Indian Institute of Science, Bengaluru, India

Almitra Patel Swachh Bharat National Expert, Bengaluru, India

S. K. Patidar National Institute of Technology, Kurukshetra, Haryana, India

Dipam Patowary Department of Energy, Tezpur University, Napaam, Tezpur, Assam, India

G. Prabakaran Rural Energy Centre, The Gandhigram Rural Institute-Deemed University, Dindigul, India

Basavaraju Prathima Department of Civil Engineering, BMSCE, Bangalore, India

Swapnil V. Punyapwar Department of Biological Sciences, BITS-Pilani, KK Birla Goa Campus, Goa, India

A. Rajor Thapar University, Ludhiana, India

Pranay A. Raut Department of Biotechnology, Priyadarshini Institute of Engineering and Technology, Nagpur, India

D. Ravi Kumar Centre for Sustainable Technologies (Formerly ASTRA), Indian Institute of Science, Bengaluru, India

T. K. Roy Department of Urban and Regional Planning, Khulna University of Engineering and Technology (KUET), Khulna, Bangladesh

Palash Kumar Saha SINTEF, Oslo, Norway

K. S. Sangunni Indian Institute of Science, Bengaluru, India; Yelahanka Lake Conservation and Restoration Group, Bengaluru, India

M. R. Sarder Department of Civil Engineering, Khulna University of Engineering and Technology, Khulna, Bangladesh

Jyoti Prakas Sarkar Department of Chemical Engineering, National Institute of Technology, Durgapur, India

M. M. Saroar Department of Urban and Regional Planning, Khulna University of Engineering and Technology (KUET), Khulna, Bangladesh

T. S. Sasi Jyothsna Environmental Consultancy, Ramky Enviro Services Private Limited, Gachibowli, Hyderabad, India

Saptarshi Sasmal CSIR-Structural Engineering Research Centre, Chennai, India

A. Schüch Department Waste and Resource Management, University of Rostock, Rostock, Germany

Roshni Mary Sebastian Department of Civil Engineering, IIT Delhi, New Delhi, India

J. Senophiyah-Mary Department of Environmental Engineering, Government College of Technology, Coimbatore, Tamil Nadu, India

Yong Chil Seo Yonsei University, Wonju, South Korea

Surya Man Shakya Department of Civil and Geomatics Engineering, Kathmandu University, Dhulikhel, Nepal

Bhavisha Sharma Department of Environment & Sustainable Development, Institute of Environment & Sustainable Development, Banaras Hindu University, Varanasi, India

M. Sharma Jadavpur University, Kolkata, India

Subodh Sharma Department of Environmental Science and Engineering, Kathmandu University, Dhulikhel, Nepal

Sushmitha Shetty Centre for Sustainable Technologies (Formerly ASTRA), Indian Institute of Science, Bengaluru, India

Dharambir Singh Chaudhary Charan Singh Haryana Agricultural University, Hisar, Haryana, India

Pushpa Singh Department of Environmental Science and Engineering, Kathmandu University, Dhulikhel, Nepal

Rajeev Pratap Singh Department of Environment & Sustainable Development, Institute of Environment & Sustainable Development, Banaras Hindu University, Varanasi, India

S. Sivasakthi Department of Environmental Engineering, Government College of Technology, Coimbatore, Tamil Nadu, India

Veena S. Soraganvi Department of Civil Engineering, Basaveshwar Engineering College, Bagalkot, Karnataka, India

David Specca Rutgers Eco Complex "Clean Energy Innovation Center", Rutgers, The State University of New Jersey, Bordentown, USA

K. Srilatha Centre for Alternative Energy Options, Centre for Environment, Jawaharlal Nehru Technological University Hyderabad, Kukatpally, Telangana, India

H. Subramanya GKVK UAS Bangalore, Bengaluru, India; Yelahanka Lake Conservation and Restoration Group, Bengaluru, India

Seema Sukhani Indian Institute of Science, Bengaluru, India

Jin Ho Sung Yonsei University, Wonju, South Korea

Srinath Suranai National Institution of Technology, Warangal, India

Hasika Suresh Centre for Sustainable Technologies (Formerly ASTRA), Indian Institute of Science, Bengaluru, India

Devadasu Sushmitha National Institution of Technology, Warangal, India

B. Thapa Department of Environmental Science and Engineering, Kathmandu University, Dhulikhel, Nepal; Soil Water and Air Testing Laboratories Pvt. Ltd., Kathmandu, Nepal

Teema Thomas Department of Civil Engineering, Thejus Engineering College, Thrissur, Kerala, India

Urmila Chaudhary Charan Singh Haryana Agricultural University, Hisar, Haryana, India

K. Yaazhmozhi Department of Environmental Engineering, Government College of Technology, Coimbatore, Tamil Nadu, India

A Review on Various Thermochemical Technologies for Resource Recovery from Sewage Sludge

Suparna Bhattacharyya and Sadhan Kumar Ghosh

1 Introduction

Our world is modernising day by day with advanced technology and latest scientific innovations. And it definitely increases the global waste production at a quite high rate. Ten years ago about 0.68 billion tonnes of waste is produced per year. Hoornweg report estimated that today, this amount has increased to 1.3 billion tonnes of waste per year, and it is estimated that by 2025, this will increase to 2.2 billion tonnes per year. Again lots of municipal sewage sludge (MSS) are produced every day causing several environmental and health-related issues by polluting soil and water resources. So proper treatment and careful yet productive Waste Management is very much required nowadays (Aggelakis et al. 2005). With increasing growth curve of sludge production, decreasing disposal outlets and increasing economic pressure low-cost solution are encouraged. Moreover, production of energy from waste management is looked forward nowadays. Waste is no more valueless, but considered as resources. And different technologies are proposed for proper waste management these days [1]. Reduction in the amount of MSS and producing energy at the same time is definitely a beneficial outcome [2].

Nowadays, government policies are becoming more strict regarding proper waste disposal. Keeping that in mind waste management processes are only encouraged if it has some positive outcomes. Disposing sewage sludge as landfills is one of the old practises, but these days, it is only encouraged if methane recovery is associated

---

S. Bhattacharyya (✉)
Department of Chemical Engineering, Jadavpur University, Kolkata, India
e-mail: suparna.ch2015@gmail.com

S. Bhattacharyya
International Society of Waste Management, Air and Water (ISWMAW), Kolkata, India

S. K. Ghosh
Department of Mechanical Engineering, Jadavpur University, Kolkata, India

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_1

with it. Alternative processes are also seen due to the limited capacity of landfills. The nutritional values of the sludge can be maintained by using the sludge it for conditioning soil and also as a fertiliser specially for fertile land and crop cultivation, though the use of sewage sludge as landfill are not too much in use nowadays, because it accelerates surface and groundwater pollution, odour and air emissions (ammonia and greenhouse gases), and the accumulation of heavy metals in soils. So currently several other waste management processes are experimented, which leads to the formation of energy. These processes are good keeping in mind the environmental and socio-economic aspects.

Among these, the thermochemical processes are mostly in use. Though having high cost of power is a major disadvantage for this, that can be considered if the production of energy is seen in these pathways [3]. Thermochemical processes include combustion/incineration, ‘advanced or emerging pyrolysis’ and gasification. Moreover, not only these processes but several co-processing are also encouraged these days like co-pyrolysis of sewage sludge and manure [4], co-digestion of MSS with poultry industry waste [5]. Not only pyrolysis but gasification process are also twisted nowadays by applying plasma gasification, steam gasification, etc. [6]. From the literature survey, [8–11] it is seen that there is very less work regarding review on MSS. Moreover, most of these works are from European countries. A very few number of works have been explored reviewing the condition of Asian countries as well as India. Again, most of the studies focus on physical and biological processes of waste treatment. Review on chemical processes of waste treatment is scarcely found. Some of the research questions that came out during the study are as follows: Which among all these processes are the most beneficial and why? Is the original process or the latest experiments with co-processing are more efficient? What are the temperature, pressure and condition in which the processes give the best result? What is the effectiveness of the process in different European and Asiatic countries.

In this study, an effort has been made for a detailed review about different thermochemical technologies of municipal sewage sludge, and tried to explore their advantages and disadvantages and to propose the best and most beneficial technology. Not only the basic ones but the paper also deals with the current co-processes which are extensively in use these days. According to the EII Brochure, 2007, co-processing can be termed as the practise where waste is used as a raw material or as a source of energy, replacing natural mineral resources and fossil fuels leading to a green technology. Some other major objectives of the paper are to show the use of these processes in different European and Asiatic countries including India. This study shows a detailed review about several thermochemical processes giving a basic idea to several industries and MSS treatment plant to move forward in which way to be benefitted to its maximum with maximum use of municipal wastes to energy. On the other hand, the paper gives a future scope for life cycle assessment (LCA) of each treatment processes individually and use of these treatment processes in other parts of the globe. Again, people can also study the technical, socio-economic and environmental aspects of these processes.

2 Research Methodology

First and foremost, a detailed literature survey was conducted and a thorough search using database like Science Direct, Google Scholar, Springer, etc. with keywords like 'municipal sewage sludge treatment, different thermochemical process for treating MSS, sewage sludge (SS) pyrolysis, plasma gasification of SS, biological treatment of sludge, comparative study of different thermal treatment of MSS, Different Reactors and condition for pyrolysis and Gasification', etc. is done. It helped to review all the scientific article regarding the subject from the last 20 years. Next, the references of these studies provided some further relevant documents. Several published articles, reports, news and presentation have been seen to get more knowledge about the study. Lastly, the help of different books was taken to understand the research gap and questions.

3 State-of-the-Art Waste-to-Energy Technologies

Different types of Waste-to-Energy technologies are discussed briefly in the followings.

3.1 Incineration

In this treatment unprocessed waste is used as a raw material and treated thermally. Incineration process takes place in presence of sufficient amount of air to oxidise feedstock. By this process, waste is converted to carbon dioxide(CO_2), water (H_2O) and non-combustible materials with solid residue state called incinerator bottom ash (IBA) in which always a small amount of residual carbon is present (DEFRA 2007). The advantages of incineration are as follows: reduction of large sludge volume, thermal destruction of several pathogens and germs, thus minimising waste odours and definitely recovery of renewable energy. The advantages are followed by some disadvantages, which are as follows: Incineration is mainly used for sludge minimization not complete disposal as 30% of the dry solids in MSS finally forms ash and combustion ash are hazardous material due to the presence of heavy metals and emission of greenhouse gases (GHG) during their combustion. Thus, additional expenses are there for ash control and disposal, though a large part of ash can be managed as construction material and in cement kiln [3, 12–15]. This disadvantage of incineration can be minimised by co-combustion of MSS with coal/lignite combustion units towards electricity production, which can improve the resulted GHG emissions and hence the public acceptability and concern.

3.2 Pyrolysis

Pyrolysis is a breakdown of chemical bonds by the use of thermal energy only according to Applied Pyrolysis Handbook-Thomas. P. Wampler, 2007. During the process of pyrolysis thermal cracking and condensation reaction are also witnessed. The products that are formed from pyrolysis can be grouped into three categories which are pyrolysis gas (containing the un-condensable low molecular gases), pyrolysis liquid or pyrolysis oil (containing the condensable volatile compounds) and char (the end solid residue). Pyrolysis is endothermic process compared to incineration process explained in Fytili and Zabaniotou 2008; Manara and Zabaniotou 2012. Some of the advantages of pyrolysis are as follows: It is less polluting than incineration because of lower operating temperature and absence of oxygen in the process. As the process of pyrolysis needs low temperature, the heavy metals are not found in the pyrolysis gas rather they are trapped in the resultant solid carbonaceous char. With these advantages, there are some disadvantages to the process like its economic viability is not so good and the process equipment are also a bit costly. Though the economic viability of the process can be improved by producing high-value pyro-oil, utilising pyrolysis gas as fuel and utilising char produced.

3.3 Gasification

Gasification is the thermochemical process that converts any carbonaceous fuel to a gaseous product with a high heating value by Gasification-Higman, Maarten Burgt 2003. Gasification mainly transforms organic solid materials to combustible gas or syngas, using O_2 between 20 and 40% of the oxygen required for total combustion. The syngas formed is a mixture of CO, H_2 and other gases, with by-products the char or slag, oils and water. The process has some benefits like steam gasification enhances H_2 production in gas and thus increases the heating value of the gas; the process is self-sufficient and no energy supply is required for the steady-state operation, followed by certain backdrops like it consists of a series of complex sequential chemical and thermal decomposition reactions [16–25].

3.4 Co-processing Methods

It is surveyed that pyrolysis, gasification originally are not so economically sustainable or beneficial, so these days, co-processing methods are becoming more famous. Co-processing is the technology where wastes are used as raw material or as a source of energy which can replace natural mineral resources and fossil fuels such as coal, petroleum and gas (energy recovery) in industrial processes. Co-pyrolysis of sewage sludge with different products like manure, animal wastes, etc. is gaining attention nowadays. The process shows some advantages like it is a better option for energetic applications. Moreover, it utilises other kinds of wastes during its process, thus increasing the economical and environmental benefits. But it should be remembered that co-processing is not always the matter for encouragement because of few drawbacks.

3.5 Plasma Gasification

Plasma gasification process is a thermal process that needs external power to heat up and sustain the high temperatures. In the process, the materials are decomposed into elements in an oxidant starved medium. Extremely high temperature helps to each higher conversion efficiency. Products formed during the process are mainly syngas, slug and ash. Plasma with high temperature breaks down nearly all the materials to their elemental form excluding the radioactive materials. Due to the high temperature required in the process, toxic compounds decompose into harmless chemical products, which is one of the major advantages of the process. The classification of plasma gasification mainly depends on the different types of plasma discharge technique used and reactor used for the process. Different types of plasma discharge techniques are as follows: (i) direct current (DC), (ii) radio frequency (RF) and (iii) microwave (MC) [6]. Different types of plasma gasification reactors are as follows: plasma fixed bed reactor, plasma moving bed reactor, plasma entrained bed reactor or plasma spout bed reactor (Tang et al. 2013) (Table 1) .

4 Technologies for Energy Recovery from Municipal Sewage Sludge (MSS)

Several types of technologies are in practise nowadays to recover energy from municipal sewage sludge (MSS) for their technical, social, economical and most importantly environmental feasibility. Some detailed studies and great technologies are already established utilising MSS to produce energy producing stuff like bio-oil, biochar, biofuel, etc., and these processes are also helpful in reducing the harmful substances of MSS to comparatively less toxic chemical compounds. In these study mainly the process of Pyrolysis and Gasification is focused. The following section shows a detailed review of these two processes.

Table 1 Benefits and drawbacks of different waste-to-energy technologies

Technologies	Benefits	Operating temperature (in Kelvin [K])	Drawbacks	Output	References
Incineration	(i) Waste volume reduced, nearly 80–95% (ii) More in practise in urban areas since the process greatly reduces the need for land and landfill spaces (iii) Solves the problem of leachate that in the landfill	673–1172	(i) The process is quite expensive to build, operate and maintain. Nearly, 38–40 lakhs INR per year is required (ii) Smoke and ashes emitted during the process including acid gases, NO_x, SO_x, heavy metals, dioxins, furans, etc. which are carcinogenic in nature (iii) The process is not so beneficial for developing countries like the developed countries since the waste produced here mainly composed of kitchen scraps which are having high moisture content of about 40–70%, which is more difficult to burn	(i) Hot flue gas which is further useful for energy production (ii) Waste heat recovery	[39}
Pyrolysis	(i) Highly toxic compounds like acid gas, dioxin are degraded by the use of high temperatures given (ii) Reduction in water volume due to high operating temperatures (iii) During the process, gases are produced which can be used as fuels which limit the supply of external fuel	573–973	(i) The process is a bit complex than the above one (ii) An air-purification installation is necessary to further treat flue gas from the pyrolysis	(i) Pyro-oil production (ii) Pyro-char further used for wastewater treatment (iii) Gas produced	emis.vito.be et al.
Gasification	(i) One of the most economic friendly procedures which have the ability to produce different forms of energy. These energies can be used to form electricity replacing the coal-generated electricity and can also be stored as fuels (ii) By-products of gasification have sulphur and ammonia which has great industrial uses	1073–1673	(i) More greenhouse gas is emitted (ii) Complex technology involved (iii) Few commercial applications	Syngas which act as a feedstock for most of the refineries	[39}

(continued)

Table 1 (continued)

Technologies	Benefits	Operating temperature (in Kelvin [K])	Drawbacks	Output	References
Co-process	(i) Much modern technique (ii) Yields good energy (iii) Environmental friendly process	Always less than 1773	(i) It is a costly process. (ii) Low greenhouse gas (GHG) production	(i) In situ energy substitution (ii) Ash produced at the end of the process becomes the constituent of the cement kiln	Baidya et al. (2016)
Plasma Gasification	(i) High energy production (ii) It does not produce greenhouse gas like methane carbon monoxide, etc. (iii) It produces syngas that can be combusted in gas tubes or reciprocating to produce electricity. The left out products can further be processed in chemical fertilisers and transportation fuels	The very high temperature required of about 5273–10,273	(i) Complex techniques (ii) Wet feedstock reduces the production of syngas (iii) Limited plant availability	Different types of gas production	[40]
Co-pyrolysis	(i) Low biochar yield due to special bond formation (ii) Biochar produced has a good thermostability (iii) Leaching and toxicity remains within the safe level	Within 673–1073	(i) The processing of multiple feedstocks requires different types of experimental setup (ii) While using biomass in the process, the feedstock may not be easily available (iii) Co-pyrolysis involves more changes in the downstream measurements and operations	(i) Bio-oil/pyro-oil (ii) Pyro-char (iii) Syngases	Link.springer.com

4.1 Pyrolysis of MSS

Pyrolysis is a thermochemical decomposition of organic substances at high temperatures in the absence of oxygen (or any halogens). During the process, chemical composition and physical phases of the substance change. It is a process of thermolysis mostly seen in organic substances. The success of the process and the yield of the product formed from pyrolysis depend mainly on the process conditions like temperature, reactor design, pressure, residence time and the original sludge characteristics. The detailed review of the process is studied thereof. Mainly two types of pyrolysis are discussed in these. Fast pyrolysis is carried at a moderate temperature of 500 °C, short gas residence time of about >2 s and rapid quenching of the vapours. The major product from these process is pyrolysis liquid commonly called bio-oil or pyrolysis oil, which can be applied as a fuel and also act as a source of valuable chemical products. On the other hand, slow pyrolysis is characterised by mild temperature of about 350–600 °C at low heating rates, and obviously, the process takes place at inert, i.e. O_2-free atmosphere. The reactors that are involved in MSS pyrolysis are fixed-fluid bed and rotary kiln reactors. But pyrolysis is less pollutant than incineration due to lower operating temperature and non-requirement of oxygen in the process.

The product of sewage sludge pyrolysis is a dark brown organic fluid with high water content. Mainly the properties of pyrolysed liquid which are helpful to serve that liquid as a fuel are important. On the other hand, Char which is the main by-product of sewage sludge pyrolysis is characterised as follows. The chars are having low calorific value, near about 5 MJ kg^{-1}, which is not at all beneficial for incineration or other kinds of energy formulation. Again, the high heavy metal content of char requires high cost for their treatment. Again there are legal restrictions to use char as landfills. But using pyrolysis char as an adsorbent to remove pollutants like H_2S and NO_x are in practise these days. But many researchers are involved to utilise char in a more economical ways that would be a better socio-environmental sustainable process.

4.2 Gasification of MSS

Gasification is a thermochemical process that converts organic fossil fuels which are rich in carbonaceous materials into CO_2, CO and H_2O. The process takes place at high temperature about 680–900 °C without combustion, within a controlled atmosphere of oxygen, steam or air. During the process, the solid organic substances change to form syngas as certain by-products like char or slag–oil and water gasification works best if the sludge can be dried up to 90% (Spinosa et al. 2011). The gaseous products formed from waste gasification are used to prepare fuel cell and are utilised to produce electricity (Vierrath and Greil 2001). A typical gasification gas is characterised by a hydrogen content of about 8.89–11.17 (vol.%), CO (6.28–10.77 vol.%),

CH_4 (1.26–2.09), C_2S (0.75–1.2 vol.%) and carbon dioxide (Fytili and Zabaniotou 2008). Gasification also contains a chain of chemical and thermal decomposition reactions. During the process, sludge undergoes a series of complex physical and chemical changes, starting with water removal. Dried MSS is then pyrolysed. The resulting volatile pyrolysis products and char undergo further reactions for the production of permanent gases. Basically, the process of gasification mainly burns out the solid wastes to form clear combustible gas having high energy value (Dogru et al. 2002). Moreover; compared to conventional gasification integrated gasification is more encouraged mainly due to intensive use of it for fuel cell (Maniatis 1999).

In the context of integrated gasification steam gasification and plasma gasification which are quite famous because of the production of high calorific value hydrogen, further several types of catalyst like K_2CO_3 are used in the process for forming ash-free coal char, which has great utility [7] (Table 2).

5 Discussions and Analysis

This paper mainly consists of a detailed review of different thermal, chemical and biochemical processes of municipal sewage sludge mainly focussing on pyrolysis and gasification. How different organic matters of sludge can be treated and how they can be transformed from Waste to resource is discussed over here. The review states that nowadays it's meaningless to consider MSS as waste and stated how efficiently energy can be produced from it. Mainly the process of Pyrolysis and Gasification is discussed over here. Different effective temperature pressure, reactors for these processes are discussed. The characteristics of the effluent are also stated. Along with this the states of pyrolysis and gasification in different European and Asiatic countries are discussed briefly, including India [25–44].

From the detailed literature study, it is found that, in several EU countries, sludge is greatly used as an agricultural manure, specially in small towns and in countrysides where the small industrial base can be localised using sludge. (Praspaliauskas et al. 2017). Latest thermal treatment techniques of sludge like incineration, pyrolysis, gasification, co-combustion, etc. are increasing day by day. These techniques are mainly used in cities or in many places are still under experimental phase. Incineration is one of the most rapidly developing sewage sludge treatment processes. It is widely used in the European countries like Germany, the United Kingdom and Denmark. Co-incineration is in huge practise in the Netherlands, France, Belgium and Czech. On the other hand, gasification is a much promising sludge disposal method (Kelessidis et al. 2012). Co-incineration is also a widely used thermal treatment technology where sewage sludge is incinerated along with other fuels. Some co-incinerated plants are cited in the cities like Klaipeda, Kaunas, Vilnius, etc. in Northern Europe. However, gasification and pyrolysis are still in an experimental phase and are in pilot scale. These processes are mainly practised in Southern part of Europe. Italy is the leading country for such studies; again, Germany and France are also some

Table 2 Comparative study of pyrolysis and gasification in context of forming energy from MSS treatment

Type of input material	Pretreatment	Temperature and other parameters	Reactor type	Observation	Special comments	References
Pyrolysis of Municipal Sewage Sludge						
Raw oil palm fibre (OPF)	Drying at 80 °C in a furnace for 24 h	**Temp**: 723–973 K **N_2 flow**: 200–1200 cm^3/min **Microwave power**: 400–900 W	Microwave muffle reactor along with power controller	Max. H_2 yield at $T = 973$ K, $P = 508.36$ W, $Q = 1200$ cm^3/min Max. Biochar yield at $T = 723$ K, $P = 400$ W, $Q = 200$ cm^3/min	Response surface methodology was used to optimise T, P and Q	Hossain et al. (2016)
Municipal sewage sludge mixed with pine bark	Biophysical sludge drying for 7 days	**Sludge: Pine bark**—2:1 **Temp**: 773–1173 K **N_2 flow**: 0.3 L/min **Pyrolysis time**: 20 min **Cooling time**: 30 min	Horizontal fixed bed reactor	As temp. rises, biochar yield decrease microstructure develops Biochar has good thermal stability. Leaching toxicity is within safe level	Adsorption of Cd^{2+} by biochar was higher than AC 900 °C is the optimal temp. for energy recovery	Tan et al. (2014) (accepted manuscript)
Municipal wastewater plant sludge	Drying at 378 K and pulverised to 106–125 μm Acid–alkali pretreatment	**Temp**: 423–723 K **N_2 flow**: Constant	Fixed bed reactor	Alkali treatment reduces gas emission: **NaOH–KOH**: 43.5–47.6% **$Ca(OH)_2$–$Mg(OH)_2$**: 16.6–25.9% Formation of H_2S at low temperature is suppressed due to alkali treatment	Harmful sulfoxides and sulphonic acid decomposed to less harmful SO_2	Cheng et al. (2016)
Sewage sludge (SS) collected from three wastewater plant	Drying at 273–278 K Ground in a ball mill and sieved to 20–40 mesh size	**Temp**: 573–973 K **Argon flow**: 300 ml/min	Fixed bed reactor	Liquid yield >40% High oxygenated compound at 573 K while nitrogenated compound at 973 K	Abundant potassium in SS3 has catalytic effect on the yield of the gas	Fan et al. (2014)

(continued)

Table 2 (continued)

Type of input material	Pretreatment	Temperature and other parameters	Reactor type	Observation	Special comments	References
Sewage sludge (SS) from the wastewater treatment plant	Drying at 273–278 K Ground and sieved Particle dia.: 0.2–0.4 mm	**Temp**: 673, 773 & 973 K **Heating rate:** 10 °C/min **Argon flow**: 200 ml/min	Fixed bed tubular reactor	Pyro-oil contains monoaromatic, PAHs, N_2 compound, O_2 compound and cyclosiloxanes Generation of long chain aliphatic amides and nitriles occurred mainly before 673 K	Proportions of monoaromatics and polyaromatic ketone increased with increasing temperature so high temperature could promote the production of phenyl ring	
Digestate from anaerobic digestion of maize and green rye	Dewatering in centrifuge and pelletized	**Temp**: 773 K Inside vapour can reach a 663K	Pyroformer, an electrically heated pyrolysis reactor with two counterrotating concentric screws	The properties of digestate pyrolysed oil were as follows: Density—1077.14 kg/m^3, calorific value—26.77 MJ/kg, flash point—54 °C, kinematic viscosity—50.55 to 473.99, water content—6.40 wt%, acid number—8.4 KOH/g	(i) Pyro-oil blended with waste cooking oil and butanol was tested in a CI engine (ii) **Emission characteristics**:**—**SO_2, CO_2, Suspended particulate matter (SPM)	Hossain et al. (2016)
Dewatered sewage sludge (SS) from municipal wastewater treatment	Drying at room temp. 293 K. Crushing and Sieving through a 100 mesh sieve	**Temp**: 673–773 K **N2 flow**: 1L/min	Indigenous pyrolysis and carbonization furnace	General properties of biochar **C**:19.88–26.52%, **H_2**:2.04–4.08%, **S**:0.87–0.905%, **pH**: 7.19–11.7 **Ash content**: 64–74%	As temp. increases, biochar yield decrease but pH, ash content and specific surface area increase	Jin et al. (2016)

(continued)

Table 2 (continued)

Type of input material	Pretreatment	Temperature and other parameters	Reactor type	Observation	Special comments	References
Raw sewage sludge (SS) and the bamboo sawdust	Sewage sludge drying at 473 K. Bamboo sawdust drying at 973 K Both feedstocks were ground and passed through a 120 mesh sieve	Co-pyrolysis of bamboo sawdust and SS. (1:1) **Temp**: 673–873 K **N2 flow**: 1L/min. **Time:** 60 min	Pyrolysis and carbonization furnace	Biochar yield is between 53.160.6%. Co-pyrolysed char had the properties pH-8.46 to 11.64, ash content-52.6–74, BET surface Analysis was 4.5–7.7	Co-pyrolysis resulted in a low biochar yield, P-H bond formation Bamboo sawdust effectively converts toxic metals in the sludge into more stable form	Jin et al. (2017)
Digestate sewage sludge (SS)	Drying at 278 K for 48 h Ground and sieved <200 mesh Commercial HZSM-5 catalyst calcined at 873 K for 5 h and pelletized and sieved to 50–70 mesh	**Temp**: 773–873 K **He flow**: Constant	Packed bed micro-reactor	C:42%, H:5.6%, O:28.3% N:4.3% High N_2 content in the biochar due to the presence of protein and microbes in wastewater stream Ash: 18.6%	Catalytic pyrolysis produces aliphatic and aromatic hydrocarbons with most of the N_2 gas converted to NH_3. At pyrolysis temperature 500 °C and catalysis temperature 600 °C, 24.41% of olefin and 19.13% of aromatics were produced	Wang et al. (2017)
Gasification of Municipal Sewage Sludge						

(continued)

Table 2 (continued)

Type of input material	Pretreatment	Temperature and other parameters	Reactor type	Observation	Special comments	References
Sewage sludge with a solid content of 15–20 wt%	(i) Crushing, dispersion and homogenisation (ii) The sludge was preheated at a temperature of 435 °C	(i) Gasification reaction temperature maintained was 600 °C (ii) A pressure of 250 MPa was feeded	Fixed bed reactor	At low temperature, methane (CH_4) and bio-oil were the main product. At high temperature, CO, CO_2 toxic gases and ash	–	Gasafi et al. (2008)
Sewage sludge sample was collected from waste treatment plant	(i) Sludge is dried via solar driers (ii) Proximate and ultimate analysis of the sludge were carried out	(i) Initial sample mass is maintained to be 35 g (ii) Temperature maintained 700–1000 °C (iii) A steam flow rate of 3 g/min was set. The steam was generated due to combustion of H_2 and O_2	Gasification reactor	Syngas and hydrogen was formed	–	Nipattummakul et al. (2010)

upcoming countries for this projects (Pyrolysis and Gasification, A. V.Bridgwater, Commission of the European Communities).

Several studies reviewed that in Asiatic countries, municipal sewage waste can be reduced by up to 90% by producing electricity from it. Several plants are successfully running by the energy produced from sludge waste through the process of Incineration and Combustion. Among the thermochemical process, incineration is mostly used for municipal sewage sludge treatment in different Asiatic countries mainly in Singapore and China. Other than incineration, biological treatment like aerobic and anaerobic digestion is also famous in Asiatic countries. Pyrolysis and gasification, on the other hand, are mainly under experimental condition over here. Further few pilot plants are in progress in several Asiatic countries (Economics 26800, Prof. Tolley & Berry).

In India, the objective of MSS treatment plant is to treat waste, reduce its volume and generate energy and electricity from it. This takes the process towards a greener approach. In India, there are several such treatment plants and several projects are studied to be under pipeline. In India, there are a total of 48 waste-to-energy plants present including 32 proposed, 4 under construction and 11 are in operation. Few plants are shut down due to some technical problems in the plant. More than thermal processes, biochemical degradation of sewage sludge is in practise. One reason behind this wide usage could be the high organic content in Indian municipal sewage waste (MSW) due to the presence of food waste. One of the upcoming plant presently under construction is the Gazipur Waste to Energy plant. India, being a multistate country, has different raw material availability in different areas. 18 plants in the country are dependent on MSW for power generation whereas 15 plants use biomass like recently a plant is proposed in South Andaman. There are three plants in Delhi and they all use MSW as raw material. Currently, Delhi is producing 16 MW/day power from waste and will be able to produce an additional 25 MW/day after the completion of construction of two more projects. Gujarat is producing 3.5 MW/day power from waste. Chhattisgarh has seven proposed projects that will be able to produce 119 MW/day of electricity in the near future (Research Article, [2]).

Lastly, this review thoroughly gives a description of different thermal processes together with some future scope. This paper will be really helpful for different municipality engineers and industrialist and for those aspirants who have research interest in this zone. Again, the work proposes some future scope like cost-estimation for these processes in detail. Anyone can further research on co-process or the biological process stated above. Other opportunities can be to find the life cycle assessment (LCA) of each of these processes or can find a detailed survey of condition of these processes in a particular country or zone.

6 Conclusion

The research work mainly contains a detailed survey of pyrolysis and gasification, two latest and efficient process of sludge treatment. Their mechanism, temperature as well as the characteristics of effluent produced in this process are given here. Not only these two but different other methods of sludge treatment are stated here. State of use of these processes in different countries in Europe and Asia including India is given.

Acknowledgements The authors would like to show her gratitude towards Prof. Sadhan Kumar Ghosh for his support and guidance during the execution of the review work and also towards Department of Chemical Engineering Jadavpur University, Centre for Quality Management, Jadavpur University and International Society of Waste Management, Air and Water (ISWMAW) for their support and help.

References

1. Zaman AU (2010) Comparative study of municipal solid waste treatment technologies using life cycle assessment method. Int J Environ Sci Technol 7(2):225–234
2. Jain P, Handa K, Paul A (2014) Studies on waste-to-energy technologies in India and a detailed study of waste-to-energy plants in Delhi. Int J Adv Res 2(1):109–116
3. Samolada MC, Zabaniotou AA (2014) Comparative assessment of municipal sewage sludge incineration, gasification and pyrolysis for a sustainable sludge-to-energy management in Greece. Waste Manag 34(2):411–420
4. Ruiz-Gómez N, Quispe V, Ábrego J, Atienza-Martínez M, Murillo MB, Gea G (2017) Co-pyrolysis of sewage sludge and manure. Waste Manag 59:211–221
5. Budych-Gorzna M, Smoczynski M, Oleskowicz-Popiel P (2016) Enhancement of biogas production at the municipal wastewater treatment plant by co-digestion with poultry industry waste. Appl Energy 161:387–394
6. Sanlisoy A, Carpinlioglu MO (2017) A review on plasma gasification for solid waste disposal. Int J Hydrogen Energy 42(2):1361–1365
7. Wu X, Wang J (2017) $K_2 CO_3$-catalyzed steam gasification of ash-free coal char in a pressurized and vertically blown reactor. Influence of pressure on gasification rate and gas composition. Fuel Process Technol 159:9–18
8. Abuşoğlu A, Özahi E, Kutlar Aİ, Al-jaf H (2017) Life cycle assessment (LCA) of digested sewage sludge incineration for heat and power production. J Clean Prod 142:1684–1692
9. Borowski S (2015) Temperature-phased anaerobic digestion of the hydromechanically separated organic fraction of municipal solid waste with sewage sludge. Int Biodeterior Biodegradation 105:106–113
10. Cao Y, Pawłowski A (2013) Life cycle assessment of two emerging sewage sludge-to-energy systems: evaluating energy and greenhouse gas emissions implications. Bioresour Technol 127:81–91
11. Di Fraia S, Massarotti N, Vanoli L, Costa M (2016) Thermo-economic analysis of a novel cogeneration system for sewage sludge treatment. Energy 115:1560–1571
12. Emami-Meibodi M, Parsaeian MR, Amraei R, Banaei M, Anvari F, Tahami SMR,… & Mostafavi SJ (2016) An experimental investigation of wastewater treatment using electron beam irradiation. Radiat Phys Chem 125:82–87
13. Fezzani B, Cheikh RB (2009) Extension of the anaerobic digestion model No. 1 (ADM1) to include phenol compounds biodegradation processes for simulating the anaerobic co-digestion of olive mill wastes at mesophilic temperature. J Hazard Mater 172(2):1430–1438
14. Gulyurtlu I, Boavida D, Abelha P, Lopes MH, Cabrita I (2005) Co-combustion of coal and meat and bone meal. Fuel 84(17):2137–2148
15. Ibrahimoglu B, Cucen A, Yilmazoglu MZ (2017) Numerical modeling of a downdraft plasma gasification reactor. Int J Hydrogen Energy 42(4):2583–2591

16. Johari K, Saman N, Song ST, Chin CS, Kong H, Mat H (2016) Adsorption enhancement of elemental mercury by various surface modified coconut husk as eco-friendly low-cost adsorbents. Int Biodeterior Biodegradation 109:45–52
17. Khalil AE, Gupta AK (2016) Fuel property effects on distributed combustion. Fuel 171:116–124
18. Kim D, Amy GL, Karanfil T (2015) Disinfection by-product formation during seawater desalination: a review. Water Res 81:343–355
19. Kwon EE, Yi H, Kwon HH (2013) Thermo-chemical process with sewage sludge by using CO_2. J Environ Manag 128:435–440
20. Lutpi NA, Jahim JM, Mumtaz T, Harun S, Abdul PM (2016) Batch and continuous thermophilic hydrogen fermentation of sucrose using anaerobic sludge from palm oil mill effluent via immobilisation technique. Process Biochem 51(2):297–307
21. Lin T, Yu S, Chen W (2016) Occurrence, removal and risk assessment of pharmaceutical and personal care products (PPCPs) in an advanced drinking water treatment plant (ADWTP) around Taihu Lake in China. Chemosphere 152:1–9
22. Li K, Wang X, Wang J, Zhang J (2015) Benefits from additives and xylanase during enzymatic hydrolysis of bamboo shoot and mature bamboo. Biores Technol 192:424–431
23. Mandal S, Mahapatra SS, Patel RK (2015) Neuro fuzzy approach for arsenic (III) and chromium (VI) removal from water. J Water Process Eng 5:58–75
24. Maragkaki AE, Fountoulakis M, Gypakis A, Kyriakou A, Lasaridi K, Manios T (2017) Pilot-scale anaerobic co-digestion of sewage sludge with agro-industrial by-products for increased biogas production of existing digesters at wastewater treatment plants. Waste Manag 59:362–370
25. Martins MNC, de Souza VV, da Silva Souza T (2016) Cytotoxic, genotoxic and mutagenic effects of sewage sludge on Allium cepa. Chemosphere 148:481–486
26. Magureanu M, Mandache NB, Parvulescu VI (2015) Degradation of pharmaceutical compounds in water by non-thermal plasma treatment. Water Res 81:124–136
27. McCrea M, Tan TK, Ting HH, Zuo X (2009) A cost-benefit analysis of different waste-to-energy technologies for the management of municipal solid waste in Singapore
28. Nowicki L, Markowski M (2015) Gasification of pyrolysis chars from sewage sludge. Fuel 143:476–483
29. Motlagh AM, Bhattacharjee AS, Goel R (2015) Microbiological study of bacteriophage induction in the presence of chemical stress factors in enhanced biological phosphorus removal (EBPR). Water Res 81:1–14
30. Niu S, Chen M, Li Y, Xue F (2016) Evaluation on the oxy-fuel combustion behavior of dried sewage sludge. Fuel 178:129–138
31. Orgill JJ, Atiyeh HK, Devarapalli M, Phillips JR, Lewis RS, Huhnke RL (2013) A comparison of mass transfer coefficients between trickle-bed, hollow fiber membrane and stirred tank reactors. Bioresour Technol 133:340–346
32. Pei J, Yao H, Wang H, Ren J, Yu X (2016) Comparison of ozone and thermal hydrolysis combined with anaerobic digestion for municipal and pharmaceutical waste sludge with tetracycline resistance genes. Water Res 99:122–128
33. Pala LPR, Wang Q, Kolb G, Hessel V (2017) Steam gasification of biomass with subsequent syngas adjustment using shift reaction for syngas production: an Aspen Plus model. Renew Energy 101:484–492
34. Rivera-Utrilla J, Sánchez-Polo M, Ferro-García MÁ, Prados-Joya G, Ocampo-Pérez R (2013) Pharmaceuticals as emerging contaminants and their removal from water. A Rev Chemosphere 93(7):1268–1287
35. Scarlat N, Motola V, Dallemand JF, Monforti-Ferrario F, Mofor L (2015) Evaluation of energy potential of municipal solid waste from African urban areas. Renew Sust Energy Rev 50:1269–1286
36. Shen Y, Linville JL, Urgun-Demirtas M, Mintz MM, Snyder SW (2015) An overview of biogas production and utilization at full-scale wastewater treatment plants (WWTPs) in the United States: challenges and opportunities towards energy-neutral WWTPs. Renew Sustain Energy Rev 50:346–362

37. Wang ZH, Zhang K, Li Y, He Y, Kuang M, Li Q, Cen KF (2016) Gasification characteristics of different rank coals at H_2O and CO_2 atmospheres. J Anal Appl Pyrol 122:76–83
38. Wang J, Chu L (2016) Irradiation treatment of pharmaceutical and personal care products (PPCPs) in water and wastewater: an overview. Radiat Phys Chem 125:56–64
39. www.greentumble.com
40. www.utagtechnology.com
41. Xiao Y, Xu S, Tursun Y, Wang C, Wang G (2017) Catalytic steam gasification of lignite for hydrogen-rich gas production in a decoupled triple bed reaction system. Fuel 189:57–65
42. Yu H, Cao W (2016) Assessment of pharmaceutical and personal care products (PPCPs) of Dalong Lake in Xuzhou by concentration monitoring and bio-effects monitoring process. Environ Toxicol Pharmacol 43:209–215
43. Zhang XY, Chen MQ, Huang YW, Xue F (2016) Isothermal hot air drying behavior of municipal sewage sludge briquettes coupled with lignite additive. Fuel 171:108–115
44. Zhao Y, Xing W, Lu W, Zhang X, Christensen TH (2012) Environmental impact assessment of the incineration of municipal solid waste with auxiliary coal in China. Waste Manag 32(10):1989–1998

Co-processing of Alternative Fuels and Resources in Indian Cement Industry—Baseline and Potential

Palash Kumar Saha and Kåre Helge Karstensen

1 Introduction

Waste generation is an inevitable output of economic activities and its environmentally sound and safe management is critical. Poor waste management is an issue in all developing countries and countries in transition. Increasing quantities of waste are disposed of in an uncontrolled manner, incinerated or dumped in landfill sites. Various wastes are increasingly considered as resources that could be used as resource input in energy-intensive industrial processes. In order to avoid loss of valuable resources and to safeguard precious land, the landfilling of waste is increasingly being prohibited or viewed as an option of last resort.

Co-processing is the use of waste as a source of energy or raw material, or both to replace natural mineral resources and fossil fuels such as coal, petroleum, coke, etc., in the manufacturing process. Basel and Stockholm Conventions highlighted the suitability of cement kiln for co-processing of hazardous and other wastes. Co-processing in a cement kiln is a scientific, sustainable, proven and established technology for disposing of hazardous and non-recyclable waste in an environmentally sound manner. This practice can be extremely attractive and cost-efficient, especially for emerging economies having insufficient waste treatment capacity.

Waste arising will increase significantly with growth in Gross Domestic Product (GDP) and living standard in India; treatment capacity for all waste streams is currently insufficient, causing local pollution, the release of greenhouse gases and a waste of valuable resources. India intends to reduce the emissions intensity of its GDP by 33–35% by 2030 from 2005's level. This means while India's GDP is pro-

---

P. K. Saha (✉) · K. H. Karstensen
SINTEF, Oslo, Norway
e-mail: palashkumar.saha@sintef.no

K. H. Karstensen
Asian Institute of Technology, Khlong Luang, Thailand

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_2

jected to increase by 5–7 times, absolute carbon emissions will increase by only 3 times by 2030 over 2005 levels. India in 2030 is projected to contribute about a tenth of global carbon emissions while being home to approximately a fifth of the global population.

Co-processing leads to 100% energy and material recovery and does not leave behind any ash for further disposal (i.e. no liability for waste generators once waste is co-processed in cement kilns). Due to its economic, environmental and social benefits, it has been recognised as one of the five important levers for large-scale reduction of CO_2 emissions from the Indian cement industry, in the low-carbon technology roadmap.

2 Co-processing Baseline

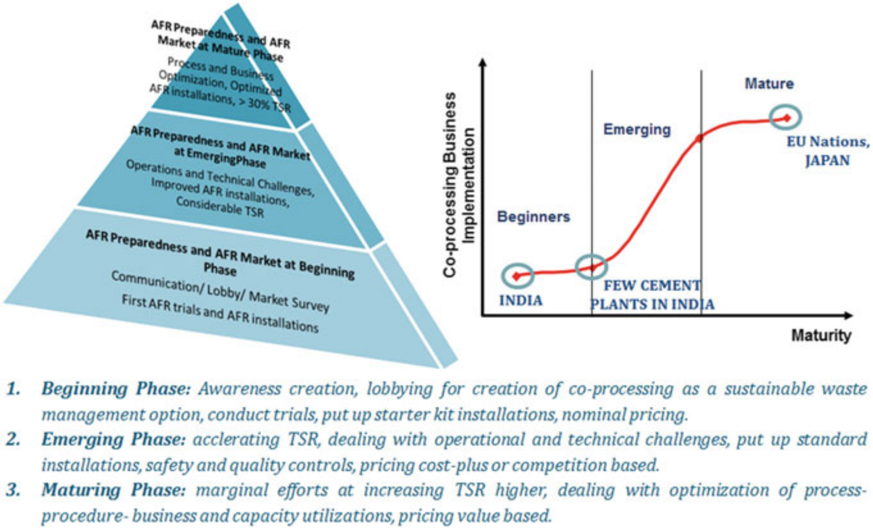
India is currently the second largest cement producer in the world. Low per capita consumption indicates large growth potential in the sector in the future. Indian cement industry consumes close to 50 million tonnes (Mt) of coal and 450 Mt of raw materials annually and responsible for 7% of India's CO_2 emissions.

Recovery of wastes and replacement of coal in the cement industry has been practiced a relatively short time in India (Fig. 1); the Thermal Substitution Rate (TSR) is 2.5% in average; compared to EU's average of almost 40% and Norway 70% (Table 1). In a status report, published by CII in May 2015 [1], the average TSR of 36 cement plants, corresponding to 109 Mt cement production capacity, was 3.55% (highest single plant substitution is around 18% TSR). The Steel and Power industry has little experience in co-processing and are generally cautious to implement co-processing as they are afraid of possible negative impacts to their processes and their 'product' quality.

The Indian cement industry is gearing up with its infrastructure, capacity and competence for enhancing Thermal Substitution Rate (TSR), including the installation of pre-processing platforms and adoption of newer technologies. This is evident from >80 numbers of co-processing trials and over 60 million USD of investment for installations, including the installation of 10 pre-processing platforms and hot discs in the pre-heater tower. There are about 54 cement plants permitted for co-processing.

3 Regulatory Framework for Co-processing

The MoEFCC has recently amended the existing regulatory framework for environmentally sound management of the waste being generated in the country. MoEFCC has notified sets of waste management rules dealing with different kinds of waste: solid waste, plastic, biomedical, construction and demolition, electronic waste and hazardous waste. These new rules advocate for adopting more scientific, technology-driven, sustainable, regulated, and participative environment management.



1. ***Beginning Phase:*** *Awareness creation, lobbying for creation of co-processing as a sustainable waste management option, conduct trials, put up starter kit installations, nominal pricing.*
2. ***Emerging Phase:*** *acclerating TSR, dealing with operational and technical challenges, put up standard installations, safety and quality controls, pricing cost-plus or competition based.*
3. ***Maturing Phase:*** *marginal efforts at increasing TSR higher, dealing with optimization of process-procedure- business and capacity utilizations, pricing value based.*

Fig. 1 Different stages of development of co-processing initiative

4 Hazardous Waste Management Rules 2016

The salient features of Hazardous and Other Wastes (Management & Transboundary Movement) Rules, 2016 include, Co-processing as preferential mechanism over disposal for use of waste as a supplementary resource, or for recovery of energy has been provided. The basic necessity of infrastructure to safeguard the health and environment from waste processing industry has been prescribed as Standard Operating Procedure (SOPs) specific to waste type. Waste Management hierarchy in the sequence of priority of prevention, minimization, reuse, recycling, recovery, co-processing, and safe disposal has been incorporated. The approval process for co-processing of hazardous waste to recover energy has been streamlined and put on emission norms basis rather than on a trial basis [4, 5].

5 Solid Waste Management Rules 2016

As per the new Municipal Solid Waste Management (Management and Handling) Rules 2016 non-recyclable waste having a calorific value of 1500 kcal/kg or more shall not be disposed of on landfills and shall only be utilised for generating energy either or through refuse-derived fuel or by giving away as feedstock for preparing refuse-derived fuel. High calorific wastes shall be used for co-processing in cement or thermal power plants. All industrial units using fuel and located within 100 km from a solid waste based RDF plant shall make arrangements within 6 months from

Table 1 Countrywise TSR from utilisation of alternative fossil wastes, mixed wastes and biomass in %

Countries	TSR (%)	Year	References
Austria	75	2014	[2]
Norway	70	2016	
Germany	65	2014	[2]
Czech Republic	62	2014	[2]
Belgium	53	2016	[3]
Poland	52	2014	[2]
United Kingdom	49	2014	[2]
Sweden	48	2016	[3]
Hungary	40	2016	[3]
France	38	2014	[2]
Ireland	29	2016	[3]
Spain	28	2014	[2]
Portugal	28	2016	[3]
Philippines	23	2014	[2]
Bulgaria	21	2016	[3]
Brazil	19	2014	[2]
United States	15	2014	[2]
Italy	14	2014	[2]
Thailand	13	2014	[2]
Canada	13	2014	[2]
Egypt	9	2014	[2]
Greece	7	2016	[3]
India	2.5	2016	Estimated

the date of notification of these rules to replace at least 5% of their fuel requirement by RDF so produced.

6 CPCB Guidelines for Co-processing of Plastic Waste in Cement Kilns 2017

The Ministry also released Guidelines for Co-processing of Plastic Waste in Cement Kilns (As per Rule Plastic Waste Management Rules, 2016 [6]) in May 2017. The guidelines elaborate upon the collection, segregation and transportation and co-processing of plastic waste in cement kiln with detailed procedures.

7 CPCB Guidelines for Pre-processing and Co-processing of Hazardous and Other Wastes in Cement Plant 2017

CPCB released guidelines for pre-processing and co-processing of hazardous and other wastes in Cement Plant in July 2017 [7]. The guidelines have been revised for complying with the conditions as specified in the Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016 [4].

- No trial runs would be necessary for grant of authorisation for co-processing of wastes in cement kilns: No trial runs would be necessary for grant of authorisation for co-processing of wastes in cement kilns since MoEFCC has notified the Emission Standards for co-processing of wastes in cement kiln vide GSR No. 497 (E) dated 10.5.2016 under the Environment (Protection) Rules, 1986. However, demonstration trials would be conducted for specific wastes such as POPs, PCBs, obsolete and date expired pesticides, ozone depleting substances, etc. Kiln-specific trial runs may be required for such wastes to study the destruction and removal efficiencies (as per the requirement of Stockholm convention). Trial/approval from CPCB would also be required of waste is fed through coal or raw material route.
- S-PCBs can issue approval without CPCB: S-PCBs may grant Authorisation to cement plants for co-processing of wastes listed in Schedule I (38 industrial processes), Schedule II (hazardous characteristics) and Schedule III (import/export of hazardous wastes) of the Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016. For co-processing of hazardous and other wastes, cement plants shall obtain Consent to Establish (CTE) and Consent to Operate (CTO) prior to obtaining authorisation under the Hazardous and Other Wastes (Management and Transboundary Movement) Rules, 2016.
- SOP for pre-processing and co-processing defined: Regular co-processing shall be carried out as per the guidelines and SOPs. Continuous Emissions Monitoring System installation is mandated in the stack for PM, SO_x and NO_x in the first phase (with data uplinked to SPCB, CPCB). There are detailed parameters mentioned for pre-qualification and fingerprint analysis of wastes, the infrastructure required for transport–storage–pre-processing and co-processing of hazardous wastes and the emission parameters.
- Inter-state transfer simplified: Facilitate movement of waste across different states and procedures to be followed for same highlighted in the document.
- Co-processing as a lever to achieve Intended Nationally Determined contribution (INDC): Utilising waste materials as AFRs will also reduce the large quantity of GHG emissions of the country which is in line with Paris agreement.

8 Co-processing Potential in India

Around 7.7 Mt of hazardous waste is currently generated annually, of which around 3.61 Mt is recyclable, 0.65 Mt is incinerable and 3.39 Mt is landfillable [8]; current disposal capacity is inadequate addressing only 40% of the landfillable and incinerable wastes generated. Cement kilns have, in general, better destruction performance for organic hazardous wastes than existing incinerators at disposal facilities in India.

Studies conducted by the Ministry of New and Renewable Energy have estimated surplus biomass availability at about 120–150 Mt per annum [9]. Gujarat, Uttar Pradesh, Maharashtra and Odisha generate 92,000 to 110,000 tonnes of industrial plastic wastes [10]. 700 000 tonnes of the used tyre is available in India, mostly in the states of Maharashtra, Tamil Nadu, Uttar Pradesh, Gujarat, Andhra Pradesh, Karnataka, Rajasthan and Madhya Pradesh [10]. Both plastic wastes and used tyres have higher energy content than Indian coal.

At present only half of ground granulated blast furnace slag generated is sent to cement plants. The estimated generation will be around 44 Mt in 2020 and about 95 Mt in 2030. Fly ash generation is expected to reach 450 Mt by 2020, and 900 Mt by 2031. Granulated blast furnace slag and fly ash when mixed with cement clinker will reduce both CO_2 from calcination of limestone and fuel-related emissions.

Therefore, more than 150 Mt of hazardous and non-hazardous wastes are available for co-processing. Considering the availability, ease of processing and potential GHG mitigation, refuse-derived fuels from MSW, biomass (e.g. rice husk, bagasse, coconut shells and wood chips.), industrial plastics; used tyres and industrial hazardous wastes/mixed industrial wastes are considered as potential AFs for utilisation in REIIs, especially cement.

For achieving 5% TSR in 2020 and 20% TSR in 2030, for every Mt of cement produced, 7000 tonnes and 25,000 tonnes of AFs need to be co-processed, respectively. In 2030, by achieving 20% TSR in a cement kiln, up to 19 Mt of Indian coal or 13 Mt of imported coal can be substituted [11].

9 Production of RDF

Presently, more than 30% of India's population lives in cities; projected to be 50% by 2050. MSW in India is generally unsegregated with high moisture content, low calorific value, odour and a wide range of particle size. As per the Planning Commission's Task Force Report (2014) [12], of the 62 Mt of Municipal Solid Waste (MSW) generated in urban India, 12 Mt is a combustible fraction which can be potentially converted to Refuse-Derived Fuel (RDF), thereby replacing 8 Mt of coal.

For dumping of 62 Mt of MSW without treatment, 1240 ha per year of precious land is required. With projected MSW generation of 165 Mt by 2031, the requirement of land for setting up a landfill for 20 years (considering 10 m high waste pile) could be as high as 66,000 ha. As per the Central Pollution Control Board (CPCB) study in 2015, there are 22 operating RDF plants in the country [13].

The principle of RDF production is recovering quality fuel fractions from the waste, particularly the removal of recyclable particles like metal, glass and converting the raw waste into a more usable form of fuel with uniform particle size and higher calorific value than raw MSW. Required quality of RDF is determined by the end use of the fuel. For example, Ministry of Urban Development (MoUD), specifies broad specification of RDF suitable for the Indian cement plants [14] as the following:

- Moisture, preferably <20%;
- Size, 2D < 120 mm, 3D < 70 mm depending on process limitation of specific cement plant;
- Chlorine, preferably <0.7% depending on particular raw mix & fuel mix;
- Calorific Value, preferably >3000 kcal/kg; the calorific value of RDF produced in Europe is in the range of 4000–6000 kcal/kg;
- Sulfur, <2%, however, depends on particular raw mix & fuel mix; and
- Free of restricted items such as PVC, explosives, batteries, aerosol containers, biomedical waste, etc.

The quantity of RDF that can be produced per tonne of MSW varies depending on the type of collection, pre-processing and composition of waste source. Usual yield of RDF from mixed MSW is in the range of 20–30%; if the waste is properly segregated yield can go as high as 80–90%. Depending on the need of the end user, RDF fluff is further processed in the densification unit to produce RDF pellets.

10 GHG Emissions Mitigation Potential Through Co-processing in India

Indian cement industry is anticipated to reach production of between 598 (low demand) and 848 Mt (high demand) by 2030. In absence of any action, CO_2 emissions from the sector will be 419–594 Mt by 2030, respectively [15]. Indian cement industry is one of best in the world in terms of energy efficiency, i.e. there seems to be a limited potential in further energy efficiency. Availability of alternative fuels and raw materials (AFRs), especially large quantities of inorganic mineral additives make clinker substitution, raw material substitution and high TSR important levers for CO_2 reduction from Indian cement industry. Work on Carbon Capture and Storage (CCS) has not yet been initiated and it will take some time for the inception of the CCS technologies in Indian cement industries.

As per the SINTEF estimates, by 2030, clinker substitution could save 47–67 $MtCO_2$; utilisation of alternative fuels, with 20% thermal substitution rate, could save 21.2–29.9 $MtCO_2$ and utilisation of alternative sources of de-carbonated lime and mineralisers could save 5.7–8 $MtCO_2$. These initiatives may reduce CO_2 emissions by 18% from business as usual scenario [16].

11 CFC Trial at ACC Limited, Kymore Cement Works

SINTEF participated on behalf of CPCB in the Test Burn with three different ozone-depleting substances, or chlorofluorocarbons (CFCs), in ACC Limited, Kymore cement works, Madhya Pradesh in December 2012. Ozone-depleting substances are regulated under the Montreal Protocol and countries are urged to destroy the five most potent CFCs gases as they destroy the ozone layer and contribute to global warming.

The full-scale demonstration involving high feeding rates of Ozone Depleting Substances (ODS), CFC gases demonstrated that the kiln was able to destroy several concentrated CFC gases effectively in an irreversible and environmentally sound manner without causing increased releases of HCl, HF or PCDD/PCDF. The destruction and removal efficiency was >99.9999% and the overall environmental performance in compliance with Indian regulation and international best practice.

The test revealed that cement kilns have a much higher disposal capacity than previously anticipated and that such undertaking can contribute significantly to reduce the release of both ODS and greenhouse gases; the destruction of 16.3 tonne of CFCs done in this demonstration was saving the release of 131 265 tonne of CO_2 to the atmosphere [17]. The global potential to prevent future emissions of ODS gases are formidable; the UN has estimated that more than 400 Mt of CO_2 equivalents will originate from discharges of cooling gases in 2015. The impact of this test is that India now has a facility with the demonstrated capability to destroy such gases in the future; a showcase which can be replicated elsewhere.

12 About SINTEF and Its Association with the Co-processing Initiatives in India

SINTEF is one of the leading applied multidisciplinary research institutions in Europe with more than 2000 professional employees. SINTEF has a long and relevant experience with capacity building and technical assistance in international projects for governments, industry and international organisations within industrial and hazardous waste management in general, and with co-processing in particular, i.e. improved energy and resource efficiency and greenhouse gas emission reduction by substitution of non-renewable fossil fuel and virgin raw materials with alternative fuels and raw materials in resource-intensive industry.

13 CPCB-SINTEF Phase I Co-processing Project (2010–2015)

CPCB and SINTEF have since 2010 cooperated in the Norwegian government supported programme ‘Recovery of alternative fuels and raw materials (AFR) and treatment of organic hazardous wastes through co-processing in resource and energy-intensive industry (REIIs) in India’. The project has been raising awareness, built capacity, shared knowledge of best international practice, and provided technical support and disseminating information to industry and authorities. This process has contributed to create confidence and a positive climate for investments, manifested by industries willingness to invest in future co-processing activities.

SINTEFs role has been to provide inputs on relevant issues of co-processing of hazardous and industrial wastes and to build capacity and knowledge among stakeholders; to assist CPCB, state PCBs and industry in implementing best practices and to convey lessons learned on possibilities and limitations in co-processing; and finally to contribute to achieve an international benchmark when it comes to process and quality performance, as well as on health, safety and environmental issues.

14 Phase II Co-processing Project (2017–2020)

SINTEF is currently working on a Norwegian government-funded project in India—'Co-processing of Alternative Fuels and Resources in the Cement Industry: Phase II' (2017–2020), which is a continuation of Phase I project (2010–2015), with a focus on the following issues:

- Provide professional technical assistance on waste related issues in the GIZ-MoEFCC SEIP project for providing technical support and capacity building on sustainable management of industrial wastes and sewage sludge, and for cleaning up of critically polluted areas in the two selected SEIP project sites—Delhi and Vapi, Gujarat;
- Demonstrate the potential to increase the TSR by utilising RDF out of MSW and dried sewage sludge;
- Strengthen the capacity of CPCB and S-PCBs on opportunities and limitations of using cement kilns for co-processing of problematic wastes;
- Strengthen the role of CPCB as a pool of competence for environmental authorities in neighbouring South Asian countries; and
- Evaluate the potential for resource conservation by utilising C&D wastes and increased use of other inorganic waste streams.

15 Conclusion

Many developed nations globally have utilised cement kilns in their countries as a sustainable solution for industrial, municipal and hazardous waste disposal (called co-processing) as this creates a win-win situation for both the local administration and the cement plants. Spiralling fuel costs, uncertainty in fuel availability and goal to reduce CO_2 emissions are drivers for enhancing AFR utilisation in Indian cement plants.

'Polluter pays principle' must be implemented for managing industrial wastes. For commodity like materials such as processed RDF, used tyres and biomass, substitution benefits in a cement plant must outweigh material costs and preparation and handling costs. Regular supply of wastes to cement plants at agreed tipping fee or price is essential for optimizing the return on investments.

By integrating co-processing and treatment of wastes in energy- and resource-intensive industry, India can forego or significantly reduce investments in costly waste incinerators; save large amounts of non-renewable fossil fuels and virgin raw materials; reduce greenhouse gas emissions; increase its waste treatment capacity and reduce exposure and negative impacts of hazardous chemicals. The aspiration of achieving 20% TSR by 2030 by the Indian cement industry is challenging but surely achievable.

References/Bibliography

1. CII (2015) Status paper on AFR usage in Indian cement industry—an initiative by CII-CMA. May 2015
2. WBCSD CSI (2014) Global cement database on CO_2 and energy information Getting the numbers right (GNR). http://www.wbcsdcement.org/pdf/GNR%20dox.pdf
3. Beer J, Cihlar J, Hensing I, Zabeti M (2017) Status and prospects of coprocessing of waste in EU cement plants. Ecofys, 26 April 2017
4. MoEFCC (2016) Hazardous and other wastes (Management and transboundary movement) rules, 2016, published in the Gazette of India, Extraordinary, Part III, Section-3, Sub-section (i), Government of India, Ministry of Environment, Forests and Climate Change, New Delhi
5. MoEFCC (2016) Solid waste management rules, 2016, published in the Gazette of India, Extraordinary, Part II, Section- 3, Sub-section (ii), Government of India, Ministry of Environment, Forests and Climate Change, New Delhi
6. CPCB (2017) Guidelines for co-processing of plastic waste in Cement Kilns (As per Rule ‘5(b)’ of Plastic Waste Management Rules 2016). Central Pollution Control Board (Ministry of Environment, Forest & Climate Change, Government of India) Parivesh Bhawan, East Arjun Nagar, Delhi—110032, May 2017
7. CPCB (2017) Guidelines for pre-processing and co-processing of hazardous and other wastes in cement plants as per H&OW(M&TBM) rules 2016. Central Pollution Control Board (Ministry of Environment, Forest & Climate Change, Government of India) Parivesh Bhawan, East Arjun Nagar, Delhi—110032, July 2017
8. Gupta PK (2012) Scenario of co-processing of wastes in India. In: CPCB and SINTEF Workshop, Bhopal, 1 Nov 2012
9. MNRE (Ministry of New and Renewable Energy). Government of India. http://mnre.gov.in/schemes/grid-connected/biomass-powercogen/. Accessed 24 Jan 2015
10. IIP (Institute of Industrial Productivity) (2014) Enhancing the use of alternative fuels and raw materials (Co-processing) in cement manufacture: white papers on selected topics
11. Saha PK, Karstensen KH (2015) Report on co-processing potential in cement, steel and power sector in India, submitted to CPCB under CPCB-SINTEF phase I co-processing project, SINTEF Building and Infrastructure, Report no. SBF2015F0049
12. Planning Commission (2014) Report of the task force on waste to energy (volume 1)—in the context of integrated MSW management, May 2014
13. CPCB (2015) Consolidated annual review report on implementation of Municipal solid wastes (Management and handling) rules, 2000, Annual review report: 2013–14
14. MoUD (2016) Municipal solid waste management manual, prepared by Central Public Health and Environmental Engineering Organisation (CPHEEO) in association with GIZ

15. WBCSD CSI (2013) Technology roadmap- low-carbon technology for the Indian cement industry, a report jointly prepared with IEA. http://www.wbcsdcement.org/index.php/technology/india-roadmap
16. Karstensen KH, Saha PK (2015) Report on potential for reduction of CO_2 emissions in cement, steel and power sectors in India. Submitted to CPCB under CPCB-SINTEF Phase I Co-processing Project, SINTEF Building and Infrastructure, Report no. SBF2015F0048
17. Karstensen KH, Parlikar UV, Ahuja D, Sharma S, Chakraborty MA, Maurya HP, Mallik M, Gupta PK, Kamyotra JS, Bala SS, Kapadia BV (2014) Destruction of concentrated chlorofluorocarbons in India demonstrates an effective option to simultaneously curb climate change and ozone depletion. Environ Sci Policy 38:237–244

Experiences on AFR Journey in India in Last 10 Years: Conceptualization to Present Day Scenario

Milind Murumkar

1 The Back Ground

There had been remarkable changes in the last 10 years on the subject of AFR in India. The thermal substitution has shown a very positive trend year-on-year, though at a very slow pace earlier and picking up later in the last 2–3 years to a level of around 4%. The basic reasons for this can be broadly assigned to the lack of knowledge on AFR usage in Indian cement industry in early years, especially on the usage of industrial waste, lack of skilled persons for handling and usage of industrial wastes, lack of proper infrastructure for storage and feeding of AFR materials to cement kilns, lack of proper understanding on the permitting process in regulatory bodies and above all the WILL to receive and use the waste materials in cement plants.

In the last 2 years, a remarkable transformation has been noticed on all the above aspects with dramatic changes in the mindset of regulatory bodies, the plant operating professionals and also in the waste generators who are shifting to co-processing as a better option over landfilling and incineration as it provides a cost-effective option to them. In April 2016, with the revised MOEF rules that incorporates co-processing as the better option for the recovery of energy, the scenario is changing fast towards higher utilization of different types of wastes in cement kilns.

Cement plants also have made proper investments to improve their infrastructure that can help in scientific disposal of industrial waste in the plants in a sustainable manner, for proper handling, storage and feeding of different types of wastes at appropriate points in the kiln system without affecting the product quality and the environment. In short, the cement plants are focusing on the higher usage of all types of waste and reduce their dependency on the conventional fuels and raw materials.

M. Murumkar (✉)
Alternate Fuels & Raw Materials, Vicat in India, Hyderabad, India
e-mail: milind.murumkar@vicat.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_3

2 The Technological Process

Co-processing is a proven sustainable development concept that reduces dependency on natural resources, reduces pollution and landfill space, thus contributing to reducing the environmental footprint.

Co-processing is also based on the principles of industrial ecology, which considers the best features of the flow of information, materials, and energy of biological ecosystems, with the aim of improving the exchange of these essential resources in the industrial world. Waste materials used for co-processing are referred to as alternative fuels and raw materials (AFR). AFR can be used alone also as fuel in cement kilns. A proper understanding of the processes, raw material characteristics and the waste compositions are the key factors that need to be assessed before the use of AFR in a particular kiln system.

The main challenges faced by any cement industry in use of AFR can be broadly classified as follows:

(a) **Management commitment**: Management's WILL to use and improve the AFR utilization in its plants. Creating suitable environment and commitments in their people to achieve the targeted short- and long-term plans. Initially, none of the plants will be willing to bring and use the waste from other industries in their plant, which is smelly, difficult to handle, store and use. Management needs to build and develop the infrastructure in a manner that it can use all types of industrial wastes like solids, semisolids and liquid waste in their plant.

(b) **Skill development and Infrastructure**: AFR utilization requires special skills in their cement plant engineers who need to be properly trained to understand the waste characteristics, their raw material and fuel characteristics and the point of dosage in their kiln. While using higher quantities of wastes in their system, process stabilities are maintained, otherwise, it may affect the quality of product and the production levels. A cement plant has to know its raw material composition and fuel composition to decide on the types of waste that can be used in their system and accordingly decide on the feeding points of different types of waste that need to be co-processed.

(c) **Regulatory requirements**: There are specific rules and guidelines for hazardous waste during transportation, storage and usage, and the cement plants have to comply with them while using hazardous materials in their plant. The equipments and storage area . need to be selected based on the availability of waste and the plans for next 10–15 years. It is better to have a proper market data mapping and have long-term agreements with the waste generators for building trust and confidence in them.

(d) **Understanding the waste and waste generators**: It is necessary to understand the pain points of the waste generating industry and work on providing total solution for managing their waste in an environmental friendly manner. Business success depends on having a good win–win model between the cement plant and the waste generating industry. Waste generators need total solution for their different wastes generated and the success in utilization of different types of waste in cement plant lies in having co-processing ability for providing total solution to the generating industry.

3 One Standing Example on AFR Usage Improvement in India

Understanding the above main factors that led to improvement in the usage of AFR in VICAT IN INDIA will help the other Indian cement industries to have an introspection of their processes and their preparedness for improving the AFR utilization in their plants.

VICAT IN INDIA is a part of Vicat group, which is an international cement company with expertise acquired through more than 160 years of research, discoveries and participation in countless construction projects all over the world. It operates two plants in India as Kalburgi cement plant and Bharathi cement plants, with an annual capacity of around 8 million tons, to produce superior quality cement since 2009. Since the inception, the focus was on utilization of AFR material in both the plants and presently we could achieve thermal substitution rate of around 20% for VICAT IN INDIA.

Vicat In India's journey started with substitution rate of around 4% in 2012 and in last 5 years it reached a level of 20%. The initial startup was on utilization of easy to use AF materials like biomass, segregated non-recyclable plastic waste, etc. Presently, we are proud to say that we can co-process different types of waste like industrial wastes (Hazardous and Non-Hazardous), tyre-derived waste, plastics-derived waste, derived waste from MSW segregation process, animal waste, waste from windmill sources, etc. We offer cradle to grave solution for different sectors like Pharma Industries, FMCG industries, Tyre industries, Municipal corporations for segregated MSW, food and beverage industries, etc.

4 Need for Proper Clarity in Understanding Waste

As discussed earlier also, a cement plant having this high-temperature profile system can practically co-process all types of wastes, without having any impact on product quality and environment. Focus and care must be taken by the cement plants during the selection of wastes, selection of equipments and selection and deployment of trained people for co-processing of any type of waste. Cement plants you know spend huge capex for creating proper blending and processing of coal and raw material in the form of stacker reclaimer, blending, storage silos, etc. Similarly, to achieve a higher TSR rate, it is advisable to have a proper preprocessing facility for blending different types of waste and prepare a recipe that is compatible to the raw material and fuel used in their plants.

5 Alignment with Community

A cement plant can certainly help the community around its plant to source agricultural waste, sorted MSW, etc., that can help in the creation of employment and earn goodwill of the community. The acceptance by the community for waste management is an important aspect for its success. Cement plants can certainly support the community around their plants by forming small groups for agricultural waste collection, MSW collection sorting, shredding and supply to the plant in such a way that this low-cost model should help the cement plants in gaining community acceptance and boost their CSR initiatives.

6 The Challenges

The challenges during utilization of hazardous waste are enormous as it is very necessary to have a proper input from waste generators about the waste characteristics and a proper MSDS to understand the precautions needed during transportation storage handling and usage of different wastes. Manpower is also required to be properly trained for the handling of these wastes in the plant and provided with required personal protection equipment, etc. Proper displays of various hazards need to be displayed in the local language at the work site. Once the waste quality and its hazards are known to the operating persons the safety aspect gets addressed well.

Our legislation is quite well defined and is in line to the developed countries a lot of work has gone in this field and regular up gradation in the policy framework and user-friendly rules and guidelines are made available by the Ministry of environment and central as well as state pollution boards.

Contrary to the earlier days, now the approval process is quite fast and adequate authorities have been given to the state and local pollution board authorities for addressing the issues and grant timely approvals. Due to this, the time lag gets drastically reduced and the process gets simplified for granting the permit.

7 Swatch Bharat an Initiative that Can Boost the AF Utilization

Large quantities of MSW are available in India in every state and in every city and can be used in cement plants if proper segregated MSW as RDF is made available to them. The basic difficulty is the quality of RDF that is being generated at the RDF plants. The RDF produced from MSW in these plants is highly heterogeneous with moisture to the tune of 30–40%, which creates problems of conveying and usage in cement plants. The problems of these RDF plants are the input MSW material received by them and they have no controls on these receipts. Some cement plants have created facilities for usage of RDF by investing in conveying systems like pneumatic or mechanical and yet the usage is very low due to high moisture and the heterogeneity of material. The RDF producing plants are trying to develop systems for improving the quality to some extent but largely no concrete steps are being taken by municipalities for improving the quality of RDF going to cement plants.

As indicated above and as indicated in the CII approach paper, India can achieve 25% TSR by 2025. In comparison to global standards we are far behind as in many countries the substitution is 60–100% also. The main differentiator is the waste characteristics and the lack of support by the required agencies for generating a good segregated quality waste. This long-term plan of achieving 25% substitution rate is as it is very challenging.

New Approaches for Solid Waste Management to Maximize Organic Waste Reutilization

Serpil Guran, Ronald MersÝky, David Specca and Margaret Brennan-Tonetta

1 Introduction

The world population is estimated to reach to 9.7 B by 2050 [1] and this growth in population will bring increased demand for energy, water, and food resources. The demand for food, in particular, is expected to increase on average by 70% by 2050 [2]. Increased population will also dramatically increase waste generation and the systems needed to manage it .

1.1 Food/Organic Waste Generation

In the US, about 40% of food produced goes unused [3]. As a result, the equivalent of $165 B in food costs are wasted each year, as well as 25% of all freshwater and a proportional amount of chemicals, energy, and land that is used in the food production process [3, 4]. The majority of waste food ends up in landfills where organic matter accounts for 16% of US methane emissions [3, 4]. In addition, getting food to the table consumes 10% of our energy and 80% of the freshwater in the US [5, 6]. Making current organic waste disposal practices cleaner and more efficient can

---

S. Guran (✉) · D. Specca
Rutgers Eco Complex "Clean Energy Innovation Center", Rutgers,
The State University of New Jersey, Bordentown, USA
e-mail: sg795@njaes.rutgers.edu

R. MersÝky
Widener University, Chester, PA, USA

M. Brennan-Tonetta
Rutgers University, The State University of New Jersey, New Brunswick, USA

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_4

reduce not only carbon emissions, but also help displace water intense fossil-based energy generation.

1.2 State of Landfills

Waste tonnages disposed in landfills have declined in recent years, first due to the downturn in the economy between 2009 and 2013, and later with the demand for further reductions in waste directed to landfills. Changes in economic and social norms favor more holistic approaches to current solid waste management practices, particularly in regards to organic wastes that have perceived value for reuse as compost/soil amendment materials. Despite concentrated efforts to manage waste by reusing, reducing, and recycling, landfilling remains the most predominant (and cost-effective) solid waste management method in the US. Although the number of landfills declined from 2500 to 1900 between 1995 and 2012, [7, 8] total landfill capacities are much larger to take advantage of economies of scale. Landfills currently accept mixed waste, which includes waste paper, food waste, manure, yard trimmings, wood, textiles, plastic, metals, glass, rubber, and leather. Approximately, 30% of landfilled waste is considered organic waste. Organic waste discarded into landfills decomposes at various rates with the more putrescible organic materials, like food waste, producing landfill gas (LFG) very quickly. Landfill gas that is collected is either flared or utilized for clean energy production, including; electricity, heat, and transportation fuel. Currently, there are 503 landfills nationwide that are utilizing LFG for energy production. An additional estimate of 545 landfills could incorporate energy production, but this has yet to be implemented [9]. Landfills are estimated to be the third largest source of anthropogenic methane emissions in the US, because of fugitive emissions and other emissions generated prior to cell closure and gas collection system installation [10, 11]. Current landfill designs and operational practices are generally not capable of collecting the majority of LFG that is quickly generated from these highly putrescible wastes. Hence, there is a growing interest in diverting organics, particularly highly putrescible food wastes, out of landfills to utilize them more efficiently for clean energy production and for compost. Currently, 23 states either ban certain organics, including leaves and grass clippings, or specifically enforce food waste disposal bans at landfills [7, 12]. In addition, large cities such as San Francisco, Seattle, Austin, and Portland have banned food waste disposal at landfills. These bans are expected to become more widespread nationally which raises an important question to be addressed: Is direct landfilling a relevant solution for future management of organic wastes? If not, how can waste management practices be optimized?

The use of waste for energy and nutrient recovery can result in both avoided emissions and increased revenue [13]. If both recoveries are performed together, the environmental and economic benefits can increase [13, 14]. In landfills, organic material residuals/nutrient is not recovered for beneficial reuse primarily due to the cost and difficulty of separating impurities from mixed MSW prior to disposal. Industrial-scale composting of organic waste does not deliver efficient solutions either, since the aerobic decomposition of the organic waste is not suitable for gas recovery. In addition, the composting process often creates significant odor problems resulting in complaints from the surrounding communities. Sending food waste to animal feeding and large-scale industrial composting applications has also been proven to be inefficient approaches.

1.3 Transitioning Traditional Linear Waste Disposal into "Closed-Loop Resource Recovery"

Neither landfilling nor industrial composting provide optimal reutilization of organic waste, and neither can achieve both energy and nutrient recovery in one process from organic waste. Therefore, there needs to be a transition from the current "Traditional Linear Waste Disposal" approach (Fig. 1) to a "Closed-Loop Resource Recovery" approach (Fig. 2) to achieve sustainability and resiliency. An alternative to direct landfilling and/or composting of organic waste is anaerobic digestion (AD) of the biodegradable organic fraction of MSW. AD is an excellent example of the closed-loop process and is considered to be a better solution for converting organic waste into clean energy. It also produces compost-based byproducts, thus extracting the maximum benefits from organic wastes [15, 16]. Closed-loop reutilization approaches can position organic waste as a valuable resource for energy generation, nutrient recovery, and reduced water consumption. In addition, anaerobic digestion will reduce GHG emissions. This is a very important feature of the AD process since research shows that landfills emit 16% of US methane emissions and manure management is responsible for about 10% of US methane emissions [17].

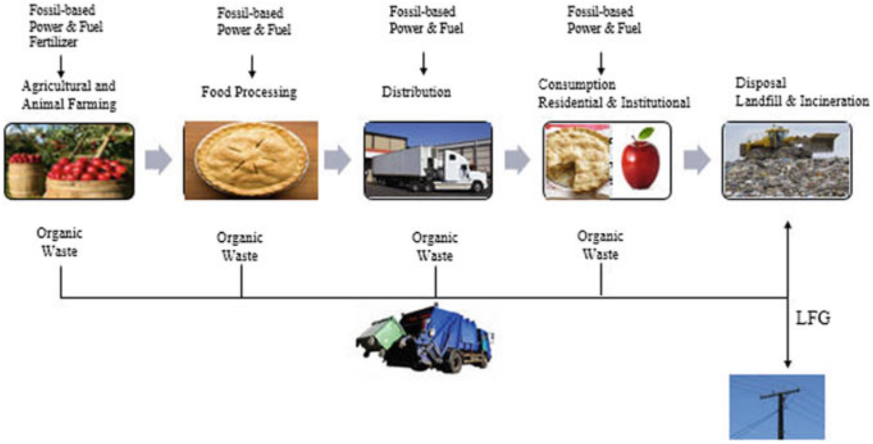


Fig. 1 Linear waste disposal and utilization

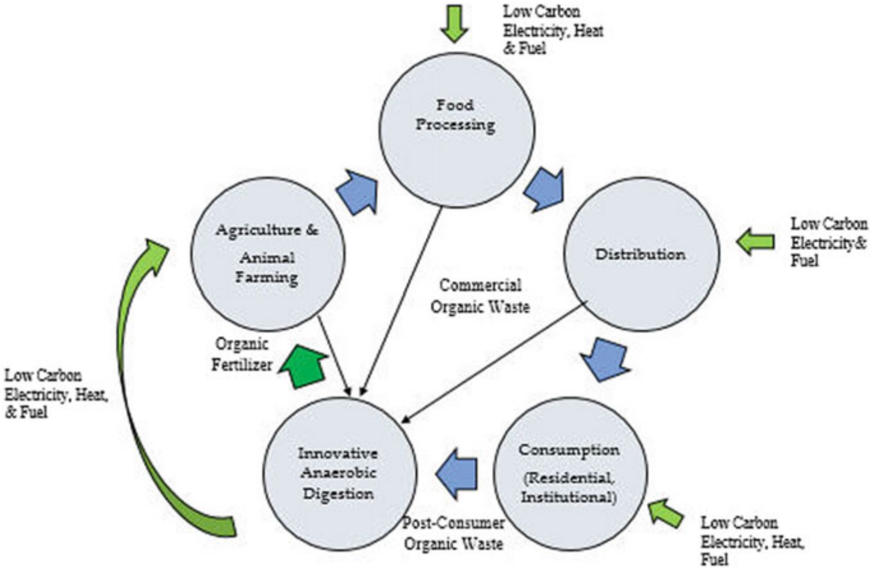


Fig. 2 Closed-loop resource recovery

1.4 Overview of Anaerobic Digestion Systems

Organic waste AD is an existing, well-known, and long practiced waste management and clean energy production technology in Europe, and has received increased attention in the United States. AD technology is an efficient, controlled, and totally enclosed system that breaks down the organic feedstock in the absence of oxygen. AD technology serves as one of the best pathways for treating organic materials because it results in better resource utilization than landfilling or aerobic composting [15]. These waste materials include food waste, yard waste, farm waste (agricultural waste, dairy poultry, and equine manure), biomass treatment byproducts, fats, and oils and wastewater. Biogas, produced from the AD process, can be utilized as a renewable energy source to generate electricity or heat alone or in a combined heat and power form (CHP). Biogas can also be processed into compressed natural gas (CNG) or liquefied natural gas (LNG) for transportation applications to displace fossil fuels after being pre-treated (Fig. 3). In addition, the biosolids and liquid digestate, which are byproducts of AD, can be utilized as fertilizers and soil amendments, thereby displacing fossil-based fertilizers and improving soil quality [16].

The conversion of organic waste to biogas is accomplished through four stages of biochemical reactions, which are known as hydrolysis, acidogenesis, acetagenesis, and methanogenesis [15, 17].

(1) Hydrolysis: The first stage of AD breaks down the organic waste feedstock into its components. In this stage, the following conversion reactions occur:

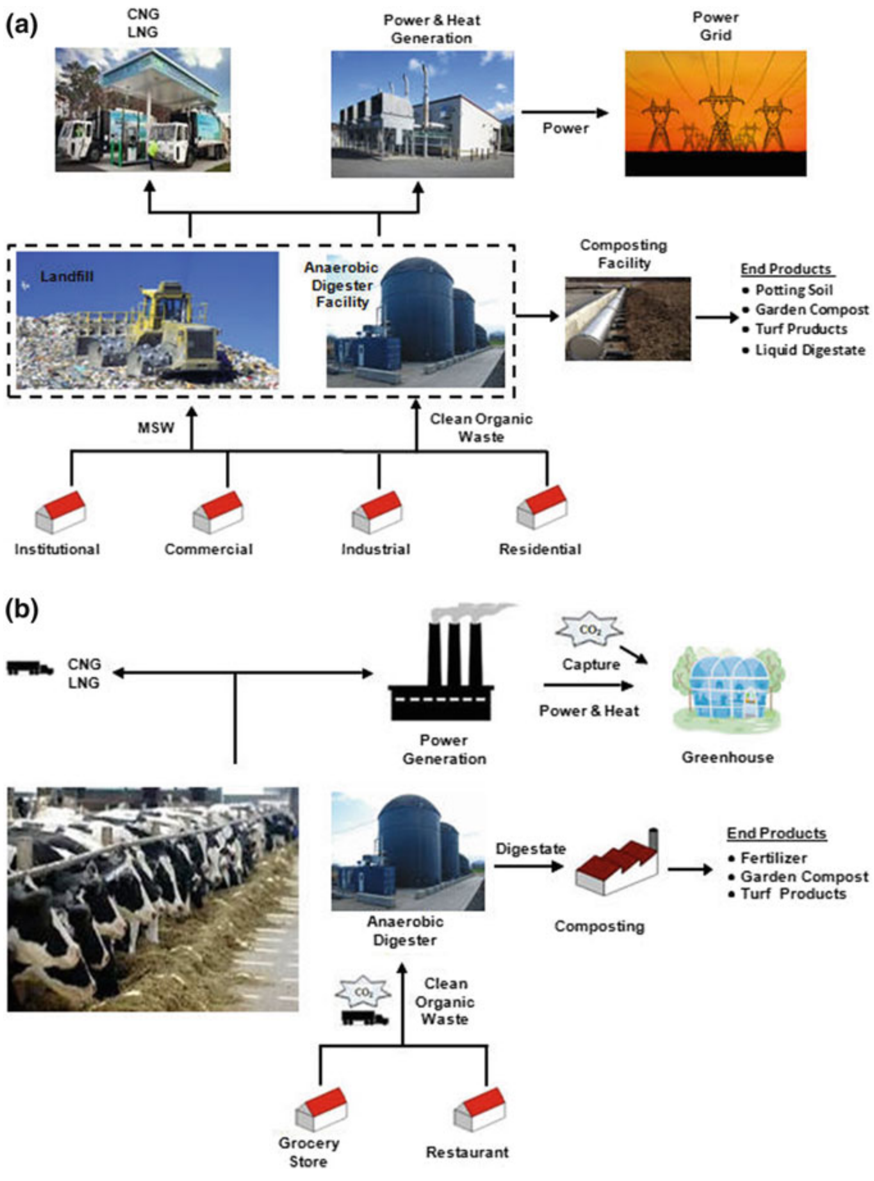


Fig. 3 **a** Co-locating digesters at landfills. **b** Co-locating digesters at dairy farms

1. Lipids → Fatty Acids
2. Polysaccharides → Monosaccharides
3. Protein → Amino Acids.

These reactions are catalyzed by enzymes excreted by bacteria such as cellulase, protease, and lipase [18]. If the biomass polymer is complex, the hydrolysis phase occurs slowly. Therefore, high lignin-containing biomass such as woody waste, is not a feasible feedstock for AD conversion. Carbohydrates, however, can be converted easily to simple sugars [15]. The chemical formula of an organic waste mixture can be presented as $C_6H_{10}O_4$ and the hydrolysis stage can convert the mixed organic waste into simple sugars [18].

$$C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + 2H_2$$

(2) Acidogenesis: During this stage, acid-forming reactions occur and products of hydrolysis are converted into primarily short chain acids such as lactic, formic, propionic, butyric, or succinic acids. In addition, ketones and alcohols are formed.
(3) Acetagenesis: This stage converts long fatty acids formed from the hydrolysis of lipids to acetate through carbohydrate fermentation. CO_2 and H_2 are also produced at this stage. The role of hydrogen as an intermediary is of critical importance to AD reactions in this stage.
(4) Methanogenesis: During this stage, methane is produced. This reaction is very sensitive to pH changes. Optimum pH levels are neutral to slightly alkaline and if the pH level becomes too acidic, essential microorganisms cannot survive and carry out the desired reactions [18, 19].

Currently, researchers are debating whether fermentation of carbohydrates to methane leads the loss of 1/3 of carbon as CO_2 [20].

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$$
$$C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2$$

Emerging research is considering the production of organic acids that are reduced electrochemically [20]. These chemicals can serve as intermediaries for the chemical industry to produce specialty chemicals and fuels to displace fossil-based counterparts. When the alternative three-stage AD approach is fully proven and demonstrated, having organic waste AD infrastructure in place will help to accelerate utilization of this new innovation.

$$C_6H_{12}O_6 \rightarrow 3C_2H_4O_2$$
$$C_2H_4O_2 + 2e^- + H^+ \rightarrow C_2H_5OH + H_2O$$

1.5 Choosing Locations for Anaerobic Digesters

AD facilities are currently being planned throughout the US to divert organic waste from landfills and to produce biogas and compost-based materials as stand-alone facilities. However, identifying a location that is logistically and technically suitable is difficult due to the high costs for infrastructure development; issues with securing clean organic waste; power generation system installation difficulties; and location-based permitting constraints. Stand-alone digesters have additional constraints since in-vessel AD, systems can only accept clean and preprocessed waste and the remaining digestate requires an aerobic composting step, adding to the equipment requirements and operational costs. As an alternative to developing stand-alone AD facilities, locating AD facilities at existing landfills should be considered as a sustainable option. Landfills are an important component of solid waste management systems and can serve as excellent locations to host AD facilities, since they have existing waste delivery and management infrastructure and permits. In addition, landfills that have an installed biogas-to-energy system can easily convert AD generated biogas utilizing the existing infrastructure without the need to install additional power generation capabilities, as would be the case with stand-alone AD systems (Fig. 3a, b). In addition, dairy farms and wastewater treatment facilities are good alternative sites for co-locating AD digesters.

Solid waste management systems (SWMSs) must proactively adapt to changing social norms, policy requirements, waste composition, and evolving energy systems to sustainably manage solid waste in the future [21]. If organic waste treatment options for food and other organic waste to energy applications are demonstrated and assessed systematically with FEW impacts in mind, along with social and economic cost–benefit analyses, then comprehensive data can be provided to landfill, county, municipal, and state decision makers. Overall, SWMS managers would understand the importance, benefits, and risks of available options leading to more informed and sound decision-making. The proposed approach, which includes a detailed implementation plan, can help inform near-term decision-making for sustainable closed-loop resource recovery and economic development. In addition, having a working AD infrastructure in place, demonstrating the value of organic waste for clean energy and bio-based fertilizer generation while reducing GHG emissions, will provide a very clear and easily understood educational opportunity for researchers and decision makers at the local, regional, and national levels.

2 Conclusions

There is an emerging need to find new approaches for solid waste management to maximize organic waste reutilization with the increased population and increased demand for food. In order to achieve energy and nutrient recovery at the same time to form organic waste, landfills can transform their operations for tomorrow's greener, cleaner, and more profitable operations. By hosting anaerobic digesters, landfills can increase their profitability, reduce carbon footprint, and avoid emerging trends of diverting organic wastes from landfills. Landfills can be part of this new approach and support creation of new innovative business plans and can play an essential role in policy-making.

References

1. Advancing sustainable materials management: facts and figures. Environmental Protection Agency, 14 Dec 2016. Web. 20. (Feb 2017). https://www.epa.gov/smm/advancing-sustainable-materials-management-facts-and-figures
2. Rewiring anaerobic digestion. In: ARPA-e workshop, Arlington, VA. (27–28 Oct 2016). https://arpa-energy.gov/sites/default/files/Marc_von_Keitz_Workshop_Introduction.pdf
3. Ahmed SI, Johari A, Hashim H, Ramli M, Alkai H (2013) Landfill gas and its renewable energy potentials in Johor, Malaysia. Int J Emerg Trends Eng Dev 1(3)
4. Arsova L (2010) Anaerobic digestion of food waste: current status, problems, and an alternative product. M.S. Thesis, Columbia University (May 2010)
5. Gunders D (2012) Wasted: how America is losing up to 40% of its food from farm to fork to landfill. NRDC Issue Paper, IP:12-06-B (Aug 2012)
6. Haaren RV, Themelis N, Goldstein N (2013) State of garbage in America. BioCycle Magazine, 2/2010, updated, 5/2011, 3/2012 (April 2013)
7. Hall KD, Guo J, Dore M, Chow CC (2009) The progressive increase of food waste in America and its environmental impact. National Institute of Diabetes and Digestive and Kidney Diseases. PLoS ONE 4(11):e7940
8. Inventory of the U.S. Greenhouse Gas Emissions and Sinks: 1990–2014, U.S. EPA: Washington, DC. Web. https://www.epa.gov/ghgemissions/inventory-us-greenhouse-gas-emissions-and-sinks-1990-2014 (2016)
9. Leib EB, Rice C, Mahoney J (2016) Fresh look at organics bans and waste recycling laws. BioCycle 57(10):16 (Nov 2016). https://www.biocycle.net/2016/11/10/fresh-look-organics-bans-waste-recycling-laws/
10. Levis JW, Barlaz MA, DeCarolis JF, Ranjithan SR (2014) Systematic exploration of efficient strategies to manage solid waste in U.S. municipalities: perspectives from the solid waste optimization life-cycle framework (SWOLF,). Environ Sci Technol 48:3625–3631
11. Levis J, Barlaz M (2011) Is biodegradability a desirable attribute for discarded solid waste? perspectives from a national greenhouse gas inventory model. Environ Sci Technol 45(13):5470–5476
12. Moriarty K (2013) Feasibility study of anaerobic digestion of food waste in St. Bernard, Louisiana. National Renewable Energy Laboratory (NREL) (Jan 2013)
13. Ostrem K (2004) Greening waste: anaerobic digestion for treating the organic fraction of municipal solid wastes. M.S. Thesis, Columbia University, Earth Engineering Center (May 2004)
14. Solano E, Dumas RD, Harrison KW, Ranjithan S, Barlaz MA, Brill ED (2002) Life cycle-based solid waste management-2. Illustrative applications. J Environ Eng 128(10):993–1005 (Oct 2002)
15. Thorneloe SA, Weitz K, Jambeck J (2007) Application of the US decision support tool for materials and waste management. Waste Manag 27:1006–1020
16. Valin H, Sands RD, Van Der Mensbrugghe D, Nelson GC, Ahammad H, Blanc E, Bodirsky B, Fujimori S, Hasegawa T, Havlik P, Heyhoe E, Kyle P, Mason-D'Croz D, Paltsev S, Rolinski S, Tabeau A, Meijl HV, Lampe MV, Willenbockel D (2014) The future of food demand: understanding differences in global economic models. Agric Econ 45:51–67. https://doi.org/10.1111/agec.12089
17. Verma S (2002) Anaerobic digestion of biodegradable organic in municipal solid wastes. M.S. Thesis, Columbia University, Department of Earth and Environmental Engineering (May 2002)
18. Webber M (2012) How to make the food system more energy efficient. Scientific American (Feb 2012)
19. Wlebe K, Gollehon N (2006) A report from the economic research service agricultural resources and environmental indicators, 2006 edition. United States Department of Agriculture, Economic Information Bulletin 16 (July 2006)

20. World Urbanization prospects, United Nations Revision report, 2014. ISBN 978-92-1-151517-6
21. Yazdani R, Barlaz M, Augenstein D, Tchobanoglous G (2012) Performance evaluation of an anaerobic/aerobic landfill-based digester using yard waste for energy and compost production. Waste Manag 32(5):912–919 (Feb 2012)

Production of Ethanol from Municipal Solid Waste of India and Nepal

B. Thapa, S. K. Patidar, N. R. Khatiwada, A. K. KC and A. Ghimire

1 Introduction

Human society cannot avoid the production of waste/used materials. With ample area disposal of the waste and used materials was easy as the generated waste/used materials were less. In Nepal, the per capita generation rate of waste varies from 0.2 to 0.28 kg/p/d and the biodegradable composition holds the share from 50.0 to 65.1% of total solid waste generated [1]. As per the study conducted by Engineering Study and Research Centre Pvt. Ltd. in 2017 [7], the average per capita household waste generation was found to be 0.115 kg/pe.d. However, based on economic status and geographic location, the generation ranged from 0.88 to 0.4 kg/household/day.

Similarly, in India, the per capita waste generation is 0.37 kg/person/day [4]. As per the study conducted by Sharholy et al. in 2008 [18], approximately 40–60% of MSW of India consists of organic fraction, 30–40% of ash and fine earth, 3–6% of paper, and others.

B. Thapa (✉) · N. R. Khatiwada
Department of Environmental Science and Engineering,
Kathmandu University, Dhulikhel, Nepal
e-mail: thapabijay88@gmail.com

N. R. Khatiwada
e-mail: nawa@ku.edu.np

S. K. Patidar
National Institute of Technology, Kurukshetra, Haryana, India
e-mail: skpatidar@nitkkr.ac.in

B. Thapa · A. Ghimire
Soil Water and Air Testing Laboratories Pvt. Ltd., Kathmandu, Nepal
e-mail: anishghimire@gmail.com

A. K. KC
Oxfam, Kathmandu, Nepal
e-mail: kajaykc@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_5

Since the generation of solid waste/used materials has increased significantly, and resources being limited, the increasing pollution level and increasing awareness and understanding of environmental problems among public have increased concerns about the necessity of other treatment options rather than land disposal. Composting, incinerating, and production of different biofuels are some of the treatment options that are gaining importance nowadays. The selection is based on technical, economical, and social factors.

The ever-increasing prices of fuels have led to energy crises in both developing and developed countries that are oil dependent [3]. By April, 2012, Nepal had 10 petroleum price hikes since early 2011 [8]. Similar was the case in India with regular hike in petroleum price. This has generated interest in alternative fuels. Bioethanol is one of them. Environmental and economical advantages for long term are the reason for using ethanol as fuel or additive to existing fuels. Studies show that using E10 (10% ethanol and 90% gasoline) does not need engine modification to the existing engines of vehicles. (Cardona et al. 2010; Mousdale 2008 as cited in [2]).

This is used as an alternative to gasoline. This has higher oxygen content, reduced CO emission, and higher octane number than gasoline. Hence, this can be used as oxygenate additive rather than methyl t-butyl ether (MTBE), which is found to be responsible for groundwater and soil contamination. With the increasing demand of ethanol as fuel, it is gaining popularity as one of the important renewable fuels based on its usage volume and market value [21].

One of the cheapest sources of bioethanol production is to use lignocellulosic materials like crop residues, grasses, sawdust, wooden chips, and solid waste. Conversion to bioethanol can be the linking chain between these two to solve the problem by managing the solid waste to produce cleaner biofuel. Municipal solid waste (MSW) can be an attractive cellulosic resource for production of bioethanol because of it's necessity of managment, easy availability and cost. However, solid wastes are not homogeneous and possible toxic content in them can be problematic in the conversion of waste to ethanol and to other products [20, 19].

The main focus of this study was to produce ethanol from food waste. The specific objectives of this research were to optimize the parameters (factors), namely, temperature and acid concentration for hydrolysis of the selected municipal wastes, to obtain the kinetics of ethanol formation, and to calculate the theoretical ethanol potential of Kathmandu Metropolitan City and Delhi.

2 Methodology

2.1 Solid Waste

Kitchen waste was collected from five houses of Beta colony, Greater Noida, UP for 3 days. The waste was sorted and the organic portion of the waste was sun dried for 3 days and then crushed into fine particles. All the waste was mixed thoroughly.

The sample was put in an airtight container and stored at 4 °C for further analysis. Characterization was limited to analysis of moisture (using [5, 6]), carbohydrate (using anthrone method), and ash content (using [14] of the sample).

2.2 Microorganisms

Saccharomyces cerevisiae was used as the microorganism for fermentation process as it can resist fermentation media up to 20% [22]. It was brought from Indian Agricultural Research Institute, New Delhi. The stock culture was maintained on potato dextrose agar (PDA) medium and inoculation was done using potato dextrose broth (PDB).

300 g of sliced potato was boiled in 1 liter distilled water for 30 min. After that, it was filtered using a cloth. The volume of that filtrate was made 1 L by adding distilled water. It was distributed in four conical flasks: two for preparing PDA medium and two for preparing PDB. For PDA, 5 g dextrose and 5 g agar was added and was boiled until the agar melts. Then, it was autoclaved for 15 min. For PDB, 5 g dextrose was autoclaved for 15 min. It was adjusted to 150 rpm in Caltan incubator shaker.

2.3 Hydrolysis

Acid hydrolysis was chosen as this process is faster, less energy consuming, and higher yield of reducing sugars [9]. Hydrolysis using concentrated acid results in corrosion [16], and hence dilute acid was used in our research. Hence, dilute-acid hydrolysis was chosen for hydrolysis process. For hydrolysis study, different combinations of temperature and acid concentrations were used varying from 1100 to 1500 °C and 0 to 10% sulphuric acid. Duplicate samples were prepared for every combination. 10 g of sample was dissolved in distilled water and conc. sulfuric acid to make the solution of 100 ml. Conical flask of 250 ml capacity was used for this. Acid and distilled water were added so as to make it to the concentration of 0, 2.5, 5, 7.5, and 10%. The different temperatures of 110, 120, 135, and 150 °C were used. The conical flask was covered with aluminum foil and was put into autoclave for 1 h. The reducing sugar was then analyzed. Each day, 10 samples of 5 different concentrations of acid were autoclaved for 1 h. After autoclaving, the samples were tested for reducing sugar using DNS method.

2.4 Fermentation

The combination with the maximum reducing sugar yield was used for studying fermentation. The product was analyzed for ethanol production analysis [24]. Further, fermentation was carried out to analyze the biomass growth [13] with varying substrate concentration. This was done in BioAge fermenter (model Bio-spin O3 A) of 3 l capacity. Temperature and pH were set to 3 °C and 4.5, respectively. The sample used was 10% w/v and inoculums were 2% w/v. The process was run for 5 days. Each day 30 ml sample would be taken out of the fermenter for analysis. Single readings of ethanol concentration and biomass concentration were taken during fermentation process each day.

2.5 Kinetic Models

The biomass growth is assumed to have depended on the concentration of cellulose. The biomass growth is assumed to follow Monod kinetic model that is given by

$$\mu = \mu_{\max} \frac{S}{Ks + S}$$

where

S	Substrate concentration (g/l)
Ks	Half velocity constant (g/l)
$\mu_{\max}$	Maximum specific growth rate (/h).

The kinetics of ethanol formation was checked for Luedeking–Piret equation described in literature review.

$$\frac{\mathrm{d}P}{\mathrm{d}t} = \alpha \frac{\mathrm{d}X}{\mathrm{d}t} + \beta X$$

where α and β are Luedeking–Piret equation parameters for growth- and nongrowth-associated product formation, respectively.

2.6 Instruments and Equipment Used

Following equipment were used for the analysis:

Instruments/equipment	Make and model
Spectrophotometer	Shimazdu UV1800
Incubator shaker	Caltan NSW 159
Centrifuge	Eppendorf centrifuge 5804 R
Furnace	Tonco Muffle furnace
Fermenter	BioAge Bio-spin 03A
Vacuum oven	Biogen
Autoclave	Thermotech Th-043

3 Results and Discussion

3.1 Characteristics of Sample

As per the analysis carried out, the moisture content was 67.9% of total weight. The carbohydrate content of the sample was found out to be 72.62% of dry weight, whereas the ash content was 8.83% of the dry weight. Others constitute 18.55%. The composition of 72.62% total carbohydrate shows the enormous potential for ethanol conversion.

3.2 Hydrolysis Results

3.2.1 Temperature Versus Sugar Yield

Based on the results obtained, for 0, 2.5, and 5% acid, sugar yield was found to be increasing with rise in temperature. For 7.5 and 10% acid concentration, the reducing sugar yield increases up to 135 °C which decreases as the temperature was raised to 150 °C as shown in Fig. 1.

3.2.2 Acid Concentration Versus Sugar Yield

The glucose yield is increased with the increase in acid concentration for 110 and 120 °C. However, after 7.5% concentration, the yield is decreased (Fig. 2).

The optimum condition for maximum reduction in sugar yield was obtained at 7.5% acid concentration at 135 °C yielding 32.636 g/100 g dry weight.

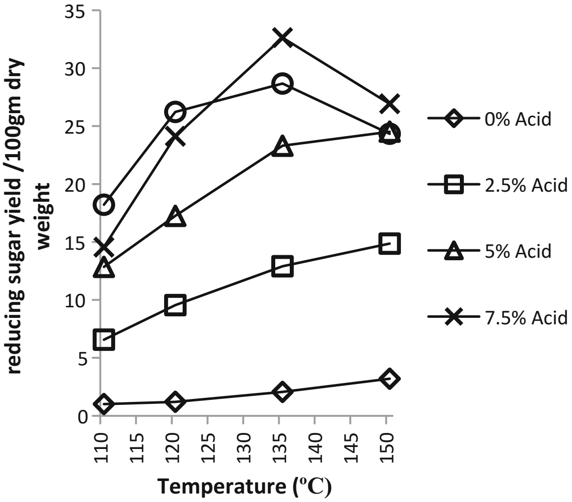


Fig. 1 Reducing sugar yield versus temperature

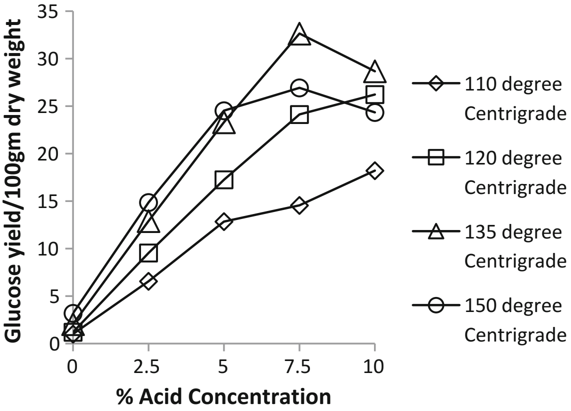


Fig. 2 Glucose yield versus acid concentration

3.3 *Fermentation Results*

The fermentation was carried out for 5 days as adopted by Manikandan and Virthagiri [13]. As shown in Figs. 3 and 4, the concentration of biomass and ethanol were increasing logarithmically. The maximum ethanol concentration reached was 13.78 g/l, whereas the maximum biomass concentration on fifth day was 5.99 g/l. The rate of biomass concentration and ethanol formation was maximum on second day, which increased from 1.22 to 1.81 g/l.d and 3.87 to 3.91 g/l.d, respectively, as shown in Figs. 5 and 6. The rate decreased as the days progressed (Fig. 7).

Fig. 3 Biomass concentration

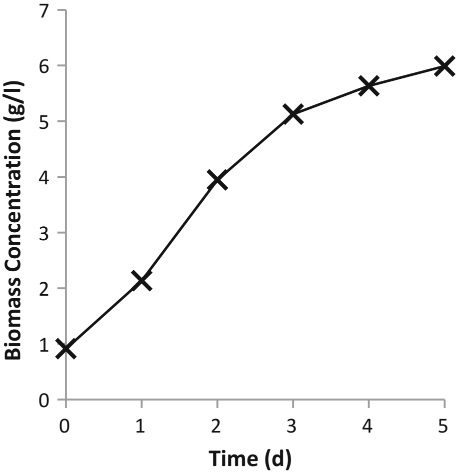


Fig. 4 Ethanol formation

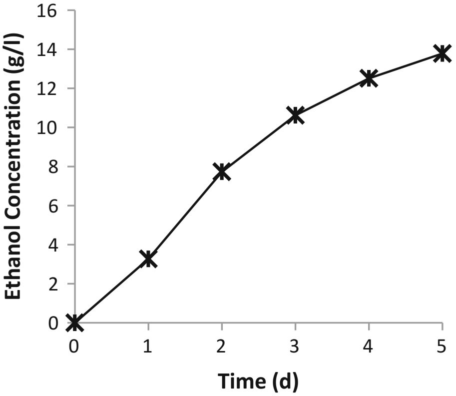
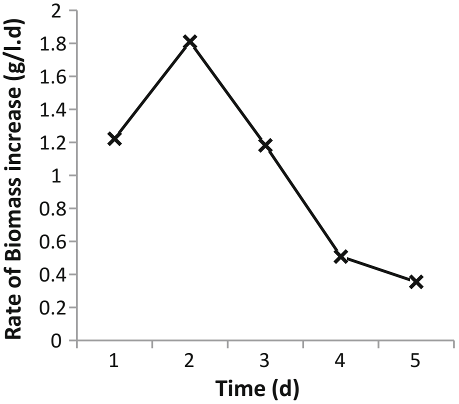


Fig. 5 Rate of biomass formation



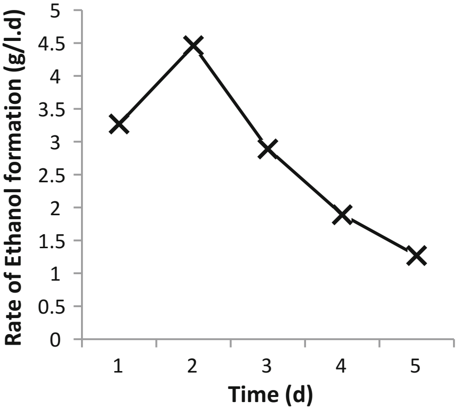


Fig. 6 Rate of ethanol formation

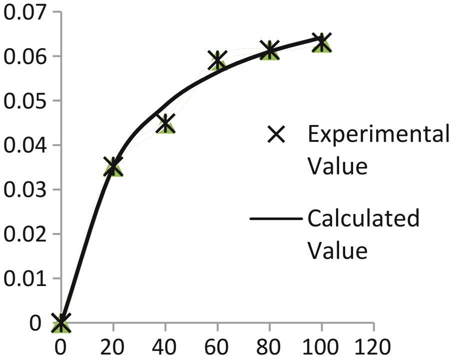


Fig. 7 Specific growth rate versus substrate concentration

3.4 Kinetics of Fermentation

3.4.1 Monod Equation

The Monod equation was found to fit the experimental data obtained. As shown in Fig. 8, the graph between 1/S and 1/μ was almost linear. From those graphs, values of Ks were found to be 26.19 g/l and μ_{max} was 0.08 h^{-1}. The value of Ks was similar to previous studies; however, the value of maximum specific growth rate is lower than that obtained in Manikandan and Virthagiri [13] and Saravanan et al. [17].

3.4.2 Luedeking–Piret Model

From Fig. 9, we can see that the values of α and β are 2.583 and 0.031, respectively.

The high value of α in this experiment implies that the production of ethanol is growth associated and depends on growth rate of biomass.

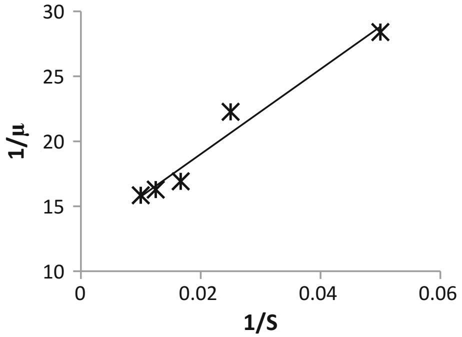


Fig. 8 1/μ versus 1/S graph

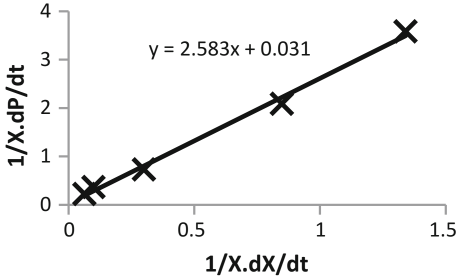


Fig. 9 Specific yield versus specific growth rate

3.5 *Ethanol Potential*

Since the total waste generation data of whole country was not available, the ethanol potential calculation was limited to the capital cities of Nepal and India.

3.5.1 Ethanol Potential for Kathmandu Metropolitan City (KMC)

As per the study conducted by CDIA, 2009 [10] and Thapa et al. [23], the composition of organic fraction being generated and disposed at landfill site of Nepal is 63.22%. The total solid waste generated at KMC being 378.6 tons.

Total organic waste content (ton/day) = 0.632 × 378.6 = 239.27,

Assuming moisture content of 67.9%,

Total dry weight (ton/day) = 0.321 × 239.27 = 76.80,

Ethanol generation (ton/d) (13.78 g/100 g) = 0.1378 × 76.80 = 10.58,

Total ethanol generated (L/d) = 10,580/0.789 = 13,414, and

Based on this study, 1 ton of MSW can generate 35.4 L of ethanol.

3.5.2 Ethanol Potential for Delhi

As per the study conducted by Annepu [4], Delhi alone is producing 11,558 tons of waste per day with the composition of organic waste and degradable being 50.89%.

Total organic waste content (ton/day) = 0.5089 × 11,558 = 5881.87,
Assuming moisture content of 67.9%,
Total dry weight (ton/d) = 0.321 × 5881.87 = 1888.08,
Ethanol generation (ton/d) (13.78 g/100 g) = 0.1378 × 1888.08 = 260.17,
Total ethanol generated (L/d) = 260,177/0.789 = 329,756.42, and
Based on this study, 1 ton of wet waste generates 28.53 L of ethanol.

3.6 Discussion

With the increase in temperature and acid concentration, the breakdown of carbohydrate (starch) and cellulose increases. Hence, with increase in acid concentration and temperature, the reducing sugar yield was found to increase. However, the reducing sugar yield was found to decrease at higher temperature. The decrease in reducing sugar yield at higher temperature can be described as the effect of saturation of reducing sugar especially glucose [12]. As the temperature is increased, the breakdown of carbohydrate especially glucan occurs with increasing temperature. It can be concluded that the reducing sugar yield is basically the function of temperature.

The ethanol produced in our study was 13.7 g/100 g of dry waste. This is very less in comparison to the similar study conducted by Kim et al [11] for food waste in South Korea. They had done enzyme hydrolysis using carbohydrase and cellulose. One possible reason may be that acid hydrolysis yields less reducing sugar than enzyme hydrolysis leading to less ethanol yield. The reducing sugar yield increases as the acid concentration increases. Furfunal can be produced at higher acid concentration and/or higher temperature, which can inhibit fermentation and is toxic to microorganisms which can reduce the ethanol production [15].

Similarly, the maximum specific growth rate in Monod equation is relatively less than obtained by Manikandan and Virthagiri [13] and Saravanan et al. [17]. The possible reasons may be, as described above, the presence of inhibitory chemicals and the presence of some dead cells accounted in biomass concentration which is not calculated in our study.

Similarly, as expected, the rate of biomass and ethanol formation was not maximum on first day, as the yeast needs some time to acclimatize. However, on later days, the rate of biomass and ethanol formation decreased because of decrease in the amount of substrate and increasing amount of product which acts as inhibitory agent.

The ethanol potential of two cities calculated was based on the literature review and results obtained in this study only. The ethanol potential can be even more than the result obtained as only acid hydrolysis was conducted and the results obtained in this study are relatively lower than that obtained in other studies.

4 Conclusion

Ethanol production from organic solid waste can provide a sustainable solution to management of solid waste. The paper investigated the optimal conditions for ethanol production using MSW. During the acid hydrolysis, the sugar yield revealed to be a function of temperature. The sugar yield increases with increase in temperature for low acid concentration and low temperature, and decreases at higher temperature. The optimum condition for acid hydrolysis was found to be 135 °C at 7.5% acid concentration. Waste sample with total carbohydrate of 72.62 g/ 100 g sample gave maximum reducing sugar yield of 32.63 g/100 g sample. Ethanol can be produced efficiently by controlled fermentation techniques from MSW using S. cerevisiae. Fermentation produced 13.78 g of ethanol per 100 g of sample. Monad equation and Luedeking–Piret model of product formation fit the experimental data very well. For, Monod equation, the half velocity constant and maximum specific growth rate were found to be 26.19 g/l and 0.08 h^{-1}, respectively. For Luedeking–Piret model of product formation, the values of α and β were found out to be 2.583 and 0.031, respectively.

References

1. ADB (2013) A report on Solid waste mangement in Nepal: current status and policy recommedation. Asian Developnment Bank, Mandaluyog, Philippies
2. Ahmad F, Tariq AJ, Kamarudin MH, Mel M (2011) Study of growth kinetic and modeling of ethanol production by *Saccharomyces cerevisiae*. Afr J Biotech 16(81):18842–18846
3. Akponah E, Akpomie O (2011) Analysis of the suitability of yam, potato and cassava root peels for bioethanol production using *Saccharomyces cerevisiae*. Int Res J Microbiol 2(10):393–398
4. Annepu RK (2012) Sustainable solid waste management in India. Master of Science in Earth Resources Engineering Thesis, Department of Earth and Environmental Engineering, Columbia University, USA
5. Ehrman T (1998) Standard method for ash in biomass. In: Chemical analysis and testing laboratory analytical procedures. Department of Energy, Midwest Research Institute (MRI)
6. Ehrman T (1998) Standard test method for moisture, total solids, and total dissolved solids in biomass slurry and liquid process samples. In: Chemical analysis and testing laboratory analytical procedures. Department of Energy, Midwest Research Institute (MRI)
7. Engineering Study and Research Centre Pvt. Ltd (2017) Solid waste management baseline study of 60 new municipalities. Solid Waste Management and Technical Support Centre, Kathmandu, Nepal
8. Englishnews.cn (2012) http://news.xinhuanet.com/english/indepth/2012-03/28/c_131494402.htm. Accessed on 5 April 2012
9. Hu R, Lin L, Liu T, Liu S (2010) Dilute sulfuric acid hydrolysis of sugar maple wood extract at atmospheric pressure. Bioresour Technol 101(10), pp 3586–3594
10. Kathmandu Metropolitan City (2009) Project report on Cities Development Initiatives for Asia (CDIA)—Kathmandu Metropolitan City, sponsored by ADB project
11. Kim JH, Lee JC, Pak D (2011) Feasibility of producing ethanaol from food waste. Waste Manage 31:2121–2125
12. Lenihan P, Walker GM, Orozco A, O'Neill E, Ahmad MNM, Rooney DW (2010) Dilute acid hydrolysis of lignocellulosic biomass. Chem Eng J 156:395–403

13. Manikandan K, Virthagiri T (2010) Kinetic and Optimization studies on ehtnaol production from Corn Flour. Int J Chem Biol Eng 3(2): 65–69
14. NREL (1988) Chemical Analysis and testing laboratory analytical procedures. Department of Energy, Midwest Research Institute (MRI)
15. Romero I, Moya M, Sánchez S, Ruiz E, Castro E, Bravo V (2007) Ethanolic fermentation of phosphoric acid hydrolysates from olive tree pruning. Ind Crops Prod 25(2):160–168
16. Ruofei H, Lu L, Liu T, Liu S (2010) Dilute sulfuric acid hydrolysis of sugar maple wood extract at atmospheric pressure. Bioresour Technol 101:3586–3594
17. Saravanan P, Pakshirajan K, Saha P (2008) Growth kinetics of an indigenous mixed microbial consortium during phenol degradation in a batch reactor, Bioresource. Technology 99(1): 205–209
18. Sharholy M, Ahmed K, Mahmood G, Trivedi RC (2008) Municipal solid waste management in Indian cities—a review. Waste Manage 28(2):459–467
19. Shi J, Ebrik M, Yang B, Wyman CE (2009) The potential of cellulosic ethanol production from municipal solid waste: a technical and economic evaluation. University of California, Riverside
20. Shi J, Sharma-Shivappa RR, Chinn M, Howell N (2009) Effect of microbial pretreatment on enzymatic hydrolysis and fermentation of cotton stalks for ethanol production. Biomass Bioenergy 33(1):88–96
21. Taherzadeh MJ, Karimi K (2008) Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review. Int J Mole. Sci 9:1621–1651
22. Talebnia F (2008) Ethanol Production from cellulosic biomass by encapsulated *Saccharomyces cerevisiae*. Doctor of Philosophy Thesis, Department of Chemical and Biological Engineering, Chalmers University of Technology, Sweden
23. Thapa B, Sapkota L, Khanal P (2009) Waste management and leachate treatment at landfill sites of Nepal. B. Tech. in Environmental Engineering Thesis, Department of Environmental Science and Engineering, Kathmandu University, Nepal
24. University of Canterbury (2012) http://www.outreach.canterbury.ac.nz/chemistry/documents/ethanol.pdf. Accessed on 4 Mar 2012

Studies on Increasing Specific Calorific Value of Producer Gas in Auto-gasification of Wooden Pallets by Steam Injection

G. Prabakaran, S. Mathiyazhagan, C. V. Dinesh Kumar, N. Gunaseelan and V. Kirubakaran

1 Introduction

Among renewable energy sources, biomass is one of the most important energy sources of the future. The sustainable power generation from the renewable energy sources is getting more attention from the world. The biomass plays important role in rural areas. The 70% of the population in India is getting 32% of primary energy from biomass only. So the biomass is a very important fuel for those peoples and also a good fuel for gasification. The biomass is most alternative fuel because it is widely spread and naturally available. Biomass gasification is one of the most promising technologies, which can help in developing the future energy systems, which can be efficient and environmentally friendly.

The solid biomass is of different types of wood, straw, municipal refuse, etc. But wood has more energy content compared to other biomass. Gasification is a thermochemical process of converting carbon materials into gaseous products using a gasifier with a gasifying medium such as air, oxygen, and steam either alone or mixture. The main combustible component in the gas is H_2, Co, and CH_4 and small amount of hydrocarbon (such as C_2H_4 and C_2H_6).

According to the Knoef's report (2000), the majority of biomass gasifiers used in the world are downdraft fixed bed gasification (DFBG) type (75%) and fluidized bed system (20%). In the DFBG, the thermochemical reaction stages can be represented in four stages—drying, pyrolysis, oxidization, and reduction, respectively.

The wood is the most available fuel and is a perfect fuel for gasification process. The theoretical air requirement for combustion process of wood was calculated. This will help to achieve an auto-gasification process. Auto-gasification can be explained as thermochemical conversion of solid combustible matter in the biomass

---

G. Prabakaran (✉) · S. Mathiyazhagan · C. V. Dinesh Kumar · N. Gunaseelan · V. Kirubakaran
Rural Energy Centre, The Gandhigram Rural Institute-Deemed University, Dindigul, India
e-mail: prabakarg11@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_6

into gaseous fuel by the bio-oxygen and catalytic ash. Bio-oxygen is the oxygen available in the biomass.

2 Literature Review

Sharma [1] reported that CO and H_2 components of PG and the calorific value are sensitive to reaction temperature. By kinetic modeling, it was found that complete char conversion takes place at a critical reaction temperature of 950 K and critical char bed length of 25 cm. The results obtained by modeling were influenced by the composition of reactants entering the reduction zone and the initial temperature.

As reported by Na et al. [2], the increase of bed height the concentration of H_2, CO, and CH_4 were also increases in the gasification process. However, beyond a certain value of bed height, the gasification became difficult due to excessive pressure drop of oxygen.

In general, gasification involves reaction of raw material with air, oxygen, steam or mixture of them at temperature higher than 700 °C to produce a gaseous product [3]. The resulting gaseous products have useful heating values, and can be used to provide heat and power or as a raw material for the synthesis of chemicals, liquid fuels, or other gaseous fuels [4]. The final product, called the producer gas is a low or medium calorific value fuel gas, depending on the gasifying medium [5].

Gasification under different gasifying mediums such as air, steam, etc., has been reported in the literature [6, 7].

In general, gasifying medium determines the calorific value of syngas produced [8] (Table 1).

Typical gas yield values for wood gasification in a downdraft gasifier are between 2 and 3 Nm^3/kg [11].

Hernández et al. [12] carried out experimental work in entrained flow gasifier in order to evaluate the effect of biomass particle size and the space residence time on the gasifier performance and the producer gas quality. It has been reported that as the concentration of all combustible species (CO, H_2, and CH_4) is increased and thus increases the heating value of gas when the biomass particle size is reduced. However, gas yield was not affected by the particle size and remained almost constant for all particle fuel conversions that are greatly improved to the value of 91.4% from 57.5% as particle size is varied from 8 mm to 0.5 mm.

Rapagnà and Latif [13] reported the steam gasification of ground almond shells, in a continuous, bench-scale fluidized bed reactor in order to evaluate the effects of particle size and operating temperature on the product yield and distribution. They reported that the H_2, CH_4, CO, and CO_2 contents were lower for larger particle size due to the greater heat transfer resistance, and hence the actual temperature inside the larger particles at which the devolatilization process takes place was found less.

Feng et al. [14] investigated the steam gasification characteristics of char derived from cyanobacterial blooms (CDCB) in a fixed bed reactor to evaluate the effect of particle size (<0.15 mm, 0.15–0.3 mm, 0.3–0.45 mm, 0.45–0.9 mm, and 0.9–3 mm)

Table 1 Types of thermal gasification [9, 10]

Gasifying agent	Gasification products	Gas heating value (MJ/m^3)	Advantages	Disadvantages/limitations
Air	CO, CO_2, H_2, CH_4, N_2, and tar	~ 5	• Moderate tar and char content	• Low heating value of gas • Large number of N2 (>50% by volume) • Gas suitable only for boiler and engine applications • Gas transportation through pipeline is difficult • Gas utilization problem can arise in combustion, particularly in gas turbine
Oxygen	CO, CO_2, H_2, CH_4, and tar	~10–12	• Moderate heating value of gas	• Additional cost of providing and using oxygen
Steam	CO, CO_2, H_2, CH_4, and tar	~15–20	• High heating value of gas • H2 rich syngas	• Lower overall efficiency due to loss of carbon in the second reactor • Requires catalytic tar reforming

on gas yield and composition. They found that the gas yield is slightly increased with an increase in particle size. However, their results indicated that gas compositions (H_2, CO, and CH_4) were not affected by particle size and remained almost constant.

3 Materials and Methods

In this process, wood is collected from local and fed to the gasifier. All the woods are of the same size. The wood characteristics have been analyzed before feeding it into the gasifier. The characteristics of the wood are tested using a muffle furnace. Then, the performance of wood has been studied through the following methods/processes:

3.1 Proximate and Ultimate Analysis
3.2 Size of Wood
3.3 Thermal Degradation of Wood
3.4 Thermogravimetric Analysis
3.5 Producer Gas Analyzer

3.1 *Proximate and Ultimate Analysis*

3.1.1 Proximate Analysis

Sl. no.	Constituent	% presented	Temperature	Initial weight (g)	Final weight (g)
1	Moisture	6.98	Max temperature 120 °C	10 g at 30 °C	9.292 g at 120 °C
2	Volatile matter	66.67	Max temperature 400 °C	9.292 g at 120 °C	2.612 g at 400 °C
3	Ash	1.6	Max temperature 600 °C	2.612 g at 400 °C	0.16 g at 600 °C

The fixed carbon content presented in the wood is 24.55% at 10 g (wood).

3.1.2 Ultimate Analysis

Parameters	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur dioxide	Ash
Symbols	C	H	N	O_2	SO_2	Ash
% presented	71.18	14.4	0.76	12.1	0.02	1.6

3.2 *Size of Wood*

The fuel particle size is one of the important parameters affecting the composition, quality, and final applications of the producer gas. The size of the particle influences the gas diffusion speed. All the woods are in rectangle shape only. The result indicated that the smaller particle size was more advantageous for production of high-quality gas. With increasing particle size, the gas composition is decreased (Fig. 1).

3.3 Thermal Degradation of Wooden Pallets

Thermal degradation study was carried out on wood of the same size but different depth levels like small, medium, and large. The temperature of the different levels of depth was monitored continuously by using data loggers and through K-type thermocouples. Also, the surface temperature was monitored. Figure 2 shows the different depth levels that were measured in wood pallet at the points $P1$, $P2$, $P3$, and $P4$. The depth levels are $P1 = 1.5$ cm, $P2 = 3.0$ cm, and $P3 = 4.5$ cm and $P4$ is the surface-level temperature.

Thermal degradation study is carried out using muffle furnace. The furnace set is set to the maximum temperature at 600 °C. From Fig. 3, it is evident that the maximum temperature reaches more than 600 up to 800 °C. Influence of the particle size on volatilization zones is different.

Figure 4 shows the muffle furnace with wooden pallets connected in data loggers through thermocouple wires and the resultant pallets after 600 °C.

3.4 Thermogravimetric Analysis (TGA)

TGA analysis was done by muffle furnace at different temperature ranges. The TGA is used to analyze the changes in physical and chemical properties of materials through the measured weight reduction with respect to time or temperature. The graph shows the result of TGA analysis (Fig. 5).

Fig. 1 Size of wood

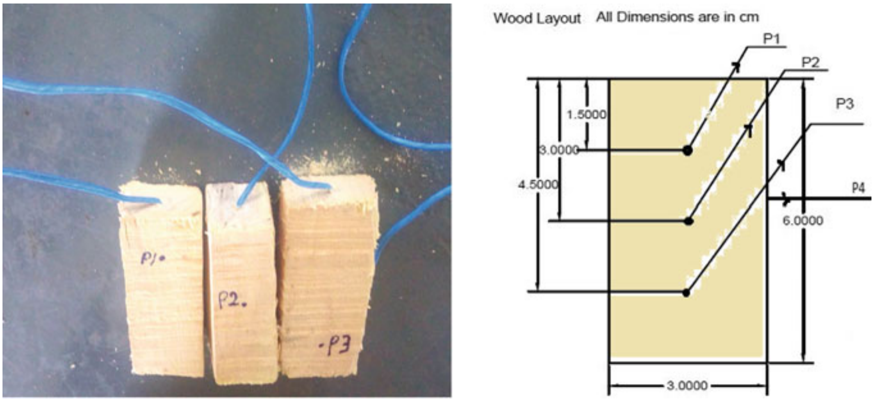


Fig. 2 Wood layout at different levels

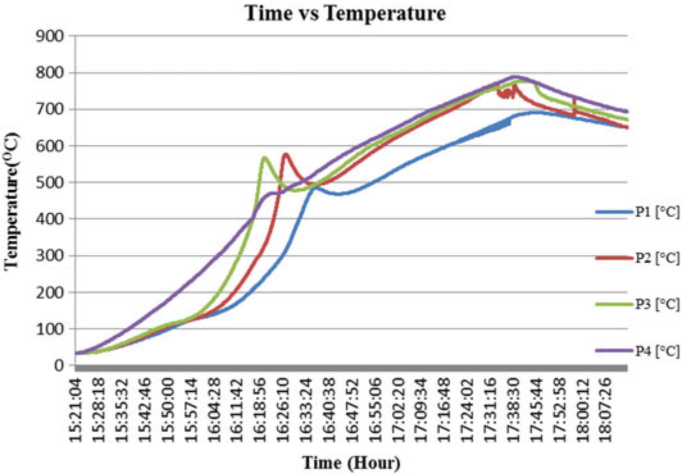


Fig. 3 Thermal degradation of wooden pallets

3.5 Producer Gas Analyzer

This gas analyzer is used to analyze the gasifier outlet gas (syngas or producer gas) compositions like carbon monoxide, hydrogen, carbon dioxide, and sulfur dioxide, and also analyze the calorific value of producer gas.

Fig. 4 Wooden pallets inside the muffle furnace

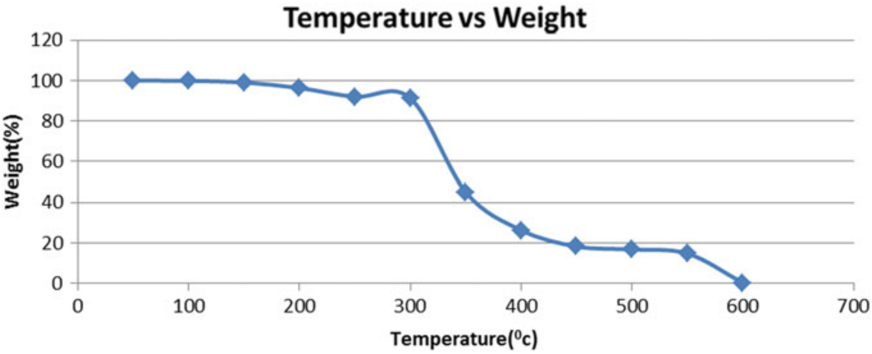


Fig. 5 TGA graph

4 Experimental Setup

The experiment was done by using downdraft gasifier, i.e., the producer gas extracted from reduction zone. Our study was carried out in two phases. First phase is normal gasification and second one is steam gasification.

4.1 Normal Gasification

In normal gasification process, the gasifier bed reaches maximum temperature at 600^0c, and then the fuel is fed. The amount of wooden pallets was 5 kg. This amount is enough to run the gasifier up to 30 min. The readings are taken using producer gas analyzer (Fig. 6).

4.2 Steam Gasification

Steam gasification is a process of steam injection to the gasifier via copper tube. The copper tube is wound and fit to the gasifier bed and the other end is connected to the water bottle. The water is filled in water bottle and also copper tubes are filled with water. The water is evaporated using bed temperature and reacts with producer gas to increase the hydrogen percentage as well as to increase the calorific value of the producer gas. Any additional energy requirement is not needed for steam generation. The gasifier combustion zone temperature was around 450 °C (Fig. 7).

5 Result and Discussion

Figure 8 shows the comparison of carbon monoxide production with and without steam gasification process. Without steam gasification more carbon monoxide is produced than with steam gasification.

Figure 9 shows the comparison of carbon dioxide production with and without steam gasification process. With steam gasification more carbon dioxide is produced than without steam gasification.

Figure 10 shows the comparison of hydrogen production with and without steam gasification process. With steam gasification more hydrogen is produced than without steam gasification.

Figure 11 shows the comparison of calorific value with and without steam gasification process. With steam gasification there is more calorific value than without steam gasification.

Fig. 6 Normal gasification

Fig. 7 Steam gasification process

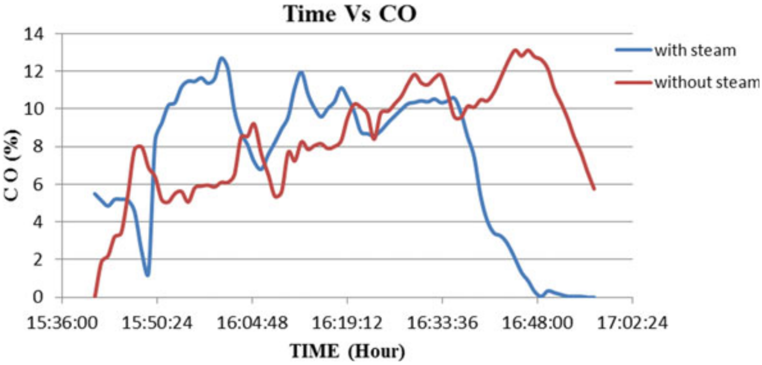


Fig. 8 Time versus carbon monoxide

Figures 12 and 13 show the thermal images of producer gas burned. The flame temperature of the producer gas burned is noted. With steam flame temperature is more compared to without steam flame temperature.

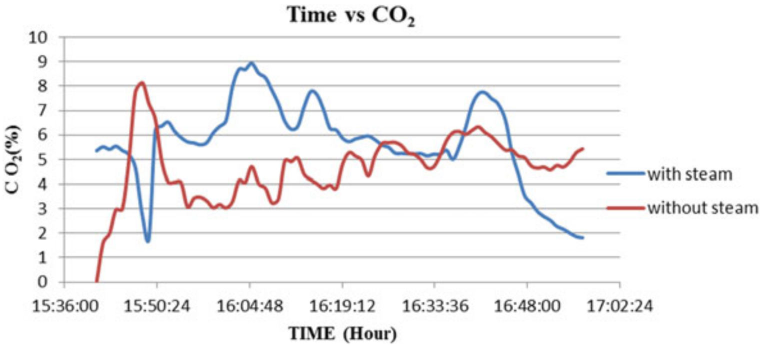


Fig. 9 Time versus carbon dioxide

6 Conclusion

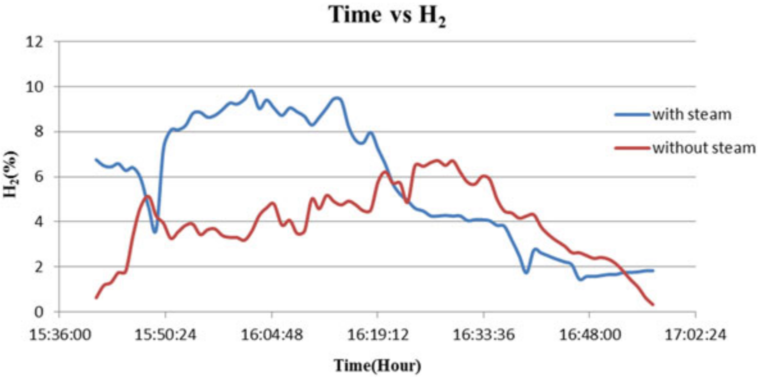


Fig. 10 Time versus hydrogen

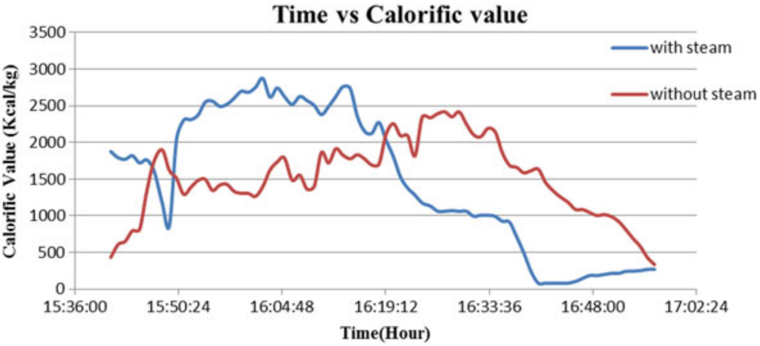


Fig. 11 Time versus calorific value

Fig. 12 Without steam

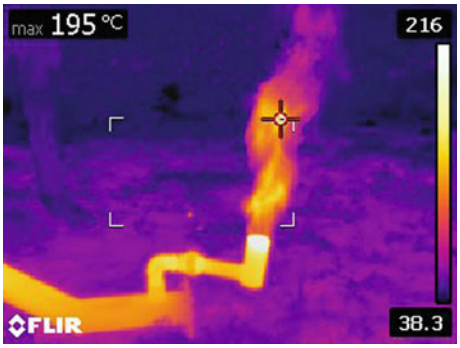


Fig. 13 With steam

In gasification process, the flamed gases are carbon monoxide and hydrogen. The calorific value of the producer gas is low and also depends on these gases. The increase in hydrogen percentage of producer gas increases its calorific value. In our work, the increase in calorific value is achieved through hydrogen enrichment using steam injection. The flame temperature measurement using thermal imager is an additional advantage.

Hydrogen production: Without steam = 6.708% and with steam = 9.807%
Calorific value: Without steam = 2257 kcal/m^3 and with steam = 2874 kcal/m^3
Flame temperature: Without steam = 195 °C and with steam = 263 °C.

Acknowledgements The authors gratefully acknowledge UGC for funding the M.Tech. Renewable Energy under Innovative Programme Scheme.

References

1. Sharma AK (2008) Equilibrium and kinetic modelling of char reduction reactions in a downdraft biomass gasifier: a comparison. Sol Energy 82:918–928

2. Na JI, Park SJ, Kim YK, Lee JG, Kim JH (2003) Characteristics of oxygen-blown gasification for combustible waste in a fixed-bed gasifier. Appl Energy 75:275–285
3. Rezaiyan J, Cheremisinoff NP (2005) https://books.google.co.in/books?hl=en&lr=&id=MEluBwAAQBAJ&oi=fnd&pg=PR2&dq=+Rezaiyan+and+Cheremisinoff,+2005&ots=AN7c3VAwi4&sig=Zx6GlHXOG__GkHGCPNDTRnm7x4#v=onepage&q=Rezaiyan%20and%20Cheremisinoff%2C%202005&f=false
4. lle Collot A-G (2006) Matching gasification technologies to coal properties. Int J Coal Geol 65:191–212
5. Subbarayudu K (2002) Liquid fuels from thermochemical conversion of biomass. PhD thesis. Indian Institute of Technology, Bombay, India
6. Guangul FM, Sulaiman SA, Ramli A (2012) Gasifier selection, design and gasification of oil palm fronds with preheated and unheated gasifying air. Bioresource Technol 126:224–232
7. Gokon N, Izawa T, Kodama T (2014) Steam gasification of coal cokes by internally circulating fluidized-bed reactor by concentrated Xe-light radiation for solar syngas production. Energy 1–9
8. Bhavanam A, Sastry RC (2011) Biomass gasification processes in downdraft fixed bed reactors: a review. Int J Chem Eng Appl 2(6):425–433
9. Bridgwater AV (2003) Renewable fuels and chemicals by thermal processing of biomass. Chem Eng J 91:87–102
10. Wang L, Weller CL, Jones DD, Hanna MA (2008) Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production. Biomass Bioenerg 32:573–581
11. Martínez JD, Mahkamov K, Andrade, Electo E. Silva Lora. Syngas production in downdraft biomass gasifier and its application using internal combustion engines. Renewable Energy 38 (2012) 1–9
12. Hernández JJ, Aranda-Almansa G, Bula A (2010) Gasification of biomass wastes in an entrained flow gasifier: Effect of the particle size and the residence time. Fuel Process Technol 91:681–692
13. Rapagna S, Latif A (1997) Steam gasification fluidised of almond bed reactor: temperature and sheels influence in a of size on product distribution. PIH S0961-9534(96)00079-7
14. Yan F, Zhang L, Hu Z, Cheng G, Jiang C, Zhang Y, Xu T, He P, Luo S, Xiao B (2010) Hydrogen-rich gas production by steam gasification of char derived from cyanobacterial blooms (CDCB) in a fixed-bed reactor: influence of particle size and residence time on gas yield and syngas composition. Int J Hydrogen Energy 35:10212–10217

Value Added By-products Recovery from Municipal Solid Waste

S. Dutta, D. Neela Priya, B. Chakradhar and T. S. Sasi Jyothsna

1 Introduction

In the current scenario, around 90 million tons of domestic or household waste, also known as municipal solid waste (MSW) is generated annually from India. A major portion of MSW (45%) consists of organic fraction like paper, vegetable waste, food waste, wood, etc., followed by (30%) inorganic waste like metals, plastics, glass, etc., and the rest (25%) being other inert waste. In major cities and towns, municipalities are involved in collection and transportation of MSW to designated sites for disposal [12]. The urban society generates amass volume of solid material as throw out due to the brisk elevation in production and consumption, This results in substantial increase in waste generated from households, commercial, public, and institutional areas. Hence, waste generation is a never-ending and ever escalating problem at all levels of its generation. The inadequacy of land, infrastructure, handling, and disposal facilities in bigger cities are some of the major challenges faced in municipal waste management. The site selection is an important task in identifying and selecting a proper disposal site. However, failure in identification of new sites for disposal of MSW and lack of space for expansion of existing facilities are some hidden threats leading to indiscriminate dumping and open burning of waste polluting the surrounding land, air, and water. In majority of states, the MSW is disposed in unauthorized and unscientific ways of dumping in low-lying areas or open burning, which involve a major threat to the environment and also to personal safety.

One of the major unforeseen causes of soil and groundwater quality deterioration is the rapid shoot up in industrialization and population [15, 21]. The increased dumping of huge quantities of domestic solid wastes in open area leads to an adverse impact on various environmental components [18]. In the low-lying areas, leachate

S. Dutta · D. Neela Priya · B. Chakradhar · T. S. Sasi Jyothsna (✉)
Environmental Consultancy, Ramky Enviro Services Private Limited, Ramky Grandiose,
Ramky Towers Complex, Gachibowli, Hyderabad, India
e-mail: srisasijyothsna.t@ramky.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_7

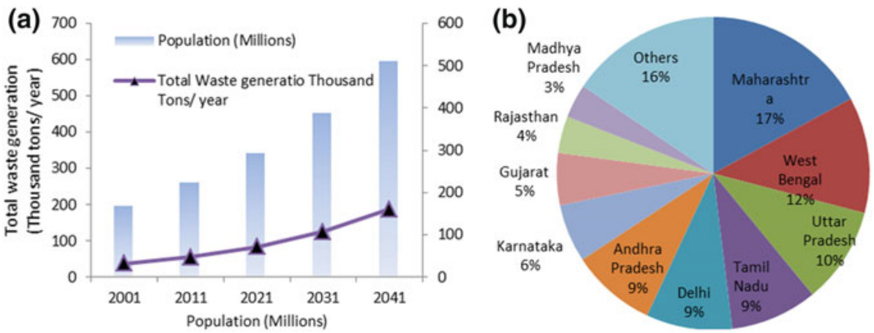


Fig. 1 **a** Waste generation in India in relation to increase in population. **b** State wise waste generation in India

generation may prominently be envisaged when the dumped solid wastes, come into contact with groundwater or rainwater [1]. The toxic compounds may enter groundwater and/or surface water through leachate runoff making the water sources unfit for consumption or for any other use [3, 13, 14, 22]. A study conducted reveals that the MSW leachate affects the nearby soil with adverse effects on the growth of the plant such as *Oryza sativa* [17]. Hence not only the groundwater and surface water even soil in nearby areas would be affected if the MSW is not scientifically handled and properly managed. Apart from these, MSW, if indiscriminately dumped in open would lead to soil and air pollution, or sometimes may become hazardous creating problems like fire accidents and dump slide like the recent Deonar dumpsite in Mumbai and Ghazipur dumpsite in Delhi.

1.1 Current Scenario in the Country

In India, MSW management is governed by Municipal Solid Wastes Rules first introduced in 2000 and revamped in 2016. According to the CPCB Report 2013, the majority of municipal corporations do not have channelized action plans for ratifying and implementation of the rules. No city can claim complete separation of waste at source of generation and it is observed that on an average, only around 70% of total generated waste is being collected. Most of the uncollected domestic waste is either mixed up and/or lost through indiscriminate disposal methods in urban areas. Studies reveal that a meager portion of only 12.45% of collected waste is disposed properly through scientifically reliable processes while the rest is disposed in open dumps [30]. The movement of wastes across jurisdictional boundaries (e.g., township, county, and state) has been an unremitting concern over the past few years, as neighborhood states and countries, without sufficient local capacity for handling and treatment, ship their wastes to other locations. Strict legislation and laws are being imposed to counter the problems of trans-boundary movement of wastes (Fig. 1).

In India, approximately 0.62 kg/person/day of MSW is generated in cities and around 0.17 kg/person/day of MSW is generated in small towns [10], consisting of approximately 40–45% of organic, and majority of the rest being potentially recyclable portion [19]. The generation of waste and its separation is influenced by various factors like the number of people in a family, the level of education and their monthly income, location of household, peer influence, gender, and land size [6, 23, 29]. Launched on October 2, 2014, by the Government of India, the "Swachh Bharat Abhiyan" or Swachh Bharat Mission (SBM) (Clean India Mission) was created to deal with the very issues of waste management, cleanliness, and sanitation on a national level. According to the report published by Ministry of Drinking Water and Sanitation (MoDWS), budget allocations were elevated by 24% from FY 2013–14 to FY 2014–15 exclusively for SBM. In FY 2015–16, an amount 3625 crores has been allotted for SBM—an increase of 27% compared to the erstwhile financial year. Central government incentive for the SWM projects will be in the form of a maximum of 35% Grant for each project. Moreover, a minimum surplus amount equivalent to 25% of GoI funding, costing to Rs. 4874 crores shall be funded by the States as State/ULB share [24].

1.2 Regulatory Affairs

In an Affidavit filed by the Government of Telangana before NGT, it is affirmed that the state has 73 ULBs which generate 7270 TPD of solid waste, of which 6596 TPD is lifted from door-to-door collection covering up to 86% of the total waste generated in the state. Only GHMC (Hyderabad) has the facility for complete processing and disposal. The Telangana state renewable energy development corporation Ltd., (TSREDCO) is also concentrating on energy projects based on municipal solid wastes.

2 Broadway Structure of Municipal Solid Waste Management

MSW consists of two categories of items, viz. organic and nonorganic. Organic fractions are either compostable or combustible. Besides, it may contain recyclables like metal, glass, plastics, etc., and inerts like bricks, stones, sand silt, etc. All available technologies aim at harnessing compostable fractions for producing compost and combustible fractions for power or steam generation. MSW collected in Indian cities is mixed as there is no system of source segregation in place. Hence, it is highly heterogeneous in shape, size, density nature, and color making it difficult to adopt any single proven technology for perfect segregation and processing (Fig. 2).

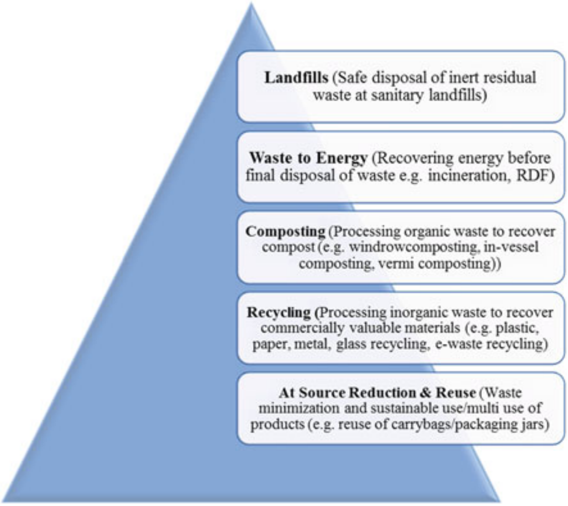


Fig. 2 General municipal solid waste management practices in India

2.1 Overview of MSW Treatment in Hyderabad

Hyderabad, the capital of Telangana state has a current population of around 6.8 million (3,943,323 persons as per 2011 census), generates an approximate quantity of 3500 MT of garbage every day. This garbage is collected is transported in covered vehicles to waste processing unit established for MSW treatment and disposal consisting of composting plant and refuse-derived fuel (RDF) for processing of around 4500 TPD of MSW, which is well equipped with various presorting and treatment facilities of MSW along with sanitary landfill facility, composting facility, RDF plant, plastic recycling facility, and leachate treatment plant that contribute to generation of value products like compost and RDF.

2.2 Description of MSW Treatment Process Adopted

The following procedure is followed for the treatment of MSW generated from Telangana state.

2.3 Pre-segregations

The incoming MSW would be first passed through a shaftless rotary screen known as trammel screen with screening size 100 mm. The undersize waste obtained after screening with less than 100 mm, predominantly consist of compostable material will be sent to composting pad. The oversize will pass through a sorting belt where big inerts like stones, recyclables like plastics, glass bottles, pet bottles, etc., will be handpicked manually. The rest would pass through a magnetic separator where ferrous material will be separated.

Screening is done in two parts. In the first section known as preparatory section, the material will be passing through screens of up to 16 mm size. The oversize material will be sent to RDF section since the rejects of screening will contain a lot of combustible material. The undersize will be stored in curing shed where further biodegradation will happen. After 1 month of curing, it will be taken up for further screening. In the secondary screening, it will pass through screens of smaller holes to produce compost of size less than 4 mm in size. Sand also will be removed using a specific gravity separator which will be dumped in sanitary landfill facility. Then, the remaining organic fractions and biodegradables will be undertaken in a compost facility (Fig. 3).

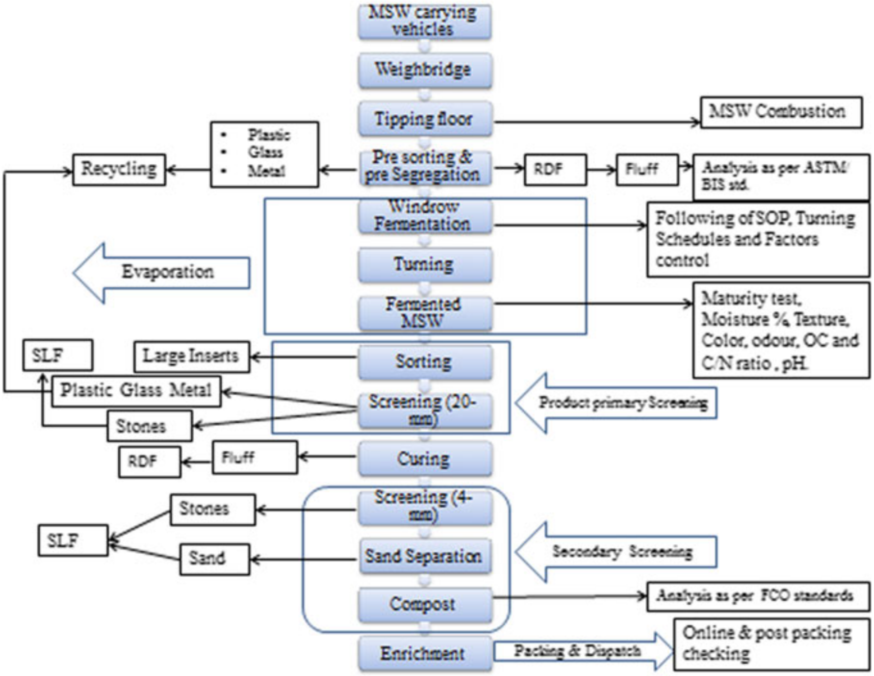


Fig. 3 Operational flowchart in MSW treatment for waste generated in Telangana state

2.4 Composting

It is the natural aerobic process of decomposition of organic solid wastes by microorganisms resulting in humus-like product, which is called compost [20]. It is a rich source of organic matter with plant growth-promoting properties and plays an important role in enhancing soil fertility, thus finding its contribution in agricultural production. Nutrient-rich compost helps in wholesome improvement of soil character by enriching the physicochemical and biological properties of soil in which it is applied.

Factors affecting aerobic composting

- Adequate population of aerobic microbes: This is ensured by inoculating the compostable mass with specially developed biological inoculums containing effective strains of aerobic microbes.
- Adequate moisture: This is done by spraying inocula biomass with an appropriate quantity of water periodically to maintain the desired moisture level.
- Proper aeration: This is ensured by turning the heaps regularly as and when required.

Composting activity consists of two processes, i.e., biological process on the composting pad (windrows) for 1 month and thereafter mechanical process of sequential screening. The daily arrival of waste from the pre-segregation section will be treated with biological inocula and is formed into separate windrows of regular shape. Each windrow will be turned every week. After 4 weeks, the material will be tested for maturity of composting.

The end product will be further enriched with useful biofertilizers and biocontrols like the N_2-fixing *Azatobactor*, *Azospirillum* which can extract nitrogen from air and phosphate-solubilizing bacteria (*Bacillus megaterium*) which can solubilize insoluble form of phosphorous in soil and antimicrobial activity exhibiting *Trichoderma viride*, *Pseudomonas fluorescence*, which acts as a biocontrols against plant pathogens. Using mixed fungal inoculum indicates changes in pH and C/N ratio aiding rapid composting [5]. The compost is a valuable input for agriculture as well as horticulture. The possibility of utilizing the composted municipal solid wastes (MSWs) was reported by Ingelmo et al. [8] as an alternative substrate for application in ornamental plants and which improved the re-vegetation of a closed landfill.

2.5 Refused-Derived Fuel

The energetic valorization of wastes has a significant role in the waste management strategies with legislation and technical notes arising in order to classify and normalize alternative fuels in the electric power plants [2]. The derived fuel from refuse can be better used in the form of gas or oil, in either conventional devices like classic engines or heaters and/or in high-efficiency devices like gas turbines, fuel cells, etc.

[27] It can also find its role alternatively as a chemical source or as raw materials for other processes. The oversize waste from pre-segregation/presorting section comes to RDF section. It is passed through magnetic separator and thereafter through a shredder for size reduction up to 15 mm. It is further passed through a screen of 15 mm size to remove fine sand and silt which are not combustible. The end product will be passed through a densifier. Finally, briquettes come out through the mold which can be used as an alternative to conventional fossil fuels like coal. The RDF has an important role as additive of fossil fuels, allowing economical savings but, moreover, the reduction of CO_2 and other greenhouse effect gases emissions.

2.6 Potential Use of Landfill Leachate

The faint brown to dark (black) colored liquid that comes out through the landfill due to percolation/seepage of rainwater or snow or moisture present in the waste is called leachate. The resulting effluent is a hazardous mixture which generally comprises of four major groups of pollutants: dissolved organic matter (COD, TOC), inorganic macro components (Ca, Na, Cl, Fe, etc.,) heavy metals (Cd, Cu, Zn, Cr, etc.,) xenobiotic compounds (pesticides, aromatic hydrocarbons, etc.), and also pathogenic microorganisms. The composition of landfill leachate is highly heterogeneous and site-specific which depends on the landfilling technology adapted, the type of waste in landfill, and the degree of waste degradation. A general set of practice on toxicity assessment exists to understand the possible health risk associated with the leachate exposure that has persuaded researchers into characterizing chemical and microbial constituents of landfill leachates. The landfill leachate generated in the treatment facility is presently not being explored for valuable product, however, it has been proposed for phytoremediation of leachate through the cultivation of nonedible crops like oil-yielding crops that would not only reduce the quantity of leachate generated but generate biofuel. Presently, the leachate is sprayed on the heap of waste for maintaining moisture and microbial population to enhance biodegradation of waste and a part of it is processed under RO treatment and reused.

Though studies reveal the presence of pathogenic microorganisms in landfill leachates, there is not much attention paid on the identification of health impacts associated with landfill leachate-borne pathogens. Some pathogenic species of *Salmonella*, *Clostridium, Enterobacter,* and *Pseudomonas* coliforms, etc., have been identified commonly at municipal solid waste sites [9]. Lai et al. [11] reported the application of old raw leachate upon wet waste bed aiding in digestion as the old leachate showed cellulolytic activity for degradation of the fresh leachate due to the presence of cellulolytic and methanogenic bacteria. In a study conducted, leachate was successfully used as a substrate in microbial fuel cell (MFC) and electricity could be generated from both single and dual chamber MFCs. The complex organic compounds of leachate could be used to generate electrical energy in MFC through anaerobic oxidation catalytically enhanced by microorganisms. Studies were conducted where sludge from wastewater treatment plant is used in brick manufacturing with noting factors as brick shrinkage, water absorption, and compressive strength [26]. Attempts have been made to incorporate waste in the production of bricks textile effluent treatment plant (ETP) sludge, petroleum effluent treatment plant sludge [16]. Also, scopes are finding to utilize the after treated leachate to be used for curing while construction. Solid state anaerobic digestion, with leachate recirculation, is found to be suitable for exploiting manure with a high solid content [4]. Nowadays, phytoremediation is also an emerging technology for the treatment of landfill leachate.

3 Alternate Technologies

Many research studies and practical applications were carried out in India and around the world for properly managing and scientific treatment of the municipal solid waste.

3.1 Waste to Energy Concept

The organic fraction of MSW can be channelized for recovering energy in the form of biodegradable as well as nonbiodegradable fraction through thermochemical and biochemical methods. Bio-methanation and incineration of RDF pellets are currently the preferred power generation technologies from MSW. Plasma pyrolysis, fermentation, laser, and microwave waste destruction are some of the emerging technologies that are being upscaled for commercial purpose with a convincible application under Indian conditions.

3.2 Biohydrogen

Biohydrogen is the H_2 obtained from dark fermentation of organic wastes produced by microalgae and bacteria. Venkata Mohan [25] has reported that for the production of biohydrogen, the biomass can be derived from woody biomass, agricultural residues, industrial wastewater, and organic fraction of MSW. Bio-hydrogen production using waste is a sustainable technology for future energy demands and simultaneously, it also contributes to the growth of a bio-based economy [28].

3.3 Pyrolysis

The thermochemical process, in which carbon-containing waste is subjected to decomposition at higher temperatures in an oxygen-free inert environment to produce bio-char, bio-oil, and gases, which have potential fuel properties, is called pyrolysis. In a comparative life cycle assessment model, the study between incineration and pyrolysis gasification, the pyrolysis method proved to have lower global warming potential due to lower residual production. It is one of the emerging technologies which are found to have the least impact on environment.

4 Conclusions

Municipal waste is an ever increasing burden of waste that has to be understood, accepted, and worked on constantly by the public, Government, and ULBs in cooperation with each other. The minimization of waste through reduce, recycle, recover, and reuse at source of generation would bring down major task of managing and treating it. However, the current treatment facilities should be improved to obtain value products as discussed in this paper that finds application in industry or agriculture. High priority should be given to treatment facilities offering waste to energy and material recycling and recovery. Constant research and projects should be encouraged on finding solutions to MSW-related issues through proper funding and collaborative works to find solutions that reach the public in time. Increased manpower as rag pickers, proper segregation of waste, integrated and scientifically sound waste treatment strategies, recycling of plastic, paper, etc., generation of microbial-rich compost, high calorific RDF, waste to energy, use of landfill cover and leachate for growing nonedible cash crops/oil-yielding crops, etc., should all be an integral part of a treatment facility that work hand in hand to minimize the problems created by MSW generation.

References

1. Akinbile CO, Yusoff MS, Shian LM (2012). Leachate characterization and phytoremediation using water hyacinth (Eichorrniacrassipes)
2. Brás I, Silva ME, Lobo G, Cordeiro A, Faria M, de Lemos LT (2017) Refuse derived fuel from municipal solid waste rejected fractions-a case study. Energy Proc 120:349–356
3. Cumar SK, Nagaraja B (2011) Environemntal impact of leachate characteristic on water quality. Environ Monit Assess 178(1–4):499–505. https://doi.org/10.1007/s10661-010-1708-9
4. Degueurce A, Tomas N, Le Roux S, Martinez J, Peu P (2016) Biotic and abiotic roles of leachate recirculation in batch mode solid-state anaerobic digestion of cattle manure. Biores Technol 200:388–395
5. Dutta S, William P, Sarangi BK, Lokhande SK, Purohit HJ, Vaidya AN (2016) Response of anaerobic digester sludge for activator aided rapid composting and its effects on compost quality. Int J Waste Resour 6(2):1–6
6. Ekere W, Mugisha J, Drake L (2009) Factors influencing waste separation and utilization among households in the Lake Victoria crescent, Uganda. Waste Manage 29(12):3047–3051
7. http://tnredcl.telangana.gov.in/MunicipalWasteBasedPowerProjects.aspx
8. Ingelmo F, Canet R, Ibanez MA, Pomares F, García J (1998) Use of MSW compost, dried sewage sludge and other wastes as partial substitutes for peat and soil. Biores Technol 63(2):123–129

9. Jones DL, Williamson KL, Owen AG (2006) Phytoremediation of landfill leachate. Waste Manage 26(8):825–837
10. Kumar S, Bhattacharyya JK, Vaidya AN, Chakrabarti T, Devotta S, Akolkar AB (2009) Assessment of the status of municipal solid waste management in metro cities, state capitals, class I cities, and class II towns in India: an insight. Waste Manage 29:883–895
11. Lai TE, Nopharatana A, Pullammanappallil PC, Clarke WP (2001) Cellulolytic activity in leachate during leach-bed anaerobic digestion of municipal solid waste. Biores Technol 80(3):205–210
12. Mor S, Ravindra K, Visscher AD, Dahiya RP, Chandra A (2006) Municipal solid waste characterization and its assessment for potential methane generation: a case study. Sci Total Environ 371(1–3):1–10
13. Naqa AE (2004) Aquifer vulnerability assessment using the DRASTIC model at Russeifa landfill, northeast Jordan. Environ Geol 47:51–62. https://doi.org/10.1007/s00254-004-1126-9
14. Raju NJ (2012) Evaluation of hydrogeochemical processes in the Pleistocene aquifers of Middle Ganga Plain, Uttar Pradesh, India. Environ Earth Sci 65:1291–1308. https://doi.org/10.1007/s12665-011-1377-1
15. Raju NJ, Shukla UK, Ram P (2011) Hydro geochemistry for the assessment of groundwater quality in Varanasi: a fast-urbanizing center in Uttar Pradesh, India. Environ Monit Assess 173(1–4):279–300. https://doi.org/10.1007/s10661-010-1387-6
16. Raut SP, Ralegaonkar RV, Mandavgane SA (2011) Development of sustainable construction material using industrial and agricultural solid waste: a review of waste-create bricks. Constr Build Mater 25(10):4037–4042
17. Rong L, Zhang C, Jin D, Dai Z (2017) Assessment of the potential utilization of municipal solid waste from a closed irregular landfill. J Clean Prod 142:413–419
18. Sharholy M (2007). Solid waste management and its impact on the groundwater system in parts of Delhi. Dissertation, JamiaMilliaIslamia (A Central University)
19. Sharholy M, Ahmed K, Mahmood G, Trivedi RC (2008) Municipal solid waste management in Indian cities: a review. Waste Manage 28:459–476
20. Singh RP, Ibrahim MH, Esa N, Iliyana MS (2010) Composting of waste from palm oil mill: a sustainable waste management practice. Rev Environ SciBiotechnol 9:331–344
21. Singh S, Raju NJ &Nazneen S (2015a) Environmental risk of heavy metal pollution and contamination sources using multivariate analysis in the soils of Varanasi environs, India. Environ Monit Assess 187. https://doi.org/10.1007/s10661-015-4577-4
22. Singh S, Raju NJ, Ramakrishna C (2015) Evaluation of groundwater quality and its suitability for domestic and irrigation use in parts of the Chandauli-Varanasi region, Uttar Pradesh, India. J Water Resour Prot 7:482–497
23. Sujauddin M, Huda SMS, Hoque AR (2008) Household solid waste characteristics and management in Chittagong, Bangladesh. Waste Manage 28(9):1688–1695
24. Swachh Bharat Mission (2017) http://www.swachhbharaturban.in/sbm/home/#/SBM
25. Venkata Mohan S (2009) Harnessing of biohydrogen from wastewater treatment using mixed fermentative consortia: process evaluation towards optimization. Int J Hyd Ener 34:7460–7474
26. Weng CH, Lin DF, Chiang PC (2003) Utilization of sludge as brick materials. Adv Environ Res 7(3):679–685
27. You SJ, Zhao QL, Jiang JQ, Zhang JN, Zhao SQ (2006) Sustainable approach for leachate treatment: electricity generation in microbial fuel cell. J Environ Sci Health A 41:2721–2734
28. Zheng HS, Guo WQ, Yang SS, Feng XC, Zhou XJ, Liu B, Ren NQ (2013) Biohydrogen production by co-fermentation of starch wastewater and sludge under thermophilic condition. In: Advanced materials research, vol 724, pp 360–364. Trans Tech Publications
29. Zhuang Y, Wu SW, Wang YL, Wu WX, Chen YX (2008) Source separation of household waste: a case study in China. Waste Manage 28(10):2022–2030
30. http://cpcb.nic.in/openpdffile.php

Urban Water Body Restoration in Semiarid Areas Using Treated Sewage: Challenges and Emerging Trends

H. N. Chanakya, Seema Sukhani, H. Subramanya and K. S. Sangunni

Abbreviation

TP	Total phosphorus
BBMP	Bruhat Bengaluru Mahanagara Palik
BDA	Bangalore Development Authority
BWSSB	Bangalore Water Supply and Sewerage Board
KSPCB	Karnataka State Pollution Control Board
LDA	Lake Development Authority
MLD	Million Liters per Day
STP	Sewage Treatment Plant
EGBR	Expanded granular bed reactor
COD	Chemical oxygen demand
DOT	Develop-Operate-transfer

H. N. Chanakya (✉) · S. Sukhani · K. S. Sangunni
Centre for Sustainable Technologies (Formerly ASTRA),
Indian Institute of Science, Bengaluru, India
e-mail: chanakya@iisc.ac.in

H. Subramanya
GKVK UAS Bangalore, Bengaluru, India

H. Subramanya · K. S. Sangunni
Yelahanka Lake Conservation and Restoration Group, Bengaluru, India

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_8

1 Introduction: Lakes in Bangalore and Associated Problems

Bangalore is known as "City of Lakes" and due to its undulating terrain, lakes form a series of hydrological connections. Traditionally, these lakes and water tanks were created to impound rainwater through storm watercourses during monsoon and any excess water would flow into the next water body downstream, preventing flooding of surrounding areas while also contributing to groundwater recharge [15]. The vision behind establishing these water tanks was to maintain the availability of water for drinking and irrigation for a stretch of 2 years. Now, out of 262 major water bodies in Bangalore (1960), only 34 (2008) are recognized as functional lakes [11]. In Bangalore, there are 189 lakes in urban areas which occupy 1005 ha [15]. LDAs performance audit (2014) found that out of 56 recently restored lakes, 47 were severely polluted. The sources of pollutants are shown in Fig. 1 [4]. The major problems observed in lakes are as follows:

- Obstruction in stormwater channel due to the encroachment of watershed area which disrupts interlinking of different lakes causing frequent flood incidences, e.g., Millers Tank [3].
- In Bangalore, the UGD lines open up into stormwater drains and often end up in lakes.
- Some degree of direct discharge of untreated wastewater/sewage from residential areas occasionally occurs [3, 8].

Bangalore population is estimated to reach 12.5 million by 2017 [8] which will result in increasing water demand which cannot be drawn from the current source, Cauvery river after stage IV. The other major source of water in the city is bore wells but groundwater levels are dwindling. Thus, it becomes necessary to restore and maintain lakes, as they can become a source of freshwater and augment groundwater.

On the basis of nutrient level, freshwater bodies are generally classified into oligotrophic (chl a <0.95 µg/L, TP <6 µg/L, nutrient poor), mesotrophic (chl a 2.6–7.3 µg/L, TP 12–24 µg/L, average level nutrients), eutrophic lakes (chl a 7.3–20 µg/L, TP 24–48 µg/L nutrient rich), and hypertrophic lakes (chl a

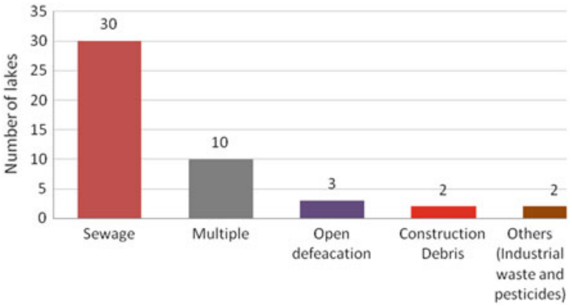


Fig. 1 Kinds of pollution in urban lakes [4]

56–155 μg/L, TP > 96 μg/L). Urban lakes (e.g., Jakkur Lake, Bangalore) are mostly manmade and are at mesotrophic or eutrophic stages. These lakes are expected to foster ecological biodiversity, moderate storm flows water impacts, prevent drought, provide sources of livelihood, aid in groundwater recharge, and act as recipient of wastewater. Lakes also influence the health, temperature fluctuations, and microclimate of the nearby areas [12]. The aim of this paper is to provide an overview of various modes and efforts of lake restoration carried out in Bangalore city through case studies and to capture their shortcomings. Also, a novel restoration model (Puttenhalli Lake, Bangalore) will be proposed which attempts to balance economic sustainability issues that have driven recent approaches along with ecological and environmental considerations.

2 History of Restoration in Bangalore

In the past century, lakes in Bangalore were managed, periodically cleaned, and maintained by the nearby communities with occasional financial aid from reigning governments. However, organic loads entering these lakes were marginal. In the twentieth century, Karnataka Revenue Department took over this responsibility and tried keeping lakes and tanks in their pristine condition [3]. Due to rapidly deteriorating condition of lakes, in 1995, National Lake Conservation Authority (NLCA) initiated Lake Conservation plan specifically for Bangalore city to implement the suggestions of the N. Lakshman Rao Commission (1986). KSPCBs comprehensive report (2000) revealed that almost all lakes in Bangalore were facing threats to water quality due to sewage influx. This paved way for convergence of various government agencies under a statutory institution called Lake Development Authority (2002) [11]. Since then, 60 lake restoration programs involving public–private governance partnerships have been initiated [8, 11]. In 2015, restoration efforts of LDA in 12 lakes were audited. The major findings are listed below [4]:

- Reduction in water spread area of almost all lakes and water bodies.
- Lack of fencing (damaged in Bellandur), in Horamavu Agara, Rachenahalli, and Nagavara Lakes.
- Encroachment by slum dwellers (Chikka Bellandur, Allalasandra lake), ITI factory (Kowdenhalli lake).
- Foaming in Bellandur Lake waste weir region (Varthur Lake).
- Ingression of untreated or mixed water in Horamavu-Agara, Vengaiahanakere, and Kowdenhalli.
- Drying of lake bed due to lack of adequate inflow during rainy season (or sewage during dry season) in Chikka Bellandur, Allasandra. In some cases, constructed inlets were defective or got clogged such as in Chokkanahalli and Kowdehalli.

These findings clearly show the gap in restoration efforts.

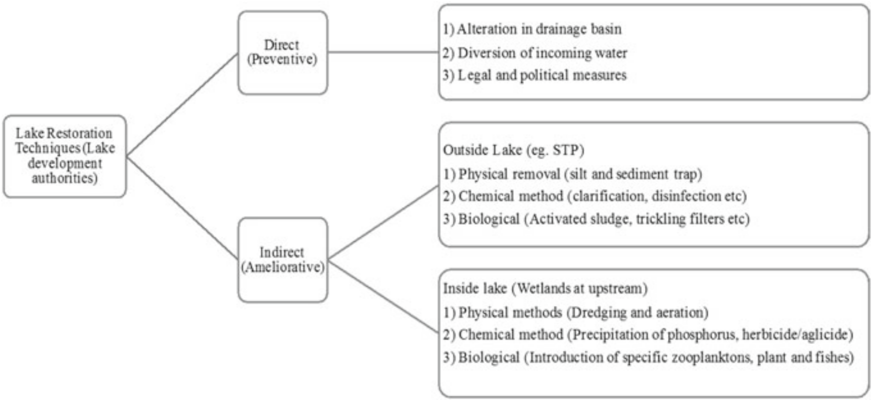


Fig. 2 Different lake restoration techniques

3 Models of Lake Restoration

Lake restoration efforts and technologies can be divided into preventive and ameliorative methods as shown in Fig. 2.

Combinations of abovementioned methods have been used to attempt restoration of lakes and tanks in Bangalore, India. The progression of these methods has been discussed below.

Ulsoor Lake: This restoration was first concerted effort to rejuvenate a sewage fed urban water body. It is situated in Eastern Bangalore in Challgatta Valley (12° 58′ 53.3″N, 77° 37′ 9.17″E) and is a man-made reservoir with an area of 50 ha [18], upstream to Bellandur tank, and being fed by Munireddy Palya and Doddakunte drain. The lake faced problems due to direct discharge of untreated sewage with average OLR being 40 g/m^2/d and a typical residence time of 25 days, seepage from UGD and dumping of solid waste and slaughterhouse wastes from the surrounding areas [10]. In 2001, desilting of the lake was carried out by BBMP which increased water holding capacity and lake depth to 11,000 MLD and 4.5 m, respectively. Along with other physical modifications such as selective inlet entry only from stormwater drain, diversion channel for sewage (900 mm pipes from eastern side of lake), silt traps, hydrophytes, and aerators were done [2, 16]. However, within a decade problems recurred. In 2013, a report by CiSTUP, IISc stated that Ulsoor lake is eutrophicated, foul smelling, and weed-infested. According to LDA, about two lakh metric tonnes of silt equivalent to 30% of actual lake depth is sitting in the lake bed. Incidents of fish kill; algal bloom, and low DO (1.1 mg/l) were reported in 2006 [17]. Similar incidences have occurred in Agara and Varthur Lakes, 2006 (Figs. 3 and 4).

Hebbal Lake: In the second phase, Hebbal and Madivala Lakes [2, 7] were restored under Indo-Norwegian Environment Programme (1997 with an aid of Rs. 198.00 million). Both preventive and ameliorative measures were taken. Hebbal Lake

Fig. 3 Eutrophied Ulsoor Lake with fish kill (2016) [14]

Fig. 4 Weed infested Hebbal Lake (2008) [5]

(13.0466°N, 77.5856°E) is a water body in northern side of Bangalore with an area of 64.5 ha [15]. With urbanization, sewage is now the only water source during summer and its diversion renders the lake completely dry [10]. In 1998, it underwent a major transformation. While desilting, the quantum of silt to be transported was so large that it was decided to pile up the excavated silt to form two islands for habitation of water birds. But it continued to receive wastewater in western side of the lake from localities and industries in catchment areas which caused heavy metal contamination in water body disturbing its ecological balance. Within a few years of its restoration, it went back to being sludge bed [1, 2]. In 2005, under DOT scheme, it was leased to East India Hotels Ltd., and in 2007; lake was drained and dredged again. Currently, it is undergoing the second phase of restoration. The lack of maintenance of the lake is one of the main problems [1, 6].

The third model of restoration was attempted in Agara Lake in the Bellanduru upstream, southeast of Bangalore city. Large quantities of sewage that passed through the lake were diverted constructing a bypass channel on its periphery with a balancing weir-like structure. Although quite linked to the sewage flow adjacent to the lake, only when storm flow occurred, the height of the water in the diversion channel increased sufficiently to allow stormwater to enter into the lake. This meant that fresh water would flow only during heavy rains and the rest of the year, the inflow would be cutoff. During many subsequent years, such storm events rarely occurred and the Agara Lake continued to remain dry, populated by emergent aquatic weeds during the major part of the year. At this stage for rejuvenation and maintenance of lakes, public–private partnership model was attempted to overcome finding finances for O&M. The Hebbal, Nagawara, and Vengaianakere Lakes were leased for 15 years to East India Hotels Ltd., Lumbini Developers and ParC Ltd., respectively.

Jakkur Lake: To maintain a balance between the water level in dry season and pollution load coming from sewage, the use of effluents from decentralized STPs was considered better. This was the basis for the fourth model of restoration tried so far. Secondary treated sewage is first fed to a wetland to capture residual nutrients. After passing through such a constructed wetland, nutrient-deficient water is allowed into the main body of the lake. Jakkur Lake (13° 04′N, 77° 36′E) in Yelahanka, is approximately 55 ha in area [9]. Earlier, this lake received untreated sewage from the nearby areas which turned it into a weed-infested and eutrophied lake (Figs. 5 and 6).

When restoration efforts were taken up, along with primary physical modifications, an STP was set up at upstream of the lake by development authorities (BDA, BWSSB) to ensure reduction of nutrient and organic carbon content. About 6–8 MLD of sewage is treated in UASB with an extended aeration system, with removal of over 60% COD (~128 mg/L), 78% BOD (~50 mg/L). An annual influx of stormwater and 0.5 MLD raw sewage from SWD also ends up in the lake. A 5 ha nutrient capturing man-made wetland now precedes entry into the larger lake. This allows rapid growth of algae and macrophytes in the wetland and helps remove a further COD, BOD, and orthophosphate. The macrophytes growing in this wetland are harvested and cleared on a weekly basis and water rich in algae and residual nutrients enter the main body

Fig. 5 Constructed wetlands

Fig. 6 BWSSB STP at Jakkur

of the lake [13, 15]. It is estimated that the hydraulic retention time (HRT) is about 50–96 days in the main water body, but water at the outlet still appears dark green and laden with algae. We may, therefore, conclude that this lake is still eutrophied. Although the Jakkur Lake has been considered as a model system for sustainable management of urban water bodies, the availability of treated water upstream, the possibility of creating a wetland midway and a 100 days HRT is difficult to achieve at all locations. It is important to note that the overall loading rate is about 0.55gN/m^2/d and 0.1gP/m^2/d requiring a primary productivity of 10–12 g/m^2/d which is close to highest recorded primary productivity. As a result, throughout the water body, there will be nutrient surplus. It is thus important to create a water intake system that lowers the nutrient intake to abilities of the primary production system or even to half these levels [13].

A fifth and poorly tried version is also included wherein constant and in situ water purification was attempted through providing nocturnal (mechanical) and diurnal (algal) supportive aeration at Bellandur Lake. Needless to emphasize, all lakes discussed here are man-made tanks built by creating an earthen bund across a shallow valley/gorges (2–25 m high) containing an impervious inner clay layer and stone pitched water face to hold water for between 2 and 3 years. The objective of this paper is capturing these learnings for future use (Fig. 7).

Fig. 7 Jakkur lake

4 Discussion

Arid and semiarid areas of India are replete with man-made lakes. South India alone has over 100,000 lakes. Urbanization and rapid change to underground drainages (UGD) are allowing the point discharge of sewage/human wastes into these water bodies putting stress on their ecological and environmental capabilities. Though constructing sewage treatment plant (STP) seems like a viable option, but their efficient functioning, treatment till secondary and tertiary stages and economic, political, and land acquisition constraints curtail these efforts. These above observations clearly indicate difficulties encountered and the presence of multiple sub-systems that need to be addressed during a restoration process. It is evident that focus of restoration efforts has been mostly dominated by developing lakes for recreational facilities to ensure peoples' participation and bring in economic viability through revenues accrued from recreational facilities. But as these lakes are being fed by surface runoff from agricultural and urban landscapes, it precludes them from functioning as pristine water bodies. There is, therefore, a middle path required where sewage, treated, or partially treated, would be the main input that work on natural processes which do not generate secondary wastes or require constant maintenance. Ecological and environmental considerations that come along with this input, therefore, need to be respected and restoration efforts cognizing them, need to be taken up.

4.1 Proposed Model for Restoration: Puttenhalli Lake (North Bangalore)

An attempt to overcome shortcomings of other restoration models is made in the restoration plan for Yelahanka Puttenahalli Lake, located in Bangalore North (12° 53′ 22.31″N, 77° 35′ 13.57″E). With an area of 10.41 ha, this lake is habitat to more than 49 species of birds, some of which include endangered and migratory birds from Northern Himalayas and Siberia. The major sources of inflow are rainfall, runoff and wastewater drain. At present, there are five inlets to the lake. The major inlets are at western (outlet of Attur Lake) and southwestern side of the lake (major source of domestic wastewater). Rest of three inlets joins the lake on North, North-eastern, and Southern part of the tank. The proposed plan is to first carry out primary physical modifications, removing encroachments, desilting, fencing the boundary, and creating a buffer zone of 30 m, to increase water holding capacity to 166.63 million liters. During rains, water will directly enter the lake after primary treatment through silt trap. Incoming sewage would be diverted through a diversion channel and led downstream to a proposed STP. During dry periods, untreated sewage would be the only water source, which, unlike all earlier attempts, will be taken in through deepest end of the lake (2.8 m) by a balancing weir. The volume taken up will be equivalent to evaporation loss (0.3–0.6 MLD). Sewage upon entry will be subjected to high rate anaerobic digestion, where mixing will happen on principle of upwelling sludge bed reactor. Anaerobic treatment (1000 m^3/d, 1d HRT) will mineralize almost 50–70% of COD input while evolving gas. The second stage in the reactor will be Euglena/protozoa which are capable of growing in holozoic mode and help in disinfection and particulate removal. Euglena at concentration 10^9 cells/L, in mixotrophic mode, can remove residual organic carbon, ~20–30% ammonia, and orthophosphates. Cholorophycean algae and aerobic bacteria would follow Euglenophycean and ensure particulates removal, volatilization of ammonia (because of increase in pH), and precipitation of phosphates, nitrification, and denitrification. A total of 50–60% residual N and 40–50% residual P loss are expected. Last two stages are similar to facultative and maturation pond (Fig. 8).

The overall residence time for sewage in the lake will be ~263 days and in the treatment unit will be ~3–5 days. In this way, the overall loading rate of nutrients would be 0.25 g N and 0.1 g/m^2/d which are well within the assimilation rate of an aquatic water body, leaving very little surplus to the end of the water body. When carbon, nitrogen, and phosphorus losses and pick up by next trophic levels are considered, this lake will be nutrient deficient after a short period, thereby lowering potential for eutrophication. In the passive anaerobic treatment system, reduction of organic carbon would occur following a Third augmentations by solar-powered diffuse aerators, to increase DO. The key features of this model are:

- Drawing the required quantity of sewage to compensate for the evaporation losses.
- Treatment of sewage by natural sequence of processes.
- To allow lake to dry up once every 4–6 years to ensure removal of aggressive species.

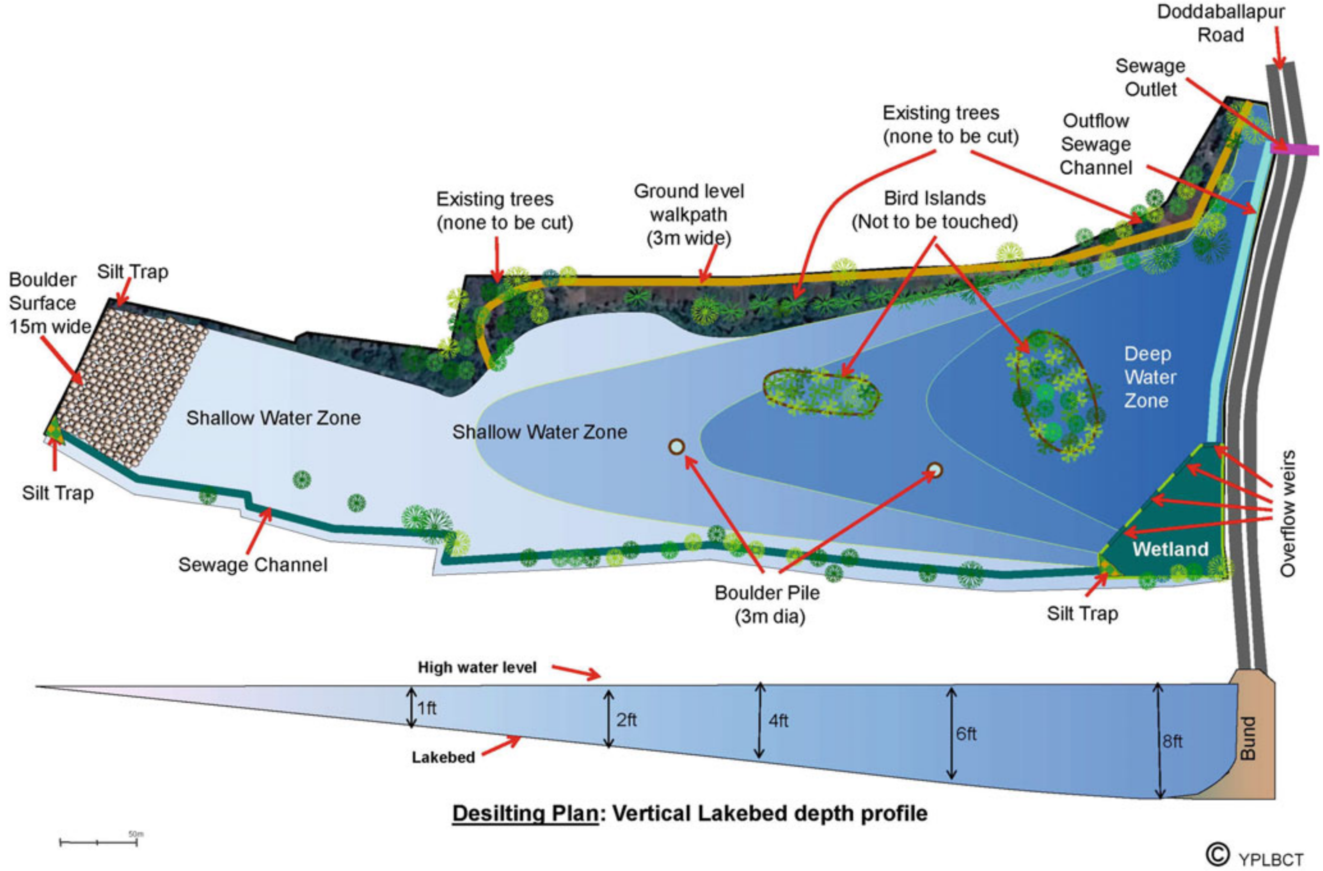


Fig. 8 Rejuvenation plan for Yelahanka Puttenahalli bird conservation reserve

- To increase the variety of avian fauna, have multiple (4–5) avian habitats to increase bird species as well as peoples' participation.

It is believed that this will form a model for future restoration efforts where input water quality in tanks and lakes is often questionable and expected to contain significant levels of sewage.

References

1. Baindur M (2014) Bangalore lake story: reflections on the spirit of a place. J Cult Geogr 31
2. Begum A, Krishna SH, Khan I, Ramaiah M, Veena K, Vinuta K (2008) Nutrients and heavy metal profile of Madivala lake, Bangalore south, Karnataka. RJC Rasayan J Chem 1(3):572–580
3. D'Souza R, Nagendra H (2011) Changes in public commons as a consequence of urbanization: The Agara lake in Bangalore, India. Environ Manage.
4. Government of Karnatka (2015) Performance audit on conservation and ecological restoration of lakes under the jurisdiction of Lake Development Authority and Urban Local Bodies
5. Hebbal lake drying—Google Search. Available: https://en.wikipedia.org/wiki/Hebbal_Lake
6. Hebbal Lake—Bangalore. Available: http://www.bangaloretourism.org/bangalore-Hebbal-Lake.php
7. Hebbal Lake| Lakes in Bangalore. Available: https://www.karnataka.com/bangalore/hebbal-lake/
8. High Court of Karnataka (2011) Preservation of lakes in the city of Bangalore, p 161
9. Inayathulla M, Paul JM (2013) Assessment of surface water chemistry of Jakkur Lake, Bangalore, Karnataka, India. Int J Sci Eng Res 4(5)
10. Indu Bhargavi R, Palavalli NM, Subramanya R (2007) Waterbodies of Bangalore, Karnatka
11. Jumbe AS, Nandini N, Tandon S, Sunitha N (2011) Bangalore lakes—issues and perspectives on pollution, restoration and management, 1699–1706
12. Mysore: a gazetteer compiled for government. Available: https://ia601407.us.archive.org/19/items/mysoregazetteerc01rice/mysoregazetteerc01rice_bw.pdf
13. Nandini N, Bheemappa K, Kumar MV, Raghavendra M (2013) Policy framework for conservation of water bodies in Bangalore. Int J Adv Res 1(4):42–45
14. Result of the tests on Ulsoor lake is alarming, says researcher. The Hindu. Available: http://www.thehindu.com/news/cities/bangalore/result-of-the-tests-on-ulsoor-lake-is-alarming-says-researcher/article8353922.ece
15. Shivakumar KV (2008) Water quality monitoring of lakes in Bangalore—Laborattory Central Laborattory KSPCB. In: Proceedings of Taal 2007 12th World Lake Conference, pp 1908–1915
16. The Hindu: Ulsoor Lake restoration on schedule. Available: http://www.thehindu.com/2003/04/18/stories/2003041809580300.htm
17. The Indian Express. Thousands of dead fish surface at Bengaluru's Ulsoor Lake; locals blame pollution. Available http://indianexpress.com/article/india/india-news-india/thousands-of-dead-fish-surface-at-bengalurus-ulsoor-lake-locals-blame-pollution/
18. Vikram L, Reddy N (2015) The role of policies of lake water management in, pp 91–99

Effect of Physical Presence of Waste Plastics in the Degradation of Municipal Solid Waste in Landfill

Anaya Ghosh, Jyoti Prakas Sarkar and Bimal Das

1 Introduction

Industrialization, rapid growth of population, urbanization and economic improvement have become major factors for the enhancement of the amount of municipal solid waste (MSW) in India. The rate of generation of MSW is increasing day by day [11, 17]. Raw vegetable waste (RVW) materials are biodegradable in nature compare to the other wastes in MSW and having a source of a major amount of carbon. Waste plastic (WP) which is one more possible health hazardous material of innumerable shapes and sizes is repeatedly found at a high scale in those wastes. Most of these waste plastics are non-biodegradable and impermeable in nature. Waste plastic (WP) materials are observed to be the foremost constituents of MSW in many municipalities after food and paper wastes. In many developing countries, the amount of plastics consumption is much higher than the world average consumption. World Bank's Urban Development Department was reported that presently the amount of municipal solid waste is 1.3 billion tonnes per year, and it will be increased to 2.2 billion tonnes per year within the year of 2025. In the year of 1950, it was assessed that the amount of world average annual plastics consumption 5 million tonnes, and presently, this amount is reached near about 100 million tonnes [4]. It means presently 20 times more plastics are produced, which becomes a major challenge for authorities of all municipalities to manage with this huge mass of plastic wastes after their use [7].

A. Ghosh (✉) · J. P. Sarkar · B. Das
Department of Chemical Engineering, National Institute of Technology, Durgapur, India
e-mail: ghoshanaya@gmail.com

J. P. Sarkar
e-mail: jpsarkar53@gmail.com

B. Das
e-mail: bimal_30@yahoo.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_9

The WPs are neither collected or segregated appropriately nor disposed of thoroughly. Consequently, chlorinated plastic materials in MSW can release harmful chemicals into the surrounding soil, which can then trickle into groundwater or other surrounding water bodies and can cause serious harm to the species that imbibe this contaminated water [2].

Risk of Biodegradable Plastics:

The modern municipal solid waste management techniques suggest a disposal method known as landfilling. Landfill areas are constantly piled high with so many different types of waste plastics. In these landfills, numerous microorganisms are present which can speed up the biodegradation of organic waste associated with plastic wastes. Although the civil authorities advice to use biodegradable plastic materials as an alternative solution. But the biodegradable plastics may indirectly affect the environment. These classes of plastics are broken down in the long run and methane is released, which is one of the very poisonous greenhouse gases that contribute significantly to global warming. Some landfill authorities are taking initiative for installing methane capture devices [19] and use it as an alternative energy. But unfortunately, most have not yet incorporated such gas collection technology. Moreover, the cost of the entire process becomes another major challenge. Due to lack of such appropriate solid waste management technologies and awareness, environment and public health are affected. Thus, increasing the amount of waste plastic becomes a big challenge for the municipal consultants and authorities.

For the last few decades, researchers are focused on recycling and reuse of waste to value added products. Some of them are interested in biodegradation of MSW in the landfills as landfill bioreactors for biogas production [1, 21, 22]. They are concentrated on developing suitable models based on the above phenomenon considering all promising complications of the system.

Review of a few recent literatures reveals that presence of waste plastics in the vegetable wastes which are inevitable components in municipal solid wastes to a certain extent enhances the biodegradation of solid wastes. A group of researchers in the aforesaid also concluded that the maximum rate of degradation is observed when the 10–15% [13–15, 18] of waste plastics is present in the vegetable waste bed in a uniformly distributed manner. They have claimed that allowing waste plastics components in the municipal solid waste landfills instead of separating from the solid wastes can increase the biodegradation rate of the solid wastes in the landfills. They justified such encouraging effect of waste plastics on the rate of degradation of vegetable waste in the bed by claiming that the distributed waste plastics increases the void pockets [13]. These void pockets can hold additional liquid leachate thus enhancing the retention of leachate in the waste bed [14]. This retained higher moisture in the bed encourages the hydrolysis stage, resulting in higher rate of degradation than that of bed free of waste plastics [20]. So finally, it may be inferred that the reasons for such enhancement are simply due to gross changes in physical parameters of the bed due to the presence of waste plastics.

The overall biochemical reaction which is involved during anaerobic digestion has been delineated below as proposed by Cossu et al. [3]:

$$\mathbf{C_aH_bO_cN_d + [(4a - b - 2c + 4d)/4]\,H_2O}$$
$$\mathbf{\rightarrow [(4a - b - 2c - 3d)/8]CH_4 + [(4a - b - 2c + 3d)/8]CO_2 + dNH_3}$$

where the complex organic compounds of the organic wastes are represented as $C_aH_bO_cN_d$. Therefore, in any particular landfill or landfill bioreactors, initially $C_aH_bO_cN_d$ and H_2O, the initial moisture content, have been contemplated as limiting reactants [12]. On the other hand, due to the existence of these impervious and non-biodegradable waste plastics in the waste bed, the hydrolysed material can be performed as an additional reactant. This impermeable nature of waste plastic thus restricts the down flow of hydrolysed material through the waste bed and helps to retain the same in the voidage made by fleecy waste plastics.

It is, therefore, necessary to study the effect of physical presence of waste plastic contents on the basic structural change and resultant hold-up of liquid inside the waste bed, compressibility of waste bed [5], the variation of voidage of the waste bed and the corresponding temporal change of the aforesaid physical parameters and also the bed height which implicates the change in volume of the waste bed [10, 16].

The present work, therefore, focuses on the studies of change of physical and structural characteristics of the MSW bed both in absence and presence of waste plastics in different proportions within the specified optimum limit.

2 Materials and Methods

2.1 Preparation of Experimental Material Samples

RVWs are collected from local vegetable markets and canteen, and WPs are picked up from different dumping sites of local municipal areas of Durgapur. Both WPs and raw vegetable waste stuffs were manually cut into small pieces having almost one square inch area and kept ready for experimentation.

2.2 Experimental Setups

Figure 1 depicts the experimental setup fabricated from transparent acrylic plastic materials for studies on biodegradation of vegetable wastes samples initially in absence of waste plastics and then with vegetable samples uniformly mixed with waste plastic samples. All the necessary arrangements in the setup are provided to observe physical changes in texture and height of the bed and to measure the pressure

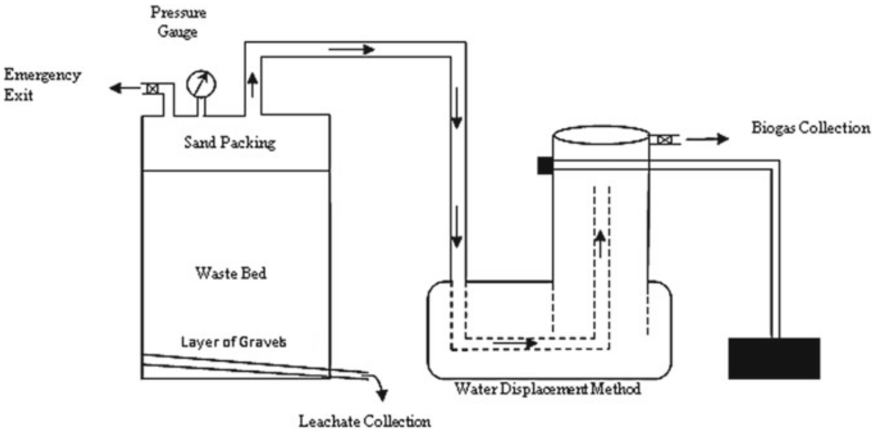


Fig. 1 Anaerobic digestion of MSW and biogas collection by water displacement method

and estimate the volume of the generated gas samples by a low range pressure gauge and by water displacement technique, respectively.

Another set of five similar small-scale cylindrical experimental setups (R-I for RVW and R-II R-III, R-IV and R-V for mixed samples) were also fabricated with transparent acrylic plastics for measurement of the liquid hold-up, voidage and compressibility of the waste beds. Figure 2 shows the diagram of one of those experimental setups having a cylindrical shape with a conical bottom for easy flow of liquid towards bottom exit tube for liquid/leachate collection. During measurement of bed compressibility, [8, 11] a plate piston of a diameter slightly smaller than the inside diameter of cylindrical bed container with necessary arrangements for placing desired weights on the piston was fabricated for compressing the waste beds samples [6]. For leachate hold-up measurement, the piston was not used and in that case, how much leachate can be held by the void pockets created by the WP was estimated by simply pouring water from the top of the beds and measuring how much water was collected from the bottom of the beds.

2.3 Experimental Procedures

2.3.1 Waste Bed Heights Study During Biodegradation

The first experimental setup (shown in Fig. 1) was initially filled with RVW samples and covered with an airtight lid and kept under strict anaerobic condition. Before packing those aforesaid waste beds, a small layer of gravels is placed at the bottom-most portion of those setups for ease of leachate percolation as well as collection. A layer of sand is packed at the top of the waste bed for creating a suitable environment

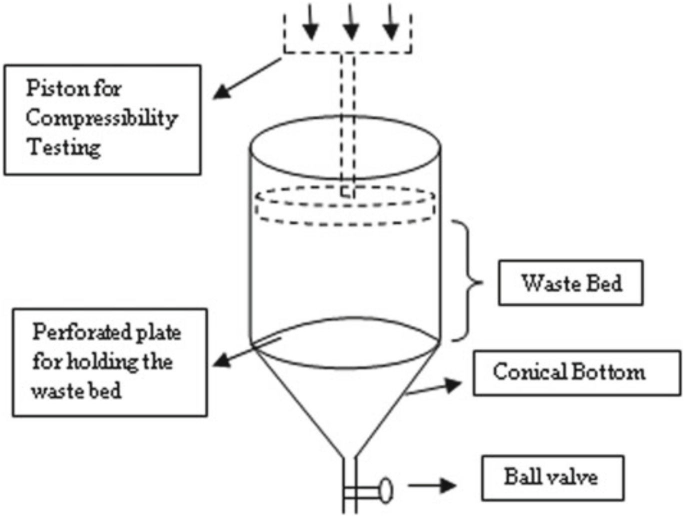


Fig. 2 Experimental setup for liquid hold-up and compressibility testing

for anaerobic digestion under ambient temperature. A special care is required for such experimental setups for carrying out the objectives of present studies. Experiments are carried out for 8 weeks under the strict anaerobic condition, and the average ambient temperate is maintained at 35 °C. The decrease in waste bed heights (WBH) of all WBs was measured minutely every day. The same procedure was repeated by filling the cylindrical bed with different samples of RVW mixed with different percentages of WP consecutively.

2.3.2 Studies of the Effect of WP Variation on the Physical Characteristics of RVW Bed

The waste beds are packed inside the second set of experimental setups with the amount of vegetable waste and waste plastics samples as described in Table 1. The physical characteristics of waste beds like voidage, compressibility and leachate hold-up [8, 9] capacity were measured accordingly and were filled RVW without WP, and rest of four (R-II, R-III, R-IV, R-V) were filled with RVW along with different percentage of WP such as 5, 10, 15 and 20% of the amount of the RVW, respectively. The amount of RVW is maintained uniform throughout all five experimental setups.

Table 1 Capacity and sample details of the experimental setups

Sl. No.	Setup	Capacity (Litre)	Percentage of WP	Weight of RVW (Kg)	Weight of WP (Kg)
1	R-I	5	0	0.5	0
2	R-I	5	5	0.5	0.01
3	R-III	5	10	0.5	0.05
4	R-IV	5	15	0.5	0.075
5	R-V	5	20	0.5	0.1

3 Results and Discussions

3.1 *Studies on the Physical Change of the First Experimental Setup Shown in Fig. 1*

Figure 3 shows the temporal change of actual bed heights in all the experimental setups (R-I, R-II, R-III, R-IV and R-V). It is observed that there is a continuous decrease in all cases of bed heights in all the WBs containing different % of WPs mixed with RVW. Such trends are justified that by the change of the individual RVW beds by the continuous degradation with respect to time results in changing the overall volume of the waste beds [13].

Percentage decrease of bed was shown in Fig. 4, where we can see that maximum percentage of decrease in bed height was achieved in the case of the bed containing 10% WP by weight. The possible reason may be due to the fact that maximum degradation occurs in the case of RVW bed having nearly 10% WP. This is happened due to the fact that higher amount of void age can hold the maximum amount of

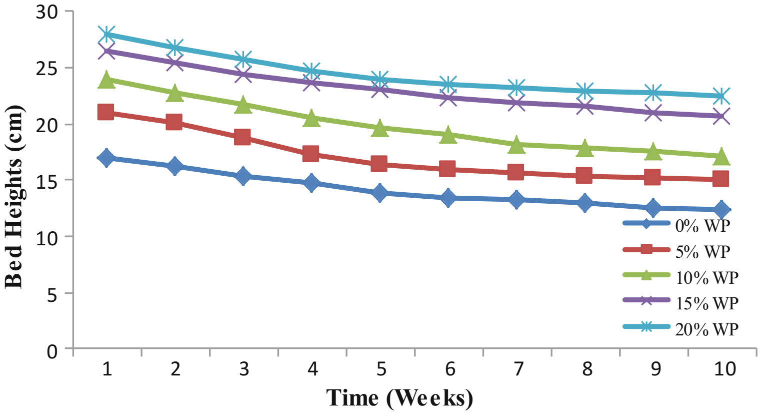


Fig. 3 Decrease of beds height with time (weekly basis)

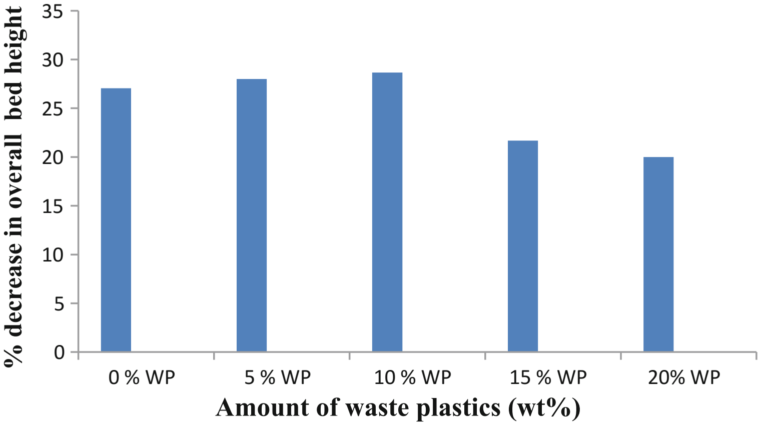


Fig. 4 Percentage decrease in overall waste bed heights

leachate inside the waste beds. The decrease in the bed's heights with further increase of waste plastics over 10% may be due to decrease in the actual RVW that contains higher % of WP all through the voids may be higher for holding the liquid leachate.

3.2 Studies on the Physical Characteristics of the Beds in Other Similar Experimental Setups Shown in Fig. 2

The voidage of the individual beds in all the five beds has been depicted in Fig. 5. The figure represents the voidage estimated theoretically from the actual measurement of the individual bed's dimensions having 0–20% WPs in the RVW. It is quite obvious that the increase in the WPs increases the voidage of the waste beds.

Figure 6 shows the indirect measurement of the actual liquid hold-up during the flow of liquid through the beds. The reason for obtaining optimum hold-up in case of bed with 10% WP may be due to the fact that although the beds with higher WP might have higher voidage, actual liquid holding capacity of the bed may not be that much as in case of 10% WP.

Figure 7 describes the compressibility characteristics of the different beds with varying % of WPs. It is observed that with the increase in the load concentration over the beds, the % reduction in height of the beds, as well as the volume of the beds diminishes continuously. It may be further noted that maximum % reduction in the height occurs in the bed with 20% of the WPs with an increase in load concentration. The maximum change in the reduction in the bed height is shown in Fig. 8, where it is observed that the bed without any plastics is having maximum compressibility characteristics than in other beds with gradually higher % of WPs in the bed. This implies the maximum change in the voidage of the bed without any waste plastics with

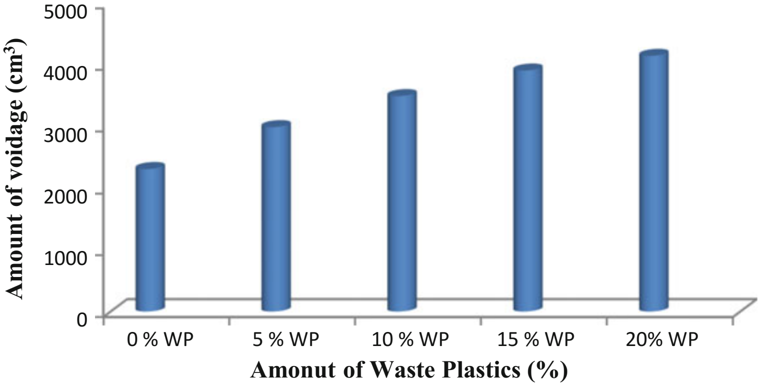


Fig. 5 Increase in voidage with increasing the amount of WP inside the WBs

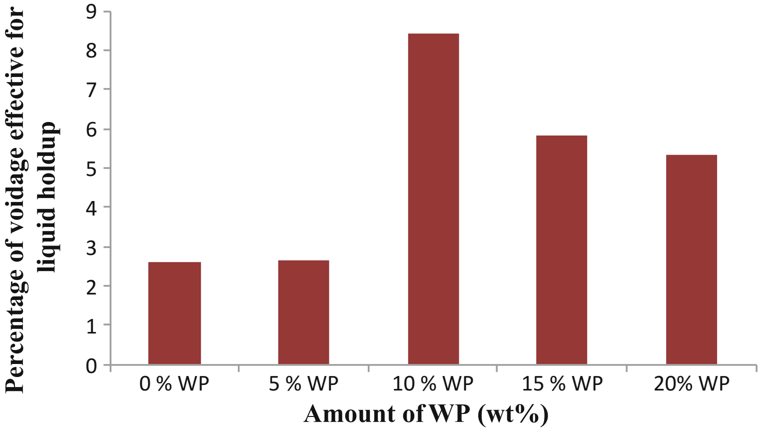


Fig. 6 Percentage of void occupied by the flowing leachate

the increase in the load concentration. The waste beds compressibility characteristics are changing with the height of the bed in the actual landfill where the bed height is very high and the individual successive layers of RVW. As we go down the bed, since different load concentration was applied by the weight of the top layers over the bottom layers, waste beds have become more compressed. Therefore, the voidage in the successive layers of the landfills will decrease continuously as we go down the bed of RVW in the actual landfill.

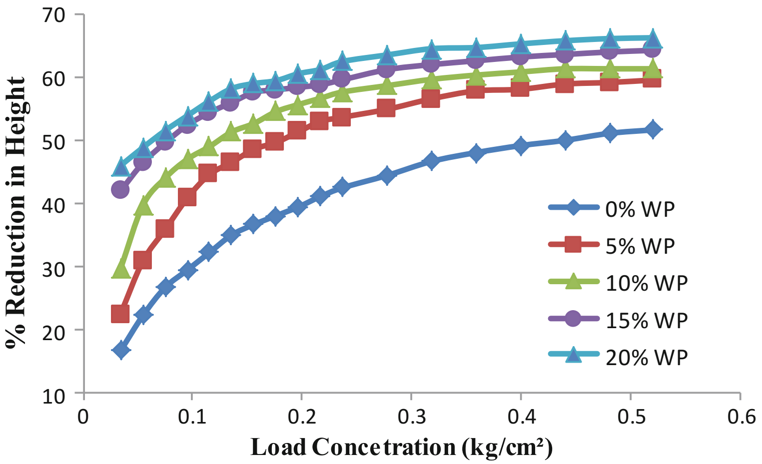


Fig. 7 Compressibility profile due to load increment of vegetable waste bed having different percentage of waste plastics

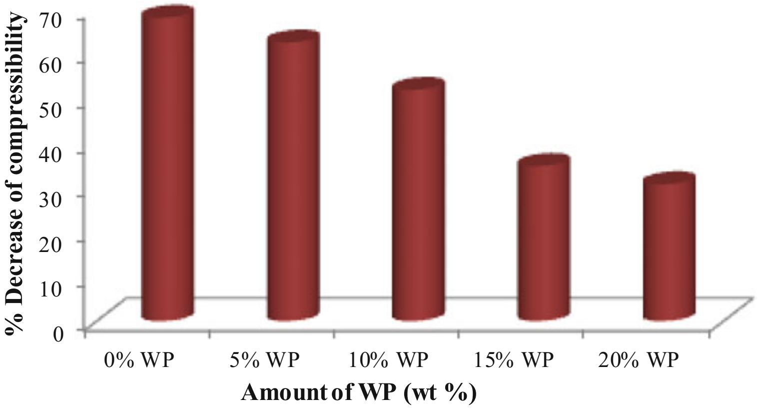


Fig. 8 Percentage of decrease in compressibility of different waste beds

4 Conclusion

The background reason for the extent of degradation of RVW in presence of WP has been studied in the aforesaid discussion. The maximum degradation in case of 10% waste plastic has been justified by the maximum amount of liquid hold-up capacity with 10% waste plastic. Although the voidage increases with the increase in % of WPs in the bed, the actual liquid/leachate hold-up capacity is optimum with 10% waste plastics.

The decrease in the overall height of a RVW bed with load concentration has been also studied showing the maximum decrease in case of RVW bed with 0% WPs in the bed. Till today, no such studies are available in the literature so far review by the author on actual degradation rate in different layers of the RVW bed neither any study is available on the change in the bed voidage throughout the height of the RVW bed.

Therefore, it is necessary to focus on the studies of the physical structural profile along the bed height and corresponding change in degradation rate along the height of the bed.

References

1. Agrahari RP, Tiwari GN (2013) The production of Biogas using kitchen waste. Int J Energy Sci (IJES) 3(6):408–413
2. Christensen TH, Kjeldsen P, Albrechtsen HJ, Heron G, Nielsen PH, Bjerg PL, Holm PE (1994) Attenuation of landfill leachate pollutants in aquifers. Critical Rev Environ Sci Technol 24(2):119–202
3. Cossu R, Andreottola G, Muntoni A (1996) Modelling landfill gas production, landfilling of waste: biogas. In: Christensen TH (ed) Landfilling of waste: leachate. London, E & FN SPON, pp 237–268
4. CPCB (2004) Central pollution control board (CPCB), 2004. Management of Municipal Solid Wastes, New Delhi, India
5. Durmusoglu E, Corapcioglu MY, ASCE F, Tuncay K (2005) Landfill settlement with decomposition and gas generation. J Environ Eng 131(9):1311–1321
6. El-Fadel M, Khoury R (2000) Modeling settlement in MSW landfills: a critical review. Critical Rev Environ Sci Technol 30(3):327–361
7. Ghosh A, Debnath B, Ghosh SK, Das B, Sarkar JP Sustainability analysis of organic fraction of municipal solid waste conversion techniques for efficient resource recovery in India through case studies. J Mater Cycles Waste Manage
8. Hossain MS, Gabr MA, ASCE F, Barlaz MA, ASCE M (2003) Relationship of compressibility parameters to municipal solid waste decomposition. J Geotech Geoenviron Eng 129(12):1151–1158
9. Hossain MS, Penmethsa KK, Hoyos KK (2009) Permeability of municipal solid waste in bioreactor landfill with degradation. Geotech Geol Eng 27:43–51
10. Hudson AP, White JK, Beaven RP, Powrie W (2004) Modelling the compression behaviour of landfilled domestic waste. Waste Manag 24(2004):259–269
11. Kaushal RK, Varghese GK, Chabukdhara M (2012) Municipal solid waste management in India—current state & future challenges: a review. Int J Eng Sci Technol (IJEST) 4(04), ISSN: 0975-5462
12. Khalid A, Arshad M, Anjum M, Mahmood T, Dawson L (2011) The anaerobic digestion of solid organic waste. Waste Manag 31(2011):1737–1744
13. Mukhopadhyay D, Sarkar JP, Dutta S (2013a) Optimization of process factors for the efficient generation of biogas from raw vegetable wastes under the direct influence of plastic materials using Taguchi methodology. Desalin Water Treat 51:(13–15), 2781–2790
14. Mukhopadhyay D, Sarkar JP, Dutta S (2013b) Optimization of process parameters for the economical generation of biogas from raw vegetable wastes under the positive influence of plastic materials using response surface methodology. J Biochem Tech 4(1): 549–553 ISSN: 0974-2328
15. Mukhopadhyay D, Sarkar JP, Dutta S (2014) Macroscopic temporal studies on the effect of waste plastic materials on anaerobic digestion of raw vegetable market wastes: experiment and modelling. Int J Environ Waste Manag 13(4):2014

16. Reddy KR, Hettiarachchi H, Giri RK, Gangathulasi J (2009) Effects of degradation on geotechnical properties of municipal solid waste from Orchard Hills landfill, USA. Geotech Geol Eng 27:43–51
17. Sharholy M, Ahmad K, Vaishya RC, Gupta RD (2007) Municipal solid waste characteristics and management in Allahabad, India. Waste Manag 27(2007):490–496
18. Singh A, Mukhopadhyay D, Sarkar JP, Dutta S (2014) Studies on effect of plastics on biodegradation of vegetable solid market waste through details analysis of leachate. J Solid Waste Technol Manag 40(3):266–284
19. Spokas K, Bogner J, Chanton JP, Morcet M, Aran C, Graff C, Golva YML, Hebe I (2006) Methane mass balance at three landfill sites: what is the efficiency of capture by gas collection systems. Waste Manag 26(2006):516–525
20. Tehhobanoglous G, Theisen H, Vigil SA (1993) Integrated solid waste management: engineering principles and management issues. McGraw-Hill Inc., Singapore
21. Themelis NJ, Ulloa PA (2007) Methane generation in landfills. Renew Energy 32(2007):1243–1257
22. Tsai WT (2007) Bioenergy from landfill gas (LFG) in Taiwan. Renew Sustain Energy Rev 11(2007):331–344

A Qualitative–Quantitative Methodological Approach for Sustainable Reclamation of Open Dumps: The Case of the Controlled Dump of Tripoli

Mervat El-Hoz

1 Introduction

Landfills have traditionally been realized as the ultimate process for the disposal of waste at minimum cost [19]. They are relatively varied with regard to the characteristics, size, and location, causing different costs and benefits of their reclamation [29]. The presence or absence of liner, leachate recirculation, and the use of soil cover change their operations. Furthermore, regulations and policies on-site-specific, local, national, and international scale are spatial [3].

Normally, and in different parts of the world, municipal solid waste landfills contain about 50–60% soil-type materials such as significantly degraded waste and cover material; 20–30% combustibles materials for instance wood, plastic, and paper; 10% inorganic materials, for example, glass concrete, and stones; and a very low percentage of metals mostly ferrous metal [26, 33, 34].

Old dumpsites are a cause of local pollution due to the absence of any type of protection for emissions reduction, and the hazardous substances leaching. There is a chance to recover significant amounts of formerly rejected waste in many municipal solid waste (MSW) dumps and landfills in the world. A remarkable remediation technology for the closed open dumpsites is landfill mining (LFM) which is well-defined as a process for removing waste materials from natural resources or minerals that have been previously placed in the ground. It is an approach that has seen worldwide over 50 years of reintroduction of forgotten resources into the materials cycle and the recovery of energy from combustible materials [12] and decreasing the environmental problems produced by landfill emissions [11], resolving traditional management problems related to solid waste deposits [22]. Traditional LFM involves the excavation, processing that includes sorting the useful materials, treatment and/or recycling of deposited materials or using for energy generation [10, 19, 23, 35]. Enhanced

---

M. El-Hoz (✉)
University of Balamand, El-Koura, Lebanon
e-mail: dr.m.elhoz@gmail.com; mervat.elhoz@balamand.edu.lb

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_10

landfill mining (ELFM) reflects an advanced form of mining. It can be defined as the safe adaptation, exploration, and integrated valorization of landfilled streams (waste to materials, WTM) and energy (waste to energy, WTE) using innovative technologies for the transformation of nonhomogeneous waste streams with respect to the strict social and environmental standards [2, 4, 12, 13, 15, 16, 18, 20, 22, 25, 26, 29, 31]. This method is obviously different from traditional landfill mining which is usually limited to land reclamation, methane, and a few valuable metals such as aluminum.

This study is aimed to propose a methodological procedure for giving practical response to the management of the open dump in the UCF. Results of the study are also discussed and their applications to other similar scenarios were evaluated.

2 Methodology

This research study uses a mix of qualitative and quantitative research approaches. Its methodology includes a five-step procedure as shown in Fig. 1. The first step involved the identification and review of relevant literature on the history of the SWM and the uncontrolled dump. Following this, data collection on waste quantities and compositions were covered. Then, meeting with the concerned stakeholders and decision makers were made. The fourth step is a fieldwork where field investigations to different treatment processes, and landfills were executed. The last step summarizes the data processing; and provides several options for solving this problem.

2.1 Literature Review

Different waste management plans were issued in Lebanon in the last two decades focused on municipal solid waste (MSW) only ignoring other wastes (e.g., industrial, commercial, medical, and hazardous). Despite these plans, Lebanon continues to depend on open dumps and sanitary landfills due to their easiness and low cost despite the limited land availability. Composting and recycling are not often implemented due to financial, administrative, and operational problems in addition to the low engineering practices in environmental protection through new technologies [8].

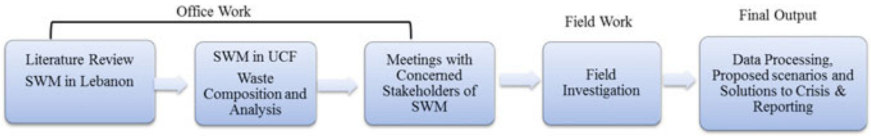


Fig. 1 Scheme of the methodology of the present study

2.2 UCF Solid Waste Management

One of the main environmental problems in UCF is solid waste management. The Tripoli dump is in operation since 1974. It is one among many uncontrolled dumping sites in Lebanon with no bottom liner and where no environmental protection actions were planned. The dump is located in the industrial zone of the city along the coastline, north to its Port and adjacent to the Abou Ali River. Figure 2 shows its geographical location.

Because of the location of this dump on the coast, air pollution due to gas emissions, odors, and fumes passed beyond its closed area, and leachate drained in the sea. Therefore, the government planned to solve the ecologically sound and health problems associated with the situation. In 1996, the UCF with the World Bank has executed a rocks breakwater of 450 m constructed around the beach side sea to contain the waste, stop it from being carried out north by sea currents, and enlarge the dumping area to 60,000 m^2. In 1999, the UCF initiated a project to rehabilitate the site and to operate it as a controlled landfill. Since then, the dumping process activities include control of incoming wastes, proper waste placement and compaction, application of daily cover, biogas flaring, and limited leachate control [5].

In 2003, under the EU-funded program, Assistance the Rehabilitation of the Lebanese Administration, the Office of the Minister of State for Administrative Reform (OMSAR) launched the solid waste management program to provide solid waste services in the country. The UCF has given the construction, 3 years operation and maintenance of a sorting plant. In 2010, the UCF established the plant, which includes a material recovery facility (MRF) for separating waste and increasing recovery of recyclables, as well as a temporary storage area to transfer the residual

Fig. 2 Geographical location of the landfill (controlled dump)

waste stream to the existing controlled dump or future composting plant and sanitary landfill in the governorate of North Lebanon [7]. The plant did not put under operation until July 2017.

The demographical development and the presence of Syrian refugees since 2012 lead to an increase of solid waste production with approximately 154,700 tons dumped in 2016 compared to 93,750 tons of 2000 and significantly higher than the foreseen amount for the year 2031, i.e., 151,279 tons/year [6, 8]. Therefore, the UCF in agreement with OMSAR program established the windrows system for a composting plant of the organic materials on a very small available area close to the site to reduce the amount of SW reaching the controlled dump. In July 2017, these plants started their operations.

Current Waste Management Practice

There is no organized solid waste reduction program but reuse and low per capita waste generation rates are common. Local communities do not practice waste segregation at source and some initiatives have been made by NGOs at a narrow level. Informal waste recovery (scavenging) in curbside containers are applied which reduce the volume of waste that is collected and transferred to the sorting plant, and then approximately 238.6 tons/day are disposed in the controlled dump.

Characteristics of the UCFs Solid Waste

The characteristics of the generated SW in the UCF contain municipal, commercial, industrial, agricultural, animal and slaughterhouse, and municipal hazardous wastes. The existing Tripoli CD receives solid waste collected from the Municipality of Tripoli, El-Mina, El-Kalamoun, Baddawi, and surrounding areas. Table 1 presents the characteristics and amount of solid wastes received at site during the last 16 years period [24].

The municipal solid wastes represent more than 85% of the total amount generated and include organic materials, paper, glass, plastic, metal, textile, and others. The average composition of the produced MSW in the UCF cities is presented in Table 2. In general, the highest ratio of total solid waste is organic. This major organic fraction of waste includes food, restaurant waste, market waste, and garden waste which are from daily market and houses of the cities.

Table 1 Solid waste generated during the last 16 years

Nature of wastes	Year 2000 (%)	Year 2005 (%)	Year 2010 (%)	Year 2016 (%)
Household wastes	92.6	92.4	92.29	89.1
Industrial wastes	0.2	0.21	0.64	0.1
Animal wastes	1.1	1.63	1.78	1.8
Agricultural wastes	0.3	0.22	0.04	0.1
Others	5.8	5.54	5.25	8.9

Table 2 Average composition of municipal solid waste generated

Composition of municipal solid waste	Waste received (%)
Organic waste	54.66
Recyclables	33.21
Plastic	15.11
Paper and cardboard	8.61
Glass	2.28
Metal	2.16
Aluminum	0.40
Textile	3.62
Wood	1.03
Hazardous wastes in MSW	9.63
Others	2.5

2.3 Meetings with Stakeholders

Meetings with the president, mayors, director, and concerned members of the municipal councils of the UCF were made. The problem reaches crisis proportions, due to the lack of sustainable solid waste technologies, complicated by diminishing CD capacity, the collapse of the CD wall a few months ago, the unavailable land for ultimate disposal besides the CD, and the not in my backyard (NIMBY) syndrome. These meetings resulted in finding an urgent applicable solution for the controlled dump as a priority. It should be noticed that the UCF pays $71/ton/day for waste management ($18/ton for collection and transportation of solid waste to the sorting plant, 25/ton for its operation, and $28/ton for the operation of the controlled dump).

As seen, this situation has not come as a surprise and CD crisis would not be solved overnight, nor will it be easy [6]. So, before decisions can be made about which technologies to implement, transparent technical information should be provided to the stakeholders to understand the function and purpose of technological options with no hidden aspects, review the main features to alleviate worries and precludes further conflicts [8].

2.4 Field Investigation

Field investigation to the site was made to visualize the nature and composition of the fill, and study the possibility of installing borehole down to depth below current elevation to be able to conduct a site characterization study. The change from land-based solid waste management to a resource-based system needs information of the characteristics of municipal solid waste. In general, the CD consists of the following three categories of solid waste:

- Biodegradable such as food waste, animal waste, leaves, grass, straws, and wood.
- Nonbiodegradable are plastic, rubber, textile waste, and metals.
- Recyclable material includes paper, cardboard, and plastic.

Having known these physical characteristics, they significantly influence the feasibility of certain treatment options.

Current Operation of the CD

The operation on the site is executed as follows:

- Receiving and weigh the waste at the entrance of the site.
- Inspecting the incoming MSW.
- Spreading and compaction of waste in layers of approximately 50 cm.
- Controlling leachate by constructing peripheral ditches to drain the leachate into pits through pumping and extracting it on daily basis, then recirculating partially leachate back into the landfill and conveying the remaining to the nearby open channel to discharge into the sea.
- Monitoring daily flare ()

Problems Facing the Dump

The following are the problems of the CD:

- Leachate treatment did not work well due to low design capacity (36 m^3/day).
- No documentation on the quantity of leachate since it is drained into the sea.
- Gas collection and flaring system are not functioning properly since September 2012 due to the increase in waste height, active dumping, need of additional well, and presence of cracks in the dump walls. The average amount of biogas used to approximates 49 m^3/h of CH_4, i.e., about 50% of the whole methane generated.
- Gas is simply released into the atmosphere causing health and environmental impacts.
- Elevation of waste is more than 39 m level in some parts of the landfill compared to 16 m in the year 2000 and exceeded the 29 m design marked for closure in 2012.
- Vertical stress and lateral pressure on the peripheral wall that leads to its failure and collapse due to sliding of waste mass.

Efforts to control this pressure were considered as a short-term solution by maintaining a 4 m deep trench around the inner face of the peripheral wall, extracting leachate through the peripheral walls, and re-grading the slopes. Figure 3 shows the current situation of the collapse of the peripheral wall.

2.5 Proposed Remedial Possibilities for Tripoli Controlled Dump

The key issues for the determination of the economic feasibility of land-based mining plans are land reclamation and energy recovery methods [30]. The selection of a

Fig. 3 Current situation of the collapse of the peripheral wall

method to solve the crisis of the current CD is a site-specific decision. It is necessary to take into consideration not only the ecological conditions, but also socioeconomic and territorial technical conditions. Site information includes information on-site history, economy, local and government planning, as well as a combination of current and future needs, available resources, type of operation, and equipment available [5]. The study assessed the current solid waste components and the treatment of existing solid waste, identified four scenarios according to different types of land reclamation to be able to come up with the best viable solution from an environmental view, and study the cost–benefit analysis of landfill mining project. The proposed scenarios are as follows:

- Scenario 1: No change, leave landfill as it is.
- Scenario 2: Reclamations with minimal change.
- Scenario 3: Reclamations with complete extracting using mobile on-site sorting plant and thermal treatment.
- Scenario 4: Reclamations with complete extracting using the current stationary sorting and composting plants.

Scenario 1: Leave controlled dump as it is (Do-nothing)

This scenario will keep odor and leachate emissions as they are and pollution will remain for years where more failures in the CD will occur. It is used as reference scenario where neither monitoring of gas and leachate nor landfill mining activities are undertaken.

Scenario 2: Closure and cover of CD

In this scenario, the gas and leachate of the dump will be managed, improve, or replace the existing infrastructure with particular emphasis on adequate periodic maintenance that will last about 15 years, in addition to monitoring and maintaining the final cover and any other long-term treatment measures required and installed. The collected gas is flared as it is designed for or can be used for combined heat and power generation through upgrading the site. Systems for the collection and treatment of leachates are in place, but the leaching of hazardous substances will continue for a long period of time. Furthermore, maintenance of the final cover and any other long-term remediation measures required and installed will be made. This is an important task in comparison with biogas flaring and leachate control. Closure of the CD will include as agreed in its operation contract:

- Construction of the final cover (capping) and
- Construction of the peripheral road.

This final cover provides a barrier over the waste materials system which is required to prevent contact with the public, minimizes leachate generation, and minimizes gas migration. Drainage swales will be constructed on the final cover system to collect and control surface water runoff. In addition, the vegetative cover layer will minimize wind erosion of the final cover sand layer.

Scenario 3: Enhanced landfill mining and reclamation (mobile plant)

First of all, this scenario is proposed from the viewpoint of waste management and within a comprehensive resource management framework. The objectives of this scenario are preservation of volume in the CD, removal of a potential source of pollution (gas emissions and leachate), mitigation of the site contamination, energy recovery, reuse of recoverable materials, reduction of management cost, and redevelopment of the site. In general, it consists of the enhanced landfill mining (ELFM) methodology. In this way, the controlled dump land which has a high value can be recovered. Moreover, in the operating section, space can be reclaimed which indicates the protection of the environment. On the other hand, the existence of new land is limited and requires political approval.

It is important to highlight that the site will be converted to a provisional storage place which is an environmentally and physically safe place that allows in situ recovery of materials and energy from waste streams. Based on the data processing of the MSW of UCF, this sustainable method consists of mechanical processes planned to recover any or all of the following:

- Recyclables incombustible (metal, glass, and dense plastic other than films).
- Organic waste.
- Inert soil material.
- Combustible (paper, textiles, rubber, wood, and plastic films).
- Recovery of space: Volume of the reclaimed landfill to reuse the additional capacity at a reduced cost and/or the value of the reclaimed land for other purposes.
- Limiting the impact of the landfill: Reduces long-term environmental impact (surrounding, social, and environmental) and thus reduces the costs of closure and post-closure.

The stored waste will be excavated from the old part and will be placed on the available 20,000 m^2 land adjacent to the site from the seaside as shown in Fig. 2. A mobile sorting system will be placed on this land. A pre-separation process will receive the mixed waste parts to identify the hazardous materials that will be treated or disposed properly and soft granules that should be excluded in the separation process. After that, the remainder is subject to progressive separation technology for additional segregation. This technology is determined by the characteristics of the removed waste such as particle size, moisture content, etc. Soil-type constituents can be used in green areas as soil amendments or fertilizers. Furthermore, soil and glass materials, plastic minerals, and construction waste can be recycled easily and reused, which means that they will be converted from waste to material (WTM). Alternatively, plastics can be used as raw materials for generating energy (WTE) which is known as waste-derived fuel (RDF). In addition, it can be burned to give back thermal power to produce electricity. RDF can be treated thermally in situ.

Scenario 4 Enhanced landfill mining (stationary plant)

It is similar to Scenario 3 but the extracted waste is transported to the stationary sorting station available next to the CD as shown in Fig. 2 after it has been upgraded to suit this type of waste. Once again, the materials separated from the waste stream are recycled and reused.

3 Discussions and Results

Scenario 1

This scenario would leave the CD in its existing condition and would not offer any protection to human health and the environment. Therefore, this solution is rejected.

Scenario 2

This scenario will include the closure, and the final capping of the site. In general, this scenario will enhance the gas collection operation; and the reduction of leachate production by covering the solid waste materials. Moreover, it provides the operation and maintenance of the site cap, and continued monitoring of gas and leachate emissions. The cost for final closure and remediation is very high and will not result in any benefit from the urban land. Therefore, the options of financing of these costs by the private sector, or through long-term loan from International Financing Institutions (European Investment Bank, European Bank for Reconstruction and Development, World Bank, etc.) are to be considered not feasible since the costs of its closing will not bring any return or future financial benefits. As a result, this scenario is also not feasible for the current situation.

Scenario 3

This scenario is simple; a mobile sorting plant will be installed on the site. This plant separates materials that can be recycled as much as possible with least time and operation requirements. The direct benefits of this scenario are low emissions of CD gas and odor. Recovery revenues where the costs are regularly balanced by the use/sale of recovered materials such as recyclable materials, waste, and soil that can be incinerated as fuel, cost reduction, or avoidance by reducing the costs of liability and closure; taking advantage of the urban economic zone, especially the high cost of land because it is adjacent to the special economic zone in Tripoli, close to the port, creating new jobs. On the other hand, indirect economic benefits comprise the high value of the controlled dump space where resources are removed, forming further space and extending its life. The CDs waste is to be completely excavated over a period of approximately 7 years.

One of the most important aspects of this scenario is the destination of the nonrecyclable part of the CD mining after the recovery of materials and on-site remediation activities that require the re-landfill. The possibility of locating an alternative landfill site was investigated. The siting of a sanitary landfill requires a reliable assessment process that should identify the best possible site for waste disposal. This site must comply with government regulations and, at the same time, reduce economic, environmental, health, and social costs. Therefore, the technical parameters used in this

Table 3 Ministry of environment site selection criteria

Criteria		Value
Siting	Distance to development zone, rural townships	1000 m
Access road	Distance to arterial road networks	500 m
Floodplain	Not within designated area as a "100-year floodplain"	100 m
Slope	Areas with slopes	<10%
Water supply	Distance away from surface water, whether permanent or intermittent	100 m
Design area	Room for future expansion of the facility	5000 m^2
Utilities	Availability of appropriate utilities (water, power, and other services)	
Sensitive areas	Distance from environmentally sensitive or protected areas	1000 m^2

part of the study were determined based on the guidelines produced by the Ministry of Environment's location selection. Nontechnical aspects such as access, availability of suitable facilities (water, energy, and other services), and expected growth and development near the facility [6]. Criteria for selecting MOE sites used in this study are presented in Table 3.

Nevertheless, there is no such site in the cities of UCF. Therefore, it was found that the most feasible solution, both in terms of environmental and financial, is the use of existing quarries in the northern governorate of Lebanon, especially those towns that have quarries and access to benefits from the wastewater treatment plant available in Tripoli. The GIS constraint maps were produced and converted into weighted geographical raster layers along the Spatial Extent of the GON cities to represent the regions which are suitable for the development of the CD. Those constraints maps were: (1) slope, (2) distance from rivers, (3) distance from residential zones, and (4) distance from roads. Two sites are found suitable for this study waiting for political decision since siting a new sanitary landfill is a very complex task.

However, from an environmental point of view, ELFM processes are not without risk because they include a number of phases (excavation, treatment, and recycling of waste), which can lead to unsafe circumstances on-site (e.g., failures in the zone under excavation, release of gases that can cause fires or explosions) and dangerous effects on public health and the environment (such as emission of particulate matter and odor and produced leachate) [19, 9]. Therefore, after reviewing operational treatment and sitemaps, 10 wells (1 per 6000 m^2) are proposed for a site characterization study as covered by phase 2 with a social benefits analysis tool to assess potential economic benefits and project costs; investment of regulatory requirements; and make a preliminary plan for workers' health and safety.

This scenario will take potential advantages of the latest collection and recycling materials technologies.

Scenario 4

This scenario involves the collection of materials as much as possible for recycling by modern technologies. This is an ambitious option where the stationary plant can separate six categories of usable materials: organic materials, combustible materials, ferrous and nonferrous metals, plastic, and building materials. Four of these six categories can be treated in different recycling plants, while the categories of combustible materials can be disposed of in the available incineration plants. Although the location of the sorting and composting plant is adjacent to the CD, the area is small; in addition to the wrong selection of the composting process used and the lack of know-how on the operating parameters that tend to reduce the effectiveness of the technology and lead to many annoying environmental problems of UCF cities. Therefore, this scenario is rejected.

4 Conclusions

This paper presents a qualitative and quantitative methodological approach for sustainable reclamation of open dump. To deal with this issue, the type, components, and all processes for its remediation need to be given serious consideration so that appropriate and workable alternatives can be designed for a better management. Different steps were followed to analyze the case and different scenarios were studied to overcome the crisis of the controlled dump in UCF cities. The findings of this study indicate that ELFM operations could potentially be feasible, for the remediation of this dump when considered in the long run. A supplementary study is necessary to cover the characteristics of dumped wastes to determine the potential benefits in addition to controls that will be required during excavation as well as the analysis of economic standards, to be able to conduct a combined environmental and economic assessment of ELFM.

Acknowledgements The author expresses her appreciation to the Urban Commune of Al-Fayhaa for its cooperation in this work.

References

1. Al-Salem SM, Lettieri P, Baeyens J (2009) Recycling and recovery routes of plastic solid waste (PSW): a review. Waste Manag 29(10):2625–2643
2. Bosmans A, Vanderreydt I, Geysen D, Helsen L (2013) The crucial role of waste-to-energy technologies in enhanced landfill mining: a technology review. Clean Prod 55(1):10–23
3. Deutz P, Neighbour G, McGuire M (2010) Integrating sustainable waste management into product design: sustainability as a functional requirement. Sustain Dev 18:229–239

4. Di Maria F, Micale C, Sordi A, Cirulli G, Marionni M (2013) Urban Mining: quality and quantity of recyclable and recoverable material mechanically and physically extractable from residual waste. Waste Manag 33:2594–2599
5. El-Hoz M (2005) Sanitary landfill extension. In: The tenth international waste management and landfill symposium, Sardinia, Italy, 3–7 Oct 2005
6. El-Hoz M (2012) Evaluation of composting processing technologies for the treatment of urban municipal solid waste. In: The twenty-seventh international conference, on solid waste technology and management, Philadelphia, PA U.S.A., March 11–14, pp 1394–1405
7. El-Hoz M (2015) Market-based system of municipal solid waste composting. Solid Waste Technol Manag 41(3):239–248
8. El-Hoz M (2017) Enhancing governance, transparency and accountability for sustainable solid waste management. In: The thirty-second international conference on solid waste technology and management, Philadelphia, PA, U.S.A., March 19–22, pp 40–58
9. Ford S, Warren K, Lorton C, Smithers R, Read A, Hudgins M (2013) Feasibility and viability of landfill mining and reclamation in Scotland (scoping study), final report, zero waste Scotland. http://ee.ricardo.com/cms/assets/Documents-for-Insight-pages/Resource-efficiency/Feasability-and-Viability-of-LFMR-Scotland-1904130.pdf
10. Frändegård P, Krook J, Svensson N, Eklund M (2013) A novel approach for environmental evaluation of landfill mining. Clean Prod 55:24–34
11. Hogland W (2002) Remediation of an old landfill site. Environ Sci Pollut Res 9(1):49–54
12. Hogland W, Marques M, Nimmermark S (2004) Landfill mining and waste characterization: a strategy for remediation of contaminated areas. Mater Cycles Waste Manag 6:119–124
13. Jain P, Townsend T, Johnson P (2012) Case study of landfill reclamation at a Florida landfill site. Waste Manag 33(1):109–116
14. Johansson N, Krook J, Eklund M (2012) Transforming dumps into gold mines: experiences from Swedish case studies. Environ Innov Soc Transit 5:33–48
15. Johansson N, Krook J, Eklund M, Berglund B (2013) An integrated review of concepts and initiatives for mining the technosphere: towards a new taxonomy. Clean Prod 55(1):35–44
16. Jones PT, Geysen D, Tielemans Y, Van Passel S, Pontikes Y, Blanpain B (2013) Enhanced landfill mining in view of multiple resource recovery: a critical review. Clean Prod 55:45–55
17. Kaartinen T, Sormunen K, Rintala J (2013) Case study on sampling, processing and characterization of landfilled municipal solid waste in the view of landfill mining. Clean Prod 55(15):56–66
18. Krook J (2010) Urban and landfill mining: emerging global perspectives and approaches. Clean Prod 18:1772–1773
19. Krook J, Svensson N, Eklund M (2012) Landfill mining: a critical review of two decades of research. Waste Manag 32(3):513–520
20. Krook J, Baas L (2013) Getting serious about mining the technosphere: a review of recent landfill mining and urban mining research. Clean Prod 55(15):1–9
21. Kurian J, Esakku S, Palanivelu K, Selvam A (2003) Studies on landfill mining at solid waste dumpsites in India. In: Proceedings Sardinia'03, ninth international Landfill symposium, Cagliari, Italy, pp 248–255
22. Kurian J, Esakku S, Nagendran R (2007) Mining compost from dumpsites and bioreactor landfills. Environ Technol Manag 7:317–325
23. Marella G, Raga R (2014) Use of the contingent valuation method in the assessment of a landfill mining project. Waste Manag 34(7):1199–1205
24. Observatory of Environment and Development (2017) Urban Commune Al-Fayhaa, Progress Report
25. Prechthai T, Padmasri M, Visvanathan C (2008) Quality assessment of mined MSW from an open dumpsite for recycling potential. Resour Conserv Recycl 53:70–78
26. Quaghebeur M, Laenen B, Geysen D, Nielsen P, Pontikes Y, Van Gerven T, Spooren J (2013) Characterization of landfilled materials: screening of the enhanced landfill mining potential. Clean Prod 55:72–83

27. Raga R, Cossu R (2013) Bioreactor tests preliminary to landfill in situ aeration: a case study. Waste Manag 33(4):871–880
28. SWEEPNET (2010) Country Report on the Solid Waste Management in Lebanon
29. Van der Zee DJ, Achterkamp MC, de Visser BK (2004) Assessing the market opportunities of landfill mining. Waste Manag 24:795–804
30. Van Passel S, Dubois M, Eyckmans J (2013) The economics of enhanced landfill mining: private and societal performance drivers. Clean Prod 55:92–102
31. Wagner TP, Raymond T (2015) Landfill mining: case study of a successful metals recovery project. Waste Manag 45:448–457
32. World Bank, SWEEPNET (2014) Cost of environmental degradation due to solid waste management practices in Beirut and Mount Lebanon, Final Draft
33. Zhao Y, Song L, Huang R, Li X (2007) Recycling of aged refuse from a closed landfill. Waste Manage Res 25(2):130–138
34. Zhou Chuanbin, Fang Wenjun, Wanying Xu, Cao Aixin, Wang Rusong (2014) Characteristics and the recovery potential of plastic wastes obtained from landfill mining. Clean Prod 80:80–86
35. Zhou C, Gong Z, Hu J, Cao A, Liang H (2015) A cost-benefit analysis of landfill mining and material recycling in China. Waste Manag 35:191–198

Recycling of Marble Waste in the Manufacturing of Ceramic Roof Tiles

Sh. K. Amin, S. A. El-Sherbiny, H. H. Abo-Almaged and M. F. Abadir

1 Introduction

With the progress of science and the increasing awareness of people's environmental protection consciousness, there is a great tendency worldwide towards recycling industrial waste by-products and their utilization in many construction materials. The recycling process not only helps decreasing the environmental pollution but also aids in lowering production costs.

Marble industry generates a lot of wastes mainly in the form of powder during sawing and polishing processes. During the cutting process, 20–30% of the block is reduced to fine powder that pollutes and damages the environment [1]. This fine waste is a highly polluting waste due to both its highly alkaline nature and high abrasiveness, which pose a health threat to the surroundings [2].

Over the past years, there has been an increasing number of researches on the use of marble waste in mortar mixes [3], catalysts [4], concrete [5–7], concrete roof tiles [8], and ceramic wall and floor tiles [9, 10].

The aim of the present work is to use the generated fine marble dust as partial replacement of a basic mixture of clay roof tiles, in order to achieve the objectives of

---

Sh. K. Amin (✉)
Engineering Research Division, Chemical Engineering and Pilot Plant Department,
National Research Centre (NRC), Affiliation ID: 60014618, Dokki, Giza, Egypt
e-mail: sheren51078@yahoo.com; dr.shereenkamel@hotmail.com

S. A. El-Sherbiny · M. F. Abadir
Chemical Engineering Department, Faculty of Engineering, Cairo University,
Giza, Egypt

H. H. Abo-Almaged
Inorganic Chemical Industries and Mineral Resources Division,
Ceramic and Building Materials Department, Refractories,
National Research Centre (NRC), Dokki, Giza, Egypt

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_11

economic, environmental, and also to achieve sustainable development saves sources of raw materials for future generations.

2 Experimental Work

2.1 Raw Materials

Two types of raw materials were used in this work: The first part is a clay roofing tiles body mixture that was kindly supplied by Sornaga Company, Egypt. This basic mixture was prepared from Egyptian raw materials. It consisted of clay mix (ball clay, Aswan clay, and shale clay) $\leq$50 wt%, sodium feldspar (albite) $\leq$20 wt%, and roofing tiles grog ($\leq$30 wt%) used as an addition to conventional mixes to reduce shrinkage, and commercial barium carbonate ($\leq$2 wt%). The second part consists of the marble fine waste which was collected from Shaq Al-Thuban cluster in Egypt.

2.2 Characterization of Raw Materials

The chemical composition of raw materials was determined using XRF by an AXIOS, Panalytical 2005, and Wavelength-Dispersive (WD-XRF) Sequential Spectrometer. X-ray powder diffraction (XRD) analysis was performed by a Brukur D8 Advanced Computerized X-ray diffractometer apparatus with monochromatized Cu Kα radiation, operated at 40 kV and 40 mA. Grain size distribution was performed according to the standard sieving procedure ASTM D 422 [11]. The powder densities of clay mix and marble fine waste were measured using the standard pycnometer method (density flask).

2.3 Tile Samples Preparation

The marble waste was dried and then ground in laboratory ball mill for 5 min. The fine waste was used to replace part of the basic mixture in percentage of weight from 0 to 30%. Rectangular samples of dimensions (150 mm × 30 mm × 25 mm) were molded with different percentage wastes using a fixed water content of 20% (on dry basis). This water content provided the best workability of mixtures. Each sample consisted of three specimens. The formed samples were dried at (110 ± 5)°C overnight and then, fired in a laboratory muffle at 1000 and 1150 °C for 3 h soaking time.

2.4 Testing of Fired Samples

For fired samples, the following tests were performed. Each time the numerical average of the three specimens was recorded.

- Linear firing shrinkage (LFS) was evaluated according to ASTM C 326 [12].
- Loss on ignition was measured according to ASTM D 7348 [13].
- Bulk density was measured according to ASTM C 20 [14].
- Water absorption was measured, and saturation coefficient was calculated according to ASTM C 67 [15].
- Transverse breaking strength of tiles was determined according to ASTM C 1167 [16].

3 Results and Discussion

3.1 Raw Materials Characterization

The chemical analyses of the two raw materials (basic raw mix of roofing tiles and marble fine waste) as obtained from XRF analyses, the percent free silica and organic matter are presented in Table 1. This table shows that the loss on ignition is highest in the case of marble waste mainly due to loss of carbon dioxide (consisting mainly of calcium carbonate), in addition to oxidation of organic matter content. Also, most of the LOI of the raw mix of roofing tiles is due to both the loss of water of hydration of clays, and its organic matter content. The fact that the free silica percent in roofing tile mix is higher due to the free silica present in clays.

On the other hand, Fig. 1 shows the mineralogical analyses of two raw materials. The raw mix for roofing tiles is composed of quartz (SiO_2), microcline ($K_2O{\cdot}Al_2O_3{\cdot}6SiO_2$), and albite ($Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$) while the XRD pattern of marble waste consists only of calcite lines ($CaCO_3$).

The cumulative screen analyses of roofing tiles mix and marble waste are shown in Fig. 2. The vertical axis represents the fraction passing from each particular screen diameter. Table 2 shows both of the volume–surface mean diameter ($\overline{D_s}$) and D_{50} values for two powders [17].

Finally, the powder density of the raw materials used in this work was found to be 2.152 gm cm^{-3} for roofing tiles mix and 2.425 gm cm^{-3} for marble fine waste.

Table 1 Chemical analysis of raw materials

Main constituents (wt%)	Raw mix	Marble waste
SiO_2	57.17	2.32
TiO_2	1.26	0.03
Al_2O_3	22.48	0.44
$Fe_2O_3^{tot.}$	7.96	0.20
MnO	0.10	–
MgO	0.76	0.48
CaO	0.68	53.75
Na_2O	1.06	0.09
K_2O	1.30	0.03
P_2O_5	0.16	0.09
SO_3	0.43	0.26
Cl	0.19	0.04
BaO	0.385	–
ZrO_2	0.039	–
Minor oxides	0.115	0.053
LOI	5.91	42.21
Free silica	19.19	0.85
Organic matter	5.84	7.10

Table 2 Volume—surface mean diameter ($\overline{D_s}$) and (D_{50}) values of raw materials

Powder (mm)	Roofing tiles mix	Marble waste
D_{50}	0.415	0.021
$\overline{D_s}$	0.41	0.036

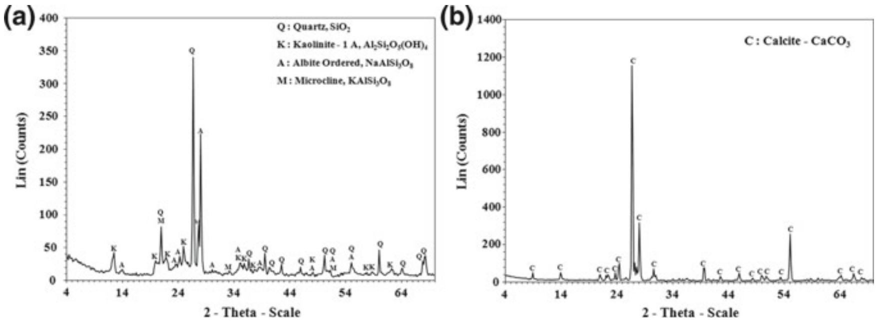


Fig. 1 XRD pattern of two raw materials, **a** Roofing tiles raw mix, **b** marble fine waste

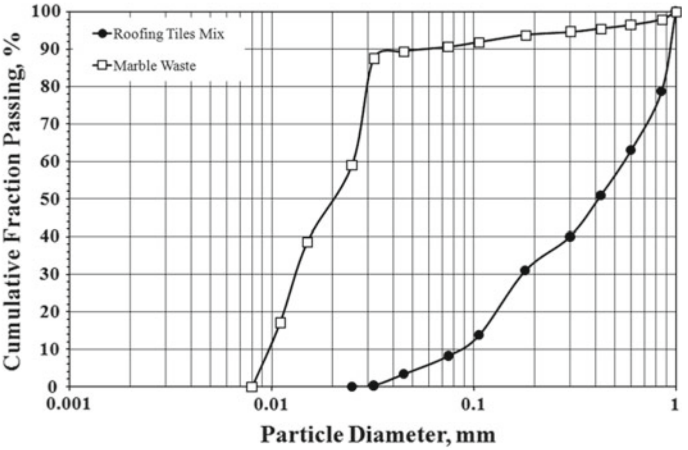


Fig. 2 Cumulative screen analysis of the raw materials

3.2 *Properties of Fired Roofing Tiles Samples*

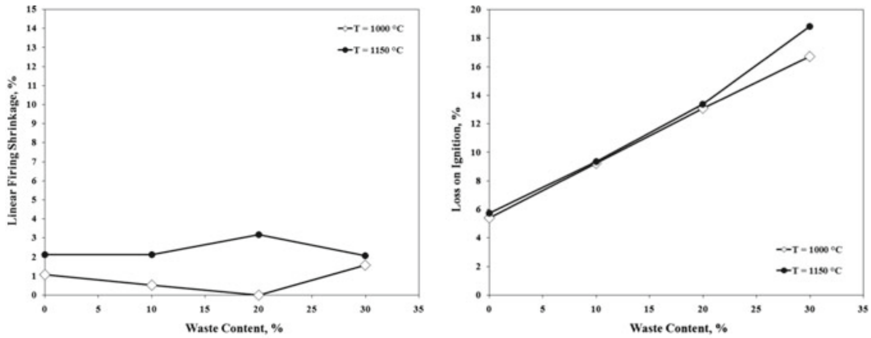
3.2.1 Firing Shrinkage

Figure 3a shows the effect of marble waste addition on linear firing shrinkage for tiles fired at 1000 and 1150 °C. As revealed from Fig. 3a, the linear firing shrinkage observed on adding marble dust for samples fired at 1150 °C did not vary but remains almost constant at about 2% at all addition levels. At 1000 °C, however, there was a decrease in shrinkage at 20% addition after which the percent shrinkage increased once more to reach 2% at higher levels of addition.

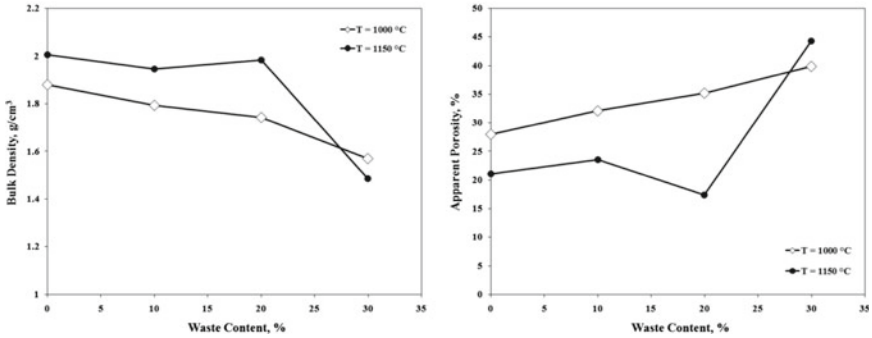
Actually, the fact that marble dust is much finer than the tiles mix should play in favor of increasing firing shrinkage once available pores between tiles mix particles are filled with calcined marble powder. It seems that this occurs at about 30% addition. Actually, this is supported by the fact that minimum porosity is achieved for a coarse to fine ratio of about 70:30 [18].

3.2.2 Loss on Ignition

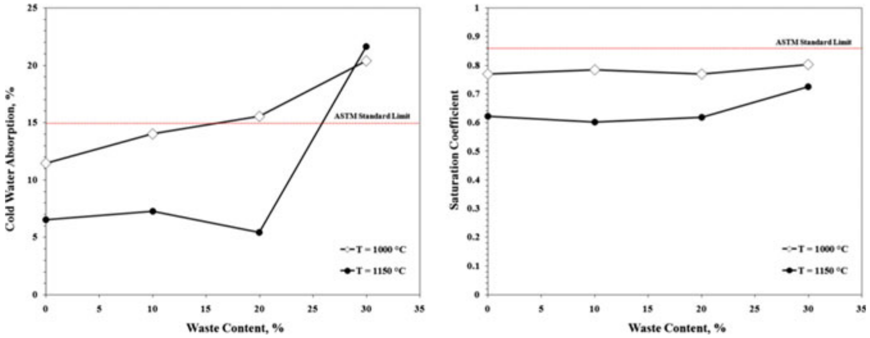
Figure 3b illustrates the effect of marble waste additions on loss on ignition, for tiles fired at different temperature. Adding marble dust to tiles mix at any level steadily increases the loss on ignition owing to loss of carbon dioxide and organic matter.



(a) Linear firing shrinkage **(b) Loss on Ignition**



(c) Bulk density **(d) Apparent porosity**



(e) Water absorption **(f) Saturation coefficient**

Fig. 3 Effect of marble waste content on physical properties of fired tiles

3.2.3 Bulk Density and Apparent Porosity

Bulk density (ρ_B) is related to the powder (true), density of the body (ρ_p), and its fractional porosity (p) by the expression:

$$\rho_B = \rho_p (1 - p) \tag{1}$$

The effect of adding marble waste on the bulk density is shown in Fig. 3c. The decrease in bulk density is not due to the difference in powder density as that of tiles mix is lower than that of marble waste. In addition at temperatures higher than 900 °C, calcium oxide (of specific gravity = 3.3) will be present. That is why the main reason for the drop in bulk density is an increase in porosity following the dissociation of calcite. At 1150 °C, the formation of a vitreous phase in reasonable amount will damp that effect resulting in a practically constant bulk density. Above 20% addition, the amount of liquid phase cannot contribute to closing all the pores formed by the evolution of carbon dioxide. This reflects in decreasing the bulk density. These results are totally compatible with the variation of apparent porosity displayed in Fig. 3d.

3.2.4 Water Absorption and Saturation Coefficient

The percent water absorption is defined as the amount of water absorbed by the body relative to its dry mass (m_D) as follows:

$$\text{Water absorption } (\%) = \frac{m_W - m_D}{m_D} \times 100\% \tag{2}$$

Figure 3e shows the variation of percent water absorption with adding marble waste. Since water absorption increases with increased porosity, it is expected that waste addition will have an inverse effect on water absorption. Additions of marble dust below 20% do not increase water absorption above the standard level of 15%.

On the other hand, the saturation coefficient is the ratio of cold water absorption to hot water absorption and should not exceed 0.86 [16]. Figure 3f reveals the decrease in saturation coefficient upon raising the firing temperature. Alternatively, the addition of marble waste does not affect that coefficient.

3.2.5 Mechanical Strength

According to ASTM C 1167 [16], the dry transverse breaking "strength" of tiles (N) defines as follows:

$$\text{Transverse breaking strength} = F \times \frac{L}{b} \tag{3}$$

where

L is the distance between two supports (mm),
b is the breadth of specimen (mm), and
F the fracture load (N).

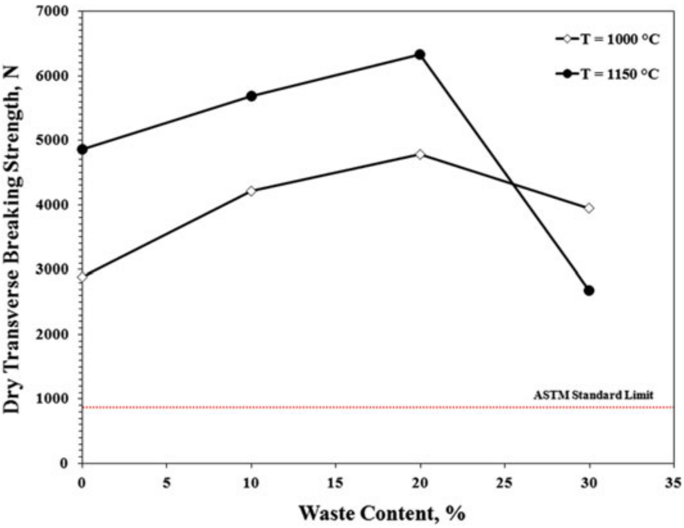


Fig. 4 Effect of marble waste content on dry transverse breaking strength

Figure 4 shows the effect of waste content on dry transverse breaking strength at different firing temperatures. As expected, the highest strength values will be achieved at the highest firing temperatures following the completion of sintering and formation of a reasonable amount of binding glassy phase.

4 Conclusion

Marble dust generated during the cutting process of marble block can reach up to 30% of raw material. This fine waste was utilized in the manufacture of ceramic roofing tiles, in order to achieve the objectives of economic, environmental, and also to achieve sustainable development saves sources of raw materials for future generations. The basic raw materials for ceramic roofing tiles and the solid waste were characterized by XRF and XRD. Marble dust was mixed with a standard mix of ceramic roofing tiles at different percentages reaching 30%, molded, dried, and fired through a fast single-firing technique in a laboratory muffle furnace. Firing was performed at 1000 and 1150 °C, for a soaking period of 3 h. Physical and mechanical properties were next measured and compared to International Standard. It was possible to obtain tiles compatible with American standard ASTM C 1167 using 10% marble waste replacement and firing at 1000 °C.

References

1. Ulubeyli GC, Artir R (2015) Properties of hardened concrete produced by waste marble powder. Procedia—Soc Behav Sci 195:2181–2190
2. Rania AH, Salah E, Safwan K (2011) Marble and granite waste: characterization and utilization in concrete bricks. Int J Biosci, Biochem Bioinform 1(4):286–290
3. Khyaliya RK, Kabeer KISA, Vyas AK (2017) Evaluation of strength and durability of lean mortar mixes containing marble waste. Constr Build Mater 147:598–607
4. Jyothi Y, Somaiah PV, Reddy KHP, Venkateshwarlu V, Swamy KK, Raju BD, Rao KSR (2017) An inexpensive and environmentally friendly activated marble waste as a catalyst for vapour phase dehydration of 1,4-butanediol to tetra-hydro-furan. Catal Commun (in press)
5. Arel HŞ (2016) Recyclability of waste marble in concrete production. J Clean Prod 131:179–188
6. Sudarshan DK, Vyas AK (2017) Impact of fire on mechanical properties of concrete containing marble waste. J King Saud Univ—Eng Sci (in press)
7. Ulubeyli GC, Bilir T, Artir R (2016) Durability properties of concrete produced by marble waste as aggregate or mineral additives. Procedia Eng 161:543–548
8. Aditya C, Halim A, Putri CF (2014) Waste marble utilization from residue marble industry as a substitution of cement and sand within concrete roof tile production. Int J Eng Res (IJER) 3(8):501–506
9. García-Ten J, Mallol G, Bou E, Silva G, Fernández J, Molina A, Romera J (2003) Recycling marble working wastes in manufacturing ceramic products, part II: ceramic wall tile manufacture. Ceram Forum Int 80(10):E30–E32
10. Erdoğan NB, Yeprem HA, Günay E, Marşoğlu M (2011) Evaluating waste marble dust as floor tile. Mater pruf 53(5):290–294
11. ASTM D 422/1963 (Reapproved 2007) Method for particle–size analysis of soils. Annual book of American Society for Testing of Material (ASTM), U.S.A., vol 04.08 (March 2014)
12. ASTM C 326/2009 (Reapproved 2014), Standard test method for drying and firing shrinkages of ceramic white ware clays. Annual book of American Society for Testing of Material (ASTM), U.S.A., vol 15.02 (April 2017)
13. ASTM D 7348/2013, Standard test methods for loss on ignition (L.O.I) of solid combustion residues. Annual book of American Society for Testing of Material (ASTM), U.S.A., vol 05.06 (September 2016)
14. ASTM C 20/2000 (Reapproved 2015) Standard test methods for apparent porosity, water absorption, apparent specific gravity, and bulk density of burned refractory brick and shapes by boiling water. Annual book of American Society for Testing of Material (ASTM), U.S.A., vol 15.01 (March 2017)
15. ASTM C 67/ 2017, Standard test methods for sampling and testing brick and structural clay tile. Annual book of American Society for Testing of Material (ASTM), U.S.A., vol 04.05 (June 2017)
16. ASTM C 1167/ 2011, Standard specification for clay roof tiles. Annual book of American Society for Testing of Material (ASTM), U.S.A., vol 04.05 (June 2017)
17. McCabe L, Smith C (2005) Unit operations of chemical engineering. 7th ed., McGraw–Hill, New York
18. Kingery WD, Bowen HK, Uhlmann DR (1976) Introduction to ceramics, 2nd edn. Wiley, New York

Treatment (Handling) of Hazardous Waste in Germany

Isabell Eickhoff, Anna-Sabina Emmerich, G. Morscheck, A. Schüch and Michael Nelles

The term “hazardous waste” refers to various waste types with defined hazardous properties that are harmful to the environment and/or the human health. Hazardous waste must be handled using special techniques and processes that ensure a safe and environmentally sound handling.

This article provides an overview of the hazardous waste situation in Germany. For this purpose, publications from the UBA [6] (Germany’s main environmental protection agency) and the Federal Ministry for the Environment, Nature Conservation, Building, and Nuclear Safety [1] are used.

“In Germany certain types of waste with hazardous properties are sometimes referred to as ‘hazardous waste’ or ‘special waste’, a term for which no clear legal definition exists in the German law” [6].

1 Hazardous Waste Classification

Depending on the literature used, there are many different definitions and categories of waste available. Waste can be generally classified into hazardous and nonhazardous waste. Hazardous waste is waste which poses a special threat to human health or the environment. Based on the physical, chemical, and biological properties, hazardous waste can be classified into:

I. Eickhoff (✉) · A.-S. Emmerich · G. Morscheck · A. Schüch · M. Nelles
Department of Waste Management and Material Flow,
University of Rostock, Rostock, Germany
e-mail: isabell.eickhoff@uni-rostock.de

M. Nelles
German Biomass Research Centre gGmbH (DBFZ), Leipzig, Germany

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_12

- Radioactive waste (e.g., waste from nuclear reactors),[1]
- Toxic waste (e.g., chlorofluorocarbons, POPs or heavy metals),
- Reactive waste,
- Corrosive waste (e.g., strong alkaline or acidic substances),
- Infectious waste (e.g., hospital waste),
- Flammable waste, or
- Explosive waste.

Hazardous waste might, therefore, cause environmental pollution or serious illnesses when ingested, inhaled, or touched and thus requires proper management strategies. Nonhazardous waste, on the other hand, does not pose a direct threat to humans or the environment. The typical sources of nonhazardous waste are municipal solid waste (MSW), nonhazardous industrial waste, agricultural waste and residues as well as construction and demolition (C&D) waste.

Classifying waste according to its hazardousness is an essential element of waste management; as such classifications determine the waste treatment methods used and the supporting waste documentation. In the EU, waste designations and classifications are governed by the Commission Decision 2000/532/EC (The European List of Waste, LoW) where all wastes that are classified as hazardous waste are marked with an asterisk next to their waste identification code. The various types of waste are hereby classified irrespectively of their disposal method.

Apart from hazardous and nonhazardous wastes, the European List of Waste also contains so-called "mirror entries" for waste streams whose hazard criteria are decisive from a legal point of view depending on hazardous substance concentrations or hazard properties. The Directive 2008/98/EC (Waste Framework Directive) defines 15 hazard criteria (H-criteria) that specify the hazardousness of those mirror entries [6] (Table 1).

The European List of Waste lays down concentration limits for certain hazard criteria. Those concentration limits are based on chemical regulations (Table 2).

R-phrases (short for Risk Phrases) are defined in Annex III of the European Union Directive 67/548/EEC. For example, R35—Causes severe burns, R34—Causes burns, or R41—Risk of serious damage to eyes.

The European Union classification of carcinogens is included in the Dangerous Substances Directive and the Dangerous Preparations Directive. It consists of three categories:

- Category 1: Substances known to be carcinogenic to humans.
- Category 2: Substances which should be regarded as if they are carcinogenic to humans.
- Category 3: Substances which cause concern for humans, owing to possible carcinogenic effects but in respect of which the available information is not adequate for making a satisfactory assessment.

---

[1] In Germany, radioactive waste is excluded from the "hazardous waste" category as it is no waste according to the German waste directive. Germany has a special law, the Radioactive Substances Act, focusing on radioactive wastes.

Table 1 Hazardous properties (Directive 2008/98/EC)

H1	Explosive	H9	Infectious
H2	Oxidizing	H10	Toxic for reproduction
H3	Flammable	H11	Mutagenic
H4	Irritant—skin irritation and eye damage	H12	Release of an acute toxic gas
H5	Specific target organ toxicity (STOT)/Aspiration toxicity	H13	Sensitizing
H6	Acute toxicity	H14	Ecotoxic
H7	Carcinogenic	H15	Waste capable of exhibiting a hazardous property listed above but not directly displayed by the original waste
H8	Corrosive		

Table 2 Hazardous waste categories based on substance concentration limits (with associated R-phrases in accordance with Annex III to the Dangerous Substances Directive [67/548/EEC])

Hazardous properties	Specification Flash point/concentration limits of one or more substances	H-criterion
Flammable	Flash point ≤55 °C	H3
Very toxic	≥0.1%	H6
Toxic	≥3%	H6
Harmful	≥25%	H5
Corrosive (R35)	≥1%	H8
Corrosive (R34)	≥5%	H8
Irritant (R41)	≥10%	H4
Irritant (R36, R37, and R38)	≥20%	H4
Carcinogenic (Cat. 1 or 2)	≥0.1%	H7
Carcinogenic (Cat. 3)	≥1%	H7
Toxic for reproduction (Cat. 1 or 2, R60 or 61)	≥0.5%	H10
Toxic for reproduction (Cat. 3, R62 or R63)	≥5%	H10
Mutagenic (Cat. 1 or 2, R46)	≥0.1%	H11
Mutagenic (Cat. 3, R40)	≥1%	H11

Table 3 Number of entries in the European List of Waste (LoW)

842 entries in the List of Waste			
408 Hazardous entries		434 Nonhazardous entries	
228 AH	180 MH	198 MNH	236 ANH

This assessment scheme is currently replaced by the GHS scheme which uses very similar category definitions.

In the European Union, the waste classification according to the European List of Waste (Commission Decision 2000/532/EC and Annex III to Directive 2008/98/EC) is used. The List of Waste (LoW) serves as a common coding of waste characteristics for many different purposes such as the grouping of hazardous wastes. The clear allocation of waste codes has a major impact on the transport of waste, installation permits (which are usually granted for the processing of specific waste codes), and decisions about recyclability of the waste or as a basis for waste statistics.

Any waste entry marked with an asterisk (*) is considered hazardous. The LoW is currently being revised and updated with regard to changes in chemical regulations. The 842 entries of the European List of Waste will then be divided into “absolute” hazardous (AH), “absolute” nonhazardous (ANH), “mirror” hazardous (MH), and “mirror” nonhazardous (MNH) entries. Thereby, each waste is either hazardous or nonhazardous (Table 3).

2 Handling of Hazardous Substances

According to Paragraph 47(1) of the German Waste Management Act (KrWG), waste prevention and management fall under the jurisdiction of the competent Federal State authorities. In Federal States imposing delivery and handover obligations for hazardous waste, the waste-generating entity is required to notify the type, quantity, and composition of the waste in question as well as the envisaged disposal facility to the local authorities. The authorities then allocate the waste to a suitable facility. Disposal techniques can vary greatly from one type of waste to another, as can the applicable regulations. This applies to the discarding of waste containing hazardous substances such as asbestos or persistent organic pollutants (POPs) or PCBs and mercury.

The Ordinance on Waste Recovery and Disposal Records governs monitoring and supervision of hazardous waste recovery and disposal. The supervision is carried out via an electronic waste tracking and record procedure (Waste Recovery and Disposal Record; Transport Form and Transfer Receipt). A Waste Recovery and Disposal Record allows for prior permission—by the waste producing entity, the waste disposal entity, and the competent authority—that a given disposal technique is environmentally sound. The Transport Forms and Transfer Receipts allow for documentation, via acknowledgement that a previously validated disposal technique has been adhered to each individual instance of waste transport. The Ordinance on Waste Recovery and Disposal Records lays down simplified rules for supporting documentation for small quantities of waste, whereby household wastes are not subject to such documentation rules.

3 Hazardous Waste Quantities and Destinations

Transport Forms used in the proof procedure are evaluated for statistics gathering purposes, whereby the competent authorities are legally required to submit information to government statistics offices. In this procedure, no statistics are gathered concerning waste disposal within a given enterprise or for trans-frontier waste deliveries, as these statistics are gathered separately.

Among the waste produced in the EU-28 in 2014, about 94.78 million tonnes (3.0% of the total waste generated—2494.7 million tonnes) were classified as hazardous waste. This was equivalent to an average of 198 kg of hazardous waste per inhabitant in the EU-28 [2].

Compared to 2010, an additional 2.0% of nonhazardous waste was generated in 2014 in the EU-28 and an additional 2.6% of hazardous waste. In 2014, the share of hazardous waste in complete waste generation was below 10.0% in all of the EU Member States (except for Estonia and Ireland, where it accounted for 41.6 and 10.3% accordingly). The very high share for Estonia was primarily due to energy production from oil shales [2] (Table 4).

The generation of hazardous waste in 2014 across European Union Member States ranged from a minimum of 27 kg per inhabitant in Greece to a maximum of 593 kg per inhabitant in Luxembourg. In Luxembourg, the high amount is mainly due to construction activities (Table 5).

Germany itself produces a total of 351 million tonnes of waste. Due to the import of different wastes from other countries, German waste treatment facilities had to handle 408 million tonnes of waste. About 6% of the total waste was hazardous waste (Table 6).

4 Special Waste from Households—Hazardous Waste in Small Quantities from Households

Many everyday products contain substances that are classified as dangerous in the broadest sense. If residual quantities of any harmful substance remain after the products' use, they become hazardous waste, which must be duly disposed of or recycled. Many German municipalities and counties offer a collection of this waste. Hazardous waste can be disposed of in waste collection centers. The disposal of hazardous waste

Table 4 Treatment of hazardous waste by waste category and waste operations [tonnes in 2014] [2]

	Total waste treatment	Deposit onto or into land (D1, D5, D12)	Land treatment and release into water bodies (D2, D3, D4, D6, D7)	Incineration/disposal (D10)	Incineration/energy recovery (R1)	Recovery other than energy recovery—backfilling	Recovery other than energy recovery—except backfilling (R2 to R11)
European Union (28 countries)	75,550,000	36,360,000	700,000	4,670,000	5,720,000	2,400,000	25,700,000
Belgium	2,140,043	589,660	0	173,011	410,133	0	967,239
Bulgaria	12,176,438	11,853,969	163,064	7171	333	0	151,901
Czech Republic	597,309	35,512	0	73,373	51,433	214,021	222,970
Denmark	1,819,120	1,195,969	0	3293	210,161	0	409,697
Germany	20,521,107	4,612,317	37,402	1,263,306	2,788,642	2,178,280	9,641,160
Estonia	10,315,094	8,983,360	0	20	15,279	0	1,316,434
Ireland	86,518	18,541	19,200	13,121	32,436	0	3220
Greece	115,015	19,303	0	2937	3211	0	89,564
Spain	2,321,536	524,712	114	354	137,387	0	1,658,969
France	7,605,065	2,672,055	0	1,520,287	1,046,249	0	2,366,474
Croatia	66,055	10,035	0	0	11,371	0	44,649
Italy	3,574,305	1,268,619	0	407,142	76,739	0	1,821,805
Cyprus	161,446	141,259	0	38	1394	0	18,755
Latvia	43,375	6681	0	11	12,119	0	24,564
Lithuania	55,457	18,168	176	1932	0	0	35,181
Luxembourg	37,843	0	0	0	35,199	0	2644
Hungary	372,580	85,563	0	81,181	21,541	0	184,295
Malta	438	0	0	438	0	0	0
Netherlands	4,483,340	1,327,555	6827	342,968	270,694	0	2,535,296
Austria	439,247	60,260	0	71,327	143,749	0	163,911
Poland	1,876,577	244,786	1426	135,443	2492	0	1,492,430
Portugal	175,169	16,354	0	16,606	16,806	0	125,403
Romania	500,394	124,535	28,152	32,457	124,292	0	190,958
Slovenia	91,696	10,675	0	9965	1443	0	69,613
Slovakia	201,819	52,534	84,669	17,290	4607	0	42,719
Finland	1,915,719	1,187,806	363,431	149,463	45,705	0	169,314
Sweden	1,092,814	426,026	0	102,739	153,013	0	411,036
United Kingdom	2,762,524	869,210	0	241,230	102,777	8549	1,540,758
Iceland	38,960	11,456	0	732	1303	0	25,469
Norway	1,566,241	799,517	1315	50,665	289,034	0	425,710
Former Yugoslav Republic of Macedonia, the	3763	3614	149	0	0	0	0

(continued)

Table 4 (continued)

	Total waste treatment	Deposit onto or into land (D1, D5, D12)	Land treatment and release into water bodies (D2, D3, D4, D6, D7)	Incineration/disposal (D10)	Incineration/energy recovery (R1)	Recovery other than energy recovery—backfilling	Recovery other than energy recovery—except backfilling (R2 to R11)
Serbia	13,493,547	13,434,944	66	0	2286	0	56,251
Turkey	6,487,595	5,831,220	0	33,329	185,314	:	437,731

Table 5 Generation of hazardous waste by waste category in 2014 [kilogram per capita] [2, 3]

	Total Waste	Chemical and medical wastes (subtotal)	Recyclable wastes (subtotal, W06 + W07 except W077)	Equipment (subtotal, W077 + W08A + W081 + W0841)	Mixed ordinary wastes (subtotal, W101 + W102 + W103)	Mineral and solidified wastes (subtotal)
European Union (28 countries)	198	61	4	21	8	104
Germany	273	79	16	18	23	136

from households at municipal collection points is usually free of charge. Only large quantities of commercial goods are charged.

Special wastes from households include, for example:

- PCB-containing capacitors and other PCB-containing waste
- Solid grease and oil contaminated equipment, oil filters, and oily metal packages
- Washing and cleaning agent waste
- Developer baths, fixing baths
- Pesticides, wood preservatives, including their packaging
- Acids and alkalis
- Laboratory chemical residues
- Hypochlorite waste (chlorine bleaching)
- Mercury and mercury-containing waste
- Compressed gas packs (aerosol cans), gas cartridges
- Hand fire extinguishers
- Old paints (non-hardened)
- Solvents, solvent mixtures, and thinners
- Fats, waxes
- Glue and adhesives
- Oils, emulsions.

Table 6 Generation of hazardous waste depending on the LoW waste type chapters in 2015 [3]

Waste types—chapters of the LoW		Total amount of waste	Amount of hazardous waste	Percentage of hazardous waste
		1000 tonnes	1000 tonnes	%
01	Wastes resulting from exploration, mining, quarrying, physical and chemical treatment of minerals	31,427.3	50.4	0.16
02	Wastes from agriculture, horticulture, aquaculture, forestry, hunting and fishing, and food preparation and processing	6092.8	1.5	0.02
03	Wastes from wood processing and the production of panels and furniture, pulp, paper, and cardboard	8551.0	0.5	0.01
04	Wastes from the leather, fur and textile industries	110.4	0.2	0.18
05	Wastes from petroleum refining, natural gas purification, and pyrolytic treatment of coal	68.1	60.3	88.55
06	Wastes from inorganic chemical processes	935.3	355.1	37.97
07	Wastes from organic chemical processes	2121.2	1269.3	59.84
08	Wastes from the manufacture, formulation, supply and use (MFSU) of coatings (paints, varnishes, and vitreous enamels), sealants, and printing inks	299.2	209.5	70.02
09	Wastes from photographic industry	24.6	18.7	76.02
10	Wastes from thermal processes	22,347.9	922.6	4.13
11	Wastes from chemical surface treatment and coating of metals and other materials; nonferrous hydrometallurgy	1732.1	591.7	34.16
12	Wastes from shaping and physical and mechanical surface treatment of metals and plastics	2592.6	115.1	4.44
13	Oil wastes and wastes of liquid fuels (except edible oils, 05 and 12)	1205.1	1413.1	117.26

(continued)

Table 6 (continued)

Waste types—chapters of the LoW		Total amount of waste	Amount of hazardous waste	Percentage of hazardous waste
		1000 tonnes	1000 tonnes	%
14	Waste organic solvents, refrigerants and propellants (except 07 and 08)	107.9	107.9	100.00
15	Waste packaging; absorbents, wiping cloths, filter materials, and protective clothing not otherwise specified	12,448.9	267	2.14
16	Wastes not otherwise specified in the list	4392.5	959.3	21.84
17	Construction and demolition wastes (including excavated soil from contaminated sites)	210,319.3	8582	4.08
18	Wastes from human or animal health care and/or related research (except kitchen and restaurant wastes not arising from immediate health care)	361.3	24.3	6.73
19	Wastes from waste management facilities, off-site waste water treatment plants, and the preparation of water intended for human consumption and water for industrial use	62,855.3	6258.9	9.96
20	Municipal wastes (household waste and similar commercial, industrial and institutional wastes) including separately collected fractions	40,163.1	114.3	0.28
		408,155.9	**21,321.7**	**5.22**

5 Recycling of Special Waste—Reduction of Special Waste

Legal regulations oblige companies to dispose of their waste in an environmentally sound manner. Disposal costs for hazardous waste are relatively high. Costs above 100 € per tonne are common. Companies are therefore interested in producing as little hazardous waste as possible. Many technologies have been redesigned accordingly. In addition, there are voluntary agreements between the industry and the supervisory or regulatory authorities. Sector-specific programs provide expertise on waste reduction.

6 Hazardous Waste Landfills (Aboveground Landfills, Underground Hazardous Waste Disposal Facility in Salt Rock)

Hazardous wastes that are not damaged by incineration or other chemical processes need to be disposed in save landfills.

In Germany, there are five landfill classes, two classes are for hazardous waste. Landfill sites must meet the following requirements:

- Suitable, secure location,
- Suitable multilayer landfill sealing system,
- Suitable installation technology for the waste,
- Compliance with the allocation values of the Landfill Ordinance.

In 2015, 2,671,100 tonnes of hazardous waste was deposited aboveground and another 120,500 tonnes underground in a total of 31 landfills for hazardous waste (including four underground disposal sites) [3].

Landfills require a special sealing system (basic and surface sealing), a combination of mineral and plastic (HDPE) sealing. The generated leachate water must be fed to a leachate treatment plant. Landfill gas must be collected and treated. Particular requirements are placed on the operation management. Special waste disposal sites are strictly monitored.

In contrast to the atmospheric processes, processes in the hydrosphere, pedosphere (ground), and lithosphere (geological layer of the earth) extend over geologically long periods of time. Mountain formation and extraction processes even take millions of years. Movements in the earth's crust range from millimeters to centimeters per year.

Underground hazardous waste disposal facilities in suitable rock formations are thus the only realistic way to avoid the long-term direct contact of pollutants with high and lasting potential and the biological cycle.

The underground landfill is intended for waste which is a danger to water and air even when orderly managed in aboveground hazardous waste disposal sites, and whose biological or thermal degradation would be technically and ecologically problematic or too expensive.

7 Chemical and Physical Treatment

Approximately, 25–30% of all hazardous waste generated in Germany is chemically and physically treated in a total of 534 plants. Thus, their dangerous ingredients are destroyed or converted into harmless ones.

The subsequent environmentally sound recovery or disposal of this waste is thus made possible. In chemical–physical treatment plants, mainly liquid hazardous waste is treated. In this case, chemical–physical reactions are used for material transformation (e.g., neutralization, oxidation, and reduction). A concentration of the dangerous ingredients (e.g., by filtration, sedimentation, distillation, and ion exchange) is frequently carried out in order to improve the reaction conditions or the economic efficiency of the process.

8 Thermal Treatment of Hazardous Waste

Waste incineration plants are treatment plants (!) which can additionally generate electricity and heat.

All of Germany's thermal waste treatment facilities comply with Directive 2010/75/EC. The European state of the art is set in the Best Available Techniques (BAT) reference document, which targets to encourage implementation of the principles regarding integrated pollution prevention and control. The EU waste incineration rules were transferred into German law via the 17th Ordinance on the Implementation of the Federal Immission Control Act (Ordinance on Waste Incineration and Co-Incineration) which applies to all waste incineration and co-incineration facilities.

Germany has 33 waste incineration facilities mainly designed for hazardous wastes (rotary kilns), most of whom are placed at chemical plants and mainly handle waste from neighboring industrial facilities. But some of those facilities have been outsourced from their chemical plants and run their own waste acquisition operations [6]. In total, 134 plants are allowed to treat hazardous waste thermally. 2,468,300 tonnes of hazardous waste were thermally treated in 2015, including 12,047,000 tonnes in rotary kilns [3].

Hazardous wastes are often a mixture of solid, pasty, and liquid substances. For such mixes, the grate incineration is inappropriate (because of the liquid portion). Therefore, the rotary kiln incineration is preferred for hazardous wastes. This technology comes from the industrial furnace sector, where it is used for the thermal treatment of industrial materials (e.g., cement) [4].

9 Process Technology

Principal components of the main thermal process, area waste hopper, charging system, and barrel lift, mainly are the rotary kiln, post-combustion chamber, and heat exchanger (boiler plant). The flue gas purification plant downstream comprises the components electrostatic precipitator, multistage flue gas scrubber, suction draught ventilator, and chimney.

In summary (according to [4]):

- Practically any waste form (including containers) can be fed.
- Rotary kilns for hazardous waste are designed with diameters between 1 and 5 m and lengths between 8 and 12 m, in exceptional cases up to 20 m.

- Because of very fast evaporation and degassing reactions of combustibles immediately after charging due to waste heterogeneity, sufficient oxygen has to be readily available, i.e., air ratios (λ) of about 1.8–2.0 are required. If the contents of the charged barrels are known before, additional oxygen can be injected in short intervals.
- Oxygen distribution along the reaction path is hardly controllable in contrast to the grate process.
- The residence time of solids (e.g., 30–60 min) can be varied by continuous speed adjustment and the degree of filling of the kiln (e.g., typically 20% of the cross section of a kiln are covered with waste) via waste mass flows. Typical waste mass flows in the range from 0.3 to 20 tonnes per hour.
- The rotary kiln may be constructed as a parallel flow or as a countercurrent device. For hazardous waste, which usually has a high calorific value, parallel flow operation prevails. Countercurrent operation is applied for waste with low calorific value ($Hu < 8$ MJ/kg) (heating up of waste in countercurrent).
- Temperatures within the rotary kiln (particularly burnout) range from 900 to 1200 °C (partly also higher). In the case of low calorific values, additional fuel has to be added through support burners, if necessary. In any case, care is taken that, depending on their composition, molten residuals can be drawn off. Generation of the smelting phase is thus integrated into the process.
- The rotary kiln with slag outlet is followed by the post-combustion chamber. Here, legal requirements for the incineration of hazardous waste such as a balance temperature of 1200 °C (statutory) and a prescribed residence time of a minimum of 2 s are fulfilled.
- Subsequently, the exhaust gas is purified (acid scrubber, alkaline scrubber, electro or fabric filter, denitrification, and activated carbon filter).
- The technology is safe, a well-perfected technology, tested over many years; broad experience has been gained during the operation of 33 plants in Germany.
- The technology is high in flexibility with regard to the range of wastes, throughputs and calorific values.
- The availability rates of plants amount to more than 7500 h per year.
- The posttreatment of residuals (smelting) is integrated into the process.

A new technology for the treatment of hazardous waste is currently under investigation. Hydrothermal carbonization (HTC) is so far mainly used for organic substrates. Literature hereby focuses on basic plant materials such as cellulose, lignin, and wood but also on special materials such as resin, wax, spores, and pollen. Some researchers even used already carbonaceous substrates such as peat, lignite, or young coal; however, those experiments required very high temperatures. Hydrothermal carbonization can be used to convert a waste product into a value-added hydrochar. During hydrothermal processes threatening, compounds contained in the waste such as pharmaceuticals, personal care products, or endocrine-disrupting compounds can be thermally treated without harming the environment or human health [5].

10 Hazardous Waste—Monitoring Instruments

The monitoring of the disposal of waste from its origin through its transport to the final recovery or disposal in suitable facilities is based on three pillars:

- the official plant monitoring in the plants,
- the legally regulated verification procedure, and
- the self-responsible monitoring of the firms themselves.

All hazardous waste is subject to official supervision in a so-called waybill method and proof procedure. The monitoring is to ensure that the waste is collected, transported, treated, and disposed of according to the rules.

References

1. BMUB (2016), Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety: http://www.bmub.bund.de
2. Eurostat (2016) http://ec.europa.eu/eurostat/data/database
3. Federal Statistical Office (2018) https://www.destatis.de
4. Scholz R, Beckmann M, Schulenburg F (1995) Waste incineration systems; current technology and future developments in Germany. In: The 3rd European conference on industrial furnaces and boilers (INFUB-3) 18.04.–21.04.1995, Lisboa (PT), S., pp 361–424. ISBN 972-8034-02-4
5. Titirici MM (2013) Sustainable carbon materials from hydrothermal processes. 1., Auflage. Wiley, New York, NY
6. UBA (Germany's Environmental Protection Agency) (2017) http://www.umweltbundesamt.de/en/tags/sonderabfall

Leaching Characteristics of Mercury Waste and Prediction of Long-Term Leaching Behaviour

**Eun Song Lee, Seung Ki Back, Jin Ho Sung, AHM Mojammal,
Joo Chan Lee, Jung Hoon Kim and Yong Chil Seo**

1 Introduction

Some of mercury species are known to be potentially highly toxic to humans in trace amounts. Elemental mercury was used as raw materials for industrial facilities and then released into the environment in the form of by-product. According to Article 11 of Minamata Convention on Mercury, mercury wastes are categorized as three types of wastes: Hg consisting waste, Hg containing waste and Hg contaminated waste. Mercury wastes are classified as hazardous wastes or general wastes and are finally landfilled. Mercury compounds contained in landfilled mercury waste are likely to be released into the environment by their leaching characteristics. Therefore, sequential extraction procedure was applied to mercury waste in order to identify the leaching characteristics of mercury waste. The sequential extraction procedure consists of five steps depending on the pH of the extraction reagent, and the major mercury compounds are leached out from different five steps. Also, leached mercury compounds in steps 4 and 5 such as mercury sulphide were chemically stable bounded. Therefore, in this study, a long-term leaching test was conducted to identify an effect of solidified and landfilled mercury waste on landfill site when exposed to the environment in the long term.

E. S. Lee · S. K. Back · J. H. Sung · A. Mojammal · J. C. Lee · J. H. Kim · Y. C. Seo (✉)
Yonsei University, Wonju 26493, South Korea
e-mail: seoyc@yonsei.ac.kr

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_13

2 Materials and Methods

2.1 Sequential Extraction Procedure (SEP)

Sequential Extraction Procedure was conducted for mercury compounds extraction by five steps. Bloom et al. [1] introduced sequential extraction method for Hg in mercury compounds [1–4]. This method was modified by Sladek et al. [2–4]. A five-step of sequence extractions was applied in order to separate the mercury compounds. Previous studies have mentioned that difficult to identify the specific chemical information. But it is possible to check the stability of mercury compounds in solid samples through this method. SEP was carried out using 0.4 ± 0.04 g of dry solid and 40 ml extraction reagent (sample: extraction reagent ratio = 1:100) in 50 ml Teflon caps. Each step solid sample was shaken with extraction reagent for 18 ± 4 h with end-over-end tumbling at 30 rpm. And then, vials were centrifuged at 1600 g as Relative Centrifuged Force (RCF) or 3000 rpm for 20 min. For the first three fractions filtered through disposable 0.4 μm nitrocellulose filter units. The residue was washed by DI water after Then, reuse the next leaching step. Hg concentration of each leachate was analysed according to US EPA method 7470 and using CVAAs type Hg analyser (RA-915+, Lumex).

2.2 Long-Term Extraction

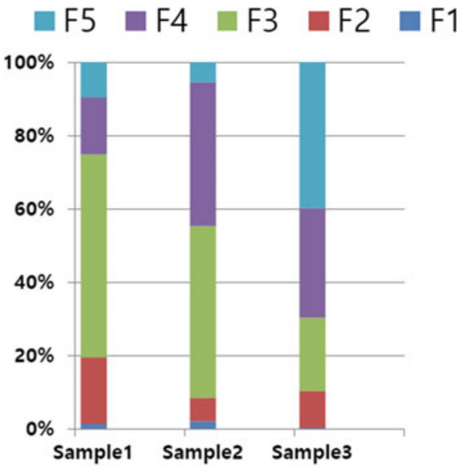
Long-term extraction experiment was carried out using solidified mercury waste with cement as a sample [5] was used to prepare the samples. Specimen mould was prepared (50-mm) cube using industrial sludge with Portland cement mixed different ratio (s/c). Ligia et al. introduced prepared samples for long-term leaching test [6]. The s/c ratio Condition A, B and C were mixed sludge with cement (s/c) by 7:3, 5:5 and 3:7, respectively. As the extraction reagent, buffer solutions of pH 4, 7 and 10 were used. And then, a solidified sample and extraction reagent were placed in a non-reactive 5.4 L glass vessel. During the experiment, do not stir and extraction reagent was replaced. The extraction reagent was replaced at intervals of 1, 3, 7 days.

3 Result and Discussion

3.1 Sequential Extraction Procedure (SEP)

In the SEP, the kinds of leached mercury compounds depending on the pH of the extraction reagent are different. In addition, the mercury compounds leached at the F1–F3 steps are considered that are likely to be easily released into the environment.

Fig. 1 Result of SEP



On the other hand, mercury compounds leached from F4 to F5 steps are considered to be chemically stable. Figure 1 shows the result of SEP of mercury waste samples. Sample 1, 2 and 3 used industrial sludge, metal production facility soil, and municipal waste incinerator F/A, respectively. Among these samples, industrial sludge contained the highest concentration of mercury in the F4–F5 steps. For this reason, solidification was carried out using cement with high concentration of mercury contained industrial sludge.

3.2 Long-Term Extraction

Figure 2 shows the result of long-term extraction test of solidified mercury waste. Leaching was proceeded in the order of washing, diffusion and reaction. Some of mercury compounds are leached at initial steps. The leaching by washing or diffusion is dominant over the reaction. The mercury content of the initial extraction reagent was found to be in excess if the hazardous waste standard value of 0.005 mg Hg/L.

4 Conclusion

This study provides a result of SEP and long-term leaching test using mercury waste. Mercury waste used in this study was categorized as hazardous waste according to the standard limit for leaching test in Waste Management Act in Korea. As a result of applying SEP, the mercury compounds leached from F1 to F3 steps are chemically unstable. On the other hand, the mercury compounds leached from F4 to F5 steps are chemically stable. As a result of the leaching test on solidified mercury-containing

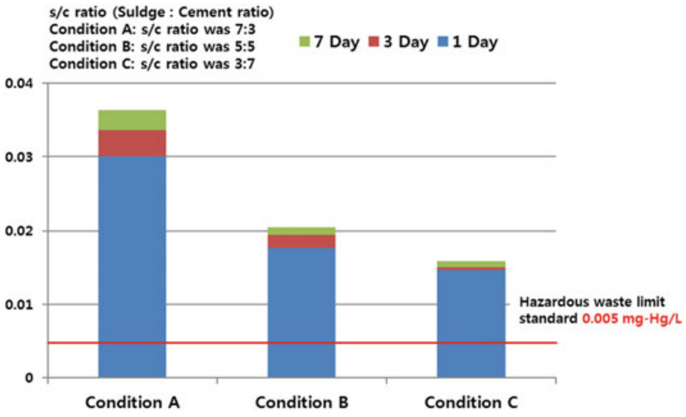


Fig. 2 Result of ongoing long-term leaching test

waste with high concentration. In the initial stage, the hazardous waste standard limit exceeded 0.005 mg Hg/L. Therefore, pretreatment needs to be applied before cement solidification of some high-concentration mercury-containing wastes and landfill. Alternatively, a treatment method other than the solidification method should be applied.

Acknowledgements This work is financially supported by Korea Ministry of Environment (MOE) as knowledge-based environmental service human resource development project.

References

1. Nicolas S, Bloom et al (2003) Analy Chimica Acta 479:233–249
2. Sladek C, Gustin MS (2003) Appl Geochem 18(4):567–576
3. Hall GEM et al (2005) Geochem Explor Environ Anal 5:107–113
4. Liu G et al (2006) Sci Total Environ 369:384–392
5. ASTM, C 109/C 109 M-07, Standard test method for compressive strength of hydraulic cement mortars
6. Tiruta-Barna L (2004) Adv Environ Res 8:697–711
7. Lee SJ, Seo Y-C et al (2004) Science Direct. Sci Total Environ 325:155–161

Current Scenario of Biomedical Waste Management in India: A Case Study

D. Neela Priya, Mayank Gupta, T. S. Sasi Jyothsna and B. Chakradhar

1 Introduction

Indian healthcare sector is growing at a 15% CAGR to reach US$280 billion by 2020 [1]. Increased life expectancy and greater health awareness have been the key contributors to this growth. With increase in population, the medical care facilities have also increased tremendously and proportionately the amount of BMW generated [2, 3]. There are a total of 14,379 hospitals having 634,879 beds in India of which about 11,054 hospitals are in rural and 3325 hospitals in urban areas to ensure availability of treatment to the people [4]. In India, the rate of generation of hospital waste is estimated to be about 0.33 million tonnes annually [5], and the quantum of waste generated is estimated to be 1–2 kg/bed/day in a hospital and 600 g/day/bed in a clinic. 85% of the hospital waste is considered as non-hazardous while 15% as infectious/hazardous [6]. There are 198 common biomedical waste treatment facilities (CBMWTFs) in operation and 28 under construction in the country. 21,870 HCFs have their own treatment facilities while 131,837 HCFs are using the CBMWTFs [7]. According to the data published by the Ministry of Environment and Forests, Climate Change (MoEF&CC), in 2011, the quantity of BMW generated every day in the country is about 405,702 kg, of which 291,983 kg (~60%) is only disposed and 40% lies unattended. This shows that BMW management has not received enough attention in India and there is an urgent need for enforcing stringent legislations in the country.

In order to regulate the environmental threat due to mismanagement of BMW, the MoEF&CC, Government of India, has framed the Biomedical Waste (Handling and Management) Rules in 1998. These rules were further amended in 2003, 2011 and 2016 [8]. Several new provisions have been added in the newly amended rules

---

D. N. Priya (✉) · M. Gupta · T. S. Sasi Jyothsna · B. Chakradhar
Environmental Consultancy, Ramky Enviro Services Private Limited, Ramky Grandiose, Gachibowli 500032, Hyderabad, India
e-mail: neelapriya.dvnl@ramky.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_14

2016 [9]. The objectives of successful management strategies could be fulfilled only when the rules are implemented by the HCUs and the operators of BMWTFs. Poorly structured and inefficiently organized healthcare systems can pose a serious threat to the healthcare workers and the environment. The correct practices of handling, segregation and storage of these wastes at HCUs are therefore vital for safe and scientific management [10]. A number of treatment technologies [11–16] are available as on today, but the choice of suitable method is based on various factors like the composition of waste generated, available space, regulatory approval, public acceptance, cost, etc.

The paper throws some light on the current situation of BMW management in India. The status of implementing the revised rules was assessed by means of a survey conducted at four different HCUs. The paper also highlights the emerging BMW treatment technologies. Based on the survey, conclusions are drawn and possible solutions are given to overcome the challenges.

2 Results and Discussions

2.1 An Overview of Biomedical Waste Management as Per BMW Rules 2016

An effective biomedical waste management comprises all the steps ranging from generation, characterization, handling, segregation, storage, transportation, treatment and disposal. The complete process of BMW management is shown in Fig. 1.

Biomedical waste can be categorized as primary and secondary sources [17] depending on the quantity of waste produced. Characterization can be assessed based on the physicochemical composition of healthcare waste which is extremely useful in establishing equipment specifications or operating parameters for treatment technologies. For example, some steam and microwave treatment systems rely on a minimum amount of moisture to be present in waste; some chemical systems are affected by the organic load and water content; incineration is influenced by the percentage of incombustibles, heating value and moisture content of waste. In some cases, physical properties such as bulk density are used to estimate storage, transport and treatment chamber capacities, specifications for compactors, shredders, etc. The classification and characteristics of BMW are shown in Table 1.

According to the BMW Rules 2016 [8], biomedical waste is classified into four categories, and the segregated waste should be disposed into the appropriate colour-coded bins/bags. Further, the treatment or disposal options are suggested based on the category/nature of the waste (Table 2). All the BMW generated at HCUs should be labelled properly as waste type, site of generation and date of generation before transportation. All the health workers handling the waste should wear adequate personal protective equipment (PPE). Each patient care area/wards should be facilitated with the coloured containers to ensure proper disposal of waste. It is required to

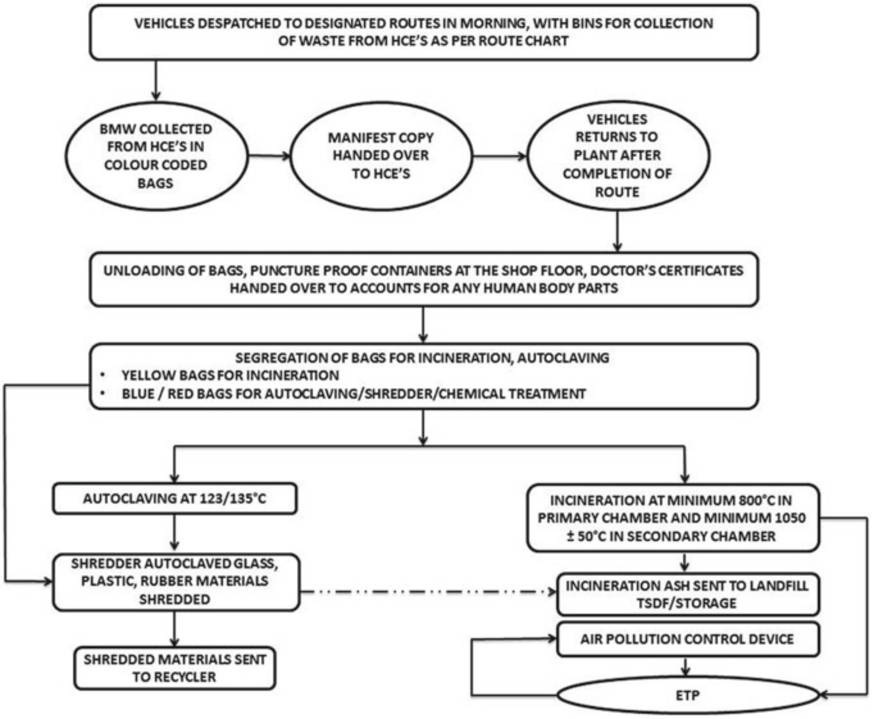


Fig. 1 Flow chart of BMW management

Table 1 Classification and characteristics of BMW

Classification of BMW	
Chemical/radioactive (hazardous healthcare waste)	5%
Infectious (hazardous healthcare waste)	10%
General (non-hazardous healthcare waste)	85%
Typical characteristics of infectious waste	
Moisture	8.5–17% by wt
Incombustibles	8% by wt
Heating value	7500 BTU/lb

maintain a waste receipt book to record the quantity of waste generated/number of bags handed over to the treatment facility.

It is the duty of the operator of CBMWTF to transport BMW from the premises of HCF to any offsite CBMWTF. Only the vehicles complying as per the existing rules should be used, and it should be of a suitable size to carry secured load, clearly marked with the name and address of the waste carrier and biohazard sign. BMW

Table 2 Collection of waste—category wise, coloured bags/containers, treatment/disposal

Colour coding	Type of bag/container	Waste category	Treatment/disposal
Yellow	Plastic bag Non-chlorinated	Human anatomical, animal, soiled Expired/discarded medicines Chemical liquid waste Microbiology and biotechnological	Incineration/plasma pyrolysis/deep burial Encapsulation/plasma Effluent treatment Sterilization
Red	Plastic bag Non-chlorinated	Recyclables such as tubing, bottles, catheters, syringes, gloves	Autoclave/microwave/hydroclave/mutilation
White translucent	Leak proof containers	Waste sharps including metals	Autoclave/sterilization/encapsulation/mutilation
Blue	Cardboard box—blue marking	Glassware	Disinfection/autoclaving/microwaving

is transported through designated route, on colour-coded, covered and leak proof trolleys to avoid spillage on road, on fixed and at reliable time which is then subjected for final treatment and disposal. The BMW should not be stored beyond a period of 48 h.

2.2 Comparison Between BMW Management Rules 2016 and 1998

An attempt was made to make a comparison between BMWM rules 2016 and 1998 with major emphasis on the revisions made in hospital protocols (Table 3).

The newly amended rules have given a clear picture on the practices to be followed by the occupier and the operator. Many improvements were made in waste segregation and some procedures were made easy. Implementation of these rules at HCUs was verified by a small survey conducted at various HCUs; the same is reflected in Sect. 2.3. However, duties of the operator were beyond the scope of the paper.

2.3 A Case Study on the Existing Scenario of BMW Management in Hyderabad

2.3.1 Need for the Study

Currently, the implementation of biomedical waste management in many hospitals is unsatisfactory, disposing the waste in an improper manner. With this background, a survey was undertaken to assess the knowledge of healthcare workers on BMW

Table 3 Major differences between BMW rules 2016 and 1998

Points	BMW Rules, 2016	BMW Rules, 1998
Application of rules	• Rules shall apply to all persons who generate, collect, receive, store, transport, treat, dispose, or handle BMW in any form • Radioactive/hazardous wastes not included	Rules shall apply to all persons who generate, collect, receive, store, transport, treat, dispose or handle BMW in any form
Provisions at healthcare facilities/duties of occupier	• HCFs shall make a provision within the premises for a safe, ventilated and secured location for storage of segregated biomedical waste • Pretreatment of infectious lab waste on-site • Use of non-chlorinated plastic bags, gloves • Effluent treatment plant (ETP) is mandatory to treat liquid waste at source • Maintain register daily and annual report to be made available on website within 2 years • Records of equipment, training, health check-up, immunization compulsory • Establish barcode System for bags/containers containing BMW to be sent for disposal • Report major accidents to SPCB—caused by fire hazards, blasts during handling of biomedical waste and the remedial action taken	• Every occupier shall take all steps to ensure that waste is handled without causing any effects • No pretreatment required • Chlorinated plastic bags • ETP not mandatory • Records and annual report not mandatory • Records not compulsory • No barcode introduction • No reporting of major accidents
Duties of CBMWTF	• Reporting of accidents and maintenance of records of equipment, training, etc.	• Records not documented
Categories	Classified into four categories based on treatment	Classified in to 10 categories
Drugs	Suggested for incineration	Discarded in black bags
Infected plastics, sharps, glass	• Infected plastics and sharps after mutilation go in for red bag and white container • Glass articles are discarded in blue cardboard box	Infected plastics, metal sharps, glass in blue container with disinfectant/autoclaving
Recycling	Plastic, sharps, glass go to authorized recyclers	Authorized recyclers not mentioned

handling and management at their HCUs and whether the newly revised rules are being reflected. **Necessary permissions and approvals were obtained from the concerned authorities before initiating the study**. The study covered a multi-speciality hospital, public sector hospital, a private nursing home and a pathological lab in Hyderabad city, Telangana, having access to CBWTF. Information on (a) the quantity of waste generated at each ward, (b) awareness of biomedical waste management rules and (c) practices with respect to segregation, use of colour coding bins/bags, sharps management, access to common waste management facilities and disposal was gathered. Researchers have approached the staff of hospitals to get the real scenario of BMW practices.

2.3.2 Materials and Methods

The observational study was carried out for a period of 2 months from July to August 2017. 15 different HCUs were surveyed. But the results of only four HCUs are presented in the paper for discussion. Different areas of the hospital such as wards, ICUs, emergency, operation theatre and laboratories were surveyed to observe the process of segregation of the waste at HCFs. The emphasis was to see whether the segregation of BMW was carried per the hospital protocol the revised rules. The knowledge of staff and healthcare workers on BMW management was assessed by asking set of prepared questions.

2.3.3 Observations and Discussions

Four HCUs were covered under the study. However, the identity of hospitals has been masked for the discussion in this paper. The observations are presented in Table 4 and discussed in detail below.

a. **Multi-specialty hospital and pathological lab**: Both the hospital and lab are in compliance with the revised Biomedical Waste (Handling and Management) Rules, 2016. The staff was totally aware of good BMW segregation practices. The colour-coded containers for waste segregation are in accordance with the new protocol and arranged at every ward. The frequency of waste removal was good. It was observed that these HCUs have well planned infrastructure, sufficient staff and health workers who are well trained. Cleanliness is maintained every nook and corner of the facilities. Quality managers make sure that the practices are being flowed properly by every staff of the hospital. The hospital had a separate storage area for the segregated wastes before it was handed over to the waste management facility. They had an ETP for treating the liquid waste from their hospital. All the records and documents were well maintained. Barcode is introduced and online updation of waste is done on a daily basis. All these activities show the concern they have towards public health and environment.

Table 4 Observations on BMW management practices at various HCUs

General information	Multi-specialty hospital	Public sector hospital	Private nursing home	Pathological lab
Total no. of beds	200	200	25	NA
Avg. bed occupancy	65	80	10	NA
Avg. in patients/day	15	25	2	NA
Avg. out patients/day	65	150	5	30
Avg. surgeries/month	275	180	5	NA
Staff position	449	180	15	25
SPCB authorization	Yes	Due	Due	Due
Waste segregation practices				
Total quantity of non-infectious waste in kg/day	52	10	2	1
Total quantity of infectious waste generated in kg/day	95	45	1.5	1
Colour coding bins	Yes	Not proper	Not aware	Yes
Open/lidded	Lidded	Open	Open	Lidded
Waste sharps mutilation	Yes	Yes	Yes	Yes
Collection at different wards	Yes	Yes	No	Yes
Frequency of removal	When filled	Sometimes	No	When filled
Duration of storage	24 h	48 h	48 h	24 h
PPE-healthcare workers	Provided	Provided	No	Yes
Lifting to storage area	Trolleys	Wheel barrow	Manually	Manually
Place of storage	Separate storage area	Dump site	No storage area	NA
Weighing the waste	Yes	No	No	NA
ETP for liquid waste	Yes	No	No	NA

(continued)

Table 4 (continued)

General information	Multi-specialty hospital	Public sector hospital	Private nursing home	Pathological lab
Records maintenance	Daily	No	No	Yes
Barcode	Yes	No	No	Yes
Online updation	Yes	No	No	No

This also shows fair investment made in BMW management by these facilities and due attention given in view of infectious wastes.

b. **Public sector hospital**: The practices of waste handling and segregation in this hospital were found to be deviating from the standard practices. Though cleanliness was maintained all around, it was observed that the housekeeping supervisors were confused about the separation of waste as per the rules. The colour-coded containers were not in accordance with the standard protocol except in the operation theatre. For bed occupancy of 175, only two healthcare workers were assigned the duty of waste segregation which was a great burden to them. This had an effect on the frequency of waste removal. However, the segregated waste was handled carefully and dumped in the storage area. The stored waste is then handed over to the waste management facility. Lack of manpower was the main reason and the health workers need proper training on the current practices of BMW management.
c. **Private nursing home**: The conditions were very poor and the infectious waste is mixed with the general waste. The healthcare workers as well as the doctors were not aware of the new rules. There was no instance of records maintenance. Authorization from SPCB was due for the past 2 years. There was no separate waste storage area. The used tubes and catheters were indiscriminately dumped at one corner.

2.4 Emerging Trends in Biomedical Waste Treatment

The present treatment of BMW in India includes thermal, chemical, biological and irradiation technologies. However, there are some limitations to overcome in the existing technologies. For example, incineration though in majority of the cases is the most preferred option; it has many disadvantages like emissions of dioxins and furans, unburned hydrocarbons, volatile heavy metals, other gases such as SO_2, NO_X and their associated compounds, incinerator ash, etc. On the other hand, autoclaving requires high temperature and pressure. Besides, it requires regular maintenance, consumes more water and power, and costly to operate. Stringent environmental legislations coupled with high operating costs involved in treatment have compelled the operators to explore new and innovative technologies. These are crucial for ensuring

Table 5 Conventional and emerging trends in BMW treatment

Conventional methods			
Type of treatment	Operating conditions	Advantages	Disadvantages
Autoclaving To sterilize medical waste prior to disposal in the standard municipal solid waste stream	**Gravity flow autoclave** Temperature—>121–149 °C Pressure—15–52 psi Residence time—>60–30 min **Vacuum autoclave** Temperature—>121–135 °C Pressure—15–21 psi Residence time—>45–30 min	• No by-products and toxic gases are emitted • Prove to be economical since the equipment can be reused	• High water and electric power consumption • Regular maintenance • Costly to operate • Requires safe operation
Incineration	• Temperature of primary chamber—800 °C and secondary chamber—1050 °C • Minimum stack height—30 m above ground level • Other parameters as per CPCB norms	• Kills pathogens and destroys the materials on which they reside • Major technique used worldwide for disposing of the amount of materials	• Incinerators—a major source of dioxins and furans • Incomplete combustion products • Incinerator ash is hazardous
Microwaving For cultures and stocks, sharps, materials contaminated with blood and body fluids, laboratory waste	• Temperatures reached are around 97–100 °C • In new systems, steam under pressure is passed, to achieve temperature >135 °C • Cycle time is around 25′ • Typically, ~2–6 magnetrons with 1.2 KW output	• Minimal emissions if no hazardous waste fed • Automated system • No liquid effluent	• High capital cost • Toxic emissions if hazardous waste fed • Any large metal item can damage shredders • Odour problems • Probability of energy leakage
Dry heat sterilization **Sharp pit/encapsulation** For waste sharps	• Temperature >185 °C • Residence period—150 min in each cycle (sterilization period 90 min) • Sharp pit or sharp encapsulation followed by autoclaving/dry heat sterilization/mutilation	• Simple • Low cost • Safe	• Not recommended for non-sharp infectious waste
Chemical disinfection Most suitable for liquid waste	• Commonly used to kill microorganisms on medical equipment and on floors and walls in healthcare facilities	• Highly efficient under good operating conditions • Some chemical disinfectants are relatively inexpensive • Reduction in waste volume	• Requires highly qualified technicians for operation • Uses hazardous substances that require comprehensive safety measures and safe disposal • Inadequate for pharmaceutical, chemical and some infectious waste

(continued)

Table 5 (continued)

Conventional methods			
Type of treatment	Operating conditions	Advantages	Disadvantages
Deep burial For anatomical waste	• A pit or trench dug about two metres deep, half filled with waste, then covered with lime within 50 cm of the surface, before filling the rest of the pit with soil	• Low cost • Relatively safe if access to site is restricted	• Safe only if access to site is limited and certain precautions are taken
Emerging technologies			
Plasma pyrolysis/gasification	• Temperature in combustion chamber—1050 ± 50 °C • Residence time—2 s • 3% Oxygen in the stack gas • Min stack height—30 m above ground level • Ash to be disposed-off as per Transboundary Movement Rules 2008/EPA Act, 1986	• Emissions are generally lower than those from traditional incinerators • Suited for large-scale, continuous operations • Waste mass and volume are drastically reduced • Gases obtained after the pyrolysis are rich in energy content and can be used to recover energy	• High capital cost and significant siting and installation requirement • High operating costs
Bio-oxidation	• First step—waste enters a pyrolysis chamber where it is heated from 200 to 1100 °F (93–590 °C) • Second step—the vapours from pyrolysis chamber are drawn into a two-stage oxidation chamber operating at 1800 and 2000 °F (980–1090 °C)	• The process results in total destruction of medical waste • Very low emissions Stack not required • Can treat the wide range of medical waste • No liquid effluents	• Despite lower emissions than conventional medical waste incinerators, the process still emits dioxin • High capital cost, large space and footprint is required
Depolymerization	• Operates at high temperatures between 150 and 350 °C (300–662 °F)	Data deficient	Data deficient

safe disposal of BMW, simultaneously minimizing the costs involved. The details of conventional and emerging technologies are listed out in Table 5.

3 Conclusions

Biomedical waste if not properly managed may have adverse effects on health and environment. Even though biomedical waste management is an issue of major concern in the country, it has not received much attention and still at a nascent stage. Raising concerns from the public and stringent legislations laid by regulatory authorities have compelled few institutions of high profile to implement good practices. However, there are many HCUs which have substandard practices. This requires regular monitoring of the practices adopted at these HCUs. Proper management of these wastes begins with segregation at source followed by handling, storage, transport, treatment and disposal. Segregation if not done may result in mixing of infectious waste with non-infectious wastes, whereby 100% of it becomes infectious/hazardous. But all these chain of activities are ultimately linked with the investments made by HCUs towards BMW management.

According to the analysis of the survey, the condition of BMW management in four HCUs varied according to the institution profile. The performance of clinics/nursing homes and public hospital was very poor and not in compliance with the current standards. Hence, there is an urgent requirement of training for the staff of the hospitals as many of staff are not clear about the standard waste management practices. It is also the responsibility of the occupier to facilitate proper training to its healthcare workers. Another major concern is the treatment and final disposal of BMW at treatment facility. Keeping in view the limitations of existing technologies, BMW treatment can be rendered safe and unobjectionable only when new and advanced technologies are explored. This would also minimize the costs incurred in treatment.

Acknowledgements The authors express their sincere thanks to M/s Ramky Enviro Services Pvt. Ltd. for constant encouragement and support to write the paper.

References

1. Healthcare Industry in India (2017) Indian Healthcare Sector, Services. https://www.ibef.org/industry/healthcare-india.aspx
2. Cheng YW, Sung FC, Yang Y, Lo YH, Chung YT, Li KC (2009) Medical waste production at hospitals and assosciated factors. Waste Manag 29:440–444
3. Patil AD, Shekdar AV (2001) Health-care waste management in India. J Environ Manag 63:211–220
4. Health Infrastructure (2017) Chapter 6, An overview of educational infrastructure and services infrastructure in the health sector in the country

5. Ranjan R, Pathak R, Singh DK, Jalaluddin M, Kore SA, Kore AR (2016) Awareness about biomedical waste management and knowledge of effective recycling of dental materials among dental students. J Int Soc Prevent Commun Dent 6:474–479
6. Manasi S (2017) Challenges in biomedical waste management in cities: a ward level study of Bangalore. Adv Recycling Waste Manag 2(1):1–8
7. New Bio-Medical Waste Management Rules will Change The way Country Used to Manage Waste Earlier (2016) Make a Big Difference to Clean India Mission: Javadekar, Press Information Bureau, Government of India, Ministry of Environment and Forests. Available at: http://pib.nic.in/newsite/PrintRelease.aspx?relid=138353%20AmitabhSrivastavaandNirmala
8. Ravindran (2011) Disposed medical waste poses danger to Karnataka's healthcare system: NATION—India Today, Rich Trash Pickings. Available at: http://indiatoday.intoday.in/story/disposed-medical-waste-karnataka-deadly-virus/1/158691.html
9. Government of India Ministry of Environment, Forest and Climate Change notification [Published in the Gazette of India, Extraordinary, Part II, Section 3, Sub-section (i)] New Delhi, the 28 March 2016. Available at: http://cpcb.nic.in/divisionsofheadoffice/hwmd/Biomedical_Waste_Management_Rules_2016.pdf
10. Praveen M, Sangeeta P, Anand SS (2012) Need of biomedical waste management system in hospitals—an emerging issue—a review. Curr World Environ 7(1):117–124
11. Hegde V, Kulkarni RD, Ajantha GS (2007) Biomedical waste management. J Oral Maxillofac Pathol 11:5–9
12. Gautam V, Thapar R, Sharma M (2010) Biomedical waste management: Incineration vs. environmental safety. Indian J Med Microbiol 28(3):191–192
13. Ferdowsi A, Ferdosi M, Mehrani MJ (2013) Incineration or autoclave? a comparative study in isfahan hospitals waste management system. Mat Soc Med 25(1):48–51
14. Zimmermann K (2017) Microwave as an emerging technology for the treatment of biohazardous waste: a mini-review. Waste Manage Res 35(5):471–479
15. Nema SK, Ganeshprasad KS (2002) Plasma pyrolysis of medical waste. Curr Sci Spec Sect Plasma Appl 83(3):271–278
16. Anurag VT, Prashant AK (2013) Biomedical waste management practices in India-a review. Int J Curr Eng Technol 3(5):399–402
17. Bio-waste Management Rules (2016) Centre for Science and Environment. Available at: http://www.cseindia.org/userfiles/bio-med-waste-ima.pdf

Investigation on the Rheological Property of Engineered Fly Ash Micro-concrete

T. Hemalatha, Jyul Bardoliwala, Maitri Mapa
and Saptarshi Sasmal

1 Introduction

In the recent past, the use of smaller size aggregates in the design of concrete such as engineered cementitious composites (ECC), textile reinforced concrete, self-compacting concrete, ultra-high-performance concrete, etc. is emerging. Felekoglu [1] has developed self-compacting filling grout (SCFG) and studied the effect of cement replacements with three types of limestone powders produced from different quarries on the rheology of the fresh SCFGs. Due to advantages such as easiness in applications, speed of construction, superior mechanical properties, etc., this type of micro-concrete is preferred for repair works. Further, self-compacting micro-concrete (SCMC) is developed using a mixture of binders and aggregates of maximum size smaller than 100 μm [2]. The rheological properties of SCMC can be improved by optimizing the high range water reducing admixture (HRWRA) dosage, water content and other ingredients [3]. In order to improve the ductile properties of SCMC mix, the polymeric or metallic fibres at varying dosages are added. These composites with fibres have control on formation of multiple micro-cracks and develop extraordinary high tensile strain capacities [4–6]. The increased amount of paste and use of superplasticizers are the requisite for developing such type of cementitious composites.

Hence, it is understood that to produce SCMC, the ingredients such as cementitious, pozzolanic, plasticizing chemical admixtures, inert filler, etc. should be carefully chosen. The physical properties of ingredients such as shape, surface morphology, fineness, particle size distribution, etc. can influence the properties of micro-concrete at both fresh and hardened states. Along with the other conventional ingredients used in the preparation of mortar, the incorporation of nano additions enhances the desired properties at both fresh and hardened states. Among all the nano-materials

T. Hemalatha (✉) · J. Bardoliwala · M. Mapa · S. Sasmal
CSIR-Structural Engineering Research Centre, Chennai, India
e-mail: hemalatha@serc.res.in

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_15

used in cement, carbon nanotubes (CNTs) [7, 8] have superior quality in enhancing the properties such as tensile and flexural strength, electrical conductivity, bridging cracks, etc. Skazlic et al. [9] developed high-performance fibre-reinforced micro-concrete (HPFRMC) having very good stability, serviceability and durability properties. For these reasons, the interest on HPFRMC has been growing to use this material for repair and rehabilitation of concrete structures. Research showed that the use of high-performance fibre-reinforced micro-concrete as repair material has both economical and technical advantages.

Further, in the sustainable point of view, it is essential to replace cement by supplementary cementitious material. Bouzoubaa and Lachemi [10] have developed and evaluated the self-compacting concrete (SCC) made with high volumes of fly ash. Tests were carried out in SCC made with different replacement of fly ash to obtain the properties of fresh concrete in terms of viscosity and stability. The mechanical properties of hardened concretes such as compressive strength and drying shrinkage were also determined. The SCCs developed with different fly ash replacement showed compressive strengths ranging from 26 to 48 MPa after 28-days of curing. The results showed that an economical SCC could be successfully developed by incorporating high volumes of Class F fly ash.

Considering the advantages of using fly ash in developing flowable concrete, in this study an attempt has been made to develop a new class of material for repair purposes. This study mainly focuses on the influence of fly ash and other ingredients on the flow behaviour of micro-concrete.

2 Experimental Details

2.1 Materials

The basic materials used for the development of self-compacting micro-concrete are cement, fly ash, lime sludge, quartz powder, water and superplasticizer. Further to enhance the properties, materials such as silica fume, polypropylene, glass fibres, steel fibres and carbon nanotubes are used.

2.2 Mix Details

Self-compacting micro-concrete (SCMC) trial mixes are prepared with cement/lime sludge and cement/quartz powder (1/1 by weight) with cement replaced by 20 and 40% of fly ash and 5% of silica fume by cement weight, respectively. Polypropylene, glass, steel fibres and multiwalled carbon nanotubes are also used. The mix details are given in later section.

2.3 Casting and Curing

SCMC mixture is prepared using Hobart mixer under room temperature. The total time for mixing is fixed as 3.5 min. First, cement/fly ash and limestone powder/Quartz powder are mixed dry for 30 s at slow speed to ensure homogeneous mixing. Gradually water is added and mixed for further 1 min at the medium speed. Finally, superplasticizer (SP) is introduced to the wet mixture and mixing is continued at a high speed of (125 rpm) for 2 min. At the end of this mixing procedure, the flowable mixture having self-levelling property is developed and poured into the moulds. Compaction is not needed because of good workability.

3 Results

In this study, it is aimed to develop a sustainable mixture for repair purposes having good workability, durability and strength properties. In view of this, micro-concrete is prepared by using special proportioning of ingredients. Generally, it is made up of one portion of cement and one portion of limestone powder for getting the consistency. In this study, as an alternate to limestone powder, lime sludge which is a waste material obtained from the paper industry is used. Further, the cement used is replaced by 20 and 40% fly ash. The purpose of using fly ash is to enhance flowability and to make the mix sustainable.

First, the mix is prepared with cement, fly ash and lime sludge. The fresh properties of mixes are tested by conducting mini slump test and mini V-funnel test as shown in Fig. 1. Hardened properties are obtained by carrying out compressive strength, split tensile and flexural strength testing.

Trials have been made by adjusting the dosage of SP to get the constant slump flow while keeping the constant water to binder ratio (0.26). The mix proportion and designation of mixes with lime sludge as major ingredient are presented in Table 1.

The dosage of superplasticizer is selected in such a way that stable flow is observed in all the mixes without any bleeding or segregation of the aggregates. Horizontal

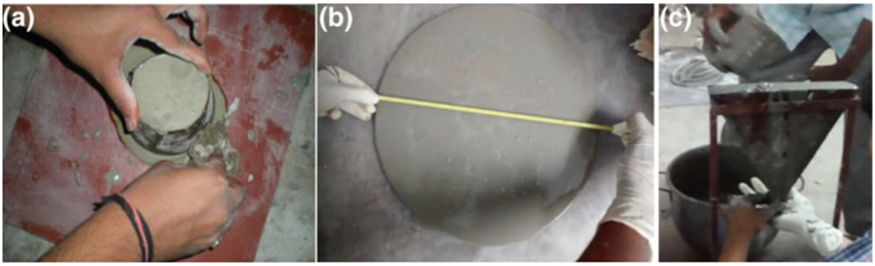


Fig. 1 **a** Mini slump test. **b** Horizontal spread. **c** V-funnel

Table 1 SCMC mixes with 20% fly ash and lime sludge

Mix I.D.	Mix combinations	SP dosage (%)
C20FALS (control mix)	C + 20% fly ash (FA) + lime sludge (LS)	2.8
C20FA5SFLS	C + 20% FA + 5% silica fume (SF) + LS	2.4
C20FAPLS	C + 20% FA + 0.25% poly propylene (PP) + LS	2.6
C20FAGLS	C + 20% FA + 0.25% glass fibre (GF) + LS	2.6
C20FASLS	C + 20% FA + 0.25% steel fibre (StF) + LS	2.4

Table 2 Fresh properties of SCMC mixes with 20% FA and lime sludge

SCMC Mix I.D.	Slump flow (mm)	V-funnel (s)
C20FALS (control mix)	260	8
C20FA5SFLS	260	8
C20FAPLS	260	10
C20FAGLS	260	9
C20FASLS	260	10

slump flow of 260 mm is obtained for all the mixes. Flow time observed during V-Funnel test is less for control mix and mix with silica fume compared to the flowability of mix with fibres. The fresh property results of lime sludge mixes are shown in Table 2.

Though the slump flow is constant, it is found that the time required for emptying the mini V-funnel is slightly increasing with fibre incorporation. It is noticed from Table 1 that for obtaining the same slump flow, the dosage of SP required for the mixes is less than that of control mix. It shows that the addition of fibres has not affected the flowability significantly. In order to obtain the strength properties, compressive strength tests are carried out on LS mixes. Figure 2 shows the compressive strength of LS mixes obtained at 7 and 28 days. It is found that the compressive strength of lime sludge incorporated mixes is found to be very low. Even with the incorporation of fibres, the strength is found to be very low. At the highest, glass fibre incorporated LS mix at 28 days recorded the strength of about 5 MPa which is considered to be very low to use it for any purposes. From this observation, it is concluded that the lime sludge mixes are not suitable for developing micro-concrete.

The mixes are then modified to have quartz powder in the place of lime sludge. The mix proportions for mixes with 20 and 40% fly ash replacement and designation of the mixes are presented in Table 3. In order to qualify the flowability tests, the slump flow and V-funnel tests have been conducted and results are presented in Table 4. From Table 3, it is noticed that the SP requirement for mixes with fibres are not increased rather it is marginally decreased in some mixes.

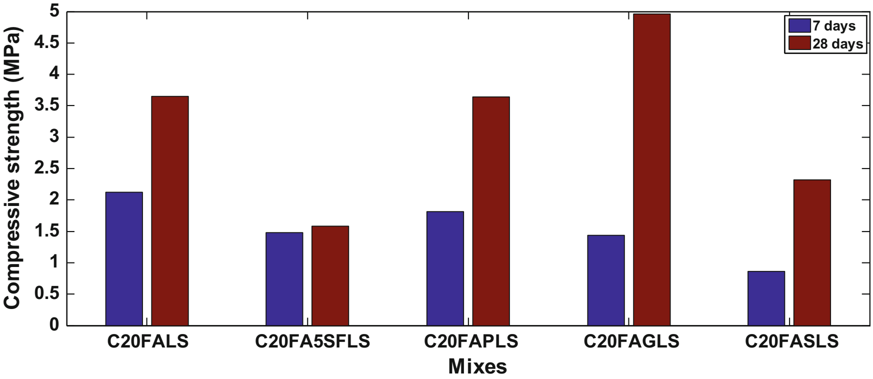


Fig. 2 Compressive strength results of lime sludge incorporated micro-concrete

Table 3 SCMC mixes with 20 and 40% FA and quartz powder

Mix I.D.	Mix combinations	SP dosage	
		20%	40%
C20FAQP/C40FAQP (control mix)	C + 20%/40% FA + quartz powder (QP)	0.65	0.53
C20FA5SFQP/C40FA5SFQP	C + 20%/40% FA + 5% SF + QP	0.63	0.53
C20FAPQP/C40FAPQP	C + 20%/40% FA + 0.5% PP + QP	0.6	0.53
C20FAGQP/C40FAGQP	C + 20%/40% FA + 0.5% GF + QP	0.6	0.53
C20FASQP/C40FASQP	C + 20%/40% FA + 0.5% StF + QP	0.6	0.53
C20FACNTQP/C40FACNTQP	C + 20%/40% FA + 0.05% CNTs + QP	0.6	0.53

From Table 4, it is noticed that the time required for emptying the V-funnel is marginally increased with fibre incorporation. However, considering the dosage of SP, the dosage used in fibre incorporated mixes is slightly less or equal. This indicates that the flowability is not affected by the introduction of fibres in micro-concretes. Further, it is noticed that the increase in fly ash replacement enhances the flowability that is indicated by the reduced dosage of SP in 40FA mixes.

Unlike lime sludge mixes, the compressive strength of quartz powder mixes is found to be high. The compressive strength of 20FA and 40FA mixes obtained at 7 and 28 days is shown in Fig. 3. It is noticed that the control mixes (20 and 40%) are having 28 days strength of about 50 and 30 MPa, respectively. As 30 MPa compressive strength can be suitable for many repair works, 40% fly ash replaced micro-concrete is considered to be a satisfactory mix. It is also noticed that with the

Table 4 Slump flow of SCMC mixes with 20% FA and quartz powder

Mix I.D.	V-funnel (s)	Mix I.D.	V-funnel (s)
C20FAQP (control mix)	9	C40FAQP (control mix)	11
C20FA5SFQP	9	C40FA5SFQP	10
C20FAPQP	12	C40FAPQP	13
C20FAGQP	10	C40FAGQP	12
C20FASQP	10	C40FASQP	12
C20FACNTQP	10	C40FACNTQP	12

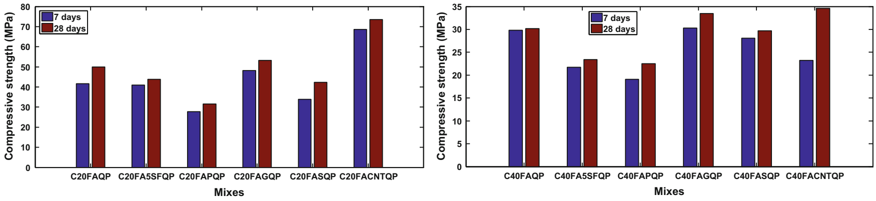


Fig. 3 Compressive strength results of quartz powder incorporated micro-concrete with 20 and 40% fly ash

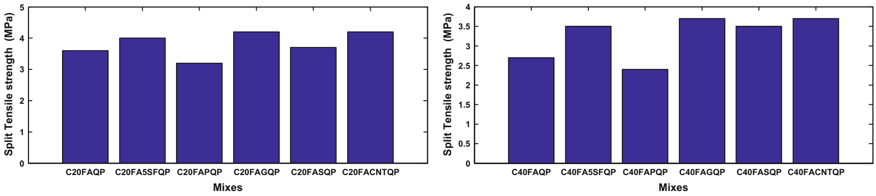


Fig. 4 Split tensile of quartz powder incorporated micro-concrete with 20 and 40% fly ash

fibre incorporation, especially with glass fibre and CNT, the compressive strength has been further increased at both replacement levels.

For a repair material, more than the compressive strength, tensile strength and flexural strength are having significance. Hence, split tensile and flexural strength are also determined for the mixes and the results are presented in Figs. 4 and 5. Among the fibres used, the increase is high in CNT incorporated mixes. In both 20FA and 40FA mixes, except for polypropylene fibres, the split tensile strength is improved.

As shown in Fig. 5, in 20FA mixes, the highest flexural strength of about 10 MPa is obtained for CNT incorporated mixes whereas in 40FA mixes, the highest value obtained is about 4.5 MPa. For many applications, the flexural strength of 4.5 MPa is sufficient; depending upon the importance of work, either 20FA or 40FA mix can be selected.

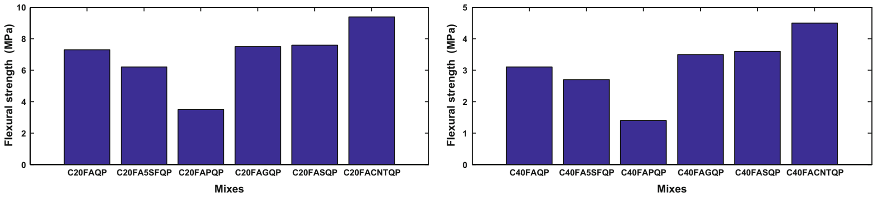


Fig. 5 Flexural strength of quartz powder incorporated micro-concrete with 20 and 40% fly ash

4 Discussions

From the poor strength results obtained for LS mixes, it is known that the lime sludge cannot be used as an alternative for limestone powder. For developing micro-concrete cement and lime sludge are used in equal proportions, especially when used in high dosages, LS is found to be not suitable in terms of both fresh and hardened properties. The requirement of higher SP dosage in LS mixes may be one of the reasons for the poor strength in LS mixes. Other reason being the low reactivity of lime sludge as it is composed of about 55% of calcium carbonate that hampers the hydration mechanism. Hydration studies are not within the scope of this study hence not presented. However, hydration studies show the evidence of low reactivity of lime sludge. On the other hand, the mixes with quartz powder showed satisfactory results in terms of both fresh and hardened properties. The advantages of using fly ash are clearly evident from the fresh property results in terms of reduced SP dosage. As reported in many literatures, in fly ash mixes, the dilution effect and spherical shape of fly ash are making the mix flowable. During the initial period, fly ash acts as a filler material providing more water available for hydration defined as dilution effect. Further, spherical shape of fly ash provides lubrication for the easy flow of particles. Another observation from the study is that there is no increase in water demand with fibre incorporation. This shows that in the absence of coarse aggregate, the fibre may not require extra water for obtaining homogeneous mixing. Further, the presence of particle size below 100 μm will help in coating the fibres for easy flowability.

5 Conclusions

Two main ingredients lime sludge and quartz powder are attempted for developing micro-concrete besides other main ingredients such as fly ash in this study. The following conclusions are made from the study. Though the properties of micro-concrete with 20% fly ash are found to be superior, the mix with 40% fly ash and quartz powder is also found to be good in terms of flowability and strength. Further, in viewpoint of sustainability, 40% fly ash mixes are found to be a suitable candidate as a repair material. Depending upon the requirement, 20FA or 40FA micro-concrete mixes can be used to suit the applications. This research would enable to introduce a new class of material with superior quality for repair purposes.

References

1. Felekoğlu B (2008) Optimization of self-compacting filling grout mixtures for repair purposes. Constr Build Mater 22:660–667
2. Felekoglu B (2009) High performance micro-concrete design. Ph.D. thesis, Dokuz Eylul University. The Graduate School of Natural and Applied Sciences, 428pp (in Turkish)
3. Felekoğlu B (2014) Rheological behaviour of self-compacting micro-concrete. Sadhana 39(6):1471–1495
4. Felekoğlu B, Tosun K, Baradan B (2009) Effects of fibre type and matrix structure on the mechanical performance of self-compacting micro-concrete composites. Cem Concr Res 39:1023–1032
5. Dawood ET, Ramli M (2011) High strength characteristics of cement mortar reinforced with hybrid fibres. Constr Build Mater 25:2240–2247
6. Dawood ET, Ramli M (2010) Development of high strength flowable mortar with hybrid fiber. Constr Build Mater 24:1043–1050
7. Konsta-Gdoutos MS, Metaxa ZS, Shah XP (2010) Multi-scale mechanical and fractural characteristics and early-age strain capacity of high performance carbon nanotubes/cement nanocomposites. Cement Concr Compos 32:110–115
8. Li GY, Wang PM, Zhao XH (2005) Mechanical behavior and microstructure of cement composites incorporating surface-treated multi walled carbon nanotubes. Carbon 43(6):1239–1245
9. Skazlic M, Bjegovic D, Serdar M (2009) Utilization of high performance fiber-reinforced micro-concrete as a repair material. In: Alexander et al (eds) Concrete repair, rehabilitation and retrofitting II. Taylor & Francis Group, London
10. Bouzoubaa N, Lachemi M (2001) Self-compacting concrete incorporating high volumes of class F fly ash preliminary results. Cem Concr Res 31:413–420

Use of Fly Ash in Mining Sector

B. Bhaskara Rao and Vimal Kumar

1 Introduction

Social and techno-economic development of any country is mainly based on the inputs of the energy in any form mainly from the source of electricity generated from the coal, gas, oil, hydro, and nuclear resources.

The resource-based power generation is given in the following table.

Fuel	MW	Percentage
Total thermal	111,324.48	65
Coal	92,418.38	54
Gas	17,706.35	10
Oil	1199.75	<1
Hydro	37,367.40	22
Nuclear	4780.00	<3
RES	18,454.52	11
Total	171,926.40	100

Source Policy perspective: India. TERI

B. Bhaskara Rao
Former General Manager (R&D) and Corporate Planning,
SCCL, Kothagudem, Andhra Pradesh, India

V. Kumar (✉)
C-FARM and Former Mission Director & Head, Fly Ash Unit,
DST, GOI, New Delhi, India
e-mail: dr.vimal.kumar@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_16

A major part of electricity in India is generated from coal (about 60–65%). Coal is being mined in India for the past more than two centuries. Since 1970 onwards, coal-based Thermal Power Plants are being installed at a rapid pace to meet the national energy requirements. Accordingly, the coal production has also increased by fivefold in the last two decades. The coal production which was about 114 million tonne during 1981 has since increased to around 700 million tonne.

The rapid increase in coal production for power generation is helping in meeting the national demand for energy. However, on the other hand, the ash generated from the power plants has become an environmental problem since Indian non-coking coal has 35–45% of ash. The ash generated from the power plants during 1980–81 was recorded as 46 million tonne, has been increased by more than fivefold to 250 million tonne during 2015–16.

2 Coal Mine Sector

Since the inception of coal mining in India, underground mining has been in practice. Keeping in view the demand for coal on a large scale, and in view of the safety of men and machinery, opencast mining was resorted to, wherever possible in place of underground coal mining besides, converting working underground mines into OC mines. Presently, 88% of coal production is from O/C mines and 12% is from underground mines.

Though presently production of coal from O/C mines is dominating, it would not continue for a longer time as the shallow depth coal reserves are being depleted very fast. Hence, the coal winning activities have to be shifted to beyond 300 m depth of deposits in underground mines, which demands high resistance support systems for roof control. In view of the mine safety and conservation of coal with high productivity, the only alternative method is the introduction of coal winning advanced technologies in conjunction with rapid ash stowing technologies by paste filling/hydraulic filling.

3 Safety and Conservation in Coal Mines

Further, it is projected that coal would continue to remain the major source of energy for power generation in the country. The estimates prepared by MoP as well as Planning Commission up to the 2031–32 year, indicate that the coal requirement and consequent generation of fly ash during the year 2031–32 would be around 1800 million tonnes of coal and 900 million tonnes of ash, respectively.

In spite of the efforts by MoEF, FAU (DST) through various notifications, the 100% utilization of ash could not be achieved to date. It is clear that efforts toward large-scale bulk utilization if not resorted to; the 100% achievement would not be possible. A few mining sectors like filling of underground mine voids, backfilling of opencast mines, admixing in OB dumps, use in opencast haul roads will have to be taken up. Ash stowing in underground mine voids enhances the good support to the overlying strata besides substantial conservation of coal and good support to the roof enhancing safety. Ash adding in OB dumps enhances the dump stability and faster revegetation. Backfilling of O/C mines with ash provides improved reclamation and revegetation. Use in haul roads enhances improved load bearing capacity with high compaction and low airborne dust. The details of these factors would be discussed in the subsequent paragraphs.

4 Constitution of C-FARM in Utilization of Thermal Coal Ash in India

Center for Fly Ash Research and Management (C-FARM), a company constituted under section 25 of Indian company's Act 1956, with eminent sr. scientists, technologists and managerial group have come together for facilitation of technology, dissemination of knowledge, know-how transfer, training of consultants and providing techno-managerial guidance for adopting developed technologies in various fields like agricultural, irrigation, development of building materials for all types of construction activities, land reclamation and revegetation, roads and highways, embankments and in U/G and opencast mines. Facilitating technical advice and guidance in all the fields is actively under progress by the experts of C-FARM. In mining, the introduction of ash filling technology on a large scale is being actively considered and is likely to be commenced shortly in some underground and opencast mines in different companies.

5 Areas of Use of Fly Ash in Mining Sector

5.1 Underground Mining

In India, various methods have been adopted for winning coal like bord and pillar mining, longwall mining, blasting gallery method and sub level caving with initial preparatory development followed by depillaring. The voids so formed by depillaring can be filled with ash in place of sand which is presently a scarce material.

- Wherever ash is available from the power plants present near the vicinity of the mines, ash stowing can be adopted instead of caving in depillaring districts, which enhances the conservation of coal, safety, and environment.
- Productivity can be improved in continuous minor technology and other intermediate technologies in conjunction with ash stowing.
- Mine supports.

- Consolidation of haulage track lines.
- Construction of ventilation walls, isolation walls and water dams with specially designed ash bricks.
- Civil construction in mines like electrical substations, rest station, reserve station, etc.
- Use of fly ash in firefighting.
- Use of fly ash in development of interlocking bricks for use in emergency firefighting isolation walls.

5.2 *Surface Mining*

- Backfilling of O/C mines.
- Consolidation of OB dumps.
- Reclamation and revegetation of abandoned OC mines.
- Reclamation and revegetation of subsidence areas caused by depillaring in underground mines.
- Construction of embankments and barriers.
- Construction of haul roads.
- Construction of drainage network.

6 Case Studies in Utilization of Ash in Mines

Considerable efforts have been made in utilizing the ash generated by coal-based thermal power plants in Andhra Pradesh, i.e., NTPC, HWP, APGENCO, Navabharat Ferro Alloy which are situated in close proximity of SCCL coal mines.

6.1 *Experimentation with NTPC Bottom Ash for Stowing at SCCL Ramagundam Mines [1]*

In the year 1993, NTPC Ramagundam (TPP) came forward with an idea of disposing of ash in underground mine voids of nearby SCCL coal mines.

Laboratory investigations were made on samples of NTPC ash by Central Institute of Mining and Fuel Research (CIMFR), Dhanbad to find its suitability for using in stowing. Based on the report, DGMS granted permission to experiment ash stowing at GDK 3 Incline mine of Ramagundam. Experiments of ash stowing were conducted in September 1994 in SS2/1 and SS4/1 depillaring panels of no. 1 seam under the technical guidance of CIMFR scientists. About 30,000 tonnes of ash was supplied to the mines by NTPC, Ramagundam.

6.1.1 Observations Made During Ash Stowing

- Some of the fines from fly ash escaped through barricades and accumulated in the sumps and low laying working places.
- Free flow of ash in the surface bunker could not be achieved due to ash moisture.
- Slow seepage of water from the barricade was observed, resulting in a delay in opening the neighboring working faces.

However, these problems were overcome in the subsequent underground stowing trials.

The following modifications were adopted.

- Vibrators were installed over the bunker for achieving free flow of ash.
- Water jets were arranged for free fall of ash from the chute.
- Opening of the chute was increased to 16″ × 16″.
- 8″ dia pipe was arranged from trough to borehole in place of … pipes.
- Flow meters were installed for controlled water supply.

6.2 Case Study of Pond Ash Stowing at SCCL Manuguru PK-1 INC., Underground Coal Mine [1]

Consequent to the MoEF Gazette Notification, in 1999, Heavy Water Board, Mumbai came forward with a proposal to dispose of the pond ash, generated by its Captive Thermal Power Station of Heavy Water Plant Manuguru, in underground mines of SCCL. Stowing with pond ash was carried out in PK 1 Incline mine under the guidance of FAU (DST), DGMS, Hyderabad and CIMFR, Dhanbad during the years 2001–2004. Before commencing experimentation, laboratory investigations were carried out by CIMFR to find suitability of pond ash for underground stowing and based on the report DGMS permission was obtained. About 10,000 cum of pond ash was stowed on a trial basis. Later regular stowing was taken up in an SQ1 panel of PK 1 Incline mine during 2005 and about 12,000 cum of pond ash was stowed (Figs 1 and 2).

6.2.1 Observations During Pond Ash Stowing

Water filtration was found to be normal as in sand stowing. As per the observations and analysis, the particle size of less than 53 μm is escaping through the barricades. This needs to be arrested by adding more additive or by improving the filter media. Persons were able to walk freely over the stowing bed after 20 min of completion of stowing. The hydrostatic pressure on the barricade is only 1 kg/sq. cm which is very low when compared to the load bearing capacity provided to the barricade. Due to ash stowing the low lying unstowed areas were also filled with fly ash, which is not

Fig. 1 Ash bunker fabricated at 60°

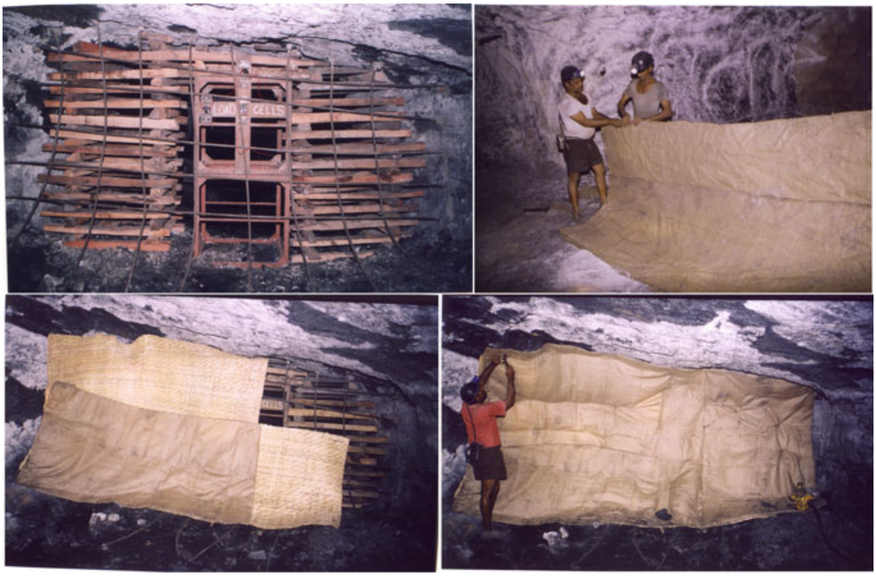


Fig. 2 Stowing barricades made of bamboo thattis and Hessian cloth

possible with sand stowing. The shrinkage factor with ash stowing was found to be only 3% when compared to the sand stowing about 10%.

Due to the high consolidation of ash and good resistance to the overlying strata, the overlying section of the same seam above the ash stowed bed could be removed safely without any roof problems.

6.3 Bottom Ash Stowing at GDK 6A Incline of SCCL [1]

Experiments were carried out with bottom ash during 2005 at GDK 6A Incline mine of Ramagundam Area, SCCL using ash from NTPC, Ramagundam.

The bottom ash collected from NTPC Ramagundam constitutes 99% of +53 μm size of ash (about 11% from +53 to 106 μm size and rest 88% of ash is +106 μm) gave very good results. About 8500 m^3 of bottom ash was stowed successfully and later discontinued due to disputes in transportation-related issues from the ash pond to the mine.

The ash water ratio was maintained at 1:0.7. The maximum rate of stowing achieved is 100 m^3/h. The shrinkage factor was observed to be less than 5%. The escapes of fines from the barricade were found to be negligible.

During the process of judicious extraction of the ribs and when the ribs were punctured to the adjacent stowed gallery, the 2.5 m high ash was self-standing like a wall and did not flow into the working area. Less shrinkage and more compaction were observed.

6.3.1 Observations During Bottom Ash Stowing

From the experiment of bottom ash stowing at GDK 6A Incline mine, it was observed that being coarser, the bottom ash stowing did not pose any technical problems. Out of the total ash generated by thermal power plants, 20% was bottom ash which can be readily used in stowing operations in underground coal mines. Thereby 20% utilization problem of total ash generated was achieved.

6.4 Ash Stowing in Jharia Division of TISCO

General Manager, Jharia Group of Mines, TISCO [2] reported that in Jharia Division about 23,000 tonnes of bed ash generated at F.B.C. Power plant has been consumed for stowing purposes. Use of ash in backfilling of abandoned open cast mines also has been carried out in TISCO besides filling in low lying areas caused by subsidence, Land Scaping, Construction of parks, etc.

6.5 Utilization of Ash for Brick Manufacturing and Filling of Low Lying Areas

Management of M/s SCCL [3] reported that SCCL has switched over to 100% use of Fly Ash bricks. SCCL received a national award for maximum utilization of fly ash products in the International Congress organized by Fly Ash Mission, DST, GOI at New Delhi during 2005. From the year 2002 to 2010, 159 million fly ash bricks were utilized in surface construction works and in underground mines. About 4 lakh cum of ash was utilized for filling the low lying areas (Figs. 3, 4 and 5).

Fig. 3 Masonry roof support with fly ash bricks

Fig. 4 Kerb walls at the man riding station

Fig. 5 Pillar sides supported with fly ash bricks

6.6 Continuous Mining with Active Fill Technology

Officers from the Directorate General of Mines Safety [4] reported that an innovative technology called "Continuous Mining with Active Fill Technology (CMAFT)" in which the voids formed after extraction of coal in the form of slice or chamber, is then immediately filled up with Fly Ash fill matrix which sets from the paste form into solid within two–three hours of filling has been developed.

6.7 Use of Ash in Opencast Mines

NTPC management in one of their presentations [5] reported that ash has been gainfully utilized in some of OC mines. Abandoned mine pits of South Balanda Colliery of Mahanadi Coalfields has been used successfully reclaimed with the ash from NTPC's Talcher Thermal Power Plant by pumping the ash in slurry form through pipes laid for about 10 km distance. The decanted water is pumped back through a Floating Pump for reclamation. Clearance was obtained from the State Pollution Control Board and DGMS. It is reported that 100% ash produced (about 1 million ton per annum) has been used on a regular basis and continuous ash filling is being done for reclamation of land in this abandoned mine.

It is also reported [6] that abandoned mines of Kajora area, ECL and Kathara area, CCL are being reclaimed with fly ash in dry form brought in dumpers from nearby Thermal Power Stations. This ash is suitably dumped and leveled for reclamation and the filled up area is then developed with suitable green cover.

Considering the limited availability of abandoned mines in the vicinity of NTPC's Coal based thermal power stations, it is proposed to use ash in operating OC mines by suitably encapsulating OB soil with ash. For a demonstration of this concept, MoC has identified Medipalli OC of SCCL and Kaniha Mine of MCL.

7 C-FARM Initiatives in Utilization of Fly Ash [7]

Appreciating the need for dissemination of knowledge, facilitation of technology/know-how transfer, training of trainers and consultants as well as providing scientific and techno-managerial guidance for adaptation of developed technologies, the C-FARM has implemented some projects, a few of them have been enumerated hereunder,

- At JSL, Jaipur, Odisha the ash generated at 250 MW TPP 100% utilization of fly ash and bottom ash was implemented.
- Reclamation of low lying areas was taken up at SP office, Jaipur, Odisha and at one of the schools in Jaipur.

- Technical advice and guidance were given to RMC plant Mumbai and for the Fly Ash concrete road at Mahindra Life Space, Mumbai.

Besides the above activities, a number of training programs and seminars were conducted for a large number of brick manufacturing units and in agriculture.

7.1 Reclamation of Laterite Mines

Centre for Fly Ash Research and Management (C-FARM) has been working for the noble cause of promoting Fly Ash Utilization in India for the last 17 years along with stakeholder agencies.

Under the guidance of C-FARM about 4.5 lakh cum voids of abandoned laterite mine at Ragadi near Jaipur have been suitably reclaimed with fly ash during 2010–11 (Figs 6 and 7).

- On the basis of expertise and work done in this area, C-FARM has prepared a Technology and Methodology Manual for Reclamation of low lying areas/abandoned quarries/laterite mines etc. which has been approved by SPCB, Odisha as well as MoEF, Govt. of India.
- The low lying areas/abandoned quarries/laterite mines reclaimed with fly ash in a manner described in above document can be safely used for habitat construction, parking lots, playgrounds and other purposes including agriculture, floriculture, horticulture, forestry etc.
- However, proper investigations and foundation design be suggested before heavy construction/usage.

Fig. 6 Abandoned laterite mine (before)

Fig. 7 Abandoned laterite mine (after)

7.2 Back Filling of O/C Pits at Talchir, Odisha of MCL and Bhupalpally Mines of SCCL

C-FARM provided technical advise and guidance for filling of 20 lac cum of fly ash generated by thermal power station located at a distance of about 30 km from O/C mine of Talcher area. The challenges of deposition of fly ash in this mine include water-filled cavity which may overflow to nearby areas/water bodies and working mines in the vicinity of the opencast pit to be reclaimed with fly ash. In addition to this, the conveying, transportation and management of fly ash at the pit including slurrification will have to be addressed.

It is proposed to use fly ash generated by KTPP, Bhupalpally, AP in underground mines and opencast mines of SCCL Bhupalpally Area (a) for stowing of underground mine voids (b) backfilling of OC mines and (c) stabilization of OB dumps.

8 Conclusions and Recommendations

From the above, it is observed that considerable efforts have been made in the utilization of fly ash generated in India. In spite of these efforts, the utilization is around 50% of the total ash generated. It is essential that in addition to the use of ash in brick, cement, roads, embankments, etc., the focus is being made on the bulk utilization in underground stowing as well as backfilling of OC mines.

Out of total ash generated by thermal power plants, 20% is bottom ash which can be readily used in stowing operations in underground coal mines along with about 65% of ash collected in the first field of ESP. The balance fly ash (about 15%) can be utilized by use of a coagulating agent for fast settling of fine particles.

Under the guidance of expert committee, C-FARM and DGMS Dhanbad, it would not be difficult to achieve 100% utilization of ash, as a large number of mines would have sufficient voids to accommodate the total ash generated in their vicinity. C-FARM would extend all its technical know-how, advise and guidance for achieving the task.

References

1. Dattatreyulu JV, Director (Operations), Veeraswamy V, Chief GM (R&D) (2010) Case study of Manuguru and Ramagundam: fly ash a good substitute of sand. In: National seminar on fly ash an opportunity for mining sector. India Habitat Centre, New Delhi, 26–27 Aug 2010, pp 10–17
2. Divakar C, General Manager, Jharia Division, TISCO (2010) Use of fly ash in mining sector—an industry's perspectives. In: National seminar on fly ash an opportunity for mining sector. India Habitat Centre, New Delhi, 26–27 Aug 2010, pp 86–92
3. Prasad DLR, Director (P&P), Ramesh Kumar B, CGM (CP&P), SCCL (2010) Experiences of SCCL on the use of fly ash and its products in project construction. In: National seminar on fly ash an opportunity for mining sector. India Habitat Centre, New Delhi, 26–27 Aug 2010, pp 157–161
4. Singh BP, Director of Mines Safety (S&T) DGMS (2010) Mining voids—a good repository of fly ash. In: National seminar on fly ash an opportunity for mining sector. India Habitat Centre, New Delhi, 26–27 Aug 2010, pp 191–192
5. Singh BP, Director (Projects) NTPC (2010) Ash utilization—future rests in mine back filling. In: National seminar on fly ash an opportunity for mining sector. India Habitat Centre, New Delhi, 26–27 Aug 2010, pp 36–41
6. A film on "Use of ash in mine filling". www.ntpc.co.in
7. www.c-farm.org

Use of Co-compost from Faecal Sludge and Municipal Organic Waste in Urban Green Space Plantation of Khulna City: Prospects and Problems

T. K. Roy, M. M. Saroar and S. M. Haque

1 Introduction

Co-composting is the composting of two or more raw materials together. Faecal Sludge (FS) and Municipal Solid Waste (MSW) are the common materials. Other materials comprise animal manure, sawdust, wood chips, slaughterhouse waste, etc. Faecal sludge is rich in plant nutrients such as nitrogen, phosphorus and potassium. In Bangladesh, faecal sludge is mainly collected from on-site sanitation systems such as pit latrines, non-sewered public toilet and septic tanks. Crude dumping of solid waste is the most common practice in Bangladesh [1].

Urban green space is a portion of city or town zoning plan that is free of structures. It serves the purpose of visual relief and buffering from building and structural mass. It may be privately or publicly owned and may or may not be accessible to the general public [2]. Green space creates recreation facilities and breathing place for city people [3, 4]. Sustainable Development Goal (SDG) and New Urban Agenda have also specific time-bound goals and targets regarding planning and management of urban open and green space.

The estimated annual volume of faecal sludge generation in Khulna City is 710,000 m^3 [5]. The city produces about 520 tons of municipal solid wastes per day, i.e. 189,800 tons per year, of which around 70% is organic in nature and suit-

T. K. Roy (✉) · M. M. Saroar
Department of Urban and Regional Planning,
Khulna University of Engineering and Technology (KUET), Khulna 9203, Bangladesh
e-mail: tusarpln@yahoo.com

M. M. Saroar
e-mail: nbipu@yahoo.com

S. M. Haque
Urban and Rural Planning Discipline, Khulna University, Khulna 9208, Bangladesh
e-mail: shamimhaque67@yahoo.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_17

able for compost [6]. Co-compost for its good quality plant nutrient value can be potentially used for urban green space plantation.

2 Objectives of the Study

The objectives of the study are as follows:

- To review the co-composting initiatives at global level and in Bangladesh.
- To identify the existing co-composting as Faecal Sludge Management (FSM) and Solid Waste Management (SWM) initiatives in Khulna City.
- To explore the prospects and problems for production and usage of co-compost in urban green space plantation of Khulna City.

3 Methodology

Reports, journal, conference and seminar papers are reviewed to identify the existing faecal sludge and solid waste management system at national and international level with a specific focus on Khulna City. Khulna Development Authority (KDA) Ordinance [7], Khulna City Master Plan 1961 and 2001, City Structure Plan 2001 and Detailed Area Plan 2014, Khulna City Corporation (KCC) Ordinance [8] are reviewed for the study. Photographs of the parks, playgrounds, roadsides, road medians and road intersections, nurseries, rooftop gardens, compost plant, Faecal Sludge Treatment Plant (FSTP), landfill sites, etc. are taken. Officials of KCC, KDA, Roads and Highways Department (RHD), experts, academics, researchers, development activists working in the field of town planning, construction and development, solid waste and sanitation management are consulted and interviewed.

4 Study Area

Khulna, the third largest industrial city in Bangladesh is the study area. It is the second largest port city of the country also. Khulna is a divisional city, which acts as regional hub of administrative, institutional, commercial and academic affairs. The city stands on the banks of the River Rupsha and the Bhairab. It lies between 22° 47′ 16″ and 22° 52′ north latitude and 89° 31′ 36″ to 89° 34′ 35″ east longitude. The city has an area of 45.65 km^2 with a population of 1.5 million. The city is divided into 31 wards.

5 Co-composting Initiatives at Global Level

Co-composting is now becoming more popular in many countries all over the world. People of Asian countries have been using fresh human excreta in agriculture for thousands of years [9]. Composting is promising practically in all countries of the world and so, more researches are important to ensure quality of the end products and improvement of the management system thereof [10].

In Japan, human excreta has been successfully collected and recycled as fertilizer for agriculture since the twelfth century. It is an example of good practice which also shows the importance of developing septage management as a business to ensure its sustainability [11]. The Faecal Sludge Treatment Plant (FSTP) in Nonthaburi City of Bangkok is one of the best operated faecal sludge treatment plants in Thailand. The plant treats about half of the faecal sludge produced in the city. The population of Nonthaburi Municipality is 264,649 with 106,074 households. The FSTP authority has own vacuum trucks. The anaerobic digestion tank capacity is 40 m^3/day. The dried sludge is used as soil conditioner, which is sold to the farmers and gardeners of Nonthaburi Municipality at a rate of 100 USD/ton [12]. The Faecal sludge (FS) and Kitchen Waste (KW) co-treatment plant inside the Changping Waste Water Treatment Plant (WWTP), owned and operated by the Beijing Municipality has been in operation since 2009. The design, construction and equipment supply tasks were assigned to a private company. Capacity of the plant is 300 tons FS and 50 tons KW per day. The final co-composted product is 10–15 tons per day. The disposal fee of FS and KW are the main source of revenue. The composted product are not sold rather it is only used for municipal landscape greening. The department of environment measures the quality of compost and equipment each month which meets the national standard for waste use as fertilizer [13].

An FSTP set up by Consortium for DEWATS Dissemination Society (CDD) and the Devanahalli Town Municipal Corporation, Bangalore, India has been operational since 2015. Area of the FSTP is about 0.17 acre, which can treat up to 6000 L of faecal sludge a day. It serves around 30,000 people. Sludge is collected by the Municipality van that is called honeysuckers. After anaerobic digestion, the sludge is dried in drying bed and the dried sludge is mixed with municipal organic waste for making co-compost, which is used in agriculture. The system is maintained with the earning from selling of co-compost and desludging fees [14]. A study on assessment of the use of treated faecal sludge compost for agriculture in Devanahalli town, Karnataka, India by Shivendra et al. [15] found that some farmers though at very low percentage were very happy to get available, good quality and the odourless compost for farming. About 74% farmers of the Municipality were not interested to use the treated sludge as manure. Only 8% people replied as ready to try once and 18% farmers were ready to surely use as manure. The compost produced from the treatment plant could be used if it would have no health effect. Direct contact with excreta is abhorred in Islamic countries. People working in close contact with FS have high health risk. Improperly treated excreta use in agriculture also has health risk [9].

6 Co-composting Initiatives in Urban Areas Other Than Khulna City in Bangladesh

In Bangladesh, municipalities or water and sewerage authorities are mainly responsible for sanitation and sewerage services. Pit emptying business is predominantly run by the manual emptiers. FSM with the introduction of mechanical collection and disposal of sludge by vacutug, establishment of FSTP, composting and co-composting from sludge etc. is gaining popularity in the urban areas of Bangladesh day by day. Recently out of 11 City Corporations, only 2 and out of 325 Municipalities (Paurashavas) less than 15 have taken the initiative to provide FSM service. Many NGOs (e.g. DSK in Dhaka) and private organizations have been involved in emptying septic tank/pit [16]. BRAC, the world largest international NGO has installed a million single pit latrines all over Bangladesh. It has desired to manage faecal sludge of these latrines and as such conducted a research with a compost company to test a co-compost technology integrating solid waste or sawdust with sludge. Co-compost turns into less bulky pellets, which are used to fertilize crops [17]. In Dhaka, there is one official sewage treatment plant available which receives sludge through a piped sewer network. The treatment plant only covers about 20% of the total sewage generated in the city.

Kushtia Municipality is providing septic tank and pit latrine emptying services through vacutug since 2004. The Municipality started managing this faecal sludge through co-composting technology since 2012 with the help from UN-ESCAP and Waste Concern. SNV Netherlands Development Organization is helping the Municipality in FSM since 2014. Now, the Municipality has four (4) Vacutugs, which have the capacity of 500, 1000, 2000 and 4000 L, respectively. The present FSTP capacity of the Municipality is about 4000 L per day, which is much lower than the actual demand of about 12,000–13,000 L per day. The Municipality also has a Coco pit filter in the FSTP for the treatment of the liquid wastewater comes from vacutug [18]. In 2013, Lakshmipur Municipality has three (3) vacutugs. The Department of Public Health Engineering (DPHE) designed and implemented the FSTP on 0.30-acre land owned by the Municipality. The treatment plant is based on planted filter bed system (Reed Bed System) and sludge drying bed. Currently, the plant receives about 42 m^3 of sludge per week [19]. Sirajganj Municipality received a 2000 L capacity vacutug from UNICEF in 2012 and started mechanical emptying service. The emptying charge for the first trip is Tk. 2500. Tk. 1500 is charged for the next trip, if needed. The existing demand for vacutug service is low and so, the Municipality is taking initiative to make the service popular. During 2013–2014, the Municipality has established an FSTP with technical support from DPHE. It is on one-acre land under GoB-ADB funded Secondary Town Water Supply and Sanitation Project. Vacutug transports the sludge in a closed container and then disposes to the filter bed [16]. Faridpur Municipality started the FSM Programme since 2014 with the financial support of Bill and Melinda Gates Foundation (BMGF) and UK-Aid with technical facilitation by Practical Action. Solar drying-based treatment facility has been developed here with 24 m^3 capacity per day. A private enterprise named Society Development

Committee (SDC) is managing the operations of the treatment plant. It is producing organic compost. Two informal sweeper groups now have been transformed into business cooperatives. They have started emptying service with the vehicle support from Municipality. A Multi-Stakeholder Steering Committee (MSSC) headed by Municipality and representatives from private enterprises, and civil society groups is now active to coordinate, support and monitoring of the FSM system [20].

7 Co-composting as Faecal Sludge and Solid Waste Management Initiatives in Khulna City

Manual emptying is found for around 81% of total desludging services and recently, mechanical emptying is brought together using vacutugs in Khulna City. In total, 68% of the population in Khulna is connected to septic tanks, of which the vast majority of 48% is connected to open drains and another 8% are directly discharging the effluent to the open ground [21, 22]. In Khulna, sludge is disposed at the solid waste dumping site of Khulna City Corporation, 10 km from the city [10]. There is a network of covered drains in one housing area (Khlishpur) of the city. It has built-in reservoir tanks in every 200–300 m and is finally linked with a large river. The network covers around 2000 households and 7–10 industries located in the area [23]. A survey conducted by KUET and AIT in 2014 estimates that about 628,070 m^3 of FS is produced every year in the KCC area [24].

KCC in funding support of Tk. 1.9 crore from the Bill and Melinda Gates Foundation through SNV Netherlands Development Organizations and technical support from AIT, Thailand and KUET, Bangladesh has established the largest FSTP in Asia on its 1.30-acre land (Fig. 1). It is on the abandoned sanitary landfill site at Rajbandh, 6 km away from Khulna City. The plant has been in operation since 2017. Daily treatment capacity of this plant is 180 thousand litres. But, due to lack of awareness and campaign among people, the FSTP has treated only 316 thousand litre sludge in the last 8 months (March–October 2017), i.e. about 40 thousand litres per month. Massive awareness campaign by KCC through the SNV in the Sanitation Month October, the sludge collection increased significantly at 119,000 litres, whereas it was insignificantly low at only 8 thousand litres in September [25].

In Khulna City, vacutug-based mechanical service is provided by KCC itself and also by Community Development Committees (CDC). There are six vacutugs having total 19,000 L capacity in Khulna City (Table 1). CDC is a community organization that provides mechanical emptying services through three different clusters in KCC with a fleet of three 1000 L capacity trucks donated by UNDP. There are also hundreds of manual emptiers plying their trade for generations.

KCC and 10 NGOs Community-Based Organizations (CBOs) are taking care of 60% of the total waste, 520 tons produced per day. In fact, most of the wastes are collected from door-to-door without any sorting and either dumped in open space or improperly landfilled. The collected waste is dumped into the nearest Secondary

FSTP of Khulna City at Rajbandh
Source: The Daily Purbanchal, 2017

Vacutugs in operation in Khulna City
Source: Author, 2017

Fig. 1 Faecal sludge and co-compost initiative in Khulna City

Table 1 Vacutugs, sludge emptying capacity and tariff in Khulna City

Owner of vacutugs	Number with capacity		Total capacity (l)	Rate of tariff per trip (Tk.)
	No.	Capacity (l)		
KCC	1	7000	7000	Tk. 3500 plus 15% VAT
	1	5000	5000	Tk. 2500 plus 15% VAT
	1	4000	4000	Not functional now
CDC	3	1000	3000	Tk. 1000
Total	6		19,000	

Source Field survey 2017

Disposal Sites (SDS). Later, KCC waste transfer trucks collect waste from those sites and dump into the Ultimate Disposal Site (UDS) at Rajbandh.

8 Existing and City Master Plan Proposed Urban Green Space Land Use in Khulna City

There are ten public parks as formal green space of different size (small and big) on 35.08-acre land in Khulna City. Shahid Hadis Park, Jatisangha Shishu Park, Khalishpur Wonderland Amusement Park, Muzgunni S S World Shishu Park, Linear Park, etc. are the mostly used parks. The parks are mostly established and maintained by Khulna City Corporation (KCC) and Khulna Development Authority (KDA). Among the different urban land uses of Khulna City, urban agriculture, urban forestry and urban greening comprise about 23% of the total area, where Crop field/Agriculture/Homestead covers about 16.30% (1839.19 acre). In the Detail Area

Plan (DAP), urban green space has been considered as one of the major existing lands uses among 16–20 categories.

9 Prospects for Production and Usage of Co-compost in Urban Green Space Plantation of Khulna City

In Khulna City, around 42,600 m^3 dried sludge (component of co-compost) can be produced per year [5]. At present, RUSTIC is the only mentionable NGO using only 46 tons of municipal organic waste and producing 30 tons of organic compost per month [6].

The amount organic waste RUSTIC used for making compost is only 0.53% (Fig. 2). The remaining 8684 tons of organic waste has the potential of making 5663 tons of compost.

There are about 50 government offices with their sub-offices and establishments in Khulna City. Only KCC has 197 acres of land property on which there are its offices and establishments. The premises of the organizations have both hardscape and softscape areas. The amount and nature of softscape green areas of the organizations vary (from 25 to 50%) depending on their purpose (Figs. 3 and 4).

There are 1532 educational and research institutes as school in Khulna City [2]. Schools, madrasas, colleges and universities use fertilizer in plantations and landscape areas of different parts of their premise. There are 1087 religious structures in KCC area. Among the structures, the number of mosques stands at 801 followed

Fig. 2 Composting from Khulna City municipal solid waste by RUSTIC at Rajbandh. *Source* Roy et al. [6]

			
Solar Park has scope for Plantation	Green coverage of Jatisangha *Shishu* Park	Golokmoni *Shishu* Park has scope for Plantation	Landscaping in Shahid Hadis Park

Fig. 3 Plantation and landscaping in Public Parks of Khulna City. *Source* Author 2017

Pot plants and landscaping in KCC

Landscaping and plantation in KDA

Pot plants in DC Office

Khulna Divisional Museum

Roads & Highways Department

Fig. 4 Landscaping of government offices as green coverage and potential co-compost users in Khulna City. *Source* Author 2017

PWD Secondary School, Boyra

Zia Secondary School, East Boyra

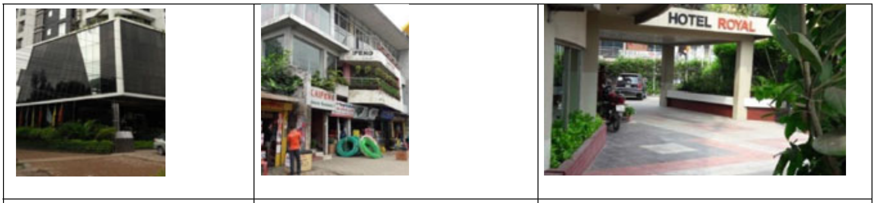
Govt. Khulna Women Polytechnic Institute

Landscaping of Govt. City College Premise

Fig. 5 Plantation and landscaping in School, college and institute as potential source of co-compost user in Khulna City. *Source* Author 2017

by 145 *mandirs* and 45 churches. In Khulna City, there are about 6000 pucca and semi-pucca structures as business and public places. There are 20 recreational establishments in Khulna City. Many of the residential and commercial buildings including hotels and restaurants have balcony plantations. Fertilizer is also used to plant the shrubs and flowers (Figs. 5 and 6).

There are about 840 pucca and semi-pucca industrial structures and establishments in Khulna City. The industries are mainly of jute, shrimp and fish processing, timber and wood processing, power plants, shipbuilding industry, small and cottage industries, etc. The DAP has a proposal of developing 21.21 km roads of varying width. The width ranges from 20 to 80 ft. Roadside, median and intersection land of the roads can be potentially used for green plantation and landscaping. Total number of roads in KCC area is 1215 and their total length is 356.64 km. Different trees, decorative plants and flowers are found in the median and intersection areas (Figs. 7 and 8). KCC is responsible for the plantation and landscaping of such medians.



Hotel City Inn Premise

Kaifeng Chinese Restaurant

Hotel Royal Int. Premise

Fig. 6 Landscaping and plantation of renowned hotels and restaurants in Khulna City. *Source* Author 2017

			
Median of KDA Majid Sarani	Median of Khanjahan Ali Road at Rupsha Ferry Ghat	Westside of Khulna-Jessore Highways in front of GPO	Westside of Khulna-Jessore Highways near Akij Medical College

Fig. 7 Landscaping and plantation in road medians and road sides as potential source of co-compost user in Khulna City. *Source* Author 2017

There exist total of 642.18 km drains in KCC. Besides drains, there are 22 canals in Khulna City. The canal and drain side land can be used for plantation and landscaping.

In the KCC area, there are about 123,739 residential building structures of various types. Residential building structures under construction are 599. Urban green can be increased if the vacant lands are used for vegetable gardens, horticulture, orchard, tree plantation, landscaping, etc. The rooftop gardeners use different types of organic and inorganic fertilizer (Fig. 9).

Nurseries are important green space. There are about 85 nurseries in Khulna City and its adjoining areas. About 87% of the nurseries are using organic compost prepared by themselves in their own nurseries (Fig. 10). Almost all the nursery owners prefer to use organic compost than chemical fertilizer [6]. Vertical expansion, i.e.

			
Royal Mor (Intersection)	Goalkhali Mor (Intersection)	Shibbari Mor (Intersection)	Joragate Mor (Intersection)

Fig. 8 Landscaping and plantation in road intersections and roundabouts as potential source of co-compost user in Khulna City. *Source* Author 2017

			
Building setback area for plantation and landscaping	Building setback area for plantation and landscaping	Rooftop gardening of a residential building in 27 no. Ward	Rooftop gardening of a residential building in 27 no. Ward

Fig. 9 Plantation and landscaping in setback area and rooftop gardens as potential source of co-compost user in Khulna City. *Source* Author 2017

			
Khulna Horticulture Nursery of RHD (Govt.)	DAE Horticulture Nursery (Govt.)	The Khulna New Market Nursery (Private)	Khulna City Nursery (Private)

Fig. 10 Agro-forestry nurseries as potential source of co-compost user in Khulna City. *Source* Author 2017

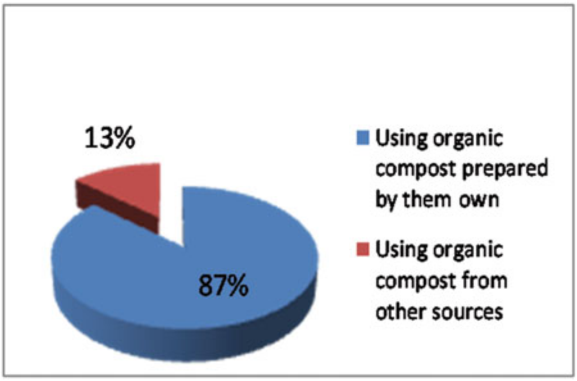


Fig. 11 Nurseries of Khulna City using organic compost. *Source* Roy et al. [6]

multi-storied and high-rise buildings with the application of Floor Area Ratio (FAR) in the city can enhance green areas in the homesteads (Fig. 11).

10 Problems of Production and Usage of Co-compost in Green Space Plantation of Khulna City

The main problems of production and usage of co-compost in green space plantation of Khulna City are:

- The organizations, i.e. KCC and NGOs have a lack of both financial and technical capacity to initiate highly technical co-composting technology.
- The City Master Plans developed by Khulna Development Authority (KDA) and policy plans prepared by KCC did not address the issues of co-composting.
- In spite of having regulatory instructions, KCC does not have any plantation and arboriculture plan.
- There exists lack of effective coordination among KCC, KDA, Khulna Water and Sewerage Authority (KWASA), Department of Agriculture (DoA), Department of Forest (DoF), Department of Environment (DoE) and relevant organizations for efficient sanitation and solid waste management of Khulna City.

- All concerned stakeholders, i.e. city people and officials staffs of the organizations related with production and usage of co-compost have lack of awareness on the importance of proper faecal sludge management, solid waste management and use of co-compost in urban green space plantation of Khulna City.

11 Recommendations to Solve the Problems of Production and Usage of Co-compost in Green Space Plantation of Khulna City

Following recommendations are made to solve the problems of production and usage of co-compost in green space plantation of Khulna City:

- Financial and technical capacity of KCC, KWASA and NGOs can be strengthened to initiate highly technical co-composting technology and management in Khulna City. Government and development partners can help to such initiatives.
- The City Master Plans developed by KDA and policy plans prepared by KCC can be reviewed and updated to incorporate the issues of co-composting. It will help to design and implement co-compost programmes and projects for Khulna City.
- KCC should prepare plantation and arboriculture plans for Khulna City as per instruction of its legal documents, i.e. Ordinance and Act. It will increase citywide green space coverage as a potential user of co-compost.
- Strategy and initiative can be taken by KCC to develop effective coordination among KCC, KDA, KWASA, DoA, DoF, DoE and relevant organizations for efficient sanitation and solid waste management focusing on production and usage of co-compost of Khulna City.
- Awareness of all concerned stakeholders, i.e. city people and officials staffs of the organizations on the importance of proper faecal sludge management, solid waste management and use of co-compost in urban green space plantation of Khulna City can be raised.

12 Conclusion

Co-compost from faecal sludge and organic solid waste is a quality soil conditioner and plant nutrient. Green space of a city acts as recreation and breathing place that promotes healthy living environment, preserves ecological balance and improves physical and mental health. In Khulna City, urban green space in the form of parks, playgrounds, urban forestry, road and waterfront greens, nursery, institutional landscaping, etc. including urban agriculture comprise about 23% of the total area under different land use. All the green space plantations require fertilizer as plant nutrients, where co-compost can be used. Co-compost is organic and environment friendly. A significant amount of co-compost from the estimated 42,600 m^3 dried sludge and

67,925 tons of compost of organic solid waste can be produced per year in Khulna City. Strengthening financial and technical capacity of sanitation service providing agencies; effective coordination among urban public and private organizations; and raising awareness of all concerned stakeholders on co-composting and green space issues is important for promoting production and usage of co-compost in urban green space plantation of Khulna city.

References

1. Enayetullah I (2015) Co-composting of municipal solid waste and Faecal sludge in Kustia Bangladesh. In: ISWA congress, 2015. Antwerp, Belgium
2. KDA (Khulna Development Authority) (2014) Draft report on “preparation of detailed area development plan for Khulna Master Plan (2001) area project. KDA, Khulna, Bangladesh
3. Roy TK (2012) Urban open space and green proposals of Khulna City master plan and their implementation. In: Proceedings of the 2nd international conference in environmental technology and construction engineering for sustainable development (ICETCESD-2012). SUST, Sylhet, Bangladesh
4. Roy TK (2013) Management of park solid wastes in Khulna City. In: Proceedings of the Waste-Safe 2013 3rd international conference on solid waste management in developing countries, KUET. Khulna, Bangladesh. ISBN: 978-984-33-7045-7
5. SNV (2015) Design of Khulna fecal sludge treatment plant by Asian Institute of Technology (AIT), Bangkok, Thailand and Khulna University of Engineering and Technology (KUET), Bangladesh
6. Roy TK, Rahman S, Dev PK (2013) Compost Fertilizer from municipal solid wastes and its application in urban agro-forestry nurseries: a case study on Khulna City. J Bangladesh Inst Plann BIP, Dhaka, Bangladesh 06:191–199
7. Khulna Development Authority Ordinance (1961) Available at http://bdlaws.minlaw.gov.bd/pdf_part.php?id=313. Accessed in July 2017
8. Khulna City Corporation Ordinance (1984) Available at http://bdlaws.minlaw.gov.bd/print_sections_all.php?id=678. Accessed in July 2017
9. WHO (2006) Guideline for the safe use of wastewater, excreta and greywater: excreta and greywater use in agriculture. World Health Organization (WHO), WHO Press, Geneva
10. Kome A (2011) Regional report Asia on landscape analysis and business model assessment in Fecal sludge management. SNV
11. Pierre J-BL, Flamand, Hidetoshi K, Xinbi Y, Satoru T (2013) A study on septage management efficiency in developing countries. In: The 11th IWA conference on small water & wastewater systems and sludge management. Harbin, China
12. Sandec (The Department of Sanitation, Water and Solid Waste for Development) (2015) SFD promotion initiative, Nonthaburi. Thailand. Available at http://www.susana.org/_resources/documents/default/3-2394-7-1451392254.pdf. Accessed on Nov 2017
13. Shikun C, Lei Z, Mingyue Z, Xue1 B, Ziful L, Mang H (2017) Assessment of two fecal sludge treatment plants in urban areas: case study in Beijing. Int J Agric Biol Eng 10(03):237–245
14. Consortium for DEWATS Dissemination Society (CDD) (2016) Pilot Faecal sludge treatment plant-Devanahalli. Available at http://www.cddindia.org/recentactivities-aug16.html. Accessed in 13 Sep 2017
15. Shivendra BT, Tejaswini M, Kamatagi P, Tejaswini PS (2016) Assessment of usage of treated Faecal sludge for agriculture. Int J Res Eng Technol 05(06):269–274
16. Rahman MM, Ali M, Ashraf (2017) A proposed operational/business model for sustainable FSM services in urban areas of Bangladesh. Available at https://www.scribd.com/document/354848001/bangladesh-fsm-review-pdf, Accessed on 12 Sep 2017

17. Smith J (2017) Human waste reuse could benefit farmers and improve public health in South Asia. International Water Management Institute (IWMI). Available at https://wle.cgiar.org/content/human-waste-reuse-could-benefit-farmers-and-improve-public-health-south-asia. Explored in Nov 2017
18. Ahmed R (2017) Faecal sludge management in Kushtia municipality. Sub-regional workshop on urban water and sanitation in South and South-West Asia, Kathmandu, Nepal
19. Rahman MM, Ali MA, Choudhury MR, Rahman MA, Redwan AM, Noor NF, Aminul IS (2016) Fecal sludge management (FSM) scenario in urban areas of Bangladesh. In: The 6th South Asian conference on sanitation (SACOSAN-VI). Dhaka, Bangladesh
20. Islam R, Stevens L, Saha UK (2015) Public private partnerships for sustainable sludge management services in Faridpur. Practical Action, Bangladesh, Bangladesh
21. Ahsan T, Ahmed IU, Alamgir M, Hasan KHM (2014) Review of legal and other governing factors related to Faecal sludge management in Bangladesh. SNV, Khulna, Bangladesh
22. Gunawan A, Schoebitz L, Strande L (2015) SFD promotion initiative, Khulna. Sandec (The Department of Sanitation, Water and Solid Waste for Development), Bangladesh
23. WaterAid (2011) Landscape analysis and business model assessment in faecal Sludge management: extraction and transportation models in Bangladesh, Bangladesh
24. SNV (2016) Co-composting of Faecal sludge and municipal organic waste for sustainable crop production in Southern Bangladesh
25. The Daily Purbanchal (2017) Available at http://purbanchal.com/2017/11/02/page-1-right-click-on-image-to-open-link-in-new-window-23/. Accessed on Nov 2017

Estimation of the Quantity of Biodegradable Volatile Solids in Waste Mixture in Khulna Applying a Three-Stage Composting Process

M. Alamin and Q. H. Bari

1 Introduction

The solid wastes generated from South Asian countries contain a large amount of organic waste with high moisture content. The organic part can be treated by biological decomposition process which is designated as composting. The solid waste composting process is a precise and effective aerobic decomposition of biodegradable part of the organic solid waste. This process involves a diversity of microorganisms, which decompose organic matter under controlled predominantly aerobic conditions. The resulting end product is a stabilized organic matter and it is a steady, dark brown, soil-like material [14] that can be used as a soil conditioner. It also contains nutrients which can have benefit as a long-term organic fertilizer. There are two types of composting systems, open and closed, of which open systems are less in the capital and operating costs but typically require more space and time. The closed system is more sophisticated with a very fast process and needs a high investment. In both open and closed system, the various phases are dominated by different communities of microorganisms depending on temperature and other important factors that prevailed in composting mass during biochemical decomposition reaction. Initial decomposition is carried out by mesophilic microorganisms, which rapidly break down the soluble, readily degradable compounds. The heat produced during reaction causes the compost temperature to rise rapidly. As the temperature rises above 40 °C, the mesophilic microorganisms become less competitive and are replaced by others that are thermophilic microorganisms. At temperatures of 55 °C and above, many microorganisms that are human or plant pathogens are destroyed. Temperature

---

M. Alamin (✉) · Q. H. Bari
Department of Civil Engineering, Khulna University of Engineering & Technology (KUET),
Khulna 9203, Bangladesh
e-mail: alamin081@gmail.com

Q. H. Bari
e-mail: qhbari@yahoo.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_18

above 65 °C kills many forms of microbes and limit the rate of further decomposition. Usually, in composting, forced aeration or turning is applied to keep the temperature below this point. Turning also reduces particle size [5] and increases biodegradation rates [16]. Regarding the spatial temperature distribution, widely varying temperatures have been reported at different locations of aerated piles, usually depending on the time passed since the start of the composting process [5, 8, 9, 11, 15]. The extent of degradation in the composting mass was predicted on the basis of outlet air temperature alone using a linear relationship between outlet air temperature and mean internal temperature of the composting mass [3]. The assessment of the areas under the temperature curves for different composting layers and their respective self-heating tests confirm the biological degradation results found by the multilayer analysis [4]. Finstein and Miller [9] noted that for any given processing duration, the higher the rate the more stable and easily handled the residue and this facilitates storage, transport, and final disposal with a minimal cost. The important factors to control a composting process include initial moisture content, temperature, carbon–nitrogen ratio (C:N), pH, and aeration [6]. Forced aeration maintains higher oxygen level than passive aeration in composting mass [1]. The key products of biochemical decomposition reaction after any effective composting system either open or closed are carbon dioxide, water, compost, and heat [2]. In the decomposition reaction, mainly the biodegradable volatile solids (BVS) are degraded. It is very important to know the amount of BVS present in the initial waste mixture for further calculation of mass balance and application in modeling and design the composting plant.

The estimation of BVS of the waste mixture and faecal sludge generated from Khulna, a South Asian city is very argent for the design of an effective composting process as it applies several projects to manage its huge solid wastes as well as faecal sludge. An estimate of BVS is performed by Bari and Koenig [2] using food waste generated in Hong Kong. The sum of the volatile solids (VS) degraded in the first stage, second stage pilot-scale tests and a further self-heating test [13] with 10% increment was estimated as biodegradable volatile solids (BVS). Therefore, the main objective of this paper was to estimate the quantity of BVS present in the initial mixture specific solid waste plus faecal sludge. The temperature variation during composting in three-stage bench-scale tests, the variation of total solids, moisture content and volatile solids are also observed.

2 Materials and Methods

Bench-scale tests were conducted using a numbers vacuum flask of 1L volume as a bench-scale reactor. The initial composting mixture was consist of two types of wastes namely (i) organic solid waste mixture (OSW) (ii) faecal sludge (FS).

2.1 Preparation of Initial Composting Mixture

Two types of wastes namely (i) solid waste mixture (ii) faecal sludge are prepared separately and then mixed together to get the initial waste mixture to start composting. (i) Organic solid waste was prepared according to waste proportion vegetable wastes: food wastes: waste paper: sawdust as 40:35:10:15. Suitable vegetable and food wastes were collected from a student's hall of KUET. Waste paper was collected from offices and sawdust were collected from a local sawmill. Sawdust was used as the bulking agent. (ii) The Faecal sludge was collected from a septic tank of KUET residential area and dried on a pre-fabricated drying bed to obtain a desired moisture content for the process. Finally, the organic solid waste mixture and faecal sludge as prepared according to the above description were mixed at four different ratios. These ratios are 90:10, 85:15, 80:20, and 75:25 (OSW:FS).

2.2 Bench-Scale Reactor

Bench-scale tests were conducted using vacuum flasks of 1L volume (Shimizu Brand, Japan) as a bench-scale reactor. In this research, the number of reactors used in first, second, and third stage bench-scale tests was 16, 12, and 8, respectively, with totally 36 numbers. About 400 g of waste mixtures is necessary to fill each of the bench-scale reactors initially. The waste inside the reactor was compacted loosely to provide proper porosity for natural and forced aeration. After putting the waste mixture into the reactor, the inlet was covered by cork to prevent excessive heat loss and the thermometers were inserted into the flask for taking reading time to time until the temperature reached ±5 °C of the ambient temperature. According to Table 1, mixture waste was filled up the reactor. The temperature of the waste mixture was continuously monitored. After final declination in temperature close to ambient, the tests were discontinued. Figure 1 shows the experimental setup.

Table 1 The experimental program of bench-scale composting test

Mix proportion	Number of reactors		
	First stage	Second stage	Third stage
90:10[a]	4	3	2
85:15	4	3	2
80:20	4	3	2
75:25	4	3	2

[a] Weight proportion organic waste mixture:faecal sludge

Fig. 1 Experimental setup of bench-scale composting tests

2.3 Experimental Program

Four sets bench-scale composting tests according to mix proportion were done using a series of reactors in three stages. The range of BVS degradation from all four sets would be estimated and described in the following sections of the paper. The experimental program is described in Table 1.

3 Experimental Results and Discussions

3.1 Temperature Variation in Different Stage

All the reactors with different mix ratio for the first stage were run for 30 days as the temperatures fall near ambient temperature. In the first stage, all reactors temperatures were raised to a maximum from 57 to 65 °C within 5 days and followed a similar fashion during their rise and fall phase. After 20 days, all reactors temperature were almost similar which are very close to ambient temperature. Temperature variations during the first stage for set PA1(75:25) are presented in Fig. 2. PA1(75:25) means reactor number 1 with waste mixture proportion OSW:FS = 75:25 for this stage.

The fresh compost released from the first stage reactors were adjusted properly with moisture (around 60% moisture content) and used as a feedstock in second-stage composting. In the second stage, all reactors were run for 15 days as the temperatures came close to ambient temperature after that time. The temperature was raised to a maximum from 54 to 60 °C within 5 days and followed a fairly similar fashion during their rise and fall phase. After 10 days all reactors temperature were similar, which are very close to ambient temperature. The temperature variations during second stage composting are presented in Fig. 3.

Compost released from the second stage reactor was adjusted properly with moisture and used as feedstock for third stage composting. In the third stage, all reactors were run for 18 days as the temperature falls toward ambient during that period. In the third stage, the reactor temperature was raised to a maximum from 33 to 38 °C within 4 days. All reactors temperature was the same which is very close to ambient temperature after 7 days. The temperature variation in third stage tests is shown in

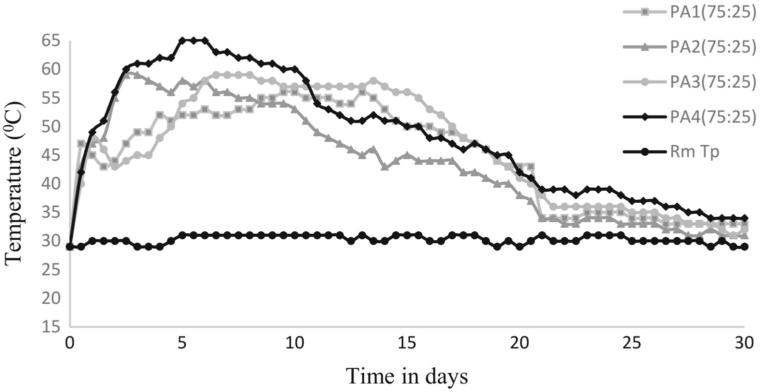


Fig. 2 Temperature variation during first stage composting process

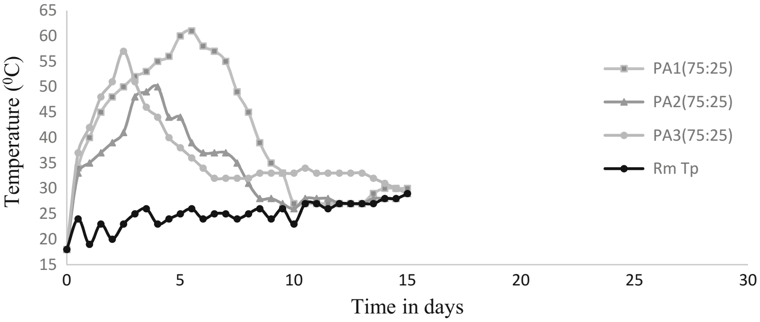


Fig. 3 Temperature variation during second stage bench-scale composting process

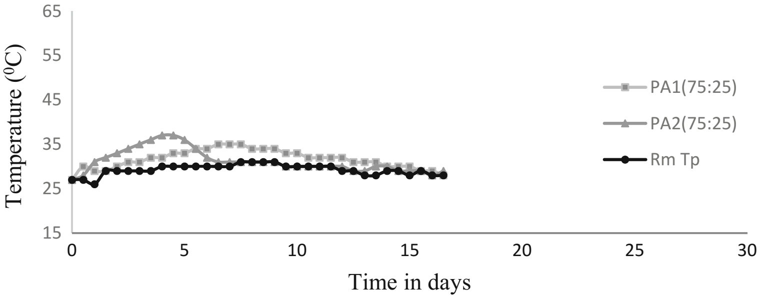


Fig. 4 Temperature variation in third stage composting process

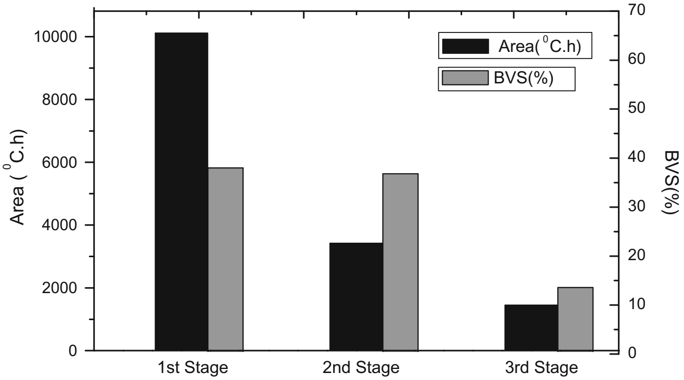


Fig. 5 First stage, second stage, and third stage area under temperature and BVS(%) reduction

Fig. 4. During first stage and second stage, the temperature was increased to high thermophilic level up to 55–60 °C within 1 week and in the third stage, there was no remarkable increase in temperature compared to ambient temperature, which indicates that the produced compost after the second stage was reached toward stability.

After comparing Figs. 2, 3 and 4, it is observed that the area under temperature curves are decreased from first to third stage and is explained in Fig. 4. Therefore, it can be concluded that the much BVS is degraded in the first stage, then second and third stage. There was very little BVS left after the second stage.

First stage, second stage, and third stage area under temperature and BVS (%) reduction are present in bar diagram Fig. 5.

3.2 Estimation of Initial Biodegradable Volatile Solids

The determination of the biodegradable fraction of VS or biodegradable volatile solids (BVS) would give a better understanding of the waste degradability and

Table 2 Estimation of initial biodegradable volatile solids (BVS) by performing three-stage bench-scale tests

Weight proportion OSW:FS	All weights in gm							
	Initial dry solids	Initial volatile solids (VS)	Final VS	VS degraded in (gm)				Estimated BVS is 1.1 times of total VS
				ST1	ST2	ST3	Total VS	
90:10	936	674	332	189	115	38	342	376
85:15	840	516	270	152	59	34	246	270
80:20	955	598	306	198	45	49	291	320
75:25	839	465	230	152	58	25	235	259

The BVS were estimated by multiplying 1.1 times the sum of VS degraded in three stages, the first stage (ST1), second stage (ST2), and third stage (ST3)

final product stability [7]. The term biodegradable volatile solids (BVS) is generally used when referring to the degradation rates or oxygen consumption rates [10]. The total initial biodegradable volatile solids (BVS) for different proportion mixture solid waste bench-scale tests were estimated from the summation of volatile solids degraded in the first, second, and third stage. According to Bari [5], it was estimated that the remaining BVS in the compost, after 63 days of effective degradation in the first stage, second stage, and the third stage would not be more than 10%. Therefore, the sum of VS degraded in three stages is increased by 10% to have a suitable estimation of initial BVS. The calculation procedure and the estimated initial amounts of BVS for different sets are presented in Table 2.

3.3 *Extent of Degradation*

The amount of biodegradable volatile solids (BVS) as estimated from Table 2 is used to determine the BVS degraded in first, second, third stages, and their overall sum with percentage degradation are presented in Table 3. For explanation: BVS = Biodegradable Volatile Solids; $i1$ = initial BVS in stage 1; Δ = amount of BVS degraded in gm; ΔT = total BVS degraded in three stage (in row 1 for 90:10, $\Delta T = (168 + 82 + 84) \times 100/386 = 88.81\%$. The total biodegradable volatile solids reduction was 83–89% after 63 days. The range of reduction is very narrow with a standard deviation of 2.78. Therefore, it can be concluded that all four sets of waste contain almost the same percentage of BVS depending on their VS content. The waste mixture proportion (75:25) of BVS was greater than other mix proportion and was 89%.

Table 3 Amount of biodegradable volatile solids (BVS) degraded (Δ) in first stage tests, second stage tests, third stage tests, and their percentage degradation

Weight proportion	BVS in ST1, duration 30 day			BVS in ST2, duration 15 day				BVS in ST3, duration 18 day				ΔT, 63 day
	$i1$	$\Delta 1$	$\%\Delta 1$	$i2$	$\Delta 2$	$\%\Delta 2$	$\%\Delta i1$	$i3$	$\Delta 3$	$\%\Delta 3$	$\%\Delta i1$	
90:10	376	168	44.74	208	82	39.29	21.71	126	84	66.64	22.36	88.81
85:15	270	103	37.98	168	102	61.15	37.93	65	28	42.38	10.21	86.12
80:20	320	103	32.05	218	145	66.71	45.33	72	19	25.91	5.86	83.24
75:25	259	91	35.29	167	104	62.07	40.17	64	36	56.26	13.81	89.26
Average			37.51				36.28				13.06	86.86
STDEV			5.39				10.20				7.00	2.78

BVS = Biodegradable volatile solids; $i1$ = initial BVS in stage 1; Δ = amount of BVS degraded in gm; ΔT = total BVS degraded in three stages

4 Conclusions

Based on the above results the following conclusions are drawn:

- The mean maximum temperature of the first stage and the second stage tests were 61 and 57 °C, respectively, and followed a similar fashion during their rise and fall phase. In the third stage, no remarkable increase in temperature was observed.
- The mean BVS reduction in different first stage tests was 37.5% of the initial estimated BVS. In a second stage, BVS reduction was 36.3% of the initial BVS and third stage BVS reduction was 13.1%.
- The total biodegradable volatile solids reduction was 83–89% after 63 days. The range of reduction is very narrow with a standard deviation of 2.78. Therefore, it can be concluded that all four sets of waste contain almost the same percentage of BVS depending on their VS content.

References

1. Alamin M, Bari QH, Islam MS, Hassan KM (2017) Safe disposal of faecal sludge using co-composting. In: Proceedings of the WasteSafe 2017—5th international conference on solid waste management in the developing countries, Khulna, Bangladesh, pp 200–213, 25–27 Feb 2017
2. Bari QH, Koenig A (2001) Effect of air recirculation and reuse on composting of organic solid waste. Resour Conserv Recy 33:93–111
3. Bari QH, Koenig A, Tao GH (2000) Kinetic analysis of forced aeration composting—I. Reaction rates and temperature. Waste Manage Res 18:303–312
4. Bari QH, Koenig A (2000) Kinetic analysis of forced aeration composting—II. Application of multilayer analysis for the prediction of biological degradation. Waste Manage Res 18:313–319
5. Bari QH (1999) Effect of different modes of aeration on composting of solid waste in a closed system. Ph.D. thesis, Deparment of Civil Engineering, The University of Hong Kong
6. Diaz MJ, Madejon E, Lopez F, Lopez R, Cabrera F (2002) Optimization of the rate vinasse/grape marc for co- composting process. Process Biochem 37:1143–1150
7. Fernandes L, Sartaj M (1997) Comparative study of static pile composting using natural, forced, and passive aeration methods. Compost Sci Utilization 5(4):65–77
8. Fernandes L, Zhan W, Panti NK, Jui PY (1994) Temperature distribution and variation in passively aerated static compost piles. Biores Technol 48:257–263
9. Finstein MS, Miller FC (1985) Principles of composting leading to maximization of decomposition rate, odor control and cost effectiveness. In: Gasser JKR (ed) Composting of agricultural and other wastes. Elsevier Applied Science Publishers, London, UK, pp 13–26
10. Haug RT (1993) The Practical Handbook of Composting Engineering. Lewis Publishers, Boca Raton, USA
11. Kuter GA, Hoitink HAJ, Rossman LA (1985) Effect of aeration and temperature on composting of municipal sludge in a full-scale vessel system. J Water Pollut Control Fed 57:309–315
12. Koenig, A, Bari QH (1998) Effect of air recirculation on single reactor and two-reactor composting system. In: 91st annual meeting and exhibition, Air and Waste Management Association, San Diego, California, USA. CD-ROM Proceedings Paper No 98-WP8601, p 15, 14–18 June
13. LAGA (LaenderarbeitsgemeinschaftAbfallbeseitigung) (1985) Memorandum M 10 Quality criteria and recommendation for application of compost from solid waste (in German). In: Kumpf W et al (eds) Muell-Handbuch. Kennzahl 6856, Lieferung 1/85. Erich Schmidt-Verlag, Berlin, pp 1–37

14. Rouse J, Rothenberger S, Zurbrügg C (2008) Marketing compost: a guide for compost producers in low and middle-income countries
15. Stentiford EI, Taylor PI, Leton TG, Mara DD (1985) Forced aeration composting of domestic refuse and sewage sludge. Water Pollution Control 84:23–32
16. Tiquia SM, Richard TL, Honeyman MS (2002) Carbon, nutrient, and mass loss during composting. Nutr Cycl Agroecosys 62:15–24.

Plasma Arc Technology: A Potential Solution Toward Waste to Energy Conversion and of GHGs Mitigation

A. Hazra, S. Das, A. Ganguly, P. Das, P. K. Chatterjee, N. C. Murmu and Priyabrata Banerjee

1 Introduction

Most of the environmental harming agents *like* Greenhouse gases (GHGs) occupy prior attention due to its adverse impact on human health. Rapid GHG emission increases its deleterious effect, which lead to global warming, acid rain, smog formation, and other direct or indirect health impact on our habitat. Human activities

---

A. Hazra · S. Das · A. Ganguly · P. Das · P. K. Chatterjee · N. C. Murmu · P. Banerjee (✉)
CSIR-Central Mechanical Engineering Research Institute (CMERI), Mahatma Gandhi Avenue, Durgapur 713209, West Bengal, India
e-mail: pr_banerjee@cmeri.res.in; priyabrata_banerjee@yahoo.co.in
URL: http://www.cmeri.res.in
URL: http://www.priyabratabanerjee.in

A. Hazra
e-mail: hazraabhijit94@gmail.com

S. Das
e-mail: Mrsaikat.das.smit@gmail.com

A. Ganguly
e-mail: a_ganguly@cmeri.res.in

P. K. Chatterjee
e-mail: pradip@cmeri.res.in

N. C. Murmu
e-mail: murmu@cmeri.res.in

P. Das
Jadavpur University, Kolkata, India
e-mail: partha_das@cmeri.res.in

N. C. Murmu
Academy of Scientific and Innovative Research, CSIR-Central Mechanical Engineering Research Institute (CMERI), Mahatma Gandhi Avenue, Durgapur 713209, West Bengal, India

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_19

and some natural events trigger the release of a huge amount of GHGs to the environment and there in its consequences are getting worse day by day. In 2010, it was estimated that globally this tremendous amount of emission from manmade actions emitted nearly 46 billion metric tons of greenhouse gases, which can be articulated in terms of carbon dioxide equivalents [1]. The emission of these long-lived gases depend upon several factors *like* economic activities (composition and efficiency of the existing economy), explosion in population, rapid industrialization, economic status, land locality, and location-dependent climatic changes, which cause a variation in the gross emission from the different countries.

Due to the indiscriminate human activities in the developing countries, it causes the release of high extent of contaminant (CO_2, CH_4, N_2O) and several other fluorinated gases which are the main composition of greenhouse gas. These gases are currently covered by agreements under the United Nations Framework Convention on Climate Change (UNFCCC) [2].

The World Resources Institute (WRI) has the climate-damaging greenhouse gases report depending upon the country-wise emissions with the latest analysis based on data coming out of its Climate Analysis Indicators Tool (CAIT). This report clearly reflects that India is the fourth largest carbon emitter country among the developing countries on the basis of per capita emission. In respect of per capita contribution to the overall emissions, India contributes very less significant amount emissions among the developing countries like China, Mexico, and Brazil while the United States' releases eight times higher than that of India. Majority of global emission is contributed by the top 10 emitting countries, where six of them are developing countries. Consequently, in respect of the total amount of global emissions, only China contributes approximately 25% of and holding the top emitter position. Rapid economic growth makes some countries *like* India, Indonesia, Brazil, Mexico, and Iran the larger contributor to the total global emissions [3].

Majority of greenhouse gases remain into the atmosphere for a prolonged period, which can be ranging from a decade to many million years. Over time, the oceans and vegetation are absorbing greenhouse gases from the atmosphere. Some extents of these gases are removed from the atmosphere by chemical reactions. The removal processes are too much slower than the accumulation of these gases into the atmosphere. The accumulation processes are accelerated by various societal activities, and as a result, the concentrations are increasing [4].

From 1990 to 2010, on view of various sectors of greenhouses gas emission, energy production industries and uses which include fuels consumption of vehicles. In fact, it becomes the largest source of greenhouse gas emissions worldwide. Rapid industrialization, urbanization, and international transport have taken proper initiatives to aggregate the energy production and use share around 71% of the total emission. Followed by this, agriculture is the major contributor, which contributes around 13%. Land-use change and forestry help to absorbs carbon dioxide, which counterbalances the emissions from other sources. Deforestation and the waste generation along with its poor management are the most severe human practices which are also responsible for greenhouse gas emission [1, 2]. Waste generation and greenhouse gas (GHG) emissions are associated with each other [5]. In total, the amount of global GHGs emission 3–4% of emissions is caused by total waste disposal [6]. In this era, waste becomes a major concern for every country due to its continuous rising and mishandling management leading to various harmful impacts on the atmosphere and human health. Waste generation has become an inevitable societal practice accumulating a huge amount of wastes throughout the globe. Many factors are responsible for this high waste generation rate, some are *like* population and their education level, monthly income plays a significant role [7]. Industrialisation [5] and enhancement of people lifestyle rapidly raises the municipal solid waste (MSW) quantity among other sources based waste like hospital waste [8, 9], radioactive waste [10] agriculture waste [11], E-waste [12]. These are categorized among the sources of generation and due to huge quantity and high rate of generation municipal solid waste draws a great attention. In 2011, worldwide the amount of generation of MSW was around 2 billion tones [13] which is expected to reach around 10 billion by 2050 [14]. In 1947, India had the amount around 6 million tons which reaches to 48 million tons with the end of this decade and followed by it was 90 million tons in 2009. Accordingly, with this rate, the quantity of generated solid waste will touch the milestone of 300 million tons by 2047 [15, 16]. Along with these factors, improper waste management is leading to severe effects in environment and livelihood [10]. In this regards, the most universal phenomenon of waste management is to reduce, recycle, and reuse which needs to be implemented in our society [10, 11]. Besides these, among various waste disposal processes, generally implemented processes are landfilling, composting, incineration [16, 17], pyrolysis, gasification [17]. Landfilling is the most common trend adopted by the community. However, due to the limitation of land for the dumping of wastes are the anthropogenic sources of GHGs like methane (CH_4) and nitrous oxide (N_2O), henceforth this process should be obsolete in the forthcoming days. While incineration can be beneficial in line with waste volume destruction but in addition, it releases environmentally toxic gases *like* SO_x, NO_x [18], and other hazardous chlorinated dioxins and furans. In the case of pyrolysis, the extent of emission is very low compared to the incineration. But some difficulties, *like* low gas productivity, a broad variation of the decomposition products are not easily get rid off because of its slow rates of heating and cool down. This makes this process limited to the product composition [17, 19]. Composting is another method, mainly applicable for degradable waste that leads to large amount of GHG like $CH_{4,}$ which have very high global warming potential (GWP) (72 times) than that of CO_2 [2]. The aforementioned waste disposal processes contribute a large amount of GHG along with some other toxic gases [14]. In view of suppressing the GHG emission through MSW disposal and generation of cleaner fuel, gasification with plasma technology is one of the advantageous thermochemical pathways that can be used. In this process, the high temperature application of plasma flames to organic solid components of MSW readily converts them to high calorific value syngas (CO and H_2) used for energy recovery. After vitrification of the inert fraction, it is converted into a non-leachable slag which can further be reused as a construction material for several useful and functional materials [20]. In this process, for efficient production of the heat energy, no fuel is needed for combustion which means no oxidant is required; therefore, this can lead to a reduction in CO_2 emission [21] and prevents the reformation of persistent organic pollutant (POPs) like dioxin, furan [22, 23] All the above factors allowing plasma treatment is a truly proximal solution for MSW [20]. Recently many agencies emphasises on sustainable energy recovery and adequate resource management which plays an efficient role in the reduction of GHGs as well as safe waste management [24, 25]. In this relevance, European Commission mentioned the significance of efficiency based on resource and focused on sustainable and inclusive growth [26]. After analyzing the GHG outputs from materials, the U.S. Environmental Protection Agency (EPA) concluded that for convenient GHG mitigation, the recycling of materials with effective waste minimization are the most suitable options [1].

2 Background

2.1 Overview of Plasma Technology

Although plasma is electrically neutral, it is considered as the fourth state of matter. It consists of neutral particles, electrons, and ions [21]. There are mainly three types of plasma: thermal, cold, and warm plasma which are known and the two are considered to be nonthermal equilibrium plasma. Among these types, thermally equilibrium plasma, i.e., thermal plasma generates very high temperature energy and temperature profile of thermal plasma makes it efficient and applicable for a broader range of waste treatment [22, 27]. On the contrary, based on the configuration of plasma it can be classified as transferred and non-transferred arc torches, which are utilized in various solid waste treatment methods. Non-transferred arc torch is more generally used in the destruction of waste material where the carrier gas (N_2, Ar, and H_2) is transformed into plasma and it is directly applied to waste materials. But in case of transferred torch reacting material should be an electrically conductive material as it behaves as an electronic linker between cathode and electronically grounded anode [15, 28]. Design and development of functional plasma gasification system can be manufactured based on certain demand considering many issues and target specific application. In this system several types of plasma generator are used and depending upon that some systems are classified as direct current (DC)/alternating current (AC), radio frequency (RF), microwave (MW), and DC-RF hybrid arc plasma system [15].

2.2 MSW Quantification and Characterisation

Rapid urbanization and population explosion have threatened the generation of wastes (MSW). Several factors affect MSW generation such as living standard, the extent of economic growth, climate variation, and variation. As an artifact rapid MSW generation in Indian cities has been found to increase approximately eight

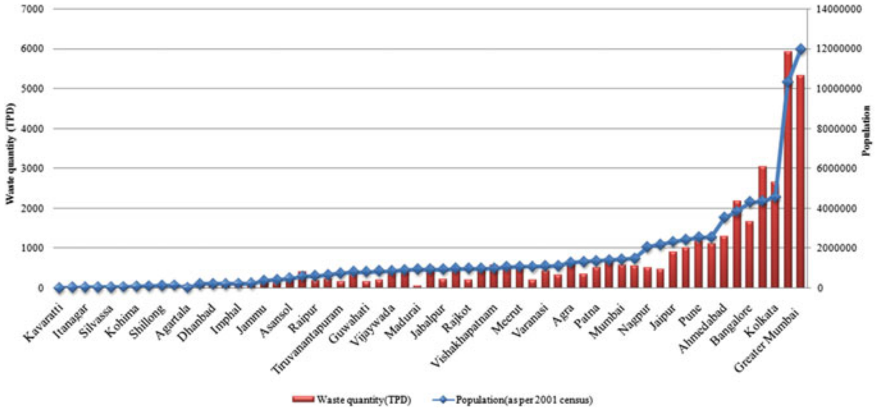


Fig. 1 Waste quantity variation with a population of Indian cities

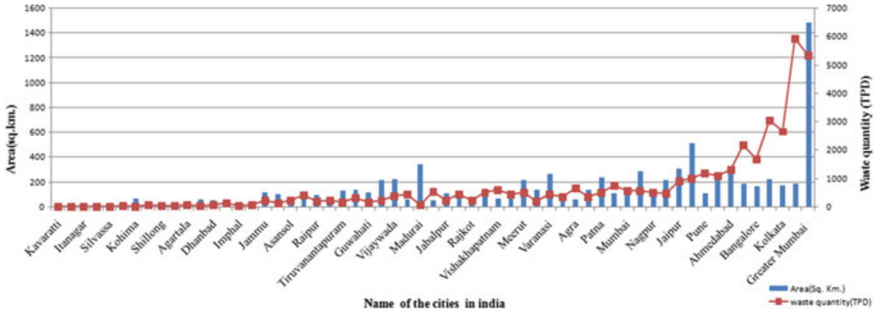


Fig. 2 Waste quantity variation with area of Indian cities

times since 1947. In respect of the per capita generation, small towns generate lower than that of the metropolitan cities. In India, the rate of MSW generation is per day ranges from 0.2 to 0.5 kg which rises at the rate of 1–1.33% annually. There are some figures (Figs. 1, 2 and 3) [29–31] providing some reflection on generated MSW of states in India which clearly indicates that rapid urbanization and explosion in dense population is the key factor in waste generation [32, 33].

In case of major Indian cities, total waste generation and waste generation rate (kg/cap/day) are compared with the area of habitable and population density (as per 2001 census), respectively. The main composition of MSW is a large compostable organic fraction (40–60%), some extent of ash and fine earth (30–40%), paper (3–6%) and plastic, glass and metals (each less than 1%). The quantity of various MSW constituent is highly depended upon the habitat and population which is shown in Table 1 [34].

Physical characteristics of MSW can be classified into compostable matters which are mainly content of fruit and vegetable peels, food waste. In this context, Paper, plastic, glass, metals, etc., are considered as recyclables materials where paints,

Table 1 Physical composition of MSW

Population series (in millions)	Cities surveyed	Waste paper	Synthetics materials, rubber, and leather	Waste glass	Metal	Bio-degradable matters	Inert material	Carbon/nitrogen ratio	CV (kcal/kg)
0.1–0.5	12	2.91	0.78	0.56	0.33	44.57	43.59	30.94	1009.89
0.5–1.0	15	2.95	0.73	0.56	0.32	40.04	48.38	21.13	900.61
1.0–2.0	9	4.71	0.71	0.46	0.49	38.95	44.73	23.68	980.05
2.0–5.0	3	3.18	0.48	0.48	0.59	56.57	49.07	22.45	907.18
5.0 and above	4	6.43	0.28	0.28	0.8	30.84	53.9	30.11	800.7

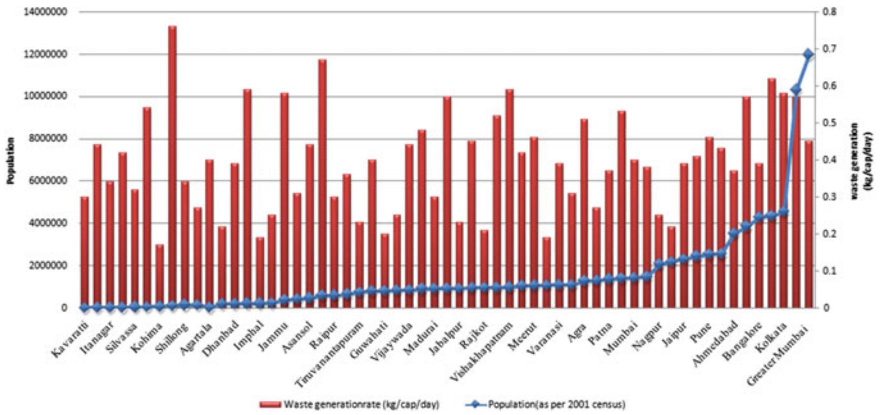


Fig. 3 Waste generation variation with a population of Indian cities

pesticides, used batteries, medicines, etc., are known as toxic substances. Soiled waste is comprised of blood stained, waste cotton, sanitary napkins, disposable syringes [35]. Combustible materials (papers, plastics, food waste, wood, textiles, disposable diapers, leather) and other organics are present in larger extent which could be a useful resource for energy recovery. The carbon and nitrogen ratio of MSW reside within 20–30 and the lower calorific value ranges between 800 and 1000 kcal/kg supports the huge potential of MSW in efficient energy recovery [32].

2.2.1 MSW Treatment Methods

Primary Storage and collection of MSW are crucial for further proper treatment. Generally, categorized bins are the ground level storage systems which are classified depending upon the nature of waste collected *like* compostable or inert [36]. The collections of these stored wastes depend upon the concerned municipalities waste collection system and greatly on societal awareness for waste management. Generally, open trucks, wheelbarrow, large size municipality bins play a major role on waste collection in India. But these are not an adequate collection process for MSW. In India, the mode of collection of MSW can be estimated with help of the data produced by the Central Pollution Control Board (CPCB) which studied over 300 Class-I cities. This aforementioned data indicate that manual collection comprises of 50%, while only by trucks the collected portion is around 49% [31, 33] though in some cities various NGOs and municipalities have taken several steps including door-to-door collection and segregation, this could be very much useful for further recycling and treatment of wastes [36, 37].

Most crucial part of waste management is the safe disposal of waste in an environment friendly manner. Accordingly, disposal of MSW requires efficient technology and resources to fulfil the environmental requirement. Till date proper management in handling those things are not adequate. The compostable parts deal with composting and vermicomposting techniques and also in some cases it is used to produce bio-methane (bio-gas). The applicability is subjected to the nature of wastes that put a limit on its usefulness. Besides this most of the MSW are disposed of as landfilling which is the most common practice in many countries. Landfilling is a burning threat as its open exposure can cause contaminants and toxins to be exposed to the environment through various media *like* rag pickers, insect, vermin [10, 38] Landfilling is dignified as a man-made source of greenhouse gases (GHGs) which primarily comprise of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) [39].

Similarly, incineration is also the most common thermal treatment for waste disposal throughout the world. Figure 4 shows the number of incineration used in various cities in Europe. In incinerators, waste material is combusted in the presence of air causes the high extent of GHGs emissions such as CO, CO_2, HCl, SO_2 including dioxins and furans, particulate matter, and many more toxins. Simultaneously the toxic contaminants in the char or ash residues can contaminate existing water bodies too. In India, there are several large and small scale based incinerators using MSW as feeding stock and some plants recover a certain extent of energy [40].

Recently in India, development and implementation of wastes to energy technologies are the initiations of environmentally friendly waste disposal. Refuse-derived fuel (RDF), pyrolysis and gasification are the most common waste to energy production techniques. Among these RDF is one of the promising technologies, which nowadays' is intended to utilized for producing power where MSW is palatalized as solid fuel. In addition, the RDF plants help to diminish the pressure of waste dumping on landfills. Combustion of the RDF is capable of generating power from MSW is technically an efficient process [32].

Pyrolysis and gasification are basically a thermochemical conversion process wherein the absence of an oxidizing agent, a solid fuel is heated for its complete decomposition or conversion to other materials. In pyrolysis bio-oil is also produced

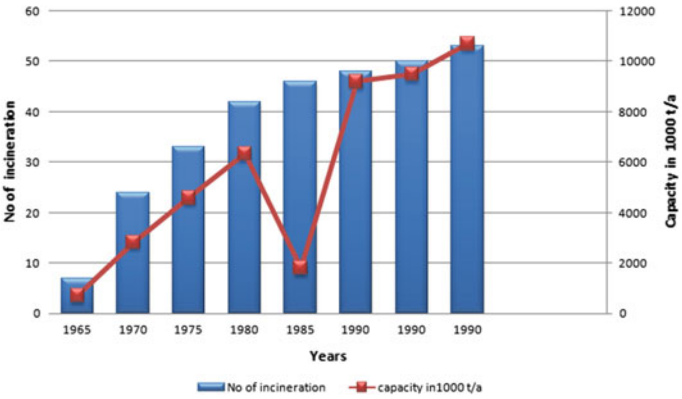


Fig. 4 No of incineration in operation in European countries with corresponding capacities

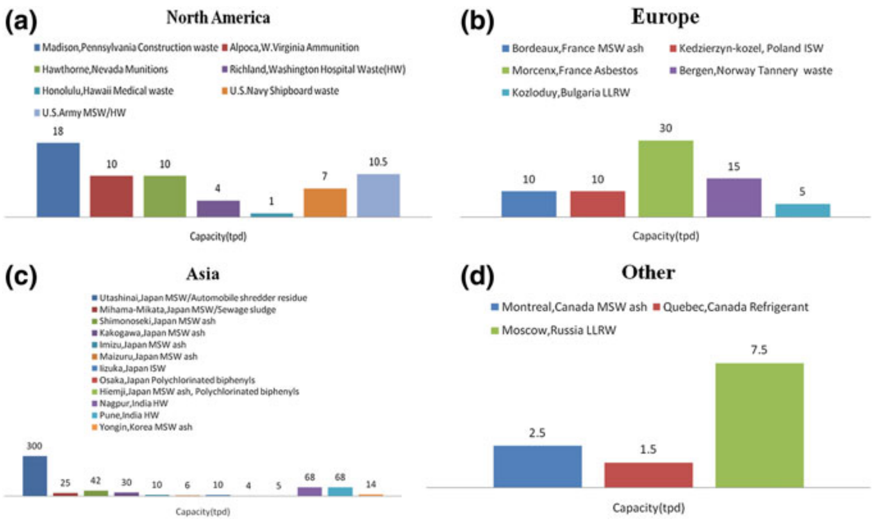


Fig. 5 Plasma technology implemented in various part of the world e.g. **a** North American zone **b** European zone **c** Asian zone **d** other

along with gas and char but low-temperature conversion generates high concentration CO *like* GHGs and some other toxins [32, 34] whereas in gasification due to application of high temperature, MSW is converted to high calorific value syngas (CO and H_2) which is further utilized for energy recovery. As Plasma arc is capable of generating very high temperature which could directly be applied to the waste material for gasification. This plasma arc-driven technology is the most emerging waste disposal as well as energy recovery technique around the world. From the Fig. 5 it can be noted that various countries utilize this technology for diverse applications.

Accordingly, some data mentioned in Table 2 where it is found that the generation of syngas utilizing plasma gasification is greater than the ordinary gasification and it regulates CO_2 emission in nature. The residual part is non-leachable vitrified solid mass which could be employed for the constructional purpose. The waste management plant also emits SO_x, NO_x and other toxins *like* dioxin, furan to a very low level (below the permissible limit) [17, 20, 41]. In India, the technology is not yet commercialized however some pilot plants operate in various sectors. Among these, the first one (NERIFIER) was installed by Narvreet Energy Research and Information (NERI) at Nohar, Hanungarh, Rajasthan. As Tata Energy Research Institute (TERI) gasification unit by Tata Energy Research Institute (TERI) second one installed at Gaul Pahari campus, New Delhi. NERIFIER operates with an efficiency of about 70–80% and waste treatment rate is 50–150 kg per hour [32].

Thus MSW could be the source of renewable energy through the utilization of plasma arc technology. Considering operation all expertise and capital cost validity, production of clean syngas with the very low emission of GHGs and other gases make this technology more viable for implementation towards safe waste management.

Table 2 Comparison between the syngas fraction of plasma gasifier and ordinary gasifier

Syngas mole fraction	MSW gasification with an ordinary gasifier	MSW gasification with plasma gasifier
H_2	17.04	43.50
CO	22.70	34.50
CO_2	4.92	0.03
H_2O	0.00	16.22
CH_4	0.00	0.01
H_2S	0.00	0.09
N_2	48.49	5.63
HCN	0.00	0.00
S	0.06	0.00
SO_2	0.00	0.00
COS	0.01	0.00
NH_3	0.00	0.00
C_2H_2	0.00	0.00
C (solid)	1.12	0.00
Syngas LHV (MJ/kg)	22.78	13.44
Syngas HHV (MJ/kg)	26.45	14.71
Feedstock flow (kg/s)	1.00	1.00

LHV Lower heating value; *HHV* Higher heating value

3 Result and Discussion

3.1 Potential of Energy Recovery from MSW

In view of energy recovery, MSW management is important for the societal benefits. In search of the efficiency of the energy recovery from MSW, one can get an idea by measuring the energy recovery from the various major components such as paper, textiles, food waste, plastics, metals, glass, and others which is shown in Fig. 6. The main resources of MSW are paper and plastics which have a higher potential in energy recovery perspective that shown in Fig. 6 [14, 42].

Variation of energy recovery value for a different component of MSW highly depends upon the calorific value of that component. In Fig. 6 it is shown that as calorific value and energy recovery proportionally related to each other then the extent of energy recovery from the textile material is lower than plastic. In the Topic of energy recovery from MSW, moisture content is a prior factor to account. High content moisture reduces the energy recovery extent as likely energy recovery from food waste was very small [14, 42]. Actually, the high proportion of moisture directly affects the heating value of MSW. Consequently, the percentage of moisture content differs from place to place as in Asian countries *like* Taiwan; Bangladesh where it

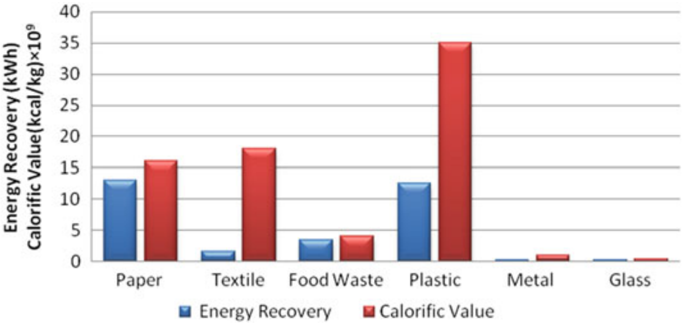


Fig. 6 Schematic representation of generated calorific value and energy recovery potential of a different constituent of MSW

ranges between 50 and 75%. In the United States and European countries, moisture content value reside between 20 and 30% [43, 44].

Composition and characteristics of MSW play a considerable role in the percentage of energy recovery. The factors such as economic status, ritual, lifestyle, literacy rate, climatic and topographical conditions also greatly influenced and characteristics of MSW [45]. In developing countries *like* India, these factors show great variation in physical, chemical composition and characteristics in comparison to the developed countries of the world [32, 44]. In Fig. 7 [29] it is shown besides Ahmadabad, the moisture content of MSW is generally high in most of the Indian cities ranging between 41 and 64%. The calorific value (CV) stays in the range of 742–2632 kcal/kg and the C/N ratio ranges from 18 to 37 [46]. It is already shown that the major content of MSW is organic wastes followed by recyclable and inert materials. From Fig. 7 one can get an idea about the waste component in various major cities of India where it also supports that organic wastes are the major constituent of MSW. Although in India along with these factors and being a high content of organic counterparts in MSW which directed the potentiality and efficiency of MSW in energy recovery perspective.

3.2 *Potential of GHG Emission and Mitigation*

Potentiality of greenhouse gas emission from MSW is very high among other sources which are shown in Fig. 6. There are high C/N ratios (Fig. 7) of MSW components, showcasing the high potential of GHGs emission caused by improper treatment. Consequently, during landfilling and uncontrolled burning of MSW a high content of CH_4, CO_2, and N_2O is released. From estimated current GHG emissions studies reveal that the largest GHG emission occurs from landfilling sectors with a major component of CH_4. After disposal, this emission continues up to several years and also from waste incineration is small compared to landfilling, around 40 metric tons

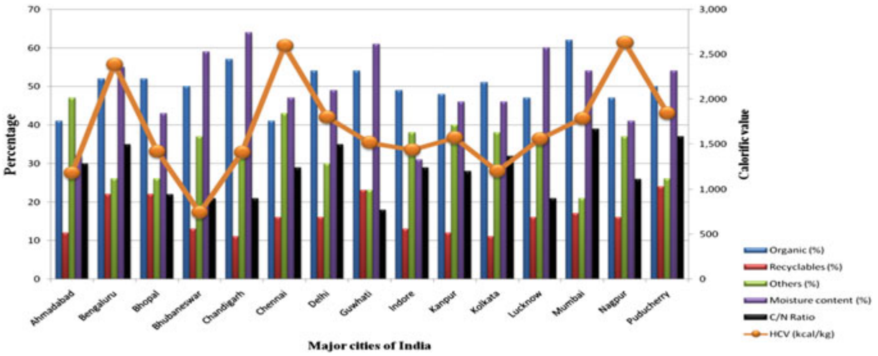


Fig. 7 Component wise characterization of MSW in Indian cities

CO_2-equivalent per year or less. CH_4 emissions from the landfill are ten times higher than the CO_2 release which reflects the potentiality of landfilling for emission of greenhouse gases [47].

Now, material recovery through recycling and energy conversion from waste is considered as the best possible option for suppression of GHG emission considering environmental and societal health. Recycling of metals and paper can effectively reduce around 1.83×10^6 kg CO_2-eq/year and 7.38×10^5 kg CO_2-eq/year respectively. As shown before the materials with lower potential value are not suitable for waste to energy recovery, that portion may be utilized by recycling. Emission of GHGs during fossil fuel burning can be reduced through the efficient generation of energy from the waste materials. As the major component of MSW has higher potential for energy recovery that leads to recovery of energy through a greener approach. Moreover, reduction, recovery, recycling of wastes and waste to energy concept consecutively leads towards the growing potential for indirect reduction of GHG emissions. Subsequently, this process also causes a decrease in waste generation and reduced energy demand and as well as the consumption of fossil fuel [48].

Many policies and initiatives like Swachh Bharat Mission (SBM) have nowadays drawn concern to reduce the indirect and direct effect of waste on the environment. Presently around 10,600 million USD for 5 years in 4041 towns are estimated for SBM which is the biggest cleanliness drive in India. In this movement, the sustainable Solid Waste Management (SWM) is considered as one of the six components, where door-to-door collection and implementation of proper disposal method for MSW are main emphasized [49].

4 Conclusion

Waste generation and greenhouse gas emission, both are the parallel process where the improper waste management methods escalating the GHG emission and its harmful effects on the environment. Some disposal practices *like* landfilling, open burning or incineration contribute a large amount of GHGs such as CH_4, N_2O which have high potential in equivalent to CO_2. Waste to energy is an efficient concept for sustainable waste management and may indirectly reduce the GHG emission by decreasing the demand for fossil fuel. Among various methods, plasma arc technology for disposal of MSW is very much efficient as it is environmentally safe and can recover energy with high volume waste destruction capability. These technologies can be an efficient alternative in the near future for sustainable waste management. Presently, SBM and other policies are emphasizing on municipal waste management which has become the biggest movement in India.

Acknowledgement Department of Science and Technology, Govt. of India sponsored DST-TSG (vide letter no.-DST/TSG/WM/2015/459) (GAP-211712) project is hereby acknowledged.

References

1. U.S EPA (2016) Climate change indicators: global greenhouse gas emissions. Climate Change Indicators in the United States, US EPAs
2. U.S EPA (2016) Technical documentation: U.S. Greenhouse Gas Emissions
3. http://timesofindia.indiatimes.com/home/environment/global-warming/Greenhouse-gases-India-fourth-biggest-emitter-but-lags-far-behind-top-three/articleshow/47807927.cms
4. Climate change indicators in the United States: atmospheric concentrations of greenhouse gases. www.epa.gov/climate-indicatorswww.epa.gov/climate-indicators. Updated Aug 2016
5. Hoornweg D, Bhada-Tata P (2012) What a waste: a global review of solid waste management. Urban Development & Local Government Unit, World Bank, Washington, DC
6. Intergovernmental Panel on Climate Change (IPCC) (2006) IPCC guidelines for National Greenhouse Gas Inventories. Waste 5, Institute for Global Environmental Strategies (IGES), Japan
7. Himabindu P, Udayashankara TH, Madhukar MA (2015) Critical review on biomedical waste and effect of mismanagement. Int J Eng Res Technol 4(03). ISSN: 2278-0181
8. Chartier Y, Emmanuel J, Pieper U, Prüss A, Rushbrook P, Stringer R, Townend W, Wilburn S, Zghondi R (2014) World Health Organization. Safe management of wastes from healthcare activities. WHO Press, World Health Organization, Appia, Geneva, Switzerland. ISBN 978-92-4-154856-4
9. Ramesh Babu B, Parande AK, Rajalakshmi R, Suriyakala P, Volga M (2009) Management of biomedical waste in india and other countries: a review. J Int Environ Appl Sci 4(1):65–78
10. Giusti L (2009) A review of waste management practices and their impact on human health. Waste Manage 29:2227–2239
11. Shanghai (2010) Manual—a guide for sustainable urban development in the 21st century (chapter 5)
12. Baldé CP, Wang F, Kuehr R, Huisman J, (2015) The global e-waste monitor—2014, United Nations University, IAS—SCYCLE, Bonn, Germany. ISBN: 978-92-808-4555-6
13. Amoo OM, Fagbenle RL (2013) Renewable municipal solid waste pathways for energy generation and sustainable development in the Nigerian context. Int J Energy Environ Eng 4:42–59

14. Chen YC (2016) Potential for energy recovery and greenhouse gas mitigation from municipal solid waste using a waste-to-material approach. Waste Manage 58:408–414
15. TERI Energy Data Directory and Yearbook (TEDDY), 2010
16. Sharholy M, Ahmad K, Mahmood G, Trivedi RC, (2006) Development of prediction models for municipal solid waste generation for Delhi city. In: Proceedings of national conference of advances in mechanical engineering, Jamia Millia Islamia, New Delhi, India, 20–21 Jan 2006
17. Asnani PU (2006) Solid waste management. India Infrastructure Report, India
18. Wanga X, Jia M, Zhang H, Pan S, Kao CM, Chen S (2017) Quantifying N_2O emissions and production pathways from fresh waste during the initial stage of disposal to a landfill. Waste Manage 63:3–10
19. Tang L, Huang H, Hao H, Zhao K (2013) Development of plasma pyrolysis/gasification systems for energy efficient and environmentally sound waste disposal. J Electrostat 71:839–847
20. Isam J, Raza SS, Valmundsson AS (2013) Plasma gasification process: modeling, simulation and comparison with conventional air gasification. Energy Convers Manag 65:801–809
21. Byun Y, Namkung W, Cho M, Chung JW, Kim YS, Lee JH, Lee CR (2010) Hwang SM demonstration of thermal plasma gasification/vitrification for municipal solid waste treatment. Environ Sci Technol 44(17):6680–6684
22. Gomez E, Rani DA, Cheeseman C, Deegan D, Wise M, Boccaccini A (2009) Thermal plasma technology for the treatment of wastes: a critical review. J Hazard Mater 161:614–626
23. Moustakas K (2005) Demonstration plasma gasification/vitrification system for effective hazardous waste treatment. J Hazard Mater 123(1–3):120–126
24. Corsten M, Worrell E, Rouw M, Duin AV (2013) The potential contribution of sustainable waste management to energy use and greenhouse gas emission reduction in the Netherlands. Res Conserv Recyc 77:13–21
25. Ryu C (2010) Potential of municipal solid waste for renewable energy production and reduction of greenhouse gas emissions in South Korea. J Air Waste Manage Assoc 60:176–183
26. European Commission (2011) A resource efficient Europe–Flagship Initiative under the Europe 2010 Strategy. European Commission, Brussels, Belgium
27. Ruj B, Ghosh S (2014) Technological aspects for thermal plasma treatment of municipal solid waste—a review. Fuel Process Technol 126:298–308
28. Huang H, Tang L (2007) Treatment of organic waste using thermal plasma pyrolysis technology. Energy Convers Manage 48:1331–1337
29. Central Pollution Control Board (CPCB) (2004) Management of municipal solid waste. Ministry of Environment and Forests, New Delhi, India
30. CPCB (2000) Status of solid waste generation, collection, treatment and disposal in metrocities, Series: CUPS/46/1999–2000
31. CPCB (2000) Status of municipal solid waste generation, collection, treatment and disposal in class I cities, Series: ADSORBS/31/1999– 2000
32. Sharholy M, Ahmad K, Mahmood G, Trivedi RC (2008) Municipal solid waste management in Indian cities—a review. Waste Manage 28:459–467
33. Bhide AD, Shekdar AV (1998) Solid waste management in Indian urban centers. Int Solid Waste Assoc Times (ISWA) 1:26–28
34. Gupta N, Yadav KK, Kumar V (2015) A review on current status of municipal solid waste management in India. J Environ Sci 37:206–217
35. Jha MK, Sondhi OAK, Pansare M (2003) Solid waste management—a case study. Indian J Environ Prot 23(10):1153–1160
36. Malviya R, Chaudhary R, Buddhi D (2000) Study on solid waste assessment and management—Indore city. Indian J Environ Prot 22(8):841–846
37. Kansal A, Prasad RK, Gupta S (1998) Delhi municipal solid waste and environment—an appraisal. Indian J Environ Prot 18(2):123–128
38. Gupta S, Mohan K, Prasad R, Gupta S, Kansal A (1998) Solid waste management in India: options and opportunities. Resour Conserv Recycl 24:137–154
39. IPCC (2013) Climate change 2013: the physical science basis. In: Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge

40. McKay G (1996) Dioxin characterisation, formation and minimisation during municipal solid waste (MSW) incineration: review. Chem Eng J 86:343–368
41. Li Jun, Liu Kou, Yan Shengjun, Li Yaojian, Han Dan (2016) Application of thermal plasma technology for the treatment of solid wastes in China: an overview. Waste Manag 58:260–269
42. Woon KS, Lo IMC (2013) Greenhouse gas accounting of the proposed landfill extension and advanced incineration facility for municipal solid waste management in Hong Kong. Sci Total Environ 458–460:499–507
43. Li X, Lu S, Xu X, Yan J, Chi Y (2001) Analysis on calorific value of Chinese cities' municipal solid waste. Zhongguo Huanjing Kexue 21:156–160
44. Zhang Y, Chen Y, Meng A, Li Q, Cheng H (2008) Experimental and thermodynamic investigation on transfer of cadmium influenced by sulphur and chlorine during municipal solid waste (MSW) incineration. J Hazard Mater 152:309–319
45. Jin J, Wang Z, Ran S (2006) Solid waste management in Macao: practices and challenges. Waste Manage 26:1045–1051
46. Syamala Devi K, Swamy AVVS, Nilofer S (2016) Municipal solid waste management in india—an overview. Asia Pacific J Res I
47. EIPPC Bureau (2006) Reference document on the best available techniques for waste incineration (BREF), integrated pollution prevention and control. European IPPC, Seville, Spain, 602p. http://eippcb.jrc.es
48. Bogner J, Ahmed MA, Diaz C, Faaij A, Gao Q, Hashimoto S, Mareckova K, Pipatti R, Zhang T (2007) Waste Management. In: Metz B, Davidson OR, Bosch PR, Dave R, Meyer LA (eds) Climate change 2007: mitigation. contribution of working group iii to the fourth assessment report of the intergovernmental panel on climate change. Cambridge University Press, Cambridge
49. Ghosh SK (2016) International cnference on solid waste management, 5IconSWM 2015 Swachhaa Bharat Mission (SBM)—a paradigm shift in waste management and cleanliness in India. Procedia Environ Sci 35:15–27

Comparative Chemical Evaluation of Vermicompost Produced by Using Different Organic Wastes

Parveen Gill, Dharambir Singh, R. K. Gupta, Urmila and Hem Lata

1 Introduction

Vermicompost enhances soil aeration and consistency by reducing earth compaction. It improves the water-holding capability of soil for the reason of its high natural material content. It enhances nutrient assimilation, micronutrients, and macronutrients status of soil.

Eisenia fetida is especially adapted to live in a decaying environment such as rotting vegetables, dung, etc., which is best for vermicomposting. The vermicompost is a better organic fertilizer is produced by worms such as the *E. fetida*, which contain humus with a good amount of nutrients so that it can be used for the plants without any detrimental effect on their vegetative growth. The total organic carbon content of cow dung with parthenium decreased and N, P, K increased as observed by Joshi and Chauhan [9].

2 Materials and Methods

The organic wastes, i.e., kitchen waste, cow dung, congress grass and a mixture of different weeds were used as substrates for vermicomposting in a ratio of 5:1 (cow dung: substrate). 16 tubs for each treatment filled with the mixtures prepared and kept in screen house under a temporary shed of straws. Gunny bags were used for coverage of all these tubs and sprinkled with water as and when required to maintain appropriate moisture level. One hundred healthy adult earthworms were inoculated into each tub subsequent to 15 days of microbial decomposition. The samples for chemical

---

P. Gill (✉) · D. Singh · R. K. Gupta · Urmila · H. Lata
Chaudhary Charan Singh Haryana Agricultural University, Hisar, Haryana, India
e-mail: parveengill135@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_20

examination (carbon, nitrogen, C/N, phosphorus, and potassium) were collected on 0, 30, 60, and 90 days.

2.1 Determination of Carbon Content

(i) **Determination of volatile solids**
One gram of fine-dried sample powder was taken in a pre-weighed china crucible and inserted into muffle furnace at 550 °C for 1 h. The losses in weight of total solids on combustion were taken as volatile solids.

(ii) **Carbon content of samples was calculated as**

$$\%\mathrm{C} = \frac{\%\ \text{Volatile Solid}}{1.724}$$

2.2 Estimation of Total Nitrogen, Phosphorous, and Potassium

Was estimated by standard Micro Kjeldahl method [3], John method [8], and flame photometer method [7], respectively.

3 Result and Discussion

The study of 90 days revealed that during the process of vermicomposting of organic waste several physical, chemical, and biological changes were observed.

The total amount of carbon decreases gradually where the maximum decrease was noted in the samples of cow dung + kitchen waste where total initial organic carbon was 37.47 g and finally the carbon was 30.9 g so this showed 6.5% decrease. The decrease in carbon content was 3.7, 1.2 and 0.72% in cow dung, congress grass and a mixture of weeds, respectively (Fig. 1).

The total amount of nitrogen increases gradually in each treatment and the maximum increase was observed in the samples of cow dung + kitchen waste, where the total initial nitrogen was 10.77 g which is 1.17% increase, so finally, the nitrogen was 22.53 g. The increment of 0.73, 0.24, and 0.12% in nitrogen was observed in cow dung, congress grass and a mixture of weeds, respectively (Fig. 2).

In Fig. 3, a decreasing trend of C:N was observed in each treatment except the best reduction in C:N from 3.47 to 1.37% (2.10%) was in the case of cow dung + kitchen waste.

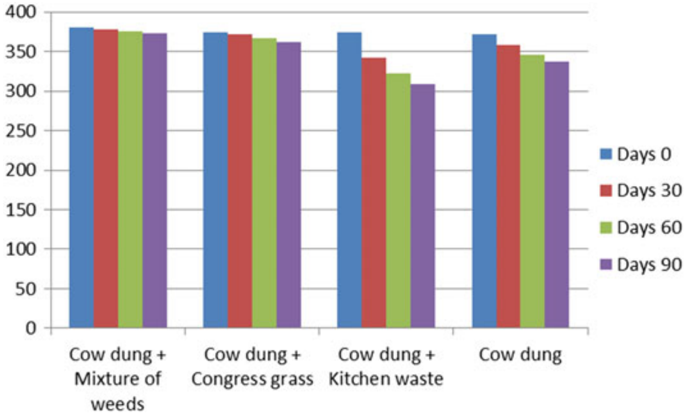


Fig. 1 Changes in organic carbon of vermicompost of different organic wastes

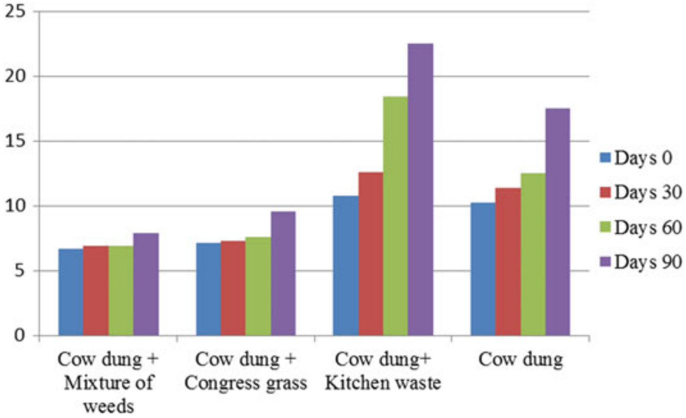


Fig. 2 Changes in organic nitrogen of vermicompost of different organic wastes

Figure 4 showed the amount of phosphorus increases gradually, where the maximum increase was found in the samples of cow dung + kitchen waste where total initial phosphorus was 0.643 g and finally, the phosphorus was 0.915 g showed 0.027% increase. The increase of 0.020, 0.012, and 0.010% phosphorus was observed in cow dung, congress grass and a mixture of weeds, respectively.

In Fig. 5, it was observed that the amount of potassium increases gradually, the maximum increase was noted in the samples of cow dung + kitchen waste. Total initial potassium was 3.05 g and finally, it becomes 5.17 g with 0.212% increase. Total potassium increase was 0.119, 0.067, and 0.038% in cow dung, congress grass, and a mixture of weeds, respectively.

In 2003, Mondini et al. [12] reported that the total organic carbon was decayed by microbial biomass from the vermicompost. A fraction of the organic carbon of

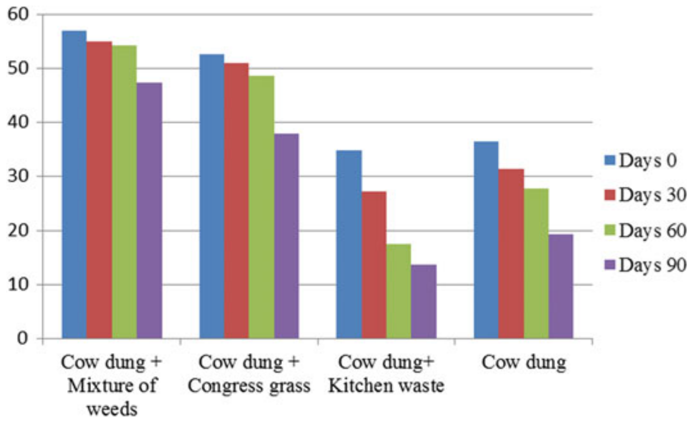


Fig. 3 Variation in C:N ratio of vermicompost of different organic wastes

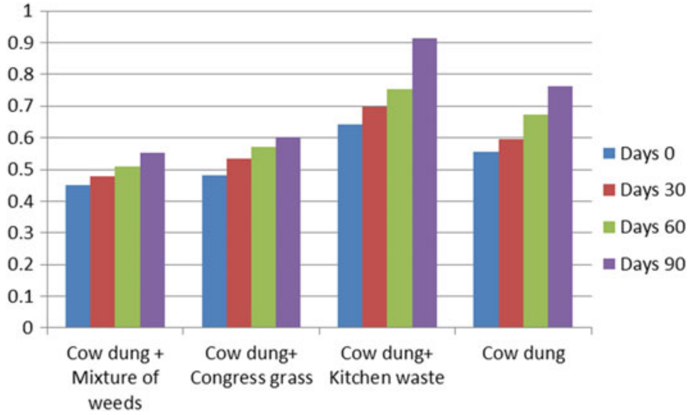


Fig. 4 Changes in organic phosphorus of vermicompost of different organic wastes

decayed residues released as CO_2 [4]. The amount of carbon decrease in compost during the initial 10 days was due to bacterial decomposition [5].

In 1995, Kale [10] reported that the nutrient profile of vermicompost varies with respect to organic waste used. The total organic carbon, C:N ratio content of cow dung with kitchen waste was decreased and increase in N, P, K was observed by Tripathi and Bhardwaj [16] and Bhardwaj [2]. Nitrogen-fixing bacteria during composting increased the nitrogen content of compost and ability of bacteria depended on the organic wastes used for composting [1].

The NPK content in the vermicompost changes from 0.38−1.76, 0.2–1.76 and 0.69–4.98%, respectively, with respect to organic waste used and vermicomposting improve the structure, fertility, and moisture-holding capacity of soil [14]. Nathia

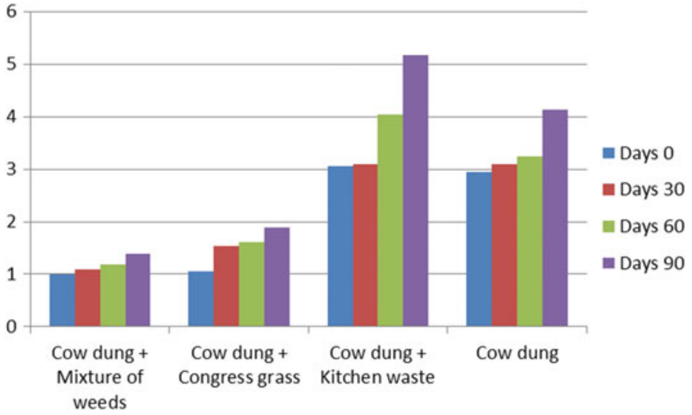


Fig. 5 Changes in organic potassium of vermicompost of different organic wastes

et al. [13] observe that NPK was greater than before and carbon level, C/N decreased after composting of organic wastes.

Enzymatic activity of alkaline phosphatase and dehydrogenase increase the total phosphorus in the vermicompost. Enzyme dehydrogenase responsible for microbial action and inoculated microbes produces alkaline phosphatase, which is helpful in phosphorus solubilizing in the compost [11].

Nutrient components of compost depend upon the type and composition of carbonic waste used. The enzymes and microbes of the digested track of earthworms increase the concentration of potassium [6, 15, 17]. There are many evidence suggesting that vermicompost due to microbial activity has a rich nutrient level. Zhang et al. [18] reported that phosphorous in vermicompost is an increase because of mobilization and mineralization of phosphorus due to phosphatase activity of earthworms gut microorganisms.

4 Conclusion

- The maximum increase NPK were observed in vermicompost formed from kitchen waste followed by cow dung, congress grass, and a mixture of different weeds so it showed that the vermicompost of kitchen waste is the best as compared with other.
- The results showed the decrease in C:N ratio in vermicompost of kitchen waste followed by cow dung, congress grass, and a mixture of different weeds.

References

1. Beauchamp CJ, Levesque G, Prevost D, Chalifour FP (2006) Isolation of free-living dinitrogen-fixing bacteria and their activity in compost containing de-inking paper sludge. Biores Technol 97:1002–1011
2. Bhardwaj A (2010) Management of kitchen waste through vermicomposting. Asian Exp Biol Sci 1(1):175–177
3. Brenner JM, Mulvancey RG (1982) Nitrogen total. Methods of soil analysis. American Society of Agronomy, Madison, pp 575–624
4. Cabrera ML, Kissel DE, Vigil MF (2005) Nitrogen mineralization from organic residues: research opportunities. J Environ Qual 34:75–79
5. Chaudhuri PS, Pal TK, Dey SK (2000) Chemical changes during vermicomposting (*Perionyx excavatus*) of kitchen wastes. Trop Ecol 41(1):107–110
6. Ismail SA (1996) Vermicompost and vermiwash. The organic farming source book, C. Alvares. The other India Press, Mopusa, Goa, pp 170–177
7. Jackson ML (1973) Soil chemical analysis. Prentice Hall Pvt. Ltd., New Delhi
8. John MK (1970) Colorimetric determination of phosphorus in soil and plant material with ascorbic acid. Soil Sci 109:214–220
9. Joshi PC, Chauhan A (2010) Composting of some dangerous and toxic weeds using *E. fetida.* J Am Sci 6(3)
10. Kale RD (1995) Vermicomposting has a bright scope. Indian Silk 34:6–9
11. Mansell GP, Syers JK, Gregg PEH (1981) Plant availability of phosphorous in dead herbage ingested by surface-casting earthworms. Soil Biol Biochem 13:163–167
12. Mondini C, Dell'Abate M, T Leita L, Beneditti A (2003) An integrated chemical, thermal and microbiological approach to compost stability evaluation. J. Environ. Qual 32: 2379–2386
13. Nathia S, Scinduja M, Suganya K, Nandhini JV, Jaya SP (2015) Experimental study on biodegradation of garden waste, market waste using *Eisenia fetida* & *Eudrilus Eugenia* and checking the quality of manure on tomato. International Journal of Engineering science & research technology 4(3):2277–9655
14. Perekh SA, Mehta MJ (2015) Vermicomposting as sustainable option for organic waste management. International Journal of Innovative and Emerging Research in Engineering 2:2394–5394
15. Stockli (1928) Studies on the influences of earthworm on the soil condition, Journal of soil 22: 45–48
16. Tripathi G, Bhardwaj P (2004) Decomposition of kitchen waste amended with cow manure using on epegeic species (*E.fetida*) and on anecic species (*Lampito mauritii*). Biores Technol 92:215–218
17. Whiston RA, Seal KL (1988) The occurrence of cellular in the earthworms, *Eisenia fetida*. Biol Wastes 25:239–242
18. Zhang BG, Li GT, Shen TS, Wang JK, Sun Z (2000) Changes in microbial biomass C, N, and P and enzyme activities in soil incubated with the earthworms *Metaphire guillelmi* or *Eisenia foetida*. Soil Biol Bioche 32:2055–2062

Status of Composting for OFMSW Treatment in Karnataka and West Bengal: Case Studies and Sustainability

Biswajit Debnath, Anaya Ghosh, Basavaraju Prathima, Khushbu K. Birawat and Sadhan Kumar Ghosh

1 Introduction

India, the 11th largest economy and 2nd most populated nation have witnessed rapid urbanization and industrialization in the past few decades, which has directly impacted the availability of natural resources in the country. Thus, it becomes a necessity to reuse and recover useful materials from the already utilized resources or as we commonly say 'waste'.

Currently, the world inhabitants are nearly 7.1 billion and as well as the generation of MSW has been estimated by the World Bank 2012 [20], almost 1300 million tonnes per year [19]. India produced 62 million tonnes (mt) of waste annually, out of which nearly 9% is plastic waste, 0.3% is biomedical waste, 12.74% is hazardous waste and 2.4% is E-waste. And the most strange fact is that only 75–80% of total generated waste per year is collected (43 million tonnes per year), 22–28% is treated (11.9 million tonnes per year) and rest of the waste is discarded in landfill site (31 million tonnes per year) [9, 7]. India is an agricultural base country in southern Asia having 29 states and 7 union territories which includes several districts municipalities and gram panchayats. The waste generation, waste composition and characteristics will

---

B. Debnath
Department of Chemical Engineering, Jadavpur University, Kolkata, India

A. Ghosh
Department of Chemical Engineering, National Institute of Technology, Durgapur, India

B. Prathima
Department of Civil Engineering, BMSCE, Bangalore, India

K. K. Birawat
Department of Civil Engineering, Global Academy of Technology, Bengaluru, India

S. K. Ghosh (✉)
Department of Mechanical Engineering, Jadavpur University, Kolkata, India
e-mail: sadhankghosh9@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_21

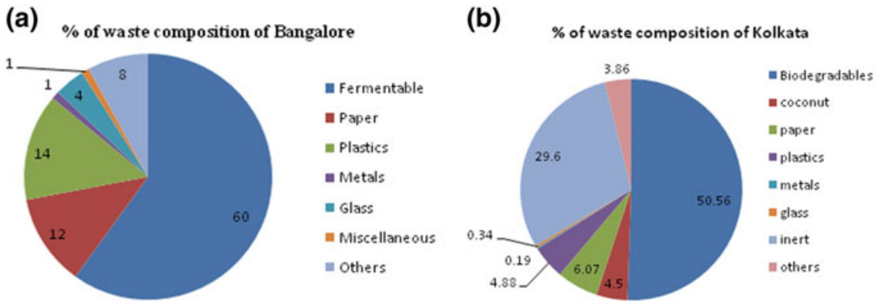


Fig. 1 **a** waste composition in Bangalore [14] and **b** Waste composition in Kolkata [3]

vary in different regions with their cultural variations, climatic changes, food habits and economy also [7]. West Bengal is the fourth populated state in India with an area 88,752 km^2, a population near about of 91,347,736 generates 12557 megatonnes solid waste per. Karnataka is the eighth populated state in India with an area 191,791 km^2, and a population near about of 61,130,704 generates 6500 megatonnes solid waste per day [2]. Kolkata, the capital of West Bengal, is the third metropolitan city which generates 3670 tonnes of solid waste per day, whereas the capital Karnataka, Bangalore is the fourth metropolitan city which generates 3700 tonnes of waste per day. The waste compositions of both metro cities are described in a pie chat are shown in Fig. 1a, b. Figure 1 represents the waste composition of Bangalore [14], whereas Fig. 1 represents the solid waste composition of Kolkata [3]. Figure 1 represents a comparative study of waste composition of both Kolkata and Bangalore. The chemical characteristics and composition of both cities are described elaborately in Table 1. In Kolkata, solid waste management is taken care by Kolkata Municipal Corporation (KMC) and also by other local bodies, non-government organizations, whereas in Bangalore, it is managed by Bruhat Bengaluru Mahanagara Palike (BBMP).

It is really important to have OFMSW treatment facilities in both Karnataka and West Bengal. The existing facilities speak for themselves as success stories. The proper valorization of the OFMSW will ensure circular economy in both the states. According to waste management rule 2016, in India, the two major treatment processes for OFMSW treatment are biogas from AD and manure from composting. In composting process, the major challenge is to get source segregated waste. Biogas is much more established and successful in India, whereas composting is comparatively less explored sector and has few success stories. The number speaks for itself as there are nearly 4 million biogas plants [16] and only 553 composting plants operating in India [5].

According to Ministry of Urban Development (MoUD), Government of India and the Central Pollution Control Board (CPCB) of India, Mysore, a major city in Karnataka has become one of the cleanest cities in India and ranked first in the Swachh Survekshan [15]. West Bengal, on the other hand, is still lagging and needs strict science policy framework, implementation and monitoring for sustainable develop-

Table 1 Details of chemical composition of MSW for Kolkata and Bangalore

City	Moisture (wt%)	pH	Loss on ignition (wt%)	Carbon (%)	Hydrogen as H_2 (%)	Oxygen O_2 (%)	Nitrogen as N (%)	Sulphur (%)	Phosphorous as P_2O_5 (%)	Potassium as K_2O (%)	Chlorid (as Cl) (%)	C/N ratio	Calorific value MJ/kg	Source
Kolkata	46	0.3–8.07	38.53	22.35	–	–	0.76	–	0.77	0.52	–	31.81	5.028	Chattopadhyay et al. [3]
Bangalore	27.35	–	–	50.44	7.72	40.39	1.08	0.39	0.26	–	0.19	35.12	13.9	Ramachandra et al. [14]

ment. Though some success stories are there in West Bengal, the sustainability is questionable. Comparison of developing systems with developed systems often offers new pathways of improvement. Hence, comparing the status of OFMSW treatment by means of composting is of relevance. Under the current investigation, an attempt has been made to compare two existing systems of Karnataka and West Bengal in the context of composting as a method of OFMSW utilization. The learning from the matured system has been taken and suggested for the developing system. A brief discussion from the perspective of sustainability has also been presented.

2 Methodology

This paper has adopted the case study approach to compare the status of composting for OFMSW treatment in two states. First, a detailed literature review was carried out in order to understand the current status of composting for OFMSW management in West Bengal and Karnataka. Then, the locations of compost plants in both the states were identified. Thereafter, the authors visited the composting facilities. Based on the field study and the literature review, the sustainability of composting for both states were analyzed. The issues and challenges were identified through this and possible suggestive measures were depicted.

3 Current Status of Composting in Karnataka and West Bengal

3.1 Karnataka

Karnataka Compost Development Corporation, (KCDC) which was established in 1965, as 1 of the 13 Municipal Solid Waste (MSW) Composting Plants in India, uses World Health Organization's technology for composting MSW. This step was taken as per the directions of Government of India. Karnataka Agro Industries Corporation (51% share), Karnataka State Co-operative Marketing Federation Limited (24.5% share) and BBMP (24.5% share) run the plant together. This is the only plant running successfully till date out of the 13 initially installed. Others were closed down within a year as the technology proven to be unsustainable with respect to the un-segregated Indian MSW. KCDC plant is set across 15.1 acres, and processes 200 MT of segregated MSW per day by composting it and the capacity will be increased to 500 MTPD after its expansion covering an area of 30 acre.

Approximately, 13–15% of compost is generated at the end of the process. The rejects are dumped at an adjacent area of the unit. KCDC is producing both organic compost (175 MTPD) and Vermicompost (15 MTPD). The organic manure is marketed under the brand name ‘Agri Gold’ (15–20 MTPD) by mixing with organic additives. The majority of these products are sold to Deptartment of Agriculture and tied-up fertilizer companies.

3.2 West Bengal

In West Bengal, the state government (KMC) is trying to develop more suitable technology and new treatment processes, proper source segregation and scientifically dumping. Previously, they are dumping in an unorganized manner in Dhapa. Now, they have introduced a composting plant that runs on source segregated waste at Uttarpara municipality, transfer station at Uttarpara-Kotrung municipality, engineered sanitary landfill at Baidyabati under the JICA project. Waste Compactor stations have also been installed at different places in Kolkata. In some municipality, they already started source separation, segregated waste collections like 115 number ward under KMC, Kolkata. Kolkata Solid Waste Management Improvement Project (KSWMIP) Kolkata Solid Waste Management Improvement Project (KSWMIP) is a resourceful project supported by Japan International Cooperation Agency (JICA). Kolkata Metropolitan Development Authority (KMDA) has taken up six ULBs of KMA, namely Uttarpara-Kotrung, Konnagar, Rishra, Serampore, Baidyabati and Champdani. The aim of this project is the proper management and disposal of MSW in the six ULBs by introducing proper source separation, proper segregated waste collection system, reuse of organic waste for composting, discontinuation of open dumping and scientific sanitary landfill with leachate treatment. The initiatives were taken by Uttarpara-Kotrung municipality and it helped the Kolkata Solid Waste Management Improvement Project (KSWMIP) to win a global award, in urban solid waste management category in the C40 Mayors' Summit held in Mexico City on 1 December 2016.

4 Case Studies

4.1 Case Studies in Mysuru

Mysore city of Karnataka, located 135 km from Bengaluru is famous for its 10-day Dasara festival. Mysuru had topped the Swachh Bharat Rankings of 476 cities in the country in 2015 and 2016. During 2017, in Swachh Bharat Rankings, Mysore grabbed fifth position among 500 cities [4]. The population of the city has grown from 0.68 lakhs in 1901 to 9.14 lakhs in 2011 [2]. The city is divided into 65 municipal wards [8, 13] with the area of 128.42 km^2.

The solid waste management in Mysuru went from an ad hoc manner at several locations into a well-planned management strategy in 2001. The municipal solid waste collection in the city is primarily based on door-to-door collection and street

Fig. 2 **a**, **b**, **c** Windrows composting process and **d** Finished product in plant at Vidyaranyapuram

sweeping followed by secondary collection and transportation. Nearly, 50% of the collected waste is processed. To achieve this, a composting plant was set up with a capacity of 200 TPD covering 12.5 acres of land at Vidyaranyapuram. Additionally, Mysore City Corporation runs 9 zero waste management plant of capacity 5–10 tonnes. The city also proposed two more composting plants with the capacity of 150 and 200 TPD.

Composting Unit 1: Vidyaranyapuram

200 MT of fresh mixed municipal waste is received at Vidyaranyapuram composting facility every day. It is presegregated through 85 mm rotary screen which segregates the mixed waste into two streams, one is organic content, which is 60% of the total waste and is transferred to windrows and the other remaining waste is rejected, which accounts to be 40% of the total waste. The organic waste sent to the windrows is less than 85 mm. The size of each windrow is 4–6 m wide and 2–2.5 m high (Fig. 2).

Cow dung slurry and microbial culture is sprayed on windrows while making the heap and turning the windrows to provide sufficient oxygen for proper composting. Leachate is controlled through absorption technique. The windrow is turned once in a week for four consecutive weeks. A reaction temperature of 40–75 °C is maintained throughout the composting process. Maintaining such a high temperature ensures that all the pathogens are killed. After composting, there is almost 45% reduction from the starting material. Then, the material is left for curing for additional 2 weeks. This

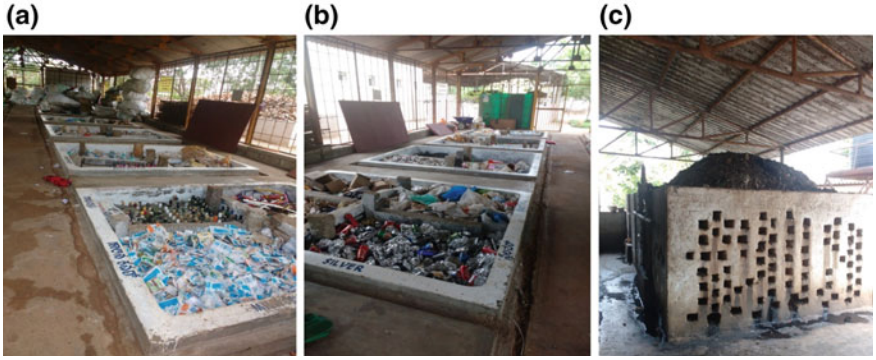


Fig. 3 **a**, **b** Storage pits for segregated waste and **c** Composting pits for OFMSW at KumbaraKoppal zero waste management plant

compost is then screened through 20 mm mesh, out of which almost 30% material is rejected. Next, the remaining material is screened through 4 mm sieves, out of which 35% of the material is rejected. The organic manure, which is almost 36 tonnes received after this step is enriched with additives. Next, it is made market ready by weighing, packing and dispatching. The compost will be sold in two variants organic soil conditioner and phosphate rich organic manure. The typical characteristics of both variants are listed in the Appendix 1.

Composting Unit 2: Kumbarakoppal

Kumbarakoppal is the northern area of Mysore; its waste management system is known as ‘Zero Waste System’, started in the year 2005. It has a capacity of 05 TPD and covers 05 wards of Mysore. It covers over 1.5 acres of land to accommodate segregation area, composting beds, shade for storage of segregated waste and parking area. 75% of the waste is segregated at source. The segregated waste is then transported to the treatment unit, where it is further segregated into 15+ categories manually by approximately 10 people to resell it and the biodegradable waste is composted on site using bins of dimensions 10’ × 10’ × 6’. After calculating total income and expenses, the net income of the plant is around INR 11,000 per month [10] (Fig. 3).

4.2 West Bengal

Composting Unit 1: Dhapa

Dhapa is situated on the eastern periphery of Kolkata, India. This area is well known for solid waste land filling where MSW of Kolkata is dumped regularly. This disposal site is owned by the Kolkata Municipal Corporation (KMC) and it has been operating since 1981 as an open dumpsite for the ‘City of Joy’. The property has an area of

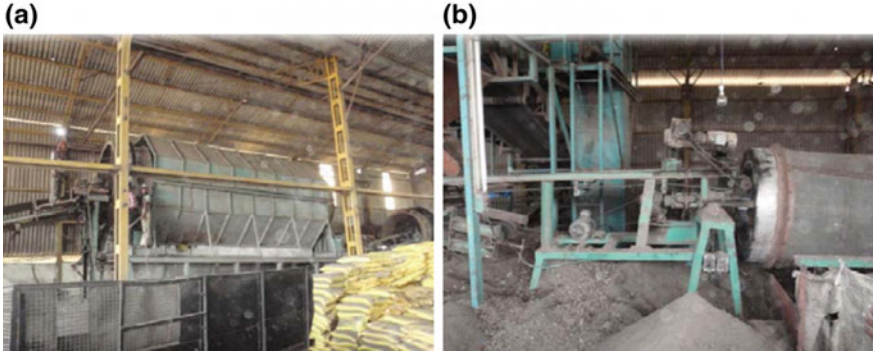


Fig. 4 **a**, **b** Equipments of the composting plant at Dhapa

land measuring 34.2 hectares (ha), out of which approximately 63% (21.5 ha) is there for waste disposal. The Dhapa landfill site has been divided into two areas—(a) the eastern area for MSW disposal that receives MSW from the waste haulers of KMC and (b) the western area for MSW disposal that receives MSW from private haulers. There is a composting facility which is situated in between these two waste disposal areas. This composting plant accepts predetermined loads of Organic Fraction of MSW (OFMSW) such as waste from food markets where the organic fraction is higher. This facility is a private firm which has a land area measuring 12.2 ha. The waste dumped at this site of Dhapa is basically mixed waste. It contains household waste, biomedical waste, market wastes, e-waste, C&D waste, glass, plastics, etc. (Fig. 4).

The waste treatment plant which was established 17 years back is a very good company and they are committed towards their goal. The plant handles almost 120 tons of waste each day whereas the installed capacity is 400 TPD. They ensure proper methodology for degradation of waste to enhance the amount of nitrogen in the manure. A culture of Bacillus sepacia and Azotobactor is used to degrade the wastes. Then the manure is separated from the unusable wastes and the pure manure is packed and sent to market. The overall process takes 45 days of time. For making the culture, they have a fermenter installed at their laboratory of 100 litres and it takes 3–4 days to prepare a batch of culture. The manure obtained is also tested in laboratory before selling to the market. This product is mainly marketed by three companies—Cormondal Fertilizer, Xl fertilizer and Nagarjun Fertilizer. Their product is a very high-quality product as they are using the best possible culture of bacteria and before releasing they also perform tests in the laboratory. Dhapa being a waste dumping ground for the whole of Kolkata region handles around 4000–4500 ton of waste daily of this waste 500 ton of waste is taken by the Eastern Organic Fertilizer Pvt. Ltd. (EOFPL) of which roughly 25% is converted to organic fertilizer which is around 100 ton on an average per day. This venture is deriving enough revenue to survive and the demand of the organic fertilizer is increasing everyday.

Fig. 5 **a**, **b** and **c** Vermicomposting process and **d** Finished product at Nimpith plant

Most importantly, 66% of their product is distributed in West Bengal. Each bag of manure consists of 50 kg of fertilizer and is sold @Rs. 400 per bag.

Composting Unit 2: Vermicomposting Plant at Nimpith

Nimpith is a village located in South 24 Parganas, West Bengal, India. Vivekananda Institute of Biotechnology (VIB), situated at Nimpith has engaged in the practice of vermicomposting. VIB is a branch of Sri Ramkrishna Ashram Krishi Vigyan Kendra which employs vermicomposting and supplies the resulting compost in the villages nearly and different areas of Sunderban (the mangrove region of West Bengal). VIB uses water hyacinth, floral waste and paddy straw as feedstock for vermicomposting. Three types of earthworm species used for this purpose—*Eisenia foetida, Eudrilus eugeniae, Perionyx excavatus*. The fertilizer produced is supplied to the different parts of Sunderban (mangrove area) and other regions in West Bengal (Fig. 5).

VIB has biogas plant operating and the digestate from that plant is added as inoculum for initial decomposition waste mixture containing 30% water hyacinth and rest market and floral waste mixture before subjected to vermicomposting. This is a pretreatment process. Sometimes, they mix cow dung, water hyacinth and floral and vegetable waste in 2:1:1 ratio and keep them for a week. Thereafter, the earthworms are added to the mixture and they are supplied with adequate nutrition. Three stages of beds are there and they are churned and transferred to subsequent beds each 15 days. 60 days time is taken for completion of the process. Finally, manual sieving is done to get fine particles of vermicompost. The produced compost has an average NPK value of 1.73, 1.6 and 4.98, respectively.

5 Discussions from the Perspective of Sustainability

Sustainability analysis is important for understanding current situation and finalising strategies for future. Life Cycle Assessment (LCA) exercise is undoubtedly the most appropriate method for evaluation of sustainability. But in this case, due to absence of reliable data, LCA was not carried out. Hence, a generalised discussion on sustainability was provided as previously reported in literature [7, 6]. Indian OFMSW is a valuable resource and composting is a very good option to convert it into biodegradable product. The two states that have been considered here are Karnataka and West Bengal. In Karnataka, there are a number of composting plants operating successfully. The sites visited are in Mysuru and both of them are using windrows method for composting. Whereas in West Bengal, currently seven composting plants are there officially that convert waste from the OFMSW. However, there are many small and medium scale composting plants operating as confirmed by one of the interviewee. The cases presented shows; one of the plants is using windrows method to produce organic compost whereas the one is using the vermicompost method. At present, there are no vermicomposting plants there in Karnataka. Vermi are very delicate and slight change is the temperature and climatic conditions can kill them. Proper maintenance is there at Nimpith West Bengal.

From the environmental point of view, both Karnataka and West Bengal has adopted the practices of composting. The utilization of OFMSW is surely an approach towards 3R. In Karnataka, only windrows method is adopted where as in West Bengal both vermicomposting and windrows is in practice. The windrows composting units in both states require electricity to run the heavy equipments such as the Trommel, sieving machines, etc. The huge amount of electricity consumption leads to carbon dioxide emission, contributing to global warming potential. However, the machineries in West Bengal are comparatively old and consume more energy. However, vermicomposting is carried out in pits; churning, mixing and sieving are carried out manually. As a result, it does not contribute to global warming potentials from electricity consumption only. But, vermicomposting process generates leachate which may contribute to impact categories such as marine ecotoxicity, freshwater ecotoxicity, eutrophication, etc. Both windrows and vermicomposting contributes towards global warming potential with significant emission of methane and nitrous oxide [1, 11]. Abiotic depletion, ozone layer depletion potential, acidification, eutrophication, photochemical oxidation are the other impact categories due to composting [12].

The socio-economic aspects are highly constricted towards the attitude of the residents and vary with region. In West Bengal, due to several issues (operational and legal mainly), either new composting plants are not running or failing at some point. Technology selection is a very critical task and that needs to the first preference in case of West Bengal. While in Karnataka, this is not an issue, however, a vermicomposting plant stopped its operation due to certain issues. This shows that Karnataka has already faced these kinds of challenges before West Bengal did. This can be easily related to the economical sustainability and learning for West Bengal. The residents of Karnataka are much more conscious and the level of aware with respect to solid waste is more than in West Bengal which ensures social sustainability. Working Hours, Child Labour, Health and Safety, Social Security, Community engagement, Equal opportunities, Safety and health of local community, Local Employment, corruption, crime, literacy, awareness, etc. are a few of the global social sustainability indicators [17, 18]. Considering these West Bengal is still lagging behind in most of them. Learning from Karnataka should be taken in order to ensure the sustainability in West Bengal.

6 Conclusion

In this study, status of OFMSW composting of two states, one matured (Karnataka) and one developing state (West Bengal), has been compared. The xase studies have been carried out in both the states to find the reality. It was found that in Karnataka, only windrows composting is being carried out whereas in West Bengal both vermicomposting and windrows composting is being practiced. Further qualitative assessment from the perspective of sustainability revealed that composting processes of both states are environmentally sustainable but from socio-economic aspects Karnataka is doing much better. It has been suggested that learning from Karnataka should be taken and must be implemented by West Bengal, direct or modified, to achieve sustainability. Comparative studies at state level are necessary for sustainable development. This study is expected to be useful for state authorities, ULBs and DMAs in strategic decision-making and framing further action plans.

Acknowledgements The author's would like to acknowledge International Society of Waste Management, Air and Water (ISWMAW) for partially funding the project. Additionally, the help and cooperation from Centre for Quality Management Systems (CQMS) Jadavpur University, Kolkata; Consortium of Researchers for Environmental Protection, Sustainability and Climate Change (CREPSCC), SJCE College, Mysore are gratefully acknowledged.

References

1. Andersen JK, Boldrin A, Christensen TH, Scheutz C (2010) Greenhouse gas emissions from home composting of organic household waste. Waste Manag 30(12):2475–2482

2. Census 2011 (2011) Ministry of Home Affairs, Government of India
3. Chattopadhyay S, Dutta A, Ray S (2009) Municipal solid waste management in Kolkata, India–A review. Waste Manag 29(4):1449–1458
4. CPCB (2016) A Status Report of Municipal Solid Waste (MSW) management in Mysuru City, Karnataka. Available from: http://cpcb.nic.in/zonaloffice/banglore/MSW_report_Mysuru.pdf. Accessed on 13 Nov 2017
5. CPCB Bulletin (2016) Vol.-I, July 2016, Government of India. http://www.cpcb.nic.in/upload/Latest/Latest_123_SUMMARY_BOOK_FS.pdf. Accessed on 8 June 2017
6. Debnath B, Chowdhury R, Ghosh SK (2018) Sustainability of metal recovery from E-waste. Front Environ Sci Eng 12(6):2
7. Ghosh A, Debnath B, Ghosh SK, Das B, Sarkar JP (2018) Sustainability analysis of organic fraction of municipal solid waste conversion techniques for efficient resource recovery in India through case studies. J Mater Cycles Waste Manage 1–17
8. Indrajeet DC, Patil DS (2017) Zero waste management system: case study—Kumbarakoppal. Mysore 6(5):768–770
9. Javadekar (2016) Solid waste management rules revised after 16 years; rules now extend to urban and industrial areas. Press Information Bureau, Ministry of Environment and Forests, Government of India. Available at: http://pib.nic.in/newsite/PrintRelease.aspx?relid=138591. Accessed 3rd June 2017
10. KCDC. Available from: http://kcdc.in/index.html. Accessed on 20 Oct 2017
11. Komakech AJ, Zurbrügg C, Miito GJ, Wanyama J, Vinnerås B (2016) Environmental impact from vermicomposting of organic waste in Kampala, Uganda. J Environ Manage 181:395–402
12. Martínez-Blanco J, Muñoz P, Antón A, Rieradevall J (2009) Life cycle assessment of the use of compost from municipal organic waste for fertilization of tomato crops. Resour Conserv Recycl 53(6):340–351
13. Naveen BP, Sivapullaiah PV (2016) Solid waste management in Bengaluru-current scenario and future challenges. Innov Ener Res 5:139. https://doi.org/10.4172/ier.1000139
14. Ramachandra TV, Bharath HA, Kulkarni G, Han SS (2018) Municipal solid waste: generation, composition and GHG emissions in Bangalore, India. Renew Sustain Energy Rev 82:1122–1136
15. Swachh Survekshan 2016 (2016) Available from: http://pib.nic.in/newsite/PrintRelease.aspx?relid=136427
16. Thomas P, Soren N, Rumjit NP, James JG, Saravanakumar MP (2017) Biomass resources and potential of anaerobic digestion in Indian scenario. Renew Sustain Energy Rev 77:718–730
17. Umair S, Björklund A, Petersen EE (2015) Social impact assessment of informal recycling of electronic ICT waste in Pakistan using UNEP SETAC guidelines. Resour Conserv Recycl 95:46–57
18. United Nations. Department of Economic (2007) Indicators of sustainable development: guidelines and methodologies. United Nations Publications
19. Vaish B, Srivastava V, Singh P, Singh A, Singh PK, Singh RP (2016) Exploring untapped energy potential of urban solid waste. Energy, Ecol Environ 1(5):323–342
20. WHAT A WASTE- A Global Review of Solid Waste Management Urban Development & Local Government Unit (2012) World Bank

A Critical Analysis on Anaerobic Digestion of OFMSW in India

Anaya Ghosh, Jyoti Prakas Sarkar and Bimal Das

1 Introduction

Anaerobic digestion of OFMSW has turned into the most promising biochemical technologies in India because of the availability of higher moisture content of MSW [1]. AD is the most suitable practice for the treatment and minimization of municipal solid waste (MSW) towards waste to energy perspective for its biogas production after the end of the process. With intensifying requirements and quick diminution of fossil fuels, biomass is a suitable alternative for the fulfilment of energy demands at present in India [2]. The first AD in India was invented in the year of 1897 by Matunga Leper Asylum in Mumbai [3]. They used human waste as a feedstock of AD process with an idea to reduce their electricity need by producing gas. The first successful attempt was taken for AD in 1937 by S.V. Desai, a microbiologist of the Indian Agricultural Research Institute (IARI). India is one of the quick progressing nations with an even-increasing economy due to its rapid growth of populations. The amount of total municipal solid waste generated per day in India is 1,41,064 tonne as evaluated by [4] and mostly it encloses 40–60% of organic waste [5, 5]. It has been described that biogas production can be accomplished at the yield of 95 m^3/tonne of MSW with the help of AD [5] and the potential of this biogas for the MSW is evaluated as 9.23 Mm^3/day [6]. This biogas is having calorific value 20–25 MJ/kg and energy potential within a range of 5.5–8 kWh/m^3 [7–9]. According to numerous reports, 4 million animal waste biogas plants are installed in India [1], whereas 645 MSW biogas plants are fabricated as per [4] report. The Government of India has taken initiatives for the implementation of biogas plants and subsidies for rural areas. The preliminary study aims the AD reaction process, operating parameters with their optimum ranges and different digesters available in India [5]. The present study also emphasizes on the rector types with the current biogas model practices

---

A. Ghosh (✉) · J. P. Sarkar · B. Das
Department of Chemical Engineering, National Institute of Technology, Durgapur, India
e-mail: ghoshanaya@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_22

in India. Various literature surveys and reports were carried out to understand the current scenario of AD process for waste management in India. With an idea of the sustainability of current AD practices in India, this paper sincerely reviews the various AD models implicated in India and the accomplishments received by the different organizations under the Government of India so far. Not only does this research aim at the assessment of the AD process on the economic, social and environmental perspectives, these reviews and the data collections would be advantageous and instructive for policymakers, stakeholders, decisions makers for recommending new framework and policies.

2 Biochemical Reactions of Anaerobic Digestion

AD is a very intricate technique which contains a numerous number of complicated biochemical reactions under oxygen-free circumstances. The digestion basically a reduction process of biodegradable wastes with the help of microorganisms and the major by-product is CH_4 (50–75%) and CO_2 (25–50%) with a slight trace of H_2S and NH_3. The methane formation in AD associated with four different biological and chemical phases: hydrolysis, acidogenesis, acetogenesis, and methanogenesis are shown in Fig. 1 [10]. The overall biochemical conversion of organic waste for AD to CH_4, CO_2 and NH_3 can be represented as

$$\begin{aligned} & C_aH_bO_cN_d + [(4a - b - 2c + 4d)/4]\,H_2O \\ & \quad \rightarrow [(4a - b - 2c - 3d)/8]\,CH_4 + [(4a - b - 2c + 3d)/8]\,CO_2 + dNH_3 \end{aligned}$$

where $C_aH_bO_cN_d$ signifies the complex organic matter of MSW [12]. A schematic diagram of anaerobic digestion process pathway, intricate solid organic waste degradation is described in Fig. 2. The first stage which involves during AD is hydrolysis or liquefaction where complex organic matter converts into soluble molecules with the help of hydrolytic bacteria [13]. Hydrolysis plays the role of rate controlling step in the overall process. It depends on the operational constraints such as pH, temperature, inhibition, substrate accessibility and bacterial population. In the second stage of AD, the organic matters including the monomers are transformed into volatile fatty acids (VFAs), acetic acids, H_2 and CO_2 by the digestion of acidogenic (fermentative) bacteria [14]. The third step is acetogenesis where monomers are assimilated by acetogenic bacteria to process CH_3COOH (acetic acid), CO_2 and H_2. At the final stage, methane is produced by methanogens and this methanogenesis step is a very complicated phase in the entire AD process because it is the slowest biochemical response of the system and very delicate to the temperature and pH of the substrate [11]. The non-digestible organic, mineral and residual material after the entire degradation process, consider as solid digestate.

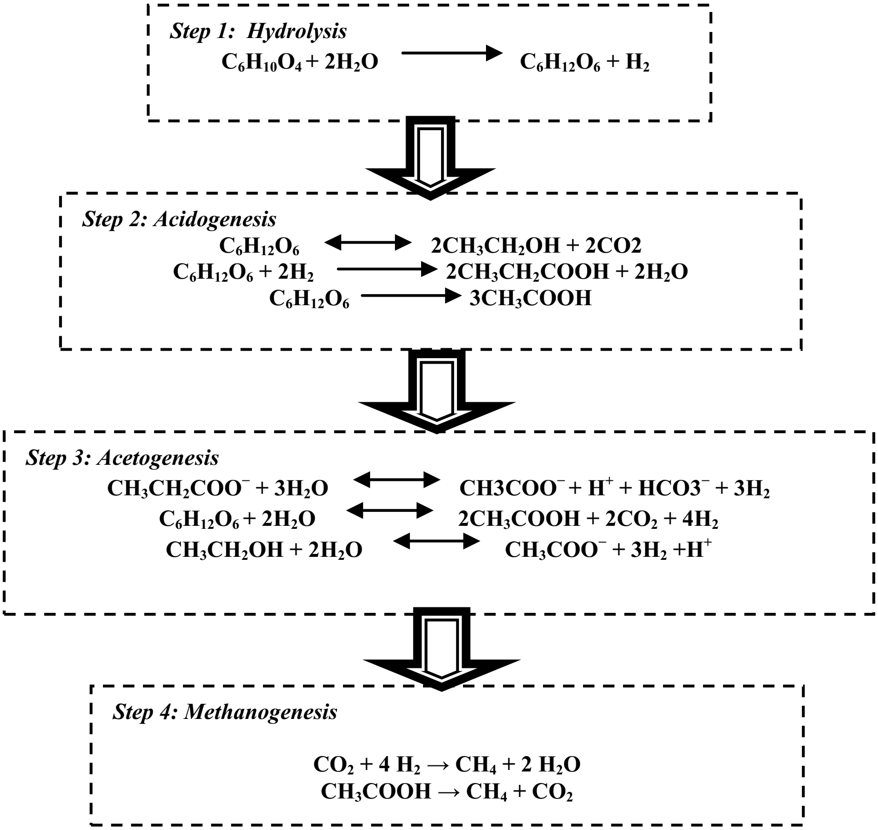


Fig. 1 Steps implicated in anaerobic oxidation of complex MSW [11]

3 Factors Affecting the Anaerobic Digestion Process for OFMSW

Depending on several process parameters, anaerobic digestion operates at an optimum circumstance for its highly sensitivity microorganisms which are implicated in methane production. Moisture content of raw OFMSW is appraised as one of the most essential factors affecting the waste stabilization. Higher amount of moisture content yields efficient biogas generation and it should be minimum 36% for a mesophilic digester with domestic vegetable waste fed [14]. The essential operating parameters of anaerobic digester like pH, temperature, volatile solids (VS), C/N ratio, hydraulic retention time (HRT), total solid content (TS) or organic loading rate (OLR), must be controlled within an optimum limit for the enhancement of the microbial activity which accelerate the process efficiency and biogas generation simultaneously [11]. The affecting process parameters for AD process of OFMSW with their optimum

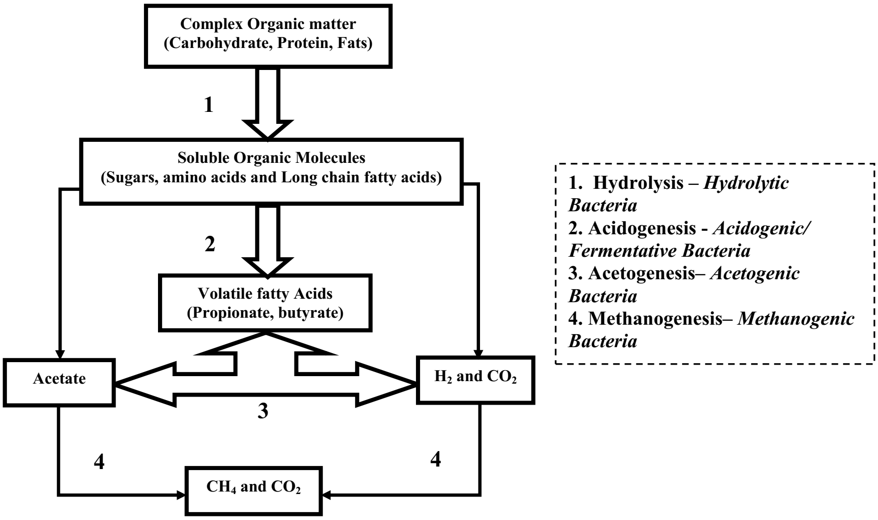


Fig. 2 Schematic diagram of anaerobic digestion process pathway [13]

Table 1 Operating process parameters and optimum conditions for AD process

Process parameters for anaerobic digestion					
Optimum range	pH	Temperature (°C)	C/N Ratio	Total solids content (TS)	Retention time (days)
	5.5–8.5 [11]	Mesophilic 25–40 °C Thermophilic 50–65 °C [8]	25–30 [16]	9.2 kg VS/m^{3}d [11]	Mesophilic 10–40 days Thermophilic 12–24 days [11, 8]

range are described in Table 1. The microbes are very sensitive to pH and temperature of the process specially the methanogenic bacteria [15, 16].

4 Existing Models of Anaerobic Digester in India

AD is one of the prime wastes to energy technology for emerging nations like India and biogas has become one of the essential renewable as well as sustainable energy sources which can be a substitution of fossil fuels. There are numerous different types of reactor technologies for AD processes and several different types of digester models are available in India [17]. AD process can be carried out into batch mode and continuous processes. In batch process, all four biochemical reaction phases of treatment process are executed in a single tank, whereas in continuous processes, it can be accomplished by continuous or semi-continuous loading, having a single stage or two-stage processes [18]. In conventional continuous AD process, all four biochemical stages are carried out in a single stage, wherein two-stage process organic wastes are decomposed first in hydrolysis–acidogenic stage reactor followed by the methanogenic reaction in upflow anaerobic sludge blanket (UASB) reactor which enhances the biodegradation efficiency [19]. The design of digesters may be diverged depending upon the waste composting, waste quantity and regional variations. Several types of models for biogas plants have been renowned in India by the Ministry of New Renewable Energy [20], Government of India, [21–23]. Two biogas digesters have been designed; one is the Chinese fixed dome digester having and the Indian floating cover biogas digester [24, 25]. The biodegradation process is identical for both reactors but the biogas collection process is much better in the case of Indian-type digester [25]. The Khadi and Village Industries Commission (KVIC) AD model is a floating dome type plant with a cylindrical digester made with steel model and very well known all over India [1], whereas Deenbandhu model, a fixed dome type plant with a hemisphere digester is rather cheaper than KVIC model. The Pragati model is also floating drum type plant having higher gas yield and it is a blend of both Deenbandhu and KVIC model with a hemisphere digester [21]. Tubular type digesters are fabricated with polyethylene tube-like bag with PVC gas collection pipeline but not applicable in case of high gas pressure system [1]. A numerous number of existing reactors and models of AD process in India have been described in Fig. 3 [1, 25].

5 Benchmark Practices of Anaerobic Digestion in India

Presently, in India, so many organizations, industries, agencies and research institutes are focused on waste management and minimization treatment process with an idea toward waste to energy recovery [2]. Anaerobic Digestion of OFMSW is one of the promising socio-economically and environmentally sustainable processes as per Indian context [6]. Ministry of New Renewable Energy (MNRE), Government of India has stepped forward to several initiatives for the implementation of both small- and large-scale biogas plants in both rural and urban areas [21]. Some private organizations like Indian Biogas Associations (IBA), Urban Local Bodies (ULBs), NGOs and Gram panchayats are also engaged for implementing biogas plants in public–private partnership (PPP) model in different possible locations in India for waste management and minimization and also for waste to energy recovery [1]. In conventional AD process, acidogenesis and methanogenesis stages are executed in a single reactor whether it may by floating dome type digester or fix dome type digester but now in the present scenario, two-stage AD process has become more efficient [9] because of the split-up of acidification and methanogenesis steps into two dissimilar reactors which expands solid handling capability and overall proficiency of AD as well as biogas production [23]. TERIs enhanced acidification and methanation (TEAM) process is an appropriate example of two-stage digestion and here methanation phase is followed up in an upflow anaerobic sludge blanket (UASB) reactor

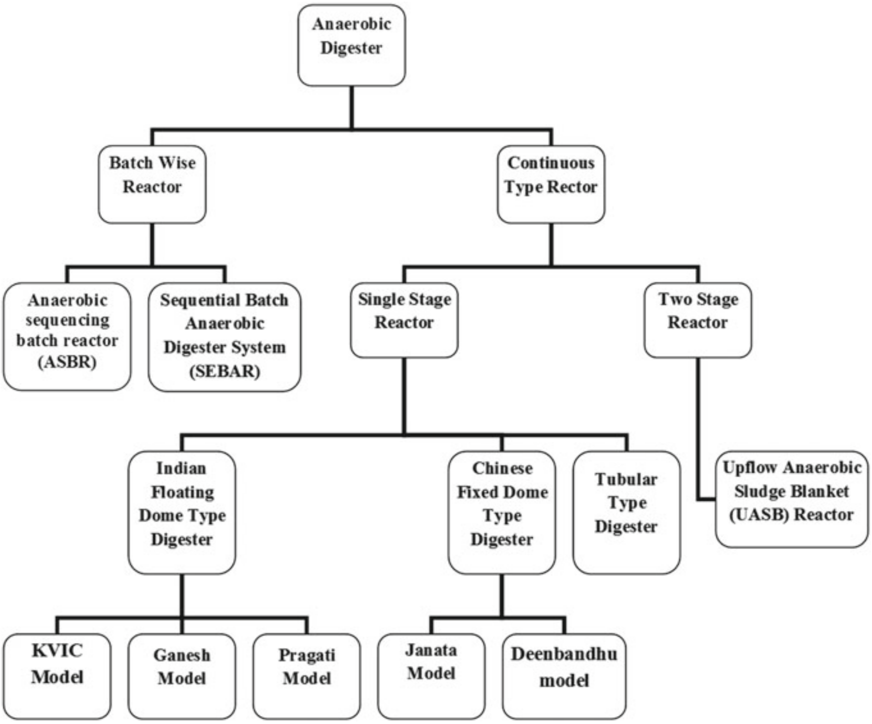


Fig. 3 Different existing reactors and models of AD process in India [1, 25]

[5]. A list of numerous success stories of biogas plants by AD in India is described in Table 2 [1].

6 Discussion and Recommendations

AD process for OFMSW management has developed various promising initiatives from the three piers of sustainability as well as waste to energy perspectives. From the environmental sustainability point of view, the practices of anaerobic digesters decrease the greenhouse gas emissions as well as reduce the global warming potential by effective utilization of waste resources. Waste to energy processes reduces the usages of woods, timbers which lead towards the diminution of deforestation to some extent. A few studies have been found on the environmental impact assessment of anaerobic digesters in India at present [1]. The global warming emanation in India, as well as other evolving nations, has been executed by reducing emanations by replacing conventional fuel sources [5], substituting of chemical fertilizers. 249 million tonnes of carbon dioxide emission can be mitigated in India by the encour-

Table 2 List of organizations using OFMSW from energy production in India

Sl No.	Organization	Feedstock	Process	Practices	Source
1.	TERI campus, Gurgaon	Food waste	Acidification and Methanation by UpFlow Anaerobic Sludge Blanket (UASB) reactor	Fuel and energy	Field visited by author
2.	KSRTC, Bangalore	Canteen wastes, food waste, OFMSW	Biomethanation	Cooking gas	Thomas et al. [1]
3.	Bellary municipality	OFMSW	Biogas through bio reactor	Power production	Thomas et al. [1]
4.	ASTRA, IISc, Bangalore	Green vegetables	Biogas through bio reactor	Fuel	Singh and Gu [26]
5.	Nisargruna Biogas plant, BARC, Mumbai	Kitchens waste, canteens waste, paper waste, green grass and leafy vegetables	two-stage anaerobic digestion	Organic manure and biogas as a fuel	Kakodkar et al. [27]
6.	Chamundi Hill, Mysore, Karnataka	Food waste	Anaerobic digestion in bio digester	Cooking Fuel	Field visited by author
7.	BBMP (Bruhat Bengaluru Mahanagara Palike)	Food waste and vegetable waste	Modified upflow anaerobic sludge blanket (UASB) process	Power generation	Ghosh et al. [5]

agement of AD [1]. Replacing biogas instead of fossil fuel diminishes the emission up to 60%, improving the air quality which is beneficial from the socio-economic perspectives. The anaerobic digesters can be a replacement of the fossil fuels and chemical fertilizer processes which minimize the expenses towards the acquisitions of conventional fuels and chemical manures for rural India. In the case of the Indian economy, 1 m^3 of biogas equivalents to 0.43 kg of LPG and nearly about Rs. 1821 can be retained per family by using biogas instead of LPG which becomes very favourable for lower income families. Presently, MNRE, Government of India is trying to implement anaerobic digesters all over rural India by imposing subsidies and instructions for operators and public awareness to consumers via different schemes.

7 Conclusion

In this study, a critical analysis of anaerobic digestion in India has been presented with special focus on reactor design and the process. The study found that a huge amount of OFMSW in India ends up in landfills which is the futility of the bioresources. Efficient policies from ministry and Government of India are solicited for effective utilization of this bioresource. Technologically, there are also scopes for improvement and innovations can increase reactor efficiency. Despite, the odds on the table more in-depth study on reactor design from the principles of chemical engineering and implementation efficient policy framework is required to ensure sustainability.

Acknowledgements The author would like to acknowledge fourth 3RINCs for organizing the field tours and International Society of Waste Management, Air and Water (ISWMAW), Jadavpur University.

References

1. Thomas P, Soren N, Rumjit NP, James JG, Saravanakumar MP (2017) Biomass resources and potential of anaerobic digestion in Indian scenario. Renew Sustain Energy Rev 77:718–730
2. Ambulkar AR, Shekdar AV (2004) Prospects of biomethanation technology in the Indian context: a pragmatic approach. Resour Conserv Recycl 40(2):111–128
3. Abbasi T, Tauseef SM, Abbasi SA (2012) A brief history of anaerobic digestion and "biogas". In: Biogas Energy. Springer, New York, NY, pp. 11–23
4. CPCB BULLETIN VOL.-I, JULY 2016, CPCB 2016 Report. Available at: http://cpcb.nic.in/openpdffile.php?id=TGF0ZXN0RmlsZS9MYXRlc3RfMTIzX1NVTU1BUllfQk9PS19GUy5wZGY=
5. Ghosh A, Debnath B, Ghosh SK, Das B, Sarkar JP (2018) Sustainability analysis of organic fraction of municipal solid waste conversion techniques for efficient resource recovery in India through case studies. J Mater Cycles Waste Manage 1–17
6. Rao PV, Baral SS, Dey R, Mutnuri S (2010) Biogas generation potential by anaerobic digestion for sustainable energy development in India. Renew Sustain Energy Rev 14(7):2086–2094
7. Surendra KC, Takara D, Hashimoto AG, Khanal SK (2014) Biogas as a sustainable energy source for developing countries: opportunities and challenges. Renew Sustain Energy Rev 31:846–859
8. Mir MA, Hussain A, Verma C (2016) Design considerations and operational performance of anaerobic digester: a review. Cogent Engineering 3(1):1181696
9. Ahammad SZ, Sreekrishnan TR (2016) Biogas: an evolutionary perspective in the Indian Context. In: Green fuels technology. Springer, Cham, pp 431–443
10. Weiland P (2010) Biogas production: current state and perspectives. Appl Microbiol Biotechnol 85(4):849–860
11. Nalo T, Tasing K, Kumar S, Bharti A (2013) Anaerobic digestion of municipal solid waste: a critical analysis. Int J Innovative Res Sci Eng Technol 3(4):224–234
12. Chanakya HN, Malayil S (2012) Anaerobic digestion for bioenergy from agro-residues and other solid wastes—An overview of science, technology and sustainability. J Indian Inst Sci 92(1):111–144
13. Jain S, Jain S, Wolf IT, Lee J, Tong YW (2015) A comprehensive review on operating parameters and different pretreatment methodologies for anaerobic digestion of municipal solid waste. Renew Sustain Energy Rev 52:142–154

14. Smith SR, Cheeseman C, Blakey N (2009) Waste management and minimization. Available at https://books.google.co.in/books?id=XoqbCwAAQBAJ&printsec=frontcover&source=gbs_ge_summary_r&cad=0#v=onepage&q&f=false
15. Beevi BS, Jose PP, Madhu G (2014) Optimization of process parameters affecting biogas production from organic fraction of municipal solid waste via anaerobic digestion. World Acad Sci Eng Technol Int J Bioeng Life Sci 1(1)
16. Dhar H, Kumar S, Kumar R (2017) A review on organic waste to energy systems in India. Biores Technol 245:1229–1237
17. Kumar S, Bharti A (2012) Management of organic waste. InTech. Available at https://www.intechopen.com/books/management-of-organic-waste
18. Zupancic GD, Grilc V (2012) Anaerobic treatment and biogas production from organic waste. In Management of organic waste. InTech. Source: https://cdn.intechopen.com/pdfs-wm/27154.pdf
19. Rajeshwari KV, Lata K, Pant DC, Kishore VVN (2001) A novel process using enhanced acidification and a UASB reactor for biomethanation of vegetable market waste. Waste Manage Res 19(4):292–300
20. The Ministry of New and Renewable Energy (MNRE) Source: http://www.mnre.gov.in Available at: https://mnre.gov.in/biogas
21. MNRE Report. Types of biogas plants a total of seven different types of biogas plant have been officially recognised by the MNES- SGP India. Available at http://www.sgpindia.org/documents/biogas_plants.pdf
22. Kishore VVN, Pant DC, Anaerobic Digesters in India. TERI University. The Energy and Resources Institute Available at: https://globalmethane.org/expo-docs/india10/postexpo/ag_kishore.pdf
23. TERI Report. TERI's enhanced acidification and methanation technology. Available at http://www.teriin.org/technology/teri-enhanced-acidification-and-methanation-technology
24. Kumar S (2012) Biogas. InTech. Available at: https://www.intechopen.com/books/biogas
25. Samer M (2012) Biogas plant constructions. In Biogas. InTech. Available at: http://cdn.intechopen.com/pdfs/31334.pdf
26. Singh J, Gu S (2010) Biomass conversion to energy in India—A critique. Renew Sustain Energy Rev 14(5):1367–1378
27. Kakodkar A, Ronge B, Patankar A, Mule S, Pawar P (2017) A concept of knowledge and technology enabled empowerment of rural Indian villages. Curr Sci 112(4):750

Biogas and Organic Fertilizer from Kitchen Waste Based Biogas Plant at Tezpur University, Assam

Dipam Patowary, Gaffer Ahmed and D. C. Baruah

1 Introduction

In recent times, the food waste management has become the focal point of many academic research and industrial organizations. It has been reported that about 1.3 billion tonnes of eatable food materials are being wasted every year worldwide [1]. Such an enormous generation of food waste has put a great deal of pressure on solid waste management corporations across nations. In one way, it has contributed to the municipal solid waste as one of the major components, whereas the detrimental effects of disposal of food waste has been severe the other way around [2, 3].

Food waste contains a huge portion of the biodegradable material, which can be converted to an efficient fuel through bioconversion techniques [4, 5]. On the application of anaerobic digestion to the staggering amount of food waste reported by Gustavsson et al. [1], biogas production of about 367 m^3 per tonne of dry food waste can be produced [6]. In addition, biogas production from food waste has been proven to be an economical route of energy recovery [7].

Biogas production from anaerobic digestion of food waste can be sought to be a better option for Tezpur University, situated in Assam, India. As much as 3000 students reside in 12 hostels of the university. With such a huge number of students in the hostels, the amount of food waste that is generated will also be quite high. In addition, all the hostels are dependent on LPG or fuelwood (in case of crisis) for meeting the cooking energy needs. An average hostel in the campus consumes about 1–2 LPG cylinders per day. This implies the massive expense incurred in procuring LPG cylinders by the hostels throughout the year.

With a view to supplementing the currently available cooking fuel, a 50 cubic meter food waste biogas plant was constructed. A previous study was carried out assessing the feasibility of the usage of the plant on a regular basis [8]. This paper

---

D. Patowary · G. Ahmed · D. C. Baruah (✉)
Department of Energy, Tezpur University, Napaam, Tezpur 784028, Assam, India
e-mail: baruahd@tezu.ernet.in

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_23

focuses on the performance of the biogas plant over a 9 months' period (January 2017–September 2017) in terms of LPG cylinders saved as well as auxiliary value addition activities performed concerning the biogas plant.

2 Materials and Methods

2.1 Construction and Operation of Biogas Plant

Prior to the construction of the biogas plant in the university, an assessment was made to determine the daily waste generated in the hostels. A daily generation of about 804 kg of food waste is generated cumulatively from all the hostels [8]. Based on the site suitability and ease of logistics, a 50 m^3 food waste biogas plant was constructed in the Patkai Men's Hostel of the university. An average quantity of about 130 kg of food waste is available on a daily basis from the selected hostel. In addition to the biogas plant, a slurry handling system is also constructed so as to handle solid and liquid digestate separately. Solid digestate available after the separation unit is fed to a 2 tonnes per annum vermicomposting unit. The complete system is shown in Fig. 1.

Fig. 1 Complete kitchen-waste-fed biogas plant with slurry handling and vermicomposting unit

2.2 Determination of Biogas Yield

This work is in continuation with the work reported in Buragohain et al. [8]. Kitchen waste of about 120 kg was fed daily in the biogas plant. Daily biogas production was measured daily. Biogas yield measurement is performed by taking into account the summation of the difference in height of the biogas holder in absence of usage and the drop during usage. The detailed method of measurement is reported in Buragohain et al. [8]. The present work shows the biogas yield of 8 months (January 2017–September 2017) with no data for the month of July 2017 as it is a vacation period at the university.

2.3 Determination of Composition of Biogas

The composition of biogas was measured daily using a Biogas Analyzer (Brand: Ambetronics Engineers Private Ltd). The detailed method of measurement is reported in Buragohain et al. [8].

2.4 Determination of Equivalent Amount of LPG

The equivalent amount of LPG with respect to the biogas consumed was performed by boiling a similar quantity of water with both the fuels and comparing the amount of each fuel utilized in boiling water. The detailed method of measurement is reported in Buragohain et al. [8].

2.5 Economic Analysis of the Biogas Plant

An economic analysis of the food waste biogas plant was performed by taking into account the maintenance cost, electrical cost, and labor cost during January 2017–September 2017. The capital cost is not considered as it has been paid back before January 2017. Money saved during each month is calculated by subtracting the incurred cost required for operating the plant from the money obtained by the numbers of LPG cylinders saved each month.

3 Results and Discussions

3.1 Determination of Biogas Yield

The biogas produced from the 50 cubic meter food waste biogas plant was monitored for a period of eight months (January 2017–September 2017), with no biogas production for July 2017 as it is a vacation month in the University. The gas production was measured in m^3 per day. During this period, the gas production varied within 6.76–14.49 m^3/day depending on the quantity of food waste fed to the reactor as well as internal and external parameters like pH and temperature. The lowest production was 6.76 m^3/day during the month of January (Fig. 2a). The dip in ambient temperature during this winter month has led to such low biogas production. Also, the values are also directly related to the quantity of feedstock fed to the plant on the previous day of gas measurement during the period of study. The highest biogas production was seen during the months of May, August, and September (Fig. 2c, d). Cumulative biogas production during the months of May, August, and September was about 390.41, 402.42, and 404.36 m^3, respectively. Temperature has played an important role in enhancing the biogas production. The biogas production during June was also high but as the plant was operated only for 15 days, it attained a low cumulative production (210 m^3) as compared to the other months. Summer air temperature was recorded to be within 33–37 °C.

During phases of low gas production, pH of the digestate was measured, and at times it Was found to dip below 6. Under these circumstances, cow dung was fed to the biogas plant until a neutralized pH was achieved. Figure 2(a–d) shows the biogas production during the months from January to September 2017.

3.2 Variation of Methane Content of Biogas

CH_4 (in %V/V) was measured during the nine months' period at an interval of seven days. It was observed during the initial phases of the study, i.e., during the months of January and February, CH_4 content varied within 40–45%. At lower concentrations, the yellow flame was observed which even led to the stoppage of burning of biogas when the analyzer measured high concentrations of CO_2 in the biogas as compared to CH_4. Formation of fatty acids inside the plant may have brought this outcome. In order to resolve the higher concentrations of carbon dioxide, cow dung was fed. It helped in the enhancement of the methane content in the biogas. After the stability was achieved in the system, food waste feeding was continued. During the period of study, the CH_4 content attained highest during the summer months from May to September. The methane content was in the ranges of 57–65% during these months.

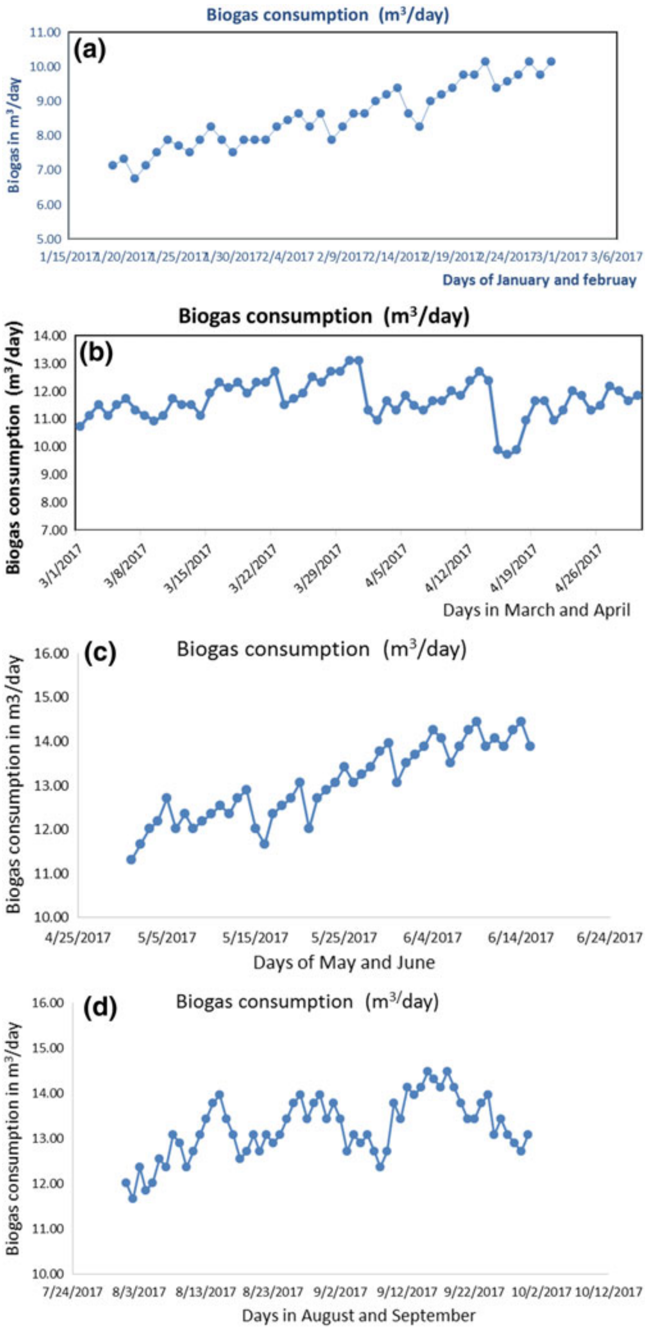


Fig. 2 **a** Biogas production from January to February, 2017 **b** Biogas production from March to April 2017 **c** Biogas production from May to June 2017 **d** Biogas production from August to September, 2017

3.3 Determination of Equivalent Amount of LPG

Based on the test to measure the equivalent amount of LPG consumed with respect to the consumption of biogas, it was found that 1 m^3 of biogas was equivalent to 0.45–0.55 kg of LPG with respect to prevailing conditions of the system. The variation in the range is due to the variation in the methane content of biogas during the analysis.

3.4 Economic Analysis of the Biogas Plant

During the period from January 2017 to September 2017, the highest number of LPG cylinders (14) was saved during the month of September. On an average, it was found out that around 10 LPG cylinders could be saved per month, which accounted for an estimated number of 123 LPG cylinders during 2017. The overall cost analysis from January 2017 to September 2017 are shown in the Table below. An amount of Rs. 28113/- of LPG could be saved during the 9 months of operation.

3.5 Digestate Slurry Handling and Conversion to Compost

The digested slurry coming out of the biogas plant is directed to a slurry handling system, where the digestate gets partially separated into a liquid form and a semi-solid form. Three vermicompost units are designed in such a way that semi-solid digestate accumulating in the handling system is extracted once in every 2 months. This form of digestate is then transferred to three vemicomposting units (each of volume 2 m^3) (Fig. 3).

Fig. 3 Separation of digestate and its conversion to vermicompost

Table 1 Economic analysis during January–September 2017

Month	Overall maintenance cost			Biogas consumption (m^3)	LPG equivalent (kg)	LPG saving (Rs.)	Gross Expenses (Rs.)	Cumulative savings (Rs.)
	Electricity cost (Rs.)	Labor wage (Rs.)	Maintenance cost (Rs.)					
January	340.03	2000.00	0.00	98.35	49.18	1904.72	2340.03	-435.31
February	307.13	2000.00	0.00	251.89	125.94	4878.12	2307.13	2570.99
March	329.06	2000.00	0.00	367.86	183.93	7124.10	2329.06	4795.04
April	340.03	2000.00	500.00	344.83	172.42	6678.07	2840.03	3838.04
May	329.06	2000.00	0.00	390.41	195.20	7560.72	2329.06	5231.66
June	340.03	2000.00	0.00	210.03	105.02	4067.52	2340.03	1727.49
July	No usage due to vacation							
August	340.03	2000.00	0.00	402.42	201.21	7793.36	2340.03	5453.33
September	329.06	2000.00	570.00	404.36	202.18	7830.99	2899.06	4931.93

Prior to transferring of the digestate, each of the units is internally laid with soil of 1-inch thickness. On the top of it, the digestate is transferred which is then covered by a layer of biodegradable materials (fallen leaves, cut grasses, etc.). This layer is again covered by another layer of digestate, which is then again covered by a layer of the biodegradable leaves. To it, a hundred earthworms (*E. foetida*) were added to each sample and water was added to keep the moisture content within 70%. The units are checked at regular intervals and the harvesting is done after 45 days.

A total of five harvests is done in a year. During the course of 9 months, three harvests have been done. A total of about 250, 370, and 270 kg have been harvested for the digestates of months January–February, March–April, and May–June, respectively. 20% of this portion is kept for gardening and farming within the Biogas plant premises, whereas, the remaining vermicompost is being sold at the rate of Rs. 10/kg. Along with the savings made from biogas usage, (as seen in Table 1), selling of vermicompost have resulted in earning an amount of Rs. 7120/-. During the nine months' operation, Rs. 35,233/- could have been saved. An estimation of about 600 kg is expected during the harvest of rest of the months.

4 Conclusions

With every academic year, with the increase in the number of students, demand for cooking energy is also showing an increasing trend. Based on this, utilization of biogas in cooking as depicted from one scenario at one of the hostels in the university seems to be a feasible choice in meeting the cooking energy demand during the period of LPG crisis. The 9-month period of study of the installed food waste biogas plant in the hostel showed a favorable option in utilizing the daily generated food waste in educational establishments. Moreover, value-added products like vermicompost generation have been quite useful in the generation of an extra revenue. Besides all the benefits, critical investigation of feedstock quality is imperative for the unhindered performance of a typical biogas plant.

References

1. Gustavsson J, Cederberg C, Sonesson U, Van Otterdijk R, Meybeck A (2011) Global food losses and food waste. FAO, Rome, pp 1–38
2. Franchetti M (2013) Economic and environmental analysis of four different configurations of anaerobic digestion for food waste to energy conversion using LCA for: a food service provider case study. J Environ Manage 123:42–48
3. Jin Y, Chen T, Chen X, Yu Z (2015) Life-cycle assessment of energy consumption and environmental impact of an integrated food waste-based biogas plant. Appl Energy 151:227–236
4. Ten Braummeler E (1993) Dry anaerobic digestion of the organic fraction of municipal solid wastes (Ph. D. thesis), Wageningen University, The Netherlands
5. Steffen R, Szolar O, Braun R (2000) Feed stock for anaerobic digestion. Making energy and solving modern waste problem. Available from www.adnett.org/dl_feedstocks.pdf
6. Yadav D, Barbora L, Rangan L, Mahanta P (2016) Tea waste and food waste as a potential feedstock for biogas production. Environ Progress Sustain Energy 35(5):1247–1253
7. IPCC (2013) Summary for Policymakers. In: IPCC Special Report on renewable energy sources and climate change mitigation
8. Buragohain S, Patowary D, Kataki S, Brahma B, Sarma GD, Patowary R, … Baruah DC (2018) Feasibility study on implementing kitchen waste-based biogas plant at Tezpur University, Assam. In: Utilization and management of bioresources. Springer, Singapore, pp 103–112

Biogas Conversion Potential of Chicken Wastes

Sreesha Malayil, Roopa Ashwath, Sunny Natekar and H. N. Chanakya

1 Introduction

Chicken and its products are the largest meat product consumed in India, where in there is a gradual shift to increased meat-based foods. This has resulted in the increased production of meat wastes from slaughterhouses, meat-processing units, and in urban chicken shops [1]. The per capita consumption of chicken in India is 2.2 kg/yr accounting for a total production of 2.6 Mtpa. A large part of this is consumed in urban areas, where the practice involves slaughtering the chicken at the time of purchase of meat. About 40% of the body weight is discarded as wastes and thus it may be reasonable to estimate a total of 1 Mtpa of which at least 40% would be in urban areas.

In the current culture, unlike the SE Asian culture, a larger number of body parts are not consumed in India. The non-edible parts include head, feet, feather, crop, skin and gastrointestinal tract contents (gizzard, crop, intestine), blood, organs, reproductive organs and bones are usually discarded as wastes [2]. Also, infected/diseased birds are excluded and generally forms (2–5% and are generally excluded at the farm itself). Thus, in urban Indian chicken wastes only dead birds would be a part of the wastes to be handled and sick and infected birds are excluded at the farm level. Traditional ways of handling wastes would involve rendering, use as animal feed where the material can be recycled and parts which are not reusable can be composted or incinerated [4]. While, converting the meat waste to useful byproducts will help generate additional income, the small size of the slaughter and sale units do not allow large-scale reuse. Composting although widely practiced is difficult in the case of chicken wastes due to high moisture content and high ambient temperatures are conducive for rapid meat decay accompanied by foul odours. As a result of the small-scale, dispersed

---

S. Malayil · R. Ashwath · S. Natekar · H. N. Chanakya (✉)
Centre for Sustainable Technologies (Formerly ASTRA),
Indian Institute of Science, Bengaluru 560012, India
e-mail: chanakya@iisc.ac.in

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_24

locations, rapid decay potential, conversion to biogas appears the most ideal way to dispose of these wastes.

A vast majority of the chicken are broilers raised for their rapid growth rates and tender meats. These birds at marketable stage weigh on an average of around 1.8–2.0 kg and as indicated earlier have about 40% discards. As mentioned earlier, these wastes are kept in polythene bags and discarded at night, most often illegally at unauthorised sites. The most sensible management options today create temporary burial yards during festive seasons where the meat waste production goes up ten times. For example, North Bangalore produced close to 120 t/d around an important festival as opposed to about 20–25 tpd on average days [MoH Per. Comm.]. Rendering of wastes has only just begun in a few cities in India and still do not handle all the renderable wastes. The rendering process simultaneously dries the material and separates the fat from the protein [3] and yields fat and a protein meal. Chicken waste has 80% moisture and energy needs to be spent to dry/incinerate it [4]. Most cities have not attempted biomethanation due to various reasons. First, there is little experience in converting meat waste into biogas except in one case of large-scale treatment in Hyderabad. Second, as indicated earlier, there is not sufficient aggregation in one place to take up clean and efficient processes. Third, because these small slaughterhouses are often very low-cost stalls and sale margins are quite low to afford aesthetic and clean treatment systems. Typical incineration today costs about Rs. 22/kg for meat and a lot more for handling feathers. Fourth, the high protein content is conducive to ammonia production and results in ammonia toxicity in AD. The aim of this study is to assess the Biochemical Methane Potential (BMP) of different parts of chicken wastes in order to assess the feasibility of biomethanation as a solution.

2 Materials and Methods

The chicken waste samples were procured from a chicken-processing factory at Krishnagiri, near Bangalore. The samples were shredded prior to preservation and then frozen until the start of the experiment. The total solids and volatile solids were estimated using the standard methods given by APHA. BMP assay was performed at various concentrations for different types of chicken waste. The inoculum for BMP assay was extracted from a Plug Flow Reactor [PFR] operating at CST, IISc [5]. Experiments were carried out in batches for 90 days in 135 ml serum bottles which were sealed with a rubber stopper and aluminium crimps. The biogas production was measured by downward displacement of acidified water. The methane content was determined using a gas chromatograph (carrier H_2, column—Hayesep A, column length—2 m, at 50 °C, carrier flow 15 ml/min, detector—thermal conductivity detector, TCD).

Table 1 TS and VS contents of different parts of the non-edible chicken

Sl. No.	Parts	Total solids (%)	Volatile solids (%)	Fraction (%) body weight	Total N
1	Head	22.7	86.3	6.9	5.3% [7]
2	Feet	29.8	83.0	4.4	5.3 [7]
3	Skin	43.3	99.0	12	NA
4	Blood	17.3	94.6	10	1%
5	Crop	17.0	95.4	NA	NA
6	Intestine	53.5	94.2	3	NA
7	Gizzard	32.0	87.1	1.5	NA
8	Trachea	14.9	87.6	2.2	NA

3 Results and Discussion

3.1 *Total Solids (TS) and Volatile Solid (VS) Analysis for Types of Chicken Waste*

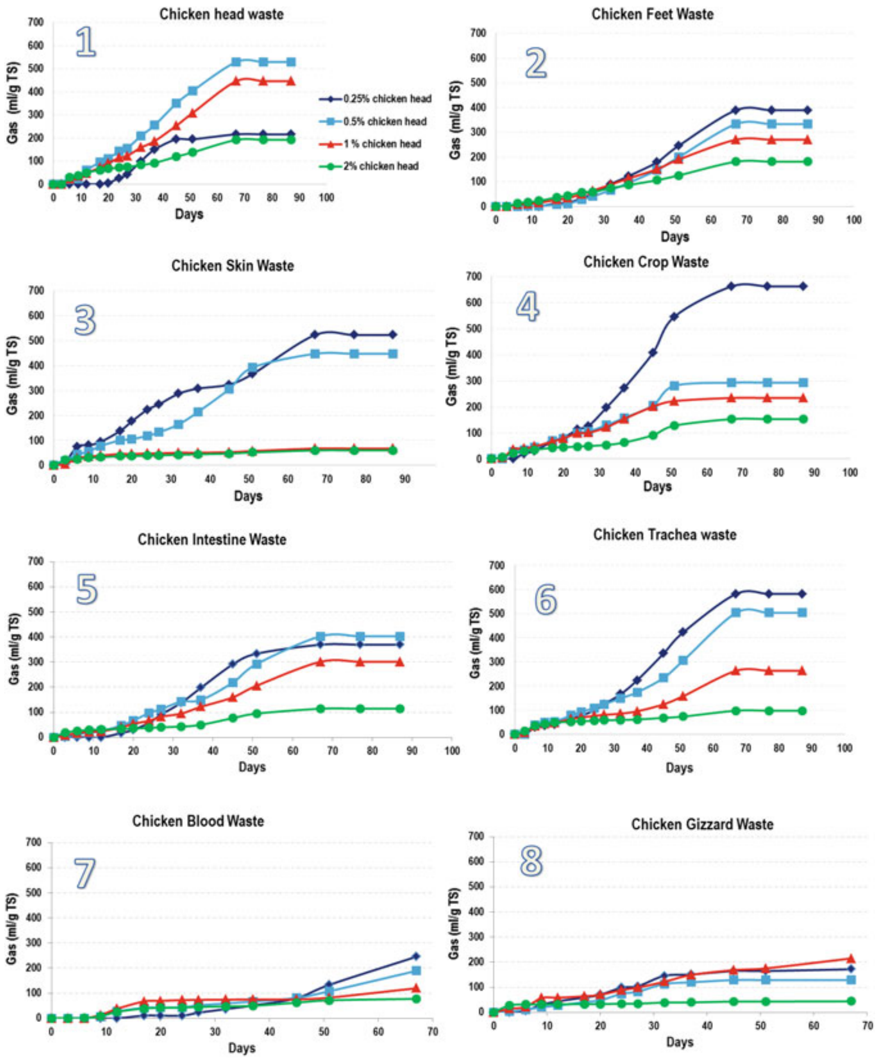
Table 1 presents the composition of different parts of chicken wastes. The skin had the highest solid content of 43.2% of which 99.8% is VS and thus suggesting a high potential for biodegradation and concomitant biogas production. In chicken, the skin constitutes about 8–10% of body weight [6]. The higher solid content in the skin is possibly due to its rapid drying compared other parts of chicken wastes. Crop had a volatile solids content of 95.4%. As expected, due to the presence of a larger extent of cartilage and bone increases the ash content of feet and therefore it had low VS. In general, the moisture contents of all the waste were >70%. This high moisture content is, therefore, conducive to rapid decay, with the production of leachate that could be foul smelling. Composting of such a material will, therefore, need to add appropriate absorbent material and will require a high level of aeration. Biomethanation, therefore, appears most suitable. Carrying out biomethanation nearer the point of generation can overcome transportation and transportation costs and yet keep the place clean and aesthetic.

3.2 *Cumulative Biogas Methane Production Potential of Various Parts of Chicken Waste*

(1) **Head**: Fig. 1(1) shows the biogas production potential of chicken head waste at substrate concentrations of 0.25, 0.5, 1 and 2% respectively. In the current study, the maximum biogas production was estimated to be 530 L/kg of wet weight or 2330 L/kg TS. We note that this level is high and beyond theoretically explained. However, from Table 1, it is evident that the head has 5.3% N and, therefore, AD

of 1 kg material would release 53 g ammoniacal-N which can be very inhibitory. Ammonia concentration of 50–70 mg/L is found to show some degree of methanogen inhibition although higher concentration has thought to be tolerated under different conditions. The maximum biogas yield for chicken head waste samples was found to be 530 ml/g TS at 0.5% concentration giving an efficiency of 83.3% as compared to theoretical yield. Initially, very less gas production was observed which may be due to acclimatisation of the substrate by microorganisms since this is a high protein material. In the case of 0.5% substrate concentration, the gas production was estimated to be 230 ml/g. Both 0.5 and 1% substrate concentration showed similar gas production rates. Increasing the substrate concentration, led to a reduction in the biogas production potential. Substrate concentration of 2% resulted in a significant decrease of biogas production and the efficiency was reduced to 70.7%. The maximum gas production was estimated to be 450 L/kg of wet waste. The decrease in biogas production may be due to the release of ammonium and free ammonia during protein degradation. Both ammonium and free ammonia are found to be inhibitory to methanogens. Sulphide is also another byproduct of amino acid fermentation. In the presence of high concentration of sulphate the H_2-consuming acetogens and sulphate-reducing bacteria compete with methanogens for hydrogen [8, 9]. Salminen and Rintala [7] have reported a biogas production potential of 300 L/kg wet weight in case of head and the current study shows a higher yield of 530 L/kg of wet weight at an inoculum to a substrate concentration of 0.5%.

(2) **Feet**: Biogas production from chicken feet is shown in Fig. 1(2). Among the various parts of chicken discarded as waste around 4.4% is feet. Chicken feet is found to have 5.3% N in the form of protein and similar to that of head. However, the VS content of feet is lesser when compared to head and expected to have a lower biogas yield. A substrate concentrate of 0.25% gave the highest gas production from feet followed by 0.5 and 1% substrate concentration. At 0.25% substrate concentration, a cumulative gas yield of 390 L/kg wet weight was achieved. Increasing the substrate concentration could have resulted in ammoniacal-N shock which decreased the activity of methanogens. Unlike chicken head where the maximum gas yields were observed at 0.5% substrate concentration in the case of feet, the optimum inoculums to substrate concentration were estimated to be 0.25% which was different. Both the substrates had similar N concentrations and this, therefore, needs further research. Ammonia produced in protein degradation in the AD of chicken waste is found as unionised ammonia which inhibits methanogens. Unionised ammonia can readily diffuse across cell membranes, unlike ammonium ion. Unionised ammonia inhibits methanogens at a concentration of 0.1–1.1 g/L, however, methanogens are capable of adapting to unionised ammonia concentration beyond this threshold level. But methane production is possible only after a certain period of adaptation in case of high ammonia concentrations. In case of both head and feet low biogas production was observed between 0 and 20d and on a long run of such reactors, this time taken for adaptation by methanogens can be avoided. Angelidaki and Ahring [10] postulated that adaptation results from the growth of new methanogens rather than metabolic changes in the methanogens already present. In addition to these small amounts of sulphide present (25–30 mg/L) can increase the ammonia inhibition. In comparison


Chicken head waste

Chicken Feet Waste

Chicken Skin Waste

Chicken Crop Waste

Chicken Intestine Waste

Chicken Trachea waste

Chicken Blood Waste

Chicken Gizzard Waste

Fig. 1 Cumulative gas production of various parts of chicken (1) head, (2) feet, (3) skin, (4) crop, (5) intestine, (6) trachea, (7) blood and (8) gizzard

with the theoretical biogas yield of protein (636 ml/g TS), an efficiency of 61.32% was observed at 0.25% substrate concentration followed by 55% efficiency at 0.5% (330 ml/g TS). Even though the volatile solid content of feet samples was 83%, there was very less gas produced. This could be due to the fact that chicken feet had lot of difficult to degrade materials such as cartilage materials, nails and a major portion of it is bones. Anaerobic bacteria are not capable of degrading the calcium phosphate element of bones and therefore these remains in the digester and hence a periodical removal of this material is required for the efficient running of large-scale biogas plants designed for chicken waste. Also, the cartilaginous material present in the chicken feet is difficult to be hydrolysed by the anaerobes and, therefore, less gas production was observed for this substrate. When both substrates (head and feet) are compared chicken head produced almost twice the biogas as feet.

(3) **Skin**: Chicken skin contributes to 12% of its total body weight. Chicken skin is found to be nutritious and in most of the countries and some parts of India, it is consumed along with the meat. However, in most of the cases, when the chicken is supplied to restaurants, hotels and even bought for consumption at households in India the meat is de-skinned and used and, therefore, found as a waste material. The biogas production from chicken skin is presented in Fig. 1(3). The maximum gas yield was observed for 0.25% substrate concentration (520 L/kg wet waste) followed by 0.5% (430 L/kg wet waste). Although substrate concentrations of 1 and 2% showed very slow signs of gas production in the initial days similar to 0.25 and 0.5% substrate concentrations, there was no further increase in the gas production. The gas production fell drastically to 67 L/kg wet material at 1% substrate concentration. This was different from other substrates such as head and feet. This could be due to the toxicity of LCFA's produced during hydrolysis of skin. Chicken skin is reported to have a high fat content of 49.8% and nitrogen content of 9.8%. It is reported that LCFA degradation may be a rate-limiting step in the anaerobic degradation of chicken waste because of slow growth of LCFA consuming bacteria since the breakdown of it requires low H_2 partial pressure [7]. LCFAs are toxic to acetogens and methanogens. The carbon chain length and saturation of LCFAs, too, affect the inhibition, saturated LCFAs with 12–14 carbon atoms and unsaturated LCFAs with 18 carbon atoms being the most inhibitory. In addition, LCFA toxicity to methanogens is synergistic, i.e. it increases in the presence of another LCFA. On the other hand, various substances, including albumin, starch, bile acids and cholesterol, may reduce the toxicity of LCFAs due to the formation of complexes or competitive adsorption at the cell wall [7]. In comparison with the theoretical biogas yield of fat (1434 ml/g TS), an efficiency of 36% was observed at 0.25% (520 ml/g TS) substrate concentration followed by 31.5% efficiency at 0.5% (450 ml/g TS). Even though the VS content was the highest for skin (99%) and expected to produce higher biogas the gas yields were close to chicken head with a VS content of 86%. This could be due to the VFA or ammonia inhibition and needs further research.

(4) **Crop**: Biogas production potential of a chicken crop is shown in Fig. 1(4). Crop and trachea (Fig. 1(4 and 6)) is the part of the oesophagus (food pipe) of the chicken, where the initial stages of digestion can occur. Hence, this part of the chicken is found to have a good amount of chicken feed present. From Fig. 1(4 and 6), it was observed that 0.25% substrate concentration gave maximum cumulative gas yield of 680 L/kg in case of crop and 600 L/kg wet waste in case of trachea with an efficiency of 90–94% as compared to theoretical protein gas yield followed by 0.5% concentration with a cumulative gas yield of 300 L/kg of wet waste efficiency of 47% in case of crop. At 1% substrate concentration, a cumulative gas reading of 220 L/kg wet weight was achieved. Chicken crop gave the highest biogas yield when compared to all the substrates under study. This could be due to the presence of carbohydrate-

rich chicken feed present in the crop of the bird. This chicken feed rich in C acted as a co-substrate with the N-rich crop which resulted in higher biogas yields. Co-digestion of wastes with varying characteristics is one way to dilute toxicants and to supply missing nutrients and suitable moisture content. Similarly, co-digesting high N-rich material such as head and feet could also yield higher gas and needs further research. Chicken crop had approximately 88% of volatile solid content which was similar to that of the head but lower than feet. However, the gas production was highest in Crop and this needs further research. Rosenwinkel and Meyer [11] showed a successful treatment of slaughterhouse waste, hog, and cow stomach contents with sewage sludge in a pilot-scale, mesophilic digester at a loading of 2.9 kg TS/m^3 d and an HRT of 17 days with a methane production of 0.23 m^3/kg TS added. In another study, methane production in a sewage sludge digester treating flotation tailings was possible at a loading of 1.5 kg TS/m^3 d and an HRT of 15 days with a methane production of 0.32 m^3/kg TS added. Brinkman [12] described a stable, thermophilic treatment of kitchen waste slurries and flotation sludges from slaughterhouse wastes in a laboratory-scale digester at a loading of less than 3.5 kg COD/m^3 d with an HRT of 32 days, but shock loads of 5–7.5 kg COD/m^3 d caused an accumulation of LCFAs and VFAs. These results clearly indicate that co-digestion is a suitable option to treat N-rich chicken waste to obtain higher gas yields.

Conclusion: Anaerobic digestion of chicken waste is a practical option for disposing of the waste when compared to composting and incineration to combine material disposal and energy production. However, not many plants are operational on chicken waste and AD of this waste is difficult due to its high N and fat content. In the current study, an attempt was made to understand the biogas production potential of various parts of chicken waste. It was seen that chicken crop produce the highest gas 680 L/kg of wet waste and the optimum gas production was achieved at 0.25% substrate concentration. Even though chicken skin had the highest VS content (99%) gas production was low. Chicken skin showed high gas production of 400–500 L/kg wet waste at 0.25–0.5% but increasing the substrate concentration from 1 to 2% reduced the gas yields to 50–60 L/kg wet waste and could to be due to LCFA inhibition due to the high fat content in chicken skin. From the above studies, it can be concluded that co-digestion of chicken waste with C-rich material could yield high gas production and stop ammonia inhibition to a certain extent.

References

1. Rivera JA, Sebranek JG, Rust RE, Tabatabai LB (2000) Composition and protein fractions of different meat by-products used for pet food compared with mechanically separated chicken (MSC). Meat Sci 55(5):53–59
2. Alao Babatunde O et al (2009) The potential of animal By-products in food systems: production, prospects and challenges. Sustainability 9:1089
3. Swan JE (1992) Animal by-product processing. Encycl Food Sci Technol 1:42–49
4. Das KC, Minkara MY, Melear ND, Tollner EW (2002) Effect of poultry litter amendment on hatchery waste composting. J Appl Poult Res 11:282–290

5. Jagadish KS, Chanakya HN, Rajabapaiah P, Anand V (1998) Plug flow digesters for biogas generation from leaf biomass. Biomass Bioenerg 14:415–423
6. Mendez-Lagunas LL, Siles-Alvarado S, Rodriguez-Ramirez J, Aquino-Gonzalez LA (2015) Fatty acid profile composition of chicken skin. Int J Chem Biomol Sci 1(3):193–196
7. Salimen E, Rintala J (2002) Anaerobic digestion of organic solids, poultry slaughter house wastes-A review. Biores Technol 83:13–26
8. Widdel F (1988) Microbiology and ecology of sulphate and sulphur reducing bacteria. In: Zehnder JB (ed) Biology of anaerobic microorganisms. Wiley, New York, pp 469–585
9. Zinder SH (1984) Microbiology of anaerobic conversion of organic wastes to methane: recent developments. ASM News 50:294–298
10. Angelidaki I, Ahring BK (1993) Thermophilic anaerobic digestion of livestock waste: effect of ammonia. Appl Microbiol Biotechnol 38:560–564
11. Rosenwinkel K-H, Meyer H (1999) Anaerobic treatment of slaughterhouse residues in municipal digesters. Water Sci Technol 40(1):101–111
12. Brinkman J (1999) Anaerobic digestion of mixed waste slurries from kitchens, slaughterhouses and meat processing industries. In: Mata-Alvarez J, Tilche A, Cecchi F (Eds) Proceedings of the Second International Symposium on Anaerobic Digestion of Solid Wastes, Barcelona, vol 1, pp 190–195

A Study on Optimization of Pretreatment for Lipid Extraction from Rice Husk Using *Oleaginous Yeast*

N. Dhivya Priya, S. Sivasakthi, R. Loganath, R. Balaji, K. Yaazhmozhi, J. Senophiyah-Mary and S. Murugan

1 Introduction

The global fossil fuel energy scenario is a complex one due to various issues out of which increasing oil price, environmental concerns, sustainability, and security are the prime factors [1]. In view of the existing fossil fuel availability and demand scenario, it is necessary to attain an equilibrium on its production–consumption. Due to these reasons and the impact of air pollution due to combustion of fossil fuels on human health, alternative sources of energy and their potential to be deployed as secondary sources of energy are being investigated on a larger scale.

N. Dhivya Priya (✉) · S. Sivasakthi · R. Balaji · K. Yaazhmozhi · J. Senophiyah-Mary
S. Murugan
Department of Environmental Engineering, Government College of Technology,
Coimbatore 641013, Tamil Nadu, India
e-mail: priya.dhivya08@gmail.com

S. Sivasakthi
e-mail: sivasakthi900@gmail.com

R. Balaji
e-mail: rbalajicivil@gmail.com

K. Yaazhmozhi
e-mail: yaazh2011@gmail.com

J. Senophiyah-Mary
e-mail: senophiyah.mary8@gmail.com

S. Murugan
e-mail: smurugan@gct.ac.in

R. Loganath
Department of Civil Engineering, Indian Institute of Engineering
Science and Technology, Shibpur 711103, West Bengal, India
e-mail: loganath.rk@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_25

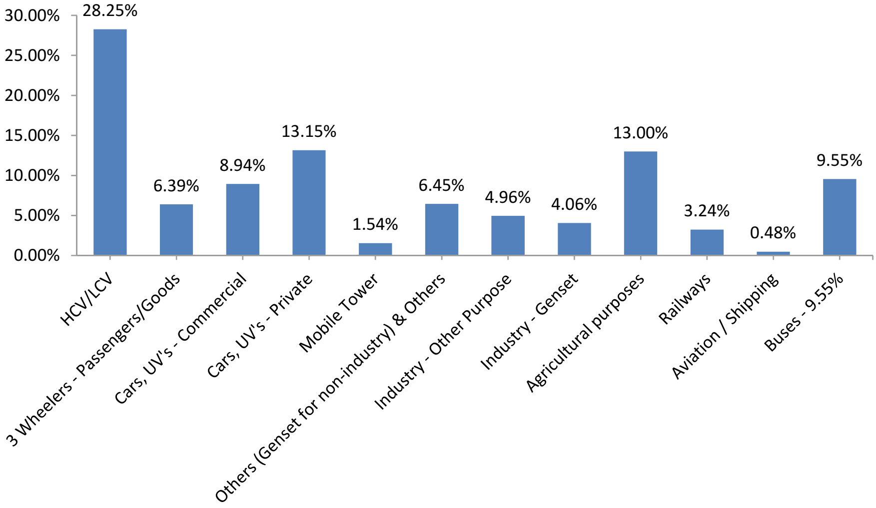


Fig. 1 All India usage share of diesel (percentage) in retail [3]

India imports fossil fuel to meet its energy demand, out of which majority is used for transportation. India imports around 1,71,729,000 tons of crude oil to meet its energy demand, incurring a cost of 6,72,220 crores [2]. Figure 1 gives the data on usage of diesel and its product in various sectors in the country in the year 2013. Transport sector consumes around 70% of the total diesel usage in the country, while nontransport sector consumes around 30%. The Replacement of even a nontransport sector by an alternative unconventional source of fuel would save at least 10,350 crores approximately [3]. The use of biodiesel as an alternative to conventional diesel has been gaining importance in the recent years.

Biodiesel is a monoalkyl ester of long-chain fatty acids, produced by the transesterification of free fatty acid with a monohydric alcohol, usually methanol [4], employing acid catalyst, alkali catalyst, or enzyme catalyst. The free fatty acids are usually derived from feedstocks like animal fat or vegetable oil [5, 6]. This definition of biodiesel confirms with the specification for biodiesel (b100)—ASTM D6751-09 to be used in compression ignition (diesel) engines. First-generation bioethanol was directly produced using food crops as feedstock which led to an increasing competition between the food and energy industries. Second-generation biodiesel, on the other hand, makes use of discarded or useless part of the food crop, rich in starch, sugar, or lingo-cellulosic content as a feedstock [7].

The main precursor raw material required for biodiesel production are lipids extracted from biomass cultured on suitable feedstock. Lipids are a class of organic compounds that are fatty acids or their derivatives, insoluble in water and soluble in organic compounds. The yield of lipids from biomass cultured on the feedstock depends directly on the availability of simple monomers such as glucose for consumption by microorganisms. The lingo-cellulosic materials in the feedstock are formed by three structural polymers: cellulose, hemicelluloses, and lignin and small quantities of other compounds [8] which must be broken down to simple monomers to effect increased growth.

A few pretreatment technologies, targeted to remove the lignin, have been developed by incorporating chemical, biological, or mechanical means [9, 10]. Because of this, carbohydrates are exposed which are further converted to simpler sugars in the following treatments. Any pretreatment processes should breakdown the cellulose and other polymers by hydrolysis and preserve it. The process should have a higher efficiency and should also facilitate easy removal of any byproducts formed [11].

Common pretreatment methods include acid and alkali pretreatment and biological methods to an extent. Acid treatment includes the use of strong acids such as H_2SO_4 or HCl or weak acids such as oxalic acid or peracetic acid. Acid treatment is less expensive because of the cheap availability of acids. It is carried out at high temperatures, so, corrosion of vessels is a serious problem. Alkali treatment uses sodium, potassium, calcium, and ammonium hydroxides at normal temperature and pressure. The main advantage of this process over acid treatment is the removal of lignin. Though these are the important treatment methods being adopted worldwide, other methods such as Ammonolysis, Wet oxidation, Ozone treatment, Microwave irradiation, etc., are being investigated extensively in recent times [7].

Rice constitutes around 20% of the world's nutritional value [8] Rice husk is the protective covering surrounding the kernel, which constitutes around 20% of the grain's weight [12] Rice husk is the second largest mill-generated source of biomass. India accounts for nearly 20% of the total rice production in the world. After processing of rice, the residual rice husk is usually burnt. It produces 18–20% ash on burning, which is comparatively high when compared to other biomass which produces 1–8% ash. Rice husk on an average contains 33% cellulose, 21% hemicellulose, 18% lignin, and 17% silica [13]. The high cellulose and hemicellulose content makes it suitable to be used as a feedstock for biodiesel production [14].

The objective of this paper is to analyze the potential of rice husk as an alternative feedstock for biodiesel production. Rice husk is to be subjected to various pretreatment techniques to depolymerize the complex sugars in it, to simple monomers. This depolymerization is to be affected by hydrolysis of rice husk, aided by acid or alkali, in the presence or absence of pressure. Optimization of the various operating parameters involved in pretreatment such as strength of acid or alkali, agitation, temperature, pressure, and reaction time are to be monitored and optimized. The species that is best suited for maximum yield of lipids is to be investigated from the chosen oleaginous yeast species on the given substrate.

2 Materials and Methods

2.1 Sample Collection

Rice husk, from the processing of local plantation in Sri Durga Mills, Coimbatore, was collected. It was ground in a conventional mixer grinder of 750 W and 0.5 L capacity. The ground sample was sieved in a fine aggregate sieve shaker for 10 min and the sample passing through 75 μm was collected. The sieved sample was further ground in a Planetary Rotating Ball mill for 2 h, with 15 loads at 150 rpm. The milled sample was stored in airtight packets at room temperature.

2.2 Pretreatment Methods

2.2.1 Alkali Pretreatment

Experimental Design

Response surface methodology (RSM), a collection of statistical and computational analysis, is used for modeling a system in which a response of interest is influenced by more than one parameter [15]. The influence and optimization of various operational parameters, namely, rate of mixing (0–300) (rpm), temperature of treatment (25–100) (°C), concentration of NaOH (0–0.6) (Normality), and time of treatment (10–60) (minutes) were studied. TOC and TN were monitored as the response parameters. A central composite design involving a quadratic model was incorporated.

Pretreatment

The experimental trails as obtained from RSM was carried out under the same conditions mentioned in a REMI 5MLH plus, magnetic stirrer with a hot plate. The pretreatment was carried out on solutions of 1 g of powdered rice husk/100 ml of distilled water. Different concentrations of alkali, i.e., 0.2–0.6 N, were employed to optimize the process. Time, temperature, and rate of mixing were preset before starting the process, and temperature was continuously monitored with an external temperature probe (PT-1000) to ensure that temperature is maintained at the present value. The sample after treatment could cool for 24 h and then filtered using a Whatman filter paper Cat No. 1001 125, with a pore size of 11 μm.

Table 1 pH required for growth of the selected species

S. No	Name of the species	pH required for growth	pH adjusted to
1	*Yarrowia lipolytica*	6.0–7.0	6.33
2	*Lipomyces starkeyi*	7.0–8.0	7.16
3	*Metschinokawia pulcherima*	5.0–6.0	5.45

2.2.2 Acid Pretreatment

This process involves the treatment of lingo-cellulosic biomass using sulphuric acid. Combination of heat and concentrated acid can be explosive. Therefore, the treatment was carried out in an autoclave under 15 psi pressure and 120 °C temperature for a time of two hours on a solution of 1 g of powdered rice husk/100 ml of water. Treatment was carried out for varying concentrations of acid, namely 1–5%. The treatment was carried out without any mixing. The sample after treatment was allowed to cool for 24 h and filtered using a Whatman filter paper Cat No. 1001 125, with a pore size of 11 μm.

2.2.3 Species Optimization

The filtered hydrolysate after optimization of pretreatment was used as a medium for culturing oleaginous yeast for lipid extraction. pH of the medium after hydrolysis was adjusted to the required optimum pH for each species as shown in Table 1. The medium was sterilized in an autoclave at a temperature of 120 °C and pressure of 15 psi. Three species of oleaginous yeast, namely, *Yarrowia lipolytica, Lipomyces starkeyi, Metschinokawia pulcherima,* were inoculated, 6% each into different conical flasks containing the sterilized medium. Inoculation was done in a laminar air flow chamber. After inoculation, the culture was kept and maintained in an orbital shaker at 25 °C temperature and 150 rpm rotation. The culture was checked continuously to maintain pH.

2.3 Analytical Methods

2.3.1 Particle Size Analyser

The size of the particle was analyzed using a particle size analyzer. A pinch of the powdered sample was added to 100 ml of double distilled water and then sonicated in a probe sonicator. The sonicated solution was then analyzed to find the size of the powdered sample by using the principle of particle diffraction index.

2.3.2 UV Visible Spectrophotometer

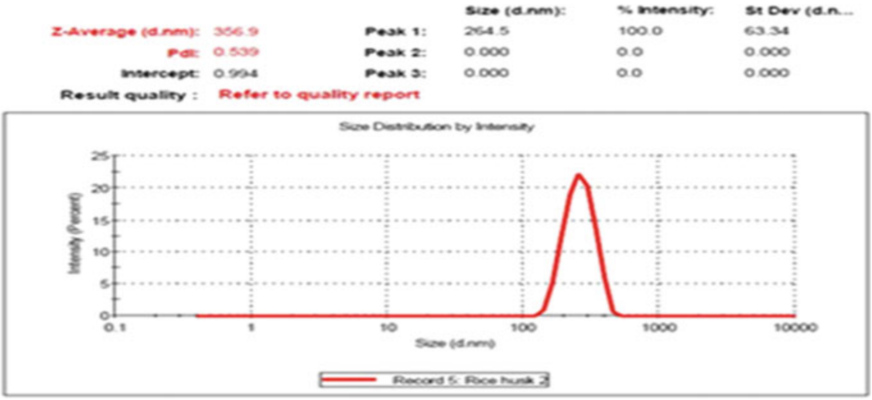
A Double beam UV Visible Spectrophotometer (Perkin Elmer Lambda, 35) was employed to trace the growth curve of the microorganism inoculated in the hydrolysate, periodically. Optical density reading at 640 nm wavelength was measured against clear hydrolysate that is not inoculated with any species as blank.

2.3.3 TOC Analyser

Total organic carbon was considered as a measure of the degree of hydrolysis of rice husk. It was analyzed in a TOC analyzer. Samples were diluted with a dilution factor of 10 using distilled water and were analyzed for total carbon and inorganic carbon from which Total Organic Carbon was found under operating conditions of 2 injections of a sample of 40 μl each for TC and IC and 4 min integration time for each, respectively. Samples were also tested for total nitrogen with operating parameters of 2 injections of 40 μl each and with an integration time of 4 min.

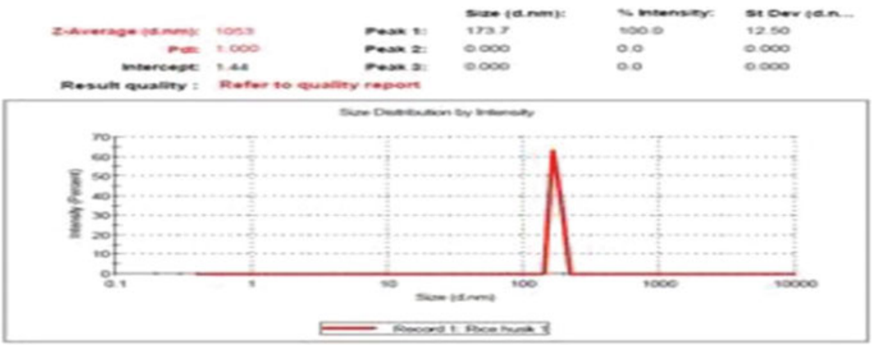
3 Results and Discussion

The particle ground in ball mill after 2 h was found to have an average particle size diameter of 356.9 nm, with a 100% peak intensity, as shown in Fig. 2. The particle size reduction even after 2 h of milling is less as compared to the size obtained after sieving (1053 nm). This might be due to the high fibrous content of rice husk, i.e., around 45% [16]. The effect of particle size reduction on lipid production is to be investigated (Fig. 3).



```
                                          Size (d.nm):   % Intensity:   St Dev (d.n...
Z-Average (d.nm): 356.9        Peak 1:    264.5          100.0          63.34
              PdI: 0.539       Peak 2:    0.000          0.0            0.000
        Intercept: 0.994       Peak 3:    0.000          0.0            0.000
  Result quality :  Refer to quality report
```

Fig. 2 Result of particle size analysis of the milled sample



Z-Average (d.nm): 1053
PdI: 1.000
Intercept: 1.44
Result quality : Refer to quality report

	Size (d.nm):	% Intensity:	St Dev (d.n...
Peak 1:	173.7	100.0	12.50
Peak 2:	0.000	0.0	0.000
Peak 3:	0.000	0.0	0.000

Fig. 3 Result of particle size analysis of powdered sample after sieving

3.1 *Acid Pretreatment*

Figure 4 shows the variation of C/N ratio with the percentage of concentrated H_2SO_4 used for treatment. Maximum value obtained for 1 g/100 ml solution was 30.33 for 3% acid solution. At mild conditions of treatment with a lower concentration of acids (1–2%), cellulose and hemicelluloses polymers are not effectively broken down which is indicated by the low value of TOC obtained (440 ppm on average) when compared to that obtained on treatment with 3percentage acid (575 ppm on an average).

At stronger treatment conditions (4 percentage to 5 percentage), though there has been a greater degree of depolymerisation, and an increase in TOC content (around 700 ppm), the treatment condition was enough to cause dissociation of lignin, thereby increasing the Total nitrogen content. This increase in total nitrogen might not favor the accumulation of lipids, as this leads to the production of new cells rather than the accumulation of lipid in the existing cells. Also, the maximum C/N ratio is far below the required amount to facilitate lipid production, i.e., C/N = 60 [17].

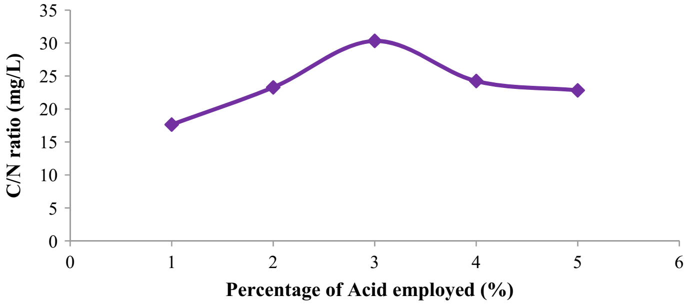


Fig. 4 Percentage of acid employed for treatment versus C/N ratio of the hydrolysate

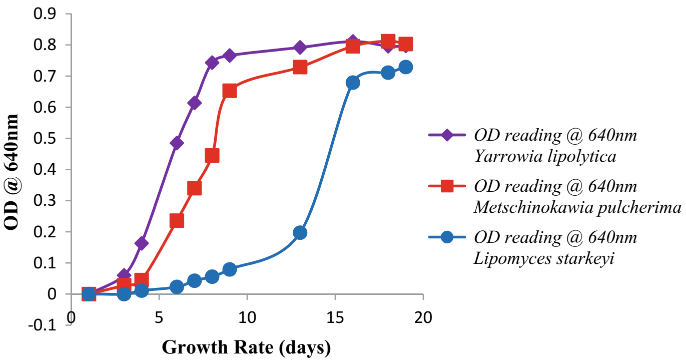


Fig. 5 Growth rate versus OD reading at 640 nm tracing growth curve of different species of oleaginous yeast for a period of 20 days

3.2 Alkali Pretreatment

30 trials were generated for optimizing temperature of treatment (B), rate of rotation(C), strength of alkali employed (A), and treatment time (D). The trials were performed experimentally and the results for TOC and TN were fed as response into Design Expert software. 3D surface model curves were analyzed for various combinations, namely, AB, AC, AD, BC, BD, and CD. The combination which yields maximum TOC was found to be 0.2-100-200-60 (A-B-C-D), with a TOC value of 1933. 8 ppm. The combination which yields the lowest TN value was found to be 0.2-50-300-60, with a TN value of 14.62 ppm. Highest C/N combination was achieved for the same combination which yielded desired TN value, i.e., 0.2-50-300-60, with a C/N value of 70.451 and an experimental desirability 1.00. This value is greater than 60, the minimum desired C/N value required for growth of oleaginous yeast [17]. ANOVA results showed an f—value of 0.0005 for the obtained quadratic model and lack of fit was insignificant.

3.3 Species Optimization

Figure 5 shows the growth curve of different oleaginous yeast species, namely, *Yarrowia lipolytica, Lipomyces starkeyi, Metschinokawia pulcherima* over a period of 20 days. The increase in OD reading indicates the growth of new cells. The graph shows the distinctive lag phase, exponential or growth phase, and stationary phase. The stationary phase is desired for lipid production as there are no new cells produced while all the consumption by the microorganism is converted and stored as lipid in the existing cells. On account of this, the species, *Yarrowia lipolytica,* is observed to have reached the stationary phase earlier than the other two species, (OD reading of 0.766 after 9 days of inoculation).

4 Conclusion

Various pretreatment techniques for particle size reduction and hydrolysis of the raw material were studied. It has been concluded that the acidic pretreatment employed for hydrolysis has proven to be ineffective due to the lower value of the maximum C/N ratio that has been achieved. Alkali pretreatment proves to be more effective than acid pretreatment as this has succeeded in achieving the minimum required C/N ratio, and the most desirable combination was found to be 0.2 N NaOH—50 °C—300 rpm—60 min. The species that gives an advantage over the other species tested, in terms of maximum growth was found to be *Yarrowia lipolytica* and the minimum time required for initiating the production of lipids was found to be 9 days at experimental conditions. However, the quality of lipid produced is a key parameter and is to be further investigated before extrapolating the process.

References

1. Abbas A, Ansumali S (2010) Global potential of rice husk as a renewable feedstock for ethanol biofuel production. BioEnergy Res 3(4):328–334
2. https://data.gov.in/catalog/importexport-crude-oil-and-petroleum-products
3. All India Study on Sectoral Demand of Petrol & Diesel—Report, Petroleum Planning and Analysis Cell, Ministry of Petroleum & Natural Gas, India
4. Lin L, Ying D, Chaitep S, Vittayapadung S (2009) Biodiesel production from crude rice bran oil and properties as fuel. Appl Energy 86(5):681–688
5. Meher LC, Sagar DV, Naik SN (2006) Technical aspects of biodiesel production by transesterification—A review. Renew Sustain Energy Rev 10(3):248–268
6. Ma F, Hanna MA (1999) Biodiesel production: a review. Biores Technol 70(1):1–15
7. Chaturvedi V, Verma P (2013) An overview of key pretreatment processes employed for bioconversion of lignocellulosic biomass into biofuels and value added products. 3 Biotech 3(5):415–431
8. Dagnino EP, Chamorro ER, Romano SD, Felissia FE, Area MC (2013) Optimization of the acid pretreatment of rice hulls to obtain fermentable sugars for bioethanol production. Ind Crops Prod 42:363–368
9. Geddes CC, Nieves IU, Ingram LO (2011) Advances in ethanol production. Curr Opin Biotechnol 22(3):312–319
10. Alvira P, Tomás-Pejó E, Ballesteros MJ, Negro MJ (2010) Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: a review. Biores Technol 101(13):4851–4861
11. Agbor VB, Cicek N, Sparling R, Berlin A, Levin DB (2011) Biomass pretreatment: fundamentals toward application. Biotechnol Adv 29(6):675–685
12. Rice husk based power generation study in the state of Punjab—report, The Energy and Resource Institute, New Delhi

13. Ma'ruf A, Pramudono B, Aryanti N (2017) March. Lignin isolation process from rice husk by alkaline hydrogen peroxide: Lignin and silica extracted. In: AIP Conference Proceedings, vol 1823, Issue 1. AIP Publishing, p 020013
14. Binod P, Sindhu R, Singhania RR, Vikram S, Devi L, Nagalakshmi S, Kurien N, Sukumaran RK, Pandey A (2010) Bioethanol production from rice straw: an overview. Biores Technol 101(13):4767–4774
15. Montgomery D, Runger G (2002) Applied probability and statistics to engineering
16. Fadaei V, Salehifar M (2012) Rice husk as a source of dietary fiber. Ann Biol Res 3(3):1437–1442
17. Chang Y, Chang K, Jang H, Hsu C (2011) May. Effect of carbon source and high C/N ratio in the cellulosic hydrolysate-based media on the crude lipid contents and unsaturated fatty acid compositions of yeasts. In: 11th International Congress on Engineering and Food, pp 1–6

Biodiesel Production from Unused Mixed Culture of Algae

R. Karmakar, A. Rajor and K. Kundu

1 Introduction

There are three main constraints of biodiesel produced form most of the feedstocks [1, 2] which are edibility of their raw material [3], high market price [4, 5] and their adverse effect on the compression ignition (CI) engine. Deposition of carbon, gumming problem clogging, etc. takes place in the engine for the higher density, viscosity and acid value of biodiesel. In spite of that research on biodiesel are being done worldwide because they are renewable and eco-friendly at the same time [6–8]. In this research work, algae was chosen as the feedstock to produce biodiesel because (i) it requires less area for growth and produce more oil compared to other crops [9, 10], (ii) it produce oxygen and absorbs carbon dioxide and (iii) in India, it is neither used as a food, nor for any other purpose. It was reported by Holbrook et al. [11] and Dassey et al. [12] that applying air mixed with more carbon dioxide increases the content of oil in the algae and biofuels produced from the culture of algae fix 0.6% CO_2 [13]. The algae which are thrown away from a canal (Simlapuri Nahar) of Ludhiana, India, were used in this experiment as they have no price value and are treated as waste material. Although algal biodiesel is not a very new fuel, it is still confined to the laboratories because of the high price of the oil. Then, the main reason behind this is the costly procedure of algae culture which is mostly done using photobioreactors [14, 15]. It was assumed that the biodiesel produced in this process (i) would be cheap as the raw material has no price value and (ii) would solve the problem of waste disposal to a little extent.

R. Karmakar (✉) · A. Rajor
Thapar University, Ludhiana, India
e-mail: rachan.in.air@gmail.com

K. Kundu
CSIR CMERI CoEFM, Patiala, India

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_26

2 Materials and Method

All the chemicals like potassium hydroxide, sulphuric acid, methanol, ethanol and n-hexane along with glassware were obtained from a local market of Ludhiana. The indigenous mixed culture of algae (*Spirulina* sp., *Euglena* sp., *Chlorella* sp., *Spyrogyra* sp. *Frustulia* sp.) was collected from the Simlapuri Nahar.

2.1 Drying of Algae

To make the process eco-friendly and economic, algae were dewatered at first by manual pressure to release water. Thin lumps of algae were prepared thereafter and kept in the sun for 2 days. This helped the algae to dry completely. Almost 10% of dried algae were derived from the wet algae.

2.2 Oil Extraction

The oil, from algae, was extracted by Soxtherm using hexane. Hexane is the solvent which extracts the oil present in algal cell. More than 90% of hexane was recovered by Soxtherm. Almost 10% of oil was extracted in this experiment.

2.3 Biodiesel Production

Before proceeding towards biodiesel production, the free fatty acid content of the oil was measured by titrimetric procedure. It was found that the algal oil has more than 20% of FFA content. Therefore, the oil has undergone acid esterification at first and alkali esterification then [16–19]. The transesterification procedure, which was used for biodiesel production from algal oil, was optimized y varying molar ratio (from 5:1 to 7:1), catalyst concentration (from 2 to 3 wt%), reaction time (from 50 to 70 min) and reaction temperature (from 55 to 62 °C). In this transesterification reaction [20, 21], methanol was used as the alcohol, potassium hydroxide (KOH) was used as the alkali catalyst and sulphuric acid (H_2SO_4) was used as the acid catalyst. The reaction was carried out inside a water bath shaker at a constant temperature. The glycerol produced in the alkali esterification reaction was separated and the biodiesel was washed by warm water. Finally, the algal oil methyl ester was kept inside a hot air oven for 1 hour so that the moisture, present in the biodiesel, gets rid of completely (Fig. 1).

Taguchi's method was used to prepare nine sets (L9 orthogonal array) of parameters for transesterification reaction (Table 1).

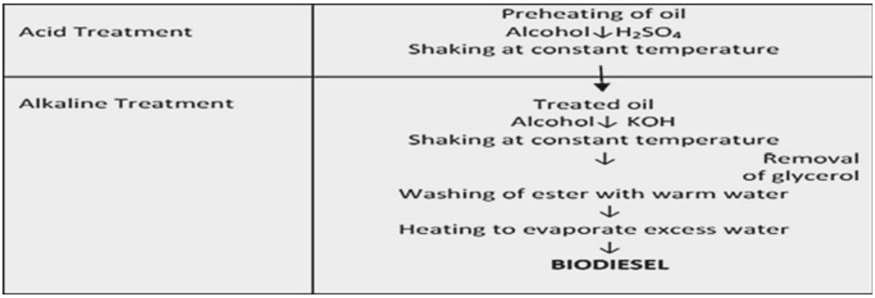


Fig. 1 Biodiesel production from algal oil

Table 1 L9 orthogonal array for transesterification

No.	Molar ratio (methanol: oil)	Catalyst conc. (wt%)	Reaction time (min)	Reaction temperature (°C)
1	5:1	2.0	50	55
2	5:1	2.5	60	60
3	5:1	3.0	70	62
4	6:1	2.0	60	62
5	6:1	2.5	70	55
6	6:1	3.0	50	60
7	7:1	2.0	70	60
8	7:1	2.5	50	62
9	7:1	3.0	60	55

2.4 Fuel Characterization

The properties of the algal biodiesel like density, viscosity, calorific value, flash and fire points, acid value, cloud and pour points, ash content and carbon residue content were characterized by standard methods.

2.5 Emission Characterization

AVL 444 di-gas analyzer was used to measure the emission of algal biodiesel. The probe of the analyzer was placed in the exhaust of Kirloskar made AV1 CI engine while it was being run by algal biodiesel. The measure of different gases was noted at different engine loads (0, 20, 40, 60, 80, 100 and 110%).

3 Result and Discussion

3.1 Yield of Biodiesel and Optimized Conditions of Transesterification

In acid esterification reaction, No. 7 combination (Table 1) yielded the best result and the FFA of the algal oil reduced down to 1.2% (Fig. 2). In alkali esterification reaction, the yield of the algal oil methyl ester increased rapidly and reached the peak (90.33%) when 6:1 molar ratio was applied with 2% KOH catalyst concentration (combination 4) (Fig. 3). The yield of the biodiesel for combination 5 was also high enough (90%). But it was not considered as the FFA of the biodiesel produced for this combination was little higher (0.29%) than that for combination 4.

From Fig. 4, it can be seen that the lowest FFA was also achieved when combination 4 was used, the free fatty acid content of the biodiesel decreased to its lowest level (0.25%). It was also found from this experiment that higher KOH concentration causes the formation of soap.

Therefore, 6:1 molar ratio, 2% catalyst concentration, 60 min reaction time and 62 °C reaction temperature were taken as the optimized conditions to produce biodiesel with the highest yield and lowest free fatty acid content. It was found that after 90 min all the glycerol settles down at the bottom of the separating funnel.

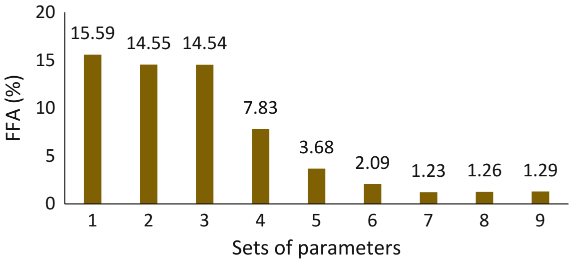


Fig. 2 Optimization of acid esterification

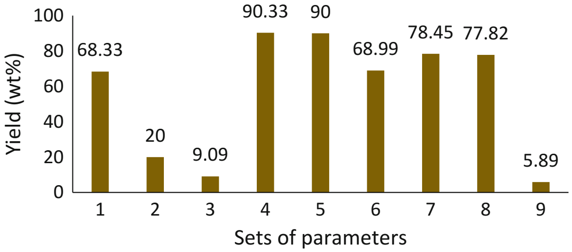
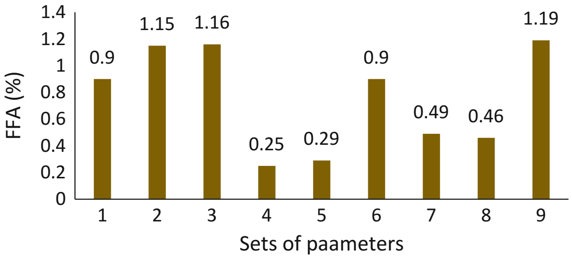


Fig. 3 Optimization of alkali esterification (yield)

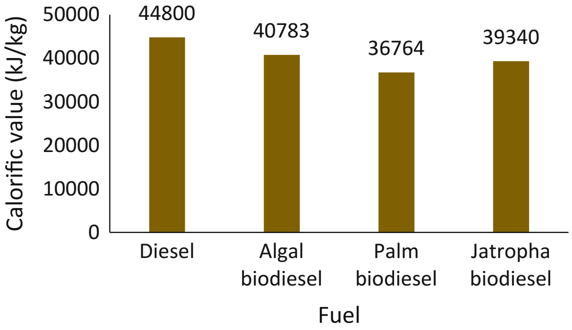
Fig. 4 Optimization of alkali esterification (FFA)



3.2 *Properties of the Algal Biodiesel*

The properties of the algal biodiesel were within the limits of ASTM standard. The calorific value is an important parameter of any fuel as it determines how much energy it would generate. The calorific value of this biodiesel was 40,783 kJ/kg which was higher than that of the biodiesel produced from palm and jatropha (Fig. 5). The density of this biodiesel at 15 °C (880.9 kg/m^3) was little higher than diesel (832 kg/m^3). The viscosity of the biodiesel at 40 °C (3.15 mm^2/s) was almost equal to the viscosity of petro-diesel (1.9–4.1 mm^2/s). The acid value of this biodiesel was 0.50 mg KOH/g. The flash and fire points of algal biodiesel (150 and 156 °C) were much higher than petro-diesel (54–96 °C). For this high flash point, the chance of any fire hazard decreases many folds. The cloud and pour points of this fuel were also low enough (1 and −2.5, respectively). Ash and carbon residue content of a fuel determines the level of deposition in the engine. Both of them, for this fuel, were 0.0105 and 0.36 wt%, respectively, which are within the limits of ASTM standard.

Fig. 5 Calorific value of different fuels



3.3 *Measurement of Emission of Algal Biodiesel*

Emission of CO, CO_2 and unburned hydrocarbon for the combustion of algal biodiesel were higher than those for the combustion of diesel at all engine loads. Only the NO_x emission for this biodiesel was higher than those for diesel. While the emission of CO_2 and NO_x were found to increase with the increase of engine load and reached their peak at overload (110%) condition (4% and 155 ppm, respectively), the emission of carbon monoxide and unburned hydrocarbon decreased regularly from 0 load condition to overload condition. The lowest CO emission (30 ppm) was found to take place at overload condition.

4 Conclusion

While most of the biodiesel is costly and produced from edible feedstocks, biodiesel produced from unused mixed culture can be a cheap and good alternative. A good yield of this biodiesel can be achieved if the optimized conditions, found in this experiment, are followed at the time of transesterification. As all the properties of this fuel are within the limit of ASTM standard, it can be used in the CI engine without any modification of the engine. Its emission has been found to be lower than that of diesel. Therefore, this is an eco-friendly fuel. The NO_x emission of this fuel, which generated in higher rate than petro-diesel, can be fixed by using de-NO_x catalyzer.

References

1. Adewale P, Dumont M, Ngadi M (2015) Recent trends of biodiesel production from animal fat wastes and associated production techniques. Renew Sustain Rev 45:574–588
2. Alcantara R, Amores J, Canoira L, Fidalgo E, Franco MJ, Navarro A (2000) Catalytic production of biodiesel from soyabean oil, used frying oil and tallow. Biomass Bioenerg 18(6):515–527
3. Pfromm P, Parman BJ, Amanor-Boadu V, Michalsky R (2011) Third generation biofuels and the food vs fuel debate: a system perspective. Int J Environ Cult Econ Soc Sustain 7(2):287–300
4. Kumar N, Mohapatra SK, Kundu K, Karmakar R (2017). Optimization of safflower oil transesterification using the Taguchi approach. Petroleum Science. Online paper 1–8. https://doi.org/10.1007/s12182-017-0183-0
5. RoyChowdhury A, Karmakar K, Kundu K, Dahake VR (2011) "Algal" biodiesel: future prospects and problems. Water Energy Int 68(11):44–51
6. Shirneshan A, Almassi M, Ghobadian B, Borghei AM, Najjafi GH (2012) Effects of biodiesel and engine load on some emission characteristics of a direct injection diesel engine. Curr World Environ 7:207–212
7. An H, Yang WM, Chou SK, Chua KJ (2012) Combustion and emission characteristics of diesel engine fuelled by biodiesel at partial load conditions. Appl Energy 99:363–371
8. Shirneshan A (2013) HC, CO, CO_2, and NOx emission evaluation of a diesel engine fuelled with waste frying oil methyl ester. Procedia Soc Behav Sci 75:292–297
9. Chisti Y (2008) Biodiesel from microalgae beats bioethanol. Trends Biotechnol 26(3):126–131

10. Chisti Y (2007) Biodiesel from microalgae. Biotechnol Adv 25(3):294–306
11. Dassey AJ, Hall SG, Theegla CS (2014) An analysis of energy consumption for algal biodiesel production: comparing the literature with current estimates. Algal Res 4:89–95
12. Holbrook GP, Davidson Z, Tatara RA, Ziemer NL, Rosentrater KA, Grayburn WS (2014) Use of microalga *Monoraphidium* sp. grown in waste water as a feedstock for biodisel: cultivation and fuel characterization. Appl Energy 131:386–393
13. Ponnusamy S, Reddy HK, Muppaneni T, Downes CM, Deng S (2014) Life cycle assessment of biodiesel production from algal bio- crude oils extracted under subcritical water conditions. Biores Technol 170:454–461
14. Nosker NH, Barbosa MJ, Vermue MH, René HW (2011) Microalgal production—a close look at the economics. Biotechnol Adv 29(1):24–27
15. Podevin M, Fotidis IA, De Francisci D, Moller P, Angelidaki I (2017) Detailing the start-up and microalgal growth performance of a full-scalephotobioreactor operated with bioindustrial wastewater. Algal Res 25:101–108
16. Dhawane SH, Kumar T, Halder G (2016) Biodiesel synthesis from *Hevea brasiliensis* oil employing carbon supported heterogeneous catalyst: optimization by Taguchi method. Renew Energy 89:506–514
17. Sorguven E, Ozilgen M (2010) Thermodynamic assessment of algal biodiesel utilization. Renew Energy 35(9):1956–1966
18. Suganya T, Gandhi NN, Renganthan S (2013) Production of algal biodiesel from marine microalga *Enteromorpha compressa* by two step process: optimization and kinetic study. Biores Technol 128:392–400
19. Pandey RK, Rai A, Kundu K, Karmakar R, Roy P, Roy Chowdhury A, Dahake VR (2013) Effect of process parameters for standardization of esterification of cotton seed oil for the production of biodiesel. Int J Curr Sci 8:74–78
20. Fernández CM, Ramos MJ, Perez A, Rodríguez JF (2010) Production of biodiesel from winery waste: extraction, refining and transesterification of grape seed oil. Biores Technol 101(18):7019–7024
21. Ragit SS, Mohapatra SK, Gill P, Kundu K (2012) Brown hemp methyl ester: transesterification process and evaluation of fuel properties. Biomass Bioenerg 41:14–20

Sustainable Algal Cultivation by Effective Utilization of MSW Digestate Slurry and Biogas By-Products—An Advanced Approach Towards Carbon Fixation and Generation of Biofuels

Afreen Aman and H. N. Chanakya

1 Introduction

Increasing fossil fuel costs due to rapidly depleting resources and global warming issues have led researchers to find alternatives to fossil fuels and one such option is biofuel from algae [1]. First-generation biofuel uses food crops and oilseed crops as primary substrates which in turn compete for freshwater/nutrients and agricultural land, therefore, creating a threat to food security [2]. This has led to the advent of second and third generation biofuels which utilize substrates like lignocellulosics and microalgae. Microalgae are a better alternative since it can be grown as a 'multi-tier' crop and in wastewater systems, rice paddies, etc. and hence do not compete with fertile land, water and therefore does not compromise food security [3]. The ability of microalgae to accumulate polysaccharides and triacylglycerides (TAG) makes them likely candidates to be used as feedstocks for biofuel production. Additionally, pressed algal biomass residue after oil extraction can be utilized to recover leftover carbon as additional fuel in the form of biogas or bioethanol [4].

Most commonly studied algae cultivation using photobioreactors is considered uneconomical due to the excessive costs and inefficiencies involved in providing illumination, water and nutrients like nitrogen, phosphorous and carbon, etc. [5]. This propels the need to identify niches and alternative nutrient resources that are suitable for culturing algae without interfering with agriculture and other human activities. Wastewater treatment plants, saline brackish water, paddy fields and fisheries deficient shores can be considered as an alternative for culturing algae as this combines energy generation, treatment of wastewater, nutrient uptake which aids in long-term sustainability [6].

A. Aman · H. N. Chanakya (✉)
Centre for Sustainable Technologies (Formerly ASTRA),
Indian Institute of Science, Bengaluru, India
e-mail: chanakya@astra.iisc.ernet.in

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_27

Every ton of MSW fermented in biogas plants produces between 750 and 800 litres of digested slurry of which over 95% is water. This needs to be disposed and there is very little effort today to address it and find productive uses for this wastewater from MSW processing. In the case of digested slurry from cattle dung biogas plants, it is easy to gradually dry it and retain the dried slurry as fertilizer for a couple of months. However, the digestate from biogas plants fed with predominantly food wastes and street sweeping (leaf litter) have different properties and cannot usually be filtered and dried into a 'cake'. We had previously studied biogas plant digestate solids as a mushroom feedstock [7], fibre [8] and possible pest repellent [9] and media for algae cultivation [10]. While we had established good cultivation characteristics, we had often encountered rapid loss of algal population through grazing by protozoans and crustaceans at certain stages [10]; this formed the inspiration for further research. In this study, we have used clear biogas slurry which is a by-product generated after anaerobic digestion of typical MSW wastes such as leafy biomass (leaf litter from street sweepings) as the culture media for growing algae. Anaerobic digestion narrows the C:N ratio of the substrate by converting C to gases like carbon dioxide and methane [8] and the resulting digester liquid emerge to become rich in nutrients like nitrogen and phosphorous. In MSW-based digesters, a significant part of the nutrients is expected to be in the dissolved form and cannot be collected as a filter cake and therefore is best utilized by algae. Such a technique of using biogas slurry, in addition, provides a low-cost alternative over the conventional mineral media.

One of the major threats to large-scale cultivation of algae is the rapid onset and multiplication (bloom) of grazers which is difficult to control under normal circumstances involving open pond cultivation. An algal bloom most often is followed by a bloom of grazers that consume the algae and result in a rapid decrease of algal biomass [11]. Yet, most grazers have specific feeding pattern on algae, being not only species-specific but also depending on the size and characteristics of algae present [12]. Thus, due to this phenomenon, controlling grazers in a natural way becomes a challenging task in large-scale algal cultivation, especially in open ponds. Digested biogas slurry contains a sizeable number of grazers that are facultative in nature such as *Paramecium*, etc. We believe that their presence can result in a new phenomenon of inter grazer competition among the species of grazers. Such competition either occurs naturally in open algal culture systems where grazers feed away on the algal population or one grazer feeds preferentially on the other grazer instead of algae and thus, it ameliorates the loss of algae to rapid grazing. When such a phenomenon occurs, the algal population reaches harvestable levels and in this way, benefits large-scale algal cultivation. This benefit accrues from biogas slurry addition to growth medium providing both nutrient source and generating harvestable algal biomass and is the focus of this paper.

Large-scale algal cultivation becomes environmentally and economically sustainable if it can be coupled with CO_2 fixation which is another objective of this research. The CO_2 and CH_4 from the anaerobic digester can be directed to algal ponds wherein CO_2 solubilizes and acts as a carbon source for algae. Thus, methane can be separated and collected as enriched biogas. Since carbon is essential for algal growth, algae will utilize the solubilized CO_2 in the form of carbonates and bicarbonates for photosynthesis and for building cell proteins, nucleic acids, etc. [13]. Microalgae have CO_2 fixation efficiency around 10–50 times greater than terrestrial plants [14], thus facilitating a path for reversing the increasing atmospheric CO_2 levels which are now considered a global problem. After lipid extraction, the resulting microalgal biomass can be used for biogas/bioethanol production by carrying out the fermentation of algae [15]. This study advocates a sustainable media alternative for algal cultivation and suggests a method for carbon sequestration that may help in the reduction of greenhouse gases in a sustainable manner.

2 Materials and Methods

2.1 Media-Based (M) Setup

For cultivation of algae, biogas slurry and media set up were used, wherein media is used as a control. Bold's Basal Media (BBM) consisted of (mg/l) $NaNO_3$, 250; K_2HPO_4, 75; KH_2PO_4, 175; $CaCl_2$, 25; NaCl, 25; $MgSO_4$, 75; $FeCl_3$, 0.3; $MnSO_4{\cdot}7H_2O$, 0.3; $ZnSO_4{\cdot}7H_2O$, 0.2; H_3BO_3, 0.2 and $CuSO_4{\cdot}5H_2O$, 0.06 [16].

2.2 Paddy Field (ALGI) Setup

This setup was designed to mimic a paddy field. The reactor had a soil base containing 5 kg soil and 10-litre water. Typically, 120 kg of urea and 75 kg of KH_2PO_4/ha are added to a paddy field. Therefore, in our reactors of surface area, 0.1 m^2, 1.2 g of urea and 0.75 g of KH_2PO_4 were added as a source of nitrogen and phosphorous, respectively. This setup also served as control when biogas slurry was used as a nutrient source.

2.3 Biogas Slurry (SL) Setup

Biogas slurry was collected from a biogas plant (PFR model), fed with leafy biomass typical of street sweepings/garden wastes at Centre for Sustainable Technologies, IISc, Bangalore. The particles in biogas slurry were allowed to settle and a 1:10 dilution of the supernatant was carried out, to avoid interference of suspended particles and for penetration of sunlight. This diluted biogas slurry was used as the culture media in two setups (1) with soil base and (2) without soil base (SL and ALGI-SL, respectively).

2.4 Paddy Field with Biogas Slurry (ALGI-SL)

This setup was similar to paddy field setup mentioned above, and the only difference was that the addition of urea and KH_2PO_4 was replaced with the slurry as growth media.

2.5 Species Consortia

The inoculum was taken from a working stock culture containing *Chlorella* sp. It was completely mixed and added to the reactors (~10^6 cells/ml, 1 L inoculum vol). The experiment was carried out for a period of 17 days with an average 9 h light period. The evaporated water was replaced with an equal amount of deionized water in the reactors. Sampling was carried out at 12 noon every day

2.6 Biomass Estimation

A sample volume of 10 ml was centrifuged at 5000 rpm for 10 min from all the setups. The pellets were washed with deionised water and dried at 60 °C [17, 18].

The following equation was used to calculate biomass productivity:

Biomass productivity (g/L/d) = $(N - N_0)/\mathrm{T}$
where N (in g/L) is the biomass concentration at the end of the cultivation period, N_0 (in g/L) is the biomass concentration at the beginning of the cultivation period and
T is the duration of the cultivation in days.

2.7 Cell Count

Grazer and algal cell counts were determined daily by using a light microscope at 400X magnification; identification of species was carried out based on the literature [19–22]. Drop count method was used for cell counting and an average algal population in five fields was taken for counting. Each sample was taken in triplicates and the cell count mentioned is an average of these replicates.

3 Results and Discussion

3.1 Biomass and Growth Rates of Algae

The biomass productivity both in terms of dry weight and total cell count was highest in ALGI with a productivity of 5.4 g/m^2/day, followed by ALGI-SL with 3.9 g/m^2/day (Fig. 1). The productivity of SL and M was 3.3 and 2.4 g/m^2/day, respectively. The average growth rate of all algal strains was found to be highest in ALGI with a growth rate of 1.5/day. *Chlorella* showed the highest growth rate of 1.4/day in slurry-based setup. *Chlorella* is one of the best species for biodiesel production hence biogas slurry appears to be a good cultivation media.

In terms of species dynamics, *Chlorella* was predominant in all reactors initially (0–6 days) and then, it was taken over by species such as *Chlorococcum*, *Diatoms*, *Anacystis*, *Scenedesmus*, *Euglena*, *Oscillatoria* after 6 days in soil-based setups. In media- and slurry-based reactors, *Chlorella* remained dominant for a period of 13 days; the other species appeared from the 13th day onwards.

3.2 The Impact of Grazers on Algal Cultivation

Biogas plant slurry contained grazers like *Paramecium* (10^4 individuals/l) and Nematodes (9 individuals/l) before inoculation. Nematodes started disappearing when they were exposed to the aerobic condition. *Paramecium* thrived till algae reached stationary phase (day 6). We observed a steep decline in the population of *Paramecium* after the sixth day. During this stage, a new species of grazers, i.e. *Daphnia* appeared.

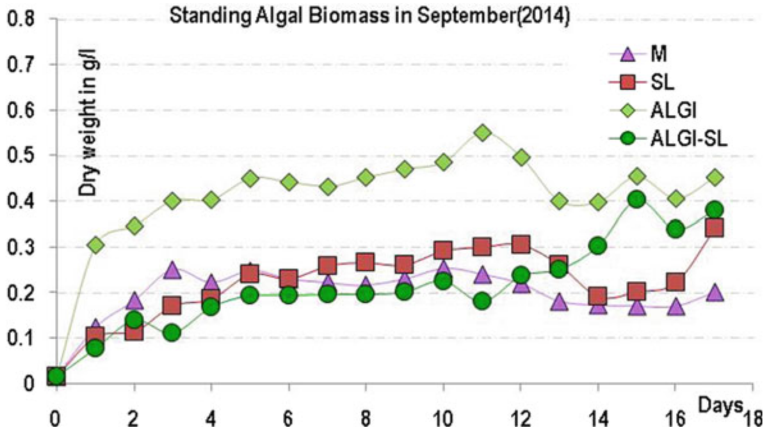


Fig. 1 Biomass yield of algae in cultivation setups

Fig. 2 *Paramecium* obseved in the setups

Fig. 3 *Daphnia* obseved in the setups

The rise in the population of *Daphnia* coincided with the decreasing population of *Paramecium* which may be attributed to their similar feed selectivity resulting in inter grazer competition. *Daphnia* persisted until the end of the experiment (Figs. 2 and 3).

The total grazer population in conventional media based setup reached a maximum of 670 individuals/l, whereas in the case of slurry-based setups, the grazer population reached a maximum of 10^6 individuals/l. *Daphnia* was the only species of grazers observed in media-based setup. In slurry-based set ups, both *Daphnia* and *Paramecium* were found, they preferred preying on *Anacystis* and *Scenedesmus* resulting in their decrease. This species specificity of grazers ensued undisturbed growth of *Chlorella* (Figs. 4 and 5).

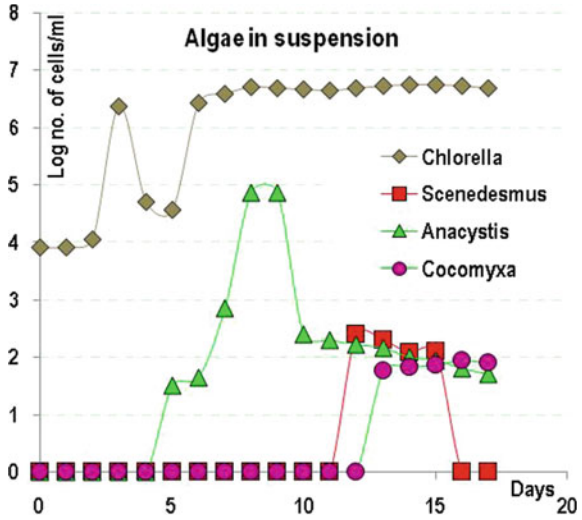


Fig. 4 Algal population in slurry-based setup

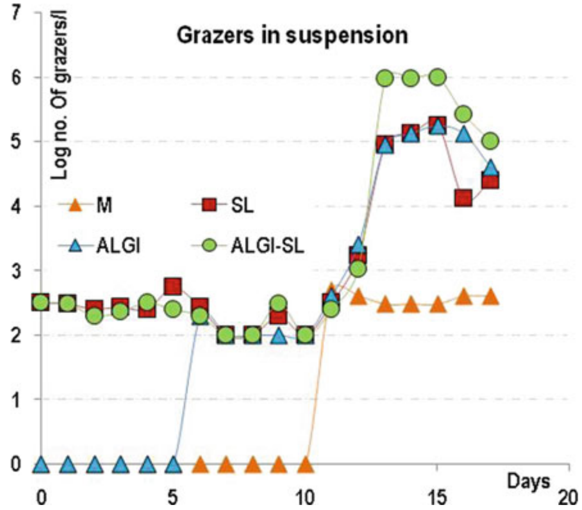


Fig. 5 Total grazer population

The biomass productivity of algae in slurry-based setups was 90% greater than that of conventional media setup. This study shows that biogas slurry can be effectively used as a substitute for conventional media as its use resulted in a better productivity of all algal species. This study also presents the possibility of using biogas slurry in paddy fields (instead of standing water).

3.3 Advanced Agriculture Setup for Future

High rate of methane and carbon dioxide emissions over the past few years have resulted in drastic climate change which needs immediate attention. This has promoted a lot of research to find effective methods to mitigate the levels of greenhouse gases responsible for rising global temperatures. CO_2 is classified as one of the most potent greenhouse gases [23]. It is important to capture and recycle CO_2 in a sustainable manner. Two approaches to this are (1) capture and recycle CO_2 and (2) reduce the use of fossil fuels.

Usage of biofuels has the potential to capture the emitted CO_2 back as organic carbon through photosynthesis.

$$2n\,CO_2 + 4n\,H_2O + \text{photons} \rightarrow 2(CH_2O)_n + 2n\,O_2 + 2n\,H_2O$$

In order to have optimum growth, algae need a large amount of CO_2 which should be supplied in the bioreactors where they are cultured. In this paper, we have tried to propose a method to meet this need of algae in a sustainable manner along with effective utilization of wastes from biogas plants. CO_2 and CH_4 emitted from biogas plant can be directed to bioreactors containing algae grown in biogas slurry as a growth medium. Algae capture CO_2 and use it for its growth, metabolism and various functions. As methane has a low solubility in water, it is collected in another chamber with only a small content of carbon dioxide. For every m^3 of biogas (1.2 kg), about 0.786 kg of CO_2 is removed and can be added to the C-footprint calculations for the process. Thus, CO_2 which is otherwise released to the atmosphere is effectively captured by algae which act as a carbon sink. This method suggests effective separation and collection of methane gas. Therefore, biogas slurry and CO_2, which are wastes generated by biogas plant are utilized effectively in an environment-friendly manner. The cultivated algae after solar drying can be used for lipid extraction process. The microalgal biomass after lipid extraction can be sent to an anaerobic digester to produce biogas (Figs. 6 and 7).

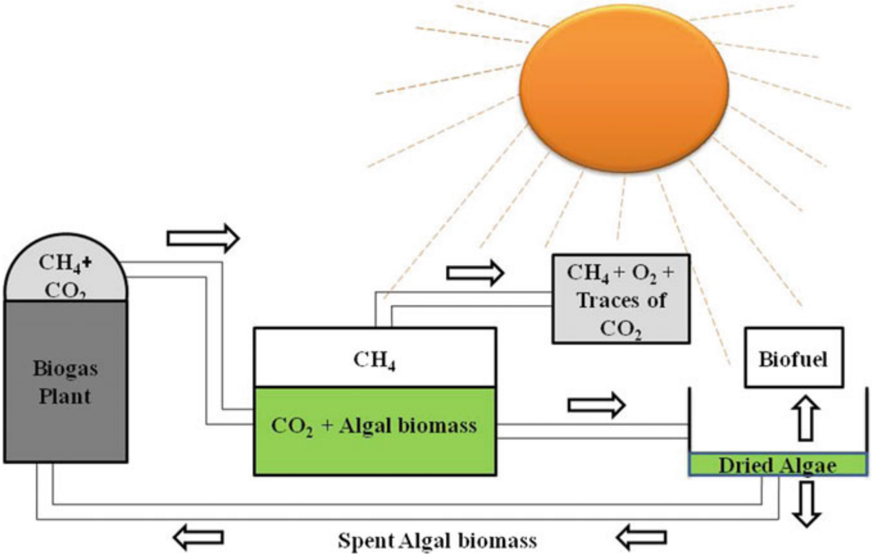


Fig. 6 Schematic representation of potential algal biomass

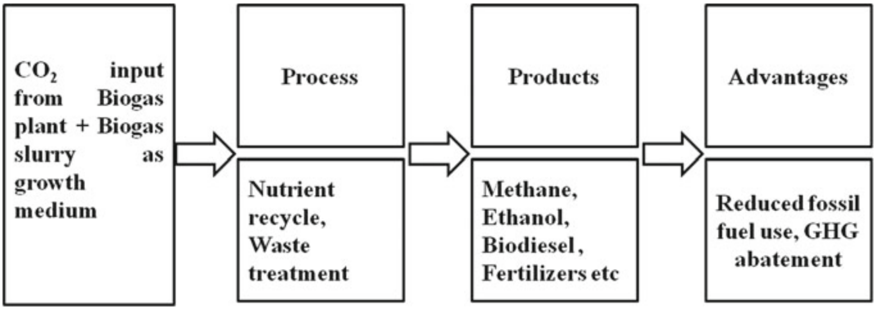


Fig. 7 Process flow diagram for sustainable biofuel production

4 Conclusion and Future Work

Digestion of MSW for biogas releases a lot of wastewater for which there is at present no sustainable recovery options. Capturing the large dissolved and colloidal nutrient pool from the digested slurry by algal cultivation offers a good route to becoming more sustainable. Second, enrichment of the algal cultivation media by bubbling biogas through it first, reduces the CO_2 content of biogas and second reduces the C-footprint of the overall process and is, therefore, a double benefit in MSW digested slurry management and greatly avoids ground and surface water contamination that is currently the problem of large-scale MSW management options. Although this research indicates the additional benefit of control of grazers that tend to devour algae when it reaches harvestable proportions in MSW digestates, there is a lot of research necessary by way of improving the overall processes and conversion efficiencies.

References

1. Hill J, Nelson E, Tilman D, Polasky S, Tiffany D (2006) Environmental, economic and energetic costs and benefits of biodiesel and ethanol biofuels. Proc Natl Acad Sci USA 103(30):11206–11210
2. Moore A (2008) Biofuels are dead: long live biofuels?—Part one. New Biotechnol 25(1):6–12
3. Chisti Y (2007) Biodiesel from microalgae. Biotechnol Adv 25(3):294–306
4. Lundquist TJ, Woertz IC, Quinn TWN, Benemann RJ (2010) A realistic technology and engineering assessment of algae biofuel. Biofuel production. Energy Biosci Inst 1–178
5. Waltz E (2009) Biotech's green gold? Nat Biotechnol 27:15–18
6. Chanakya HN, Mahapatra D, Sarada MR, Abitha R (2013) Algal biofuel and mitigation potential in India. Mitig Adapt Strat Glob Clim Change 18(1):133–136
7. Chanakya HN, Malayil S Vijayalakshmi C (2015) Cultivation of *Pleuritus* spp. on a combination of anaerobically digested plant material and various agro residues. Energy Sustain. Dev. 27:84–92
8. Chanakya HN, Malayil S (2012) Anaerobic retting of banana and areca nut wastes in a plug flow digester for recovery of fiber, biogas and compost. Energy Sustain Dev 27:231–235
9. Chanakya HN, Malayil S (2012) Anaerobic digestion for bioenergy from agro residues and other solid wastes-an overview of science, technology and sustainability. J Indian Inst Sci 1(92):111–143
10. Abitha R, Chanakya HN, Aman A, Shwetha U (2015) Biogas slurry—an alternative growth media for algae cultivation in agriculture systems with simultaneous reduction algal predation. Carbon Sci Technol 7(2):99–108
11. Anderson MJ, Underwood AJ (1997) Effects of gastropod grazers on recruitment and succession of an estuarine assemblage: a multivariate and univariate approach. Oecologia 109:442–453
12. Lehman JT, Sandgren CD (1985) Species specific rates of growth and grazing loss among freshwater algae. Limnol Oceanogr 30:9046
13. Shirvani T, Yan XY, Inderwildi OR, Edwards PP, King DA (2011) Life cycle energy and green house gas analysis for algae-derived biodiesel. Energy Environ Sci 4:3773–3778
14. Khan SA, Hussain MZ, Prasad S, Bannerjee UC (2009) Prospects of biodiesel production from microalgae in India. Renew Sustain Energy Rev 13(9):2361–2372
15. Uggetti E, Sialve B, Trably E, Steyer JP (2014) Integrating microalgae production with anaerobic digestion a biorefinery approach. Biofuels, Bioprod Biorefin 8(4):516–529
16. Kanz T, Bold HC (1969) Physiological studies, morphological and taxonomical investigation of Nostoc and Anabaena in culture. University of Texas, Austin (TX), p 6924
17. Rao AR, Dayananda C, Sarada R, Shamala TR, Ravishankar GA (2007) Effect of salinity on the on the growth of green alga *Botrycoccus braunii* and its constituents. Biores Technol 98:560–564
18. Sarada R, Bhattacharya S, Ravishankar GA (2002) Optimization of culture conditions for growth of the green alga *Haematococcus pluvialis*. World J Microbiol Biotechnol
19. Lehman JT, Sandgren CD (1985) Species specific rates of growth and grazing loss among freshwater algae. Limnol Oceanogr 30:9046
20. Hessen DO, Donk EV (1993) Morphological changes in *Scenedesmus* sp induced by substances released Daphnia. Arch Hydrobiol 127:129–140
21. Bergquist AM, Carpenter SR (1986) Limnetic herbivory: effects on phytoplankton population and primary productivity. Ecology 67:1351–1630

22. Agrawal AA (1998) Algal defense, grazers, and their interactions in aquatic trophic cascades. Acta Oecol 19(4):33l–337
23. Harrington L, Foster R (1999) Australian residential building sector greenhouse gas emissions 1990–2010. Final Report, Energy Efficient Strategies, Australian Greenhouse Office

Pyrolysis of Garden Waste: Comparative Study of *Leucaena leucocephala* (Subabul Leaves) and *Azadirachta indica* (Neem Leaves) Wastes

K. Srilatha, D. Bhagawan and V. Himabindu

1 Introduction

Biomass has been considered as a potential and renewable energy that can be used to produce a variety of chemicals and materials [10, 16]. The benefits of biomass over conventional fossil fuels are their low sulfur and nitrogen contents and no net CO_2 emissions to the atmosphere [10, 31]. Biomass resources cover a wide range of materials like agriculture wastes, energy crops, organic wastes, and forest residues. Agriculture waste, a readily available biomass, is produced annually worldwide and is massively underutilized [35].

The large amount of agriculture waste is presently utilized as a raw material for paper industry or as animal feed sources in developing countries. Then mostly and subsequently the collection and disposal of these waste are becoming more difficult and expensive, it is left unused as a waste material or simply burned in the fields, thereby creating significant environmental problems.

The conversion techniques may be physical, biological, chemical, or thermal to give solid, liquid, and gas products. Among various conversion techniques, biomass pyrolysis becomes attractive as it offers a flexible way of agricultural biomass resources into bio-oil [14] as pyrolysis is one of the few biofuel technologies that can handle a range of biomass feedstocks (agri-residues, forest residues, energy crops, municipal solid wastes), and is an attractive option for expanding the possibilities of using less desirable biomass.

Pyrolysis is a thermochemical decomposition of biomass at elevated temperature in the absence of oxygen [12, 25]. Bio-oil is the main pyrolysis product, char and gases are the by-products. Bio-oil from fast pyrolysis can be combusted in industrial boilers/furnaces [21] or upgraded into ethanol and biodiesel to be used with existing

---

K. Srilatha (✉) · D. Bhagawan · V. Himabindu
Centre for Alternative Energy Options, Centre for Environment,
Jawaharlal Nehru Technological University Hyderabad, Kukatpally, Telangana, India
e-mail: latha.hasini@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_28

infrastructure and vehicle technologies [22, 24] to replace fossil fuels [6]. Biochar can be used for water purification, power generation [19, 26], and as a soil amendment to improve soil quality and sequester carbon [30, 36]. Furthermore, small pyrolysis plants are compatible with the existing agriculture and forestry infrastructure, providing significant flexibility for the feedstock [22]. Consequently, there is increasing attention on furthering the applications of this technology.

The techno-economic analysis of biomass pyrolysis is very important for the economic feasibility of converting agricultural biomass to bio-oil by using pyrolysis [3, 4, 27, 28]. There existed many researches on the techno-economic analysis of biomass pyrolysis in the literature. Although several studies have already discussed pyrolysis technologies [2, 11, 33], usage of pyrolysis products [13, 22], upgrading of pyrolysis products [2, 37], co-pyrolysis [1], and catalytic pyrolysis process [18], there are no studies highlighting either recent technological advances or economic and environmental performance of this technology. Therefore, we must focus on synthesis of technical challenges, recent developments, and opportunities in pyrolysis technologies, as well as their potential as a viable environmental and economic alternative to fossil fuels. Therefore, the aim of the present work is to evaluate the economic feasibility of a biofuel plant to produce bio-oil using pyrolysis in (JNTUH) India. The results will be helpful for the industrial application of biomass pyrolysis. In the present study, pyrolysis studies on *L. leucocephala* (Subabul leaves) and *A. indica* (Neem leaves) were carried out in a fixed bed reactor at different reaction times of 2 and 3 h at a reaction temperature of 650 °C using Liquified Petroleum Gas (LPG).

2 Materials and Methodology

2.1 Materials

Leucaena leucocephala and *A. indica* leaves were used in this study collected from JNTUH premises, Hyderabad, Telangana, India. The dried samples were used for the pyrolysis experiment.

2.2 Experimental Procedure

Pyrolysis of *L. leucocephala* and *A. indica* were performed in a indigenously designed fixed bed reactor (Fig. 1) under atmospheric pressure using LPG (Liquified Petroleum Gas) at different reaction time of 2 and 3 h at reaction temperature of 650 °C. 250 g of dry biomass of *L. leucocephala* and *A. indica* samples were loaded into the reactor and heat was given to the system for a required time. Once the reaction time is over, the reactor is cooled and then bio-oil and biochar collected from the system. The

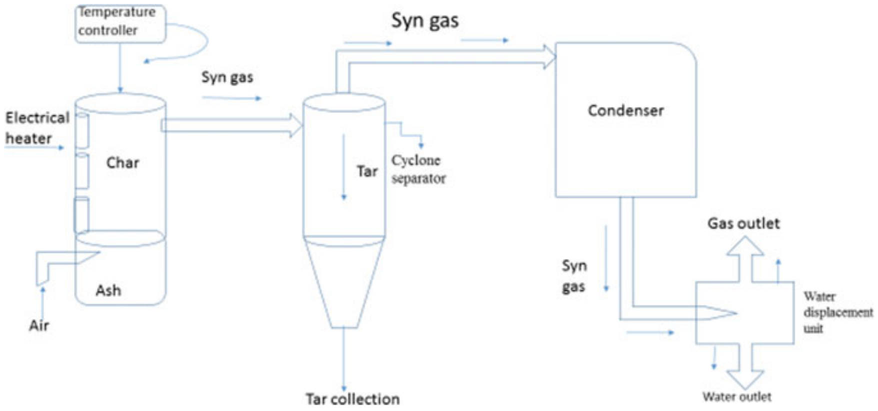


Fig. 1 Schematic view of pyrolysis unit

gas samples were collected in the Tedlar bags and analyzed by GC. In this pyrolysis technique, the biomass has been converted into bio-oil, biochar, and gas products.

The following equations were used to calculate the yield of bio-oil, biochar, and gas [23].

$$\begin{aligned}\text{Yield of bio - oil (wt\%)} = {} & \text{(weight of measuring cylinder with bio - oil)} \\ & -\text{(weight of empty measuring cylinder)}/\text{(weight of feed)} \times 100\end{aligned}$$

$$\begin{aligned}\text{Yield of bio - char (wt\%)} = {} & \text{(weight of reactor after reaction)} \\ & -\text{(weight of empty reactor)}/\text{(weight of feed)} \times 100\end{aligned}$$

$$\begin{aligned}\text{Yield of gas(wt\%)} &= 100\% \ - \text{(Yield of bio - oil (wt\%) + Yield of bio - char(wt\%))} \\ \text{Conversion(\%)} &= 100\% \ - \text{(Yield of bio - char(wt\%))}\end{aligned}$$

2.3 *Characterization Methods*

The proximate analysis (moisture content, ash content, volatile matter and fixed carbon) of sample was analyzed before and after the experiment according to ASTM. The calorific value was analyzed using bomb calorimeter. The elemental composition of C, H, N, and S was analyzed using CHNS analyzer. The FTIR analysis was analyzed using FTIR analyzer over a range of 400–4000 cm^{-1} with the sample powder diluted in KBr. The gas samples obtained from the experiment were analyzed using Agilent Gas Chromatography. The organic fraction of the bio-oil was analyzed

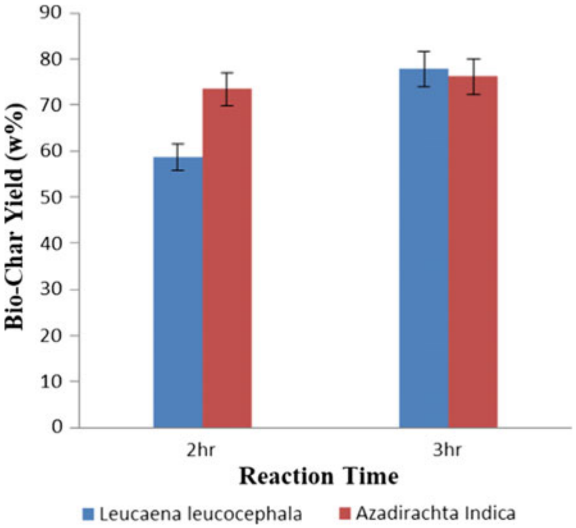


Fig. 2 Yield of biochar from *Leucaena leucocephala* and *Azadirachta indica* at constant temperature of 650 °C. *Experimental conditions* Quantity of biomass = 250 g, reaction temperature = 650 °C and reaction time = 2 and 3 h

using Gas Chromatography-Mass Spectrometry (Agilent GCMS). The carrier gas was He and column flow rate of 1 ml/min. A DB-5MS column (30 m × 0.25 mm × 0.25 μm) was used for the separation. Compounds were identified by the library of mass spectra.

3 Results and Discussions

3.1 Effect of Reaction Time

The *L. leucocephala* and *A. indica* samples were performed in a fixed bed pyrolysis unit with a two different reaction time (2 and 3 h) at 650 °C reaction temperature using LPG. The yields of biochar, bio-oil, and gas yield of both *L. leucocephala* and *A. indica* samples were shown in Figs. 2, 3 and 4.

From Figs. 2, 3 and 4, it was observed that for *L. leucocephala*, 2 h of reaction time 589 wt% of biochar yield; 19 wt% of bio-oil yield and 23 wt% of gas yield were observed and for the 3 h of reaction time 78 wt% of biochar yield; 19 wt% of bio-oil yield and 3 wt% of gas yield and for *A. indica* 2 h of reaction time 73 wt% of biochar yield; 13 wt% of bio-oil yield and 14 wt% of gas yield were observed and for the 3 h of reaction time 76 wt% of biochar yield; 21 wt% of bio-oil yield and 3 wt% of gas yield were observed.

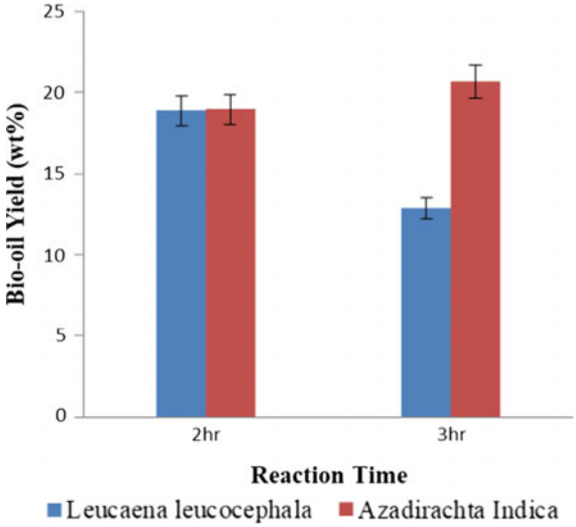


Fig. 3 Yield of bio-oil from *Leucaena leucocephala* and *Azadirachta indica* at constant temperature of 650 °C. *Experimental conditions* Quantity of biomass = 250 g, Reaction temperature = 650 °C and Reaction time = 2 and 3 h

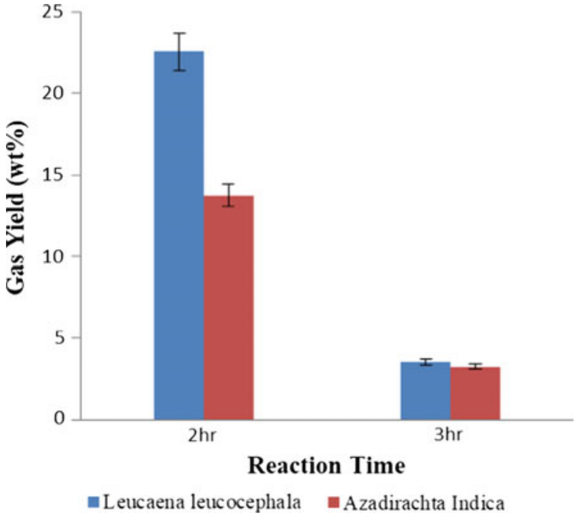


Fig. 4 Yield of Gas from *Leucaena leucocephala* and *Azadirachta indica* at constant temperature of 650 °C. *Experimental Conditions* Quantity of biomass = 250 g, reaction temperature = 650 °C and reaction time = 2 and 3 h

3.2 Characterization Methods

3.2.1 Proximate Analysis

The proximate analyses [the Moisture Content (MC), Ash Content (AC), Volatile Matter (VM), Fixed carbon content(FC)] of both *L. leucocephala* and *A. indica* samples were analyzed according to standard ASTM tests [5] and were shown in Table 1.

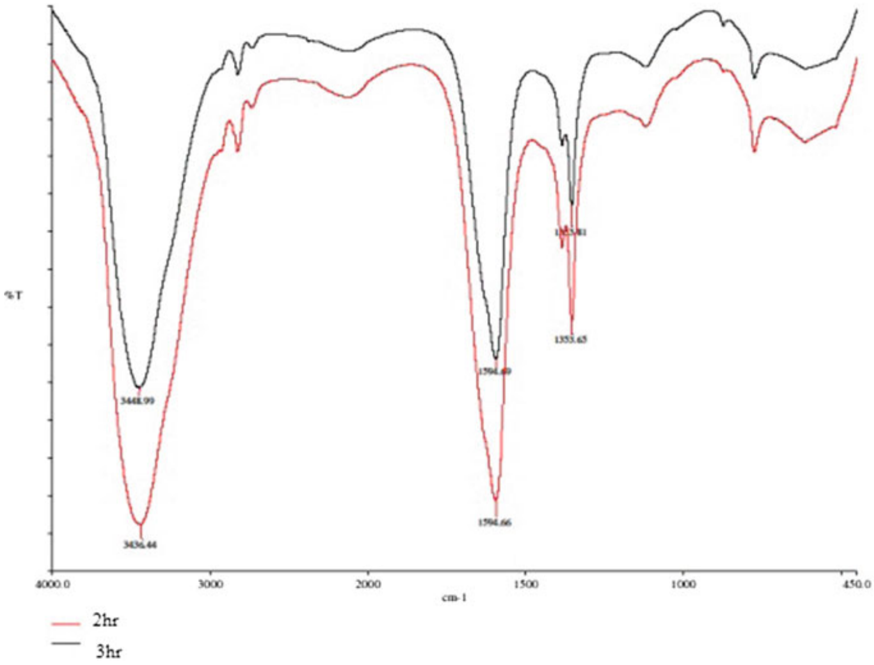


Fig. 5 FTIR spectra of *Leucaena leucocephala* (Subabul leaves)

Before the reaction *L. leucocephala* have a high fixed carbon as 88 wt% with 1 wt% moisture content, 5 wt% ash content and 6 wt% volatile matter and after reaction, the moisture content has been decreased to 0.4 wt% for 2 h and 0.1 wt% for 3 h of reaction; ash content has been increased to 36 wt% for 2 h and 39 wt% for 3 h of reaction; and volatile matter has been decreased to 38.6 wt% for 2 h and 24.9 wt% for 3 h of reaction and for *A. indica*, 84 % with 4 wt% moisture content, 4 wt% ash content and 7 wt% volatile matter and after reaction, the moisture content has been decreased to 0.5 wt% for 2 h and 2 wt% for 3 h of reaction; ash content has been increased to 1.5 wt% for 2 h and 22 wt% for 3 h of reaction; and volatile matter has been decreased to 76 wt% for 2 h and 46 wt% for 3 h of reaction.

With increasing the temperature, ash content and volatile matter increased with decreasing the moisture content, fixed carbon, and calorific value.

3.2.2 Ultimate (CHNS) Analysis

The elements C, H, N, and S were analyzed for both *L. leucocephala* and *A. indica* before and after reaction in a CHNS analyzer and were shown in Table 2.

3.2.3 Determination of Calorific Value

The calorific values of *L. leucocephala* and *A. indica* of biochar were determined by using bomb calorimeter and were shown in Table 3.

Before the reaction *L. leucocephala* have 3949.8 cal/g and after 2 h reaction of time, it has been decreased to 3886.6 cal/g for 2 h and 3182.6 cal/g for 3 h of reaction time and in case of *A. indica*, it followed the reverse trend. The significant calorific values of *L. leucocephala* showed that these locally available renewable resources can potentially be converted to a substantial amount of bio-oil, biochar, and gas products from effective pyrolysis technique.

3.2.4 FTIR Analysis

The FTIR analysis of *L. leucocephala* and *A. indica* was determined by FTIR analyzer. The FTIR spectra of *L. leucocephala*) were shown in Fig. 5 and that of *A. indica* were shown in Fig. 6. For *L. leucocephala* of 2 h of reaction time, the peak at 3436.44 cm^{-1} is corresponds to stretching vibrations is originated due to stretching of O–H groups for intramolecular hydrogen bond. The peak at 1594.66 cm^{-1} is corresponds to stretching vibrations is originated due to aromatic skeleton vibrations involving both C–C stretching. The peak at 1353.65 cm^{-1} is corresponds to stretch-

Table 1 Proximate analysis

S. No.	Samples	Reaction time (h)	Moisture content (wt%)	Ash content (wt%)	Volatile matter (wt%)	Fixed Carbon (wt%) FC = 100 − (MC + VM + AC)
1	Initial *Leucaena leucocephala*		1	5	6	88
2	*Leucaena leucocephala*	2	0.4	36	25	38.6
3	*Leucaena leucocephala*	3	0.1	39	36	24.9
4	Initial *Azadirachta indica*		4	4	7	84
5	*Azadirachta indica*	2	0.5	1.5	14	76
6	*Azadirachta indica*	3	2	22	30	46

Table 2 CHNS analysis

S. No.	Sample name	C (wt%)	H (wt%)	N (wt%)	S (wt%)
1	*Leucaena leucocephala*-before reaction	60.43	2.72	3.11	0.22
2	*Leucaena leucocephala*-after reaction	50.01	2.69	2.28	0.11
3	*Azadirachta indica*-before reaction	61.47	1.94	2.23	0.12
4	*Azadirachta indica*-after reaction	55.04	4.67	2.89	0.15

Table 3 Calorific value

S. No.	Samples	Calorific value (Cal/g)
1	Initial *Leucaena leucocephala*	3949.8
2	*Leucaena leucocephala*—2 h of reaction time	3886.6
3	*Leucaena leucocephala*—3 h of reaction time	3182.6
4	Initial *Azadirachta indica*	2654.6
5	*Azadirachta indica*—2 h of reaction time	3754.6
6	*Azadirachta indica*—3 h of reaction time	4766.6

ing vibrations is originated due to the stretching of C–H stretching, CH_2 wagging, C = O, C–O bonds of acetyl esters, and C–O stretching, respectively.

For *L. leucocephala* of 3 h of reaction time, the peak at 3448.44 cm^{-1} is corresponds to stretching vibrations is originated due to stretching of O–H groups for intramolecular hydrogen bond. The peak at 1549.69 cm^{-1} is corresponds to stretching vibrations is originated due to aromatic skeleton vibrations involving both C–C stretching. The peak at 1353.81 cm^{-1} is corresponds to stretching vibrations is originated due to stretching of C–H stretching, CH_2 wagging, C = O, C–O bonds of acetyl esters, and C–O stretching, respectively.

For *A. indica* of 2 h of reaction time, the peak at 3436.44 cm^{-1} is corresponds to stretching vibrations is originated due to stretching of O-H groups for intramolecular hydrogen bond. The peak at 1595.04 cm^{-1} is corresponds to stretching vibrations is originated due to aromatic skeleton vibrations involving both C–C stretching. The peak at 1353.08 cm^{-1} is corresponds to stretching vibrations is originated due to

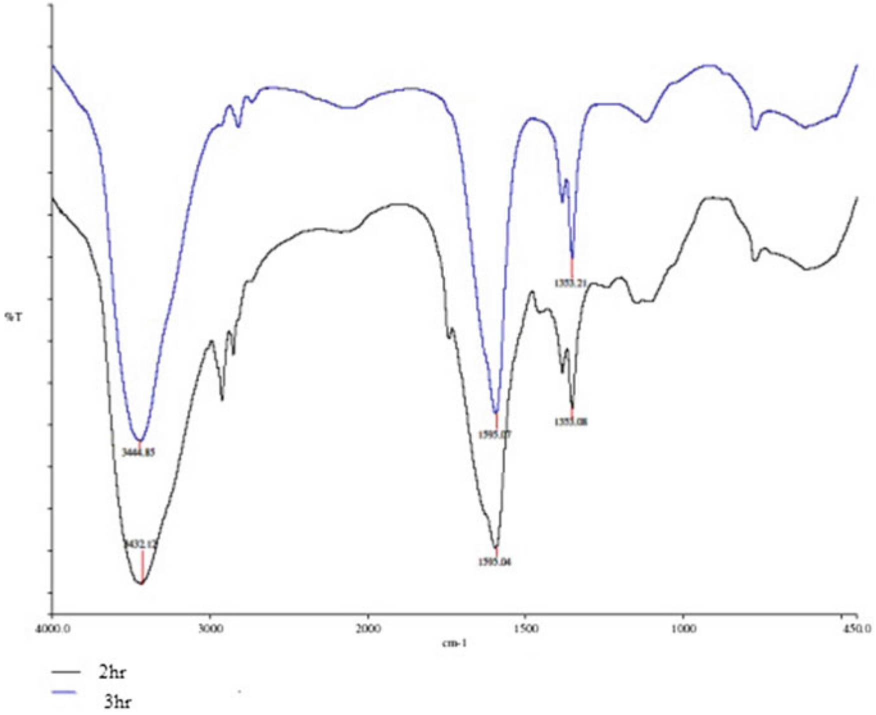


Fig. 6 FTIR spectrum of *Azadirachta indica* (Neem leaves)

stretching of C–H stretching, CH_2 wagging, C = O, C–O bonds of acetyl esters, and C–O stretching, respectively.

For *A. indica* of 3 h of reaction time, the peak at 3444.85 cm^{-1} is corresponds to stretching vibrations is originated due to stretching of O–H groups for intramolecular hydrogen bond. The peak at 1595.07 cm^{-1} is corresponds to stretching vibrations is originated due to aromatic skeleton vibrations involving both C–C stretching. The peak at 1353.21 cm^{-1} is corresponds to stretching vibrations is originated due to stretching of C–H stretching, CH_2 wagging, C = O, C–O bonds of acetyl esters, and C–O stretching, respectively.

The presence of OH group in both *L. leucocephala* and *A. indica* samples might be attributed to the dehydration of biomass, and at the same time, a large amount of moisture was released during the pyrolysis reaction [7, 17, 40]. The presence of C–H group represents the CH_4 and C_2 hydrocarbon in the gas products obtained during the pyrolysis reaction [17, 38]. The FTIR spectrum of pyrolysis obtained in the present study is matched with the previous literature [15].

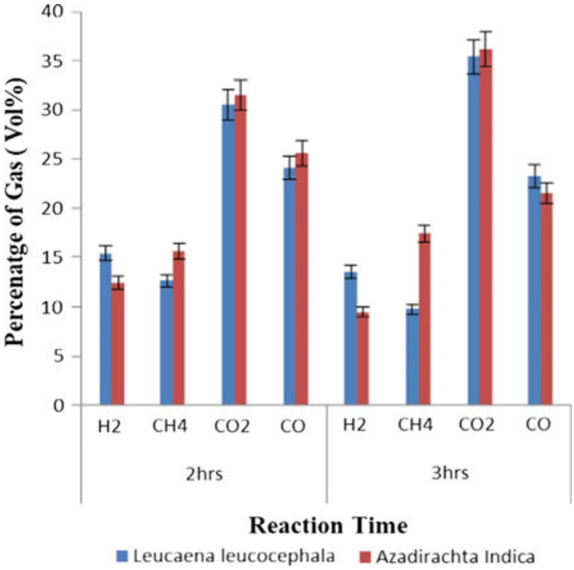


Fig. 7 Yield of gas from *Leucaena leucocephala* and *Azadirachta indica* at constant temperature of 650 °C. *Experimental conditions* Quantity of biomass = 250 g, reaction temperature = 650°C and reaction time = 2 and 3 h

3.2.5 Gas Chromatography (GC) Analysis

The gas samples were collected in Teddlar^{TM} bags during the pyrolysis reaction for both *L. leucocephala* and *A. indica* samples and analyzed using Agilent Gas Chromatography (GC) and gases obtained were shown in Table 4 and pictorial representation was shown in Fig. 7. The calibrated data of hydrogen, carbon dioxide, carbon monoxide, and methane were obtained using the standards—hydrogen and methane (99.99 volume%, BOC Ltd., India).

With increasing reaction time, the hydrogen, methane, carbon monoxide, and carbon dioxide will be decreased.

The gaseous products obtained during pyrolysis mainly consist of carbon dioxide (CO_2) and carbon monoxide (CO) due to the decarbonylation and decarboxylation reactions occurring during pyrolysis in inert (nitrogen) atmosphere [23, 39]. The other gases like methane (CH_4) and hydrogen (H_2) are formed during the pyrolysis reaction.

3.2.6 GCMS Analysis

GCMS was applied to identify the organic compounds obtained from the bio-oil, which was obtained from both *L. leucocephala* and *A. indica* samples. Identification of the GCMS peaks in most cases was based on a comparison with spectra from the NIST 98 spectrum library. The peaks obtained from the GCMS analysis were shown in Table 5.

Table 4 Gases obtained during pyrolysis

S. No.	Sample name	Reaction time							
		2 h				3 h			
		H_2 (vol.%)	CH_4 (vol.%)	CO_2 (vol.%)	CO (vol.%)	H_2 (vol.%)	CH_4 (vol.%)	CO_2 (vol.%)	CO (vol.%)
1	*Leucaena leucocephala*	15.4	12.6	30.5	24.1	13.5	9.8	35.4	23.2
2	*Azadirachta indica*	12.4	15.6	31.5	25.6	9.5	17.4	36.2	21.5

Table 5 Chemical compounds in bio-oil (GCMS)

S. No.	Name	Molecular weight	Molecular formula
1	2-Furan methanol	98	$C_5H_6O_2$
2	5-hydroxymethylfuran	98	$C_5H_6O_2$
3	2-Cyclopenten-1-one, 3-methyl	96	C_6H_8O
4	2,4-diethyl furan	96	C_6H_8O
5	Phenol	94	C_6H_6O
6	Phenol,2-methoxy	124	$C_7H_8O_2$
7	Piperdine-2,5-dione	113	$C_5H_7NO_2$
8	α-methyl-α-propylsuccinimide	155	$C_8H_{13}NO_2$
9	Propylphosphomiacid, fluoroanhydride, octyl ester	238	$C_{11}H_{24}FO_2P$
10	3-Quinuclidinol	127	$C_7H_{13}NO$
11	Phenol, 3-ethyl	122	$C_8H_{10}O$
12	Phenol, 2,3-dimethyl	122	$C_8H_{10}O$
13	Phenol, 2-ethyl	122	$C_8H_{10}O$
14	Phenol, 2,6-dimethoxy	154	$C_8H_{10}O_3$
15	3,5-dimethoxy-4-hydroxytoluene	168	$C_9H_{12}O_3$
16	Phenol, 4-methoxy-3-(methoxymethyl)-	168	$C_9H_{12}O_3$
17	2,5-dimethoxy benzyl alcohol	168	$C_9H_{12}O_3$
18	Pyrrolo[1,2-a]pyrazine-1,4-dione, hexahydro-3-(2-methylpropyl)-	210	$C_{11}H_{18}N_2O_2$
19	Palmitic acid	256	$C_{16}H_{32}O_2$
20	Cyclo(leucylopropyl)	210	$C_{11}H_{18}N_2O_2$

Pyrolysis bio-oil contains phenolic compounds, furans, ketones, acids, alcohols, esters, and hydrocarbons. The GCMS analysis of both *L. leucocephala* and *A. indica* samples bio-oil obtained from present study shows that its composition is similar to the previous literature by Wang and Guo etc. [9, 20, 29, 34]. Thus, bio-oil is a complex mixture with a number of chemical compounds. Furfural and phenolic compounds are the main chemical compounds in the bio-oil of biomass [8, 15, 32].

The bio-oil produced during pyrolysis is highly oxygenated and requires upgradation step for use as a fuel [23].

4 Conclusion

In this study, the pyrolysis of *L. leucocephala* and *A. indica* samples experiments was performed in a fixed bed reactor for the conversion of waste to energy. The bio-oil obtained from the pyrolysis consists mainly of furfural and phenolic compounds which are the main compounds of bio-oil and the obtained bio-oil after upgradation can be used as a fuel. The biochar obtained during pyrolysis can be used for the soil amendment and gaseous products can be used as a fuel in industries for chimneys.

Acknowledgements The authors would like to thank TEQIP-II for sponsoring funds for providing funds to Pyrolysis unit.

References

1. Abnisa F, Daud WMAW (2014) A review on co-pyrolysis of biomass: an optional technique to obtain a high-grade pyrolysis oil. Energy Convers Manag 87:71–85
2. Ahmad M, Rajapaksha AU, Lim JE, Zhang M, Bolan N, Mohan D et al (2014) Biochar as a sorbent for contaminant management in soil and water: a review. Chemosphere 99:19–33
3. Anex RP, Aden A, Kazi FK, Fortman J, Swanson RM, Wright MM et al (2010) Techno economic comparison of biomass-to-transportation fuels via pyrolysis, gasification, and biochemical pathways. Fuel 89:S29–S35
4. Badger P, Badger S, Puettmann M, Steele P, Cooper J (2010) Techno-economic analysis: preliminary assessment of pyrolysis oil production costs and material energy balance associated with a transportable fast pyrolysis system. Bio-Resources 6:34–47
5. Basu P (2010) Biomass gasification and pyrolysis: practical design and theory. Elsevier, MA, US
6. Biederman LA, Harpole WS (2013) Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis. GCB Bioenergy 5:202–214
7. Bilba K, Ouensanga A (1996) Fourier transform infrared spectroscopy study of thermal degradation of sugar cane baggase. J Anal Appl Pyrol 38(1–2):61–73
8. Biswas B, Pandey N, Bishit Y, Singh R, Kumar J, Bhasker T (2017) Pyrolysis of agriculture biomass residues: comparative study of corn, cob, wheat straw, rice straw and rice husk. Bioresource Technology
9. Boucher ME, Chaala A, Roy C (1998) Biomass Bioenergy 14 (2):103–113
10. Bridgewater A, Grassi G (1991) Biomass pyrolysis liquids upgrading and utilisation. Elsevier Applied Science, England
11. Bridgwater AV (2003) Renewable fuels and chemicals by thermal processing of biomass. Chem Eng J 91:87–102
12. Bridgwater T (2006) Biomass for energy. J Sci Food Agric 86:1755–1768
13. Bridgwater AV (2012) Review of fast pyrolysis of biomass and product upgrading. Biomass Bioenergy 38:68–94
14. Bridgwater A, Peacocke G (2000) Fast pyrolysis processes for biomass. Renew Sustain Energy Rev 4:1–73
15. Chen TJ, Wu C, Liu RH, Fei WT, Liu SY (2011) Effect of hot vapor filteration on the characterization of bio-oil from rice husks with fast pyrolysis in a fluidized bed reactor. Biresour Technol 102:6178–6185
16. Chum HL, Overend RP (2001) Biomass and renewable fuels. Fuel Process Technol 71:187–195
17. Chutia Rahul Singh, Kataki Rupam, Bhasker Thallada (2014) Charcterization of liquid and solid product from pyrolysis of Pongamia glabra deoiled cake. Biores Technol 165:336–342

18. Dickerson T, Soria J (2013) Catalytic fast pyrolysis: a review. Energies 6:514–538
19. Downie A, Munroe P, Cowie A, Van Zwieten L, Lau BM (2012) Biochar as a geoengineering climate solution: hazard identification and risk management. Crit Rev Environ Sci Technol 42:225–250
20. Guo Y, Wang Y, Wei F et al (2001) Chem Ind Eng Progr 18:7–13
21. Han J, Elgowainy A, Dunn JB, Wang MQ (2013) Life cycle analysis of fuel production from fast pyrolysis of biomass. Bioresour Technol 133:421–428
22. Kanaujia PK, Sharma YK, Garg MO, Tripathi D, Singh R (2014) Review of analytical strategies in the production and upgrading of bio-oils derived from lignocellulosic biomass. J Anal Appl Pyrolysis 105:55–74
23. Krishna BB, Biswas B, Kumar J, Singh R, Bhasker T (2016) Role of reaction temperature on pyrolysis of cotton residue. Waste Biomass Valor 7:71–78
24. Laird DA, Brown RC, Amonette JE, Lehmann J (2009) Review of the pyrolysis platform for coproducing bio-oil and biochar. Biofuels, Bioprod Biorefin 3:547–562
25. Lehto J, Oasmaa A, Solantausta Y, Kytö M, Chiaramonti D (2014) Review of fuel oil quality and combustion of fast pyrolysis bio-oils from lignocellulosic biomass. Appl Energy 116:178–190
26. Mahmood AS, Brammer JG, Hornung A, Steele A, Poulston S (2013) The intermediate pyrolysis and catalytic steam reforming of Brewers spent grain. J Anal Appl Pyrolysis 103:328–342
27. Meier D, van de Beld B, Bridgwater AV, Elliott DC, Oasmaa A, Preto F (2013) State-of-the-art of fast pyrolysis in IEA bioenergy member countries. Renew Sustain Energy Rev 20:619–641
28. Meyer PA, Snowden-Swan LJ, Rappe KG, Jones SB, Westover TL, Cafferty KG (2016) Field-to-fuel performance testing of lignocellulosic feedstocks for fast pyrolysis and upgrading: techno-economic analysis and greenhouse gas life cycle analysis. Energy Fuels. https://doi.org/10.1021/acs.energyfuels.6b01643
29. Peng W.M, Wu Q.Y (2000) New Energy Sour. 22 (11): 39–44
30. Popp J, Lakner Z, Harangi-Rakos M, Fari M (2014) The effect of bioenergy expansion: food, energy, and environment. Renew Sustain Energy Rev 32:559–578
31. Probstein RF, Hicks RE (1982) Synthetic fuels. McGraw-Hill Book Company, New York
32. Tsai W, Lee M, Chang Y (2007) Fast pyrolysis of rice husk: product yields and copositions. Bioresour Technol 98:22–28
33. Vamvuka D (2011) Bio-oil, solid and gaseous biofuels from biomass pyrolysis processes—an overview. Int J Energy Res 35:835–862
34. Wang SR, Luo ZY, Tan H et al (2004) J Eng Thermophys 25(6):1049–1052
35. Williams PT, Nugranad N (2000) Comparison of products from the pyrolysis and catalytic pyrolysis of rice husks. Energy 25:498–513
36. Wright MM (2008) Techno-economic evaluations of biofuel technologies. Iowa State University
37. Xiu S, Shahbazi A (2012) Bio-oil production and upgrading research: a review. Renew Sustain Energy Rev 16:4406–4414
38. Yang HP, Yan R, Chen HP, Lee DH, Liang DT, Zheng C (2006) Mechanism of palm oil waste pyrolysis in a packed bed. Energy Fuels 20(3):1321–1328
39. Yang HP, Yan R, Chen HP, Lee DH, Zheng CG (2007) Characteristics of hemicellulose, cellulose and lignin pyrolysis. Fuel 86(12–13):1781–1788
40. Yang H, Yan R, Chin T, Liang DT, Chen H, Zheng C (2004) Thermo gravimetric analysis-Fourier transform infrared analysis of palm oil waste pyrolysis. Energy Fuels 18(6):1814–1821

Technological Options for Biogenic Waste and Residues—Overview of Current Solutions and Developments

A. Schüch, G. Morscheck and Michael Nelles

1 Introduction

Globally, it is becoming increasingly clear that organic waste can not only cause massive environmental impacts, including climate-harming emissions by illegal dumping, burning or even untreated landfilling but also is a valuable resource for energy generation and recycling. The transition from waste disposal to a circular economy is in progress [3, 12, 49, 47, 58]. The "circular economy involves reusing, repairing, refurbishing and recycling existing materials and products to keep materials within the economy wherever possible. It is generally opposed to a traditional, linear economic model, which is based on a 'take-make-consume-throw away' pattern" [20]. In many countries, the source segregation and recycling are recognized as a chance (e.g., [13, 39]). The segregation of biowaste is mandatory for all European countries, binding the EU Waste Directive 2008/98/EC [8, 36, 37]. Despite this, the share of recycled and composted waste varies among Europe. Due to its decades of tradition, Germany is on a comparatively good level in the separate biowaste collection and recycling, although the collection rate varies widely. As high-quality recycling option for biowaste currently the biogas production combined with a post-composting is favored [37, 49, 58].

There is still unused potential available, for example, one-third percent of the technical potential of waste biomass in Germany is treated but not energetically used [10]. Worldwide, the demand for biomass will increase to meet the demand for material and energetic use [29, 53]. At the same time, the amount of biogenic waste and residues increases. Seven billion people (in 2011) produce around 1.3 billion Mg dry matter (DM) organic waste (based on 1.5 kg organic waste per person and

---

A. Schüch (✉) · G. Morscheck · M. Nelles
Department Waste and Resource Management,
University of Rostock, Rostock, Germany
e-mail: andrea.schuech@uni-rostock.de

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_29

day and 65% water content of the waste). Around one-third of this is food waste (0.51 billion Mg DM), since globally 30% of the food is wasted [53].

The proper treatment and the highest possible use of this waste streams are of particular importance because of their environmentally harmful emissions. Moreover, no competition for food and feed exists. Facing the increasing demand, the efficient use of biomass gains more attention. Especially in low-income or developing countries, biomass is used with simple technologies as energy source mainly for cooking what causes a pressure to the local forest and environment and health problems by the emissions as reported, for example, by Lohri et al. [38].

2 Management of Biodegradable Waste and Source Segregation

Despite the fact that the total waste amount in Europe came back to the level of 1995, waste management is far from a zero-waste implementation. The avoidance of waste inclusive biodegradable waste is the best option to reduce the waste amount and to save resources. That is why the prevention is on top of most preferred measurements of the European waste hierarchy.

For biodegradable waste, an adapted hierarchy of preferred options is to find (Fig. 1). Following this, the backyard or home composting has to be preferred before decentralized composting plants, followed by centralized composting and/or anaerobic digestion. This hierarchy is for sure to adapt to local conditions [14, 26, 40, 42, 54]. So at low populated regions, decentralized solutions could have a better environmental impact than centralized. Last option should be the incineration.

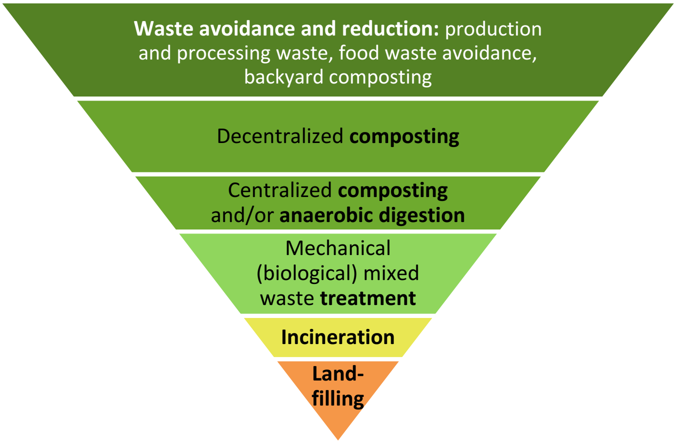


Fig. 1 Organic waste (management) hierarchy

3 Relevant Legal Framework in Europe

The DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL amending Directive 2008/98/EC on waste (WFD) is the binding law for waste in Europe, which was revised in 2018. “Biowaste” is defined as biodegradable garden and park waste, food and kitchen waste from households, restaurants, caterers and retail premises and comparable waste from food processing plants. “Biodegradable waste” is a broader definition and includes biowaste and commercial food waste, not collected as part of the MSW, forestry residues, waste from agriculture (not all residues have waste status—e.g., manure or straw), wastes from the food and beverage industry, and sewage sludge. “Biodegradable municipal waste” (BMW) includes beside the separate collected “Biowaste” also the organic fraction in the municipal residual waste (not segregated). The EU action plan for the Circular Economy formulates targets: the EU member states have to ensure that by 31 December 2023 that biowaste is either collected separately or recycled at source; by 2035, the amount of municipal waste landfilled has to be reduced to 10% or less of the total amount of municipal waste generated; EU target for recycling 65% of municipal waste by 2030.

End-of-waste (EoW) is defined by Article 6 of the WFD in the following terms: “certain specified waste shall cease to be waste [within the meaning of point (1) of Article 3[1]] when it has undergone a recovery, including recycling, operation and complies with specific criteria to be developed in accordance with the following conditions:

(a) The substance or object is commonly used for a specific purpose;
(b) A market or demand exists for such a substance or object;
(c) The substance or object fulfills the technical requirements for the specific purpose referred to in (a) and meets the existing legislation and standards applicable to products; and
(d) The use of the substance or object will not lead to overall adverse environmental or human health impacts.”

The quality of recycling products is directly influenced by the quality of source segregation. For example, good working collection accepted systems for e-waste, glass, plastics, and batteries have a positive impact on the impurity content of segregated biowaste. It should be clear that any contaminated input material should be banned from use in composting/digestion operations with the aim to obtain EoW material. Compost and digestate made from segregated biodegradable waste fulfill normally this. New technical solutions and its end products have to be designed in compliance with these criteria.

---

[1] ‘Waste’ means any substance or object which the holder discards or intends or is required to discard.

4 State-of-the-Art and Current Research of Organic Waste Treatment Technologies

Generally the state-of-the-art waste treatment options for biodegradable municipal waste not changed as shown in Fig. 1. But the waste management has to adjust the changing needs of the society and is developing from waste disposal to a circular economy.

Biogenic waste and raw materials are to be used even more efficiently in the green or bioeconomy [48]. Current research focuses on integrated biorefinery concepts [11, 21], the production of basic chemicals, specialized fibers or fillers [5, 23], biocomposites [4, 35], or chars based on biodegradable waste. The (new) combination of technologies can lead to new or better products or enhance the energy efficiency. Ding et al. [17] describe, for example, the pretreatment of food waste by hydrothermal carbonization followed by a two-stage anaerobic digestion. The aim should be to produce high-value bioproducts of the valorization [11]. In the future, energy-efficient biowaste treatment plants are not only intended to safely fulfill their disposal and recycling function, but also to supply electricity demand orientated and to link sectors such as transport and heat sector in an optimal way. Besides these new developments, traditional and proven technologies retain their importance.

4.1 Generation of Energy and Recycling Products in Combination

This concept is not new and implemented in the combination of anaerobic digestion and post-composting or in cascading bioeconomy concepts. The development continues and new technological options are investigated to enhance the efficiency, to create new products or to make the final products more attractive for the market (e.g., [3, 33]). In the field of high-quality recycling in the form of combined biogas production and subsequent production of compost, there is also room for improvement in Germany. Here, the most of the segregated biowaste is composted, but the number of combined AD and composting plants is slowly growing. The final products are biogas and compost or (separated) liquid fertilizer (digestate). Since the market price and valuable for longer transport for this digestate is low, a posttreatment could be useful. This reaches from a liquid–solid separation until the production of high-quality fertilizers as, for example, struvite. One idea is the pressing of organic waste to separate an easy and slow degradable fraction. This was already implemented for biowaste by the company Sutco in 2014 in Gescher, Germany with a throughput of 60,000 t/a fresh mass (reference list at www.sutco.de/). About two-thirds of biowaste with high percentage of food waste can be converted into an easily degradable liquid substrate by the pressing, reported by Micolucci et al. [41]. A positive energy balance of the needed treatment and energy generation can be reached. Micolucci et al. [41]

found that the energy production is nearly doubled compared to energy consumption. The solid fraction is composted and used as organic fertilizer.

In Germany, the renewable energies will focus on volatile wind and solar power. The biogas plants inclusive of the waste digestion plants are encouraged to generate energy demand oriented. Different concepts are used: the storage of biogas and CHP generation in times with higher market prices and low wind and solar power at the grid. For this, higher gas storage capacity and CHP units are necessary. One possibility to decrease the gas storage demand is the flexible biogas production by adapted feeding strategies. Several research and demonstration projects are implemented and reported (e.g., [12, 58, 2, 56]). One other option is to decouple the biogas production and the use by an upgrade to biomethane and storage and transport by the natural gas grid. Limiting are the availability of the natural gas grid and the economic feasibility for small plants (<500 kW electrical equivalent capacity). Research and development is done to find applicable upgrade solutions with high efficiency, e.g., by using membranes [43, 52].

4.2 Composting

Composting could be defined as "a process of controlled decomposition of biodegradable materials under managed conditions, which are predominantly aerobic and which allow the development of temperatures suitable for thermophilic bacteria as a result of biologically produced heat" [36].

Currently, the main part of the segregated biowaste is treated by composting. Low emissions could be reached with good plant operation and aeration of the waste. A proven, effective but space-consuming low-cost method is the vermicomposting. A huge number of research works to this are done until today. Advanced technical concepts with high throughput run closed in chambers, boxes, tunnels, drums, or windrows in halls with active aeration and biofilter for exhaust gas cleaning.

The selection of the most suitable composting technology depends strongly on the local conditions. The higher the population density the more centralized the plant should be. A comparison of home composting with centralized industrial composting was made by Martínez-Blanco et al. [40]. Main results are that the production of composters and gaseous emissions are the main responsible for the home composting impacts, whereas for centralized composting, the main contributions come from collection and transportation of organic waste, electricity consumption, disposed waste (impurities), and emissions of volatile organic compounds. Martínez-Blanco et al. [40] suggest that home composting may be an interesting alternative or complement in areas with low population density.

To use the energetic potential of biodegradable waste, the combination of anaerobic digestion and a subsequent composting step is state-of-the-art and more diverse as the single technological options.

4.3 Anaerobic Digestion

The anaerobic digestion (AD) is a process of controlled decomposition of biodegradable materials under controlled conditions under absents of oxygen. Organic waste and residues contain different fractions more or less suitable for conversion into biogas via anaerobic digestion. The so called “wet digestion” technologies are suitable for kitchen and canteen waste as well as for sludges. For waste and residues with woody compounds the dry fermentation or percolation are the state-of-the-art solutions. By continuous stirred tank reactor (CSTR), a broad range of biodegradable wastes was treated. Liquid biowaste as vinasse, molasses, and dairy waste could be treated in UASB or fixed bed reactors, which avoids the elution of microorganism. Worldwide, the number of anaerobic digestion for waste management is constantly growing for municipal and industrial waste as well as for agricultural waste [3].

Since quantity and quality of many biodegradable residues and the segregated biowaste vary with the season, co-digestion concepts could lead to a better and stable methane production and economic feasibility [28, 30, 63]. This technically and economic useful concept is limited by legal regulations when biomass with a waste status is used. The plant has to be considered as waste treatment plant with additional requirements regarding control and emissions.

To enhance the substrate utilization rate, an alkali pretreatment or posttreatment of digestate is promising. Different options for biowaste and agricultural residues are investigated by the research of Francavilla et al. [22] and Engler et al. [19].

Ongoing is the combination of AD with a biomethanation by using the CO_2 content of the biogas and addition of hydrogen (H_2) produced by surplus electricity via electrolysor (e.g., [62]). Pilots are currently implemented in Germany.

4.4 Thermal Treatment/Incineration

The thermal treatment is a state-of-the-art energy conversion technology for dry biomass as woody wastes residues, straw, or dry sewage sludge at different application scales. While the utilization of available straw is at a low level in Germany, this is well developed in Denmark. The thermal use is the most efficient in cogeneration. In developing countries, often a simple incineration for cooking or heating of wood of charcoal as open fire is common which causes environmental and health problems. For recycling of ashes, a mono-incineration is useful.

4.5 Thermochemical Conversion

Thermal conversion processes could be divided into the groups: incineration, gasification and pyrolysis and results in different products from solid to gaseous. The conversion is running under different process conditions in terms of temperature and pressure. Depending on temperature and retention time different proportions of gas, pyrolysis oil and coal are produced, as described in Gerdes [24]. An actual overview about thermochemical conversion with over 100 relevant technological variants was prepared by Quicker et al. [55].

The energy for **gasification** process is generated by partial oxidation of the fuel. As gasification fluid air or steam could be used. Advantages are: an energy-rich gas is produced, which can be utilized in a CHP process or the synthesis gas further upgraded to platform chemicals or biomass-to-liquid (BTL) fuels by means of Fischer–Tropsch synthesis. Stage of development: Until now, the synthesis to BTL or platform chemicals only working in pilot scale for high-quality woody biomass. There are research activities to gasify the organic fraction of mixed municipal solid waste for use in CHP [55].

The torrefaction is a particular type of pyrolysis where biomass is heated at oxygen exclusion and temperatures approx. 250–300 °C [55]. Volatile, lower calorific compounds, and water are evaporated. By this, the lower heating value (LHV) of the biomass is increased and the combustion characteristics improved (see Sect. 5.4 Solid biofuels). This technology is suitable for: woody biomass and lignocellulosic biowaste with approx. 50% water content. The stage of development: process in pilot phase.

Pyrolysis: biomass with water content up to 30% could be treated and heated at oxygen exclusion at a temperature of 800 °C (Pyreg with 180 kg/h) respectively 400–500 °C (Intermediate Pyrolysis with 100 kg/h) at slightly negative pressure. The retention time is 5–30 min. Products are pyrolysis gas, oil, and coal and different proportions depending on the process control [55]. Research and pilot plants treated successfully digestate, sewage sludge, slaughterhouse waste, and green waste. For example, investigations to produce carbon adsorbents using sludge from paper mill effluent treatment were done by [31] at 800 °C and a retention time of 150 min (heating rate 10 °C min^{-1}).

Hydrothermal processes are particular types of pyrolysis at elevated pressure. This technology is suitable for biomass and biowaste with high water content, e.g., sewage sludge, feces, or wet biowaste with water content of 60–80%. An overview of the different processes gives Table 1.

Currently, a lot of activities in research and development (e.g., [1, 34, 45]) up to industrial applications are running at hydrothermal carbonization (HTC). One of the main advantage for wet substrates as sewage sludge is the better drainable charcoal. Continuous processing is introduced in pilot scale up to industrial scale, e.g., a commercial HTC plant for sewage sludge in China by TerraNova Energy GmbH with 14,000 t/a in the first project phase (up to 40,000 t/a). Other companies at the market are: Artec Biotechnologie GmbH, AVA-CO_2 Schweiz AG, CS carbonSolutions Deutschland GmbH, Grenol GmbH, Ingelia, KWT Rosenkranz GmbH, SmartCarbon AG, SunCoal Industries GmbH [55].

Table 1 Process parameters for hydrothermal processes [55]

	Hydrothermal carbonization (HTC)	Hydrothermal liquefaction (HTL)	Hydrothermal gasification (HTG)	Vapothermal carbonization (VTC)
Reactant	Water, liquid	Water, liquid	Water, supercritical	Saturated steam
Temperature (°C)	170–250	250–350	600–700	180–250
Pressure	10–40 bar	50–200 bar	250–300 bar	16–42 bar
Retention time	2–16 h	10–15 min	1–5 min	3 h
Additive/catalyst	Citric acid, $FeSO_4$	Alkali carbonate, alkali hydroxide	Usually no	No
Main product	Charcoal	Phenol rich oily liquid	H_2, CO_2, CH_4	Charcoal
Product separation	Dewatering, drying	Phase separation hydrophilic—hydrophobic	Phase separation gashouse—liquid	Drying

5 Selected Bioproducts

5.1 Production of Platform Chemicals

The production of volatile fatty acids (VFAs), e.g., acetic acid, butyric acid, and propionic acid by dark fermentation is possible for a broad range of organic wastes [7, 9]. Promising results are reached by using slaughterhouse waste. The purification and extraction could be expensive. Membrane separation or extractive fermentation could be suitable solutions for the processing. Results for direct utilization of VFAs in fermented broth for biolipid production are encouraging [59].

Also, the production of lactic acid (LA) by using biodegradable waste is possible. The potential of LA and its importance as a platform chemical is well visible on the chemical market. A research showed an LA production using segregated biowaste via batch fermentation at 37 °C, in which a fermentation period of 24 h resulted in high yields of lactic acid (up to 37 g/kg). The fermentation residues were used as co-substrate in biomethane production yielding up to 618 ± 41 Nml CH_4 g/L volatile solids [18]. By using food waste (FW) for simultaneous saccharification and fermentation (SSF) and separate enzymatic hydrolysis and fermentation (SHF), an yield of 0.29 g LA/g_{FW} respectively 0.33 g LA/g_{FW} could be reached [15].

By dark fermentation, various products could be generated: acetic acid, butyric acid, propionic acid, caproic acid, lactic acid, ethanol, formic acid, and H_2 in different proportions [7, 9].

The potential restructuring of a pulp and paper process employing the sulfite process through fractionation of spent sulfite liquor (SSL) for the production of phenolic compounds as antioxidants, lignosulfonates, and succinic acid was evaluated by Koutinas et al. [35] as part of the FP7 research project BRIGIT.

Also by thermochemical conversion, the production of platform chemicals is possible, e.g., furane [70].

5.2 Biohydrogen

There is a lot of research to optimize the fermentation process to produce pure biohydrogen (H_2), e.g., by dark [7] or photofermentation. By dark fermentation, diverse organic wastes can be used and reach higher H_2 production rates than photofermentation. Organic waste as additional media components is tested by several authors with H_2 production rates between 1.16 and 36.53 ± 0.53 mmol/L medium, while the concentration of the media was between 2.5 and 10 g/L. The research of [51] is focused on the valorization of the increasing amount of waste glycerin from biodiesel production in combination with egg shells. In batch and semicontinuous tests (7.5 L volume), a maximum H_2 production rate of 41.16 ± 0.95 mmol/L could be reached [51]. Another option to produce H_2 from biodegradable waste is the production and direct utilization of volatile fatty acids (VFAs) in fermented broth [59].

5.3 Conversion to Liquid Biofuels

The use of used vegetable oil and animal fat to produce biodiesel is implemented at industrial scale and state of the art [21]. The use of biodegradable waste for alcohol production as ethanol, methanol or butanol [16] is challenging, since for a successful process a good quality with low impurities and degradation is necessary. Additionally, the seasonal variation of the composition may cause problems. Research of [61] has shown that decentralized level for the production of ethanol using the Simultaneous Saccharification and Fermentation (SSF) process by using source separated household biowaste is possible. At pilot scale (200 L bioconversion reactor), a maximum ethanol production of 29.12 g/L was achieved what represented approximately 63% of the maximum theoretical yield based on the substrate sugar content [61].

The production of liquefied biogas is possible also for biogas from biodegradable wastes. The production of liquefied natural gas (LNG) is a proven technology to make natural gas transportable by trucks or ships. Research and new developments are focused to adapt the technology for liquefied biomethane (LBM) or liquefied biogas (LBG) to the smaller scale of biogas plants [44]. An increasing importance is expected as biofuel for truck and ships.

Possibilities of thermal processes to produce liquid biofuels are described in chapter Thermochemical conversion.

5.4 Conversion to Solid Biofuels

Compaction technologies to produce pellets or briquettes from straw, grass or other residues as solid fuels are common. The challenge is to meet the requirements of emissions in small incinerations and applications and to avoid the accumulation of slags by the low smelting point. Research is working at optimal compositions to replace wood pellets. One possibility to improve the characteristics of solid biofuels is the torrefecation or carbonization by using different kinds of waste biomass. Vakalis et al. [65] and Lohri et al. [38] found a significant heating value increase of torrefied household biowaste. Processed to fuel briquettes these products have an economic value and market that can potentially foster waste collection and enhance cost recovery of SWM systems [38]. At the same time, this utilization pathway contributes to a sustainable energy supply, based by own resources.

5.5 Recovery of Phosphorous

Phosphorus (P) is an essential crop nutrient, making it indispensable in maintaining food security for a continuously growing world population. Most mined phosphate rock is used in agriculture, although up to 46% of the P supplies are lost globally through agricultural runoff and erosion [68]. The natural resources are limited and the mined phosphate increasingly polluted. Biodegradable residues such as slaughterhouse waste, sewage sludge contain a considerable amount of P. The recovery is possible in different ways. Promising is the mono-incineration and chemical treatment recovery from ashes or the precipitation of P as magnesium ammonium phosphate ($MgNH_4PO_4$ $6H_2O$, struvite) from digested sludge [57, 67]. A good but different plant availability and fertilization effect of the recovered P, digestate, compost, or biochar was found by several authors (e.g., [6, 60, 66, 67]). Currently, the most P-recovery technologies are not economic feasibility. This will change with increasing market prices.

6 Challenges of the Implementation of Future Technologies

6.1 Ecological Aspects

The positive ecological effects of a proper waste management are scientifically proven especially for biodegradable waste as mentioned in Thomsen et al. [63], Mihai and Ingrao [42], Güereca et al. [27], Giovanis [25]. Further improvements can contribute to even higher greenhouse gas savings while a suboptimal process control or leakages could lead to increased site emissions of a treatment plant what negates the greenhouse gases (GHG) saving effect [32]. Future technologies are in competition with already established technical solutions. Sometimes, an advanced solution with a higher quality of final products needs a higher effort for the preparation or transport, what affect the GHG balance. The aim should be to implement the more sustainable option. Research of Thomsen et al. [63] showed that with increased circular bioresource management system at the example of Denmark, the GHG savings and other positive effects could be significant reached compared with status quo. Investigation in the Baltics showed that separate collection of biowaste and anaerobic digestion is the optimal solution for the countries Estonia, Lithuania [54].

At the same time, biowaste treatment facilities are faced with impurity content (e.g., [39]) and increasing requirements concerning emission control. In Europe, recycling products as compost and digestate have to fulfill at least the "End-of-Waste" criteria [20]. The collection system itself has also an impact on the biowaste quality: for example, the offering of free curbside recycling services is a way to offset the illegal disposal of recyclables [25].

6.2 Economical and Social Aspects

Advanced technological options for biogenic waste and residues are commonly more expensive and have higher requirements regarding the material input quality, plant management, workflow, and level of knowledge of the staff. All this influence the economic feasibility and broad implementation of new technologies. Also, the education and qualification in the field of waste management and circular economy have to be considered. The consequent and regular public relation work and information are the best way the reach a quality of source separated organic waste [61], also or especially in developed countries. In other regions, the implementation of high-quality recycling of organic waste is hindered by low environmental awareness.

Rapidly growing nations such as China are faced with the problems of fast-growing megacities and inadequate disposal systems [13, 50]. The cities have to handle enormous amounts of food waste [17]. Here, spaces saving and advanced waste management technologies are needed. Against this, Germany is especially in the rural areas confronted with the problem of demographic change and decreasing population density [37].

Especially the waste collection and logistics have to be adapted to changing requirements and (also financing) limitations. The management and treatment of biogenic waste and residues is not economically feasible without any refinancing system [64]. It has to be recognized as a social obligation. In many countries of the world refinancing systems, e.g., fees for the waste collection and treatment are lacking (e.g., [69, 46]). The implementation of a polluter pay principle, e.g., by pay-as-you-throw (PAYT), helps to obtain acceptance but the financial burden of the population has to be balanced. Otherwise, waste management measures are not accepted and not supported. A (part) substitution system can lead to a better acceptance by lower gate fees. Tock and Schummer [64] estimated in a case study in a developing country gate fees in the range of 10–18 €/t together with electricity feed-in tariffs in the range of 160–240 €/MWh, the economic viability of a biogas plant with CHP would be given. The implementation of a new technology is much easier when this can offer a better efficiency and lower treatment cost, higher quality of recycling products and higher GHG savings and better living conditions.

7 Conclusions

It should be noted that the transition from waste disposal to a circular economy is in progress. But the implementation varies worldwide considerable. The already established reliable treatment methods for biodegradable waste together with new developments offer a broad variety of solutions to improve the current recycling level of biodegradable waste. The proper treatment and the highest possible use of this waste are of particular importance to avoid environmentally harmful and greenhouse gas emissions. The identification of local adapted technologies and waste management strategies is still challenging, but good examples can serve as best practice.

In the future, the circular economy will be strongly connected with the bioeconomy. The way to this so-called green economy is long, but it gains more and more importance at policy, industry, and research. To make the transition from traditional waste disposal to circular and green economy happens, the awareness and the own volition of the population to support this development by a good source separation is necessary. Besides technology, economy and ecology also social aspects are to consider. The source segregation is a key element for high-quality recycling products. These more valuable products could contribute to economic feasible management concepts. Biodegradable waste can be a valuable resource for energy generation and recycling. In many countries, its separate collection and high-quality utilization were recognized as an opportunity for an added value.

Acknowledgements The presented work is part of the running research project "Network Stability with Wind and Bioenergy, Storage and Loads (Netz-Stabil)", ESF/14-BM-A55-0021/16. The authors are grateful to the Excellence Initiative of the Federal State Mecklenburg-Western Pomerania funded by the European Social Fund for Germany (ESF) for the support of the research.

References

1. Afolabi OOD, Sohail M, Thomas CLP (2017) Characterization of solid fuel chars recovered from microwave hydrothermal carbonization of human biowaste. Energy 134:74–89. https://doi.org/10.1016/j.energy.2017.06.010
2. Aichinger P, Kuprian M, Probst M, Insam H, Ebner C (2015) Demand-driven energy supply from stored biowaste for biomethanisation. Bioresour technol 194:389–393. https://doi.org/10.1016/j.biortech.2015.06.147
3. Alibardi L, Ragazzi M (2016) Biowaste to fuel–what's leading research and applications? Waste Manag (New York, N.Y.) 47:1–2. https://doi.org/10.1016/j.wasman.2015.11.034

4. Angelini S, Cerruti P, Immirzi B, Santagata G, Scarinzi G, Malinconico M (2014) From biowaste to bioresource. Effect of a lignocellulosic filler on the properties of poly(3-hydroxybutyrate). Int J Biol Macromol 71:163–173. https://doi.org/10.1016/j.ijbiomac.2014.07.038
5. Angelini S, Cerruti P, Immirzi B, Scarinzi G, Malinconico M (2016) Acid-insoluble lignin and holocellulose from a lignocellulosic biowaste. Bio-fillers in poly(3-hydroxybutyrate). Eur Polymer J 76:63–76. https://doi.org/10.1016/j.eurpolymj.2016.01.024
6. Bachmann S, Wentzel S, Eichler-Löbermann B (2011) Codigested dairy slurry as a phosphorus and nitrogen source for *Zea mays* L. and *Amaranthus cruentus* L. Z. Pflanzenernähr. Bodenk. 174(6):908–915. https://doi.org/10.1002/jpln.201000383
7. Bastidas-Oyanedel J, Bonk F, Thomsen MH, Schmidt JE (2015) Dark fermentation biorefinery in the present and future (bio)chemical industry. Rev Environ Sci Biotechnol 14(3):473–498. https://doi.org/10.1007/s11157-015-9369-3
8. Bernad-Beltrán D, Simó A, Bovea MD (2014) Attitude towards the incorporation of the selective collection of biowaste in a municipal solid waste management system. A case study. Waste Manag (New York, NY) 34(12):2434–2444. https://doi.org/10.1016/j.wasman.2014.08.023
9. Bonk F, Bastidas-Oyanedel J, Schmidt JE (2015) Converting the organic fraction of solid waste from the city of Abu Dhabi to valuable products via dark fermentation–Economic and energy assessment. Waste Manag (New York, NY) 40:82–91. https://doi.org/10.1016/j.wasman.2015.03.008
10. Brosowski A, Thrän D, Mantau U, Mahro B, Erdmann G, Adler P et al (2016) A review of biomass potential and current utilisation—status quo for 93 biogenic wastes and residues in Germany. Biomass Bioenergy 95:257–272. https://doi.org/10.1016/j.biombioe.2016.10.017
11. Budzianowski WM (2017) High-value low-volume bioproducts coupled to bioenergies with potential to enhance business development of sustainable biorefineries. Renew Sustain Energy Rev 70:793–804. https://doi.org/10.1016/j.rser.2016.11.260
12. Cimpan C, Rothmann M, Hamelin L, Wenzel H (2015) Towards increased recycling of household waste: Documenting cascading effects and material efficiency of commingled recyclables and biowaste collection. J Environ Manag 157:69–83. https://doi.org/10.1016/j.jenvman.2015.04.008
13. de Clercq D, Wen Z, Fan F (2017) Performance evaluation of restaurant food waste and biowaste to biogas pilot projects in China and implications for national policy. J Environ Manag 189:115–124. https://doi.org/10.1016/j.jenvman.2016.12.030
14. Colón J, Cadena E, Colazo AB, Quirós R, Sánchez A, Font X, Artola A (2015) Toward the implementation of new regional biowaste management plans. Environmental assessment of different waste management scenarios in Catalonia. Resour Conserv Recycl 95:143–155. https://doi.org/10.1016/j.resconrec.2014.12.012
15. Demichelis F, Pleissner D, Fiore S, Mariano S, Gutiérrez IMN, Schneider R, Venus J (2017) Investigation of food waste valorization through sequential lactic acid fermentative production and anaerobic digestion of fermentation residues. Bioresour Technol 241:508–516. https://doi.org/10.1016/j.biortech.2017.05.174
16. Demirbas MF, Balat M, Balat H (2011) Biowastes-to-biofuels. Energy Convers Manag 52(4):1815–1828. https://doi.org/10.1016/j.enconman.2010.10.041
17. Ding L, Cheng J, Qiao D, Yue L, Li Y-Y, Zhou J, Cen K (2017) Investigating hydrothermal pretreatment of food waste for two-stage fermentative hydrogen and methane co-production. Bioresour Technol 241:491–499. https://doi.org/10.1016/j.biortech.2017.05.114
18. Dreschke G, Probst M, Walter A, Pümpel T, Walde J, Insam H (2015) Lactic acid and methane. Improved exploitation of biowaste potential. Bioresour Technol 176:47–55. https://doi.org/10.1016/j.biortech.2014.10.136
19. Engler N, Scholwin F, Sutter R, Nelles M (2015) Performance enhancement of biogas digesters by post-treatment and recirculation of digestate. Forte Village_S. Margherita di Pula (CA)—Italy (Symposium proceedings (DVD), sardinia_2015, 15th international waste management and landfill symposium, 5–9 October 2015), 11 p

20. European Commission (ed.) (2014) End-of-waste criteria for biodegradable waste. Subjected to Biological Treatment (compost & digestate). Joint Research Centre. Publications Office of the European Union (Technical Proposals. JRC Scientific and Policy Reports), Luxembourg. Available online at http://jrc.es/EURdoc/JRC87124.pdf
21. Fava F, Totaro G, Diels L, Reis M, Duarte J, Carioca O, Ferreira B et al (2015) Biowaste biorefinery in Europe. Opportunities and research & development needs. New Biotechnol 32(1):100–108. https://doi.org/10.1016/j.nbt.2013.11.003
22. Francavilla M, Beneduce L, Gatta G, Montoneri E, Monteleone M, Mainero D (2016) Waste cleaning waste. Ammonia abatement in bio-waste anaerobic digestion by soluble substances isolated from bio-waste compost. Biochem Eng J 116:75–84. https://doi.org/10.1016/j.bej.2016.02.015
23. García A, Gandini A, Labidi J, Belgacem N, Bras J (2016) Industrial and crop wastes. A new source for nanocellulose biorefinery. Ind Crops Prod 93:26–38. https://doi.org/10.1016/j.indcrop.2016.06.004
24. Gerdes C (2001) Pyrolyse von biomasse-abfall: thermochemische konversion mit dem hamburger-wirbelschichtverfahren dissertation, Universität Hamburg 2001. URN: urn:nbn:de:gbv:18-5563. http://ediss.sub.uni-hamburg.de/volltexte/2001/556/
25. Giovanis E (2015) Relationship between recycling rate and air pollution. Waste management in the state of Massachusetts. Waste Manag (New York, NY) 40:192–203. https://doi.org/10.1016/j.wasman.2015.03.006
26. Gomes AP, Matos MA, Carvalho IC (2008) Separate collection of the biodegradable fraction of MSW. An economic assessment. Waste Manag (New York, NY) 28(10):1711–1719. https://doi.org/10.1016/j.wasman.2007.08.017
27. Güereca LP, Gassó S, Baldasano JM, Jiménez-Guerrero P (2006) Life cycle assessment of two biowaste management systems for Barcelona, Spain. Resour Conserv Recycl 49(1):32–48. https://doi.org/10.1016/j.resconrec.2006.03.009
28. Hidalgo D, Martín-Marroquín JM (2015) Biochemical methane potential of livestock and agri-food waste streams in the Castilla y León Region (Spain). Food Res Int 73:226–233. https://doi.org/10.1016/j.foodres.2014.12.044
29. Hoogwijk M, Faaij A, Eickhout B, de Vries B, Turkenburg W (2005) Potential of biomass energy out to 2100, for four IPCC SRES land-use scenarios. Biomass Bioenergy 29(4):225–257
30. Hungría J, Gutiérrez MC, Siles JA, Martín MA (2017) Advantages and drawbacks of OFMSW and winery waste co-composting at pilot scale. J Cleaner Prod 164:1050–1057. https://doi.org/10.1016/j.jclepro.2017.07.029
31. Jaria G, Silva CPa, Ferreira CIA, Otero M, Calisto V (2017) Sludge from paper mill effluent treatment as raw material to produce carbon adsorbents. An alternative waste management strategy. J Environ Manag 188:203–211. https://doi.org/10.1016/j.jenvman.2016.12.004
32. Jensen MB, Møller J, Mønster J, Scheutz C (2017) Quantification of greenhouse gas emissions from a biological waste treatment facility. Waste Manag (New York, NY). https://doi.org/10.1016/j.wasman.2017.05.033
33. Jimenez J, Lei H, Steyer J-P, Houot S, Patureau D (2017) Methane production and fertilizing value of organic waste. Organic matter characterization for a better prediction of valorization pathways. Bioresour Technol 241:1012–1021. https://doi.org/10.1016/j.biortech.2017.05.176
34. Kannan S, Gariepy Y, Raghavan GSV (2017) Optimization and characterization of hydrochar produced from microwave hydrothermal carbonization of fish waste. Waste Manag (New York, NY) 65:159–168. https://doi.org/10.1016/j.wasman.2017.04.016
35. Koutinas A, Alexandri M, Pateraki C, Vlysides A, Papapostolou H (2014) Development of an advanced biorefinery concept based on valorization of pulp and paper industry waste streams. New Biotechnol 31:S39. https://doi.org/10.1016/j.nbt.2014.05.1700
36. Lasardi K (2009) Implementing the Landfill Directive in Greece. Problems, perspectives and lessons to be learned. Geogr J 175(4):261–273. https://doi.org/10.1111/j.1475-4959.2009.00342.x
37. Lemke A, Schüch A, Morscheck G, Nelles M (2016) Impact of demographic change for bio-waste-management in German rural areas. In: Lasaridi K, Manio T (eds) ORBIT 2016

Abstract Book. Organic resources & biological treatment. 10th international conference on circular economy and organic waste. Heraklion, Crete, Greece, 48 (auf USB Stick 6 Seiten)
38. Lohri CR, Rajabu HM, Sweeney DJ, Zurbrügg C (2016) Char fuel production in developing countries—a review of urban biowaste carbonization. Renew Sustain Energy Rev 59:1514–1530. https://doi.org/10.1016/j.rser.2016.01.088
39. Malamis D, Bourka A, Stamatopoulou E, Moustakas K, Skiadi O, Loizidou M (2016) Study and assessment of segregated biowaste composting. The case study of Attica municipalities. J Environ Manag https://doi.org/10.1016/j.jenvman.2016.09.070
40. Martínez-Blanco J, Colón J, Gabarrell X, Font X, Sánchez A, Artola A, Rieradevall J (2010) The use of life cycle assessment for the comparison of biowaste composting at home and full scale. Waste Manag (New York, NY) 30(6):983–994. https://doi.org/10.1016/j.wasman.2010.02.023
41. Micolucci F, Gottardo M, Cavinato C, Pavan P, Bolzonella D (2016) Mesophilic and thermophilic anaerobic digestion of the liquid fraction of pressed biowaste for high energy yields recovery. Waste Manag (New York, NY) 48:227–235. https://doi.org/10.1016/j.wasman.2015.09.031
42. Mihai F-C, Ingrao C (2016) Assessment of biowaste losses through unsound waste management practices in rural areas and the role of home composting. J Cleaner Prod. https://doi.org/10.1016/j.jclepro.2016.10.163
43. Miltner M, Makaruk A, Harasek M (2017) Review on available biogas upgrading technologies and innovations towards advanced solutions. J Cleaner Prod 161:1329–1337. https://doi.org/10.1016/j.jclepro.2017.06.045
44. Nachtmann K (2017) LNG – künftige Herstellungs- und Anwendungsstrategien als alternativer Kraftstoff. Presentation at the C.A.R.M.E.N. e. V. – Symposium 2017 at the 11.07.2017 in Straubing, Germany
45. Narzari R, Bordoloi N, Sarma B, Gogoi L, Gogoi N, Borkotoki B, Kataki R (2017) Fabrication of biochars obtained from valorization of biowaste and evaluation of its physicochemical properties. Bioresour Technol 242:324–328. https://doi.org/10.1016/j.biortech.2017.04.050
46. Nassour A, Elnaas A, Hemidat S, Nelles M (2016) Development of waste management in the Arab region. In: Waste management. TK, Neuruppin, pp 117–128. http://www.vivis.de/phocadownload/Download/2016_wm/2016_WM_117-128_Nassour.pdf
47. Nelles M, Grünes J, Morscheck G (2016) Waste management in Germany—development to a sustainable circular economy? Procedia Environ Sci 35:6–14. https://doi.org/10.1016/j.proenv.2016.07.001
48. Nelles M (2017) Kreislaufwirtschaft in Deutschland - internationales Vorbild oder nur noch 2. Liga? Editorial. *Müll und Abfall* 49(4):153
49. Nelles M, Brosowski A, Morscheck G, Schüch A (2016a) Biogenic waste and residues in Germany—amount, current utilisation and perspectives. In: Waste management and research: the journal of the international solid wastes and resource utilisation 2016, pp 1609–1615
50. Nelles M, Eickhoff I, Lemke A, Morscheck G, Nassour A, Schüch A, Zhou Y (2017) Disposal of biogenic fractions in the PR of China. In: Kuehle-Weidemeier M (ed) Waste-to-resources 2017. VII international symposium MBT and MRF. Proceedings. With assistance of K. Buescher, pp 179–195
51. Pachapur VL, Das RK, Brar SK, Le Bihan Y, Buelna G (2017) Valorization of crude glycerol and eggshell biowaste as media components for hydrogen production. A scale-up study using co-culture system. Bioresour Technol 225:386–394. https://doi.org/10.1016/j.biortech.2016.11.114
52. Park A, Kim YM, Kim JF, Lee PS, Cho YH, Park HS et al (2017) Biogas upgrading using membrane contactor process. Pressure-cascaded stripping configuration. Sep Purification Technol 183:358–365. https://doi.org/10.1016/j.seppur.2017.03.006
53. Piotrowski S, Carus M, Essel R (2015) Global bioeconomy in the conflict between biomass supply and demand. Hürth (7). In: Nova paper on bio-based economy
54. Pubule J, Blumberga A, Romagnoli F, Blumberga D (2015) Finding an optimal solution for biowaste management in the Baltic States. J Cleaner Prod 88:214–223. https://doi.org/10.1016/j.jclepro.2014.04.053

55. Quicker P, Neuerburg F, Noël Y, Huras A, Eyssen R, Seifert H et al (2017) Sachstand zu den alternativen Verfahren für die thermische Entsorgung von Abfällen. Projektnummer 29217 UBA-FB 002102: Umweltbundesamt (UBA TEXTE, 17)
56. Raussen T, Wagner J (2017) EEG 2017 in der abfallwirtschaftlichen Praxis—Chancen für Bio- und EEG 2017 in der abfallwirtschaftlichen Praxis—Chancen für Bio- und Grüngutverwertungsanlagen. Renewable Energy Sources Act (EEG 2017) in waste management practice—chances for organic recycling plants. In: Müll und Abfall, vol 7. pp 328–334. https://www.muellundabfall.de/MA.07.2017.328
57. Sartorius C, von Horn J, Tettenborn F (2012) Phosphorus recovery from wastewater—expert survey on present use and future potential. Water Environ Res 84(4). https://doi.org/10.2175/106143012x13347678384440
58. Schüch A, Morscheck G, Lemke A, Nelles M (2016) Bio-waste recycling in Germany—further challenges. Procedia Environ Sci 35:308–318. https://doi.org/10.1016/j.proenv.2016.07.011
59. Singhania RR, Patel AK, Christophe G, Fontanille P, Larroche C (2013) Biological upgrading of volatile fatty acids, key intermediates for the valorization of biowaste through dark anaerobic fermentation. Bioresour Technol 145:166–174. https://doi.org/10.1016/j.biortech.2012.12.137
60. Sortino O, Montoneri E, Patanè C, Rosato R, Tabasso S, Ginepro M (2014) Benefits for agriculture and the environment from urban waste. Sci Total Environ 487:443–451. https://doi.org/10.1016/j.scitotenv.2014.04.027
61. Sotiropoulos A, Vourka I, Erotokritou A, Novakovic J, Panaretou V, Vakalis S et al (2016) Combination of decentralized waste drying and SSF techniques for household biowaste minimization and ethanol production. Waste Manag (New York, NY) 52:353–359. https://doi.org/10.1016/j.wasman.2016.03.047
62. Sprafke J, Schüch A, Nelles M (2017) Possibilities of biogas enhancement by hydrogen addition as contribution to the energy transition. In: Conference proceedings of the international conference on solid waste management, 7IconSWM 2017. Proceedings under preparation
63. Thomsen M, Seghetta M, Mikkelsen MH, Gyldenkærne S, Becker T, Caro D, Frederiksen P (2017) Comparative life cycle assessment of biowaste to resource management systems—a Danish case study. J Cleaner Prod 142:4050–4058. https://doi.org/10.1016/j.jclepro.2016.10.034
64. Tock L, Schummer J (2017) Sustainable waste-to-value biogas plants for developing countries. Waste Manag (New York, NY) 64:1–2. https://doi.org/10.1016/j.wasman.2017.05.014
65. Vakalis S, Sotiropoulos A, Moustakas K, Malamis D, Vekkos K, Baratieri M (2016) Thermochemical valorization and characterization of household biowaste. J Environ Manag. https://doi.org/10.1016/j.jenvman.2016.04.017
66. Vassilev, N, Martos E, Mendes G, Martos V, Vassileva M (2013) Biochar of animal origin. A sustainable solution to the global problem of high-grade rock phosphate scarcity? J Sci Food Agric 93(8):1799–1804. https://doi.org/10.1002/jsfa.6130
67. Vogel T, Nelles M, Eichler-Löbermann B (2015) Phosphorus application with recycled products from municipal waste water to different crop species. Ecol Eng 83:466–475. https://doi.org/10.1016/j.ecoleng.2015.06.044
68. Vogel T, Kruse J, Siebers N, Nelles M, Eichler-Löbermann B (2017) Recycled products from municipal wastewater: composition and effects on phosphorus mobility in a sandy soil. J Environ Qual 1–9. https://doi.org/10.2134/jeq2016.10.0392
69. Wolfgang P-S (2012) Entwicklung eines sektoralen Ansatzes zum Aufbau von nachhaltigen Abfallwirtschaftssystemen in Entwicklungsländern vor dem Hintergrund von Klimawandel und Ressourcenverknappung. Darmstadt/Rostock: Dissertation am Lehrstuhl Abfall- und Stoffstromwirtschaft, Universität Rostock
70. Zhang Z, Zhao ZK (2010) Microwave-assisted conversion of lignocellulosic biomass into furans in ionic liquid. Biores Technol 101(3):1111–1114. https://doi.org/10.1016/j.biortech.2009.09.010

Decentralized Utilization of Urban Biomass Waste and Solar Energy for Cooling System—A Proposed Model

Rahul Baidya, Tapobrata Bhattacharya
and Sadhan Kumar Ghosh

1 Introduction

The demand for energy associated with air conditioning is increasing noticeably in recent years, causing abrupt peak demand in consumption of electricity. Alternative energy utilization for the same is increasingly seen as the answer towards sustainability. Further, the high-rise condominiums (gated communities) in India have to manage their own waste in a decentralized manner as laid down in the Waste Management Rule 2016, which emphasizes on source segregation and decentralized disposal, thereby increasing emphasis on resource efficiency and waste utilization. The cooling system, i.e., refrigeration and air conditioning requires a large amount of electricity. There is a need for development of a sustainable system that utilizes alternative source of energy for household applications like cooling system and kitchen fuel/heating requirements. The waste composition for the city of Kolkata, in India, amounts to 55–60% organic waste on a per capita basis. There lies huge potential for energy recovery from urban biomass waste that is composed of organic fragments of municipal solid waste (OFMSW). Moreover, the potential of harvesting solar energy is enormous: a solar parabolic trough reflector for extraction of solar power in conjunction with biogas energy and molten salt for heat storage.

A hybrid energy recovery system utilizing OFMSW and solar energy is proposed consequently. The proposed model incorporates three subsystems: vapor absorption refrigeration system (VARS) (LiBr—Water system) for air conditioning, solar energy extraction system (SEES), and biogas generation system (BGS). The proposed system employs the decentralized model of waste management as household organic

---

R. Baidya (✉) · S. K. Ghosh
Department of Mechanical Engineering, Jadavpur University, Kolkata, India
e-mail: rahulbaidya.ju@gmail.com

R. Baidya · T. Bhattacharya
Centre for Research and Innovation, Department of Mechanical Engineering,
Institute of Engineering & Management, Kolkata, India

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_30

waste acts as feed for the BGS. The biogas generated acts as energy source during night and on cloudy days, for VARS system. SEES powers the system on sunny days, both for air conditioning as well as for domestic hot water requirement. Solar thermal systems, in addition to their role as low-cost renewable resource, are especially suited for air conditioning and refrigeration requirement, on account of the fact that availability of solar radiation and cooling needs usually coincide seasonally [1, 2]. There exists a variety of systems for solar energy extraction [3]; one of the prominent being PTCs (parabolic trough concentrating system). A PTC system focuses the solar insolation, parallel to the collector axis on to a focal line. A receiver pipe is placed in this focal line through which heat transfer fluid flows. The collectors are usually provided with a solar tracking system to enhance its efficiency. The tracking system can be of 1-axis or 2-axis types [4, 5].

Hammad et al. [6] designed and tested a solar-powered LiBr–H_2O absorption refrigeration cycle at the University of Jordan. Osman [7] used an integrated solar cooling system utilizing three types of solar subsystems for air conditioning a residential building in Kuwait. Lizarte et al. [8] compared experimentally an indirectly air-cooled commercial absorption chiller to a directly air-cooled absorption chillers prototype. Lizarte et al. [9] studied an innovative directly air-cooled absorption chiller prototype and calculated COP, SCOP values, solar fraction, etc. Syed et al. [10] investigated a solar cooling system consisting of a 35 kW LiBr/H_2O absorption machine energized by 49.9 m^2 of flat-plate collectors.

In keeping with new Waste Management rules 2016, the new high-rise condominiums have to dispose/recycle their waste in-house. Conversion of this waste to methane provides an effective option. The production potential of methane largely depends on the quantity and type of material added to the system [11]. Anaerobic digestion (AD) is a multistage biological process. The organic waste is converted to a gaseous product consisting of methane (50–70% by volume), carbon dioxide (25–40% by volume) and minute quantity of hydrogen sulfide, water vapor, and ammonia [12–14]. AD of organic fragments of MSW provides a solution to the waste management problem [15]. AD digestion takes place due to number of microorganisms, thus it depends on different factors like pH, temperature, HRT, C/N ratio, etc.; it is a relatively a slow process. Lack of process stability and low loading rates are some of the limitations associated with it [16, 17]. Elango et al. [18] carried out experiments to study the production potential of biogas from municipal solid waste (MSW) and domestic sewage by using anaerobic digestion process. El-Mashad and Zhang [19] evaluated the effect of manure-screening on the biogas yield. Tchobanoglous and Burton [20] studied the potential of digester gas in large plants. Kisaalita et al. [21] analyzed biodigesters coupled with absorption refrigeration systems in Uganda. Gomri [22] presented a numerical study of solar/natural gas single effect lithium bromide absorption chiller. Holm-Nielsen et al. [23] in his paper suggested the utilization of biogas as an energy source for heat, steam and/or electricity and cooling system. Bruno et al. [24] analyzed the different configurations of absorption cooling integrated into biogas CCHP systems from environmental and economic aspect.

A commercial electric vapor absorption refrigerator connected to a PTC for the preservation of perishable food was investigated for its effectiveness by Raheman and

Gupta [25]. Sumathy et al. [26] introduced a case study for solar thermal applications in an energy-intensive food industry in India. Rajeshwari et al. [27] experimentally analyzed anaerobic digestion of vegetable market waste in a two-stage digester. The hydrolysis and acidification process was carried out by a continuous sprinkling of water over the waste in a 100 l mild steel solid bed digester.

The leachate produced from the acidification phase was treated in 24.6 l Upflow Anaerobic Sludge Blanket Reactor (UASB) reactor for production of biogas. There is a dearth of sufficient literature on biogas utilization in the Indian context. The proposed hybrid system with relay control is the first of its kind. The model once successfully developed will make decentralized waste management and solar energy extraction a viable alternative energy source for high-rise condominiums. Until now, research has concentrated on decoupled systems that employ either solar energy or biogas; hybrid systems with multidirectional approach have not been reported. The main goal of the project is to solve the dual problem of waste disposal and alternative energy utilization in a decentralized manner and provide a cost-effective energy solution for high-rise condominiums and office spaces having in-house canteens/food courts in Indian cities. The study aims to reduce the burden on the existing waste management system as almost 55–60% waste will be recycled at source. The digested by-product can be reused as fertilizer for gardens. Additionally, the utilization of solar power for cooling system and hot water or steam for kitchen use will further reduce the carbon footprint of the high-rise condominiums. The proposed system will arguably provide a holistic solution of waste management and alternative resource utilization. The objective of the current study is to find a comprehensive system design which can address the urban waste management issues and simultaneously utilize alternative source of energy. The study proposes a decentralized cooling system for a storied apartment block, utilizing organic fragments and simultaneous production of energy from waste, by the path of anaerobic digestion and harnessing solar energy through PTCs for operating the VARS for cooling arrangements. The organization of the paper is as follows: Sect. 2 explains the methodology adopted for the study. Section 3 discusses and analyzes the potential based on the proposed design. Section 4 presents the future scope of work and concludes the papers.

2 Materials and Method

First, an extensive literature review has been carried out to gauge the present practices in solar energy utilization for the cooling system. The biogas utilization for cooling has also been studied but the study reveals scant results in this aspect. The waste management practices and utilization of organic fragments for biogas production were also reviewed. Second, based on the review and secondary data, a holistic system design was developed and a system structure was proposed for a high-rise building. A one-year data on waste management practices was taken from the preexisting literature to support the system design. Finally, the holistic system design and its innovativeness were discussed.

3 Results and Discussion

Waste management across the globe and specifically in India is a major problem. With new norms for decentralized waste dispsoal, energy recovery from the waste is given utmost priority, biogas production from organic fragments of municipal solid waste (OFMSW) is need of the hour for the gated communities. The study aims to address some of the issues by carrying out the development of a comprehensive system that utilizes solar energy extraction system (SEES) and biogas generation system (BGS) to produce cooling effects. The proposed biogas generation system (BGS) will be designed or adapted based on the Rajeshwari et al. [27], and the designed reactor is a multiphase system with two-stage reaction stage with the first stage having a fixed bed type reactor. The reactor will be fabricated out of PVC-based materials. There will be six tanks for the acidification stages followed by a leachate storage tank. A UASB reactor will be used for the second stage which is the methanogenesis stage. The UASB reactor is to be maintained at a desired temperature by placing it in an insulated chamber equipped with a heat convector controlled by a temperature sensor. The leachate storage tank is outfitted with a 0.5 mm stainless steel mesh to filter the suspended particles. The leachate will be recirculated over the solid bed reactor of first stage by using a 0.75 hp chemical pump. The sprinkling rate will be controlled by bypass valves and the rate was monitored by using a water flow meter. An arrangement for removal of the digested waste from the bottom of the reactor will be provided by means of a gate valve on each of the first stage reactor. Feeding of the waste was done from the top of the reactor (1st stage), which was tightly sealed with a gasket to provide an anaerobic conditions.

The hopper 1 and hopper 2 are made of MS grade material, and it will be used for feeding the waste into the reactor in between the hopper and there will be an arrangement of shredder for reducing the size of the waste so as to increase the rate of digestion in the reactor. A screw feeder will be also incorporated for feeding the waste to different inline reactors. A level indicator is to be incorporated in the first stage reactor so as to control the feeding frequency. A control valve will be there for controlling the feeding of each first stage reactor. The digestate from the first stage tank will be dried in a mechanical open drying system; the dried waste will be used as manure in the garden. Once the leachate is produced, it will go into the leachate storage tank from there on it will be pumped at the desired rate to the UASB to maintain the sludge blanket and the recycled leachate will be used as manure in the community garden. The biogas produced in the UASB will be stored in a tank with pressure indicator; the gas will be used for firing the gas burner in the generator of VARS and also in domestic kitchens of the complex. The firing will be controlled by a relay arrangement based on the temperature of the fluid in the generator of VARS (Fig. 1).

The SEES will consist of PTCs which will be designed on the roof of the high rise. The collector will absorb the concentrated solar heat by a running thermal liquid, pumped via high temperature pump. The collector will be single axis tilting device the tilting will be controlled by an electric motor. The flow rate will be controlled

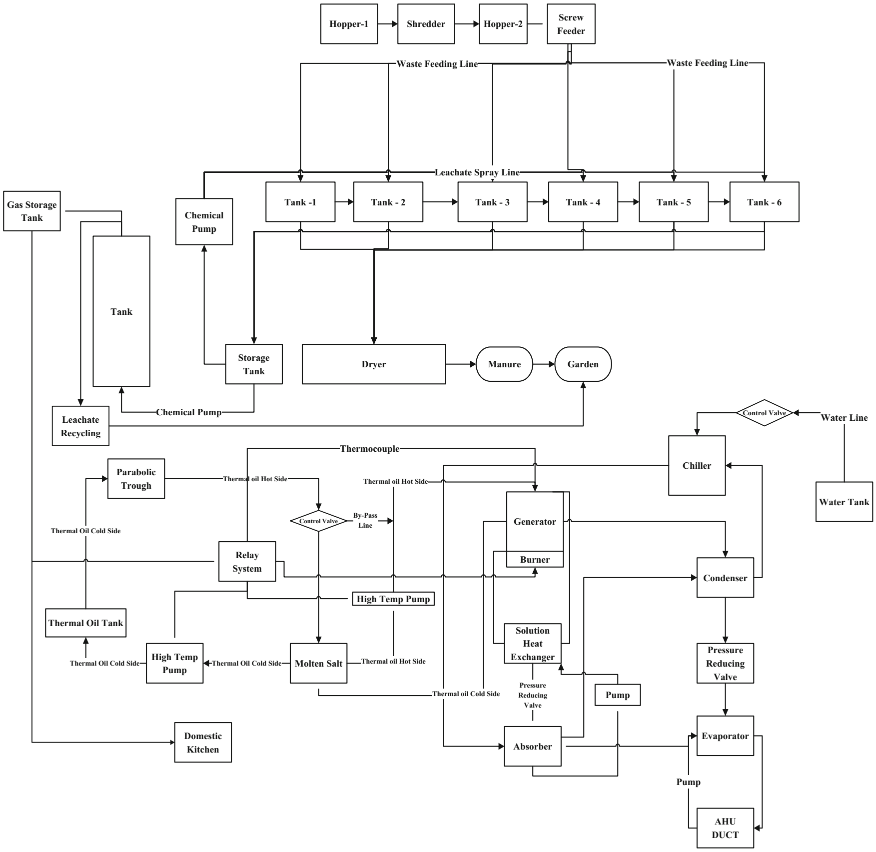


Fig. 1 Block diagram of the proposed system

by a control valve. The thermal liquid will transfer the heat to a molten salt storage tank and simultaneously a bypass pipeline will directly transfer the thermal heat to the generator of the VARS. The thermal liquid will then flow through the molten salt storage tank and will complete the cycle. The secondary circuit will also be designed to transfer the heat from the molten salt storage tank when the required temperature starts falling. A heat pump will be connected for the circulation of the thermal oil in the secondary circuit. This activation of the heat pump in the secondary circuit will be carried out with the utilization of the relay system. The heat pump in the parabolic circuit will be also controlled by the solar radiation sensor. The flow rate and generator will be designed based on the heat requirement and cooling load requirement. This will be again controlled by the relay systems which control the mass flow rate of the fluid via a control valve (Fig. 1).

The vapor absorption system is LiBr–H_2O based cycle. The VARS components were designed with mild steel (MS) with anti-corrosive lining with the size of each of the generators, absorber, evaporator, and condenser to be 3 l. The solution heat exchanger was also made of MS and similarly, the pipes for different connection in the VARS were also made of MS. The chiller was designed of SS pipes and SS fins with a dedicated water supply from water tank. A chemical pump will be used to increase the pressure on the top side of the cycle that is of generator and condenser. Two pressure reducing valve will reduce the pressure in the lower side of cycle that is absorber and evaporator. A water pump will be also there for AHU duct, and the incoming air in duct is cooled by circulating the cold water from the evaporator. The setup will be housed on an open rooftop shed with parabolic trough hosed in open space. The proposed system will provide a business solution to number of organizations; it will provide a sustainable way of utilizing waste and alternative energy. The system will also address the issues presently persistent in the waste management system. The setup will be able to develop renewable energy methodology. The system can be laid into modular units which allow for ease of installation and maintenance. The configuration can be customized over a wide range of capacities: from single house to storied condominiums and office complex. The low energy input necessary for the VARS system makes it an ideal choice to serve air conditioning load. The usage of solar insolation and treated waste for generation of biogas to run the pumps yield twofold benefits: a low-cost alternative to fossil fuels and sustainable disposal of processed waste.

4 Conclusion

The proposed system will help to address waste management problem and renewable energy utilization by involving the urban development authorities and town planners. The system design will have a positive impact on the environment as the system does not produce any harmful emission during the functioning. Further, it reduces the waste going to the landfill and produces manure as a by-product and the SEES utilizes solar energy which would have been otherwise remained unutilized. The system will reduce the carbon footprint of the high rise by utilizing alternative energy source and simultaneously utilizing OFMSW. The system is going to reduce the use of conventional resources for cooling arrangement. Further for cooking purpose, the system will provide biogas produced in the reactor. The system as a whole with BGS, SEES, and VARS will help the environment in a number of diverse aspect including waste management system.

Acknowledgements Authors acknowledge the support provided by the UK India Educational Research Initiative (UKIERI) project, "Waste-to-energy—DSS for planning and implementation in India" at the department of mechanical engineering, Jadavpur University, India and Aston University, UK. The authors acknowledge the support by International Society of Waste Management, Air and Water" (ISWMAW).

References

1. Kalkan N, Young EA, Celiktas A (2012) Solar thermal air conditioning technology reducing the footprint of solar thermal air conditioning. Renew Sustain Energy Rev 16(8):6352–6383
2. Kim DS, Ferreira CI (2008) Solar refrigeration options–a state-of-the-art review. Int J Refrig 31(1):3–15
3. El Fadar A, Mimet A, Azzabakh A, Pérez-García M, Castaing J (2009) Study of a new solar adsorption refrigerator powered by a parabolic trough collector. Appl Therm Eng 29(5):1267–1270
4. Bakos GC (2006) Design and construction of a two-axis Sun tracking system for parabolic trough collector (PTC) efficiency improvement. Renew Energy 31(15):2411–2421
5. Mousazadeh H, Keyhani A, Javadi A, Mobli H, Abrinia K, Sharifi A (2009) A review of principle and sun-tracking methods for maximizing solar systems output. Renew Sustain Energy Rev 13(8):1800–1818
6. Hammad MA, Audi MS (1992) Performance of a solar LiBr-water absorption refrigeration system. Renew Energy 2(3):275–282
7. Osman MG (1985) Performance analysis of a solar air-conditioned villa in the Arabian gulf. Energy Convers Manag 25(3):283–293
8. Lizarte R, Izquierdo M, Marcos JD, Palacios E (2013) Experimental comparison of two solar-driven air-cooled LiBr/H_2O absorption chillers: indirect versus direct air-cooled system. Energy Build 62:323–334
9. Lizarte R, Izquierdo M, Marcos JD, Palacios E (2012) An innovative solar-driven directly air-cooled LiBr–H_2O absorption chiller prototype for residential use. Energy Build 47:1–11
10. Syed A, Izquierdo M, Rodriguez P, Maidment G, Missenden J, Lecuona A, Tozer R (2005) A novel experimental investigation of a solar cooling system in Madrid. Int J Refrig 28(6):859–871
11. Converti A, Del Borghi A, Zilli M, Arni S, Del Borghi M (1999) Anaerobic digestion of the vegetable fraction of municipal refuses: mesophilic versus thermophilic conditions. Bioprocess Biosyst Eng 21(4):371–376
12. Singh KJ, Sooch SS (2004) Comparative study of economics of different models of family size biogas plants for state of Punjab, India. Energy Convers Manag 45(9):1329–1341
13. Igoni AH, Ayotamuno MJ, Eze CL, Ogaji SOT, Probert SD (2008) Designs of anaerobic digesters for producing biogas from municipal solid-waste. Appl Energy 85(6):430–438
14. Angelidaki I, Ellegaard L (2003) Codigestion of manure and organic wastes in centralized biogas plants. Appl Biochem Biotechnol 109(1–3):95
15. Miranda ML, Hale B (2005) Paradise recovered: energy production and waste management in island environments. Energy Policy 33(13):1691–1702
16. Van den Berg L, Kennedy KJ (1983) Comparison of advanced anaerobic reactors. In: Proceedings of the 3rd international symposium Anaerobic Digestion. Agosto, vol 14, No 19, pp 71–89
17. Fehrenbach H, Giegrich J, Reinhardt G, Sayer U, Gretz M, Lanje K, Schmitz J (2008) Kriterien einer nachhaltigen Bioenergienutzung im globalen Maßstab. UBA-Forschungsbericht 206:41–112
18. Elango D, Pulikesi M, Baskaralingam P, Ramamurthi V, Sivanesan S (2007) Production of biogas from municipal solid waste with domestic sewage. J Hazard Mater 141(1):301–304
19. El-Mashad HM, Zhang R (2010) Biogas production from co-digestion of dairy manure and food waste. Biores Technol 101(11):4021–4028
20. Burton F (1991) Tchobanoglous, g. wastewater engineering treatment, disposal and reuse. Metcalf and Eddy, Inc, p. 1334
21. Kisaalita WS, Tippie A, Faircloth W, Franklin J, Boyer B (2006) Comparative feasibility analysis of alternative renewable energy sources for small milk cooling plants of Southwestern Uganda. Ama, Agric Mechanization in Asia, Africa & Latin America 37(4):69
22. Gomri R (2013) Simulation study on the performance of solar/natural gas absorption cooling chillers. Energy Convers Manag 65:675–681

23. Holm-Nielsen JB, Al Seadi T, Oleskowicz-Popiel P (2009) The future of anaerobic digestion and biogas utilization. Biores Technol 100(22):5478–5484
24. Bruno JC, Valero A, Coronas A (2005) Performance analysis of combined microgas turbines and gas fired water/LiBr absorption chillers with post-combustion. Appl Therm Eng 25(1):87–99
25. Raheman H, Gupta CP (1989) Development of a solar-energy-operated vapour-absorption-type refrigerator. Appl Energy 34(2):89–98
26. Sumathy K, Yeung KH, Yong L (2003) Technology development in the solar adsorption refrigeration systems. Prog Energy Combust Sci 29(4):301–327
27. Rajeshwari KV, Lata K, Pant DC, Kishore VVN (2001) A novel process using enhanced acidification and a UASB reactor for biomethanation of vegetable market waste. Waste Manage Res 19(4):292–300

A Performance Study on the Bioleaching Process by the Production of Organic Acids Using HPLC/UV

J. Senophiyah-Mary, R. Loganath and T. Meenambal

1 Introduction

1.1 Electronic Waste

Electronic waste (e-waste) recycling which has been a successful business among the unskilled labours of the informal sectors among the various parts of the world plays a significant role in contaminating the entire living environment. Electronic waste which contributes only a few in percentages to the municipal solid waste being generated contributes a lot to the heavy metal contamination which in future gets accumulated to all the living cells in one way or the other. Due to the increasing advancements in the technology and the increased planned obsolescence, there is a huge amount of e-waste generated all over the world [1]. Electronic waste is the costliest waste ever identified. It has various metals like copper, nickel, lead, tin, arsenic, bromine and precious metals like gold, silver and platinum within it on the surface of the printed circuit board (PCB). This board is a layer of three which has a plastic/ceramic thick surface with which a thin layer of copper contributes about 70% of the total metal present in the board, and was coated with a lavish layer of epoxy

---

J. Senophiyah-Mary (✉)
Department of Civil Engineering, Government College of Technology,
Coimbatore 641013, Tamil Nadu, India
e-mail: senophiyah.mary8@gmail.com

R. Loganath
Department of Civil Engineering, Indian Institute of Engineering
Science and Technology, Shibpur, Howrah 711103, West Bengal, India
e-mail: loganath.rk@gmail.com

T. Meenambal
Department of Civil Engineering, Madanapalli Institute of Technology, Madanapalli,
Chittor 517325, Andhra Pradesh, India
e-mail: tmeenambal_gct@yahoo.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_31

resin [2]. Those metals are in its purest form which requires only extraction rather than purification which is simpler while comparing to the extraction and purification from its ores [3, 4]. Improper treatment of e-waste leads to the generation of secondary pollutants which could again be a mess for treating them completely.

1.2 Treatment of E-Waste

There are various treatment processes like pyrometallurgy, hydrometallurgy, bio-hydrometallurgy and cryo-metallurgy [5]. Other than hydrometallurgy process the rest of them have not been implemented in large scale, while hydrometallurgy is a successful procedure in the extraction of metals and also in the generation of secondary pollutants which causes adverse effects in humans like eye irritation, nausea, even turn carcinogenic. Bioleaching could be an effective way for the extraction of metals and converting them into either nanoparticles or oxides of the metals. In order to extract the metals from e-waste, the bioleaching process requires microorganism for the synthesis of organic acids which help to leach out the metal from the PCB. They differ depending on the type of microorganisms used for the treatment. Microorganism used may be bacteria, fungi and algae [6].

1.3 Biological Treatment

Bioleaching is an ancient technique for the onsite extraction of metals from its ores [7]. Microorganisms require carbon and some minerals for their growth and multiplication. In bioleaching process, the microbes synthesise organic acids that convert the insoluble metals into soluble form with where the microbes utilise a few amounts for their growth. They undergo processes like acidolysis, complexolysis and redoxolysis. These processes require the organic acid for the conversion of metals. The organic acids differ depending on the microorganism used. The microorganism might be a fungus or a bacterium which synthesises organic acid for the leaching of metals [8] while all bacteria, fungi and algae are under research for the extraction of metals. Out of which *Acidothiobacillus* species and *Chromobacterium* species has been used widely in research as they extract various specific metals in a short span. Fungi are well known for its wide growth in the area of low food content. Bread mold is the best example which grows in a place until the moisture content retains. They are easy to cultivate in lab and grows for a long-time span. They have been used extensively in research for the extraction of metals and have found that many fungi were also metal specific as they have high tolerant to metals.

The synthesis of organic acid by the fungus mainly deals with the substrate composition so that the organic acid gets generated. The composition of the media plays a key role in the production of organic acids. It was also well stated that *Aspergillus niger* is well known for the production of organic acids like citric acid, oxalic acid, succinic acid and gluconic acid that helps in the conversion of metals. The presence of certain metals hinders the production of these organic acids like Manganese [9, 10]. The hydrogen ion concentration (pH) plays a significant role in the bioleaching process. The production of organic acid varies the pH of the medium. It was found that oxalic acid, succinic acid was at pH 3–5 and citric acid was produced at a pH lesser than pH-3. Another factor that greatly influences the leaching process is the substrate concentration [11].

The objective of the study was to find out the synthesis of organic acids by *A. niger* in the presence of e-waste in five different concentrations during the extraction of metals. This paper highlights that the concentration of the particle influences the leaching efficiency where the powdered sample was replaced with the plated sample. Metals like Lead, Nickel, Chromium, Zinc and Copper has been analysed with the help of Atomic Absorption Spectroscopy and the percentage of metals extracted were studied. The organic acids were analysed with the help of high pressure liquid chromatography (HPLC) and the effect of metal leaching efficiency due to the organic acid were studied. The influence of concentration in the production of organic acids and the influence of organic acid in the leaching of metals has been studied.

2 Materials and Methods

2.1 Strains

Aspergillus niger (A. niger) was procured from MTCC, Pune. The freeze-dried culture was mixed with deionised water and then it was plated onto a Borosil Petri dish containing Potato dextrose agar and Sabourad Dextrose Agar (SDA). The 7-day-old spores of *Aspergillus niger* were cultivated with the help of tween-80 and the spores were poured into a 250 ml Erlenmeyer flask containing Bioleaching medium which was a mixture of Sucrose-100 g/L, Sodium Nitrate-1.5 g/L, KH_2PO_4-0.5 g/L, $MgSO_4$. $7H_2O$-0.025 g/L, KCl -0.025 g/L, Yeast extract −1.6 g/L, pH 5.5 [6]. The culture was placed in an orbital shaker at 150 rpm at 25 °C. A blank sample was taken to know the presence of organic acids in it.

2.2 Electronic Waste

The electronic waste used was the printed circuit board (PCB) which was collected from Green era recyclers, Coimbatore. In order to lower the consumption of resources the plate has not been shredded instead the plate has been cut into small plates. The boards were washed with distilled water and then with 7 N sodium chloride (NaCl) to avoid contamination and to remove the epoxy coating. It was then dried. The boards were coated with epoxy resin to avoid rusting of the metals of PCB when it contacts the atmosphere. The epoxy coating is a barrier for the microbes to react with the metals. This coating suppresses the growth of microbes and hence reduces the production of organic acids. It was removed with the addition of sodium hydroxide followed by overnight shaking and sonication [12, 13]. The epoxy coating removed PCBs were washed with distilled water until the pH of the left-out sample reaches pH 7.

2.3 Bioleaching

Two types of bioleaching are in practice, one step and two-step bioleaching process. Out of which two-step bioleaching has been implemented in this study as it has shown high efficiency in various literatures [6, 14]. The epoxy resin coating removed e-waste plate (2–10 g) was added to the 7-days-old culture of *A. niger* which was inoculated in the Bioleaching medium. pH plays a significant role in the bioleaching process and so the pH was checked intermittently with the help of Orion pH metre. The samples were placed in an orbital shaker at 150 rpm, 25 °C for 14 days.

2.4 Analytical Techniques

2.4.1 High-Pressure Liquid Chromatography

To analyse the organic acids capillary electrophoresis, HPLC and Ion exchange has been widely used in olden days [15]. Still, HPLC is easily available analytical equipment while comparing to Capillary Electrophoresis (CE) as the awareness about CE is very low though the testing cost is too low while comparing to HPLC. A qualitative test can be done for the identification of organic acids synthesised by the microbes with the help of high-pressure liquid chromatography (HPLC). A retention time of 30 min could give a history of the short chain organic acids being generated by the fungus. Various literatures have been surveyed and the retention times of various organic acids have been studied and listed in Table 1.

A Shimadzu LC2010, Japan HPLC apparatus was equipped with an isocratic pump and a UV–visible detector set at 210 nm to determine the organic acids. A 10 μl sample was injected through the injection valve. The samples were separated isocratically through an amino column (250 mm × 4.6 mm diameter), particle size diameter of 0.5 mm and a pore size of 120 Å. The column temperature was set at 42 °C. The mobile phase was 0.004 N sulfuric acid [16] and it was fed at a flow rate 0.6 mL/min. The day 1 sample was run as blank which contains the bioleaching medium alone to confirm that there is no production of organic acid present in the sample before leaching. The 14 days culture was centrifuged and diluted before it ran in the HPLC as followed by Sanarico, 2003 [17].

Table 1 Types of organic acids and their retention times [18]

S. no	Types of organic acid	Retention time (min)
1.	Oxalic acid	7
2.	Citric acid	8.4
3.	Tartaric acid	9
4.	Malic acid	10.2
5.	Succinic acid	12.8
6.	Lactic acid	13.1
7.	Formic acid	14.4
8.	Acetic acid	15.6
9.	Propionic acid	18.7
10.	Butyric acid	23.3

Table 2 Data of different metallic lamps used for AAS

S. no	Lamps (types)	Wavelength (nm)	Slit width (nm)	Current (mA)
1.	Copper	324.8	0.5	4
2.	Nickel	232	0.2	4
3.	Chromium	357.9	0.5	7
4.	Lead	283.3	0.5	5
5.	Zinc	213.9	0.2	5

2.4.2 Atomic Absorption Spectroscopy

The metals leached by the microbes were analysed by Atomic Absorption Spectrometer (AAS) were various lamps were used in it as mentioned in Table 2.

3 Results and Discussion

3.1 Growth of Microbes

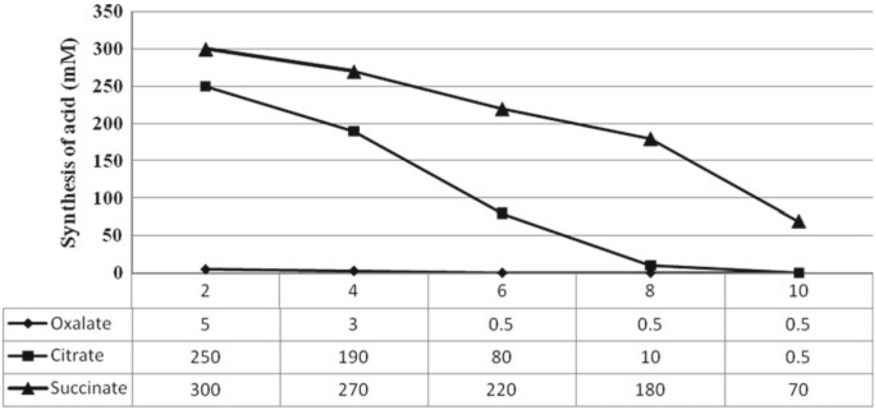
The growth of microorganisms in both the conical flask was monitored every day by taking dry weight of the sample. They attained a partial growth at the 7th day. But as soon as the e-waste was added, there was a sudden shock so that the microbes could not sustain for a while. Continuous stirring made them grow again in the same environmental conditions. After 7 days of inoculation with the samples, the bioleaching medium showed colour changes representing the leaching processes. Whereas *A. niger* is a spore-bearing microbe and it needs little skill for the cultivation of spores from the plate. *A. niger* is a well-known microbe. They help maintain the pH at 1–3. The pH of the medium is maintained by the organic acid produced by the microbes [19]. It was proven that the organic acids produced are citric acid and oxalic acid rather than other microbes. It was found that these acids are the cursors to leach out metals.

3.2 Bioleaching

The 14 days result of two-step bioleachate was analysed with the help of AAS to facilitate the presence of metals in the medium. The bioleachate was centrifuged and filtered before AAS analysis. The initial metal concentration was analysed with the help of chemical leaching. There are various parameters that influence the bioleaching process namely pH, temperature, microorganism, sample size and sample concentration. Out of which the organic acid production due to the presence of plated e-waste has been chosen as the area of study to find out its influence. The morphology of the microbe changes with respect to the size of the sample. It showed a small pebble-shaped structure in the lower concentration whereas the medium turned out to be clumsy in higher concentrations.

3.3 Organic Acid Production

The mobile phase was eluted for 30 min in order to check the baseline and, in another 20 min, the column was ready for the injection of samples. A retention time of 30 min was set for the analysis of the sample. The peaks at a retention time of 5.6–23.3 min indicated the presence of organic acids. The pH of the bioleaching medium of *A. niger* decreases due to this and it was observed clearly in the peaks. Initially, the pH of the medium was found to be 5.5 and after 7 days the pH of the medium was found to be increased up to pH 2.3 which promises that there was the production of organic acids in the sucrose medium. At once, the samples (2–10 g) were added there was a sudden change in pH of the bioleachate which did not last for more than 2 days. There was a proper growth and the microbes started synthesising organic acids. The presence of oxalic acid was confirmed at the retention time of 7 and it was found to be high at approximately 400 mM of oxalate which later decreases as the concentration increase. The production of citric acid is very tedious because it rarely gets produced during the addition of any waste but in this case, the production has been seen and it showed that the size of the particle altered the production of organic acid. Citric acid is well known to leach out metals and this has been achieved in this case. The succinic acid was produced at a high rate and it also decreases with respect to the concentration of e-waste. The principle behind the fact that the presence of plastic content in the bioleaching medium would be too high when a powdered sample is added to the medium which turns toxic for the microbes and so plated sample could help increase the production of organic acid and thereby increase the leaching efficiency.



	2	4	6	8	10
◆ Oxalate	5	3	0.5	0.5	0.5
■ Citrate	250	190	80	10	0.5
▲ Succinate	300	270	220	180	70

Fig. 1 Production of organic acids with respect to the sample concentration and synthesis of acid

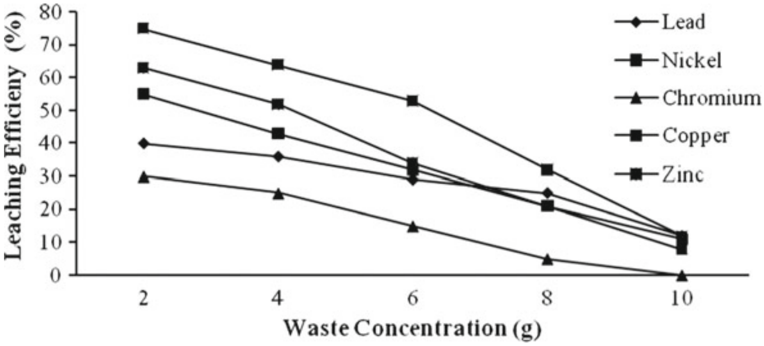


Fig. 2 Leaching efficiency of metals with respect to the waste concentration and leaching efficiency

3.4 *Metal Leaching Efficiency*

As stated earlier organic acid helps in the leaching process. It was clear that the organic acid produced was lump sum which could leach metals (Fig. 1). The peaks present in Fig. 2 showed that the leaching efficiency was high when the concentration of the e-waste was 2–6 g and was found to decrease when the production of organic acid decreases. Sayer added that the addition of any waste to the *A.niger* medium hinders the production of citrate but that was not seen found to be reduced in this case [19]. AAS results showed that the bioleachate of *A. niger* showed nearly 75% of copper which gradually reduced when the addition of e-waste plate increases and so happened for other samples too. And hence *A. niger* suits good for the leaching with the production of citric acid when e-waste metal plates were added to leach metals like copper, nickel, zinc, copper and lead.

4 Conclusion

The bioleaching is a process which helps to leach out the metals from its ore/waste with low or no emission of gasses with the help of microorganisms. The organic acid synthesised differs depending on the microorganisms. *A. niger* was found to synthesise citric acid, oxalic acid and succinic acid which helps in leaching of metals. This study revealed that the citrate production of *A. niger* was not hindered when e-waste was added as a plated sample rather the production of acids were very less when other wastes were introduced. This could help leach out the metals out of it. But the leaching efficiency could be reduced not only because of the organic acids synthesis but also because of the metal concentration. Thus, the leaching efficiency of metals requires organic acid which would be hindered initially when the plated samples were added while the production does not alter when the addition of e-waste gets added up in different concentration and so the leaching efficiency gradually increases.

References

1. Mary JS, Meenambal T (2016) Inventorisation of e-waste and developing a policy-bulk consumer perspective. Procedia Environ Sci 35:643–655
2. Senophiyah-Mary J, Loganath R, Shameer PM (2018) Deterioration of cross linked polymers of thermoset plastics of e-waste as a side part of bioleaching process. J Environ Chem Eng 6:3185–3191
3. Garlapati VK (2016) E-waste in India and developed countries: management, recycling, business and biotechnological initiatives. Renew Sustain Energy Rev 54:874–881
4. Dwivedy M, Mittal R (2012) An investigation into e-waste flows in India. J Clean Prod 37:229–242
5. Barai K, Tiwary C, Chattopadhyay P, Chattopadhyay K (2012) Synthesis of free standing nanocrystalline Cu by ball milling at cryogenic temperature. Mater Sci Eng, A 558:52–58
6. Mary JS, Meenambal T (2015) Solubilisation of metals from e-waste using Penicillium chrysogenum under optimum conditions, Infrastructure development for environmental conservation and sustenance 28–30 October, 2015, p 285
7. Brombacher C, Bachofen R, Brandl H (1997) Biohydrometallurgical processing of solids: a patent review. Appl Microbiol Biotechnol 48:577–587
8. Brandl H, Faramarzi MA (2006) Microbe-metal-interactions for the biotechnological treatment of metal-containing solid waste. China Particuol 4:93–97
9. Burgstaller W, Schinner F (1993) Leaching of metals with fungi. J Biotechnol 27:91–116
10. Devevre O, Garbaye J, Botton B (1996) Release of complexing organic acids by rhizosphere fungi as a factor in Norway spruce yellowing in acidic soils. Mycol Res 100:1367–1374
11. Brandl H (2001) Heterotrophic leaching. In: British mycological society symposium series. pp 383–423
12. Charles JM (1967) Process for removing organic coatings, in, Google Patents
13. Belcak EJ, Corcoran LF (1976) Coatings removal composition containing an alkali metal hydroxide, an oxygenated organic solvent, and an amine, in, Google Patents
14. Brandl H, Bosshard R, Wegmann M (2001) Computer-munching microbes: metal leaching from electronic scrap by bacteria and fungi. Hydrometallurgy 59:319–326
15. Kenney BF (1991) Determination of organic acids in food samples by capillary electrophoresis. J Chromatogr A 546:423–430

16. Schneider A, Gerbi V, Redoglia M (1987) A rapid HPLC method for separation and determination of major organic acids in grape musts and wines. Am J Enol Vitic 38:151–155
17. Sanarico D, Motta S, Bertolini L, Antonelli A (2003) HPLC determination of organic acids in traditional balsamic vinegar of Reggio Emilia. J Liq Chromatogr Relat Technol 26:2177–2187
18. Andersson R, Hedlund B (1983) HPLC analysis of organic acids in lactic acid fermented vegetables. Zeitschrift für Lebensmitteluntersuchung und-Forschung A 176:440–443
19. Sayer JA, Gadd GM (2001) Binding of cobalt and zinc by organic acids and culture filtrates of Aspergillus niger grown in the absence or presence of insoluble cobalt or zinc phosphate. Mycol Res 105:1261–1267

Urban Mining and the Metal Recovery from E-Waste (MREW) Supply Chain

Biswajit Debnath, Ranjana Chowdhury and Sadhan Kumar Ghosh

1 Introduction

E-waste has become a mini-catastrophe and its amount has reached a record level of nearly 42 million metric tonnes in 2014 [4, 10]. The demand for EEE is ever increasing and the driving force behind this demand is often the technological advancement coupled with short innovation cycles and business strategies which shortens the lifespan of the equipments [15]. In 2014, the BRICS nations were responsible for 25% of the total e-waste generated in the world [17]. It has been predicted that by 2017, 72 million tonnes of e-waste will be generated [4].

E-waste is a complex material and contains different types of basic metals, rare earth metals, polymers, glass, glass fibre, etc. (Fig. 1). With the depletion of primary resources and increasing demand for metals in the market, it is legible to recover metals from e-waste and reuse them in the manufacturing process of new ones reducing the mining activities. A comparatively new term *urban mining* has come into the picture. It extends the concept of *landfill mining* to the reclamation process of elements and compounds from the anthropogenic stockpiles [3]. The basic objective of urban mining is to recover resources from urban waste and put them back into the supply chain. It is important to extract and process the anthropogenic stocks accompanied by the economical benefits. This is the primary reason that the term urban mining has become almost synonymous with the extraction of metals from e-waste as the metal concentration (expensive and rare earth) is comparatively high [7]. Several studies have been reported in the context of urban mining. Debnath et al. [13] have proposed the frameworks for Metal Recovery from E-Waste (MREW) to address the

---

B. Debnath · R. Chowdhury
Department of Chemical Engineering, Jadavpur University, Kolkata, India

S. K. Ghosh (✉)
Department of Mechanical Engineering, Jadavpur University, Kolkata, India
e-mail: sadhankghosh9@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_32

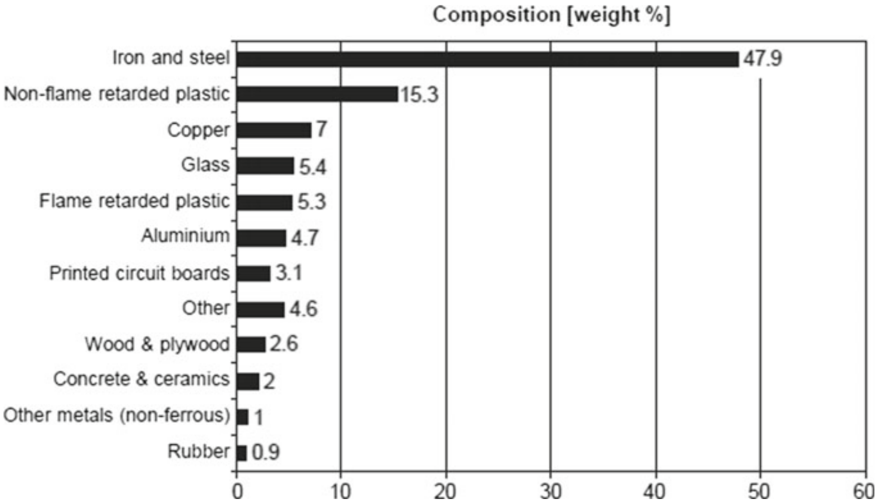


Fig. 1 Composition of e-waste [14]

issue of urban mining. Supply chain network (SCN) of e-waste is interesting and complex [9]. It is imperative to have an efficient and sustainable SCN for proper e-waste management. Aravindhan et al. [1] have provided some insight into how supply chain strategies can help e-waste management. There are several issues and challenges in e-waste supply chains and the sustainability of the business depends on it [15219]. Country-specific supply chain mapping has been approached by different researchers. It is of great interest to identify how the supply chain of e-waste differs in developed and developing countries [9, 16]. Ghosh et al. [17] has mapped the high level supply chain for the BRICS nations and also proposed a sustainable high level SCN for them taking learning from developed nations. Barletta et al. [5] have provided the prerequisites for a high level framework for designing sustainable units in the e-waste supply chain. Reported literatures focus on country-specific supply chain mapping, optimisation models, risk assessments, etc. Hence, focus on the e-waste supply chain issues was there. However, for urban mining, it is crucial to address the issue of metal recovery and that has not been addressed in the reported literature. The research questions that arise are—how MREW can help in addressing the urban mining concept? How essential it is to have an efficient supply chain for MREW? What is the supply chain framework of the MREW? The study aims to answer these questions with the background concept of MREW. A supply chain framework for the MREW has also been developed.

Table 1 Metal percentage in PCBs

Metal	Ores (%)	PCBs (%)
Copper	0.5–3.0	12.0–29.0
Zinc	1.7–6.4	0.1–2.7
Tin	0.2–0.85	1.1–4.8
Lead	0.3–7.5	1.3–3.9
Iron	30–60	0.1–11.4
Nickel	0.7–2.0	0.3–1.6
Gold	0.0005	0.0029–0.112
Silver	0.0005	0.01–0.52

Source Bizzo et al. [6]

2 Methodology

First, a detailed literature survey was carried out. Several search engines were explored with keywords such as ‘E-waste supply chain’, ‘WEEE supply chain’, ‘Urban Mining’, etc. The literature was critically reviewed and the relevant ones were segregated. Cross-references were also considered for review. Based on the findings of Ghosh et al. [17] and Debnath et al. [13] and the authors’ experience in visiting different e-waste recycling facility around the world, a supply chain framework was developed for an MREW. The relevant literatures have been cited and additional information from the associated cross-literatures has been also properly referred.

3 Urban Mining of E-Waste

The concept of *urban mining* is associated with recovery of materials and energy from urban waste and puts them back into the economy. Such a concept must be coupled with circular economy concept to design policy frameworks for sustainable development. The anthropogenic stock available for urban mining is not limited to e-waste, but the overall concept has somehow become synonymous with resource recovery from e-waste. There is special relevance to this with respect to the goal no. 13 of the Ha Noi 3R goals which encompasses the concept of urban mining [18]. The key reason for this is due to the concentrations of metals that are more in PCBs compared to the ores (Table 1) [6].

E-waste is a heterogeneous material and contains different types of basic metals, valuable metals, rare earth elements (REE), polymers, ceramics, glass, etc. From the perspective of urban mining, all of these are resources which can be recovered via technological intervention. In general, physical recycling processes are implemented for the segregation of separate streams such as metals, glass, polymers, etc. Thermochemical, pyrometallurgical, hydrometallurgical and biometallurgical technologies can be employed for further resource recovery from the resultant material streams from physical processing of e-waste. These technologies have been discussed in detail previous reported literatures [10, 11, 20].

4 The Relevance of MREW to Urban Mining

The business of e-waste is particularly of interest due to the presence of metals. Recovery of metals from e-waste is expected to play a major role in the resource circulation. Technologies such a pyrolysis, leaching, electro-chemical refining, pyrometallurgic extraction of metals, bio-leaching, etc. are in existence which are helpful in metal recovery from e-waste (MREW) [13]. We have discussed the concept of MREW in details in our previous work [13]. As the primary intention of urban mining is the resource recovery from 'urban ore' (or anthropogenic stockpile) and its proper circulation, the MREW has direct relevance to it. Though the metals are the particular focus, several other things can be recovered from e-waste. E-waste consists of a significant amount of polymers. These polymers may be recycled to make nice products or can be used for new product development. The printed circuit boards (PCBs) are metal-polymer-glass fibre matrix which is a source of useful materials. Pyrolysis of PCBs followed by mechanical separation can lead to recovery of metals, pyro-oil and glass fibre [12]. All of these are recyclables and have market value and pyrolysis can be considered as a pretreatment process for MREW [13]. Based on the size and average composition of e-waste, the resources that can be recovered can be estimated and accordingly the recovery path may be chosen. Another important issue is the economic sustainability, which must be ensured while realisation of urban mining via MREW facilities [8]. Some generalised insight on economic sustainability of MREW has been discussed in the previous paper [13]. Though much more innovations are required, MREW technologies are expected to play a pivotal role in urban mining of e-waste.

5 Findings and Discussions

5.1 Supply Chain Framework for Urban Mining Considering MREW

Despite the technological advancements and maturity over time, it is imperative to have a very efficient supply chain network to balance the supply and the demand for materials and ensure circular economy. Based on the findings of Ghosh et al. [17] and Debnath et al. [13], literature findings, brainstorming and the authors' experience in visiting several e-waste recycling facilities, a supply chain framework has

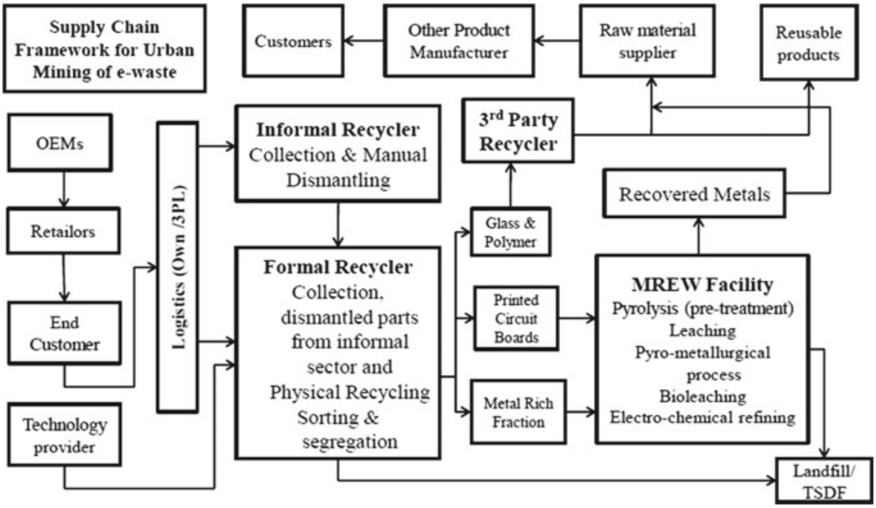


Fig. 2 Supply chain framework for urban mining of e-waste considering MREW facility

been developed (Fig. 2). The framework is intended for urban mining of e-waste considering MREW facility.

The supply chain framework can be divided into three parts—the supply side, the internal operations side and the demand side. OEMs, retailers, customers and the technology providers are in the supply side. The informal sector, formal recyclers and the MREW facility are in the internal operations side whereas; third party recyclers, raw material suppliers, reusable product manufacturer and customers of recycled products are in the demand side.

5.2 *Discussions*

The developed supply chain framework (Fig. 2) has considered the MREW facility for the recovery of metals from e-waste. The supply side considers the traditional stakeholder flow from OEM to end customers. The logistics for e-waste to recycling facilities has been kept as a choice of the users. To some extent, the door-to-door collection of the informal sector makes it independent of the users. After the collection and dismantling at the primary recycling facilities, the recovered fractions enter the MREW facility. In the MREW, all possible routes of metal recovery have been considered including pyrolysis as a pretreatment process. This is where the urban mining gets a boost. The existence of the dedicated MREW facility for metal recovery is the key and the strongest point here is to ensure the resource recovery. The circularity of resources is ensured by the demand side where the third party recyclers are involved in recycling the resulting fractions and the recycled product manufacturers convert these into products which can be sold in the market. Some portion of recovered e-waste can be considered as raw materials and these are then supplied to different places by the raw material suppliers, which mean the material re-enters the value chain. This conforms to the concept of circular economy. Nonetheless, the supply chain framework will undoubtedly help in realising the concept of urban mining in a unique way and ensure sustainability.

6 Conclusions

In this paper, the concept of urban mining has been addressed with respect to e-waste as a very important anthropogenic stockpile. The concept of MREW has been taken as basis and its relevance to the urban mining of e-waste. Furthermore, a supply chain framework has been developed which considered MREW facility to address urban mining of e-waste. The urban mining is a new concept and this study focusing on enhancing urban mining of e-waste gives it a boost. The unique concept of the MREW facility will no doubt be a thing to be explored in the future for the researchers. The proposed framework will help in enhancing urban mining and ensuring sustainability. It is also believed that more studies of such kind accompanied by case studies will be beneficial for the overall community.

Acknowledgements The authors would like to acknowledge International Society of Waste Management, Air and Water (ISWMAW) for partially funding the project. Additionally, the help and cooperation from Dr. Prasanta Kumar Dey, Aston University; Centre for Quality Management Systems (CQMS) Jadavpur University, Kolkata; Consortium of Researchers for Environmental Protection, Sustainability and Climate Change (CREPSCC) are gratefully acknowledged.

References

1. Aravindhan L, Raaghavan P, Vivek Narayanji SG, Jaysri Thangam A (2012) Impact of supply chain strategies on the reduction of e-waste. Int J Interscience Manage Rev 2(2):26–29
2. Baidya R, Debnath B, Ghosh SK (2016) Analysis of E-waste supply chain framework in india using the analytical hierarchy process. In: Proceedings of 6th on waste management and resource utilization IconSWM 2016, Jadavpur University, India, pp 1181–1188
3. Baccini P, Brunner P (2012) Metabolism of the antroposphere: analysis, evaluation, design. The MIT Press, Cambridge. ISBN 9780262016650
4. Baldé CP, Wang F, Kuehr R, et al (2015) The global e-waste monitor–2014. United Nation University
5. Barletta I, Johansson B, Reimers J, Stahre J, Berlin C (2015) Prerequisites for a high-level framework to design sustainable plants in the e-waste supply chain. Procedia CIRP 29:633–638
6. Bizzo WA, Figueiredo RA, de Andrade VF (2014) Characterization of printed circuit boards for metal and energy recovery after milling and mechanical separation. Materials 7(6):4555–4566
7. Cossu R, Williams ID (2015) Urban mining: concepts, terminology, challenges. Waste Manag 45:1–3
8. Cossu R (2013) The urban mining concept. Waste Manage 33(3):497–498

9. Debnath B, Baidya R, Ghosh SK (2015) Simultaneous analysis of WEEE management system focusing on the supply chain in India, UK and Switzerland. Int J Manuf Ind Eng 2(1):16–20
10. Debnath B, Roychoudhuri R, Ghosh SK (2016) E-waste management–a potential route to green computing. Procedia Environ Sci 35:669–675
11. Debnath B, Chowdhury R, Ghosh SK (2016b) An analysis of e-waste recycling technologies from the chemical engineering perspective. In: Proceedings of 6th waste management and resource utilization IconSWM 2016, Jadavpur University, India, pp 1189–1195
12. Debnath B, Chowdhury R, Ghosh SK (2017) An analysis of e-waste recycling technologies from the chemical engineering perspective. In: Proceedings of CHEMCON 2017, Haldia Institute of Technology, India, pp 1189–1195
13. Debnath B, Chowdhury R, Ghosh SK (2018) Sustainability of metal recovery from e-waste. Front Environ Sci Eng, Springer (Accepted for publication.)
14. ETC/RWM (2003) European topic centre on resource and waste management (Topic Centre of the European Environment Agency) part of the European Environment Information and Observation Network (EIONET), http://waste.eionet.eu.int/waste/6
15. Ghosh SK, Baidya R, Debnath B, Biswas NT, De D, Lokeswari M (2014a) E-waste supply chain issues and challenges in India using QFD as analytical tool. In: Proceedings of international conference on computing, communication and manufacturing, ICCCM 2014, pp 287–291
16. Ghosh SK, Singh N, Debnath B, De D, Baidya R, Biswas NT, Ghosh SK, Lili L, Dey PK, Li J (2014b) E-waste supply chain management: findings from pilot studies in India, China, Taiwan (ROC) and the UK. In: The 9th international conference on waste management and technology, Beijing China, 29–31 October, 2014, pp 1131–1140
17. Ghosh SK, Debnath B, Baidya R, De D, Li J, Ghosh SK, Tavares AN (2016) Waste electrical and electronic equipment management and Basel Convention compliance in Brazil, Russia, India, China and South Africa (BRICS) nations. Waste Manage Res 34(8):693–707
18. Ha Noi Declaration (2013) Available from: https://www.env.go.jp/en/focus/docs/files/20130318-67.pdf. Accessed on 3 Dec 2017
19. Hazra J, Sarkar A, Sharma V (2011) E-waste supply chain management in India: opportunities and challenges. Clean India J 7
20. Khaliq A, Rhamdhani MA, Brooks G, Masood S (2014) Metal extraction processes for electronic waste and existing industrial routes: a review and Australian perspective. Resources 3(1):152–179

Fast Thermal Degradation of Biomass Using Scrapped Solar Cell with Special Focus on Photovoltaic (PV) Waste Disposal

G. N. Lalith Pankaj Raj Nadimuthu, V. Madhan Karthik, M. Mohanraj and V. Kirubakaran

1 Introduction

India is the world's second largest populated country in the world. India is the world's third largest producer and fourth largest consumer of electricity in the world. The amount of electrical energy consumption in India for the year 2016–2017 is 1127 kWh per capita. The per capita energy consumption in India is 768 kWh. The electrical energy demand in India was met by fossil fuels and renewable energy in which both of the energy shares 67.1 and 30.8%. India is a country which is located in tropical region gets Sun radiation throughout the year. Because of the increase in global pollution and greenhouse gas emission from all over the world, renewable energy came into play. The GHG emissions from the electricity power generation are 2019.6 $MtCO_2$. The solar energy is one of the widely used energy for power generation all over the world and in India and it accounts 12.6 GW units of energy. The government of India aims to achieve the usage of renewable energy by 175 GW in 2022. In the field of renewable energy where the electricity from the solar photovoltaic cell will give more yield in India. The major problem with the solar PV cell is Disposal after use. There is going to be very huge amount of Solar PV panels will come into landfills after their use of 25–30 years. After the lifetime usage of solar panels, the disposal is going to be a big problem to the environment. Since it is non-degradable material and has high risk of harmfulness associated with it. So, it cannot be dumped into the environment as landfill. For that, the disposal of aged solar cells technique is to be identified effectively.

G. N. Lalith Pankaj Raj Nadimuthu · V. M. Karthik (✉) · M. Mohanraj · V. Kirubakaran
Rural Energy Centre, The Gandhigram Rural Institute-Deemed University,
Dindigul, Tamil Nadu, India
e-mail: madhankartikk007@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_33

2 Literature Review

Vekes Balasundrama et al., gave the concept of catalytic reaction techniques of biomass and chemical material in the combustion process. Here, they used alumina (Al2O3) as a catalyst was used in addition with nickel (Ni) and cerium (Ce) as promoter at fixed loading by weight percent of 20 wt% Ni: 5 wt% Ce: 75 wt% Al_2O_3.

Cui Quan, Aimin Li and Ningbo Gao [1] clearly gave the idea to carry out the Thermal analysis of the Waste Electrical and Electronics Equipment (WEEE). Author shows the thermogravimetric analysis and kinetics studies of the various electronic wastes like keyboards, PCB and telephone wires, which intern helps us to proceed with our research.

Mahsa Baniasadi, Alessandro Tugnoli* and Valerio Cozzani provide us the idea of catalytic reaction of biomass like chicken manure for pyrolysis proces [2].

3 Methodology

3.1 Segregation

In general, the solar panels are arranged with individual solar cells in the order of series and parallel combination. In this paper, the individual single solar cells are segregated from the solar panels with the help of some hand tools. The process of expulsion of solar cells from the aged solar panels done with the knowledge of chipping out the cells with the help of hand tools. Finally, the cells are broken into small pieces for studying the reduction of weight.

3.2 Incineration

This is the process of high-temperature disposal method in which involves complete combustion of hazardous materials. In the first process, the aged solar cells that are made to small pieces burn at 1000 °C in furnace body. During the burning of materials, the weight and volume occupied by the aged solar cells started decreasing. In the next process, some amount of wood powders are used as a fuel to accelerate the burning of solar cells. It retains the heat in the crucible so that even after attaining the set temperature, the heat in the crucible remains for some more time so that the toxic gases present in the cells comes out. Various proportions of wood and solar cells combination were studied. The toxicity and pollutants presented in the materials are removed at low temperature which it prevents from land pollution.

Table 1 Properties of sample

Sample	% of wood powder	% of powdered solar cell
1	100	0
2	90	10
3	80	20
4	70	30
5	60	40
6	50	50

3.3 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) measures the rate of change in the weight of a material as a function of temperature or time in controlled atmospheric conditions. This study is mainly used to obtain the thermal stability of a particular Materials and their composition of materials. It will give the properties of weight loss or gain of that particular material [5].

4 Experimental Details

In the process, we have taken the aged solar panels and separated the solar cells from panels crushed into small pieces. The small pieces of solar cells are kept in crucible and weight is measured in a weighing scale. The crucible is kept in furnace and made to attain the temperature of 1000 °C in a static environment of burning. Then weight reduction was observed is not in a promising manner.

After that, the different proportions of wood powders and solar cells are made to different samples and kept in furnace for 500 °C. The samples of different proportions of the weight were measured and observations are noted down.

The various sample proportions are shown in Table 1.

The samples are taken in a total weight of 10 g, and there are six samples with above-shown proportions of mentioned above.

Figure 1 shows the final status of the various samples of wood and solar which are burned at 500 °C in a muffle furnace, which in turn shows the type of combustion process.

Figure 2 shows the comparison between the combustion of both the sample (i.e.) 100% Wood powder and sample 6 (i.e.) 50:50% of the Wood powder and the solar cell powder.

From the comparison, we observed that the 50:50% gives good result than the other combinations. So we decided to find the suitable biomass [4]. Then, we took the various biomass like rice husk, coconut husk, tea waste, palm trunk, groundnut shell and did the above-mentioned procedure of 50% of biomass and 50% of solar cell powder.

Fig. 1 Samples at 500 °C

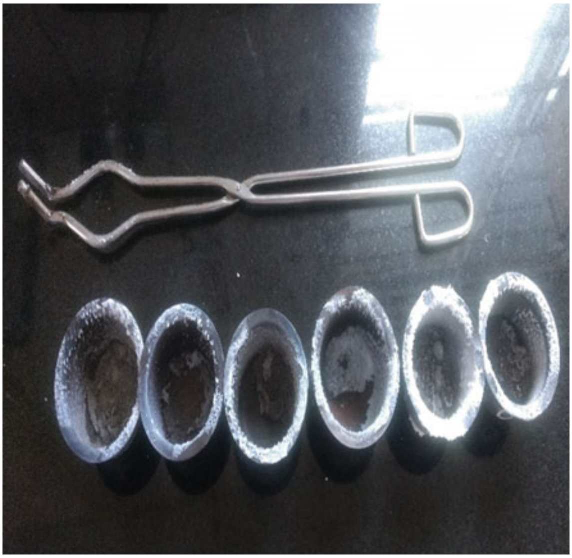


Fig. 2 Comparison of 100% wood and 50% wood

Figure 3 shows the thermal image of the crucible with the sample 6, which shows the temperature gain of sample 6 (Wood: PV cell) accurately with that maximum temperature of 523 °C inside the crucible (Figs. 4 and 5).

The various biomass are included in the study, the biomass like rice husk, coconut husk, tea waste, palm trunk, groundnut shell and wood powder. From our previous study results, we took 50–50% sample and biomass are taken in a crucible for combustion analysis. Figure 6 gives the thermography of palm trunk, Fig. 7 gives the thermography of rick husk, Fig. 8 shows the thermography of tea waste, Fig. 9 shows the

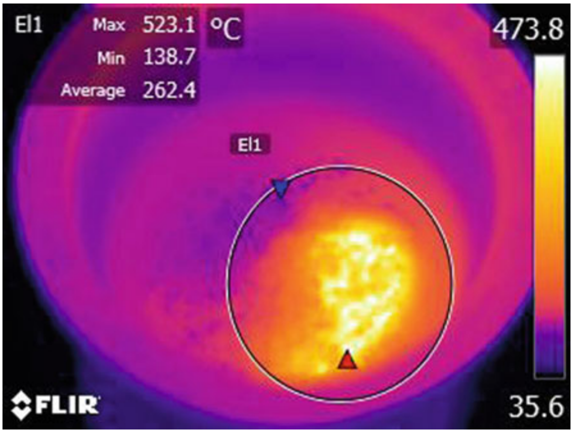


Fig. 3 Thermal image of sample 6

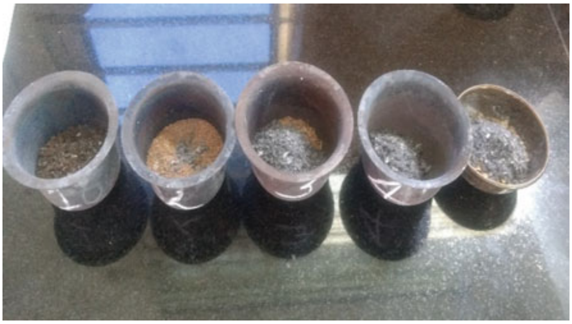


Fig. 4 Various samples of biomass (unburnt)

Fig. 5 Various samples of biomass (Burnt)

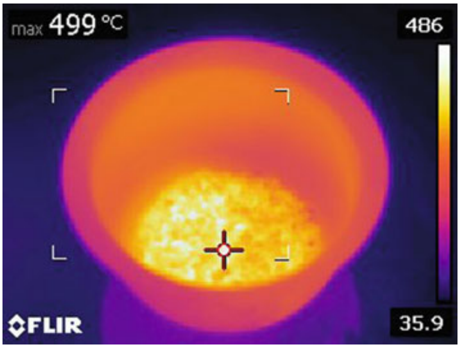


Fig. 6 Biomass sample of palm trunk

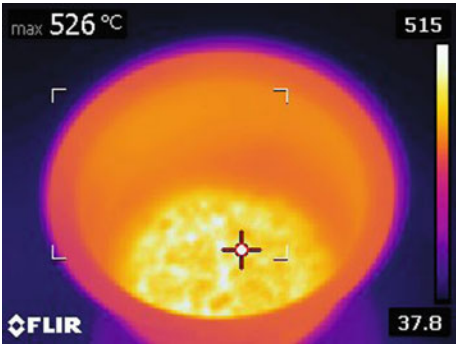


Fig. 7 Biomass sample of rice husk

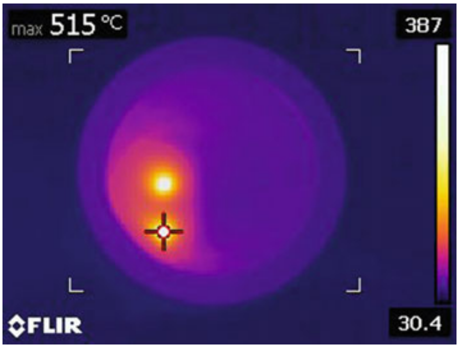


Fig. 8 Biomass sample of tea waste

thermography of coconut trunk, Fig. 10 gives the thermography of groundnut shell.

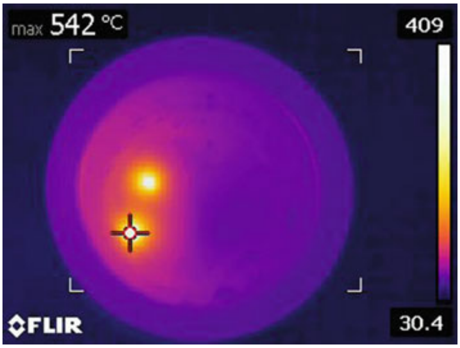


Fig. 9 Biomass sample of coconut trunk

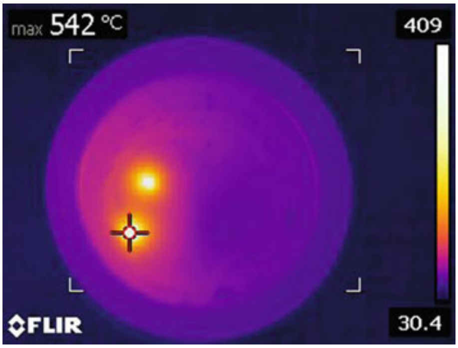


Fig. 10 Biomass sample of groundnut shell

5 Findings and Observation

The isothermal degradation of solar cells inside the Muffle furnace is continuously monitored. Under the static environment of the muffle furnace, the toxic gas compounds become degraded by high-temperature incineration treatment. During this point of firing of solar cells homogenous exothermic heat energy is released which has potential of high energy content which can be utilized for various purposes. The toxic level of the solar cells is found to reduced and imparts less pollutant to the landfill. The thermal degradation and its characteristic behaviour are monitored for the set temperature of the incineration process inside the muffle furnace. The burnt solar cells are collected at the final stage for further study. The percentage reduction in various samples ratios are calculated and tabulated below Table 2.

Graph 1 clearly shows the percentage weight reduction at 500 °C versus sample. This is evident that the co-combustion process of 50% wood powder and 50% solar cell powder makes a huge difference in terms of percentage weight reduction, which is about nearly 33.03%.

Graph 2 gives the thermogravimetric analysis curve which gives the percentage weight reduction with respect to that of temperature.

Various biomass samples are taken and the results are tabulated.

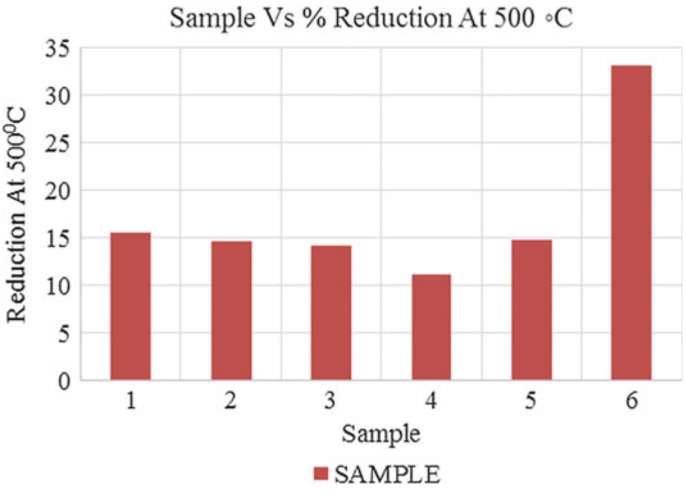
The percentage removal of ash content for various biomass samples is calculated using this formula [3].

$$\%\ \text{Removal of Ash} = \frac{\text{Final Weight} - \text{Intial Weight}}{\text{Sample Weight}} * 100$$

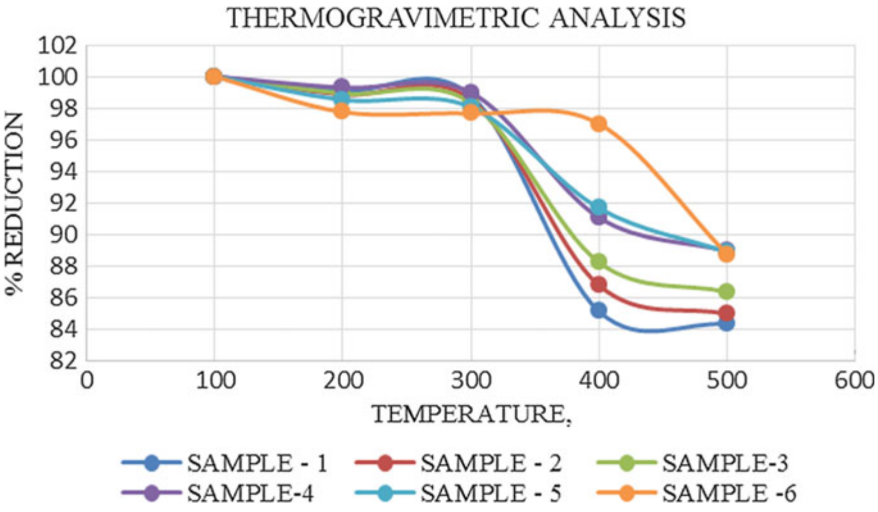
The various samples of percentage of ash content for scrapped PV with biomass and without scrapped PV biomass were calculated and tabulated below. Table 3 gives the percentage of Ash without Scrapped solar PV cell. Table 4 gives the Percentage

Table 2 Percentage reduction of various sample ratios

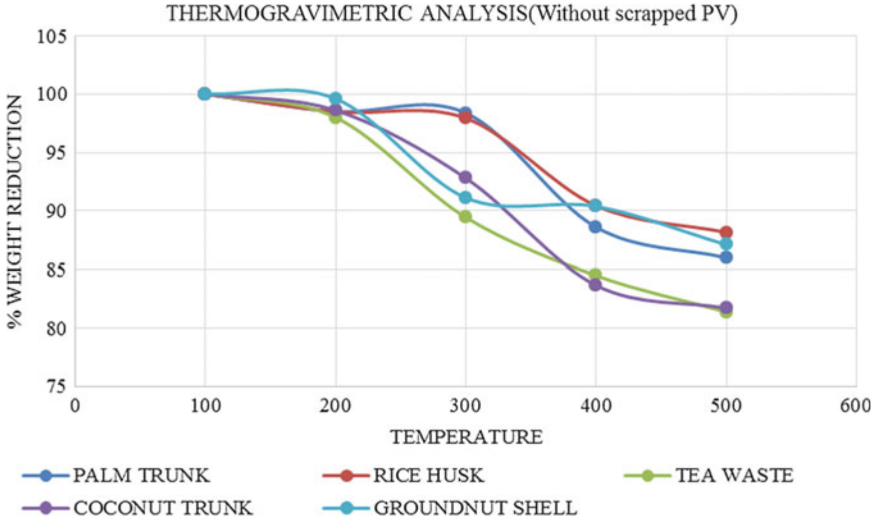
Sample	% reduction 100 °C	% reduction 200 °C	% reduction 300 °C	% reduction 400 °C	% reduction 500 °C
1	0.898120757	1.223742737	14.89348118	15.70434375	15.59139785
2	1.149857373	1.468279415	13.24326117	15.06313159	14.56164555
3	1.078378713	1.667148701	11.77953146	13.6594637	14.23012064
4	0.718108529	1.024659576	8.942483572	11.07140438	11.08541893
5	1.489241112	1.944612739	8.347176891	11.12631188	14.82645123
6	2.257058222	2.351429994	2.99892521	11.26431961	33.03724482



Graph 1 Sample versus % weight reduction



Graph 2 Thermogravimetric analysis of various samples



Graph 3 Thermogravimetric analysis (without scrapped PV biomass)

of ash with scrapped solar PV cell, Table 5 gives the comparison of Biomass weight reduction with and without scrapped solar PV cell. Graph 1 gives the sample vs weight reduction, Graph 2 shows the Thermogravimetric analysis of sample, Graph 3 represents the Thermogravimertic analysis of sample without scrapped solar PV cells, Graph 4 represents the thermogravimetric analysis of sample with scrapped solar PV cells, Graph 5 gives the overall comparison of weight reduction and sample.

Table 3 Percentage of ash for various biomass and without scrapped PV cell

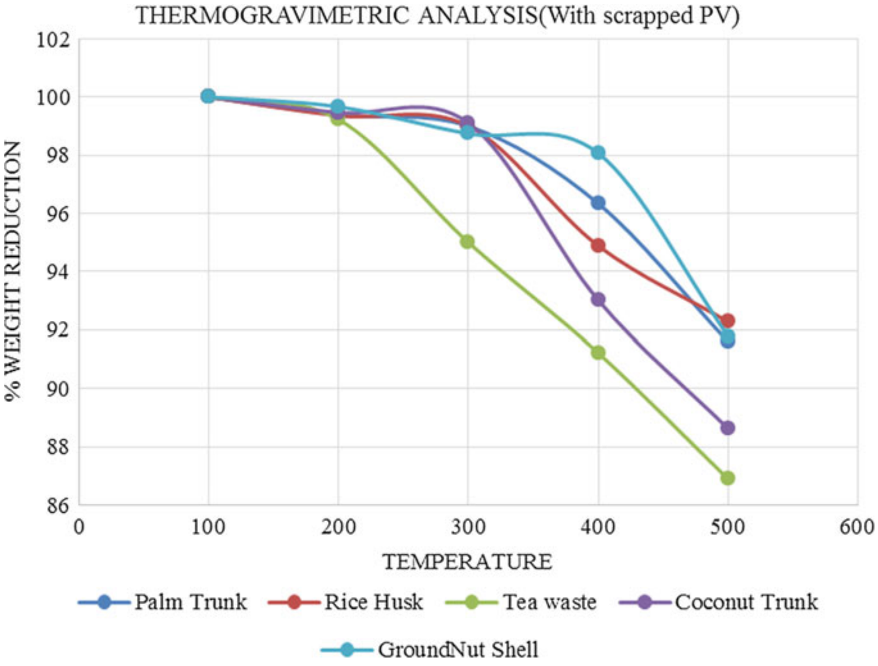
S. no	Biomass	Crucible weight (g)	Initial weight (g)	100 °C	200 °C	300 °C	400 °C	500 °C	Without scrapped PV (%)
1	Palm trunk	48.47	58.47	57.6	57.5	51.8	50.2	49.6	12
2	Rice husk	41.2	51.2	50.4	50.1	46.3	45.1	44.2	30.9
3	Tea waste	32.27	42.27	41.4	37.8	35.7	34.4	33.3	10.6
4	Coconut trunk	35.2	45.2	44.5	41.9	37.8	36.9	35.9	7.9
5	Groundnut shell	37.78	47.78	47.5	43.5	43.1	41.6	39.7	19.6

Table 4 Percentage of ash for various biomass and with scrapped PV cell

Sl. no.	Biomass	Crucible weight (g)	Initial weight (g)	100 °C	200 °C	300 °C	400 °C	500 °C	With scrapped PV (%)
1	Palm trunk	36.99	46.99	46.7	46.5	45.2	43.0	41.5	45.1
2	Rice husk	49.028	59.028	58.6	58.4	56.0	54.4	53.8	48.02
3	Tea waste	28.094	38.094	37.8	36.1	34.7	33.1	32.2	41.76
4	Coconut trunk	38.42	48.42	48.1	47.9	45.0	42.9	42.1	37.2
5	Groundnut shell	37.66	47.66	47.5	47.0	46.7	43.7	42.3	46.7

Table 5 Comparison of percentage weight reduction between without scrapped PV cell biomass and with scrapped PV cell biomass

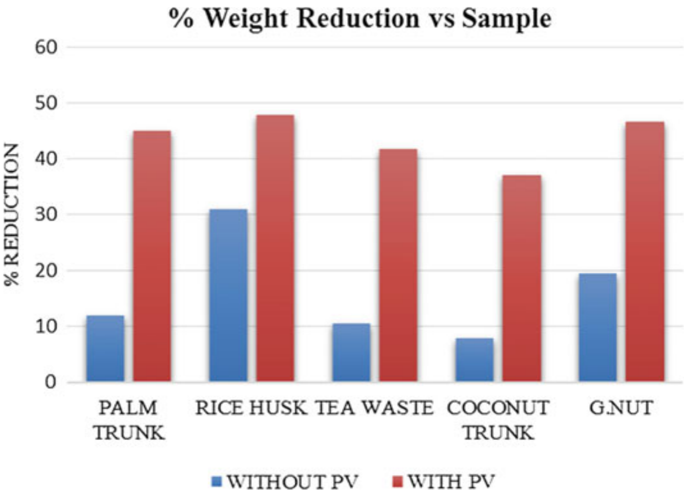
Sl. no.	Samples	Without scrapped PV cell (%)	With scrapped PV cell (%)
1	Palm trunk	12	45.1
2	Rice husk	30.9	48.02
3	Tea waste	10.6	41.76
4	Coconut trunk	7.9	37.2
5	Ground nutshell	19.6	46.7



Graph 4 Thermogravimetric analysis (with scrapped PV biomass)

6 Conclusion

From the analysis of various biomass catalysed with scrapped photovoltaic cells, it is observed that by adding the scrapped photovoltaic cells, the degradation rate of biomass increases during the combustion process. Rice husk shows the highest consistent reduction in weight as it measures 48.02% and the groundnut shell 46.7% and palm trunk 45.1% comes next to it. The tea waste and coconut trunk shows least weight reduction of only 41.7% and 37.2%, when compared with all other biomass samples. Rice husk is widely used fuel for gasification, and by adding the scrapped



Graph 5 Comparison of percentage weight reduction between without scrapped PV cell biomass and with scrapped PV cell biomass

solar cells with the rice, husk the combustion temperature will become lower and also it increases the quality of producer gas.

Acknowledgements The authors gratefully acknowledge UGC for funding the M. Tech. Renewable Energy under Innovative Programme scheme.

References

1. Quan C, Li A, Gao N (2013) Combustion and pyrolysis of electronic waste: thermo gravimetric analysis and kinetic model. Int Symp Environ Sci Technol Procedia Environ Sci 18(2013):776–782
2. Baniasadi M, Tugnoli* A, Cozzani V (2016) Optimization of catalytic upgrading of pyrolysis products. The Italian Association of Chemical Engineering, ISBN 978-88-95608-40-2, ISSN 2283-9216
3. Kirubakaran V, Sivaramakrishnan V, Premalatha M, Subramanian P (2007) Kinetics of autogasification of poultry litter. Int J Green Energy 4:519–534 ISSN: 1543-5075/1543-5083
4. Kirubakaran V, Sivaramakrishnan V, Nalini R, Sekar T, Premalatha M, Subramanian P (2007) A review on gasification of biomass. Renew Sustain Energy Rev 13(2009):179–186
5. Balasundram V, Ibrahim* N, Samsudin MDH, Kasmani RM, Hamid MKA, Isha R, Hasbullah H (2017) Thermogravimetric studies on the catalytic pyrolysis of rice husk, vol 56, 2017. A publication of The Italian Association of Chemical Engineering, ISBN 978-88-95608-47-1; ISSN 2283-9216

Optimisation of Copper Removal from E-Waste Using Bioleaching Technique by Activated Mosambi Peels

J. Senophiyah-Mary, Teema Thomas, R. Loganath and T. Meenambal

1 Introduction

The electronic waste grows exponentially which has been found during the investigations executed by the European Union (EU). It was found that the growth rate of e-waste increases at a rate of 3–5% every year. The United Nations have also assessed that the world has created a serious damage by producing nearly 50 million tonnes of e-waste every year [1–3]. A similar situation applies to cell phones and other handheld electronic gadgets utilised as a part of present society. Every year, more than 130 million cell phones in the USA and more than 105 million versatile telephones in Europe achieve their finish of life and are discarded. Accordingly utilised EEE, normally known as e-waste and known as Waste Electrical and Electronic Equipment (WEEE), has turned into a genuine social issue and natural thread to numerous

---

J. Senophiyah-Mary (✉)
Department of Civil Engineering, Government College of Technology,
Coimbatore 641013, Tamil Nadu, India
e-mail: senophiyah.mary8@gmail.com

T. Thomas
Department of Civil Engineering, Thejus Engineering College,
Thrissur 680584, Kerala, India
e-mail: teemathomas111@gmail.com

R. Loganath
Department of Civil Engineering, Indian Institute of Engineering
Science and Technology, Shibpur, Howrah 711103, West Bengal, India
e-mail: loganath.rk@gmail.com

T. Meenambal
Department of Civil Engineering, Madanapalli Institute of Technology, Madanapalli,
Chitoor 517325, Andhra Pradesh, India
e-mail: tmeenambal_gct@yahoo.co.in

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_34

nations around the world. E-waste likewise contains various dangerous substances, counting plastics and substantial metals [4–7].

More than 70% of metal in the printed circuit board is copper. The need of copper increases every day as there is an exponential growth in electronic industries has been chosen and the conductivity of copper is high. Due to the crude extraction process, they get dissolved in the groundwater and contaminate the soil, and bioaccumulates in plants, animals and even in human and removal of copper are crucial from all these substances [8]. The WHO has recommended 2.0 mg/L as permissible limit in drinking water. It also causes itching, dramatisation, keratinisation of the hands and soles of feet. They also cause gastrointestinal irritation and damages liver, kidney if consumed in large. Inhalation while acid or pro-metallurgical treatment causes lung cancer. Hence, the removal of copper from the leachate is necessary to make the environment healthy [9–13].

Bioleaching was found to be the safest way of treatment of the printed circuit board which is the heart of any electronic device that has a large amount of metals with it. The microbes that help in the leaching process are symbiotic because they uptake a small amount of metal for their growth and give out a large amount of organic acid that leaches the metal to the medium creating a pool of metal which needs a further treatment because of the disposal to the environment [14, 15]. And so the activated carbon has been used in the extraction of metals from the bioleachate. Many low-cost adsorbents have been practised in the metal removal from wastewater and so this technique has been used in the metal extraction which could then be used in many techniques [12, 14, 16, 17]. Many fruit wastes were tried by various researchers out of which mosambi peels were chosen for the experiment because it is a well-known fruit peel with a rich source of fibre. The time taken for optimising the experiment is more and so trials were conducted based on the outcome of Design-Expert software which reduced the use of time and material. Thus, the software lessens the time by providing a consolidated result and therefore this is a time-saving experiment which can be easily implemented [18–22].

The objective of this present study, the effects of the pH, temperature, agitation speed, dosage, concentration, contact time and their interactions on the efficient removal of copper were investigated. The DOE was used to optimise the copper removal efficiency through the bioleaching treatment process. The parameters were optimised for the removal of copper by Central Composite Design (CCD) by feeding six factors of three levels combined with RSM. A statistical model was developed to calculate the copper removal efficiency percentage from the printed circuit board. The statistical quadratic models were validated by another set of experiments at the optimum operating conditions based on the DOE results.

2 Materials and Methods

2.1 *Adsorbate*

Bioleachate of e-waste was used as a source for the extraction of copper which acts as an adsorbate. Bioleachate was prepared previously with various effective microorganisms [15]. Bioleachate was centrifuged by Large Volume Centrifuge (Sigma 2-16 KL model) and the supernatant was collected. The solution with metals is then diluted several times for adsorption process.

2.2 *Adsorbent—Mosambi Activated Carbon (MAC)*

The mosambi peel was collected from local fruit juice shop and washed several times. They are then chopped to a size of 1 cm^2. It was then sun-dried for 24 h so that the consumption of other sources of energy would be reduced. It was dried in a hot air oven at 100 °C for 12 h. The dried peels were then activated with the help of thermal activation which includes carbonising the sample at 500 °C for 4 h in a muffle furnace and activating the sample at 800 °C for 10 min. They are then ground then sieved through 75 μm sieve and stored. The samples were then ground well in planetary Ball mill for conversion of still smaller particles and it was analysed for various characteristics.

2.3 *Atomic Absorption Spectrophotometer*

Experiments were carried out at room temperature (25–30 °C) in batch method. Batch method was selected due to its simplicity and reliability. The experiments were carried out by taking 10 ml of 10 ppm e-waste bioleachate sample in a 15 ml falcon tube and after pH adjustment, a 10 mg of dried adsorbent was added. The flask was agitated at 150 rpm for 60 min using an orbital shaking incubator. After shaking, the sample suspension was allowed to settle. The residual biomass adsorbed with metal ion was filtered using whatman-1 filter paper. Copper ions were estimated using (Agilent 200 Series) Atomic Absorption Spectrophotometer *(*AAS). The percent removal of copper from the solution was calculated by the following equation:

$$\text{Percentage removal of copper} = \frac{c_i - c_f}{c_i} \times 100$$

where

C_i initial copper concentration (ppm),
C_f final copper concentration in the solution (ppm)

2.4 Response Surface Methodology

Design-Expert 7.1.5 was used, and a 2^3 factorial design with six central points and six axial points was selected. The behaviour of the system is explained by the following second-order polynomial empirical model.

$$y = \beta_0 + \sum_{i=1}^{n} \beta_i X_i + \sum_{i=1}^{n} \beta_{ii} X_i^2 + \sum_{i<1}^{n} \sum_{j=1}^{n} \beta_{ij} X_i X_j + \varepsilon \tag{1}$$

where y is the response, β_0 is the constant coefficient, x_i $(i = 1 - n)$ are non-coded variables, β_i is are the linear interaction coefficients, β_{ii} are the quadratic interaction coefficients and β_{ij}s (i and $j = 1 - n$) are the second-order interaction coefficients and are residuals for each experiment

Data were processed for Eq. (1) using the Design-Expert 7.1.5 program, including an ANOVA to evaluate the interaction between the process variables and the response. The quality of the fit of the polynomial model was expressed by the coefficient of determination (R^2), and its statistical significance was checked by the F-test in the same program.

3 Results and Discussion

Response Surface Methodology was applied to resolve the optimum conditions of the experiment with six different factors, including the pH, temperature (°C), agitation speed (RPM), dosage (mg/L), concentration (ppm), and contact time (mins) to obtain maximum percent copper removal efficiency. The optimisation was obtained by an optimisation condition using the numerical optimisation method that was built into the software, Design-Expert 7.1.5. As a result, the equation has been formalised as shown in Eq. (2) which was the objective function of the software. This optimisation method helped to explore the design gap using the accomplished model to find an optimum parametric condition that meets the goals of maximum percentage removal of copper.

$$\begin{aligned}\text{Copper Removal Efficiency} = {} & +84.60 + 2.27 * A + 1.01 * B + 3.48 * C + 0.99 * D \\ & - 3.11 * E - 0.04 * F - 0.26 * A * B - 1.11 * A * C \\ & + 2.14 * A * D + 1.31 * A * E + 3.56 * A * F \\ & - 1.5 * B * C + 2.28 * B * D + 1.46 * B * E \\ & + 1.82 * B * F + 2.13 * C * D + 1.80 * C * E \\ & - 0.079 * C * F - 0.33 * D * E - 0.95 * D * F \\ & - 2.12 * E * F + 3.03 * A2 + 1.53 * B2 - 1.97 * C2 \\ & - 2.47 * D2 + 3.03 * E2 + 2.5 * F^2\end{aligned} \tag{2}$$

Table 1 Coded values for the predictions of the percentage of copper removal efficiency

S. no	Variable	Low factorial	Central factorial	High factorial
1.	pH	3	4	5
2.	Temperature (°C)	25	32.5	40
3.	Agitation speed (RPM)	100	300	200
4.	Dosage (mg/L)	0.01	0.10	0.55
5.	Concentration (PPM)	50	200	125
6.	Contact time (min)	20	300	160

where

$A =$ pH, $B =$ Temperature, $C =$ Agitation speed, $D =$ Dosage, $E =$ Concentration, $F =$ Contact time

The unfavourable conditions were indicated by a negative coefficient of the model components. In the case of copper removal efficiency (Y_1), the unfavourable conditions come from the components *E, F, AC, BC, CF, DE, DF, EF,* C^2 and D^2. On the other hand, positive coefficients indicate favourable condition of responses. For the percentage of copper removal efficiency, the favourable effects come from the model components *A, B, C, D, AD, AE, AF, BD, BE, BF, CD, CE,* A^2, B^2, E^2 and F^2.

ANOVA was applied to determine the statistical significance of the statistical models for a percentage of the copper removal as shown in Table 1. After consequent evaluation of the coefficient, the probability values (p) were compared with the Fisher's value (F). Thus, small $p < 0.05$ indicate the significant of the model parameters, whereas $p > 0.10$ indicate the insignificant factors. The insignificant factor indicated that the optimal levels were located at the experimental limit [23–25].

The design of experimental (DoE) run matrix using the six variables ($n = 6$) was generated using a central composite design (CCD) with three levels ($\pm\alpha$, ± 1 and 0). The low, middle and high level values of each variable were designated as −1.68, 0 and +1.68. The coded levels and natural values of each variable are represented in Table 1. The experimental design consisted of six-star points (coded as $\pm\alpha$), eight factorial points (coded as ± 1) and three centre points (coded as zero), resulting in 40 randomised runs.

The three-dimensional response surfaces were plotted to find out the interrelationship between the variable levels and responses to which an optimum condition can be developed. Figure 1a clearly explains the responses of copper removal efficiency when there is a change in contact time and temperature. When the temperature increases with respect to contact time the removal efficiency increases because it was well known that temperature could increase the adsorption. An optimum temperature of 32.4 °C could help fastening the removal efficiency. The contact time with varying temperature also influences the leaching efficiency. The copper removal efficiency increases with increase in contact time. 92% of copper could be removed when a

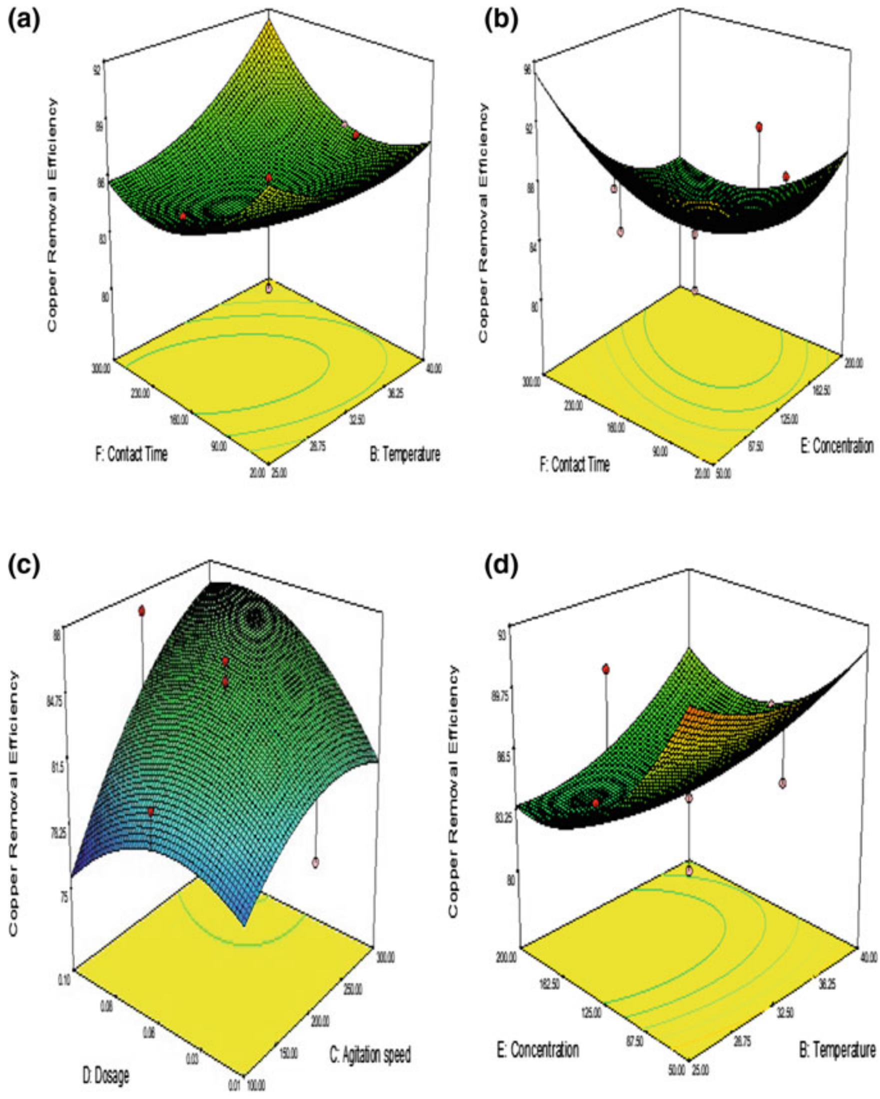


Fig. 1 3D plots that shows the effects for copper removal efficiency for **a** interaction between temperature (B) and contact time (F), **b** interaction between concentration (E) and contact time (F), **c** interaction between agitation speed (C) and dosage (D), **d** interaction between temperature (B) and concentration (E)

contact time of 300 min was given. Thus, Fig. 1a states that the temperature alters the treatment efficiency though it was given a higher contact time. And so, an optimum temperature of 32.5 °C and a contact time of 160 min could be an optimum condition for the removal of copper using MAC.

Figure 1b explains the removal efficiency of copper when the parameters like contact time and concentration are varied. The high concentration of the sample requires a longer time for the complete adsorption. As the MAC synthesised was microporous and it has to form two layers and so a small disturbance during the analysis of copper removal could alter the result. Rather the contact time increases the copper removal efficiency increases irrespective of whatever the concentration would be, but it purely depends on the type of the adsorbent. Figure 1c illustrates the fact that the dosage and agitation speed playa significant role in the copper removal efficiency. There is a clear picture in the figure which clearly states the quality of MAC. When dosage concentration increases, removal efficiency showed a sudden decline whereas when agitation speed increases the removal efficiency increases. The moisture absorbing capacity of MAC is high and so when agitation speed lowers there is a formation of clogs whereas agitation speed increases the clog disappears the removal efficiency increases. So, agitation speed is a principal factor in adsorption process. An optimum speed of 220 rpm with a dosage concentration of 0.06 mg showed good leaching efficiency. Figure 1d exemplifies the fact that the increase in temperature increases the leaching efficiency with respect to the concentration of the sample. The increase in concentration decreases the removal efficiency of copper. The increase in temperature increases the removal efficiency of copper. The temperature could also alter the characteristics of the sample and so an optimum temperature of 32.5 °C would give out good leaching efficiency but it was clearly seen in figure that lower concentration could also give good leaching efficiency while the concentration of the sample should be 125 mg/L to get a better removal efficiency of copper.

4 Conclusions

The Mosambi Activated Carbon was prepared using thermal activation and the removal of copper from bioleachate sample was tested using adsorption process. Parameters like temperature, agitation speed, concentration of sample and dosage amount of MAC were optimised with the help of the 3D plot given by the Response Surface Methodology which gave out the results to be a sample concentration of 125 mg/L at a temperature of 32.5 °C and agitation speed of 200 min was given with a dosage of 0.055 mg of MAC would help remove copper with a percentage of 90–93% from waste PCB which was highly dependent on the agitation speed.

References

1. Herat S, Agamuthu P (2012) E-waste: a problem or an opportunity? Rev Issues Challenges Solutions Asian Countries Waste Manage Res 30:1113–1129
2. Sustainable Innovation (2009) Technology transfer industrial sector studies. Recycling–from e-waste to resources

3. Schwarzer S, De Bono A, Giuliani G, Kluser S, Peduzzi P (2005) E-waste, the hidden side of IT equipment's manufacturing and use
4. Canning L (2006) Rethinking market connections: mobile phone recovery, reuse and recycling in the UK. J Bus Ind Mark 21:320–329
5. Grant K, Goldizen FC, Sly PD, Brune M-N, Neira M, van den Berg M, Norman RE (2013) Health consequences of exposure to e-waste: a systematic review. Lancet Glob Health 1:e350–e361
6. Song Q, Li J (2014) A systematic review of the human body burden of e-waste exposure in China. Environ Int 68:82–93
7. Song Q, Li J (2014) Environmental effects of heavy metals derived from the e-waste recycling activities in China: A systematic review. Waste Manag 34:2587–2594
8. Senophiyah-Mary J, Loganath R, Shameer PM (2018) Deterioration of cross linked polymers of thermoset plastics of e-waste as a side part of bioleaching process. J Environ Chem Eng 6:3185–3191
9. Ahluwalia SS, Goyal D (2007) Microbial and plant derived biomass for removal of heavy metals from wastewater. Biores Technol 98:2243–2257
10. Kadirvelu K, Thamaraiselvi K, Namasivayam C (2001) Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. Biores Technol 76:63–65
11. Kim J, Kwak S-Y (2017) Efficient and selective removal of heavy metals using microporous layered silicate AMH-3 as sorbent. Chem Eng J 313:975–982
12. Kobya M, Demirbas E, Senturk E, Ince M (2005) Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Biores Technol 96:1518–1521
13. Mary JS, Meenambal T (2016) Inventorisation of e-waste and developing a policy-bulk consumer perspective. Procedia Environ Sci 35:643–655
14. Mary JS, Meenambal T (2018) Removal of copper from bioleachate of electronic waste using banana-activated carbon (BAC) and comparison with commercial-activated carbon (CAC). In: Utilization and management of bioresources, Springer, Berlin, 2018, pp 233–242
15. Mary JS, Meenambal T (2015) Solubilisation of metals from e-waste using Penicillium chrysogenum under optimum conditions. Inf Dev Environ Conserv Sustenance 285
16. Kadirvelu K, Namasivayam C (2003) Activated carbon from coconut coir pith as metal adsorbent: adsorption of Cd (II) from aqueous solution. Adv Environ Res 7:471–478
17. Seco A, Marzal P, Gabaldón C, Ferrer J (1997) Adsorption of heavy metals from aqueous solutions onto activated carbon in single Cu and Ni systems and in binary Cu–Ni, Cu–Cd and Cu–Zn systems. J Chem Technol Biotechnol 68:23–30
18. Dhiman N, Shukla S, Kisku G (2017) Statistical optimization of process parameters for removal of dyes from wastewater on chitosan cenospheres nanocomposite using response surface methodology. J Clean Prod 149:597–606
19. Ghafari S, Aziz HA, Isa MH, Zinatizadeh AA (2009) Application of response surface methodology (RSM) to optimize coagulation–flocculation treatment of leachate using poly-aluminum chloride (PAC) and alum. J Hazard Mater 163:650–656
20. Halim SFA, Kamaruddin AH, Fernando W (2009) Continuous biosynthesis of biodiesel from waste cooking palm oil in a packed bed reactor: optimization using response surface methodology (RSM) and mass transfer studies. Biores Technol 100:710–716
21. Myers RH, Montgomery DC, Anderson-Cook CM (2016) Response surface methodology: process and product optimization using designed experiments. Wiley, New Jersey
22. Šereš Z, Maravić N, Takači A, Nikolić I, Šoronja-Simović D, Jokić A, Hodur C (2016) Treatment of vegetable oil refinery wastewater using alumina ceramic membrane: optimization using response surface methodology. J Clean Prod 112:3132–3137
23. Botha G, Oliveira J, Ahrné L (2012) Quality optimisation of combined osmotic dehydration and microwave assisted air drying of pineapple using constant power emission. Food Bioprod Process 90:171–179

24. Bustillo-Lecompte CF, Ghafoori S, Mehrvar M (2016) Photochemical degradation of an actual slaughterhouse wastewater by continuous UV/H 2 O 2 photoreactor with recycle. J Environ Chem Eng 4:719–732
25. Bustillo-Lecompte CF, Mehrvar M (2017) Treatment of actual slaughterhouse wastewater by combined anaerobic–aerobic processes for biogas generation and removal of organics and nutrients: an optimization study towards a cleaner production in the meat processing industry. J Clean Prod 141:278–289

Removal of Copper from Bioleachate of E-Waste Using Orange Activated Carbon (OAC) and Comparison with Commercial Activated Carbon (CAC)

J. Senophiyah-Mary, Teema Thomas, R. Loganath and T. Meenambal

1 Introduction

1.1 E-Waste

Electronic waste is the waste electrical and electronic utensils which are not appropriate for its actual intended use. E-waste is an evolving threat to the environment. Treatment should be done in a proper and formal way to make it non-toxic. Management of e-waste is a tedious process when considering its environmental and economic aspects. Since it contains numerous poisonous elements, the existence waste directly or in between the treatment in unstable condition create a harmful condition for the whole biotic life and underground water [1]. There are many hazardous compounds present in e-waste like americium, mercury, sulfur, BFRs (Brominated flame retardants), cadmium, lead, beryllium oxide, etc. [2, 3]. Heavy metal contamination

---

J. Senophiyah-Mary (✉)
Department of Environmental Engineering, Government College of Technology,
Coimbatore 641013, Tamil Nadu, India
e-mail: senophiyah.mary8@gmail.com

T. Thomas
Department of Civil Engineering, Thejus Engineering College,
Thrissur 680584, Kerala, India
e-mail: teemathomas111@gmail.com

R. Loganath
Department of Civil Engineering, Indian Institute of Engineering
Science and Technology, Shibpur 711103, West Bengal, India
e-mail: loganath.rk@gmail.com

T. Meenambal
Department of Civil Engineering, Madanapalli Institute of Technology, Madanapalli,
Chitoor 517325, Andhra Pradesh, India
e-mail: tmeenambal_gct@yahoo.co.in

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_35

is one of the supreme leading environmental complications today. Heavy metals are non-biodegradable and it can result in biomagnification and cause various diseases in human beings and other living things. Various electronic wastes are disposed in various forms into the environment that causes this pathetic situation.

1.2 E-Waste Treatment

These days, it turned out to be a trend to treat the electronic waste informally to get precious metals out of it. And after the simple acid treatment and getting the precious metals, they throw out the leachate to the environment. This leads to serious environmental issues due to the presence of even a small amount of poisonous metals or elements which are leached out through the acid treatment. This leachate also contains an infinitesimal number of precious elements. The separation of materials from the leachate is a tedious process. Informal treatments damage the worker's health worse and at the same time, the toxic fumes degrade the environment which would be given out during the treatment process and the direct disposal of leachate into the environment would contaminate the underground water [4, 5]. Even though there are many formal treatment systems for e-waste, they use enormous chemicals which are again a source of energy [6]. One such efficient method for the treatment of e-waste is the bioleaching process.

1.3 Bioleaching

Bioleaching makes use of the natural capability of the living microorganisms to convert the insoluble metals existing in the waste to a liquefied form. There are two types of bioleaching: direct leaching and indirect leaching. Direct leaching makes use of the organic acids formed by the microbes, to oxidize the insoluble poisonous metals, converting them into ions which convert them to be soluble. In indirect leaching, the medium present gets oxidized with the help of the bacteria that oxidizes the metal. Generally, free metal ions will form after oxidization of anionic part of targeted metal [3, 7, 8].

This process is a time-consuming process but efficient and less harmful compared to other treatment methods. The bioleachate is a pool of metals called lixiviant pool (pool of metals) [8]. Extraction/separation of metals from bioleachate should be done before disposing it into the environment. This can be done by many methods like cementation, adsorption, solvent extraction, ion exchange, gold recovery by biosorbents, coal–oil agglomeration, gold desorption and recovery from biomass, but in that simplest and efficient method is adsorption [9]. There are many choices for adsorbents but in that, activated carbon has higher voice because of its numerous properties which result in the most efficient adsorption of metals.

1.4 Activated Carbon

Activated carbon is an inert microporous carbon with the enormous internal surface area (up to 1500 m^2/g). Organic molecules in the liquids or gases can be attracted to the surface. Activated carbon encompasses:

(i) Bulk atoms those are neutral,
(ii) Surface atoms are the actual 'adsorption' atoms
(iii) Corner atoms are very responsive towards metals.

Activated carbon is able to adsorb a wide variety of organic substances, oxidizing materials and some of the heavy metals from liquid. Adsorption process is a natural phenomenon in which molecules from the gas or liquid phase are bonded to the surface of the solid. The microspores are developed primarily at the time of carbon activation and result in the large surface area for adsorption can be occurring.

1.5 Activated Fruit Waste

Activated carbon is available commercially, but a trial has been done to prepare an activated carbon from some municipal solid waste and check the ability of activated waste to adsorb metals from e-waste leachate. Thus, a possibility has been checked to find out the treating efficiency of an emerging waste using another waste [7]. Almost any organic matter with a higher percentage of carbon could be activated to enrich its ability to adsorb. Numerous investigations have been conducted for the proper management of fruit wastes into wealthy products. Processes like incineration, vermin-composting and anaerobic digestion were executed for the conversion of fruit wastes into beneficial products. And conversion of fruit waste into bio-adsorbents for the wastewater treatment was also proposed. Fruit peels would be a good suggestion as a resource for the preparation of activated carbon. Fruit wastes that have been generated from fruit shops, bakeries, soft drink producers and hotels are mostly thrown out into open spaces. This can be converted to a value-added product like activated carbon for treating another problematic waste treatment like e-waste. Orange has been chosen in this study which is rich in cellulose, hemicelluloses, lignin, fiber and pectin which converts the orange to be a highly potent adsorbent [10–14]. Characteristic study was done using particle size analyzer, zetasizer, surface area analyzer and Fourier Transform Infrared Spectroscopy (FTIR).

The main target of this work is to extract the copper from leachate of e-waste which could be used in various applications. The adsorption technique was used to extract the metals out of the leachate. Orange peel was found to be a rich source of hydroxyl group which could adsorb metals out of the leachate with prior activation. The characteristic study of Orange Activated Carbon (OAC) were done with the help of Fourier Transform Infrared Spectroscopy, T-plot have been analyzed with the help of surface area analyzer, zeta potential and particle size has been analyzed for the same to find out the characteristics of OAC. The removal efficiency of copper was determined by analysis of samples using Atomic Absorption Spectroscopy.

2 Materials and Methods

2.1 Adsorbate

Bioleachate of e-waste was used as a source for the abstraction of copper which perform as an adsorbate. Bioleachate was made earlier with various selective microbes. Centrifuge of bioleachate was done by Large Volume Centrifuge (Sigma 2-16 KL model) and its supernatant liquid was collected. The solution with metals is then diluted several times for further process.

2.2 Adsorbent—Orange Activated Carbon (OAC)

The orange peel was collected from local fruit juice shop and washed several times. They are then chopped to a size of one inch. It was sun-dried for 24 h so that the consumption of other sources of energy would be reduced. It was dehydrated in a hot air oven at 100 °C for 12 h. The dried peels were then activated with the help of thermal activation which includes carbonizing the sample at 500 °C for 4 h in a muffle furnace and activating the sample at 800 °C for 10 min. They are then ground then sieved through 75 μm sieve and stored. The samples were then ground well in planetary Ball mill (VB ceramics) for conversion of still smaller particles and it was analyzed for various characteristics.

2.3 Initial Metal Concentration Analysis

Initially, the metal concentration (taken as 1000 ppm) of bioleachate was assessed using Atomic Absorption Spectroscopy (AAS) followed by serial dilutions of sample and marked as I_i (concentration of copper). It was then proportioned to 10 ppm and used as a main sample for the entire adsorption process.

2.4 Stock Solution Preparation

1000 ppm copper solution was prepared using 1 g copper turnings in 50 ml of 5 M nitric acid and then diluted to 1 liter in a volumetric flask with deionized water. This sample was then made to a concentration of 1–10 ppm for further calibration standard curve examined in Atomic Absorption Spectroscopy (AAS).

2.5 Experimental Procedure—Batch Adsorption

Investigates were done at room temperature (25–30 °C) in batch mode adsorption method. Batch method was selected due to its ease and reliability. The tests were done by taking 10 ml of 10 ppm e-waste bioleachate sample in a 15ML falcon tube and after pH adjustment a 10 mg of dehydrated adsorbent was added. The flask was agitated at 150 rpm for 60 min using an orbital shaking incubator. After shaking, the sample suspension could settle. The remaining biomass adsorbed with metal ion was clarified using whatman-1 filter paper. Copper ion concentration were estimation using Atomic Absorption Spectrophotometer (AAS)-Agilent 200 Series. The percent removal of copper in the solution was determined by the following equation:

$$\text{Percentage removal of copper} = \frac{C_i - C_f}{C_i} \times 100$$

where

C_i initial copper concentration (ppm),
C_f final copper concentration in the solution (ppm).

2.6 Characteristics Study of Adsorbent

2.6.1 FTIR (Fourier Transform Infrared Spectroscopy)

FTIR (PerkinElmer Spectrum Version 10.4.2) was made use for this process. It was done to define the functional groups which are very beneficial for the adsorption process. It investigates the surface carbon-oxygen groups. Orange activated carbon of particle size less than 75 μm were primarily oven dried for 24 h at a temperature of 100 °C. The oven-dried samples were added with finely powdered Potassium Bromide (KBr) at a proportion of 1:100. FTIR spectra were documented by running a background followed by scanning the sample at a resolution of 8 cm^{-1} and with 8 scans per sample.

2.6.2 Moisture Content Analysis

Activated carbon is known to absorb moisture and so an initial analysis has been done to find out the moisture content present in it. The moisture content would become a drawback during the adsorption process. Moisture content analysis was done in

WENSAR Halogen Moisture Analytical Balance (HMB 100) at a temperature of 100 °C. The moisture content in percentage of weight was noted.

2.6.3 Particle Size Analysis

Particle size analysis of activated carbon was done in Malvern particle size analyzer. For this analysis, 0.1 g of orange activated carbon was centrifuged in a solvent so that the dispersed solution would be easier for the analysis. The particles with higher weight would settle at the bottom which cannot be monitored in this machine.

2.6.4 Zeta Potential Analysis

As per the result of particle size analysis, the suitability of zeta potential investigation of adsorbent was determined. The zeta potential measurements can be done in Malvern Zetasizer. Zeta analysis should be done only after the pH determination. The samples were injected to the cuvette containing electrodes and measurements were noted for 20 times for a single sample to get accuracy then average of reading would be read by the instrument.

2.6.5 Surface Area Analysis

Adsorption amount is governed by the gas pressure, adsorption temperature, and characteristics of adsorbent liquid and adsorptive gas. In a nitrogen adsorption isotherm, the temperature is set as constant and the gas supplies are limited, thus the isotherm fluctuations with respect to the solid property [15]. A measurement of specific surface area of the orange activated carbon has been made by N_2 adsorption at temperature 77 K, using a surface analyzer (Belsorp surface area analyzer). The pore size of the sample was analyzed so that varies plots could be taken with which the surface area would be analyzed. The results were obtained by using Belsorp adsorption/desorption data analysis software version 6. 3. 2. 1. Themesoporous volume was calculated by subtracting Micropore volume from total pore volume [16].

3 Results and Discussion

3.1 E-Waste Bioleachate

Characteristics of e-waste bioleachate was analyzed by monitoring the pH using Orion pH meter and the concentration of copper ions present in sample was measured by means of Atomic Absorption Spectroscopy (AAS) using copper flame at a wavelength of 324 nm, slit width of 0.5 nm, an ampere of 4 mA of current was fed to analyze copper. pH of Bioleachate of e-waste showed that the sample was acidic in nature(pH 4). AAS result of the same sample shows that it contains approximately 500 ppm copper metal was present in it.

3.2 Characteristic Study of Orange Activated Carbon

The pH was noted to be 8.56 for OAC while that of commercial activated carbon (CAC) was that of 8.7. Activated carbon with a pH of 6–8 is more preferable for wastewater treatment [17]. This shows that OAC could be used as an alternate for CAC acidic or basic nature of activated carbon directs the chemically reactive oxygen groups are present on its surface.

3.3 Moisture Analysis

The moisture content present in the OAC was found to be 7.03%. This shows that the adsorption of any other heavy metals would not be hindered by the penetration of water. The moisture content analysis was done for 3 h within which the result showed only 7.03% and after that, there were no water molecules. Moisture analyzer could also increase the pore size of the sample which could be used as an activation process but the energy consumption is high and so it would not be affordable.

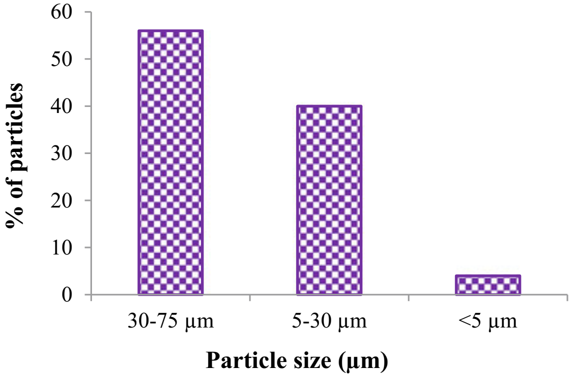
3.4 Particle Size Analysis of OAC

Though the particles were ground with planetary ball mill, there was no uniform sized sample may be because of the time given for milling. The particle size analysis results of OAC showed it had particles less than 30 µm. The activated samples were sieved with a 75 µm sieve which was then milled, and it was noted from the result that there were particles with size of 5–30 µm which was less than 50% whereas there were particles with nano size which was less than 5% while the rest of the particle lies between 30 and 75 µm. This reduces the scope of more characteristic analysis of activated carbon (Fig. 1).

3.5 Zeta Potential Measurements

Zetasizer is used mainly for nanosized particles to find out the ion interactions. The potential analysis can only be conducted if particle size of sample lies in the

Fig. 1 Particle size analysis of OAC



nanoscale. As the sample is a mixture of nanoparticles as well as microparticles it showed a better result. The zeta size potential was found to be +70 mV which proved that the particles could settle and could form flocs.

3.6 FTIR Analysis

FTIR (Fourier transform infrared spectroscopy) Perkin Elmer was used for this process. It was done to determine the functional groups which are very useful in adsorption process. On comparing the IR spectra of OAC and CAC presence of various groups in them could be predicted. OAC and CAC displayed bands in the region 4000-3500 cm^{-1} could be indicated to O-H, N-H, C-H stretching and bands around 1600-950 cm^{-1} were attributed to polysaccharide or protein, ester, which have a strong adsorption of gold metal ion and base metal ions, such as nickel, lead, copper, iron. The peak between 1600 cm^{-1} and 950 cm^{-1} proves that the synthesised activated carbon as well as the commercial activated carbon has the affinity to adsorb metals (Fig. 2).

3.7 Surface Area Analysis

The adsorption amount is articulated by the thickness of the adsorption layer. The graph as shown in Fig. 3 shows that they have two slopes in it. This is because the pores are micropores and they are homogenous too. In the primary stage of adsorption, the adsorption extent increases significantly due to adsorption into micropores, nevertheless the thickness of the adsorption does not rise much, as its result, the slope of t-plot becomes sharp. After completion of adsorption into micropores, adsorption occurs on the surface. This results in the gradual slope of the curve [18]. The pore

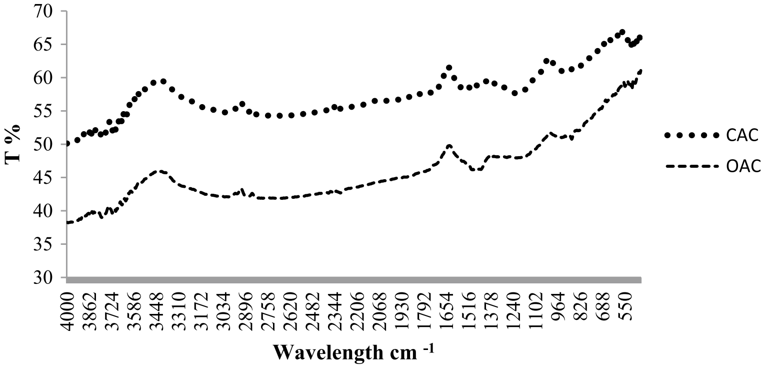


Fig. 2 FTIR spectra for OAC and CAC

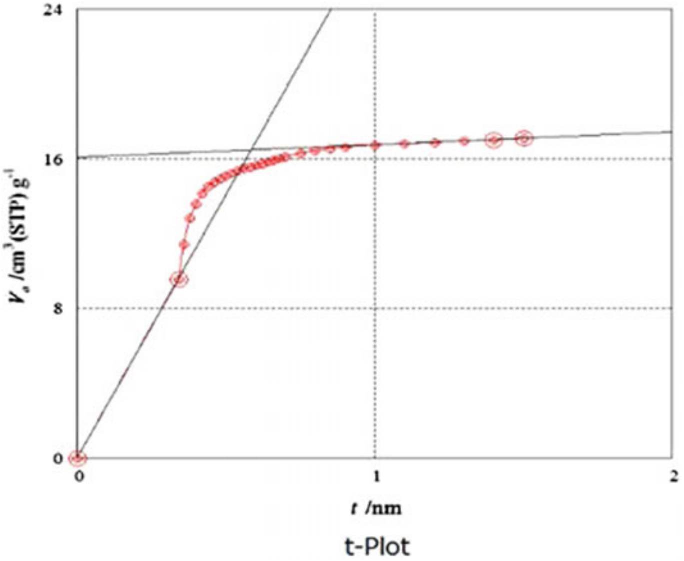


Fig. 3 t-Plot of OAC

surface area can be determined by deducting the external surface area and the internal surface area which was found to be 40 m^2/g which states that the pores are micropores and lie between 2 and 30 nm.

3.8 Adsorption of Copper

Two sets of bioleachate sample were taken with which 0.1 g of OAC and CAC was added. The adsorption studies stated that the OAC is suitable for adsorption of metals with its pores. The copper removal percentage was found to be 87.78% was the CAC showed a result of 97% which stated that the OAC thus synthesized could be replaced with CAC which could reduce the depletion of fossil fuels.

4 Conclusions

Orange peel getting into municipal solid waste mainly from fruit juice shops can be used efficiently by converting it into adsorbent for treating e-waste bioleachate since it shows similar characteristics and adsorption properties as commercial activated carbon; it can be efficiently replacing commercial activated carbon (CAC). It was also examined that they could adsorb more than 85% of copper from e-waste bioleachate for 10 ml of e-waste bioleachate treated with 0.1 g of OAC. Since activation process only consumes expense and considering the conversion of municipal solid waste into a wealthy product like efficient adsorbent, and OAC is preferable for e-waste treatment.

References

1. Needhidasan S, Samuel M, Chidambaram R (2014) Electronic waste–an emerging threat to the environment of urban India. J Environ Health Sci Eng 12:36
2. Pramila S, Fulekar M, Bhawana P (2012) E-waste-a challenge for tomorrow. Res J Recent Sci 1:86–93
3. Senophiyah-Mary J, Loganath R, Shameer PM (2018) Deterioration of cross linked polymers of thermoset plastics of e-waste as a side part of bioleaching process. J Environ Chem Eng 6:3185–3191
4. Blade CP, Forti V, Gray V, Kuehr R, Stegmann P (2017) The global e-waste monitor, in, United Nation University (UNU). International Telecommunication Union (ITU) and International Solid Waste Association (ISWA), Bonn, Geneva, Vienna, p 2017
5. Mary JS, Meenambal T (2016) Inventorisation of e-waste and developing a policy-bulk consumer perspective. Procedia Environ Sci 35:643–655
6. Sheng PP, Etsell TH (2007) Recovery of gold from computer circuit board scrap using aqua regia. Waste Manage Res 25:380–383
7. Mary JS, Meenambal T (2018) Removal of copper from bioleachate of electronic waste using banana-activated carbon (BAC) and comparison with commercial-activated carbon (CAC). In: Ghosh SK (ed) Utilization and management of bioresources. Springer, Kolkata, pp 233–242
8. Mary JS, Meenambal T (2015) Solubilisation of metals from e-waste using Penicillium *chrysogenum* under optimum conditions. In: Infrastructure development for environmental conservation and sustenance, pp 285–293
9. Syed S (2012) Recovery of gold from secondary sources—a review. Hydrometallurgy 115:30–51

10. Bernard E, Jimoh A (2013) Adsorption of Pb, Fe, Cu and Zn from industrial electroplating wastewater by orange peel activated carbon. Int J Eng Appl Sci 4:95–103
11. Ajmal M, Rao RAK, Ahmad R, Ahmad J (2000) Adsorption studies on Citrus reticulata (fruit peel of orange): removal and recovery of Ni (II) from electroplating wastewater. J Hazard Mater 79:117–131
12. Li X, Tang Y, Cao X, Lu D, Luo F, Shao W (2008) Preparation and evaluation of orange peel cellulose adsorbents for effective removal of cadmium, zinc, cobalt and nickel. Colloids Surf, A 317:512–521
13. Li X, Tang Y, Xuan Z, Liu Y, Luo F (2007) Study on the preparation of orange peel cellulose adsorbents and biosorption of Cd 2+ from aqueous solution. Sep Purif Technol 55:69–75
14. Feng N, Guo X, Liang S, Zhu Y, Liu J (2011) Biosorption of heavy metals from aqueous solutions by chemically modified orange peel. J Hazard Mater 185:49–54
15. De Boer J, Linsen B, Osinga TJ (1965) Studies on pore systems in catalysts: VI. The universal t curve. J Catal 4:643–648
16. Karagöz S, Tay T, Ucar S, Erdem M (2008) Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption. Biores Technol 99:6214–6222
17. Qureshi K, Bhatti I, Kazi R, Ansari AK (2008) Physical and chemical analysis of activated carbon prepared from sugarcane bagasse and use for sugar decolorisation. Int J Chem Biomol Eng 1:145–149
18. De Boer J, Lippens B, Linsen B, Broekhoff J, Van den Heuvel A, Osinga TJ (1966) Thet-curve of multimolecular N2-adsorption. J Colloid Interface Sci 21:405–414

Removal of Copper from Bioleachate of E-Waste Using Lemon Activated Carbon (LAC) and Comparison with Commercial Activated Carbon (CAC)

J. Senophiyah-Mary, Teema Thomas, R. Loganath and T. Meenambal

1 Introduction

1.1 E-Waste

One of the outgrowths of population growth is waste generation. Out of which electronic waste has a major role which contains toxic metal introduction to environment. Management of e-wastes is a pronounced threat and has become a formidable social issue. Many countries including India, China etc., find it difficult to regulate the problem due to the same. Proper treatment should be done to make it nontoxic and at the sometime to make use of precious and rear elements present in e-waste [1]. Treatment and extraction of elements of e-waste is a tedious process considering its environmental aspects. It contains numerous poisonous elements, which can make acute and chronic health issues in human beings and making environmental imbal-

---

J. Senophiyah-Mary (✉)
Department of Environmental Engineering, Government College of Technology,
Coimbatore 641013, Tamil Nadu, India
e-mail: senophiyah.mary8@gmail.com

T. Thomas
Department of Civil Engineering, Thejus Engineering College,
Thrissur 680584, Kerala, India
e-mail: teemathomas111@gmail.com

R. Loganath
Department of Civil Engineering, Indian Institute of Engineering
Science and Technology, Shibpur 711103, West Bengal, India
e-mail: loganath.rk@gmail.com

T. Meenambal
Department of Civil Engineering, Madanapalli Institute of Technology, Madanapalli,
Chitoor 517325, Andhra Pradesh, India
e-mail: tmeenambal_gct@yahoo.co.in

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_36

ance. E-waste disposal directly or in between the treatment (Leachate) makes the condition unstable to whole biotic life and environment. There are many toxic contents present in e-waste like americium, mercury, sulfur, BFRs (Brominated flame retardants), cadmium, lead, beryllium oxide, etc. [2–4]. Heavy metal toxicity is one of the most prominent environmental troubles facing today and its main reason is e-waste. Heavy metals are nonbiodegradable and it can result in biomagnification and may cause various health issues [3]. Various electronic waste disposals in its different forms into the surroundings cause these pathetic environmental situations. E-waste leachate can make a worse condition to ground water source pointing out the serious issue faced by e-waste.

1.2 E-Waste Treatment

E-waste contains a good amount of valuable metals within it and so crude treatment has been practiced by the informal sector, to recover the valuable metals and then dispose the leachate in an improper way. Toxic metals like chromium mercury, lead, etc. make environmental to be instable even due to its slight presence. This leachate also contains precious elements like gold silver. The extraction of various metals present in the leachate is a tedious process. Acid treatments done by improper precautions make the workers' health poorer and result in environmental degradation due to toxic fumes [3]. Even though there are many proper treatment systems for e-waste, they are following chemical processes and they are expensive too. Most efficient and eco-friendly treatment method is biological treatment and in those biological methods, bioleaching process is having more importance because of its selective extraction capability.

1.3 Bioleaching

Bioleaching use the microbes to convert metals that exist in the waste in a solid form into its soluble form. There are two methods of bioleaching:

- *Direct leaching*: It utilizes organic acids formed by the action of microbes to oxidize the insoluble toxic metals, converting it into ions which they become soluble
- *Indirect leaching*: Metal oxidizing bacteria are utilized to oxidize the metal surrounding the microbe. Normally, the anion of the target metal compounds gets oxidized, which give out free metal ions in aqueous medium. This process takes more time but efficient and less harmful compared to other treatment methods, but results in leachate (pool of metals) [1, 5–9].

Before the disposal of leachate into surroundings, proper treatment should be done by many methods like cementation, adsorption, solvent extraction, ion exchange, gold recovery by Coal–Oil Agglomeration (CGA), bio-sorbents, gold desorption, and recovery from biomass, but in that, simplest and efficient method is adsorption. But in that, adsorption is simplest method. Activated carbon is having numerous properties which result in most efficient adsorption of metals.

1.4 Activated Carbon

Activated carbon contains microporous and it is inactive carbon with a large internal surface area (up to 1500 m^2/g). On the external portion, carbon-based molecules from liquids or gases can be adsorbed. Activated carbon contains greater part of atoms those are neutral, surface atoms which are the actual "adsorption" atoms, and corner atoms are very reactive and more react with metals. Activated carbon can adsorb organic constituents, oxidizing materials (like chlorine and ozone), and selected heavy metals from liquids. In adsorption process, molecules from the gas or liquid state are bonded to the surface of the solid matter. The microspores are made at the time of carbon activation and result in the big surface area for adsorption to occur [10–13].

1.5 Activated Fruit Waste

Commercially activated carbon is available, but the possibility of waste activation makes more promising case of reusability and reduction of municipal waste. For the activation, citrus fruit peels are collected such as lemon and checked the adsorption capacity of metals from e-waste bioleachate. Any organic matter with a large percentage of carbon could be activated to enhance its adsorption properties. Disposal of fruit wastes can be effectively done by processes like vermin-composting, incineration and anaerobic digestion, etc. At the same time, conversion of fruit residues into bioadsorbents for wastewater treatment was also done efficiently [10, 14–19]. Lemon peels are prominent for the preparation of activated carbon. Lemon wastes that have been generated from fruit shops, bakeries, soft drink producers, and hotels are mostly thrown out into open spaces, and can be transformed to a value-added product like activated carbon for treating e-waste. Lemon is rich in cellulose, hemicelluloses, lignin, fiber, and pectin which convert the lemon to be a highly potent adsorbent. Characteristic study was conducted using particle size analyzer, zetasizer, surface area analyzer and Fourier Transform Infrared Spectroscopy (FTIR).

The main objective of this work is to remove the copper from leachate of e-waste. The adsorption technique was used to extract the metals out of the e-waste bioleachate. Lemon peel was found to be rich source of hydroxyl group which could adsorb metals out of the leachate with prior activation. Functional group analysis has been analysed with Fourier Transform Infrared Spectroscopy (FTIR) and T-plot have been analyzed with the help of surface area analyzer. Zeta potential and particle size has been done for both LAC and CAC. The removal efficiency of copper was determined by analysis of samples using Atomic Absorption Spectroscopy.

2 Materials and Methods

2.1 Adsorbate

Bioleachate of e-waste was used as a sample for the study on removal of the copper. Selective microorganisms were used for the preparation of bioleachate [9]. E-waste bioleachate was centrifuged by Large Volume Centrifuge (Sigma 2-16 KL model) and the supernatant was collected. Diluted sample is taken for further process.

2.2 Adsorbent—Lemon Activated Carbon (LAC)

The lemon peel was accrued from local fresh fruit juice shop and cleaned with double distilled water for several times. Chopped lemon pieces were sundried for 24 h to reduce other sources of dehydration. It was then oven dried at 100 °C for 24 h. After removing the moisture from the peels then carbonized at 500 °C for 4 h in a muffle furnace and activated at 800 °C for 10 min. Activated samples were then ground well in planetary Ball mill (VB ceramics) for conversion of still smaller particles and it was analyzed for various characteristics.

2.3 Initial Metal Concentration Analysis

Initial copper concentration of bioleachate (taken as 1000 ppm) was analyzed using Atomic Absorption Spectroscopy (AAS) followed by serial dilutions of sample and marked as I_i (concentration of copper). It was then diluted to 10 ppm and used as a main source for the further process.

2.4 Stock Solution Preparation

Stock solution of copper was prepared using 1 g copper turnings in 50 ml of 5 M nitric acid and then diluted to 1 L in a volumetric flask with deionised water (100 ppm copper solution). This sample was then prepared to 1–10 ppm for getting standard curve for the analysis in Atomic Absorption Spectroscopy (AAS).

2.5 Experimental Procedure—Batch Adsorption

Trials were conducted by batch mode adsorption technique and carried out at room temperature (25–30 °C). Batch method is simple and can be analyzed easily. The experiments were done by taking 10 ml of 10 ppm e-waste bioleachate sample in a 15 ml falcon tube and after pH adjustment a 0.1 g of dried adsorbent was added. The flask was agitated at 150 rpm for 1 h using an orbital shaking incubator. After settling of sample, the residual biomass adsorbed with metal ion was filtered using Whatman-1 filter paper. Copper ions concentration were estimation using (agilent 200 Series) Atomic Absorption Spectrophotometer (AAS). The percent removal of copper from the solution was calculated by the following equation:

$$\text{Percentage removal of copper} = \frac{C_\text{i} - C_\text{f}}{C_\text{i}} \times 100$$

where

C_i = initial copper concentration (ppm) and
C_f = final copper concentration in the solution (ppm).

2.6 Characteristics Study of Adsorbent

2.6.1 FTIR (Fourier Transform Infrared Spectroscopy)

FTIR (PerkinElmer Spectrum Version 10.4.2) was used for determining the functional groups which have high influence in adsorption process. It investigates the surface carbon–oxygen groups present in lemon-activated carbon. LAC of particle size less than 75 μm were first dried up for 24 h at a temperature 100 °C. The dried samples were mixed with finely divided potassium bromide (KBr) at a proportion of 1:100. FTIR spectra were plotted by running a background followed by scanning the sample at a resolution of 8 cm^{-1} and with 8 scans per sample.

2.6.2 Moisture Content Analysis

Activated carbon will absorb moisture so it is necessary find out the moisture content present in it. The moisture content reduces effect of adsorption process. Moisture content analysis was done in WENSAR Halogen Moisture Analytical Balance (HMB 100) at a temperature of 100 °C. The moisture content in percentage of weight was determined.

2.6.3 Particle Size Analysis

Particle size analysis of LAC was done in Malvern particle size analyzer. For this analysis, 0.1 g of LAC was centrifuged in a solvent so that the dispersed solution would be easier for the analysis. The particles with higher weight would settle at the bottom which cannot be monitored in this machine.

2.6.4 Zeta Potential Analysis

According to the result of particle size analysis, the suitability of zeta potential investigation of adsorbent was determined. The zeta potential measurements can be done using (Malvern Zetasizer). Zeta analysis was done after the pH measurements. The samples were injected to the cuvette containing electrodes and measurements were taken for 20 times for single sample for more accurate result.

2.6.5 Surface Area Analysis

The extent of adsorption is influenced by the gas pressure, adsorption temperature, and the properties of adsorptive gas and adsorbent liquid. During BET isotherm analysis, the constant temperature is maintained and the gas supplies are reduced, thus the isotherm variations according to the solid property [20]. A measurement of specific surface area of the LAC has been made by N_2 adsorption at temperature 77 K, using a surface analyzer (Belsorp surface area analyzer). The pore size of the sample was analyzed so that various plots could be taken with which the surface area would be analyzed. The results of LAC analysis were obtained by using Belsorp adsorption/desorption data analysis (software version 6. 3. 2. 1). The mesoporous volume was determined by subtracting micropore volume from total pore volume [21].

3 Results and Discussion

3.1 E-Waste Bioleachate

After the bioleaching process, the bio-leachate was collected and subjected to characteristic study such as pH, and metals has been analysed by Atomic Absorption Spectrometry (AAS) using copper flame of wavelength of 324 nm, slit width of 0.5 nm, an ampere of 4 mA of current was fed to analyze copper. pH of Bioleachate of e-waste have the pH of 4 which is acidic in nature. AAS result of sample shows that it contains approximately 500 ppm copper metal was present in it.

3.2 Characteristic Study of Lemon Activated Carbon

The pH of LAC was 8.16 while that of CAC was that of 8.7. Activated carbon with a pH of 6–8 is most preferable for wastewater treatment [22]. This shows that LAC could be used as an alternate for CAC acid or basic nature of adsorbent indicates the chemically active oxygen groups on its surface.

3.3 Moisture Analysis

The moisture content present in the LAC was found to be 9.55%. This shows that the adsorption would not be hindered by the penetration of water. The moisture content analysis was done for 3 h and result showed only 9.55% and after that there were no water molecules. Moisture analyzer could also increase the pore size of the sample which could be used as an activation process but the energy consumption is very high.

3.4 Particle Size Analysis of LAC

Though the particles were ground with planetary ball mill, there was no uniform sized sample may be because of the time given for milling. The particle size analysis results of LAC showed it had particles less than 30 μm. The LAC samples were sieved with a 75 μm sieve which was then milled, and it was noted from the result that there were particles with size of 5–30 μm which was less than 50% whereas there were particles with nanosize which was less than 5% while the rest of the particle lie between 30 and 75 μm. This reduces the scope of more characteristic analysis of LAC (Fig. 1).

3.5 Zeta Potential Measurements

Zetasizer is used mainly for nanosized particles to find out the ion interactions. The potential analysis can only be conducted if particle size of sample lies in the nanoscale. As the sample is a mixture of nanoparticles as well as micro particles, it showed a better result. The zetasize potential was found to be +82 mV which proved that the particles could settle and could form flocs.

Fig. 1 Particle size analysis of LAC

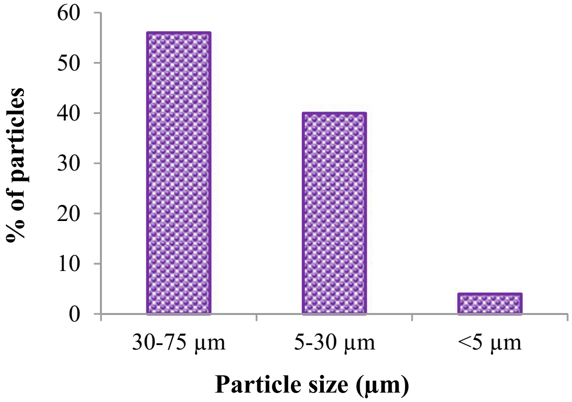
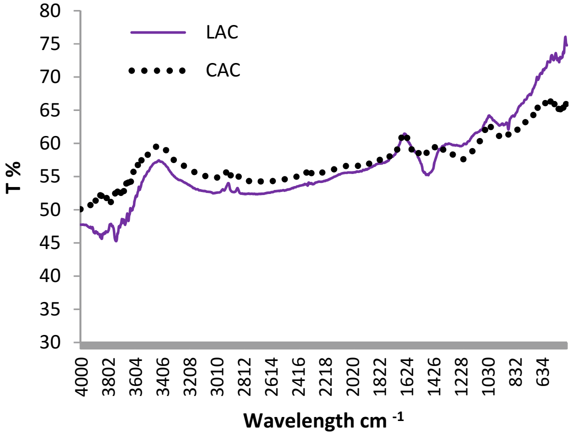


Fig. 2 FTIR spectra for LAC and CAC



3.6 FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) Perkin Elmer was used for this process. Figure 2 shows the result of FTIR of LAC and CAC. Presences of functional groups which have high influence in adsorption process were checked through FTIR analysis. On comparing the IR spectra of LAC and CAC, the existence of various groups in them could be assessed. From the obtained result, the peaks of LAC and CAC show that similar bands in the region 4000–3500 cm^{-1} indicates O–H, N–H, C–H stretching and bands around 1600–950 cm^{-1} were indicates the presence of polysaccharide or protein, ester, which have a strong attraction to both gold metal ion and base metal ions, such as copper, iron, nickel, lead. Both the peaks of activated carbon show that between 1600 and 950 cm^{-1}(1461 cm^{-1}) shows the affinity towards copper metal which is more useful for adsorption of Cu.

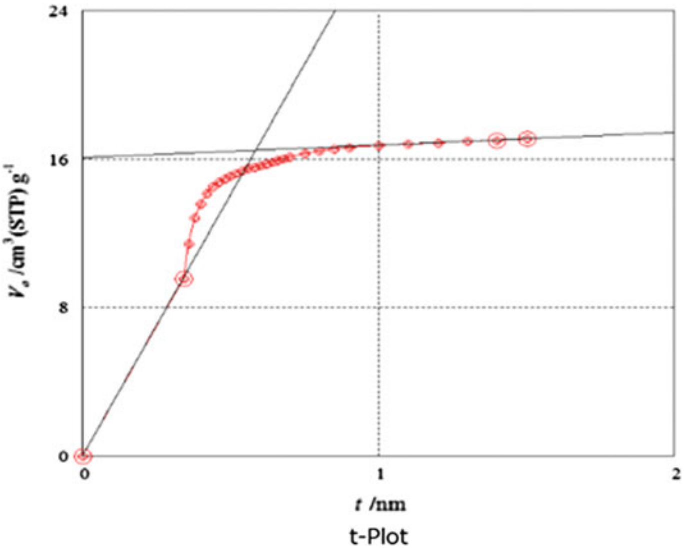


Fig. 3 t-plot of LAC

3.7 Surface Area Analysis

The adsorption amount is stated by adsorption layer thickness. T-plot of surface area analysis is shown in Fig. 3. In that, they have two slopes in it. This is because the pores are micropores and they are homogenous too. In the primary stage of adsorption, the adsorption amount increases considerably due to adsorption into micropores, but the thickness of the adsorption does not surge so much, as a result, the slope of t-plot turns into sharp. When adsorption into micropores is accomplished, adsorption occurs only on the surface of adsorbent. As it affects the slope of the curve and thus becomes gradual [23]. The pore surface area can be calculated by subtracting the external surface area and the internal surface area which was found to be 40 m^2/g which states that the pores are micropores and lie between 2 and 30 nm.

3.8 Adsorption of Copper

Two samples of e-waste bioleachate were taken with 0.1 g of LAC and CAC was added and agitated at 150 rpm for 1 h. The adsorption studies stated that LAC are suitable for adsorption of metals with its pores. The percentage removal of copper was found to be 85.7% were the CAC showed a result of 97% which stated that the LAC thus synthesized could be replaced with CAC considering municipal waste management and which could reduce the depletion of fossil fuels.

4 Conclusions

Lemon peel getting into municipal solid waste mainly from fruit juice shops can be used efficiently by converting it into activated carbon for treating e-waste bioleachate since it shows similar characteristics and adsorption properties as Commercial Activated Carbon (CAC). It was also understood that they could remove 85.7% of copper from e-waste bioleachate for 10 ml of e-waste bioleachate treated with 0.1 g of LAC. Since activation process only consumes expense and considers the conversion of municipal solid waste into wealthy product like efficient adsorbent, LAC is preferable for e-waste treatment.

References

1. Senophiyah-Mary J, Loganath R, Shameer PM (2018) Deterioration of cross linked polymers of thermoset plastics of e-waste as a side part of bioleaching process. J Environ Chem Eng 6:3185–3191
2. Kandola BK, Biswas B, Price D, Horrocks AR (2010) Studies on the effect of different levels of toughener and flame retardants on thermal stability of epoxy resin. Polym Degrad Stab 95:144–152
3. Kumar SA, Narayanan TS (2002) Thermal properties of siliconized epoxy interpenetrating coatings. Prog Org Coat 45:323–330
4. Xing M, Zhang F-S (2013) Degradation of brominated epoxy resin and metal recovery from waste printed circuit boards through batch sub/supercritical water treatments. Chem Eng J 219:131–136
5. Bosshard PP, Bachofen R, Brandl H (1996) Metal leaching of fly ash from municipal waste incineration by *Aspergillus niger*. Environ Sci Technol 30:3066–3070
6. Brandl H (2008) Microbial leaching of metals, 2nd edn. Wiley Online Library, London
7. Brandl H (2001) Heterotrophic leaching. In: British mycological society symposium series, pp 383–423
8. Brandl H, Bosshard R, Wegmann M (2001) Computer-munching microbes: metal leaching from electronic scrap by bacteria and fungi. Hydrometallurgy 59:319–326
9. Mary JS, Meenambal T (2015) Solubilisation of metals from e-waste using *Penicillium chrysogenum* under optimum conditions. In: Infrastructure Development for Environmental Conservation and Sustenance, pp 285–293
10. Baccar R, Bouzid J, Feki M, Montiel A (2009) Preparation of activated carbon from tunisian olive-waste cakes and its application for adsorption of heavy metal ions. J Hazard Mater 162:1522–1529
11. Bernard E, Jimoh A (2013) Adsorption of Pb, Fe, Cu and Zn from industrial electroplating wastewater by orange peel activated carbon. Int J Eng Appl Sci 4:95–103
12. Gratuito M, Panyathanmaporn T, Chumnanklang R-A, Sirinuntawittaya N, Dutta A (2008) Production of activated carbon from coconut shell: optimization using response surface methodology. Biores Technol 99:4887–4895
13. Hameed B, Din AM, Ahmad A (2007) Adsorption of methylene blue onto bamboo-based activated carbon: kinetics and equilibrium studies. J Hazard Mater 141:819–825
14. Kadirvelu K, Thamaraiselvi K, Namasivayam C (2001) Removal of heavy metals from industrial wastewaters by adsorption onto activated carbon prepared from an agricultural solid waste. Biores Technol 76:63–65
15. Kobya M, Demirbas E, Senturk E, Ince M (2005) Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. Biores Technol 96:1518–1521

16. Namasivayam C, Kavitha D (2002) Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste. Dyes Pigm 54:47–58
17. Seco A, Marzal P, Gabaldón C, Ferrer J (1997) Adsorption of heavy metals from aqueous solutions onto activated carbon in single Cu and Ni systems and in binary Cu–Ni, Cu–Cd and Cu–Zn systems. J Chem Technol Biotechnol 68:23–30
18. Zhong Z-Y, Yang Q, Li X-M, Luo K, Liu Y, Zeng G-M (2012) Preparation of peanut hull-based activated carbon by microwave-induced phosphoric acid activation and its application in Remazol Brilliant Blue R adsorption. Ind Crops Prod 37:178–185
19. Mary JS, Meenambal T (2018) Removal of copper from bioleachate of electronic waste using banana-activated carbon (BAC) and comparison with commercial-activated carbon (CAC). In: Ghosh SK (ed) Utilization and management of bioresources. Springer, Kolkata, pp 233–242
20. De Boer J, Linsen B, Osinga TJ (1965) Studies on pore systems in catalysts: VI. The universal t curve. J Catal 4:643–648
21. Karagöz S, Tay T, Ucar S, Erdem M (2008) Activated carbons from waste biomass by sulfuric acid activation and their use on methylene blue adsorption. Biores Technol 99:6214–6222
22. Qureshi K, Bhatti I, Kazi R, Ansari AK (2008) Physical and chemical analysis of activated carbon prepared from sugarcane bagasse and use for sugar decolorisation. Int J Chem Biomol Eng 1:145–149
23. De Boer J, Lippens B, Linsen B, Broekhoff J, Van den Heuvel A, Osinga TJ (1966) Thet-curve of multimolecular N2-adsorption. J Colloid Interface Sci 21:405–414

A Study on the Merits and Demerits of the Extraction of Metals by Thermal Cracking Treatment of WPCB with Different Thermal Furnaces

R. Balaji, J. Senophiyah-Mary, R. Loganath, K. Yaazhmozhi and N. Dhivya Priya

1 Introduction

E-waste is a term which includes all the electrical and electronic equipment (EEE) and its constituent parts that have been left over by the people as waste without the purpose of reuse. The e-waste being generated has both the toxic as well as valuable materials [1, 2]. Though it is an emerging issue due to its toxicity level, it is a great platform for the business people to recycle the e-waste to obtain the valuable materials [3–5]. India produces tonnes of e-waste and it is one the largest electronic waste producers in the world which ranks 5th among them. Nearly 70% of electronic wastes from India are majorly contributed by Computer devices. Out of which, telecom sector holds 8%, electric and electronic equipment holds 7% of the yearly electronic waste generation. Nearly 75% of e-wastes are generated from the Government public sector companies and private sector companies, whereas the 16% of e-wastes are only generated from individual household. E-waste accounts for heavy metals such as

---

R. Balaji · J. Senophiyah-Mary (✉) · K. Yaazhmozhi · N. Dhivya Priya
Department of Environmental Engineering, Government College of Technology,
Coimbatore 641013, Tamil Nadu, India
e-mail: senophiyah.mary8@gmail.com

R. Balaji
e-mail: rbaljaicivil@gmail.com

K. Yaazhmozhi
e-mail: yaazh2011@gmail.com

N. Dhivya Priya
e-mail: priya.dhivya08@gmail.com

R. Loganath
Department of Civil Engineering, Indian Institute of Engineering
Science and Technology, Shibpur,
Howrah 711103, West Bengal, India
e-mail: loganath.rk@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_37

nickel, lead, cadmium and chromium in it and most of them are found in the landfills and groundwater [6–8]. These pollutants are responsible for the contamination of the environment. In India, Extended Producer Responsibility is introduced by E-waste (Management and Handling) Rules 2016 to take back the used goods by the corresponding producer. As the implementation of EPR was improper, there is an increase in growth rate of e-wastes are generated and compounded annually, out of which 95% recycling is done by the unskilled informal sector [9, 10]. The present e-waste management rules in India are very difficult to implement because of its numerous factors such as hurdles faced during the inventorisation process, vigorous growth of informal sector which involved in recycling and majorly lack of awareness among people who dump the obsolete e-waste in their household itself [11, 12] .

Printed Circuit Board (PCB) has a composition of metals, plastics and some amount of glass materials and ceramics [13]. The possible metal elements in the PCBs are Pb, Al, Cr, Cd, Sn, Zn, Ti, Hg and As along with some precious metals such as gold, silver and palladium. Some rare earth metals are also used in PCBs [14, 15]. Recoveries of precious metals are achieved because of greater affinity for Copper [16, 17]. Heavy metal concentration is high in PCB when compared with e-waste. The possible heavy metals in PCBs are Pd, Cr, Hg, As and Cd that are available in surplus quantity [18]. The cost of metal recovery from E-Scrap is much less as compared to the extraction of these metals from mining ores. Electronic waste and WPCB recycling help in recovery of metals to a very large extent, and also help in the preservation of natural resources [19–21]. The process of recycling e-waste provides a better solution for the e-waste management also the environmentally sound living habitat. For the world scenario, the growth rate of e-waste is likely to hit by 23.5%. Similarly, for the Indian scenario from 2015 to the upcoming 5 years, the generation rates are expected to be 26%. The general methods adopted for the treatment of e-waste PCBs are pyrometallurgy, hydrometallurgy and biohydrometallurgy. Pyrometallurgy is the process used for the recovery of metals using high different temperatures for the treatment. Hydrometallurgy is the process in which metal extraction is done using aqueous solutions [16, 22, 23]. Biohydrometallurgy is the process which deals with the microorganism that converts solid metal to a dissolved form [24]. Both the formal as well as the informal sectors were involved in the treatment process.

Pyrometallurgical treatment process can be achieved with the help of Muffle furnace and the horizontal tubular furnace and the gaseous emissions are opened to the atmosphere. Chemical Vapour Deposition (CVD) is equipment used to extract or convert WPCB sample into its purest metallic form for the pyrometallurgical treatment process. Two gases were used in the CVD chamber [25, 26]. Namely, hydrogen and argon out of which argon is a non-reactive inert gas which is used to flush out the metal oxides formed during the treatment processes. And the H_2 gas is used to reduce the oxidised metals that are been formed due to the excess heat generated during the process. This equipment has a provision to collect the oxides that have been analysed with the help of gas chromatography, as well as atomic absorption spectroscopy [17].

Muffle furnace equipment is used for the continuous heating for processing samples and material, here the samples are secluded from all sorts of external sources such as fuels and gases which help in the combustion process [27]. Heating is done in the absence of air which enhances the oxides formation which is carried out in the Muffle furnace. No gas is collected from the muffle furnace since the outlet is open to the atmosphere [28]. The sample lags the metallic phase, this is because the thin metals present in the tubular furnace get crumbled and get oxidised during the treatment process. But in case of tubular furnace, the e-waste is heated to 950 °C under inert atmosphere for 20 min. Argon gas which flushes out the gases emitted during the treatment at a rate of 200 mL/min [29, 30].

The main advantage of pyrometallurgical treatment process is the metals recovered from the treatment process can be directly used for further metal utilisation needed for the industry, which means it results in the pure form of metal oxides and in some cases metal foil itself recovered [31]. But this differs from the type of PCBs used for the treatment. It also requires low skilled supervision. The major disadvantage is the emission of toxic substances which may affect the environment, but the study has been made in the presence of inert atmosphere which may give a possibility of low toxic emission compared to all the other processes.

The main objective of this was to study the merits and demerits of the extraction process under different thermal furnaces. As the PCB is a combination of metals and plastics, the deterioration effect of plastics in WPCB was also studied. Though there are many techniques to leach out, metals pyrometallurgy is a known technique to extract the metals direct to use and also reduces time. This study has been extended to know the amount of metals that were obtained as a result of this treatment and various analysis techniques have been used to know the concentration and types of substances present in it. The toxic emissions that get emitted during the treating process were also studied.

2 Materials and Methods

2.1 Material Collection

WPCB plate samples are collected from Green Era Recyclers. WPCB of varied sizes is cut into 2 cm × 2 cm which should be rich in metal composition and is weighed. Semicircular alumina boat of size 2 cm inner diameter is needed in order to make the PCB fit in the alumina crucible.

2.2 CVD Chamber

The metals rich in PCBs are cut into the proper size and placed in the semicircular alumina boat. A metal rod helps in pushing the alumina boat to the centre portion of the CVD chamber, now the boat is directly below the heating furnace. Pressure in the tubular furnace is adjusted to vacuum and then the temperature is set to 950 °C for the duration of 20 min. The hydrogen gas is passed during the initial stage for the flow rate of 200 mL/min for the duration of 1 h in order to enhance the reduction process. Then it is followed by the argon gas which results in flushing out the gases inside the tubular furnace thus resulting the inert atmosphere to the chamber. The outlet of the tubular furnace is led into the container filled with water. The toxic emissions coming out from the furnace during the treatment process are collected in the container and it should be used for the analysis of toxic oxides present in it. The CVD chamber can cool down and the product obtained after the treatment process is metallic phase, slag phase and gaseous Phase. The slag phase may contain some metals, and the residual metals can be recovered using Vibrated Gas–Solid Fluidised Bed (VGFB) apparatus [32, 33].

2.3 Muffle Furnace

Samples are weighed and placed in the crucible and kept inside the muffle furnace at 950 °C for 20 min. The only difference between tubular furnace and muffle furnace is the existence of inert atmosphere. In muffle furnace, the metals are recovered in the crucible. Here, also the metal oxides are formed in the absence of air (Fig. 1).

2.4 Thermo-Gravimetric Analyser

Thermo-gravimetric analyser is used in order to determine the temperature at which complete degradation of the polymers occurs. TGA also gives the value of weight loss

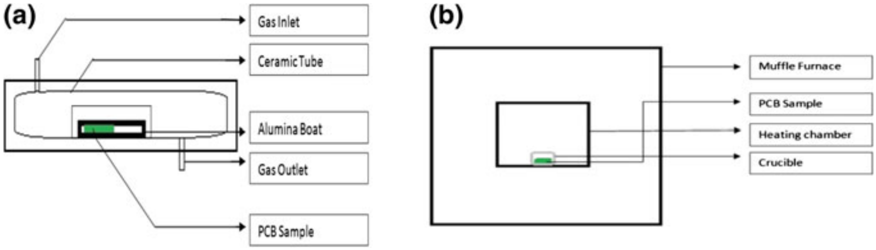


Fig. 1 **a** Tubular furnace. **b** Muffle furnace

Table 1 Instrumental parameters for AAS determination of metals

S. no.	Metals	Wavelength (nm)	Slit width (nm)	Current (mA)
1	Cu	324.8	0.5	4
2	Ni	232	0.2	4
3	Cr	357.9	0.5	7
4	Zn	213.9	0.2	5
5	Pb	283.3	0.5	5

in percentage at different temperatures for different time periods. Thus, the weight loss in percentage of the substance is valued as the function of temperature or time. Here, both the plate samples as well as powdered samples may be used for optimising the temperature which gives the degradation temperature of the substance. The plate sample weighing 0.2 mg is analysed with an initial temperature of 32 °C and the degradation completes by 920 °C. For experimental purpose a temperature of 950 °C is optimised for both the Muffle and Tubular furnace.

2.5 Atomic Absorption Spectroscopy

Atomic absorption spectroscopy is used in order to find out the initial metal concentration of the samples. Here, the initial sample and the treated samples are used for the analysis. Samples should be weighed before and after the treatment process. The product obtained from Muffle Furnace as well as tubular furnace is weighed in order to find out the percentage of weight which has been converted into toxic emissions during the treatment process. The solid metallic form obtained is converted into its soluble form by using concentrated nitric acid. Similarly, the weighed untreated e-waste plate is also made into its soluble form. For finding out the initial metal concentration, stock solution of different ppm (i.e.) 1–10 ppm is made for different metals like Cu, Zn, Cr, Pb and Ni. And serial dilution is done for treated and untreated e-waste solutions in order to avoid high absorbance value during sample testing. Then, the unknown initial concentration of metals for the sample is found out from the absorbance value (Table 1).

3 Results and Discussion

It is observed that the degradation of plastics in e-waste samples likely to be increased from 300 to 500 °C. After 500 °C, there is a steady degradation found and weight loss after the 500 °C is also found to be stable. From the analysis, the complete degradation of e-waste sample occurs at 920 °C. No further weight reduction is observed in the analysis value. Hence, 950 °C is used for the further treatment process (Fig. 2).

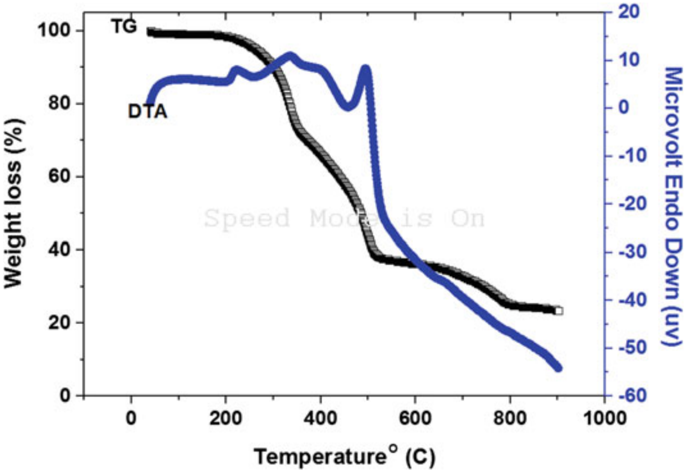


Fig. 2 A thermo-gravimetric analysis of a PCB sample

The process of Thermal Cracking Treatment of WPCB under CVD chamber at inert atmosphere generates carbon slag. In general, the bond between carbon and copper is very less hence the separation of metal and slag is much easier than all the other process. This study shows that this method of recycling WPCB results in direct metal recovery in large quantity and also generates the least amount of by-products [34]. Recent research reveals that thermal processing of e-waste and WPCB provides an alternate methodology for utilisation of energy from it if inclusive toxic control features are established in the treatment unit [24, 35]. The pyrolysis at 950 °C resulted in copper alloys. Copper foils contain Pb and Ni levels as low as 0.34 and 0.49%, and it will be recovered directly in single step smelting process. Copper foils are obtained after the pyrolysis of WPCBs [11, 24]. By using Atomic absorption spectroscopy, the metal concentration for different metals such as Cu, Cr, Pb, Zn and Ni are found out. From the result, it is found that Cu metal concentration is found to be 400 mg/l and Pb as 7.5 mg/l and finally Ni as 10 mg/l for the untreated e-waste plate. No metal concentrations are found for Zinc and Chromium (Fig. 3).

It is observed that weight loss in muffle furnace is much higher when compared to the tubular furnace. It is also observed that metals undergo reduction and metal alloys are formed in the tubular furnace that is identified with the help of colour pattern obtained after the treatment process. But in case of muffle furnace metals are oxidised and are no such metallic phase is obtained as in the tubular furnace. Other than metallic phase, slag is retained in the crucible which not dispersible medium during acid treatment. The slag is removed, and metallic phase is segregated in an easier manner. From which the treated e-waste contains approximately 20% of metallic weight as a combination of alloy. The metallic alloy is further acid treated in order to find out the metal concentration in that treated samples by using Atomic absorption spectroscopy. During acid treatment, the metals in the alloy are turned

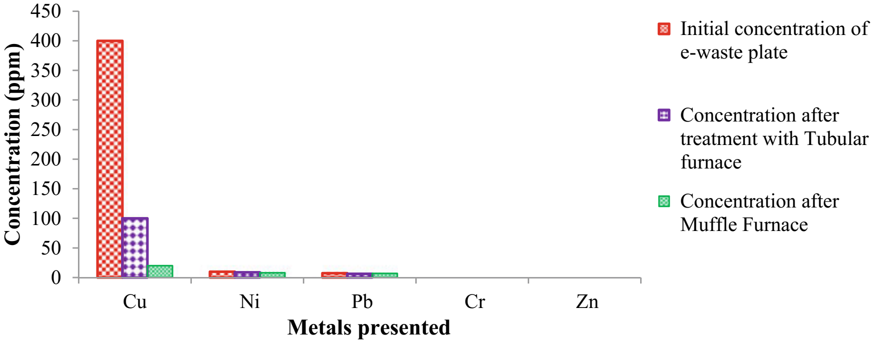


Fig. 3 Concentration of metals identified using AAS

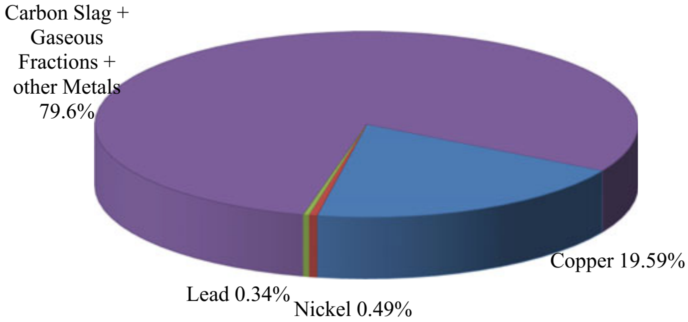


Fig. 4 Percentage weight of recovered metals

into gaseous phase, which is confirmed through the Red fumes coming out during the effervescence (Fig. 4).

3.1 Merits and Demerits

Pyrometallurgical method is one of the cheapest and best suited methods for metal removal from WPCB when underwent through a large-scale metal separation mechanism. At high temperatures, the removal efficiency is greatly influenced, and the rate of reaction is quite high for the thermal cracking treatment process. At high temperatures, it is much easier to separate the metal from the residue left after the treatment, since the product vapourises at high temperature. Metal extraction by tubular furnace gives an efficient outcome (i.e.) metals is extracted as an alloy and it can be separated uniquely by means of smelting process under different temperatures . But the question is while going for a large-scale production, the power consumption for the treatment process will be too high and there may be a possibility of low productivity in large-scale productions. Hence, tubular furnace in series may be suggested for large-scale efficient production. Published research shows that pyrometallurgical process is a profitable and efficient method to achieve WPCBs harmless recycling and resource utilisation [36]. Recycling e-waste and WPCB is a major solution to the meet the energy need for our self which is increasing in our day-to-day life. At the same time, natural resources can be conserved which are at the depleting stage. Electronic waste recycling and management should be implemented throughout the world to ensure a sustainable future. At very high temperature, the existence of metals in carbon residues is very few, which confirms that the quality of carbon obtained as a by-product is in extremely good condition [16, 19, 37, 38]. The emitted organic gases from the pyrolysis process can be utilised as an alternate heating source needed for the pyrolysis of PCBs [3, 39].

4 Conclusion

Pyrometallurgy using tubular furnace helps in direct recovery of metals which can be reused further. No additional costlier methods needed for separating the metals from the metallic alloy. Toxic metals are also recovered as an alloy during the treatment process. It requires no skilled supervision during the treatment process. It is one of the time-consuming processes than hydrometallurgy and biohydrometallurgy, since it may take a long time for leeching and for chemical separation of metals. Here, the reduction in cost of epoxy coating removal from PCBs is also achieved. The only major problem faced during the treatment process is the emission of toxic metal oxides as gases. Necessary modifications have to be done in order to minimise the toxic emissions below the standards. At high temperature, the product obtained after the treatment process are metallic phase, carbonaceous slag and gaseous fractions. The thermal cracking of plastics and polymers will result in gaseous emission which may contain carbon dioxide, carbon monoxide and methane.

References

1. Brandl H, Bosshard R, Wegmann M (2001) Computer-munching microbes: metal leaching from electronic scrap by bacteria and fungi. Hydrometallurgy 59:319–326
2. Osibanjo O, Nnorom I (2007) The challenge of electronic waste (e-waste) management in developing countries. Waste Manage Res 25:489–501
3. Huang K, Guo J, Xu Z (2009) Recycling of waste printed circuit boards: a review of current technologies and treatment status in China. J Hazard Mater 164:399–408
4. Sohaili J, Muniyandi SK, Mohamad SS (2012) A review on printed circuit board recycling technology. J Emerg Trends Eng Appl Sci (JETEAS) 3:12–18
5. Mary JS, Meenambal T (2016) Inventorisation of e-waste and developing a policy-bulk consumer perspective. Procedia Environ Sci 35:643–655
6. Coman V, Robotin B, Ilea P (2013) Nickel recovery/removal from industrial wastes: a review. Resour Conserv Recycl 73:229–238

7. Mary JS, Meenambal T (2018) Removal of copper from bioleachate of electronic waste using banana-activated carbon (BAC) and comparison with commercial-activated carbon (CAC). In: Ghosh SK (ed) Utilization and management of bioresources. Springer, Kolkata, pp 233–242
8. Mary JS, Meenambal T (2015) Solubilisation of metals from e-waste using *Penicillium chrysogenum* under optimum conditions. In: Infrastructure development for environmental conservation and sustenance 2015, pp 285–293
9. F.a.C.C. Ministry of Environment (2016) Published in the Gazette of India, extraordinary part-II, section-3, sub-section (i), Government of India
10. Joseph K (2007) Electronic waste management in India–issues and strategies. In: Eleventh international waste management and landfill symposium, Sardinia
11. Xiu F-R, Weng H, Qi Y, Yu G, Zhang Z, Zhang F-S, Chen M (2017) A novel recovery method of copper from waste printed circuit boards by supercritical methanol process: preparation of ultrafine copper materials. Waste Manage 60:643–651
12. Cayumil R, Khanna R, Ikram-Ul-Haq M, Rajarao R, Hill A, Sahajwalla V (2014) Generation of copper rich metallic phases from waste printed circuit boards. Waste Manage 34:1783–1792
13. Cui J, Zhang L (2008) Metallurgical recovery of metals from electronic waste: a review. J Hazard Mater 158:228–256
14. Bizzo WA, Figueiredo RA, de Andrade VF (2014) Characterization of printed circuit boards for metal and energy recovery after milling and mechanical separation. Materials 7:4555–4566
15. Szałatkiewicz J (2014) Metals content in printed circuit board waste. Pol J Environ Stud 23:2365–2369
16. Awasthi AK, Li J (2017) Management of electrical and electronic waste: a comparative evaluation of China and India. Renew Sustain Energy Rev 76:434–447
17. Shuey S, Taylor P (2005) Review of pyrometallurgical treatment of electronic scrap. Min Eng 57:67–70
18. Senophiyah-Mary J, Loganath R, Shameer PM (2018) Deterioration of cross linked polymers of thermoset plastics of e-waste as a side part of bioleaching process. J Environ Chem Eng 6:3185–3191
19. Kumar A, Holuszko M (2016) Electronic waste and existing processing routes: a Canadian perspective. Resources 5:35
20. Yu J, Williams E, Ju M (2009) Review and prospects of recycling methods for waste printed circuit boards. In: Sustainable systems and technology, 2009. ISSST'09. IEEE international symposium on, IEEE, 2009, pp 1–5
21. Kan Y, Yue Q, Liu S, Gao B (2018) Effects of Cu and CuO on the preparation of activated carbon from waste circuit boards by H3PO4 activation. Chem Eng J 331:93–101
22. He J, Duan C (2017) Recovery of metallic concentrations from waste printed circuit boards via reverse floatation. Waste Manage 60:618–628
23. Cayumil R, Ikram-Ul-Haq M, Khanna R, Saini R, Mukherjee P, Mishra B, Sahajwalla V (2017) High temperature investigations on optimising the recovery of copper from waste printed circuit boards. Waste Manage 73:556–565
24. Luda MP (2011) Integrated waste management, Online
25. Chen Z, Ren W, Gao L, Liu B, Pei S, Cheng H-M (2011) Three-dimensional flexible and conductive interconnected graphene networks grown by chemical vapour deposition. Nat Mater 10:424
26. Mohammadi A, Hasan M-A, Liedberg B, Lundström I, Salaneck W (1986) Chemical vapour deposition (CVD) of conducting polymers: polypyrrole. Synth Met 14:189–197
27. Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D, Crocker D (2008) Determination of structural carbohydrates and lignin in biomass. Lab Anal Proced 1617:1–16
28. Aspila K, Agemian H, Chau A (1976) A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. Analyst 101:187–197
29. Kavousi M, Sattari A, Alamdari EK, Firozi S (2017) Selective separation of copper over solder alloy from waste printed circuit boards leach solution. Waste Manag 60:636–642
30. Khanna R, Cayumil R, Mukherjee P, Sahajwalla V (2014) A novel recycling approach for transforming waste printed circuit boards into a material resource. Procedia Environ Sci 21:42–54

31. Khaliq A, Rhamdhani MA, Brooks G, Masood S (2014) Metal extraction processes for electronic waste and existing industrial routes: a review and Australian perspective. Resources 3:152–179
32. Zhang G, He Y, Wang H, Zhang T, Wang S, Yang X, Xia W (2017) New technology for recovering residual metals from nonmetallic fractions of waste printed circuit boards. Waste Manage 64:228–235
33. Cayumil R, Khanna R, Rajarao R, Mukherjee P, Sahajwalla V (2016) Concentration of precious metals during their recovery from electronic waste. Waste Manage 57:121–130
34. Garlapati VK (2016) E-waste in India and developed countries: management, recycling, business and biotechnological initiatives. Renew Sustain Energy Rev 54:874–881
35. Ghosh B, Ghosh M, Parhi P, Mukherjee P, Mishra B (2015) Waste printed circuit boards recycling: an extensive assessment of current status. J Clean Prod 94:5–19
36. Wang H, Zhang S, Li B, Pan DA, Wu Y, Zuo T (2017) Recovery of waste printed circuit boards through pyrometallurgical processing: a review. Resour Conserv Recycl 126:209–218
37. Sahajwalla V, Cayumil R, Khanna R, Ikram-Ul-Haq M, Rajarao R, Mukherjee P, Hill A (2015) Recycling polymer-rich waste printed circuit boards at high temperatures: recovery of value-added carbon resources. J Sustain Metall 1:75–84
38. Jadhav U, Su C, Hocheng H (2016) Leaching of metals from large pieces of printed circuit boards using citric acid and hydrogen peroxide. Environ Sci Pollut Res 23:24384–24392
39. Hall WJ, Williams PT (2007) Processing waste printed circuit boards for material recovery. Circuit world 33:43–50

Bioremediation of Lead Compound Using *Acinetobacter sp. 158*; Optimization of Media and Cell Growth Dynamics

Moumita Bose, S. Datta and Pinaki Bhattacharya

Nomenclatures

C_{G}	Concentration of substrate glucose (kg/m^3)
C_{B}	Concentration of biomass (kg/m^3)
k	Maximum specific cell growth rate (hour^{-1})
K_{S}	Saturation constant for lead (kg/m^3)
t	Time of incubation (hours)
$Y_{B/G}$	Yield factor

1 Introduction

It is now well established that to bring down the level of heavy metal contaminated industrial effluents below the permissible limit, bioremediation route is the only possible solution. Although bioremediation of most of the heavy metals is well explored [1–4], interestingly, not many reports on investigations are available on the bioremediation of metallic lead and its compounds. Many industries such as coating, automotive, storage batteries, and aeronautical steel industries generate a large quantity of wastewater containing medium to high concentration of lead and its compounds which are highly toxic to human and aquatic bodies. Understanding the potential threat of this heavy metal to the environment and living bodies different statutory agencies have made stringent rules for discharging effluent containing

---

M. Bose (✉) · S. Datta
Chemical Engineering Department, Jadavpur University, Kolkata 700 032, India
e-mail: moumita405@gmail.com

P. Bhattacharya
Department of Chemical Engineering, Heritage Institute of Technology, Kolkata 700 107, India

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_38

lead and its compounds. Such ultralow discharge standard can only be made by coupling conventional physiochemical treatment with the bioremediation process. The bioremediation technique although apparently looks simple but in reality, it needs a thorough bioprocess engineering study to make the process economically viable, eco-friendly as well as user friendly. It is felt that there are enough scopes to add new knowledge through a programmed setup experiment followed by suitable modeling and simulation, which can be directly used for bioreactor design [5, 6].

In the present investigation, in order to make the target bioremediation process industrially acceptable with regards to cost-effectiveness, an attempt has been made to optimize the percentage of lead removal using the key constituents of growth medium, viz., glucose as well as key microenvironmental parameter pH and shaking speed as independent variables. The well-accepted statistical optimization technique response surface methodology (RSM) has been used for this purpose. The optimized value of the independent variables is expected to make the process cost-effective.

An attempt has also been made to study in detail the cell growth dynamics as well as the substrate concentration—time histories in batch mode operation by using the optimized value of the initial substrate concentration obtained through response surface methodology experiment. Experimental data so obtained have been fitted to the Monod's substrate uninhibited cell growth rate model for the purpose of predicting the cell growth. The two intrinsic kinetic parameters present in the Monod's equation have been evaluated experimentally.

2 Materials and Methods

- Lead nitrate [Pb $(NO_3)_2$] (A.R grade), SRL, India.
- Tryptone glucose yeast extract (TGY) broth, sodium hydroxide (NaOH) (L.R grade), HIMEDIA, India.
- Nitric acid (HNO_3), sulphuric acid (H_2SO_4), alcohol, sodium sulfite, Di-potassium hydrogen phosphate glucose, Rochelle salt (A.R grade) MERCK, India.
- Di nitro salicylic acid (DNSA) (GR grade), (L.R grade) LOBA CHEMIE Pvt. Ltd, India.

2.1 Preparation of Bacterial Culture

Acinetobacter sp. 158 was previously isolated from battery industry waste mud. In the present study, the 24 h fresh culture of that bacterial cell grown in lead-incorporated tryptone glucose yeast extract (TGY) broth was used as inoculum. Aqueous solution of lead nitrate was used as a lead supplement.

2.2 Estimation of Concentration of Glucose

Concentration of glucose was measured using Di nitro salicylic acid (DNSA) method [7]. Initially, 1gm of Di nitro salicylic acid (DNSA), 200 mg crystalline phenol, and 50 mg sodium sulfite were dissolved in 100 ml 1% aqueous sodium hydroxide (NaOH) solution. Simultaneously, a solution of 40% sodium potassium tartrate (Rochelle salt) was prepared by adding 20 gm Rochelle salt in 50 ml distilled water.

2.2.1 Procedure

1 ml supernatant broth was taken in a 200 ml beaker and was diluted to a hundred times by adding distilled water. 1 ml of this diluted supernatant was transferred to a test tube and 2 ml distilled water, 3 ml Di-nitro salicylic acid (DNSA) solutions were added to it. The test tube was kept in a boiling water bath for 5 min until dark red color appeared. At this stage, 1 ml of 40% sodium potassium tartar ate (Rochelle salt) solution was added to it. The solution was cooled and its optical density was measured at 510 nm wavelength. The optical density was used to determine the concentration of glucose with the help of a previously prepared standard plot of optical density against the known concentration of glucose.

2.3 Determination of Concentration of Bacterial Biomass

The concentration of biomass was estimated using the dry cell measurement method following the protocol described earlier [5].

2.4 Estimation of Lead

Monitoring of removal of lead was made following the similar procedure published earlier [5].

2.5 Optimization of Lead Removal Using Response Surface Methodology

Since *Acinetobacter sp. 158* has tremendous potential of removing lead from lead-containing industrial waste, a cost-effective method is needed for large-scale production of the lead-resistant bacterium. The bacterium uptakes lead by intracellular accumulation so the bacterial growth is directly related to lead removal. The primary step toward cost reduction is to identify optimum growth conditions as well as optimum lead removal conditions and operating parameters.

Experimentally the optimized conditions are determined by changing one variable keeping all others variables are constant and observing its effect on the cell response. This optimization procedure is almost arbitrary and real-time situation provides no fruitful information. Presently, with the advent of response surface method technique for optimizing process parameters theoretically, the scenario is completely changed. It is a fantastic approach to get optimized condition by performing a minimum number of experiments.

Optimization of media compositions for any biological system the principal emphasis rests on carbon source. In the present investigation, an attempt has been made to optimize the percentage of lead removal by that bacterium based on the concentration of carbon source, pH, and rotational speed.

2.5.1 Procedure

The principle of optimization is based on central composite design (CCD). According to CCD design, the total number of treatment combinations is $2^a + 2a + n_0$, where 'a' is the number of independent variables and n_0 the number of repetitions of the experiments at the center point.

The principal of optimization followed here include two consecutive steps. Initially, the total number of treatment combinations is determined by performing central composite design (CCD). In the next step response, surface methodology was applied to solve the multivariate polynomials and subsequently optimization of the response variable. Thus, response surface methodology is based on three steps: (i) design and experiments; (ii) response surface modeling through regression; (iii) optimization. The functional relationship between the response variables is best represented by a second-order polynomial equation given in Eq. 1.

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{i=1}^{k} \beta_{ij} X_i X_j + \varepsilon \tag{1}$$

where $X_1, X_2, \ldots, X_k$ are the input variables, which impact the response Y; β_0 (independent term of regression equation), β_i ($i = 1, 2, \ldots, k$) (linear term of regression equation), β_{ii} ($i = 1, 2, \ldots, k$) (second-order term of regression equation), and β_{ij} ($i = 1, 2, \ldots, k$; $j = 1, 2, \ldots, k$) (interactive term of regression equation) are unknown parameters; ε is a random error. In the present investigation, the response variable (Y) is the percentage of lead removal and X_1, X_2, X_3 are concentration of glucose, pH of the medium, and rotational speed, respectively [8–10].

Design-Expert 8.7.0.1 software was used for regression and graphical analysis of the simulated data. The central composite design (CCD) was used to perform 20 experiments for 2^3 three factorial designs and six replicates at the center point; six star points were employed to the second-order polynomial model. The optimum

Table 1 Experimental ranges and levels of independent variables for set 1 experiment

Independent variables with symbol	$-\alpha$	-1	0	+1	$+\alpha$
Concentration of Glucose (X_1) (Kg/m^3)	0.454622	2.5	5.5	8.5	10.54538
pH (X_2)	5.318207	6	7	8	8.681793
Rotational speed (X_3) (rpm)	103.1821	110	120	130	136.8179

values of the selected variables were obtained by solving the regression equation at the desired values of the process responses. Each of the parameters was coded at five levels $-\alpha$, -1, 0, +1, $+\alpha$. The range and level of the variables in coded units obtained through response surface methodology study are given in Table 1.

2.5.2 Determination of Optimum Percentage of Lead Removal

Twenty experiments were conducted under batch mode condition in Erlenmeyer flasks. The temperature was maintained at 37 °C. The intention of this experiment to study the effect of concentration of glucose, pH of the solution, and shaking speed on the percentage of lead removal by the lead resistant strain. Media pH was adjusted by using 0.1 (N) HNO_3 and 0.1 (N) NaOH according to the experimental sets given by software.

Each Erlenmeyer flask contained a calculated amount of TGY broth and was subjected to autoclaving at 0.2 MPa at 121 °C for 15 min before inoculation. Then the metered amount of aqueous lead nitrate solution was added into each flask under the aseptic condition to maintain 250 ppm lead concentration in media. After that, each of the flasks was inoculated with the pure culture solution of the lead-resistant strain. Percentage of lead removal (the response variable) was determined by estimating lead following the procedure mentioned under Sect. 2.4.

2.6 Concentration-Time History of Limiting Carbon Source Glucose

In order to find out the growth kinetics of the isolated microorganism at the optimum value of the concentration of glucose obtained using response surface methodology, a set of batch experiment was carried out in 100 ml Erlenmeyer flask. Erlenmeyer flasks each containing a calculated amount of broth were taken and autoclaved at 0.2 M Pa and 121 °C for 15 min. Fixed amount of previously sterilized aqueous solution of lead nitrate was incorporated into each flask under the aseptic condition to maintain metal concentration 0.25 kg/m^3. Each flask was then inoculated with the isolated pure strain inside the laminar flow chamber and was marked serially. Once the inoculation was over, all the shake flasks except that marked 1 were kept inside incubator under shaking. The temperature was maintained at 37 °C.

Metered amount of aliquot from the flask marked 1 was taken in a centrifuge tube and centrifuged at 5000 rpm for 20 min. After separation of the solid residue from the liquid, the concentration of the dry cell mass was measured by the method outlined earlier. The concentration of the glucose was determined by DNSA study from the liquid supernatant mentioned under Sect. 2.2. After a definite time interval, the flask marked 2 was taken out from the incubator and a similar experiment was conducted as in the case of the flask marked 1. These experiments were repeated for each of the flasks to get the cell mass growth-time history as well as substrate-time history. In order to find out the experimental data at 0 time one flask was analyzed immediately after inoculation.

3 Result and Discussion

In order to investigate the potential effectiveness of the candidate bacterium *Acinetobacter sp. 158* as lead tolerant, the phase contrast microscopic observation was made and the result is shown in Fig. 1. It is evident from the figure that the isolated cells have formed profuse spores to tolerate lead metallic shock and eventually has been transformed into a lead-resistant bacterium.

3.1 Optimization of Growth Media and Growth Parameters

Table 2 presents the experimental design data obtained through central composite design for the experiment. In order to develop a quantitative relation between the

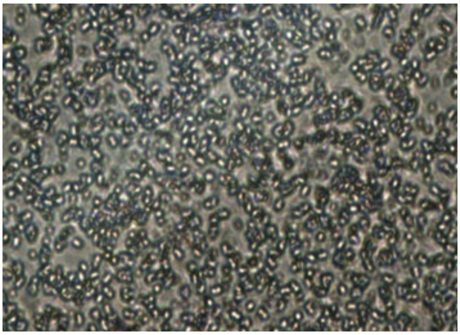


Fig. 1 Phase contrast microscopic observation of endospore staining

Table 2 Central composite design data for RSM experiment

Run	X_1 (coded) (Kg/m^3)	X_2 (coded)	X_3 (coded) (rpm)	Observed values of percentage of lead removal	Predicted values percentage of lead removal
1	+α	0	0	11	10.16
2	+1	−1	+1	11.9	12.45
3	0	+α	0	16	14.19
4	−1	−1	−1	10.6	10.85
5	0	0	−α	22.2	22.71
6	−1	−1	+1	10.7	11.48
7	0	0	0	57.38	57.45
8	0	0	0	57.39	57.45
9	0	−α	0	12	11.65
10	0	0	0	57.4	57.45
11	+1	−1	−1	11.5	11.66
12	0	0	0	57.41	57.45
13	−1	+1	−1	11.4	12.36
14	+1	+1	−1	12.3	12.97
15	0	0	0	57.38	57.45
16	+1	+1	+1	12.7	13.96
17	−1	+1	+1	11.9	13.26
18	−α	0	0	10.2	8.89
19	0	0	0	57.37	57.45
20	0	0	+α	24.8	23.14

response and the independent variables for that experiment, Eq. (1) was subjected to multiple regression analysis only the known process parameters involved in that experiment.

The resulting Eq. (2) is the desired predicted response for cell growth.

$$\begin{aligned}\mathbf{Y} &= \mathbf{57.44967 + 0.367766X_1 + 0.75619X_2 + 0.422693X_3}\\ &\quad \mathbf{- 0.05X_1X_2 + 0.025X_1X_3 + 0.05X_2X_3 - 16.9431X_12}\\ &\quad \mathbf{- 15.741X_2^2 - 12.3822X_3^2}\end{aligned} \tag{2}$$

The significance of Eq. (2) was determined by F-value and the analysis of variance (ANOVA) by fitting the data of all selected independent variables in the response surface quadratic model obtained in the individual set. This is shown in Table 3.

The significance of each coefficient was verified by *F* values and *P* values following the principle that larger the magnitude of *F* values and smaller the *P* values the more significant is the corresponding coefficient.

In this case, values greater than 0.1000 indicate the model terms are not significant. Table 3 indicates that in the present model equation X_2, X_1^2, X_2^2, X_3^2 are significant

Table 3 Significance of coefficients present in Eq. (2)

Model term	Coefficient estimate	Standard error	F-value	p-value
Intercept	57.44967	0.494981		
X_1	0.376766	0.328409	1.316175	0.2780
X_2	0.75619	0.328409	5.301911	0.0441
X_3	0.422693	0.328409	1.656616	0.2271
X_1X_2	−0.05	0.429086	0.013578	0.9095
X_1X_3	0.025	0.429086	0.003395	0.9547
X_2X_3	0.05	0.429086	0.013578	0.9095
X_1^2	−16.9431	0.319697	2808.711	<0.0001
X_2^2	−15.741	0.319697	2424.303	<0.0001
X_3^2	−12.3822	0.319697	1500.4592	<0.0001

Table 4 Analysis of variance for set 2 experiment

Source of variation	Sum of squares	Degree of freedom	Mean square	F-value	Probability > F
Model	8330.864	9	925.6515	628.4459	<0.0001
Residual	14.72922	10	1.472922		
Lack of fit	14.72813	5	2.945626		
Pure error	0.001083	5	0.000217		
Total	8345.593	19			

C.V% = 4.549472; R^2 = 0.998235; Pred R^2 = 0.986659; Adj R^2 = 0.996647

Table 5 Optimum values of independent variables and the percentage of lead removal

Glucose concentration (kg/m^3)	pH	Rotational speed (rpm)	Predicted optimum value of percentage of lead removal	Experimental optimum value of percentage of lead removal
5.55	7.04	120.75	57.42	57.38

model terms. Analysis of variance is shown in Table 4. The F values of the model as indicated by the analysis of variance are 628.45. This value along with the probability (less than 0.05) indicates the validity of the predicted cell response equation in the present case.

In order to understand the quantitative dependence of the percentage of lead removal on the independent variables, a set of 3D plots (Fig. 2 through Fig. 4) have been constructed with the operating parameters. All these plots establish the optimum lead removal percentage simultaneously optimum cell growth conditions. The optimum value of the percentage of lead removal and the corresponding values of the three selected independent variables are given in Table 5 (Fig. 3).

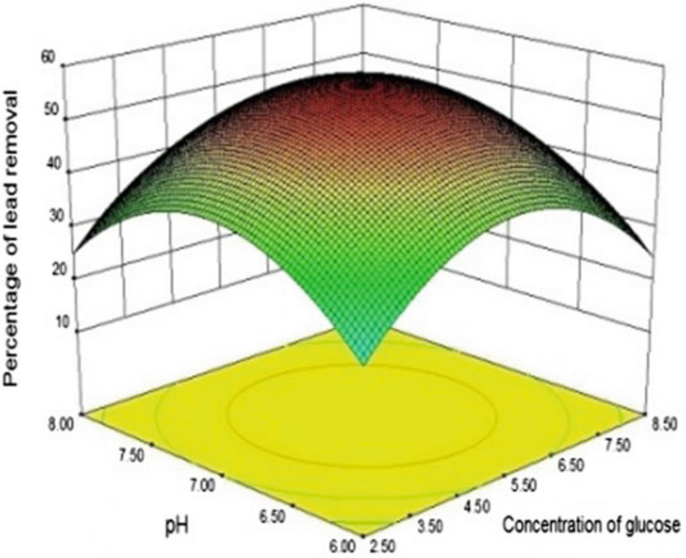


Fig. 2 3D plot of optimum percentage of lead removal against the concentration of limiting carbon source (glucose) (kg/m^3) and pH

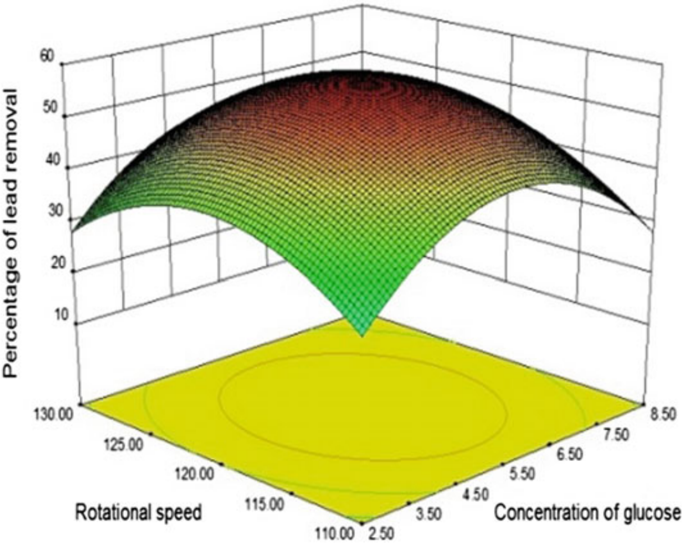


Fig. 3 3D plot of optimum percentage of lead removal against limiting carbon source (glucose) (kg/m^3) and rotational speed (rpm)

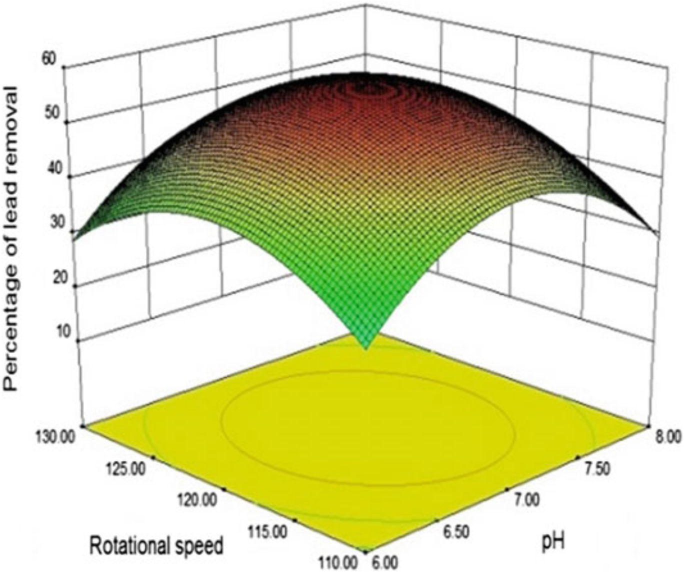
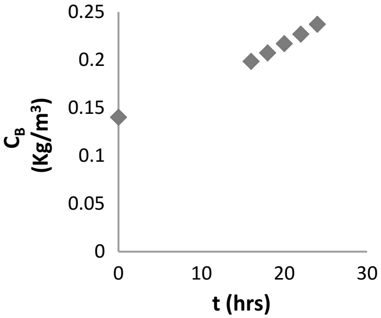


Fig. 4 3D plot of optimum percentage of lead removal against pH and rotational speed (rpm)

3.2 Cell Growth Dynamics

Time history plots of cell growth and substrate depletion have been constructed from the experimental data. These are shown in Figs. 5 and 6 respectively. A section of S-shaped curve obtained in Fig. 5 leads to the possibility of cell dynamics to be explained by Monod's substrate uninhibited model equation. A close inspection of Fig. 6 reveals that the substrate depletion dynamics is exponential in nature. Such observations further strengthen the applicability of the Monod equation in the present cell growth dynamics.

Fig. 5 Cell growth as a function of time with initial glucose concentration as a parameter



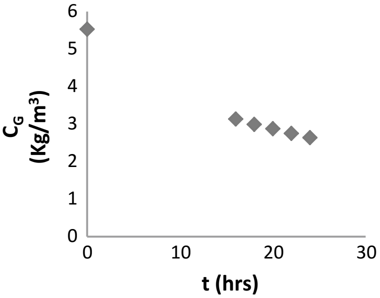


Fig. 6 Depletion of glucose as a substrate with time for optimum initial glucose concentration obtained from RSM

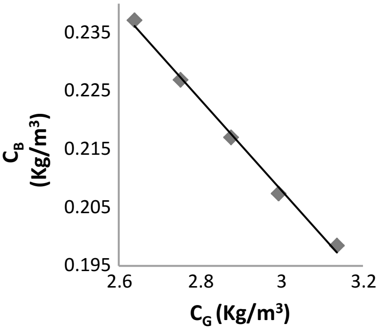


Fig. 7 Yield coefficient curve

3.2.1 Development of Theoretical Equations of Cell Growth Dynamics

The nature of cell growth as well as the depletion of substrate shown in Figs. 5 and 6, respectively, dictate the applicability of Monod's substrate uninhibited model equation in the present case. The model equation is given by.

$$\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}t} = \frac{kC_{\mathrm{G}}C_{\mathrm{B}}}{K_{\mathrm{S}} + C_{\mathrm{G}}} \tag{3}$$

In the above equation, C_{G} = concentration of substrate glucose (kg/m^3), C_{B} = concentration of biomass (kg/m^3), k = maximum specific cell growth rate, hour^{-1}, K_{S} = saturation constant for glucose, (kg/m^3), t = time of incubation, (hour).

In Eq. (3), concentration of substrate has been eliminated in terms of concentration of cell using the yield of cells as follows:

$$\mathrm{Y}_{\mathrm{B}/\mathrm{G}} = -\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}C_{\mathrm{G}}} \tag{4}$$

C_B Vs C_G should yield a straight line having slope $\mathrm{Y}_{B/G}$. This is shown in Fig. 7. A linear plot so obtained has a slope of 0.078. Integration of Eq. (4) gives

$$\left(C_B - C_{B_0}\right) == Y_{B/G}\left(C_{G_0} - C_G\right)$$

Fig. 8 Linear plot of integrated Monod's equation

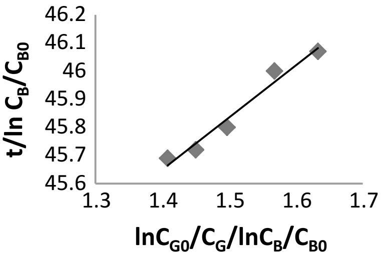


Table 6 Cell yield and intrinsic kinetic parameters of Monod's equation

Yield coefficient $\left(\frac{\text{kg of cell}}{\text{kg of glucose}}\right)$	Substrate saturation constant (kg/m^3)	Maximum specific reaction rate (Hour^{-1})
0.078	0.321	0.02427

Or,

$$C_G = C_{G_0} + Y_{G/B}\left(C_B - C_{B_0}\right) \tag{5}$$

And,

$$C_B = C_{B_0} + Y_{B/G}\left(C_{G_0} - C_G\right) \tag{6}$$

Integrating Eq. (3) with suitable substitution and rearranging the following linear form of the equation is obtained [11]

$$\frac{t}{\ln\frac{C_B}{C_{B0}}} = \frac{M}{k}\frac{\ln\frac{C_{G0}}{C_G}}{\ln\frac{C_B}{C_{B0}}} + \frac{M+1}{k} \tag{7}$$

Where,

$$M = \text{a constant} = \frac{K_S}{C_{G_0} + C_{B_0}Y_{B/G}} \tag{8}$$

A plot of $\frac{t}{\ln\frac{C_B}{C_{B0}}}$ against $\frac{\ln C_{G0}/C_G}{\ln C_B/C_{B_0}}$ is shown in Fig. 8. The linear plot so obtained confirms the validity of Monod's equation to predict cell growth dynamics in the present case.

The two intrinsic kinetic parameters k and K_S present in Monod's equation have been evaluated by combining slope and intercept obtained from Fig. 8. The values of $Y_{B/G}$ k and K_S are given in Table 6.

The cell growth dynamics can be represented by the following equation, and therefore can be shown as follows:

For cell growth,

$$\frac{\mathrm{d}C_\mathrm{B}}{\mathrm{d}t} = \frac{0.02427 C_\mathrm{B} C_\mathrm{G}}{0.321 + C_\mathrm{G}} \frac{\text{kg cell formed}}{(\text{hr})\left(\text{m}^3\right)} \tag{9}$$

In order to validate the general applicability of the proposed cell growth dynamics equation experimental data not used for simulating purpose have been used to compare with the predicted values. It is observed that the experimental and simulated data match well within the acceptable confidence level. Thus, Eq. (9) is capable of predicting cell growth rate in presence of a predetermined concentration of lead.

4 Conclusion

Understanding the importance of optimum culture condition used for cell growth, in the present investigation a programmed statistical optimization study has been carried out to identify the optimum condition pertaining to initial concentration of carbon source, pH, and rotational speed of the medium. A widely accepted statistical tool, viz., RSM has been used for optimization and resulting 3D plots yielded the optimized value of the independent variables. Studies on cell growth dynamics using this optimum values resulted in a quantitative dynamic equation capable of predicting cell growth concentration under transient condition.

Acknowledgements One of the authors (M.B.) gratefully acknowledges the University Grants Commissions, Govt. of India for providing financial support for this work.

References

1. Wang X, Nie Z, He L, Wang Q, Sheng X (2017) Isolation of As—tolerant bacteria and their potentials of reducing As and Cd accumulation of edible tissues of vegetables in metal (loid)-contaminated soils. Sci Total Env 579:179–189
2. Mahbub MR, Kannan K, Naidu R, Mallavarapu M (2016) Mercury resistance and volatilization by *Pseudoxanthomonas sp.* SE1 isolated from soil. Environ Technol Innov 6:94–104
3. Mala JGS, Sujatha D, Rose C (2015) Inducible chromate reductase exhibiting extracellular activity in Bacillus methylotrophicus for chromium bioremediation. Microbiol Res 170:235–241
4. Davolos D, Pietrangeli B (2013) A molecular study on bacterial resistance to arsenic-toxicity in surface and underground waters of Latium (Italy). Ecotoxicol. Environ Saf 96:1–9
5. Bose M, Datta S, Bhattacharya P (2017) Studies on isolation, characterization and cell growth dynamics of a lead resistant bacterium *Acenetobacter 158*. Environ Technol Innov 8:103–112
6. Ghoshal S, Bhattacharya P, Chowdhury R (2011) De-mercurization of wastewater by *Bacillus cereus* (JUBT1): Growth kinetics, biofilm reactor study and field emission scanning electron microscopic analysis. J Hazard Mater 194:355–361

7. Miller GL (1959) Use of dinitrosalicylic acid reagent for determination of reducing sugar. J Anal Chem 31:426–428
8. Myers Raymond H, Montgomery DC (2002) Response surface methodology: process and product optimization using designed experiment. Wiley-Interscience Publication, New York, NY
9. Box G, Hunter JS (1957) Multi-factor experimental designs for exploring response surfaces. Ann Math Stat 28:195–241
10. Ferda G, Zümriye A (2008) Use of response surface methodology (RSM) in the evaluation of growth and copper(II) bioaccumulation properties of *Candida utilis* in molasses medium. J Haz Mat 154:731–738
11. Levenspiel O (2013) Chemical Reactor Omnibook-soft cover. Lulu. com.

Rapid In Vitro Proliferation of *Tinospora Cordifolia* Callus Biomass from Stem and Leaf with Phytochemical and Antimicrobial Assessment

Vidyadhar V. Gedam, Swapnil V. Punyapwar, Pranay A. Raut and Anup D. Chahande

1 Introduction

Extensive variety of secondary metabolites viz. tannins, terpenoids, alkaloids, and flavonoids are richly available in plants, with profound antimicrobial properties [1]. Plants that possess strong antimicrobial potential against pathogens are considered as a valuable source of medicinal compounds and are likely to have lesser side effects in comparison with modern medicines. Antibiotic discovery was a critical moment in medical history that has revolutionized medicine in many regards, and myriad lives have been saved consequently. But, it is unfortunate that the injudicious use of these drugs has been conjoined with the prompt development of resistant strains of microorganisms. Thus, there is a need to investigate such plants and isolate commercially useful secondary metabolites.

Tinospora cordifolia (Wild) Miers (Menispermaceae) is a big, woody climber. The early stem is green in color, cylindrical shape, and smooth in nature [2, 3]. Its developed stem has warts on the surface, hanging floating roots, and peeling bark which is creamy white in color. *Tinospora cordifolia* is a widely used shrub in ayurveda. This species is also efficiently used in the treatment of allergic rhinitis due to its immunomodulatory or immunostimulatory, antitumor, cognition,

---

V. V. Gedam (✉)
Environmental Engineering and Management, National Institute of Industrial Engineering (NITIE), Mumbai, India
e-mail: vgedam@nitie.ac.in

S. V. Punyapwar
Department of Biological Sciences, BITS-Pilani, KK Birla Goa Campus, Goa, India
e-mail: svpunyapwar@gmail.com

P. A. Raut · A. D. Chahande
Department of Biotechnology, Priyadarshini Institute of Engineering and Technology, Nagpur, India

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_39

anti-inflammatory, anti-neoplastic, antihyperglycemia, antihyperlipidemia, antioxidant, antituberculosis gastrointestinal and hepatoprotection, anti-osteoporotic, antiangiogenic, antimalarial, anti-allergic, and antimicrobial, and side effect prevention from cancer chemotherapy characteristics [4–7].

Plant researchers were attracted and paid attention due to phytochemical properties of medicinal plants and also due to the development of more sophisticated analytical tools. These sophisticated analytical tools played a real role in the search of new assets of unanalyzed materials for pharmaceutical research. Various important biochemical contents have been screened from various parts of plants and their effects have been studied [8–10]. Among such phytochemicals few have antimicrobial activity. Plants that possess strong antimicrobial potential against pathogens are considered as a valuable source of medicinal compounds and are likely to have lesser side effects in comparison with modern medicines. Typical medicines were increasingly accessible to the use of antimicrobial and other types of drugs specifically resulting from plants. For the last 20 years, there has been a fast rate of (plant) species loss, which is the motivating factor for the renewed interest in plant antimicrobials [11].

In current study, *T. cordifolia* is subjected to different hormone concentrations for biomass production from different plant parts. It also focuses on the assessment of antimicrobial activity of *T. cordifolia* stem and leaf extract. The antimicrobial activity of *T. cordifolia* is estimated against three standard strains, i.*e., E-coli*, *P. aeruginosa*, and *B. subtilis* with aqueous, methanolic, and ethanolic extracts with the help of standard well diffusion method.

2 Material and Methods

2.1 In Vitro Propagation

Fresh and strong plants of *Tinospora cordifolia* were collected from Manas Ayurveda and Shreeshaila Ayurvedic Nursery in Nagpur. Leaf, node, internode, and shoot tips were chosen for propagation. Explants were first washed under tap water and surface sterilized by 70% ethanol. Further, washed with double distilled water to remove the traces of ethanol from the explants. The washed explants were treated with 2% Bavistin for 4 min and rinsed with distilled water 2–3 times. Finally, treated with 0.1% mercuric chloride for 3–4 min and again washed with sterilized double distilled water to remove all traces of mercuric chloride.

Explants were inoculated on the MS (Murashige and Skoog) media supplemented with various concentrations of growth hormones such as NAA, BAP, Kinetin, and 2,4,D. Sterilized leaf explants of diameter 0.5 mm were inoculated on the MS media supplemented with various combinations of NAA (2.0 and0.5 mg/lit), BAP (1.5,2.5 and 3.0 mg/lit), and 2,4,D (0.5,1.0 and 2.0 mg/lit) used for rapid induction of callus. For nodal and shoot tip explants, combination of NAA (0.5 and 2.0 mg/lit) with

BAP (1.5, 2.0, 2.5 and 3.0 mg/lit) and 2, 4, D (2.0 and 2.5 mg/lit) with Kinetin (0.5 and1.0 mg/lit) are used. Subculturing was done in 20 days after induction of callus. The days of callus induction and multiple shoot induction from single shoot and shoot formation from callus were observed and data is recorded.

2.2 Phytochemical Screening

Extract Preparation

Tinospora cordifolia plant parts and calluses are sun dried for 4–5 days and thinly powdered. This powdered plant is then used for the extraction process. Three types of extracts were prepared with different solvents, i.e., aqueous, ethanolic, and methanolic extracts that were prepared using standard protocols.

a. Aqueous extract:

4 g of powdered plant and callus powder were dissolved into 50 ml lukewarm autoclaved double distilled water. Temperature of the mixture is maintained at 50–60 °C for 2 h, and then filtered with the help of Whatman's filter paper no. 1. This extract was dried. Half of this dried mass is dissolved into DMSO and remaining half is dissolved into the respective solvent.

b. Ethanolic extract:

4 g of powder was dissolved into 50 ml of 70% ethanol and maintained at 40–50 °C, and allowed to reduce up to ¼ of its quantity. The mixture is then filtered with Whatman's filter paper no. 1. Extract is then allowed to evaporate and the half of this dried material is then dissolved into 5 ml of DMSO. Remaining half is dissolved in the ethanol.

c. Methanolic extract:

4 g of powder was dissolved into 50 ml of 70% methanol and maintained at 40–50 °C, and allowed to reduce up to ¼ of its quantity. The mixture is then filtered with Whatman's filter paper no. 1. Extract is then allowed to evaporate and the half of this dried material is then dissolved into 5 ml of DMSO. Remaining half is dissolved in the methanol.

2.3 Well Plate Diffusion for Antimicrobial Activity

The nutrient agar plates were prepared by pouring the sterilized media in autoclaved Petri plates and then allowing it to solidify. Then, evenly spread 20 μl of microbial culture on the plate with the help of spreader and wait for 10 min. Wells are bored on the nutrient agar plates with the help of sterilized borer and named as replica 1 (R1) replica 2 (R2), replica 3 (R3), replica 4 (R4), replica 5 (R5), and replica 6 (R6). 200 µl of aqueous, methanolic, and ethanolic of *Tinospora cordifolia* extract were added in wells, respectively. Plates are then set for overnight incubation. Results were observed on next day [12].

3 Results and Discussion

3.1 In Vitro Propagation

Diverse explants of *Tinospora cordifolia* were selected for callus propagation. Node and internode explants were inoculated on MS supplemented with different concentrations of BAP, KIN, and 2, 4, D which showed different responses.

Callus induction was observed within 7 days or more depending upon the concentration of the growth regulators. Callus best results were obtained on 2,4,D (1 mg/lit) alone. Our results of callus induction are in harmony with the results obtained by Bhalerao et al. [13]. The combination of BAP and 2,4,D gave moderate results.

For nodal explant, BAP (1.5 mg/lit) and 2,4,D (2 mg/lit) concentration was better than the other combinations (Table 1).

Mature callus was obtained within 22–25 days after inoculation. Callus yield from leaf explant showed higher potential as compared to shoot and nodal explant.

Table 1 Induction of callus with dissimilar concentrations of NAA, BAP, KINETIN, and 2,4,D for leaf node and internode

Growth regulators (mg/lit)				Explants		
NAA	BAP	2,4,D	KIN	Leaf	Node	Internode
_	_	1.0	_	H	_	_
0.5	0.3	_	_	M	_	_
_	3.0	0.5	_	M	_	_
_	2.0	2.5	_	L	_	_
_	_	1.0	3.0	M	_	_
_	2.0	12.0	_	H	_	_
_	1.5	2.0	_	_	L	_
_	2.0	2.5	_	_	M	_
0.5	3.0	_	_	_	_	H
_	2.0	1.0	_	_	_	L

H denotes high callusing, **M** denotes moderate callusing, **L** denotes little callusing. (If callus initiation and growth is visible within 5–7 days, it can be considered as high callusing denoted by **H**. If the callus is grown visibly within 10–15 days, it can be considered as moderate callusing denoted by **M** and if it takes more than 20 days, it can be considered as low denoted by **L**)

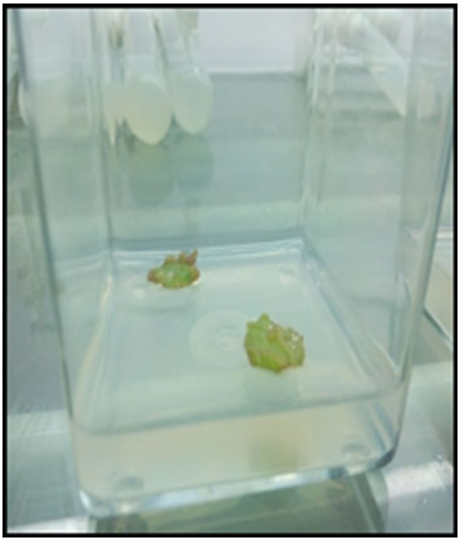


Fig. 1 Induction of callus

Similar pattern of variation in callus induction by different explants was observed in the research of Verma et al. [14].

After 30 days of callus-induced culture, a phenolic exudation issue was observed in shoot formation, media was observed with different colors, explants were observed with browning, and the buds were broken; therefore, additional analysis was required to regulate the phenolic leakage, and the procedures were identified by giving different phenolic exudation regulatory substances. To prevent the browning of explant, ascorbic acid is added in the MS media. Similar measures were taken up by Sivakumar et al. [15] (Fig. 1).

3.2 Shoot Induction

The shoots were directly inoculated on the medium with growth hormones such as KIN and BAP, which shows initiation of shoot in 7–10 days, and visible growth of 6 mm was observed within 25 days. Multiple shoot induction from single shoot was prominent, i.e., approximately three shoots were arising from a single shoot. The best combination that works for the multiple shoot formation is BAP (2 mg/lit) and KIN (1 mg/lit). For shoot induction from shoot tip explant itself, the best working concentration is KIN and BAP (Table 2).

Above table shows the response given by the shoot tip explant for various concentrations of BAP and KIN. The response was recorded after each 25 days of interval (Fig. 2).

Table 2 Response of shoot induction by different growth regulators

Concentration of growth hormones (mg/lit)		Response of shoot induction
BAP	KIN	
1.0	2.0	L
2.0	2.0	M
2.0	1.0	M
2.0	_	L
0.2	0.1	H

L indicates low response, **M** indicates moderate response, **H** indicates high response (If shoot induction starts within 15 days, it is considered as high response denoted by **H**. For 20–30 days, it can be considered as moderate denoted by **M** and for 30–50 days, it can be considered as low denoted by **L**)

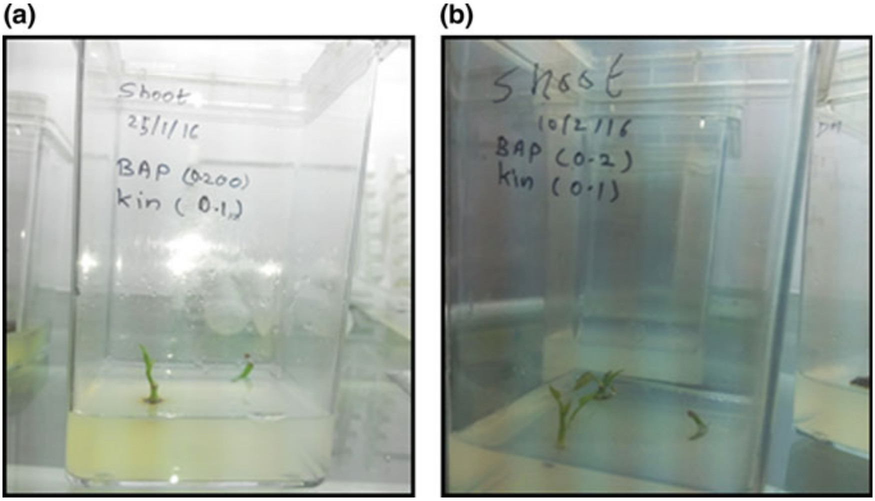


Fig. 2 Multiple shoots induction. **a** Shoots at Day—0 of inoculation, **b** multiple shoot induction

3.3 Phytochemical Screening

The initial phytochemical screening of leaves and stems of *T. cordifolia* highlights the presence of different bioactive secondary metabolites which might be responsible for their medicinal attributes. Phytochemical study of the leaf and stem extract of *Tinospora cordifolia* shows the presence of alkaloids, carbohydrates, proteins and amino acid, tannins, flavonoid, steroids, terpenoids, cardiac glycosides and saponins, phenol, anthocynide, and phlobatannins (Table 3).

Current study signifies the presence of carbohydrates, phenols, proteins, saponins, flavonoids, alkaloids, and steroids in all extracts. Tannins are present in methanolic and ethanolic extract. Terpenoids are present only in methanolic extract. Cardiac glycosides are also present only in methanolic extract.

Table 3 Phytochemical screening of *Tinospora cordifolia* extract

Sr. no	Phytochemical tests	Aqueous extract	Methanolic extract	Ethanolic extract
1	Carbohydrates	P	P	P
2	Phenols	P	P	P
3	Proteins and amino acids	P	P	P
4	Saponins	P	P	P
5	Tannins	A	P	P
6	Terpenoids	A	P	A
7	Flavonoids	P	P	P
8	Anthocynide	A	A	A
9	Steroids	P	P	A
10	Cardiac glycosides	A	P	A
11	Phlobatannins	A	A	A
12	Alkaloids	P	P	P

P indicates the presence and **A** indicates the absence of corresponding secondary metabolites methanol (MET), ethanol (ETH), and aqueous (AQS)

Our results are similar in context of antimicrobial activity to the research of Rani et al. [16] in which data indicates the presence of alkaloids, amino acid, phenolic compounds, flavonoids, saponins, steroids, and cardiac glycosides. Most of the phytochemical components were found in methanolic extract due to high solubility of active compound of *T. cordifolia* in this solvent as compared to other solvents.

The parameters affecting the selection of solvent includes the amount of photochemical to be extracted, rate of extraction, variety of different compounds to be extracted, variety of inhibitory compounds to be extracted, simplicity during handling of the extracts, toxicity of the solvent during bioassay process, potential health hazard of the extract, etc. The main aim for using diverse solvents when screening for photochemical in plant materials is validated and proved in this study. Alkaloids play important role during metabolic as well as living system controlled development, and also they play a major role in shielding function in animals and are mostly used as medicine, specifically steroidal alkaloids. Presence of flavonoids and phenolic compounds relate to multiple biological properties such as antioxidant, free radical scavenging ability, anti-inflammatory, anti-carcinogenic, etc. Some of these phytochemicals can significantly reduce the risk of cancer due to polyphenol antioxidant and anti-inflammatory effects.

3.4 Antimicrobial Activity

In present study, all extracts viz. aqueous ethanolic and methanolic extracts show the antimicrobial activity against the standard microbial stains. The efficiency of antimicrobial can be found out by measuring the zone of inhibition shown by the extracts in the standard well diffusion method. The radius of the zone of inhibition around the well shows the potential of the antimicrobial extract to inhibit the growth of the antimicrobial culture.

The undiluted extract and first dilution have shown antimicrobial activity but subsequent dilutions of all methanolic, ethanolic, and aqueous extract have not shown any antimicrobial activity. Best results were seen for *E. coli* followed by *B. subtilis*, and then for *P. aeruginosa*.

Among the three extracts, the best antimicrobial activity is shown by methanolic, ethanolic, and aqueous extracts which are redissolved in DMSO. The crude extracts which were redissolved in respective solvent show lower zone of inhibition than DMSO extracts (Fig. 3).

The circle highlights the concentration of the extract producing best inhibitory zone for respective strains of organisms (Fig. 4).

- *E. coli:* Ethanolic (DMSO), methanolic (DMSO), and aqueous (DMSO) show ZI.
- *P. aeruginosa*: Crude ethanol, aqueous (DMSO), and methanolic (DMSO) show ZI.
- *B. subtilis*: Methanolic (DMSO), ethanolic (DMSO), and crude ethanol show ZI (where ZI indicates zone of inhibition).

Results in above studies resemble to the results of this experiment. The best result observed for leaf extract dissolved in DMSO for *E. coli*, followed by *B. subtilis*, and *P. aeruginosa.*

Our results were confirmed by the study conducted by Amane [17] in which the aqueous extract and ethanolic extract of *Tinospora cordifolia* showed antimicrobial

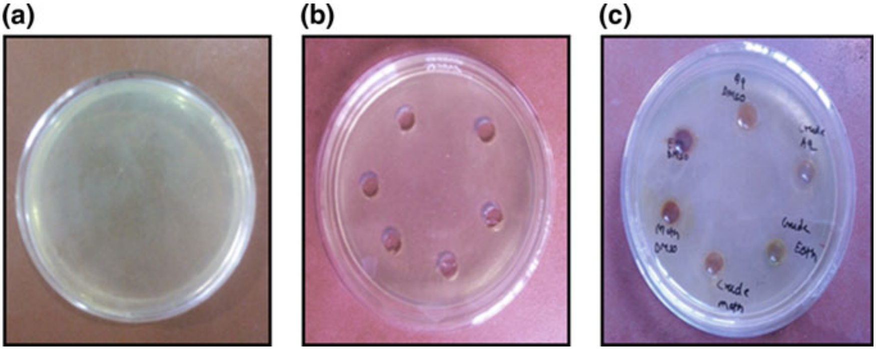
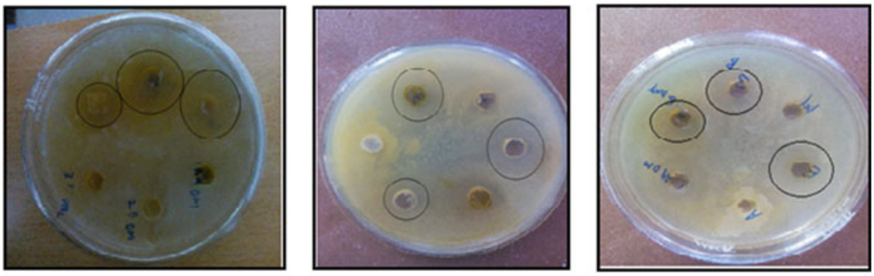


Fig. 3 Well diffusion method. **a** shows the agar plate without wells, **b** shows agar plate with wells, and **c** shows agar plates containing various extracts of *T. cordifolia*



E.coli *P.aeruginosa* *B. subtilis*

Fig. 4 Antimicrobial activities of extracts on different microbes

Table 4 Antimicrobial activity of different extracts against different organisms

Sr. No	Microbial strain	Extract					
		Aqueous extract		Methanolic extract		Ethanolic extract	
		AQU (DMSO)	AQU	MET (DMSO)	MET	ETH (DMSO)	ETH
1	*E. coli*	+	_	+	_	+	_
2	*P. aeruginosa*	+	_	+	_	_	+
3	*B. subtilis*	_	_	+	_	+	+

"+" = presence of antimicrobial activity in the respective extract and "_" = absence of antimicrobial activity in the respective extract.

activity against standard strains of *Escherichia coli*, *Staphylococcus aureus,* and *Pseudomonas aeruginosa*.

Research of Khan [18] with the help of agar disk diffusion method confirmed antimicrobial activity against *Escherichia coli*, *Staphylococcus aureus*, and *Bacillus subtilis*. At 2 mg and 4 mg concentrations of methanolic callus extract, inhibition was obtained for both the organisms. This sums up our successful study of antimicrobial activity of *Tinospora cordifolia* (Table 4).

4 Conclusion

Wealth of medicinal plants is rapidly diminishing over the time due to reasons such as genetic erosion, loss of biodiversity, urbanization, expansion of agriculture, increasing deforestation, and construction of dams. If it goes on, then there will be complete loss of some of the most important sources of drugs forever. Secondary metabolites are currently being produced commercially from plants' extraction process. Therefore, large-scale plant tissue culture is an attractive alternative compared to traditional methods. However, for industrial scale commercial production, this technology has led to only few realizations in spite of promising results. On other hand, regeneration procedures have been identical and standardized for many medicinal plants to meet demand and supply gap as well as conservation. As a result of the overexploitation of plant material for typical medicinal purposes, the standardization of the regeneration protocols for *Tinospora cordifolia* medicinal plant is very important. The regeneration protocol described and developed in the present work will benefit the protection of *Tinospora cordifolia*, which was extensively used in traditional medicine. The extract of *Tinospora cordifolia* may contain carbohydrates, phenols, proteins, alkaloids, terpenoids, tannins, saponins, flavonoids, steroids, and cardiac glycosides which are responsible for its various activities. The compound which is responsible for its antimicrobial activity is present in very low concentration, so there is a need to concentrate the compound. Advanced techniques like TLC and HPLC can be used to precisely collect the data of compounds resulting in antimicrobial and other activity.

References

1. Cowan MM (1999) Plant products as antimicrobial agents. Clin Microbiol Rev 12(4):564–582
2. Rana V, Thakur K, Sood R, Sharma V, Sharma TR (2012) Genetic diversity analysis of *Tinospora cordifolia* germplasm collected from northwestern Himalayan region of India. J Genet 91:99–103
3. Parthipan M, Aravindhan V, Rajendran A (2011) Medico-botanical study of Yercaud hills in the Eastern Ghats of Tamil Nadu, India. Anc Sci Life 30:104–109
4. Upadhyay AK, Kumar K, Kumar A, Mishra HS (2010) *Tinospora cordifolia* (Willd.) Hook. f. and Thoms. (Guduchi)-validation of the ayurvedic pharmacology through experimental and clinical studies. Int J Ayurveda Res 1:112–121
5. Sharma U, Bala M, Kumar N, Singh B, Munshi RK, Bhalerao S (2012) Immunomodulatory active compounds from *Tinospora cordifolia*. J Ethnopharmacol 141:918–926
6. Patel SS, Shah RS, Goyal RK (2009) Antihyperglycemic, antihyperlipidemic and antioxidant effects of Dihar, a polyherbal ayurvedic formulation in streptozotocin induced diabetic rats. Indian J Exp Biol 47:564–570
7. Jagetia GC, Rao SK (2006) Evaluation of the antineoplastic activity of guduchi (*Tinospora cordifolia*) in Ehrlich ascites carcinoma bearing mice. Biol Pharm Bull 29:460–466
8. Sardhara RA, Gopal S (2015) Qualitative phytochemical screening of different solvent extracts of *Tinospora cordifolia* stem and lantana camara flower. Int Res J Pharm Appl Sci 3(5):210–213
9. Pathan A, Kamble A, Chowdhury S, Laware S (2015) Sequential extraction and quantification of tinospora cordifolia leaf pigments and metabolites. Int J Curr Microbiol App Sci 4(3):638–644
10. Tilton F, Nair A, Mumdhaj H, Abdulla S, Dheeba B (2013) Inhibitory potentials of *Tinospora cordifolia* leaf extracts against pathogenic bacteria and colon cancer cell line. Int J Adv Res Biotechnol 2(12):027–037
11. Lewis WH, Elvin-Lewis MP (1995) Medicinal plants as sources of new therapeutics. Ann Mo Bot Gard 82:16–24
12. Bauer AW, Perry DM, Kirby WMM (1959) Single disc antibiotic sensitivity testing of *Staphylococci*. AMA Arch Intern Med 104:208–216
13. Bhalerao BM, Kasote DM, Nagarkar BE, Jagtap SD, Vishwakarma KS, Pawar PK, Maheshwari VL (2012) Comparative analysis of radical scavenging and immunomodulatory activities of *Tinospora cordifolia* growing with different supporting trees. Acta Biol Szeged 56(1):65–71

14. Verma KC, Sapra S, Bagga A, Baigh MA (2014) Antioxidant activity assay of stem and in vitro callusing of *Tinospora cordifolia* (Miers.). J Spices Aromatic Crops 23(1):91–97
15. Sivakumar V, Dhana Rajan MS, Sadiqi AM, Jayanthi M (2014) In vitro Micropropagation of *Tinospora cordifolia* (Willd.) Miers ex Hook. F. & Thoms—An Important Medicinal Plant. J Pharmacogn Phytochem 3(2):5–10
16. Rani J, Singh L, Singh H, Kapoor M, Singh G (2015) Preliminary phytochemical analysis of different solvent extracts from leaf and stem of *Tinospora cordifolia*. Int J Phytother 5(3):124–128
17. Amane H, Kaore S, Kaore N (2014) In vitro study of antimicrobial properties of *Tinospora cordifolia* (guduchi). Int J Pharma Bio Sci 5(1):747–753
18. Khan N, Garg M, Tamboli ET, Khan M, Sharma VK, Kumar S, Kumar A (2013) Comparative assessment of antibacterial activity of *Tinospora cordifolia* (willd) Miers leaves and its callus. Pelagia research library 4(1):56–59

Bioremediation of Gurugram–Faridabad Dumpsite at Bandhwari

Raaginii Jaain and Almitra Patel

1 Gurugram–Faridabad Bandhwari Dumpsite

The Bandhwari dumpsite, located along the Gurugram–Faridabad highway, had 25 lakh tons of garbage in the form of a mountain 100 ft in height and 400 ft in length, covering close to 15 acres of the 34-acre dumpsite (Photo 1) . This garbage had been dumped without treatment on a daily basis for 3 years. It had generated leachate covering over 10 acres land (Photo 2) and flowing through the back wall into a forest quarry, from where 900 tankers of leachate were removed in 2016 before bioremediation began. Some of the leachate ponds inside the site were over 10 ft deep. This piled up waste and its unbearable stench, plus flies and birds were causing problems to nearby villages of up to 10 kms away.

2 Processing of Old Waste and Leachate Treatment

The Municipal Corporation of Gurugram (MCG) engaged Raaginii Jaain, Swachh Bharat Mission National Expert, in October 2016 to bio-remediate the Bandhwari dumpsite as recommended by Almitra. H. Patel, Swachh Bharat Mission National Expert and Member, Supreme Court Committee for Solid Waste Management.

The processing of waste in the Bandhwari dumpsite began on October 17, 2016 and ended 10 months later. The initial step was to treat the leachate that had covered the entire dumpsite (Photo 3).

R. Jaain (✉)
Swachh Bharat National Expert, Mumbai, India
e-mail: raaginiijaain@gmail.com

A. Patel
Swachh Bharat National Expert, Bengaluru, India

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_40

Photo 1 Aerial view of 100 ft Bandhwari dump in October 2016

Photo 2 Aerial view of large leachate pools at Bandhwari dump. October 2016

The leachate pools were treated with GE biocultures. Aeration is important for rapid multiplication of microbes, which is indicated by fine bubbles rising from the bottom. Aeration was provided first by a JCB and later by a compressor pump (Photo 4).

Step-like levels called terraces were first formed. Using earthmovers, deep vertical trenches were dug out along both sides of the waste heap and connected by similar deep trenches across the top, so as to form huge windrows for aerating the waste. Odor control and composting GE biocultures were continuously sprayed on all newly exposed surfaces using back-pack sprayers, to speed up the process of decomposition and treatment of leachate (Photo 5).

Photo 3 Waste floating on leachate pools was removed manually with rakes

Photo 4 Leachate pool aeration using a JCB bucket

The trenches also helped to drain out the leachate into existing pools for biotreatment, which digested their organic content and dried up almost all the pools (Photo 6).

These giant windrows were successively turned once a week for 4 weeks to provide aeration. The specialized bioculture along with aeration caused no new leachate to

Photo 5 Cutting trenches for aeration and leachate drainage

Photo 6 Leachate draining out of a sliced heap of waste

be produced from the garbage. Old waste heap height reduced progressively over 10 months (Photo 7).

Photo 7 Huge windrows formed by slicing and trenching brought down the heap height

3 Fresh Waste Processing

Bandhwari dumpsite receives close to 1800 MT of waste on a daily basis from Gurugram and Faridabad. Bioremediation and volume reduction of the original heap created space for windrow formation of fresh waste. Creative space management was the biggest challenge. The fresh waste windrows, 2 meters high, were sprayed with composting and odor-control biocultures, turned twice weekly and doubled up as volume reduced to create space for fresh incoming waste windrows. After four weekly turnings, volume reduced by 40% through loss of moisture and decomposition (Photo 8).

The process of bioremediation with the usage of GE bioculture causes the organic content of mixed waste to be digested. The biological heat generated destroys pathogens and reduces moisture content so that no leachate is produced; waste volume reduction of 40% is observed in one month after four turnings of the windrows and the waste is dry enough for screening. No smell means no anaerobic conditions, hence no methane (a greenhouse gase) is now released. Windrows with fresh waste have been observed to get stabilized by the fifth week and old waste windrows by week 6 or 7. Both are then ready to be biomined.

4 Biomining

Over a 10-month period, both 25 lakh tons of old waste as well as 6 lakh tons of fresh waste received during that time was fully stabilized, to release no leachate, methane, or smelly anaerobic gases (Photo 9).

The biomining (screening) process of these bioremediated windrows was begun and clearing out of 1000 tons from the dumpsite was demonstrated. The MCG hired

Photo 8 Fresh waste unloaded and moved back to form windrows above the unloading spot

Photo 9 All old plus fresh waste bioremediated in windrows, ready for biomining

a consultant to build screeners from the damaged machinery present in the abandoned composting plant, shut down since 2013 after a fire. Through this, economical screening of 60, 35, 16, 8, and 4 mm fractions was possible at the dumpsite (Photo 10).

Photo 10 Different size fractions after screening are made ready for off-site use

The different size fractions that are obtained by biomining have various markets, with 80–90% of it being usable or even sold commercially. The fine fraction containing compost-plus-soil (called bioearth) can be used for agriculture and gardening. The coarser organic material is useful for forest and quarry revegetation. Plastics go for recycling and nonrecyclable thin film plastic can be shredded for adding on heated aggregate to make improved asphalt roads. RDF with moisture below 20% goes to coal boilers or brick kilns. The inert rejects can go as fill material for low lying land or landscaping or even road subgrade. With the process of biomining after bioremediation, 100% recovery of the former dumpsite land is possible, leaving about 10% rejects on site, raised slightly above ground level.

5 Results

Through the process of bioremediation, the height of the garbage mound was reduced from 30 to 5 m. The dumpsite was completely free of smell, flies, and birds after biotreatment. On December 20, 2017, 11 peacocks came and rested on one windrow for a long while.

About 95% of the original leachate present in the dumpsite and within the waste was digested by biocultures. Even with the advent of the monsoons in 2017, there has been no increase in the leachate quantities, leaving leachate present only in four small pools (Photo 11).

On the instructions of the Gurugram Municipal Corporation, possession of the site was handed over in good condition to M/S Ecogreen on December 20, 2017,

Photo 11 By December 2017, nearly 95% percent of the original leachate present had been drained out and digested, with leachate present in only in a few small pools

as shown in Photo 11. The repaired screening equipment used for biomining trials was also left on site. This as well as all other equipment on site is the property and responsibility of the Gurugram Municipal Corporation (GMC). We thank the former and present commissioners of GMC for the opportunity to demonstrate the success of bioremediation on a huge scale into a huge waste heap in a site with minimal free space, and to demonstrate the utility and saleability of 1000 tons of screened biomined fractions.

6 Recommendations

Bioremediation of old dumps totally removes permanently the source of both leachate and methane. If it is done on a large scale countrywide, it is the quickest and most cost-effective way to meet India's greenhouse gas reduction targets.

Anaerobic Digestion of Biodiesel Residues for Energy and Revenue Generation

Himanshu Kumar Khuntia, H. N. Chanakya, Naveen Janardhana and Sushmitha Shetty

1 Introduction

The manufacturing of biodiesel from inedible oilseed crops and trees such as *Pongamia pinnata, Jatropha curcas, Simarouba glauca, Madhuca indica,* etc., on non-agricultural and wastelands has gained momentum in India. India has planned to substitute petro-diesel with biodiesel to the tune of 30% by 2020. A large extent of biodiesel wastes will emerge in cities where biodiesel plants will come up very quickly. The inedible oil yileding crops and trees can be grown on less fertile lands (wastelands) that are considered unfit to grow cash crops, have a comparatively lower water and nutrient demand and similar lipid yields as edible oilseed crops. The processing of biodiesel leads to the production of various residues such as (i) seed cover/pod/husk, (ii) deoiled cakes, (iii) waste glycerol, (iv) biodiesel wash water, etc. The above-said residues are distributed across the farmers, oil expellers and biodiesel processing industries; therefore, their cumulative energy potential remains unrecognized today. Multiple options to maximize energy recovery and derivation of value-added products from the residues have been reported such as combustion, gasification of the deoiled cakes and husk, waste glycerol as a binder for pelletization of agro-residues, AD of deoiled cake to biogas, purification of pure glycerol from waste glycerol, AD of waste glycerol to biogas, fermentation of glycerol to hydrogen, methanol and ethanol, etc. [1–4]. All the above-said attempts were focused on reusing a single residue; a single pathway of waste utilization often leads to a lower level of harvestable energy and/or economic potential of the residues. This research was initiated to estimate the total mass and energy of the residual biomass generated during the processing of biodiesel from *PP* and *JC*. Secondly, evaluate the efficacy of AD in order to convert the residues into energy and to understand the inhibitory

---

H. K. Khuntia · H. N. Chanakya (✉) · N. Janardhana · S. Shetty
Centre for Sustainable Technologies (Formerly ASTRA),
Indian Institute of Science, Bengaluru, India
e-mail: chanakya@astra.iisc.ernet.in

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_41

effects of these residues on the anaerobic bacteria. Finally, assess the agronomic, economic and social benefits of the overall process.

2 Materials and Methods

The experiments such as total solids (TS), volatile solids (VS) and total lipids were conducted as per the standard methods [5]. The composition of biomass was determined by the methods described by APHA et al. 1975, 2000 [6–8]. A bomb calorimeter was used to estimate the calorific value of all the residues. The constituents of impure glycerol such as water content [9], soap and catalyst [10], glycerol [11] were estimated. The maximum possible biogas yield was estimated by a method called as bio-methane potential (BMP). The BMP of residues was studied in glass vials of 125 ml as shown in Fig. 1 and the data was simultaneously analysed [12, 13].

3 Results and Discussion

A comparative study based on agronomic perspective revealed that the yields of biodiesel per hectare of land were lower in *JC* with respect to *PP* by 3.5–5.5 times, in addition, the net production costs estimated per ton of biodiesel were also lower in *PP* than *JC* by 10–15%. In contrast, an industrial perspective of calculations based on per ton pods indicates a comparatively lower net production by 1–5% costs and 23% higher biodiesel yield in *JC*. The life cycle of biodiesel production irrespective of the type of oilseed yields two main categories of residues, lignocellulosics (pods/shells, deoiled cakes) and impure glycerol (IG). An estimated 7.88 and 5.83 kg of residues

Fig. 1 The 125 ml glass vials used to study the bio-methane potential (BMP) of the organic residues

are produced from *PP* and *JC,* respectively, per kg of biodiesel production. The total energy locked in these residues amounts to 128.61 and 103.13 MJ, that is, 3.46 and 2.63 times higher than the energy of 1 kg biodiesel derived from *PP* and *JC*, respectively (Fig. 2). The pods and deoiled cakes contributed 50% and 37.5% of the total residues by weight in the case of *PP*, whereas in *JC* nearly 35 and 48.75% existed in the form of pods and deoiled cakes, respectively. Multiple factors contribute to the profitability of the biodiesel industries such as (i) feedstock, (ii) lipid content in the kernel and (iii) cost of oilseed kernel. The oilseed kernel, accounts for 74–83 and 87.5–90% of the net biodiesel production costs in case of *PP* and *JC*, respectively. In addition to the sale of biodiesel, additional revenues can be generated by the purification and selling of 99% pure glycerol, currently sold at ₹27 per litre in India [14]. However, this method of extraction of 99% glycerol from IG is difficult and expensive due to the presence of other impurities; therefore, makes this process uneconomical due to a drastic reduction in costs of 99% pure glycerol to <₹7.37 ($0.11) per kg in the international market [15]. The AD of all the above-said residues is therefore an alternative method of energy generation that could pave way for revenue generation. The presence of higher lignin and lipids in the feedstock, however, make the AD process challenging; therefore, several strategies were adopted in this study to enhance their biodegradability [16, 17] that are as follows (i) subject AD at different ratios of substrate/innoculum (S/I) in order to reduce the substrate inhibitions and (ii) removal of the inhibitory components from the substrates such as lipids from deoiled cakes, methanol from impure glycerol to ensure efficient AD. The BMP study estimated the biogas yield of 646 ml/g VS in PDC followed by JDC, JFS and PP of 310, 239 and 99 ml/g VS, respectively, at S/I ratios of 0.25, 1, 1, 1. The lipid content in *PP* and *JC* deoiled cakes were 17.24 and 8.98%, respectively, (although categorized as lignocellulosics), and therefore pose difficulties in degradation. An increase in the S/I ratio in high lipid content substrates such as deoiled cakes inhibited anaerobic bacteria, observed as lower biogas production volume, longer initial lag phase (λ), lower gas production rates (μ). On the other hand, the removal of lipids from the deoiled cakes by solvent extraction methods made them amenable to digestion at higher S/I ratios. However, at a lower S/I ratio of 0.25, the mineralization of lipids was estimated to contribute 1508 ml biogas/g lipids, and similar results of biogas generation from co-digestion of lipid-based substrates have been reported previously [12, 13].

The transesterification of inedible oil to biodiesel generates 0.1–0.15 kg of glycerol per kg of biodiesel [15, 18]. Our study estimated 0.3–0.6 kg of impure glycerol (IG) residues containing 18 and 31% glycerol in the impure pongamia glycerol (IPG) and impure jatropha glycerol (IJG), respectively, and the remaining was composed of methanol, water, soap, unreacted oil, methyl esters and catalyst. The components in IG other than glycerol are known to inhibit AD; however, the inhibitory effects could be reduced by the following methods (i) conducting the BMP study at lower S/I ratio of 0.25 and (ii) sequential removal of all the components from the IG's and subjecting the remaining/leftover fraction to BMP at higher S/I ratio. The methanol content in IPG and IJG was estimated to be 30.5 and 31.25%, respectively, and its removal via distillation showed improvement in degradability. The biogas potential

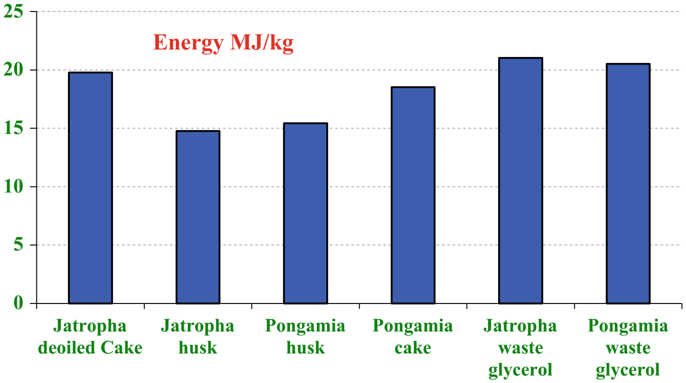


Fig. 2 The calorific value of the residues measured in bomb calorimeter

of IPG and IJG was estimated to be around 880 and 580 ml/g VS, respectively, at a S/I ratio of 0.25. The glycerol content in the IPG and IJG contributed nearly 15 and 25% of the total biogas volume and the remaining was contributed by the degradation of soap, lipids and other carbonaceous residues. The co-digestion of both IPG and IJG with deoiled cakes can solve multiple issues that are as follows (i) the deoiled cakes contain N, P and inorganic nutrients essential for AD, and therefore the addition of supplementary nutrients for digesting glycerol can be avoided and (ii) the lignocellulosic residues can be digested along with the IG in a single digester, avoiding the need to build multiple biogas plants to carry out the processes. The optimum mixing ratio for co-digestion of deoiled cakes and IG was found to be 1:1 (TS:VS). The co-digestion of IPG:PDC had a BMP of 630 ml, similarly, the biogas yield from IJG:JDC was 590 ml.

Biogas containing an average of 50% CH_4 and CO_2 is estimated to have an Iw of 17.894 at a calculated price of ₹16.52. It can be considered as a substitute of natural gas/compressed natural gas (CNG; Bio-CNG with >90% CH_4) that are mainly used in transportation, in addition used as a heating source for several industrial applications. The total biogas potential for the PP residues was estimated to be higher than *JC, and* therefore offered 2–3 times higher returns. Instead of selling the residues or converting them to energy by conventional methods such as burning, the biogas production, especially from *PP* residues provides 2–3 times higher economic returns, whereas in *JC* the returns via the AD route offer marginal gains than the conventional methods. In other words, the net production costs of biodiesel from *PP* can be reduced by 30–80% and 19–40% in JC. The feeding of the *PP* substrates into a plug-flow anaerobic digester (PFR, Fig. 3) at a loading rate of 1 ton (TS) per day offers a simple payback period of 2.29 years, whereas at a similar PFR size and loading rates the JC residues yield payback of 6.02 years. An average biogas plant has an operational lifespan of >15 years, and thus offering an excellent source of revenue generation. Moreover, the AD process is known to contribute a comparatively lower GHG emissions, the residual/digestate slurry can be composted or used as a soil

Fig. 3 The bench-scale plug flow biogas reactor (PFR) designed at CST used to convert the residue into biogas

conditioner to enhance the plant growth and crop yield. The demand for biodiesel is dwindling due to stark competition from cheaper non-renewable fuels such as petroleum diesel. In its current state of manufacturing, biodiesel is expensive, and thus alternative methods of revenue generation such as biogas production from the residues can enhance the financial gains.

4 Conclusion

The byproducts generated with every kg of biodiesel production from *PP* and *JC* amounts to a total of 7.88 and 5.83 kg, respectively, with an equivalent energy of 128.61 and 103.13 MJ, respectively. The AD of the residues of *PP* and *JC* yields 3.07 and 1.83 m^3 of biogas, with an overall energy of 55.8 and 33.3 MJ, respectively. The cost of petroleum derived 99% pure glycerol has reduced significantly in the international market, and therefore extraction of pure glycerol form impure glycerol is uneconomic. The methanol content in the impure glycerol accounting to 30.5–31.25% can be distilled and reused in the transesterification process. The leftover mass can be then subjected to AD to reduce microbial inhibitions else co-digested with deoiled cakes at 1:1 ratio. The conversion of residue to biogas can reduce the overall production costs of PP and JC biodiesel by 30–80 and 19–40%, respectively. The dissemination of waste through the AD route seems more economically feasible for *PP* residues over *JC* and also offers a faster return on investment.

References

1. Barik D, Murugan S (2015) Assessment of sustainable biogas production from deoiled seed cake of karanja-an organic industrial waste from biodiesel industries. Fuel 148:25–31
2. Siles López JÁ, de los Martín Santos ÁM, Pérez AFC, Martín AM (2009) Anaerobic digestion of glycerol derived from biodiesel manufacturing. Bioresour Technol 100:5609–5615
3. Speers AM, Young JM, Reguera G (2014) Fermentation of glycerol into ethanol in amicrobial electrolysis cell driven by a customized consortium. Environ Sci Technol 48:6350–6358
4. Chaudhary N (2011) Biosynthesis of ethanol and hydrogen by glycerol fermentation using Escherichia coli. Adv Chem Eng Sci 1:83–89
5. American Public Health Association (1999) American Water Works Association, Water Environment Federation, W.E. Federation, Standard Methods for the Examination of Water and Wastewater, Stand. Methods, p 541
6. Sluiter A, Ruiz RO, Scarlata C, Sluiter J, Templeton D (2004) Determination of extractives in biomass. Biomass Anal Technol Team Lab Anal Proced: 1–8
7. Sluiter A, Hames B, Ruiz R, Scarlata C, Sluiter J, Templeton D (2010/2011) Determination of structural carbohydrates and lignin in biomass determination of structural carbohydrates and lignin in biomass. Natl Renew Energy Lab. NREL/TP-510-42618
8. Sadasivam S, Manickam A (1996) Biochemical methods, 2nd edn, New Age International Pvt Ltd
9. Moisture Karl Fischer. Volumetric method; AOCS official method, Ea 8–58. AOCS, Urbana (1997)
10. Soap in Oil Titrimetric Method; AOCS Recommended Practice Cc 17-95; AOCS, Urbana (1997)
11. ASTM D7637 (2015) Standard test method for determination of glycerin assay by titration Sodium Meta. ASTM D7637(10):8–11
12. Chanakya HN, Khuntia HK, Mukherjee N, Aniruddha R, Mudakavi JR, Thimmaraju P (2015) The physicochemical characteristics and anaerobic degradability of desiccated coconut industry waste water. Environ Monit Assess 187:772
13. Khuntia HK, Chanakya HN, Siddiqha A, Thomas C, Mukherjee N, Janardhana N (2017) Anaerobic digestion of the inedible oil biodiesel residues for value addition. Sustain Energy Technol Assess 22:9–17
14. Gunatilake H (2011) South Asia Working Paper Series Financial and Economic Assessment of Biodiesel Production and Use in India Financial and Economic Assessment of Biodiesel Production
15. Yang F, Hanna MA, Sun R (2012) Value-added uses for crude glycerol—a byproduct of biodiesel production. Biotechnol Biofuels 5:1–10
16. Song Z, Yang G, Guo Y, Zhang T (2012) Comparison of two chemical pretreatments of rice straw for biogas production by anaerobic digestion. BioResources 7:3223–3236
17. Chen Y, Cheng JJ, Creamer KS (2008) Inhibition of anaerobic digestion process: a review. Bioresour Technol 99:4044–4064
18. Yazdani SS, Gonzalez R (2007) Anaerobic fermentation of glycerol: a path to economic viability for the biofuels industry. Curr Opin Biotechnol 18:213–219

Creating Value Addition for MSW Biogas Plants: Increasing Mushroom Yields with Biogas Plant Digester Liquid

Hasika Suresh, H. N. Chanakya and Sreesha Malayil

1 Introduction

India's increasing population accompanied by rapid urbanization has led to increased municipal solid waste (MSW) production in metropolitan cities. Waste is generated from domestic households, restaurants and eateries, local factories, gardens, etc. This generated waste contains >80% decomposable substances [1]. If recycled efficiently, the locked nutrients can be returned to the soil. Currently, India has about 5 million biogas plants, and >90% run on cow dung as feedstock. An alternative feed for an urban biogas plant could be this MSW, agro-residues, leaf litter, etc. [2]. Organic fraction of the MSW (OFMSW) also has a good fraction of straw which is used as a packing material for fruits and vegetables. This forms a good feedstock for biogas production in modern biomass biogas plants. This straw waste could also be used a substrate to grow a variety of mushrooms (before and after anaerobic digestion) contributing significantly to sustainability.

Under anaerobic conditions in a BGP, microbes act on the organic fractions of MSW (cellulose, hemicellulose, and pectin) to convert it into biogas. MSW BGPs yield yields three outputs namely, (1) biogas ($CH_4 + CO_2$), (2) biogas digester residue (BDR), and (3) biogas digester liquid (BDL). Usually, lignin and some cellulosics are recalcitrant under anaerobic conditions as most microbes do not have the enzyme or access to degrade this complex lignin molecule. Yet, a part of this partial lignin breakdown product is leached into BDL. Basidiomycete fungi have enzymes that have the potential to degrade lignin into simpler sub-units [3, 4].

Unlike the typical straw feedstock, there is more easily accessible nitrogen in the form of bacterial protein in the biogas digester residue and is best suited for basidiomycete growth, a secondary colonizer. BDR can be converted to compost

---

H. Suresh · H. N. Chanakya (✉) · S. Malayil
Centre for Sustainable Technologies (Formerly ASTRA),
Indian Institute of Science, Bengaluru, India
e-mail: chanakya@astra.iisc.ac.in

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_42

and vermi-composting but the economic returns are low as these are priced around ₹2–5/kg. On the other hand, converting BDR to mushrooms in combination with other substrates for the species *Pleurotus sajor-caju* is remunerative yielding 2–3 kg mushroom per kg of BDR accruing about ₹2–300 [5].

The BDL, on the other hand, has accessible nitrogen and phosphorous emerging from the original biomass or MSW feedstock fed to the biogas plant. In typical MSW plants installed across the country, biogas digester liquid is poorly used and most often consigned to the drains. This in addition to the partial breakdown products of lignin also has several long-chain volatile fatty acids (LCVFAs) that are known to repel insects. The release of micronutrients from breakdown of MSW and leaf litter biomass makes the BDL rich in, minerals and micronutrients. All these can stimulate basidiomycete growth if used alone on existing straw-based mushroom bags. We examine this possibility in this study [6]. Few additional uses of the BDL evolved are used as a pest repellent, for algal cultivation and as a fertilizer [ref]. In this study, the efficiency of *P. djamor* to pick up the locked nutrients from the BDL of a leaf biomass fed biogas plant is examined. Its growth pattern and biological efficiency are reported.

2 Materials and Methods

2.1 Materials and BDL

Ready-to-use fruit bags were used in this study and were bought from Biocentre, Bangalore. The substrate (paddy straw) and spawn were mixed in the ratio 10:1. Once inoculated, these bags were incubated in the dark for 25 days until the mycelia were well formed (spawn-run) and uniformly distributed all over the surface. After this stage, small holes were made around the bag to facilitate pinhead formation and consequent emerging of fruiting bodies allowing easy harvesting of mushrooms (Fig. 1). Four bags were sprayed with 100 mL water each, every day (Control) and six bags was sprayed with 100 mL BDL every day. The BDL was taken from the outlet of a plug flow reactor fed with a leafy biomass. It was filtered using a 50 μm mesh and maintained frozen for future use.

2.2 Sampling of Substrate

Ten grams of the residual straw samples were collected from various bags at regular intervals until the end of the third flush of mushrooms (~30 days) and dried rapidly. The dried straw was powdered and sieved through a 50 μm mesh and stored for further analysis. A detailed analysis of the different organic fractions in the substrate was done using a sequential extraction protocol [7].

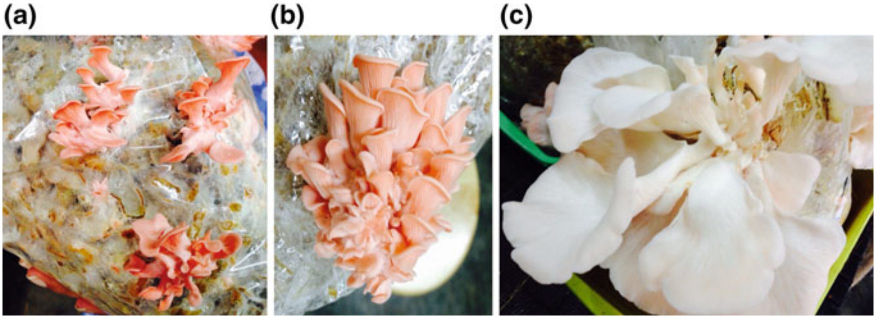


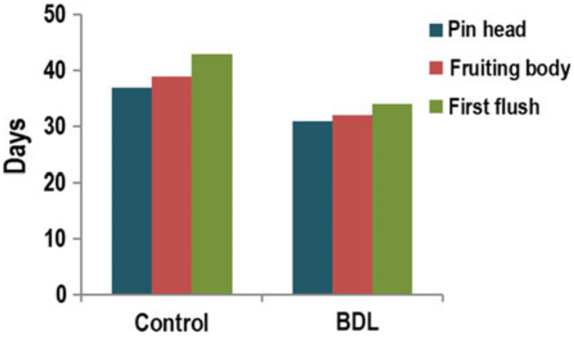
Fig. 1 *Pleurotus djamor* growth stages. **a** Pinhead formation **b** Fruiting body **c** Harvest stage Hasika Suresh et al./Global Waste Management 2017

3 Results and Discussion

3.1 Mushroom Yields

The mushroom bags supplemented with BDL was found to have faster growth in terms of the time at which pinhead formation was observed, fruiting body became visible as well as the first flush could be recovered and carried out with water sprayed bags as control (Fig. 2). The pinhead formation occurred in 32 days after the inoculation of the spawn for BDL sprayed bags as opposed to 36 days in the water sprayed bags. The time required for fruiting bodies to emerge and enlarge was shortened from 42 days in control to 37 days with BDL sprayed bags. Spraying of BDL could narrow the C:N ratio of the substrate. BDL was found to have locked organic nitrogen which leads to faster growth and higher yields of mushrooms. The first flush of mushrooms in the BDL sprayed bags was seen on 46 days as opposed to 52d in the case of water sprayed controls. The maximum biological efficiency for the control bags was 288%, and that of BDL sprayed bags was found to be 558%. The maximum efficiency till date was reported for *Hypsigus ulmarius*, which was 437% [8].

Fig. 2 Growth stages of *P. djamor*



3.2 *Dry Matter and Organic Fractions Retained*

The powdered substrate samples were analyzed at regular intervals for dry matter loss and its organic constituents over the experiment duration. The substrate in the BDL sprayed bags showed 40% loss on 34d itself, after which, it showed a gradual decline to a final 75% at the end of the third flush (60d). The control bags also displayed a similar degradation pattern, showing a loss 70% dry matter at the end of Day 60 (Fig. 3). One may expect higher yields of mushroom to correspond to higher dry matter loss, but this was not the case with *P. djamor*. In other species such as *P. florida*, the DM loss increased with BDL spray and with no differences with *H. ulmarius* [6, 8].

Calculating the individual components of biomass retained at various stages of decomposition gives a better understanding of the components and its rate of degradation (Fig. 4). Lignin, thought to be recalcitrant in most cases, showed significant degradation or loss with degradation time. Generally, most studies indicate that lignin component of the biomass is recalcitrant under anaerobic conditions and is not decomposable or convertible to biogas. BDL appears to have significant content of lignin breakdown products (CST, unpublished study). In the control bags, there was 76.64% degradation while around 66.90% lignin was lost in the BDL sprayed bags at the end of three flushes. There was higher cellulose degradation in the BDL sprayed bags (88.03%) as compared to the control (77.84%). Hemicellulose degradation was about the same (~90%) in both the setups. This softened biomass could be composted or even employed for bioethanol production [9].

4 Conclusion

Straws, leaf litter, and bagasse form a significant part of MSW and are best processed by biomethanation so as to provide economic output (biogas) and compost. Biogas plants lose a lot of valuable components in the biogas digester liquid (BDL) and are rarely tapped as an economic output. Using BDL as a supplement for growing

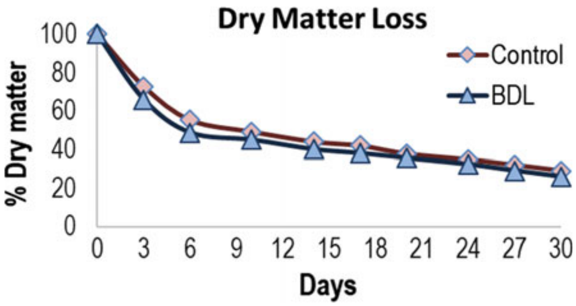


Fig. 3 Dry matter loss in control and BDL sprayed bags

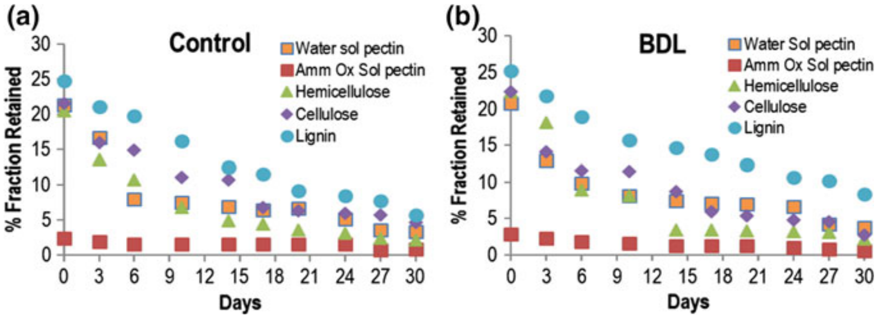


Fig. 4 Organic fraction retained in substrate during the mushroom growth

P. djamor not only reduces the harvest time in terms of pinhead formation, fruiting body, and collection, it also increases the yields of the mushroom by nearly 50% over unsprayed control in this experimental setup. This has not been reported before and forms a new value addition mechanism for MSW biogas plants. Spraying of BDL could narrow the C:N ratio of the mushroom substrate leading to faster growth and higher yields of the mushroom.

References

1. Chanakya HN, Malayil S (2013) Techno-economic potential for value added products from digestion of urban solid wastes and rural residues. Dyn Biochem Process Biotechnol Mol Biol 6(special Issue 2):38–42
2. Chanakya HN, Malayil S (2012) Anaerobic digestion for bioenergy from agro-residues and other solid wastes—an overview of science, technology and sustainability. J Indian Inst Sci 92(1):111–144
3. Hasewaga H, Ichinohe T, Ainai A, Nakamura T, Akiyama Y, Maeyama JI, Odagiri T, Chiba J et al (2010) Induction of cross-protective immunity against influenza A virus H5N1 by an intranasal vaccine with extracts of mushroom mycelia. J Med Virol 82(1):128–137
4. Barbosa Raposo NR, Zimmermann Franco DC, Gonçalves de Carvalho GS, Rocha PR, da Silva Teixeira R, Da Silva AD (2012) Inhibitory effects of resveratrol analogs on mushroom tyrosinase activity. Molecules 17(10):11816–11825
5. Ganguli NK, Chanakya HN (1994) Mushroom cultivation on spent biomass from biogas plant. Curr Sci India 66:70–73
6. Chanakya HN, Malayil S, Vijayalakshmi C (2015) Cultivation of *Pleurotus* spp. on a combination of anaerobically digested plant material and various agro-residues. Energy Sustain Dev 27:84–92
7. Chesson A (1978) Maceration of linen flax under anaerobic conditions. J Appl Bacteriol 45:219–230
8. Malayil S, Chanakya HN, Ashwath R, Suresh H (2017) Biogas digester liquid as a supplement for higher yields of *Hypsizgus ulmarius*. Environ. Technol. Innov. 8:269–281
9. Vikram S, Binod P, Sindhu R, Singhania RR, Devi L, Nagalakshmi S, Pandey A et al (2010) Bioethanol production from rice straw: an overview. Biores Technol 101(13):4767–4774
10. Yoswathana N, Phuriphipat P, Treyawutthiwat P, Eshtiaghi MN (2010) Bioethanol production from rice straw. Energy Res J 1(1):26

Comparative Study on Adsorption of Dye Solutions Using Silver Nanocomposites

M. Sharma, P. Das and S. Datta

1 Introduction

Removal of dye effluents from wastewater has become a crucial topic in wastewater treatment that needs immediate attention. Dyes that are used by industries, viz. textiles, tanning, leather, food processing, cosmetics, paper and pulp, etc. are discarded in water bodies without proper treatment. These effluents are causing serious health issues in human as well as other species. The dye molecules are complex in structure and have an aromatic ring that causes cancer and is also responsible for gene mutation [1, 2]. Also when they are disposed in water bodies, the dye particles form a thin layer on the water which prevents light penetration and also disturbs the aquatic ecosystem. Moreover, the continuous exposure of human being to these dye particles may cause serious health hazard [3]. The dyes used in this experiment are Methylene Blue and Malachite Green. Methylene blue is a heterocyclic aromatic chemical compound which is usually used as a stain and as medication. Excessive inhalation and consumption of the dye can cause dizziness, headache, mental confusion, nausea, vomiting, abdominal pain and bladder irritation (Methylene Blue, The American Society of Health-System Pharmacists ([4] and Wikipedia). Malachite Green (MG) is a Triarylmethane dye used in pigment industry for materials such as silk, leather and paper is used as biological stain for microscopic analysis of cell and tissues. It has been reported to cause carcinogenesis, mutagenesis, chromosomal fractures,

---

M. Sharma (✉) · P. Das
Jadavpur University, Kolkata, India
e-mail: moumitasharma21@gmail.com

P. Das
CSIR-Central Mechanical Engineering Research Institute (CMERI),
Durgapur, West Bengal, India

S. Datta
Chemical Engineering Department, Jadavpur University, Kolkata, India

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_43

teratogenecity, respiratory toxicity and developmental abnormalities [5]. We can see that the above-mentioned dyes have manifold advantages as well as disadvantages. So to prevent ourselves from the hazardous effect of the dye particles, proper treatment of the effluent is necessary before dumping them in water bodies (lakes, rivers, drains, canals, sea, etc.).

Numerous physical, biological and chemical methodologies were used to treat these hazardous dye effluents [3, 6, 7, 8]. However, most of them are either expensive or time-consuming. However, with the recent evolution of Science and Technology, many novel techniques are coming forward. Among these techniques, Green Synthesis of nanoparticles has obtained massive significance not only in wastewater treatment but also in other fields like pharmaceuticals, cosmetics and electronics [9–11]. Moreover, the process saves time as well as cost-efficient. Green Synthesis is a novel technique where parts of a plant are used for the synthesis of nanoparticles. Various parts of the plant like seeds, leaves, flowers, peels of skin, stem, bark, root, etc. can be used for the synthesis of the nanoparticles [12–22].

Innumerable experiments were performed on the degradation of dyes using nanoparticles from plant extracts but the literature on comparative study for the removal of two dyes having optimal experimental condition are very few. In this experiment, silver nanocomposites were first prepared from the leaf extract of Indian lilac (Neem) and Basil. Indian Lilac and Basil leaves were used since they are renowned antimicrobial Ayurvedic herbs. Then, experiments were performed using the nanocomposites for the degradation of Methylene Blue and Malachite Green dye solution keeping the operating parameters (adsorbent dose, dye concentration, rotational speed, time, temperature, etc.) similar in both the cases. The results were compared graphically.

2 Materials and Methodology

The leaves of Indian Lilac (Neem) and Basil were obtained from Rajpur to Sonarpur area of West Bengal. The soil required for preparation of the nanocomposite was also collected from the same area. The chemicals and dyes (Silver nitrate, Methylene Blue and Malachite Green) were bought from Merck, Germany.

2.1 Preparation of the Nanoparticles

The leaves used in the process were first thoroughly washed and chopped into fine pieces separately. Then, 20 g of chopped neem and basil leaves were boiled in 200 ml of distilled water separately for 15 min. A pale greenish solution is obtained in both cases which is the required leaf extract. Now, Silver nitrate solution (1 mM) is prepared and 95 ml of that solution is taken in a beaker. To that silver nitrate solution, 5 ml of both the leaf extracts were added separately and introduced in a microwave for 10 min for complete reduction. As the solution is taken out, a change in the colour is observed from pale green to dark brown which signifies the formation of silver nanoparticles.

2.2 Preparation of the Nanocomposite

Since soil act as a natural adsorbent, it was added with the silver nanoparticles which are formed to prepare the required nanocomposite. For the nanocomposite, a fixed amount of properly dried and churned soil is taken in a conical flask and silver nanoparticles containing solution is added to it. Then, it is placed in a shaker incubator for 24 h for proper mixing. After taking out, it is allowed to settle overnight. The supernatant solution is removed and the bottom product is dried is a hot air oven. The dried soil was then churned and sieved and thus the final adsorbent is obtained [23].

2.3 Preparation of Dye Solution

Methylene Blue (MB) and Malachite Green (MG) dye having molecular weight 319.85 g/mol and 364.91 g/mol, molecular formula $C_{16}H_{18}ClN_3S$ and $C_{23}H_{25}N_2$ and having maximum absorption peak λ_{max} 667 nm and 618 nm were bought from Merck (Germany). Double distilled water is then added to the solid dye to prepare the required concentration of dye solution. The pH concentration of the solution can be changed by adding 0.1 N Hydrochloric acid (HCl) and 0.1 N Sodium hydroxide (NaOH) solution.

2.4 Characterization Done

The surface plasmon resonance of the nanoparticles formed in the colloidal mixture is measured using a UV–visible spectrophotometer (Lambda 25 Perkin Elmer) in a range of 400–700 nm. Furthermore, the batch studies are also conducted using the UV–visible spectrophotometer. The size and the morphological characterization of the silver nanoparticles formed in the composites are determined using SEM. A thin layer of metal (gold) using a sputter coater is used to coat the samples for providing a better image, to arrest the electrical charge accumulation, and microscopic analysis were performed using Scanning Electron Microscope (Model Hitachi S 3000 N) with an electron acceleration voltage of 20 kV for excitation of the samples. Transmission Electron Microscope was also used to determine the structure and morphology. The presence of different functional groups in the three composites can be measured by using the FTIR analysis since each group has a specific energy absorption band.

The analysis of two components was done in an FTIR spectrophotometer (Perkin Elmer Spectrum version 10.4.4 model) in a wavelength range of 4000–400 cm^{-1}. Analysis of configuration of the nanocomposite adsorbent was carried out using X-ray diffractometer equipment with a Cu Kα radiation source and Braggs angle ranging from 20° to 80° for the three adsorbents to find out the crystalline nature of the two composites.

2.5 Batch Studies

The batch studies were performed in 250 mL conical flasks with 100 mL of dye solution. A certain weighed amount of two nanocomposites were added separately to the dye solution in separate flasks. The flasks were agitated at a speed of 120 rpm in an incubator shaker at 308 K. The effect of initial dye concentration (100–500 mg L^{-1}), nanocomposite dosage (0.025–0.2 g/L) and agitation speed (80–150 rpm), contact time (10–120 min) were evaluated. At regular time intervals, samples were collected and centrifuged for analysis of the residual dye concentration in the solutions. The amount of dye adsorbed per unit of nanocomposite for all three of the adsorbents was determined according to a mass balance equation:

$$q_e = \frac{(c_i - c_e)V}{m}$$

The percent removal (%) of dye was calculated using the following equation:

$$\left\{\frac{c_i - c_e}{c_i}\right\} * 100$$

where C_i is the initial dye concentration (mg L^{-1}), C_e is the equilibrium dye concentration in solution (mg L^{-1}), V is the volume of the solution (L) and m is the mass of the nanocomposite in g.

3 Result and Discussion

3.1 Characterization Results of the Nanocomposites

The silver nitrate solution is added to the *Ocimum Sanctum* and *Azadirachta Indica* leaf extracts and heated for complete bioreduction, and there is a change in the colour of the solution from pale green to Dark brown. That colour change indicates the synthesis of the Silver nanoparticles as shown in Fig. 1.

A fixed amount of both the nanoparticles containing samples were taken and maximum absorption peak was measured in a UV-VIS spectrophotometer. For the

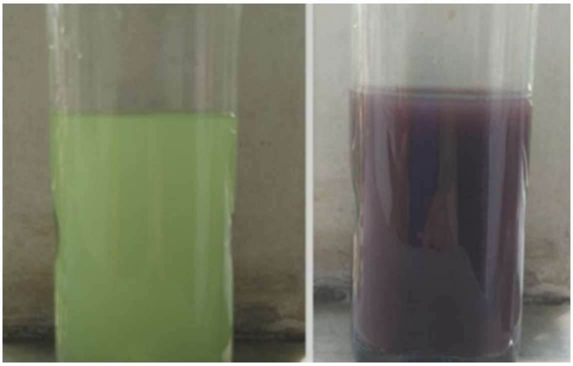


Fig. 1 This figure depicts the colour change observed

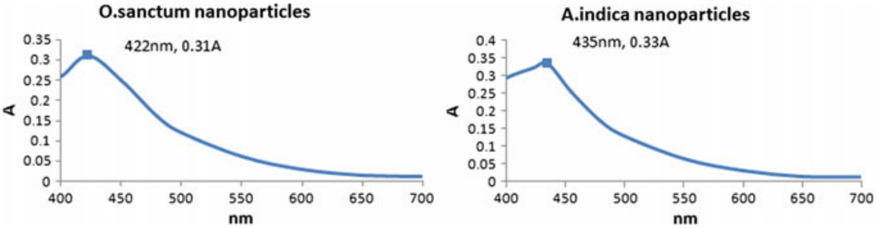


Fig. 2 This figure represents the UV-VIS spectroscopy diagram of AgNP formed from *O. sanctum* and *A. Indica*, respectively

O. sanctum and *A. indica* containing solutions, absorption peak obtained is at 422 and 435 nm which both indicates the formation of silver nanoparticles as shown in Fig. 2.

The TEM image of the soil-AgNP from *O. sanctum* and *A. indica* were also provided in Fig. 3. The morphology of the silver nanoparticles formed was spherical and the size ranges around 50 nm which was quite a match to the previous reports.

The SEM images of the two adsorbents are shown in Fig. 4. The figure indicated that the silver nanoparticles were spherical, oval and irregular polygonal for both the adsorbents with average size of 38.7 nm.

Fourier-Transform Infrared spectral analysis was carried out for the two adsorbents, which showed range of absorbance bands in 400–4000 cm^{-1} as shown in Fig. 5. The peaks of the absorption bands for adsorbent made of basil leaf were at 3960, 2929.4, 2120.4, 1659.5, 1465.4, 1316.6, 1075.2, 776.5 and 693.4 cm^{-1} which is due to the presence of phenolic group, ketones, triple bond C–C and C–N groups, protein amide I, Carbonyl group C=O, esters, carboxyl groups, aromatic C–H bonding patterns, alkenes, respectively. The peaks of the absorption bands for adsorbent made of neem leaf were at 721, 1637.27, 2364.3, 3334.1 and 3745.08 cm^{-1} suggesting alkenes, carbonyl groups, protein amide I, aromatic rings, Hydroxyl group, Triple bond C–N, alcohols and phenols [3]. A trace amount of chloride, carboxyl group, disulfide, tertiary ammonium ions and hydrogen bonds were also observed [1].

XRD analysis of Ag-nanocomposite form *A. indica* and *O. sanctum* leaves demonstrated the crystalline nature of the adsorbents as shown in Fig. 6. The maximum peaks for the silver nanocomposite from *O. sanctum* were observed at 27.8, 32.3, 38.1, 46.3, 54.9, 67.5^0 and 76.7^0, respectively which index to (1 1 0), (1 1 1), (2 0 0), (2 1 1), (2 2 0), (1 0 3) and (0 0 4), respectively, for face-centred cubic silver as well as silver oxide. And, maximum peaks for the silver nanocomposite from *O. sanctum* were observed at 27.9, 38.3, 44.3, 64.3 and 77.50 and the corresponding values of lattice plane are indexed at (1 1 1), (2 0 0), (2 2 0) and (3 1 1) of face-centred cubic silver [18]. The major components present in nanocomposites were Silver (Ag),

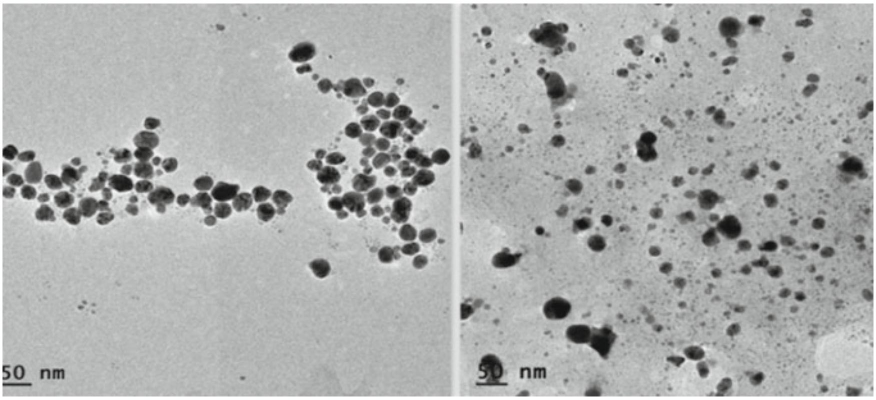


Fig. 3 This figure represents the TEM image of *O. sanctum* nanocomposite and *A. indica* nanocomposite, respectively

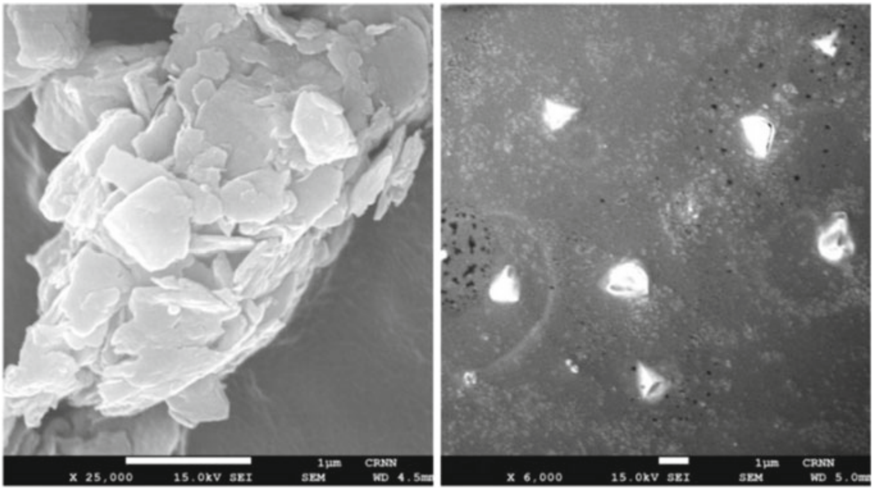


Fig. 4 This figure represents the SEM image of *O. Sanctum* nanocomposite and *A. indica* nanocomposite, respectively

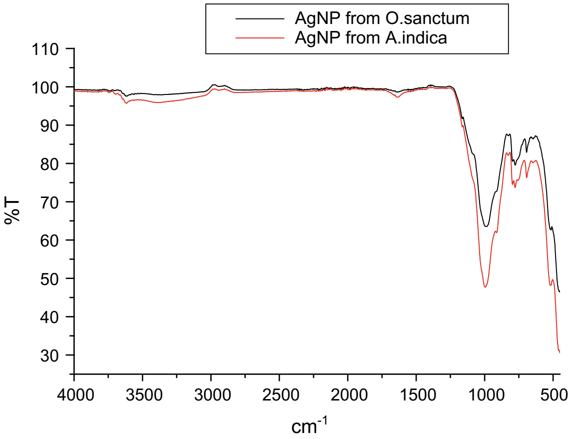


Fig. 5 This figure represents the FTIR image of the two adsorbents

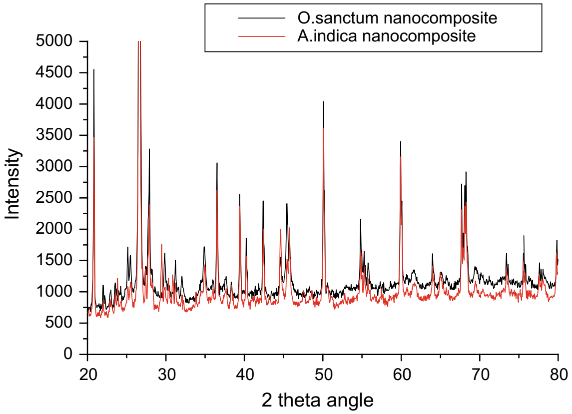


Fig. 6 This figure represents the XRD image of the two adsorbents

quartz, feldspar, mica, amphibole, kaolinite and calcite due to the presence of soil in the composite.

3.2 *Result for Batch Experiment*

In the batch experiment, a comparative study for the removal of dyes was done between two dye containing solutions—Methylene Blue and Malachite Green of same concentration using Silver nanocomposites from the two leaves extracts (*O. sanctum* and *A. indica*). The experiment is performed to check which dye is getting adsorbed rapidly and efficiently in between the two dye solutions keeping all the regulating parameters (Temperature, pH, agitation speed, etc.) same.

3.2.1 Effect of Mass of Adsorbents

Five conical flasks were taken with 100 ml solution of Methylene Blue dye of concentration 10 ppm, and in the 25, 50, 75, 100 and 200 mg of nanocomposite made of *O. sanctum* were added separately and placed in a shaker incubator at speed of 120 and temperature 308 K. The same process was carried out for nanocomposites made of *A. indica* and percentage removal was obtained. The whole experiment was repeated with Malachite Green dye. We observe that the increase in the adsorbent dosage also shows a gradual increase in percentage removal for all the three adsorbents which may be due to increase in surface area and availability of more binding sites. It is observed that the percentage removal is higher in Methylene blue dye. In the Fig. 7, MB and MG represent the dyes Methylene Blue and Malachite Green, respectively.

3.2.2 Effect of Dye Concentration

The effect of the dye concentration for both the dyes at 2.5, 5, 10, 20, 25, 50 and 100 mg L^{-1} for two adsorbents at adsorbent dose 100 mg, temperature 308 K and pH 2 were shown in Fig. 8. It was observed that in the first two curves for Methylene Blue, the amount of dye adsorbed has decreased with increase in the dye concentration as shown in the figure above. It may be due to the fact that as the amount of Methylene Blue increases, the nanocomposite particles get saturated and loses its ability to adsorb more dye molecules. But in the case of Malachite Green dye, it was observed that with increase in dye concentration for all the two composites, there was increase in percentage removal followed by a decrease and at the end, it increases again.

3.2.3 Effect of Contact Time and Agitation Speed

For both Methylene Blue and Malachite Green dyes, the experiment of contact time was performed for times—15, 30, 60,90 and 120 min at pH 2, temperature 308 K, adsorbent dose 100 mg and 120 rpm. It was observed that the percentage removal

Fig. 7 Effect of Adsorbent dose

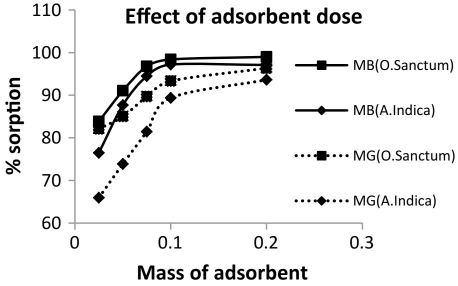
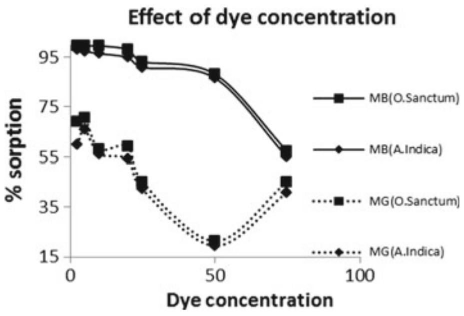


Fig. 8 Effect of dye concentration



keeps on increasing with increase in contact time but after a certain time when it reaches equilibrium, there was no further change in the removal. It may be due to the fact that contact time increases the availability of active sites while further increase causes immobilization of the cationic dyes on the silver nanoparticles shown in Fig. 9.

A similar trend was observed in agitation speed experiment. In case of the agitation speed experiment for both the dyes with the increase on rpm from 80 to 150, the percentage removal also increases as shown in Fig. 10. This may be due to more agitation the dye molecules react more with the nanocomposites causing higher adsorption.

Fig. 9 Effect of time with respect to Percentage sorption

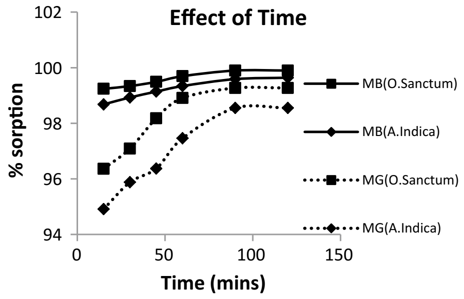
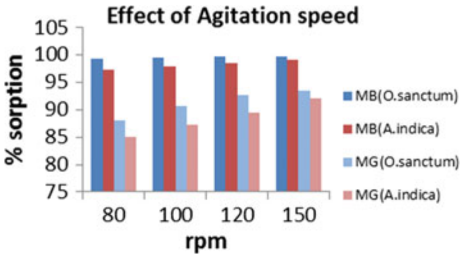


Fig. 10 Effect of agitation speed



3.3 Adsorption Isotherm

For both the Methylene Blue (Dye 1) and Malachite Green dye (Dye 2), the adsorption isotherm study is done since an adsorption isotherm represents the equilibrium relationship between the adsorbate adsorbed on the surface of adsorbent and concentration of adsorbate at constant temperature. The Langmuir isotherm model is best fitted for both the dyes as shown in Figs. 11 and 12. Langmuir isotherm is usually relevant for a monolayer adsorption on a surface having a finite number of identical sites [24, 25]. Hence, monolayer adsorption of the dye is obtained in both the cases [26].

The values of the coefficients (q_0, K_L and R^2) from the correlation are provided in Table 1 for both the dyes.

Fig. 11 Langmuir isotherm model for Methylene Blue dye

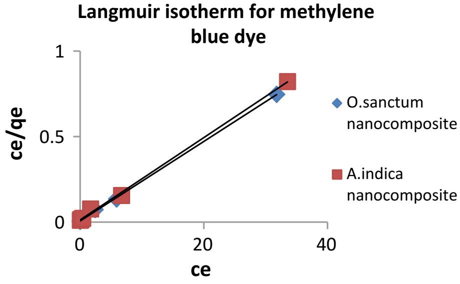


Fig. 12 Langmuir isotherm model for Malachite Green dye

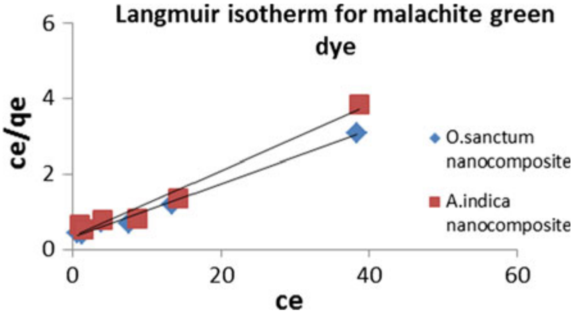


Table 1 Correlation coefficient of Langmuir isotherm

Langmuir parameters	Soil-AgNP (*O. sanctum*)		Soil-AgNP (*A. indica*)	
	Dye 1	Dye 2	Dye 1	Dye 2
q_0 mg/g	43.48	14.085	41.667	11.494
K_L L/mg	3.833	0.223	1.846	0.257
R^2	0.999	0.988	0.998	0.973

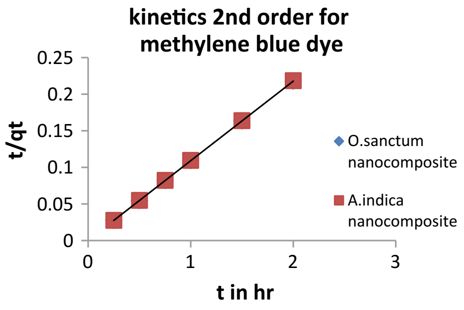


Fig. 13 Kinetic study of Methylene Blue dye

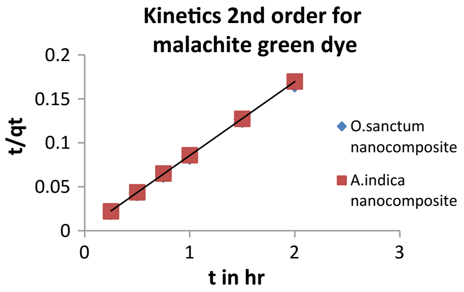


Fig. 14 Kinetic study of Malachite Green dye

Table 2 Correlation coefficient of Ho-McKay's model

Kinetics 2nd order coefficients	Dye 1	Dye 2	Dye 1	Dye 2
	Soil-AgNP (*O. sanctum*)	Soil-AgNP (*O. sanctum*)	Soil-AgNP (*A. indica*)	Soil-AgNP (*A. indica*)
q_e	0.108	0.082	0.108	0.082
K_2	0.001	0.001	0.001	0.001
R^2	0.999	0.999	0.999	0.999

3.4 Kinetics Studies

The kinetic study generally predicts the adsorbate uptake rate and forecast the residence time of dyes on the solid–liquid interface. For both the dyes, the Lagergren's pseudo-first-order and Ho-McKay's pseudo-second-order models were applied to the experimental data using the two adsorbents. The plot between t/q_t versus t (shown in Figs. 13 and 14) for the two adsorbents showed excellent fit to the pseudo-second-order equation [27]. K_2 ($g\ mg^{-1}\ min^{-1}$) value from second-order kinetics is quite the same for all the two adsorbents with R^2 value 0.999. It can thus be concluded that the reaction has followed a pseudo-second-order mechanism and not a pseudo-first-order mechanism [24, 25]. Table 2 represents the Ho-McKay's correlation coefficient.

Fig. 15 Vant Hoff plot for Methylene Blue dye

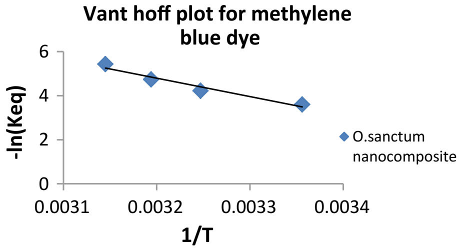
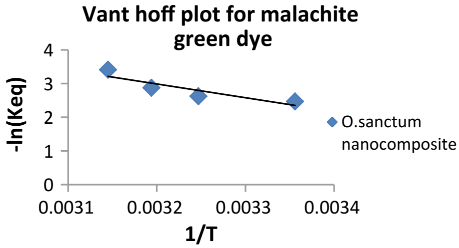


Fig. 16 Vant Hoff plot for Malachite Green dye



3.5 *Thermodynamic Studies*

To conclude whether the two processes are spontaneous in nature or not, the thermodynamic studies are necessary. Gibbs free energy change (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) were calculated for both the dyes using Van't Hoff plot to check the feasibility of the process and to validate the nature of the adsorption process. In Figs. 15 and 16 below, the Van't Hoff plots for Methylene Blue and Malachite Green dye are given using *O. sanctum* nanocomposite. Similar plots were drawn for the other two adsorbents (figure not shown). Table 3 shows the values of different thermodynamic parameters obtained. The study concluded that both the processes are spontaneous, exothermic in nature and has an affinity towards the dye molecules.

Table 3 Correlation coefficient from Van't Hoff model

Parameters		ΔH^0 (KJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})	ΔG^0 (25 °C) (KJ mol^{-1})	ΔG^0 (30 °C) (kJ mol^{-1})	ΔG^0 (35 °C) (kJ mol^{-1})
Soil-AgNP (basil leaf)	Dye 1	−8.39	31.63	−8.92	−10.46	−10.81
	Dye 2	−4.301	16.39	−4.85	−6.21	−6.72
Soil-AgNP (neem leaf)	Dye 1	−5.38	21.78	−8.62	−9.82	−10.26
	Dye 2	−4.11	15.76	−4.31	−5.05	−5.26

4 Conclusion

The TEM and SEM results proved that the nanoparticles formed from the Basil and Neem leaf extract are spherical in shape with size of 50 nm. XRD studies revealed the presence of silver and silver oxide. The presence of aromatic ring, alcohol group, amide, alkane, aldehyde, alkene, carboxyl and carbonyl groups were obtained from FTIR studies. In the comparative study, the percentage removal of dye particles was maximum for Methylene Blue using the *O. sanctum* nanocomposite which is 99.6%. The Langmuir isotherm and Ho-Mckay's model also showed an excellent fit to the experimental results. Thus from the above, we can conclude that the use of silver nanocomposite is a cost-efficient, eco-friendly and time- and energy-saving process for the treatment of hazardous dye materials.

References

1. Pandian CJ, Palanivel R, Dhananasekaran S (2015) Green synthesis of nickel nanoparticles using *Ocimum sactum* and their application in dye and pollutant adsorption. Chin J Chem Eng 23:1307–1315
2. Ahmad R (2009) Studies on adsorption of crystal violet dye from aqueous solution onto *Coniferous pinus* bark powder (CPBP). J Hazard Mater 171:767–773
3. Sun Q, Kai X, Li J, Zheng M, Chen Z, Yu CP (2014) Green synthesis of silver nanoparticles using tea leaf extract and evaluation of their stability and antibacterial property. Colloids Surf A 444:226–231
4. Methylene blue, The American Society of Health-System Pharmacists (2016)
5. Srivastava S, Sinha R, Roy D (2004) Toxicological effects of malachite green. Aquat Toxicol 66(3):319–329
6. Babuponnusami A, Muthukumar K (2014) A review on Fenton and improvements to the Fenton process for wastewater treatment. J Environ Chem Eng 2:557–572
7. Wan C, Li J (2016) Cellulose aerogels functionalized with poly pyrrole and silver nanoparticles: in-situ synthesis, characterization and antibacterial activity. Carbohyd Polym 146:362–367
8. Mazaheri H, Ghaedi M, Asfaram A, Hajati S (2016) Performance of CuS nanoparticle loaded on activated carbon in the adsorption of methylene blue and bromophenol blue dyes in binary aqueous solutions: Using ultrasound power and optimization by central composite design. J Mol Liq 219:667–676
9. Kumar DA, Palanichamy V, Roopan SM (2014) Green synthesis of silver nanoparticles using *Alternanthera dentata* leaf extract at room temperature and their antimicrobial property. Spectrochim Acta Part A Mol Biomol Spectrosc 127:168–171
10. Joseph S, Mathew B (2015) Microwave-assisted green synthesis of silver nanoparticles and the study on catalytic activity in the degradation of dyes. J Mol Liq 204:184–191
11. Prabhu S, Poulose EK (2012) Silver nanoparticles: mechanism of antimicrobial action, synthesis, medical applications, and toxicity effects. Int Nano Lett 2:32–42
12. Baghizadeh A, Ranjbar S, Gupta VK, Asif M, Pourseyedi S, Karimi MJ, Mohammadinejad R (2015) Green synthesis of silver nanoparticles using seed extract of *Calendula officinalis* in liquid phase. J Mol Liq 207:159–163
13. Saeed A, Sharif M, Iqbal M (2010) Application potential of grapefruit peel as dye sorbent: kinetics, equilibrium and mechanism of crystal violet adsorption. J Hazard Mater 179:564–572
14. Alishah H, Seyedi SP, Ebrahimipour SY, Esmaeili-Mahani S (2016) A green approach for the synthesis of silver nanoparticles using root extract of *Chelidonium majus*: characterization and antibacterial evaluation. J Clust Sci 27:421–429

15. Saha J, Begum A, Mukherjee A, Kumar S (2017) A novel green synthesis of silver nanoparticles and their catalytic action in reduction of methylene blue dye. Sustain Environ Res 27:245–250
16. Kumar R, Ghosal G, Jain A, Goyal M (2017) Rapid green synthesis of silver nanoparticles (AgNPs) using (*Prunus persica*) plants extract: exploring its antimicrobial and catalytic activities. J Nanomed Nanotechnol 8:452
17. Senthilkumaar S, Kalaamani P, Subburaam CV (2006) Liquid phase adsorption of crystal violet onto activated carbons derived from male flowers of coconut. J Hazard Mater 136:800–808
18. Dhand V, Soumya L, Bharadwaj S, Chakra S, Bhatt D, Sreedhar B (2016) Green synthesis of silver nanoparticles using *Coffea Arabica* seed extract and its antibacterial activities. Mater Sci Eng C 58:36–53
19. Kumar B, Smita K, Cumbal L, Debut A (2015) Green synthesis of silver nanoparticles using Andean Blackberry fruit extract. Saudi J Biol Sci
20. Benakashani F, Allafchian AR, Jalali SAH (2016) Biosynthesis of silver nanoparticles using *Capparis spinosa L.* leaf extract and their antibacterial activity, Karbala. Int J Mod Sci 2:251–258
21. Ibrahim HMM (2015) Green synthesis and characterization of silver nanoparticles using banana peel extract and their antimicrobial activity against representative microorganisms. J Radiat Res Appl Sci 8:1–11
22. Jamil M, Murtaza G, Mehmood A, Bhatti TM (2015) Green synthesis of silver nanoparticles using leaves extract of *Skimmia laureola*: characterization and antibacterial activity. Mater Lett 153:10–13
23. Satapathy MK, Das P (2014) Optimization of crystal violet dye removal using novel soil-silver nanocomposite as nanoadsorbent using response surface methodology. J Environ Chem Eng 2:708–714
24. Transport processes and unit operations, Christie Geankoplis, 3rd edn
25. Unit operations of Chemical Engineering, Mcabe and Smith, 6th edn
26. Langmuir I (1916) The constitution and fundamental properties of solids and liquids. J Am ChemSoc 38:2221–2295
27. Ho YS, McKay G (1999) Pseudo-second-order model for sorption processes. Proc Biochem 34:451–465

Performance of TiO_2 Photocatalytic Nanomaterial in Removal of Lead from Sanitary Landfill Leachate Using Sunlight

Naveen N. Desai and Veena S. Soraganvi

1 Introduction

Developing countries are the highest Municipal Solid Waste (MSW) producers, due to the growing urbanization and industrilization. In India, it is estimated that about 115000 MT of Municipal Solid Waste (MSW) is generated daily in the country [1]. The social and environmental effects caused by MSW have received great attention in recent decades. The policies, plans, strategies, and techniques have been developed in the field of MSW management for waste recovery, reuse, recycling, and energy generation by incineration and sanitary landfilling for the final rejects [2]. Most of the developed and developing countries have adopted sanitary landfilling as the general technique for their MSW disposal because of its low-cost and well-established methods [3]. Major pollutants emerge from sanitary landfill sites are biogas and leachate. The environmental problems experienced by the leachate is evading of leachate from the site and the subsequent contamination of surrounding land and water [4]. The difficulty associated with treating MSW landfill leachate involves highly variable composition and high concentration of recalcitrant organic compounds, ammonia, and heavy metals [5].

Heavy metals are one of the major concerns in the sanitary landfill leachate. Heavy metals enter in the landfill by electroplating waste, painting waste, used batteries, etc., when these wastes degradation takes place in acidic condition leads to a high metal concentration in the leachate [6]. Heavy metals disturb the natural biological balance and inhibit self-purification process [7]. Heavy metal ions, for example, Pb^{2+},

---

N. N. Desai (✉)
Department of Civil Engineering, B.L.D.E.A's V.P. Dr. P.G.H. College of Engineering & Technology, Vijayapur 586103, Karnataka, India
e-mail: dnaveen_009@yahoo.co.in

V. S. Soraganvi
Department of Civil Engineering, Basaveshwar Engineering College, Bagalkot 587103, Karnataka, India

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_44

Cd^{2+}, Cr^{6+}, Zn^{2+}, and Hg^{2+} have toxic and nonbiodegradable properties, can cause serious health issues in human being and animals [8].

Heavy metal lead (Pb^{2+}) can cause harmful effects such as anemia, abdominal pain, irritability, as well as it disturbs functioning of the brain resulting in memory loss and headache.

In recent years, various techniques have been developed for effective removal of heavy metal from water and wastewater, those are adsorption, reverse osmosis, membrane filtration, ion exchange, and electrochemical technologies. Among these techniques, adsorption offers flexibility in design and operation, which produces high-quality-treated effluent [9].

In recent years, nanomaterials are used for treating heavy metals, organic, and inorganic compounds from water and wastewater. These nanomaterials are used as an adsorbent and photocatalyst. Photocatalytic nanomaterials are metal oxides which includes ferric oxide, aluminum oxides, titanium oxides, manganese oxides, and magnesium oxides.

In nanosized metal oxides, semiconductor photocatalysis has gained more attention because of its outstanding efficiency in environmental purification. TiO_2 is one of the broadly used semiconductor photocatalysts [3]. One of the widely used semiconductor photocatalysts is TiO_2. TiO_2 gained a prominent place in research due to its nontoxicity, cost-effective, high chemical stability, and has highly oxidizing power, which makes it a competitive candidate for many photocatalytic applications [10]. Heterogeneous photocatalysis uses artificial or natural solar UV rays for degradation most of the heavy metals in water and wastewater. The reduction of Cr^{6+} under visible light is studied by using TiO_2 photocatalytic. Methanol, methanal, and formic acid are used as electron donors in photocatalysis process and quickest rate of chromium reduction was found in formic acid [11]. The photocatalytic reduction of Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}, is studied under solar energy with the parabolic trough and TiO_2 as a photocatalyst. Citric acid is used as a hole scavenger and results show that 97% reduction of copper and other metals reduction is significantly low compared to nickel 36.4%, zinc 22.2%, and lead 41.4% [12, 13]. Photocatalytic reduction of nickel and zinc is more in alkaline pH and acidic pH is favorable for chromium reduction [12, 13]. Photocatalytic degradation of phenol by titanium dioxide was investigated with varying pH, irradiation time, and dosage of TiO_2. A total of 94.5% degradation of phenol is achieved in 150 min of irradiation time [14].

In the present work, the UV/TiO_2 photocatalyst is used for the degradation of lead ($Pb2^{+}$) in the aqueous solution. TiO_2 characterization study is performed on particle size, specific surface area, and surface morphology. The parabolic trough collector is used as solar photoreactor. This photoreactor brings efficiently solar photons and chemical reagents in contact with TiO_2 photocatalyst. Factors affecting the performance of TiO_2 photocatalysis are considered as pH, contact time, dosage, and different lead concentrations in Design of Experiments (DOE).

2 Materials and Methods

2.1 *Chemicals*

A stock lead solution is prepared by dissolving 1.599 gm of lead nitrate $Pb(NO_3)_2$ in deionized distilled water. When the solution is completely acidified, 10 ml redistilled HNO_3 and diluted to 1 L with deionized distilled water. 1 ml = 1 mg (1000 mg/l). Different concentrations of lead solutions are obtained by using stock lead solution.

The pH is varied as 4, 7, and 10 in aqueous solution, buffer solutions are prepared with reagents such as Disodium Hydrogen Phosphate (Na_2HPO_4). The Disodium Tetra borate ($Na_2B_4O_7$) is commonly known as borax and Boric acid or Hydrogen Borate (H_3BO_3). The titanium dioxide (TiO_2) used for the work is Sisco Research Laboratories Private limited.

2.2 *Design of Experiments (DOE)*

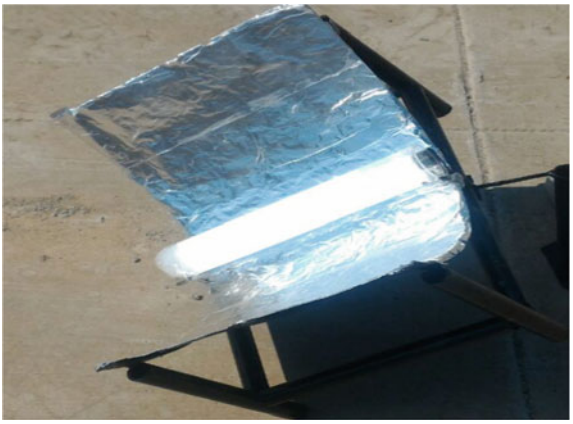
Various factors are influencing the degradation of lead under photocatalytic process. To know the key factors and their interaction effects in the photocatalytic process, a statistical tool DOE was used. Four influencing factors were considered for the study which is pH, initial concentration of aqueous solution, adsorbent dosage, and irradiation time. Design Expert Software version 7.0 is used with two-level factorial design. It is used in most of the experiments because of its simplicity, versatility and can be used for many factors. A total of 30 runs were obtained with Design expert software 7.0 for adsorbent dosage (A), pH (B), initial concentration of aqueous solution (C), and the irradiation time (D) in randomized fashion.

2.3 *Experiments*

The experiments were carried out in a batch sequence under natural sunlight at Vijayapur, (16.83°N 75.71°E) Karnataka state, India. The parabolic trough (Fig. 1) is used with an angle of 45° to receive the maximum sunrays. A 100 ml glass tube is used as a container for experimental work. For proper circulation of TiO_2 with aqueous lead solution air is supplied. At the end of each experiment, the filter paper is used for the separation of TiO_2 particles. The lead analysis was done by using Atomic Absorption Spectroscopy (Varian 240). The lead removal efficiency is calculated according to

$$R = \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \times 100$$

Fig. 1 Parabolic trough



where C_{in} and C_{out} are initial and residual concentrations of the metal ion, respectively.

3 Results and Discussion

3.1 *Characterization of TiO_2*

3.1.1 X-Ray Diffraction (XRD)

Crystal Structure and Crystallite Size

The X-ray diffraction of photocatalytic TiO_2 is carried out to determine the crystal structure and crystallite size. The XRD pattern of TiO_2 is shown in Fig. 2. The results show six peaks at 25.29, 37.92, 48.09, 53.86, 55.12, and 62.7. The 2θ peaks at 25.29° and 48.09° confirm the TiO_2 used for the study is anatase form according to JCPDS Card No. 21-1272. The TiO_2 nanomaterials are available in the crystallographic structures to form as anatase, rutile, and brookite. Among these three structures, anatase exhibits higher photocatalytic activity compared to the others, because of its indirect band gap semiconductor. Rutile exhibits direct band gap semiconductor. Anatase having band gap of 3.2 eV which is larger than of rutile 3.0 eV.

Average crystallite size is calculated by considering the 2θ peak values. The average crystallite size is estimated from the Full Width Half Maximum (FWHM) of diffraction peak using Debye-Scherer formula. This Debye-Scherer formula is the simplest and widely used one.

$$D = \frac{0.94\lambda}{\beta \cos\theta} \tag{1}$$

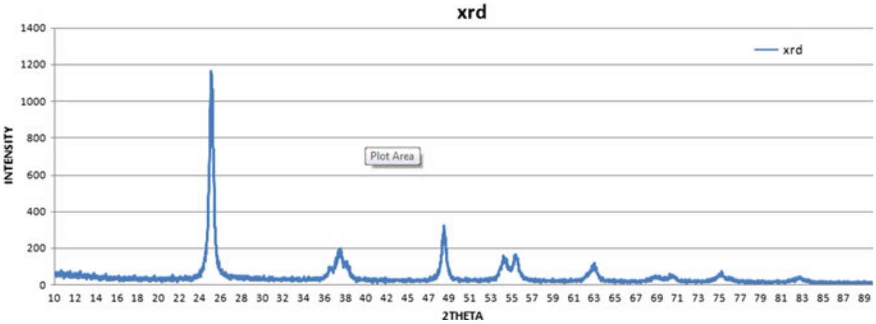


Fig. 2 XRD pattern of TiO_2 nanoparticles

where λ—wavelength of X-ray (0.1540 nm), β—FWHM, θ—diffraction angle, and D—crystallite size. The average crystallite size obtained by the above equation is 19 nm. The samples intensity of the XRD peaks reflects that the smaller the crystal size, the broader the peak and confirming small size crystallite.

Specific Surface Area (SSA)

SSA is a surface area per unit mass, and this property is important for adsorption, heterogeneous catalysis, and reactions on surfaces. As the size of material decreases, the specific surface area and surface-to-volume ratio increases. The SSA can be calculated as per the Eqs. 2 and 3. The results obtained by both the equations are same. The observed results are tabulated in Table 1.

$$\mathrm{SSA} = \frac{\mathrm{SA}_{\mathrm{Part}}}{V_{\mathrm{Part}} \times \rho} \tag{2}$$

$$S = \frac{6000}{D_{\mathrm{p}} \times \rho} \tag{3}$$

where SSA and S = specific surface area, V_{Part} = particle volume, $\mathrm{SA}_{\mathrm{part}}$ = surface area, D_{p} = the size (Spherical Shaped), and ρ = density of the material.

The results show that 120.32 m^2/gm SSA is responsible for the enhanced photocatalytic degradation of lead. The high specific surface area of TiO_2 nanoparticles facilitates reaction/interaction between the TiO_2 as the interacting media, which

Table 1 Specific surface area of TiO_2 nanoparticles

Particle size (nm)	Surface area (nm^2)	Volume (nm^3)	Density (g cm^{-3})	SSA (m^2 g^{-1})
19	1134.262	3597.82	2.62	120.32

mainly occurs on the surface or at the interface and strongly depends on the surface area of the material.

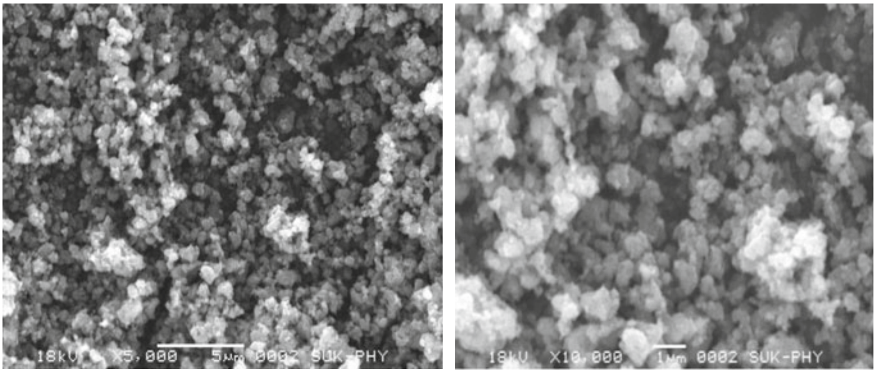
3.1.2 Scanning Electron Microscope (SEM)

The surface morphology is studied by Scanning Electron Microscopy (SEM) in the physical Instrumentation Facility Centre (PIFC), Department of Physics, Shivaji University, Kolhapur, Maharashtra. The SEM images of TiO_2 at different magnifications are shown in Fig. 3a, b, which confirms that the TiO_2 used for the study is spherical in shape.

3.2 *Response Surface Methodology (RSM)*

RSM application helps in optimizing the critical factors and provides a useful data about the response nature. Figure 4 indicates the relevant fitted response surfaces for the design. It shows % removal of Pb^{2+} versus variables in the response surface plots. The interaction among variables and removal efficiency can be observed at the curvature of the plots. The response surface plots as shown in Fig. 4 indicate the dependency of variables such as dosage, pH, irradiation time, and lead concentration with respect to percentage removal of lead from the aqueous solution.

The effect of initial concentration of lead and pH values is shown in Fig. 4a with percentage removal of lead. The results obtained from the graph show that increasing in pH as well as concentration of lead leads to remove maximum percentage of lead from aqueous solution. At higher pH, the movement of holes and electrons in photocatalyst is faster compared to acidic media.



(a) 5,000 (b) 10,000.

Fig. 3 SEM images of TiO_2 nanoparticles with different magnification

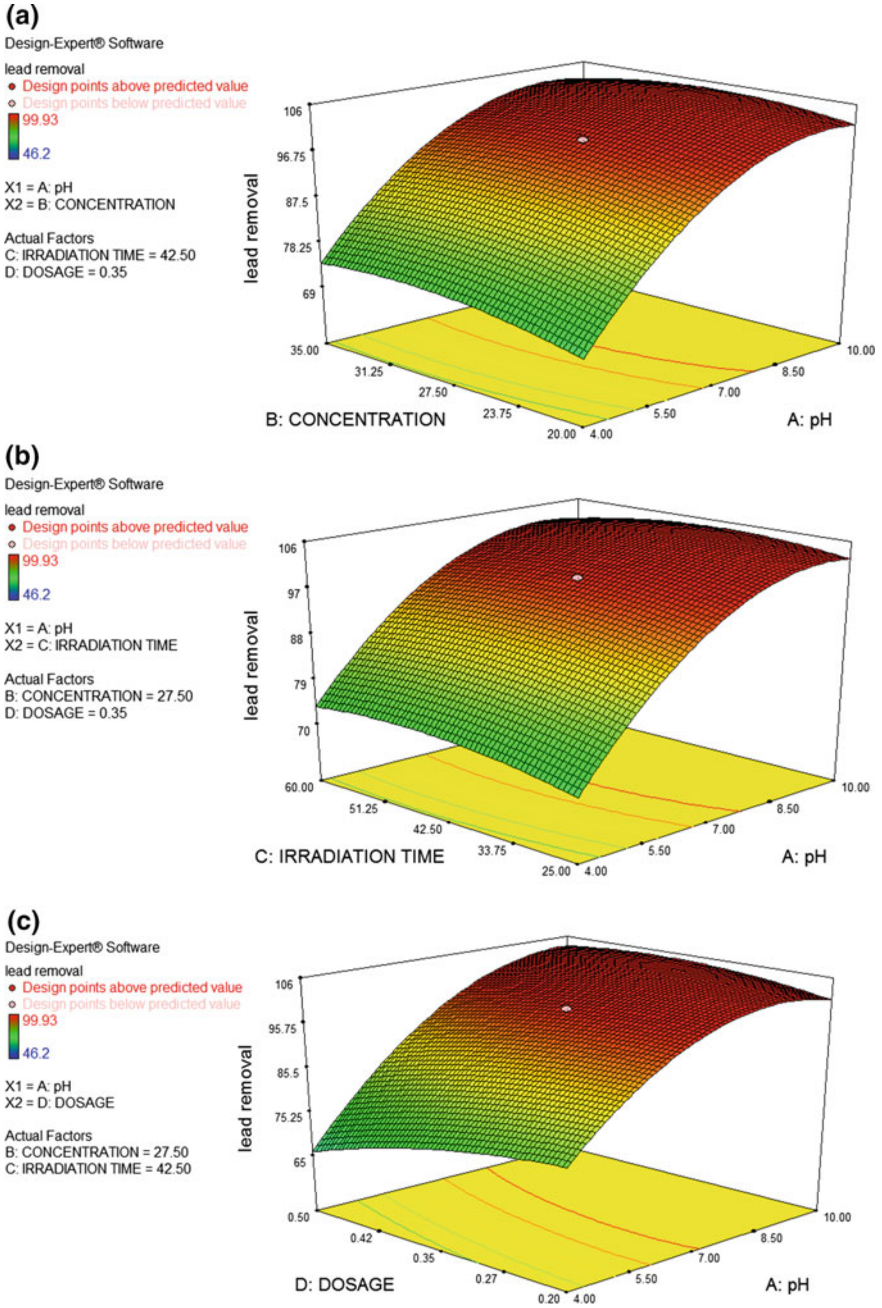


Fig. 4 Profiles for predicted values for removal percentage of lead

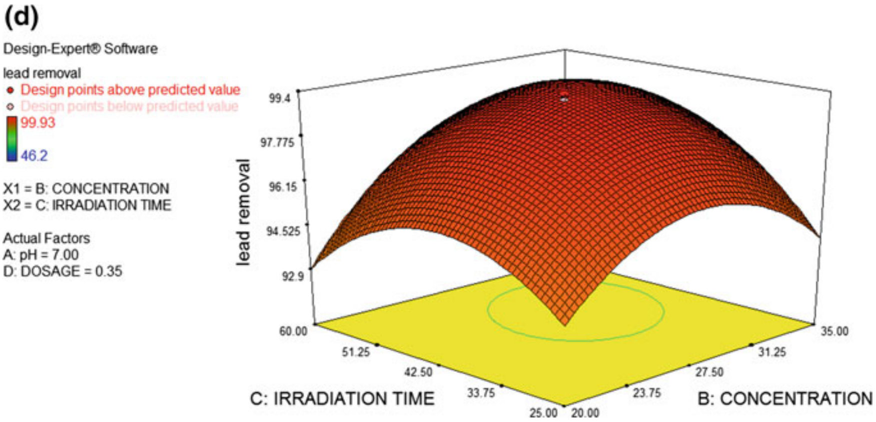


Fig. 4 (continued)

Figure 4b demonstrates the change in the lead as a function of pH and irradiation time. As the irradiation time increases, the percentage removal of lead increases. This is because of longer irradiation time accelerates mixing and dispersion of adsorbent into the solution and provides more vacant sites in the metal ions. Furthermore, an increase of irradiation time leads to precipitation of the adsorbed lead back to the solution.

Figure 4c represents the lead removal in terms of pH and dosage variables. As the dosage increases, the lead removal efficiency increases. The increase in lead removal efficiency is due to the density of increased dosage particles in the area of illumination. This density will help in increasing availability of catalyst sites for the adsorption. Further, an increase of dosage levels reduces the light absorption coefficient which in turn reduces the lead removal efficiency. Lower adsorbent dosage with alkaline pH causes a higher adsorption capacity, due to deprotonation of the more adsorption sites.

Figure 4d represents variation of the initial concentration and irradiation time. From the results, it is seen that the initial concentration of lead with 27.50 mg/l and 35 min contact time will help in maximum percentage removal of lead. It indicates that high adsorption capacities of ions were observed at initial irradiation time, due to probable saturation of the adsorbent surface as a result of air-assisted mixing and dispersion of adsorbent and metal ions in solution.

3.3 Optimization of Parameters

The surface profiles (Fig. 4) obtained by the study are utilized for optimizing the process of lead removal. The overall response provided by the plots with different variables are studied individually and found that maximum percentage removal of the lead was 99.38% at optimum conditions of 42.5 min = contact time, 0.35 g/l = adsorbent dose, initial lead concentration = 27.5 mg/l, and pH = 7.

4 Conclusions

In this study, the TiO_2 photocatalytic nanomaterial is used for the removal of lead from aqueous solution. The TiO_2 characteristics study such as XRD and SEM results confirm that the selected photocatalytic TiO_2 is an anatase with spherical in shape. The crystallite size is approximately 19 nm and specific surface area of 120.32 m^2/gm. It is observed that the TiO_2 is having small crystal size and high SSA which proves to be an efficient photocatalyst for the removal of lead from leachate. Central Composite Design (CCD) and RSM are used to find the effects of different factors, interactions among the various operating parameters and optimizing the process. With the results, we can conclude that the optimum operating variables are 42.5 min = irradiation time, 0.35 g/l = dosage, 27.5 mg/l = lead concentration, and pH = 7 is required to achieve maximum percentage removal of lead. The said photocatalyst and the operating conditions can help in the study of lead removal from sanitary landfill leachate.

References

1. Position paper on the solid waste management sector in India (2009) Department of economic affairs, Ministry of Finance, Government of India
2. El-Salam MMAbd, Abu-Zuid GI (2015) Impact of landfill leachate on the groundwater quality: a case study in Egypt. J Adv Res 6:579–586
3. Hassan M, Zhao Y, Xie B (2016) Employing TiO_2 photocatalysis to deal with landfill leachate: Current status and development. Chem Eng J 285:264–275
4. Mahmud K, Hossain MD, Shams S (2012) Different treatment strategies for highly polluted landfill leachate in developing countries. Waste Manag 32(11):2096–2105
5. Meeroff DE, Bloetscher F, Reddy DV, Gasnier F, Jain S, McBarnette A, Hamaguchi H (2012) Application of photochemical technologies for treatment of landfill leachate. J Hazard Mater 299–307
6. Esakku S, Palanivelu K, Joseph K (2003) Assessment of heavy metals in a municipal solid waste dumpsite. Workshop on Sustainable Landfill Management, 3–5 Dec 2003, pp 139–145
7. Talalaj IA (2015) Release of heavy metals from waste into leachate in active solid waste landfill. Environ Prot Eng 41:83–89
8. Wang X, Guo Y, Yang L, Han M, Zhao J, Cheng X (2012) Nanomaterials as sorbents to remove heavy metal ions in wastewater treatment. Environ Anal Toxicol, ISSN: 2161-0525
9. Hua M, Zhang S, Pan B, Zhang LW, Lv QZ (2012) Heavy metal removal from water/wastewater by nanosized metal oxides: a review. J Hazard Mater 211–212:317–331
10. Castellote M, Bengtsson N (2011) Principal of TiO_2 photocatalysis. Applications of titanium dioxide photocatalysis to construction materials. Springer, Dordrecht. ISBN 978-94-007-1296-6
11. Zhang X, Song L, Zeng X, Li M (2012) Effects of electron donors on the TiO_2 photocatalytic reduction of heavy metal ions under visible light. Energy Procedia 17(Part A):422–428

12. Kabra K, Chaudhary R, Sawhney RL (2008) Solar photocatalytic removal of metal ions from industrial waste water. AIChE Environ Prog 27(4):487–495
13. Kabra K, Chaudhary R, Sawhney RL (2008) Solar photocatalytic removal of Cu(II), Ni(II), Zn(II) and Pb(II): speciation modeling of metal–citric acid complexes. J Hazard Mater 155:424–432
14. Alalm MG, Tawfik A (2014) Solar photocatalytic degradation of phenol in aqueous solutions using titanium dioxide. Int J Chem Mol Nucl Mater Metall Eng 8(2):136–139

Bioconversion of Waste Conversion Gases to Liquid Fuels: Challenges and Opportunities

Aastha Paliwal, H. N. Chanakya and Himanshu Kumar Khuntia

1 Introduction

India has gone a big way to convert MSW to methane and purify the same to CNG grade to create Bio CNG that has been recently accorded permissions at the national level [1, 2]. Bio CNG replaces fossil fuel-derived CNG that is transported from afar, results in large footprints. The current biomethanation plants that handle between 5 and 100 tpd, result in 300–6000 m^3/d biogas (4000 m^3 methane, 2.4 tpd of methane) [3]. This is a very small scale for catalytic methanol production [4] and therefore requires a simpler technology that also operates at a small scale. Biogas production from MSW at the above scale is almost always used to generate 'green' electricity in India which in turn can at best provide about 1.5 kWh/m^3 biogas (₹8/m^3). Converting the same to methanol would yield 1L methanol (@60% efficiency) fetching ₹20 on the market today. This will allow methanol to be stored on site as a compact liquid instead of paving way for frequent flaring of excess methane/biogas. This will also allow green energy to be produced from MSW with higher profit margins and potential for a greater number of entrepreneurs in the process.

Energy is a key input in driving the country's economic growth and development [5, 6]. Therefore, the growth of the nations is estimated to create a 28% increase in world energy consumption by 2040 (777 EJ in 2040 from 607 EJ in 2015) [7, 8]. This necessitates the need for an alternative source of energy for India more than ever. Saraswat and Bansal report methanol and dimethyl ether (DME) as potential fuel alternatives to contain increasing import demands of fuel and to improve the energy security of India [9]. Methanol (CH_3OH) as a fuel alternative with energy density of 23 MJ/Kg [10], octane number 109, is a slow-burning, energy-efficient fuel [11]. It is a clean energy carrier which produces lesser NO_x, SO_x, particulate matter

---

A. Paliwal · H. N. Chanakya (✉) · H. K. Khuntia
Centre for Sustainable Technologies (Formerly ASTRA),
Indian Institute of Science, Bengaluru, India
e-mail: chanakya@iisc.ac.in

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_45

and tailpipe emissions than gasoline. Easy storage, transportation and potential of use in existing infrastructure with minimum modification and production potential through multiple routes make methanol a preferred fuel alternative. The resource base for methanol is very diverse [6], natural gas, shale gas, fossil fuels, effluent gas from power plants, syngas, methane/biogas from landfill and biomass (animal waste, agricultural waste and domestic waste) are the potential starting material for methanol production [12].

Biomethanol (methanol produced with biomass as starting material [6]) production enables the integration of waste management and generation of clean and green alternate of fuel by capturing the energy stored in organic waste as methanol. Carbon dioxide fixed by plants (direct or indirect source of all organic material) in its lifetime makes this route of methanol production carbon neutral [12]. Gasification, pyrolysis, electrolysis, biosynthesis and photoelectrochemical are the processes for biomethanol production [6]. Biosynthesis of methanol has recently gained momentum. It involves the conversion of methane to methanol using methane-oxidizing bacteria, methanotrophs. The objective of this study was to bring forward different microbial species capable of carrying out the process, their metabolic requirement, isolation source and growth conditions. Finally, we attempt to capture the current status and bottlenecks in the feasibility of this process.

2 Biosynthesis of Methanol from Biomass

2.1 Resource Base

About 62 MT/yr of municipal waste and 249 MT/yr of surplus crop residue [13] are generated in India and can be processed through anaerobic digestion or gasification to obtain methane. 16 million metric tons of CO_2 equivalent of methane generated annually from landfills is another methane source from solid waste [14]. The methane produced through these routes serves as the feed gas for methanotroph-based conversion to methanol. Figure 1 represents the stages involved in the conversion of waste to methanol, and input energy processes like temperature regulation, compression unit, pumps, flow regulators, etc. have not been mentioned in the diagram. Bioreactor is the central part of the process of biosynthesis. Bioreactor is fed with a fixed ratio of methane and oxygen, where methanotrophs use methane as their carbon source. These bacteria which otherwise oxidize methane to carbon dioxide are stimulated in the bioreactor to terminate the process after methanol production.

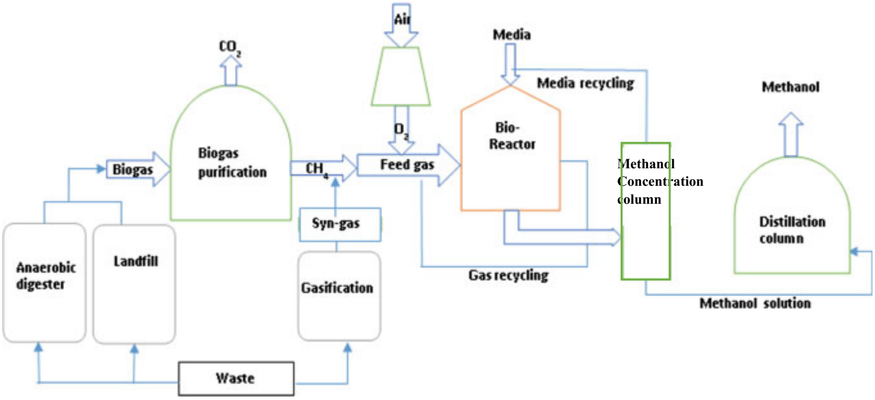


Fig. 1 Block diagram of biosynthesis of biomethanol. Waste is treated through either biological route (anaerobic digester, landfill) or through thermal route (gasification). The effluent gases: biogas in the case of anaerobic digestion and landfill and syngas in the case of gasification are processed to obtain methane. Methane along with oxygen serves as feed gas. In the bioreactor, methanotrophs are present which use methane as the carbon source and partially oxidize it to methanol using oxygen. Methanol is then concentrated in the methanol concentration column, and from here, growth media is recycled into the bioreactor and concentrated methanol is transferred to distillation column to obtain pure methanol

2.2 *Methanotrophs*

Methanotrophs, the methane-oxidizing, Gram-negative bacteria, are believed to be the largest sink of methane (second most significant greenhouse gas). Both aerobic and anaerobic forms of bacteria exist. Anaerobic methane oxidizers (ANME) clades (ANME-1,2,3) are phylogenetically associated with methanogens and form three different clusters related to order methanosarcinales and methanomicrobiales [15–17]. Aerobic form of these bacteria was first classified in 1970 by Whittenbury in five groups based on their morphology, resting stage and fine structure [18]. Today, these aerobic bacteria can be broadly classified into three groups [19] on the basis of their phylogenetic relationship, group 1, gammaproteobacteria (example *Methylomonas albus* BG8), group 2, alphaproteobacteria (*Methylosinus trichosporium* OB3b) [20] and group 3, verrucomicrobia (*Methylacidiphilum infernorum*) [21].

2.2.1 History

Two scientists, Kaserer (1905) and Sohngen (1906), simultaneously reported methanotrophs, methane-converting bacteria [22]. In 1915, Miinz, studied the physiology of methanotrophs [22]. In few years to follow, the presence of methanotrophs was reported from different sources, Giglioli and Masoni in 1914 reported bacterias widespread occurrence in Italian soils; Harrison and Aiyer, 1914 and 1916, investigated methanotrophs in Indian swamp rice soils. Dworkin in 1956 and Foster in 1958 isolated a number of methanotrophs, different varieties of same species, *Pseudomonas methanica.* In 1960s, two new species of methanotrophs, *Methanomonas methanooxidans* [23] and *Methylococcus capsulatus* [18], were isolated. In 1970, Whittenbury and colleagues isolated hundreds of aerobic methane-oxidizing bacteria and classified them in five groups. The potential of methanotrophs to oxidize a wide range of substrate was established by 1970s, its application in bioremediation intrigued many applied microbiologists and several studies were undertaken for the same in 1980s [24]. Anaerobic oxidation of methane was discovered in 1976; yet the causal organism was identified approximately 20 years later [18]. Late in the 1990s, production of methanol by partial oxidation of methane using biocatalyst (methanotrophs) was tried and is now an active area of research. Figure 2 represents the trend of the research.

2.2.2 Sources

Stable gas exchange environments with continuous availability of oxygen and methane host largest and most active populations of aerobic methane-oxidizing bacteria [19]. Freshwater, rice paddy fields, swamps and marshes, rivers, ponds and lake surface sediments, activated sewage sludge, coal mine surfaces, meadow and deciduous forest soils and wetlands are some of the common habitats of methanotrophs [19]. Anaerobic methanotroph is common inhabitants of marine sediments [17], anoxic marine water, sediments of soda lakes, freshwater sediments, sulphate methane transition zone, cold and hot seeps, etc. [19].

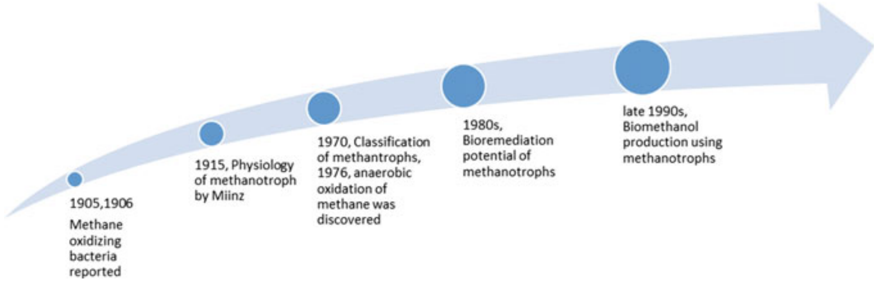


Fig. 2 Major leaps in research with methanotrophs. Methanotrophs were first isolated in 1906, and by 1970, bacteria were classified into five different classes. Around 1970s, the ability of methanotrophs to oxidize broad range of substrate such as alkanes, alkenes, ethers, alicyclic, heterocyclic and aromatic compounds were investigated, anaerobic methanotrophs were isolated in 1976 and by 1980s, application of aerobic methanotrophs for bioremediation was investigated. Since the late 1990s, active research in exploiting these bacteria for partial oxidation of the methane to produce methanol has been undertaken

2.2.3 Growth Conditions of Aerobic Methanotrophs

Common growth media for methanotrophs is NMS (nitrate (KNO_3) mineral salt), AMS (Ammonium (NH_4Cl) mineral salt) [18] and ANMS (ammonium nitrate mineral salt (both KNO_3 and NH_4Cl are present)). 5.8–7.4 is the pH range for growth of majority of aerobic methanotrophs [18]. Ammonium salts as a source of nitrogen are used by all aerobic methanogen, majority grows on nitrite and nitrate, while only a few are able to grow on urea, cas amino acids and yeast extracts. Common temperature for growth of mesophiles is 25–30 °C (*Methylomonas, Methylosinus*, etc.), 2–10 °C for psychrophiles (*Methylobacter psychrophilus*, *Methylosphaera hansonii*) and 40–45 °C for thermotolerant aerobic methanotrophs (*Methylococcus* and *Methylocaldum*) [19].

2.2.4 Metabolic Pathway

Figure 3 represents the metabolic pathway of methanotrophs. Methanotrophs obtain energy by conversion of methane to formaldehyde and carbon dioxide. Metabolic pathway involves the conversion of methane → methanol → formaldehyde → formic acid → carbon dioxide [25].

Three different carbon assimilation pathways exist in methanotrophs, RuMP pathway allowing for synthesis of key intermediates for central metabolic routes from formaldehyde is operational in type 1 methanotrophs, type 2 methanotrophs use serine pathway and have a functional TCA cycle and type 3 methanotrophs use Carbon–Benson–Bassham (CBB) cycle for carbon assimilation [20]. Independent of the fate of carbon from methane, the first step is conversion of methane to methanol, conversion which begins with breaking stable C–H bonds of methane, requiring 438.38 kJ/mol [26]. Methanotrophs obtain this energy by activation of molecular oxygen. Methane monooxygenase (MMO), the enzyme involved in the conversion, activates oxygen using its metal centre (iron in sMMO and copper in pMMO) [27].

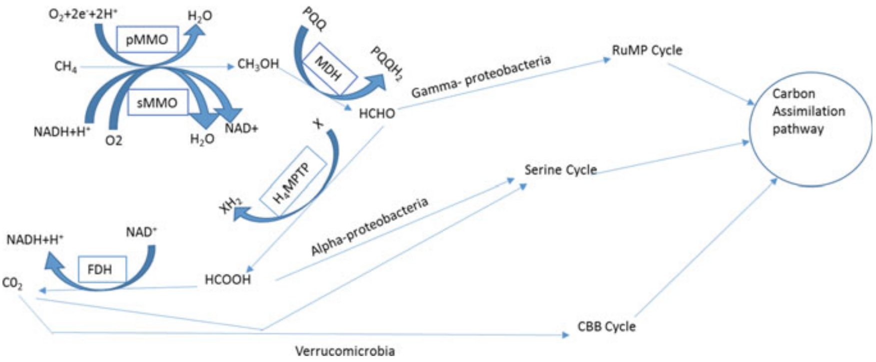


Fig. 3 Metabolic pathway of methanotrophs adapted from [20]

2.3 Methanol Production Using Methanotrophs

Methanotrophs can serve as biocatalysts for conversion of methane to methanol by [28] expression of active MMO in high concentration in cell and by inhibiting methanol dehydrogenase (MDH), next enzyme in the pathway, to block the pathway after methanol synthesis [25]. Two variants of MMO have been reported in methanotrophs, soluble (sMMO) and particulate (pMMO). These two variants have different specific activities, susceptibility to inhibitors and stability [25]. The enzyme pMMO, a membrane-bound variant of MMO, has higher affinity for methane and is, therefore, a desired variant for methanol production. Expression of pMMO over sMMO can be selected in bacteria by the provision of copper (present at active site of pMMO) in growth media, in 5 μM concentration [29]. Methanol dehydrogenase inhibitors added to the growth media are EDTA, thiotreitol, cyclopropane, NaCl and cyclopropanol [28–31]. Addition of MDH inhibitor blocks the source of reducing equivalent needed for methanol synthesis, and this necessitates the addition of an external source of reducing equivalent (formate) in the growth media. Formate is converted to carbon dioxide in the cell, and this conversion produces a reducing equivalent which then is utilized for methanol formation. One mole of formate is required to produce reducing equivalents needed for one mole of methanol formation.

3 Current Status

Methylomonas trichosporium is the most investigated organism for the study of methanol biosynthesis with growth temperature around 30 °C [20] and near neutral pH [25, 28, 32]. High cell densities are used to compensate for the low specific productivity rate. The shortest doubling time reported for these bacteria is 3–5 h but when employed for methanol production, the doubling rates go up to 48 h [18, 27, 28, 30, 32–34]. This could be due to the methanotrophs being near stationary phase when cultured for methanol production and impaired metabolic process which reduces the net energy available to the bacteria. An equimolar 1:1 ratio of methane to oxygen [30, 32, 33], the stoichiometric ratio for methanol production in the cell, is the most common ratio of these gases in the feed. Due to differences in the solubility of these gases, the equimolar ratio in gaseous phase provides a concentration ratio of methane to oxygen of ~1:2 in liquid phase, ensuring enough oxygen. Most of the studies conducted a focus on optimization of growth media for enhancing methanol production and are all small-scale studies with reactor volume <50 ml (Table 1).

Table 1 Examples of studies conducted on methanol production using methanotrophs

Bacteria	Scale of study	Ratio of methane to oxygen (v/v)	Product conc. (mg/l)	Bacterial conc. (dry cell weight) (mg/ml)	Reference
Methylosinus trichosporium OB3b	10 ml (for batch) 50 ml (Semi-continuous)	1.08:1 (Batch) 1.08:1 (semi-continuous)	179 (batch) 2.06/hr (semi-continuous)	2.5	[32]
Methylomonas DH-1	24 ml	3:1	1340	2.4	[28]
Methylosinus trichosporium OB3b	10 ml (anaerobic reactor)	1:1	1100	17	[30]
Methylosinus trichosporium IMV 3011	100 ml	1:1	0.55	3	[33]
M. trichosporium OB3b	12 ml	2:1	393	0.21	[25]
Methylosinus trichosporium OB3b	3 l	5:1	438	0.6	[34]

4 Bottlenecks in the Biosynthesis Process

- Broad substrate range for MMO [20].
- Low specific productivity rate (grams of methanol produced/gram of bacteria/hour) of methanotrophs for methanol necessitates high cell densities in bioreactor. 0.0752 g of methanol per gram of bacteria per hour is the maximum reported specific productivity [28].
- For every molecule of methanol, cell produces one water molecule; this requires reducing equivalents. Blocking the pathway at methanol production starves cell of these reducing equivalents which are otherwise generated later in the pathway; this limits continuous methanol production by cell and necessitates the provision of external source of reducing equivalent [20].
- Methanol toxicity at low concentration limits methanol accumulation in the reactor. Highest reported methane tolerance is 7%, where cells are able to grow without inhibition with methanol as a substrate [28].
- Knowledge gaps at genetic level, poor understanding of energy balance involved in the pathway, poor understanding of reducing equivalent donor to pMMO [25] and absence of required genetic tools for engineering methanotrophs are the major challenges in genetic engineering of the cell with higher and more efficient methanol productivity [35].

- Low solubility (methane—20.16 mg/l, oxygen—36.56 mg/l at 30 °C) [36, 37] and diffusion rates (methane—$0.19 * 10^{-4}$ cm^2/s and $0.23 * 10^{-4}$ cm^2/s for oxygen) [38, 39] of gases makes volumetric mass transfer a major challenge.

5 Conclusion

Conversion of surplus methane to methanol overcomes the complexities of compressing and purifying methane (from MSW) to Bio CNG levels and attendant energy losses. As a fuel source, methanol is preferred over methane because of its easy storage, transportation, diverse endpoint use, better fuel efficiencies and easy blending with diesel and petrol. Organic solid waste as required source of methane increases the economic feasibility and makes conversion process sustainable. Chemical conversion of methane requires temperature of 200–900 °C and 5–20 MPa pressure [40], high purity gases and expensive metal catalysts. Most of these limitations can be circumvented with biological route. Although still at early stage of research with major biological and technological challenges, methanotroph-aided methanol production offers a new approach to sustainable development and value addition for MSW conversion to methanol.

References

1. Dhussa A (2004) Biogas in India. MNRE, India
2. Bamboriya ML (2013) Biogas generation, purification and bottling: development in India. India
3. Chanakya HN, Malayil S (2012) Anaerobic digestion for bioenergy from agro-residues and other solid wastes—an overview of science, technology and sustainability. J Indian Inst Sci 92(1):111–144
4. Pedersen TH, Schultz RH (2012) Technical and economic assessment of methanol production from biogas. Department of Energy Technology, University of Aalborg, Denmark
5. Yergin D, Bocca R (2012) Energy for economic growth. Report, Geneva, Switzerland
6. Shamsul NS et al (2014) An overview on the production of bio-methanol as potential renewable energy. Renew Sustain Energy Rev 33(42):578–588
7. EIA (2017) International energy outlook 2017. Report, US
8. IEA (2015) India energy outlook. Report, Paris, France
9. Saraswat VK, Bansal R India's Leapfrog to Methanol Economy. Retrieved from: http://niti.gov.in/content/india%E2%80%99s-leapfrog-methanol-economy
10. Biofuels, The Fuel of the Future 2010. Retrieved from http://biofuel.org.uk/bioalcohols.html
11. Anderson JE et al (2010) Octane numbers of ethanol- and methanol-gasoline blends estimated from molar concentrations. Energy Fuels 24(12):6576–6585
12. Nicholas RJ (2003) The methanol story: a sustainable fuel for the future. J Sci Ind Res 62:97–105
13. Bio-Residue Map of India. Retrieved from: http://lab.cgpl.iisc.ernet.in/atlas/Atlas.aspx
14. Joshi R, Ahmed S (2016) Status and challenges of municipal solid waste management in India: a review. Cognet Environ Sci 2:1139434
15. Knittel K, Boetius A (2009) Anaerobic oxidation of methane: progress with an unknown process. Annu Rev Microbiol 63:311–334
16. Anthony C (1982) The biochemistry of methylotrophs. Academic Press, London, p 431

17. Boetius A et al (2000) A marine microbial consortium apparently mediating anaerobic oxidation of methane. Nature 407:623–626
18. Whittenbury R, Phillips KC, Wilkinson JF (1970) Enrichment, isolation, and some properties of methane-utilizing bacteria. Microbiology 61:205–218
19. Hanson RS, Hanson TE (1996) Methanotrophic bacteria. Microbiol Rev 60(2):439–471
20. Fei Q et al (2014) Bioconversion of natural gas to liquid fuel: opportunities and challenges. Biotechnol Adv 3:596–614
21. Sharp CE et al (2014) Distribution and diversity of verrucomicrobia methanotrophs in geothermal and acidic environments. Environ Microbiol 16(6):1867–1878
22. Hutton WE, Zobell CE (1949) The occurrence and characteristics of methane-oxidizing bacteria in marine sediment. J Bacteriol 58(4):463
23. Bowman J (2006) The methanotrophs—the families methylococcaceae and methylocystaceae. Prokaryotes 5:266–289
24. Hinrichs Ku et al (1999) Methane-consuming archaebacteria in marine sediments. Nature 398(6730):802–805
25. Hwang IY et al (2015) Batch conversion of methane to methanol using *Methylosinus trichosporiu*m OB3b as biocatalyst. Microbiol Biotechnol 25(3):375–380
26. Blanksby SJ, Ellison GB (2003) Bond dissociation energies of organic molecules. Acc Chem Res 36(4):255–263
27. Park D, Lee J (2013) Biological conversion of methane to methanol. Korean J Chem Eng 30(5):977–987
28. Hur DH et al (2016) Highly efficient bioconversion of methane to methanol using a novel type 1 *Methylomonas* sp. DH-1 newly isolated from brewery waste sludge. Chem Technol Biotechnol 92(2):311–318
29. Hwang IY et al (2014) Biocatalytic conversion of methane to methanol as a key step for development of methane-based bio-refineries. J Microb Biotechnol 24(12):1597–1605
30. Duan C (2011) High-rate conversion of methane to methanol by *Methylosinus trichosporium* OB3b. Biores Technol 102(15):7349–7353
31. Frank J et al (1989) On the mechanism of inhibition of methanol dehydrogenase by cyclopropane-derived inhibitors. FEBS J 184(1):187–195
32. Furuto et al (1999) Semicontinuous methaol biosynthesis by *Methylosinus trichosporium* OB3b. J Mol Catal 144:257–261
33. Xin JY et al (2009) Production of methanol from methane by methanotrophic bacteria. Biocatal Biotransform 22(3):225–229
34. Kim HG et al (2010) Optimization of lab scale methanol production by *Methylosinus trichosporium* OB3b 15(3):476–480
35. Kalyuzhnaya MG et al (2015) Metabolic engineering in methanotrophic bacteria. Metab Eng 29:142–152
36. Duan Z, Mao S (2006) A thermodynamic model for calculating methane solubility, density and gas phase composition of methane-bearing aqueous fluids from 273 to 523 K and from 1 to 2000 bar. Geochim Cosmochim Acta 70(13):3369–3386
37. Vendruscolo F et al (2012) Determination of oxygen solubility in liquid media. ISRN Chemical Engineering
38. Guo H et al (2013) In situ Raman spectroscopic study of diffusion coefficients of methane in liquid water under high pressure and wide temperatures. Fluid Phase Equilib 360:274–278
39. Han P, Bartels DM (1996) Temperature dependence of oxygen diffusion in H_2O and D_2O. J Phys Chem 100(13):5597–5602
40. Sheets JP et al (2016) Biological conversion of bio-gas to methanol using methanotrophs isolated from solid-state anaerobic digestate. Biores Technol 201:50–57

Assessing the Effect of Temperature on Performance of the High Altitude Anaerobic Digesters

Pushpa Singh, Subodh Sharma, Bivek Baral, N. R. Khatiwada and Surya Man Shakya

1 Introduction

According to BSP [3], biogas is the mixture of gas which is produced by methanogenic bacteria while the organic matter is decomposed in an anaerobic condition. It is composed of methane (60–70%), carbon dioxide (30–40%), and some other gases. It is about 20% lighter than air. Biogas is similar to that of LPG as it is odorless that burns with a clear blue flame.

Proper functioning of biogas system leads benefits to users including renewable energy sources, organic waste transformed to high-quality fertilizer, improvement of hygienic conditions through reduction of pathogens, reduction of firewood used for cooking and heating, and the improvement of quality of soil, water, air, and vegetation [10]. Mainly studies concern in biogas production has been conducted in countries having warm weather and at sea level. At intermediate altitudes (1000–3000 m above

---

P. Singh (✉) · S. Sharma · N. R. Khatiwada
Department of Environmental Science and Engineering,
Kathmandu University, P.O. Box-6250, Dhulikhel, Nepal
e-mail: singhpushpa07@gmail.com

S. Sharma
e-mail: subodh@ku.edu.np

N. R. Khatiwada
e-mail: nawa@ku.edu.np

B. Baral
Department of Mechanical Engineering,
Kathmandu University, P.O. Box-6250, Dhulikhel, Nepal
e-mail: bivek@ku.edu.np

S. M. Shakya
Department of Civil and Geomatics Engineering, Kathmandu University,
P.O. Box-6250, Dhulikhel, Nepal
e-mail: suryamanshakya@yahoo.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_46

the sea level), there have been only a few studies, whereas above 3000 m over the sea level, no studies have been published.

Anaerobic digestion is normally operated at defined and constant temperatures. Nevertheless, a situation exists in which the reactors are subjected to repeat in sudden and abrupt changes of temperature. The anaerobic digestion process is classified into three different temperature ranges, namely psychrophilic (<20 °C), mesophilic (20–40 °C), and thermophilic (>40 °C) [5]. The microorganisms involved in anaerobic digestion are characterized by optimal temperature and upper limit that would cause immediate death of the considered group of bacteria [4].

The methane production from anaerobic digestion of livestock manures depends on various parameters including hydraulic retention time, temperature, and solid loading [6]. In many researches, a strong temperature effect has been observed and bio-methanation process at mesophilic and thermophilic ranges is more favorable [8]. There is severe lack of fundamental knowledge concerning the anaerobic digestion at psychrophilic digestion [7].

The main aim of this work was to assess the type of feed used in anaerobic digesters for biogas production at different temperature ranges. The cow dung was found to have highest biogas production under mesophilic condition that that of psychrophilic. From the experiment conducted and the graphical representation, mesophilic temperature was found to be more efficient for the higher yield of biogas. Hence, at high altitude having cold climatic condition, heating is required for the production of a sufficient amount of biogas.

2 Study Area

The research was carried out in Moharigaun of Jumla district. It is one of the remote and underdeveloped districts of Nepal. The temperature of the district from November through January is very low, which also make it difficult to travel across the district. The livelihoods get impacted during pre- and post-monsoon winds as the air is very dry. The topography of Jumla is characterized by three parts: high hill and rocky mountain partially covered by snow; lower hill with grazing meadows; and low lands where most agriculture and towns are found. August to November is the main tourist season in the district. Jumla is located at elevation of 915–4679 m above sea level. The average temperature in Jumla varies between 30 °C (it is hottest from May through July) and 12 °C, although during winter (November January) it can reach –11 °C.

3 Materials and Methods

Different substrates such as cow dung (CD), horse dung (HD), and sheep dung (SD) were collected from Moharigaun of Jumla district, whereas human feces (HF) and vegetable (potato) residue were collected from houses from Dhulikhel. For the purpose of this study, cow dung was used as inoculum. A sample of fresh cow dung was collected from household area near Dhulikhel. The inoculum was prepared by mixing fresh cow dung with the same weight of water. Cow dung is used as inoculum because of neutral pH, as it contains naturally occurring microbes responsible for anaerobic degradation, high buffering capacity, provides an array of digestion and is available in large quantities. Total solid is determined for estimation of water content of feedstock and volatile solid is carried out along with total solids.

Biochemical Methane Potential (BMP) test was conducted to determine the methane yield of feedstock. The feedstock sample and inoculum were weighted and filled into sample bottle of 125 ml leaving 1/3 for headspace. Then, the bottles were maintained at C:10 °C, G:17 °C, H1:32 °C, and H2:42 °C in a thermostat water bath. The temperature was monitored at regular interval of 12 h. A laboratory scale mini digesters were designed to carry out the experiment. A plastic tank with 25 l capacity was used and two valves were fitted in the tank. The inlet valve was used to feed the digester, whereas outlet valve was used to empty the digester. The digesters were kept air-tight to prevent from entering atmospheric air and gas leakage and ensured that the digestion is anaerobic. Each of the eight digesters was filled with 8.5 l of inoculum leaving 1/3 for headspace in digester. The digester worked under uncontrolled pH, which is without acid or base addition. The digesters were adjusted for 3 days before feeding. The digesters were vigorously shaken by hand, and then incubated in ply box (acts as an insulator) with occasional manual shaking where water was maintained at temperature 17 and 42 °C under mesophilic and thermophilic conditions. Temperature monitoring was performed at regular interval of 12 h. A thermometer was used to determine the daily temperature. The potato residues were cut into small pieces by a knife to increase the surface area of organic matter and digestibility.

Various substrates were weighted, mixed together, and fed into digester according to Table 1. Then, water was added depending on total solid concentration. The digesters were fed semi-continuously, once per day. As biogas production began in digester, it was delivered to bottle (5 l) containing water. The biogas was measured daily by water displacement method. Gas production was lacking near the final stage of decomposition of the organic matters. The gas production from the sample bottles for the BMPs test was measured daily by using syringe injection method.

Table 1 Substrate weight (gm) for daily feeding of digesters

S. No.	Digester mixing	Cow dung	Horse dung	Sheep dung	Human feces	Potato residue
1	D1	89		8		3
2	D2	68		6	24	2
3	D3	34	61	3		2
4	D4	31	55	3	11	

4 Results

4.1 Physical Analysis

The amount of total solids found in cow dung, horse dung, human feces, and sheep dung are 23.12, 23.28, 8.6 and 53.98%, respectively. Whereas, volatile solids found in cow dung, horse dung, human feces, and sheep dung are 19.72, 18.18, 7.45 and 43.8%, respectively.

4.2 Biogas Production from BMP

In this project, cow dung, sheep dung, horse dung, human feces, and inoculum were used as feedstock. The experiment was conducted for 45 days. The biogas production by CD and HD was slow at starting, then gas production increased after few days as shown in Fig. 1. This is because of the lag phase of microbial growth at the beginning and due to exponential growth of methanogens, high production of biogas was observed later. According to past literature, the horse dung consists of about one half of straw which was disposed of from the feed of the animals or as bedding in the stables together with the excrement, and due to high lignin, the microorganism can hardly ferment the straw which leads to extremely long residence time in the anaerobic digester. This was the main reason behind the declination of gas production after few days of setup. In human feces, there was a rapid increase in biogas during the first day reaching to highest gas production and then quickly, production went on decreasing as shown in Fig. 2. As there is an occurrence of methane from human intestine, hence, methanogenic organisms grow in the human alimentary tract. Since methane gas formation process is already completed so the production is rapid in HF. According to past literature, the reason for less production of gas from human excreta is the low ratio C/N which about 6–10, which is lower than the ratio of C/N that is expected on biogas production by 25–30. In the case of SD, the gas production is at the initial phase but after few days from setup, the gas production is decreased and at some stages it is zero. To start and accelerate fermentation process, small amount of digested slurry, containing methane-forming bacteria is added to freshly charged plant, this is known as seeding. The inoculum was used as seeding for the substrate and also it helps in enhancing the amount of gas production. Hence, low gas production can be seen in RF. Among various types of feed used cow dung is very efficient regarding gas production as it contains high percentage of organic carbon value and also due to the presence of predominant bacteria called *rumen* in cow dung.

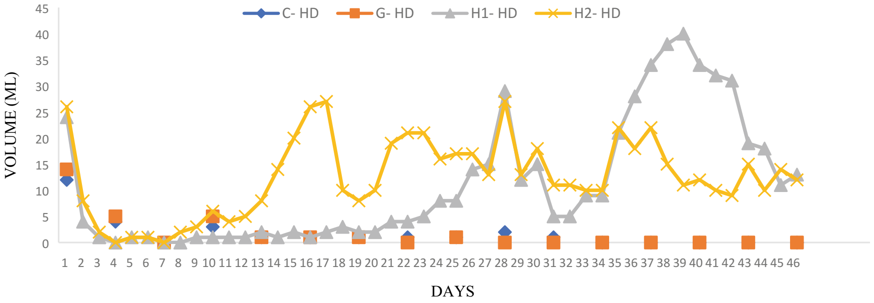


Fig. 1 Gas production from horse dung at four different temperatures

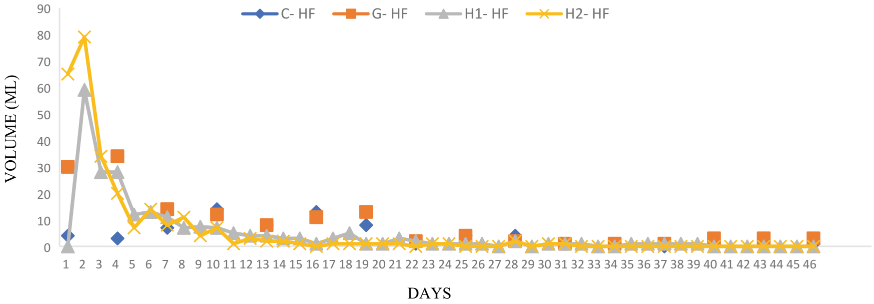


Fig. 2 Gas production from human feces at four different temperatures

4.3 Biogas Production from Digester

Calculations from Table 1 are used for feeding in four different mini digesters which is kept at temperature of 17 and 42 °C. The feeding for each digester was of different compositions so that the gas production rate is also different from different feeds used. The gas production capacity of the mesophilic temperature was efficient. Liden [1], concluded the result of the past research on the production of biogas from cow dung and cowpea have shown that flammable biogas can be produced from these wastes through anaerobic digestion. These wastes are always available in our environment and can be used as a source of fuel if managed properly. The study further revealed that cow dung as animal manure has great potentials for generation of biogas and its use should be encouraged due to its early retention time and high volume biogas yields. The Digester 4 with the composition of cow dung, horse dung, sheep dung, and human feces produces more gas which is 4.12 L in 22 days from 2.2 kg substrates as shown in Figs. 3 and 4 which represents the volume of gas produced as a function of time.

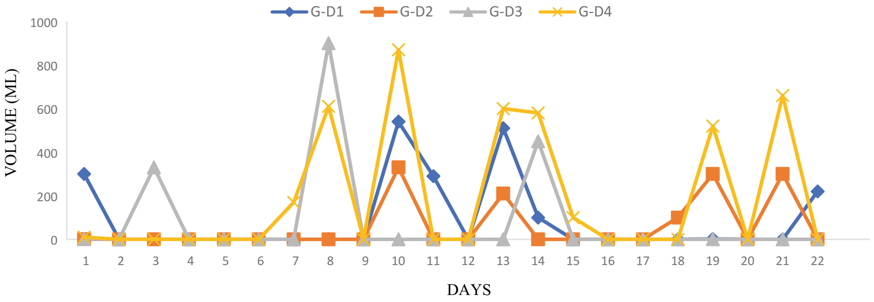


Fig. 3 Gas production at psychrophilic temperature

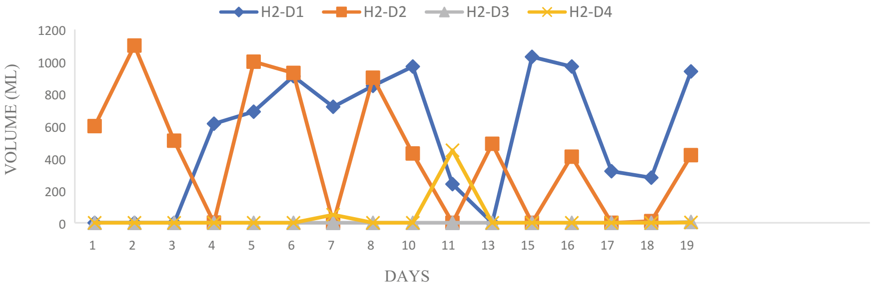


Fig. 4 Gas production at mesophilic temperature

4.4 Temperature Variation

The temperature was monitored and maintained at regular interval of 12 h., no any sharp decrease in temperature was noted as shown in Figs. 5 and 6. The considered regime used in the case is two temperature ranges, i.e., psychrophilic and mesophilic range. According to Liden et al. [2], the rise or fall of the temperature for 5 °C is normal and this change of temperature is acceptable. The real variation of temperature is also of 5–6 °C, which means that the processes were fully under control. The temperature maintained for the mini digesters were psychrophilic and mesophilic temperature and the change in temperature is also about 5–6 °C. The total change in temperature is acceptable hence the process was fully under control.

5 Discussion

The initial rise and gradual fall in gas production was observed in the cow dung, horse dung, sheep dung, greenhouse residue, human feces, and reference, due to carbon dioxide produced by the aerobic bacteria which used up the available oxygen trapped in the mixture to breakdown complex compounds to simpler forms. As

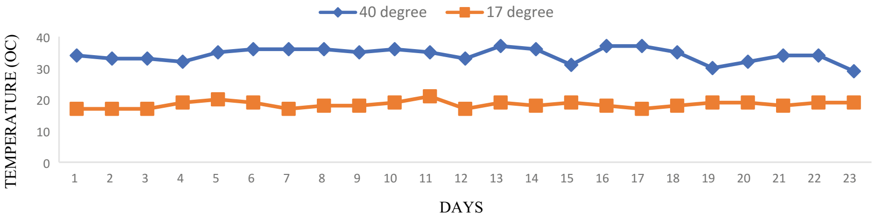


Fig. 5 Temperature variation for the anaerobic digestion process

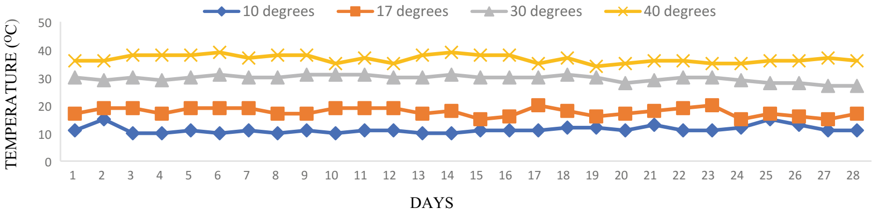


Fig. 6 Temperature variation for the BMPs test

the amount of oxygen available in the BMP bottle and digester was being used up, the amount of carbon dioxide being produced decreased until all the oxygen was used up. At this point, the activity of the aerobic bacteria was halted and anaerobic activity of methanogenesis took over. The methane-forming bacteria have a very slow growth rate, hence explaining the gradual rise in gas production and after the initial fall, methane gradually builds up. The hydrogen used to reduce carbon dioxide was obtained from the degradation of organic compounds. Gas production was affected by temperature due to the fact that the bacteria population responsible for both fermentation and gas production were known to carry out these activities better at thermophilic temperature range. Human feces have maximum potential for biogas generation because it has more methane gas composition. Human feces were mixed with cow dung to enhance the gas production rate, where cow dung have already greater C:N ratio, Tafdrup [10]. Due to the forced cyclic variations of temperature, it causes large cyclic variations in the rate of gas production and the methane content. Low-ambient temperatures, <20 °C, causes drastic reduction in the efficiency of anaerobic process due to low growth rate of the constituent bacterial consortium. The cold temperature retards the growth rate of the microbes responsible for AD; this tends to a drop in biogas production at high altitude.

6 Conclusion

Locally available and abundant wastes have been investigated to establish the possibility of utilizing them as an alternative source of energy. Thus, results indicated that cow dung, horse dung, and human feces have high biogas formation potential in comparison to other substrates. An effective way to prolong the period of the highest gas production and to improve biogas yield the co-digestion with suitable substrate mixture is necessary. From the experiment conducted, mesophilic temperature was found to be more efficient for the higher yield of biogas. As Jumla district is at higher altitude having cold climatic condition, and for the production of sufficient amount of biogas, heating is required. Hence, for the effective and efficient biogas production, heating is required in the case study area.

7 Recommendation

Previous study was conducted for the effects of temperature on anaerobic digestion process of Jumla district. In order to make the study more relevant, the different composition of feeds was used to investigate the maximum amount of gas production at different temperatures. There were plenty of studies regarding socioeconomic, gender-related issues, adopting aspects of biogas plants done, but only few studies regarding the temperature effects on anaerobic digestion at higher altitude. Pilot installations (family size) are necessary to provide more realistic insights for realistic firewood replacement figures and operational challenges, Singh et al. [9]. This project work was completed in a short period of time with only available facilities. Due to time constraints and apparatus unavailability, some recommendations are as follows: instead of water displacement method for gas measurement, other advanced technology can be used for preventing leakages. In rural population, biogas is the main source of renewable energy but it is also an abundant and appropriate source of energy for urban population, having potential to replace fossil fuel. Hence, research and proper interest must be given toward the advanced use of biogas.

Acknowledgements We would like to extend our heartfelt wishes and gratitude to the team of this research work, Ms. Gyanu Giri and Ms. Luniva Bajracharya. We are particularly grateful to Department of Environmental Science and Engineering, Kathmandu University, Nepal, Alex Zahnd, Christoph Hugi and Thomas Gross. We acknowledge financial support received through the Seed Money Programme by ETH Global Switzerland. We are indeed to the households of Jumla for providing the substrates for the research work.

References

1. Alvarez R, Vilica S, Liden G (2006) Biogas production form Ilama and cow manure at high altitude. Biomass Bioenerg 30:66–75
2. Alvarez R, Liden G (2008) The effect of temperature variation on biomethanation at high altitude. Bioresour Technol 99(15):7278–7284
3. BSP-Nepal (2005) BIOGAS as renewable source of energy in Nepal, theory and development. Kathmandu

4. Chen M (1983) Adaptation of mesophilic anaerobic sewage fermentor population to thermophilic temperatures. Appl Environ Microbiol 45(4):1271–1276
5. El-Mashad HM, Zeeman G, van Loon WKP, Gerard PAB, Lettings G (2004) Effect of temperature and temperature fluctuation on thermophilic anaerobic digestion of cattle manure. Biores Technol 95(2):191–201
6. Hashimoto AG (1982) Methane from cattle waste: effect of temperature, hydraulic retention time, and influent substrate concentration on kinetic parameter (K). Biotechnol Bioeng 24:2039–2052
7. Kashyap DR, Dadhich KS, Sharma SK (2003) Biomethanantion under psychrophilic conditions; a review. Biores Technol 87:147–153
8. Nozhevnikova AN, Kosyurbenco OR, Parshina SN (1999) Anaerobic manure treatment under extreme temperature conditions. Water Sci Technol 40(1):215–221
9. Singh KJ, Sooch SS (2004) Comparative study of economics of different models of family size biogas plants for state of Punjab, India. Energy Convers Manag 45(910):1329–1341
10. Tafdrup S (1995) Viable energy production and waste recycling from anaerobic digestion of manure and other biomass materials. Biomass Bioenerg 9:303–314

Recyclable Materials as Catalysts for Nonbiodegradable Organics in Water Treatment

S. B. Jonnalagadda, Suresh Maddila and Venkata D. B. C. Dasireddy

1 Introduction

The use of chlorinated organics, in particular, chloro phenols is wide in varied spheres of industries and environment, as solvents, precursors in synthesis, preservatives, and pesticides to mention a few. Those are refractory compounds with long life persisting in water systems and soils and are mutagenic in nature [1]. They have a tendency to accumulate in organisms and animal tissue. These nonbiodegradable chemicals entering into water systems are of serious health concern. Their removal poses serious challenges. Furthermore, chlorophenols are bio-refractory and once released into ecosystems, over a period of time, tend to accumulate in animal tissue. This raises an urgent need for efficient dechlorination methods to eliminate chloro functionalities from both concentrated and diluted industrial effluents which pollute the groundwater [2].

While the removal of these toxic organics from wastewater effluents prior to entering the water bodies is a solution to the problem, addressing the issue varied techniques have been investigated. Although the removal of organic pollutants by adsorption/desorption approach is cost-effective, most of the adsorbent materials are not recyclable. Hence, the disposal of the secondary pollutants are again to be addressed. Furthermore, the disposal of solid disposal consisting of chlorinated organics by incineration has the danger of producing potentially more toxic gasses. The complexity of the biologically nondegradable can be degraded partially by oxidative methods, by the use of advanced oxidation processes (AOPs) for their effective degradation to small and safer molecules. The AOPs, a combination of one or more techniques, such as use of oxygen, oxidants, UV/Visible light, and catalysts were proved to be effective in elimination of toxic organics even at low concentrations. Literature reports show many of the aromatic compounds can be degraded to smaller

---

S. B. Jonnalagadda (✉) · S. Maddila · V. D. B. C. Dasireddy
School of Chemistry and Physics, University of KwaZulu-Natal, Durban, South Africa
e-mail: jonnalagaddas@ukzn.ac.za

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_47

molecules, such as carboxylic compounds and aldehydes [3]. The use of appropriate catalysts, UV, etc., which facilitate the increase in hydroxyl radical concentration can give greater efficiencies.

Heterogeneous materials, solid catalysts are preferred over homogeneous catalysts due to the scope for easy recovery and recyclability. In the AOPs, using ozone as oxidant, the characteristics of catalyst, in particular The basicity and acidity of surface plays a vital role in enhancing their ability to absorb ozone as it facilitates the faster decomposition ozone to hydroxyl radicals [4]. Cost-effective and eco-friendly catalyst materials are crucial for the viable process of treatment of toxic organics in water systems. Over the years, many support materials such as hydrotalcite-like compounds(HTlcs), zeolites, clays, etc., have been explored as support materials with varied metals have been loaded/exchange as active materials to enhance their overall activity. HTlcs with high anionic exchange capacity, approximately (100–150 cmol(+)/kg), allow the ion exchange with the anions in the water systems. Wide choice of cations have been loaded modifying the properties of the HTLcs and those upon calcination are known to give well-mixed oxides. Their thermal stability, high surface area, with the formation of very small stable metal crystallites under reducing conditions, synergetic effects between elements in the active and support are of vital importance to act as good catalysts [5]. In this study, we focussed on the scope of Zn or Mg VCO_3 and VPO_4 hydrotalcites, as heterogeneous catalysts for the ozone-initiated dechlorination and degradation of chloromethylphenol (CMP), a widely used precursor in pharmaceutical and chemical industries.

2 Preparation of Catalysts

The layered double hydroxides $MgVCO_3$, $ZnVCO_3$, $MgVPO_4$, and $ZnVPO_4$ HTlcs with 1:0.8:0.2 (molar ratio) by coprecipitation method were prepared at constant pH [6]. The solution with metal nitrates of Mg, V, and Zn at desired concentrations, 0.35 mol NaOH and 0.15 mol Na_2CO_3/ammonium hydrogen phosphates were simultaneously mixed slowly at 50 mL/h, in one liter beaker, under constant stirring at 35 °C, while pH maintained between 10 and 11.5. The precipitate formed was aged for 18 h at 65 °C and the precipitate obtained was recovered by filtration. The precipitate was repeatedly washed with deionized water until it is free of nitrate ion. The wet precipitate was dried at 80 °C for 12 h to obtain the HTlcs. The prepared HTlcs was calcined at 500 °C for 4 h, to obtain the material labeled as HTlc 500.

3 Ozonalysis Experiments

For the ozone aeration experiments, O_3 was generated by passing compressed oxygen through a Fischer Ozone 500 generator, which converted oxygen to ozone by the electric discharge via the corona discharge method. All the experiments were carried out in a semi-batch reactor, out under the controlled conditions of room temperature (20 ± 1) °C using 25 mL 10% w/v of 4-chloro-3-methylphenol (CMP) in water and aerating the ozone-rich oxygen stream at flow rate (100 ml/min) and fixed ozone concentration (0.05 M) for 5 h.

4 Product Identification

Control experiments showed no progress of the reaction in absence of ozone, with oxygen bubbling alone. During the ozone aeration, aliquots of reaction mixture were collected at 30 min intervals for analysis. The organic components from the aliquot were extracted and analyzed by GC-MS. Two products were separated and identified by GC-MS. The peaks appeared at retention time, 9.5–13.0 refer to varied carboxylic acid compounds formed due to further degradation of the main products of the reaction. The peak at retention time 9.8 refers to the first product degradation of oxalic acid (OA). Further, the degradation of hydroxyl-3-methylfumaric acid (HMFA) is confirmed by injecting the substrate, which elutes at the retention time of 12.6. Based on the results from the mass spectra and the reference standards, the first oxidation product was identified as hydroxyl-3-methylfumaric acid (HMFA) and the second product was oxalic acid (OA). The ^{1}H-NMR spectrum of HMFA exhibited broad two singlet protons for the COOH group at δ 11.92 ppm and singlet at δ 8.01 ppm for the OH group, respectively. The LC-MS mass spectrum showed m/z peak at 147 $(M+H)$. Similarly, oxalic acid showed a broad singlet at δ 13.05 ppm for COOH protons. Furthermore, the LC-MS mass spectrum showed at m/z at 91 $(M+H)$. The functional groups observed in the ^{1}H-NMR and LC-MS spectrum were in good agreement with spectra corresponding to hydroxyl-3-methylfumaric acid and oxalic acid. Further, the qualitative test (limewater) confirmed the release of CO_2 during the ozonation reaction and suggested partial mineralization of the target compound.

5 Effect of the pH

In aqueous solutions, pH is a key parameter for ozone stability. While molecular ozone relatively stable in acidic conditions, under alkaline conditions rate decomposition of ozone and formation of ·OH radical are accelerated. Relative to molecular ozone, with higher oxidation potential, the hydroxyl radical attacks the organic species much faster. Thus, if hydroxy radical is the reactive species, it is expected to enhance the rate of degradation of CMP under alkaline pH. On the other hand, the pH and water affect the surface property of the catalysts, which are covered by surface hydroxyl groups. For the calcined mixed metal oxide catalysts from the hydrotalcite precursors, under different pH conditions, there exists proton transference on the catalyst surface.

The effect of initial pH (3, 7, and 11) on the degradation of CMP was investigated over a 120 min ozonation duration using the uncalcined and calcined catalysts. Sodium hydroxide or sulfuric acid was used to adjust the solution to the required pH and the solution was exposed to ozone stream with flow rate of 1.0 L/min. The profiles of percentage conversion as function time, obtained under varied pH conditions using different catalyst materials. The observation of the curves indicates that the percentage conversion of substrate increased with pH for the carbonate supported catalysts, indicating that ·OH play the lead role in the oxidative attack. Among the uncalcined catalysts, $ZnVCO_3$ catalysts showed high conversion followed by $MgVCO_3$ catalysts. Interestingly, the effect of pH is inversed over the PO_4 precursors. As the pH increased, the percentage conversion of phenol decreased suggesting with these catalysts molecular ozone could be reactive species. Calcined catalysts also followed the same trend as uncalcined catalysts but all the calcined catalysts exhibited higher conversions relative to uncalcined catalysts. The presence of the proton transference on the surface of the mixed metal oxides, which are formed from hydrotalcite precursors, might be the probable reason for the high conversion of CMP over calcined catalysts. The surface proton species have associations with the adsorption of organic on the catalysts. From the results, it can be deduced that depending on the solution pH, the catalyst enhances the degradation of the chlorinated organic substrate, through faster conversion of molecular ozone to hydroxyl and other radicals, which have higher reactivity.

All the catalysts with carbonate precursors showed low conversion range in acidic medium. To confirm the full conversion (100%), a time-line analysis is conducted. Calcined catalysts showed the 100percentage conversion ~180 min whereas the uncalcined catalysts achieved the full conversion in ~210 min. This could be probably due to the proton species, which are associated with the surface of the calcined catalysts, which increase the adsorption of organics on the catalyst surface. The catalysts with Zn metal (calcined and uncalcined) showed the greater conversion efficiency compared to the Mg-containing catalysts. This could be probably due to the less acidity of catalysts containing Zn metal relative to the catalysts containing Mg metal, which increases the adsorption of the acidic phenols on the catalyst surface containing Zn metal. The selectivity toward HMFA is high for the uncalcined catalysts compared to the calcined catalysts. As the reaction duration increased, the selectivity toward HMFA decreased with increased conversion to OA. All the carbonate-based catalysts showed low conversion at acidic pH, while hydrotalcites with PO_4 precursors showed the optimum conversion in acidic medium. While all calcined catalysts showed high conversion relative to the uncalcined catalysts, the calcined catalysts with Zn metal showed better conversions compared to the catalysts with the Mg metal. Selectivity toward HMFA decreased with the time of the reaction as HMFA is further oxidized to OA, resulting in increased selectivity toward OA (Fig. 1). The selectivity toward OA is not influenced by the time on line analysis since the starting material is 100% converted to form OA.

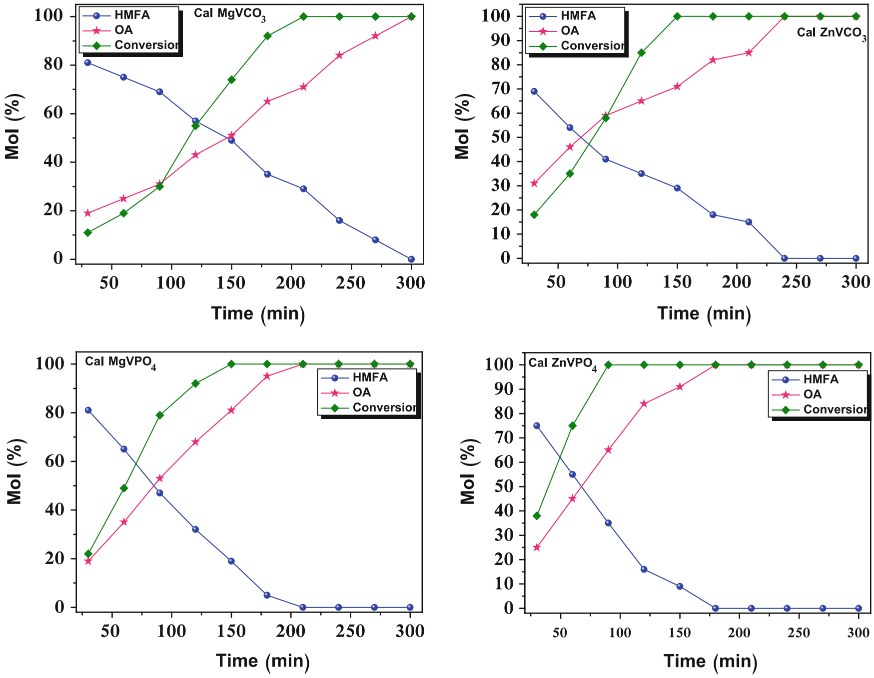


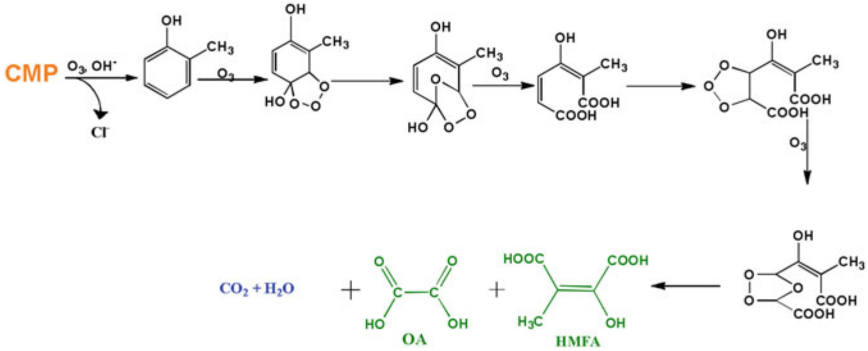
Fig. 1 Percentage conversion of CMP and product profile with ozone aeration with four catalysts: Calcined ZnV/CO_3 or PO_4 and MgV/CO_3 or PO_4 hydrotalcites

6 Effect of Transition Metal in Hydrotalcite

The catalytic activity exhibited by different catalysts studied was due to the synergy in the active sites of transition metal and the precursor on the catalyst surface and catalyst surface area of the catalyst showed marginal effect. While different catalyst materials have different catalytic efficiencies, the efficacy of specific catalyst toward degradation of different organic substrates varies due to their differences in adsorption abilities to those compounds and the adsorption of organic model substances on the catalyst's surface plays important role in its oxidative degradation [7]. Furthermore, the main characteristic that determines the activity of the catalyst is acidity and basicity. The hydroxyl groups formed at metal oxide surface behave as Bronsted acid sites, while the Lewis acids and Lewis base sites are, respectively, located on the metal cation and coordinatively unsaturated oxygen. Both Bronsted and Lewis acid sites are considered to contribute as active catalytic centers of metal oxide [8].

7 Proposed Mechanism

In general terms, it is proposed that CMP binds to an active site on the catalyst surface, lowering the activation energy. Either molecular ozone and/or the reactive radicals generated by the decomposition of ozone on the catalyst surface, in oxidative attack abstract electrons from the aromatic molecule. This causes the dechlorination of the aromatic subtract and its oxidative degradation. The desorbed product/intermediate is further oxidized leading to smaller molecules, such as carboxylic acids. The ozone initiated catalyzed degradation of CMP probably occurs in a number of sequential steps, initiating the hydroxylation aromatic ring and finally to the breakdown and partial mineralization of organic compound, the transformation of aromatics to aliphatic by the destruction of ring structures (Scheme 1) [6].



Proposed mechanism for the ozone facilitated catalysed degradation of chloromethylphenol

The hydroxylation of the aromatic ring is considered to be an initial and important step in the reaction sequence. With high redox potential of ·OH radical ($E_0 = 2.8$ V), generated by the heterogeneous surface of the catalyst, $^-$OH plays the vital role in the degradation of the chlorophenol. The reaction of $^-$OH with the aromatic compounds, which involve its electrophilic addition to the aromatic ring with the formation of a ·OH is well-known. It is proposed that, at first, $^-$OH could attack the chlorophenol molecule selectively bound on catalyst surface, resulting in the occurrence of electron transfer and dechlorination (Scheme 1).

The dihydroxy toluene was reported to react with ·OH to form methyldienedioc acid, followed by its cleavage, degradation, and mineralization through oxidative processes. However, the intermediate was detected only under relatively mild oxidizing conditions. Due to the strong electrophilic effect of hydroxyl groups, the C–C bonds between the adjacent hydroxyl groups are known to be destabilized. Such destabilized bonds undergo oxidative ring opening reactions easily leading to aliphatic compounds [9]. The cleavage of the compound under strong oxidative conditions was so rapid that no detectable amount of methyldienedioc acid remains. The aliphatic acids formed get further oxidized leading to other smaller compounds and partial mineralization to CO_2 and H_2O.

8 Conclusions

Calcined Zn or Mg/VPO_4 catalysts were efficient under acidic pH and Zn or Mg/VCO_3 exhibited improved activity under alkaline pH. Phosphate-containing catalysts proved to be better catalysts than carbonate catalysts. The oxidation CMP was quantitative with 100percentage conversion and 100% dechlorination. The hydroxyl-3-methylfumaric acid (HMFA) and oxalic acid (OA) are the oxidation products and mineralization occurred at tertiary level.

References

1. Chao T, Guibin J (2005) Chemosphere 59:321–326
2. Esplugas S, Gimenez J, Contreras S, Pascual E, Rodriguez M (2002) Water Res 36(4):1034–1042
3. Chetty EC, Maddila S, Southway C, Jonnalagadda SB (2012) Ind Eng Chem Res 51:2864–2873
4. Li P, He C, Cheng J, Ma ChY, Dou BJ, Hao ZP (2011) Appl Catal B 101:570–579
5. Maddila S, Dasireddy VDBC, Oseghe EO, Jonnalagadda SB (2013) Appl Cat B 142:129–141
6. Ernst M, Lurot F, Schrotter JC (2004) Appl Catal B Environ. 47:15–25
7. Wang Q, Tay HH, Guo Z, Chen L, Liu Y, Chang J, Zhong Z, Luo J, Borgna A (2012) Appl Clay Sci 55:18–26
8. Ndabankulu NO, Maddila S, Jonnalagadda SB (2016) Glob NEST J 18(2):242–250
9. Wang H, Wang JL (2007) Appl Catal B Environ 77(1–2):58–65

Characterization of Essential Oil Extracted from a Kitchen Waste: Lemon Peel

M. R. Sarder and M. Alamgir

1 Introduction

The essential lemon oil is aromatic compound that is commonly used in the perfume, drug, and food sectors. Essential oil is a mixture of over than two hundred distinct compounds. EO is mostly made of monoterpene and sesquiterpene hydrocarbons and their oxygenated by-products such as aliphatic aldehydes, alcohols, ketones, and esters. EO is generally found in scented plants. The specific gravity of water is frequently more than EO. The compounds obtained from EO are soluble into most of the organic solvent such as diethyl ether, hexane, and ethyl acetate. EO in the presence of air and temperature are vaporized; consequently they might be named as volatile oil [1, 5]. The most significant is that the EO can be manufactured by distillation process and EO is not glycerol esters. The EO of lemon or citrus genus belongs to the Rutaceae family. Limonene is a single-cycle monoterpene, which is present in lemon peel [6]. Limonene can be observed as 32–98% into citrus EO [9]. The EO of some various kinds of lemon and citrus fruits has been examined through GC/MS analysis and noticed that the EO was mainly made of limonene, C-pinene, sytronelal, sabinene, neral, geranial, linalool, and acetate neryl at various concentrations depending on the sort of cultivar [8].

Citrus is one of the world's main fruit, which is produced in various places especially in tropical and subtropical environment. Generally, the quantity of citrus generation is estimated as 105 million metric tons (MMT) per year in the world. Furthermore, to large scale of citrus fruit is consumed as fresh fruits and the large amount of juice has been produced from citrus fruits. In the citrus fruit handling industry, after citrus juice extraction lots of wastes in terms of peels, pulps, and seeds have been generated equivalent to around 50% of the fresh treated fruit, these wastes can be

---

M. R. Sarder (✉) · M. Alamgir
Department of Civil Engineering, Khulna University of Engineering and Technology, Khulna, Bangladesh
e-mail: razibsarder08@gamil.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_48

recycled as a possible source of valuable by-products. Particularly, the citrus shells, commonly termed as agro-manufactured waste, are a probable source of beneficial supplementary plant metabolites and necessary oils [3]. Different kinds of bioactive constituents, specifically flavonoids, coumarins, carotenes, linalool, terpenes, etc., are present into EO of lemon peel [7]. Lately, Lemon peels EO have also been discovered for their inherent anti-oxidant and antimicrobial potentials [5].

2 Study Area

This research was done at KUET campus, Khulna of Bangladesh offering a special focus in the technological advancement, engineering education, and investigation. At present, it has about 5000 students, 18 academic departments under 3 faculties, 3 institutions and having a count of population is around 7000 such as students, teachers, officers, and other workers. The university having an area of 101 acre area appears at the northwest corner of Khulna City, about 12 km from the city center as shown in Fig. 1.

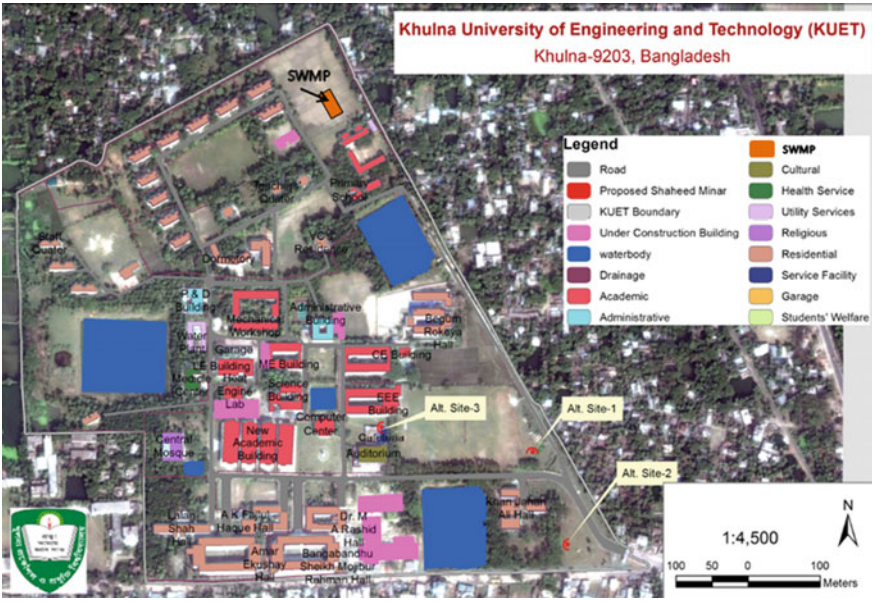


Fig. 1 Layout plan of KUET campus showing the location of WMP

3 Materials and Methods

3.1 Extraction of Essential Oils

For the characterization of essential oil extracted from lemon peel available in Bangladesh, at first peel has been removed with a knife from fresh lemon properly so that no oil gland of peel has been damaged. These peels have been cut into small pieces. Lemon peels were exposed to hydro-refinement for 4 h using Clevenger kind equipment shown in Fig. 2. The oil has been separated from water–oil combination with the help of dichloromethane (DCM) solvent by a separating funnel. The DCM contains oils and some water, water was removed over anhydrous sodium sulfate and DCM has been removed by passing nitrogen gas through DCM-oils mixture and oils have been kept in a wrapped vessel at 4 °C until further enquiry.

3.2 Gas Chromatography–Mass Spectrometry Analysis

The GC-MS investigation of the EO was done by a GC (Model: CP 3800 Varian) constructed with a MS (Model: Saturn 2200 Varian)-fused silica tube column (30 m × 0.25 m i.d., film thickness 0.25 µm). An electron ionization scheme with ionization force of 70 eV has been used in GC-MS/MS detection. Helium gas has been applied as a hauler gas at a continual flow speed of 1 ml/min. The temperature of injector and mass transmission line has been fixed at 220 and 280 °C, respectively. The oven heat

Fig. 2 Hydro-distillation process using Clevenger apparatus

range has been designed for 50–200 °C at 8 °C/min, then detained isothermal for 20 min and finally conveyed up to 280 °C at 10 °C/min and adopted for 10 min and the whole run time has been set as 57.57 min. The comparative amount of the EO elements was shown as fraction by highest area standardization. The determination of the constituents of the necessary oils has been assigned in the comparison to their holding indices, comparative to a series n-alkane indices on the ZB-1 capillary column and GC–MS spectra from the Wiley 6.0 MS data and literature data and whenever possible, by co-injection with authentic compounds [2, 4].

4 Results and Discussions

From the field-level investigation, it has been noticed that the SW generation rate at KUET campus has been found as 0.099 kg/capita/day during September 2016 to March 2017. Figure 3 represents the monthly SW generation at different month and noticed that SW has been generally increased from previous year.

Figure 4 symbolizes the composition of SW produced at KUET campus where food and vegetable, paper and plastic waste have been found as predominant and their percentage amount has been observed as 52.04, 42.01, and 3.70%, respectively. Small amount of lemon peel, eggshells, and other wastes have been generated as 0.30, 0.20, and 1.75%, respectively, in 7 months from September 2016 to March 2017.

Figure 5 delineates the essential oil analysis through GC-MS process and 125 numbers of compounds have been identified. In which limonene; phosphoric acid, tribornyl ester; Bicyclo[2.2.1]heptane,7,7-dim ethyl-2-methylene;

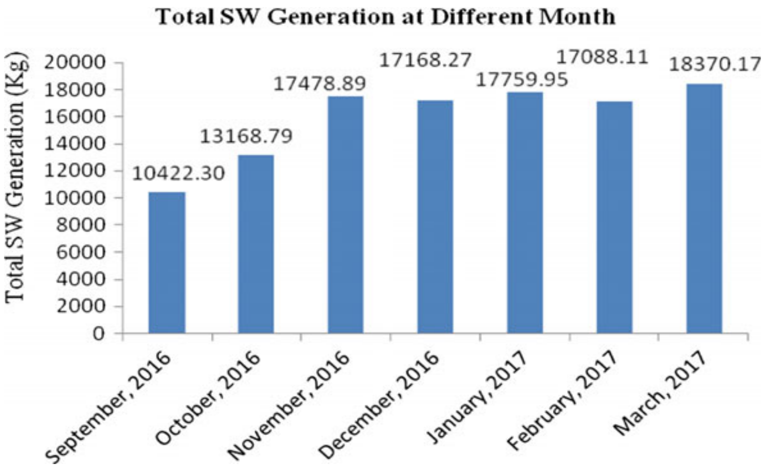


Fig. 3 Solid waste generation at different months

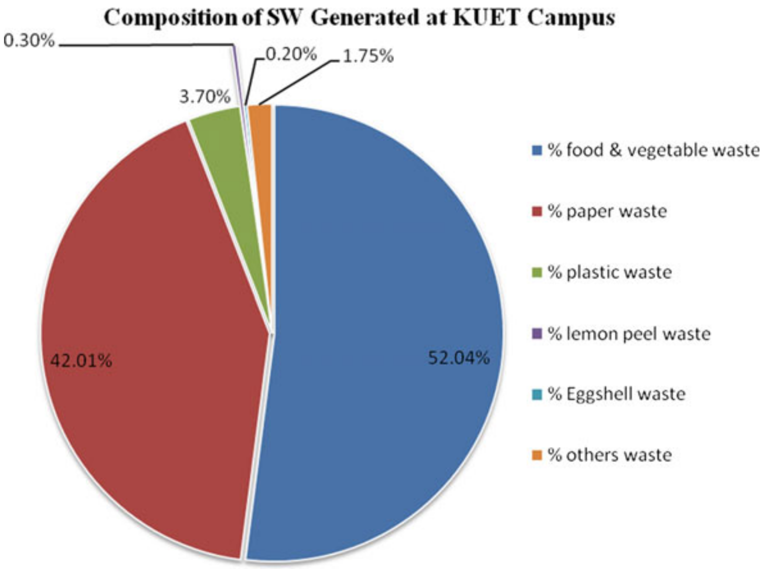


Fig. 4 Composition of SW generation at KUET campus

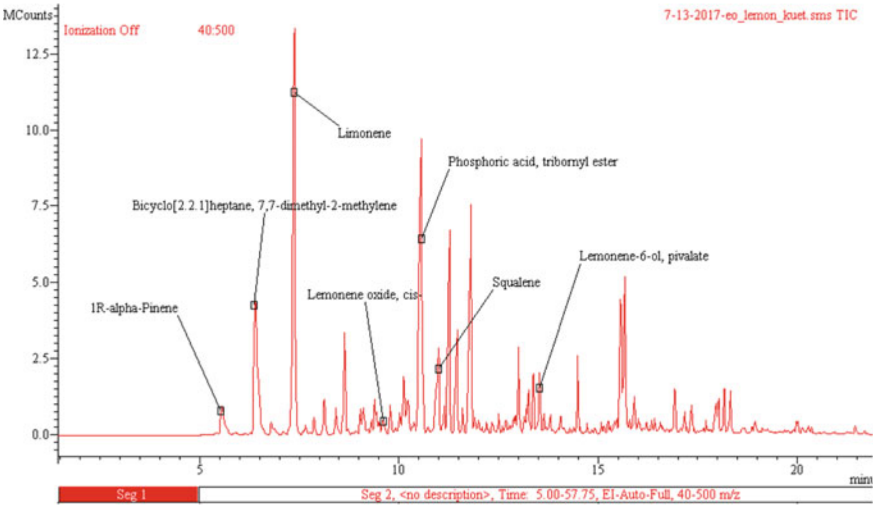


Fig. 5 GC-MS analysis of different elements of essential oil obtained from lemon peel

1,4-Methano-1H-indene,octahydro-1,7a-dimethyl-4-(1-methylethenyl); Squalene; Bicyclo[2.2.1]heptan-2-ol,1,3,3-trimethyl-, (1S-endo); 1R-alpha-Pinene have been found as predominant.

Table 1 represents the chemical composition of essential oils extracted from lemon peel and major component is found as Limonene and is 13.21%. From the GC-MS analysis, 125 numbers of compounds has been identified and among the major compounds are limonene; Phosphoric acid, tribornyl ester; Bicyclo[2.2.1]heptane,7,7-dim ethyl-2-methylene; 1,4-Methano-1H-indene,octahydro-1,7a-dimethyl-4-(1-methylethenyl); Squalene; Bicyclo[2.2.1]heptan-2-ol,1,3,3-trimethyl-, (1S-endo); 1R-alpha-Pinene; Artemiseole; Butanoic acid, 3,7-dimethyl-2,6-octadienyl ester, (E); Limonen-6-ol, pivalate; Bicyclo[3.1.1]hept-2-ene,2, 6-dimethyl-6; 2-Cyclohexen-1-ol, 1-methyl-4-(1-methylethyl)-, trans; Caryophyllene oxide; Diepicedrene-1-oxide; alpha-Methyl-alpha-[4-methyl-3-pentenyl]oxiranemethanol; Isoaromadendrene epoxide; alpha-Bisabolol; trans-p-Mentha-2,8-dienol; cis-p-Mentha-2,8-dien-1-ol, Bicyclo[3.1.1]hept-3-en-2-ol,4,6,6-trimethyl-, [1S-(1α,2β,5α)]-; exo-2-Hydroxycinede; 1-Naphthalenol,decahydro-1,4a-dimethyl-7-(1-methylethylidene)-, [1R-(1α,4aβ,8aα)]-; 7-Oxabicyclo[4.1.0]heptanes, 1-methyl-4-(1-methylethenyl)-; 6-Nonenal,3,7-dimethyl-; Bornyl chloride; Caryophyllene oxide; Ether,p-menth-6-en-2-yl methyl; Cyclohexane,1-ethenyl-methyl-1-methyl-2,4-bis(1-methylethenyl)-, (1α,2β,4β)-; 2,6-Odadien-1-ol, 3,7-dimethyl-,acetate; Dibutyl phthalate; Phenol,4,4’-(1-methylethylidene)bis-; 1,2-Cyclohexanediol,1-methyl-4-(1-methylethenyl)-; 1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-; 1,3-Dioxolan-2-one, 3-methyl-3-(4,8-dime; 2-Methyl-Z,Z-3,13-octadecadienol; Aromadendrene oxide-(2); Farnesene epoxide,E-; Epoxy-alpha-terpenyl acetate; 9,19-Cyclolanostan-24-one,3-acetoxy-25.

From this research, it has been observed that the lemon peel powder is an efficient cleaner for glass, ceramic utensils, and floor tiles. This is due to the presence of limonene, which is the main agent present in the lemon peel. Also, this study suggests the spray obtained from the mixture of lemon peel, vinegar, and water (1:2:8) is used as an effective air freshener, floor cleaner, and as an insect repellent due to it has present lots of aromatic and anti-insecticidal, antibacterial, and anti-fungicidal compounds.

5 Conclusions

The results obtained in the experimental study can be concluded as the following:

- The total SW generation rate at KUET campus has been found as 0.099 kg/capita/day during September, 2016 to March, 2017, out of which 0.30% wastes come from lemon peel.
- Essential oil has been extracted through distillation process from lemon peel and yield of oil has been found as 2.31% of fresh lemon peel. Characterization of EO has been executed through GC-MS analysis and about 125 numbers of components have been identified. The major compound has been seen as limonene as 13.21%, which is low than the expected amount and this happen may be due to the losses during heating due to its volatile nature; however, rigorous investigation is needed to find out the actual quantity.

Table 1 Chemical composition of essential oil extracted from lemon peel

Name of the Compound	RT	Area	Area%	R. Match	BC
1R-alpha-Pinene	5.550	6.721E6	1.48	900	VM
Bicyclo[2.2.1]heptane,7,7-dimethyl-2-methylene	6.395	3.003E7	6.61	823	VM
2,6-Dimethyl-1,3,5,7-octatetraene,E,E-	6.876	1.009E6	0.22	806	TF
(+)-4-Carene	7.093	446651	0.10	889	MV
Limonene	7.379	6.000E7	13.21	N/A	VB
Spiro[2, 4]hepta-4,6-diene	7.656	1.016E6	0.22	914	TF
1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)	7.867	1.781E6	0.39	884	TF
.alpha.-Methyl-.alpha.-[4-methyl-3-pentenyl]oxiranemethanol	8.123	4.163E6	1.59	776	TS
Bicyclo[2.2.1]heptan-2-ol,1,3,3-trimethyl-, (1S-endo)	8.641	1.145E7	2.52	723	VM
Ether,p-menth-6-en-2-yl methyl	9.027	1.988E6	0.44	700	VV
trans-p-Mentha-2,8-dienol	9.109	3.709E6	0.82	848	VV
p-Menth-2-en-7-ol,cis-	9.227	609308	0.13	756	VV
Limonene oxide, cis-	9.312	1.225E6	0.27	860	VV
cis-p-Mentha-2,8-dien-1-ol	9.393	3.103E6	0.68	832	VV
trans-Pinocarveol	9.504	1.340E6	0.29	783	VV
7-Oxabicyclo[4.1.0]heptane, 1-methyl-4-(1-methylethenyl)-	9.601	2.215E6	0.49	778	VV
Bicyclo[3.1.1]hept-3-en-2-ol,4,6,6-trimethyl-, [1S-(1α,2β,5α)]-	9.783	3.065E6	0.67	801	VV
1-Cyclohexene-1-methanol,.alpha.,2,6,6	9.916	773126	0.17	701	VV
Bornyl chloride	10.024	2.193E6	0.48	871	VV
Artemiseole	10.125	6.607E6	1.45	769	VV
2-Cyclohexen-1-ol, 1-methyl-4-(1-methylethyl)-	10.224	5.182E6	1.14	769	VV
Benzenemethanol, .alpha.,.alpha,.alpha.,4-trime	10.387	1.230E6	0.27	741	VV
Phosphoric acid, tribornyl ester	10.555	4.863E7	10.68	701	VV
2-Cyclohexen-1-ol, 3-methyl-6-(1-methylethyl)-	10.720	514900	0.11	823	TF
Squalene	10.995	1.449E7	3.19	713	VV
exo-2-Hydroxycinede	11.130	2.880E6	0.63	762	VV
6-Nonenal,3,7-dimethyl-	11.598	2.245E6	0.49	717	VV
1-Acetyl-2-(2’-oxo-propyl)-cyclopentane	11.899	938923	0.21	799	TF
Z,Z,Z-4,6,9-Nonadecatriene	12.193	732783	0.16	766	TF

(continued)

Table 1 (continued)

Name of the Compound	RT	Area	Area%	R. Match	BC
Epoxy-.alpha.-terpenyl acetate	12.504	1.426E6	0.31	794	TF
7-Oxabicyclo[4.1.0]heptane,1-methyl-4-(2-methyloxiranyl)-	12.922	754216	0.17	760	TF
1,2-Cyclohexanediol,1-methyl-4-(1-methylethenyl)-	13.141	1.793E6	0.39	791	VV
2,6-Odadien-1-ol, 3,7-dimethyl-,acetat	13.211	1.866E6	0.41	817	VV
Limonen-6-ol, pivalate	13.376	5.850E6	1.29	764	VV
Butanoic acid, 3,7-dimethyl-2,6-octadien	13.524	6.004E6	1.32	762	VV
Ethanone,1-(6-methyl-7-oxabicyclo[4.1.0]hept-3-en-3-yl)-	13.694	452686	0.10	758	VV
Cyclohexane,1-ethenyl-methyl-1-methyl-2,4-bis	13.805	1.899E6	0.42	881	VV
Z-(13,14-Epoxy)tetradec-11-en-1-ol acet	14.008	632227	0.14	729	VV
2-Methyl-Z,Z-3,13-octadecadienol	14.062	1.550E6	0.34	815	VV
trans-p-Mentha-2,8-dienol	14.117	354815	0.19	799	VV
1,3-Cyclohexadiene-1-methanol, 4-(1-methylethyl)-	14.382	639924	0.14	791	VV
Bicyclo[3.1.1]hept-2-ene,2, 6-dimethyl-6	14.490	5.167E6	1.14	875	VV
1,6,10-Dodecatriene,7,11-dimethyl-3-methylene	14.724	817502	0.18	892	VV
1-Hexadecanol	15.084	699543	0.15	868	MV
1,6,10-Dodecatriene,7,11-dimethyl-3-methylene	15.313	455590	0.10	841	VV
Azulene,1,2,3,5,6,7,8,8a-octahydro-1,4-	15.467	1.075E6	0.24	891	VV
1,4-Methano-1H-indene,octahydro-1,7a-	15.668	1.707E7	3.76	836	VV
9,19-Cyclolanostan-24-one,3-acetoxy-25	16.046	795320	0.18	813	VV
Farnesene epoxide,E-	16.220	1.411E6	0.31	861	VV
9-(3,3-Dimethyloxiran-2-yl)-2,7-dimethyl	16.340	997885	0.22	770	VV
1,6,10-Dodecatrien-3-ol,3,7,11-trimethy	16.422	1.235E6	0.27	815	VV
9,19-Cyclolanostan-24-one,3-acetoxy-25	16.566	1.296E6	0.29	779	VV
Caryophyllene oxide	16.926	4.911E6	1.54	896	VV
Lanceol, cis	17.344	2.953E6	0.65	849	VV
Alloaromaclendrene oxide-(1)	17.646	422078	0.09	771	VV
Tetracyclo[6.3.2.0(2,5).0(1,8)]tridecan-	17.714	1.024E6	0.23	817	VV
Isoaromadendrene epoxide	17.959	3.996E6	0.88	796	VV
1-Naphthalenol,decahydro-1,4a-dimethyl	18.020	2.648E6	0.58	836	VV
Diepicedrene-1-oxide	18.159	4.675E6	1.03	791	VV

(continued)

Table 1 (continued)

Name of the Compound	RT	Area	Area%	R. Match	BC
.alpha.-Bisabolol	18.325	3.954E6	0.87	893	VB
Hexadeca-2,6,10,14-tetraen-1-ol,3,7,11,	18.635	438282	0.10	868	VV
Aromadendrene oxide-(2)	18.942	1.525E6	0.34	823	VV
Isoaromadendrene epoxide	19.906	486534	0.11	780	VV
1,2-Epoxy-5,9-cyclododecadiene	19.980	884340	0.19	802	VV
Longifolene chloride	20.009	965214	0.21	714	VV
Cedren-13-ol,8-	20.124	828643	0.18	798	VV
7,9-Di-tert-butyl-1-oxaspiro(4,5)deca-6,	21.452	981910	0.22	838	VV
Dibutyl phthalate	22.383	1.824E6	0.40	922	VB
Phytol	26.282	416916	0.09	851	BB
Phenol,4,4’-(1-methylethylidene)bis-	28.856	1.753E6	0.39	901	BB
1,2-Benzenedicarboxylic acid, diisooctyl	44.812	898137	0.20	901	BB

- Limonene can be used as a cleaner, flavoring, and to make medicine. Most of the compounds presents into essential oil have insect repellent capacity and aromatic nature. From this research, it has been observed that the lemon peel can be used as utensils cleaner, pest repellent, air freshener, and for aromatic purposes.

References

1. Aberoomand AP, Nekoei M, Larijani K, Bahraminasab S (2011) Chemical composition of the essential oils of Citrus sinensis cv. valencia and a quantitative structure–retention relationship study for the prediction of retention indices by multiple linear regression. J Serb Chem Soc 76(12):1627–1637
2. Adam RP (2001) Identification of essential oil components by gas chromatography/quadrupole mass spectroscopy. Allured Publishing Corporation, Carol Stream, IL, USA
3. Andrea V, Nadia N, Teresa RM, Andrea A (2003) Analysis of some Italian lemon liquors (Limoncello). J Agricu Food Chem 51(17):4978–4983
4. Joulain D, Konig WA (1998) The Atlas of Spectral Data of Sesquiterpene Hydrocarbons. E. B.-Verlag, Hamburg, pp 1–657
5. Kamal GM, Anwar F, Hussain AI, Sarri N, Ashraf MY (2011) Yield and chemical composition of Citrus essential oils as affected by drying pretreatment of peels. Int Food Res J 18(4):1275–1282
6. Kamaliroosta L, Zolfaghari M, Shafiee S, Larijani K, Zojaji M (2016). Chemical identifications of citrus peels essential oils. J Food Biosci Technol, Islamic Azad University, Science and Research Branch 6(2):69–76
7. Mondello L, Casilli A, Tranchida PQ, Dugo P, Dugo G (2005) Comprehensive two dimensional GC for the analysis of citrus essential oils. Flavour Fragr J 20:136–140
8. Samdja J, Rondeau P, Sing ASC (2005) Volatile constituents of five citrus petitgrain essential oils from reunion. Flavour Fragr J 20(4):399–407
9. Svoboda KP, Greenaway RI (2003) Lemon scented plants. Int J Aromather 13(1):23–32. https://doi.org/10.1016/S0962-4562(03)00048-1

Arsenic (V) Remediation Using Adsorption-Induced Ultrafiltration Process and Management of Toxic Sludge in Glass Formation

D. Mukherjee, S. Ghosh, S. Majumdar and K. Annapurna

1 Introduction

Arsenic contamination in water is becoming a severe threat to the mankind, as well as the natural flora and fauna. Average arsenic concentration of arsenic in groundwater in Bengal basin have even reached 5 mg/L [1], higher arsenic concentration have also been found in several locations like in contaminated groundwater of mining areas, geothermal water and near oilfield very high arsenic concentration of about 200 mg/L have been observed [2]. Chronic exposure to arsenic-contaminated groundwater causes skin, cardiovascular, renal, haematological and respiratory disorders [3]. Various treatment processes like adsorption, ion exchange, coagulation, precipitation and membrane-based technologies have been developed for removing arsenic (V) from the environment [4]. Recent trends have been on combination processes of two different technologies [5] involving membranes of different polymeric materials. In view of the lower thermal, mechanical and chemical stability of the

---

D. Mukherjee · S. Ghosh (✉) · K. Annapurna
Academy of Scientific and Innovative Research (AcSIR),
CSIR-Central Glass and Ceramic Research Institute, Kolkata, India
e-mail: sourja@cgcri.res.in; sourja.g@gmail.com

D. Mukherjee
e-mail: debarti.chemistry@gmail.com

K. Annapurna
e-mail: annapurnak@cgcri.res.in

D. Mukherjee · S. Ghosh · S. Majumdar
Ceramic Membrane Division, CSIR-Central Glass and Ceramic
Research Institute, 196, Raja S.C. Mullick Road, Kolkata 700032, India

K. Annapurna
Glass Science and Technology Section,
CSIR-Central Glass and Ceramic Research Institute, Kolkata, India

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_49

polymeric membranes compared to their inorganic counterparts, the present study is focused on application of ceramic ultrafiltration membranes in combination with adsorption using iron oxide nanoparticles, for arsenic (V) remediation from water [6]. Iron oxide nanoparticles (α-Fe_2O_3) (FeIII-NP) have been synthesized using a cost-effective green method showing high adsorption capacity of 38.48 mg/g for arsenic (V) [7]. Adsorption process was followed by ultrafiltration using nano γ-Al_2O_3 coated macroporous clay–alumina membranes for efficient separation of the nanoparticles and production of high-quality permeate. Central composite design (CCD) was employed for designing of experiments to be performed for assessing the effects of different independent parameters affecting membrane filtration performance, viz. transmembrane pressure (TMP) and the cross-flow velocity (CFV). Response surface methodology (RSM) employing Design-Expert 6.0.8 Portable version was used for optimization of the independent parameters has also been done targeting maximization of the response, i.e. the permeate flux.

Sludge management is another issue which needs to be focused for environmental reasons. Reuse and recycling of the hazardous sludge produced emerges as the best option for sludge management considering economic and environmental aspect. Effective solidification of sludge with various fillers like clay, cement and lime for bricks production has been reported [8]. The present study focuses on a novel method of arsenic sludge immobilization. Vitrification has been chosen for the toxic component immobilization because of their high thermal, mechanical, chemical stability, negligible leaching when exposed to harsh conditions and manageable glass formation temperature [9]. Arsenic (V) containing α-Fe_2O_3 nanoparticles sludge has been utilized in making of amber coloured soda lime silicate glass. The main objective of glass making lies in utilizing the refining property of arsenic (V) adsorbed in the sludge. Formation of bubbles is reduced during glass melting resulting in formation of homogenous glass sample. The produced glass can be used in reagent bottles, ornamental purpose and various other applications.

2 Materials and Methods

2.1 Arsenic Removal Using the Combination Process

The synthesized Fe(III)-NP nanoparticles were used in combination with ceramic UF membrane filtration for arsenic (V) removal at the optimized pH and adsorbent dosage [7]. Accordingly, the feed solution taken was 5 mg/L of arsenic (V) solution (Merck, Germany) with 1 g/L as the adsorbent dosage.

2.1.1 Ceramic UF Membrane Preparation

The macroporous tubular ceramic support tubes having outer diameter: inner diameter of 8 mm: 6 mm and length of 150 mm, were indigenously synthesized by extruding a paste of clay and alumina followed by firing at 1450 °C. The tubes were ultrasonicated by water and acetone successively, followed by drying at 110 °C to remove any impurities which may block the pores. These were then coated with the slurry prepared from the mixture of Boehmite powder (Pural SB, SASOL, Germany) having purity of 74% and γ-Al_2O_3 of 40 nm particle size of (Presi, France) [6]. Polyvinyl alcohol (Sigma Aldrich, USA) was used as binder, plasticizer used was Polyethylene glycol (Merck, Germany) and nitric acid (Merck, India) as peptizing agent for proper sol formation.

The prepared membrane was characterized in terms of field emission scanning electron microscopy [FESEM, Zeiss, Germany], pore diameter by BET method using Quantachrome Autosorb Automated Gas Sorption System (USA). Molecular weight cut-off (MWCO) of the membrane was estimated by measuring the rejection of PEG of different molecular weights. The clean water permeability of the membrane was estimated by obtaining the permeate flux of deionized water by varying the transmembrane pressure (TMP) in the range of 1–3 bar, maintaining a fixed cross-flow velocity (CFV) of 2.4 L min^{-1}.

2.1.2 Cross-Flow Filtration

The experimental feed solution was filtered using the prepared UF membrane. The effect of various parameters like TMP and CFV on the permeate flux has been studied using RSM. The effect of filtration time upon permeate flux decline was also studied by performing the UF membrane filtration for 150 min at a stretch. After completion of each run, the UF membrane was washed with water and clean water permeability was rechecked. The main parts of the filtration setup included a jacketed feed tank, 5 L (SS), tubular membrane module (SS) and variable speed pump for controlling the feed flow velocity during recirculation. Permeate sample was collected from the port present at the bottom of the membrane module while the retentate, being concentrated in As (V) containing adsorbent, was recycled back to the feed tank.

2.2 Statistical Analysis of Membrane Performance Using RSM

The permeate flux of the ultrafiltration process was optimized using RSM. Transmembrane pressure (TMP) across the membrane and cross-flow velocity (CFV) of the arsenic feed solution were found to affect the permeate flux; hence, these two parameters were chosen as independent parameters while permeate flux was selected

Table 1 Experimental range and levels as set up by the central composite design (CCD)

Independent variable	Range and level		
	−1	0	+1
TMP [bar] (A)	1	2.5	4
CFV (m/s) (B)	1	2	3

as dependent experimental response. The experimental range and the corresponding levels of the parameters selected have been listed in Table 1. Total of 13 experiments with 5 replicates as set up using CCD were conducted. The experiments were performed accordingly. The α value is chosen to be face-centered ($\alpha = 1$). $\alpha = 1$ signifies placement of the axial points on the cube portion of the experimental design. When the operational limits in the design are the cube points, designation of $\alpha = 1$ becomes a good choice.

2.3 Immobilization of the Spent Adsorbent

The sludge produced in the process involving arsenic (V) adsorbed iron oxide nanoparticle separated after membrane filtration was immobilized in glass matrix. Borosilicate glass with a variety of modifiers was chosen for the study. The compositions (wt%) for 100 g batch of the two glasses includes 45 SiO_2 −6.5 Na_2O—13.5 B_2O_3—11 Fe_2O_3—2 Al_2O_3 −4CaO—10 PbO—8 Li_2O (G-1) and 52.79 SiO_2 −24.9 B_2O_3—12.44 Na_2O—7.85 TiO_2 −2.02 Fe_2O_3 (G-2), respectively. The sources of Na_2O, CaO, B_2O_3, Li_2O were Na_2CO_3, $CaCO_3$, H_3BO_3, Li_2CO_3, respectively. For Fe_2O_3, the arsenic-containing sludge was used. The raw materials were purchased from Sigma Aldrich, USA. Rapid melting quenching method was adopted for formation of the glasses. The materials taken in proper ratio were mixed well to attain a homogenous and uniform batch. The batches were then placed in alumina crucible, charged at 1100 °C and 1350 °C in the furnace and melted at 1200 °C and 1450 °C, for G-1 and G-2, respectively. Stirring was done with a platinum rod to attain homogeneity and avoid formation of bubbles. The glass melt was given a rectangular shape by casting in a stainless steel mould. It was then annealed at 700 °C for about 2 h to relieve the internal stress. The prepared glass samples were characterized in terms of X-Ray Diffraction (XRD, Philips 1710 diffractometer) from $2\theta = 5°–80°$ using Cu as anode material. The microstructure of glass was analysed using Field Emission Scanning Electron microscopy (FESEM, Zeiss, Germany). Density was measured by Archimedes principle and refractive index was found at wavelengths of 473, 532, 632.8, 1064 and 1552 nm using Metricon M2010 Prism Coupler. The properties, viz. Poisson's ratio (σ), Young's modulus (E), shear modulus (G), bulk modulus (K), longitudinal modulus (L), mean ultrasonic velocity (U_{m}) and Vicker's hardness (H_{V}), were also measured for assessing the mechanical stability.

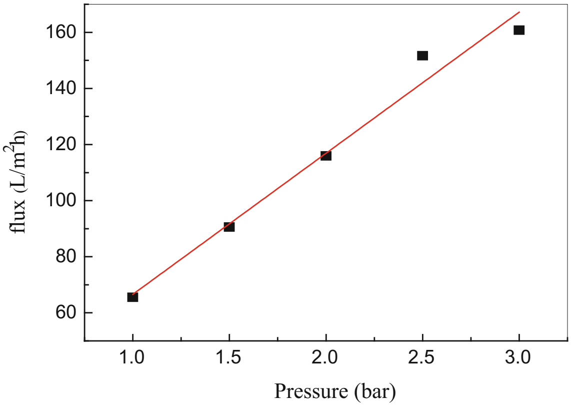


Fig. 1 Clean water permeability of UF membrane

3 Results and Discussions

3.1 Arsenic (V) Removal Using the Combination Process

3.1.1 Characterisation of the Prepared UF Membrane

The clean water permeability of the membrane was obtained by estimating the permeate flux of deionized water at different transmembrane pressures (1–3 bar). Stabilization time of 5 min was provided at each pressure to attain a constant flux. From the plot of permeate flux versus TMP as shown in Fig. 1, the value of the clean water permeability was estimated to be 55.55 $\text{Lm}^{-2}\ \text{h}^{-1}\ \text{bar}^{-1}$. The pore diameter and molecular weight cut-off (MWCO) was found to be 5.5 nm and 35 KDa, respectively [6].

The FESEM image of the membrane has been shown in Fig. 2. The surface topology of the membrane (Fig. 2a) shows the presence of nanosized spherical particles which are the nano γ-Al_2O_3 particles. Coating of thickness 15 μm over the porous support is clearly visible from the cross-sectional view of the coated membrane in Fig. 2b. This proves successful coating of γ-Al_2O_3 over the clay–alumina support tubes.

3.1.2 Cross-Flow Membrane Filtration

The arsenic-containing feed solution was filtered using the prepared ultrafiltration membrane. The effect of various parameters like TMP and CFV on permeate flux has been studied by RSM. Permeate flux was measured and permeate sample was collected for determination of the arsenic content, total suspended solids (TSS) and turbidity while retentate was recycled back to the feed tank. The effect of time on flux was also studied during filtration operation up to 150 min. After completion

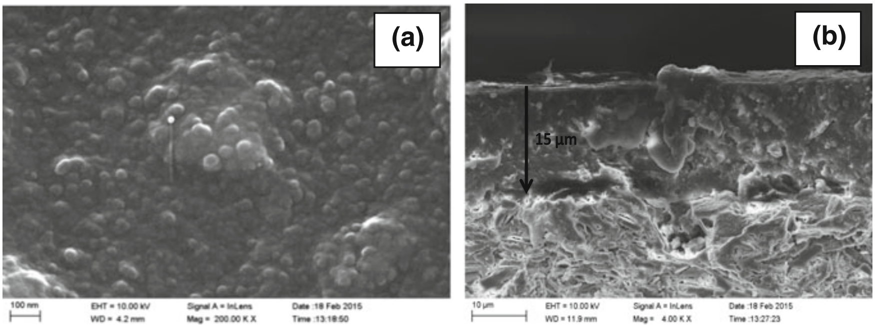


Fig. 2 FESEM image of the UF membrane: **a** surface and **b** cross section

of each filtration cycle, the membrane was thoroughly washed with deionized water and clean water permeability was checked. The arsenic concentration in the permeate sample after filtration for 150 min was 0.115 mg/L at TMP of 4 bar and CFV of 1 m/s. The permeate sample was free of TSS and turbidity reduced from 765 NTU to 0.736 NTU.

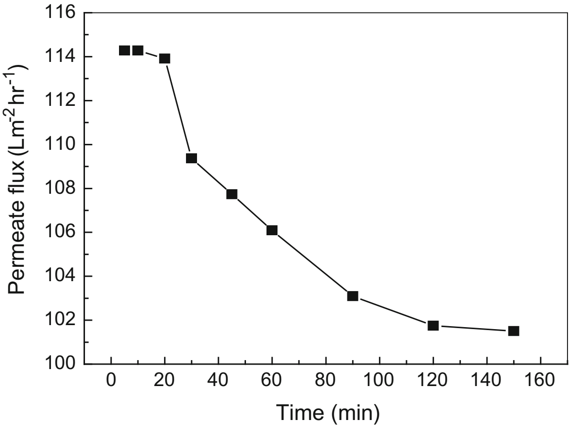
To study the extent of fouling during membrane filtration, the filtration was carried out for 150 min at a stretch. The decline in the permeate flux was 11% which can be seen from Fig. 3. Basically, fouling occurs due to the blockage of the pores and hence formation of a filter cake. In this study, the size of the nanoparticles is about 100 nm while the membrane has a pore diameter of 5.5 nm. This size difference causes the particles to deposit on the surface of the membrane and hence blocking of the pores, thus reducing the permeate flux. In cross-flow membrane filtration, steady-state condition is reached when convective transport of the solute towards the membrane becomes equal to transport of the solute in opposite direction, i.e. from the membrane surface to the bulk solution [10]. In this case, fouling was temporary in nature as the clean water permeability could be retained back on washing the membrane successively with water.

3.2 Statistical Analysis of Membrane Performance by RSM

The experimental design had been set up by CCD and experiments were conducted accordingly. The second-order quadratic model was used for fitting of experimental data. The relationship among the independent influencing factors viz., TMP (A) and the dependent response permeate flux is given by quadratic equation (Eq. 1) represented in terms of coded factors

$$\text{Flux} = +96.08 + 33.82 \times A + 1.59 \times B - 6.88 \times A^2 + 0.68 \times B^2 + 0.34 \times A \times B \tag{1}$$

Fig. 3 Effect of time on permeate flux



A synergistic effect of TMP and CFV is found as indicated by the positive sign in their corresponding regression coefficient values. Increase in permeate flux occurs with increasing TMP and the CFV which is justified by the equation. The ANOVA analysis performed for the UF membrane filtration of arsenic–iron oxide solution indicates that A, B and A^2 are significant terms ($p < 0.05$).

A good match was found between the experimental and predicted response, which is clear from the plot as given in Fig. 4a having coefficient of determination (R^2) value of 0.9990. Moreover, the negligible difference (less than 0.2) exists between the predicted and adjusted R^2 value (0.9975 and 0.9982, respectively). The model F-value was found to be 0.8852 indicating lack of fit is insignificant. The contour plot as generated from RSM has been represented in Fig. 4b. It shows that the permeate flux increases with the increase in the cross-flow velocity and the transmembrane pressure as is also evident from the obtained regression equation. However, the effect of TMP is much more on the flux compared to the CFV as can be seen from the contour plot generated. The effect of increase in the pressure is evident to cause an increase in the permeate flux as this is the main driving force for the membrane filtration process.

The optimized conditions obtained with the target of maximizing the permeate flux are CFV, 1 m/s and TMP, 4 bar resulting in permeate flux of 121.78 $\mathrm{Lm}^{-2}\ \mathrm{h}^{-1}$ with desirability of 0.967.

3.3 *Immobilization of the Arsenic-Containing Sludge*

XRD characterization of the glass samples G-1 and G-2 revealed the presence of broad peaks as observed in Fig. 5a, b, respectively, showing their amorphous nature which infers the absence of phase separation in the matrix [11].

Absence of any specific crystal structure, grains and grain boundaries in the samples had been represented by their respective FESEM micrographs in Fig. 6a, b,

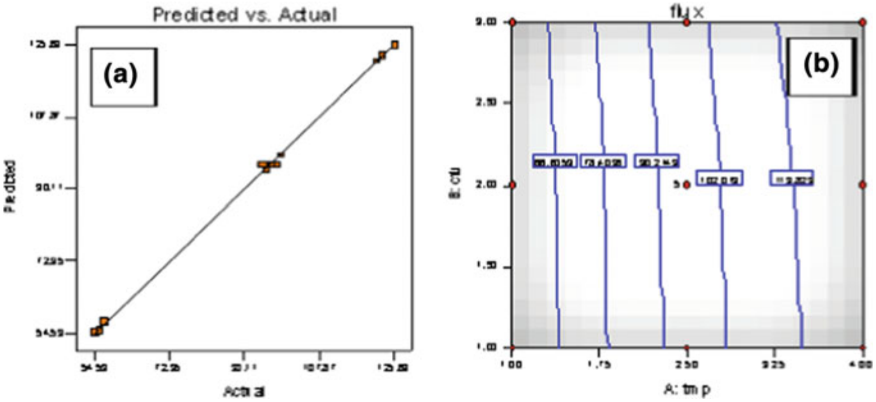


Fig. 4 **a** Plot of predicted vs. experimental response, and **b** contour plot showing the effect of TMP and CFV on the permeate flux

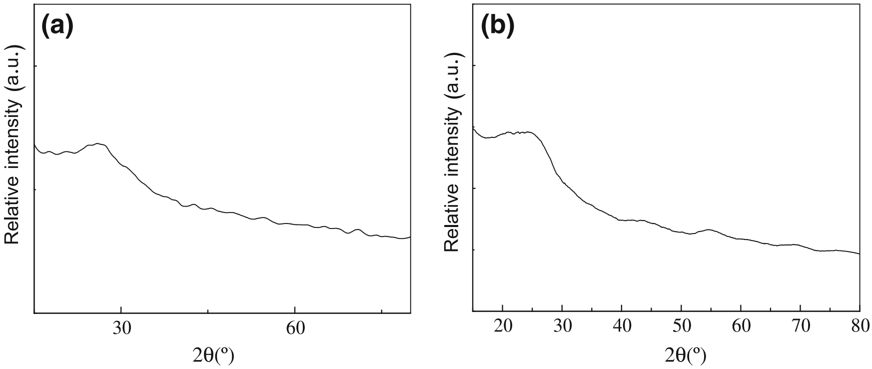


Fig. 5 X-ray diffraction plot of **a** G-1 and **b** G-2

respectively, showing the amorphous state of G-1 and G-2. The EDX analysis shows the presence of iron, which is due to the presence of the spent adsorbent. Arsenic was below the instrumental detectable limit for which no specific peak of arsenic could be detected.

Different physical properties of the glass samples have been represented in Table 2. The respective values are comparable with commercial glasses proving that incorporation of spent adsorbent does not create any appreciable difference [12, 13].

4 Conclusions

The combination process of adsorption integrated with ceramic ultrafiltration membrane-driven filtration was successfully applied for arsenic (V) remediation from

Table 2 Physical properties of the prepared glass samples

Properties											
Glass	ρ (g/cc)	μ	U_L (m/s)	U_S (m/s)	L (GPa)	G (GPa)	K (GPa)	σ	E (GPa)	U_m (m/s)	H_V (kgf/mm^2)
G-1	2.3699	1.59	6326	3595	95.98	30.62	53.58	0.261	77.16	3996.56	704.22
G-2	2.3047	1.54	5634	3194	98.04	24.51	42.88	0.260	61.76	3551.49	540.02
Commercial glass	2.23	1.47	5724	3429	73.06	26.22	38.09	0.22	64	3793.89	652.61

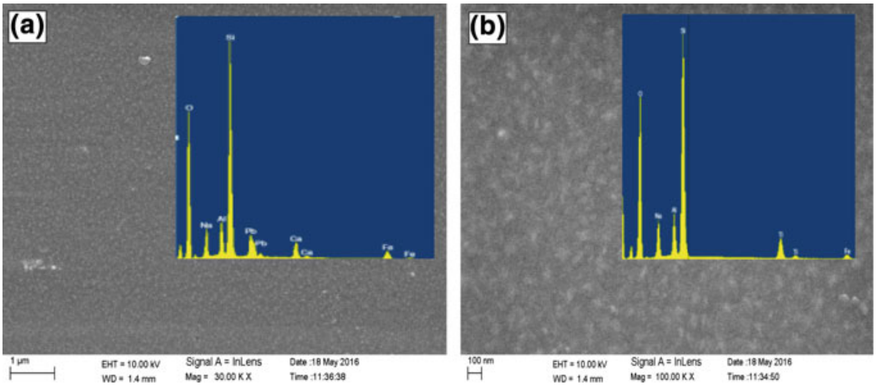


Fig. 6 FESEM image of the arsenic immobilized glass samples: **a** G-1 and **b** G-2

water. The iron oxide nanoparticles showed about 99% removal efficiency for arsenic (V). Ultrafiltration membrane prepared by coating of nano γ-Al_2O_3 on macroporous ceramic substrates enabled an effective filtration of the arsenic-containing solution with adsorbent. Permeate samples showed turbidity of 0.736 NTU and no TSS content. The RSM study for the membrane filtration showed that the permeate flux increased with increase in the TMP and CFV. R^2 value of 0.99 shows good similarity between the experimental, i.e. the actual and the quadratic model predicted responses. The CFV and TMP for optimum permeate flux was 1 m/s and 4 bar, respectively. The decline in permeate flux of 11% was observed indicating partial membrane fouling. Sludge generated by UF membrane filtration of iron oxide nanoparticles adsorbed with arsenic (V) was successfully utilized in the preparation of borosilicate glasses which is a novel approach for immobilization of toxic components. The proposed process involving toxic component remediation and solid waste management would be a cost-effective and eco-friendly approach for arsenic remediation.

Acknowledgements The financial support from the Council of Scientific and Industrial Research (CSIR), Government of India, is gratefully acknowledged for completion of this work.

References

1. Mandal BK, Suzuki KT (2002) Arsenic round the world: a review. Talanta 58:201–235
2. Gebreyowhannes YB (2009) Effect of silica and pH on arsenic removal by iron-oxide coated sand. MSc Thesis, Unesco-IHE
3. Sharma VK, Sohn M (2009) Aquatic arsenic: toxicity, speciation, transformations, and remediation. Environ Int 35:743–759
4. Sanchez J, Rivas BL (2010) Arsenic extraction from aqueous solution: electrochemical oxidation combined with ultrafiltration membranes and water-soluble polymers. Chem Eng J 165:625–632

5. Arar O, Kabay N, Sanchez J, Rivas BL, Bryjak M, Pena C (2014) Removal of arsenic from water by combination of electro-oxidation and polymer enhanced ultrafiltration. Environ Prog Sustain Energy 33:918–924
6. Sarkar S, Ghosh S, Banerjee P, Larbot A, Cerneaux S, Bandyopadhyay S, Bhattacharjee C (2014) Preparation and characterization of single layer ultrafiltration alumina membrane directly over porous clay-alumina tubular and capillary support for textile effluent treatment. T Indian Ceram Soc. https://doi.org/10.1080/0371750X.2014.882246
7. Mukherjee D, Ghosh S, Majumdar S, Annapurna K (2016) Green synthesis of α-Fe_2O_3 nanoparticles for arsenic(V) remediation with a novel aspect for sludge management. J Environ Chem Eng 4:639–650
8. Mahzuz HMA, Alam R, Alam MN, Basak R, Islam MS (2009) Use of arsenic contaminated sludge in making ornamental bricks. Int J Environ Sci Tech 6:291–298
9. Donald IW, Metcalfe BL, Taylor RNJ (1997) The immobilization of high level radioactive wastes using ceramics and glasses. J Mater Sci 32:5851–5887
10. He Y, Li G, Jiang Z, Wang H, Zhao J, Su H, Huang Q (2011) Diafiltration and concentration of Reactive Brilliant Blue KN-R solution by two-stage ultrafiltration process at pilot scale: technical and economic feasibility. Desalination 279:235–242
11. Kaushik CP, Mishra RK, Sengupta AK, Das D, Kale GB, Raj K (2006) Barium borosilicate glass—a potential matrix for immobilization of sulfate bearing high-level radioactive liquid waste. J Nucl Mater 358:129–138
12. Chorfa A, Madjoubi MA, Hamidouche M, Bouras N, Rubio J, Rubio F (2010) Glass hardness and elastic modulus determination by nanoindentation using displacement and energy methods. Ceramics—Silikáty 54:225–234
13. Bouras N, Madjoubi MA, Kolli M, Benterki S, Hamidouche M (2009) Thermal and mechanical characterization of borosilicate glass. Phys Procedia 2:1135–1140

Microwave-Assisted Alkali-Peroxide Treated Sawdust for Delignification and Its Characterisation

Devadasu Sushmitha and Srinath Suranai

1 Introduction

The production of bioethanol from lignocellulosic biomass can be the most exciting alternatives to compensate the fossil fuels. Nevertheless like conventional heating, microwave heating requires lesser time for processing with the equal or higher efficiency. As compared to the traditional heating which is having prolonged pretreatment times (say until 12 h), in this contest, microwave heating could be a promising thing as it considerably decreases the processing time for dissolution of hardwood, and increase the efficiency of the pretreatment. The operating conditions for depolymerisation of lignin were different for different types of lignocellulosic biomass such as softwood, hardwood, etc. for these reasons, intensive work has been done on pretreatment of biomass and investigation was increased in the past years [1].

Studies on microwave irradiation of biomass is done in the past, mostly on sugar cane bagasse, corn and corn stover due to an abundance of unutilised waste resources in countries [2, 3].

Using sugar cane bagasse, 48% of lignin was removed by depolymerisation of polysaccharide at processing conditions of 28% v/v ammonium hydroxide solution, and with an operating temperature of 130 °C for 1 h [4].

In another paper, Morritis used the same sugar cane bagasse, irradiated with microwave for 5 min with distilled water, phosphoric acid of pH 3, and 100% glycerol, was reported that the highest separation of hemicelluloses and cellulose was occurred [5].

The solubility of green tea residue was up to 74% by pretreatment using microwave and sodium hydroxide (1%) at a temperature of 120–200 °C, for a reaction time of 5 min [5]. In fact, we can observe that there was a less reaction time for effective removal of lignin, and with the highest yields of cellulose and hemicelluloses using

---

D. Sushmitha (✉) · S. Suranai
National Institution of Technology, Warangal, India
e-mail: sushmitha.devadasu@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_50

microwave reactor. Moreover, using microwave reactor alone could limit the reaction time, but along with the combination of most efficient pretreatment methods, combinations of different equipment could expect good results regarding effective delignification, and it is in purity.

Bussemaker and co-workers used with a combination of ultrasound, in oxidative environments to depolymerise the lignocellulosic biomass in the presence of alkali [6]. Their studies are performed on specialised equipment that merges the use of ultrasound and microwave then compares, the results with those obtained with microwave alone. Therefore from the previous studies, proves that simultaneous use of microwave and ultrasound for less residence time, and there by ultilizing non-oxidizing compounds gives higher yeilds of main compounds (that is cellulose, hemicellulose, and lignin) but with less purity.The pretreatment with oxidizing compounds results in lesser yeilds but with higher purity.

Ultrasound-assisted pretreatment of lignocellulosic biomass gives a higher purity in the individual components using different chemical pretreatments, but the efficiency of lignin removal was reduced to 50% [5]. Tatijarern et al. understood the worth of Thai Mission grass (*Pennisetumpolystachyon*) and discovered as a new weedy raw material for synthesis of monomeric sugar.

Ming-Guo Ma studied the production of nano cellulose composites and derivatives, using microwave irradiation along with 3% (w/v) NaOH, at 120 °C for 10 min; he separated nearly 85% lignin from Mission grass. And from the solid residue of treated mission grass, they observed an excellent reducing sugar content (34.3 ± 1.3 g per 100 g of dried biomass), mainly of 31.1 ± 0.8 g of reducing sugar per 100 g of dried biomass.

In a two-stage microwave and a chemical process, sugar yield was 40.9 g per 100 g of dried biomass, Using 1% (w/v) H_2SO_4, 15:1 liquid-to-solid ratio (LSR) at a temperature of 200 °C for only 5 minutes of processing time [7].

In this paper, an attempt was made to use microwave-assisted alkali peroxide pretreatment of sawdust, for varying powers from 350 to 700 watts, and simultaneously the increasing temperatures were recorded, that is approximately 45–90 °C. Experiments were conducted with varying hydrogen peroxide concentrations, i.e. from 0.2 to 1 M keeping the sodium carbonate concentration as constant 0.2 M. The results of the treated and untreated sawdust was analysed using sophisticated equipment such as UV spectroscopy, Fourier transform infrared spectroscopy FTIR, Scanning electron microscopy SEM, X-Ray Diffraction (XRD) and Thermogravimetric analysis (TGA).

2 Materials and Methods

2.1 Materials

Teak sawdust was collected from a local industrial mill located in Warangal, India. All chemicals were procured and utilized with out any purification, Sodium carbonate is procured from HiMedia chemicals, and hydrogen peroxide from Fisher scientific chemicals, and distilled water/deionised water is used for all experiments.

Ragas Scientific Microwave system has internal dimensions of W 36 cm × H 21 cm × D 43 cm having ten adjustable power levels, ranging from 140 to 700 W that can be adjusted during operation with a frequency of 2450 MHz. Inside the system, there exists a beam reflector for perfect distribution of microwaves for its maximum utilisation of processing place. A provision for temperature indicator is allotted on top with a flexible probe like IR sensor.

2.2 Microwave-Assisted Alkali Pretreatment

A microreactor with varying power ranging from 140 to 700 W was used for operations. Sawdust to the liquid ratio is taken as 1:10 with a sodium carbonate concentration as 0.2 M and hydrogen peroxide as 1 M. Contents were mixed well with a magnetic stirrer and kept in a microwave reactor for a different power staring with 350–700 W and various times from 15 s to 1.15 min. The mixture is filtered, and the filtrate is sent to lignin analysis by UV spectroscopy.

2.3 Methodology for Lignin Removal

The filtrate after filtration of microwave-assisted pretreated sawdust has a pH around 12, and this was reduced to pH 5–8 with HCl, precipitated one is separated by centrifuging, at 10,000 rpm within 10 min. The supernatant was collected in a separate vessel, and its pH was further reduced to 2, to precipitate soluble lignin. Then the contents are centrifuged, similarly, as above conditions, and the supernatant is discarded, pellet obtained was soluble lignin. Wet soluble lignin was dried in a vacuum oven at 50 °C for 30 min.

2.4 Characterisation Techniques and Methods

Quantification of total lignin content is measured gravimetrically using UV spectroscopy by dissolving extracted lignin, by Acetyl bromide soluble lignin method.

Precipitated lignin was mixed with 25 v/v% of acetyl bromide in acetic acid, kept in the water bath for 50 °C for 30 min. The mixture was cooled and then, an addition of 2.5 ml of glacial acetic acid, 0.5 ml of 0.5 M hydroxylamine hydrochloric acid and 1.5 ml of 0.5 M NaOH was added and analysed in spectroscopy at 300 nm.

Spectrum 100 Optica FTIR Spectrophotometer of Perkin Elmer (NITW, Telangana, India) is used for FTIR analysis of treated biomass. The pretreated and dried sawdust was mixed with spectroscopic grade KBr powder in 1:3 ratio and pelletised like thin 1 mm circular disc. This pellet is placed in a pellet slot for FTIR analysis under mid range from 400 to 4000 cm^{-1}.

Scanning Electron Microscopy (SEM) the micrographs of raw and pretreated sawdust, by scanning electron microscopy were obtained by TescanVega-3 MUT. To understand the structure, fine powder of untreated and pretreated sawdust was first coated with gold and operated at 15 kV electron beam voltage with a secondary electron detector.

X-Ray Diffraction (XRD) patterns were collected from a powder X-ray diffractometer (PANalytical X^1pert powder Model) at operating conditions of 45 mV and 30 mA, for a 2 theta range of 5–30° at 0.016° step intervals, with step input of 34.925 s.

Thermo Gravimetric Analysis (TGA), Thermax 700 Thermo Scientific TGA analyser was used to know about the thermal behaviour of treated and untreated sawdust. 2 mg of sample was used for a temperature range of 20–1000 °C,at a constant heating rate of 10 °C in inert atmosphere nitrogen (99.5% nitrogen).

3 Results and Discussion

3.1 Effect of Hydrogen Peroxide Concentration

The impact of hydrogen peroxide influences more for lignin removal. The sodium carbonate concentration has taken constant (Na_2Co_3) 0.2 M (by observing the previous studies) varying the hydrogen peroxide concentration from 0.2 to 1 M, the removal of lignin was found to nearly 69%. Delignification from sawdust can be due to the strong alkali helps in cleavage of ester, ether and glycosidic linkages that connect lignin and hemicellulose, and also the dissociation reactions of water with hydrogen peroxide, produces hydroxide radicals, and hydrogen radicals. These radicals act strongly on carbohydrate and lignin linkages to degrade lignin (Fig. 1; Table 1).

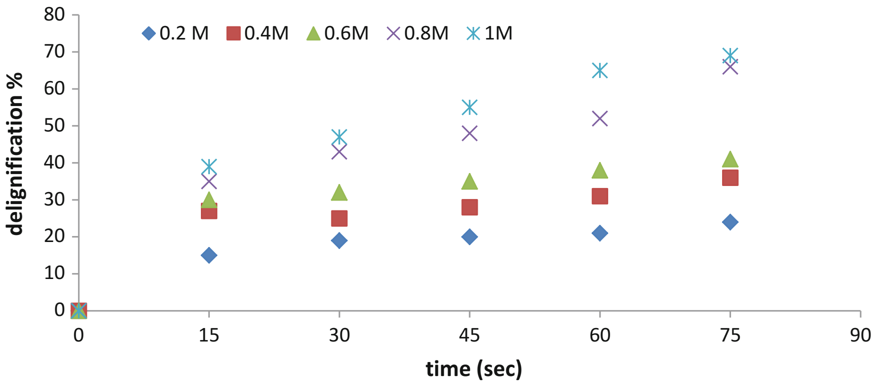


Fig. 1 Effect of hydrogen peroxide concentration on the percentage of lignin removal

3.2 Impact of Power and Temperature

The microwave power is varied from 350 to 700 W. Therefore at 700 W power, highest delignification is obtained 700 W power, and furthermore, it is observed that by increasing the microwave power level, the pretreatment time can be decreased with some limitations [8–10].

The characteristics of heating in a microwave irradiated reaction system are directly affected by dielectric properties of a material. Dielectric characteristics of material like dielectric constant (ε') and dielectric loss (ε''), which decides the extent of heating of the material, under microwave irradiation. One of the most interesting dielectric properties can be loss tangent and is denoted by the term tan δ. It can be expressed as a specific material can transform the electromagnetic energy into heat for a particular temperature and frequency. The quotient of dielectric loss (ε'') and the dielectric constant (ε') are termed as loss tangent (tan δ) [8, 11, 12]. The absorption of high microwaves, in turn, gives fast and efficient heating at low dielectric loss factor (ε'') media such as water, acts as a reaction media. There are some critical points to be to consider in the microwave heating process that are the penetration depth, relaxation time, etc.

Table 1 Effect of hydrogen peroxide concentration on the removal of lignin percentage

H_2O_2 (M)	Delignification (%)	Rate constant (min^{-1})	Correlation coefficient
0.2	24	0.0466	0.893
0.4	36	0.08	0.921
0.6	41	0.0071	0.853
0.8	57	0.0128	0.895
1	69	0.238	0.935

Water acts as the enhancer in the microwave energy absorption, dielectric loss tangent (δ) of water is 0.123 [10]. It serves as a barrier to maintain equal and quick transfer of energy to biomass. It also consumes some of the power to vaporise. Too much of water also reduces the positive effect of energy transfer by decreasing the increased temperature by the presence of free water. Therefore, there is a need to check the water level that can use absorption of microwave up to the maximum extent. There should be a balance between microwave energy absorption and energy required by water must be kept adequately to achieve maximum utilisation of the reactants, by increasing the interfacial area, thereby increases mass transfer rates effectively.

Unlike a microwave, conventional cooking type pretreatment does not depend on penetration depth inside the processing flask. Common vessels used in a traditional type of experiments are borosilicate glass, and the purpose of that is to transfer the energy to the reaction medium, by dissipating heat through conventional currents, which is very inefficacious. But in the microwave irradiation, heating can happen from the inside of the reaction vessel (that means volumetric heating), since borosilicate glass is capable of allowing the microwaves to pass through it, with a dielectric loss tangent of tan δ = 0.0010. So, by using borosilicate glass, there could be a better coupling of the microwave energy along with molecules exists in the processing medium [13–15].

The scientific microwave has a flexible probe for temperature measurement with a IR sensor. The table shows a variation of power and temperature at 1.15 min of reaction time since from the above parameters, alkali concentration and biomass loading gave higher delignification at that particular reaction time (Table 2).

From the graph between ln(k) versus 1/T, the activation energy required for treating sawdust under an alkali peroxide environment with microwave gives 98.8 kcal/mole (Fig. 2).

Table 2 Effects of power and temperature on delignification

Power (W)	Temperature (°C)	Delignification (%)	Rate constant k (min^{-1})	R^2 correlation coefficient
350	45	14	0.02272	0.97
420	54	25	0.0322	0.98
490	63	46	0.04	0.97
560	72	58	0.0454	0.98
700	90	64	0.05	0.98

4 Characterisation Results

4.1 Fourier-Transform Infrared Radiation (FTIR)

The results gave a graph between wavelength and absorption. The quantification of biomass is performed through 'beers law quant application' provided in the Perklin software. The correlation gave good results for lignin quantification at the corresponding lignin peaks.

The intensity of each peak corresponds to the presence of a chemical structure of a component.

The bands 3414 and 990 cm^{-1}, corresponding to the cellulose as it represents O–H stretching, C–O valence vibration in cellulose and 1280 cm^{-1}, in particular, C–H bending crystalline cellulose for sawdust and in the figure, it was low for raw saw dust and high for pretreated sawdust [13].

Similarly, the peaks 1246 and 1212 and 1250 cm^{-1} corresponds to hemicelluloses stands for weak C–O stretching, acetylated hemicelluloses [6]. The FTIR results show weak intensity of lignin bands for pretreated biomass implies the low concentration of lignin. Generally, lignin peaks at 1510 and 1606 cm^{-1} wave numbers, the lignin absorbance peak was lower as compared to the untreated sawdust, this explains about the better lignin removal for a higher concentration of alkali peroxide under microwave irradiations at 90 °C for 1.15 min (Fig. 3).

4.2 Scanning Electron Microscopy (SEM)

Morphological changes can read by examining the SEM micrographs. The significant structural changes can be analysed by reviewing the micrographs. The appearance of gaps on pretreated sawdust in the upper right most corner of the second SEM image shows that removal of lignin and presence of cellulose microfibrils are visible,

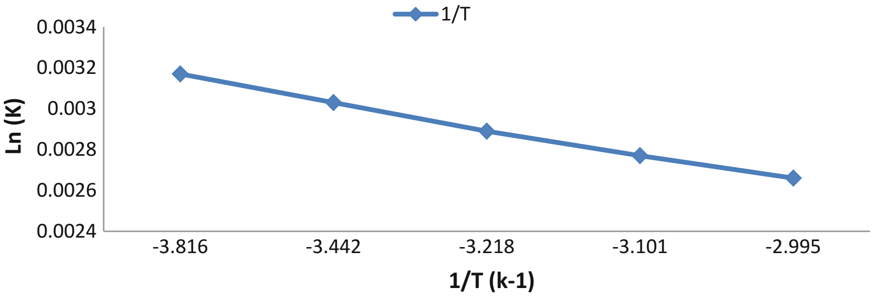


Fig. 2 Graph between 1/T versus ln(k)

whereas in the raw sawdust, wholes and microfibrils were absent which indicates that the lignin was attached to sawdust (Fig. 4).

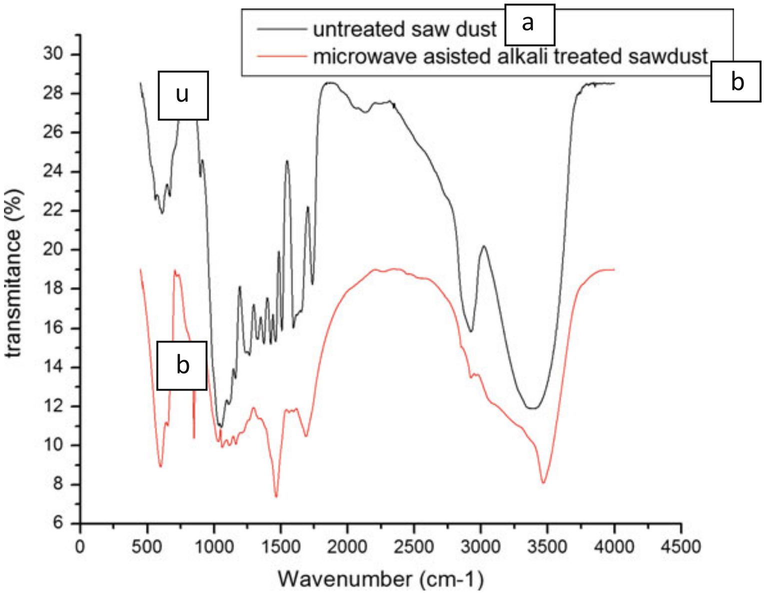


Fig. 3 FTIR graphs between wavenumber (cm^{-1}) and transmittance for **a** untreated sawdust and **b** alkali-assisted microwave-treated sawdust

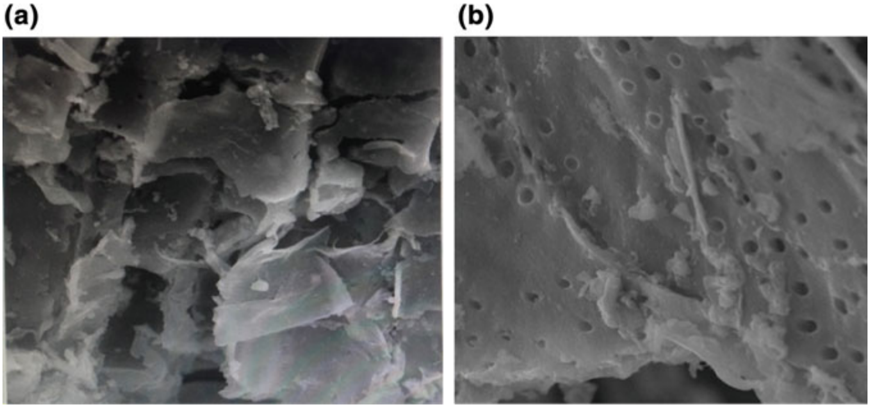


Fig. 4 SEM images of **a** untreated sawdust and **b** alkali-assisted microwave-treated sawdust

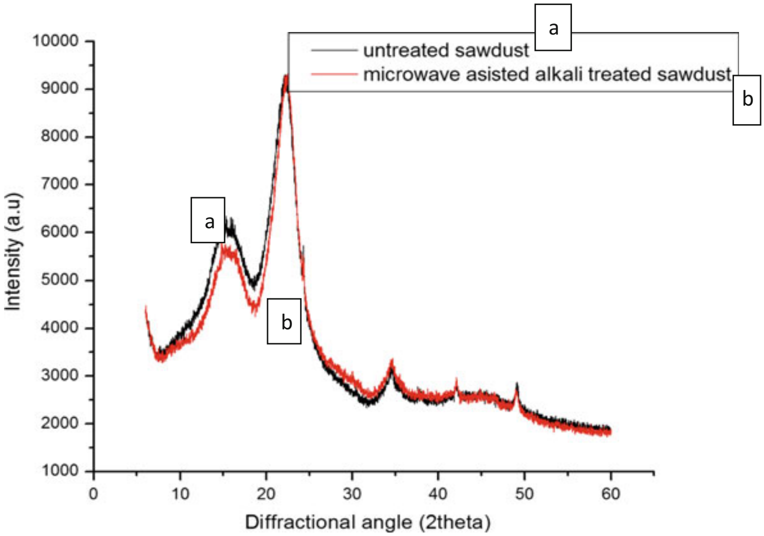


Fig. 5 XRD profiles of **a** untreated sawdust and **b** alkali-treated sawdust (Na_2co_3 0.2 M, H_2O_2 1 M at 1.15 min of microwave reaction time)

4.3 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) patterns were collected from a powder X-ray diffractometer (PANalytical X^{1}pert powder Model) at an operating condition 45 mV and 30 mA, for a 2 theta range of 5–30° at 0.016° step intervals, with step input of 34.925 s. Crystalline index (CrI) can be expressed as the percentage of crystalline material in the biomass, and is calculated with

$$\text{CrI}\ (\%) = \frac{(I_{002} - I_{\text{am}})}{I_{002}} * 100$$

where I_{002} is the maximum intensity of 002 peaks at 2 theta = 23° and

I_{am} is the intensity at 2 theta = 19°.

Crystallinity index for untreated and microwave-assisted alkali peroxide-treated sawdust was 49 and 67%, respectively, this shows amorphous nature of the sawdust got removed on treatment, and there was an increase in crystal nature of treated sawdust under microwave-assisted alkali peroxide-treated sawdust (Fig. 5).

4.4 Thermo Gravimetric Analysis (TGA)

It is clear from the TGA graphs, of untreated and microwave-assisted alkali-treated sawdust, the weight loss occurred in three stages. In the first stage, there is no significant loss of weight happened from 50 to 210 °C, and this can be known as drying period, at this stage degradation of hemicelluloses starts. In the second stage, that

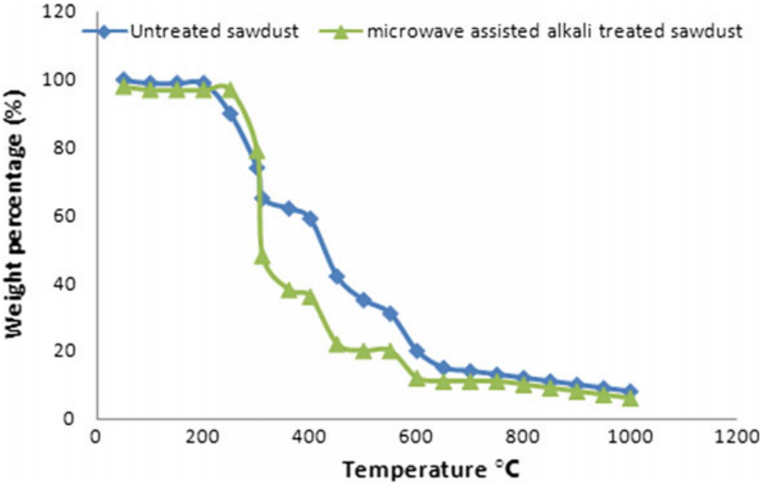


Fig. 6 TGA graphs of microwave-assisted alkali peroxide-treated sawdust and untreated sawdust

is 200–350 °C, devolatisation starts, and decomposition of hemicelluloses, cellulose and some parts of lignin occur. There is 50–53% weight loss of untreated sawdust, and 63–65% weight loss of microwave-assisted pretreated sawdust. Finally, in the third stage, which is from 310 to 500 °C from Fig. 4, about 20% weight loss in untreated sawdust and 9% weight loss in microwave-assisted alkali-treated sawdust. Then after 600 °C, there is no noticeable weight loss both in untreated and microwave–alkali-treated sawdust (Fig. 6).

4.5 Conclusion

There was an increased 35% of lignin removal achieved as compared to the conventional method. Optimal temperature of 90 °C, occurred at 700 watts is considered to be the best delignification temperature using microwave irradiation. The activation energy required for delignification was shown as 98.8 kcal/mole. The characterisation results like FTIR, SEM and TGA gave reasonable results as explained above. So, further work can be a combination of microwave and ultrasound equipment can expect higher efficiency and purity of lignin.

References

1. Tolbert A (2014) Characterization and analysis of the molecular weight of lignin for biorefining studies © 2014 Society of Chemical Industry and John Wiley & Sons, Ltd. Biofuels, Bioprod

Bioref. https://doi.org/10.1002/bbb

2. Ethaib S (2015) Microwave-assisted pretreatment of lignocellulosic biomass: a review. J Eng. Sci Technol (2)
3. De Souza R (2015) Theoretical aspects of microwave irradiation practices springer link. In: Production of biofuels and chemicals with microwave, part of the Biofuels and biorefineries book series BIOBIO, Volume 3, pp 3–16
4. Chen C, Boldor D, Aita G, Walker M (2012) Ethanol production from sorghum by microwave-assisted dilute ammonia pretreatment. Biores Technol 110:190–197
5. Shengdong Z, Ziniu Y, Yuanxin W, Xia Z, Hui L, Ming G (2005) Enhancing enzymatic hydrolysis of rice straw by microwave pretreatment. Chem Eng Commun 192:1559–1566
6. Bussemaker MJ, Xindong Mu, Zhang D (2013) Ultrasonic pretreatment of wheat straw in oxidative and nonoxidative conditions aided with microwave heating. Ind Eng Chem Res 52(35): 12514–12522, American Chemical Society
7. Moretti MMD, Bocchini-Martins DA, Nunes CDC, Villena MA, Perrone OM, da Silva R, Boscolo M, Gomes E (2014) Pretreatment of sugarcane bagasse with microwaves irradiation and its effects on the structure and on enzymatic. Appl Energy 122:189–195
8. Rivers DB, Emert GH (1987) Lignocellulose pretreatment—A comparison of wet and dry ball attrition. BiotechnolLett 9(5):365–368
9. Kim KH, Hong J (2001) Supercritical CO_2 pretreatment of lignocellulose enhances enzymatic cellulose hydrolysis. Bioresour Technol l77(2):139–144
10. Kovacs K, Macrelli S, Szakacs G, Zacchi G (2009) Enzymatic hydrolysis of steam-pretreated lignocellulosic materials with Trichoderma atroviride enzymes produced in-house. Biotechnol Biofuels 2:14. https://doi.org/10.1186/1754-6834-2-14
11. Arthur J, Kim DH, Eckert RM, Charles A, Hallett Jason P, Liotta CL (2006) From wood to fuels: integrating biofuels and pulp production. Ind Biotechnol 2(1):55–65
12. Bensah EC, Mensah M (2013) Chemical pretreatment methods for the production of cellulosic ethanol: technologies and innovations. Int J Chem Eng 2013:21
13. Sun Y, Cheng JY (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresour Technol 83(1):1–11
14. Balat M, Balat H, Oz C (2008) Progress in bioethanol processing. Prog Energy Combust 34(5):551–573
15. Alizadeh H, Teymouri F, Gilbert TI, Dale BE (2005) Pretreatment of switchgrass by ammonia fibre explosion (AFEX). Appl Biochem Biotech 121:1133–1141

Physiological, Biochemical, Growth, and Yield Responses of Radish (*Raphanus sativus* L.) Plants Grown on Different Sewage Sludge–Fly Ash Mixture (SLASH) Ratios

Bhavisha Sharma and Rajeev Pratap Singh

1 Introduction

Sustainable environmental management of solid wastes has become a significant issue of global concern. Rapidly growing rates of global population and urbanization coupled with ongoing industrial development have further escalated the generation of various types of solid wastes like sewage sludge (SS) and fly ash (FA) [23, 33]. SS is also referred to as biosolids that originate as a waste by-product of sewage treatment process [27], whereas coal FA is mainly an industrial waste produced as a result of coal combustion in thermal power plants and different industrial processes [13]. Both of these waste products are generated in enormous amounts and are disposed off openly at dumpsites occupying large area of land and also deteriorating the air, water, and soil quality of adjacent areas due to accumulation, leaching, and increased bioavailability of heavy metals, and other contaminants posing a threat to human health and environment. Rising solid waste generation has also been a key factor in increasing environmental pollution worldwide [34]. Hence, safe disposal of such wastes is not only a major challenge but also a deepening environmental concern these days.

Over the time, using SS and FA in agriculture has become quite popular around the world. SS is an abundant source of organic matter, and many essential micro- and macro-plant nutrients (N, P, and K); however, presence of toxic heavy metals, pathogens, and other organic micro-pollutants has caused apprehension about its use [2, 32]. FA although lacking macronutrients viz. nitrogen and organic carbon, contains many micronutrients like Ca, Si, Fe, Mg, Na, K, S, Mo, Ni, Cu, Co, Cd,

---

B. Sharma · R. P. Singh (✉)
Department of Environment & Sustainable Development, Institute of Environment & Sustainable Development, Banaras Hindu University, Varanasi, India
e-mail: rajeevprataps@gmail.com

B. Sharma
e-mail: bhavisha.sharma@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_51

Pb, Zn, etc., and improves soil structure and water holding capacity [33]. Land application of these wastes has multiple benefits like improvement in soil's physico-chemical properties, recycling of beneficial plant nutrients, substitute to inorganic fertilizers, alkaline stabilization of SS using FA in place of lime to ameliorate acidity, reduce bioavailability of heavy metals and pathogenic microbes [12], along with agronomic and economic benefits. Apart from these benefits, combining SS and FA as mixture (SLASH) can be evaluated as an approach to integrated solid waste management, wherein wastes from two different waste streams (i.e., municipal and industrial) are utilized simultaneously to produce a mixture which is more stable and less likely to cause environmental pollution than their individual application [20]. This approach enables to tap potential benefits of SS in boosting plant growth and FA which serves as a composting ingredient to neutralize acidic SS thereby minimizing the bioavailability of heavy metals and the attendant injury to plants and crops. It also helps in treating both SS and FA as a valuable resource and not as waste being in conformity with the principles of integrated waste management hierarchy, which states recycling of wastes to be more environmentally preferred than disposal methods like landfilling, open and ocean dumping, and incineration [22].

The present study is an attempt to investigate the potential of SLASH mixtures as a plant growth medium through assessment of physiological, biochemical, growth, and yield responses of test plant Radish (*Raphanus sativus* L.) to determine the best mixture(s) which can be used further at different amendment rates/doses in soil to derive maximum fertilizing benefits for plants and minimum environmental risk.

2 Materials and Methods

2.1 Study Area

The experiment was conducted at the agricultural field of Institute of Environment and Sustainable Development, Banaras Hindu University, a suburban area of Varanasi, Uttar Pradesh, India between December 2016 and February 2017. This period of the year is characterized by mean monthly maximum temperature between 20.5 and 27.39 °C and mean monthly minimum temperature between 11.74 and 12.67 °C. The total rainfall during the experimental period was 5.08 mm. The mean maximum relative humidity ranged between 95.64 and 84.96% and mean minimum relative humidity between 76.09 and 38.10%.

2.2 Experimental Design and Raising of Plants

SS collected from Bhagwanpur sewage treatment plant, Varanasi was air dried and ground properly to make it homogeneous and FA was collected from Hindalco Indus-

Table 1 Description of different SLASH (sewage sludge–fly ash) mixture ratios

1	Control	Agricultural farm soil (AFS)
2	**SLASH A** (4:1)	4 parts sewage sludge + 1 part fly ash
3	**SLASH B** (4:2)	4 parts sewage sludge + 2 parts fly ash
4	**SLASH C** (4:3)	4 parts sewage sludge + 3 parts fly ash
5	**SLASH D** (4:4)	4 parts sewage sludge + 4 parts fly ash

tries Ltd., Renukoot, Sonbhadra, Uttar Pradesh, India. Pot experiment was carried out using Radish (*Raphanus sativus* L.) as the test plant grown at different SS and FA mixture ratios (SLASH). The treatments used in experiment comprised of SS and FA mixed uniformly in four different ratios viz. 4:1, 4:2, 4:3, and 4:4 designated as A, B, C, and D respectively. The SLASH mixture ratios were prepared in heaps as follows: A [4(SS): 1(FA)], B [4(SS): 2(FA)], C [4(SS): 3(FA)], and D [4(SS): 4(FA)] (Table 1) and left in the field for 10 days. Agricultural field soil was dug up to a depth of 30 cm, air dried and thereafter mixed uniformly, served as control. There were three pots of each treatment along with control. The pots were filled with the prepared SLASH mixtures uniformly and left for 5 days to stabilize. Necessary moisture levels were maintained and then six seeds were sown manually in each pot at equal distances. Thinning was done after germination of seeds to keep three plants in each pot. The test plants were grown upto maturity in the soil and different treatments were given using standardized agronomic practices. Identical light, water, and temperature conditions were maintained for all the treatments during the growth period of plants. Climatic variables like minimum and maximum temperature, rainfall, humidity, etc., were measured throughout the growing period of the plant. Selected physiological and biochemical parameters were quantified during vegetative and reproductive phases of plants for assessing the impact of different SLASH mixtures on pigments, metabolite contents, and antioxidants. Upon maturity, plants were harvested to examine the crop responses with respect to following parameters: morphological characteristics, biomass accumulated, and yield.

2.3 Analyses of Morphological or Growth Parameters, Biomass, and Yield

For the analysis of morphological or growth parameters and biomass determination, Radish plants were harvested in triplicate from different pots of each treatment at 45 and 65 DAS. Morphological parameters viz. root and shoot lengths, number of leaves (plant^{-1}), leaf area, and component-wise biomass were assessed. Leaf area measurements were done using portable leaf area meter (Model Systronics 211). For determination of biomass, after initial washing of plants to remove adhering soil particles, oven drying of separated parts (root and shoot) at 80 °C was done to achieve constant weight. Thereafter, separated plant parts were weighed individually to assess biomass accumulation expressed as g plant^{-1}. Yield was expressed in g pot^{-1} by calculating fresh weight of root (belowground part) per pot at the time of harvest.

2.4 Estimation of Physiological and Biochemical Parameters

Physiological and biochemical activities of test plant Radish were measured by estimation of photosynthetic pigments, antioxidants, and different metabolites in fully expanded fresh leaves of Radish plants sampled manually at 40 and 60 DAS and stored in deep freezer. These estimations were done through methods given by Machlachlan and Zalik [19] and Duxbury and Yentsch [9] for chlorophyll and carotenoid contents, respectively, Lowry et al. [18] for foliar protein content, Bray and Thorpe [6] for total phenol, Bates et al. [4] for proline, Britton and Mehley [7] to estimate peroxidase activity, Fahey et al. [10] for thiol content, and Heath and Packer [14] for lipid peroxidation.

2.5 Statistical Analysis

The data were subjected to one-way analysis of variance (ANOVA) using SPSS version 20 software. Duncan's multiple range test was performed as post hoc to test the significance of difference between the treatments.

3 Results and Discussion

3.1 Physiological Response

Raphanus sativus (Radish) plants grown at all the SLASH mixture ratios (viz. A, B, C, and D) showed significant increase in photosynthetic pigments reported as total chlorophyll as compared to the control plants (grown in agricultural farm soil) at 45 DAS (Fig. 1). However, at 65 DAS total chlorophyll content in Radish plants decreased, even though the content was higher in plants grown in all the SLASH mixtures as compared to control plants (Fig. 2). Increase in photosynthetic pigments (total chlorophyll) initially at 45 DAS can be ascribed to higher nutrient availability to plants provided by SS which is an ample source of essential plant nutrients (N, P, K, Mg S, Ca, Mn, Zn, etc.) [28], and its decrease at 65 DAS may be linked to increased degradation or lowered biosynthesis of chlorophyll molecules due to heavy metal induced oxidative stress [12, 26]. Alvarenga et al. [2] also reported increased chlorophyll content in *Lolium multiflorum* L. due to SS amendment which resulted in higher readily available form of total nitrogen ($N\text{-}NH_4^+$) content. Significant rise in accessory pigment carotenoid was also observed in Radish plants grown in different SLASH mixtures as compared to control plants at both ages of observations, i.e., 45 and 65 DAS (Figs. 1 and 2). Gupta and Sinha [11] reported an increase in carotenoid content in mung bean plants (*Vigna radiata* L. var. PDM 54) grown at 10 and 25% FA amendment. Increased carotenoid content which is a non-enzymatic antioxidant clearly indicates toward the active defense mechanism of Radish plants to protect the chlorophyll pigment against oxidative stress owing to heavy metals [15, 25]. Chl a/b ratio decreased due to different SLASH mixtures at both ages of observation; however, significant decrease was observed only in plants grown in SLASH mixture D at 45 DAS (Fig. 1). Chl a/b ratio is a good indicator of environmental stress and an increase in chl a/b ratio is the tolerance mechanism adopted by plants in presence of heavy metals [17]. Total chl/carotenoids ratio increased in plants grown across all the SLASH amendment mixtures at 45 DAS (Fig. 1); however, at 65 DAS total chl/carotenoids ratio decreased significantly in SLASH mixture B, C, and D plants (Fig. 2). Higher total chl/car ratio indicates greater production of chlorophyll as compared to carotenoids in Radish plants grown on different SLASH mixture ratios and reduction may be caused by heavy metals.

3.2 Biochemical Response

Lipid peroxidation quantified as malondialdehyde (MDA) concentration increased significantly in Radish plants grown on different SLASH mixture ratios as compared to those grown on control soil at both the ages, i.e., 45 and 65 DAS (Figs. 3 and 4). Increased lipid peroxidation (LPO) in plants grown on SS and FA mixture, quantified as malondialdehyde (MDA) content is a reliable indication of oxidative damage or peroxidation of membrane lipids caused by reactive oxygen species (ROS) generated due to heavy metal stress [17]. Proline content showed significant rise in plants grown at different SLASH mixtures as compared to respective control plants at both ages of observation (Figs. 3 and 4). Minimum increment in proline content was seen in SLASH mixture B followed by mixture A at 65 DAS (Fig. 4). Proline increment in plants is an indication of environmental stress and provides stress tolerance through scavenging of hydroxyl radicals, protection against dehydration of enzymes, and osmoregulation [24]. Peroxidases are important enzymatic antioxidant in plants involved in free radical detoxification. Peroxidase activity in Radish plants was reported to increase significantly in all the SLASH mixtures at 45 and 65 DAS (Figs. 3 and 4) as compared to plants grown in control soil except for SLASH mixture D which significantly decreased at 65 DAS (Fig. 4) indicating heavy metal induced oxidative stress. Protein content in Radish increased signifi-

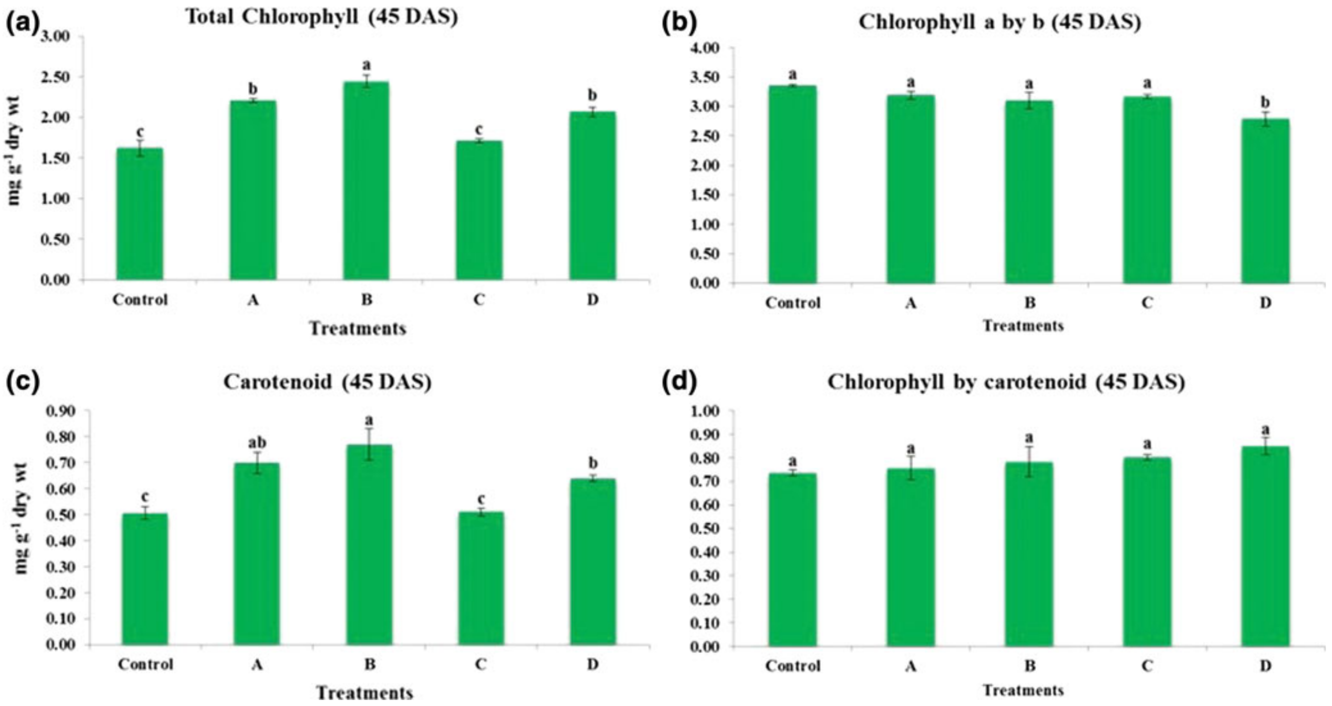


Fig. 1 Variations in physiological parameters **a** Total chlorophyll, **b** Chlorophyll a by b, **c** Carotenoids, and **d** Total chlorophyll by carotenoids of *Raphanus sativus* plants grown in control soil and SLASH mixture ratios at 45 DAS (Mean ± 1SE). Bars with different letters in each group show significant difference at $p < 0.05$

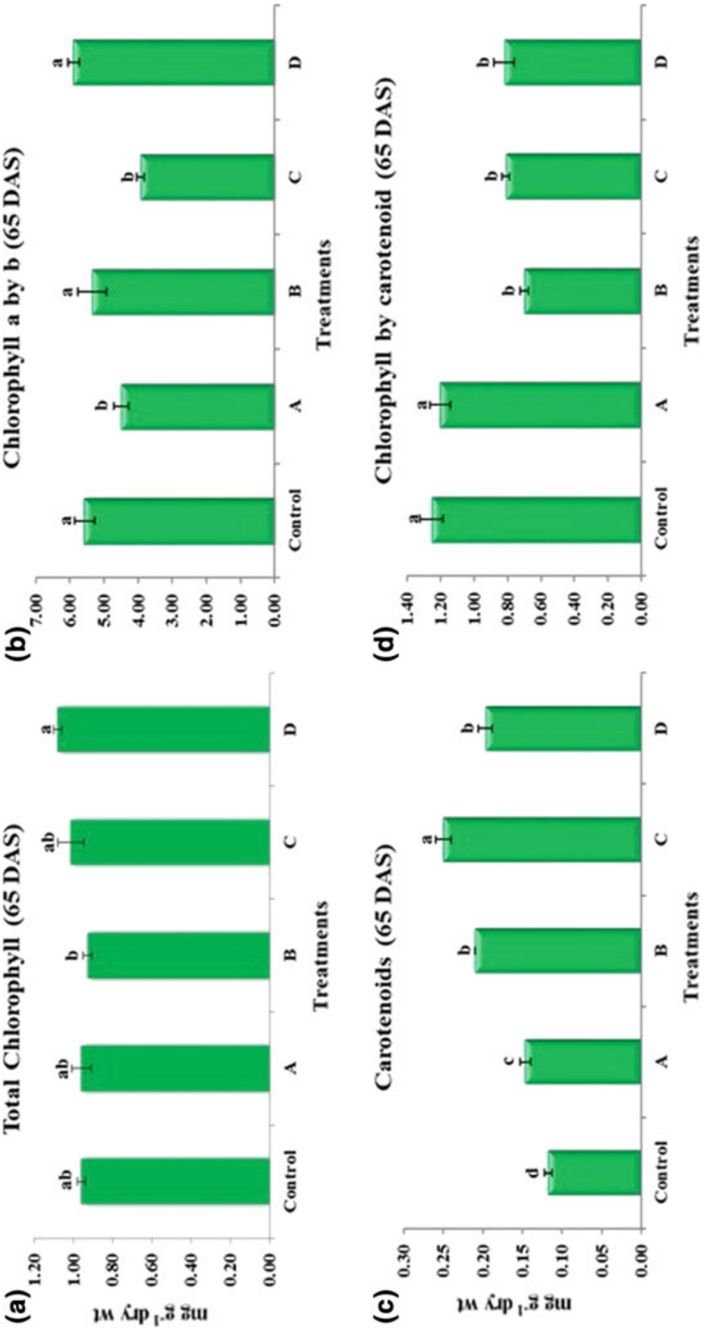


Fig. 2 Variations in physiological parameters **a** Total chlorophyll, **b** Chlorophyll a by b, **c** Carotenoids, and **d** Total chlorophyll by carotenoids of *Raphanus sativus* plants grown in control soil and SLASH mixture ratios at 65 DAS (Mean ± 1SE). Bars with different letters in each group show significant difference at $p < 0.05$

cantly under all the SLASH mixtures as compared to those grown in control soil; however, the increase was higher at 45 DAS than 65 DAS (Figs. 3 and 4). Maximum increment in protein content was shown by plants grown in SLASH mixture B and A at 45 DAS (Fig. 3). Similar findings of increased lipid peroxidation, proline content, peroxidase activity, and protein content in plants (*B. vulgaris, A. esculentus* and *O. sativa, and V. radiata*) grown on SS and FA amendments have been reported by many researchers [11, 23, 26, 28, 29]. The results are also in agreement with the findings of Gupta et al. [12] who also reported increased foliar protein content in *Brassica campestris* L. (cv. Pusa Jaikisan) grown in mixtures of tannery sludge and FA in the ratio of 4:1 (A) and 4:2 (B) in comparison to control plants at different amendment rates. Higher protein content in Radish plants under different SLASH ratios may be credited to the higher availability of organic matter and nitrogen contents due to SS [22, 27]. It could also be due to heavy metal stress [26] as both SS and FA contain heavy metals. Thiol content in Radish increased significantly across all the SLASH mixtures, in comparison to control plants at 45 DAS; however, at 65 DAS significant increase was seen only in plants grown at SLASH mixture B (Figs. 3 and 4). Thiols help in fighting oxidative stress induced by heavy metals as an important part of non-enzymatic defense adopted by plant cells through detoxification of metals and phytochelatin synthesis [8, 11]. Significant increase in thiol content was also reported in nodulated alfalfa plants due to application of SS [3]. Phenol, a secondary metabolite, also plays an important role in providing resistance against many stresses in plants and protects the plants against oxidative stress through scavenging of free radicals [25, 29]. Phenol content increased significantly in Radish plants grown in different SLASH mixtures as compared to respective control at both 45 DAS and 65 DAS (Figs. 3 and 4). Both Singh and Agrawal [26] and Singh et al. [25] reported a decrease in foliar phenol content in *Beta vulgaris* grown at different SS and FA amendment rates, respectively.

3.3 Morphological or Growth and Yield Response

In the present study, growth parameters of Radish such as root length, shoot length, number of leaves, leaf area, root biomass, shoot biomass, and total biomass increased significantly in plants grown in different SLASH mixtures as compared to control plants at both ages of observation (45 and 65 DAS) except for a decrease shown by parameter root length in SLASH mixture D (at 45 DAS) (Table 2). Maximum increment in growth parameters at 45 DAS was shown by Radish plants grown in SLASH mixture A followed by C; and at 65 DAS it was seen in plants grown on SLASH mixture A followed by B (Table 2). Similarly, yield of Radish increased significantly in all the SLASH mixtures; however, maximum increase was shown by plants grown in mixture A (87.8%) followed by C (87.5%) and B (84.8%), respectively (Table 2). Positive morphological response or increase in growth parameters and yield in plants due to SS and/or FA amendments have been reported in many studies such as Singh and Agrawal [28, 30, 31] (lady's finger [*Abelmoschus esculentus* L. var Varsha uphar],

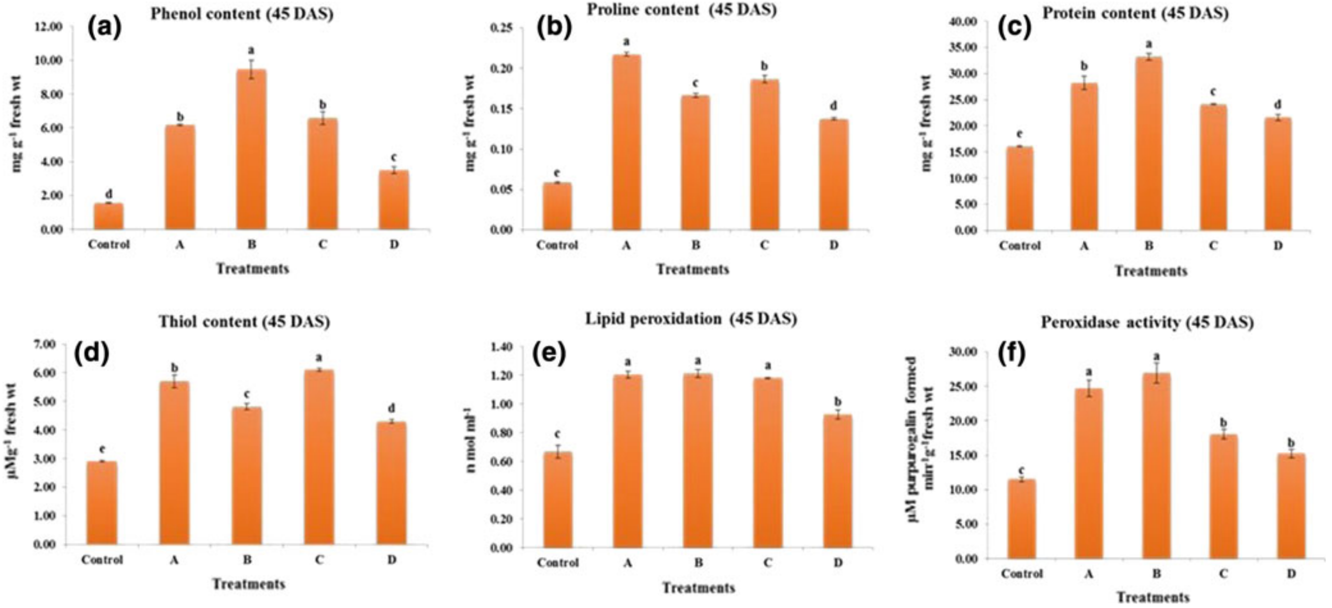


Fig. 3 Variations in biochemical parameters **a** Phenol content, **b** Proline content, **c** Protein content, **d** Thiol content, **e** Lipid peroxidation, and **f** Peroxidase activity of *Raphanus sativus* plants grown in control soil and SLASH mixture ratios at 45 DAS (Mean ± 1SE). Bars with different letters in each group show significant difference at $p < 0.05$

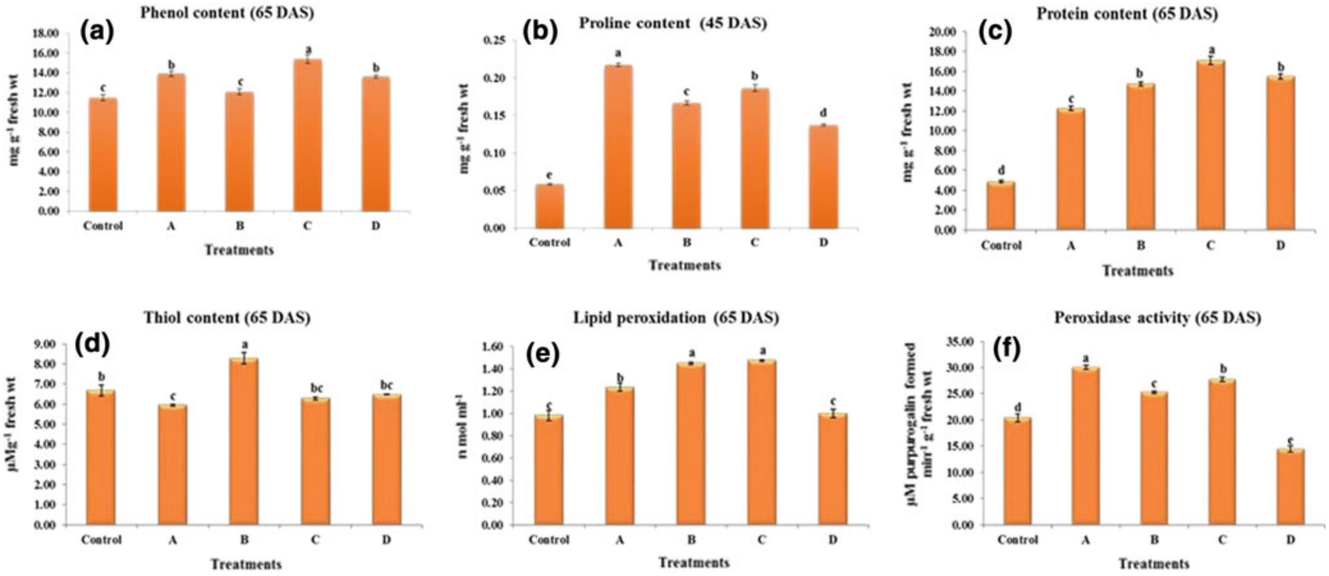


Fig. 4 Variations in biochemical parameters **a** Phenol content, **b** Proline content, **c** Protein content, **d** Thiol content, **e** Lipid peroxidation, and **f** Peroxidase activity of *Raphanus sativus* plants grown in control soil and SLASH mixture ratios at 65 DAS (Mean ± 1SE). Bars with different letters in each group show significant difference at $p < 0.05$

Table 2 Variations in different morphological characteristics of *Raphanus sativus* plants grown in control soil and different SLASH ratios at 45 and 65 DAS (Mean ± 1SE)

	Treatments				
Parameters	Control	SLASH A	SLASH B	SLASH C	SLASH D
45 DAS					
Root length (cm)	12.8 ± 0.9^{bc}	16.17 ± 1.09^{a}	12.93 ± 1.11^{bc}	14.7 ± 1.01^{ab}	11.47 ± 0.59^{c}
Shoot length (cm)	19.7 ± 0.86^{b}	37.33 ± 1.09^{a}	39.20 ± 0.56^{a}	39.60 ± 1.00^{a}	37.70 ± 0.61^{a}
Leaf number (plant^{-1})	5.00 ± 0.0^{d}	9.67 ± 0.33^{a}	7.67 ± 0.33^{bc}	8.33 ± 0.67^{b}	7 ± 0.00^{c}
Leaf area (cm^{2})	51.1 ± 3.3^{d}	910.0 ± 44.95^{a}	523.73 ± 31.3^{b}	628.9 ± 53.9^{b}	400.23 ± 11.48^{c}
Root biomass (g plant^{-1})	0.03 ± 0.00^{e}	0.40 ± 0.00^{a}	0.10 ± 0.01^{d}	0.25 ± 0.00^{b}	0.12 ± 0.00^{c}
Shoot biomass (g plant^{-1})	0.21 ± 0.01^{d}	3.97 ± 0.24^{a}	1.73 ± 0.09^{c}	2.70 ± 0.15^{b}	1.44 ± 0.07^{c}
Total Biomass (g plant^{-1})	0.24 ± 0.0^{d}	4.36 ± 0.24^{a}	1.83 ± 0.09^{c}	2.95 ± 0.15^{b}	1.56 ± 0.07^{c}
65 DAS					
Root length (cm)	11.97 ± 0.4^{c}	22.47 ± 1.74^{a}	18.47 ± 1.41^{b}	18.23 ± 1.09^{b}	19.73 ± 0.90^{ab}
Shoot length (cm)	17.5 ± 0.76^{b}	41.33 ± 2.01^{a}	38.67 ± 2.13^{a}	38.10 ± 1.35^{a}	37.93 ± 1.85^{a}
Leaf number (plant^{-1})	5.00 ± 0.0^{d}	13.67 ± 0.33^{a}	13.33 ± 0.88^{a}	11.00 ± 0.58^{b}	9.00 ± 0.58^{c}
Leaf area (cm^{2})	77.5 ± 5.76^{c}	1257.3 ± 103.3^{a}	1339.03 ± 126^{a}	680.70 ± 47.3^{b}	682.17 ± 28.77^{b}
Root biomass (g plant^{-1})	0.10 ± 0.01^{d}	1.39 ± 0.08^{a}	0.80 ± 0.03^{b}	0.43 ± 0.02^{c}	0.42 ± 0.02^{c}
Shoot biomass (g plant^{-1})	0.39 ± 0.02^{d}	6.24 ± 0.21^{a}	5.33 ± 0.44^{b}	2.42 ± 0.19^{c}	2.40 ± 0.13^{c}
Total Biomass (g plant^{-1})	0.48 ± 0.02^{d}	7.63 ± 0.14^{a}	6.13 ± 0.47^{b}	2.85 ± 0.21^{c}	2.81 ± 0.15^{c}
Yield (g pot^{-1})	1.82 ± 0.04^{d}	14.93 ± 0.14^{a}	12.01 ± 0.18^{b}	14.63 ± 0.21^{a}	10.03 ± 0.44^{c}

Different letters in each group show significant difference at $p < 0.05$.
A= 4:1 Sewage sludge: Fly Ash;
B= 4:2 Sewage sludge: Fly Ash;
C= 4:3 Sewage sludge: Fly Ash;
D= 4:4 Sewage sludge: Fly Ash

rice [*Oryza sativa* L. cv. Pusa sugandha 3], and mung bean [*Vigna radiata* L.]), Bhat et al. [5] (Radish [*Raphanus sativus* L.]), Latare et al. [16] (wheat [*Triticum aestivum* L. cv. Malviya 234]), Ajaz and Tyagi [1] (cucumber [*Cucumis sativus*]), Gupta and Sinha [11] (mung bean [*Vigna radiata* L. var PDM 54]), Sajwan et al. [21] (sorghum sudangrass [*Sorghum vulgaris*]), and Wong and Selvam [35] (*Brassica chinensis*). However, significant reductions in growth parameters in palak plants (*Beta vulgaris* L. var. Allgreen H-1) grown in different SS and FA amendments were reported by Singh and Agrawal [26] and Singh et al. [25], respectively. Significant increase in growth parameters and yield in Radish plants in the present study can be ascribed to higher availability of plant growth promoting macro- and micronutrients present in SS and FA, whereas reduction in these parameters occurs due to higher concentration of heavy metals in plant tissues causing phytotoxicity or due to variable tolerance of different plant species to heavy metals and salt stress [13, 22, 35].

4 Conclusions

The present study clearly showed significant rise in biochemical parameters (viz. proline, protein, carotenoids, phenol, thiol, and peroxidase activity) and plant productivity (chlorophyll content, total biomass, leaf area, and yield) of Radish plants grown on SLASH mixtures A, B, and C indicating toward strong antioxidant defense of Radish plants against heavy metal stress to maintain increments in their growth parameters, biomass accumulation, and yield. Hence, SLASH mixtures A, B, and C may be a good option to utilize as a fertilizer supplement (at different amendment rates/doses) or plant growth medium for Radish plants, but the amendment rates/doses in soil should be strictly regulated to avoid food chain contamination and risk to human health due to heavy metals.

Acknowledgements Authors are thankful to Head, Department of Environment and Sustainable Development (DESD), Banaras Hindu University, Varanasi for providing necessary facilities during the research work. Ms. Bhavisha Sharma is also thankful to University Grants Commission, New Delhi for providing Senior Research Fellowship.

References

1. Ajaz S, Tiyagi S (2003) Effect of different concentrations of fly-ash on the growth of cucumber plant, Cucumis sativus. Arch Agron Soil Sci 49:457–461
2. Alvarenga P, Palma P, Mourinha C, Farto M, Dores J, Patanita M, Cunha-Queda C, Natal-da-Luz T, Renaud M, Sousa JP (2017) Recycling organic wastes to agricultural land as a way to improve its quality: a field study to evaluate benefits and risks. Waste Manage 61:582–592
3. Antolín MC, Muro I, Sánchez-Díaz M (2010) Application of sewage sludge improves growth, photosynthesis and antioxidant activities of nodulated alfalfa plants under drought conditions. Environ Exp Bot 68(1):75–82

4. Bates LS, Waldren RP, Teare ID (1973) Rapid determination of free proline for water-stress studies. Plant Soil 39(1):205–207
5. Bhat MA, Kirmani NA, Agrawal HP, Bhat MI, Wani MA (2011) Heavy metal phytotoxicity to radish (Raphanus sativus L.) in a digested sludge-amended gangetic alluvium. Soil Sediment Contamin An Int J 20(6): 733–743
6. Bray HG, Thorpe WV (1954) Analysis of phenolic compounds of interest in metabolism. Methods Biochem Anal 1:27–52
7. Britton C, Mehley AC (1955) Assay of catalase and peroxidase. In: Colowick SP, Kalpan NO (eds) Methods in Enzymology, vol II. Academic Press Inc., New York, p 764
8. Dietz KJ (2005) Plant thiol enzymes and thiol homeostasis in relation to thiol-dependent redox regulation and oxidative stress. In: Smrinoff N (ed) Antioxidants and reactive oxygen species in plants, Blackwell Publishing Ltd, pp 25–52
9. Duxbury AC, Yentsch CS (1956) Plankton pigment monographs. J Marine Res 15:91–101
10. Fahey RC, Brown WC, Adams WB, Worsham MB (1978) Occurrence of glutathione in bacteria. J Bacteriol 133(3):1126–1129
11. Gupta AK, Sinha S (2009) Growth and metal accumulation response of Vigna radiata L. var PDM 54 (mung bean) grown on fly ash-amended soil: effect on dietary intake. Environ Geochem Health 31(4):463–473
12. Gupta AK, Mishra RK, Sinha S, Lee BK (2010) Growth, metal accumulation and yield performance of Brassica campestris L. (cv. Pusa Jaikisan) grown on soil amended with tannery sludge/fly ash mixture. Ecol Eng 36(8):981–991
13. Gupta AK, Singh RP, Ibrahim MH, Lee BK (2012) Fly ash for agriculture: implications for soil properties, nutrients, heavy metals, plant growth and pest control. Agroecology and strategies for climate change. Springer, Netherlands, pp 269–286
14. Heath RL, Packer L (1968) Photoperoxidation in isolated chloroplasts: I. Kinetics and stoichiometry of fatty acid peroxidation. Arch Biochem Biophys 125(1):189–198
15. Kenneth E, Pallet KE, Young J (2000) Carotenoids. antioxidants in higher plants in Taiwan. Bull Environ Contam Toxicol 61:497–504
16. Latare AM, Kumar O, Singh SK, Gupta A (2014) Direct and residual effect of sewage sludge on yield, heavy metals content and soil fertility under rice–wheat system. Ecol Eng 69:17–24
17. Lopareva-Pohu A, Verdin A, Garçon G, Sahraoui ALH, Pourrut B, Debiane D, Waterlot C, Laruelle F, Bidar G, Douay F, Shirali P (2011) Influence of fly ash aided phytostabilisation of Pb, Cd and Zn highly contaminated soils on Lolium perenne and Trifolium repens metal transfer and physiological stress. Environ Pollut 159(6):1721–1729
18. Lowry OH, Rosebrough NJ, Farr AL et al (1951) Protein measurement with the Folin phenol reagent. J Boil Chem 193(1):265–275
19. Maclachlan S, Zalik S (1963) Plastid structure, chlorophyll concentration, and free amino acid composition of a chlorophyll mutant of barley. Can J Bot 41(7):1053–1062
20. Masto RE, Sunar KK, Sengupta T, Ram LC, Rout TK, Selvi VA, George J, Sinha AK (2012) Evaluation of the co-application of fly ash and sewage sludge on soil biological and biochemical quality. Environ Technol 33(8):897–905
21. Sajwan KS, Paramasivam S, Alva AK, Sahi SV (2006) Fly ash-organic byproduct mixture as soil amendment. In: Soil and water pollution monitoring, protection and remediation, pp 387–399
22. Sharma B, Sarkar A, Singh P, Singh RP (2017) Agricultural utilization of biosolids: a review on potential effects on soil and plant grown. Waste Manage 64:117–132
23. Sharma B, Kothari R, Singh RP (2018) Growth performance, metal accumulation and biochemical responses of Palak (Beta vulgaris L. var. Allgreen H-1) grown on soil amended with sewage sludge-fly ash mixtures. Environ Sci Pollut Res 25:12619–12640
24. Sharma SS, Schat H, Vooijs R (1998) In vitro alleviation of heavy metal-induced enzyme inhibition by proline. Phytochemistry 49(6):1531–1535
25. Singh A, Sharma RK, Agrawal SB (2008) Effects of fly ash incorporation on heavy metal accumulation, growth and yield responses of Beta vulgaris plants. Bioresour Technol 99(15):7200–7207

26. Singh RP, Agrawal M (2007) Effects of sewage sludge amendment on heavy metal accumulation and consequent responses of Beta vulgaris plants. Chemosphere 67(11):2229–2240
27. Singh RP, Agrawal M (2008) Potential benefits and risks of land application of sewage sludge. Waste Manage 28(2):347–358
28. Singh RP, Agrawal M (2009) Use of sewage sludge as fertiliser supplement for Abelmoschus esculentus plants: physiological, biochemical and growth responses. Int J Environ Waste Manage 3(1–2):91–106
29. Singh RP, Agrawal M (2010) Biochemical and physiological responses of rice (Oryza sativa L.) grown on different sewage sludge amendments rates. Bull Environ Contam Toxicol 84(5):606–612
30. Singh RP, Agrawal M (2010) Variations in heavy metal accumulation, growth and yield of rice plants grown at different sewage sludge amendment rates. Ecotox Environ Safe 73(4):632–641
31. Singh RP, Agrawal M (2010) Effect of different sewage sludge applications on growth and yield of Vigna radiata L. field crop: metal uptake by plant. Ecol Eng 36(7):969–972
32. Singh RP, Singh P, Ibrahim MH, Hashim R (2012) Land application of sewage sludge: physicochemical and microbial response. Reviews of environmental contamination and toxicology. Springer, New York, pp 41–61
33. Singh RP, Sharma B, Sarkar A, Sengupta C, Singh P, Ibrahim MH (2014) Biological responses of agricultural soils to fly-ash amendment. In: Reviews of environmental contamination and toxicology. Springer International Publishing, 232, pp 45–60
34. Singh RP, Sarkar A (2015) Waste management: challenges, threats and opportunities. Nova Science Inc., New York. ISBN 978-1-63482-150-6
35. Wong JWC, Selvam A (2009) Growth and elemental accumulation of plants grown in acidic soil amended with coal fly ash–sewage sludge co-compost. Arch Environ Contam Toxicol 57(3):515–523

Anaerobic Digestion Potential of Leaf Litter: Degradability and Gas Production Relationships

D. Ravi Kumar, H. N. Chanakya and S. Dasappa

1 Introduction

Leaf litter is a predominant fraction of the organic fraction of the municipal solid waste, and leaf litter constitutes almost 35% of the overall waste collected at many locations [1]. Usually, the leaf litter is composted [2], and leaf decomposition is one of the major factors either in the case of composting or degradation towards biogas production. Leaves have the potential to produce twice as much as produced by cow dung [3]. Leaves could be thin and easily decomposable or could be highly recalcitrant having lower photosynthetic rates [2]. Studies on certain varieties of available leafy biomass feedstock have been carried out with some success [4]. The properties of leafy biomass make it difficult to digest in many conditions [5].

This study focuses on the degradability and biogas production of some fast-growing tropical biomass and attempts to understand its feasibility towards biogas production. Also, various model fits are studied, namely Monod kinetics, linear kinetics and Modified Gompertz kinetics. This study also looks into the pattern of gas production and separation of gas production based on their properties.

2 Materials and Method

Substrate: Five leafy biomass substrates were chosen, viz., Mango leaves, Rubber (Ficus elastica), Acacia (Acacia auriculiformis), Bamboo and Syzigium leaves. The choice of the substrates was dependent on their availability and importance. Inoculum: Inocula were collected from the pre-existing biogas reactor fed with biomass.

D. Ravi Kumar · H. N. Chanakya (✉) · S. Dasappa
Centre for Sustainable Technologies (Formerly ASTRA),
Indian Institute of Science, Bengaluru, India
e-mail: chanakya@iisc.ac.in

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_52

The inocula were collected in jerry cans and sealed. Intermittent degassing was done until gas production subsided.

BMP: Biochemical methane potential was performed in serum bottles of 135 ml with a working volume of 70 ml. Since the substrate-to-inoculum (S/I) ratio plays an important role [6], an S/I of 0.25 was chosen making sure the system does not undergo acid accumulation due to any process imbalances. The gas volume was measured though downward displacement of water that was moderately acidified to prevent CO_2 solubilization. The gas quality was measured using gas chromatography fitted with Haysep A column with a thermal conductivity detector (TCD). Hydrogen was used as carrier gas maintained at a flow rate of 30 (ml/min).

Gompertz kinetics: Modified Gompertz model was used to ascertain behaviour and fit of the gas production data. Factors like specific gas production rate and lag time or lag phase were also determined [7].

$$Y = A * e^\wedge\left\{-e^\wedge((\mu * e)/A(\lambda - t) + 1)\right\}$$

A—maximum gas production, μ—specific gas production rate and λ—lag time/phase.

3 Results and Discussions

The leaves are abundantly found in tropical countries large foliage, with large canopy and can be obtained as leaf litter [8]. The results obtained are shown in the table below.

Among the five leafy biomass Syzigium has the highest gas production of about 225 (ml/gVS) and least gas is obtained in the case of rubber leaves. As compared to other biomass such as Parthenium and weed like paper mulberry, the gas yields are a lot lower [4]. Acacia leaves showed a similar behaviour when compared with earlier studies [4]. It was observed that the volatile solid degradation occurs within a period of 20–30 days (not shown here). Bamboo leaves being an extension of the stem has lower gas production. All the biomass showed methane production of greater than 45%, except in the case of Acacia. This shows that there is insufficient acidogenesis leading to methanogenic starvation. The pH of all samples at the end of 100 days was found to be within optimum range.

4 Gompertz Fit and Inference

An initial linear and Monod fit showed poor correlation. This can be ascertained to the behaviour of the solid substrate, whose behaviour is different as compared to pure soluble substrate [9]. Gompertz fit of the gas production shows that the correlation/fit is significant, with an R^2 of 0.94–0.98. From Table 1, the specific gas production rate is high in case of Syzigium while at the same time, it has the highest lag phase or

Table 1 Cumulative gas production and Gompertz parameters

Substrate	Cumulative gas production (ml/gVS)	Specific gas production rate (μ/day)	Lag time (λ, day)
Mango	213 ± 20	6.2	2.8
Rubber	125 ± 25	3.5	5.8
Acacia	90 ± 10	2	0
Bamboo	179 ± 15	2.6	7.8
Syzigium	223 ± 30	7.2	7.3

lag time. On the other hand, though Acacia had no lag phase, it has extremely low specific gas production rate.

When looked at the lag phase and specific gas production rate, it could be observed there is a significant difference in the gas-specific gas production rates and lag phase. This could be due to the binding properties or the structure of the bundle fibres. Chanakya and Sreesha [10] in their paper had shown that the presence and different binding of lignin within the fibres (areca nut and banana stem) played a significant role in the degradation. Similarly, parallels could be drawn that the significant differences in gas production extent, specific rates and lag phase could be due to the structure.

5 Conclusion

This study with the tropical leafy biomass shows a limited gas as compared to certain other leafy biomass studied in the literature. A small lag phase does not necessarily mean higher gas production as can be seen from the Gompertz fit data. Though not conclusive, it can be shown that the structure might play a role in the gas production. Gompertz fits well with the gas production data as compared to Monod and linear kinetics.

References

1. Sateesh Kumar R, Chanakya HN, Ramachandra TV (2001) Feasible solid waste management, CES Tech. Report No 86, Centre for Ecological Sciences, Bangalore, p 145
2. Mehta N, Dinakaran J, Patel S, Laskar AH, Yadava MG, Ramesh R (2013) Changes in litter decomposition and soil organic carbon in a reforested tropical deciduous cover (India). Ecol Res 28:239–248. https://doi.org/10.1007/s11284-012-1011-z
3. Jagadish KS, Chanakya HN, Rajabapaiah P, Anand V (1998) Plug flow digestors for biogas generation from leaf biomass. Biomass Bioenerg 14:415–423. https://doi.org/10.1016/S0961-9534(98)00003-8

4. Chanakya HN, Srikumar KG, Anand V, Modak J, Jagadish KS (1999) Fermentation properties of agro-residues, leaf biomass and urban market garbage in a solid phase biogas fermenter. Biomass Bioenerg 16:417–429. https://doi.org/10.1016/S0961-9534(99)00015-X
5. Chanakya HN, Venkatsubramaniyam R, Modak J (1997) Fermentation and methanogenic characteristics of leafy biomass feedstocks in a solid phase biogas fermentor. Bioresour Technol 62:71–78. https://doi.org/10.1016/S0960-8524(97)00139-9
6. Hashimoto AG (1982) Effect of inoculum/substrate ratio on methane yield and production rate from straw. Biotechnol Bioeng 24:9–23. https://doi.org/10.1002/bit.260240103
7. Davis ML, Mounteer LC, Stevens LK, Miller CD (2012) 2D motility tracking of *Pseudomonas putida* KT2440 in growth phases using video microscopy 111:605–11. https://doi.org/10.1016/j.jbiosc.2011.01.007.2d
8. Chanakya HN, Sharma I, Ramachandra TV (2009) Micro-scale anaerobic digestion of point source components of organic fraction of municipal solid waste. Waste Manag 29:1306–1312. https://doi.org/10.1016/j.wasman.2008.09.014
9. Vavilin VA, Rytov SV, Lokshina LY (1996) A description of hydrolysis kinetics in anaerobic degradation of particulate organic matter. Bioresour Technol 56:229–237. https://doi.org/10.1016/0960-8524(96)00034-X
10. Chanakya HN, Sreesha M (2012) Anaerobic retting of banana and arecanut wastes in a plug flow digester for recovery of fiber, biogas and compost. Energy Sustain Dev 16:231–235. https://doi.org/10.1016/j.esd.2012.01.003

Hydrogen Generation from Biorefinery Waste: Recent Advancements and Sustainability Perspectives

Biswajit Debnath and Sadhan Kumar Ghosh

1 Introduction

The COP21 has started a new movement on climate change and sustainability globally. The energy demand is also increasing every day which makes it imperative to develop clean and alternative sources of energy. Biohydrogen produced from biomass and other natural resources is a promising candidate as a clean source of energy. These are advantageous because it is readily available, there are no harmful emissions involved, green, high-energy content (122 kJ/g), sustainable and renewable. One of the major challenges is the sustainable production of biohydrogen and subsequent storage. These days, the demand of hydrogen has increased quite a few times as the hydrogen-powered bus, ships and trains are being demonstrated. Other than that, hydrogen has applications in chemical and petrochemical industries. Hydrogen demand is also increasing for fuel cell applications and worldwide demand was projected 475 billion m^3 in 2013. World demand of hydrogen will rise by 3.5% annually through 2018 [1]. Hydrogen market is expected to grow at a CAGR of 5.2%, from \$117.94 billion in 2016 to \$152.09 billion in 2021 [2]. Today nearly, 98% of hydrogen is fossil fuel based. As reported by Singh and Wahid [3], 40% of the World's hydrogen is produced either from natural gas or by steam reforming of hydrocarbons, 30% is produced from oil which is primarily used within the refineries itself, coal gasification produces another 18% and the remaining amount is obtained by electrolysis of water. However, these processes are energy intensive, quite expensive as well as not environmentally sound. Biological hydrogen production is a comparatively promising alternative to the traditional one. There are two popular methods for

---

B. Debnath
Department of Chemical Engineering, Jadavpur University, Kolkata, India

S. K. Ghosh (✉)
Department of Mechanical Engineering, Jadavpur University, Kolkata, India
e-mail: sadhankghosh9@gmail.com

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_53

biohydrogen production—(a) the photo-fermentative process, which employs photosynthetic organisms (such as algae or bacteria) and (b) dark fermentation process that uses ability of certain organisms to ferment a substrate. The identification of proper substrates for future industrial-scale economic applications of the hydrogen fermentation technology is a big challenge. Apart from that the yield of hydrogen varies in a wide range from a given substrate present in different feedstocks, which make things more difficult [4]. Hence, it is essential to overcome these obstacles to enable the commercialization of biohydrogen production from biomass.

Biodiesel is arguably the most widely used biofuel in the world today and by 2020 biodiesel could contribute to nearly 20% of the transportation fuels. To meet the ever-increasing demand of biofuel, biodiesel production leads to the generation of huge amount of waste glycerol. Stoichiometrically, 10 kg of waste glycerol is produced per 100 kg of biodiesel produced [5]. Biodiesel companies in EU and USA are finding it really costly to dispose this huge quantity of waste glycerol. A number of impurities are present in waste glycerol such as methanol, soaps, residual fatty acids, salts and heavy metals [6]. Due to the presence of impurities, waste glycerol appears to be a bit yellowish, and hence it is also known as yellow glycerol. Purification of this yellow glycerol is energy intensive and economically challenging. Hence, it is quite important to seek new and innovative ways of utilizing yellow glycerol in a sustainable manner. In recent years, hydrogen production from glycerol has caught the attention of the researchers. The chief reason behind this is the utilization of hydrogen for clean energy generation using the fuel cells. Bioethanol, another widely used biofuel, which is blended with gasoline in major, can be manufactured from cornstarch, paper and other lignocellulosic biomasses. The demand of bioethanol is also quite high and a lot of researchers are now shifting their focus on the conversion of biomass to bioethanol. The plants which are established for conversion of lignocellulosic biomass to ethanol are termed as the second-generation biorefinery. These biorefineries produce a lot of waste water. It generated nearly 920 m^3 of waste water per day. Other biorefineries such as olive mill biorefinery [7], winery [8], cellulose fermentation units, xylose fermentation units, potato processing units, soya bean processing units, tofu manufacturing units, etc. also produce waste water. The presence of different organic acids and organic compounds makes this waste water suitable for hydrogen production. The microbial fuel cell (MFC) is the technology that is being explored for hydrogen generation from waste water or biorefinery effluents. Research work is being carried out on use of MFC and their efficiencies to establish this technology.

The demand of hydrogen has increased over the last few years. Biomass and biorefinery waste streams are potential candidates for conversion of hydrogen. Research trends focus on individual technology development, opportunities for different feedstocks for hydrogen generation and potential of some methods for this purpose. Good review on potential of biorefinery waste streams is scant. The sustainability of these processes is also not very clear. In this study, a comprehensive idea about the potential of biorefinery waste stream has been presented and the sustainability of the processes has been discussed.

2 Methods and Materials

This study is based on published literature including book chapters, conference proceedings, reports, journal papers, etc. Different databases were explored to obtain the literature. Keywords such as 'Hydrogen generation from waste water', 'Hydrogen from Biorefinery waste water', 'Hydrogen from glycerol', etc. were employed for this purpose. The publications were found in the areas of hydrogen generation from biowaste via different pathways, hydrogen generation from glycerol and waste water using different technologies and catalysts. Literatures relevant to the study were screened and reviewed keeping in mind the sustainability parameters. In this study, four sustainability parameters (environmental, operational, economical and social) were considered for providing a generalised view on the sustainability aspects.

3 Hydrogen Generation from Biorefinery Waste Streams

3.1 Hydrogen Generation from Waste Glycerol

Waste glycerol from the biodiesel manufacturing units is a big issue. Hydrogen generation from waste glycerol is one of the green ways of utilization of waste glycerol. Several thermochemical and biochemical technologies have been explored by the researchers for conversion of glycerol to hydrogen such as steam reforming [9], steam gasification [10], pyrolysis [10], aqueous-phase reforming [11], partial oxidation reforming [12], oxidative steam reforming [13], supercritical water reforming [14], dark fermentation [15], photofermentation [16], etc. Sharma et al. [17] studied hydrogen production in a batch hydrogen producing bioreactor setup from waste glycerol and compared with pure glycerol. Single chamber microbial fuel cell setup was used to investigate the electricity generation from glycerol in a continuous mode at different concentrations. Finally, an economic evaluation was carried out to find the benefits of coupling anaerobic bioenergy technologies. Remon et al. [18] studied the effect of impurities (such as acetic acid, methyl alcohol and potassium hydroxide) in steam reforming of yellow glycerol in the presence of catalyst, both theoretically and experimentally, for hydrogen production. The experimental study was done in a fluidized bed reactor at 823 K using nickel as catalyst considering all the impurities. It was found that methanol alone does not affect the process much but acetic acid and potassium hydroxide decrease the initial production of gases. This effect is highest for KOH as it enhances the char formation. Luo et al. [19] carried out liquid-phase reforming of aqueous glycerol in subcritical water in the presence of bimetallic nickel–cobalt catalysts on alumina supports promoted by cerium. Hydrogen selectivity was increased due to the presence of cobalt and nickel which enhanced the C–C bond breaking. The optimal Ni:Co ratio was found to be 1:3 with 2% added cerium for suppressing methane selectivity and higher catalyst activity. Catalyst deactivation was noted due to deposition of carbon. Ozgur and Uysal [20] used Pt/Al_2O_3 catalyst for hydrogen generation from glycerol via aqueous-phase reforming (APR). Two reactor configurations were used for the experiments—(a) an autoclave reactor and (b) a continuous fixed bed reactor. Effects of reaction temperature, feed flow rate and feed concentration were investigated on product distribution. It was found that the decrease in glycerol concentration in feed increases the hydrogen concentration in product gas. 503 K was found to be the optimum temperature and 0.1 ml/min feed rate gave maximum gas production rate.

Dou et al. [21] presented a continuous method for hydrogen production from glycerol. The method employs enhanced-sorption chemical looping steam reforming technique. This is based on redox reactions integrated with in situ carbon dioxide removal. The $NiO/NiAl_2O_4$ catalyst was used for this purpose which is a low-cost catalyst. The catalyst converted steam and glycerol to hydrogen, whereas CaO helped to remove the CO_2 simultaneously from the system. Best results (above 90% hydrogen generation) were achieved in autothermal operation for reforming reactor at 773–873 K temperature, steam-to-carbon ratio of 1.5–3.0. Calles et al. [22] presented a study of hydrogen production by glycerol steam reforming using Mg- and Ca-modified Ni/SBA-15 catalysts at 873 K. The Ni/Ca/SBA-15 catalyst achieved the highest glycerol conversion of 98.4% with a hydrogen content of 53 vol.%. The catalyst was found to be stable during the reaction time and lowest coke deposition occurred. Steam glycerol reforming (SGR) has been attempted by many other researchers for hydrogen generation. Sanchez and Comelli [23] used nickel and nickel–cobalt impregnated on alumina as catalysts. Araque et al. [24] performed glycerol steam reforming using two catalysts $Ce_2Zr_{1.5}Co_{0.5}O_{8-\delta}$ (CZCo) and $Ce_2Zr_{1.5}Co_{0.47}Rh_{0.07}\ O_{8-\delta}$(CZCoRh) mixed oxides. Dou et al. [25] used a commercial Ni-based catalyst for hydrogen generation from glycerol and a dolomite-based sorbent was used for in situ carbon dioxide removal evolved within the process. Sanchez et al. [26] used Ni/Al_2O_3 catalyst for the same at atmospheric pressure, 873–973 K temperature, 16:1 water-to-glycerol ratio and 3.4–10 h^{-1} weight hourly space velocity(WHSV). Wang et al. [27] used Ni–Mg–Al-based catalysts in a fixed bed reactor for SGR. So, it can be seen that different types of catalysts have been used for steam reforming of glycerol but a big portion of it has relied on commercial nickel catalysts or Ni-based bimetallic or other Ni-based catalysts.

A quick glimpse of different thermochemical and biochemical technologies along with hydrogen gas yield has been illustrated in Table 1. It is clear that the thermochemical technologies leave a mark for the preference mainly because of the yield of hydrogen is greater than the biochemical ones. However, that is not the main reason because from the perspective of technological maturity most of the thermochemical technologies are matured and are being utilized in different sectors of waste to energy. Pyrolysis and gasification are two widely used technologies which make them suitable to be implemented in the industrial scale. Whereas, steam reforming and autothermal reforming processes are quite complex in terms of operation and monitoring. Co-pyrolysis and co-gasification are comparatively new comers and are promising but needs more intervention to put them into limelight. Despite these advantages, these technologies require high energy and thus leave a lot of environ-

Table 1 Overview of hydrogen generation from glycerol using different technologies

Technology	Reaction conditions	Reactor type	Yield of hydrogen	References
Thermochemical technologies				
Hydrothermal gasification by supercritical water	923 K and 5 wt% glycerol	Continuous tubular reactor	26.44–35.85 mmol/g feed in 1 min	[28]
Supercritical water gasification	773 K, 45 Mpa and 7% glycerol concentration	Chrome-vanadium steel batch tubular reactor	27.9 mol%	[29]
Steam gasification	1073 K, Ni/Al_2O_3 catalyst, steam-to-glycerol Weight ratio 0:100–50:50	Fixed bed reactor	Hydrogen yield increased by 15 mol%	[30]
Steam reforming	723–926 K, Ni–Cu–Al, Ni–Cu–Mg, Ni–Mg catalysts	Continuous fixed bed reactor	Hydrogen yield 5–10%	[31]
Steam reforming	1173 K, Pt–Al catalyst, 0.12 mol/min glycerol flow per kg of catalyst.	Reformer	70% yield of pure glycerol (which was nearly 100%)	[32]
Steam reforming	673–723 K, $Ni/CeO_2/Al_2O_3$ catalyst	Electrolessly plated Pd/Ag alloy membrane reactor	5.82 mol-H_2/mol of glycerol	[33]
Two-step reforming	953 K, 37 wt%, Ni–Co/Al–Mg catalyst	Fluidised bed reactor	67 vol.% H_2	[34]
Supercritical water conversion	873 K, 25 Mpa	Batch autoclave	10 mol H_2 per kg of Glycerol	[35]
Hydrothermal Reforming	573–623 K, 8.5–31 Mpa	Hastelloy-C batch reactor	8.89% mol of H_2 per mole of carbon in feed.	[36]
Autothermal Reforming	773 K, 1–3 bar, $Ni/CeO_2/Al_2O_3$ catalyst, Space Velocity 5 h^{-1}	Packed bed reactor	85.3% at O_2/glycerol ratio of 0.15	[37]
Pyrolysis	923 K	Laminar flow reactor	44 mol% per mole of glycerol	[38]

(continued)

Table 1 (continued)

Technology	Reaction conditions	Reactor type	Yield of hydrogen	References
Co-pyrolysis with olive Kernel	993 K, 25 wt% olive kernel with crude glycerol	Laboratory pyrolyzer	~46 vol.%	[39]
Co-gasification with olive kernel	1123 K, 49 wt% crude glycerol in olive kernel	Fixed bed reactor	33% (v/v)	[40]
Gasification via air	1223–1773 K, excess air ratio 0.17–0.32	Entrained flow gasifier	24 vol.%	[41]
Gasification via oxygen	1223–1773 K, excess air ratio 0.4–0.7	Entrained flow gasifier	38–42 vol.%	[41]
Biochemical technologies				
Dark fermentation	308 K, 48 h, pH 7, Soil microbial inoculums	Two-Chamber MFC reactor	0.55 mol/mol glycerol	[15]
Dark fermentation	310 K, *Enterobacter aerogenes* HU-101	Packed bed reactor	63 mmol/l/h	[42]
Dark fermentation	303 K, pH 6, *Enterobacter aerogenes* NBRC 12010	Bioelectrochemical two compartment reactor	0.77 mol/mol glycerol	[43]
Photofermentation	303 K, 150 W halogen light, *R. palustris*	125 ml serum bottles as bioreactor	6 mol of H_2/mol glycerol	[16]
Photofermentation	303 K, 200 W/m^2 light intensity, *R. palustris*	125 ml serum bottles as bioreactor	6.1 mol hydrogen/mole of crude glycerol	[44]
Photo + Dark fermentation	303 K, 175 W/m^2 light intensity, *R. palustris*	50 L CSTR	6.9 mol hydrogen/mole of glycerol	[45]

mental footprints. Compared to them, the biochemical processes are greener and in most of the cases require much less energy input for their operation. These technologies are comparatively naive and require much attention in order to improve hydrogen yield. Researchers around the world are trying to develop these biochemical processes via research work and process intensifications. Major advancement in this field includes reactions in the continuous reactor medium [42, 46].

3.2 Hydrogen Generation from Waste Water

Globally, the ethanol production facilities are the predominant biorefineries. The growth of such biorefineries is increasing every day with the increasing energy demand. The South American sugar cane ethanol fermentation facilities have produced nearly double volume ethanol since the last decade. On the other hand, corn ethanol production has surged dramatically in the last few years in USA which surpasses Brazilian production. These facilities also produce a lot of waste water. Waste water is also generated from different food and beverage industries, e.g. brewery waste water [47]., soy sauce waste water [48], sugar refinery waste water [49], dairy waste water [50], tofu waste water [51], palm oil mill effluent [52], olive mill waste water [53, 54], etc. Breweries generate a huge amount of waste water containing sugar, alcohols, vitamins, amino acids, other organic acids, etc. which is suitable for hydrogen generation [55, 56]. Carbon content is comparatively lower in this kind of waste water compared to the nitrogen content [57]. Hydrogen can be generated from this kind of waste water using photofermentation method. Soy sauce processing waste water is highly acidic having a pH of four. It contains several molecules including glucose, proteins, organic acids, iron (Fe) and molybdenum (Mo) which is suitable for hydrogen generation by the route of fermentation. Anam et al. [58] have reported a study on hydrogen generation from this type of waste water. He adjusted the pH to seven and then sterilized the samples by autoclaving before applying the photofermentation technique. It was found that glucose acts as the primary substrate followed by organic acids for hydrogen generation. Hydrogen generation is also possible by photofermentation route using sugar refinery waste water as substrate [59]. Dairy waste water and tofu waste water are also good candidates for hydrogen generation. Dairy waste water is rich in milk, milk fats, whey particles and vitamins [56]. Preprocessing is important for this type of waste water before using them as substrate [60]. Tofu waste waters are also high in organic loads. It contains sucrose, starch, other reducing sugars, proteins, VFAs and a few other compounds [56]. In this case, preprocessing is also important. A few studies on hydrogen generation from tofu waste water is available in literature [51, 57, 58]. Hydrogen generation from palm oil mill effluent and olive mill waste water is also achievable. Palm oil mill effluent contains huge amount of suspended solids, organic compounds, oil and grease. BOD and COD value of this type of effluent can be as high as 30,000 and 50,000 mg/l, respectively [52]. Olive mill waste water treatment is one of the burning issues today. Huge number of publications was found in this area. Raw olive mill waste water is considered as a hazardous water pollutant because it contains high amount of organic matter contributing to high BOD and COD values and has a dark brownish colour. This type of waste water contains sugar, pectins, tannins, lipids, volatile acids, polyalcohols, polyphenols, etc. [56]. Due to the presence of these different types of substrates, olive mill waste water is a very suitable candidate for generation of hydrogen. However, inhibiting compounds such as polyphenols are there and hence preprocessing is imperative in this case [59, 60]. An overview

Table 2 Overview of hydrogen generation from different types of waste water using fermentation

Waste Water	Pretreatment	Microorganism	pH	Productivity	References
Brewery	Filtration and autoclaving	*Rhodobacter sphaeroides* O.U. 001	7	2.75 mL H_2/L/h	[47]
Soy Sauce	Autoclaving and pH neutralization	*Rhodobium marinum*	7–7.2	N/A	[48]
Sugar Refinery	Filtration, centrifugation, autoclaving	*Rhodobacter sphaeroides* O.U.001	7	5 mL H_2/L/h	[49]
Tofu	N/A	*Rhodobacter sphaeroides* RV	N/A	18.33 mL H_2/L/h	[51]
Tofu	Autoclaving	*Rhodobacter sphaeroides* TJ-0803	N/A	14.2 mL H_2/L/h	[58]
Palm oil mill effluent	Presettling, centrifugation, filtration, autoclaving	*Rhodopseudomonas palustris* PBUM001	7	10 mL H_2/L/h	[52]
Olive mill	Clay pretreatment, pH neutralization, sterilization	*Rhodobacter sphaeroides* O.U.001	6.8	5.45 mL H_2/L/h	[60]
Olive mill	Clay pretreatment	*Rhodobacter sphaeroides* O.U.001	6.8	0.0081/lit/h	[61]
Olive mill	Filtration, pH neutralization, autoclaving	*Rhodobacter sphaeroides* O.U.001	6.8–7	9 mL H_2/L/h	[59]
Olive mill	Centrifugation, adsorption, pH neutralization, autoclaving	Rhodopseudomonas palustris 6A	6.8–7.1	1.54 mL H_2/L/h	[62]
Olive mill	Adsorption	*Rhodopseudomonas palustris* 420L	6.8–7.2	5.28 mL H_2/L/h	[54]

of hydrogen generation from different types of waste waters has been presented in Table 2.

Microbial fuel cells (MFC) is the most well-known technology today that is being explored for hydrogen generation from different waste water effluents. MFCs require certain pretreatment steps before feeding into the MFCs [78]. Researchers have explored different types of waste waters that can be used as substrate for hydrogen generation using MFCs. A brief idea has been presented in the table below (Table 3).

Biorefineries that use lignocellulosic biomass for production of biofuels generates huge amount of waste water. This waste water contains biodegradable organic matter which can be used for hydrogen generation using MFCs. Since biomass pretreatment

Table 3 Different substrates for hydrogen production using MFC

Type of waste water	Source	References
Effluents from fermentation	Cellulose, xylose, spent wash, corn stalk, corn-cob hydrolysate, sugar beet juice, molasses effluent, leachate from landfill and yellow glycerol	[15, 63–70]
Lignocellulosic biorefinery by-products	Furanic and phenolic effluent, switchgrass pyrolysis aqueous stream, refinery effluent (oil free), hydrolysate of wheat straw pyrohydrolysis	[71–74]
High strength waste water	Potato processing and dairy Manure, industrial waste water and food processing effluent, swine waste water, winery waste water	[8, 75–77]

Adopted from [79]

is an inevitable step for the lignocellulosic biorefineries, it is an increased cost for the operation of biorefinery but certainly an opportunity for energy generation. Furanic and phenolic compounds, and furfural and hydroxymethyl furfural are generated in huge amount during the pretreatment process of the lignocellulosic biomass which acts as inhibitors. These inhibitors are nuisance for downstream fermentation. MFCs can be placed following the pretreatment and these inhibitors can be utilized as substrates for hydrogen production. The removal of these inhibitors will also increase fermentation efficacy [74]. The discharge effluent after fermentation contains residual sugar, ethanol and organic acids, which are ideal substrates for MFCs for hydrogen production. Nearly 750–8900 m^3/h and 1260–7200 m^3/h of hydrogen could be produced by MFCs from existing starch-based and lignocellulosic-based biorefineries in the USA, respectively [79].

4 Discussions from the Sustainability Perspective

The COP21 agreement on climate change aims to limit the temperature increase of the atmosphere by 2° by 2020. One of the major issues of climate change is greenhouse gases, carbon dioxide being the mostly blamed. As a result, the whole world is now trying to cut down the carbon dioxide emission from their processes. Hydrogen is a clean fuel as it doesn’t generate CO_2 as by-product and it is the new big thing. Hydrogen can be generated from biorefinery waste streams, i.e. yellow glycerol, waste water, effluents, etc. The basic processes employed for hydrogen generation from biorefinery waste streams are fermentation (photo and/or dark) using microbial fuel cells (MFC). Both of these technologies are limited to either lab scale or in the pilot scale. However, fermentation is being practiced in an industrial scale for manufacturing alcohol but certainly not for hydrogen generation. Hence, it is important to look in details about the sustainability of these processes.

4.1 Environmental Sustainability

The environmental sustainability of any process is characterized by the factors by which it ensures the minimum impact on the environment. It is hard to look into the whole process without a life cycle assessment exercise. However, if we look at things from a systems approach, it is possible to predict the environmental impact it may have. Since the biorefineries are being operated separately and different processes are being implemented in large scale, the waste generated is also quite high in volume. Disposal of this waste streams in the environment without prior treatment will have enormous effect on the flora and fauna. MFC and fermentation are the technologies which can be used as end-of-pipeline processes to generate biohydrogen from the substrate present in the waste streams. In case of glycerol, thermochemical processes are suitable for hydrogen production. Employing these methods, ensure proper utilization of these waste streams which ensures circular economy and since hydrogen is a green product, it can be commented that the processes are environmentally sustainable. But one should keep in mind that during the operation of the biorefineries as well as the technologies concerned for hydrogen generation, the energy input is based on fossils fuel. This implies an ample amount of environmental impact with respect to carbon dioxide emission. If the power source is renewable like solar, wind or hydro, then the processes may be considered as green or the emissions may be neglected. In a published literature, it was found that the emissions from a biorefinery are more than that of a petrochemical refinery in USA based on reported data and subsequent analysis [80]. Other than that, in most of the cases, it is required to dilute the waste water streams with water which also increases water demand and increases water footprint. Several other factors are there such as acidification, eutrophication, etc. but those can only be covered by an LCA exercise as mentioned earlier.

4.2 Operational Sustainability

The operational sustainability of any process is dictated by the ease of the processes to be employed (operating parameters) and to some extent the nature of the processes (exothermicity, safety features, residence time, etc.). There are different operating parameters which are important in order to understand the process itself first and thereafter the sustainability of the concerned process. The identification of feedstock is really an important thing as this technology evolved from basic research should have future industrial-scale commercial applications. The suitability of feedstock depends on two things—(a) types of substrate present in the stream and (b) the amount of inhibitory substances (either in pure form or to be evolved during operation). In the aforementioned technologies, pretreatment is an inevitable step for production of hydrogen which is an operational barrier. Another important issue is the presence of the inhibitory compounds in the waste streams which inhibits the processes. Sometimes, inhibitory compounds are formed during the processes. For example, ammonium ion, which is formed due to breakdown of nitrogenous compounds such as proteins and amino acids. There are some factors which are also specific to the technology, like in case of the photofermentation, the physical appearance of the waste water is a factor. Intense dark-coloured waste water streams owe their appearance to the organic matter present. The more intense the colour of the waste water, lesser the light penetration. Sometimes, presence of a mixture of different types of carbon substrates is also a factor. Other than these, there is no benchmark process for hydrogen generation from these streams. At this point, the operational sustainability is questionable. However, optimization of process parameters, process intensification and development of decision support systems (DSS) will lead towards sustainability in this front.

4.3 Economical Sustainability

We are pretending to march towards a sustainable future with biofuels and biorefineries have given us much opportunity to generate clean fuel from the waste they generate. Waste glycerol from biodiesel units can be used to generate hydrogen. It has been found that nickel- and platinum-based catalysts give maximum yield of hydrogen. But, in some cases, catalyst poisoning and catalyst deactivation are one of the major issues. The processes adopted for glycerol to hydrogen conversion are still yet to be established as a benchmark process as economic feasibility of these processes are still questionable. Fermentation is a very old process which is helpful in some ways but more R&D work is required for developing the technology for full-fledged operations. Moreover, the whole process has many other preprocessing and post-processing steps which adds on to operating cost. MFCs are still in the research phase. Hydrogen storage is a big problem and using MFCs in a fully developed biorefinery is not yet feasible. The main barrier is the economic aspects of the technology. Moreover, the maintenance cost is also an issue. From the overall analysis, the economical sustainability is not very clear but certainly the pitfalls are clear and rings true. The practical implementations are yet to be achieved and more research and development in this field are required. We also need to change our thinking from silos approach to the systems approach. This will certainly help us to achieve the circular economy.

4.4 Social Sustainability

Social sustainability of any process is complex enough to go about. The behaviour, mentality and other social indicators change with geographical region. Religion also plays a big role in this case. With respect to the technologies above, it is quite hard to predict the social sustainability. However, the industrial implementation of these methods will certainly create job opportunities. The society will also be benefitted with the use of green fuels and the use of green technologies in the industries. However, the price of the green fuel and the initial investment in the use of these green fuels in an individual level may not be well accepted in the early stages. Overall, with time and advancement in the technologies, more the products will be commercialized, more it will be socially accepted and we will march towards social sustainability. Further, social LCA may be carried out for detailed analysis.

5 Conclusion

Recently, there is a growing trend of research on biorefinery and biohydrogen production from different sources which are basically part of biorefineries. While the major work is focused on silos thinking, this study takes a systems approach to look at things from the perspective of circular economy. While the biorefineries are producing green fuels and other green products, the waste generated by the biorefineries are rare discussed in forums or in popular academics. Most importantly, the sustainability of the processes adopted in these biorefineries is not clear. With the COP21 agenda and the buzzword being climate change an ample amount of push is there on production of clean fuels, i.e. hydrogen. This study reviews existing literature and performs a sustainability analysis on hydrogen generation from the waste streams originated from the biorefineries. It was found from the literature that basically two processes are there for hydrogen generation form biorefinery waste—(a) fermentation (photo and dark) and (b) using MFCs. The analysis reveals that environmental and social sustainability of these processes are somewhat sustainable, whereas the operational and economical sustainability is questionable. It was suggested to perform LCA analysis to find the detailed environmental impact of these processes on the environment. Moreover, optimization of process parameters and finding solutions to remove inhibitory compounds are also necessary. It is also suggested to carry out techno-economic feasibility of the processes and to go about social LCA to ensure further sustainability of the processes. The findings of the paper will no doubt help the stakeholder in decision-making and to develop science-policy framework for further development.

Acknowledgements Authors acknowledge the support of International Society of Waste Management, Air and Water (ISWMAW). We would also like to thank Ms. Aryama Raychaudhuri, Research Scholar, NEERI for her valuable inputs during the preparation of the paper.

References

1. World Hydrogen (2014) Industry study with forecasts for 2018 & 2023. Available from: http://www.freedoniagroup.com/industry-study/world-hydrogen-3165.htm. Accessed 6th Apr 2017
2. Hydrogen Generation Market by Generation & Delivery Mode (Captive, Merchant), Technology (Steam Methane Reforming, Partial Oxidation, Gasification, and Electrolysis), Application (Refinery, Ammonia Production, and Methanol Production), & Region - Global Forecast to 2021 (2015) Available from: http://www.marketsandmarkets.com/PressReleases/hydrogen.asp. Accessed 6th Apr 2017
3. Singh L, Wahid ZA (2015) Methods for enhancing bio-hydrogen production from biological process: a review. J Ind Eng Chem 21:70–80
4. Urbaniec K, Bakker RR (2015) Biomass residues as raw material for dark hydrogen fermentation–A review. Int J Hydrogen Energy 40(9):3648–3658
5. Yang F, Hanna MA, Sun R (2012) Value-added uses for crude glycerol–a byproduct of biodiesel production. Biotechnol Biofuels 5(1):1
6. Chatzifragkou A, Papanikolaou S (2012) Effect of impurities in biodiesel-derived waste glycerol on the performance and feasibility of biotechnological processes. Appl Microbiol Biotechnol 95(1):13–27
7. ElMekawy A, Diels L, Bertin L, De Wever H, Pant D (2014) Potential biovalorization techniques for olive mill biorefinery wastewater. Biofuels, Bioprod Biorefin 8(2):283–293
8. Cusick RD, Bryan B, Parker DS, Merrill MD, Mehanna M, Kiely PD, Liu G, Logan BE (2011) Performance of a pilot-scale continuous flow microbial electrolysis cell fed winery wastewater. Appl Microbiol Biotechnol 89(6):2053–2063
9. Adhikari S, Fernando SD, To SF, Bricka RM, Steele PH, Haryanto A (2008) Conversion of glycerol to hydrogen via a steam reforming process over nickel catalysts. Energy Fuels 22(2):1220–1226
10. Valliyappan T (2004) Hydrogen or syn gas production from glycerol using pyrolysis and steam gasification processes. Doctoral dissertation, University of Saskatchewan Saskatoon
11. Lehnert K, Claus P (2008) Influence of Pt particle size and support type on the aqueous-phase reforming of glycerol. Catal Commun 9(15):2543–2546
12. Dauenhauer PJ, Salge JR, Schmidt LD (2006) Renewable hydrogen by autothermal steam reforming of volatile carbohydrates. J Catal 244(2):238–247
13. Kamonsuangkasem K, Therdthianwong S, Therdthianwong A (2013) Hydrogen production from yellow glycerol via catalytic oxidative steam reforming. Fuel Process Technol 106:695–703
14. Byrd AJ, Pant KK, Gupta RB (2008) Hydrogen production from glycerol by reforming in supercritical water over Ru/Al_2O_3 catalyst. Fuel 87(13):2956–2960
15. Chookaew T, Prasertsan P, Ren ZJ (2014) Two-stage conversion of crude glycerol to energy using dark fermentation linked with microbial fuel cell or microbial electrolysis cell. New Biotechnol 31(2):179–184
16. Sabourin-Provost G, Hallenbeck PC (2009) High yield conversion of a crude glycerol fraction from biodiesel production to hydrogen by photofermentation. Biores Technol 100(14):3513–3517
17. Sharma Y, Parnas R, Li B (2011) Bioenergy production from glycerol in hydrogen producing bioreactors (HPBs) and microbial fuel cells (MFCs). Int J Hydrogen Energy 36(6):3853–3861
18. Remón J, Mercado V, García L, Arauzo J (2015) Effect of acetic acid, methanol and potassium hydroxide on the catalytic steam reforming of glycerol: thermodynamic and experimental study. Fuel Process Technol 138:325–336
19. Luo N, Ouyang K, Cao F, Xiao T (2010) Hydrogen generation from liquid reforming of glycerin over Ni–Co bimetallic catalyst. Biomass Bioenerg 34(4):489–495
20. Özgür DÖ, Uysal BZ (2011) Hydrogen production by aqueous phase catalytic reforming of glycerine. Biomass Bioenerg 35(2):822–826

21. Dou B, Song Y, Wang C, Chen H, Yang M, Xu Y (2014) Hydrogen production by enhanced-sorption chemical looping steam reforming of glycerol in moving-bed reactors. Appl Energy 130:342–349
22. Calles JA, Carrero A, Vizcaíno AJ, Garcia-Moreno L (2014) Hydrogen production by glycerol steam reforming over SBA-15-supported nickel catalysts: Effect of alkaline earth promoters on activity and stability. Catal Today 227:198–206
23. Sanchez EA, Comelli RA (2014) Hydrogen production by glycerol steam-reforming over nickel and nickel-cobalt impregnated on alumina. Int J Hydrogen Energy 39(16):8650–8655
24. Araque M, Vargas JC, Roger AC (2011) Hydrogen production by glycerol steam reforming over CeZrCo fluorite type oxides. Catal Today 176(1):352–356
25. Dou B, Dupont V, Rickett G, Blakeman N, Williams PT, Chen H, Ding Y, Ghadiri M (2009) Hydrogen production by sorption-enhanced steam reforming of glycerol. Biores Technol 100(14):3540–3547
26. Sánchez EA, D'Angelo MA, Comelli RA (2010) Hydrogen production from glycerol on Ni/Al_2O_3 catalyst. Int J Hydrogen Energy 35(11):5902–5907
27. Wang C, Dou B, Chen H, Song Y, Xu Y, Du X, Luo T, Tan C (2013) Hydrogen production from steam reforming of glycerol by Ni–Mg–Al based catalysts in a fixed-bed reactor. Chem Eng J 220:133–142
28. Dianningrum LW, Choi H, Kim Y, Jung KD, Susanti RF, Kim J, Sang BI (2014) Hydrothermal gasification of pure and crude glycerol in supercritical water: a comparative study. Int J Hydrogen Energy 39(3):1262–1273
29. Yang F, Hanna MA, Marx DB, Sun R (2013) Optimization of hydrogen production from supercritical water gasification of crude glycerol—byproduct of biodiesel production. Int J Energy Res 37(13):1600–1609
30. Valliyappan T, Ferdous D, Bakhshi NN, Dalai AK (2008) Production of hydrogen and syngas via steam gasification of glycerol in a fixed-bed reactor. Top Catal 49(1–2):59–67
31. Wang C, Dou B, Chen H, Song Y, Xu Y, Du X, Zang L, Luo T, Tan C (2013) Renewable hydrogen production from steam reforming of glycerol by Ni–Cu–Al, Ni–Cu–Mg, Ni–Mg catalysts. Int J Hydrogen Energy 38(9):3562–3571
32. Slinn M, Kendall K, Mallon C, Andrews J (2008) Steam reforming of biodiesel by-product to make renewable hydrogen. Biores Technol 99(13):5851–5858
33. Lin KH, Lin WH, Hsiao CH, Chang HF, Chang ACC (2012) Hydrogen production in steam reforming of glycerol by conventional and membrane reactors. Int J Hydrogen Energy 37(18):13770–13776
34. Remón J, Jarauta-Córdoba C, García L, Arauzo J (2016) Analysis and optimisation of H_2 production from crude glycerol by steam reforming using a novel two step process. Fuel Process Technol 145:130–147
35. Yu-Wu QM, Weiss-Hortala E, Barna R, Boucard H, Bulza S (2012) Glycerol and bioglycerol conversion in supercritical water for hydrogen production. Environ Technol 33(19):2245–2255
36. Onwudili JA, Williams PT (2010) Hydrothermal reforming of bio-diesel plant waste: products distribution and characterization. Fuel 89(2):501–509
37. Lin KH, Chang ACC, Lin WH, Chen SH, Chang CY, Chang HF (2013) Autothermal steam reforming of glycerol for hydrogen production over packed-bed and Pd/Ag alloy membrane reactors. Int J Hydrogen Energy 38(29):12946–12952
38. Stein YS, Antal MJ, Jones M (1983) A study of the gas-phase pyrolysis of glycerol. J Anal Appl Pyrol 4(4):283–296
39. Skoulou VK, Manara P, Zabaniotou AA (2012) H_2 enriched fuels from co-pyrolysis of crude glycerol with biomass. J Anal Appl Pyrol 97:198–204
40. Skoulou VK, Zabaniotou AA (2013) Co-gasification of crude glycerol with lignocellulosic biomass for enhanced syngas production. J Anal Appl Pyrol 99:110–116
41. Yoon SJ, Choi YC, Son YI, Lee SH, Lee JG (2010) Gasification of biodiesel by-product with air or oxygen to make syngas. Biores Technol 101(4):1227–1232
42. Ito T, Nakashimada Y, Senba K, Matsui T, Nishio N (2005) Hydrogen and ethanol production from glycerol-containing wastes discharged after biodiesel manufacturing process. J Biosci Bioeng 100(3):260–265

43. Sakai S, Yagishita T (2007) Microbial production of hydrogen and ethanol from glycerol-containing wastes discharged from a biodiesel fuel production plant in a bioelectrochemical reactor with thionine. Biotechnol Bioeng 98(2):340–348
44. Ghosh D, Tourigny A, Hallenbeck PC (2012) Near stoichiometric reforming of biodiesel derived crude glycerol to hydrogen by photofermentation. Int J Hydrogen Energy 37(3):2273–2277
45. Sarma SJ, Brar SK, Le Bihan Y, Buelna G (2013) Bio-hydrogen production by biodiesel-derived crude glycerol bioconversion: a techno-economic evaluation. Bioprocess Biosyst Eng 36(1):1–10
46. Escapa A, Manuel MF, Morán A, Gómez X, Guiot SR, Tartakovsky B (2009) Hydrogen production from glycerol in a membraneless microbial electrolysis cell. Energy Fuels 23(9):4612–4618
47. Seifert K, Waligorska M, Laniecki M (2010) Brewery wastewaters in photobiological hydrogen generation in presence of *Rhodobacter sphaeroides* OU 001. Int J Hydrogen Energy 35(9):4085–4091
48. Anam K, Habibi MS, Harwati TU, Susilaningsih D (2012) Photofermentative hydrogen production using *Rhodobium marinum* from bagasse and soy sauce wastewater. Int J Hydrogen Energy 37(20):15436–15442
49. Yetis M, Gündüz U, Eroglu I, Yücel M, Türker L (2000) Photoproduction of hydrogen from sugar refinery wastewater by *Rhodobacter sphaeroides* OU 001. Int J Hydrogen Energy 25(11):1035–1041
50. Seifert K, Waligorska M, Laniecki M (2010) Hydrogen generation in photobiological process from dairy wastewater. Int J Hydrogen Energy 35(18):9624–9629
51. Zhu H, Ueda S, Asada Y, Miyake J (2002) Hydrogen production as a novel process of wastewater treatment—studies on tofu wastewater with entrapped *R. sphaeroides* and *mutagenesis*. Int J Hydrogen Energy 27(11):1349–1357
52. Jamil Z, Annuar MSM, Ibrahim S, Vikineswary S (2009) Optimization of phototrophic hydrogen production by *Rhodopseudomonas palustris* PBUM001 via statistical experimental design. Int J Hydrogen Energy 34(17):7502–7512
53. Eroğlu İ, Tabanoğlu A, Gündüz U, Eroğlu E, Yücel M (2008) Hydrogen production by *Rhodobacter sphaeroides* OU 001 in a flat plate solar bioreactor. Int J Hydrogen Energy 33(2):531–541
54. Pintucci C, Giovannelli A, Traversi ML, Ena A, Padovani G, Carlozzi P (2013) Fresh olive mill waste deprived of polyphenols as feedstock for hydrogen photo-production by means of *Rhodopseudomonas palustris* 42OL. Renew Energy 51:358–363
55. Madukasi EI, Zhou JJ, He C (2012) Photosynthetic bacteria organic wastewater treatment: effect of anaerobic-pretreatment. Int J Res Chem Environ 2(2):188–195
56. Ghosh S, Dairkee UK, Chowdhury R, Bhattacharya P (2016) Hydrogen from food processing wastes via photofermentation using purple non-sulfur bacteria (PNSB)–A review. Energy Convers Manage 14:299–314
57. Zhu H, Suzuki T, Tsygankov AA, Asada Y, Miyake J (1999) Hydrogen production from tofu wastewater by *Rhodobacter sphaeroides* immobilized in agar gels. Int J Hydrogen Energy 24(4):305–310
58. Zheng GH, Wang L, Kang ZH (2010) Feasibility of biohydrogen production from tofu wastewater with glutamine auxotrophic mutant of *Rhodobacter sphaeroides*. Renew Energy 35(12):2910–2913
59. Padovani G, Pintucci C, Carlozzi P (2013) Dephenolization of stored olive-mill wastewater, using four different adsorbing matrices to attain a low-cost feedstock for hydrogen photo-production. Biores Technol 138:172–179
60. Eroğlu E, Eroğlu İ, Gündüz U, Yücel M (2008) Effect of clay pretreatment on photofermentative hydrogen production from olive mill wastewater. Biores Technol 99(15):6799–6808
61. Eroğlu E, Eroğlu İ, Gündüz U, Türker L, Yücel M (2006) Biological hydrogen production from olive mill wastewater with two-stage processes. Int J Hydrogen Energy 31(11):1527–1535
62. Pintucci C, Padovani G, Giovannelli A, Traversi ML, Ena A, Pushparaj B, Carlozzi P (2015) Hydrogen photo-evolution by *Rhodopseudomonas palustris* 6A using pre-treated olive mill wastewater and a synthetic medium containing sugars. Energy Convers Manage 90:499–505

63. Dhar BR, Elbeshbishy E, Hafez H, Lee HS (2015) Hydrogen production from sugar beet juice using an integrated biohydrogen process of dark fermentation and microbial electrolysis cell. Biores Technol 198:223–230
64. Lalaurette E, Thammannagowda S, Mohagheghi A, Maness PC, Logan BE (2009) Hydrogen production from cellulose in a two-stage process combining fermentation and electrohydrogenesis. Int J Hydrogen Energy 34(15):6201–6210
65. Li XH, Liang DW, Bai YX, Fan YT, Hou HW (2014) Enhanced H_2 production from corn stalk by integrating dark fermentation and single chamber microbial electrolysis cells with double anode arrangement. Int J Hydrogen Energy 39(17):8977–8982
66. Lu L, Ren N, Xing D, Logan BE (2009) Hydrogen production with effluent from an ethanol–H_2-coproducing fermentation reactor using a single-chamber microbial electrolysis cell. Biosens Bioelectron 24(10):3055–3060
67. Mahmoud M, Parameswaran P, Torres CI, Rittmann BE (2014) Fermentation pre-treatment of landfill leachate for enhanced electron recovery in a microbial electrolysis cell. Biores Technol 151:151–158
68. Modestra JA, Babu ML, Mohan SV (2015) Electro-fermentation of real-field acidogenic spent wash effluents for additional biohydrogen production with simultaneous treatment in a microbial electrolysis cell. Sep Purif Technol 150:308–315
69. Nam JY, Yates MD, Zaybak Z, Logan BE (2014) Examination of protein degradation in continuous flow, microbial electrolysis cells treating fermentation wastewater. Biores Technol 171:182–186
70. Wang A, Sun D, Cao G, Wang H, Ren N, Wu WM, Logan BE (2011) Integrated hydrogen production process from cellulose by combining dark fermentation, microbial fuel cells, and a microbial electrolysis cell. Biores Technol 102(5):4137–4143
71. Lewis AJ, Ren S, Ye X, Kim P, Labbe N, Borole AP (2015) Hydrogen production from switchgrass via an integrated pyrolysis–microbial electrolysis process. Biores Technol 195:231–241
72. Ren L, Siegert M, Ivanov I, Pisciotta JM, Logan BE (2013) Treatability studies on different refinery wastewater samples using high-throughput microbial electrolysis cells (MECs). Biores Technol 136:322–328
73. Thygesen A, Marzorati M, Boon N, Thomsen AB, Verstraete W (2011) Upgrading of straw hydrolysate for production of hydrogen and phenols in a microbial electrolysis cell (MEC). Appl Microbiol Biotechnol 89(3):855–865
74. Zeng X, Borole AP, Pavlostathis SG (2015) Biotransformation of furanic and phenolic compounds with hydrogen gas production in a microbial electrolysis cell. Environ Sci Technol 49(22):13667–13675
75. Kiely PD, Cusick R, Call DF, Selembo PA, Regan JM, Logan BE (2011) Anode microbial communities produced by changing from microbial fuel cell to microbial electrolysis cell operation using two different wastewaters. Biores Technol 102(1):388–394
76. Tenca A, Cusick RD, Schievano A, Oberti R, Logan BE (2013) Evaluation of low cost cathode materials for treatment of industrial and food processing wastewater using microbial electrolysis cells. Int J Hydrogen Energy 38(4):1859–1865
77. Wagner RC, Regan JM, Oh SE, Zuo Y, Logan BE (2009) Hydrogen and methane production from swine wastewater using microbial electrolysis cells. Water Res 43(5):1480–1488
78. Lu L, Ren ZJ (2016) Microbial electrolysis cells for waste biorefinery: a state of the art review. Biores Technol 215:254–264
79. Borole AP, Mielenz JR (2011) Estimating hydrogen production potential in biorefineries using microbial electrolysis cell technology. Int J Hydrogen Energy 36(22):14787–14795
80. Sengupta D, Hawkins TR, Smith RL (2015) Using national inventories for estimating environmental impacts of products from industrial sectors: a case study of ethanol and gasoline. Int J Life Cycle Assess 20(5):597–607

Quantifying Temporal Variations in Incinerability of Municipal Solid Waste

Roshni Mary Sebastian, Dinesh Kumar and Babu J. Alappat

1 Introduction

MSW management strategies have transformed over the years owing to variations in the quantum and characteristics of the MSW generated. The heterogeneity and the quantities of the waste generated complicate the treatment and disposal operations [9, 21]. The United Nations Development Programme (UNDP) surveys convey problems related to MSW management to be one of the most acute issues in urban areas globally, second only to unemployment [33]. Increasing the rate of urbanisation and economic growth are anticipated to intensify the complexity of the same. The formulation of an integrated waste management scheme can help a country attain sustainable development to some extent [11]. The composition of the MSW is instrumental in devising the treatment strategies [13]. However, economic development has caused substantial variations in the composition of MSW. The ramifications of this are particularly noticeable in developing countries like India which recorded a GDP growth rate of 3.47% in 1982 to 8.01% in 2015 as per the World Bank online database [31]. While food fraction continued to be the major constituent of the MSW, the inert matter reportedly reduced by nearly half to 25% by 2005 in India [14]. Furthermore, the absence of source segregation leaves highly mixed MSW for disposal. While landfilling was one of the most widely adopted disposal techniques across the world, the downsides to it are numerous, namely the release of greenhouse gases (GHG) like CH_4, soil and groundwater pollution and degradation of the aesthetics of the locality, to name a few. Besides, the unavailability of land for disposal of huge quantities of MSW makes the technique an unfavourable choice. This triggered a

---

R. M. Sebastian (✉) · B. J. Alappat
Department of Civil Engineering, IIT Delhi, New Delhi 110016, India
e-mail: roshnimary@gmail.com

D. Kumar
North Delhi Municipal Corporation, New Delhi 110002, India

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1_54

change in the environmental legislation and policies, with Landfill Directive, 1999, Municipal Solid Waste (Management and Handling) Rules, 2000, etc. coming into effect. The former was enforced in Europe, while the latter in India, with an intention of reducing the landfilling of the biodegradable fraction. Subsequently, the demand for an integrated waste management scheme with minimal landfilling emerged.

Integrated municipal solid waste management entails the choice of appropriate treatment and disposal techniques to achieve specific objectives. Waste reduction, reuse and recycle (3Rs), material and energy recovery, biological and thermal treatment techniques and landfilling are fundamental to integrated solid waste management [29]. Biological techniques like composting are normally preferred due to its low pollution potential and production of beneficial by-products. However, the treatment duration spans from at least 2–3 weeks to as high as 4–5 months [29]. Moreover, poorly segregated waste feed results in poor compost quality. Although manual and automated segregation operations can produce specific waste streams for material and energy recovery operations, the overall economy of operation may get disturbed. As a result, there is an evident need for a treatment technique that has low residence time while not being environmentally disruptive. Thermal treatment techniques, namely incineration can reduce waste volumes by almost 90%, in a residence time extending from a few seconds to couple minutes. In addition to energy recovery, which can offset the operational costs to some extent, waste transportation costs can also be considerably reduced as waste incineration units can be set up near the collection or disposal sites [20]. In Europe, nearly 53% of the total waste incineration was performed in Denmark followed by Sweden [13]. Despite the huge reliance on waste incineration in developed countries, it was not widely adopted in developing countries. This was due to the high organic and inert fraction in the MSW, which reduced the overall heat content of MSW. Since the average heat content in developing countries was in the range of 800–1200 kcal/kg, auxiliary fuel supply becomes mandatory to sustain combustion. There are cases of incineration plants lying obsolete in Malaysia, India and other developing countries due to poor thermal properties of the waste feed.

It thus becomes quintessential to assess the feasibility of the waste incineration prior to its implementation. Quantification of the incinerability of MSW, or the amenability of MSW to be burned completely to sterile ash, with minimal environmental impact, optimum energy recovery and economic sustainability are crucial for assessing the feasibility of operation. A decision-making tool named *i*-Index which can estimate the incinerability of MSW sans detailed characterisation has been developed by the authors in this regard. The aim of the present study is to illustrate the application of *i*-Index by using it to investigate the variation in the incinerability of MSW generated in a developed country as opposed to a city from a developing country. Variation in the composition of the MSW generated in the UK and New Delhi shall be adopted to draw comparisons in the fluctuations in its incinerability over the period from 1980 to 2005. The subsequent sections give a detailed account of the same.

2 Study Areas

There are numerous studies on MSW management in the UK [1, 2, 3, 8] and Delhi [4, 5, 12, 15, 23, 28].

Population and economic growth considerably increase the generation rates of MSW. In the UK, despite a steady population growth of 0.035% in 1981 to 0.776% in 2016, the total population remains at 65 million, which is a sharp contrast to India, where in spite of a decrease in annual population growth from 2.322% in 1982 to 1.148% in 2016, the total population is at an alarming 1.32 billion. Although the rate of urbanisation in the UK and India have gradually reduced in the last decade from about 2.341–2.039% and 2.857–2.329%, respectively, in the period from 2002 to 2016 as per World Bank database, the variation in the composition of MSW generated from both the cases are quite dissimilar. Figure 1 illustrates the variation in the population and economic growth during the study period.

Figure 2 shows the areas chosen for the present study. Table 1 shows the composition of MSW generated in the study areas from 1981 to 2005 [1, 7, 28]. The composition of MSW had quite a difference in the UK in contrast to New Delhi. While the former had a higher fraction of combustibles like paper, plastic and textiles, food and inert fraction were higher in the latter. Moreover, there has also been an economic growth, which although unsteady, has improved the waste characteristics considerably. For instance, the plastic content of the waste in Delhi increased from 1.5 to 6.1% in 20 years, which has been a very gradual but steady increase.

A similar trend was also observed in the MSW generated in the UK. Consequently, the net heat contents had wide differences which are evident from Fig. 3. As per conventionally followed thumb rules, the MSW can be incinerated for energy recovery, if the calorific value is roughly above 1500 kcal/kg. Autogenous incineration is, however, possible above 2400 kcal/kg approximately. While MSW generated

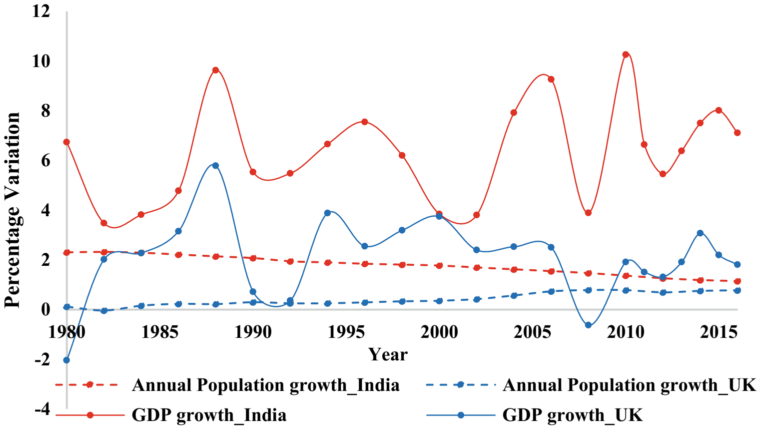


Fig. 1 Economic and population growth in the study areas over the years

Fig. 2 Study areas **a** The UK **b** Delhi

in the UK may be autogenously incinerated during the study period, it is quite the contrary in Delhi, which has relatively poor thermal characteristics. The primary aim of waste incineration is not energy recovery, but disposal of the MSW generated with minimal environmental impact. Relying on conventional techniques which assess the feasibility based on the thermal properties alone may not be ideal. The *i*-Index can mitigate such erroneous assumptions.

Table 1 Composition of MSW generated in the study areas across different years

Component (%)	Delhi 1982 (IHPH 1982)	Delhi 1995 [19]	Delhi 2002 [30]	Delhi 2004 [16]	UK 1981 [1]	UK 1992 [1]	UK 1996 [7]	UK_2005 [18]
Biodegradables	57.7	38	38.6	37.8	21.4	30.9	33.5	32.7
Paper	5.9	5.6	5.6	6.0	35.7	25.1	26.4	23.3
Plastic	1.5	6.0	6.0	6.1	7.1	15.3	8.9	23.7
Textile					2.7		8.8	2.3
Metal	0.6	0.3	0.2	0.4	8.9	13.2	3	6.2
Glass and Crockery	0.3	1.0	1.0	1.3	8.9	7.3	5.7	4.3
Bioresistant	5.1	14.0	13.9	15.62	–	–	–	–
Yard wastes	–	–	–	–	12.5	–	–	–
Inert	28.9	34.8	34.7	32.0	3.7	4.4	13.7	7.5

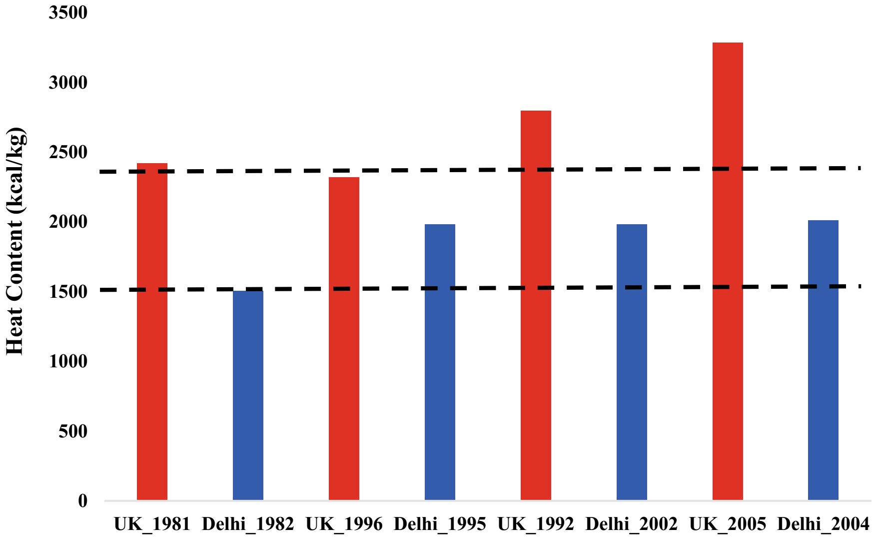


Fig. 3 Variation in the heat contents of MSW

The waste management regime in the UK involves the active individual involvement of authorities of Wales, Northern Ireland and Scotland, all of whose strategies are targeted at diverting the waste from landfills, as per the Landfill Directive.

This reduced the quantity of MSW being landfilled from 80% in 2001 to nearly 49% in 2010. This was met with a simultaneous increase in material recovery operations. Figure 4 prepared using Eurostat data demonstrates the variation in MSW generation and treatment rates over the years in the UK. This illustrates a steady increase in waste incineration, with an uninterrupted decrease in landfilling. Delhi, on the other hand, treats merely 26% of the generated waste as per Central Pollution Control Board (CPCB) reports [6]. Earlier reports suggest nearly 90% of landfilling of MSW in India [27]. However, most of the existing landfills have exhausted their capacities and with an acute shortage of land for disposal of wastes, waste incineration which can reduce waste volumes by almost 90% in a matter of a few seconds to minutes is perhaps, more reliable.

The first waste-to-energy plant in India was set up in Delhi at Timarpur in 1987, which, in spite of state-of-the-art technology was a failure. The Ministry of New and Renewable Energy (MNRE) and the Ministry of Urban Development (MoUD) presently records 5 fully functional, 4 non- functional, 31 under construction and 21 under tendering stage waste-to-energy plants in India [17]. Europe, on the contrary, holds nearly 47.6% of the waste-to-energy market and nearly, 520 waste-to-energy plants were accounted to be operational in Europe in 2013 [32].

Despite the increase in waste generation, the waste collection and segregation services are poor in India while major metros like Delhi record 70–90% collection efficiency, smaller cities and rural areas record much less collection rates [6, 27].

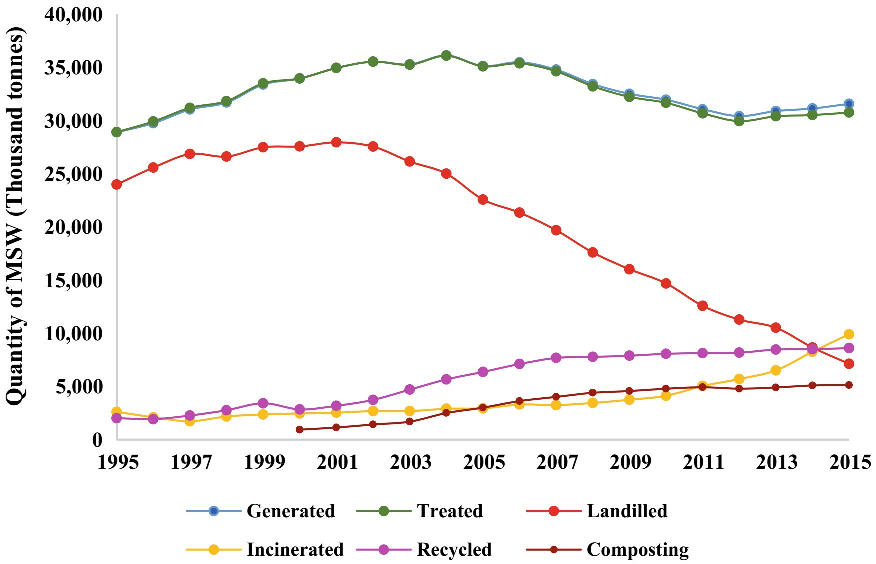


Fig. 4 Quantity of MSW generated and treated in the UK

Furthermore, the collected MSW is highly heterogeneous, owing to the absence of source segregation. While thermal treatment may prove to be a reliable treatment route, it may not always be feasible depending on the properties of the feed. For instance,

(a) Material recovery operations, including informal recycling activities may reduce the combustible fraction of MSW feed
(b) Heterogeneity of the MSW may affect the thermal properties of the feed, like moisture content, ash content, etc.
(c) Variation in the composition of the feed over the years
(d) Seasonal fluctuation of MSW properties

To ensure the feasibility of a cost-intensive technology like incineration, it is necessary to quantify the incinerability of the MSW feed. To facilitate this decision-making, the *i*-Index has been formulated. The *i*-Index incorporates the various criteria which have the potential to influence the feasibility of incineration of MSW. With waste-to-energy technology gradually becoming an inalienable part of integrated waste management and MSW composition varying over the years, *i*-Index can aid in estimating the variations in the incinerability of MSW over the years and facilitate the design of the waste-to-energy plant in accordance with that. The study aims at assessing the variation in the incinerability of MSW generated in the UK and Delhi, during the period from 1981 to 2005. The data reported by various governmental agencies as well as previous researchers have been used for the determination of the same. A brief account of the computation of *i*-Index is given in the following section.

3 Quantification of Incinerability of MSW Using *i*-Index

The *i*-Index is a composite indicator which is used to estimate the incinerability of MSW. Incinerability of MSW is affected by the pollution potential, energy recovery as well as the financial aspect of the incineration process and how the various properties of the MSW affect these criteria. However, this being a multi-criteria decision-making problem, opinions of the experts from the field was collected during various stages of its formulation, right from the parameter selection to its normalisation [24]. The relative weightage of the chosen parameters were determined using analytic hierarchy process (AHP) [22]. Besides the ranking of the parameters, this technique can help isolate the inconsistent comparisons and rectify the anomalies in the responses. The relative weightages of the parameters thus obtained are listed in Table 2. The normalisation of the parameters to convert them to a uniform scale was done implicitly by graphical method.

The computation of the index was then done by weighted linear summation technique.

$$\text{Incinerability Index or } i\text{-Index} = \frac{\sum_1^n w_i P_i}{\sum_1^n w_i} \quad (1)$$

where P_i is the normalised values of parameters obtained from the graph and w_i their corresponding weightages. The index is designed as an increasing scale indicator, with a maximum of 100 and minimum of 1.

In addition to estimating the incinerability of MSW, the *i*-Index may also be used to determine the degree of pretreatment required to make the MSW feed incinerable.

Table 2 Input parameters and the relative weightages for *i*-Index

Rank	Parameter	Relative weightage
1	SO_2 released per kg of MSW feed (g/kg MSW)	0.161
2	Heat Content of MSW feed (kcal/kg)	0.151
3	CO_2 released per kg of MSW feed (kg/kg MSW)	0.148
4	Quantity of auxiliary fuel required to maintain 1000 °C inside the furnace (kg/ton MSW)	0.137
5	% Volatiles in MSW feed	0.124
6	Specific heat of MSW feed	0.097
7	Bulk Density of MSW feed	0.092
8	% Moisture in MSW feed	0.090
Total		1.000

The current study investigates the application of the *i*-Index to assess the variations in incinerability of MSW over the years.

4 Variation in Incinerability of MSW Over the Years

The variation in the composition of MSW generated in the UK and Delhi has already been listed in Table 1. The various input parameters to compute the index were obtained from the literature. Table 3 shows the input parameters for the study areas during different years and the normalised values for the same. The *i*-Index values were calculated for the UK and New Delhi using the reported data by the weighted linear summation technique. The variation in the *i*-Index values over the years is presented diagrammatically in Fig. 5.

Table 3 Values of input parameters and the corresponding normalised values

Parameter	Delhi (1982)	Normalised value (P_i)	Delhi (1995)	Normalised value (P_i)	Delhi (2002)	Normalised value (P_i)	Delhi (2004)	Normalised value (P_i)
Bulk density (kg/m^3)	550	60.28	480	61.7	485	60.7	475	61.86
CO_2 (kg/kg MSW)	0.96	64.8	1.09	59.7	1.09	58.96	1.09	59.7
Heat content (kcal/kg)	1506.4	48.51	1982.2	67.7	1980	66.3	2010.5	67.99
Moisture content (%)	33.3	73.7	24.62	77.99	24.84	77.96	26.58	77.4
Auxiliary fuel (kg/T MSW)	91.3	16.89	72.9	24.1	73.43	23.88	73.7	24.1
SO_2 (g/kg MSW)	4.14	17.78	4.69	7.69	4.718	7.44	4.64	8.5
Specific heat (kJ/kg K)	2.55	26.7	2.03	51.75	2.04	51.75	2.14	45.7
Volatile content (%)	45.8	51.7	50.25	64.1	50.18	64.2	50.6	64.5

(continued)

For MSW generated in Delhi, the *i*-Index value increased by 12.13% in 1995 to become 49.3 from 43.3. This can be due to the increase in plastic fraction to nearly 6%. Further, booming literacy rates might have caused an increase in the paper fraction of MSW. Improved standards of living increased the purchasing power which may have increased the combustible fraction in MSW. This was simultaneously met with a mild decrease in food fraction, due to the increased use of packaged food products. However, past 1995, *i*-Index remained nearly constant up to 2004. After the initial increase in the combustible fraction, the composition underwent negligible changes and hence no major change in the *i*-Index value from 1995 to 2004.

Following the Landfill Directive, integrated waste management underwent phenomenal changes in the UK. Moreover, landfill tax was also levied on the weight of the MSW disposed at a landfill @ 95 €/ton which further accelerated the material recovery operations [10]. Subsequently, there has been a steady increase in the recycling rate from the year 1996. Further, it was mandatory to significantly decrease the amount of biodegradable materials landfilled and targets were set accordingly. The

Table 3 (continued)

Parameter	UK 1981	Normalised value (P_i)	UK 1992	Normalised value (P_i)	UK 1996	Normalised value (P_i)	UK 2005	Normalised value (P_i)
Bulk density (kg/m^3)	150	95.18	150	95.18	175	94.35	125	96
CO_2 (kg/kg MSW)	1.14	56.8	1.06	60.8	1.05	61.3	1.25	53
Heat content (kcal/kg)	2419	83	2797	87.95	2317	82	3282.3	94.2
Moisture content (%)	20.4	80.48	15.58	85.4	21.38	79.87	20.5	80.3
Auxiliary fuel (kg/T MSW)	28.36	57.5	8.7	82.1	38.1	47.8	11.5	76.5
SO_2 (g/kg MSW)	3.00	46.48	2.77	53.9	2.85	51.47	2.46	61.7
Specific heat (kJ/kg K)	1.98	51.78	1.82	61.92	2.08	47.89	2.11	47.03
Volatile content (%)	54.3	70.7	60.9	74.89	53.65	70.24	60.8	74.94

Note P_i is the normalised parameter value obtained from normalisation curves

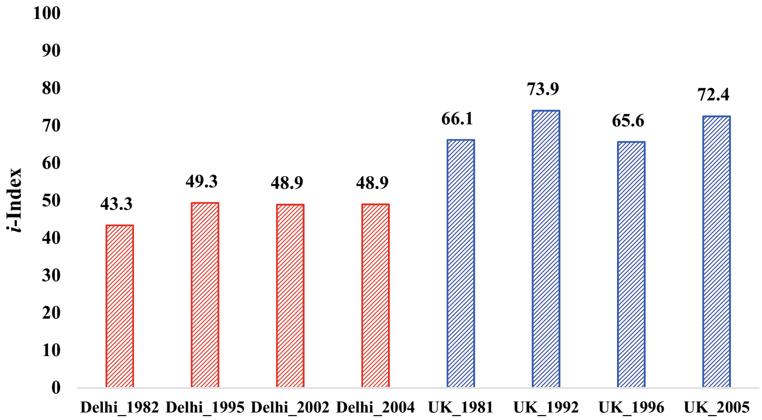


Fig. 5 *i*-Index values for MSW generated in the UK and Delhi during 1981–2005

aim was to reduce the amount of biodegradable fraction landfilled in 2010 by 75% of the value in 1995 significantly.

MSW generated in 1981 in the UK had an *i*-Index of 66.1, which is far higher than that in a like Delhi. The incinerability improved over the years, as evident from the *i*-index values in Fig. 5. The policy changes may have elicited a reduction in *i*-Index value by nearly 11% in mere 4 years. In 2005, the *i*-Index of MSW was observed to have undergone almost 9% growth. With Renewable Obligation Orders of 2002, 2003 and 2005, the electricity distributors are required to supply a fraction of electricity from renewable energy sources. This opened up the market avenues for waste incineration furthermore. Although material recovery operations may adversely affect the *i*-Index and thus the incinerability to some extent, the feed may remain incinerable, as evident from the *i*-Index value of 65.6 in 1996 in the UK.

Higher *i*-Index values for MSW from the UK are indicative of appreciably high feasibility of incineration. On the contrary, the *i*-Index values for MSW generated in Delhi are relatively lower. The index indicates how poor thermal characteristics of MSW shall disrupt the self-sustainability of incineration. Although auxiliary fuel supply can rectify this, the economy of operation may be affected. Without detailed characterisation studies, the index value expresses the incinerability of MSW as well as the feasibility of MSW incineration for energy recovery. With a yearly variation of *i*-Index available, the incinerability of MSW can be projected to future years so that waste-to-energy facilities are planned in accordance with that.

5 Conclusion

The *i*-Index, which is a composite indicator for quantifying the incinerability of MSW was used to determine the variation of incinerability of MSW generated in the UK and Delhi in the period from 1981 to 2005. The UK being a developed country exhibited a high value of the *i*-Index with 66.4 in 1981 which increased to 72.4 in 2005. With MSW management policies being amended in the UK to minimise landfilling, this is a reassuring fact, as it opens avenues for thermal treatment techniques. On the contrary, a major metro like Delhi in a developing country reports a low value of 43.3 in 1982 to 48.9 in 2004. Besides an increase in the initial years, there has not been much of a variation in the incinerability, as apparent from the *i*-Index values. In spite of that, there is three waste-to-energy plants currently operational in Delhi actively disposing of nearly 6250 TPD of MSW as per Delhi government statistics. Self-sustained incineration may not be a feasible option in such a scenario, but incineration for waste disposal and energy recovery is feasible in Delhi, as observed from *i*-Index values. Planning of waste-to-energy facilities to cater to the MSW feed in future years can also be facilitated using similar studies.

Acknowledgements The authors would like to express their gratitude to the panel of experts for their valuable responses and suggestions.

References

1. Bridgwater AV (1986) Refuse composition projections and recycling technology. Resour Conserv 12:159–174. https://doi.org/10.1016/0166-3097(86)90008-8
2. Burnley SJ (2007) A review of municipal solid waste composition in the United Kingdom. Waste Manag 27:1274–1285. https://doi.org/10.1016/j.wasman.2006.06.018
3. Burnley SJ, Ellis JC, Flowerdew R, Poll AJ, Prosser H (2007) Assessing the composition of municipal solid waste in Wales. Resour Conserv Recycl 49:264–283. https://doi.org/10.1016/j.resconrec.2006.03.015
4. Chakraborty M, Sharma C, Pandey J, Gupta PK (2013) Assessment of energy generation potentials of MSW in Delhi under different technological options. Energy Convers Manag 75:249–255. https://doi.org/10.1016/j.enconman.2013.06.027
5. Chakraborty M, Sharma C, Pandey J, Singh N, Gupta PK (2011) Methane emission estimation from landfills in Delhi: a comparative assessment of different methodologies. Atmos Environ 45:7135–7142. https://doi.org/10.1016/j.atmosenv.2011.09.015
6. CPCB (2013) Status Report on Municipal Solid Waste Management. Cent. Pollut. Control Board (Ministry Environmental For. Gov. India Parivesh Bhawan, East Arjun Nagar pp 1–13
7. Daskalopoulos E, Badr O, Probert SD (1998) Municipal solid waste: a prediction methodology for the generation rate and composition in the European Union countries and the United States of America. Resour Conserv Recycl 24:155–166. https://doi.org/10.1016/S0921-3449(98)00032-9
8. DEFRA (2004) Review of environmental and health effects of waste management: municipal solid waste and similar wastes, Department for Environment, Food and Rural Affairs Nobel House, 17 Smith Square, London
9. Gupta N, Yadav KK, Kumar V (2015) A review on current status of municipal solid waste management in India. J Environ Sci 37:206–217. https://doi.org/10.1016/j.jes.2015.01.034

10. HM Revenue and Customs (2013) A general guide to Landfill Tax
11. Ikhlayel M (2018) Development of management systems for sustainable municipal solid waste in developing countries: a systematic life cycle thinking approach. J Clean Prod 180:571–586. https://doi.org/10.1016/j.jclepro.2018.01.057
12. Jain P, Handa K, Delhi N (2014) Studies on waste-to-energy technologies in India & a detailed study of waste-to-energy plants in Delhi 2:109–116
13. Karak T, Bhagat RM, Bhattacharyya P (2012) Municipal solid waste generation, composition, and management: the world scenario. Crit Rev Environ Sci Technol 42:1509–1630. https://doi.org/10.1080/10643389.2011.569871
14. Kaushal RK, Varghese GK, Chabukdhara M (2012) Municipal solid waste management in India-current state and future challenges: a review
15. Kumar A (2013) Existing situation of municipal solid waste management in NCT of Delhi, India 1:6–17
16. MCD (2004) Feasibility study and master plan report for optimal solid waste treatment and disposal for the entire state of Delhi based on public and private partnership solution. Municipal Corporation of Delhi, Delhi, India
17. MoUD (2016) Municipal solid waste management manual Part 1: an overview, CPHEEO, MoUD
18. Mühle S, Balsam I, Cheeseman CR (2010) Comparison of carbon emissions associated with municipal solid waste management in Germany and the UK. Resour Conserv Recy 54
19. NEERI (1996) Solid waste management in MCD Area. National Environmental Engineering Research Institute, Nagpur, India
20. Quina MJ, Bordado JCM, Quinta-ferreira RM (2005) Air pollution control in municipal solid waste incinerators. In: The impact of air pollution on health, economy, environment and agricultural sources
21. Rathi S (2006) Alternative approaches for better municipal solid waste management in Mumbai, India. Waste Manag 26:1192–1200. https://doi.org/10.1016/j.wasman.2005.09.006
22. Saaty TL (1994) How to make a decision: the analytic hierarchy process. In: INTERFACES. The Institute of Management Sciences, pp 19–43
23. Sebastian RM, Alappat B (2016) Thermal properties of Indian municipal solid waste over the past, present and future years and its effect on thermal waste to energy facilities. Civ Eng Urban Plan Int J 3:97–106. https://doi.org/10.5121/civej.2016.3208
24. Sebastian RM, Kumar D, Alappat BJ (2018) Comparative assessment of incinerability of municipal solid waste over different economies. Detritus (Accepted)
25. Sebastian RM, Kumar D, Alappat BJ (2019) A technique to quantify incinerability of municipal solid waste. Resour Conserv Recycl 140, 286–296. https://doi.org/10.1016/j.resconrec.2018.09.022
26. Sebastian RM, Kumar D, Alappat B (2018) Comparative assessment of incinerability of municipal solid waste over different economies, detritus. 2:89–95
27. Sharholy M, Ahmad K (2008) Municipal solid waste management in Indian cities—a review 28:459–467. https://doi.org/10.1016/j.wasman.2007.02.008
28. Talyan V (2008) State of municipal solid waste management in Delhi, the capital of India 28:1276–1287. https://doi.org/10.1016/j.wasman.2007.05.017
29. Tchobanoglous G, Theisen H, Vigil S (1993) Integrated solid waste management: engineering principles and management issues. McGraw-Hill, New York
30. TERI (2002) Performance measurements of Pilot Cities. Tata Energy Research Institute, New Delhi, India
31. Vij D (2012) Urbanization and solid waste management in India: Present practices and future challenges 37:437–447. https://doi.org/10.1016/j.sbspro.2012.03.309
32. World Energy Council (2016) World energy resources: waste to energy. World Energy Council, UK
33. Zhu D, Asnani PU, Zurbrügg C, Anapolsky S, Mani S (2008) Improving municipal solid waste management in India: a sourcebook for policy makers. 10.1596\978-0-8213-7361-3

Author Index

S. K. Ghosh (ed.), *Waste Valorisation and Recycling*,
https://doi.org/10.1007/978-981-13-2784-1