Sustainable Agriculture Reviews 34

Mu. Naushad
Eric Lichtfouse *Editors*

Sustainable Agriculture Reviews 34

Date Palm for Food, Medicine and the Environment

Springer

Sustainable Agriculture Reviews

Volume 34

Series Editor
Eric Lichtfouse
Aix-Marseille Université, CNRS, IRD, INRA
Coll France, CEREGE
Aix-en-Provence, France

Other Publications by Dr. Eric Lichtfouse

Books
Scientific Writing for Impact Factor Journals
https://www.novapublishers.com/catalog/product_info.php?products_id=42242

Environmental Chemistry
http://www.springer.com/978-3-540-22860-8

Sustainable Agriculture
Volume 1: http://www.springer.com/978-90-481-2665-1
Volume 2: http://www.springer.com/978-94-007-0393-3

Book series
Environmental Chemistry for a Sustainable World
http://www.springer.com/series/11480

Sustainable Agriculture Reviews
http://www.springer.com/series/8380

Journal
Environmental Chemistry Letters
http://www.springer.com/10311

Sustainable agriculture is a rapidly growing field aiming at producing food and energy in a sustainable way for humans and their children. Sustainable agriculture is a discipline that addresses current issues such as climate change, increasing food and fuel prices, poor-nation starvation, rich-nation obesity, water pollution, soil erosion, fertility loss, pest control, and biodiversity depletion.

Novel, environmentally-friendly solutions are proposed based on integrated knowledge from sciences as diverse as agronomy, soil science, molecular biology, chemistry, toxicology, ecology, economy, and social sciences. Indeed, sustainable agriculture decipher mechanisms of processes that occur from the molecular level to the farming system to the global level at time scales ranging from seconds to centuries. For that, scientists use the system approach that involves studying components and interactions of a whole system to address scientific, economic and social issues. In that respect, sustainable agriculture is not a classical, narrow science. Instead of solving problems using the classical painkiller approach that treats only negative impacts, sustainable agriculture treats problem sources.

Because most actual society issues are now intertwined, global, and fast-developing, sustainable agriculture will bring solutions to build a safer world. This book series gathers review articles that analyze current agricultural issues and knowledge, then propose alternative solutions. It will therefore help all scientists, decision-makers, professors, farmers and politicians who wish to build a safe agriculture, energy and food system for future generations.

More information about this series at http://www.springer.com/series/8380

Mu. Naushad • Eric Lichtfouse
Editors

Sustainable Agriculture Reviews 34

Date Palm for Food, Medicine and the Environment

Springer

Editors
Mu. Naushad
Department of Chemistry, College of Science
King Saud University
Riyadh, Saudi Arabia

Eric Lichtfouse
Aix-Marseille Université
CNRS, IRD, INRA
Coll France, CEREGE
Aix-en-Provence, France

ISSN 2210-4410 ISSN 2210-4429 (electronic)
Sustainable Agriculture Reviews
ISBN 978-3-030-11344-5 ISBN 978-3-030-11345-2 (eBook)
https://doi.org/10.1007/978-3-030-11345-2

This Springer imprint is published by the registered company Springer Nature Switzerland AG.
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Preface

This book reviews the applications of date palm for food, medical, and environmental sectors. About 100 million of date trees are cultivated globally, out of which 90% are grown in the Middle East and North Africa regions. The annual global production of dates was 7.5 million tons in 2008. Date palm is an important crop in semiarid and arid regions of the world including North Africa, the Middle East, Southern Europe, Central and South America, India, and Pakistan. Date palms are scientifically named *Phoenix dactylifera* L. and belong to the Arecaceae family. The date palm is one of the oldest cultivated trees, and its fruit has been a dietary staple around the world for many centuries. The fruit is used for food, environmental, and medical applications.

Date palm tree (**a**, **b**), date fruits (**c**), and date seeds (**d**)

Date pulps contain dietary fibers and easily digestible sugars (70%) including glucose, sucrose, and fructose. Pulps also contain vitamins such as biotin, thiamine, riboflavin, and ascorbic and folic acid and are also rich in iron, cobalt, calcium, copper, potassium, magnesium, fluorine, manganese, phosphorus, sulfur, boron, sodium, copper, selenium, and zinc. Consumption of 100 g of dates supplies more than 15% of the recommended daily allowance for copper, selenium, magnesium, and potassium.

Moreover, date fruits have phenolic compounds and flavonoid constituents with free radical scavenging and antioxidant activities. The date palm fruit has been used in traditional medicines for the cure of various contagious diseases. Thus, regular use of dates provides protection from prostate, endometrial, colon, lung, breast, and pancreatic cancers.

Date palm wastes are efficient adsorbents owing to cost-effective and adsorption potential for the exclusion of various contaminants. Date stones and date palm leaves are a freely and abundantly available biomass. Therefore, the transformation of date biomass waste into activated carbon can be useful for drinking water purification, wastewater treatment, and removal of dyes, pesticides, phenols, and toxic metal ions.

Health benefits and the importance of the date palm fruit for human wellness are discussed in Chap. 1. Chapter 2 highlights the nutritional and antioxidant constituents of dates. Chapter 3 presents the nutritional and pharmacological effects of date fruits. In Chap. 4, various techniques for the extraction of lipids from date pits are reviewed. Chapter 5 depicts the potential for biogas production from date palm fruit and explains the upsides and obstacles of the anaerobic digestion technology. Using waste date pits for biofuel production is discussed in Chap. 6. Chapter 7 presents extraction techniques used for getting date seed oils from different sources and leading to different yields. Chapter 8 reviews the production of glucose and lactic acid from cellulosic date palm wastes by enzymatic fermentation. Chapter 9 explores the applications of date palm fibers as low-cost adsorbent for wastewater treatment. Chapter 10 reports the adsorption of metal ions by date stone-based activated carbon. Chapter 11 presents the removal of toxins from the environment using date palm seeds. Chapter 12 reviews the development and application of date palm-based activated carbon for decolorizing textile effluents. Chapter 13 discusses nitrate and phosphate removal from aqueous solutions using date palm-assisted nanocomposite materials.

Riyadh, Saudi Arabia Mu. Naushad
Aix-en-Provence, France Eric Lichtfouse

Acknowledgments

First of all, we would like to thank God Almighty for giving us the strength, knowledge, and ability to undertake this book project and to persevere and complete it satisfactorily. Without his blessings, this achievement would not have been possible.

This book is the outcome of the remarkable contribution of experts from various interdisciplinary fields of science and covers the most comprehensive, in-depth, and up-to-date research and reviews. We are thankful to all the contributing authors and their coauthors for their esteemed work. We would like to express our gratitude to all the authors, publishers, and other researchers for granting us the copyright permissions to use their illustrations. Although every effort has been made to obtain the copyright permissions from the respective owners to include citation with the reproduced materials, we would still like to offer our deep apologies to any copyright holder if unknowingly their right is being infringed.

Dr. Mu. Naushad expresses his deep gratitude to the Chairman of the Department of Chemistry, College of Science, King Saud University, Saudi Arabia, for his valuable suggestions. He has great pleasure in acknowledging his gratitude to his friends and colleagues for their good wishes, encouragement, and affections. Above all, he wants to thank his parents and all his family members who supported and encouraged him in spite of all the time it took him away from them.

Finally, Dr. Mu. Naushad extends his appreciation to the Deanship of Scientific Research at King Saud University for the financial support.

Mu. Naushad
Eric Lichtfouse

Contents

1 Date Palm as a Healthy Food 1
P. Senthil Kumar and P. R. Yaashikaa

2 Analysis of Antioxidants and Nutritional Assessment of Date Palm Fruits 19
B. M. Gnanamangai, S. Saranya, P. Ponmurugan, S. Kavitha, Sudhagar Pitchaimuthu, and P. Divya

3 Nutritional and Therapeutic Applications of Date Palm 41
Prabu Periyathambi, Hemalatha Thiagarajan, and Suganthan Veerachamy

4 Chemical Composition of Date Pits: Potential to Extract and Characterize the Lipid Fraction 55
Asif Ahmad and Hifsa Imtiaz

5 Biogas Production from Date Palm Fruits 79
P. Senthil Kumar and C. Femina Carolin

6 Valorization of Waste Date Seeds for Green Carbon Catalysts and Biodiesel Synthesis 105
Ala'a H. Al-Muhtaseb, Farrukh Jamil, Lamya Al Haj, Eyas Mahmoud, Mohamed Becherif, Umer Rashid, Sikander Rafiq, A. E. Atabani, and Gopalakrishnan Kumar

7 Different Extraction Methods, Physical Properties and Chemical Composition of Date Seed Oil 125
Jawhar Fakhfakh, Sahar Ben-Youssef, Mu. Naushad, and Noureddine Allouche

8 Date Palm Waste: An Efficient Source for Production of Glucose and Lactic Acid 155
Muhammad Tauseef Azam and Asif Ahmad

9 Application of Date-Palm Fibres for the Wastewater Treatment 179
Marija Nujic, Natalija Velic, and Mirna Habuda-Stanić

10 Recent Updates on Heavy Metal Remediation Using Date Stones (*Phoenix dactylifera L.*) – Date Fruit Processing Industry Waste 193
N. Sivarajasekar, J. Prakashmaran, Mu. Naushad, Bader Z. ALFarhan, S. Poornima, S. Sivapriya, V. Gayathri, T. Pradeepika, V. Raghu, S. Sivamani, Swapnil Dharaskar, and Nirajan Dhakal

11 Removal of Toxins from the Environment Using Date Palm Seeds 207
Basma Al-Najar, Mohamed Bououdina, J. Judith Vijaya, Radhika R. Nair, and Tetiana Tatarchuk

12 Date Palm Based Activated Carbon for the Efficient Removal of Organic Dyes from Aqueous Environment 247
Shamik Chowdhury, Sharadwata Pan, Rajasekhar Balasubramanian, and Papita Das

13 Date Palm Assisted Nanocomposite Materials for the Removal of Nitrate and Phosphate from Aqueous Medium 265
Mirna Habuda-Stanić, Marija Nujic, Blanca Magdalena Gonzalez Silva, Sveinung Sægrov, Stein Wold Østerhus, and Mario Šiljeg

About the Editors

Mu. Naushad is presently working as associate professor in the Department of Chemistry, College of Science, King Saud University (KSU), Riyadh, Kingdom of Saudi Arabia. He obtained his MSc and PhD in Analytical Chemistry from Aligarh Muslim University, Aligarh, India, in 2002 and 2007, respectively. He has vast research experience in the multidisciplinary fields of Analytical Chemistry, Materials Chemistry, and Environmental Science. He holds over 250 publications in the international journals of repute and several US patents. He has >5300 citations with a Google Scholar h-index of >45. He has successfully run several research projects funded by the National Plan for Science and Technology (NPST) and King Abdulaziz City for Science and Technology (KACST), Kingdom of Saudi Arabia. He is the editor/editorial member of several reputed journals like *Scientific Reports* (Nature), *Process Safety and Environmental Protection* (Elsevier), *Journal of Water Process Engineering* (Elsevier), and *International Journal of Environmental Research and Public Health* (MDPI). He is also the associate editor for *Environmental Chemistry Letters* (Springer) and *Nanotechnology for Environmental Engineering* journal (Springer). He has been awarded the Scientist of the Year Award 2015 from the National Environmental Science Academy, Delhi, India, and Almarai Award 2017, Saudi Arabia.

Eric Lichtfouse, PhD, born in 1960, is an environmental chemist working at the University of Aix-Marseille, France. He has invented carbon-13 dating, a method allowing to measure the relative age and turnover of molecular organic compounds occurring in different temporal pools of any complex media. He is teaching scientific writing and communication and has published the book *Scientific Writing for Impact Factors*, which includes a new tool – the micro-article – to identify the novelty of research results. He is founder and chief editor of scientific journals and series in environmental chemistry and agriculture. He got the Analytical Chemistry Prize by the French Chemical Society, the Grand Prize of the Universities of Nancy and Metz, and a Journal Citation Award by the Essential Indicators.

About the Authors

Asif Ahmad Department of Food Technology, PMAS-Arid Agriculture University, Rawalpindi, Pakistan

Institute of Food and Nutritional Sciences, Pir Mehr Ali Shah, Arid Agriculture University, Rawalpindi, Pakistan

Bader Z. ALFarhan King Abdulaziz City for Science and Technology, Riyadh, Saudi Arabia

Lamya Al Haj Department of Biology, College of Science, Sultan Qaboos University, Muscat, Oman

Noureddine Allouche Laboratory of Organic Chemistry LR17ES08 (Natural Substances Team), Department of Chemistry, Faculty of Sciences of Sfax, Sfax, Tunisia

Ala'a H. Al-Muhtaseb Department of Petroleum and Chemical Engineering, College of Engineering, Sultan Qaboos University, Muscat, Oman

Basma Al-Najar Department of Physics, College of Science, University of Bahrain, Sakheer, Kingdom of Bahrain

A. E. Atabani Energy Division, Department of Mechanical Engineering, Faculty of Engineering, Erciyes 20 University, Kayseri, Turkey

Muhammad Tauseef Azam Institute of Food and Nutritional Sciences, Pir Mehr Ali Shah, Arid Agriculture University, Rawalpindi, Pakistan

Rajasekhar Balasubramanian Department of Civil & Environmental Engineering, National University of Singapore, Singapore, Singapore

Mohamed Becherif Department of Energy, FCLab, FR CNRS 3539, Bourgogne Franche-Comte University/UTBM, Belfort, France

Sahar Ben-Youssef Laboratory of Organic Chemistry LR17ES08 (Natural Substances Team), Department of Chemistry, Faculty of Sciences of Sfax, Sfax, Tunisia

Mohamed Bououdina Department of Physics, College of Science, University of Bahrain, Sakheer, Kingdom of Bahrain

Shamik Chowdhury Department of Civil & Environmental Engineering, National University of Singapore, Singapore, Singapore

Papita Das Department of Chemical Engineering, Jadavpur University, Kolkata, India

Nirajan Dhakal Environmental Engineering and Water Technology Department, IHE Delft Institute for Water Education, Delft, The Netherlands

Swapnil Dharaskar Department of Chemical Engineering, School of Technology, Pandit Deendayal Petroleum University, Gandhinagar, Gujarat, India

P. Divya Department of Biotechnology, K. S. Rangasamy College of Technology, Tiruchengode, Tamil Nadu, India

Jawhar Fakhfakh Laboratory of Organic Chemistry LR17ES08 (Natural Substances Team), Department of Chemistry, Faculty of Sciences of Sfax, Sfax, Tunisia

C. Femina Carolin Department of Chemical Engineering, SSN College of Engineering, Chennai, India

V. Gayathri Laboratory for Bioremediation Research, Unit Operations Lab, Department of Biotechnology, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India

B. M. Gnanamangai Department of Biotechnology, K. S. Rangasamy College of Technology, Tiruchengode, Tamil Nadu, India

Mirna Habuda-Stanić Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, Osijek, Croatia

Hifsa Imtiaz Department of Food Technology, PMAS-Arid Agriculture University, Rawalpindi, Pakistan

Farrukh Jamil Department of Petroleum and Chemical Engineering, College of Engineering, Sultan Qaboos University, Muscat, Oman

Department of Chemical Engineering, COMSATS University Islamabad, Lahore, Pakistan

J. Judith Vijaya Catalysis and Nanomaterials Research Laboratory, Department of Chemistry, Loyola College, Chennai, India

S. Kavitha Department of Biotechnology, K. S. Rangasamy College of Technology, Tiruchengode, Tamil Nadu, India

Gopalakrishnan Kumar Institute of Chemistry, Bioscience and Environmental Engineering, Faculty of Science and Technology, University of Stavanger, Stavanger, Norway

Eyas Mahmoud Department of Chemical and Petroleum Engineering, United Arab Emirates University, Al-Ain, UAE

Radhika R. Nair Catalysis and Nanomaterials Research Laboratory, Department of Chemistry, Loyola College, Chennai, India

Mu. Naushad Department of Chemistry, College of Science, King Saud University, Riyadh, Saudi Arabia

Marija Nujic Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, Osijek, Croatia

Stein Wold Østerhus Department of Civil and Environmental Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway

Sharadwata Pan School of Life Sciences Weihenstephan, Technical University of Munich, Freising, Germany

Prabu Periyathambi Centre for Nanobiotechnology, Vellore Institute of Technology (VIT), Vellore, TN, India

Sudhagar Pitchaimuthu Multi-functional Photocatalyst & Coatings Group, SPECIFIC, College of Engineering, Swansea University (Bay Campus), Swansea, Wales, UK

P. Ponmurugan Department of Botany, Bharathiar University, Coimbatore, Tamil Nadu, India

S. Poornima Laboratory for Bioremediation Research, Unit Operations Lab, Department of Biotechnology, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India

T. Pradeepika Laboratory for Bioremediation Research, Unit Operations Lab, Department of Biotechnology, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India

J. Prakashmaran Department of Food Science and Nutrition, Periyar University, Salem, Tamil Nadu, India

Sikander Rafiq Department of Chemical Engineering, COMSATS University Islamabad, Lahore, Pakistan

V. Raghu Laboratory for Bioremediation Research, Unit Operations Lab, Department of Biotechnology, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India

Umer Rashid Institute of Advanced Technology, Universiti Putra Malaysia, Serdang, Selangor, Malaysia

Sveinung Sægrov Department of Civil and Environmental Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway

S. Saranya Department of Biotechnology, K. S. Rangasamy College of Technology, Tiruchengode, Tamil Nadu, India

P. Senthil Kumar Department of Chemical Engineering, SSN College of Engineering, Chennai, India

Mario Šiljeg Faculty of Geotechnical Engineering, University of Zagreb, Varaždin, Croatia

Blanca Magdalena Gonzalez Silva Department of Civil and Environmental Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway

S. Sivamani Chemical Engineering Section, Salalah College of Technology, Salalah, Sultanate of Oman

S. Sivapriya Laboratory for Bioremediation Research, Unit Operations Lab, Department of Biotechnology, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India

N. Sivarajasekar Laboratory for Bioremediation Research, Unit Operations Lab, Department of Biotechnology, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India

Tetiana Tatarchuk Department of Chemistry, Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine

Educational and Scientific Center of Material Science and Nanotechnology, Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine

Hemalatha Thiagarajan Biological Materials Laboratory, CSIR-Central Leather Research Institute (CLRI), Chennai, TN, India

Suganthan Veerachamy Department for Sensors and Biomedical Technology, School of Electronics Engineering [SENSE], Vellore Institute of Technology (VIT), Vellore, TN, India

Natalija Velic Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, Osijek, Croatia

P. R. Yaashikaa Department of Chemical Engineering, SSN College of Engineering, Chennai, India

Chapter 1
Date Palm as a Healthy Food

P. Senthil Kumar and P. R. Yaashikaa

Abstract Date is an extremely rich-nutritious fruit that could develop in an exceptionally poor condition also. Date fruit is an imperative item on the planet and assumes a significant part in the monetary and political life in date developing districts. Date palm (*Phoenix dactylifera* L.) is a monocotyledon plant that experiences different stages amid aging. Despite the fact that more than three-fourths of the fruit comprises of sugars, the rest is extremely rich in vitamins, dietary strands, phenolic mixes or antioxidants, and minerals. An extremely profitable compound, for example, oleic acid could be removed from the seed with other unsaturated fats and utilized as food for humans and animals.

The medical advantage of dates is another vital viewpoint. Date concentrate could shield human bodies from the harm of free radicals or responsive oxygen species and even weaken the impact of diarrheal movement and turned out to be compelling as neuroprotective against two-sided regular carotid artery impediment. Lately, a lot of research has been carried on the various medical advantages of dates including identification and evaluation of different classes of photochemical with an awesome potential uses in the developing sectors of important sustenance and nutraceuticals. The health benefits and the importance of date palm fruit for human wellbeing are discussed in this chapter.

Keywords Date palm · Growth and development · Industrial uses · Medical applications · Healthy food · Nutritional constituents · Destruction

1.1 Introduction

Plants serve as a major natural source of nutrients to humans and animals. A transcending date palm (*Phoenix dactylifera*) resembles somewhat like a coconut tree, yet its enormous groups of organic product offer something which is sweeter.

P. Senthil Kumar (✉) · P. R. Yaashikaa
Department of Chemical Engineering, SSN College of Engineering, Chennai, India
e-mail: senthilchem8582@gmail.com

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_1

Apart from their richness, caramel flavoured and delicate, chewy substance, it's nothing unexpected that dates which are weighing about 70% sugar are normally alluded to as "nature's treat"(Farag 2016). Dates might be as sweet as confection; however they convey much more supplements – and potential medical advantages. The family Phoenix is composed of 17 palm species, for example, *canariensis*, *dactylifera*, *sabal*, *rupicola*, *reclinata*, and so forth. It is an individual from the palmae family (Arunachalam 2012). These palms are well known things in close ice free atmospheres around the globe. This palm is moderately developing when youthful, yet once the storage compartment achieves its full distance across the development rate increments and it grows completely in spring and summer. It is tolerant to very much depleted soils. The *Phoenix dactylifera* is a palm tree which is oftentimes planted for its elaborate characteristics. This palm is best utilized along lanes, on grounds and in parks. The developed *Phoenix dactylifera* dates are of red shading and contain a seed about 1 cm long. Fruits of date palm are not harmful but rather have a repulsive taste which renders them unfit for utilization yet when it is ripped totally this natural product is sweet (Ibrahim et al. 2001). The utilization of date pits as an animal feed in the customary way is still likely the most widely recognized practice. Date palms begin to hold up fruits at 4 years old to 5 years and achieve full development at 10 years old to 12 years contingent upon neighbourhood conditions influencing rate of development and improvement. Blossoms (flowers) are borne in strands on clusters at the highest point of the tree. The quantity of bundles per tree changes from 3 to 10 and each pack incorporates several strands and a huge number of individual dates. Contingent upon the flesh consistency and dampness content at gather when completely ready, date palm cultivars are partitioned into three gatherings, in particular delicate, semi-dry and dry. The fruit of any specific crop when left on the palm or presented to unreasonable curing conditions will lose dampness and build up a hard surface.

Dates with a hard surface texture are classified as second-grade dates. These dry dates are filled with nutrients with more benefits (Besbes et al. 2009). Different classifications can be found inside a similar gathering depending on natural product attributes, size and sugar content. Dates are devoured new, dried, or in different handled structures (Al-Abid et al. 2007). They are regularly devoured crisp in the wake of picking particularly at the fresh ripped stage. In a few cultivars, fruits are expended at the physiological development stage itself. Most dates, in any case, are devoured at the completely ready stage. The fruits at this stage are portrayed by low dampness content and hence are perfect for long period storage to be expended out of season. Any losses while collecting and handling in postharvest and advertising are high in most creating nations because of the frequency of physical, physiological and obsessive issue and to bug infection. Free radicals are involved in incessant incendiary ailments including rheumatoid joint inflammation. Free radicals assume an imperative part in the seriousness of rheumatoid joint inflammation and patients normally endure high oxidative pressure (Chaira et al. 2007). Antioxidants either engineered or normal are scavengers of free radicals and effectively affect human wellbeing and infection counteractive action. They may have a conceivable part in enhancing the incendiary condition in rheumatoid joint inflammation patients (Rahmani et al. 2014). The fluid concentrate of date organic product had in vitro cell reinforcement movement because of the nearness of mixes with powerful free-radical-scavenging action. So it was of significance to think about the antioxidant action of a consumable part of date natural products separates in vivo, in order to affirm their action in an organic framework. Since the palatable part of natural products has been demonstrated to contain phenolic mixes, the methanolic and water concentrates may indicate mitigating action (Mohamed and Al-Okabi 2004; Biglari et al. 2008). In addition to its antioxidant activity, date palm fruits also terminate allergic responses and the fruit extracts acts as an anti-allergic agent (Karasawa and Otani 2012). The geographic origin of the date palms can be explored by determining the phenolic content (Mansouri et al. 2005; Saleh 2011).

Date palm is socio-financially and customarily critical for populaces where the way of life flourishes. Foundation of date palm forests made difference migrant populaces in the past to settle and sort out groups and start cultivating. These populaces turned into a centre point for advertising or exchanging items, a creature, and different items. A totally new industry has additionally been produced in late years around the date palm and dates (El Hadrami and Al-Khayri 2012). The dates have a high substance of sugars, which can possibly build serum glucose and triacylglycerol levels, and also serum oxidative pressure and weight file. No information is directly accessible on the impacts of information utilization by solid subjects on their serum glucose, lipids, and oxidative status (Rock et al. 2009).

1.2 Date Palm – Growth and Development

Date palm is a dioecious plant with singular male and female trees. The tree takes 5–7 years to blossom, and henceforth drawn out stretches of time are required before the sex of the plant is identified. It is quiet east to proliferate the female trees by branches or by utilizing tissue culture methods. In date palm, formative capture of sterile sex organs happens before the finish of cell division. It is trailed by the gifted cell separation and advancement of unisexual blossoms. Direct root meristem recoloring with chromomycin is adequate to distinguish the sex of the date palm plant. Blooms have three carpels yet on fertilization just a single creates and two prematurely end. The state of the fruit is generally pretty much elongated or ellipsoidal (Hammadi et al. 2009). Figure 1.1 represents unripe and riped date palm in unripe and dried date palm seed. The seed, or pit, is hard and stogie formed, somewhat pointed at the finishes, from grey to darker in shading, and with a little developing life. The seed of the date palm fruit is bizarre where it stores the nourishment materials for the developing embryo not as starch, but rather as hemi-celluloses (Ashraf and Hamidi-Esfahani 2010).

Fertilization is a standout amongst the most vital pre-collect factors influencing fruit quality in the date palm. In commercial estate, artificial pollination either using hand or mechanical means is used in case of female trees using pollens from male trees. Choice of a decent pollinizer is of primary significance in the date palm, as the sort of the pollen parent influences fruit size and time taken for fruit aging, and

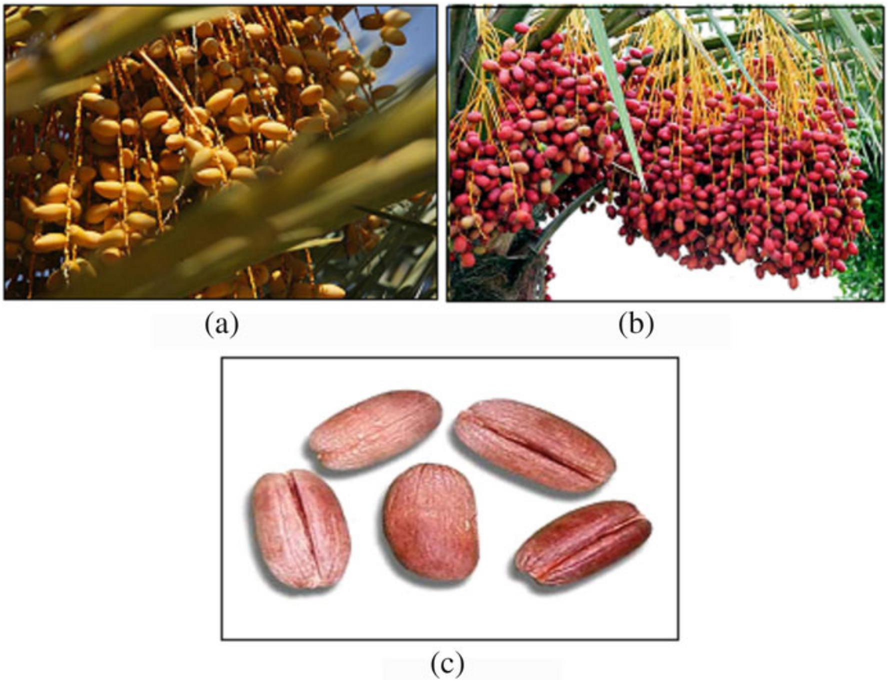


Fig. 1.1 Date palm – (**a**) Unripe date palm. (Reproduced from http://www.junglemusic.net/New%20Plant%20Arrivals/Images3/Phoenix%20dactylifera%20fruit%20closepu%20(Large)%20(Small).JPG (**b**) Riped date palm. (Reproduced from http://realpalmtrees.com/palm-tree-store/canary-island-date-palm-seeds-pkg.html) (**c**) Date palm seed

additionally the chemical constituent of the organic product. Such impacts of the pollen male parent on different parts of date fruit improvement are alluded to as mataxenia (Bazza 2008). Because of its nutritional properties, date fruit as such can have an extensive range of applications, but at present the processing applications are very limited (Kamal-Eldin et al. 2012).

Fermentation is one of the most seasoned advancements ever utilized for the protection of sustenance and determining esteem included nourishment items from sustenance materials over the globe. Fermentation using microbes yield a few esteem included items for fluctuated applications other than the expansion of nourishment such as yogurt, vinegar, mixed drinks and so forth that are specifically consumed (Cagno et al. 2017). All natural products, plant and animal items that fit to be utilized as nourishment have been subjected to microbial fermentation with a specific end goal to infer advance results and items, for example, natural acids, amino acids, vitamins, and so forth (Chandrasekaran and Bahkali 2013). In spite of the fact that date palm sap is the rich wellspring of microbes, it could likewise fill in as a substrate during fermentation. As of late lignocellulosic biomass speaks to the most imminent feedstock for ethanol generation. Fermentative microflora from date palm could be used for fermentation using ethanol fermenting significant feedstocks. These microbes could be altered using hereditary and metabolic building strategies for higher production of ethanol (Gupta and Kushwaha 2011).

1.3 Variables Influencing Date Palm Development and Improvement

- **Precipitation and Humidity**

High precipitation and dampness at the time of blooming or later phases of fruit improvement may restrain the creation of date palms to an indistinguishable degree from deficient warmth unit. High stickiness and precipitation amid later phases of fruit advancement may cause certain physiological issue. Moreover, low relative moistness amid the fruit aging time frame may cause some physiological issue. High stickiness and precipitation pronouncedly affect the procedure of fertilization. Early precipitation amid flowering in the spring may cause the disease of the shut spathes with inflorescence spoil.

- **Temperature**

For appropriate date fruit maturing on the date palm, it is basic that the developing season is hot and free of precipitation amid the aging time frame. The normal ideal every day temperature from blooming until the point when the fruit aging is around 21 °C for early aging cultivars, 24 °C for mid season cultivars, and 27 °C for late maturing cultivars.

- **Mineral nourishment**

The presence of nitrogen is essential for effective growth and efficiency of date palm tree, and it is less delicate to other mineral supplements, for example, iron and boron, as contrasted to other fruit trees, for example, citrus.

- **Growth regulators**

The real increment in size of fruit is accomplished by the enlargement or vacuolation of the cells framed amid the early period of mitotic action. Auxins and gibberellins, splashed onto fruit groups, have been found to build fruit size and defer fruit maturing, with conflicting consequences for fruit compound structure. The inclination of the date palm flower to set parthenocarpic fruit if not pollinated might be identified with levels of endogenous hormones in the ovary of unpollinated flowers. Parthenocarpic date palm organic products may likewise be acquired by treating unpollinated flowers with hormones such as auxins, cytokinins or gibberellins. Such fruit are of low quality when contrasted with fruits delivered by hand fertilization and they won't age completely. Fruit aging is typically postponed in trees conveying a substantial harvest, which can be helped by fruit or bundle diminishing at a beginning period of development, with the goals of adjusting the quantity of green leaves and the quantity of fruiting packs (Yahia and Kader 2011).

1.4 Nourishing Constituents of Date Palm

Date palm fruits were found to contain the accompanying supplement creation:

- Carbohydrates – 44–88%
- Sugars – 60–80%
- Fats – 0.2–0.4%
- Proteins – 2.3–5.6%
- Fibres – 6.4–11.5%

The natural fruit are additionally rich in potassium, calcium and iron with little measures of protein (2%), lipids (under 2%), copper, chloride, zinc, sulphur and vitamins A, B1, B2 (Hasnaoui et al. 2010; Nehdi et al. 2010). Dates are rich wellsprings of copper, potassium, magnesium, selenium, and direct of calcium, iron, manganese, and phosphorus; and their normal utilization is accounted for to give the expected supplements to the human body. The high potassium and low sodium substance in dates are attractive for individuals experiencing hypertension. The presence of mixes, for example, phenolics with a possibility to scavenge free radicals, high antimutagenic impacts and to fortify the insusceptible framework may contribute towards the different pharmacological impacts (Baliga et al. 2011; Abdul and Allaith 2008). The unrefined fibre, which contains gelatin, lignin, hemicelluloses and cellulose, speaks to around 2–4% of fruit dry weight. Gelatin assumes an essential part in date surface. The protein substance of dates, which is accounted for to be of high nutritive esteem, goes in the vicinity of 1.5 and 2.0%, and the rough fat substance runs in the vicinity of 2.5 and 7.4%. The seed oil is made out of 45% oleic, 25% palmitic, 10% stearic and 10% linoleic corrosive, with some capric and caprylic corrosive substance. The relish and nature of dates are influenced by their natural acidic substance. The date palm kernel weighs about 12–15% of date palm fruit. It is filled with 5–6% of proteins, 10–13% of fat, 46–51% of fibre, 1–2% of ash and nearly 10% of moisture content in it (Mariod et al. 2017). The causticity of the fruit tends to increment with fruit development and afterward diminishes toward the start of the aging stage, while pH increments at development. High pH esteem means that dates is of high quality. Date corrosiveness achieves the largest amount amid the time of most quick development and reductions amid development and maturing. Palmitic corrosive is the most prevailing corrosive took after by capric and caprylic acids. Date fruits at the completely develop organize are rich in useful parts, including phenolic mixes. Tannins are the most prevailing phenolic mixes in date leafy foods intently connected with the fruit maturing process (Al-Farsi and Lee 2008; Sahari et al. 2007). Dates comprise 70% starches, the vast majority of which is as sugars. In many assortments, the sugar content is totally modified sugar, which is quickly consumed by the human body. There is a specific absence of data on utilitarian constituents of dates and their potential incentive as useful nourishments. Useful sustenance is defined as those nourishments that give health benefits beyond fundamental nutrition (Assirey 2015; Sirisena et al. 2015).

1.5 Physiological Clutters

A few physiological issues can influence dates, consequently influencing their quality in the market.

- **Obscuring**

Both enzymatic and non-enzymatic browning happens in dates and increments with higher dampness content and higher temperatures. Enzymatic browning can be restrained at low oxygen focuses and low temperatures.

- **Skin division (puffiness)**

Skin division happens when the skin winds up dry, hard and fragile, and isolates from the flesh. It is said to be serious when the skin isolates from the flesh in an inflatable like manner. This issue creates amid aging of delicate date cultivars, which change in vulnerability. High temperature and high stickiness at a phase before the start of aging may incline the dates to skin division. Puffiness or indented partition, caused by high temperature as well as high dampness before the start of aging, may increment amid curing and influences just delicate cultivars.

- **Sugaring**

Sugar spotting is described by the presence of light-shaded spots under the skin and in the flesh and happens primarily in delicate date cultivars otherwise called rearrange sugar dates in which glucose and fructose are the principle sugars. Rate and importance of sugar spotting increases with increase in capacity temperature and time. Sugar spotting diminishes as the temperature diminishes and when the dampness content falls beneath 22%. So stockpiling at suggested temperatures limits this issue. Sugaring might be diminished by delicate warming of the influenced dates, however returned if adverse conditions conquer.

- **Discolouration**

Because of their high dampness content, delicate date cultivars are defenceless to a physiological issue known as inner breakdown which causes dark discolouration of fruits, on the off chance that they are not put away at the right temperature.

- **White and Black Nose**

White nose is portrayed by the nearness of a stained ring close to the calyx territory, which at times covers half of the fruit. It has been recommended that dry breezes for a long time amid the rutab phase of maturing can make the basal locale of the fruit age more than the rest, causing the ring appearance. This physiological issue might be because of calcium inside the fruit with the basal end containing less calcium than the apical end. Dark nose is fruit checking at the tip area of the fruit that turns dull shading. It is caused by high moistness.

- **Splitting**

It can be caused by various climatic conditions. Over-hydration, caused by a sudden increment in stickiness, for example, unseasonal rain, can offer ascent to an adjustment in turgor weight inside the fruit, bringing about splitting.

1.6 Market Preparation Before Commercialization

There are few preparatory stages for date palm fruit before it is provided in the market for commercialization (Mahmoudi et al. 2008). Figure 1.2 demonstrates the steps engaged with advertising readiness.

1.7 Applications of Date Palm

Date palm owing to its vast nutrient and mineral content is widely used for various purposes. Figure 1.3 represents the benefits of date palm in various sectors.

1.7.1 Medical Advantages

Medicinal and health nourishments have as of late gotten tremendous enthusiasm among the wellbeing experts and the general population. Subsequently, the

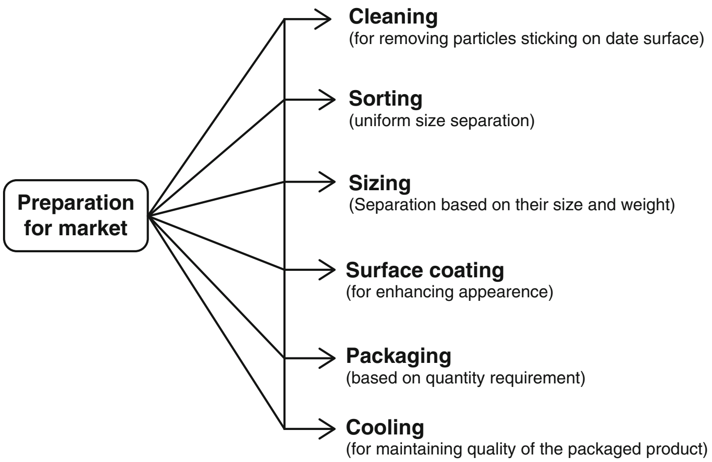
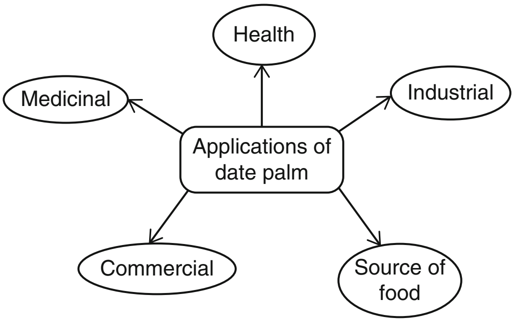


Fig. 1.2 Preparatory steps before commercialising

Fig. 1.3 Applications of date palm



worldwide wellbeing market has been overwhelmed with such items guaranteeing to enhance wellbeing and also avoid ceaseless ailments. Due to expanded business misuse of therapeutic sustenance, all assortments of products of the soil were re-assessed for their phytochemical piece and medical advantages under both research facility conditions and clinical settings (Vayalil 2012).

- **Gut Regularity**

Consuming dates can help counteract clogging. They're a phenomenal wellspring of dietary fiber. A lot of the fruit's fiber is insoluble, the kind that advances ordinary absorption. Concentrates of dates mash and palm sap have stimulatingly affect GIT movement. All the more imperatively, the outcomes contribute toward the approval of the conventional utilization of dates mash and palm sap for the treatment of stomach related issue such as constipation (Souli et al. 2014).

- **Cardiovascular Benefits**

Dates are a decent wellspring of a few cardio-defensive supplements, including potassium, copper and magnesium. Having ample potassium in one's eating regimen can help diminish hypertension, which may thusly bring down the danger of showing stroke or heart attack. Copper and magnesium are imperative for blood veins. Copper likewise keeps up the connective tissues in the heart and veins, while magnesium maintains typical heart rhythms. Moreover, dates are a decent wellspring of beta-D-glucan, a solvent fibre that can be especially compelling at decreasing elevated cholesterol levels (Ishurd et al. 2002).

- **Absence of additional sugars**

Dates can be consumed to fulfil one's sweet tooth while entirely constraining or previous the additional sugars found in numerous refined nourishments - likewise ensures cardiovascular wellbeing. Added sugars, or with any sort of sugar used to sweeten a supper or sustenance item, have been connected to stoutness, hypertension and undesirable cholesterol levels. Expending excessively numerous additional sugars is related with a significantly more serious danger of dying from coronary illness.

1.7.2 Potential Benefits

Vitamin C is absent in dates which is an important antioxidant commonly found in most of the fruits. They are as yet a decent wellspring of phytochemicals, in any case, which are generally present as phenols and carotenoids. A portion of these mixes display huge cancer prevention agent movement; they adequately protect cells from free-radical harm (Hamada et al. 2002). An eating routine rich in cell reinforcements or one focused on fruits, vegetables and other entire nourishments is generally thought to help ensure against growth, coronary illness and other perpetual conditions (Al-Humaid et al. 2010). Additionally presence of chemical constituents enhances the benefits of dates (Alshowiman 1990).

1.7.3 Minerals from Date Palm

- **Potassium**

Important electrolyte potassium is rich in dates. Potassium helps to control liquid levels and helps bring down the circulatory strain. It additionally makes the body less delicate to sodium, so people are more averse to endure a substantial spike in circulatory strain after a sodium-rich dinner. Expending potassium likewise benefits the nervous system, as the nerves depend on potassium communicates with each other.

- **Polyphenols**

Dates likewise contain polyphenols, a kind of gainful substance found in some plant-based nourishments. Polyphenols work as cancer prevention agents, shielding the cells from oxidative harm to the DNA, cell lipids and proteins that generally would cause ailment. While the impacts of date polyphenols on people requires assist examination, they demonstrate potential for ensuring one's wellbeing.

- **Dietary Fibre**

Dates fill in as a rich wellspring of starches, including dietary fibre. Fibre goes through the stomach related framework unaltered. Devouring fruits that contain fibre secures against coronary illness, and dietary fibre likewise benefits people with type 1 and sort 2 diabetes. Fibres are the strong insoluble piece of date substance, basically made out of cellulose, hemicellulose, insoluble proteins and lignin. The measure of these filaments is higher in beginning periods of fruit life. In any case, amid the aging procedure, cellulase and pectinase chemicals show in the natural product separate insoluble polymers into littler dissolvable atoms. These filaments can be utilized as dietary strands because of oil and water take-up, and swelling limit (Shafiei et al. 2010).

Other advantages

- Date palm fruits help in expanding platelet count in patients experiencing dengue fever.
- Immune framework gets fortified and bone loss is prevented.
- Whole framework picks up vitality with expanded platelet count.
- It gives different minerals (potassium, fibre, and so on.) and vitamins required for development of human body.
- Night visual impairment (blindness) and paleness (anaemia) can be avoided.

1.7.4 Industrial and Commercial Applications

Date palm tree is fundamentally planted for its fruits. It has different uses too in the commercial and modern aspects. Besides, a portion of these results equalled or are more imperative than the date fruit itself (Weber 2010). Date palm tree requires heaps of daylight. The normal and most direct business utilization of date palm tree is in arranging. Seeing avenues fixed with date palm trees will bring out an extraordinary and tasteful atmosphere to the region. It can withstand high and low temperature yet should not dip under 20 °F. Dates seed oils, which are rich in a few unsaturated fats are utilized as a part of cleansers and beauty care products. High tocol content is present in date palm than other oils such as olive, etc. This indicates better oxidative stability of date palm (Nehdi et al. 2018). The chemical nature of date seed oil makes it reasonable as an element for oxalic acid. Date seed medical advantages incorporate defensive impacts against early diabetic complexities, counteract DNA harm, and secure liver and kidney. Regardless of its little size, date seed can be subjected to burning and utilized as a viable charcoal. The date leaves stalk or spine is long and thin yet is solid and can stand the heaviness of a few men. They are utilized as rooftop rafters, networks, wall, flooring for little cabins, basic furniture, and so on (Khan and Khan 2016). Date palm fruits are broadly delivered and speak to rich wellsprings of sugar, fibre, and phenolic cancer prevention agents. Date fruits give high sustenance crude materials because of its conceivable utilization at three advancement stages from an extensive variety of assortments. In spite of the high generation, date fruits are underutilized and more engaged research is expected to increase the value of this yield. Date fruits have a tremendous degree and potential for use as nourishment due to their wholesome and financial esteem. There is a vast potential to particularly create healthy products using the high-esteem fibre and phenolic cancer prevention agents found in the fruits and seeds (Ghnimi et al. 2017).

Table 1.1 Medical applications of different parts of date palm

S. No	Parts of date palm	Uses
1.	Leaf	Aphrodisiac and liver treatment
2.	Flower	Fever, purgative and blood complaints
3.	Fruit	Leprosy, bronchitis, asthma, fever, vomiting and tuberculosis
4.	Seed	Inflammation, laxative, lesions and wounds
5.	Gum	Genitor-urinary system diseases and diarrhea

1.7.5 Therapeutic Uses

Taking date fruits once a day amid pregnancy will help reinforce the uterine muscles. It will aid the conveyance and deflect the post-conveyance dying. Dates are rich in potassium, glycine, and threonine that will enact prolactin which is the milk hormone. It will advance the stream of milk, which is useful for a breastfeeding lady. Along these lines, it regards keep eating dates even after pregnancy. Dates are rich in Vitamins A, B1, B2, B3, B5 and C, fiber, calcium, phosphorus, sulfur, potassium, copper, magnesium, and manganese. In spite of its sugar content, it is utilized to re-establish wellbeing to the iron deficient and delicate because of its extraordinary wellspring of supplement content. The most ideal route is to eat them crisp and not in cooking or squeezing. The date is a low-glycemic record sustenance and its high characteristic sugar substance won't essentially raise your glucose levels. Date fruits to give alleviation from fever, astringent, bronchial asthma, chest and throat contaminations. Table shows remedial utilizations of various parts of date palm (Kwaasi 2003) (Table 1.1).

1.7.6 Source of Food

The date is the staple sustenance. Dates are additionally prepared into glue, syrup, stick, jam, date solid shapes, date sugar powder, date vinegar and even date liquor. Dates are presently promoted as chocolate secured dates and sprinkled with slashed walnuts and raisins. Most agriculturists will do specific separating while date fruits are creating for more profitable collect. These winnowed date fruits will be dried out, grounded and blended with different grains and utilized as feedstock (Ibrahim 2004). Overload dried dates are given as sustenance to animals such as horse and camels. The terminal bud and youthful date leaves, which are rich in phosphorus, potassium, nitrogen, and fiery debris, can be transformed into a serving of mixed greens or cooked as a vegetable dish (Al-Farsi and Lee 2011; Al-Shahib and Marshall 2003).

1.8 Destruction of Date Palm

In the same way as other different plants, a few palms are in risk of ceasing to exist in view of human action. In spite of the fact that date palm development in the date developing districts of the world has a long history, yet the endeavours consumed for the advancement of this imperative yield, though important, yet still deficient and fall beneath desires. The item quality is still low, the field and post-harvest misfortunes are very high and the date items and side-effects can no uncertainty be enhanced and the product blend more differentiated (Jaradat and Zaid 2004). Production of Date palm is confronting significant issues, for example, low yields because of the absence of research, the spread of bugs, and additionally promoting imperatives. In the course of the most recent decade, profitability has declined in the customary developing zones. Pests and diseases caused by them have caused huge impacts upon date generation. Bayoud sickness which is caused by parasite undermines the date palms (Gassouma 2004). Therefore, the expenses of date production have outperforms incomes. In the meantime, the transportation of dates has declined to a base. Lessening in the profitable limit of date palms and the corruption of the nature of generation itself are the fundamental markers of debasement. Thus, the likelihood to gain a salary outside the desert garden, have incited mass movement. The maintaining date palms for the most part are limited. The outcome of this disregard is the running wild of the palm-forests, thickly developed with date palms, diminishing harvests and, subsequently. Regardless of the significance and expansive culture territories of ordinary date palm development, field and postharvest depletion are high, and techniques for estimating item quality and the utilization of date items and side-effects require change (Awad 2007). Amid the most recent 50 years, date palm forests have been subjected to corruption because of broad misuse coming about and because of the expansion in both the human populace and the quantity of residential animals. Likewise, the expanded capacity of most of the populace to profit by circumstances displayed by present day innovation has driven them to desert their date palms. Common variables have additionally added to the debasement of date palms, for example, dry spell, soil saltiness, bugs, natural change, and a decrease in the nature of ground water. Intense lack of trained and experienced workers with expanded wage requests, bringing about the disregard of numerous rural procedures required for appropriate date palm production. There is a recognizable shortcoming of government organizations for the augmentation and security of horticultural movement. Expanded pervasion of bugs and sicknesses bringing about a critical decrease in the efficiency of trees and have contributed altogether in destruction of date palm. The change of the present status of date palm development in the date producing nations and the upgrade of the nature of date items have turned out to be basic need that can't be overplayed (El-Juhany 2010).

Date palms must be comprehended to exist inside complex biological, social and economic organizations. Commercial products incorporate an expansive number of adjusted ecotypes. This perpetual dioecious plant is of extraordinary financial intrigue. To create natural dates, agriculturists must guarantee that natural organic composts are utilized to improve the sandy soil, and the dated must be permitted to age completely on the trees. The makers ought to consider, when fitting, the conceivable outcomes offered by naturally developed dates, as the natural market is developing quickly in numerous created nations. Thusly, as an ever-increasing number of buyers swing to natural sustenance, retailers will search for an entire scope of producing natural organic dates (Williams 2008).

1.9 Conclusion

Date palm is a customary product in the Arab world which has the ability to withstand unfavourable climatic conditions. The circulation of date palm is exceptionally impossible to miss due to the inalienable prerequisite for hot atmosphere which is important for effective fertilization and fruit setting. Lately, in light of overexploitation, the decent variety of the date palm forests has declined. The generation and use of the date fruits likewise differs from nation to nation because of the impact of current ecological conditions. There are various components which impede the generation of date palm, for example, significant nuisances and sicknesses, saltiness and dry spell, poor gather and postharvest hones. For a great many years date palm was engendered through ordinary reproducing which is a tedious and repetitive process. The utilization of the tissue culture systems gave date palm an enhanced productivity contrasted with different yields. The required data when accessible will upgrade our insight and thankfulness for the utilization of dates in our every day count calories. Because of its wealth and ease, dates remain a species with enormous potential and incalculable conceivable outcomes for future examination. Considering the way that dates are generally modest, nutritious and are without dangerous impacts it is protected to propose that their utilization ought to be prescribed on a day by day the reason for better wellbeing, essentialness, and force.

References

Abdul A, Allaith A (2008) Antioxidant activity of Bahraini date palm (*Phoenix dactylifera* L.) fruit of various cultivars. Int J Food Sci Technol 43:1033–1040. https://doi.org/10.1111/j.1365-2621.2007.01558.x

Al-Abid M, Al-Shoaily K, Al-Amry M, Al-Rawahy F (2007) Preparation of caramel colour from dates. Acta Hortic 736:537–541. https://doi.org/10.17660/ActaHortic.2007.736.53

Al-Farsi MA, Lee CY (2011) Chapter 53 – usage of date (*Phoenix dactylifera* L.) seeds in human health and animal feed. In: Nuts and seeds in health and disease prevention, pp 447–452. https://doi.org/10.1016/B978-0-12-375688-6.10053-2

Al-Farsi MA, Lee CY (2008) Nutritional and functional properties of dates: a review. Crit Rev Food Sci Nutr 48:877–887. https://doi.org/10.1080/10408390701724264

Al-Humaid AI, Mousa HM, El-Mergawi RA, Abdel-Salam AM (2010) Chemical composition and antioxidant activity of dates and dates–camel-milk mixtures as a protective meal against lipid peroxidation in rats. Am J Food Technol 5:22–30. https://doi.org/10.3923/ajft.2010.22.30

Al-Shahib W, Marshall RJ (2003) The fruit of the date palm: it's possible use as the best food for the future. Int J Food Sci Nutr 54:247–259. https://doi.org/10.1080/09637480120091982

Alshowiman SS (1990) Chemical-composition of some date palm seeds (*Phoenix dactylifera* L) in Saudi-Arabia. Arab Gulf J Sci Res 8(1):15–24

Arunachalam V (2012) 4 – Date palm. In: Genomics of cultivated palms, pp 49–59. https://doi.org/10.1016/B978-0-12-387736-9.00004-2

Ashraf Z, Hamidi-Esfahani Z (2010) Date and date processing: a review. Food Rev Int 27 (2):101–133. https://doi.org/10.1080/87559129.2010.535231

Assirey EAR (2015) Nutritional composition of fruit of 10 date palm (*Phoenix dactylifera* L.) cultivars grown in Saudi Arabia. J Taibah Univ Sci 9(1):75–79. https://doi.org/10.1016/j.jtusci.2014.07.002

Awad MA (2007) Increasing the rate of ripening of date palm fruit (*Phoenix dactylifera* L.) cv Helali by preharvest and postharvest treatments. Postharv Biol Technol 43:121–127. https://doi.org/10.1016/j.postharvbio.2006.08.006

Baliga MS, Baliga BRV, Kandathil SM, Bhat HP, Vayalil PK (2011) A review of the chemistry and pharmacology of the date fruits (*Phoenix dactylifera* L.). Food Res Int 44(7):1812–1822. https://doi.org/10.1016/j.foodres.2010.07.004

Bazza M (2008) Irrigated date palm production in the Near East. In: Proceedings of workshop on "Irrigation of Date Palm and Associated Crops", in collaboration with Faculty of Agriculture, Damascus University Damascus, Syrian Arab Republic, 2007, FAO/RNE pp 1–15

Besbes S, Drira L, Blecker C, Deroanne C, Attia H (2009) Adding value to hard date (*Phoenix dactylifera* L.): compositional, functional and sensory characteristics of date jam. Food Chem 112(2):406–411. https://doi.org/10.12691/ajfn-5-2-4

Biglari F, AlKarkhi AFM, Easa AM (2008) Antioxidant activity and phenolic content of various date palm (*Phoenix dactylifera*) fruits from Iran. Food Chem 107:1636–1641. https://doi.org/10.1016/j.foodchem.2007.10.033

Cagno RD, Filannino P, Cavoski I, Lanera A, Mamdouh BM, Gobbetti M (2017) Bioprocessing technology to exploit organic palm date (*Phoenix dactylifera* L. Cultivar Siwi) fruit as a functional dietary supplement. J Funct Foods 31:9–19. https://doi.org/10.1016/j.jff.2017.01.033

Chaira N, Ferchichi A, Mrabet A, Sghairoun M (2007) Chemical composition of the flesh and the pit of date palm fruit and radical scavenging activity of their extracts. Pak J Biol Sci 10 (13):2202–2207

Chandrasekaran M, Bahkali AH (2013) Valorization of date palm (*Phoenix dactylifera*) fruit processing by-products and wastes using bioprocess technology–review. Saudi J Biol Sci 20:105–120. https://doi.org/10.1016/j.sjbs.2012.12.004

El Hadrami A, Al-Khayri JM (2012) Socioeconomic and traditional importance of date palm. Emir J Food Agric 24:371–385

El-Juhany LI (2010) Degradation of date palm trees and date production in Arab countries: causes and potential rehabilitation. Aust J Basic Appl Sci 4(8):3998–4010

Farag KM (2016) Date palm: a wealth of healthy food. Reference module in food science. Encyclopedia of Food and Health 356–360. https://doi.org/10.1016/B978-0-12-384947-2.00215-4

Gassouma MS (2004) Pests of the Date Palm (*Phoenix dactylifera*). In: Regional workshop on Date Palm Development in the Arabian Peninsula, Abu Dhabi, UAE, pp 29–31

Ghnimi S, Umer S, Karim A, Kamal-Eldin A (2017) Date fruit (*Phoenix dactylifera* L.): an underutilized food seeking industrial valorization. NFS J 6:1–10. https://doi.org/10.1016/j.nfs.2016.12.001

Gupta N, Kushwaha H (2011) Date palm as a source of bioethanol producing microorganisms. In: Date palm biotechnology. Springer, Dordrecht, pp 711–727. https://doi.org/10.1007/978-94-007-1318-5_33
Hamada JS, Hashi IB, Sharif FA (2002) Preliminary analysis and potential uses of date pits in foods. Food Chem 76:135–137. https://doi.org/10.1016/S0308-8146(01)00253-9
Hammadi HR, Mokhtar M, Elbekkay FA (2009) New approach for the morphological identification of date palm (*Phoenix dactylifera* L.) cultivars from Tunisia. Pak J Bot 41(6):2671–2681
Hasnaoui A, Elhoumaizi MA, Asehraou A, Hakkou A (2010) Chemical composition and microbial quality of main varieties of dates grown in Figuig Oasis of Morocco. Int J Agric Biol 12:311–314
Ibrahim AF, Attalla AM, El-Kobbia AM, Mostaffa LY (2001) Physico-chemical characteristics of fruits and pits of some date palm cultivars as affected by cultivars and seasons. Second international conference on Date Palms, Al-Ain, United Arab Emirates
Ibrahim HM (2004) Date palm in the Gulf Council Countries (GCC): present status, constraints and prospective. In: Regional workshop on date palm development in the Arabian Peninsula. Abu Dhabi, UAE pp 29–31
Ishurd O, Sun CR, Xiao P, Ashour A, Pan YJ (2002) A neutral beta-D-glucan from dates of the date palm, *Phoenix dactylifera* L. Carbohydr Res 337(14):1325–1328. https://doi.org/10.1016/S0008-6215(02)00138-6
Jaradat AA, Zaid A (2004) Quality traits of date palm fruits in a center of origin and center of diversity. Food Agric Environ 2(1):208–217, WFL Publisher Science and Technology
Kamal-Eldin A, Hashim IB, Mohamed IO (2012) Processing and utilization of palm date fruits for edible applications. Recent Pat Food Nutr Agric 4:78–86. https://doi.org/10.2174/2212798411204010078
Karasawa K, Otani H (2012) Anti-allergic properties of a matured fruit extract of the date palm tree (*Phoenix dactylifera* L.) in mite-sensitized mice. J Nutr Sci Vitaminol 58(4):272–277. https://doi.org/10.3177/jnsv.58.272
Khan H, Khan SA (2016) Date palm revisited. Res J Pharm, Biol Chem Sci 7(3):2010–2019
Kwaasi AAA (2003) Date palms. Encyclopedia of food sciences and nutrition, 2nd edn. Elsevier Science, London, pp 1730–1740
Mahmoudi H, Hosseininia G, Azadi H, Fatemi M (2008) Enhancing date palm processing, marketing and pest control through organic culture. J Org Syst 3:29–39
Mansouri A, Embarek G, Kokkalou E, Kefalas P (2005) Phenolic profile and antioxidant activity of the Algerian ripe date palm fruit (*Phoenix dactylifera*). Food Chem 89(3):411–420. https://doi.org/10.1016/j.foodchem.2004.02.051
Mariod AA, Mirghani MES, Hussein I (2017) Chapter 29 – *Phoenix dactylifera* date palm kernel oil. Unconventional oilseeds and oil sources, pp 181–185. https://doi.org/10.1016/B978-0-12-809435-8.00029-9
Mohamed DA, Al-Okabi S (2004) In vivo evaluation of antioxidant and anti-inflammatory activity of different extracts of date fruits in adjuvant arthritis. Polish J Food Nutr Sci 13:397–402
Nehdi I, Omri S, Khalil MI, Al-Resayes SI (2010) Characteristics and chemical composition of date palm (*Phoenix canariensis*) seeds and seed oil. Ind Crop Prod 32(3):360–365. https://doi.org/10.1016/j.indcrop.2010.05.016
Nehdi IA, Sbihi HM, Tan CP, Rashid U, Si A-R (2018) Chemical composition of date palm (*Phoenix dactylifera* L.) seed oil from six Saudi Arabian cultivars. J Food Sci 83(3):624–630. https://doi.org/10.1111/1750-3841.14033
Rahmani AH, Aly SM, Ali H, Babiker AY, Srikar S (2014) Therapeutic effects of date fruits (*Phoenix dactylifera*) in the prevention of diseases via modulation of anti-inflammatory, anti-oxidant and anti-tumour activity. Int J Clin Exp Med 7(3):483–491
Rock W, Rosenblat M, Borochov-Neori H, Volkova N, Judeinstein S, Elias M, Aviram M (2009) Effects of date (*Phoenix dactylifera* L., Medjool or Hallawi variety) consumption by healthy subjects on serum glucose and lipid levels and on serum oxidative status: a pilot study. J Agric Food Chem 57(17):8010–8017. https://doi.org/10.1021/jf901559a

Sahari MA, Barzegar M, Radfar R (2007) Effect of varieties on the composition of dates (*Phoenix dactylifera* L.). Food Sci Technol Int 13:269–275. https://doi.org/10.1177/1082013207082244

Saleh EA (2011) Phenolic contents and antioxidant activity of various date palm (*Phoenix dactylifera* L.) fruits from Saudi Arabia. Food Nutr Sci 02(10):1134–1141. https://doi.org/10.4236/fns.2011.210152

Shafiei M, Karimi K, Taherzadeh M (2010) Palm date fibers: analysis and enzymatic hydrolysis. Int J Mol Sci 11:4285–4296. https://doi.org/10.3390/ijms11114285

Sirisena S, Ng K, Ajlouni S (2015) The emerging Australian date palm industry: date fruit nutritional and bioactive compounds and valuable processing by-products. Compr Rev Food Sci Food Saf 14(6):813–823. https://doi.org/10.1111/1541-4337.12162

Souli A, Sebai H, Rtibi K, Chehimi L, Sakly M, Amri M, El-Benna J (2014) Effects of dates pulp extract and palm sap (*Phoenix dactylifera* L.) on gastrointestinal transit activity in healthy rats. J Med Food 17:782–786. https://doi.org/10.1089/jmf.2013.0112

Vayalil PK (2012) Date fruits (*Phoenix dactylifera* Linn): an emerging medicinal food. Crit Rev Food Sci Nutr 52:249–271. https://doi.org/10.1080/10408398.2010.499824

Weber RW (2010) On the cover – date palm. Ann Allergy Asthma Immunol 105(4):A4. https://doi.org/10.1016/j.anai.2010.09.001

Williams N (2008) Palm breach. Curr Biol 18(22):R1039–R1041. https://doi.org/10.1016/j.cub.2008.10.057

Yahia EM, Kader AA (2011) 4 – Date (*Phoenix dactylifera* L.). In: Postharvest biology and technology of tropical and subtropical fruits pp. 41–79:80e–81e. https://doi.org/10.1533/9780857092885.41

Chapter 2
Analysis of Antioxidants and Nutritional Assessment of Date Palm Fruits

B. M. Gnanamangai, S. Saranya, P. Ponmurugan, S. Kavitha, Sudhagar Pitchaimuthu, and P. Divya

Abstract This chapter highlights on the nutritional and antioxidant constituents of dates. Date palm (*Phoenix dactylifera* L) assumes a vital role in traditional treatment. Dried date fruit serves as the staple food in many countries of the world for a considerable period of time. Dates are found to be rich in carbohydrates (77.13 g/100 g), predominantly glucose and fructose, but low in proteins (2.61%) and fats (0.35%). Date fruit offers a wide range of essential nutrients and potential health benefits. They also serve as a good source of many vitamins, dietary fiber, minerals, phenolics, carotenoids and antioxidants. Nutritional and medicinal activities of date fruit are related to its chemical compositions, mainly phytochemicals. Due to these important functional compounds, dates exhibit various health benefits by preventing various diseases. Date fruit has antioxidant, anti-mutagenic, anti-inflammatory, gastro-protective, hepato-protective, nephro-protective, anticancer, immune-stimulant activities, antidiabetic, hypocholestrolemic and many other. The chapter likewise depicts the techniques by which the date varieties were shown to exhibit strong antioxidant activity. Considering the detailed information on nutritional and health promoting components, dates are deliberated as an ideal supplement, providing a wide range of essential nutrients and potential health benefit to mankind.

Keywords Antioxidant · Nutrition · Medicinal value · Date palm · Functional food · Antioxidant methods · DPPH method · ABTS method · TEAC method · FRAP method · ORAC method

---

B. M. Gnanamangai (✉) · S. Saranya · S. Kavitha · P. Divya
Department of Biotechnology, K. S. Rangasamy College of Technology, Tiruchengode, Tamil Nadu, India
e-mail: mythumithras@gmail.com

P. Ponmurugan
Department of Botany, Bharathiar University, Coimbatore, Tamil Nadu, India

S. Pitchaimuthu
Multi-functional Photocatalyst & Coatings Group, SPECIFIC, College of Engineering, Swansea University (Bay Campus), Swansea, Wales, UK
e-mail: vedichi@gmail.com

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_2

2.1 Introduction

Date palm is traditional fruit of Saudi Arabia. They are well known for its nutritive value and are widely used as functional/traditional/medicinal food to maintain the health and improve the health of diseased one. They are more than 60 popular varieties of Date palm grown all over the world for its dietary benefits. The nutritional value of the fruit varies based on the cultivars, place of cultivation and the nature of the fruit.

Cultivars of date palm, all the cultivars have their distinct nutritive value starting from moisture content, carbohydrate, fat, protein, iron, calcium, dietary fibres, vitamins and minerals. Based on the climatic conditions and environmental features the fruits are produced from the flowers of the palm tree within a period of 5 to 6 months.

Date palm serves as an energy rich food that occupies the daily meal of Arabian food habits. The taste, nutritive value and visual appeal of fruit mainly depends on the cultivational lands that are adequate for the better growth of palm tree.

The final factor that determines the date fruits nutritional value are fruiting stages which include kimri, khalal, rutab and tameer. Kimri is the initial stage of the fruit that contains high moisture content of about 85% with increased fruit weight. Khalal in second stage of fruit ripening where the fruits look fresh and hard. Rutab is the second stage where the fruits are at ripe stage and tends to have crispy and succulent nature. The final stage, tameer is the tender, succulent ripe stage of the fruit that is used as edible part on processing all over the world. Based on the nature of the fruit stages all the biochemical parameters differ accordingly due to changes in the ripening enzymes.

2.2 Medicinal Value of Dates in Nutritive Aspects

The date fruits contain wide variety of compounds that makes it to serve as functional food. The compounds of date varieties were reported to have antioxidant. Rutab and tamer stage of dates were analysed earlier for its functional and nutritive compounds. Besides all the difference exhibited between different cultivars, cultivation places and the fruit stages of cultivation popular varieties does exhibit significant changes in all nutritional aspects. Some potential functional activities are more common on all popular varieties of date palm.

Nutritional aspects of all dried date palm varieties in coherence with the functional medicine were analysed in the present article.

Nutritive value of dates were analysed based on the following aspects and their average values as calculated from various research articles on dates were listed in Table 2.1.

Table 2.1 Average quantification of nutrients from the reported date varieties

Nutrient	Average quantity	Nutrient	Average quantity
Protein (%)	2.61	Mo (mg/100 g)	0.14
Carbohydrates (g/100 g)	77.13	Se (μg/100 g)	0.28
Lipid (%)	0.35	A Retinol (IU)	23.85
Ash (%)	1.68	B1 Thiamine (mg/100 g)	78.67
Moisture (%)	17.66	B2 Riboflavin (mg/100 g)	116.5
Fat (%w/w)	7.08	B3 Niacin (mg/100 g)	0.1442
Total sugar (g/100 g)	59.88	B6 Pyridoxal (mg/100 g)	0.207
Fibre (%w/w)	3.98	B9 Folate (μg/100 g)	53.75
Dry matter (%)	82.63	C Ascorbic (mg/100 g)	0.39
Nitrogen (g/100 g)	0.48	K Phylloquinone (μg/100 g)	2.70
Fructose (g/100 g)	29.39	Phenolics (mg/100 g)	239.51
Glucose (g/100 g)	30.41	Al (mg/100 g)	1.42
Sucrose (g/100 g)	11.65	As (mg/100 g)	0.03
Mg (mg/100 g)	64.42	Ba (mg/100 g)	0.04
Na (mg/100 g)	40.11	Cd (mg/100 g)	0.01
Ca (mg/100 g)	56.01	Cr (mg/100 g)	0.06
P (mg/100 g)	65.21	Ni (mg/100 g)	4.63
K (mg/100 g)	373.89	Pb (mg/100 g)	0.01
Mn (mg/100 g)	106.76	Sr (mg/100 g)	0.82
Fe (mg/100 g)	1.72	V (mg/100 g)	0.003
Zn (mg/100 g)	0.57	Bo (mg/100 g)	3.63
Cu (mg/100 g)	0.31	Fl (μg/100 g)	0.15
Mg (mg/100 g)	54.1	Cl (mg/100 g)	161
Co (μg/100 g)	1.93	Pb (mg/100 g)	0.02

I. Moisture
II. Carbohydrate
III. Protein
IV. Vitamins and minerals
V. Fat, fatty acids and lipids
VI. Dietary fibre
VII. Phytochemicals

2.2.1 Moisture Content

Moisture content of the date palm fruits are high to 85% at kimri stage and reduce to 13.25% in tameer stage of date variety like Davee. The average moisture content of popular varieties of the date fruit as collected from all literature support is 17.66%.

Reduced moisture content of the date fruit makes it suitable as staple energy food. It can store more calories that can serve better during the fasting period. The dryness of the date fruit prevents them from infestation and loss of nutrients due to contamination. Tameer stage of the date fruit are good to store and use them as energy rich food for a good life span of time for about 1 year.

2.2.2 Carbohydrate Content

Total carbohydrate can be correlated to the moisture/water content of the dates where ripening and dried stage of date fruit shows difference in the total carbohydrate content. Mere high amount of carbohydrates in dried dates make them religious food for breaking the fasting which in turn provides high Kcal of energy.

The average total carbohydrate of the dried dates are 77.13 g/100 g and 308.52 Kcal of energy which are calculated from most popular varieties and calculated for most of the dates as reported earlier (Al-Harrasi et al. 2014; Al-Farsi and Lee 2008; Habib and Ibrahim 2011; Al-Shahib and Marshall 2003).

The total carbohydrate includes the glucose, sucrose, fructose, mannose, cellulose and starch. Except sucrose other sugar were reported to increase in the dried fruit stage (Al-Farsi and Le 2008). The average fructose content in the dates were about 29.39 g/100 g and the ratio of glucose to fructose were almost ≤ 1 (Ismail et al. 2006) which indicates the higher concentration of fructose in dried date fruits. Higher amount of sucrose percentage were reported only in fresh dates and were negligible and non-detectable in dried dates (Al-Farsi and Lee 2008).

Although the total available sugar like glucose and fructose are more in dates. They also possess wide other minerals, phytochemicals like phenolics (Ranilla et al. 2008), flavonoids (Hong et al. 2006) and carotenoids (Boudries et al. 2007) and dietary fibre (Elleuch et al. 2008) were reported to reduce the availability of the sugar to blood (Weickert and Pfeiffer 2008). Alternative sugars like fructose which are significantly high in date varieties increases the sweetness of the fruit and exhibits high satiety value with lower amount of date consumption (Al-Farsi and Lee 2008). However over eating of dates or any dried fruit can increase the calories (Gardner 2017).

Natural fructose rich foods are being used in traditional medicine to treat diabetes mellitus. Fructose in dates were attributed to negative co-relation of glycemic index (GI) values. As of Ali et al. (2009) low GI index reported for three varieties in Oman. Low GI value foods contribute high in reducing the blood sugar value during post prandial assessment. Among all varieties, it was reported that Deglet Nour containing 38% of sucrose as low GI fruit due to the fact that it reduces the availability of carbohydrates for digestion (Duke 2001). Date fruits consumed in isocaloric amount did not raise the blood sugar level were reported for Sukkari date varieties (Famuyiwa et al. 1992).

2.2.3 Protein

Protein content in various date varieties are comparatively high due to the presence of various aminoacid content (Al-Farsi and Lee 2008). Nitrogen content (Al-Harrasi et al. 2014) and water reduction (Al-Shahib and Marshall 2003) may be reason for high protein content in date on comparing to other fruits like apple, banana and orange (Al-Shahib and Marshall 2003). The average protein content changed from 2.0% to 6.4% that differs accordingly to the ripening stages of the date fruit (Al-Orf et al. 2012). The present analysis revealed an average protein content of about 2.61% (calculated from the data revealed by most of the date varieties). Nitrogen were estimated in the range of 0.25–0.5g/100g. Nitrogen is an essential element to form amino acids and hence the amino acids were reported to be high at ripening stages and were significantly more in dried dates to 2.14 g/100g. These amino acids in turn play vital role in protein synthesis and metabolism that are essential for ripening of date fruits. Dates were reported to be rich in glutamic and aspartic acid (Al-Shahib Marshall 2003). The protein of dates contains 23 amino acids at high concentration. On comparing with other fruits that are commonly known for health benefits.

Although the proteins from dates cannot meet the RDI of about (0.84 g/kg/day), they help in serving many essential amino acids as that of egg-protein (Bouaziz et al. 2008). Highest concentration of aspartic acid, glutamic acid, proline and alanine in dates like Dan mali, Fari and Dagalla were reported to serve as building blocks of protein that are essential for various meatabolism (Uba et al. 2015). These amino acids also serve to act as precursors for proteins, receptors, hormones that involve in cell signalling, gene expression nutrient transport and immunity for the growth, metabolism and normal function of healthy human body (Wu 2010; Wang et al. 2013).

2.2.4 Vitamins and Minerals

Dietary minerals play essential role in all major functions of human body. There are number of essential macronutrient minerals, micronutrient minerals and trace elements that helps to prevent diabetes, cancer, hypertension and other cardiovascular disease and some dietary supplements serves to replenish the mineral loss due to the above disease. Date palm fruit varieties serves as one such dietary food to prevent, regulate and treat the disease that are caused due to the minerals imbalance. Some of the mineral reported in the date fruits are calcium, phosphorus, sodium, potassium, magnesium, iron, zinc, copper, manganese, cobalt. Molybdenum, selenium, aluminium, arsenic, barium, cadmium, chromium, nickel, lead, strontium and vanadium.

Although, mineral supplements through drug formulation like tablets, sachets and injections are available, they provide many side effects due to its pain in manifestation schedule and as well as absorption problems which induces gastritis, headache, nausea and anorexia (El-Zoghbi 1997). Date palm fruits were reported as the richest source of dietary minerals and vitamins (Vayali 2012).

The date varieties have shown significant changes among the mineral contents both qualitatively and quantitatively that were earlier reported to be attributed to genetic difference (Marzouk and Kassem 2011) time of harvest, ripening stages (Amira et al. 2011), place of cultivational parameters like water, soil minerals and environmental factors (Marzouk and Kassem 2011). The average mineral quantities at dried stage were reported in the Table 2.1 for most varieties reported. Some major findings that can be enumerated includes, overall all mineral content was comparatively less in dried date fruits (1.7%) as described by Al-Shahib and Marshall (2003), than any stage of fresh date fruit. The potassium content was reported to be high with sodium constituent in low level. It also contains higher level of iron followed by other trace elements like selenium and fluoride were reported controversy in many date varieties. Selenium and fluorides are not reported in all the popular date varieties (Habib and Ibrahim 2011), but were reported to have high industrial valorization due to the presence of selenium (Ghnimi et al. 2017) (Al-Farsi and Lee 2008). Some minerals like iodine and fluoride were not reported in many of the date varieties (Vayalil 2012).

Post diabetic complications includes, kidney failure, high pressure, muscle spasm, vision impairment, depression, mental illness, etc., all these complications can be correlated to the deficiency of micronutrient status. Some of the minerals investigation revealed the diabetes mellitus prevention are Mg, Zn, Cr, Mn, Cu and Se (Table 2.2).

Date fruits contribute as a moderate source of vitamins with a total of ten enzyme presence where, vitamin A is detected in lower quantities. It is rich in water soluble vitamins and play major role in vital function of the human body. Vitamin C is reported to protect liver by Al-Mamary et al. (2011). Effectiveness of date fruits in curing anaemia was possible due to the effective absorption of iron through vitamin C.

2.2.5 Dietary Fibre

Date palm varieties excel as a richest source of dietary fibres. The widely consumed tamer stage of date fruit contains 3% of dietary fibre, it meets 32% of fibre with 100 g consumption as recommended by RDA 25g/day. The dietary fibres contains small proportion of soluble and large amounts of insoluble polysaccharides, lignins and tannin components that are widely indigestible.

Soluble polysaccharides in date dried fruits are pectin and hydrocolloids that are decreased in dried dates. The insoluble polysaccharides include cellulose, hemicellulose and lignin. Indigestible dietary fibres aids in two mechanism they are retarding the absorption ability of anti-nutritional factors by matrix gel formation using

Table 2.2 Role of minerals and vitamins with respect to various functions in the body

Minerals	
Mg	Energy dependent transport system glycosis, oxidative energy metabolism, release of insulin
Zn	Insulin synthesis, secretion, signalling
Cr	Enhances insulin action
Cu	Alters glucose homeostasis
Mn	Alters glucose homeostasis
Se	Glucose uptake, regulate glycolysis, gluconeogenesis, fatty acid synthesis and pentose phosphate path activates gene of antioxidant enzyme to stimulate defence system against cancer
Ca	In combination with Na, Mg, K provides ionic balance to vascular membrane, vasodilation
K	Increases serum potassium, endothelium-dependent vasodilation, stimulation of Na protein. Electrolyte balance, prevent development & progression of hypertension
Vitamins	
B complexes B1, B2, B3, B5, B6 and B9	Coenzyme of enzyme reactions
	Carbohydrates, fats and protein metabolism
Vitamin C	Iron absorption, hepato-protective effects, prevents oxidation
Choline	Structural integrity of cell membrane cholinergic neurotransmission, source of methyl groups
Betaine	Osmolyte, source of methyl group, maintain liver, heart and kidney health

soluble polysaccharides. The other mechanism is the bulking the faecal mass through high water and oil holding capacity of insoluble polysaccharides.

The highest ratio of insoluble polysaccharides therefore are reported to involve in increasing faecal transit time. The dietary fibre plays a vital role in reducing the availability of soluble carbohydrates by involving them in matrix formation and as well as bulking properties. It induces satiety value and contributes much to glucose metabolism by improving insulin sensitivity, secretion of gut hormones and other metabolic and inflammatory markers associated with metabolic disorder and syndrome like lactose intolerance and irritable bowel syndrome. Altogether fibre consumption regulates glucose absorption by optimal insulin secretion with decreased Hb A1C level in diabetes (Jenkins et al. 2008; Mohammad and Habibi 2011). Hence date fruits are reported to be potential factor to prevent the development of diabetes and its progression (Vayalil 2012).

The soluble polysaccharides in the dietary fibre of date palm varieties prevents Atherosclerosis by slowing down the process of intestinal absorption of cholesterol where by its deposition in arteries are prevented and hence conditions like coronary heart disease (Baliga et al. 2011) stroke (Lusis 2002) and hyperlipidemia (Abuelgassim 2010) are prevented. The fibre in date fruit have hypo-cholesterolemic effects by reducing the absorption of cholesterol, reduced insulin secretion and short chain fatty acids produced during formation of dietary fibre inhibits hepatic cholesterol biosynthesis. Date fibre also contains 0.5–3.9% of pectin. Pectin rich foods reduces metabolic risk factors associated with heart disease by reducing the cholesterol level in blood (Al-Shahib and Marshall 2003). Although the level of pectin decreases to 0.5% in tameer stage of date fruits due to high level of pectin esterase activity it is considered as the higher level compared to other fruits (El-Zoghbi 1997).

In addition, the dietary fibre also reduces the availability of toxic compounds that induces hepatotoxicity by low faecal transit time, which also reduces constipation by serving as laxative (Al-Farsi and Lee 2008). Dietary fibre reduces the risk of intestinal, bowel and colon cancer (Marlett et al. 2002). This property of date fruit are mainly attributed to two anti-neoplastic glucans namely (1-3)- β-D glucan with various (1-6) linked mono, di and trisaccharide branches and (1-3)-β-D glucopyranosyl residues (Ishurd and Kennedy 2005; Ishurd et al. 2004; Ishurd et al. 2007). Similarly, the β- glucans doses were reported to have increased apoptotic activity in prostate cancer cell line PC-3 by decreasing the cell viability (Fullerton et al. 2000).

Dietary fibres act as direct scavengers of exogenous and as well as endogenous mutagens through increased faecal mass and its enhanced gastrointestinal transit (Al-Qarawi et al. 2003). Apart from the above said disease and disorders the date palm dietary fibre serves as antimicrobial agents (Shafiei et al. 2010), laxative (Al-Qarawi et al. 2003) and prevents diventricular diseases (Marlett et al. 2002).

2.2.6 Fats Fatty Acids and Lipids

Fat content in dried date fruits were very low and differs significantly among the cultivars. The fat content of the date fruit is present in two parts of the date fruit; skin of date fruits and seeds of date fruits. Drying causes increased fat in date fruits (Al-Farsi and Lee 2008). The major role of fat in date fruits is to prevent the escape of nutrients, contamination, and moisture etc., (Shafiei et al. 2010). The flesh of date contains 0.2–0.5% saponificable oils (Al-Hooti et al. 1998).

The fatty acids were reported to be in date fruits as saturated and unsaturated forms (Al-Shahib and Marshall 2003). The saturated fatty acids include (apric, lauric, myristic, palmitic, stearic, margaric, arachidic, henscicosanoic, behenic and tricosanoic acids. The unsaturated fatty acids in date fruit includes, palmitoleic, oleic, linoleic and linolenic acids. The date fruits without seeds contains mainly eight fatty acids that includes myristic palmitic, stearic, margaric, arachidic, hencicosanoic, oleic and linoleic.

The low amount of fat in date fruits is the main reason for the hypocholesterolimic effects of dates fruits (Al-saif et al. 2007). Medjool dates consumption for 4 weeks reduced the VLDL-cholesterol levels by 8–15% (Rock et al. 2009).

2.2.7 Phytochemicals and Their Antioxidant Potentials

Phytochemicals are non-nutrient bioactive component that are mainly responsible for scavenging the toxic radicals through antioxidant formation after oxidative stress, which is the major causative for most of the chronic diseases (Al-Harrasi et al. 2014). Some of the phytochemicals of date fruits that are reported to act as bioactive components are phenols, phenolic acids, carotenoids, isoflavons, lignans, flavonoids, tannins and sterols. Role of these phytochemicals in disease prevention and their levels present in date fruits were enlisted in Table 2.3.

Total phenolic compounds were estimated in various date varieties and similarly the phenolic acids were estimated and fractionated in many varieties like Omani (Al-Farsi and Lee 2008), algeriani (Thompson et al. 2006), fard (Vayalil 2002), khalas etc., most of the studies have proved dates as the highest source of antioxidants and it is attributed to the total phenols and phenolic acids. Among this phenols and phenolic acids, the most predominant phenol reported to be high in detection and quantification is ferrulic acid (Vayalil 2002). The phenolic contents in varieties were reported as non-stable (Karasawa et al. 2011). Since they play vital role in antioxidant activity, which also varied from 40% to 80% (Al-Harrasi et al. 2014). Studies on the factors affecting the total phenolics should be implemented to produce varieties with stable estimate of phenolics and antioxidant activity. Flavanoids are also important phenolic compounds and were widely studied in different varieties and stages (Chaira et al. 2009; Hong et al. 2006; Biglari et al. 2008).

2.3 Methods for the Evaluation of Antioxidant Potential

Some of the methods commonly employed for preparing date palm extracts and determining their antioxidant potential are discussed in details below with emphasis on and their mechanism of actions. The observed values for various varieties found across countries are tabulated for better understanding.

2.3.1 Date Palm Extract Preparation

The date palm extracts are prepared from various parts of the plant like seeds, fruits (unripe, fresh ripe and dried stages), skin, leaves, cluster and pollen (Habib and Ibrahim 2011; Lemine et al. 2014; Vayalil 2002). They are subjected to multiple steps for preparing extracts including (i) cleaning, (ii) drying, (iii) cutting or grinding, (iv) solvent extraction, (v) centrifugation (vi) freeze drying or solvent evaporation (Vayalil 2002). The crude extract thus prepared is subjected to one or many of the antioxidant potential evaluation methods.

Table 2.3 Phytochemicals of date varieties and its function

Phytochemical	Quantity	Function	References
Carotenoid:			
B Carotene	3–10%	Protects testicular functions and have gonadotropic and hepatoprotective activity	Boudries et al. (2007), Eustache et al. (2009), Said et al. (2010), Jana et al. (2008), Ipatova et al. (2003), Zheng et al. (2005), Srinivasan et al. (2005), Janbaz et al. (2005) and Domitrovic et al. (2008)
Lutein	89–94%		
Minor Carotenoids	2–8%		
Phenols:			
Cinnamic acids, acetylated flavonols, caffeoglshikimic aacid hexoside, caffeoyl-sinapoyl monohexoside, dihexoside, hydroxyl benzoates, hydroxyl cinnamates	30,000 ppm (3.0 g/100 g)	Less glucose absorbance, antioxidant activity, inhibits Angiotensin II converting enzymes and reduces hypertension and anticancer	Duke and Beckstrom Sternberg, (2007), Neori et al. (2013) and Surh (2003)
Phenolic acids:			
Gallic acid, protocatechuic, *p*-hydroxyl benzoic, vanillic, caffeic, dactyliferic acid, ellagic acid, syringic, *p*-coumaric ferulic, *o*-coumaric	14.18–49.67 mg/100g (bound) 6.1–14.8 mg/100g (free)	Hepatoprotective	Vayalil (2012), Mansouri et al. (2005), Al-Farsi and Lee (2008), Al-Farsi et al. (2005), Ipatova et al. (2003), Zheng et al. (2005), Srinivasan et al. (2005), Janbaz et al. (2005) and Domitrovic et al. (2008)
Tannins:			
Flavanoids, flavones, flavonols, flavanones, procynidines, proanthocyanidins, flavonoid glycosides (luteolin, quercetin, apigenin), Chrysoeriol, isohamnetic, anthocyanins	0.0162–5446 g/kg	Hepatoprotective	Hong et al. (2006), Tomas lorente and ferreres, (1988), Al-Hooti et al. (1997), Ipatova et al. (2003), Zheng et al. (2005), Srinivasan et al. (2005), Janbaz et al. (2005) and Domitrovic et al. (2008)
Sterols:			
Phytosterols:			
Campesterol, β-sitosterol, lupenone, lupeol, 24-methylene cy-cloartanol, propylidene cholesterol	1.83–2.57%	Hepatoprotective, inhibits cholesterol synthesis and causes hypocholestrolemia	John et al. (2007) and Liolios et al. (2009)
Phytoestrogens:			
Isoflavones, lignans, genistein, daidzein		Anticancer and antidiabetic	Bhathena and Velasquez (2002)

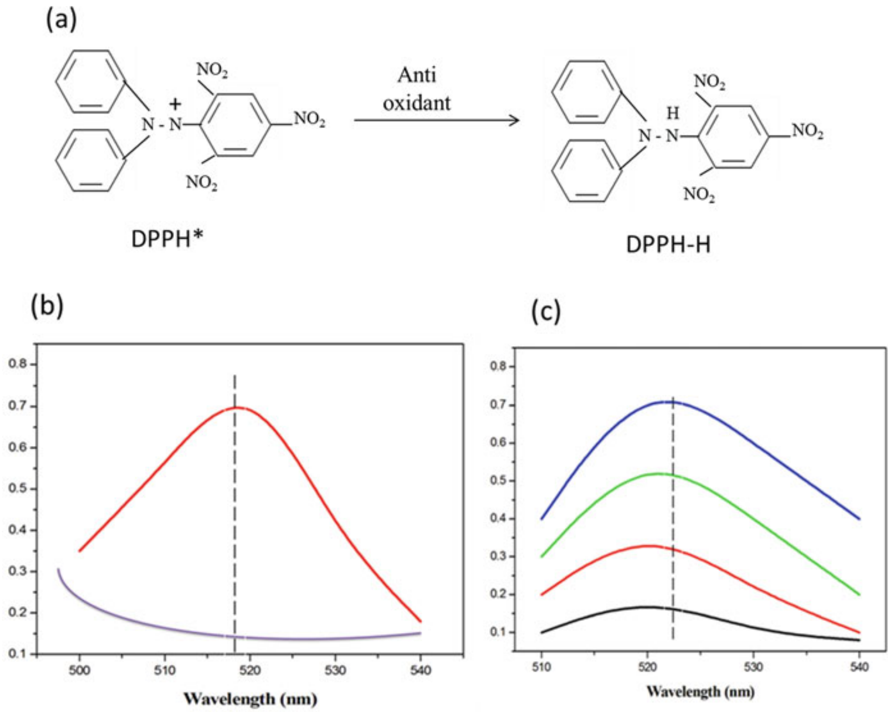


Fig. 2.1 (**a**) DPPH reaction with anti-oxidant (Stasko et al. 2007). (**b**) Absorption spectra of oxidized and reduced DPPH, (**c**) Absorption spectra for DPPH containing varying concentration of antioxidants

2.3.2 The DPPH Method

The DPPH assay is the most commonly used colorimetric assay for the determination of antioxidant potential from date palm varieties. DPPH (2,2-diphenyl-1-picrylhydrazyl) (Fig. 2.1) is a dark crystalline solid which yields a deep violet solution. It has strong radical scavenging capacity and upon reaction with a free radical sequesters them completely and turns pale yellow or colourless (Shimamura et al. 2014). The proportion of discoloration was found to linearly increase with increase in antioxidant content. In other words, samples with higher antioxidant potential would promote greater extent of discoloration of purple pigment. The antioxidant source would act as an electron donating species. Trolox is (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) and ascorbic acid are used as standard antioxidant for the construction of calibration curve or as positive control in DPPH assays (Lemine et al. 2014).

The antioxidant potential is expressed by multiple methods. It is either expressed as μmol Trolox Equivalent Antioxidant Capacity (TEAC)/100 g dried material (Lemine et al. 2014) or EC50 (effective concentration or the amount of antioxidant required to decrease the initial concentration of DPPH by 50%) (Saleh et al. 2011). % DPPH inhibition is calculated as follows (Singh et al. 2012).

$$\%DPPH\ Inhibition = \frac{\left(Abs_{control} - Abs_{sample}\right)}{\left(Abs_{control}\right)} \times 100$$

It is based on the fact that antioxidant potential is directly related to the reducing power of electron donating capacity of the test article. The degree of discolouration is proportional to the hydrogen donating capacity of the test sample (Singh et al. 2012). The exact mechanism of antioxidant property of the test article needs to be evaluated before relying on this method for antioxidant potential evaluation studies. The solution prepared has limited stability and hence this method is not recommended for long duration assays (Benzie and Strain 1999; Stasko et al. 2007).

2.3.3 The ABTS Method or TEAC (Trolox Equivalent Antioxidant Capacity) Method

The cation radical of ABTS ($ABTS^+$) upon loss of electron yields bluish-green colored substance to form 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulphonic acid). The absorption maximum was determined to be 743 nm (Biskup et al. 2013). In the presence of hydrogen donation atom (test article and standard Trolox) the charges are quenched and the solution is decolorized. Hence the antioxidant efficacy is expressed in terms of Trolox equivalence/mass of test article.

Reactive ABTS (cationic radical form) is generated by treating it with oxygenating reagents such as potassium permanganate or manganese dioxide (Miller and Rice-evans 1997). It yields the bluish – green chromogenic substance in solution which upon reduced to yield a discoloured product. The antioxidant potential is monitored by measuring absorbance at 743 nm to determine the decrease in absorbance (Fig. 2.2). Thus a lesser absorbance at 743 nm indicated a greater antioxidant efficacy of the test article.

Some of the significant advantages of ABTS assay are that this can be applied at different pH conditions and can be used for organic and aqueous extracts (Prior et al. 2005). Hence the assay is flexible and suffers little or no difference when used under various conditions. Hence this method is widely used for date palm varieties as well as fruit and vegetable extracts, soft beverages such as tea and coffee and alcoholic beverages.

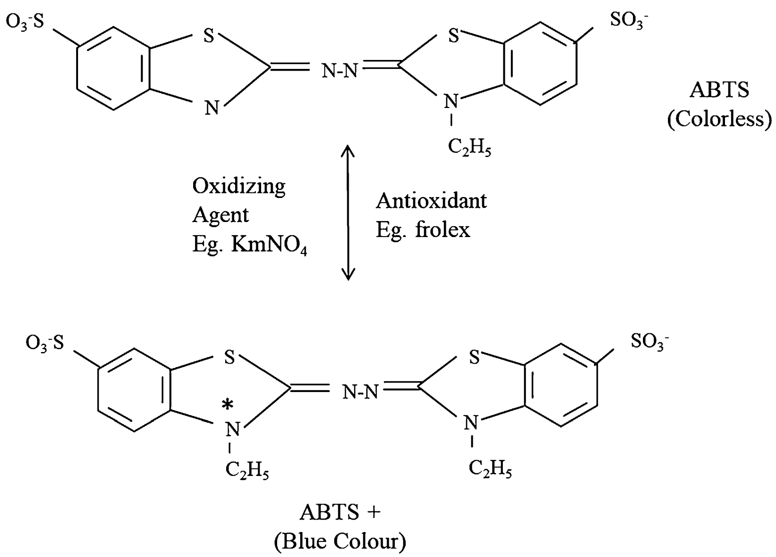


Fig. 2.2 $ABTS^+$ reaction with anti-oxidant

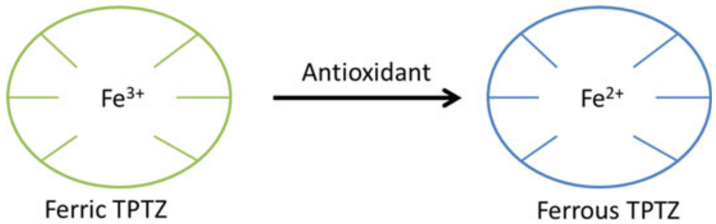


Fig. 2.3 FRAP reducing activity

2.3.4 The FRAP (Ferric Reducing Antioxidant Power) Method

The capability of antioxidants to reduce ferric (FE^{3+}) form of substance to ferrous (Fe^{2+}) form of substance are measured in FRAP method (Fig. 2.3). The complex ferric ion used is 2,4,6-tri(2-pyridyl)-1,3,5-triazine reacts with antioxidants (standard trolax or ascorbic acid and test article) and produces an intense blue coloured ferrous ion complex (Antolovich et al. 2002). The product formation can be monitored by increase in absorbance using a spectrophotometer at 593 nm. The results can be expressed as Trolox equivalents or ascorbic acid equivalents or Fe^{2+} equivalents depending on the standard used for the method.

FRAP assays are carried out in acidic conditions (pH 3.6) in order to maintain the solubility of iron in ferric and ferrous form. The electron transfer is also achieved at lower pH facilitating the applicability of the method (Hagerman et al. 1998).

The FRAP method is simple, fast and efficient method which finds is applications in antioxidant estimation from body fluids, food and plant extracts. The method is successfully employed for determining the antioxidant potential of date palm varieties also (Singh et al. 2012).

Such variety of assays provides a platform for evaluation of antioxidant potential for date palm varieties or any target of interest.

2.3.5 The ORAC Method

ORAC (Oxygen Radical Absorbance Capacity) is been used as a method of measuring antioxidant potential of date varieties (Al-Farsi et al. 2005). In this method, AAPH (2,2′-azobis(2-amidinopropane) dihydrochloride) is an active reagent used for generating free radicals in the reaction mixture. This in turn attacks the fluorescene (fluorophore) whose decay is monitored in a timely fashion. The presence of antioxidants in the sample can thus delay the decay in fluorescence of a fluorophore. Final results are calculated based on the difference between the areas under the curve generated from the decay curve of fluorescene with and without antioxidants (Fig. 2.4). Trolox is used as a standard in most cases (Wang et al. 1996; Cao et al. 1993; Ou et al. 2001) and the results are expressed as micromoles of Trolox equivalents per gram of dry weight.

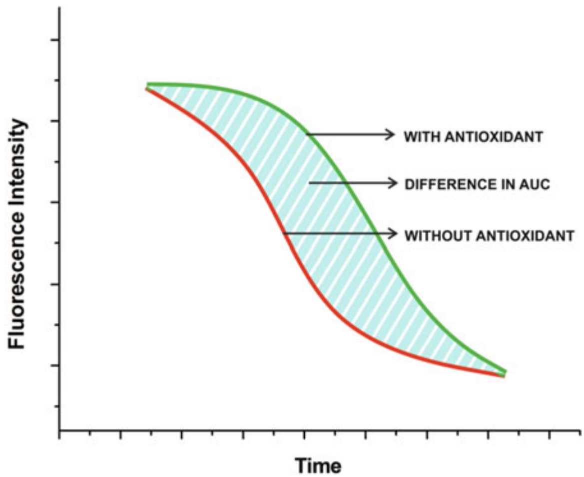


Fig. 2.4 ORAC fluorescence decay curve

2.3.6 Antioxidant Activity of Three Varieties of Dates Grown in Sultanate of Oman (Singh et al. 2012)

Three varieties of Omani dates were subjected to antioxidant activity estimation using multiple methods such as DPPH method, ABTS method, Superoxide anion scavenging method and FRAP method (Table 2.4). Overall it was concluded that Fardh variety showed maximum antioxidant efficiency at both stages tested (fresh and dried stages).

2.3.7 Antioxidant Activity of Three Varieties of Dates Grown in Oman (Al Farsi et al. 2005)

Antioxidant activity reduces during drying by comparing fresh and sun-dried dates of three varieties through ORAC method was studied in Oman date fruits (Table 2.5). It is states that sun-drying could cause a significant loss in antioxidant activity (30–40% depending on the variety). Khalas variety was concluded to have higher antioxidant potential through ORAC method.

Table 2.4 Antioxidant activities three varieties of Omani dates by DPPH, FRAP, ABTS and Superoxide anion scavenging activity methods

	Variety name					
	Khasab		Khalas		Fardh	
Assay	Tameer	Rutab	Tameer	Rutab	Tameer	Rutab
Total antioxidant activity assay (ABTS method)	92%	85%	84%	56%	87%	92%
DPPH radical scavenging activity	70%	63%	72%	63%	73%	65%
Superoxide anion scavenging activity	30%	41%	29%	34%	44%	43%
Order of FRAP electron donating capacity	6	4	3	1	4	1

Table 2.5 ORAC values of three varieties of Omanian dates by ORAC method.

	ORAC values (μmol of TE/g)	
	Stage	
Variety name	Fresh	Sun dried
Fardh	17,335	9986
Khasab	11,687	8212
Khalas	20,604	12,543

2.3.8 Antioxidant Activity of Two Varieties of Dates Grown in Israel (Rock et al. 2009)

The antioxidative properties of Medjool and Hallawi date varieties were determined by DPPH and FRAP methods (Table 2.6). Medjool was found to be slightly better in reducing the DPPH absorbance by 44% when compared to 39% by Hallawi, whereas the FRAP activity of Hallawi was found to be 24% greater than Medjool.

2.3.9 Antioxidant Activity of Six Varieties of Dates Grown in Mauritius (Lemine et al. 2014)

A study conducted to evaluate six varieties of Mauritian dates at two different edible stages such as Blah (slightly crunchy edible stage) and Tameer (dried stage). It was shown that the Blah stage exhibited the highest antioxidant activity compared to their Tameer stage in all varieties (Table 2.7).

2.3.10 Antioxidant Activity of Seven Varieties of Dates Grown in Algeria (Mansouri et al. 2005)

Antiradical efficiency (AE) or antiradical power (ARP) of seven varieties of algerian dates was evaluated earlier (Table 2.8). It was found that the Tantbouchte variety showed maximum AE, followed by Deglet-Nour. The lease AE values were observed for Tazizaout and Ougherouss varieties.

Table 2.6 Antioxidant activities of two varieties of Israeli Dates by DPPH and FRAP methods

Assay	Variety name	
	Medjool	Hallawi
DPPH radical scavenging activity	44%	39%
FRAP electron donating capacity	~650 mg vitamin C/100 g)	~790 mg vitamin C/100 g)

Table 2.7 Antioxidant activity of six varieties of Mauritanian date palm by DPPH method

Antioxidant potential (μmol TEAE/100 g DM)		
Variety name	Stages	
	Blah (Khalal)	Tameer
Ahmar dl	108.4	98.9
Ahmar denga	99.1	98.7
Bou seker	129.3	78.7
Tenterguel	90.5	75.6
Lemdina	103.4	95.8
Tijib	114.3	99.3

Table 2.8 Antioxidant activity of seven varieties of Algerian dates by DPPH method

Variety name	Antiradical efficiency ($1/EC_{50}$) or (1/μg sample/μg DPPH)
Tazizaout	0.08
Ougherouss	0.10
Akerbouche	0.10
Tazerzait	0.10
Tafiziouine	0.12
Deglet-Nour	0.17
Tantbouchte	0.22

Table 2.9 Antioxidant activity of four varieties of Tunesian dates by ABTS and DPPH methods

Variety name	ABTS (μmol Trolox equivalents/ 100 g fresh weight)	Antiradical efficiency ($1/EC_{50}$) or (1/μg phenolic sample per μg DPPH)
Khouet Kenta	1148.11	1.96
Kentichi	1008.46	1.68
Deglet Nour	866.82	1.53
Allig	891.31	0.72

2.3.11 Antioxidant Activity of Four Varieties of Dates Grown in Tunisia (Saafi et al. 2009)

Antioxidant activities of four varieties of Tunisian dates were evaluated by ABTS method and DPPH method (Table 2.9). From the APTS method, the Khouet Kenta variety was found to possess highest antioxidant potential. The increasing order of antioxidant activity by ABTS method was found to be Deglet Nour < Allig < Kentichi < Khouet Kenta.

The same varieties were evaluated for antioxidant activity by DPP method. In case of DPPH method, the antioxidant activities were expressed as AE or APR, where the larger the ARP, the more efficient the antioxidant is. Khouet Kenta variety showed the highest level of antiradical efficiency even in DPPH method. The increasing order of antioxidant activity by DPPH method was found to be Allig < Deglet Nour < Kentichi < Khouet Kenta.

2.4 Conclusion

Dates as a food supplement were determined to contain required levels of carbohydrate, proteins, vitamins, crude fibres and essential minerals. Consequently, dates are also delicious with sweet taste that provides us good satiety feel that gives an extensive variety of essential nutrients with many potential health benefits. Investigation on phytochemicals and antioxidants from dates are beneficial against diabetes and cancer.

Antioxidant activities were estimated from date varieties grown in various parts of the world by several available methods. Most common methods such as DPPH, ABTS, ORAC and FRAP are discussed in the previous sections. The antioxidant capacity estimates by a single method is never written as total antioxidant activity, as there are multiple mechanisms in which a plant variety can function as an antioxidant. Multiple methods used for antioxidant capacity measurement can be broadly classified assays which estimate hydrogen atom transfer (HAT methods) and assays which estimate electron transfer (ET methods). ORAC is a HAP based method whereas DPPH, APTS and FRAP are ET based methods. In order to understand the mode of action of antioxidants present in a variety, it is imperative to use multiple methods (Dudonne et al. 2009; Huang et al. 2005). This principle was further strengthened by the statement that all reductants are not necessarily antioxidants, whereas all antioxidants will function as reductants (Prior and Cau 1999). With this detailed analysis on the regimen of date fruit antioxidants, they can be used to fractionate many functional compounds and treat them against many prime diseases.

References

Abuelgassim AO (2010) Effect of flax seeds and date palm leaves extracts on serum concentrations of glucose and lipids in alloxan diabetic rats. Pak J Biol Sci 13:s1141–s1145. https://doi.org/10.3923/pjbs.2010.1141.1145

Al-Farsi MA, Lee CY (2008) Nutritional and functional properties of dates: a review. Crit Rev Food Sci Nutr 48:877–887. https://doi.org/10.1080/10408390701724264

Al-Farsi M, Alasalvar C, Morris A, Baron M, Shahidi F (2005) Comparison of antioxidant activity, anthocyanins, carotenoids, and phenolics of three native fresh and sun-dried date (*Phoenix dactylifera* L.) varieties grown in Oman. J Agric Food Chem 53(19):7592–7599. https://doi.org/10.1021/jf050579q

Al-Harrasi A, Rehman NU, Hussain J, Khan AL, Al-Rawahi A, Gilani SA, Al-Broumi M, Ali L (2014) Nutritional assessment and antioxidant analysis of 22 date palm (*Phoenix dactylifera*) varieties growing in Sultanate of Oman. Asian Pac J Trop Med 7(Suppl 1):S591–S598. https://doi.org/10.1016/S1995-7645(14)60294-7

Al-Hooti S, Sidhu JS, Qabazard H (1997) Physicochemical characteristics of five date fruit cultivars grown in the United Arab Emirates. Plant Foods Hum Nutr 50:101–113. https://doi.org/10.1007/BF02436030

Al-Hooti S, Sidhu JS, Qabazard H (1998) Chemical composition of seeds of date fruit cultivars of United Arab Emirates. J Food Sci Technol 35:44–46

Ali A, Al-Kindi YSM, Al-Said F (2009) Chemical composition and glycemic index of three varieties of Omani dates. Int J Food Sci Nutr 60:51–62. https://doi.org/10.1080/09637480802389094

Al-Mamary M, Al-Habor M, Al-Zubairi AS (2011) The in vitro antioxidant activity of different types of palm dates (Phoenix dactylifera) syrups. Arab J Chem 7:964–971. https://doi.org/10.1016/j.arabjc.11.014

Al-Orf SM, Mona HM, Norah A, Al-Atwai, Al-Zaidi H, Dehwah A, Dehwah S (2012) Review: nutritional properties and benefits of the date fruits (*Phoenix dactylifera* L.). Bull Natl Nutr Inst Arab Republic Egypt 39:97–129

Al-Qarawi AA, Ali BH, Al-Mougy SA, Mousa HM (2003) Gastrointestinal transit in mice treated with various extracts of date (*Phoenix dactylifera* L.). Food Chem Toxicol 41(1):37–39. https://doi.org/10.1016/S0278-6915(02)00203-X

Al-Saif MA, Khan LK, Alhamdan AAH, Alorf SM, Harfi SH, Al-Othman AM, Arif Z (2007) Effect of dates and Gahwa (Arabian coffee) supplementation on lipids in Hypercholesterolemic hamsters. Int J Pharmacol 3:123–129. https://doi.org/10.3923/ijp.2007.123.129

Al-Shahib W, Marshall RJ (2003) The fruit of the date palm: its possible use as the best food for the future. Int J Food Sci Nutr 54:247–259. https://doi.org/10.1080/09637480120091982

Amira EA, Guido F, Behija SE, Manel I, Nesrine Z, Ali F, Mohamed H, Noureddine HA, Lotfi A (2011) Chemical and aroma volatile compositions of date palm (*Phoenix dactylifera* L.) fruits at three maturation stages. Food Chem 127:1744–1754. https://doi.org/10.1016/j.foodchem.2011.02.051

Antolovich M, Prenzler PD, Patsalides E, McDonald S, Robards K (2002) Methods for testing antioxidant activity. Analyst 127(1):183–198. https://doi.org/10.1039/B009171P

Baliga S, Baliga V, Kandathil S (2011) A review of the chemistry and pharmacology of the date fruits (*Phoenix dactylifera* L.). Food Res Int 44:1812–1822. https://doi.org/10.1016/j.foodres.2010.07.004

Benzie IF, Strain JJ (1999) Ferric reducing/antioxidant power assay: direct measure of total antioxidant activity of biological fluids and modified version for simultaneous measurement of total antioxidant power and ascorbic acid concentration. Methods Enzymol 299:15–27. https://doi.org/10.1016/S0076-6879(99)99005-5

Bhathena SJ, Velasquez MT (2002) Beneficial role of dietary phytoestrogens in obesity and diabetes. Am J Clin Nutr 76:1191–1201. https://doi.org/10.1093/ajcn/76.6.1191

Biglari F, Alkarkhi AFM, Easa AM (2008) Antioxidant activity and phenolic content of various date palm (*Phoenix dactylifera*) fruits from Iran. Food Chem 107:1636–1641. https://doi.org/10.1016/j.foodchem.2007.10.033

Biskup I, Golonka I, Gamian A, Sroka Z (2013) Antioxidant activity of selected phenols estimated by ABTS and FRAP methods. Postepy Hig Med Dosw (Online) 67:958–963. https://doi.org/10.5604/17322693.1066062

Bouaziz MA, Besbes S, Blecker C, Wathelet B, Deroanne C, Attia H (2008) Protein and amino acid profiles of Tunisian Deglet Nour and Allig date palm fruit seeds. Int J Trop Subtrop Hortic 63:37–43. https://doi.org/10.1051/fruits:2007043

Boudries H, Kefalas P, Hornero-Mendez D (2007) Carotenoid composition of Algerian date varieties (*Phoenix dactylifera*) at different edible maturation stages. Food Chem 101(4):1372–1377. https://doi.org/10.1016/S0278-6915(02)00203-X

Cao G, Alessio HM, Cutler RG (1993) Oxygen-radical absorbance capacity assay for antioxidants. Free Radic Biol Med 14(3):303–311. https://doi.org/10.1016/0891-5849(93)90027-R

Chaira N, Mrabet A, Ferchichi A (2009) Evaluation of antioxidant activity, phenolics, sugar and mineral contents in date palm fruits. J Food Biochem 33:390–403. https://doi.org/10.1111/j.1745-4514.2009.00225.x

Domitrovic R, Jakovac H, Grebic D, Milin C, Radosevic-Stasic B (2008) Dose- and time-dependent effects of luteolin on liver metallothioneins and metals in carbon tetrachloride-induced hepatotoxicity in mice. Biol Trace Elem Res 126:176–185. https://doi.org/10.1007/s12011-008-8181-0

Dudonne S, Vitrac X, Coutière P, Woillez M, Merillon JM (2009) Comparative study of antioxidant properties and total phenolic content of 30 plant extracts of industrial interest using DPPH, ABTS, FRAP, SOD, and ORAC assays. J Agric Food Chem 57(5):1768–1774. https://doi.org/10.1021/jf803011r

Duke JA (2001) Handbook of phytochemical constituents of GRAS herbs and other economic plants. CRC Press, Boca Raton

Duke JA, Beckstrom-Sternberg S (2007) Dr. Duke's ethnobotanical databases. http://www.ars-grin.gov/duke/plants.html

Elleuch M, Besbes S, Roiseux O, Blecker C, Deroanne C, Drira NE, Attia H (2008) Date flesh: chemical composition and characteristics of the dietary fibre. Food Chem 111(3):676–682. https://doi.org/10.1016/j.foodchem.2008.04.036

El-Zoghbi M (1997) Biochemical changes in some tropical fruits during ripening. Food Chem 49:33–37. https://doi.org/10.1016/0308-8146(94)90229-1

Eustache F, Mondon F, Canivenc-Lavier MC, Lesaffre C, Fulla Y, Berges R, Cravedi JP, Vaiman D, Auger J (2009) Chronic dietary exposure to a low-dose mixture of genistein and vinclozolin modifies the reproductive axis, testis transcriptome, and fertility. Environ Health Perspect 117:1272–1279. https://doi.org/10.1289/ehp.0800158

Famuyiwa OO, Elhazmi MAF, Aljasser SJ, Sulimani RA, Jayakumar RV, Alnuaim AA, Mekki MO (1992) A comparison of acute glycemic and insulin-response to dates (*Phoenix-dactylifera*) and oral dextrose in diabetic and nondiabetic subjects. Saudi Med J 13(5):397–402

Fullerton SA, Samadi AA, Tortorelis DG, Choudhury MS, Mallouh C, Tazaki H, Konno S (2000) Induction of apoptosis in human prostatic cancer cells with betaglucan (Maitake mushroom polysaccharide). Mol Urol 4:7–13

Gardner E (2017) Alternative sugars: dates. Br Dent J 223(6):393. https://doi.org/10.1038/sj.bdj.2017.792

Ghnimi S, Umer S, Karim K-EA (2017) Date fruit (*Phoenix dactylifera* L.): an underutilized food seeking industrial valorization. NFS J 6:1–10. https://doi.org/10.1016/j.nfs.2016.12.001

Habib HM, Ibrahim WH (2011) Nutritional quality evaluation of eighteen date fruit varieties. Int J Food Sci Nutr 60(S1):99–111. https://doi.org/10.1080/09637480802314639

Hagerman AE, Riedl KM, Jones GA, Sovik KN, Ritchard NT, Hartzfeld PW, Riechel TL (1998) High molecular weight plant polyphenolics (Tannins) as biological antioxidants. J Agric Food Chem 46(5):1887–1892. https://doi.org/10.1021/jf970975b

Hong YJ, Tomas-Barberan FA, Kader AA, Mitchell AE (2006) The flavonoid glycosides and procyanidin composition of Deglet Nour dates (*Phoenix dactylifera*). J Agric Food Chem 54:2405–2411. https://doi.org/10.1021/jf0581776

Huang D, Ou B, Prior RL (2005) The chemistry behind antioxidant capacity assays. J Agric Food Chem 53(6):1841–1856. https://doi.org/10.1021/jf030723c

Ipatova OM, Prozorovskaia NN, Rusina IF, Prozorovskii VN (2003) Antioxidant properties of a leaf extract from Aronia (*Aronia melanocarba*) containing proanthocyanidins. Biomed Khim 49:165–176

Ishurd O, Kennedy JF (2005) The anti-cancer activity of polysaccharide prepared from Libyan dates (*Phoenix dactylifera* L.). Carbohydr Polym 59(4):531–535. https://doi.org/10.1016/j.carbpol.2004.11.004

Ishurd O, Zgheel F, Kermagi A, Flefla M, Elmabruk M (2004) Antitumor activity of beta D glucan from Libyan dates. J Med Food 7(2):252–255. https://doi.org/10.1089/1096620041224085

Ishurd O, Zgheela F, Kermagia A, Flefleaa N, Elmabruka M, Kennedy JF, Ashour A (2007) (1–3)-β D-glucans from Lybian dates (*Phoenix dactylifera* L.) and their anticancer activities. J Biol Sci 7 (3):554–557. https://doi.org/10.3923/jbs.2007.554.557

Ismail B, Haffar I, Baalbaki R, Mechref Y, Henry J (2006) Physico-chemical characteristics and total quality of five date varieties grown in the United Arab Emirates. Int J Food Sci Technol 41:919–926. https://doi.org/10.1111/j.1365-2621.2005.01143.x

Jana K, Samanta PK, Manna I, Ghosh P, Singh N, Khetan RP, Ray BR (2008) Protective effect of sodium selenite and zinc sulfate on intensive swimming-induced testicular gamatogenic and steroidogenic disorders in mature male rats. Appl Physiol Nutr Metab 33:903–914. https://doi.org/10.1139/H08-065

Janbaz KH, Saeed SA, Gilani AH (2005) Studies on the protective effects of caffeic acid and quercetin on chemical-induced hepatotoxicity in rodents. Phytomedicine 11:424–430. https://doi.org/10.1016/j.phymed.2003.05.002

Jenkins DJ, Kendall CW, McKeown-Eyssen G (2008) Effect of a low-glycemic index or a high cereal fiber diet on type 2 diabetes: a randomized trial. JAMA 300:2742–2753. https://doi.org/10.1001/jama.2008.808

John S, Sorokin AV, Thompson PD (2007) Phytosterols and vascular disease. Curr Opin Lipidol 18:35–40. https://doi.org/10.1097/MOL.0b013e328011e9e3

Karasawa K, Uzuhashi Y, Hirota M, Otani H (2011) A matured fruit extract of date palm tree (*Phoenix dactylifera* L.) stimulates the cellular immune system in mice. J Agric Food Chem 59:11287–11293. https://doi.org/10.1021/jf2029225

Lemine FMM, Ahmed MVOM, Maoulainine LBM, Bouna ZAO, Samb A, Boukhary AOMSO (2014) Antioxidant activity of various Mauritanian date palm (*Phoenix dactylifera* L.) fruits at two edible ripening stages. Food Sci Nutr 2(6):700–705. https://doi.org/10.1002/fsn3.167

Liolios CC, Sotiroudis GT, Chinou I (2009) Fatty acids, sterols, phenols and antioxidant activity of Phoenix theophrasti fruits growing in Crete, Greece. Plant Foods Hum Nutr 64(1):52–61. https://doi.org/10.1007/s11130-008-0100-1

Lusis AJ (2002) Atherosclerosis. Nature 14:233–241. https://doi.org/10.1038/35025203

Mansouri A, Embarek G, Kokkalou E, Kefalas P (2005) Phenolic profile and antioxidant activity of the Algerian ripe date palm fruit *(Phoenix dactylifera*). Food Chem 89:411–420. https://doi.org/10.1016/j.foodchem.2004.02.051

Marlett JA, McBurney MI, Slavin JL (2002) Position of the American Dietetic Association: health implications of dietary fiber. J Am Diet Assoc 102:993–1000. https://doi.org/10.1016/j.jada.2008.08.007

Marzouk HA, Kassem HA (2011) Improving fruit quality, nutritional value and yield of Zaghloul dates by the application of organic and/or fertilizers. Sci Hortic 127:249–254. https://doi.org/10.1016/j.scienta.2010.10.005

Miller NJ, Rice-Evans CA (1997) Factors influencing the antioxidant activity determined by the $ABTS^{\cdot+}$ radical cation assay. Free Radic Res 26(3):195–199. https://doi.org/10.3109/10715769709097799

Mohammad B, Habibi N (2011) Date seeds: a novel and inexpensive source of dietary fiber. In: International conference on food engineering and biotechnology, vol 9, pp 323–326

Neori BH, Judeinstein SA, Greenberg N, Volkova M, Rosenblat M, Aviram M (2013) Date (*Phoenix dactylifera* L.) fruit soluble phenolics composition and antiatherogenic properties in nine israeli varieties. J Agric Food Chem 61(18):4278–4286. https://doi.org/10.1021/jf400782v

Ou B, Hampsch-Woodill M, Prior RL (2001) Development and validation of an improved oxygen radical absorbance capacity assay using fluorescein as the fluorescent probe. J Agric Food Chem 49(10):4619–4626. https://doi.org/10.1021/jf010586o

Prior RL, Cao G (1999) In vivo total antioxidant capacity: comparison of different analytical methods. Free Radic Biol Med 27(11–12):1173–1181. https://doi.org/10.1016/S0891-5849(99)00203-8

Prior RL, Wu X, Schaich K (2005) Standardized methods for the determination of antioxidant capacity and phenolics in foods and dietary supplements. J Agric Food Chem 53:4290–4302. https://doi.org/10.1021/jf0502698

Ranilla LG, Kwon YI, Genovese MI, Lajolo FM, Shetty K (2008) Antidiabetes and antihypertension potential of commonly consumed carbohydrate sweeteners using in vitro models. J Med Food 11(2):337–348. https://doi.org/10.1089/jmf.2007.689

Rock W, Rosenblat M, Borochov-Neori H, Volkova N, Judeinstein S, Elias M, Aviram M (2009) Effects of date (*Phoenix dactylifera* L., Medjool or Hallawi variety) consumption by healthy subjects on serum glucose and lipid levels and on serum oxidative status: a pilot study. J Agric Food Chem 57:8010–8017. https://doi.org/10.1021/jf901559a

Saafi EB, Arem AE, Issaoui M, Hammami M, Achour L (2009) Phenolic content and antioxidant activity of four date palm (*Phoenix dactylifera* L.) fruit varieties grown in Tunisia. Int J Food Sci Technol 44:2314–2319. https://doi.org/10.1111/j.1365-2621.2009.02075.x

Said L, Banni M, Kerkeni A, Said K, Messaoudi I (2010) Influence of combined treatment with zinc and selenium on cadmium induced testicular pathophysiology in rat. Food Chem Toxicol 48:2759–2765. https://doi.org/10.1016/j.fct.2010.07.003

Saleh EA, Tawfik MS, Abu-Tarboush HM (2011) Phenolic contents and antioxidant activity of various date palm (*Phoenix dactylifera* L.) fruits from Saudi Arabia. Food Nutr Sci 2 (10):1134–1141. https://doi.org/10.4236/fns.2011.210152

Shafiei M, Karimi K, Taherzadeh MJ (2010) Palm date fibers: analysis and enzymatic hydrolysis. Int J Mol Sci 11:4285–4296. https://doi.org/10.3390/ijms11114285

Shimamura T, Sumikura Y, Yamazaki T, Tada A, Kashiwagi T, Ishikawa H, Matsui T, Sugimoto N, Akiyama K, Ukeda H (2014) Applicability of the DPPH assay for evaluating the antioxidant capacity of food additives – inter-laboratory evaluation study. Anal Sci 30(7):717–721. https://doi.org/10.2116/analsci.30.717

Singh V, Guizani N, Essa MM, Hakkim FL, Rahman MS (2012) Comparative analysis of total phenolics, flavonoid content and antioxidant profile of different date varieties (*Phoenix dactylifera* L.) from Sultanate of Oman. Int Food Res J 19(3):1063–1070

Srinivasan M, Rukkumani R, Ram Sudheer A, Menon VP (2005) Ferulic acid, a natural protector against carbon tetrachloride-induced toxicity. Fundam Clin Pharmacol 19:491–496. https://doi.org/10.1111/j.1472-8206.2005.00332.x

Stasko A, Brezova V, Biskupic S, Misi KV (2007) The potential pitfalls of using 1,1-diphenyl-2-picrylhydrazyl to characterize antioxidants in mixed water solvents. Free Radic Res 41 (4):379–390. https://doi.org/10.1080/10715760600930014

Surh YJ (2003) Cancer chemoprevention with dietary phytochemicals. Nat Rev Cancer 3 (10):768–780. https://doi.org/10.1038/nrc1189

Thompson LU, Boucher BA, Liu Z, Cotterchio M, Kreiger N (2006) Phytoestrogen content of foods consumed in Canada, including isoflavones, lignans, and coumestan. Nutr Cancer 54:184–201. https://doi.org/10.1207/s15327914nc5402_5

Tomas Lorente F, Ferreres F (1988) Flavonoid sulphates in fruits of *Phoenix dactilifera*. J Agrochem Food Technol 28(4):581–585

Uba A, Abdullahi MI, Yusuf AJ, Ibrahim ZYY, Lawal M, Nasir I, Abdullahim FT (2015) Mineral profile, proximate and amino acid composition of three dates varieties (*Phoenix dactylifera* L.). Der Pharma Chemica 7(5):48–53

Vayalil PK (2002) Antioxidant and antimutagenic properties of aqueous extract of date fruit (*Phoenix dactylifera* L. Arecaceae). J Agric Food Chem 30 50(3):610–617. https://doi.org/10.1080/10715760600930014

Vayalil PK (2012) Date fruits (*Phoenix dactylifera* Linn): an emerging medicinal food. Crit Rev Food Sci Nutr 52(3):249–271. https://doi.org/10.1080/10408398.2010.499824

Wang H, Cao G, Prior RL (1996) Total antioxidant capacity of fruits. J Agric Food Chem 44:701–705. https://doi.org/10.1021/jf950579y

Wang Z, Wu Z, Dai Y, Yang J, Wang W, Wu G (2013) Glycine metabolism in animals and humans: implications for nutrition and health. AminoAcids 45(3):463–477. https://doi.org/10.1007/s00726-013-1493-1

Weickert MO, Pfeiffer AFH (2008) Metabolic effects of dietary fiber consumption and prevention of diabetes. J Nutr 138(3):439–442. https://doi.org/10.1093/jn/138.3.439

Wu G (2010) Functional amino acids in growth, reproduction, and health. Adv Nutr 1:31–37. https://doi.org/10.3945/an.110.1008

Zheng QS, Sun XL, Xu B, Li G, Song M (2005) Mechanisms of apigenin-7-glucoside as a hepatoprotective agent. Biomed Environ Sci 18:65–70

Chapter 3
Nutritional and Therapeutic Applications of Date Palm

Prabu Periyathambi, Hemalatha Thiagarajan, and Suganthan Veerachamy

Abstract Date palm (*Phoenix dactylifera* L. Arecaceae family) is an ancient crop of Southwest Asia, widely known for its nutritional and therapeutic values. Date fruits are rich in carbohydrates, dietary fibres, proteins, minerals, vitamins etc. The therapeutic potential of date fruit is well documented in Ayurveda (Indian traditional medicine) and Middle Eastern folklore. Date fruits are highly nourishing and possess immense health benefits, which is highly attributed to the presence of phytochemicals viz., polyphenols, flavonoids, anthocyanins etc. This chapter speaks about the nutritional and pharmacological effects of date fruit. Date fruit is a real gift to mankind, because it's a unique combination of a natural product being tastier, inexpensive encompassing high nutritional and medicinal properties.

Keywords Date palm · *Phoenix dactylifera* · Fruit · Nutritional · Antioxidant · Anti-inflammation · Anticancer · Antimicrobial · Neuroprotection · Hepatoprotection

3.1 Introduction

Date palm (*Phoenix dactylifera* L.) is one of the most important tree species in the oasis areas of Northern Africa and Middle East countries. Date palm trees play a major role in creating favourable conditions in the oasis areas, to protect it from

P. Periyathambi (✉)
Centre for Nanobiotechnology, Vellore Institute of Technology (VIT), Vellore, TN, India
e-mail: prabubiochemi87@gmail.com

H. Thiagarajan
Biological Materials Laboratory, CSIR-Central Leather Research Institute (CLRI), Chennai, TN, India
e-mail: hemabiotek.t@gmail.com

S. Veerachamy
Department for Sensors and Biomedical Technology, School of Electronics Engineering [SENSE], Vellore Institute of Technology (VIT), Vellore, TN, India
e-mail: suganthan.v@vit.ac.in

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_3

desertification. Date palm is one of the oldest plants in the World, which is cultivated by mankind throughout the world (Ghnimi et al. 2017). They were widely cultivated in many places of Asia, Africa, Arabian countries, and in Middle East. Similarly, date palm also being cultivated in places like Palestine from several million years ago where they do extensive farming in the regions of Jericho, Jordan Valley and Gaza strip. It is also considered to be rich in nutrition, therapeutic, socio-economic tree with all the environmental attributes that makes it to grow in all kinds of climatic conditions (Goor 1967).

Date palm belongs to Arecaceae family (Angiosperms, Monocotyledon), which consists of about 200 genera and more than 2500 species. The genera Phoenix consists of about 14 species, including *Phoenix dactylifera* L. The name dactylifera translates to "finger-bearing" which represents the fruit clusters produced by this plant (Ashraf and Hamidi-Esfahani 2011). The genome of date palm was re-sequenced to yield insights into the diversification of a fruit tree crop (Hazzouri et al. 2015). Regular consumption of dates protects the liver and helps to reduce the level of alkaline phosphatase. Previous reports have stated that consuming date fruits would help people in safeguarding against cardiovascular disease (CVD), which is the major cause of mortality worldwide. Date fruits help to reduce the blood pressure, cholesterol level and lipid oxidation. However, all the understanding behind this mechanistic observation is still unknown.

3.2 Nutritional Value of Date Palm

Depending on the cultivation, soil and environmental conditions the chemical composition of date palm varies with its ripening stage. During its ripening phase, it starts to lose its moisture content by undergoing a conversion of glucose to fructose. Amongst the various components found in date palm, carbohydrates play a major role for about 78% in particular sugars, and also supplies a high energy source to the human body (Makki et al. 1998). Further, the content of carbohydrate in date palm varies from 50 to 90 g/100 g. Several authors have reported that at the early stage, date palm consists of a small amount of fructose and glucose (Tang et al. 2013).

Further, the region of production and its variety can considerably affect the glucose and total sugar content found in date palm fruit (Ahmed et al. 1995; Ismail et al. 2006; Ali et al. 2009). During the digestion process of the date fruit, the glucose and fructose get readily absorbed which leads to an instant elevation in blood sugar levels. (Liu et al. 2000). Almost 50% of the sugars in date fruit is present in the form of fructose which double the amount of glucose which induces a feeling of satiety.

Date palm fruits are rich in dietary fibre source which further depends on the stage of the ripening process (Al-Shahib and Marshall 2003). These date palm consists of both soluble and insoluble fibres viz., cellulose, pectin, lignin etc. At the ripening stage of the fruit, the enzymes slowly break down into few soluble components by rendering the date palm softer and tender (Fennema 1996). Pectin is considered as the most important fibre in date palm which gets accumulated during the initial stage of fruit growth. The dietary fibre found in date palm fruit further donates to their main nutritional value, as they are used in fibre-based food preparation and dietary supplements. An average amount of 100 g of daily intake of date palm fruit can meet the recommended dietary allowance of about 32% for dietary fibre (Marlett et al. 2002). The excess amount of insoluble fibre can lead to satiety and due to increased stool weight, it produces a laxative effect. These dietary fibres found in date palm fruit reveals many therapeutic effects viz., it lowers the blood cholesterol levels and it is also shown to lower the risk of several other diseases like hypertension, diabetes, bowel cancer and cardiovascular diseases (Marlett et al. 2002; Cummings et al. 1992).

These date palm fruit also consists of proteins and lipids in the range of 1–3% of its total composition. During the ripening process, the proteins found in date palm fruit play a prominent role in non-oxidative browning and precipitation of tannins (Barreveld 1993). Many essential amino acids are also found in the date fruits which are favourable for the human needs. Further, the date seeds are also a rich source of dietary fibre, phenolics and antioxidants (Almana and Mahmoud 1994; Hussein et al. 1998).

Date palm fruit comprises a wide range of both saturated and unsaturated fatty acids viz., capric, lauric, myristic, palmitic, stearic, oleic, linoleic and linolenic acids. In addition, date palm fruit comprises of a wide range of vitamins and minerals like selenium, copper, potassium, magnesium, iron, phosphorus and calcium. The high content of potassium and low sodium concentration found in date palm is beneficial for persons suffering from hypertension. On the other hand, boron and vitamins significantly aid in rheumatism and in the treatment of brain cancer. Date fruits act as natural supplements for iron deficiency without causing any adverse effects (Tang et al. 2013).

In addition to these compositions, date palm fruit also contain various phytochemicals like carotenoids, phenolics, glycosides and flavanols (Shahidi and Naczk 2004; Al-Farsi et al. 2005; Biglari et al. 2008). These carotenoids and phenolics found in date palm provide antioxidant and antimutagenic activity. It is further reported that most of the antioxidants found in date palm fruit is hydrophilic in nature. Further, date palm fruits not only act as good source of natural antioxidants, but also, they help in improving the products flavor and color due to their high content in active phenolics (Mansouri et al. 2005; Vayalil 2002; Biglari et al. 2008; Vinson et al. 2005). In particular, date palm fruit is considered as a moderate source of carotenoids compared with other dried fruits. Although all carotenoids in general do not act as provitamin A, date palm contributes to the human requirement of vitamin A (Hart and Scott 1995; Boudries et al. 2007). In addition, date palm fruit is found to have high medicinal properties.

3.3 Therapeutic Applications of Date Palm

The therapeutic applications of date palm are well recognized in Middle Eastern folklore and Indian traditional Medicine. The Holy Book "*Al-Qur'an* also mentions the nutritional significance and health benefits of dates. Date fruits decoction along with salt is given as a remedy for dehydration associated with diarrhoea in the Middle East (Al-Qarawi et al. 2005). Consumption of date fruits, particularly in the morning on an empty stomach helps to overcome the adverse effects of toxic material that the subject has been exposed to. Date palm is well recognized in Ayurveda (Indian Traditional Medicine) for its various therapeutic values viz., lower respiratory tract infections, sciatica, oedema, microbial infections, alcohol intoxication etc. (Nadkarni, 1976). Date fruits are high energy foods; with its potent antioxidant and antimutagenic activities it is found to provide strength, fitness and it is used as a cure against number of ailments and diseases including fever, stomach disorders, memory disturbances, nervous disorders, cancer, cardiovascular disorders and also proved to boost the immunity (Vayalil 2002; Allaith 2008).

3.3.1 Antioxidant Activity

Bouhlali et al. (2017a) examined different varieties of date palm and have reported that they possess antioxidant activity which strongly correlated with the polyphenol and flavonoid content. Vinson et al. (2005) report that date fruits contain the highest concentration of polyphenols among the dried fruits. This characteristic feature could be attributed to their greater exposure to sunlight and extreme temperature. Antioxidants are nature's defence which act against the reactive oxygen species (ROS), which play a significant role in many diseases. Antioxidants neutralise the free radicals, making them harmless to other cells. In most cases, the production of endogenous antioxidants is insufficient to meet out the needs, wherein exogenous supplementation would help to protect the body from the deleterious effects of ROS. Antioxidants viz., polyphenols, carotenoids, tannins etc., present in date fruits confer them with potent free radical scavenging property and antioxidant potential. Also, date fruits enhance the activity of antioxidant enzymes viz., superoxide dismutase and catalase (Ceballos- Picot et al. 1996; Al-Farsi and Lee 2008). Thouri et al. (2017) reports that date seeds also possess antioxidant potential and it could also be used as a cheap source of natural antioxidant.

3.3.2 Anti-Inflammatory Activity

Taleb et al. (2016) further reported that the anti-inflammatory activity of date is strongly linked to its secondary metabolites and anti-oxidant nature. Free radicals play a key role in the upregulation of inflammatory response. Secondary metabolites viz., phenolics and flavonoids act as suppressor of NF-KB and function as anti-inflammatory agents. Hence, the anti-inflammatory effect of dates could be attributed to the presence of polyphenol (viz., gallic acid, ferullic acid, cafferic acid etc) and flavonoids (rutin, quercetin, luteolin etc). The difference in anti-inflammatory activities of different date varieties largely depend on the variations in their phenolic and flavonoid content (Bouhlali et al. 2017b). Zhang et al. (2013) analysed the various extracts of ajwa date fruit and confirm that the bioactive compounds present in them possess strong antioxidant and anti-inflammatory properties. The compounds inhibited cyclooxygenase enzymes viz., Cox-1 and Cox-2, the important mediators of inflammation. Al-Okbi and Mohammed (2012) investigated the effects of methanolic and water extracts of date fruit in adjuvant induced arthritis in rats, a model of chronic inflammation. They infer that the extracts were able to significantly reduce the foot swelling, despite normalizing the plasma levels of antioxidants. Algerin date fruit extract was able to decrease the edema size, levels of homocysteine and C-reactive protein in formalin – induced edema test in rats (Kehili et al. 2016).

3.3.3 Anticancer Activity

Presence of polyphenols, flavonoids, folic acid etc., are one of the significant advantages of date fruits. Consumption of dates builds up immunity and cancer protection. Khan et al. (2017) investigated the effect of ajwa date fruit extract on rat model of hepatocellular carcinoma and proved that date fruit extracts were able to reverse the liver to normal conditions by restoring the antioxidant enzymes, liver enzymes, cytokine balance etc. Ishrud and John (2005) provide evidence in mice regarding the anticancer activity of date fruits. Lybian date fruit extract possessed the ability to hinder the growth of sarcoma in female mice. The results of Al-Sayyed et al. (2014) state that date fruits provide potent protection against DMBA-induced mammary cancer in rat. Date fruit exerted their effects at various stages viz., initiation, promotion and progression stages of carcinogenesis. Regular intake of date fruits could improve the health of the colon by inhibiting the proliferation of colon cancer cells and also it enhances the growth of beneficial bacterial cells. Digested date extract and polyphenol extract strongly inhibited the growth of human epithelial colorectal adenocarcinoma cells (Caco-2) (Eid et al. 2014). This anticancer property of date fruit is due to the presence of phenolics and flavonoids which play a major role in up-regulation of apoptotic molecules such as p53, caspases and Bax or they act by downregulating the anti-apoptotic molecules viz., Akt, Bcl-2, nuclear factor κB (NFκB) etc. (Ishrud and John, 2005).

3.3.4 Neuroprotective Activity

Date palm fruits are an excellent source of dietary fibre, rich in total phenolics and natural antioxidants, such as anthocyanins, ferulic acid, protocatechuic acid and caffeic acid. Presence of these polyphenolic compounds, bestows it with neuroprotective action. Dietary supplementation of date fruits lowers the risk and progression of Alzheimer's disease (Subash et al. 2015). Dehghanin et al. (2017) analysed the effects of date seed extract in rat model of Alzheimer's disease and reported that DSE significantly restored memory and learning impairments. It significantly reduced the caspase-3 expression level and the number of degenerated neurons. Date extract offered potential neuroprotection against cerebral ischemia induced by bilateral common carotid artery occlusion in rats (Pujari et al. 2011). In Ayurveda date palm is known as *Kharjura* and is recommended for the treatment of psychosis, anxiety, cognitive dysfunction and nervous system disorders (Shanmugapriya and Patwardhan 2012). Date fruits exhibited profound cerebroprotective activity against cerebral ischemia in mice (Kalantaripour et al. 2012). Presence of sterols, ascorbic acid and flavonoids are attributed for this effect. Sheikh et al. (2016) investigated the neuropharmacological and analgesic properties of date fruit in rats and reported that the presence of polyphenols viz., catechin, epicatechin and trans-ferulic acid could be attributed to the above effect.

3.3.5 Nephroprotective Activity

Al-Qarawi et al. (2008) reviewed the effects of extract of date flesh and pits and reported that they were able to significantly reduce the plasma creatinine and urea concentration in gentamicin induced nephrotoxicity in rats. Also, they ameliorated the proximal tubular damage. Presence of versatile antioxidants viz., melatonin, tocopherols and vitamin C could be the factors behind nephroprotection.

3.3.6 Hepatoprotective Activity

The hepatoprotective effect of date extracts were proved by El Arem et al. (2014) in experimental rats. The results of the study conclude that the date extract could significantly protect the liver, by lowering the levels of hepatic marker enzymes (viz., aspartate transaminase, lactate dehydrogenase, alanine transaminase, gamma glutamyl transferase), hepatic thiobarbituric acid reactive substances (TBARS) and by enhancing the activities of antioxidants (superoxide dismutase, catalase etc). The studies of Saafi et al. (2011) also coincide with the above findings, wherein date fruit extracts serve a hepatoprotective action against dimethoate induced oxidative stress in liver. Date fruits were also able to reverse the effects of carbon tetrachloride induced liver damage in experimental rat (Attia et al. 2016). The antioxidant, antiapoptotic and antifibrotic activities of date extract are primarily responsible for this hepatic protection (Elsadek et al. 2017).

3.3.7 Anti-Diabetic Activity

Date seeds also possess high nutrients, high energy values and good fatty acids. Hasan and Mohieldien (2016) studied the effect of date seed extract on streptozotocin induced diabetic rats. Date seed extract restored kidney and liver function and balanced the oxidative stress in diabetic experimental animals. The study clearly states the antidiabetic property of date seed extracts. Micheal et al. (2013) investigated the effects of diosmetin glycoside (isolated from the epicarp of date fruit), in alloxan induced diabetic experimental animals. The results showed that there was a marked improvement in the serum glucose level, liver function, antioxidant enzymes with a significant reduction in cholesterol and triglycerides. Date fruits could induce antidiabetic action by enhancing the output of insulin and by inhibiting the absorption of glucose. Flavonoids, steroids, phenols and saponins present in dates could be responsible for the above action. Phenolics present in dates are potent inhibitors of alpha glycosidase and alpha amylase, which leads to the reduction of carbohydrates digestion and absorption that may counteract the hyperglycemic condition (Ranilla et al. 2008). A study done by Miller et al. (2003) in healthy volunteers revealed that consumption of dates either alone or in mixed meals with plain yoghurt have a low glycaemic index. Intake of date fruit by diabetic patients helps to control their glycemic index and lipid profile.

3.3.8 Anti-Microbial Property

Samad et al. (2016) infer that date/date extracts could be widely used in the nutraceutical and pharmaceutical industries owing to their antibacterial and antioxidant properties. Methanolic extract of ajwa datefruit exhibited antibacterial activity against *Staphylococcus aureus, Bacillus cereus, Serratia marcescens* and *Escherichia coli.* Aqueous extract of date palm seeds and pollen possess antifungal activity against *Fusarium oxysporum* (Bentrad et al. 2017a). Presence of polyphenols in date extracts is responsible for their antifungal activity (Boulenouar et al. 2011), while presence of fatty acids viz., palmitic, stearic, oleic, linoleic acid etc. confer date fruits with their antibacterial property (Bentrad et al. 2017b). Date extracts from Tunisian cultivars possessed antimicrobial activity against both gram positive and gram negative bacteria; especially a profound activity was present against *E.coli* (Kchaou et al. 2016).

3.3.9 Effect on Infertility Issues in Male

El Arem et al. (2017) reported that date extracts offered protection over dichloroacetic acid induced oxidative damage in testes of male rats. This observed therapeutic potency of ADE might be due to several contributing factors, mainly due to the mineral (zinc, selenium, copper, iron, calcium, cobalt, magnesium, manganese) and vitamin (A, B, C) composition of these fruits (Baliga et al. 2011). Presence of polyphenolic compounds viz., flavonoids which are highly effective against ROS-mediated injury, also contribute towards protection of testicles (Garcia and Castillo 2008). Presence of quercetin, an essential bioflavonoid in date extracts is also one of important component responsible for the testicular protective effect. Quercetin prevents the formation of free radicals in cells and inhibits lipid peroxidation. Arsenic induced testicular damage in rats was significantly prevented by the antioxidant and antiapoptotic properties of quercetin (Baltaci et al. 2016). Microelements found in date palm pollen extract viz., estrone, sterols and other agents have a positive effect on male fertility. Also, date palm pollen extract suspension augments the plasma levels of estradiol and testosterone (Bahmanpour et al. 2006; Mahran et al. 1976).

3.3.10 Effect on Labour and Lactation in Female

Zangeneh et al. (2009) report that consumption of date fruits in late pregnancy accelerates labour and it increases the pain threshold level. Presence of fatty acids in date fruits aids in saving energy and strengthening uterus muscles. Al Kuran et al. (2011) report that date fruits influence oxytocin receptors, stimulates the uterine muscles to respond more comfortably to oxytocins, and better prepares the uterus and cervix for delivery. The study concludes that consumption of date fruits in that last 4 weeks of pregnancy reduces the need for induction, augments labour and produces a favourable delivery outcome. Khadem et al. (2007) further added that date fruits have the potential to reduce postpartum haemorrhage. Kordi et al. (2014) report that cervical dilation was higher in women consuming date fruit. Hence consumption of date fruit is recommended for pregnant women, especially in the last week of gestation. The labour intervention was also reduced by date fruits without adversely affecting the mother and infant (Razali et al. 2017). The presence of potassium, glycine and threonine in date fruits are thought to activate the production of prolactin. Date fruits are also recommended as galactogogue in feeding mothers, due to the presence of oxytocin (Tang et al. 2013).

3.3.11 Anti-Hemolytic Activity

Bacterial toxin of Streptolysin O (SLO) is generated by *Streptococcus pyogenes*, which causes the hemolysis of erythrocytes. Abuharfeil et al. (1999) report that the date fruit extract was able to neutralise the hemolytic activity of SLO at low concentrations. Date fruit extract even has the ability to inhibit the hemolytic activity of snake and scorpion venoms (Sallal et al. 1997). Bouhlali et al. (2016) infer that date fruit extract exhibited considerable anti-hemolytic activity in rabbit blood induced with AAPH (free radical generator), which positively correlated with the polyphenols and flavonoid content. Flavonoids and other polyphenols enhance the erythrocyte membrane stability, while the antioxidants scavenge the lipid peroxyl radicals generated by AAPH.

3.3.12 Other Medical Benefits

Dates decoction is used as an eye-lotion as it helps in the maintenance of eye hygiene and a remedy for ophthalmic disorders (Tang et al. 2013). Due to the rich phenolic content date fruits are considered as a cleansing agent and astringent in intestinal troubles. The aqueous extracts of dates have been shown to have antidiarrheal effects in rats (Al-Taher 2008).

3.4 Conclusion

The date is an ideal fruit with a delicious sweet taste. It is rich in nutrients viz., carbohydrates, vitamins, minerals etc. It is an excellent source of fibre and contains many potent phytochemicals such as polyphenols, flavonoids, anthocyanins, carotenoids etc. The various properties of date fruits especially antioxidant, anticancer, anti-inflammatory, neuroprotection, hepatoprotection etc., could be attributed to the presence of these phytochemicals. Consumption of date fruits on a regular basis offers potential health benefits viz., strength, fitness, immunity etc. Though, the chapter summarizes the nutritional and therapeutic applications of date palm, a thorough investigation of the molecular mechanisms involved is yet to be defined. Unravelling such paths will throw more light on this Middle East fruit, thereby paving the way for its addition in nutraceuticals and pharmaceutical supplements.

References

AAl-Sayyed HF, Takruri HR, Shomaf MS (2014) The effect of date palm fruit (*Phoenix dactylifera* L.) on the hormone 17-β-estradiol in 7,12-dimethylbenz (α) anthracene induced mammary cancer in rats. Med J Nutrition Metab 7(1):5–10. https://doi.org/10.3233/MNM-140001

Abuharfeil NM, El Sukhon S, Msameh Y, Sallal AJ (1999) Effect of Date Fruits, *Phoenix Dactyliferia L.*, on the Hemolytic Activity of Streptolysin O. Pharm Biol 37(5):335–339. https://doi.org/10.1076/phbi.37.5.335.6051

Ahmed IA, Ahemed AWK, Robinson RK (1995) Chemical composition of date varieties as influenced by the stage of ripening. Food Chem 54:305–309. https://doi.org/10.1016/0308-8146(95)00051-J

Al-Farsi MA, Lee CY (2008) Nutritional and functional properties of dates: a review. Crit Rev Food Sci Nutr 48:877–887. https://doi.org/10.1080/10408390701724264

Al-Farsi M, Alasalvar C, Morris A, Baron M, Shahidi F (2005) Compositional and sensory characteristics of three native sundried date (*Phoenix dactylifera* L.) varieties grown in Oman. J Agric Food Chem 53:7586–7591. https://doi.org/10.1021/jf050578y

Ali A, Al-Kindi YS, Al-Said F (2009) Chemical composition and glycemic index of three varieties of Omani dates. Int J Food Sci Nutr 60(S4):51–62. https://doi.org/10.1080/09637480802389094

Al-Kuran O, Al-Mehaisen L, Bawadi H, Beitawi S, Amarin Z (2011) The effect of late pregnancy consumption of date fruit on labour and delivery. J Obstet Gynaecol 31:29–31. https://doi.org/10.3109/01443615.2010.522267

Allaith AAA (2008) Antioxidant activity of Bahreini date palm (*Phoenix dactylifera*) fruit of various cultivars. Int J Food Sci Tech 43:1033–1040. https://doi.org/10.1111/j.1365-2621.2007.01558.x

Almana HA, Mahmoud RM (1994) Date-palm seeds as an alternative source of dietary fibre in Saudi bread. Ecol Food Nutr 32:261–270. https://doi.org/10.1080/03670244.1994.9991406

Al-Okbi SY, Mohamed DA (2012) Preparation and evaluation of functional foods in adjuvant arthritis. Grasas Aceites 63:394–402. https://doi.org/10.3989/gya.130811

Al-Qarawi AA, Abdel-Rahman H, Ali BH, Mousa HM, El-Mougy SA (2005) The ameliorative effect of dates (*Phoenix dactylifera L.*) on ethanol induced gastric ulcer in rats. J Ethnopharmacol 98:313–317. https://doi.org/10.1016/j.jep.2005.01.023

Al-Qarawi AA, Abdel-Rahman H, Mousa HM, Ali BH, El-Mougy SA (2008) Nephroprotective action of Phoenix dactylifera. In gentamicin-induced nephrotoxicity. Pharm Biol 46 (4):227–230. https://doi.org/10.1080/13880200701739322

Al-Shahib W, Marshall RJ (2003) The fruit of date palm: it's possible uses as best food for the future. Int J Food Sci Nutr 54(4):247–259. https://doi.org/10.1080/09637480120091982

Al-Taher AY (2008) Possible antidiarrheal effect of date-palm (*Phoenix dactylifera* L.) aqueous extracts in rats. Scientific Journal of King Faisal University (Basic and Applied Sciences) 9:1429–1435

Ashraf Z, Hamidi-Esfahani Z (2011) Date and Date Processing: A Review. Food Rev Int 27 (2):101–133. https://doi.org/10.1080/87559129.2010.535231

Attia H, Al-Rasheed N, Mohamad R, Al-Rasheed N, Al-Amin M (2016) The antifibrotic and fibrolytic properties of date fruit extract via modulation of genotoxicity, tissue-inhibitor of metalloproteinases and nuclear factor- kappa B pathway in a rat model of hepatotoxicity. BMC Complement Altern Med 16(1):414. https://doi.org/10.1186/s12906-016-1388-2

Bahmanpour S, Talaei T, Vojdani Z, Panjehshahin MR, Poostpasand A, Zareei S, Ghaeminia M (2006) Therapeutic effect of *Phoenix dactylifera* pollen on sperm parameters and reproductive system of adult male rats. Iran J Med Sci 31:8–12. http://ijms.sums.ac.ir/index. php/IJMS/article/view/2180/666

Baliga MS, Baliga BRV, Kandathil SM, Bhat HP, Vayalil PK (2011) A review of the chemistry and pharmacology of the date fruits (*Phoenix dactylifera* L.). Food Res Int 44:1812–1822. https://doi.org/10.1016/j.foodres.2010.07.004

Baltaci BB, Uygur R, Caglar V, Aktas C, Aydin M, Ozen OA (2016) Protective effects of quercetin against arsenic-induced testicular damage in rats. Andrologia 48(10):1202–1213. https://doi.org/10.1111/and.12561

Barreveld WH (1993). Date-Palm Products. Bulletin No 101. Food and Agriculture Organization of the United Nations, Rome. http://www.fao.org/docrep/t0681e/t0681e 00.htm

Bentrad N, Gaceb-Terrak R, Benmalek Y, Rahmania F (2017a) Studies on chemical composition and antimicrobial activities of bioactive molecules from date palm (*phoenix dactylifera* L.) Pollens and seeds. Afr J Tradit Complement Altern Med 4(3):242–256. https://doi.org/10.21010/ajtcam.v14i3.26

Bentrad N, Gaceb-Terrak R, Rahmania F (2017b) Identification and evaluation of antibacterial agents present in lipophilic fractions isolated from sub-products of Phoenix dactilyfera. Nat Prod Res 31(21):2544–2548. https://doi.org/10.1080/14786419.2017.1314282

Biglari F, Abbas FM, Alkarkhi FM, Azahar ME (2008) Antioxidant activity and phenolic content of various date palm (*Phoenix dactylifera*) fruits from Iran. Food Chem 107:1636–1641. https://doi.org/10.1016/j.foodchem.2007.10.033

Boudries H, Kefalas P, Hornero-Mendez D (2007) Carotenoid composition of Algerian date varieties (*Phoenix dactylifera*) at different edible maturation stages. Food Chem 101:1372–1377. https://doi.org/10.1016/j.foodchem.2006.03.043

Bouhlali ET, Bammou M, Sellam K, Benlyas M, Alem C, Filali-Zegzouti Y (2016) Evaluation of antioxidant, antihemolytic and antibacterial potential of six Moroccan date fruit (*Phoenix dactylifera* L.) varieties. J King Saud Univ Sci 28(2):136–142. https://doi.org/10.1016/j.jksus.2016.01.002

Bouhlali ET, Ramchoun M, Alem C, Ghafoor K, Ennassir J, Zegzouti YF (2017a) Functional composition and antioxidant activities of eight Moroccan date fruit varieties (*Phoenix dactylifera* L.). J Saudi Soc Agric Sci 16(3):257–264. https://doi.org/10.1016/j.jssas.2015.08.005

Bouhlali ET, El Hilaly J, Ennassir J, Benlyas M, Alem C, Amarouch M-Y, Filali-Zegzouti Y (2017b) Anti-inflammatory properties and phenolic profile of six Moroccan date fruit (*Phoenix dactylifera* L.) varieties. J King Saud Univ Sci 30(4):519–526. https://doi.org/10.1016/j.jksus.2017.08.011

Boulenouar N, Marouf A, Cheriti A (2011) Antifungal activity and phytochemical screening of extracts from *Phoenix dactylifera* L. cultivars. Nat Prod Res 25(20):1999–2002. https://doi.org/10.1080/14786419.2010.536765

Ceballos-Picot I, Witko-Sarsat V, Merad-Boudia M, Nguyen AT, Thévenin M, Jaudon MC, Zingraff J, Verger C, Jingers P, Latscha BD (1996) Glutathione antioxidant system as a marker of oxidative stress in chronic renal failure. Free Radic Biol Med 21:845–853. https://doi.org/10.1016/0891-5849(96)00233-X

Cummings JH, Bingham S, Heaton KW, Eastwood MA (1992) Fecal weight, colon cancer risk, and dietary intake of non-starch polysaccharides (dietary fibre). Gastroenterology 103:1783–1789. https://www.gastrojournal.org/article/0016-5085(92)91435-7/abstract

Dehghanian F, Kalantaripour TP, Esmaeilpour K, Elyasi L, Oloumi H, Pour FM, Asadi-Shekaari M (2017) Date seed extract ameliorates β-amyloid-induced impairments in hippocampus of male rats. Biomed Pharmacother 89:221–226. https://doi.org/10.1016/j.biopha.2017.02.037

Eid N, Enani S, Walton G, Corona G, Costabile A, Gibson G, Rowland I, Spencer JP (2014) The impact of date palm fruits and their component polyphenols, on gut microbial ecology, bacterial metabolites and colon cancer cell proliferation. J Nutr Sci 3:e46. https://doi.org/10.1017/jns.2014.16

El Arem A, Ghrairi F, Lahouar L, Thouri A, Behija Saafi E, Ayed A, Zekri M, Ferjani H, Haouas Z, Zakhama A, Achour L (2014) Hepatoprotective activity of date fruit extracts against dichloroacetic acid-induced liver damage in rats. J Funct Foods 9:119–130. https://doi.org/10.1016/j.jff.2014.04.018

El Arem A, Lahouar L, Saafi EB, Thouri A, Ghrairi F, Houas Z, Neffati F, Achour L (2017) Dichloroacetic acid-induced testicular toxicity in male rats and the protective effect of date fruit extract. BMC Pharmacol Toxicol. 18:17. https://doi.org/10.1186/s40360-017-0127-8

Elsadek B, El-Sayed ES, Mansour A, Elazab A (2017) Abrogation of carbon tetrachloride-induced hepatotoxicity in Sprague-Dawley rats by Ajwa date fruit extract through ameliorating oxidative stress and apoptosis. Pak J Pharm Sci 30(6):2183–2191. http://www.pjps.pk/wp-content/uploads/pdfs/30/6/Paper%2017.pdf

Fennema OR (1996) Food Chemistry, 3rd edn. Dekker M, New York, pp 365–339. https://www.zuj.edu.jo/download/food-chemistry-3rd-ed-o-fennema-9ed-marcel-dekker-1996-ww-pdf/

Garcia OB, Castillo J (2008) Update on uses and properties of citrus flavonoids: new findings in anticancer, cardiovascular, and anti-inflammatory activity. J Agric Food Chem 56:6185–6205. https://doi.org/10.1021/jf8006568

Ghnimi S, Umer S, Karim A, Kamal-Eldina A (2017) Date fruit (*Phoenix dactylifera* L.): An underutilized food seeking industrial valorization. NFS Journal 6:1–10. https://doi.org/10.1016/j.nfs.2016.12.001

Goor A (1967) The history of the date through the ages in the holy land. Econ Bot 21(4):320–340. https://doi.org/10.2307/4252895

Hart D, Scott KJ (1995) Development and evaluation of HPLC method for the analysis of carotenoids in fruits, and the measurement of the carotenoid content of vegetables and fruits commonly consumed in UK. Food Chem 54:101–111. https://doi.org/10.1016/0308-8146(95)92669-B

Hasan M, Mohieldein A (2016) In vivo evaluation of anti diabetic, hypolipidemic, anti-oxidative activities of saudi date seed extract on streptozotocin induced diabetic rats. J Clin Diagn Res 10(3):FF06–FF12. https://doi.org/10.7860/JCDR/2016/16879.7419

Hazzouri KM, Flowers JM, Visser HJ, Khierallah HS, Rosas U, Pham GM, Meyer RS, Johansen CK, Fresquez ZA, Masmoudi K, Haider N, El Kadri N, Idaghdour Y, Malek JA, Thirkhill D, Markhand GS, Krueger RR, Zaid A, Purugganan MD (2015) Whole genome re-sequencing of date palms yields insights into diversification of a fruit tree crop. Nat Commun 6:8824. https://doi.org/10.1038/ncomms9824

Hussein AS, Alhadrami GA, Khali YH (1998) The use of dates and date pits in broiler starter and finisher diets. Bioresour Technol 66:219–223. https://doi.org/10.1016/S0960-8524(98)00054-6

Ishruda O John FK (2005) The anticancer activity of polysaccharide prepared from Libyan dates (*Phoenix dactylifera* L.). Carbohydr Polym 59:531–535. https://doi.org/10.1016/j.carbpol.2004.11.004

Ismail B, Haffar I, Baalbaki R, Mechref Y, Henry J (2006) Physico-chemical characteristics and total quality of five date varieties grown in United Arab Emirates. Int Food Sci and Technol 41:919–926. https://doi.org/10.1111/j.1365-2621.2005.01143.x

Kalantaripour T, Asadi-Shekaari M, Basiri M, Najar AG (2012) Cerebroprotective effect of date seed extract (*Phoenix dactylifera*) on focal cerebral ischemia in male rats. J Biol Sci 12:180–185. https://doi.org/10.3923/jbs.2012.180.185

Kchaou W, Abbès F, Mansour RB, Blecker C, Attia H, Besbes S (2016) Phenolic profile, antibacterial and cytotoxic properties of second grade date extract from Tunisian cultivars (*Phoenix dactylifera* L.). Food Chem 194:1048–1055. https://doi.org/10.1016/j.foodchem.2015.08.120

Kehili HE, Zerizer S, Beladjila KA, Kabouche Z (2016) Anti-inflammatory effect of Algerian date fruit (*Phoenix dactylifera*). Food Agric Immunol 27:820–829. https://doi.org/10.1080/09540105.2016.1183597

Khadem N, Sharaphy A, Latifnejad R, Hammod N, Ibrahimzadeh S (2007) Comparing the efficacy of dates and oxytocin in the management of postpartum hemorrhage. Shiraz E-Medical Journal 8(2):64–71. https://cdn.shopify.com/s/files/1/0820/4871/ files/MEDJOULS -_Comparing the Efficacy of Dates and_Oxytocin in_the_Management of_Postpartum Hemorrhage.pdf

Khan F, Khan TJ, Kalamegam G, Pushparaj PN, Chaudhary A, Abuzenadah A, Kumosani T, Barbour E, Al-Qahtani M (2017) Anti-cancer effects of Ajwa dates (Phoenix dactylifera L.) in diethylnitrosamine induced hepatocellular carcinoma in Wistar rats. BMC Complement Altern Med 17:418. https://doi.org/10.1186/s12906-017-1926-6

Kordi M, Aghaei MF, Tara F, Nemati M, Taghi SM (2014) The Effect of Late Pregnancy Consumption of Date Fruit on Cervical Ripening in Nulliparous Women. J Midwifery Womens Health 2(3):150–156. https://doi.org/10.22038/JMRH.2014.2772

Liu S, Willett WC, Stampfer MJ, Hu FB, Franz M, Sampson L, Hennekens CH, Manson JAA (2000) Prospective study of dietary glycemic load, carbohydrate intake and risk of coronary heart diseases in U.S women. Am J Clin Nutr 71:1455–1461. https://doi.org/10.1093/ajcn/71.6.1455

Mahran GH, Abdel-Wahab SM, Attia AM (1976) A phytochemical study of date palm pollen. Planta Med 29:171–175. https://doi.org/10.1055/s-0028-1097648

Makki M, Hamooda A, Al-Abri A (1998) The Date Palm, Culture, Operation and Maintenance. Modern Color Publishers, Muscat. https://www.crcpress.com/Dates-Production-Processing-Food-and-Medicinal-Values/Manickavasagan-Essa-Sukumar/p/book /9781439849453

Mansouri A, Embarek G, Kokkalou E, Kefalas P (2005) Phenolic profile and antioxidant activity of the Algerian ripe date palm fruit (*Phoenix dactylifera*.). Food Chem 89:411–420. https://doi.org/10.1016/j.foodchem.2004.02.051

Marlett JA, Mc Burney MI, Slavin J (2002) Position of the American Diabetic Association: Health implications of dietary fiber. J Agric Food Chem 102:993–1000. https://doi.org/10.1016/j.jada.2008.08.007

Michael HN, Salib JY, Eskander EF (2013) Bioactivity of Diosmetin Glycosides Isolated from the Epicarp of Date Fruits, *Phoenix dactylifera*, on the Biochemical Profile of Alloxan Diabetic Male Rats. Phytother Res 27:699–704. https://doi.org/10.1002/ptr.4777

Miller CJ, Dunn EV, Hashim IB (2003) The glycaemic index of dates and date/yoghurt mixed meals. Are dates 'the candy that grows on trees'? Eur J Clin Nut 57:427–430. https://doi.org/10.1038/sj.ejcn.1601565

Nadkarni KM (1976) Indian Matria Medica, vol 1. Bombay Popular Prakashan, Mumbai. https://trove.nla.gov.au/version/21887031

Pujari RR, Vyawahare NS, Kagathara VG (2011) Evaluation of antioxidant and neuroprotective effect of date palm (*Phoenix dactylifera L.*) against bilateral common carotid artery occlusion in rats. Indian J Exp Biol 49:627–633. https://pdfs.semanticscholar.org/ 1d2b/a9458ea3aa4a23b469929331f22c7bf38e6e.pdf

Ranilla LG, Kwon YI, Genovese MI, Lajolo FM, Shetty K (2008) Antidiabetes and antihypertension potential of commonly consumed carbohydrate sweeteners using *in vitro* models. J Med Food 11:337–348. https://doi.org/10.1089/jmf.2007.689

Razali N, Mohd Nahwari SH, Sulaiman S, Hassan J (2017) Date fruit consumption at term: Effect on length of gestation, labour and delivery. J Obstet Gynaecol 37(5):595–600. https://doi.org/10.1080/01443615.2017.1283304

Saafi EB, Louedi M, Elfeki A, Zakhama A, Najjar MF, Hammami M, Achour L (2011) Protective effect of date palm fruit extract (*Phoenix dactylifera L.*) on dimethoate induced-oxidative stress in rat liver. Exp Toxicol Pathol 63(5):433–441. https://doi.org/10.1016/j.etp.2010.03.002

Sallal AK, Rim J, Amr ZS, Disi AM (1997) Inhibition of haemolytic activity of snake and scorpion venom by date extract. Biomed Lett 55(217):51–56. http://jglobal.jst.go.jp/en/public/200902115410640922

Samad MA, Hashim SH, Simarani K, Yaacob JS (2016) Antibacterial properties and effects of fruit chilling and extract storage on antioxidant activity, total phenolic and anthocyanin content of four date palm (*Phoenix dactylifera*) Cultivars. Molecules 21(4):419. https://doi.org/10.3390/molecules21040419

Shahidi F, Naczk M (2004) Phenolics in Foods and Nutraceuticals. CRC Press, Boca Rotan. https://www.crcpress.com/Phenolics-in-Food-and-Nutraceuticals/Shahidi-Naczk/p/book/9781587161384

Shanmugapriya M, Patwardhan K (2012) Uses of date palm in Ayurveda. In: Manickavasagan A, Essa MM, Sukumar E (eds) Dates: production, processing, food, and medicinal values. CRC Press, Boca Raton, pp 377–385. https://www.crcpress.com/Dates-Production-Processing-Food-and-Medicinal-Values/Manickavasagan-Essa-Sukumar/p/book/9781439849453

Sheikh BY, Zihad SMNK, Sifat N, Uddin SJ, Shilpi JA, Hamdi OA, Hossain H, Rouf R, Jahan IA (2016) Comparative study of neuropharmacological, analgesic properties and phenolic profile of

Ajwah, Safawy and Sukkari cultivars of date palm (*Phoenix dactylifera*). Orient Pharm Exp Med 16(3):175–183. https://doi.org/10.1007/s13596-016-0239-5

Subash S, Essa MM, Braidy N, Awlad-Thani K, Vaishnav R, Al-Adawi S, Al-Asmi A, Guillemin GJ (2015) Diet rich in date palm fruits improves memory, learning and reduces beta amyloid in transgenic mouse model of Alzheimer's disease. J Ayurveda Integr Med 6(2):111–120. https://doi.org/10.4103/0975-9476.159073

Taleb H, Maddocks SE, Morris RK, Kanekanian AD (2016) Chemical characterisation and the anti-inflammatory, antiangiogenic and antibacterial properties of date fruit (*Phoenix dactylifera* L.). J Ethnopharmacol 194:457–468. https://doi.org/10.1016/j.jep.2016.10.032

Tang ZX, Shi LE, Aleid SM (2013) Date fruit: chemical composition, nutritional and medicinal values, products. J Sci Food Agric 93:2351–2361. https://doi.org/10.1002/jsfa.6154

Thouri A, Chahdoura H, El Arem A, Omri Hichri A, Ben Hassin R, Achour L (2017) Effect of solvents extraction on phytochemical components and biological activities of Tunisian date seeds (var. Korkobbi and Arechti). BMC Complement Altern Med 17:248. https://doi.org/10.1186/s12906-017-1751-y

Vayalil PK (2002) Antioxidant and antimutagenic properties of aqueous extract of date fruit (*Phoenix dactylifera* L. *Arecaceae*). J Agric Food Chem 50:610–617. https://doi.org/10.1021/jf010716t

Vinson JA, Zubik L, Bose P, Samman N, Proch J (2005) Dried fruits: excellent in-vitro and in-vivo antioxidants. J Am Coll Nutr 24:44–50. https://doi.org/10.1080/07315724.2005.10719442

Zhang CR, Aldosari SA, Vidyasagar PS, Nair KM, Nair MG (2013) Antioxidant and antiinflammatory assays confirm bioactive compounds in Ajwa Date fruit. J Agric Food Chem 61:5834–5840. https://doi.org/10.1021/jf401371v

Zangeneh F, Moezi L, Amir Zargar A (2009) The effect of palm date, fig and olive fruits regimen on weight, pain threshold and memory in mice. Iranian Journal of Medicinal and Aromatic Plants. 25:149–158

Chapter 4
Chemical Composition of Date Pits: Potential to Extract and Characterize the Lipid Fraction

Asif Ahmad and Hifsa Imtiaz

Abstract Date palm *Phoenix dactylifera* L., is recognized as an oldest plant and is grown for its palatable fruit and pit in various Arab countries for centuries. Its fruit is considered as an important source of dietary carbohydrates, fibers, antioxidant compounds, definite unique profile of vitamins and minerals especially the pits are tremendous reservoirs of lipids and protein components. The considerable amount of oil fraction in date pits is not only characterized with stability but also with biological activities and potential health benefits. A variety of techniques are available in scientific literature for extraction of date pit lipid fraction demonstrated significant amount of neutral fats, high molecular weight triglycerides, and sterol contents. Fractionation of pits lipids by Gas-liquid chromatography revealed more unsaturated fatty acids (e.g. oleic acid), less saturated fatty acids (lauric acid) and average amounts of myristic, palmitic and linoleic acids. The greater oil proportion of date seeds make it efficient use as renewable resource with significant value addition to the agricultural products and most commonly recognized for cosmetics, and food products usage. Presence of bioactive substances in this oil makes it a suitable candidate for variety of nutraceuticals and value-added food products.

Keywords Date pits · Lipid extraction · Liquid · Saturated fatty acids · Sterols · Unsaturated fatty acids · Lauric acid · Fibers · Fractionation · Gas-liquid chromatography

4.1 Date Palm

Date palm usually recognized as Phoenix dactylifera is considered as an ancient (5500–3000 BCE) cultured date crop that possess nutraceutical, economical and ornamental advantages. It is most commonly cultivated in arid and semi-arid areas worldwide because of religious, traditional, ecological, and social expansion of

A. Ahmad (✉) · H. Imtiaz
Department of Food Technology, PMAS-Arid Agriculture University, Rawalpindi, Pakistan
e-mail: asifahmad@uaar.edu.pk; hifsaimtiaz786@gmail.com

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_4

individuals present. Especially the Middle East and African countries are leading regions regarding date palm cultivation, production and export (Vayalil 2012). The fruit of date palm is generally considered as monocotyledonous and its tree usually found at a highness of 1500 m in well prepared drained loams. Currently, areas of many countries like Iraq, Iran, Saudi Arabia, Algeria, Egypt, Libya, Pakistan, Morocco, and Oman are famous for date palm cultivation. However, due to unique nutraceutical characteristics, date is consumed as major food item in numerous areas of Asian, Arabian, and various African countries (Assirey 2015). Date palm possess unique characteristic compared to other fruit crops due to its consumption at any of the various ripeness stages such as Rutab, Khalal and Tamar. It can be consumed both in fresh and dried form but on commercial level dried dates are mostly preferred because of their extensive shelf life. The ripening stages and choice of the varieties have a great influence on the sensory (taste, texture) nutritional and phytochemical properties that varies greatly in various regions. It was estimated that there are almost more than 5000 date varieties cultivated in various areas worldwide, among which Aseel, Dhakki, Zahidi, Majdool, Mabrook, Halawi, Lasht, Deggla and Bamy are considered as the most common ones (Khalid et al. 2016, 2017a, b).

4.2 Development of Date Pit as Value Added Product

There is a growing trend for cultivation of date palm across the globe due to increased utilization of date palms by the different food processing industries. Rising demands for dates and its products enhanced its production that touches to an amount of about 7.2 million tons in 2016, (Al-Alawi et al. 2017) and this accounts almost 720,000 tons of date seeds (10% of total datet palm). Moreover, about 1.3 billion tons of foodstuff and products waste formed annually all through the supply chain could fed almost two billion persons devoid of any detrimental effect on atmosphere as significantly recognized by FAO (Rodrigo et al. 2014). Nowadays, food waste is considered as “one of the great paradoxes of our times”, and it is the best deteriorating resources to bring into account for producing various other valuable food products. Various research studies demonstrated the use of different food industry waste in formulation of value added products and could also efficient source of economic profits for industry, farmers, food safety and product sustainability. In past, due to insufficient research on date pits, these are mostly used as feed for livestocks or as fertilizers. Today in modern times, extensive scientific research on date pits and their extracts make it possible to open up new avenues for its use. Modern scientific literature on date pits indicated wide range of applications in food, cosmetics and pharmaceutical products (Salah et al. 2012). For instance, date flesh and pits can be used to make nutritious granola bar that could be a great source of dietary fibers, antioxidants and other nutrients (Abu-Qaoud 2015; Ahmad et al. 2017).

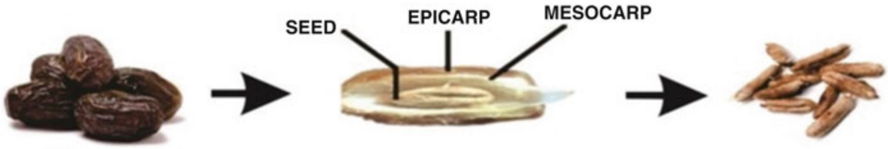


Fig. 4.1 Date palm and seed parts

Generally, the date palm fruit is comprising of fleshy pericarp and pit or seed (Fig. 4.1). Besides date flesh, seeds are recognized to possess high extractable value-added constituents. Various research studies on chemical composition of dates proved that pits are largely wasting byproducts of industries due to their biological and technological transformation. Consequently, a larger proportion of date palm pits might effortlessly be collected from various date based treating productions or by employing their wasted byproducts (Hossain et al. 2014; Khalid et al. 2017b).

Date pits often underutilized and considered as low value agricultural by-products. Their actual potential was not discovered in last century, now it is considered as good source of nutritional components having vast applications in products formulation. For example, date pits are considered as a good precursor for the formulation of carbon, used as most popular and effective adsorbent in various industries (Yaish and Kumar 2015). It is also good in galactomannan, glucomannan and heteroxylan that had been extracted and characterized from date seeds. Ample amounts of carbohydrates (62.90%), crude fiber (19.99–39.66%) and lipids (7.87–9.76%) are also available in date pits. (Al-Humaid et al. 2010; Khalid et al. 2016). However, nowadays major consideration was given towards the lipids or oil extraction of date seeds due to their potential industrial and biological applications. Some studies demonstrated a diversified physiochemical configuration and fatty acid description in date pit oils. Date seeds oil was found to possess higher amounts of oleic acid (47.66%) and lauric acid 17.39%, however linoleic (10.54%), palmitic acid (10.20%) and myristic acid (10.06%) were also found in moderate to low levels (Elbasheer et al. 2012; Khalid et al. 2017a).

4.3 Nutritional Composition of Date Flesh and Pits

Date fruits and pits are recognized as enriched with various nutritional characteristics. The nutritive configuration of date palm flesh and pit has been described by various research studies. It was found that dates flesh and seed contains higher amounts of reducing sugars in addition to other amino acids, proteins and fats. Whereas, the date pits possess greater proportions of proteins, crude fat and crude fiber as compared to date flesh (Khalid et al. 2017a, b). Recent studied specified the proximate configuration of date flesh and pits and depicted the presence of moisture, ash, glucose, fructose, galactose and maltose, protein, fats and fibers in date pits and flesh. The details of these chemical constituents are as under:

4.3.1 Carbohydrates

Date fruits are considered as an energy dense food because of their rich carbohydrate constituents. Glucose and fructose are among the chief reducing sugars while sucrose as non-reducing and other polysaccharides such as starch and cellulose contribute as minor carbohydrate composition. The content of glucose, fructose and sucrose in date flesh varies and mainly depend upon date varieties, maturity stages and moisture contents. Studies suggested that date sugar content increases during Kimri, Khalal and Tamar stages, as the total soluble solids and sugars significantly increases with reduction in moisture levels (Abbès et al. 2011). Carbohydrate content gain special importance in date fruits as it is regarded as significant characteristic of both fresh and dried fruits on commercial basis. Sugar content comprises 50–80% of total date weight as 1 kg of dates provides 3000 calories. Dates are classified as sweeter or less sweet on basis of reducing or non-reducing content of dates. Comparing with date flesh, date seeds or pits comprises of almost 83.0% of carbohydrates among which, 42% of cellulose, 8% of hemicellulose, 25% of total sugar and other components are present (Ahmed and Theydan 2012). Date seeds signify almost 10–15% of total date fruit of which major contributors are insoluble fiber type carbohydrates (cellulose, hemicellulose). Similarly, carbohydrates are considered as major storage reservoirs in date seed endosperm mostly in (1 → 4) β-D mannan form. Several other hemicellulose portions that were recognized in date pits are mainly comprises of water-soluble gluco- and galacto-mannans and an alkali soluble heteroxylans. An alkali-soluble heteroxylans in date pits are generally composes of xylose (82%) and 4-O-methylglucuronic acid (17%) with minor quantity of arabinoses and very few traces of galactose, glucose and mannose contents (Assirey 2015).

4.3.2 Dietary Fibers

Date palm kernel or seeds are good source of total, soluble and insoluble dietary fibers. Dietary fiber in date flesh can be characterized as insoluble fiber that comprises of cellulose, hemicellulose, lignocellulose, lignin, and insoluble proteins. Dietary fiber signify almost 6.4–11.5% of total date weight of which insoluble fiber ranges between 84% and 94%. However, the cellulose, hemicellulose, and lignin contribute 1.55%, 1.28%, and 2.01% of total date fiber, respectively (Breil et al. 2016). The nutritional constituents of date especially fiber greatly varies with different varieties and ripening stages. For example, the total fiber content of Deglet Nour is 8.09% and in Kentichi 20.25%. It significantly rises during kimri stage (6.1–12.3%) compared to the tamer stage (2.01–3.10%) of maturity. Not only date flesh but seeds are also regarded as excellent source of dietary fibers 77.8–80.2 g/ 100 g that constitute 10–20% of fresh date weight (Al-Daihan and Bhat 2012). The dietary fiber content of date pits has higher concentrations than date flesh. For example, Ajwa date palm has TDF constituents ranges between 6.20% and 8.70% while the Ajwa date pit has total dietary fiber of 26.4–33.9% (Khalid et al. 2017b). The various studies conducted on chemical analysis of dietary fiber demonstrates some important functional properties in food industry greatly associated with date fiber. For example: possession of higher water-binding capability, higher oil-holding capacity, emulsifying properties, pseudoplasticity behavior of suspensions, and gel formation. Moreover, to improve the nutraceutical properties in food products, dietary fiber can extensively be employed as an important constituent in many foodstuffs (dairy, soup, meat, bakery products and jams) generally recognized to alter texture related properties and enhance the high fat foods stability (Saafi-Ben Salah et al. 2012; Khalid et al. 2016).

4.3.3 Protein

The protein and fat contents of dates gain special importance due to their high concentrations and biological values. Dates provide almost 1–7% of total protein content and essential amino acids that play important role in human body. Date protein content deliver most important 16–20 types of amino acids, that are not even existing in fruits (orange, apples and banana) and other products. The most important amino acids present in date palm cultivars comprises of histidine, lysine, arginine, aspartic acid, threonine, glutamic acid, proline, glycine, alanine, cystine, valine, methionine, isoleucine, leucine, tyrosine, and phenylalanine (Samad et al. 2016). Moreover, dates isoleucine content is 800 times greater than apple and 5000 times greater lysine content than oranges. Not only date flesh but date seeds also contains considerable amount of protein constituent. Soluble proteins like albumin, globulin, prolamine and glutelin constitute main portion of date seeds that is 5–6% of total date proteins (Zhang et al. 2013).

Majority of essential and sulphur containing amino acids (methionine, cystine) comprises relatively considerable amount of date seed proteins compared to other seed protein products (soybean, peanuts, cottonseed). Glutamic acid, aspartic acid and arginine specified almost half of the total amino acids that are extracted from Ruzeiz and Sifri cultivars. Lysine is present in greater concentrations whereas the tryptophan is the only amino acid that is present in limited amounts in date seed fractions (Akasha et al. 2012). A brief composition of date flesh and pits are demonstrated in Table 4.1.

Table 4.1 Nutritional composition of date palms and pits

Components	Date flesh %	Date pits %	References
Moisture	9.7–17.7	8.6–12.5	Sadiq et al. (2013) and Parvin et al. (2015)
Lipids	0.5–3.3	5.7–8.8	Al-Orf et al. (2012) and Assirey (2015)
Protein	1.1–3.0	4.8–6.9	Deng et al. (2012)
Ash	1.4–2.0	0.8–1.1	Saleh et al. (2011) and Paranthaman et al. (2012)
Dietary fiber	5.9–18.4	67.6–74.2	Basuny and Al-Marzooq (2011)
Carbohydrates	72.8–85.4	2.4–4.7	El Arem et al. (2014) and Baliga et al. (2011)
Energy	357.95	399.69	Eid et al. (2013) and Agboola and Adejumo (2013)

4.3.4 Minerals and Vitamins

Dietary minerals are recognized as indispensable chemical constituents which are vital for numerous human functions like skeletal structure maintenance, cellular and biochemical reactions and functions. Hence the adequate amount of these minerals is necessary for optimum growth and maintenance of human physiological and metabolic functions. Regarding their importance dates fruit (flesh and pits) could highly considered as excellent sources of mineral constituents. Several studies reported that potassium content in date flesh of several varieties could be as higher as 0.9%. However, the most important minerals in date fruits are Ca, K, P and Mn (Kumar et al. 2014; Khalid et al. 2016). Dates are also preferred to various other fruits because of their high content of potassium, phosphorus and iron. Several studies demonstrated the higher percentage of iron content as compared to zinc and copper which is considerably present in lower amounts in date fruit. The beneficial fluorine content of date flesh has advantageous affects for preventing tooth decay. Similarly, selenium play important role in cancer prevention, providing antioxidant properties and improvement of human immune system (Sun et al. 2013). Date seeds are also found to be enriched with greater amounts of various minerals like Mg, Ca, P, Na, K, Al, Cd, S and Pb in various proportions. Additionally, in some of the varieties potassium contribute 0.5% of total date seed minerals. Whereas iron, manganese, zinc and copper confer major concentrations regarding micronutrients. Various studies stated that the major differences in the minerals content of date flesh and seeds are due to various date varieties, soil type and quantity of fertilizer. As the Saudi Arabian dates comprises of minor quantity of phosphorus ranges (0.19–0.26%) whereas the selenium component contribute 1.48–2.96 mg/g of total minerals proportion compared to other date varieties (Habib and Ibrahim 2009).

The important vitamins like vitamin A (exist as β- carotene or provitamin A), vitamin C (ascorbic acid), vitamin B1 (thiamine), niacin and riboflavin are reported in date fruits. Among various date cultivars Ajwa dates comprises of relatively high provitamin A and vitamin C content. Due to these important vitamin components, dates are regarded as an ideal food because they proposed important nutritional components with significant potential health benefits (Habib et al. 2014).

4.3.5 Lipids

The lipid contents are regarded as most important components of date's fruits and gain special importance due to their nutritional significance. Although the date flesh comprises of only a small fraction of fat contents but date seeds are considered as much more concentrated source of lipids. Previous research studies demonstrated the narrow range of lipid contents in different date varieties but significantly varies along with maturity stages. For example the fat content generally declines from 0.5% to 0.1% from the Kimri to the Tamer maturity stages. The total lipid content in date seeds ranges from 5.05% to 12% while the oil contents that are 30–45% of total seed lipids have potential applications at industrial and pharmaceutical level (Al-Humaid et al. 2010; Akbari et al. 2012).

4.3.5.1 Free Fatty Acids

The most important fatty acids determined in date pits oil were comprising of oleic (C18:1), linoleic (C18:2), palmitic (C16:0), myristic (C14:0), and lauric (C12:0) acid that altogether contribute almost 90–95% of the total fatty acids. However, most of the fatty acids profile composition described in oil of the date pits may significantly differs among various varieties, and along with climatic and growing conditions (Amani et al. 2013). Similarly, among the major SFA (saturated fatty acids) possess by date–pits are: lauric acid (0.10–38.71 g), myrsitic acid (3.11–18.13 g), palmitic acid (0.41–15.19 g), and stearic acid (1.56–6.04 g) are present in greater concentrations. Likewise, palmitoleic acid (0.07–1.51 g) and oleic acids (32.15–54.10 g) are the chief MUFA (monounsaturated fatty acids) while linoleic acids (4.32–21.10 g) and linolenic acids (0.02–1.68 g) are the major PUFA (polyunsaturated fatty acids) but are present in relatively lower amounts (Akbari et al. 2012). Regarding the beneficial fatty acid profile, the date seed oil usually has low degree of unsaturation that exhibited good flavour and frying stability. Oleic acid in date pits as dominant component could considered advantageous to human health owing to its low saturated level and high potential to decrease LDL cholesterol along with greater oxidative constancy although the linoleic acid and linolenic acid is essential regarding growth of healthy human skin yet these posses less oxidative stability (Farooq et al. 2013).

4.3.5.2 Sterols

The studies based on GC analysis of date pits oil demonstrated the extraction of trimethylsilyl derivatives of sterols. The major sterol components determined comprises of cholesterol, campesterol, stigmasterol, β-sitosterol, avenasterol and stigmastadienl. Moreover, the β-sitosterol and campesterol were among the most important constituents of date seed oils that contribute almost 90% of total sterol fractions. Among which β-sitosterol add 83.31% and campesterol 9.10% of total sterols in seed oils. In some date varieties avenasterol is comparatively higher than other sterols e.g. Allig and Deglet Nour seed oil contains 4.50 against 0.45% of other sterols and greatly related with antioxidant effects (Al-Mssallem et al. 2013). Phytosterols was also found ranges from 0.50% to 0.90% for Allig and Deglet Noor varieties respectively. Phytosterols from date seed oils along with dietary fibers of date seed have a capacity to significantly lower the total and LDL cholesterol levels in hyperlipidemic individuals by preventing the intestinal cholesterol absorption. Despite this, date seed oil sterols can be highly beneficial for use as therapeutic agents for hypercholesterolemia treatments (Nigam and Singh 2011).

4.3.6 Antioxidant Compounds

4.3.6.1 Phenolic Contents

Date pits are considered as an excellent reservoirs of phenolics constituents (3112–4420 mg gallic acid) and antioxidants (570–919 μmol) (Ahmad et al. 2012). Various studies reported that comparing with various other edible oils (olive oil) date seed oils are regarded as rich source of phenolic contents (21–62 mg gallic acid) when extracted with numerous solvents (acetone–water, ethanol–water, methanol–water). Among several date varieties, Iranian date seeds had comparatively highest antioxidant and radical scavenging activity that could be employed for various pharmaceutical and commercial purposes (Suresh et al. 2013). Among various date seed phenolics gallic acid, protocatechuic acid, p-hydroxybenzoic acid, vanillic acid, caffeic acid, p-coumaric acid, ferulic acid, m-coumaric acid and o-coumaric acid were recognized to be present in variable concentrations. While the hydroxybenzoic acid (9.89 mg), protocatechuic acid (8.84 mg), and m-coumaric acid (8.42 mg) were the phenolic constituents that contribute major antioxidant potential of date seeds (Waly et al. 2015).

4.3.6.2 Flavonoids

The flavonoids are regarded to be most abundant phenolic constituents present in date fruits. These polyphenols are mostly existing in date flesh with enormous health advantages such as antioxidant as well as radical scavenging activities. Due to antioxidant potential these phenolic compounds are operative in reducing cardiovascular and chronic diseases with positive response towards damaged cells proliferation. Date fruit is enriched with various flavonoids that mostly comprises of quercetin, isoquercetin, and rutin and can be determined using HPLC technique (Hossain et al. 2014; Kaleem et al. 2016). The various antioxidant flavonoids vary within different varieties same is true for date palm kernel or pits. However, the total flavonoids contents of Ajwa date palm is 2.79–4.35 mg/100 g whereas the date pit consists of 1.35–3.67 mg/100 g of quercetin content as predominant flavonoid. Similarly, the various amounts of these compounds significantly differ among pits and flesh of date fruits due to variations in genetic considerations, experimental situations, and hydration levels. Phytochemicals (phenolics and flavonoids) in date fruit have strong antioxidant potential and possess major health advantages like reducing diabetes, prevention of cancerous cells, and cardiovascular disorders. The therapeutic potential of date pits flavonoids is comparable to other fruits flavonoids in combating microbial and viral infections (Biglar et al. 2012; Ahmad et al. 2015; Khalid et al. 2017a).

4.4 Extraction of Lipids from Date Pits

There are different methods employed for lipid extraction from date pits either using different solvents like hexane and petroleum ether or by using microwave and ultrasonic extraction. However, solvent extraction methods consume more time with high usage of solvents. Modern technologies make use of techniques like microwave and ultrasound extraction for optimum extraction of lipids. Thus more beneficial in terms of time, cost reduction, solvent consumption and power effectiveness. These methods could also improve stability of compounds to be extracted, process simplification, and quality and quantity of extraction and extract respectively. The total lipids or oil extracted through these methods could possess better oxidative stability than most of the vegetable oils even used in comparison with olive oil. Due to its unique characteristics date pit oils possess wide variety of applications in pharmaceuticals, cosmetics, and food products (Jassim and Naji 2010). Some other methods used for lipids extraction of date pits are explained as follows:

4.4.1 Folch Method

Combination of various organic solvents have been suggested to use for extraction of lipids from date pits and other sources. Folch method is one of this kind of method based on extraction of fats by employing mix of solvents. Lipids from the endogenous cells are extracted using chloroform–methanol (2:1 by volume). In detail, the one-fourth of the saline solution was equilibrated with the normal homogenized cells with efficient mixing. The resulted mixture formed as a result of this combination was placed for some time for the separation of two layers and as a result lipids settled down in the top layer phase. This method was introduced in past for lipids extractions and after some modifications it formed the basics of all extraction procedures. The same procedure with some amendments is still employed for the assessment of date pits lipid extraction spectrophotometrically. Usually, the large number of samples are rapidly and easily processed by using this method. However, it lacks sensitivity in results in comparison with other modern processes (Ullah et al. 2011).

4.4.2 Bligh and Dyer Method

Bligh and Dyer method is another useful technique for lipid extraction and partitioning, protein exist at interface of two liquid phases in this technique. This method also have some similarity to Folch method, but the only difference is found between solvent-solvent and solvent-tissues ratio. During this process lipids from standardized cells suspension were extracted by employing 2:1 (v/v) methanol-chloroform (Breil et al. 2017). Then the desired lipids are extracted using chloroform phase and processed by numerous procedures. However, the above gravimetric method is most extensively employed by the date pits processors for lipids and oil estimation on commercial level. There are some basics improvements which have been made in order to modify this method. The major kind of modification is the prevention of acidic and denatured lipids binding by the addition of 1 M sodium chloride instead of water. Also the basic reason behind the preference of this method over others is that during lipid extraction from date pits, further addition of 0.2 M phosphoric acid and hydrochloric acid (Reis et al. 2013) to the NaCl solution resulted in progressive lipid recovery with very short time duration. Correspondingly, another kind of modification is the accumulation of 0.5% acetic acid to the water phase which significantly resulted in increased reclamation of acidic phospholipids. A more recent report suggested that such type of lipid extraction was verified to be the most proficient method for the date pits lipids extraction (Yao and Schaich 2015).

4.4.3 Ultrasonic-Assisted Extraction

The Ultrasound assisted extraction is considered as substitute to other lipid extraction methods, without problems that are associated with other conventional lipid extraction methods of cell disruption. This method is regarded as more simple that may result product of high purity. This technique offer an ecofriendly, economical, less time consuming, and product with greater quality. Comparatively, lower temperatures adopted in this technique ensure lower energy inputs (Chemat and Khan 2011). The ultrasonic waves generated in this process cause quick cycles of compression/decompression, resulted in the production of extremely confined power waves, that disrupts lipid containing cells in date pits. Sonication with high frequency waves resulted in cracking of cell membrane for lipids fractionation. The sonicators that are most commonly used during this process are hot and bath types that are most commonly employed for batch as well as for continuous operations. In the bath type processors, usually the shape and capacity of vessel determines the quantity and organization of transducers (Lee et al. 2012). The basic benefit related to this procedure as compared to microwave reactors is its formation and generation of low temperature and energy, thus resulted in less denaturation of heat sensitive lipid molecules. Additionally, the beads and chemical substances does not required to be excluded in the end time process that cast off additional cost. Though, extended sonication some time resulted in free radical formation, that may be detrimental to the extracted oil quality (Hosikian et al. 2010).

4.4.4 Microwave Extraction Method

Earlier, the microwave radiations applications were only restricted to samples digestion for estimation of metals and organic contaminants extraction. The microwave technology has greatly recognized as quick, safe and cost effective method for lipids extraction (Kim et al. 2012). In this method usually polar material or dielectric is introduced in electric field generated by microwaves, resulted in heat release due to various frictional forces among inter and intra molecular surfaces. During intracellular heating in this method, high energy water vapors formed, resulted in disruption of lipids containing cells, opening of cell membranes thereby intercellular lipid metabolites are extracted (Amarni and Kadi 2010). Consequently, the quick pressure and heating system generated within biological structure, forced compounds out from cell matrix, significantly resulted in best-quality extracts production along with recovery of better lipids compounds. It was suggested that microwave treated lipids cells of date pits possess greater oil yields, because of numerous cell wall cracks, resulted in extraction and transesterification of oils into biodiesels (Ghasemi et al. 2016).

The microwave extraction method is preferred compared to other methods because of its low equipment cost, less reaction time, small operating cost involved, and efficient extraction. This method is demonstrated to be more suitable for biodiesel recovery from reaction mixture in a very short time of 15–20 min, as compared to conventional time consuming (6–7 h) heating method. Conversely, the drawback associated with microwave method is the high cost involved on commercial level applications (Lee et al. 2010).

4.4.5 Nile Red Fluorescence Extraction of Lipids

The Nile red is considered as an intense fluorescent lipophilic dye highly employed to determine the intracellular lipids quantity in algae, selective novel herbs and date pits. Generally the efficiency of Nile red is effected by various cell membrane diffusion levels and greatly depends on the time required for highest fluorescence emission (Sitepu et al. 2012). Moreover, the Nile Red is recognized as the most appropriate method of oil extraction and estimation, highly used to determine the accumulated lipids through fluorescence microscopy after the accumulation of Nile Red in cellular lipids. This method is more easy, simple, modernized, efficient and preferred, that used fluorescence plate reader for lipids quantification and highly recognized for most of the lipids containing seeds including date pits, algae and yeasts (Rumin et al. 2015; Takeshita et al. 2015). Similarly, several studies demonstrated that this method provides more stable values by using 20% dimethyl sulfoxide during its growth phase. However, the fluorescence power capabilities highly reduced with enhancing dimethyl sulfoxide concentrations. This method demonstrated to added up more lipids fraction with passage of time using sodium chloride solution. Conversely, the penetration of Nile Red across the cell membrane highly depends on process conditions and type of cell for lipids extraction (Hounslow et al. 2017). Generally, the fluorometric process does required lipid to be extracted; but for the fluorometric dye penetration through the material is necessary. This method is also used for algal and yeast lipids extraction but for oilseeds like date pits, its efficiency is highly enhanced by adding dimethyl sulfoxide and Nile Red along with acetone (Natunen et al. 2015).

4.4.6 Expeller Press Oil Extraction

Expeller press is considered as one of the oldest and simplest oil extraction method from raw seeds. This conventional technique is equally effective in case of dried dates seeds (Demirbaş 2008). The oil extraction is proportional to higher mechanical pressure that is applied to date seeds mass to break down the cell structure, then to rupture them for lipid extraction. Higher extraction efficacy can only be achieved by applying pressure in a specific range, too much high pressure effect the lipids quality due to accumulation of high heat and also cause obstruction problems (Boldor et al. 2010). This technique can be combined with use of chemicals/solvents for enhanced recovery. The limitations with these extraction technique is the longer time of extraction and initial high costs. Additionally, for mechanical pressing, input material of low moisture content is desirable that require additional drying and thus incur extra energy and production costs (Ranjith et al. 2015). Another important drawback during date seed oil extraction is hindrance of oil due to rigid cell wall structure that is mostly not happens in most of the vegetables oil solvent extraction. By adopting mechanical expression process, several natural pigments also get their way into the crude oil that have to remove during refining process by using either solvent extraction or carbon adsorption method, that yet again responsible for additional cost. Other problems associated with this type of method comprises of higher energy and maintenance costs, skilled labors requirement, and less efficiency in comparison with other methods (Johnson and Wen 2009).

4.4.7 Bead Beating Extraction

Another mechanical method of cell disruption most commonly used is bead beating, where cell is directly damaged by high rated spinning of seed extract slurries along with quality beads. All cell types including date seeds could be processed by cell disruption using grinding beads opposite to seed cells. Moreover, due to usage of multiple shaking vessels in a bead mill with vibrant platform, such kind of bead extraction method is regarded as best for seed samples that required same handling settings for disruption. (Lee et al. 2012). However, improved oil extraction efficiencies could be acquired, when beads were agitated along with cell culture. The cooling jacket often used inside the mill to protect the heat sensitive cell molecules, and also to minimize the heat generated during entire process. Numerous types of beads are usually employed for varied cell categories, however the beads made up of zirconium oxide, or titanium carbide could significantly increase the distraction rates and extraction efficacy of date seeds probably due to their greater density and hardness (Šoštarič et al. 2012). The overall comparison of all lipids extraction methods is demonstrated in Table 4.2.

4.4.8 Superior Solvent Extraction Methods

In this type of solvent extraction method usually chloroform is used as the main lipid extracting solvent that enhances its effectiveness and efficiency. However, on commercial level during large-scale lipids extraction employing these procedures is excluded due to ecological and health threats. Consequently, many researchers have been developing the least-toxic, but more operative, alternatives such as by using ethanol, isopropanol, butanol, acetic acid esters, hexane, and numerous solvents in combinations for date pitsoil extraction (Sheng et al. 2011). Moreover, the usage of above described solvents highly dependent on the lipids classes required to be extracted. Though, in a latest research studies, the extracted lipid fraction was highly recovered by using 2-ethoxyethanol (2-EE) in comparison with other common solvent extraction methods (chloroform, methanol and hexane) (Jones et al. 2012). A general description of date pit oil extraction steps along with solvent fractionation is presented in Fig. 4.2.

To further improve the efficiency of extraction process, ASE (accelerated solvent extraction) process, employing heat and pressure, was introduced. This method highly shortens the extraction time, and thus resulted in efficient solvent recovery for re-usage, thus minimize the operating costs. Recently, most of the modern solvent extraction as well as combined solvent/physical extraction methods are being developed for lipid extraction by various researchers all over the world. Although, the organic solvent extraction methods have possess various disadvantages when executed on commercial level (Cooney et al. 2009).

4.4.9 Extraction of Lipids Classes

The better and efficient method was developed by (El-Sharnouby and Al-Eid 2009) for extraction of various lipid classes, that is a modified form of the Folch/Bligh and

Table 4.2 Comparison of different methods for lipid extraction from date pits

Method	Efficiency	Cost involved	Energy requirements	Safety concerns	References
Use of organic solvents (chloroform/methanol)	Moderate	High due to use of solvents	Energy intensive	Health and environmental hazards	Habibi-Najafi (2011) and Wang et al. (2013)
Pressurized solvent extraction	High	High because of solvent used and pressurized nitrogen	High energy requirements	Environmental and regulatory issues	Juhaimi et al. (2014) and Al-Mssallem et al. (2013)
Isotonic extraction	Moderate high	Higher cost of solvents	Energy intensive	Less hazardous	Kelley et al. (2015) and Al-Harrasi et al. (2014)
Expeller pressing	Low moderate	Higher cost	Energy intensive	High heat generation and possible damaged to compounds	Sadiq et al. (2013) and Orabi and Shawky (2014)
Bead beating	Moderate	Cost-effective	Energy intensive, high pressure usage	Difficult to scale up	Halaby et al. (2014) and Bonsegna et al. (2011)
Microwave	Very high	High maintenance and initial setup cost	Too high energy demands (for cooling)	Easy to scale up, but yet need to be standardized at commercial level	Camus et al. (2013) and Chang et al. (2015)
Sonication method	High	High cost	Energy intensive –energy requires for cooling and sonication	Poor product quality due to the loss during the process	Filipe and McLauchlan (2015) and Umate (2012)
Electroporation	Very high	High maintenance cost	Less energy	Favorable but detailed pilot-scale studies need to be carried out	Wahlroos et al. (2015) and Besbes et al. (2004)

Dyer method. This procedure provides improved recovery of nearly all chief lipid classes and is based on using MTBE(Methyl-tert-butyl ether) as a solvent, and offers the most precise lipidemic profile. This can only be possible to acquire due to the development of a lipid-containing low density organic upper phase, that resulted in more easy and accurate lipid extractions. Briefly, 1.5 ml of methanol was mixed rigorously for 200 ml sample (vortexing), moreover after adding 5 ml of MTBE, the solution was incubated for 1 h at normal room temperature (Saura-Calixto 2012). Likewise, phase separation during the process was developed by the addition of 1.25 ml of water to the solution and permitted to stand at room temperature. The top

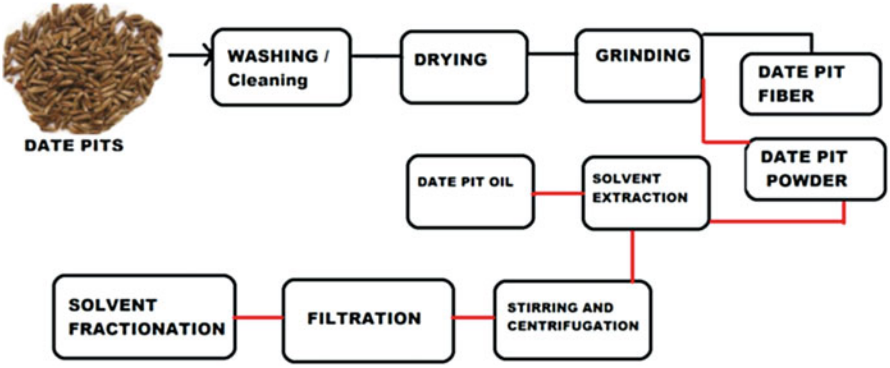


Fig. 4.2 Extraction method for date pit oil and bioactive substances

organic phase was extracted by centrifugation and the lower phase was re-extracted by adding 2 ml of MTBE/methanol/water (10/3/2.5, v/v/v) to accomplish complete recovery of lipidic profile (Lemine et al. 2014). However, the excessive solvent remained could be easily drained off by vacuum drying of both the organic phases including lipid extract. Additionally, the resultant extracted lipids were retained for better storage by dissolving in 200 ml of chloroform/methanol/water (60/30/4.5, v/v/v) or can be directly employed for further studies (Mahmoud and El-Bana 2013). All these type of procedures are appropriate for lipid extraction from all kinds of lipid-bearing cells, containing date pits (El-Sohaimy and Hafez 2010).

4.4.10 Hydrolysis of Lipids by Supercritical Transesterification

Transesterification is recognized as an efficient method to make lipids extracts in the form of solid and liquid fractions. Generally, in this method wet lipids fractions from date seeds are processed for lipids extraction followed by trans esterification. Briefly, wet lipids mass was retained in stainless steel reactors, submerged in isothermic fluidized bath for specific time followed by water cooling process (Shin et al. 2014). Continuous hydrolysis reaction between two reactors carried out, followed by drying of pits extract and again mixed with water in huge reactors and the reaction was persistent for 1 h at 250 °C. Repeatedly continuous dehydration and drying process transforms the wet lipidic biomass into compact fraction, consequently the appropriate filters were used under light vacuum conditions for efficient separation of aqueous and solids phase (Han et al. 2011). Additionally, the detailed experimental procedure was carried out for the determination of special effects resulted by reaction time, temperature, ethanol filling yield and crude biodiesel configuration. Although, the resulted seed oil was checked to verify its quality characteristics to meet the standards by using appropriate methods. Yet, the described process has to be verified for its commercial utilization for date pits (Zhao and Zhang 2013).

4.4.11 Hexane: Isopropanol (HIP) Lipid Extraction

The hexane based lipid extraction method was used to quantify the lipid contents found in tissues using mixed solvent as hexane and isopropanol, followed by washing of extract and removal of non-lipid residues using sodium sulphate solution. Various studies demonstrated the use of HIP method was better and offer less residual level of solvents in final product. Gravimetric methods were usually recognized as best methods for the determination of lipids content weight directly, however the hexane-isopropanol was considered to be efficient for polar lipids extraction (Shimada et al. 2014). Moreover, the basic advantages of gravimetric methods are: total fat measurement, more quantitative process, least equipment requirements, less workers required, simpler and easier to accomplish. However, this method have several limitations including less accuracy of lipid weight, compositional analysis of fats, lowest detection level of lipids. This method require shorter time and resemble Folch method that required much shorter time for oil extraction as compared to gravimetric and soxhlet method (Murphy 2012).

4.5 Future Perspectives

Date seeds are considered as byproducts of various date fruit industries. Numerous studies demonstrated the potential of date seeds as a source of edible oil. In addition to oil, some other nutritional constituents like dietary fiber, protein, minerals, phenolic that present in significant amount make date seeds as an effective functional food ingredient. Hence the potential usage of date seeds in numerous industries is favorable for developing value added products. Having favorable lipids and fatty acid profile in date pits, it is recommended to use it for development of nutraceutical products, as an edible cooking oil, and for formulation of different oil based products (margarines), because of its higher oxidative stability and thermal resisting properties and have good shelf life capabilities for extensive storage time period. Furthermore, as date seed oil possess unique unsaturation degree in comparison to other vegetable oils, therefore highly recommended as a vegetable oil substitutes in many food industries.

Besides possessing wide variety of applications date seed offers great number of challenges. As there are less information regarding date seed oils, more research studies are required for determination of oil safety regarding its use as important constituent in pharmaceutical and food industry for the development of edible and non-edible products. Additionally, there is great need to meet the challenges of using suitable extraction methods from date seeds to attain the high oil production. Although date pits are also accessible at very low or without any cost, so the seed pits oil extraction could be possible and possess important worth considerations on commercial level. As the date seeds are recognized as discarded byproducts and have possess high probability to be used as ingredients for various food products formulation, for extraction of beneficial bioactive components, water sanitization, and biomass production. However, the future research studies require to be concentrated on technological development for commercialized production and biomaterials specification for their safety concerns and functionality needs. Presently the systematic health entitlements regarding date pits are at its initial stages so more research studies are requires for establishment of their safety and efficiency. Different studies were demonstrated to extract the date pits extract using numerous solvents, though it is more essential to improve more technological advancements for oil and other bioactive components extracted compounds to be employed for cosmetics, pharmaceutical and food products.

4.6 Conclusion

The various functional components of Date palm *Phoenix dactylifera* L., and pits described in this chapter constitute promising alternatives to various other crops as it is recognized an oldest plant and cultured for its desirable fruit and pits in various Arab countries for centuries and also preferred because of its nutraceutical and economical benefits. Compared to date flesh, pits are highly recognized as an important source of dietary carbohydrates, proteins, fibers, antioxidant compounds, definite indispensable vitamins and minerals. Especially the lipid fraction of date pits constitute major portion along with higher amounts of beneficial oleic acid and lauric acid, however linoleic acid, palmitic acid and myristic acid were present in lower amounts respectively. The different extraction methods described here establish favorable alternates to recover date pit lipid fraction either using different solvents like hexane and petroleum ether or by using microwave and ultrasonic extraction. However, solvent extraction methods are less prefer because of excessive time consumption and usage of greater amount of solvents. Also the basic reason behind the less usage of organic solvents for oil extraction is highly related to the harmful effects associated with these compounds. Consequently, various type of modern technologies like microwave, expeller pressing and ultrasound extraction provide more benefits in terms of time and cost reduction, solvent consumption and power effectively. These methods could also improve stability of compounds to be extracted, process simplification, and quality and quantity of extraction and extract respectively.

An important drawback in the research studies of date oil extraction is the process scale-up, comprising the process cost and efficiency analysis. The most of the research studies regarding oil extraction from date seeds have been accomplished on lab scale. That out comes about a very little information regarding availability and development of this process on large scale. Consequently, additional studies should be conducted using greater amounts of date seeds biomass to analyses the oil extraction efficacy and to compared with results studies previously identified for lab-scale process.

References

Abbès F, Bouaziz MA, Blecker C, Masmoudi M, Attia H, Besbes S (2011) Date syrup: effect of hydrolytic enzymes (pectinase/cellulase) on physico-chemical characteristics, sensory and functional properties. LWT Food Sci Technol 44:1827–1834. https://doi.org/10.1016/j.lwt.2011.03.020

Abu-Qaoud H (2015) Date palm status and perspective in Palestine. In: Date palm genetic resources and utilization. Springer, Boca Raton, pp 423–439. https://doi.org/10.1007/978-94-017-9707-8

Agboola OS, Adejumo A (2013) Nutritional composition of the fruit of the Nigerian wild date palm, Phoenix dactylifera. World J Dairy Food Sci 8:196–200. https://doi.org/10.5829/idosi.wjdfs.2013.8.2.81178

Ahmad T, Danish M, Rafatullah M, Ghazali A, Sulaiman O, Hashim R, Ibrahim MNM (2012) The use of date palm as a potential adsorbent for wastewater treatment: a review. Environ Sci Pollut Res 19:1464–1484. https://doi.org/10.1007/s11356-011-0709-8

Ahmad A, Kaleem M, Ahmed Z, Shafiq H (2015) Therapeutic potential of flavonoids and their mechanism of action against microbial and viral infections – a review. Food Res Int 77:221–235. https://doi.org/10.1016/j.foodres.2015.06.021

Ahmad A, Irfan U, Amir RM, Abbasi KS (2017) Development of high energy cereal and nut granola bar. Int J Agric Bio Sci 1(3):13–20

Ahmed MJ, Theydan SK (2012) Equilibrium isotherms, kinetics and thermodynamics studies of phenolic compounds adsorption on palm-tree fruit stones. Ecotoxicol Environ Saf 84:39–45. https://doi.org/10.1016/j.ecoenv.2012.06.019

Akasha IA, Campbell L, Euston SR (2012) Extraction and characterisation of protein fraction from date palm fruit seeds. World Acad Sci Eng Technol 70:292–294. https://doi.org/10.1999/1307-6892/3421

Akbari M, Razavizadeh R, Mohebbi G, Barmak A (2012) Oil characteristics and fatty acid profile of seeds from three varieties of date palm (Phoenix dactylifera) cultivars in Bushehr-Iran. Afr J Biotechnol 11:12088–12093. https://doi.org/10.5897/AJB12.1084

Al-Alawi RA, Al-Mashiqri JH, Al-Nadabi JS, Al-Shihi BI, Baqi Y (2017) Date palm tree (Phoenix dactylifera L.): natural products and therapeutic options. Front Plant Sci 8:845. https://doi.org/10.3389/fpls.2017.00845

Al-Daihan S, Bhat RS (2012) Antibacterial activities of extracts of leaf, fruit, seed and bark of Phoenix dactylifera. Afr J Biotechnol 11:10021–10025. https://doi.org/10.5897/AJB11.4309

Al-Harrasi A, Rehman NU, Hussain J, Khan AL, Al-Rawahi A, Gilani SA, Al-Broumi M, Ali L (2014) Nutritional assessment and antioxidant analysis of 22 date palm (Phoenix dactylifera) varieties growing in Sultanate of Oman. Asian Pac J Trop Med 7:S591–S598. https://doi.org/10.1016/S1995-7645(14)60294-7

Al-Humaid A, Mousa H, El-Mergawi R, Abdel-Salam A (2010) Chemical composition and antioxidant activity of dates and dates-camel-milk mixtures as a protective meal against lipid peroxidation in rats. Am J Food Technol 5:22–30. https://doi.org/10.3923/ajft.2010.22.30

Al-Mssallem IS, Hu S, Zhang X, Lin Q, Liu W, Tan J, Yu X, Liu J, Pan L, Zhang T (2013) Genome sequence of the date palm Phoenix dactylifera L. Nat Commun 4:ncomms3274. https://doi.org/10.1038/ncomms3274

Al-Orf SM, Ahmed MH, Al-Atwai N, Al-Zaidi H, Dehwah A, Dehwah S (2012) Review: nutritional properties and benefits of the date fruits (Phoenix dactylifera L.). Bull Nat Nutr Inst Arab Rep Egypt 39:97. https://doi.org/10.9755/ejfa.2016-01-104

Amani MA, Davoudi MS, Tahvildari K, Nabavi SM, Davoudi MS (2013) Biodiesel production from Phoenix dactylifera as a new feedstock. Ind Crop Prod 43:40–43. https://doi.org/10.1016/j.indcrop.2012.06.024

Amarni F, Kadi H (2010) Kinetics study of microwave-assisted solvent extraction of oil from olive cake using hexane: comparison with the conventional extraction. Innov Food Sci Emerg Technol 11:322–327. https://doi.org/10.1016/j.ifset.2010.01.002

Assirey EAR (2015) Nutritional composition of fruit of 10 date palm (Phoenix dactylifera L.) cultivars grown in Saudi Arabia. J Taibah Univ Sci 9:75–79. https://doi.org/10.1016/j.jtusci.2014.07.002

Baliga MS, Baliga BRV, Kandathil SM, Bhat HP, Vayalil PK (2011) A review of the chemistry and pharmacology of the date fruits (Phoenix dactylifera L.). Food Res Int 44:1812–1822. https://doi.org/10.1016/j.foodres.2010.07.004

Basuny AMM, Al-Marzooq MA (2011) Production of mayonnaise from date pit oil. Food Nutr Sci 2:938. https://doi.org/10.4236/fns.2011.29128

Besbes S, Blecker C, Deroanne C, Drira N-E, Attia H (2004) Date seeds: chemical composition and characteristic profiles of the lipid fraction. Food Chem 84:577–584. https://doi.org/10.1016/S0308-8146(03)00281-4

Biglar M, Khanavi M, Hajimahmoodi M, Hassani S, Moghaddam G, Sadeghi N, Oveisi MR (2012) Tocopherol content and fatty acid profile of different Iranian date seed oils. Iran J Pharm Res IJPR 11:873

Boldor D, Kanitkar A, Terigar BG, Leonardi C, Lima M, Breitenbeck GA (2010) Microwave assisted extraction of biodiesel feedstock from the seeds of invasive Chinese tallow tree. Environ Sci Technol 44:4019–4025. https://doi.org/10.1021/es100143z

Bonsegna S, Bettini S, Pagano R, Zacheo A, Vergaro V, Giovinazzo G, Caminati G, Leporatti S, Valli L, Santino A (2011) Plant oil bodies: novel carriers to deliver lipophilic molecules. Appl Biochem Biotechnol 163:792–802. https://doi.org/10.1007/s12010-010-9083-0

Breil C, Meullemiestre A, Vian M, Chemat F (2016) Bio-based solvents for green extraction of lipids from oleaginous yeast biomass for sustainable aviation biofuel. Molecules 21:196. https://doi.org/10.3390/molecules21020196

Breil C, Abert Vian M, Zemb T, Kunz W, Chemat F (2017) "Bligh and dyer" and Folch methods for solid–liquid–liquid extraction of lipids from microorganisms. Comprehension of solvatation mechanisms and towards substitution with alternative solvents. Int J Mol Sci 18:708. https://doi.org/10.3390/ijms18040708

Camus G, Vogt DA, Kondratowicz AS, Ott M (2013) Lipid droplets and viral infections. Methods Cell Biol 116:167–190. https://doi.org/10.1016/B978-0-12-408051-5.00009-7. Elsevier

Chang W, Zhang M, Zheng S, Li Y, Li X, Li W, Li G, Lin Z, Xie Z, Zhao Z (2015) Trapping toxins within lipid droplets is a resistance mechanism in fungi. Sci Rep 5:15133. https://doi.org/10.1038/srep15133

Chemat F, Khan MK (2011) Applications of ultrasound in food technology: processing, preservation and extraction. Ultrason Sonochem 18:813–835. https://doi.org/10.1016/j.ultsonch.2010.11.023

Cooney M, Young G, Nagle N (2009) Extraction of bio-oils from microalgae. Sep Purif Rev 38:291–325. https://doi.org/10.1080/15422110903327919

Demirbaş A (2008) Production of biodiesel from algae oils. Energy Sources Part A Recover Util Environ Eff 31:163–168. https://doi.org/10.1080/15567030701521775

Deng G-F, Shen C, Xu X-R, Kuang R-D, Guo Y-J, Zeng L-S, Gao L-L, Lin X, Xie J-F, Xia E-Q (2012) Potential of fruit wastes as natural resources of bioactive compounds. Int J Mol Sci 13:8308–8323. https://doi.org/10.3390/ijms13078308

Eid NM, Al-Awadi B, Vauzour D, Oruna-Concha MJ, Spencer JP (2013) Effect of cultivar type and ripening on the polyphenol content of date palm fruit. J Agric Food Chem 61:2453–2460. https://doi.org/10.1021/jf303951e

El Arem A, Thouri A, Zekri M, Saafi EB, Ghrairi F, Zakhama A, Achour L (2014) Nephroprotective effect of date fruit extract against dichloroacetic acid exposure in adult rats. Food Chem Toxicol 65:177–184. https://doi.org/10.1016/j.fct.2013.12.023

Elbasheer EE, Abdalla RS, Elhussein AR, Gadkariem EA (2012) Physico-chemical characteristics of date seed oil grown In Sudan. Am J Appl Sci 9(7):993–999. https://doi.org/10.3844/ajassp.2012.993.999

El-Sharnouby GA, Al-Eid SM (2009) Utilization of enzymes in the production of liquid sugar from dates. Afr J Biochem Res 3:041–047. https://doi.org/10.5897/AJBR

El-Sohaimy S, Hafez E (2010) Biochemical and nutritional characterizations of date palm fruits (Phoenix dactylifera L.). J Appl Sci Res 6:1060–1067. https://doi.org/10.11648/j.ajls.20150304.14

Farooq M, Ramli A, Subbarao D (2013) Biodiesel production from waste cooking oil using bifunctional heterogeneous solid catalysts. J Clean Prod 59:131–140. https://doi.org/10.1016/j.jclepro.2013.06.015

Filipe A, McLauchlan J (2015) Hepatitis C virus and lipid droplets: finding a niche. Trends Mol Med 21:34–42. https://doi.org/10.1016/j.molmed.2014.11.003

Ghasemi NF, González González LM, Chan W, Schenk PM (2016) Progress on lipid extraction from wet algal biomass for biodiesel production. Microb Biotechnol 9:718–726. https://doi.org/10.1111/1751-7915.12360

Habib HM, Ibrahim WH (2009) Nutritional quality evaluation of eighteen date pit varieties. Int J Food Sci Nutr 60:99–111. https://doi.org/10.1080/09637480802314639

Habib HM, Platat C, Meudec E, Cheynier V, Ibrahim WH (2014) Polyphenolic compounds in date fruit seed (Phoenix dactylifera): characterisation and quantification by using UPLC-DAD-ESI-MS. J Sci Food Agric 94:1084–1089. https://doi.org/10.1002/jsfa.6387

Habibi-Najafi MB (2011) Date seeds: a novel and inexpensive source of dietary fiber. In: ICFEB 2011. pp 62-B018

Halaby MS, Farag MH, Gerges AH (2014) Potential effect of date pits fortified bread on diabetic rats. Int J Nutri Food Sci 3:49–59. https://doi.org/10.11648/j.ijnfs.20140302.16

Han Y, Wen Q, Chen Z, Li P (2011) Review of methods used for microalgal lipid-content analysis. Energy Procedia 12:944–950. https://doi.org/10.1016/j.egypro.2011.10.124

Hosikian A, Lim S, Halim R, Danquah MK (2010) Chlorophyll extraction from microalgae: a review on the process engineering aspects. Int J Chem Engg 2010:1–11. https://doi.org/10.1155/2010/391632

Hossain MZ, Waly MI, Singh V, Sequeira V, Rahman MS (2014) Chemical composition of date-pits and its potential for developing value-added product – a review. Pol J Food Nutri Sci 64:215–226. https://doi.org/10.4236/fns.2011.29128

Hounslow E, Noirel J, Gilmour DJ, Wright PC (2017) Lipid quantification techniques for screening oleaginous species of microalgae for biofuel production. Eur J Lipid Sci Technol 119:1500469. https://doi.org/10.1002/ejlt.201500469

Jassim SA, Naji MA (2010) In vitro evaluation of the antiviral activity of an extract of date palm (Phoenix dactylifera L.) pits on a Pseudomonas phage. Evid Based Complement Alternat Med 7:57–62. https://doi.org/10.1093/ecam/nem160

Johnson MB, Wen Z (2009) Production of biodiesel fuel from the microalga Schizochytrium limacinum by direct transesterification of algal biomass. Energy Fuel 23:5179–5183. https://doi.org/10.1021/ef900704h

Jones J, Manning S, Montoya M, Keller K, Poenie M (2012) Extraction of algal lipids and their analysis by HPLC and mass spectrometry. J Am Oil Chem Soc 89:1371–1381. https://doi.org/10.1007/s11746-012-2044-8

Juhaimi FA, Ghafoor K, Özcan MM (2014) Physicochemical properties and mineral contents of seven different date fruit (Phoenix dactylifera L.) varieties growing from Saudi Arabia. Environ Monit Assess 186:2165–2170. https://doi.org/10.1007/s10661-013-3526-3

Kaleem M, Ahmad A, Khalid S, Azam MT (2016) HPLC condition optimization for identification of flavonoids from Carissa opaca. Sci Int (Lahore) 28(1):343–348

Kelley LA, Mezulis S, Yates CM, Wass MN, Sternberg MJ (2015) The Phyre2 web portal for protein modeling, prediction and analysis. Nat Protoc 10:845. https://doi.org/10.1038/nprot.2015.053

Khalid S, Ahmad A, Masud T, Asad M, Sandhu M (2016) Nutritional assessment of Ajwa date flesh and pits in comparison to local varieties. J Plant Anim Sci 26:1072–1080

Khalid S, Khalid N, Khan RS, Ahmed H, Ahmad A (2017a) A review on chemistry and pharmacology of Ajwa date fruit and pit. Trends Food Sci Technol 63:60–69. https://doi.org/10.1016/j.tifs.2017.02.009

Khalid S, Ahmad A, Kaleem M (2017b) Antioxidant activity and phenolic contents of Ajwa date and their effect on lipo-protein profile. Funct Foods Health Dis 7(6):396–410. https://doi.org/10.31989/ffhd.v7i6.337

Kim Y-H, Choi Y-K, Park J, Lee S, Yang Y-H, Kim HJ, Park T-J, Kim YH, Lee SH (2012) Ionic liquid-mediated extraction of lipids from algal biomass. Bioresour Technol 109:312–315. https://doi.org/10.1016/j.biortech.2011.04.064

Kumar A, Negi YS, Choudhary V, Bhardwaj NK (2014) Characterization of cellulose nanocrystals produced by acid-hydrolysis from sugarcane bagasse as agro-waste. J Math Phys Chem 2:1–8. https://doi.org/10.12691/jmpc-2-1-1

Lee J-Y, Yoo C, Jun S-Y, Ahn C-Y, Oh H-M (2010) Comparison of several methods for effective lipid extraction from microalgae. Bioresour Technol 101:S75–S77. https://doi.org/10.1016/j.biortech.2009.03.058

Lee AK, Lewis DM, Ashman PJ (2012) Disruption of microalgal cells for the extraction of lipids for biofuels: processes and specific energy requirements. Biomass Bioenergy 46:89–101. https://doi.org/10.1016/j.biombioe.2012.06.034

Lemine FMM, Samb A, Zein el Abidine OB, Ahmed MVOM, Djeh T-KO, Boukhary AOMSO (2014) Assessment of physicochemical diversity in fruit of Mauritanian date palm (Phoenix dactylifera L.) cultivars. Afr J Agric Res 9:2167–2176. https://doi.org/10.5897/AJAR2013.8250

Mahmoud A, El-Bana H (2013) Evaluation of olive and palm byproducts in feeding camels. Pak J Nutr 12:879. https://doi.org/10.3923/pjn.2013.879.885

Murphy DJ (2012) The dynamic roles of intracellular lipid droplets: from archaea to mammals. Protoplasma 249:541–585. https://doi.org/10.1007/s00709-011-0329-7

Natunen K, Seppälä J, Schwenk D, Rischer H, Spilling K, Tamminen T (2015) Nile Red staining of phytoplankton neutral lipids: species-specific fluorescence kinetics in various solvents. J Appl Phycol 27:1161–1168. https://doi.org/10.1007/s10811-014-0404-5

Nigam PS, Singh A (2011) Production of liquid biofuels from renewable resources. Prog Energy Combust Sci 37:52–68. https://doi.org/10.1016/j.pecs.2010.01.003

Orabi SH, Shawky SM (2014) Effect of date palm (Phoenix dactylifera) seeds extracts on hematological, biochemical parameters and some fertility indices in male rats. Int J Sci Basic Appl Res 17:137–147. https://doi.org/10.3923/ajb.2014.119.130

Paranthaman R, Kumar PP, Kumaravel S (2012) HPLC and HPTLC determination of caffeine in raw and roasted date seeds (Phoenix dactylifera L). J Chromatogr Sep Tech 1:249–253. https://doi.org/10.1002/jsfa.6387

Parvin S, Easmin D, Sheikh A, Biswas M, Sharma SCD, Jahan MGS, Islam MA, Shovon M, Roy N (2015) Nutritional analysis of date fruits (Phoenix dactylifera L.) in perspective of Bangladesh. Am J Life Sci 3:274–278. https://doi.org/10.11648/j.ajls.20150304.14

Ranjith KR, Hanumantha Rao P, Arumugam M (2015) Lipid extraction methods from microalgae: a comprehensive review. Front Energy Res 2:61. https://doi.org/10.3389/fenrg.2014.00061

Reis A, Rudnitskaya A, Blackburn GJ, Fauzi NM, Pitt AR, Spickett CM (2013) A comparison of five lipid extraction solvent systems for lipidomic studies of human LDL. J Lipid Res 54:1812–1824. https://doi.org/10.1194/jlr.M034330

Rodrigo R, Libuy M, Feliu F, Hasson D (2014) Polyphenols in disease: from diet to supplements. Curr Pharm Biotechnol 15:304–317. https://doi.org/10.2174/138920101504140825113815

Rumin J, Bonnefond H, Saint-Jean B, Rouxel C, Sciandra A, Bernard O, Cadoret J-P, Bougaran G (2015) The use of fluorescent Nile red and BODIPY for lipid measurement in microalgae. Biotechnol Biofuels 8:42. https://doi.org/10.1186/s13068-015-0220-4

Saafi-Ben Salah EB, Flamini G, El Arem A, Issaoui M, Dabbou S, BenYahia L, Ferchichi A, Hammami M, Achour L (2012) Compositional characteristics and aromatic profile of date palm seeds from seven varieties grown in Tunisia. Int J Food Sci Technol 47:1903–1908. https://doi.org/10.1111/j.1365-2621.2012.03049.x

Sadiq I, Izuagie T, Shuaibu M, Dogoyaro A, Garba A, Abubakar S (2013) The nutritional evaluation and medicinal value of date palm (Phoenix dactylifera). Int J Mod Chem 4:147–154

Salah EBS-B, El Arem A, Louedi M, Saoudi M, Elfeki A, Zakhama A, Najjar MF, Hammami M, Achour L (2012) Antioxidant-rich date palm fruit extract inhibits oxidative stress and nephrotoxicity induced by dimethoate in rat. J Physiol Biochem 68:47–58. https://doi.org/10.1007/s13105-011-0118-y

Saleh EA, Tawfik MS, Abu-Tarboush HM (2011) Phenolic contents and antioxidant activity of various date palm (Phoenix dactylifera L.) fruits from Saudi Arabia. Food Nutr Sci 2:1134. https://doi.org/10.4236/fns.2011.210152

Samad MA, Hashim SH, Simarani K, Yaacob JS (2016) Antibacterial properties and effects of fruit chilling and extract storage on antioxidant activity, total phenolic and anthocyanin content of four date palm (Phoenix dactylifera) cultivars. Molecules 21:419. https://doi.org/10.3390/molecules21040419

Saura-Calixto F (2012) Concept and health-related properties of nonextractable polyphenols: the missing dietary polyphenols. J Agric Food Chem 60:11195–11200. https://doi.org/10.1021/jf303758j

Sheng J, Vannela R, Rittmann BE (2011) Evaluation of methods to extract and quantify lipids from Synechocystis PCC 6803. Bioresour Technol 102:1697–1703. https://doi.org/10.1016/j.biortech.2010.08.007

Shimada TL, Takano Y, Shimada T, Fujiwara M, Fukao Y, Mori M, Okazaki Y, Saito K, Sasaki R, Aoki K (2014) Leaf oil body functions as a subcellular factory for the production of a phytoalexin in Arabidopsis. Plant Physiol 164:105–118. https://doi.org/10.1104/pp.113.230185

Shin H-Y, Ryu J-H, Bae S-Y, Crofcheck C, Crocker M (2014) Lipid extraction from Scenedesmus sp. microalgae for biodiesel production using hot compressed hexane. Fuel 130:66–69. https://doi.org/10.1016/j.fuel.2014.04.023

Sitepu I, Ignatia L, Franz A, Wong D, Faulina S, Tsui M, Kanti A, Boundy-Mills K (2012) An improved high-throughput Nile red fluorescence assay for estimating intracellular lipids in a variety of yeast species. J Microbiol Methods 91:321–328. https://doi.org/10.1016/j.mimet.2012.09.001

Šoštarič M, Klinar D, Bricelj M, Golob J, Berovič M, Likozar B (2012) Growth, lipid extraction and thermal degradation of the microalga Chlorella vulgaris. New Biotechnol 29:325–331. https://doi.org/10.1016/j.nbt.2011.12.002

Sun X, Lu C, Zhang W, Tian D, Zhang X (2013) Acetone-soluble cellulose acetate extracted from waste blended fabrics via ionic liquid catalyzed acetylation. Carbohydr Polym 98:405–411. https://doi.org/10.1016/j.carbpol.2013.05.089

Suresh S, Guizani N, Al-Ruzeiki M, Al-Hadhrami A, Al-Dohani H, Al-Kindi I, Rahman MS (2013) Thermal characteristics, chemical composition and polyphenol contents of date-pits powder. J Food Eng 119:668–679. https://doi.org/10.1016/j.jfoodeng.2013.06.026

Takeshita T, Takeda K, Ota S, Yamazaki T, Kawano S (2015) A simple method for measuring the starch and lipid contents in the cell of microalgae. Cytologia 80:475–481. https://doi.org/10.1508/cytologia.80.475

Ullah SR, Murphy B, Dorich B, Richter B, Srinivasan K (2011) Fat extraction from acid-and base-hydrolyzed food samples using accelerated solvent extraction. J Agric Food Chem 59:2169–2174. https://doi.org/10.1021/jf104001d

Umate P (2012) Comparative genomics of the lipid-body-membrane proteins oleosin, caleosin and steroleosin in magnoliophyte, lycophyte and bryophyte. Genomics Proteomics Bioinformatics 10:345–353. https://doi.org/10.1016/j.gpb.2012.08.006

Vayalil PK (2012) Date fruits (Phoenix dactylifera Linn): an emerging medicinal food. Crit Rev Food Sci Nutr 52:249–271. https://doi.org/10.1080/10408398.2010.499824

Wahlroos T, Soukka J, Denesyuk A, Susi P (2015) Amino-terminus of oleosin protein defines the size of oil bodies-topological model of oleosin-oil body complex. J Plant Biochem Physiol 3:155. https://doi.org/10.4172/2329-9029.1000155

Waly MI, Al-Ghafri BR, Guizani N, Rahman MS (2015) Phytonutrient effects of date pit extract against azoxymethane-induced oxidative stress in the rat colon. Asian Pac J Cancer Prev 16:3473–3477. https://doi.org/10.7314/APJCP.2015.16.8.3473

Wang W, Wu Z, Dai Z, Yang Y, Wang J, Wu G (2013) Glycine metabolism in animals and humans: implications for nutrition and health. Amino Acids 45:463–477. https://doi.org/10.1007/s00726-013-1493-1

Yaish MW, Kumar PP (2015) Salt tolerance research in date palm tree (Phoenix dactylifera L.), past, present, and future perspectives. Front Plant Sci 6:348. https://doi.org/10.3389/fpls.2015.00348

Yao L, Schaich K (2015) Accelerated solvent extraction improves efficiency of lipid removal from dry pet food while limiting lipid oxidation. J Am Oil Chem Soc 92:141–151. https://doi.org/10.1007/s11746-014-2568-1

Zhang C-R, Aldosari SA, Vidyasagar PS, Nair KM, Nair MG (2013) Antioxidant and anti-inflammatory assays confirm bioactive compounds in Ajwa date fruit. J Agric Food Chem 61:5834–5840. https://doi.org/10.1021/jf401371v

Zhao S, Zhang D (2013) A parametric study of supercritical carbon dioxide extraction of oil from Moringa oleifera seeds using a response surface methodology. Sep Purif Technol 113:9–17. https://doi.org/10.1016/j.seppur.2013.03.041

Chapter 5
Biogas Production from Date Palm Fruits

P. Senthil Kumar and C. Femina Carolin

Abstract In order to explore the renewable energy resources like biogas, there is a need to find the appropriate feedstock to avoid the depletion of fossil fuels and environmental deterioration. Date palm fruit is a suitable raw material with health promising features. Palm fruits also have the capability to produce biogas at a high quantity. Anaerobic digestion of palm fruit is a most valuable technique that has been evaluated as a promising feedstock to generate biogas like methane. In the event of biogas production, the anaerobic procedure assumes an essential part which gives higher help to the high amount of biogas generation. It is generally connected for the treatment of organic waste like palm natural products because of its high natural substance which helps in the generation of biogas.

This chapter features the elements which impacting or influencing the anaerobic procedure and different kind of anaerobic reactors, for example, continuous stirred tank reactors, anaerobic filtration, anaerobic fluidized bed reactors, anaerobic contact process, upflow anaerobic sludge blanket reactors and so forth used for the methane gas generation. These reactors are organic procedures that have been disclosed to upgrade the biogas generation. This chapter also depicts the potential for biogas production from date palm fruit and additionally it reveals the upsides and obstacles for anaerobic digestion technology. Procedures to additionally enhance these methodologies alongside future research are outlined in this chapter.

Keywords Renewable energy · Biogas · Palm fruits · Anaerobic digestion · Continuous stirred tank reactors · Anaerobic filtration · Anaerobic contact process

5.1 Introduction

Date palm (*Phoenix dactylifera*) is an essential antiquated monocots plant in the Saudi Arabia. It is made up of various natural products including leaves and seeds. Date palm parts are highly utilized in date creation and their primary utilization are to

P. Senthil Kumar (✉) · C. Femina Carolin
Department of Chemical Engineering, SSN College of Engineering, Chennai, India
e-mail: senthilchem8582@gmail.com

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_5

enhance organic matter of soil (Alananbeh et al. 2014). Date palm tree is an imperative tree for dry areas of the word, and it has constantly assumed an essential part in the social existences of the general population (Elluech et al. 2008). World date fruit generation achieved in excess of 7.7 million tons in 2014. An expected 12 million tons of date palm waste comprising of date palm trunk, fronds (stems and leaves), date flesh, and seeds are created on the planet consistently. The product of the date palm is one of the wealthiest natural product based wellsprings of protein. Date palm is one of the major natural products delivered in moisture free districts. It is a critical business edit in various districts of the world and is viewed as the third generally essential palm species in the worldwide farming industry, after coconut. The seeds of the date organic product, which are discarded after the date preparing, additionally contain 5–7% protein by weight. Various attempts were tried to utilize the date waste in a useful way. It produces a fruit date that is appreciated in all parts of the world. Because of this reasons the worldwide interest for dates and in addition its generation keeps on increasing. The present chapter is based on the efforts to extract energy from date palm fruit as methane-rich biogas.

5.1.1 Properties and Characteristics of Date Palm Fruit

Date palm fruit has an important part due to the upsides like agricultural, food providing, therapeutic, profitable, architectural, environmental characteristics and their various applications. As of late, this organic product has picked up noteworthy significance in worldwide business also. Amid the most recent two centuries, the world generation of dates has dramatically increased. Date organic products (*Phoenix dactylifra*) are of extraordinary significance in human sustenance attributable to their high substance of fundamental supplements, which incorporate various biomolecules (Lattieff 2016). Dates are rich in specific supplements and give a wellspring of quick vitality because of their high sugar content (70–80%). The vast majority of the sugars in dates are as fructose and glucose, which are effectively consumed by the human body. It has been built up that the date palm fruit product has different therapeutic properties like cancer prevention agent, antimutagenic, antioxidant, antimicrobial. The date organic product is recorded in society solutions for the treatment of different irresistible illnesses and cancer. Customarily they are utilized for sustenance, or to deliver desserts, sweet syrup (Dibs in Arabic), vinegar and alcoholic items. Sugars are the real substance components of the date, for the most part including glucose, fructose and little measures of cellulose and starch. The high health giving sugars of date palm squanders are great hotspots for organism maturation potential toward bio-energy creation (Gupta and Kushwaha 2011). The real parts of date palm biomass are cellulose, hemicelluloses and lignin. Additionally, date palm has high unstable solids substance and low humidity.

5.1.2 Global Production

Date palm is one of the primary rural items in the Middle East also. The date palm *Phoenix dactylifera*, a tropical and subtropical tree, having a place with the family Palmae (Arecaceae) is one of humankind's most established developed plants. It has assumed an essential part in the everyday existence of the general population throughout the previous 7000 years. Tons of dates are generating from million date palm trees per year excluding secondary products like palm midribs, leaves, stems, fronds and coir. The generation of date palm fruits has been raised from 2.3 million tons in 1974 to 7.6 million tons in 2010. The heft of this yield comes, in a specific order, from Iraq, Egypt, Saudi Arabia, Iran, United Arab Emirates, Pakistan, Algeria, Sudan, Libya, and Tunisia (Bhansali 2010). The Arab world has in excess of 84 million date palm trees with the greater part in Egypt, Iraq, Saudi Arabia, Iran, Algeria, Morocco, Tunisia and the United Arab Emirates. In Iraq, nine million trees cover the center and southern parts of the nation, bringing about a surplus generation of dates also, other optional biomass. It is created to a great extent in the hot dry locales of the world especially in Gulf Cooperation Council (GCC) nations, and Saudi Arabia is one of the world's significant maker of dates. The availability of date palm trees in Saudi Arabia is about 23 million trees, which deliver about 780,000 tons of dates for every year (Al-Abdoulhadi et al. 2011). Dates creation in Saudi Arabia incredibly expanded for the previous two centuries and is likewise paralleled by high utilization. *P. dactylifera* is the essential yield in Oman, which transfers 82% of all organic product crops creation in the nation. Algeria produces in excess of 400 distinct assortments of dates with a yearly creation of more than 400,000 tons.

5.1.3 Feedstocks of Biogas Production

The target on biogas production through better feedstock is increasing. The things like difficulties of inefficient biogas yield, high maintenance time, and high operating cost obstruct the most extreme execution of biogas creation in the anaerobic digestion process. These restrictions are profoundly reliant upon the accessibility, synthesis, and degradability of the feedstock utilized for biogas generation. The extraordinary potential lies in biogas generation from different feedstocks, for example, crop residues, livestock residues, municipal waste, landfill waste, food waste, and lignocellulosic feedstocks in light of their accessibility and plenitude. Nonetheless, the greater part of these feedstocks has moderate corruption rates and in that capacity requires longer maintenance times. Moreover, a portion of these feedstocks contains harmful intermediates or contain harmful mixes, which repress the biogas generation process. Biogas can be delivered from locally accessible natural source by anaerobic processing. Locally accessible waste items for biogas generation include solid waste; sludge; and date palm wastes. Biogas is commonly created just from source that are effortlessly used by the microbial group in charge of changing these feedstocks into biogas. The improvement of imaginative innovations going for the usage of feedstocks that are promptly accessible however not effectively degradable would bring about an expansion in biogas creation. The real reasons why a few feedstocks are not perfect for biogas creation are: (a) they can't be processed by microbes, (b) assimilation by microbes is extremely troublesome to accomplish, (c) assimilation could be accomplished however in a moderate manner, and (d) the availability of inhibitors in the feedstock or the creation of inhibitory mixes amid microbial debasement.

5.1.4 Date Palm Fruit as a Main Source

Among the extraordinary types of inexhaustible feedstocks, biomass is without a doubt a standout amongst the most encouraging (Messineo et al. 2012). Around 16% of worldwide last vitality utilization originates from inexhaustible assets, with 10% of all vitality from customary biomass, essentially utilized for warming, and 3.4% from hydroelectricity. The biomass can be used for improving the quality of soil after proper treatment (Converti et al. 1999). The biogas quality depends on the type of waste material, characteristics of the material and also the fermenting conditions. The nature of biogas created by natural waste materials does not stay steady but rather shifts with the time of assimilation. An extensive variety of warm and biochemical innovations are available to change over the energy put away in date palm biomass to helpful types of energy. Due to the availability of moisture free in the date palm fruits, it is well appropriate for the thermal treatment like combustion, gasification and pyrolysis. Then again, the huge unpredictable solids in date palm biomass demonstrates its probability towards biogas creation in anaerobic absorption plants, conceivably by co-digestion with sludge, animal wastes and food wastes. By the fermentation process, the carbohydrate content of date palm fruits can be converted into a biofuel. Various researches have been carried out the co-digestion process of agro waste for biogas production. *Phoenix dactylifera* has assumed a critical part of the everyday existence of the general population for the last 7000 years. Today overall generation, use and industrialization of dates are consistently expanding because date natural products have acquired incredible significance in human nourishment attributable to their rich substance of fundamental supplements. The current investigation, intended to evaluate out of the biogas generation from date palm source.

5.2 Biogas Generation

In the current decades, creation and utilization of biogas have pulled in particular consideration in view of vitality deficiency and rising costs of fuel in bringing in nations. In later a long time, administrations of India and China have started far-reaching endeavors to create biogas to manage the quick increment of the imported oil value. Biogas creation from natural waste items is a good choice since it joins both energy recovery and waste administration (Radeef et al. 2016). Biogas can be used for on-location warm vitality and power. Biogas speaks to a standout amongst the most very refreshing openings to use certain classifications of biomass to satisfy in part the earth vitality needs. Biogas normally alludes to a blend of gases delivered through the natural disruption of natural matter in the nonappearance of oxygen. The resultant vitality discharge permits biogas to be utilized as a biofuel to replace ordinary fossil vitality sources (coal, oil, flammable gas) in power and warmth generation, and furthermore as an adaptable sustainable power source to fuel vehicle. It also used to replace the diesel generated and local grid power. The generated biogas can be utilized for warm age, and after that sold to the next adjacent industrial facility. The part of biogas generation and catching innovation should be considered also. The establishment and working of biogas creation frameworks can give numerous advantages to clients and the more extensive group. Focal points incorporate vitality manageability, asset protection and natural preservation. The high use of reducing petroleum derivatives is considered unsustainable in view of their fewer source and nonrenewable nature. Biogas got from different natural sources can decrease the overwhelming reliance on these draining common assets and address the vitality weakness worries because of its inexhaustible (He et al. 2012). A few reports show that anaerobic process of the natural division of strong waste gives hopeful measures of biogas. Biogas is for the most part made out of 48–65% methane, 36–41% carbon dioxide, up to 17% nitrogen, <1% oxygen, 32–169 ppm hydrogen sulfide and hints of different gases (Ward et al. 2008). Not at all like a petroleum product, does biogas not contribute much to the environmental impact, ozone consumption or corrosive rain (Nath and Das 2004). This is one of the fundamental causes that anaerobic processing is an extremely vital part in addressing vitality difficulties of the future generations. The valorization of the created biogas is that it is vitality effective because of the low outflow of risky contaminations, for instance, volatile organic compounds (VOC) (Appels et al. 2011).

5.3 Anaerobic Digestion Process

Enthusiasm for anaerobic digestion (AD) has been consistently developing in the course of the most recent decades, being increasingly as often as possible advanced by national projects for vitality generation from inexhaustible assets. Anaerobic assimilation is an innovation confronting developing regards and expansive uses (Clarke and Alibardi 2010; Levis et al. 2010). Anaerobic assimilation is thought to be an eco-compelling innovation since it produces sustainable power source as methane, and furthermore decreases the discharge of ozone-harming substances by means of the biogas recovery (Kaewmai et al. 2013). Anaerobic Digestion (AD) is a natural procedure, which diminishes natural contamination and produces sustainable power source (biogas). This sort of bioprocess is viewed as an elective vitality source to non-renewable energy source. The capacity of anaerobic digestion process has identified newly which has the potential to convert biologically the hydrogen and carbon-di-oxide of sources into methane storage uses (Burkhardt et al. 2015). The high biodegradability and dampness substance of food waste are perfect attributes for biogas generation and digestate are utilized for conditioning the soil or as supplement feedstock. Biogas creation through anaerobic absorption innovation has progressed massively throughout the years. Because of high energy request and ecological worries as the total population expands, the drive for anaerobic digestion is inside research and the business for manageable energy. Anaerobic assimilation has been a standout amongst the most generally utilized handled for the adjustment of biosolid waste, for example, from the agro and civil waste to modern waste. In order to boost its effectiveness, anaerobic assimilation is currently generally utilized at fullscale to debase different natural feedstocks.

Anaerobic digestion is exceptionally ideal because of its ability of vitality recuperation by transformation of solids into biogas, odor decrease, and disposal of pathogens and mass decrease of solids. In anaerobic digestion, the organic biodegradable material is corrupted by microbes under conditions without oxygen, where biogas is delivered normally. Biogas is included for the most part 60–70% CH_4, 30–40% CO_2 and low measures of other trace gases. It incorporates assorted types of anaerobic microbes, which are in charge of the corruption of organic compounds and need time to adjust to the new condition before they begin to devour on organic matter to develop. To create biogas from absorbable materials by anaerobic absorption, the decay of natural squanders happens in four procedures at the same time: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Yang et al. 2015a, b). Steps associated with the anaerobic digestion process are indicated in the Fig. 5.1. Controlling these phases in an appropriate way of balance between their rates prompts the gas production to higher. Hydrolysis is a basic rate constraining procedure which corrupts insoluble natural materials, for example, lipids, polysaccharides, proteins and cellulose into its spine constituents (e.g. fatty acids furthermore, amino acids). The products from hydrolysis process are additionally separated into hydrogen (H_2, CO_2, acetic acid derivatives and volatile fatty acid (VFA) by acidogenesis process and further these products get converted in another product which is utilized for methanogenesis. In the next step, VFAs are processed to create acetic acid derivatives and H_2 by H_2 creating microbes/acetogens. In the last process where CH_4 is produced by an assortment of methanogenic microscopic organisms. The proficiency of this framework primarily relies upon the structure of the microbial group and natural variables, for instance, pH and temperature (Weiland 2010). The different gatherings of microscopic organisms taking part in the anaerobic

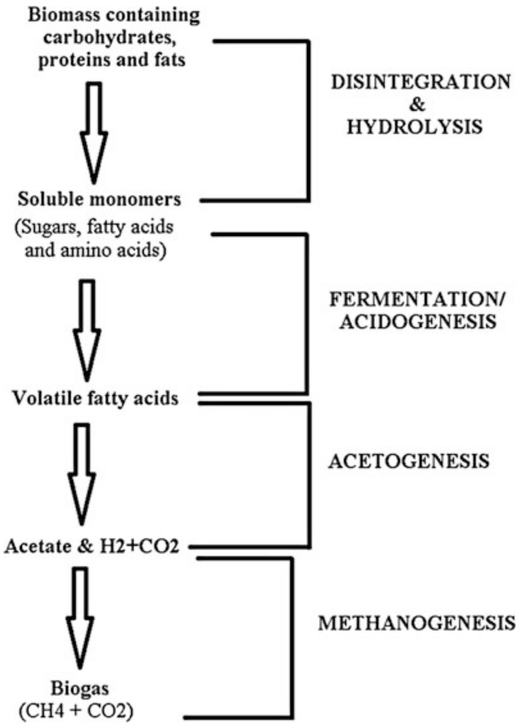


Fig. 5.1 Steps involved in the anaerobic digestion process

digestion have diverse ideal pH extents and large guarantee of effective assimilation and gas generation. The procedure of biogas age from strong natural waste is frequently completed by a few distinctive anaerobic microorganisms.

The procedure of acidogenesis also, methanogenesis need diverse pH for ideal process control. Acidogenic microbes are less delicate and just require pH over 5, while methanogenic microbes are more suitable at pH range of 6.5–7.2 (Kathirvale et al. 2004; Appels et al. 2008). Hence, the ideal pH extend is 6.8–7.4 where both the microbes gathering can coincide. The VFAs produced amid the anaerobic processing prompts the decrement in the pH. However, it can be countered by the creation of alkalinity as carbon dioxide, ammonia furthermore, bicarbonate by the methanogenesis microbes. The methane-producing process needs separate degradation phases to be executed by the bacteria fermentative bacteria, syntrophic acetogens, homoacetogens, hydrogenetrophic methanogens and aceticlastic methanogens. The relationship among the above mentioned microbes adds to proficient anaerobic digestion and biogas creation (Weiland 2010). The last stage, directed by methane forming microorganisms, is the most essential phase in biogas creation where the methanogens change over their essential substrates including acetic acid derivation, hydrogen and carbon dioxide into methane. In methane development pathway, 75% of methane generation gets from decarboxylation of acetic acid derivation and 25% begins from CO_2 and H_2.

The board utilization of this innovation originates from its potential preferences methanogenic procedure of anaerobic processing, and additionally on biodegradability. To detoxify the phenolic compounds, pretreatment was found to be necessary. A wide assortment of anaerobic frameworks has been created to particularly treat squander anaerobically. Anaerobic assimilation in this way speaks to an adaptable procedure that can be utilized as conclusive change process in a biorefinery chain for every one of those substrates furthermore, remaining streams not further convertible to high esteem items. Including, the generation of methane, a decrease of 30– half of the waste volume requiring extreme transfer, and a rate of pathogen obliteration, especially in the thermophilic procedure. The execution of the anaerobic procedures can be restricted by the inhibitory impacts of the phenolic mixes exhibit in palm effluent. Some straightforward phenolic mixes and polyphenols inhibitory affect both general anaerobic assimilation and on the

5.3.1 Factors Affecting Anaerobic Digestion Process

Anaerobic digestion, a microbial-subordinate organic process, is exceedingly subject to the presence of great environment to survive and process. Accordingly, the microbial groups will be straightforwardly influenced by the feedstock properties. This is on account of the feedstock, which assumes a part as the nourishment to be processed by the microorganisms, includes the significant living conditions inside the anaerobic assimilation framework. The microorganisms that take an interest in the process might be particular for each debasement step and in this manner could have distinctive ecological necessities. The anaerobic assimilation of natural material is a difficult process, including various diverse debasement steps. For the most part, the natural factors have a range, ideal esteem or pattern to take after for having a fruitful anaerobic assimilation process. Subsequently, the exploration techniques which had been and to be done for enhancing the biogas generation in view of the ecological variables will have a correct pathway to approach. Other than the natural factors, the cautious operational ability will be required with a specific end goal to guarantee a steady and fruitful anaerobic processing framework to work successfully and consistently. The biogas yield is influenced by numerous elements includes type and creation of substrate, microbial arrangement, temperature, pH, biodegradability and nutrient content. The factors influencing and affecting the anaerobic digestion are well explained in this chapter. Diminish in biogas generation was seen on account of fruit also, vegetable waste because of fast fermentation of these squanders, bringing about a bringing down of the pH in the bioreactor. Besides, the creation of bigger unstable unsaturated fats from such waste under anaerobic conditions restrains the action of methanogenic microbes. The expansion of co-substrates, for example, abattoir waste and sludge of fruit and vegetable waste stimulate the biogas generation under anaerobic conditions. In the meantime, these central understandings supported different of biogas generation upgrade techniques.

5.3.1.1 Temperature

Numerous analysts have announced noteworthy impacts of temperature on the microbial group, process energy and dependability also, methane yield. Temperature is an imperative parameter that significantly impacts anaerobic procedures. The working temperature is the main factor of the population of microbes' presence, particularly the assorted variety of the methanogen group in the anaerobic reactor (Leven et al. 2007). Underneath temperatures amid the procedure are known to diminish microbe development, substrate use, rates, and biogas generation (Trzcinski and Stuckey 2010). In addition, low temperatures may likewise bring about a release of cell vitality, a spillage of intracellular substances or on the other hand entire lysis Conversely, high temperatures bring down biogas yield because of the creation of unstable gases, for example, ammonia which stifles methanogenic exercises (Fezzani and Cheikh 2010). Based on the three diverse temperature ranges namely psychrophilic (0–20 °C), mesophilic (20–42 °C) and thermophilic (42–75 °C), the anaerobic digestion process delivers the biogas. There are two regular temperature levels connected in the traditional anaerobic assimilation, which are mesophilic and thermophilic temperatures. Both temperature ranges have upsides and downsides from various viewpoints. Mesophilic anaerobic digestion has higher stability than the thermophilic. This can be clarified there is more differing microbial group can be found in mesophilic (37 °C) bioreactor. It moderately lower volume of biogas and will bring down volume loading compared with thermophilic anaerobic assimilation. The task in the mesophilic extend is more steady and requires a little vitality cost (Fernandez et al. 2008). Despite the fact that thermophilic anaerobic assimilation can accomplish higher natural substance corruption, it is constantly identified with the issue of the delicate process with inclined unstable unsaturated fat gathering. Other than that, there was a contention as far as vitality discussion because of the lower methane content had been created by a thermophilic reactor. Generally speaking, a temperature extends between 35– 37 °C is viewed as reasonable for the creation of methane and a change from mesophilic to thermophilic temperatures can cause a sharp reduction in biogas creation until the fundamental population has expanded in number. Thermophilic are known to have a rate-advantage over the others because of a quicker response time and higher volumetric stacking rate, and accordingly exhibiting higher biogas efficiency. Psychrophilic are in huge consideration especially as far as creating biogas from low-quality wastewaters.

5.3.1.2 The pH

A basic parameter which impacts the methanogens and which directly affects the biogas and methane generation. Most anaerobic frameworks work at close unbiased pH since methane aging happens inside the pH 6.5 e8.5 territories with the ideal range from 7.0 to 8.0. Through neutralization process, the pH range was maintained that need excessive utilization of chemicals, for example, sodium carbonate/bicarbonate or calcium carbonate since a few streams have outrageous pH esteems, and hydrolysis also, acidogenesis stages will diminish pH esteems. Extraordinary pH conditions amid anaerobic activity can't just furious natural execution and methane yield yet additionally influence film porousness and life expectancy. The methanogens are powerless to the encompassing pH esteem, which just can survive only under pH scope of 6.5–7.8. A scope of pH esteems appropriate for anaerobic assimilation has been revealed by different specialists, however, the ideal pH for methanogenesis has been observed to be around 7.0.

5.3.1.3 Nutrient Content

The most essential wholesome substance, for example, carbon and nitrogen are basic to help the anaerobic organic process. Nitrogen is fundamental for protein union and basically needed as a supplement by the microbes in the anaerobic reactors. Nitrogenous mixes in the natural squander are normally proteins which are changed over to ammonium by anaerobic processing (Sawayama et al. 2004). As ammonium, nitrogen adds to the adjustment of the pH esteem in the bioreactor where the procedure is occurring. The stability between carbon and nitrogen substance will be needed for a natural assimilation framework, which is usually depicted as carbon to nitrogen (C/N) proportion. The C/N proportion in the natural material assumes a vital part in anaerobic processing. The unequal supplements are viewed as a critical factor constraining anaerobic processing of natural squanders. Moderate debasement will be experienced when C/N proportion is too high, while the other way around will cause the gathering of the inhibitors, for example, alkali. For the generation of new cell mass microorganisms acclimatize ammonium. Smelling salts in high focus may prompt the hindrance of the natural procedure also, it restrains methanogenesis. For the change of nourishment and C/N proportions, co-absorption of natural blends are utilized (Cuetos et al. 2008).

5.3.1.4 Substrate Characteristics

Not a wide range of substrate is appropriate for experiencing the anaerobic assimilation, particularly when the biogas generation is the objective. For case, the poor mass exchange because of the lower water content, imbalance of nutrients and lower biodegradability. The rate of anaerobic processing is emphatically influenced by the sort, accessibility and nature of the substrate (Zhao et al. 2010). Distinctive sorts of carbon source support diverse gatherings of organisms. Before beginning an anaerobic procedure, the substrate must be portrayed for starch, lipid, protein also, fiber substance. The substrate ought to likewise be portrayed for the amount of methane that can conceivably be delivered under anaerobic conditions. Contrasted with lignocellulosic biomass, date palm fruit is substantially more desirable to be processed anaerobically due to its good characteristics. Other than of C/N proportion, COD: N: Phosphorus (P) proportion had additionally been expected to keep up the digester activity (Annachhatre 1996). The prerequisites of different components as large-scale and micronutrient must be considered too. Sugars are viewed as the most imperative natural segment of municipal waste for biogas creation. Starch could go about as a compelling minimal effort substrate for biogas generation contrasted with sucrose and glucose (Su et al. 2009). The strong substance of the substrate in the bioreactor can essentially influence the execution of the procedure and the measure of methane delivered during the process.

5.3.1.5 Biodegradability

The biodegradability of the organic matter by the microbes is one of the major variables for a successful anaerobic assimilation process. It will specifically impact the rate of substrate use by primarily restricting the procedure of hydrolysis. This is generally portrayed as the biodegradability, which is significantly reliant on the constituents of the substrate. The water content basically restricts the mass exchange and organic matter solubilization inside the digester framework. In this way, the anaerobic assimilation of the high strong substrate will experience more difficulties and issues. Next, the unpredictability of substrate constituents, for example, the sugars, proteins, and lipids, will decide the biodegradability essentially. Moreover, the degradation of non-structural carbohydrates, lipids, proteins are more difficult to degrade due to its strong chemical bonding. Henceforth, the carbohydrate pretreatment or anaerobic digestion for a superior biogas generation. Other than that, the substrate with huge content of lipids (fat) was observed to be corrupted slower due to the availability of long-chain unsaturated fats (LCFAs).

5.3.1.6 Biomass Retention

Biomass maintenance is one of the basic observing factors for anaerobic assimilation. For this, the most widely recognized method is to decide the population of microbes in an anaerobic reactor by which it is particularly depicted as mixed liquor volatile suspended solids (MLVSS).

5.4 Anaerobic Reactors

Anaerobic bioreactors have significant use for quick processing of strong natural waste constituents to decrease the ecological stack (Agdag and Sponza 2007). Bioreactor configuration has been found to apply a strong effect on the execution of a digester. an assortment of new bioreactor plans has been produced lately, which encourage a fundamentally higher rate of response for the treatment of food waste. Favorable position of anaerobic waste treatment frameworks as means for the recuperation of non-regular vitality is progressively being perceived around the world. Anaerobic deterioration is an organically intervened process, indigenous to nature, and fit for treating squanders radiating from civil, agriculture, and modern exercises. These prompted improvement of different reactors, which are equipped for holding a considerably higher biomass focus than customary digesters. It is hard to assess the focal points and weaknesses of every framework in connection with other ideas. The most well-known anaerobic reactors are Anaerobic sequencing batch bioreactor, Anaerobic filtration, Plug flow reactor, Continuous stirred tank reactors, Lagoon system, Anaerobic fluidized bed reactor, up-flow anaerobic sludge blanket reactor, Anaerobic contact digester. This chapter discuss the anaerobic digestion strategy for the improvement of production biogas through date palm fruit waste. The methodology must be applicable and possible, and this will require a solid comprehension of the compelling elements of biogas generation by anaerobic digestion.

5.4.1 Anaerobic Filtration

The primary showing of this treatment framework originated from Young and McCarty, who productively worked an up-flow anaerobic channel to treat the rum refinery wastewater. It is widely in scale studies for the treatment of palm waste materials. Channel clogging is a noteworthy issue in the activity of anaerobic channels. Anaerobic filtration contains a channel medium where anaerobic microbial population—life forms that live without oxygen—can build up themselves. Such channels are generally used in the wastewater treatment. Such channels are generally utilized in the treatment of wastewater. An anaerobic channel is an anaerobic reactor with at least one filtration chambers in the arrangement. The principal anaerobic channels outlined utilized characteristic materials as help media, for example, stone and rock. These had a low voidage and obstructed with biomass and solids quickly. Plastic raschig rings were used in which the increase the time interval between blockages yet did not defeat the issue completely. As wastewater courses through the channel, particles are caught and the natural issue is corrupted by the dynamic biomass that is connected to the surface of the channel material. The channels can be worked under either an up-stream or on the other hand down-stream condition. The up-stream condition contains a high convergence of suspended biomass shaping a biofilm in the structure of the settled bed. The downstream bed contains a huge concentration of inorganic sulfur between the BOD and inorganic compounds. Upflow anaerobic channels (UAF) can be worked at either mesophilic or thermophilic temperature ranges. Thermophilic anaerobic filters are highly suitable for the treatment for high concentrated wastewaters particularly for the palm oil effluent (Mustapha et al. 2003). The anaerobic filtration has been effectively utilized in the treatment of date palm effluent on account of the advantages credited to it, which incorporates little reactor volume with low water powered maintenance time, capacity to withstand stun loadings, no strong partition/reusing and reasonableness of the

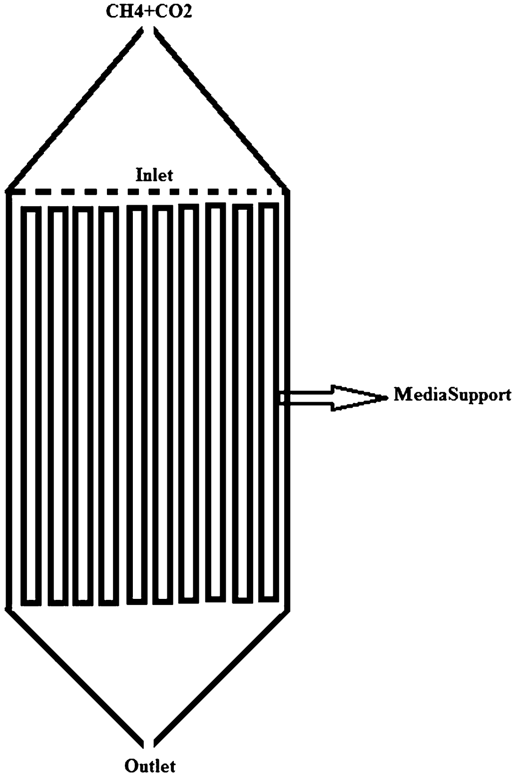


Fig. 5.2 Anaerobic filtration

reactor (Poh and Chong 2009). Anaerobic channels are utilized as an auxiliary treatment in family level or decentralized wastewater treatment frameworks. With respect to any anaerobic assimilation process, biogas can be recouped and changed to vitality or light. It is highly utilized for the personal contact between the inflow and microbial biomass, in this way taking into account a biomass maintenance time longer than the HRT. Reusing can be connected for high-quality wastewaters. In this manner, the AF shows incredible versatility for biomass to another carbon source and to natural load vacillations. Contrasted with an anaerobic contact process, the AF shown better sludge settlement. Accordingly, the AF could be more reasonable to treat wastewaters with bringing down suspended solids. The higher speculation cost ought to likewise be considered in applications. Figure 5.2 represents the diagram of anaerobic filtration.

5.4.2 Plug Flow Reactor

Anaerobic plug flow reactors have been accounted for to be proficient for dry anaerobic assimilation forms. This reactor is economical what's more, simple to

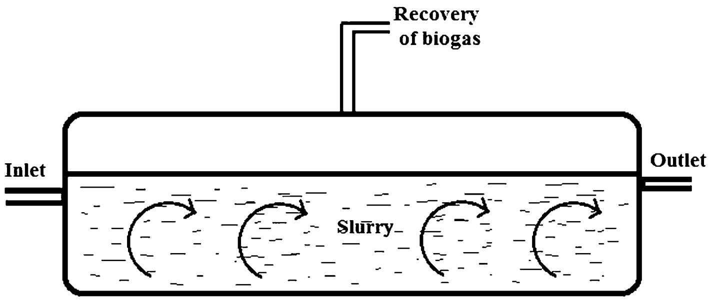


Fig. 5.3 Plug flow reactor

assemble which make them an appropriate innovation to enhance the occupations of the farmers (Lansing et al. 2010). The schematic representation of plug flow reactor is depicted in Fig. 5.3. The execution of biogas generation relies upon biomass substance creation and also process factors, for example, sustain focus, water driven maintenance time, pH, and temperature. The anaerobic plug flow reactor (APFR) is another customary process giving low groupings of VFA in the effluent, a high level of sludge maintenance and stable reactor execution. Plug flow reactors are long, direct troughs normally arranged over the ground. This kind of reactor is effective regarding productivity and conversion when compared with the ordinary single-phase CSTR. The APFR includes no inside disturbance and is stacked with the thick fertilizer of 11–14% aggregate solids and functions admirably at mesophilic or thermophilic temperature. The maintenance time is generally 15–20 days (Rajeshwari et al. 2000). This type of reactor has been accounted for to have the most noteworthy achievement rate in the United States, where 42% out of the 242 anaerobic digesters working at domesticated animals cultivates in 2015. This sort of reactor was used to give low beginning venture cost, high productivity and moderately simple activity and support in case of semi-solid waste (Sharma et al. 2000). Subsequently, in both industrialized and creating nations, the reactor has huge tendency to deliver biogas. Additionally, the reactor has been tried tentatively utilizing substrates, for example, pig manure, cattle deposits and urban natural squander, and so forth.

A plug flow reactor, a sort of reactor which is isolated into acidogenic and methanogenic stages along the stream way of the reactor, could enhance the reactor stability and treatment proficiency. By and by, a few deficiencies, for example, bring down mass exchange because of the absence of blending, warm stratification and strong sedimentation issues have been accounted in certain studies (Lansing et al. 2010). These issues can be controlled by the usage of compressors in plug stream reactors. The impellers permit insignificant blending for higher execution in the reactors. Plug flow reactor is constrained to cases in which the substrate contains low measures of sand, soil, coarseness that these polluting influences settle at the base of the reactor and prompt stratification of the reactor substance, requiring unavoidable release and cleaning of the digester. In addition, light coasting particles amass at the highest point of the reactor and cause crusting issues. Nowadays, a mixed plug flow reactor was utilized to maintain a strategic distance from the settlement of particles at the base and to make an inflexible layer on the reactor substance.

5.4.3 Continuous Stirred Tank Reactors

The traditional continuous stirred tank reactor (CSTR) is the most regular suspended microbial development framework and has been generally used to create hydrogen (Fang and Liu 2002). CSTRs (Continuous Stirred Tank Reactors) are in round and hollow or rectangular shapes and utilize mechanical turbines for blending. Continuous stirred tank reactors are also known as closed tank digesters. The potential for natural transformation from the substrate to methane can be incredibly expanded because of the overall high shear pressure and serious blending (Ozgun et al. 2013). CSTR works at a persistent stream of reactants and items with a steady makeup in the reactor including exit stream having an indistinguishable synthesis from the tank. The mechanical instigator of the CSTR gives more zone of contact with the biomass in this way upgrading gas generation. CSTR utilizes microorganisms to process the natural substances in the wastewater under anaerobic condition. Amid this procedure, the BOD of the profluent is diminished in the meantime delivering biogas. To heighten this innovation and keep up a reasonable populace of the moderate developing methanogens, the CSTRs are generally joined with an inside or then again outer biomass division and reusing framework (Reungsang et al. 2013) A CSTR coupled film framework can accomplish a promising methane yield up to hypothetical esteem. Also, CSTR, for the most part, works at a lower biomass fixation (e.g. 5 g/L MLSS) contrasted with other high rate anaerobic reactors because of deposition of waste control issues, which comes about in a lower OLR (Organic Loading Rate) connected to the framework, constraining the biomethane potential from high stacking wastewater. Various digesters are being connected for AD process in both laboratory usage and in industrial use, continuous stirred tank reactor (CSTR) is one of most generally utilized for the anaerobic processing of high-strong food waste like date palm waste. A solitary CSTR is easy to work yet less effective in feedstock processing and biogas generation due to the “short circuit”. The short circuit in CSTR is found to be a major downside in the generation of biogas. Associating two reactors in arrangement (serial assimilation) is a suitable method to defeat the issues from single CSTR to build the biodegradation rate and also acquire more biogas generation. A few investigations have stressed the attainability of serial arrangement of CSTR. Blending yields better collaboration amongst microorganisms and substrates diminishes impediment to mass transmission and reduces the gathering of safe intermediates (Chong et al. 2013). Due to continuous blending in the reactor, the microorganisms get suspended. Application of biogas distribution expanded the COD evacuation proficiency, bio-methane age effectiveness, biomass maintenance capacity and the solids retention time (SRT) of CSTR. CSTR is simple to work and minimal effort without immobilization transporter. Besides, it normally takes shorter start-up time compared with the anaerobic sludge blanket reactor and biofilm frameworks. Good mixing stimulates the contact between the organisms and food waste by consuming more energy. The activity of a traditional single CSTR is straightforward yet less proficient in based on the effluent quality. Therefore, a two-stage framework was found to have the more typical sort of framework. The two-stage CSTR framework is well known because of the effortlessness of the framework inactivity and its low capital when compared with the one stage CSTR. Also, the downsides related to the framework's structure and activity mode make it difficult to hold a high microbial population in the reactor. Because of blending and ceaseless blending, fast fermentation occurs, resulting in substantial VFA creation, which could prompt AD process. Recently, advances have concentrated on CSTR variations to make reactor execution through reactor volume enhancement.

5.4.4 Lagoon System

Anaerobic ponds or lagoons is most useable palm fruit anaerobic treatment around 85% of the plant implemented this technique inferable from just its low capital and operational cost This approach viably empowers about 100% catch of the biogas created in all the lagoon ponds to decrease smell and GHGs (Green House Gas) outflows to the environment. Lake framework is one of the commonest treatment innovation because of its cost adequacy. An alternative to lessen digester cost is utilizing more affordable digester plans and lower cost development materials. This line of thinking can prompt be considering a persistent stream 'earthen digester', worked at encompassing temperatures, which is like present anaerobic ponds. This framework depends principally on microbial action to decrease natural material and supplements. Anaerobic lagoons are working as digesters where microbes break down the natural issue. Anaerobic tidal ponds are regularly used to treat modern wastewater or creature squanders from dairy or then again swine cultivates, or to fill in as the primary treatment advance in frameworks utilizing at least two lagoons in an arrangement. The anaerobic ponds digesters are intended for a generally low stacking rate worked with a long maintenance time and work well under warm climatic conditions and intensely subject to the surrounding temperature.

5.4.5 Anaerobic Fluidized Bed Reactor

Over the most recent two decades, anaerobic fluidized-bed reactors (AFBRs) started to be utilized as a part of food waste because of their ability for keeping high biomass fixations furthermore, thin biofilm thickness. In anaerobic fluidized bed reactor, the barrier for bacterial connection and development is little dormant particles, for example, fine sand or alumina, kept in suspension by a quick upward stream of approaching wastewater. The design considerations provide more prominent protection from inhibitors and higher OLR. Moreover, execution of a thin biofilm on these medium particles and a great connection to biomass take into consideration great mass move effectiveness in the AFBR. AFBR depends on worthy fluidization attributes, for example, bed-extension tallness also, gas, fluid, and strong hold-ups. In any case, gas generation in AFBRs may acquire a bed-compression impact, bringing about the decrease of contact time between mass fluid and bioparticles, particularly for a huge scale AFBR. Anaerobic fluidized bed reactor (AFBR) is the treatment techniques for low-quality wastewater and it provides the excellent mass conversion between the substrate and the medium like a solid particle. FBR is a progressed stuffed bed framework, which allows the development of the bed amid activity (Alade et al. 2011). AFBR setup has pulled in an expanding consideration due to the maintenance of biomass onto a strong inactive biofilm bearer material with a huge particular surface region (Karadag et al. 2015). The reactors have been broadly utilized for the treatment of numerous food waste since the most recent two decades. The bearer materials are fluidized by the influent stream as well as through distribution of the supernatant fluid (Barca et al. 2015). FBR is a sort of anaerobic reactor gadget that has the limit of doing a few multiphase synthetic responses. The high up-flow fluid speeds give a bed development of just about 100%. The effectiveness of the fluidized bed reactor relies upon the idea of help material (Sowmeyan and Swaminathan 2008). The opposite stream fluidized reactor indicated high stability when over-burden is connected (Alvarado-Lassman et al. 2008). Little permeable fluidized media hold high biomass focuses in the reactor and in this way diminished HRT. Lower HRT (High Retention Time) and more prominent CH_4 generation demonstrated an advantage of fluidized bed over an anaerobic process.

Figure 5.4 shows the pictorial diagram of anaerobic fluidized bed reactor. In any case, gas generation in AFBRs may bring about a bed-compression impact, bringing about the diminishment of contact time between mass fluid and bioparticles, particularly for a substantial scale AFBR. The FBR can withstand high OLRs and a superior methane gas creation. Moreover, the capacity to evacuate surface strong particles of local wastewater utilizing the AFBR is superior to that of the UASB. This kind of reactor is more compelling for the treatment of soluble, or surface material nourish that is effectively biodegradable, for example, whey, whey permeates, black liquor condensate, etc. However, membrane fouling is a limitation for anaerobic fluidized bed reactors. It has been accounted for that proteins are the prevailing supporters of layer fouling at low temperature (Gao et al. 2014). To wipe out or diminish layer fouling, analysts have exhibited that a small amount of strong media such as granular activated carbon (GAC) or powder activated carbon (PAC) can be included, in light of the fact that they can successfully adsorb microbial metabolic items (Akram and Stuckey 2008).

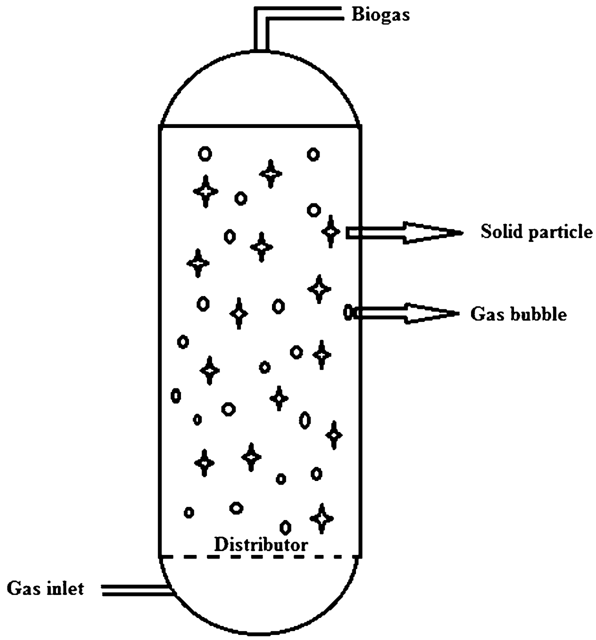


Fig. 5.4 Anaerobic fluidized bed reactor

5.4.6 Upflow Anaerobic Sludge Blanket Reactor

The UASB idea was produced by Lettinga et al. in the 1970s for methane creation. The up-flow anaerobic sludge blanket (UASB) reactor is the noticeable extensions in anaerobic processing framework for wastewater treatment and in excess of 1000 such sort of reactors is utilized as a part of worldwide (Tiwari et al. 2006; Chong et al. 2012). UASB reactor (Fig. 5.5) is very simple, compact and widely applied for the treatment of waste for the production of gas. The principle structure of the reactor is a thick slime bed situated in the base, which ensures great wastewater and biomass contact. This procedure has been successfully used to treat the extensive variety of modern profluent. The mystery of such a novel reactor configuration lies in its capacity to hold a high centralization of biomass as well settable methanogenic slop granules in a thick slop bed at the base of the reactor; furthermore, besides, catch the created biogas through a gas-liquid separator (GLS) at the top. This reactor demonstrates a great execution for high-suspended strong wastewater and produces a huge volume of methane. The creation of fermentative hydrogen relies upon the impacts of HRT (High Retention Time) and OLR (Organic Loading Rate). The biomass and sludge from the organic waste settle in UASB reactor and the sludge gets digested by this reactor when the organic waste be in contact with the sludge. UASB reactor has been effectively been utilized for the treatment of various modern effluents incorporating those with high natural substance fit for restraining assimilation (Demirel and Scherer 2008). The suspended natural solids of date palm effluent have a high biogas potential which makes the transformation innovation

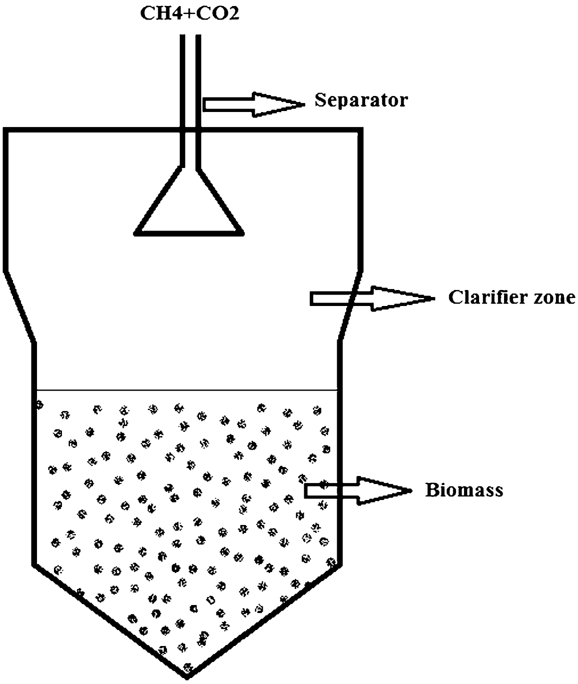


Fig. 5.5 Up flow anaerobic sludge blanket reactor

practical, which are the main thrust of UASB. Among the remarkable preferences, UASB requires low volume and space, highlights higher stream speed and biogas generation and fundamentally higher natural load rates. Moreover, the accessibility of granular permits treatment of higher COD stacking rates and providing satisfactory treatment at bringing down HRTs than is conceivable with the anaerobic filters (AF). UASB reactors can utilize thick bacterial granules, which fill in as a channel to counteract bacterial washout and which additionally give a bigger surface territory for speedier biofilm advancement and enhanced methanogenesis.

5.4.7 Anaerobic Contact Reactor

The anaerobic contact reactor is comprised of digester and sedimentation tank. The anaerobic contact reactor (ACR) is widely utilized for wastewater with high quantity of surface solids In a few cases, high-rate mesophilic ACRs have been shown to be a manageable innovation for an extensive variety of modern wastewater, for example, food industry wastewater (Senturk et al. 2012) and pulp and paper mills (Capela et al. 2009). These reactors introduce comparative highlights to their oxygen-consuming partners like activated sludge reactors. Anaerobic contact assimilation includes the utilization of digester and sedimentation tank whereby the processed wastewater is left to coagulate and the wastewater is reused once more into the

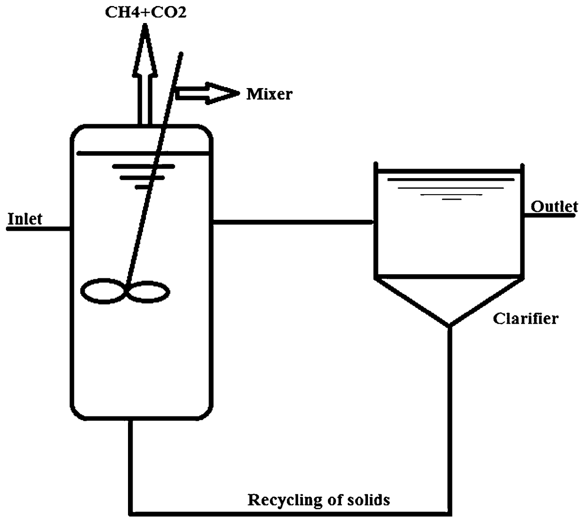


Fig. 5.6 Anaerobic contact reactor

digester. ACR is more invaluable than regular anaerobic reactors, for example, up-flow anaerobic sludge blanket reactors (UASB). Figure 5.6 Schematic representation of anaerobic contact reactor.

Revealed focal points incorporate the contact procedure, quickly accomplished consistent state times because of blending, adequately short water powered maintenance times and moderately high gushing quality, less affected by stun stacking, ideal pH and constrained biomass washout. In order to maintain the organisms' quantity, the settled solids are move towards the reactor. The clarifier or pilgrim may have gravity settling or vacuum buoyancy. Settlement must be helped by degassing, cooling, filtration, or slanted plates. This approach was fruitful for the treatment of processed solids and enabled one to acquire fantastic effluents. Gas-lift blending is well known in these sorts of digesters. Great blending is likewise fundamental in this sort of reactor to guarantee uniform substrate and biomass concentration. Traditionally blending has been by paddles in a draft tube. Much of the system of the paddle type is submerged in the digester and maintenance is exceptionally troublesome. Another strategy for mixing is directed distribution of the digesters contents. Present day digesters are a large portion of the size and blending is significantly simpler.

5.5 Conclusions and Recommendations

Date palm natural product, a standout amongst the most nutritive and complete organic products regarding medical advantages is a perfect substrate for inferring a scope of significant worth included items in sustenance and nutraceutical businesses in the upcoming future utilizing bioprocessing innovations which will have a massive extension for the biogas production. For supporting the future manageable palm fruit advancement, more exhaustive research on improving the biogas creation from date palm by anaerobic assimilation is basically required. Keeping in mind the end goal to guarantee the execution of anaerobic assimilation, RSM improvement of the manipulable elements (temperature, pH) by utilizing the specific bioreactor is very encouraged. The present chapter plainly shows that anaerobic assimilation is a standout amongst the best organic procedures to treat a wide assortment of date palm fruit. Additionally, this chapter demonstrates that anaerobic digestion is a standout amongst the best natural procedures to treat a date palm fruit for biogas generation. In any case, unique variables for example, substrate and co-substrate structure and quality, natural components (temperature, pH), microbial elements add to the proficiency of the anaerobic assimilation process and should be improved to accomplish the greatest advantage from this innovation as far as both vitality creation furthermore, natural waste administration. The examined reactors can be further investigated by taking into consideration of different measures, for example, extraordinary co-substrates, pre-treatment advances, added substances etc. the major elements of anaerobic assimilation and cost adequacy must be considered for the future activities. By working the anaerobic digester effectively, the used techniques had a positive reaction to the biogas creation. The prime preferences of this innovation incorporate that the procedure at the same time prompts minimal effort generation of biogas, which could be indispensable for meeting future vitality needs. In any case, unique components, for example, substrate and co-substrate structure and quality, ecological components (temperature, pH), furthermore, microbial flow add to the productivity of the anaerobic assimilation process and should be enhanced to accomplish most extreme advantage from this innovation. This innovation has enormous application later on for maintainability of both condition and horticulture, with the generation of energy as an additional advantage.

This chapter focuses the way that there is an extraordinary research movement around the globe, both in nations that deliver date palm and those in nations where the production is low yet the consumption is high. The anaerobic assimilation is a perplexing procedure, which the execution came about will be effectively affected by alternate variables, for example, organic loaded, start-up effectiveness, operation conditions, bioreactor design etc. The cooperation impacts of these diverse components might be amplified and turned out to be more imperative than its individual impact. The efforts were made to basically upgrade the biogas volumetric creation, yet not underlined to enhance the biogas quality. The basic examination of newer literature shows that much advance has been made in the innovative work of anaerobic systems for biogas creation. The green points of view of anaerobic reactors are biogas creation, high profluent quality, squander minimization, high limit, and impression proficiency (diminishing capital expenses) and bring down vitality prerequisites. Most research on reactors has concentrated on researching customary setups, for example, up-flow anaerobic sludge blanket reactor anaerobic fluidized bed reactor, continuous stirred tank reactors and so forth. The anaerobic pond is the basic strategy to produce biogas because of its minimal effort. The most suitable reactor for the generation of biogas from the date palm fruit is Upflow anaerobic sludge blanket reactor (UASB) as it produces higher measures of biogas, for example, biomethane and biohydrogen. Be that as it may, it can't release completely clear profluent. For the further improvement of biogas AD that consideration be given to the blend of at least two of the previously mentioned factors influencing proficiency and to advance anaerobic digestion efficiency.

References

Agdag ON, Sponza DT (2007) Co-digestion of mixed industrial sludge with municipal solid wastes in anaerobic simulated landfilling bioreactors. J Hazard Mater 140:75–85. https://doi.org/10.1016/j.jhazmat.2006.06.059

Akram A, Stuckey DC (2008) Flux and performance improvement in a submerged anaerobic membrane bioreactor (SAMBR) using powdered activated carbon (PAC). Process Biochem 43:93–102. https://doi.org/10.1016/j.procbio.2007.10.020

Al-Abdoulhadi IA, Dinar HA, Ebert G, Buttner C (2011) Effect of salinity on leaf growth, leaf injury and biomass production in date palm cultivators. Indian J Sci Technol 4:1542–1546. https://doi.org/10.17485/ijst/2011/v4i11/30283

Alade AO, Jameel AT, Muyibi SA, Karim MA, Alam MZ (2011) Application of semi fluidized bed bioreactor as novel bioreactor system for the treatment of palm oil mill effluent (POME). Afr J Biotechnol 10(81):18642–18648. https://doi.org/10.5897/AJB11.2767

Alananbeh KM, Bouqellah NA, Al Kaff NS (2014) Cultivation of oyster mushroom *Pleurotus ostreatus* on date-palm leaves mixed with other agro-wastes in Saudi Arabia. Saudi J Biol Sci 21 (6):616–625. https://doi.org/10.1016/j.sjbs.2014.08.001

Alvarado-Lassman A, Rustrian E, Garcia-Alvarado MA, Rodriguez-Jimenez GC, Houbron E (2008) Brewery wastewater treatment using anaerobic inverse fluidized bed reactors. Bioresour Technol 99:3009–3015. https://doi.org/10.1016/j.biortech.2007.06.022

Annachhatre AP (1996) Anaerobic treatment of industrial wastewaters. Resour Conserv Recycl 16:161–166. https://doi.org/10.1016/0921-3449(95)00053-4

Appels L, Baeyens J, Degreve J, Dewil R (2008) Principles and potential of the anaerobic digestion of waste-activated sludge. Prog Energy Combust Sci 34(6):755–781. https://doi.org/10.1016/j.pecs.2008.06.002

Appels L, Lauwers J, Degr_eve J, Helsen L, Lievens B, Willems K, Impe JV, Dewil R (2011) Anaerobic digestion in global bio-energy production: potential and research challenges. Renew Sustain Energy Rev 15:4295–4301. https://doi.org/10.1016/j.rser.2011.07.121

Barca C, Soric A, Ranava D, Giudici-Orticoni MT, Ferrasse JH (2015) Anaerobic biofilm reactors for dark fermentative hydrogen production from wastewater: review. Bioresour Technol 185:386–398. https://doi.org/10.1016/j.biortech.2015.02.063

Bhansali RR (2010) Date palm cultivation in the changing scenario of Indian arid zones: challenges and prospects. In: Ramawat KG (ed) Desert plants: biology and biotechnology. Springer, Berlin/Heidelberg, pp 423–459. https://doi.org/10.1007/978-3-642-02550-1_20

Burkhardt M, Koschack T, Busch G (2015) Biocatalytic methanation of hydrogen and carbon dioxide in an anaerobic three-phase system. Bioresour Technol 178:330–333. https://doi.org/10.1016/j.biortech.2014.08.023

Capela I, Bile MJ, Silva F, Nadais H, Prates A, Arroja L (2009) Hydrodynamic behavior of a full-scale anaerobic contact reactor using residence time distribution technique. J Chem Technol Biotechnol 84:716–724. https://doi.org/10.1002/jctb.2104

Chong S, Sen TK, Kayaalp A, Ang HM (2012) The performance enhancements of upflow anaerobic sludge blanket (UASB) reactors for domestic sludge treatment – a state-of-the-art review. Water Res 46:3434–3470. https://doi.org/10.1016/j.watres.2012.03.066

Chong MF, Chen J, Oh PP, Chen ZS (2013) Modeling study of chemical phase equilibrium of canola oil transesterification in a CSTR. Chem Eng Sci 87:371–380. https://doi.org/10.1016/j.ces.2012.11.002

Clarke WP, Alibardi L (2010) Anaerobic digestion for the treatment of solid organic waste: what's hot and what's not. Waste Manag 30:1761–1762. https://doi.org/10.1016/j.wasman.2011.03.021

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 Eng 21:371–376. https://doi.org/10.1007/s004490050

Cuetos MJ, Gomez X, Otero M, Moran A (2008) Anaerobic digestion of solid slaughterhouse waste (SHW) at laboratory scale: influence of co-digestion with the organic fraction of municipal solid waste (OFMSW). Biochem Eng J 40:99–106. https://doi.org/10.1016/j.bej.2007.11.019

Demirel B, Scherer P (2008) The roles of acetotrophic and hydrogenotrophic methanogens during anaerobic conversion of biomass to methane: a review. Rev Environ Sci Biotechnol 7:173–190. https://doi.org/10.1007/s11157-008-9131-1

Elleuch M, Besbes S, Roiseux O, Blecker C, Deroanne C, Drira NE, Attia H (2008) Date flesh: chemical composition and characteristics of the dietary fibre. Food Chem 111:676–682. https://doi.org/10.1016/j.foodchem.2008.04.036

Fang HHP, Liu H (2002) Effect of pH on hydrogen production from glucose by a mixed culture. Bioresour Technol 82:87–93. https://doi.org/10.1016/S0960-8524(01)00110-9

Fernandez J, Perez M, Romero LI (2008) Effect of substrate concentration on dry mesophilic anaerobic digestion of organic fraction of municipal solid waste (OFMSW). Bioresour Technol 99:6075–6080. https://doi.org/10.1016/j.biortech.2007.12.048

Fezzani B, Cheikh RB (2010) Two-phase anaerobic co-digestion of olive millwastes in semi-continuous digesters at mesophilic temperature. Bioresour Technol 101:1628–1634. https://doi.org/10.1016/j.biortech.2009.09.067

Gao D-W, Hu Q, Yao C, Ren N-Q (2014) Treatment of domestic wastewater by an integrated anaerobic fluidized-bed membrane bioreactor under moderate to low temperature conditions. Bioresour Technol 159:193–198. https://doi.org/10.1016/j.biortech.2014.02.086

Gupta N, Kushwaha H (2011) Date Palm as a Source of Bioethanol Producing Microorganisms. In: Date Palm Biotechnology. Springer, Berlin/Germany, pp 711–727. https://doi.org/10.1007/978-94-007-1318-5_33

He Y, Bagley DM, Leung KT, Liss SN, Liao BQ (2012) Recent advances in membrane technologies for biorefining and bioenergy production. Biotechnol Adv 30:817–858. https://doi.org/10.1016/j.biotechadv.2012.01.015

Kaewmai R, H-Kittikun A, Suksaroj C, Musikavong C (2013) Alternative technologies for the reduction of greenhouse gas emissions from palm oil mills in Thailand. Environ Sci Technol 47:12417–12425. https://doi.org/10.1021/es4020585

Karadag D, Koroglu OE, Ozkaya B, Cakmakci M (2015) A review on anaerobic biofilm reactors for the treatment of dairy industry wastewater. Process Biochem 50(2):262–271. https://doi.org/10.1016/j.procbio.2014.11.005

Kathirvale S, Muhdyunus M, Sopian K, Samsuddin A (2004) Energy potential from municipal solid waste in malaysia. Renew Energy 29(4):559–567. https://doi.org/10.1016/j.renene.2003.09.003

Lansing S, Martin JF, Botero RB, da Silva TN, da Silva ED (2010) Methane production in low-cost, unheated, plug-flow digesters treating swine manure and used cooking grease. Bioresour Technol 101(12):4362–4370. https://doi.org/10.1016/j.biortech.2010.01.100

Lattieff FA (2016) A study of biogas production from date palm fruit wastes. J Clean Prod 139:1191–1195. https://doi.org/10.1016/j.jclepro.2016.08.139

Leven L, Eriksson ARB, Schnürer A (2007) Effect of process temperature on bacterial and archaeal communities in two methanogenic bioreactors treating organic household waste. FEMS Microbiol Ecol 59:683–693. https://doi.org/10.1111/j.1574-6941.2006.00263.x

Levis JW, Barlaz MA, Themelis NJ, Ulloa P (2010) Assessment of the state of food waste treatment in the United States and Canada. Waste Manag 30(8–9):1486–1494. https://doi.org/10.1016/j.wasman.2010.01.031

Messineo A, Volpe R, Marvuglia A (2012) Ligno-cellulosic biomass exploitation for power generation: A case study in Sicily. Energy 45:613–625. https://doi.org/10.1016/j.energy.2012.07.036

Mustapha S, Ashhuby B, Rashid M, Azni I (2003) Start-up strategy of a thermophilic upflow anaerobic filter for treating palm oil mill effluent. Process Saf Environ Prot:Trans Inst Chem Eng Part B 81:262–266. https://doi.org/10.1205/095758203322299798

Nath K, Das D (2004) Improvement of fermentative hydrogen production: various approaches. Appl Microbiol Biotechnol 65:520–529. https://doi.org/10.1007/s00253-004-1644-0

Ozgun H, Dereli RK, Ersahin ME, Kinaci C, Spanjers H, Van Lier JB (2013) A review of anaerobic membrane bioreactors for municipal wastewater treatment: integration options, limitations and expectations. Sep Purif Technol 118:89–104. https://doi.org/10.1016/j.seppur.2013.06.036

Poh PE, Chong MF (2009) Development of anaerobic digestion methods for palm oil mill effluent (POME) treatment. Bioresour Technol 100:1–9. https://doi.org/10.1016/j.biortech.2008.06.022

Radeef W, Shanableh A, Merabtene T (2016) Impact of date palm seed size on biogas production from date seeds/wastewater treatment sludge mixtures. Int J of Thermal Environ Eng 13(1):1–6. https://doi.org/10.5383/ijtee.13.01.001

Rajeshwari K, Balakrishnan M, Kansal A, Lata K, Kishore V (2000) State-of-the-art of anaerobic digestion technology for industrial wastewater treatment. Renew Sust Energ Rev 4:135–156. https://doi.org/10.1016/S1364-0321(99)00014-3

Reungsang A, Sreela-or C, Plangklang P (2013) Non-sterile bio-hydrogen fermentation from food waste in a continuous stirred tank reactor (CSTR): performance and population analysis. Int J Hydrog Energy 38:15630–15637. https://doi.org/10.1016/j.ijhydene.2013.03.138

Sawayama S, Tada C, Tsukahar K, Yagishita T (2004) Effect of ammonium addition on methanogenic community in a fluidized bed anaerobic digestion. J Biosci Bioeng 9:65–70. https://doi.org/10.1016/S1389-1723(04)70167-X

Senturk E, İnce M, Engin GO (2012) The effect of transient loading on the performance of a mesophilic anaerobic contact reactor at constant feed strength. J Biotechnol 164:232–237. https://doi.org/10.1016/j.jbiotec.2012.08.016

Sharma V, Testa C, Lastella G, Cornacchia G, Comparato M (2000) Inclined-plug- flow type reactor or anaerobic digestion of semi-solid waste. Appl Energy 65:173–185. https://doi.org/10.1016/S0306-2619(99)00084-7

Sowmeyan R, Swaminathan G (2008) Evaluation of inverse anaerobic fluidized bed reactor for treating high strength organic wastewater. Bioresour Technol 99:3877–3880. https://doi.org/10.1016/j.biortech.2007.08.021

Su H, Cheng J, Zhou J, Song W, Cen K (2009) Improving hydrogen production from cassava starch by combination of dark and photo fermentation. Int J Hydrog Energy 34:1780–1786. https://doi.org/10.1016/j.ijhydene.2008.12.045

Tiwari M, Guha S, Harendranath CS, Tripathi S (2006) Influence of extrinsic factors on granulation in UASB reactor. Appl Microbiol Biotechnol 71:145–154. https://doi.org/10.1007/s00253-006-0397-3

Trzcinski AP, Stuckey DC (2010) Treatment of municipal solid waste leachate using a submerged anaerobic membrane bioreactor at mesophilic and psychrophilic temperatures: analysis of recalcitrants in the permeate using GC-MS. Water Res 44:671–680. https://doi.org/10.1016/j.watres.2009.09.043

Ward AJ, Hobbs PJ, Holliman PJ, Jones DL (2008) Optimization of the anaerobic digestion of agricultural resources. Bioresour Technol 99:7928–7940. https://doi.org/10.1016/j.biortech.2008.02.044

Weiland P (2010) Biogas production: current state and perspectives. Appl Microbiol Biotechnol 85:849–860. https://doi.org/10.1007/s00253-009-2246-7

Yang L, Huang Y, Zhao M, Huang Z, Miao H, Xu Z, Ruan W (2015a) Enhancing biogas generation performance from food wastes by high solids thermophilic anaerobic digestion: effect of pH adjustment. Int Biodeterior Biodegrad 105:153–159. https://doi.org/10.1016/j.ibiod.2015.09.005

Yang L, Xu F, Ge X, Li Y (2015b) Challenges and strategies for solid-state anaerobic digestion of lignocellulosic biomass. Renew Sust Energ Rev 44:824–834. https://doi.org/10.1016/j.rser.2015.01.002

Zhao Y, Wang A, Ren N (2010) Effect of carbon sources on sulfidogenic bacterial communities during the starting-up of acidogenic sulfate-reducing bioreactors. Bioresour Technol 101:2952–2959. https://doi.org/10.1016/j.biortech.2009.11.098

Chapter 6
Valorization of Waste Date Seeds for Green Carbon Catalysts and Biodiesel Synthesis

Ala'a H. Al-Muhtaseb, Farrukh Jamil, Lamya Al Haj, Eyas Mahmoud, Mohamed Becherif, Umer Rashid, Sikander Rafiq, A. E. Atabani, and Gopalakrishnan Kumar

Abstract The decreasing availability of fossil fuels and environmental issues associated with their use has placed a greater emphasis on biofuels production as a competent alternative source to produce energy in the current era. Production of biofuels from plant-based oil has a good prospect as a competent alternative to fossil fuels. The concept of utilizing waste date pits for biofuels production is promising due to its abundant availability in Oman. Present work reports, a better way to

A. H. Al-Muhtaseb (✉)
Department of Petroleum and Chemical Engineering, College of Engineering, Sultan Qaboos University, Muscat, Oman
e-mail: muhtaseb@squ.edu.om

F. Jamil
Department of Petroleum and Chemical Engineering, College of Engineering, Sultan Qaboos University, Muscat, Oman

Department of Chemical Engineering, COMSATS University Islamabad, Lahore, Pakistan

L. Al Haj
Department of Biology, College of Science, Sultan Qaboos University, Muscat, Oman

E. Mahmoud
Department of Chemical and Petroleum Engineering, United Arab Emirates University, Al-Ain, UAE

M. Becherif
Department of Energy, FCLab, FR CNRS 3539, Bourgogne Franche-Comte University/UTBM, Belfort, France

U. Rashid
Institute of Advanced Technology, Universiti Putra Malaysia, Serdang, Selangor, Malaysia

S. Rafiq
Department of Chemical Engineering, COMSATS University Islamabad, Lahore, Pakistan

A. E. Atabani
Energy Division, Department of Mechanical Engineering, Faculty of Engineering, Erciyes
20 University, Kayseri, Turkey

G. Kumar
Institute of Chemistry, Bioscience and Environmental Engineering, Faculty of Science and Technology, University of Stavanger, Stavanger, Norway

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_6

valorize the waste biomass (Date pits) is adopted in order to get environment friendly catalyst which will be effectively used for producing biodiesel. The produced carbon material was impregnated with KOH to enhance the efficiency and analyzed by SEM, XRD, EDX and BET. The production of biodiesel was analyzed by parametric studies involving following process parameters which include process temperature, reaction time, type of catalysts along with methanol to oil ratio. The maximum yield obtained was 91.6% for following parametric value such as temperature 65 °C, for C3 (6 wt% KOH on carbon) catalyst when 9:1 methanol to oil ratio was used. Moreover, the verification for quality of produced biodiesel was done by comparison with standards recognized internationally (ASTM and EN). The produced biodiesel possessed a cetane number of 60.31, density 881 kg/m^3, flash point 141 °C, viscosity was measured to be 4.24 mm^2/s, low temperature properties which includes cloud point, cold filter plugging point and pour point were 3.9 °C, −0.62 °C, −1.4 °C respectively thus these properties identify the quality of produced biodiesel. Thus, all properties were within the ranges provided standards of ASTM and EN. Thus, it can be concluded that Date pits biomass is potential alternative source for catalyst synthesis along with biodiesel.

Keywords Waste biomass, carbon catalyst · Biodiesel · Energy source

6.1 Introduction

Currently, fossil fuels are sources for energy production and only source for energy supply (Bae and Kim 2017; Abas et al. 2015; Mohr et al. 2015). As in the last century world observed the industrial revolution, this enhanced the economic activity which lead toincrease the energy demand and utilization (Vertes et al. 2010), carbonaceous fuel which are fossil-based emerged as a main source for production of energy and in transportation (Fig. 6.1) (Shafiee and Topal 2009). In 2014, oil consumption was approximately 92 million barrels per day worldwide (2015) and is expected to reach 116 million barrels per day in 2030 (Cherubini 2010). This hasty upsurge in oil usage has led to questions regarding its readiness and issues related to environmental caused by combusting fossil fuels.

As shown in Fig. 6.2, the depletion of fossil oil reserves is due to rapid industrial growth and population growth which caused the increase in demand for fossil fuel. 42% of the world's energy is produced by consuming fossil oil indicating the importance of fossil fuel as the major source for economic development. According to the 2016 report of the Energy Information Administration (EIA) report, it is estimated that the world's total energy consumption will increase by 71% between 2000 and 2030 based on population increment and welfare. The usage of oil, coal and gas will increase by 30–50% of current value and 75% of energy produced will be from coal, gas and oil in 2040 (Grammelis et al. 2016; Di Gianfrancesco 2017). Oil production may its maximum in 2030. Meanwhile, conventional fossil oil is

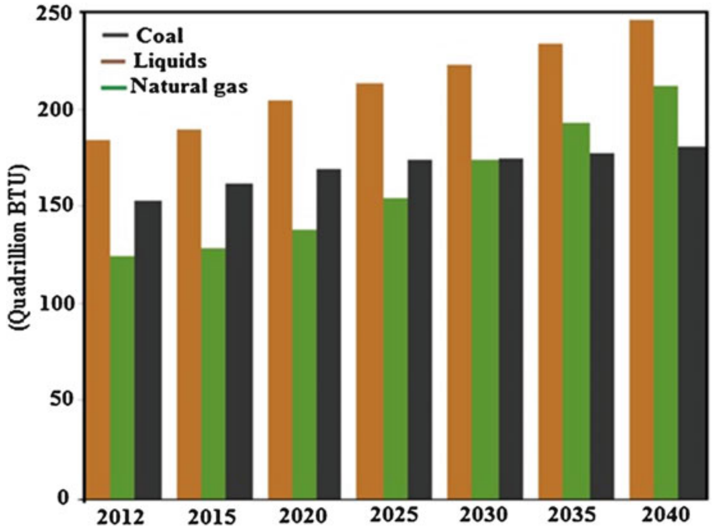


Fig. 6.1 Worldwide fossil fuel energy consumption from 2012 to 2040 (EIA 2012)

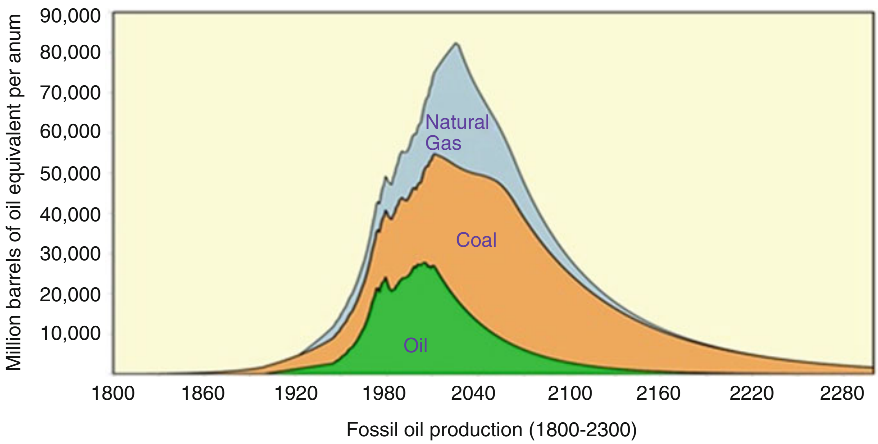


Fig. 6.2 Fossil reserves exploration and usage worldwide and their consumption (Archibald 2014)

expected to be constrained by reduced supply owing to physical depletion and decreased accessibility to oil possessing area (Capellán-Pérez et al. 2014; Utama et al. 2014). Due to depletion of fossil fuel reserves the transportation sector may be affected to a large extent as it consumes more than 50% of oil being produced worldwide (Dewulf et al. 2005; Vertes et al. 2010; Panwar et al. 2011). Similarly, the chemical industry is expected to be second most affected sector due to a decreased supply of fossil oil. The demand for fuel increases ostensibly due to increasing need for fertilizers, plastics, electricity and chemicals which puts pressure on the available energy supply and infrastructure.

Based on the trend followed by oil consumption, it can be concluded that fossil oil supply will not be able to meet demand in the coming era. Therefore, environmental and availability concerns related to the usage of fossil-based fuels can be overcome by utilizing alternative energy sources. Hence, renewable and sustainable resources such as wind, biomass and solar energy can counterpoise the concerns related to fossil fuels (Tiwari and Mishra 2011). Moreover, among all alternative energy resources mentioned, biomass is the most suitable alternative based on the fact that it is an enriched source of carbon. Also, it can serve as a source of energy as well as biochemicals and catalysts. In spite of this solar and wind can only serve as a source of energy (Demirbas 2007; Maczulak 2009).

6.2 Biomass as an Alternative Source

Biomass is the material resulting from resources naturally present in the environment or biological matter derived from living organisms (Klass 2006; Vertes et al. 2010). It possesses a complex chemical nature and its composition relies on factors such as location and environment of its growth. Biomass is regarded as renewable as its production is the result of photosynthesis as a result of energy captured from sunlight, which leads to the growth of plants (Ptasinski 2016; Ringsmuth et al. 2016). Meanwhile, when biomass itself or its derived products are combusted, CO_2 is released into the environment where it may be recaptured as seen in Fig. 6.3, which shows the complete carbon cycle (Rosillo-Calle and Woods 2012). It is thought to be the best potential alternative to fossil-based fuels based on its sustainability and reliability as a competent source of organic compounds, which can be utilized as green fuels, chemicals and materials. Thus, moving towards the

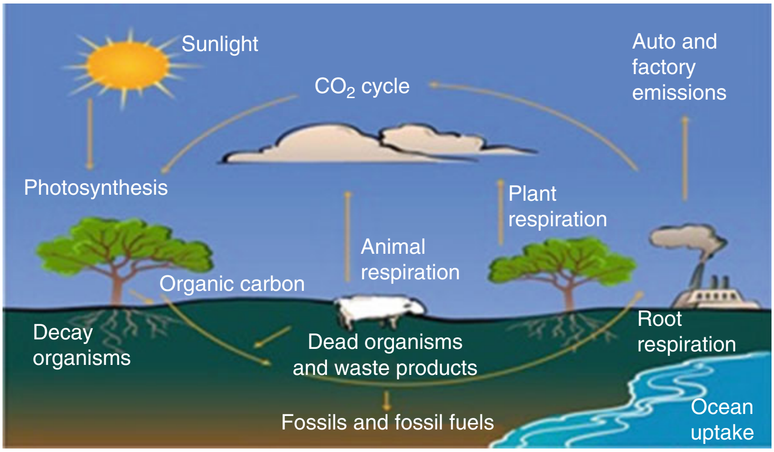


Fig. 6.3 Carbon cycle for all kinds of emissions and use of CO_2 for photosynthesis (Carbon-Cycle 2018)

sustainable energy sources causes the urgent need for the valorization of biomass. Therefore, bringing biomass-derived fuels, chemicals and materials to the commercial level requires the development of efficient technologies and this leads this to be one of the main research domain of current era.

Sustainability and environmental related issues regarding biomass usage have been considered in terms of industrial-scale production of biofuels based on the first generation biofuels. First generation biofuels were derived from edible feedstocks which may lead to food versus fuel controversy and reduce biodiversity (Vertes et al. 2010). Thus, this is considered to be the major drawback for the biofuels production that may increase the edible oil prices and causes food scarcity in a specific area of biofuel production and it can be overcome by using non-edible feedstocks.

The sustainability of biomass depends on its source type and it should be abundantly available for producing biofuels and chemicals. One can prove the sustainability of biomass based on some parameters such as growth on abandoned agricultural land, crop waste, harvested plants from forests and organic waste generated from industrial and domestic purposes (Tiwari and Mishra 2011; Toka et al. 2014). Moreover, biomass used for biofuels production should have high energy density. Biomass processed auxiliaries and produced fuels along with waste are considered to biodegrade either by bacteria or other biological means more rapidly as compared to fossil-derived products and waste (Ptasinski 2016).

6.3 Feedstock Selection

Almost 90% of biofuels are being produced from edible oils due to a global imbalance in the market demand and food supply by their high prices and the reduction of food sources it should be shifted towards non-edible oils sources (Mofijur et al. 2013). Due to the presence of some toxic components in non-edible oils such as protein curcin and purgative in jatropha plants, castor plant contains protein ricin, glucoside cerberin in fruits of sea mango and flavonoids pongamiin and karajiin in karanja oil, they are not considered good for health (Banković-Ilić et al. 2012). Non-edible oil-producing plants are grown all over the world but of different types. Also, while considering the plantation of non-edible plants, they can be grown over barren lands not suitable for cultivation and moreover, help to reduce CO_2 as well from the environment. Worldwide production of different kinds of feedstocks is shown in Table 6.1. In addition, biofuels produced from non-edible resources can become a major poverty alleviation program for rural areas by providing them with energy security and upgrading the non-farm rural sector (Jamil et al. 2018). Finally, all these factors lead to the feasibility of considering the sustainability of biofuels production.

There are some issues also related to the non-edible oils for biofuels production such as they have a high acid value which refers to high contents of free fatty acids, high viscosity and high oxygen contents which can affect the engine performance during their combustion (Yusuf et al. 2011). However, it must be pointed out that

Table 6.1 Different kind feedstocks available in different regions

Country	Feedstock
USA	Waste oil/soybeans/peanut
Canada	Rapeseed/animal fat/soybean/yellow grease
Mexico	Waste oil/animal fat
Germany	Rapeseed
Italy	Rapeseed/sunflower
France	Rapeseed/sunflower
Spain	Lin seed/sunflower
Greece	Cotton seed
UK	Waste cooking oil/rapeseed
Sweden	Frying oil/animal fat
Ireland	Rapeseed
India	Jatropha/rapeseed/sunflower
Malaysia	Palm oil
Indonesia	Palm oil/jatropha/coconut
Singapore	Palm oil
Philippines	Coconut/jatropha
Thailand	Palm oil/jatropha/coconut
China	Waste cooking oil/rapeseed/jatropha
Brazil	Soybeans/palm oil/castor/cotton oil
Argentina	Soybeans
Japan	Waste cooking oil
New Zealand	Waste cooking oil/tallow
GCC	Date palm

global biofuel feedstocks should not rely on certain sources as it could bring harmful influence in the long run. The world's dependence on the fossil fuels is the perfect example. Therefore, biofuels feedstock should be as diversified as possible, depending on their geographical locations in the world.

6.4 Biomass Availability

Date palm is considered the main crop in Oman which occupies 54 percent of total agricultural land in the country (El Hag et al. 2002, 2014). Date palm exists in large amounts in Oman with around 200 cultivated varieties and a production rate of about 270,000 metric tons per year from an area of 31,500 hectares. The total production of dates in Oman reached 308,000 tonnes in 2013 from 281,000 tonnes in the previous year, according to the latest data released by the Ministry of Agricultural and Fisheries (2014). The ministry had conducted a detailed survey of the most important crop of the country during 2013. It revealed that out of the 308,000 tonnes, only 7000 tonnes were exported. According to the statistics, the local consumption within the country was 164,000 tonnes when the population of the country was 2,159,000

(2014). On average, a single person consumed 60 kg of dates annually. This is in addition to 1,710,000 expatriates, who, on average consumed around 20 kg of dates per person. Oman ranks ninth in the world dates production, however, its export share is only around 4% of all dates produced (Manickavasagan et al. 2012). Majority of dates are used for human consumption (51%), while animal consumption constitutes 22%. This would deliver around 62,000 metric tons of residues that represent 23% of the total date production.

6.4.1 *Potential of Utilizing Waste Date Pits for Biofuel Production*

Based on Date palm production it can be reported that Oman can potential candidate for supplying biomass waste for biofuel production. Date palm waste (pits) has outstanding potential as an substitute energy supply as it evades the use of the edible parts of the plant, hence does not compete with the food supplies for biodiesel synthesis. The by-product from dates is date pits. They are largely available in Oman and are usually very cheap. They can, therefore, be used as a source for producing biofuel. The residues of date palm tree and spoiled dates comprise economic and environmental burden to be managed. Interestingly, date pits contain 15–20% volatile compounds that can be a potential source for biofuel production. There are two main pathways used to obtain oil such as fermentation for bioethanol production and oil extraction and transformation of that oil to biofuel. The fermentation process could be time-consuming while the yield is low. For these reasons, obtaining biofuel from oil extracted from date pits is a preferred method and so the biofuel production from date pits would be a very attractive option. Amani et al. (Amani et al. 2013) produced biodiesel from the oil extracted from date pits by transesterification and reported that the biodiesel produced fulfilled international standards for biodiesel. Azeem et al. (2016) studied the potential of various varieties of date pits for biodiesel production. They found that biodiesel from waste date pits possesses the fuel properties which meet the international standards. Biofuel production from renewable resources in Oman such as date pits will not only help in recycling the vast amount of waste materials produced in the country but will also provide the local and governmental authorities with the economic and technical benefits of biofuel. The use of biofuel may replenish any future shortage of fossil fuels due to continuous population growth and will decrease the greenhouse gas emission.

6.4.2 *Waste Date Pits*

Date pits (*Phoenix Dactylifera L.*), were collected from a local “Dates” farm in Muscat. The pits were brown in visual appearance as shown in Fig. 6.4. As pits were

Fig. 6.4 Waste date pits (**a**) original form, (**b**) powder of waste date pits and (**c**) grinder used for grinding

collected from the farm, they were treated as waste. So, first of all, they were cleaned and then washed with water in order to remove dirt and pulp. The pits (15–20 wt% moisture content) were then sun-dried for 6–7 days, followed by overnight drying in an oven at 70 °C to completely remove the moisture content from date pits. The dried pits were rigid and hard. Hence, the strong mechanical grinder was used to grind them into powder form. The powdered material obtained after grinding was sealed so as to avoid moisture contamination and open just before use. The grinder used for grinding the waste date pits is shown in Fig. 6.4c. Ground date pits were used to extract the oil in a Soxhlet apparatus in which hexane was used as a solvent. Standard method AOCS was adopted for extraction.

6.5 Biodiesel

The term biodiesel refers to the alkyl esters of plant oils and animal fats produced by transesterification (Bart et al. 2010a, b, Knothe 2010). Biodiesel ought to be a combination of saturated and unsaturated fatty acids and monoalkyl esters derived from edible and non-edible sources. It is considered as an alternative fuel to conventional diesel if it complies with international standards (American Society of Testing and Materials ASTM D6751 and European standard EN 14214) (Bart et al. 2010a, b; Chen et al. 2013, Aransiola et al. 2014, Baroi and Dalai 2015). The increasing trend of adopting the biodiesel as a competent alternative to fossil diesel is due to its physiochemical properties and energy content which allows it to be used directly or in blended form with conventional diesel in compressed-ignition engines without modification (Gerhard et al. 1997).

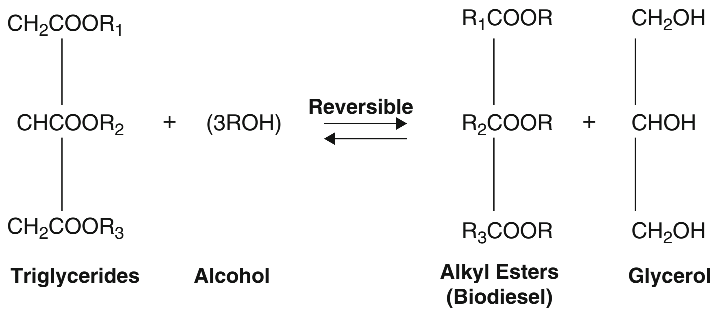


Fig. 6.5 Transesterification of triglyceride to form alkyl ester and glycerol as a by-product (Demirbas 2008)

Transesterification refers to the reaction in which triglycerides react with alcohol in the presence of suitable catalysts and give monoalkyl ester (Demirbas 2007; Demirbas 2008) as shown in Fig. 6.5. This is also known as alcoholysis and considered to be most suitable technique compared to others used for upgrading plant-based oils and animal fats to consumable fuel for energy production or transportation purposes (Jitputti et al. 2006; Meher et al. 2006). The product fuel obtained from this process is known as biodiesel and is one of the most commonly used and commercialized products from plant-based oils and animal fats. Transesterification is not a new method; it was first reported in 1853 in which alcoholysis of castor oil was done with ethanol, but the desired product was glycerol (Demirbas 2005). It is considered to be cheapest among other techniques used for upgrading plant-based oils and animal fats and to overcome the major problem of the higher viscosity of oils (Yan et al. 2007; Liang et al. 2009a, b). The important factors, which one should consider before applying transesterification for upgrading oils are fatty acid content, the water content in oil, amount of saturated component in fatty acids and components which cannot be converted such as sterols, hydrocarbons and tocopherols. The water content of oil should be less than 0.5% because it leads to hydrolysis of oil to generate FFAs, which cause soap formation in the presence of alkaline catalysts (Chouhan and Sarma 2011; Lin et al. 2011). The amount of saturated components does not affect the process as such but it can lead to poor properties of biodiesel produced. Meanwhile, the percentages of non-convertible should not exceed 1.5%. If they are more than that, this indicates that there is some contamination in oil and it should be filtered before transesterification (Mofijur et al. 2013).

6.5.1 *Biomass Collection and Catalysts Synthesis*

Date pits were gathered from nearby food processing factory located in Muscat, Oman. Firstly the date pits were grinded and powdered material was washed in order

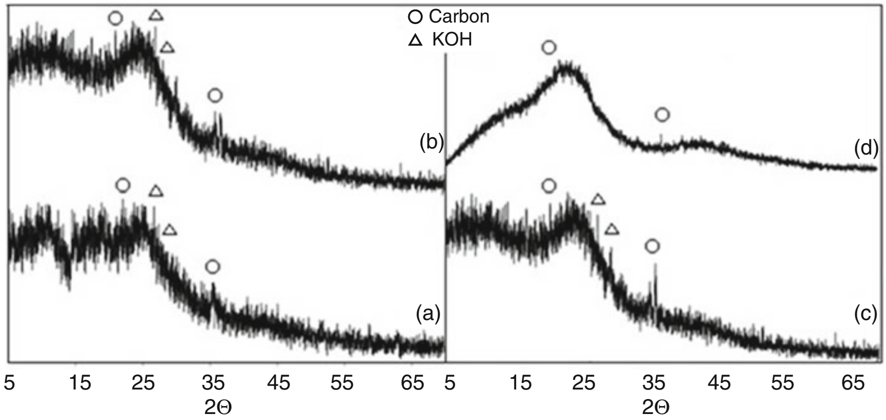


Fig. 6.6 XRD results: **(a)** catalysts C1; **(b)** catalysts C2; **(c)** catalysts C3 and **(d)** pristine carbon (Abu-Jrai et al. 2017)

to remove all impurities. The washed material was placed in oven for 6 h at 110 °C so as to remove moisture from powdered biomass. After drying the material was carbonized in muffle furnace at 500 °C in absence od oxygen for 4 hand heating rate applied was 3.5 °C/min. Further on the the carbonized material was further washed to remove all kind of impurities and obtained pristine carbon. The pristine carbon was dried in oven for four hours at 110 °C. The pristine carbon was further modified by imprehnating with KOH solution in different amounts (2 wt%, 4 wt% and 6 wt %). Pristine carbon was mixed with aqeous solution of KOH for almost 24 h at atmospheric conditions so as to impregnate KOH in carbon. The pristine carbon material modified with KOH in several ratios was first filtered and then dried. The produced catalysts were denoted as C1 (2 wt% KOH with carbon), C2 (4 wt% KOH with carbon) and C3 (6 wt% KOH with carbon).

X-ray powder diffraction (XRD) patterns were measured on PANalytical (Xpert PRO instrument, USA) fitted out with revolving anode and CuKα radiations. The analysis were carried out in continuous θ/2θ scan refraction mode for synthesized catalysts. The results of XRD for pristine carbon along with modified carbon with KOH are given in Fig. 6.6. Two prominent peaks are seen in pattern for pristine carbon such as 21°-24° and 35°–43° whixh relates to pure carbon and graphite respectively. Thus there were several peaks present in paterns given for modified form of catalysts which can be related due to impragnation of KOH. The peaks which ranges between 26°– 35° can be due to KOH in modified forms of pristine carbon derived from waste Date pits biomass. Thus it can be concluded based on patterns given by XRD that KOH has been succesfully impregnated in presitine carbon.

Scanning Electron Microscope (SEM) was used to measure crystal and surface morphology in SEM (JEOL JSM-7900F instrument, Japan). Images shown in Fig. 6.7 are for pristine carbon alond with its modified forms. It was observed from images that there was not any margin change between images. Moreover the

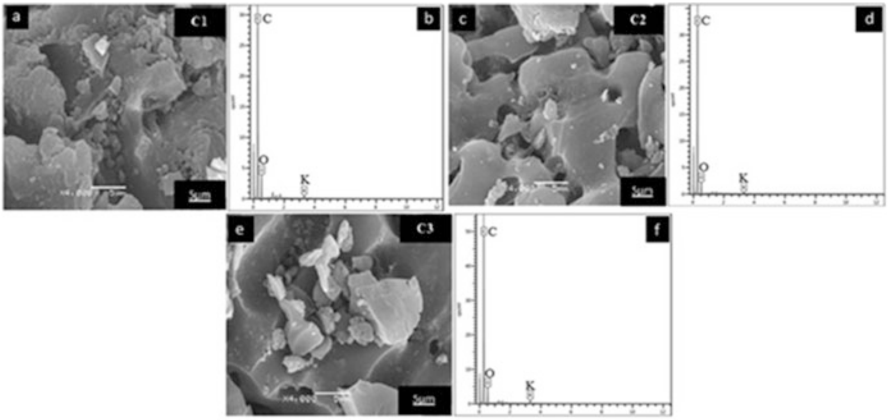


Fig. 6.7 SEM images for **(a)** pristine carbon with 2 wt% of KOH (C1); **(b)** EDS of C1; **(c)** carbon with 4 wt% of KOH; **(d)** EDS of C2; **(e)** carbon with 6 wt% of KOH and **(f)** EDS of C3. (Abu-Jrai et al. 2017)

Table 6.2 BET results for pristine carbon along with its modified forms

Sample ID	S_{BET} (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
C	432.1	0.22	6.62
C_1	229.5	0.17	6.41
C_2	218.2	0.15	6.19
C_3	210.5	0.14	5.98

images shows that there are not agglomerates present which lead to observation that KOH is dispersed uniformly on the waste date pits carbon and small changes in the images as shown in Fig. 6.7a, b and c might be due to increment in the concentration of KOH. Further EDX results gave assurance of well distribution of KOH on parent carbon material.

The catalysts were further analyzed through BET analyzer (ASAP 2020, Micromeritics Instruments Inc., Norcross, GA, USA) using nitrogen gas (99.995% pure) to determine surface properties such as surface area, size of pores and volume of pores as carbon material is highly porous. The measurements done in BET are shown in Table 6.2. It was observed that significant decrement in surface area and pore volume in modified form of pristine carbon which can be attributed to the fact that KOH articles occupied the pores up to some extent which affect the activity of catalysts. However, the final shows that pore size is up to marks so that it can support trans esterification.

So, it can be concluded based on all characterization that efficient catalysts have been synthesized with uniform distribution of KOH on parent carbon material. Moreover, it can stated that as amount of KOH is being increased tends to enhance the active site for trans esterification to produce biodiesel. Pore channel is basic requirement for biodiesel formation based on BET results it can be concluded that synthesized catalysts have definite pore channel along with active sites. As shown that all catalysts possess pore diameter even higher than the diameter of triglyceride molecule 5.8 nm (Wan Omar and Amin 2011). Thus it can be concluded that C3 can be more active attributed from the fact that it can provide more basic sites and suitable pore channel.

6.5.2 Biodiesel Production

Oil was extracted using a paper thimble (43 mm, Whatman International Ltd., Maidstone England), Firstly the powder biomass was placed in thimble and cotton was used to cover it from top and placed in Soxhlet assembly for oil extraction. Extraction process was done for 7 h while using n-hexane as solvent and once extraction time is over the mixture of oil and solvent are separated by using rotary evaporator (Buchi, Switzerland). To produce transesterification was carried out in two neck flask and experiments were done according to plan developed by using RSM software using Taguchi's method as mentioned in Table 6.3. Parameters under consideration were temperature, methanol-to-oil ratio, time, and catalysts type against the yield of biodiesel which set as response factor calculated experimentally based on Eq. 6.1.

$$Yield = \frac{wt\ of\ methyl\ produced}{wt\ of\ oil\ as\ feed} \times 100 \tag{6.1}$$

6.5.3 ANOVA Analysis

Significance of all process variables was determined through statistical analysis known to be ANOVA. First of all a model is predicted based on experimental data

Table 6.3 Plan for experiment developed using RSM

Time (min)	Temperature (°C)	Catalyst type	Alcohol: Oil	Yield (%)
80	65	1	15	82.1
80	60	3	12	70.1
40	70	3	15	77.4
80	70	2	9	83.7
60	65	3	9	91.6
60	70	1	12	84.8
40	60	1	9	75.3
60	60	2	15	73.1
40	65	2	12	82.9

Table 6.4 ANOVA analysis for transesterification of date pits oil

Source	F-value	p-value Prob > F
Model	65.97	0.015
Time (min)	23.32	0.041
Temperature (°C)	142.8	0.007
Alcohol: Oil	31.74	0.033
ANOVA analysis		
Standard deviation	0.95	
Corrected value (%)	1.18	
R-squared	0.995	
Signal/noise	25.682	

obtained by RSM and p-value test predicts which model is most suitable for current process. For p-value test the value should be less than 0.05 then it is significant with more than 95% confidence level. Further on coefficient of determination (R^2) gave another prediction for most significant model for current process and its variance from experimental data. In order to examine the current process ANOVA analysis is performed and shown in Table 6.4.

As discussed earlier that for significant model p-value should be less than 0.05 thus for current process model p-value is 0.015 which gave the understanding that model is significant with more than 95% level of confidence. In similar value this p-value also indicates the significance for each parameter along with interaction parameter and cross products. Thus, ANOVA study told that how nominal affect is of parameters on yield of biodiesel and based on results it can be revealed that the most significant effect was of temperature on yield of biodiesel. The predicted model is shown in Eq. 6.2.

$$\text{Yield} = 80.11 - 1.58A[1] + 3.06A[2] - 7.28B[1] + 5.42B[2] + 3.42D[1] - 0.84D[2] \quad (6.2)$$

High level of accuracy is obtained when CV is low which is the actual indicator for good agreement between experimentally determined values of biodiesel yield and values taken based on model predicted from ANOVA analysis. Moreover this was further justified by high value near to 1 of R^2 which gave good fitting of experimental value with model predicted value. Thus this can be also observed from the plot shown in Fig. 6.8 as actual yield and predicted yield has good coincidence between each as they are almost linear with each other. Similarly, it can be seen in Fig. 6.8 that response values calculated based on the predicted and actual experimental value were in good agreement.

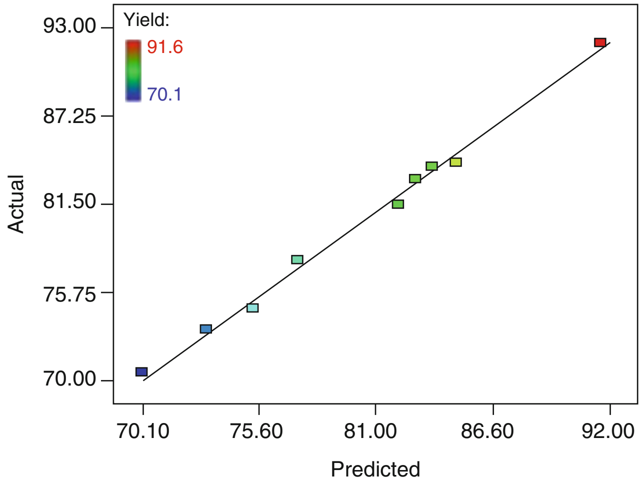


Fig. 6.8 Biodiesel yield actual vs predicted values (Abu-Jrai et al. 2017)

6.5.4 *Parametric Study*

In order to examine the effect of process parameters on biodiesel yield a detailed parametric is conducted as shown in Fig. 6.9. First of all process time was considered and other parameters were constant. It can be observed from figure that as the time is increased biodiesel yield start increasing but this behavior was upto certain time and after that the decreasing trend was observed. Thus trend the of time can be attributed to fact that initially time was not enough for reactants to interact and form the product. Moreover as time start increasing the yield increased lead to observation that reactants got enough time to interact and form the product but the decrement in yield may be attributed to the observation that due to difficulty in separation of downstream process while the reaction is reversible thus cause the decrement in yield of biodiesel. Process temperature is one of the important parameter to be analyzed and as shown in figure it can be observed that initially at low temperature biodiesel yield was quite low. However with the increment in temperature a significant increase in yield was observed. Similarly to time temperature also gave similar kind of trend. The yield increased up to certain limit and after that the yield decreased by increasing temperature. This observation can be related to the fact that but increasing the temperature the affinity of reactants increases and they react to form biodiesel. However, as the temperature is increased further the availability of methanol in reaction vessel starts decreasing thus causing the reversible reaction and tending to decrease the biodiesel yield. (Gurunathan and Ravi 2015). Another parameter studied was methanol to oil ratio and its effect on biodiesel is shown by Fig. 6.9c. As the reaction is reversible based on this fact excess methanol is provided so as move reaction into forward direction and according to stoichiometric calculation, molar ratio of methanol to oil 3:1 is required only for transesterification

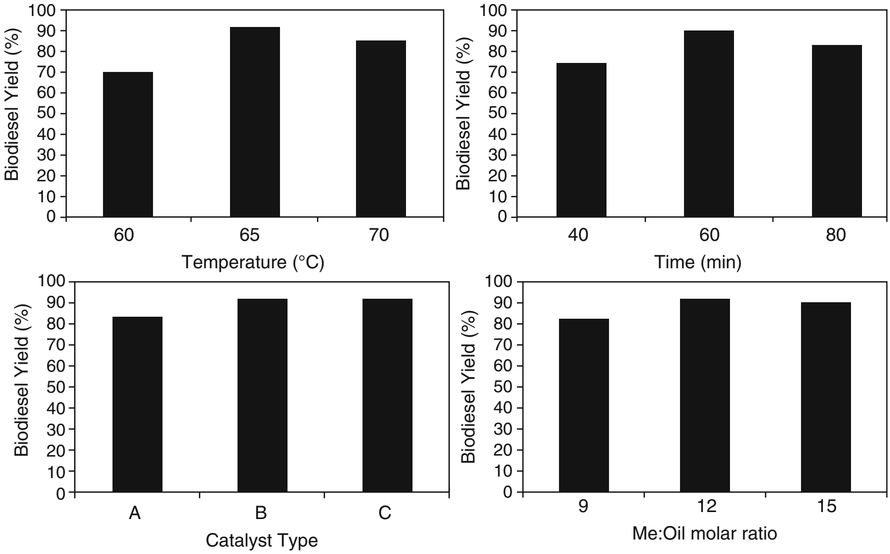


Fig. 6.9 Biodiesel yield with respect to temperature, time, catalyst type and methanol to oil ratio

reaction. Based on the trend shown in the figure it can be said that by increasing ratio tend to increasing the yield of biodiesel but increasing the ration further yield of biodiesel decreased tending to the observation that higher ratio may obstruct the separation of byproducts and leading to decrement in biodiesel yield. In the last effect a catalyst loading was studied and tend in shown in Fig. 6.9d. It can be observed that both catalyst C1 and C2 gave lower yield of biodiesel as compared to C3. This can be related to the fact that in C3 there was more quantity of KOH and thus this tends to provide more active sites for the reaction. Based on the parametric study conducted it can be suggested that optimum conditions are 65 °C process temperature, for 1 h reaction time when C3 catalysts was used with methanol to oil ratio 9:1 and biodiesel yield was 91.6%.

6.5.5 Quality of Biodiesel

Quality of any fuel synthesized is to be determined before claiming its suitability to be used as fuel. Thus several techniques given by international standards ASTM and EN were considered for evaluation f produced biodiesel. It was observed that biodiesel produced gave cetane number 60.31 that fulfill the minimum requirement defined by standards. One of major drawback of biodiesel to be used as a fuel is its bad low temperature properties in colder regions. But the produced biodiesel gave better low temperature properties which were cloud point 3.7 °C, pour point is −1.6 °C and cold filter plugging point −0.62 °C. Thus for Phoenix dactylifera kernel oil, low-temperature properties are quite considerable. Moreover, other measured properties include flash point and calorific values which were 141 °C and 43.24 MJ/kg respectively. As flash point refers to the temperature above which fuel may ignites thus for produced biodiesel flash point is hgher than the minimum limit defined by standards. Further on kinematic viscosity and density of produced biodiesel was observed to be at 40 °C was 4.24 mm^2/s and 881 kg/m^3, respectively. One of major property which can help to establish the observation that either fuel storage is safe or not in terms of corrosion is acid value and for produced biodiesel is 0.32 mg KOH/g and this less than the limit defined by ASTM and EN standards thus enables its storage and transportation safe.

6.6 Conclusions

All parts of the world are facing issues regarding the depletion of fossil reserves due to excess usage and ever-increasing demand. Moreover, combustion of fossil fuels causes environmental pollution due to emission of excess CO_2, thus all these issues lead the search for an alternative source for energy production and transportation sector. Biomass is considered to be a promising alternative for reducing demand and consumption of fossil-based fuel reserves. In Oman, abundantly available biomass from agricultural waste is date pits which are valorized in present research work to biofuels and catalysts. First of all, grinded date pits were used to extract the oil in Soxhlet apparatus in which hexane was used as solvent. Standard method AOCS was adopted for extraction.

Date palm waste (pits) were effectively engaged for oil extraction and carbon post oil extraction wss engaged in catalysts synthesis successfully to produced biodiesel. Moreover, it was revealed based on characterization that impregnated material was uniformly distributed and gave equal number of active sites for biodiesel production. Based on the parametric study conducted it can be suggested that optimum conditions are 65 °C process temperature, for 1 h reaction time when C3 catalysts was used with methanol to oil ratio 9:1 and biodiesel yield was 91.6%. Moreover produced biodiesel was suitable for commercial usage as fuel based on fuel properties measurement and there comparison with standards ASTM and EN.

So, the conclusive remark for overall research work reported was to valorize waste date pits which are abundantly available in Oman. All aspects were considered, such that the oil extracted was subjected to the production of biofuel such as biodiesel. Moreover, biodiesel was produced in the presence of heterogeneous carbon catalysts which help to overcome issues related to usage of conventional homogeneous catalysts. The synthesized catalyst was highly active which makes biodiesel production economical.

References

Abas N, Kalair A, Khan N (2015) Review of fossil fuels and future energy technologies. Futures 69 (0):31–49. https://doi.org/10.1016/j.futures.2015.03.003

Abu-Jrai AM, Jamil F, Al-Muhtaseb A a H, Baawain M, Al-Haj L, Al-Hinai M, Al-Abri M, Rafiq S (2017) Valorization of waste date pits biomass for biodiesel production in presence of green carbon catalyst. Energy Convers Manag 135:236–243. https://doi.org/10.1016/j.enconman.2016.12.083

Amani MA, Davoudi MS, Tahvildari K, Nabavi SM, Davoudi MS (2013) Biodiesel production from Phoenix dactylifera as a new feedstock. Ind Crop Prod 43(0):40–43. https://doi.org/10.1016/j.indcrop.2012.06.024

Aransiola EF, Ojumu TV, Oyekola OO, Madzimbamuto TF, Ikhu-Omoregbe DIO (2014) A review of current technology for biodiesel production: state of the art. Biomass Bioenergy 61 (0):276–297. https://doi.org/10.1016/j.biombioe.2013.11.014

Archibald D (2014) The Twilight of Energy Abundance. SPE Asia Pacific Oil & Gas Conference and Exhibition. Adelaide, Australia, Society of Petroleum Engineers

Azeem MW, Hanif MA, Al-Sabahi JN, Khan AA, Naz S, Ijaz A (2016) Production of biodiesel from low priced, renewable and abundant date seed oil. Renew Energy 86:124–132. https://doi.org/10.1016/j.renene.2015.08.006

Bae C, Kim J (2017) Alternative fuels for internal combustion engines. Proc Combust Inst. https://doi.org/10.1016/j.proci.2016.09.009

Banković-Ilić IB, Stamenković OS, Veljković VB (2012) Biodiesel production from non-edible plant oils. Renew Sust Energ Rev 16(6):3621–3647. https://doi.org/10.1016/j.rser.2012.03.002

Baroi C, Dalai AK (2015) Process sustainability of biodiesel production process from green seed canola oil using homogeneous and heterogeneous acid catalysts. Fuel Process Technol 133:105–119. https://doi.org/10.1016/j.fuproc.2015.01.004

Bart JCJ, Palmeri N, Cavallaro S (2010a) 1 – Biodiesel as a renewable energy source. Biodiesel Science and Technology, Woodhead Publishing pp 1–49

Bart JCJ, Palmeri N, Cavallaro S (2010b) 12 – Analytical methods and standards for quality assurance in biodiesel production. In: Biodiesel science and technology. Woodhead Publishing, Oxford, pp 514–570

Capellán-Pérez I, Mediavilla M, de Castro C, Carpintero Ó, Miguel LJ (2014) Fossil fuel depletion and socio-economic scenarios: an integrated approach. Energy 77(0):641–666. https://doi.org/10.1016/j.energy.2014.09.063

Carbon Cycle (2018.) https://eo.ucar.edu/kids/green/cycles6.htm

Chen K-T, Wang J-X, Dai Y-M, Wang P-H, Liou C-Y, Nien C-W, Wu J-S, Chen C-C (2013) Rice husk ash as a catalyst precursor for biodiesel production. J Taiwan Inst Chem Eng 44 (4):622–629. https://doi.org/10.1016/j.jtice.2013.01.006

Cherubini F (2010) The biorefinery concept: using biomass instead of oil for producing energy and chemicals. Energy Convers Manag 51(7):1412–1421. https://doi.org/10.1016/j.enconman.2010.01.015

Chouhan APS, Sarma AK (2011) Modern heterogeneous catalysts for biodiesel production: a comprehensive review. Renew Sust Energ Rev 15(9):4378–4399. https://doi.org/10.1016/j.rser.2011.07.112

Demirbas A (2005) Biodiesel production from vegetable oils via catalytic and non-catalytic supercritical methanol transesterification methods. Prog Energy Combust Sci 31 (5–6):466–487. https://doi.org/10.1016/j.pecs.2005.09.001

Demirbas A (2007) Progress and recent trends in biofuels. Prog Energy Combust Sci 33(1):1–18. https://doi.org/10.1016/j.pecs.2006.06.001

Demirbas A (2008) Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. Energy Convers Manag 49(1):125–130. https://doi.org/10.1016/j.enconman.2007.05.002

Dewulf J, Van Langenhove H, Van De Velde B (2005) Exergy-based efficiency and renewability assessment of biofuel production. Environ Sci Technol 39(10):3878–3882. https://doi.org/10.1021/es048721b

Di Gianfrancesco A (2017) 1 – The fossil fuel power plants technology. In: Materials for Ultra-Supercritical and Advanced Ultra-supercritical Power Plants. Woodhead Publishing, Cambridge, MA, pp 1–49

El Hag MG, Al-Merza MA, Al Salti B (2002) Growth in the Sultanate of Oman of small ruminants given date byproducts-urea multinutrient blocks. Asian Australas J Anim Sci 15(5):671–674

Gerhard K, Robert OD, Marvin OB (1997) Biodiesel: the use of vegetable oils and their derivatives as alternative diesel fuels. Fuels and chemicals from biomass, vol 666. Am Chem Soc, pp 172–208

Grammelis P, Margaritis N, Karampinis E (2016) 2 – Solid fuel types for energy generation: Coal and fossil carbon-derivative solid fuels A2 – Oakey, John. In: Fuel Flexible Energy Generation. Woodhead Publishing, Boston, pp 29–58

Gurunathan B, Ravi A (2015) Process optimization and kinetics of biodiesel production from neem oil using copper doped zinc oxide heterogeneous nanocatalyst. Bioresour Technol 190:424–428. https://doi.org/10.1016/j.biortech.2015.04.101

Jamil F, Al-Haj L, Al-Muhtaseb Ala'a H, Al-Hinai Mohab A, Baawain M, Rashid U, Ahmad Mohammad NM (2018) Current scenario of catalysts for biodiesel production: a critical review. Rev Chem Eng 34:267–297

Jitputti J, Kitiyanan B, Rangsunvigit P, Bunyakiat K, Attanatho L, Jenvanitpanjakul P (2006) Transesterification of crude palm kernel oil and crude coconut oil by different solid catalysts. Chem Eng J 116(1):61–66. https://doi.org/10.1016/j.cej.2005.09.025

Klass DL (2006) Biomass for renewable energy, fuels, and chemicals. Academic Press An Imprint of Elsevier

Knothe G (2010) 1 – Introduction. In: The Biodiesel Handbook, 2nd edn. AOCS Press, pp 1–3

Liang X, Gao S, Wu H, Yang J (2009a) Highly efficient procedure for the synthesis of biodiesel from soybean oil. Fuel Process Technol 90(5):701–704. https://doi.org/10.1016/j.fuproc.2008.12.012

Liang X, Gao S, Yang J, He M (2009b) Highly efficient procedure for the transesterification of vegetable oil. Renew Energy 34(10):2215–2217. https://doi.org/10.1016/j.renene.2009.01.009

Lin L, Cunshan Z, Vittayapadung S, Xiangqian S, Mingdong D (2011) Opportunities and challenges for biodiesel fuel. Appl Energy 88(4):1020–1031. https://doi.org/10.1016/j.apenergy.2010.09.029

Maczulak AE (2009) Renewable energy: sources and methods (Green Technology), Facts on File

Manickavasagan A, Essa MM, Sukumar E (2012) Dates production, processing, food and medical values. CRC Press, New York

Meher LC, Vidya Sagar D, Naik SN (2006) Technical aspects of biodiesel production by transesterification—a review. Renew Sust Energ Rev 10(3):248–268. https://doi.org/10.1016/j.rser.2004.09.002

Mofijur M, Masjuki HH, Kalam MA, Atabani AE, Shahabuddin M, Palash SM, Hazrat MA (2013) Effect of biodiesel from various feedstocks on combustion characteristics, engine durability and materials compatibility: a review. Renew Sust Energ Rev 28(0):441–455. https://doi.org/10.1016/j.rser.2013.07.051

Mohr SH, Wang J, Ellem G, Ward J, Giurco D (2015) Projection of world fossil fuels by country. Fuel 141(0):120–135. https://doi.org/10.1016/j.fuel.2014.10.030

Panwar NL, Kaushik SC, Kothari S (2011) Role of renewable energy sources in environmental protection: a review. Renew Sust Energ Rev 15(3):1513–1524. https://doi.org/10.1016/j.rser.2010.11.037

Ptasinski KJ (2016) Efficiency of biomass energy. Wiley

Ringsmuth AK, Landsberg MJ, Hankamer B (2016) Can photosynthesis enable a global transition from fossil fuels to solar fuels, to mitigate climate change and fuel-supply limitations? Renew Sust Energ Rev 62:134–163. https://doi.org/10.1016/j.rser.2016.04.016

Rosillo-Calle F, Woods J (2012) The biomass assessment handbook: bioenergy for a sustainable environment. Earth Scan

Shafiee S, Topal E (2009) When will fossil fuel reserves be diminished? Energy Policy 37 (1):181–189. https://doi.org/10.1016/j.enpol.2008.08.016

Tiwari GN, Mishra RK (2011) Advanced renewable energy sources. RSC

Toka A, Iakovou E, Vlachos D, Tsolakis N, Grigoriadou A-L (2014) Managing the diffusion of biomass in the residential energy sector: an illustrative real-world case study. Appl Energy 129 (0):56–69. https://doi.org/10.1016/j.apenergy.2014.04.078

Utama NA, Fathoni AM, Kristianto MA, McLellan BC (2014) The end of fossil fuel era: supply-demand measures through energy efficiency. Procedia Environ Sci 20(0):40–45. https://doi.org/10.1016/j.proenv.2014.03.007

Vertes AA, Qureshi N, Blaschek HP, Yukawa H (2010) Biomass to biofuels. Wiley, U.S.

Wan Omar WNN, Amin NAS (2011) Biodiesel production from waste cooking oil over alkaline modified zirconia catalyst. Fuel Process Technol 92(12):2397–2405. https://doi.org/10.1016/j.fuproc.2011.08.009

Yan S, Lu H, Liang B (2007) Supported CaO catalysts used in the transesterification of rapeseed oil for the purpose of biodiesel production. Energy Fuel 22(1):646–651. https://doi.org/10.1021/ef070105o

Yusuf NNAN, Kamarudin SK, Yaakub Z (2011) Overview on the current trends in biodiesel production. Energy Convers Manag 52(7):2741–2751. https://doi.org/10.1016/j.enconman.2010.12.004

Chapter 7
Different Extraction Methods, Physical Properties and Chemical Composition of Date Seed Oil

Jawhar Fakhfakh, Sahar Ben-Youssef, Mu. Naushad, and Noureddine Allouche

Abstract Vegetable oils are naturally found in a wide range of plants. Each plant provided separate and distinctive oil. However, only few of these plants are exploited for their economic importance. Vegetable oils have a major role in human nutrition. They provide a high energy source and contain distinctive fatty acids which are essential for health and these are not developed by the human body. The major source of vegetable oils is the seeds of annual plants and oil-bearing trees. Nowadays and with the word increase demand on vegetable oils, oil-processing industries searches for new exploitable sources. Recycling agricultural wastes constitutes one of the pertinent alternatives for the production of edible oils. Date palm seeds are promising source for this purpose.

The aim of this chapter is to present up–to–date data on the different extraction techniques used for getting Date seed oils (DSO) from different sources and leading to different yields.

These extraction techniques included (i) cold pressure; (ii) conventional solid-liquid extraction like maceration, Bligh-Dyer and Soxhlet extractions; and (iii) non-conventional extractions such as microwave, ultrasound and supercritical fluid extractions using either petroleum solvents like hexane and petroleum ether or MeTHF as green solvent for the first two techniques and CO_2 for the last one. Cold pressure, supercritical fluid and green solvent extractions afforded the safer oils while Soxhlet extractions give the better yields.

In order to evaluate the compositional quality as well as the nutritional and sensory properties of DSOs, several physicochemical properties like refractive index, color perception, melting point, viscosity, iodine value, saponification value, and peroxide value were assessed.

J. Fakhfakh (✉) · S. Ben-Youssef · N. Allouche
Laboratory of Organic Chemistry LR17ES08 (Natural Substances Team), Department of Chemistry, Faculty of Sciences of Sfax, Sfax, Tunisia
e-mail: jawharfakhfakh@yahoo.fr

M. Naushad
Department of Chemistry, College of Science, King Saud University, Riyadh, Saudi Arabia

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_7

Date seeds contain between 3 and 16.5% oil. DSO contains different types of fatty acids (FA) from which the most abundant were oleic (C18:1 ω9; 25.89–55.10%), lauric (C12:0; 8.4–45.88%), linoleic (C18:2 ω6; 2.47–19.23%), palmitic (C16:0; 8.3–16.22%) and myristic (C14:0; 0.04–18.76%) acids of which oleic acid is the predominant. Lauric and oleic acids are the main saturated and unsaturated fatty acids of DSO respectively. Other FAs exist in trace level. DSO has low acidity (0.15–0.90%) and low peroxide value (3.16–6.91 meq O_2/kg) allowing its possible use in food applications. DSO could resist thermal treatments for long period (30–40 h long) and could be utilized in frying and cooking. Additionally, DSO contains tocophereols and tocotrieneols which together exist in an average of 70.75 mg/g oil. Phytosterols exist also in minor amounts in DSO and constitute most of the unsaponifiable matter of which β-sitosterol was found to be the predominant (76%) followed by Campesterol (29.90%) and Δ^5-Avenasterol (29.56%). 96–99% of DSO is triacylglycerids composed mainly by LaMM + LaLaP with 18.9% of relative composition followed by LaMP + MMM (15.31%), LaOO + PLL+ MPL (12.86%) and LaPO (11.33%).

Keywords Date palm seed oil · Oil extraction · Soxhlet · Maceration · Microwave · Ultrasound · Green extraction · Supercritical fluid · Chemical composition · Physicochemical properties

7.1 Introduction

Since earlier ages, humans are using fats and oils for food as they are easily extracted from their source. Fats are usually from animal source whereas oils from vegetable source. Eating habits of people, especially the consumption of fats and oils, are very influenced by climate and availability. Seeds of annual plants as well as oil-bearing trees represent the largest source of vegetable oils. Oil-bearing plants like olive, coconut and palm provide oil from the fruit pulp rather than the seed of the fruit. Palm also can afford oil from its seed's kernel. Seeds of annual plants require a relatively temperate climate whereas oil-bearing tree fruits grow in a relatively warm climate. The highest oil yields are usually provided by most of the fruits and kernels of oil-bearing trees. Oil-bearing trees have a long productive life. Their annual production changes from 1 year to another depending on several effects. This productivity, therefore, cannot be geared to variable market requirements that change from year to year.

In the last few decades, many people have changed their diet by shifting their consumption from animal fats to vegetable oils. In fact, vegetable oils have competitive pricing and attractive nutritional and healthy concerns like higher levels of polyunsaturated fat and lower levels of saturated fat and cholesterol. This has led to several repercussions such as the increase of world's vegetable oils demand; changes of source oils regarding the medical, chemical and biological studies results; development of genetically modified oil seeds plants and search of new vegetable oils sources. One of the most promising alternatives is the use of agricultural wastes as a new source of edible oils from which we can distinguish date palm seeds.

The date palm tree (*Phoenix dactylifera* L.) is distributed over the arid and semiarid regions of the north hemisphere of the earth. Date palm constitutes the most important fruit tree; and constitutes a basic source of economy and remuneration for many people living in Saharian regions (Besbes et al. 2004a, b). Date processing industries and home consuming can furnish a large quantity of date seeds either directly from the gap-conditioning or from the stations palm grove. The weight of date seeds varies between 10 and 15% of date mass (Hussein et al. 1998) and contains about 4–16.5% crude oil (Aris et al. 2013; Biglar et al. 2012; Al-Farsi et al. 2007; Besbes et al. 2005; Jamil et al. 2016).

Date seeds are considered for a long time as an agro-industrial waste and used either as an additive for animals and poultry feed materials or a conventional soil fertilizer (Vandepopuliere et al. 1995). They were also used traditionally to make coffee in the Arabian Peninsula (Ali-Mohamed and Khamis 2004) and to get oil either for pharmaceutical or cosmetic products (Ben-Youssef et al. 2017). Literature reported several works focused on lipid extraction and chemical composition of DSO from different varieties.

In this chapter we aimed to recover the different used methods for the extraction of lipids from date seeds along with the chemical composition and physicochemical properties of the extracted oils. The extraction methods included mainly cold pressure, solvent extraction, ultrasound and microwave assisted extractions.

7.2 Date Seed Oil Extraction

7.2.1 Cold Pressed Oil

Nowadays, and comparing with oils obtained by conventional solvent extractions, cold-pressed oils attracted much more worldwide interest thanks to their nutritional and health benefits as well as their richness in bioactive components (Nederal et al. 2012), and leads to an increase in the demand for bioactive compounds of plant origin (Czaplicki et al. 2011). Indeed, the consumption of bioactive compounds like vitamins A, D, K and E, lipoic acid, omega fatty acids such as oleic, linoleic and linolenic ones, and many phenolic components like hydroquinones (Gulaboski et al. 2013) contributes efficiently in the cure of a lot of diseases. Additionally, many phenolics like flavonoids are required due to their therapeutic potential that includes anti-imflammatory, anti-artherogenic anti-microbial, anti-allergenic, antioxidant, anti-thrombotic and vasodilatory properties (Balasundram et al. 2006).

Cold-pressed oils are exempt of any trace of extracting solvent. Temperature during extraction does not attain an elevated level that could detriment the ingredients and cause loss of nutrients by oxidation or induce the formation of dangerous toxins in seeds and seeds oil. Many standards and amendments required that oils should be obtained only by mechanical processes, such as expelling or pressing, without the application of heat. In any way this temperature should not exceed 50 °C (Codex Alimentarius Commission 1981; Lutterodt et al. 2010; Parry et al. 2006; Siger et al. 2008).

Oils extracted in this way retain their genuine flavor, aroma, and nutrients. The major disadvantage lies in the low oil yield obtained by this process compared with that obtained with conventional solvent extraction. Despite, cold pressed oil is much safer due to its emptiness of solvent residues (Lutterodt et al. 2011).

It is well known that cold-pressed oils contain higher levels of natural antioxidants (Lutterodt et al. 2010) that improves shelf-life stability and safety without the requirement of additional synthetic antioxidants (Yu et al. 2002).

Little data were available on research works tackling the subject of cold-pressed DSOs of which we can mention especially that reported by Gecgel et al. (2015). In their work Gecgel et al. (2015) have studied several cold pressed oils in term of their physicochemical properties and FA composition. Detailed data are reported in Table 7.3.

7.2.2 Conventional Extractions

Wide researches in literature was reported on the conventional solid-liquid extraction (SLE) of lipids and oils from date seeds using maceration and soxhlet methods with different solvents such as petroleum ether, n-hexane (Besbes et al. 2004b; Biglar et al. 2012; Nehdi et al. 2010; Kazemi and Dadkhah 2012), chloroform, methanol (Herchi et al. 2014), ethanol and acetone (Al-Sumri et al. 2016) (other references are displayed in Table 7.1).

7.2.2.1 Soxhlet Extraction

Franz von Soxhlet invented the Soxhlet extraction technique in 1879 for the determination of fat in milk. Since then, it has been widespread for the extraction in agricultural chemistry before becoming the most used tool for solid–liquid extraction in many fields like foodstuffs, pharmaceutics and environment. Soxhlet apparatus (Fig. 7.1) is still conventional in laboratories and has been the standard and reference method for solid–liquid extraction in maximum cases (Virot et al. 2007). Soxhlet extraction is a repeated cycles of solvent extraction. Generally, and in the phytochemistry field, air dried plant material, like seeds, is ground to fine powder, placed in a porous cartridge, sometimes called thimble, and then putted in the extractor. The solvent, contained in the flask, is brought to a boil, which transfers it to the upper part. Here, it is condensed through a refrigerant located at the top of the installation and accumulates around and inside the cartridge. When the solvent reaches the upper level of the siphon, the mixture is returned to the flask by pressure difference, where it is again evaporated. Several extraction cycles are thus carried out (Jensen 2007). Some standards have fixed the duration of the operation at 8 h (ISO 659–1988 1988). Compared to other techniques, if Soxhlet extraction gives the best extraction yield,

Table 7.1 Yields of date seed oil recovery based on selected extraction methods

Extraction method	Solvent extraction	Operational conditions	Percentage of oil based on dry matter (%)	References
Soxhlet	Petroleum ether	15 g	12.7	Basuny and Al–Marzooq (2011)
		40–60 °C		
		18 h		
Soxhlet	Petroleum ether	15 g	10.19–12.67	Besbes et al. (2004a, b, 2005)
		40–60 °C		
		18 h		
Soxhlet	Petroleum ether	Seed to solvent ratio (1/3)	6.4–13.2	Kazemi and Dadkhah (2012)
		Reflux		
		1.5 h		
Soxhlet	Hexane	40 g	10.36	Nehdi et al. (2010)
		Reflux		
		8 h		
Sohxlet	Petroleum ether	20 g	10.13–12.37	Chaira et al. (2007)
		Reflux		
		Time not indicated		
Sohxlet	n-hexane	20 g	4.62–7.72	Biglar et al. (2012)
		Reflux		
		8 h		
Sohxlet	Petroleum ether	Weight not indicated	0.26 and 8.33	Saafi et al. (2008)
		Reflux		
		8 h		
Sohxlet	MeOH	Same conditions	9.78	Al-Sumri et al. (2016)
	EtOH	5 g	8	
	Acetone	Reflux	9.5	
		4 h		
Soxhlet	Petroleum ether	10 g	8.7–10.0	El-Shurafa et al. (1982)
		Reflux		
		8 h		
Soxhlet	Hexane	50 g	8.5	Jadhav et al. (2016)
		78 °C		
		3 h		
Soxhlet	Petroleum ether	6 h	7.11	Herchi et al. (2014)
		Reflux		
		Time not indicated		
Soxhlet	n-hexane	15 g	4.44–7.24	Ben-Youssef et al. (2017)
	MeTHF	Reflux	5.02–5.97	
		8 h		

(continued)

Table 7.1 (continued)

Extraction method	Solvent extraction	Operational conditions	Percentage of oil based on dry matter (%)	References
Soxhlet	Hexane	Weight not indicated	5.89–7.83	Nehdi et al. (2018)
		Reflux		
		8 h		
Soxhlet	Hexane	Weight not indicated	16.5	Jamil et al. (2016)
		70 °C		
		7 h		
Soxhlet	Hexane	Operational conditions not indicated	8.2	Reddy et al. (2017)
Soxhlet	Hexane	Weight and temperature not indicated	5.66	Bouhlali et al. (2017)
		8 h		
Soxhlet	Hexane	Weight not indicated	5.05–6.08	Boukouada and Yousfi (2009)
		Reflux		
		6 h		
Soxhlet	Hexane	750–900 g	5.064–6.833	Abdalla et al. (2012)
		Reflux		
		4–6 h		
Soxhlet	Petroleum ether	Weight not indicated	5.77–10.71	Al-Juhaimi et al. (2018)
		5 h		
		Reflux		
Macertion	n-hexane	100 g	5.12	Herchi et al. (2014)
		20 °C		
		4 h		
Soxhlet	(Chloroform-methanol 2:1 v/v)	Same conditions	9.3	Yousuf and Winterburn (2017)
	Hexane	4 g	5.3	
	Petroleum ether	140 °C	3.4	
		4 h		
Maceration	Petroleum ether	Operational conditions not indicated	5.71–8.77	Habib and Ibrahim (2009)
Macertion	n-hexane	50 g	4.2	Jadhav et al. (2016)
		Room temperature		
		3 days		
Macertion	n-hexane	Same conditions	4.44	Ben-Youssef et al. (2017)
	MeTHF	15 g	4.04	
		Room temperature		
		30 min		

(continued)

Table 7.1 (continued)

Extraction method	Solvent extraction	Operational conditions	Percentage of oil based on dry matter (%)	References
Bligh and Dyer's method	($CHCl_3$-MeOH 2:1 v/v)	50 g	5.70	Herchi et al. (2014)
		Room temperature		
		Time not indicated		
Ultrasound	n-hexane	Same conditions	6.18	Ben-Youssef et al. (2017)
	MeTHF	15 g	5.57	
		Reflux		
		30 min		
Ultrasound	n-hexane	50 g	8.5	Jadhav et al. (2016)
		20 °C		
		45mn		
Microwave	n-hexane	Same conditions	5.52	Ben-Youssef et al. (2017)
	MeTHF	15 g	4.74	
		30 min		
SC-CO_2	CO_2	Extraction pressure 41.4 MPa	3.0	Aris et al. (2013)
		T° 70 °C		
		40 min		
		CO_2 flow rate 24 mL/min		
		Particle size 0.5 mm.		

the obtained extracts are much more complex, and the major inconvenient is the abundance of artifacts coming from the long exposition of the extracted compounds to heat and air oxygen which are the major source of chemical modifications. In addition, long operation time required, large solvent volumes, evaporation and concentration needed at the end of the extraction, and insufficiency for thermolabile analytes (Virot et al. 2007) constitutes other potential disadvantages of this technique.

Soxhlet extraction is the most cited technique in the literature used for extracting oil from date seeds (see references displayed in Table 7.1). It is sometimes used as reference against the other techniques because it gives, generally, the best yield of oil.

7.2.2.2 Maceration

This technique consisted on soaking plant material with solvent in a stoppered flask. The mixture is then submitted to continuous stirring an allowed to stand at room temperature for several hours or days until suitable phytochemicals are extracted (Handa et al. 2008). The obtained mixture is clarified by filtration or decantation

Fig. 7.1 Soxhlet extractor

after standing. The kind of used solvent decided the nature of the extracted compounds from plant material (Thakur and Arya 2014).

7.2.3 Green Extractions

7.2.3.1 Petroleum-Based Solvents

Hexane and petroleum ether have been used for decades as solvents for fats and oils extraction from plants (Virot et al. 2008). These solvents have various qualities for easy extraction of lipids such as easily removal by evaporation from the extracts, stability and convenient boiling point (Fine et al. 2013). However, many researches dealt with the toxic and hazardous effects of these solvents and considered the fact that they are sourced from fossil resources and registered under the REACH Regulation as a category 2 reprotoxic and as a category 2 aquatic chronic toxic (Sicaire et al. 2015).

7.2.3.2 Green Solvents

Nowadays, the environment friendly procedures become more interesting. To protect the environment and to develop the green chemistry, these petroleum solvents should be replaced by bio-based solvents (Chemat 2014; Battershill et al. 1987). These bio-solvents are generally produced from agricultural sources and many researches approve that they are greater potential candidates to replace petroleum solvents (Breil et al. 2016; Sicaire et al. 2015).

7.2.3.3 Green Method Extractions

Green technologies have a lot of advantages as reducing cost, time (completed in minutes instead of hours with high reproducibility), solvent consumption and power. In addition, they keep the stability of extracted compounds, simplify process and improve the extraction qualitatively and quantitatively (Arslan and Ozcan 2010; Chemat et al. 2008; Maskan 2000; Tiwari 2015). Limited research has been used the green extraction of oil and lipids in date seed (Ben-Youssef et al. 2017) using Ultasound and Microwave with bio-sourced solvent (MeTHF).

7.2.4 Microwave Extraction

This method makes possible to extract plant material at atmospheric pressure. It consists on placing the plant material in a reactor in a microwave oven. The internal heating of the plant with the solvent allowed the dilatation of plant cells conducting to the release of organic compounds. A refrigerant system located outside the microwave oven allows solvent condensation.

Microwaves are non-ionizing radiation in the electromagnetic spectrum of microwaves between 300 MHz and 300 GHz and having a wavelength between infrared and radio waves. The energy of the electromagnetic wave is discriminated as an energy vector thanks to the friction, the shocks and the molecular agitation produced by the migration of the ions and the dipolar rotation. The propagation of electromagnetic energy acts as a non-ionizing radiation that causes molecular motions of ions and rotation of the dipoles, but does not affect molecular structure. Many advantages with using microwave, that is a non-contact heat source, as: reduced thermal gradients, more effective heating, faster energy transfer, selective heating, reduced equipment size, faster start-up, faster response to process heating control, increased production and reducing of process steps (Paré and Bélanger 1997).

7.2.5 Ultrasound Extraction

The history of ultrasound is rooted in the study of sound with Isaac Newton's first theory that the sound is a waves in 1687 (Mason 1998). The difference between sound and ultrasound is the wave frequency. Those mechanical waves are able to move in an elastic medium at a frequency greater than the maximum limit of audibility of the human ear (16 kHz). Power ultrasonic operating at intensity between 20 and 100 kHz are used for extraction of plant molecules. When low frequency ultrasound is in a liquid it names the phenomenon of cavitation that is responsible for cell damage, transient micro-bubbles implode violently after reaching a critical size. The bubbles, thus, lead to destruct the cell walls (Chemat et al. 2011). More clearly, when the ultrasound transmits through any medium, it induces a series of compressions and rarefactions in molecules of the medium. Such alternating pressure changes cause the formation and, ultimately, the collapse of bubbles in a liquid medium. This phenomenon of creation, expansion, and implosive collapse of microbubbles in ultrasound-irradiated liquids is known as "acoustic cavitation". The implosion of cavitating bubbles generates also high-velocity inter-particle collisions, turbulence at a microscopic level and agitation in microporous particles of the vegetal sample that hastens the diffusion (M. Virot et al. 2008). Cavitation bubbles formed are roughly divided into two types: transient cavitations and stable cavitations (Tiwari 2015). The main advantage of ultrasound technique is to provide cell wall destruction at low temperature. Figure 7.2 shows the ultrasound apparatus used by Ben-Youssef et al. (2017) for the extraction of DSO using hexane and MeTHF as extracting solvents. Further details of these extractions are presented in the next sections.

Fig. 7.2 Ultrasound apparatus

7.2.6 Supercritical Fluid Extraction

Supercritical fluid extraction is widely used nowadays thanks to its many advantages towards the conventional large-scale extraction procedures due to strict rules against the use of volatile organic solvents (Bernardo-Gil et al. 2006; Bernardo-Gil et al. 2011; Pinto et al. 2011). Fluid passed in its supercritical state when its temperature and pressure reached or exceed its critical point.

Supercritical fluid extraction is highly selective because of the possibility to control the density of the used solvent such as carbon dioxide. CO_2 has high diffusion capacity and high solvating power making it more efficient for the extraction of compounds from a plant matrix (Herrero et al. 2010). The solvent is removed from the matrix by its depressurization which brings it back to its normal gaseous phase, leaving little or no residues (Abbas et al. 2008). Carbon dioxide (CO_2) is the most used solvent in the supercritical fluid extraction. It is naturally abundant, nontoxic, nonpolluting, inexpensive, inert, non-flammable and has a relatively low critical temperature (31.1 °C) and pressure (7.38 MPa) (Pinto et al. 2011; Norhuda and Jusoff 2009). Also, carbon dioxide has been globally admitted as safe by European Food Safety Authority (EFSA) and U S Food and Drug Administration (FDA) (Herrero et al. 2010). The limitation of this technique comes mainly from the requirement of supercritical technology and expensive equipments which increases the cost compared to conventional liquid extraction.

7.3 Physicochemical Properties of Date Seed Oil

Extraction yields as well as physicochemical properties like refractive index, color perception, melting point, viscosity, iodine value, saponification value, and peroxide value are usually assessed for oils in order to evaluate their compositional quality as well as their nutritional and sensory properties.

7.3.1 Extraction Yields Based on the Extraction Method

Dry date seeds contain between 3 and 16.5% of oil depending on the growth conditions, the stage of harvest and the source of raw material such as location and variety.

Table 7.1 summarizes the yield of obtained DSO based on the used method and the operating conditions. Surprisingly, there is a little academic information on the extraction yield and the chemical composition of cold pressed DSO. The majority of scientific works deals with solvent extracted oils that give a better oil yield necessary for further studies.

Several researches have used hexane and petroleum ether to extract DSOs using a Soxhlet apparatus (Abdalla et al. 2012; Al-Juhaimi et al. 2018; Basuny and Al–Marzooq 2011; Bouhlali et al. 2017; Boukouada and Yousfi 2009; Chaira et al. 2007; Reddy et al. 2017; Saafi et al. 2008). Hexane and petroleum ether having closer chemical and physical properties gave generally closer oil extracts in terms of yield and composition. As showed in Table 7.1 the yields obtained with hexane using Soxhlet method ranges from 4.44% (wt) (Ben-Youssef et al. 2017) and 16.5% (wt.) (Jamil et al. 2016). In their study Jamil et al. (2016) have used a ratio of solvent to seed of 4:1; 70 °C as operating temperature and 7 h as time course while Ben-Youssef et al. (2017) have used an extraction time of 8 h under reflux. Other authors have described the use of petroleum ether with Soxhlet for DSO recovery. The obtained yield ranged between 3.4% (wt.) (Yousuf and Winterburn 2017) and 13.2% (wt.) (Kazemi and Dadkhah 2012). Yousuf and Winterburn (2017) have used 4 h of extraction duration and 100 °C as operating temperature against just 1.5 h of extraction time under reflux used by Kazemi and Dadkhah (2012). Despites, the first yield is much lower than the second one. This could be due either to the used amount of solvent or, much likely, to the difference in the used date varieties.

Also, Yousuf and Winterburn (2017) have compared oil extraction from date seeds using three different solvent systems namely hexane, methanol/chloroform mixture and petroleum ether with different extraction times and particule sizes. The best yields were obtained with a particule size of ≤1 mm and an operating time of 4 h for the three solvent systems and were as 9.3% (wt.) with (chloroform-methanol 2:1 v/v) at 160 °C, 5.3% (wt) with hexane at 140 °C and 3.4% (wt.) with petroleum ether at 100 °C. Lipid extraction using (chloroform-methanol 2:1 v/v) as solvent is also known as Bligh and Dyer (1959) method. This method was used by Herchi et al. (2014) and afforded 5.70% (wt) of DSO. In this study authors have used maceration at 100 °C instead of Soxhlet technique.

Maceration with organic solvent is also used as an extraction method for the recovery of oil from date seeds. Most of the works were done with hexane or petroleum ether giving a yields ranging from 4.2% (wt) with hexane (Jadhav et al. 2016) to 8.77% with petroleum ether (Habib and Ibrahim 2009).

In a recent study Ben-Youssef et al. (2017) have elaborated the study of MeTHF (2-methyltetrahydrofuran) as green solvent and conducted a comparison of this solvent with hexane as petroleum solvent using several techniques as Soxhlet, maceration, microwave and ultrasound extractions. In this study they have used three date varieties (Deglet Noor, Allig and Belah). The best yields for the three varieties were obtained by Soxhlet for 8 h. Seeds of Deglet Nour gives the best extracted oil yield of 7.24% (wt) with hexane as solvent. However, MeTHF afforded the best yields for Allig and Belah (5.74% (wt) and 5.02% (wt), respectively) which allows to MeTHF to be a good candidate as an alternative solvent for lipids extraction from Allig and Bellah.

In the same work, Ben-Youssef et al. (2017) have used microwaves and ultrasound techniques for the extraction of lipids from Deglet Noor variety using, and makes a comparison with conventional extractions. Hexane and MeTHF afforded always comparable yields whatever the used extraction procedure. Ultrasound and microwaves gives higher yields than maceration but slightly lower than Soxhlet with just 30 min against 8 h for Soxhlet.

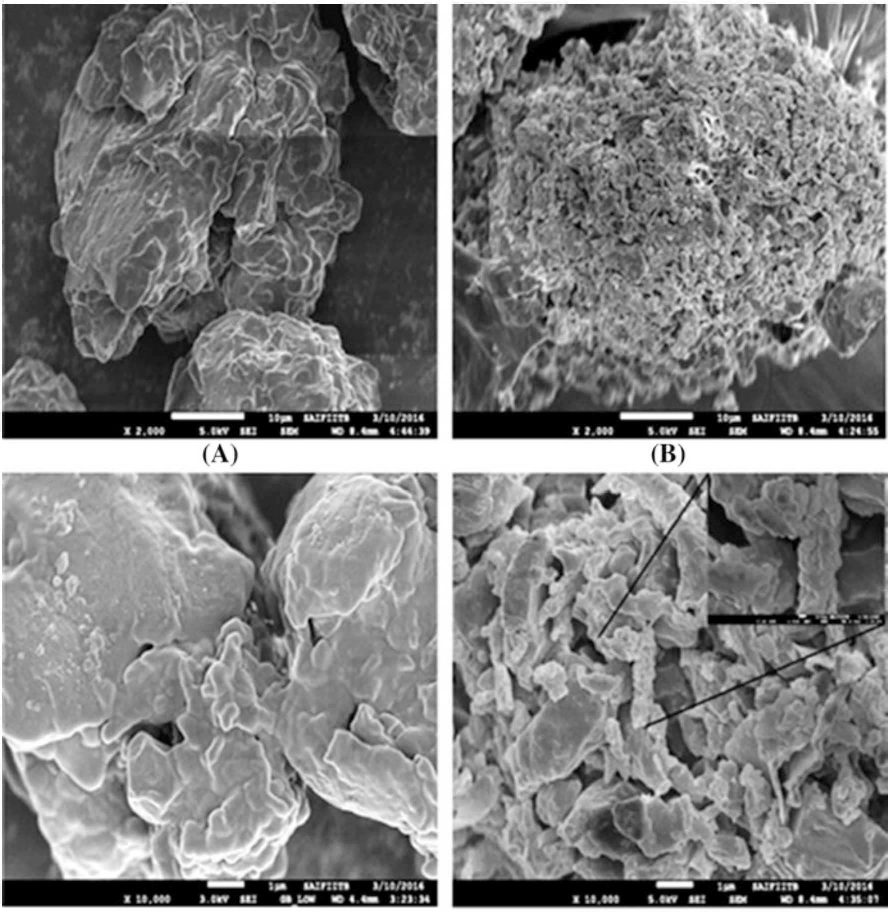
Jadhav et al. (2016) have also used ultrasound-assisted extraction method for extracting oil from date seeds using hexane as solvent. They have found the following optimum parameters: 45 min as sonication time; solvent-to-seed ratio of 5; 30% of 750 W as applied power and 20 °C as operating temperature. Compared with conventional solvent extraction methods, the ultrasound-assisted extraction method was described to be a more efficient due to short extraction time and low energy consumption. On the other hand, while yield obtained with ultrasound method was higher than that obtained with maceration method; it was close to the yield given by the Soxhlet extraction method.

Authors have assigned these results to the enhancement of the permeability of the solvent into the plant tissues throw physical effects of cavitations occurring onto the surface of the date seeds leading to the formation of cracks, crevices, and microfractures onto seed surfaces as consequences of cell walls disruption. Then, it will be easier for the solvent to reach the cell tissues and extract their containing oil efficiently.

In order to visualize the ultrasonic effect on seed surfaces, Jadhav et al. (2016) resorted to field emission scanning electron microscopy (FE-SEM) technique to compare images of fresh date seed and ultrasonically treated date seed which are illustrated here in Fig. 7.3. The Fig. 7.3 (a) and (c) show the regular, intact, smooth state of the raw date seed's surface. Figure 7.3 (b) and (d) exhibit the new state of this surface after treatment with ultrasound where microfractures and crevices appeared clearly.

Aris et al. (2013) have used supercritical carbon dioxide (SC-CO_2) for the extraction of oil from date seeds and have optimized the operational conditions for to obtain the highest oil yield. In this study they have used a particle size of 0.5 mm of ground date pits and they have obtained 3.0% as the highest oil yield when they have used an extraction pressure of 41.4 MPa, a temperature of 70 °C, an operating time of 40 min and a CO_2 flow rate of 24 mL/min. The obtained yield is too low as compared to conventional extractions. This could be due to the dissolving power and the degree of compatibility of carbon dioxide with the extracting oil.

On the other hand, It is well known that particle size of the ground seeds, the type of the used solvent and the extraction time, are the major parameters affecting the yield of oil (Ali et al. 2015). Al-Sumri et al. (2016) have studied these parameters using methanol, ethanol and acetone as solvents, different particle sizes of crushed seeds and different time of extraction. The better conditions were found by using methanol as solvent brought to a temperature of 15 °C above its boiling point, a particle size range of 0.212–1 mm and an extraction time of 4 h.



(A) (B) (C) (D)

Fig. 7.3 (**a**) and (**c**): Scanning electron microscopy (SEM) images of raw date seed amplified 2000× and 10,000× respectively. (**b**) and (**d**): SEM images of date seed after ultrasonic treatment amplified 2000× and 10,000× respectively. (Adopted from Jadhav et al. (2016) with permission)

7.3.2 Moisture, Volatiles and Refractive Index

In a recent study, Gecgel et al. (2015) measured a yield of moisture and volatiles contents of 0.6% (wt.) for CPDSO. Low moisture content is required for cold-pressed oils in order to sustain their quality and to lengthen their shelf-life (Teh and Birch 2013). This value is higher than the Codex Alimentarius Commission requirements fixing a maximum limit of 0.2% of moisture and volatiles content of cold-pressed oils (Codex Alimentarius Commission Codex Stan 1981).

The refractive index is an indicative physicochemical parameter easy to get for oils. it essentially depends on the carbon chains length and the number of double bonds existing in the FAs containing oil (O'Brien 2004) and very sensible to the oxidative processes (Gray 1978). Refractive indexes of DSOs obtained from different sources are very comparative. They ranged between 1.456 and 1.479 (Table 7.2).

Compared to other cold-pressed vegetable oils such as grape, walnut, safflower, argan, flax, pomegranate and golden berry that were obtained by similar conditions, CPDSO showed the lowest value for refractive index (1.4586), while pomegranate seed oil had the highest refractive index (1.5110). On the other hand CPSO showed a comparative refactive index when compared to DSOs obtained by other processes such as soxhlet extraction, maceration, microwave extraction (Table 7.2). The low value of DSO refractive index indicated that their FAs may be composed of medium-short hydrocarbon chains (Besbes et al. 2004a, b).

7.3.3 Color Perceptions

Oil's appearance plays a crucial role in their potential applications and customer perceptions (Parker et al. 2003). Since that, and in order to get measured and comparative parameters, color perception of oils was estimated by color-values measurements. Generally, a vegetable oils color comes from the existence of coloring pigments such as β-carotene, chlorophyll and tocopherols (Teh and Birch 2013; Raziq et al. 2012). High Chlorophyll content could indicate an unsuitable pressing conditions and leads to an unpleasant green or brown color of oil (Matthaus and Brühl 2003). While color measurements can be used for color classification, we found no scales or details developed for this classification. However, it is possible to estimate the amount of chlorophyll and carotenoids in an oil sample spectrophometrically by measuring the absorbance of an oil solution and following the procedure cited by Minguez –Mosquera et al. (1991). Usually cyclohexane is used as solvent in which case measurements should be done over a UV-Vis spectrometer at 470 and 670 nm, where 470 nm is related to the maximum absorption of the carotenoid fraction; and 670 nm is due to that of the chlorophyll fraction. The applied coefficient values of specific extinction were E0 = 2000 for lutein accounted as the major compound in the carotenoid fraction and E0 = 613 for pheophytin taken as the predominant pigment in the chlorophyll fraction. Thus, the applied formulas for quantifying pigments were as follows (Nehdi et al. 2014; Herchi et al. 2014):

$$\text{Chlorophyll (mg/kg)} = \left(A_{670} \times 10^6\right)/(613 \times 100 \times d).$$
$$\text{Carotenoid (mg/kg)} = \left(A_{470} \times 10^6\right)/(2000 \times 100 \times d).$$

Table 7.2 Physicochemical properties and minor constituents of some date seed oils

Parameter	References										
	Gecgel et al. (2015)	El- Shurafa et al. (1982)	Nehdi et al. (2010)	Besbes et al. (2004a) and (2004b)	Nehdi et al. (2018)	Reddy et al. (2017)	Herchi et al. (2014)			Bouhlali et al. (2017)	Boukouada and Yousfi (2009)
Extraction method	Cold pressed	Sx/PE	Nd	Sx/PE	Sx/H	Sx/H	Mc/H	Sx/PE	BD	Sx/H	Sx/H
Refractive index	1.4586	Nd	1.456	1.457–1.462[a]	1.4642	Nd	Nd	Nd	Nd	Nd	1.4778–1.4792
Acid value (mg KOH/g oil)	0.30	1.41–2.04	Nd	1.06–2.10[a]	Nd	1.83	1.28	1.37	1.10	1.083–1.813	1.35 -1.38
FFA (as oleic acid %)	0.15	2.36–4.08	0.59	0.53–1.05[a]	0.36–0.67	0.9	0.85	0.90	0.75	Nd	Nd
Peroxide value (meq O_2/kg)	3.6	Nd	3.62	1.6–2.5[a]	3.26–5.62	1.24	11.90	10.37	9.15	1.243–1.01	Nd
Iodine value (g/100 g)	51.27	48.32–66.28	76.66	44.1–45.5[a]	54.07–59.15	73.6	55.13	54.60	59.27	45.40–58.02	67.22–74.80
Saponification value (mg KOH/g oil)	155.9	201.1–224.4	191.28	Nd	204.62–207.73	208.33	198	193	190	202.33–222.74	204.84–215.87
Sterols (mg/kg)	Nd	Nd	336.07	3000–3500[b]	Nd	Nd	Nd	Nd	Nd	Nd	5417–7884
Tocopherols and tocotrienols (mg/100 g oil)	Nd	Nd	51.54	53.35–70.05[b]	44.73–110.82	Nd	Nd	Nd	Nd	Nd	Nd
Carotenoids (mg/100 g oil)	Nd	Nd	5.51	Nd	Nd	Nd	11.24	10.41	12.76	Nd	Nd

[a]Taken from reference Besbes et al. (2004b); [b]Taken from reference Besbes et al. (2004a)

Nd not determined, *Sx* Soxhlet method; *Mc* maceration method, *BD* Bligh and Dyer method, *H* hexane, *PE* petroleum ether

In these equations A represents the absorbance and d the spectrophotometer cell thickness usually 1 cm. Results are expressed in mg (of pigment)/kg (of date seed oil).

Following this method Herchi et al. (2014) have measured the amount of chlorophyll and carotenoid pigments in the seed oil of "Kentichi" date variety and have found 2.18 and 11.24 mg/kg oil of chlorophyll and carotenoids respectively when using maceration with hexane as an extracting method. These values are quite similar to those found in the same study by soxhlet method using petroleum ether as solvent and were 2.10 and 10.41 mg/kg oil of chlorophyll and carotenoids respectively.

Chlorophylls and carotenoids play an opposite role in oil protection against photo-oxidative deterioration. In fact, while chlorophylls speed up this deterioration by initiating the photosensitized oxidation of esters and unsaturated FAs in the presence of oxygen and light energy (Choo et al. 2007; Frankel 2005), carotenoids protect oils against the deterioration of photooxidation by deactivating the singlet oxygen and acting as light filters (Fakourelis et al. 1987; Perrin 1992).

7.3.4 Melting Point

Natural oils do not have an appropriate melting point. While pure compounds have sharp and distinct melting points, fats and oils that are complex mixtures of substances do not become completely liquid until they pass through a gradual softening. Triglycerides and fatty acids, the major oil's components, are the most depending melting point's compounds. The broad stability of their different crystal forms allowed distinctive melting points. Thus, it is more suitable to consider melting range instead of melting point. In recent studies, melting behavior of DSOs was concluded from DSC (Differential Scanning Calorimetry) experiments. In fact, the obtained DSC thermogram is characteristic of the considered oil and can be served as a fingerprint. Nehdi et al. (2010) reported a melting peak of 3.71 °C and a melting enthalpy of 62.08 J/g for DSO. This melting point is higher than those of several seed oils such as M. porifera (Fatnassi et al. 2009) and this could be due to the high content on saturated FAs compared to the other oils.

Besides, DSC is considered as a fast and very useful tool for determining differences between oils, for example between refined and natural oils or between fresh and rancimat ones. Besbes et al. (2005) have used DSC to study the effect of heating on the quality characteristics of DSO, and particularly its oxidation stability during storage following an accelerated test in a Rancimat system at a temperature of 100 °C. In this study, the oxidative stability of DSO was found to be much higher than that of most vegetable oils. Also, it was reported that DSO could resist thermal treatments for long period (30–40 h long) and could be used in frying and cooking. As a result, DSO may have a good shelf–life and could be stored safely for a relatively long period (Besbes et al. 2005). In this way, authors have used absorptivity in the UV range of seed oils as a tool for the analysis of their oxidative states since it was demonstrated that the formation of hydroperoxides depends on the double bonds in polyunsaturated FAs and their conjugation state, and could be easily measured by oil's absorbance in the UV spectrum (Shahidi and Wanasundra 1997). Usually, researchers consider specific absorption at 232 nm (K_{232}) and 270 nm (K_{270}) that are proportional to the amounts of primary and secondary oxidation products, respectively (Gharby et al. 2015). Besbes et al. (2005) have measured the absorptivity of two DSOs cultivars before and during rancimat treatment. The initial values were about $K_{232} = 2.1$ and 1.1 for Allig and Deglet Noor respectively and $K_{270} = 0.5$ for the two varieties. Authors ascribed the higher initial absorptivity at 232 nm of Allig seed oil to its elevated sensitivity to heating during the extraction procedure which conducted to higher content of oxidation primary products. In parallel, authors have checked the viscosity of these two oils during rancimat test and they have concluded that she evolved in the same way as absobtivity at 232 nm. Concerning viscosity, Deglet Nour has an initial viscosity of 20 mPa s which is closer to that of raspberry seed oil (26 mPa s) (Oomah et al. 2000) but lower than that Allig seed oil (40 mPa s) as well as those of most of other vegetable oils who ranged between 50 and 100 mPa s. The authors referred the difference in viscosity between the seed oils of the two date varieties to the fact that Allig seed oil contains more unsaturated FAs content while Deglet Noor seed oil is rich in short-medium hydrocarbon chain length FAs.

7.3.5 *Other Physicochemical Properties*

Literature data showed two different ways for presenting the free acidity. We can find either Free Fatty Acid (FFA) expressed as oleic acid (%) or Acid value given in mg KOH/g oil. Table 7.2 showed that the acid values of DSO vary between 0.94 and 2.10 (mg KOH/g oil). It was found also that FFAs of DSO ranged between 0.15 and 0.9 (% oleic acid) except for that found for six Libyan varieties by El-Shurafa et al. (1982) ranging between 2.36 and 4.08 (% oleic acid) which is too high. In the former cases, FFA values are low and comparable to many other edible oils like sunflower oil (1.4%) (Nehdi et al. 2013), and soybean oil (0.86%); (Nehdi 2011). The low acidity is an indicative of the high quality of the studied DSOs and allowed their possible use in food applications.

Peroxide values of DSOs ranged usually from 1 to 5 meq O_2/kg except for the oils studied by Herchi et al. (2014) which are higher than 9 meq O_2/kg. The low peroxide values compared to that of sunflower oil (6.07 meq O_2/kg) (Nehdi et al. 2013), is due to the low oxidation state of the DSOs. DSOs exhibited a saponification values varying between 191.28 and 224.4 mg KOH/g oil. It is comparable to those of some vegetable oils such as olive and soybean oils (188 and 192 mg KOH/g oil respectively) (O'Brien 2004). These high saponification values could be explained by the high contents of the DSOs on short-chain FAs (C12, C14) since it is known that the saponification value is inversely proportional to the carbon chain length of the FAs (Nehdi et al. 2018).

The iodine value depends on the oil's unsaturation degree. DSOs with an iodine values varying between 44.1 and 76.6 (g I_2/100 g) possessed a high content of saturated FAs. These iodine values are lower than those of sunflower oil (118.0 g I_2/100 g) (Nehdi et al. 2013) and soybean oil (122.56 g I_2/100 g) (Nehdi 2011). The relatively high iodine value in DSO is a strong sign of the presence of many unsaturated bonds in the FAs and thus can be classified as drying oils (Boukouada et al. 2014).

7.4 Chemical Composition of Date Seed Oil

7.4.1 Fatty Acid and Triglyceride Composition

The FA profiles of several DSOs are presented in Table 7.3. The most abundant FAs of all of the studied DSOs were oleic (C18:1 ω9; 25.89–55.10%), lauric (C12:0; 8.4–45.88%), linoleic (C18:2 ω6; 2.47–19.23%), palmitic (C16:0; 8.3–16.22%) and myristic (C14:0; 0.04–18.76%) acids. Generally, these five FAs characterize all of the DSOs but with different amounts that depends on the date source. Oleic FA (C18:1) is always the most predominant FA of DSOs.

When oleic acid, the most abundant FA in DSO, is followed by lauric acid, the oil is considered as oleic-lauric oil. When it is followed by linoleic or palmitic acids the oil is regarded as oleic-linoleic or oleic-palmitic type respectively. For example, Besbes et al. (2004a) have described Deglet Nour seed oil as an oleic–lauric oil and Allig seed oil as oleic–linoleic oil. While, Al-Hooti et al. (1998) reported that DSOs were either oleic–linoleic or oleic–palmitic oils. According to this classification, and following data displayed in Tables 7.3 and 7.4, oils reported by Habib and Ibrahim (2009), Habib et al. (2013), Suresh et al. (2013) can be considered as Oleic-Myristic types because Myristic acid follows directly oleic acid in terms of abundance.

Beside these major FAs, some minor ones are commonly present in the majority of DSO namely capric (C10:0), pentadecenoic (C15:1), myristoleic (C14:1), palmitoleic (C16:1 ω7) and linolenic (C18:3 ω3) acids. Their amounts did not exceed 2% and vary from variety to another. However, Table 7.4 reported data from the literature indicating minor FAs found in some DSOs that are not commonly found in all oils such as caprylic (C8:0), tridecyclic (C13:0), pentadecanoic (C15:0), hexadecenoic (C16:1 ω9), margaric (C17:0), isomargaric acid (C17:0), margaroleic (C17:1), vaccenic (C18:1 ω7), arachidic (C20:0), eicosenoic (C20:1), C20:1 ω7, Gondoic (C20:1 ω9), behenic (C22:0), Eruric (or brassidic) (C22:1 ω9), tricosylic (C23:0), lignoceric (C24:0), cerotic (C26:0) and 9,10-Epoxystearic acids (Al-Shahib and Marshall 2003; Azeem et al. 2016; Azodi et al. 2014).

In the most studied DSO, the amount of Saturated FA and unsaturated FA were comparable indicating that no class of FA was dominant. Overall, the degree of unsaturation of these DSO is lower than that of common vegetable oils. This may be due to the low content on linoleic acid of DSO as compared to vegetable oils. Generally, oils with high oleic FA contents showed good flavor and frying stability.

Table 7.3 Common fatty acid composition (%) of date seed oils

Fatty acid	References						
	Besbes et al. (2004a)	Besbes et al. (2004b)	Basuny and Al–Marzooq (2011)	Habib and Ibrahim (2009)	Saafi et al. (2008)	Ben-Youssef et al. (2017)	Ben-Youssef et al. (2017)
Capric (C10:0)	0.8–0.07	0.44–0.68	0.25	–	–	0.48	0.5
Lauric (C12:0)	17.8–5.81	22.56–24.34	35.31	–	17.39	22.2	22.6
Myristic (C14:0)	9.84–3.12	10.33–11.17	0.04	10.43–18.23	10.06	10.2	9.1
Myristoleic (C14:1)	0.09–0.04	0.33	–	–	–	–	–
Pentadecenoic acid (C15:1)	10.9–15.0	–	–	–	–	–	–
Palmitic (C16:0)	–	8.30–8.47	12.58	11.31–14.20	10.20	9.02	9.5
Palmitoleic (C16:1 ω7)	0.11–1.52	0.12–0.18	–	0.11–1.14	0.59	–	–
Stearic (C18:0)	5.67–3.0	2.57–2.65	3.30	2.70–6.05	3.06	3.47	3.5
Oleic (C18:1 ω9)	41.3–47.7	39.17–42.13	39.50	41.40–52.30	47.66	45.5	44.6
Linoleic (C18:2 ω6)	12.2–21.0	11.66–11.99	8.20	7.90–13.90	10.54	9.11	9.0
Linolenic (C18:3 ω3)	1.68–0.81	1.01–1.39	0.81	0.03–0.40	0.46	–	–

It is beneficial for health due to its minimal trans-isomer level, low saturation level and its potential to reduce LDL cholesterol in the blood as well as high oxidative stability (Liang and Liao 1992). DSOs displayed low content of linoleic acid in comparison to the commonly used vegetable oils and lower degree of unsaturation. Linolenic acid was reported to be crucial for the healthy growth of human skin (Bruckert et al. 2001).

Ben-Youssef et al. (2017) have used High Performance Thin-Layer Chromatography (HPTLC) for the analysis of extracted oils. Only triacylglycerides (TAGs) (99.66–100%) were detected along with traces of diacylglycerides (DAGs) (0.29–0.34%) when using MeTHF as solvent. These results are in a good agreement with those reported by Besbes et al. (2004b) who got about 97.26–96.90% of TAGs and 0.23–0.22% of DAGs in oils from Deglet Nour and Allig varieties. Nehdi et al. (2010) have used a reverse phase HPLC equipped with a refractive index detector for the identification of the triacylglycerol (TAG) composition of DSO. In this study it was found that the main TAGs was LaMM + LaLaP ECN40 with 18.9% of relative composition, followed by LaMP + MMM ECN42 (15.31%), LaOO + PLL + MPL ECN44 (12.86%) and LaPO ECN44 (11.33%). Other TAGs with relative composition less than 10% are also present and were identified as: POL + MOP + MOO +

Table 7.4 Fatty acid composition (%) of date seed oils presenting uncommon fatty acids

Fatty acid	Reference					
	Nehdi et al. (2018)	Al-Shahib and Marshall (2003)	Azodi et al. (2014)	Azeem et al. (2016)	Nehdi et al. (2010)	Habib et al. (2013)
Caprylic (C8:0)	0.20–0.25	0.0–0.8	0.00–0.65	0.25–0.41	0.08	–
Capric (C10:0)	0.24–0.32	0.0–0.6	0.28–0.44	0.28–0.48	0.11	–
Lauric (C12:0)	15.90–18.67	24.1–8.4	23.05–23.40	26.56–29.86	10.24	–
Tridecyclic (C13:0)	0.02–0.07					
Myristic (C14:0)	9.77–12.31	14.4–10.3	11.66–11.78	18.76–16.58	7.51	10.43–18.23
Pentadecanoic acid (C15:0)	0.02–0.07	–	–	0.04–0.05	0.07	0.04–0.73
Pentadecenoic acid (C15:1)		–	–	–	0.03	–
Palmitic (C16:0)	9.49–10.28	10.6–12.8	10.80–12.03	14.15–16.22	9.83	11.31–14.20
Palmitoleic (C16:1 ω7)	0.04–0.07	–	–	0.06–0.13	0.06	0.13–1.14
Hexadecenoic (C16:1 ω9)	0.02–0.05	–	–	–	0.07	
Margaric (C17:0)	0.02–0.07	–	–	0.07–0.13	0.15	0.03–0.17
Isomargaric (C17:0)		–	–	0.03–0.19	–	–
Margaroleic (C17:1)	0.02–0.03	–	–	–	0.08	0.05–0.10
Stearic (C18:0)	2.44–3.23	2.7–5.4	3.1–3.2	2.97–4.39	1.66	2.52–6.05
Vaccenic (C18:1 ω7)	0.30–0.34	–	0.60–0.65	0.23	0.10	–
Oleic (C18:1 ω9)	45.40–50.09	40.0–52.2	39.56–40.73	25.89–31.52	50.00	41.40–55.10
Linoleic (C18:2 ω6)	7.41–8.91	7.1–11.8	8.42–8.67	2.47–3.63	19.23	7.90–13.90
Linolenic (C18:3 ω3)	0.01–0.06	–	0.00–0.33	–	0.11	0.03–0.40
Arachidic (C20:0)	0.25–0.49	0.5–0.1	0.00–0.45	0.25–0.52	0.19	0.27–0.59
Eicosenoic (C20:1)		0.9–0.1	–	–	–	0.33–0.56
C20:1 ω7	0.02–0.07	–	–	–	–	–
Gondoic (C20:1 ω9)	0.37–0.52	–	–	0.42–0.58	0.32	–
Behenic (C22:0)	0.15–0.36	0.5–0.0	–	0.21–0.31	0.09	0.01–0.17

(continued)

Table 7.4 (continued)

	Reference					
Fatty acid	Nehdi et al. (2018)	Al-Shahib and Marshall (2003)	Azodi et al. (2014)	Azeem et al. (2016)	Nehdi et al. (2010)	Habib et al. (2013)
Eruric (or brassidic) (C22:1 ω9)		–	–	0.14–0.75	0.02	–
Tricosylic (C23:0)	0.01–0.1	–	–	0.05–0.14	0.02	–
Lignoceric (C24:0)	0.07–0.19	–	–	0.13–0.42	0.02	–
Cerotic (C26:0)	0.03–0.04		–			
9,10-Epoxystearic acid	0.03–0.06	–	–	–	–	–

SLL ECN46 (6.82%); LaMO ECN42 (4.98%); LaLaM ECN38 (4.64%); PPL ECN46 (4.63%); POO ECN48 (3.81%); OOO ECN48 (3.77%); OOL ECN46 (2.44%); LaLaLa ECN36 (2.11%); POP ECN48 (2.05%); OLL ECN44 (1.29%); SOO ECN50 (1.08%); POS ECN50 (1.06%); LaLaO ECN40 (1.04%); LLL ECN42 (0.67%); LaPP ECN44 (0.34%) and MPP ECN46 (0.33%). It is worthy reminding here that:

(i) The equivalent carbon number (ECN) is calculated as the total carbon number in all acyl chains minus 2 times the number of double bonds, i.e., ECN = CN – 2DB.
(ii) TAGs are usually symbolized by their three fatty acids that compose them, written in the following abbreviations: La: Lauric, M: Myristic, O: Oleic, L: Linoleic, S: Stearic and P: Palmitic acids.

7.4.2 Tocopherols and Tocotrienols

In many vegetable oils studies, Tocopherols and tocotrienols are broadly investigated. Their antioxidant properties make them as active as vitamin E and so very important for human health. Also, their antioxidant potential contributes considerably to the conservation of oil from air oxidation and sunlight deterioration and improves its shelf-life. In a recent study Nehdi et al. (2018) have investigated six date palm cultivars in term of their tocopherols and tocotrienols contents. They have found four tocopherols (α-, β-, γ- and δ-tocopherol) and three tocotrienols (α-, γ- and δ-tocotrienol) which together exists in an average of 70.75 mg/g oil of the six studied varieties. This value is higher than those found for olive and peanut oils giving only

23.39 and 66.73 mg/g oil respectively. Tocotrienols are slightly abundant in DSO than tocopherols with a respective percentage of 49.25 and 41.16% among which γ-tocopherol and α-tocotrienol are the most predominants, compared to their homologues, with an abundance of 23.61% and 30.19% respectively.

7.4.3 Sterol Composition

Phytosterols is the common name of vegetable sterols. They exist in minor amounts in oils but constitute most of the unsaponifiable matter. Analysis of phytosterols fraction in the unsaponifiable matter of oil is very useful for tracking commercial frauds (Lercker and Rodriguez-Estrada 2000), checking authenticity or detecting adulterations. Thus, oil's sterol composition was considered as a fingerprint. Besides, their antioxidant properties make their determination of major interest (Maestro-Durán and Borja-Padilla 1993). In most DSOs studies, β-sitosterol was found to be the predominant sterol (76%) followed by campesterol (29.90%) and Δ^5-avenasterol (29.56%). Other minor sterols were Δ^5–24-stigmastadienol (9.20%), Δ^7-avenasterol (3.99%), stigmasterol (3.69%), Δ^7-stigmastenol (2.68%) and very low amount of cholesterol (1.42%) (Nehdi et al. 2010). The average total sterol content in DSO is 300–350 mg/100 g oil (Besbes et al. 2004b). DSO's sterol composition is comparable to that of olive oil, one of the most consumed oil in the Mediterranean region. β-sitosterol is the most predominant phytosterol in olive oil with a mean content of about 83% depending on the studied variety and growth conditions. Other major sterols found in olive oil are Δ^5-avenasterol, campesterol and stigmasterol. While the minor sterols were identified as cholesterol, Δ^5–24-stigmastadienol, brassicasterol, Δ^7-avenasterol, 24-methylenecholesterol, sitostanol, clerosterol, Δ^7-sigmastenol and campestanol (Kyçyk et al. 2016).

7.5 Conclusion

This review described the different methods used by several researchers for the extraction of date seeds oil. Despite high production, date seeds are underutilized and considered for a long time as waste. DSO is promising alternative for common edible oils since it was found that it possessed the required physicochemical and chemical parameters. Conventional petroleum solvent extractions like maceration or Soxhlet extraction gives the better yield while cold pressure extraction, microwave, ultrasound and supercritical extractions allowed fewer yields but safer oil especially when microwave and ultrasound are used with green solvents like MeTHF. MeTHF is an agro-solvent produced from some vegetable wastes. It is environmental friendly, safe for human health and has physical and chemical properties similar to hexane. Its use in association with new technologies like microwave and ultrasound leads to several benefits like reducing solvent consumption and time, and better quality and stability of the obtained oil. Although application of SC-CO_2 extraction is harmless towards health and environment, it gives the lowest yield. The chemical and physicochemical characteristics of the extracted oils were found to be different across date varieties and sources. Despite, all of the studied DSOs were of economical interests. They are edible and useful for pharmaceutical or cosmetic purposes. More focused research is needed to optimize the better conditions and processes in order to obtain DSO with better quantity and quality which leads to the development of technology for industrial utilization and commercial production.

References

Abbas KA, Mohamed A, Abdulamir AS, Abas HA (2008) A review on supercritical fluid extraction as new analytical method. Am J Biochem Biotechnol 4(4):345–353. https://doi.org/10.3844/ajbbsp.2008.345.353

Abdalla RSM, Albasheer AA, El-Hussein ARM, Gadkariem EA (2012) Physico-chemical characteristics of date seed oil grown in Sudan. Am J Appl Sci 9(7):993–999. https://doi.org/10.3844/ajassp.2012.993.999

Al-Farsi M, Alasalvar C, Al-Abid M, Al-Shoaily K, Al-Amry M, Al-Rawahy F (2007) Compositional and functional characteristics of dates, syrups and their by-products. Food Chem 104:943–947. https://doi.org/10.1016/j.foodchem.2006.12.051

Al-Hooti S, Sidhu JS, Qabazard H (1998) Chemical composition of seeds date fruit cultivars of United Arab Emirates. J Food Sci Technol 35:44–46

Ali-Mohamed AY, Khamis ASH (2004) Mineral ion content of the seeds of six cultivars of Bahraini date palm (*Phoenix dactylifera*). J Agric Food Chem 52(21):6522–6525. https://doi.org/10.1021/jf030518x

Ali MA, Al-Hattab TA, Al-Hydary IA (2015) Extraction of date palm seed oil (*phoenix dactylifera*) by soxhlet apparatus. Int J Adv Eng Technol 8(3):261–271

Al-Juhaimi F, Ozcan MM, Adiamo OQ, Alsawmahi ON, Ghafoor K, Babiker EE (2018) Effect of date varieties on physico-chemical properties, fatty acid composition, tocopherol contents, and phenolic compounds of some date seed and oils. J Food Process Preserv 42(7):1–6. https://doi.org/10.1111/jfpp.13584

Al-Shahib W, Marshall RJ (2003) Fatty acid content of the seeds from 14 varieties of date palm *Phoenix dactylifera* L. Int J Food Sci Technol 38(6):709–712. https://doi.org/10.1046/j.1365-2621.2003.00723.x

Al-Sumri A, Al-Siyabi N, Al-Saadi R, Al-Rasbi S, Al-Dallal A (2016) Study on the extraction of date palm seed oil using Soxhlet apparatus. Int J Sci Eng Res 7(12):1266–1270

Aris NA, Norhuda I, Adeib IS (2013) Extraction of *Phoenix Dactylifera* (Mariami) seeds oil using supercritical carbon dioxide (SC-CO_2). Int J Chem Environ Eng 4(1):32–37

Arslan R, Ozcan MM (2010) Study the effect of sun, oven and microwave drying on quality of onion slices. LWT – Food Sci Technol 43(7):1121–1127. https://doi.org/10.1016/j.lwt.2010.02.019

Azeem MW, Hanif MA, Al-Sabahi JN, Khan AA, Naz S, Ijaz A (2016) Production of biodiesel from low priced, renewable and abundant date seed oil. Renew Energy 86:124–132. https://doi.org/10.1016/j.renene.2015.08.006

Azodi RA, Hojjatoleslamy M, Shariati MA (2014) Comparison of chemical properties of kabkab and shahani palm kernel. AJSR 1(1):17–19

Balasundram N, Sundram K, Samman S (2006) Phenolic compounds in plants and agri-industrial by-products: antioxidant activity, occurrence, and potential uses. Food Chem 99(1):191–203. https://doi.org/10.1016/j.foodchem.2005.07.042

Basuny AMM, Al–Marzooq MA (2011) Production of mayonnaise from date pit oil. Food Nutr Sci 2:938–943. https://doi.org/10.4236/fns.2011.29128
Battershill JM, Illing HPA, Shillaker RO, Smith AM (1987) n-Hexane. In: Health & safety executive toxicity review, vol 18. Department of Health and Human Services Public Health Service National Institutes of Health, London, pp 7–248
Ben-Youssef S, Fakhfakh J, Breil C, Abert-Vian M, Chemat F, Allouche N (2017) Green extraction procedures of lipids from Tunisian date palm seeds. Ind Crop Prod 108(1):520–525. https://doi.org/10.1016/j.indcrop.2017.07.010
Bernardo-Gil MG, Lopes IMG, Casquilho M, Ribeiro MA, Esquível MM, José E (2006) Supercritical carbon dioxide extraction of acorn oil. J Supercrit Fluids 40(3):344–348. https://doi.org/10.1016/j.supflu.2006.07.026
Bernardo-Gil MG, Ricardo R, Luísa BR, Luís CD, Francisco G, Paula E (2011) Supercritical extraction of carob kibbles (*Ceratonia siliqua* L.). J Supercrit Fluids 59:36–42. https://doi.org/10.1016/j.supflu.2011.08.007
Besbes S, Blecker C, Deroanne C, Drira NE, Attia H (2004a) Date seeds: chemical composition and characteristic profiles of the lipid fraction. Food Chem 84:577–584. https://doi.org/10.1016/S0308-8146(03)00281-4
Besbes S, Blecker C, Deroanne C, Lognay G, Derira N, Attia H (2004b) Quality characteristics and oxidative stability of date seed oil during storage. Food Sci Technol Int 10:333–338. https://doi.org/10.1177/1082013204047777
Besbes S, Blecker C, Deroanne C, Lognay G, Drira N, Attia H (2005) Heating effects on some quality characteristics of date seed oil. Food Chem 91:469–476. https://doi.org/10.1016/j.foodchem.2004.04.037
Biglar M, Khanavi M, Hajimahmoodi M, Hassani S, Moghaddam G, Sadeghi N, Oveisi MR (2012) Tocopherol content and fatty acid profile of different Iranian date seed oils. Iran J Pharm Res 11 (3):873–878
Bligh EG, Dyer WJ (1959) A rapid method of total lipid extraction and purification. Can J Biochem Physiol 37(8):911–917
Bouhlali ET, Alem C, Ennassir J, Benlyas M, Mbark AN, Zegzouti YF (2017) Phytochemical compositions and antioxidant capacity of three date (*Phoenix dactylifera* L.) seeds varieties grown in the South East Morocco. J Saudi Soc Agric Sci 16:350–357. https://doi.org/10.1016/j.jssas.2015.11.002
Boukouada M, Yousfi M (2009) Phytochemical study of date seeds lipids of three fruits (*Phoenix dactylifera* L) produced in Ouargla region. Annales de la Faculté des Sciences et Sciences de l'Ingénieur 1(3):66–74
Boukouada M, Ghiaba Z, Gourine N, Bombarda I, Saidi M, Yousfi M (2014) Chemical composition and antioxidant activity of seed oil of two Algerian date palm cultivars (Phoenix dactylifera). Nat Prod Commun 9(12):1777–1780
Breil C, Meullemiestre A, Vian M, Chemat F (2016) Bio-based solvents for green extraction of lipids from oleaginous yeast biomass for sustainable aviation biofuel. Molecules 21:1–14. https://doi.org/10.3390/molecules21020196
Bruckert F, Casavant T, Satre M (2001) Aromatic di–alanine repeats (AdAR) are structural motifs characteristic of the soluble N–ethylmaleimide–sensitive factor attachment protein (SNAP) family. Proteins 45(1):40–46. https://doi.org/10.1002/prot.1121
Chaira N, Ferchichi A, Mrabet A, Sghairoun M (2007) Chemical composition of the flesh and the pit of date palm fruit and radical scavenging activity of their extracts. Pak J Biol Sci 10 (13):2202–2207. https://doi.org/10.3923/pjbs.2007.2202.2207
Chemat F (2014) Alternative solvents for natural products extraction. Ph.D. thesis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China
Chemat F, Tomao V, Virot M (2008) Ultrasound-assisted extraction in food analysis. In: Handbook of food analysis instruments by Semih Ötles. CRC Press, Boca Raton, pp 85–103. https://doi.org/10.1201/9781420045673.ch5

Chemat F, Zill-e-Huma, Khan MK (2011) Applications of ultrasound in food technology: processing, preservation and extraction. Ultrason Sonochem 18(4):813–835. https://doi.org/10.1016/j.ultsonch.2010.11.023

Choo WS, Birch J, Dufour JP (2007) Physico-chemical and quality characteristics of cold-pressed flaxseed oils. J Food Compos Anal 20:202–211. https://doi.org/10.1016/j.jfca.2006.12.002

Codex Alimentarius Commission Codex Stan 19–1981. http://www.codexalimentarius.net/search/advancedsearch.do. Accessed 12 July 2018

Czaplicki S, Ogradowska D, Derewiaka D, Tanska M, Zadernowski R (2011) Bioactive compounds in unsaponifiable fraction of oils from unconventional sources. Eur J Lipid Sci Technol 113 (12):1456–1464. https://doi.org/10.1002/ejlt.201000410

El-Shurafa MY, Ahmed HS, Abou-Naji SE (1982) Organic and inorganic constituent of dates palm pit (seeds). J Date Palm 2:275–284

Fakourelis N, Lee EC, Min DB (1987) Effects of chlorophyll and β-carotene on the oxidation stability of olive oil. J Food Sci 52(1):234–235. https://doi.org/10.1111/j.1365-2621.1987.tb14018.x

Fatnassi S, Nehdi IE, Zarrouk H (2009) Chemical composition and profile characteristics of Osage orange *Maclura pomifera* (Rafin.) Schneider seed and seed oil. Ind Crop Prod 29(1):1–8

Fine F, Vian MA, Tixier A-SF, Carre P, Pages X, Chemat F (2013) Les agro-solvants pour l'extraction des huiles végétales issues de graines oléagineuses. OCL 20(5):1–6. https://doi.org/10.1051/ocl/2013020

Frankel EN (2005) Lipid oxidation, 2nd edn. The Oily Press, Bridgwater

Gecgel U, Demirci AS, Dulger GC, Gecgel U, Tasan M, Arici M, Ay O (2015) Some physico-chemical properties, fatty acid composition and antimicrobial characteristics of different cold-pressed oils. Riv Ital Sostanze Gr 92(3):187–200. https://doi.org/10.13140/RG.2.1.2381.3208

Gharby S, Harhar H, Guillaume D, Roudani A, Boulbaroud S, Ibrahimi M, Ahmad M, Sultana S, Ben Hadda T, Chafchaouni-Moussaoui I, Charrouf Z (2015) Chemical investigation of *Nigella sativa* l. Seed oil produced in Morocco. J Saudi Soc Agric Sci 14(2):172–177. https://doi.org/10.1016/j.jssas.2013.12.001

Gray JI (1978) Measurement of lipid oxidation. J Am Oil Chem Soc 55(6):539–546. https://doi.org/10.1007/BF02668066

Gulaboski R, Mirceski V, Mitrev S (2013) Development of a rapid and simple voltammetric method to determine total antioxidative capacity of edible oils. Food Chem 138(1):116–121. https://doi.org/10.1016/j.foodchem

Habib MH, Ibrahim WH (2009) Nutritional quality evaluation of eighteen date pit varieties. Int J Food Sci Nutr 60(S1):99–111. https://doi.org/10.1080/09637480802314639

Habib MH, Kamal H, Ibrahim WH, Dhaheri ASA (2013) Carotenoids, fat soluble vitamins and fatty acid profiles of 18 varieties of date seed oil. Ind Crop Prod 42:567–572. https://doi.org/10.1016/j.indcrop.2012.06.039

Handa SS, Khanuja SPS, Longo G, Rakesh DD (2008) Extraction technologies for medicinal and aromatic plants, 1st edn. United Nations Industrial Development Organization and the International Centre for Science and High Technology, Trieste

Herchi W, Kallel H, Boukhchina S (2014) Physicochemical properties and antioxidant activity of Tunisian date palm (*Phoenix dactylifera* L.) oil as affected by different extraction methods. Food Sci Technol Campinas 34(3):464–470. https://doi.org/10.1590/1678-457x.6360

Herrero M, Mendiola JA, Cifuentes A, Ibáñez E (2010) Supercritical fluid extraction: recent advances and applications. J Chromatogr A 1217(16):2495–2511. https://doi.org/10.1016/j.chroma.2009.12.019

Hussein AS, Alhadrami GA, Khalil YH (1998) The use of dates and date pits in broiler starter and finisher diets. Bioresour Technol 66(3):219–223

ISO 659–1988 (1988) International organization for standardization (ISO). ISO, Geneva

Jadhav AJ, Holkar CR, Goswami AD, Pandit AB, Pinjari DV (2016) Acoustic cavitation as a novel approach for extraction of oil from waste date seeds. ACS Sustain Chem Eng 4(8):4256–4263. https://doi.org/10.1021/acssuschemeng.6b00753

Jamil F, Al-Muhtaseb AH, Al-Haj L, Al-Hinai MA, Hellier P, Rashid U (2016) Optimization of oil extraction from waste "date pits" for biodiesel production. Energy Convers Manag 117:264–272. https://doi.org/10.1016/j.enconman.2016.03.025

Jensen WB (2007) The origin of the Soxhlet extractor. J Chem Educ 84(12):1913–1914. https://doi.org/10.1021/ed084p1913

Kazemi M, Dadkhah A (2012) Antioxidant activity of date seed oils of fifteen varieties from Iran. Orient J Chem 28(3):1201–1205. https://doi.org/10.13005/ojc/280315

Kyçyk O, Aguilera MP, Gaforio JJ, Jiménez A (2016) Sterol composition of virgin olive oil of forty-three olive cultivars from the world collection olive Germplasm Bank of Cordoba. J Sci Food Agric 96(12):4143–4150. https://doi.org/10.1002/jsfa.7616

Lercker G, Rodriguez-Estrada MT (2000) Chromatographic analysis of unsaponifiable compounds of olive oils and fat-containing food. J Chromatogr A 881(1–2):105–129. https://doi.org/10.1016/S0021-9673(00)00455-6

Liang T, Liao S (1992) Inhibition of steroid 5x–reductase by specific aliphatic unsaturated fatty acids. Biochem J 285(2):557–562. https://doi.org/10.1042/bj2850557

Lutterodt H, Luther M, Slavin M, Yin JJ, Parry J, Gao JM, Yu L (2010) Fatty acid profile, thymoquinone content, oxidative stability, and antioxidant properties of cold-pressed black cuminseed oils. LWT – Food Sci Technol 43(9):1409–1413. https://doi.org/10.1016/j.lwt.2010.04.009

Lutterodt H, Slavin M, Whent M, Turner E, Yu L (2011) Fatty acid composition, oxidative stability, antioxidant and antiproliferative properties of selected cold-pressed grape seed oils and flours. Food Chem 128(2):391–399. https://doi.org/10.1016/j.foodchem.2011.03.040

Maestro-Durán R, Borja-Padilla R (1993) Actividad antioxidante de esteroles y ácidos orgánicos naturales. Grasas Aceites 44(2):208–212. https://doi.org/10.3989/gya.1993.v44.i3.1096

Maskan M (2000) Microwave/air and microwave finish drying of banana. J Food Eng 44(2):71–78

Mason TJ (1998) Chapter 6: Power ultrasound in food processing – the way forward. In: Ultrasound in food processing. Blackie Academic and Professional, Thomson Science, London, pp 105–126

Matthaus B, Brühl L (2003) Quality of cold-pressed edible rapeseed oil in Germany. Nahrung/Food 47(6):413–419. https://doi.org/10.1002/food.200390092

Minguez-Mosquera MI, Rejano-Navarro L, Gandulrojas B, Sanchez Gomez AH, Garrido-Fernandez J (1991) Color-pigment correlation in virgin olive oil. J Am Oil Chem Soc 68 (2):332–336. https://doi.org/10.1007/BF02657688

Nederal S, Skevin D, Kraljic K, Obranovic M, Papesa S, Bataljaku A (2012) Chemical composition and oxidative stability of roasted and cold pressed pumpkin seed oils. J Am Oil Chem Soc 89 (9):1763–1770. https://doi.org/10.1007/s11746-012-2076-0

Nehdi I (2011) Characteristics, chemical composition, and utilisation of *Albizia julibrissin* seed oil. Ind Crop Prod 33(1):30–34. https://doi.org/10.1016/j.indcrop.2010.08.004

Nehdi I, Omri S, Khalil MI, Al-Resayes SI (2010) Characteristics and chemical composition of date palm (*Phoenix canariensis*) seeds and seed oil. Ind Crop Prod 32:360–365. https://doi.org/10.1016/j.indcrop.2010.05.016

Nehdi IA, Sbihi H, Tan CP, Al-Resayes SI (2013) Evaluation and characterization of *Citrullus colocynthis* (L.) Schrad seed oil: comparison with *Helianthus annuus* (sunflower) seed oil. Food Chem 136(2):348–353. https://doi.org/10.1016/j.foodchem.2012.09.009

Nehdi IA, Mokbli S, Sbihi H, Tan CP, Al-Resayes SI (2014) *Chamaerops humilis* L. var. *argentea* André date palm seed oil: a potential dietetic plant product. J Food Sci 79(4):C534–C539. https://doi.org/10.1111/1750-3841.12420

Nehdi IA, Sbihi HM, Tan CP, Rashid U, Al-Resayes SI (2018) Chemical composition of date palm (*Phoenix dactylifera* L.) seed oil from six Saudi Arabian cultivars. J Food Sci 83(3):624–630. https://doi.org/10.1111/1750-3841.14033

Norhuda I, Jusoff K (2009) Supercritical carbon dioxide (SC-CO_2) as a clean technology for palm kernel oil extraction. J Biochem Technol 1(3):75–78

O'Brien RD (2004) Fats and oils: formulating and processing for applications, 2nd edn. CRC Press LLC, Boca Raton/London/New York/Washington, DC

Oomah BD, Ladet S, Godfrey DV, Liang J, Girard B (2000) Characteristics of raspberry (*Rubus idaeus* L.) seed oil. Food Chem 69(2):187–193. https://doi.org/10.1016/S0308-8146(99)00260-5

Paré JRJ, Bélanger JMR (1997) Instrumental methods in food analysis. Elsevier Science, Amsterdam

Parker TD, Adams DA, Zhou K, Harris M, Yu L (2003) Fatty acid composition and oxidative stability of cold-pressed edible seed oils. J Food Sci 68(4):1240–1243

Parry J, Su L, Moore J, Cheng Z, Luther M, Rao JN, Wang JY, Yu L (2006) Chemical compositions, antioxidant capacities, and antiproliferative activities of selected fruit seed flours. J Agric Food Chem 54:3773–3778. https://doi.org/10.1021/jf060325k

Perrin JL (1992) Les composés mineurs et les antioxgènes naturels de l'olive et de son huile. Revue Française des Corps Gras 39:25–32

Pinto LF, Ndiaye PM, Ramos LP, Corazza ML (2011) Phase equilibrium data of the system CO_2 + glycerol + methanol at high pressures. J Supercrit Fluids 59:1–7. https://doi.org/10.1016/j.supflu.2011.08.002

Raziq S, Anwar F, Mahmood Z, Shahid SA, Nadeem R (2012) Characterization of seed oils from different varieties of watermelon [*Citrullus lanatus* (Thunb.)] from Pakistan. Grasas Aceites 63 (4):365–372. https://doi.org/10.3989/gya.022212

Reddy MK, Rani HD, Deepika CN, Samrawat S, Akshara V, Rajesh K (2017) Study on physico-chemical properties of oil and powder of date palm seeds (*Phoenix dactylifera*). Int J Curr Microbiol App Sci 6(12):486–492. https://doi.org/10.20546/ijcmas.2017.612.059

Saafi EB, Trigui M, Thabet R, Hammami M, Achour L (2008) Common date palm in Tunisia: chemical composition of pulp and pits. Int J Food Sci Technol 43:2033–2037. https://doi.org/10.1111/j.1365-2621.2008.01817.x

Shahidi F, Wanasundra UN (1997) Methods of measuring oxidative rancidity in fats and oils. In: Food lipids: chemistry, nutrition, and biotechnology, 4th edn. Akoh CC, New York, pp 377–396. https://doi.org/10.1201/9781420046649.ch14

Sicaire AG, Vian M, Fine F, Joffre F, Carré P, Tostain S, Chemat F (2015) Alternative bio-based solvents for extraction of fat and oils: solubility prediction, global yield, extraction kinetics, chemical composition and cost of manufacturing. Int J Mol Sci 16:8430–8453. https://doi.org/10.3390/ijms16048430

Siger A, Nogala-Kalucka M, Lampart-Szczapa E (2008) The content and antioxidant activity of phenolic compounds in cold-pressed plant oils. J Food Lipids 15(2):137–149. https://doi.org/10.1111/j.1745-4522.2007.00107.x

Suresh S, Guizani N, Al-Ruzeiki M, Al-Hadhrami A, Al-Dohani H, Al-Kindi I, Rahman MS (2013) Thermal characteristics, chemical composition and polyphenol contents of date-pits powder. J Food Eng 119(3):668–679

Teh SS, Birch J (2013) Physicochemical and quality characteristics of cold-pressed hemp, flax and canoal seed oils. J Food Compos Anal 30(1):26–31. https://doi.org/10.1016/j.jfca.2013.01.004

Thakur N, Arya V (2014) Preliminary phytochemical analysis of the extracts of *psidium* leaves. Middle-East J Sci Res 19(11):1421–1424. https://doi.org/10.5829/idosi.mejsr.2014.19.11.11415

Tiwari BK (2015) Ultrasound: a clean, green extraction technology. Trends Anal Chem 71:100–109. https://doi.org/10.1016/j.trac.2015.04.013

Vandepopuliere JM, Al-Yousef Y, Lyons JM (1995) Dates and date pits as ingredients in broiler starting and coturnix quail breeder diets. Poult Sci 74(7):1134–1142. https://doi.org/10.3382/ps.0741134

Virot M, Tomao V, Colnagui G, Visinoni F, Chemat F (2007) New microwave-integrated Soxhlet extraction an advantageous tool for the extraction of lipids from food products. J Chromatogr A 1174:138–144. https://doi.org/10.1016/j.chroma.2007.09.06

Virot M, Tomao V, Ginies C, Visinoni F, Chemat F (2008) Microwave-integrated extraction of total fats and oils. J Chromatogr A 1196–1197:57–64. https://doi.org/10.1016/j.chroma.2008.05.023
Yousuf RG, Winterburn JB (2017) Waste date seed oil extract as an alternative feedstock for poly (3-hydroxybutyrate) synthesis. Biochem Eng J 127:68–76. https://doi.org/10.1016/j.bej.2017.08.007
Yu L, Haley S, Perret J, Harris M (2002) Antioxidant properties of extracts from hard winter wheat. Food Chem 78(4):457–461. https://doi.org/10.1016/S0308-8146(02)00156-5

Chapter 8
Date Palm Waste: An Efficient Source for Production of Glucose and Lactic Acid

Muhammad Tauseef Azam and Asif Ahmad

Abstract Plant based by-products are naturally available in large quantities and they can be exploited as cheap and feasible substrate for their biological transformation into valuable products. Date palm is a good example from plant source having a great value for its by-products owing to presence of cellulosic material that can be converted into valuable products like glucose and lactic acid as an option to reduce environmental pollution. Production of glucose from cellulosic date palm waste can be achieved with the help of cellulose enzyme from selective microorganisms. Similarly, date palm cellulosic material can also be converted into lactic acid with the help of lactic acid bacteria through fermentation process. Conditions may be optimized for the production of glucose and lactic acid during fermentation process. Lactic acid production is decreased if the substrate concentration is high initially in the fermentation experiment while maximum production is achieved by increasing the enzyme concentration in the experiment. The desirable yield of glucose can be achieved at 50 °C and pH of 5.0. Adopting a two-step hydrolysis process can increase the glucose production by 94.88% in 24 h process. Lactic acid yield can be achieved maximum at temperature 40–45 °C and pH 6. These results are promising and these suggest that yield of sugar and lactic acid from date palm waste is practical and it may be employed as a best practice to minimize the environmental pollution by using date palm cellulosic by-products as an inexpensive source. This chapter envisage the suitability of date palm waste as inexpensive cellulosic source for obtaining commercially valuable products i.e. glucose and lactic acid.

Keywords Date palm · Biological waste · Cellulosic waste · Cellulase enzyme · Glucose · Lactic acid · Lactic acid bacteria · Enzymatic fermentation

M. T. Azam · A. Ahmad (✉)
Institute of Food and Nutritional Sciences, Pir Mehr Ali Shah, Arid Agriculture University, Rawalpindi, Pakistan
e-mail: tauseefazam@ymail.com; asifahmad_1@yahoo.com

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_8

8.1 Introduction

Date palm (*Phoneix dactylifera*) trees are considered as one of the oldest tree of the world. These are ancient cultivated plants and their history goes back to 10,000 years ago (Al-Shahib and Marshall 2003). It is produced as principal agriculture product in North Africa and Middle East region. Saudi Arabia and Egypt are the major countries which are famous for their date production. It is cultivated across the globe and it is estimated that about 3% of the world's cultivable area is occupied by date palm. From this cultivable area, global marketable date production has reached about 8 million metric tons (mmt) tons per year (Zamzam et al. 2018). Date plant is mainly cultivated for its nutritional value however, its medicinal properties is also available in scientific literature. These health properties are attributed to presence of bioactive compounds including antioxidants and phenolics which can be exploited in curing diseases like cancer, diabetes, microbial infections etc. (Khalid et al. 2017a). On nutrition side, date fruit is rich in carbohydrate (80%), protein (2–6%) and fiber (6.4–11.5%) while fats (0.2–0.4%) exists in minor amounts. Besides these date palm also contains traces of important minerals and vitamin (Al-Farsi* and Lee 2008). The presence of these nutrients in variable amounts to maintain the health are also supported by other scientists (Al-Shahib and Marshall 2003; Khalid et al. 2017b).

Date is mainly cultivated for its fruit, however, it also provides large amount of valuable products that are useful for many applications of daily life. It also provides raw material for many industrial products as well (Agoudjil et al. 2011). Date palm fronds are very famous agricultural by-products that have been used as feed stuff in animal diet (Chandrasekaran and Bahkali 2013). Date palm waste products includes tree trunk, leaves (midrib, leaflets, spines, sheath), stems, fruit stalk, spikelets, spath, fronds, seeds, date pits and coir etc. (Chao and Krueger 2007). Date pit mass is about 10–15% of the total mass of the date fruit. Date pit contains about 10% of crude oil and cellulose (Hamada et al. 2002). Date palm waste products could be utilized for the production of different valuable products like glucose and lactic acid.

Dates can be used for fermentation process to produce different biochemical products like alcohol, organic acids and glucose etc. (Naik et al. 2010). The conversion of cellulosic waste into useful products remained at priority in the last few decades. Conversion of cellulosic date palm waste into glucose and lactic acid is important for environment as such agricultural wastes utilize a lot of land resources and when the process of decomposition starts, air in the surrounding area stinks which is responsible for the dissemination of microbes. In this way such agricultural wastes brings a lot of pressure to the environment. However, this conversion of agricultural waste into useful products like energy, proteins and chemicals remained costly due to cost of cellulosic material, and cellulosic enzymes where technical problems also creates hindrance in cellulosic saccharification (Goyal et al. 2008).

Date palm contains huge amount of cellulose i.e. 45.3%, hemicellulose i.e. 29.12% and lignin amount is around 25.82%. Fermentation technology is the one which is used to produce valuable products from waste materials. Lignocellulosics are not easily saccharified by enzyme like cellulases to produce sugar until it is carried through different processes like physical, chemical and mechanical pretreatments which remove undesired inhibitory complexes like lignin complex. Such complexes reduce the crystallinity whereas polymerization process of cellulose molecules helps the exposure of substrate for action of enzyme by increasing the surface area (Agbor et al. 2011).

Lactic acid is a very useable organic acid which is produced by the action of lactic acid producing bacteria through the process of fermentation. Wide range of application for lactic acid has been reported in the literature for various industries like pharmaceutical, leather, biodegradable plastic and food industry (Vijayakumar et al. 2008). Lactic acid is employed as pH regulator, acidulant and flavor enhancer in these industries. Lactic acid keep higher amount of chemical reactivity because of carboxylic and hydroxyl group so it is involved in variety of conversions into useful chemical components (Rogers et al. 2006). In recent decades, lactic acid fermentation drew higher attention due to increased demand for new biomaterial such as biodegradables and biocompatible polylactic acid (PLA) (Lim et al. 2008). PLA is used for making bioplastics which has wide applications. There are many economic and efficiency problems in lactic acid fermentation but scientist are focusing to discover new and effective nutritional resources using progressive fermentation techniques so they can achieve high substrate conversion along with high productivity. Use of cheap agricultural waste materials such as date palm cellulosic waste for the yield of important products like lactic acid through process of fermentation is attractive (de Oliveira et al. 2018).

There are various reports available relating to production of glucose and lactic acid from date palm and other agricultural waste products. This study represents the review of production of glucose and lactic acid from date palm by fermentation technology. Suitability of date palm as a cellulosic waste for the production of valuable products is also part of discussion.

8.2 Glucose

Glucose is a monosaccharide (simple sugar). Its chemical formula is $C_6H_{12}O_6$ and it contains aldehyde group. Commercial production of glucose involves the hydrolysis, enzymatic hydrolysis of complex carbohydrates or fermentation of biological wastes from different sources i.e. sugarcane bagasse, rice, wheat, corn husk (Raman 2010). Glucose has wide industrial applications. It is used for the synthesis of many other useful products e.g. vitamin C, citric acid, ethanol, amino acids, sorbitol, gluconic acid etc. (Pandey 2003).

8.2.1 Raw Material for the Production of Glucose

For the production of glucose in large quantities, it is important that raw material or substrate used must be cheap and easily available. Substrate must be clean with less

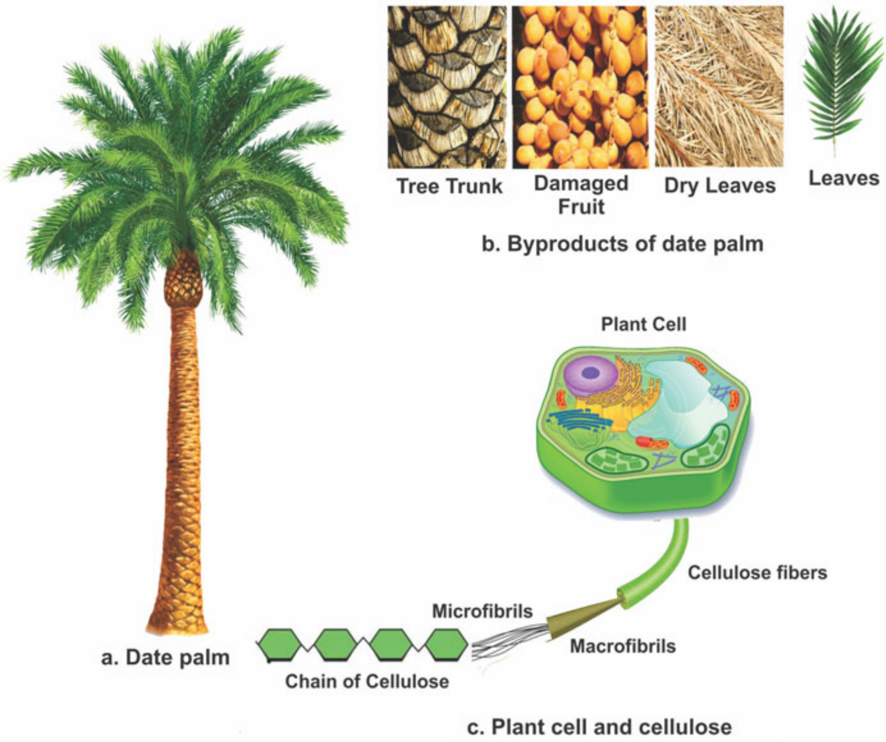


Fig. 8.1 Date palm and its cellulosic by-products with depiction of cellulose fibers

contaminant and it should give large production rate/yield without requirement of extra processing and in this way it reduces the cost of production. Availability is also important; substrate must be available all the year easily (Kimura et al. 2016). Date palm waste material provides the desired starting material for glucose production. During regular date palm collection activity a lot of material is produced which cannot be utilized by man as a food but this waste material can be used as part of feed for animals or it can be used as substrate for the production of useful products as it contains cellulose (Nancib et al. 2015). The details of such date palm waste is shown in Fig. 8.1.

8.2.2 Microorganisms Involved in the Production of Glucose

Cellulases are the main enzymes which are used as a source for the production of glucose from cellulosic material. These enzymes may be isolated from bacterial strain *Geobacillus stearothermophilus* Y-1. Separate saccharification and fermentation of lignocellulosic biomass is also recommended because of its much higher temperature and substrate range (Himmel et al. 2010). Achieving complete cellulose hydrolysis is a difficult process, however, it can be achieved by utilizing three types of cellulases, i.e. glucosidase, exoglucanases and endoglucanases. Glucosidase can cleave glucose units from cello-oligosaccharides; exoglucanases has high efficiency to cleave cellobiosyl units from the end of cellulose whereas endoglucanases can cleave internal glucosidic bonds (Scully et al. 2015).

8.2.3 Enzymatic Hydrolysis of Date Palm Waste

Date fruits are collected and cleaned manually and thoroughly to remove dust or any other unnecessary substance present on it. Date pulp is removed usually and date seeds are separated manually by splitting the fruit. Regular tap water is added into the date fruit in a way that two parts of water is mixed with one part (by weight) of fruit. Heat (80 °C) is then applied to the mixture for 02 h with continuous stirring by a rod. Cellulosic material from date fruit is removed by the process of centrifugation at the rotor speed of 20,000 revolutions per minute (rpm) for 10 min. After completion of the process of centrifugation, supernatant is obtained which is important as it serves as carbon source in the experiment.

Hydrolysis of cellulosic substrate is required and it is performed at appropriate conditions. Culture growth for fermentation process is carried out by initial inoculation of bacterial cultures from primary agar plates into a 50 mL tube containing 5 mL of medium nutrient broth and incubation at 50 °C with continuous shaking at 200 rpm. This culture stock is enough for preparation of media (250 mL) in a flask containing 50 mL Bushnell Haas medium (BHM) media. Recipe of production medium (BHM) includes: $CaCl_2$ (0.02 g/L), KH_2PO_4 (1 g/L), $FeCl_3 \cdot 6H_2O$ (0.05 g/L), K_2HPO_4 (1 g/L), Tween 80 (0.2%) $MgSO_4 \cdot 7H_2O$ (0.2 g/L) and yeast extract (1.0 g/L). As source of carbon, leaves of date palm pre-treated with 2.0% alkaline solution can be used (Yadav et al. 2011).

For the fermentation process, the optimized conditions for production of cellulose enzyme can be achieved at pH 7.0 and mild temperature i.e. 45 °C with shaking at shaker incubator at 200 rpm to avoid clump formation in media. Centrifugation process helps in removal of insoluble cells and materials, when centrifugation is performed for 10 min at 10,000 rpm. The supernatant is now free of cells and it could be used as the enzyme source (Alrumman 2016).

For enzymatic hydrolysis, experimental conditions could be optimized and then date palm cellulosic waste (2%) can be mixed with cellulase enzyme (optimized units) in a 100-mL Erlenmeyer flask containing buffer (acetate buffer. pH 5.0). For inhibition of microbial growth in the media, sodium azide can be added. To carry out the enzymatic hydrolysis successfully, flasks can be incubated at 50 °C for 24 h at shaker incubator with continuous shaking at 200 rpm. During hydrolysis, complex sugars would be broken down into simple ones and after successful saccharification procedure, centrifugation is again performed at 400 rpm at 30 °C to remove the unhydrolyzed substrate. Hydrolyzed product should be well mixed with sodium acetate (0.167%) and is supplemented with yeast extract (6%), $FeSO_4.7H_20$ (0.1%),), $NaPO_3$ (0.167%), $MnSO_4.H_2O$ (0.005), $MgSo_4.7H_20$ (0.1%) made to final volume 50 ml in a 100 ml flask. To prevent acidification, $CaCO_3$ is added because acidification will alter the pH of the medium that in turn affects the efficiency of whole process (Nancib et al. 2015).

8.3 Lactic Acid

The first organic acid which is discovered by a Swedish Chemist Carl Wilhem Scheele in 1780 by fermentation process in sour milk was lactic acid. Its chemical formula is $C_3H_6O_3$ and it is also known as 2-hydroxypropionic acid (Datta et al. 1995). History of lactic acid discovery and production is described in Table 8.1. It is an essential metabolic product and is available as metabolic intermediate in all living organisms. Naturally, it is also available in numerous fruits and vegetables and can also be produced in lab and industrial conditions through microbial fermentation. Lactic acid has different physical and chemical characteristics which are presented in Table 8.2. Lactic acid is produced commercially by the process of fermentation in many countries since its production is started in the United States in 1881 (Wang et al. 2015).

8.3.1 Potential Applications of Lactic Acid

Lactic acid is an important naturally occurring organic compound which has tremendous uses in our daily life. There are four main and important fields in which lactic acid is used i.e. cosmetics, food, chemical industry and pharmaceutics. The potential fields and products where lactic acid has tremendous applications are represented in Fig. 8.2.

Table 8.1 The history of lactic acid production

Sr #	Developments	Year	References
1	Discovered by Scheele	1780	Mohanty et al. (2016)
2	First industrial production	1881	Martinez et al. (2017)
3	First usage in leather and textile processes	1894	Saxena (2015)
4	Used for armoured tank coolant and glycerol substitute	1939-1945	Harding and Harrison (2016)
5	Synthetic production of lactic acid to make stearoyl-2-lactylates	Early 1960's	Carocho et al. (2015)

Table 8.2 Physical and chemical properties of lactic acid

Sr #	Property	Characteristics	References
1	Optical activity	Exists as L(+), D(−) and racemic mixture	Chafran et al. (2016)
2	Crystallization	Forms colourless monoclinic crystals when highly pure	Salas-Papayanopolos et al. (2017)
3	Color	None or yellowish	Carrasco et al. (2010)
4	Odour	None	Carrasco et al. (2010)
5	Consistency	Syrupy liquid	Carrasco et al. (2010)
6	Solubility/miscibility/hygroscopicity	Soluble in all proportions with water; miscible with water, alcohol, glycerol, furfural; insoluble in chloroform, carbon disulphide; hygroscopic	Salas-Papayanopolos et al. (2017)
7	Volatility	Low	Salas-Papayanopolos et al. (2017)
8	Self-esterification	In solutions of >20%, forming a cyclic dimer or a linear polymer	Södergård and Stolt (2002)
9	Reactivity	Versatile, e.g. as organic acid or organic alcohol	Wasewar et al. (2004)
10	Physical	Formula weight: 90.1; melting point 18 °C, boiling point 122 °C at 15 mm Hg; density 1.2; specific gravity 1.248	Södergård and Stolt (2002)

Cosmetic industry is the main industry which utilizes lactic acid in a lot of formulations. It is an important ingredient in moisturizers for its water retaining properties and it can help in pH regulation and microbial growth inhibition. Lactic acid is a natural product and it is considered safer for its use in cosmetic industry. It has some additional properties like it can be used as skin lightening agent as it inhibits formation of tyrosinase (John et al. 2007).

Lactic acid is considered safe and it is approved by US FDA for its use as additive to food. Now lactic acid is widely used as flavoring agent, pH regulator, mineral fortification agent and inhibitor of microbial growth in food items. It is used in poultry and meat industry to improve the shelf life of products and to control the growth of pathogenic microbes. Lactic acid is used as flavoring agent on salads, pickles, backed food items, beverages etc. due to its acidulant properties. Lactic acid is also used in confectionaries for its ability to control pH and to add flavor in candies etc. (John et al. 2007).

There are a lot of chemical processes which involves use of lactic acid. Lactic acid and its derivatives are part of many chemical products. In chemical industry, lactic

Fig. 8.2 Potential applications of lactic acid

acid represents itself as an excellent solvent. It is safe as it is natural product and it has great solubility property so it is used as cleaning agent to remove polymer and resin. Lactic acid is used for the manufacturing process of different herbicides and pharmaceutical products (Martinez et al. 2013). It has excellent descaling properties so it is used for the production of cleaning products like toilet and bathroom cleaners. It is utilized as pH regulator, neutralizer, antimicrobial product and metal complexing agent. Product of lactic acid e.g. Ethyl lactate is produced naturally and it does not have any toxicological effects so it is used in the preparation of many anti-acne formulations (John et al. 2007; Datta and Henry 2006). Lactic acid is comprised of very reactive functional groups i.e. carboxylic group and a hydroxyl group. These functional groups are involved in variety of chemical conversions to produce different chemicals e.g. propylene oxide, acetaldehyde, acrylic acid and propanoic acid etc. Production of biodegradable plastic i.e. polylactic acid (PLA) is achieved because of lactic acid which is used for food packaging and for making of trash bags, containers and short shelf-life trays (John et al. 2007).

In the pharmaceutics, lactic acid has wide applications. Lactic acid is employed in production of n different varieties of important medical preparations including surgical items, tablets, artificial body parts etc. It is used in preparation of intravenous solutions (I.V.) which serves as electrolyte to replenish all the nutrients in human body e.g. Hartmann’s solutions or Lactated Ringer’s solution. Lactic acid is also used in dialysis solution for dialysis process (John et al. 2007).

Table 8.3 Quantitative comparison of production of lactic acid from different substrates

Sr.no.	Substrates	Production of lactic acid in g/L	References
Expensive substrates			
1.	Barley	162.00	Linko and Javanainen (1996)
2.	Wood	108.00	Moldes et al. (2001)
3.	Beet molasses	90.00	Kotzamanidis et al. (2002)
Cheap alternative substrates			
4.	Cellulose	24.00	Yáñez et al. (2003)
5.	Corn cob	24.00	Miura et al. (2004)
6.	Waste paper	23.10	Yáñez et al. (2005)

8.3.2 Raw Material for the Production of Lactic Acid

There are lots of reported investigations which attempt to search for the feasible and cheap cellulosic raw materials for the economical lactic acid production. Any cellulosic waste of date palm can be used as a substrate for fermentation process (Nancib et al. 2015). Recent reports regarding the use of different raw materials for the lactic acid production and their quantitative comparison is listed in Table 8.3.

Use of cellulosic waste as raw material/substrate is preferred for being utilized for the lactic acid production as it is feasible, cheap and available round the year. It mainly contains xylan, arabinan, galactan and lignin. There are several published reports regarding production of lactic acid by using different raw materials which contain cellulose. It is reported that pure cellulose can be utilized through the processes of enzymatic hydrolysis and fermentation for lactic acid yield (Venkatesh 1997; Yáñez et al. 2003). There are reports on the use of corn stover, waste paper, wheat bran, wood, wheat straw, alfalfa fiber and corn cob for the reasonable and economic lactic acid production. It is investigated that yield of lactic acid is enhanced by using cellulase and pectinase enzymes synergistically (Sreenath et al. 2001). Different lactic acid bacteria e.g. *L. pentosus* and *L. brevis* can be co-cultured for the lactic acid production. They were reportedly used for complete hydrolysis of substrate i.e. wheat straw into lactic acid (Garde et al. 2002). During pretreatment process of substrate, different compounds were produced e.g. furfural, 5-hydroxymethyl furfural, and acetic acid. These compounds have inhibitory action during fermentation process and they hinder hydrolysis of lignocellulosic material. To decrease inhibitory action of these compounds several methods are studied including physical and chemical treatment of hydrolysate. It is possible to minimize the inhibition of fermentation process if lactic acid bacteria are adapted directly on substrate based medium i.e. wood hydrolysate (Wee et al. 2004).

Commonly agricultural and industrial waste products e.g. whey and molasses are exploited to get valuable products such as lactic acid. Whey is very important as it contains fats, protein, minerals and lactose. Whey is obtained from dairy source. If whey substrate is supplemented with additional nitrogen source e.g. yeast extract, it will be completely hydrolyzed. It makes the production of lactic acid viable economically as it utilizes all the nutrients completely (Kulozik and Wilde

1999; Schepers et al. 2002). Whey protein hydrvolysate can be added into whey medium and hydrolyzed into lactic acid (Amrane and Prigent 1998; Kulozik and Wilde 1999).

During production process of sugar, molasses is produced which is a waste product and contains large quantities of sucrose. There are several reports available regarding the use of molasses in the process of lactic acid production (Shukla et al. 2004). For efficient fermentation process there is a requirement for supplementation of fermentation media with extra nutrients. Media can be supplemented by using yeast extract but it is expensive and it increases the production cost. Corn steep liquor can be used as alternatives of yeast extract in the media. Corn steep liquor is obtained from the corn. Most of the nitrogenous compounds which are part of corn steep liquor relies on the steeping process and it contains proteins, amino acids and peptides.

Media supplementation is advantageous and it is studied that wheat bran or rice bran contains fermentable sugars and their use brings lots of nutritious value to media (Wee et al. 2005). Other media supplementations are also reported to increase nutritious value of media including use of ram horn waste and vinification lees (Bustos et al. 2004). Electrodialyzed fermentation water contains nutrients which can be employed by gram positive lactic acid bacteria to produce lactic acid by enzymatic fermentation. There is published data regarding the use of electrodialyzed fermentation water which demonstrate that it enhances the efficiency of fermentation water (Wee et al. 2005).

8.3.3 Pretreatment of the Date Palm Waste

The cellulosic waste of date palm e.g. plant leaves, leaves stalks and fibers of date palm can be used as a cellulosic substrate. These waste date palm plant materials can be ground and pretreated by two methods. (1) alkaline pretreatment and (2) acid-steam pre-treatment. Alkaline pretreatment method involves treatment of substrate with 2 N NaOH at room temperature for at least 48 h while during acid steam pretreatment process substrate has reaction with H_2SO_4 (1%) at high temperature (120 °C) for 100 min. After pretreatment procedures, the plant waste must be cleaned. Tap water can be used to thoroughly wash the treated substrate. By using water, substrate gets neutralized. Substrate is then dried at 70 °C in hot oven. Dried material will then thoroughly ground for further processing by using Wiley Mill (Model 2 Thomas Co., USA). Grinding process will generate particle size $\leq$1 mm, which is preferable. Smaller sized particles have more surface area that increases its availability for enzyme action. Substrate may be comprised of major contents i.e. cellulose, hemicellulose and lignin (Bozoglu and Ray 2013).

8.3.4 Micro-organisms Used for the Production of Lactic Acid

Commonly used microorganisms for the lactic acid production from cellulosic waste material are known as lactic acid bacteria. Lactic acid bacteria are mainly gram positive bacteria which can produce lactic acid by the process of fermentation into the fermentation medium when they are cultured on substrate which contain cellulose or hemicellulose (Wee et al. 2006). On the basis of mechanism of action utilized to achieve the final product i.e. lactic acid, lactic acid bacteria are of two different types i.e. homofermentative and heterofermentative. Those bacteria which have ability to convert glucose into lactic acid exclusively are known as homofermentative lactic acid bacteria while the heterofermentative lactic acid bacteria are group of those bacteria which can produce lactic acid as well as some other products such as CO_2 and alcohol (ethanol) (Fig. 8.3) (Wee et al. 2006).

Only the homofermentative lactic acid bacteria belonging to genus *Lactobacillus* are preferably employed for the lactic acid production commercially because of their higher conversion, yield and rate of metabolism (Table 8.4).

There are reports for the use of batch culture of *L. helveticus* and *L. rhamnosus* to get lactic acid. Substrates used in the experiment were concentrated cheese whey and lactose (Berry et al. 1999; Schepers et al. 2002). There are investigations regarding the use of different substrates for the conversion into lactic acid by using *L. bulgaricus*. Kinetic models were also established for the lactic acid production (Burgos-Rubio et al. 2000). Investigations were conducted on studying the effects of variation of temperature and use of nitrogen from different sources on lactic acid production by *L. casei* strain (Hujanen et al. 2001; Roukas and Kotzekidou 1998). Investigations were made to study the kinetics of lactic acid production from lactose by using *L. plantarum* and *L. amylophilus* (Fu and Mathews 1999; Altaf et al. 2005). Lactic acid can also be produced by using *L. pentosus* from vine-trimming wastes (Bustos et al. 2004).

Investigations are made and it is obvious that some other strains other than the *lactobacilli* from lactobacillus genus can also be employed for lactic acid production e.g. *lactococci*. There are reports on the lactic acid production by cassava starch by using *Lactococcus lactis* with *Aspergillus awamori* together and attempts are made to establish the model of kinetics of lactic acid production by using strain *Lactococcus lactis* from substrate of whole wheat flour (Åkerberg et al. 1998).

However, after reviewing a lot of investigation reports, it is obvious that among the genus *Lactobacillus* the most commonly used species is *L. delbrueckii* which can be employed for lactic acid yield. It is reported for its use in many reports related to enzymatic fermentation and lactic acid production (Kotzamanidis et al. 2002; Alrumman 2016). Another species, a homofermentative lactic acid producer i.e. *L. casei* subsp. *rhamnosus* can also be employed for fermentation process. Bacterial stock cultures can be preserved in *Lactobacilli* MRS (Chang et al. 1999)

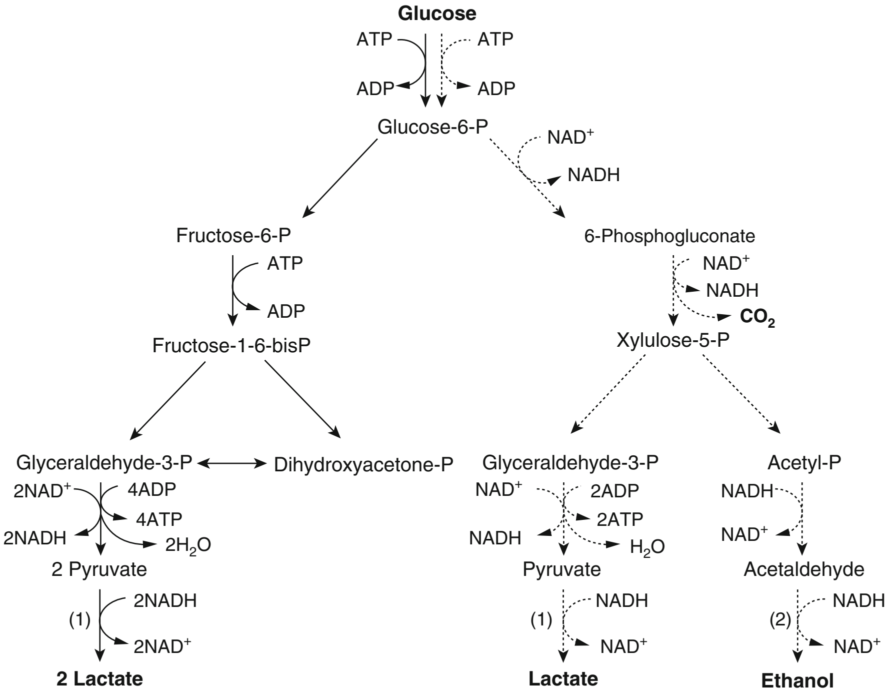


Fig. 8.3 Lactic acid synthesis via different metabolic pathways by using enzyme (*1*) lactate dehydrogenase (*2*) alcohol dehydrogenase. (Courtesy Wee et al. 2006)

Table 8.4 Biotechnological production of lactic acid by using different starting materials

Sr. #	Raw material	Organism	References
01	Cassava	*Lactobacillus amylovorus*	Xiaodong et al. (1997)
02	Molasses	*Lactobacillus delbrueckii*	Kotzamanidis et al. (2002)
03	Potato	*Lactobacillus amylovorus*	Yun et al. (2004)
04	Rice	*Lactobacillus sp.*	Yun et al. (2004)
05	Rye	*Lactobacillus paracasei*	Richter and Berthold (1998)
06	Barley	*Lactobacillus casei*	Linko and Javanainen (1996)
07	Cellulose	*Lactobacillus coryniformis*	Yáñez et al. (2003)
08	Wheat	*Lactobacillus lactis*	Hofvendahl and Hahn-Hägerdal (1997)
09	Waste paper	*Lactobacillus coryniformis*	Yáñez et al. (2005)
10	Wood	*Lactobacillus delbrueckii*	Moldes et al. (2001)
11	Whey	*Lactobacillus casei*	Büyükkileci and Harsa (2004)

media in −20 °C refrigerator with glycerol 25% (v/v) (Nancib et al. 2015). *L. rhamnosus* and *L. acidophilus* also have very good fermenting efficiency for the lactic acid yield from date cellulose as a substrate. However, certain modification are required in setting conditions in order to get the desired results (Alrumman 2016).

8.3.5 Inoculum Preparation

Bacterial culture preparation is an important step in the fermentation experiments. Bacterial culture can be prepared by transferring (1 mL) of the glycerol stock solution to the Erlenmeyer flask which already contains 100 mL MRS medium in liquid form. In order to achieve the exponential growth of bacteria, flask can be incubated for 12 h at 38 °C. For the process of fermentation, Fermenter contains production medium which can be inoculated with a portion of starter culture. Usually, 10% starter culture or inoculum in MRS medium is required for fermentation process (Bozoglu and Ray 2013).

8.3.6 Fermentation Conditions

Fermentation conditions for both batch and Fed –batch cultures are different. For batch culture, stirred tank fermenter is required which has a fermentation capacity of 1 L. For fermentation, 5 N NH_4OH solution is added in the medium which maintains the pH at 6. Cultures are usually incubated with continuous shaking at speed of 200 rpm at 38 °C.

For Fed-batch culture, stirred tank fermenter (LKB, Bromma, Sweden) is required which has fermentation capacity of 10 L. Fed-batch can be started with the addition of feeding medium. Feeding medium has date palm fruit juice (glucose 100 g/L) as main constituent which should be added continuously into fermenter at different feeding rates i.e. (18, 22, 33, 75 and 150 mL/h) (Nancib et al. 2015). Batch Fermentation can be done in 24 h after inoculation.

8.3.7 Fermentation Process in Lactic Acid Production

Lactic acid is produced from the cellulosic date palm waste by fermentation process in which substrate is biodegraded with the help of enzymes obtained from microorganisms into products i.e. lactic acid and ethanol. Lactic acid is produced from glucose with the help of process of glycolysis and it is available either in levorotatory (L) configuration or dextrorotatory configuration (D) (Fig. 8.4) (Martinez et al. 2013).

Fermentation process is completed in different stages that are carried out in bio reactor. Firstly, samples are prepared for fermentation process (Fig. 8.5).

Fermentation processes is employed to get valuable products e.g. lactic acid and it is of many types e.g. Batch, fed-batch, repeated batch and continuous fermentation process. Advantage of using batch and fed batch culture is that it gives higher lactic acid concentrations while other kind of fermentation processes e.g. continuous cultures gives higher productivity and fermentation processes can be continued for the longer time in this case (Oh et al. 2003).

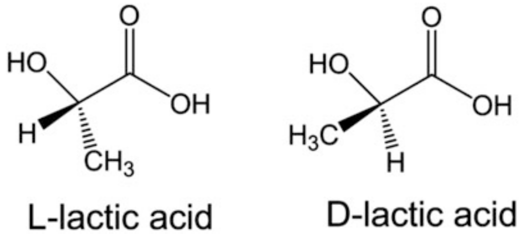


Fig. 8.4 Enantiomers of lactic acid

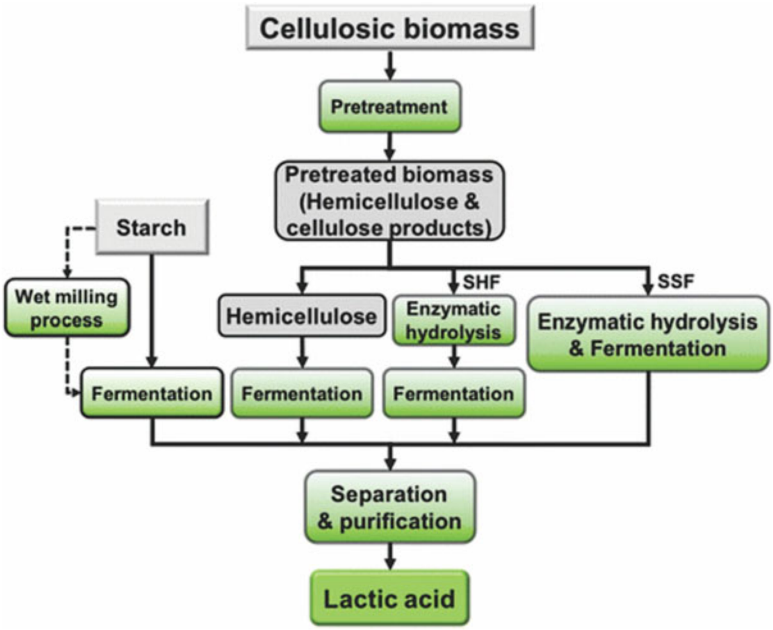


Fig. 8.5 Flow diagram for production of lactic acid

Two types of fermentation is mostly used for fermentation of date palm. One is batch fermentation whereas other one is fed batch fermentation.

8.3.7.1 Batch Fermentation

Batch fermentation is an excellent method that is used for commercial production of lactic acid at industrial level. However, it is observed that during batch fermentation, productivity and yield of lactic acid is decreased because of some issues. Presence of larger amount of initial substrate concentration cause inhibition of lactic acid production during batch fermentation process (Hujanen et al. 2001).

8.3.7.2 Fed Batch Culture

Another type of fermentation process is fed-batch culture. This type of culture is constantly provided with substrate quantity and in addition it must have some mechanism for the transfer of broth of fermentation. Fed batch fermenter has some advantages over the batch fermenter that it is more efficient and productivity of biomass is higher in this case as it is continuous and constantly provided with the substrate. It is beneficial as final production of desired product i.e. lactic acid in this case is enhanced as nutrients are provided continuously in the process (Ding and Tan 2006). (Roukas and Kotzekidou 1998; Nancib et al. 2015). Data regarding the use of fed batch process to get lactic acid biotechnologically is scanty.

High productivity of lactic acid can be achieved by using repeated batch and continuous fermentation processes. It was reported that lactic acid is produced at a rate of 6.4 g/L by using repeated batch fermentation system with very low production cost as compared to traditional fermentation processes as only 26% yeast extract is used in such experiments (Oh et al. 2003). Lactic acid production was also attempted by cell retention in cell recycle culture system using *L. rhamnosus*. Lactic acid was obtained 92 g/L in cell recycle bioreactor successfully.

8.3.7.3 Kinetics

The study of kinetics is important to design and control biological reactors. It is extremely important to obtain maximum yield. The Hanson and Tsao in 1972 studied about kinetics of batch and continuous fermentation on a glucose-yeast extract medium at controlled pH levels. They give a detail idea about maintenance of pH during fermentation process and suggested that any change in pH affects the fermentative process (Eş et al. 2018). Stieber and Gerhard in 1979 succeeded in developing a mathematical model for the continuous process that also carry dialysis for the production of ammonium lactate from deproteinized whey (Hofvendahl and Hahn–Hägerdal 2000). In structured models for fermentations the compositions of biomass remain constant during the processes which are responsible to limits their applicability to experiments with different operating conditions. It is suggested by Nielsen in 1991 that a theoretical study of lactic acid fermentation that was based on simple structured model of *Streptococcus cremoris*, in which the cell physiology is taken into consideration (Dien et al. 2003). These kinds of models and their modifications suggest better characterization of lactic acid fermentation in different situations such as non-growth conditions. These models can be modified into suitable way depending on other parameters of fermenting process and conditions. Nielsen also claimed that their model described experimental observations as *S. cremoris* carbohydrate adaptation and substrate preference on mixtures of galactose, glucose and lactose (Dien et al. 2003). These models suggest idea about setting the optimal condition for desired process.

8.3.8 Fermentation Equipment and Technology

The target of producing lactic acid by active microbial organisms usually follows basic established technology. The utilization of right technology and right microorganism is extremely important in carrying out effective fermentation.

In conventional fermentation methods the use of free microbial cells in batch or continuous fermenters is good choice but they usually require the separation of cells from the medium at the end of each process. Whereas, on the other hand, immobilization of cells on solid supports or their entrapment in a gel matrix can introduce diffusional resistances but it requires additional expenses which are associated with the immobilization step (Kailasapathy 2013).

Product inhibition in lactic acid fermentation processes is a serious problem and its effect on lactic acid productivity has been reported by various authors (Carroll and Somerville 2009). It has been studied that due to product inhibition, the benefits of continuous fermentation are not fully achieved in lactic acid processes. In case, if substrate concentrations in the reaction is very low then specific growth rate of the microorganism can be more dependent on the concentration of the product as compare to substrate (Keller and Gerhardt 1975). So, processes that remove the product from the fermentation medium could easily improve the efficiency of the system. In such cases, the dialysis culture system was utilized which can remove lactic acid from the medium and restore the efficiency of the system (Friedman and Gaden 1970). The system maintained a low lactate concentration after the log phase which causes the increase in specific microbial growth rates and lactic acid production. The study also claims that these results inveterate the product inhibition effect in lactic acid fermentation. It was suggested that relative to non-dialysis continuous or batch processes, the dialysis continuous fermentation endorsed the use of more concentrated substrate that causes increase in the efficiency of substrate conversion into product i.e. lactic acid (Friedman and Gaden 1970). Monitoring of process variables is very important in a fermentation process. A semi-on-line monitoring system is required to study the lactic acid fermentation process which can successfully measure the Glucose, lactic acid, protein, and optical density in a computer based controlled fermenter (Nielsen et al. 1990). The authors reported that the response of this system was very fast and reliable and that it can be used for the study of mathematical fermentation models that may help in designing appropriate protocols (Spann et al. 2018).

Lactic acid produced in fermentation processes needs to be recovered or extracted and then purified. However, few fermentation problems make its difficult. For example, to control the pH of the lactic acid fermentation, many chemicals such as ammonia, calcium carbonate, or sodium hydroxide are added into the medium. But, calcium carbonate causes precipitation of calcium lactate, which in turn hinders the production of a polymer-grade material from lactic acid. Whereas the continuous removal of lactic acid from the fermentation medium can be a solution to this problem, by avoiding the lowering of the pH of the broth. A system which is known as reactive liquid-liquid extraction (RLLE) that uses amines can achieve this target (San-Martín et al. 1992). Extractive fermentation process can be used to get high yield of lactic acid by *Lactobacillus delbrueckii* utilising a tertiary amine (Alamine 336) and oleyl alcohol, at acidic pH was also studied by (Berry et al. 1999). In general the processes used for the recovery of lactic acid or lactate salts from the fermentation medium are a significant part of the total cost of the process (Nampoothiri et al. 2010).

8.4 Factors Affecting Yield of Glucose and Lactic Acid

8.4.1 Effect of Pretreatments on Wastes of Date Palm on Yield of Glucose and Lactic Acid

It is experimentally proved that if date palm cellulosic waste material is pretreated that will give rise to increased production of glucose as compared to starting material which is non-treated. It is because of activity of cellulose enzyme which is more active on pretreated substrate date palm waste as compared to non-treated substrate material. The low production of glucose may be due to the presence of high content of lignin in non-treated substrate which makes it difficult for the large enzymatic protein molecules to act on the structure of plant cell wall which is complex and packed. So, pre-treatment of the substrate which contains lignocellulose is necessary for activity of enzyme effectively. Pretreatment with alkaline solution lowers down the hardness and crystalline nature of cellulose in plant leaves as compared with leaf bases and it also increases the surface area available for the activity of cellulose enzyme. The maximum glucose production i.e. 19.57% (4.37 mg/mL) is achieved in date palm leaves then in leaf bases, 15.66% (3.47 mg/mL) respectively (Nancib et al. 2015). The alkaline pre-treatment process is very important factor that affects the production of valuable products because it can dissolve the complicated complexes of lignin and hemicelluloses and swelling of the cellulose (Hofvendahl and Hahn–Hägerdal 2000). Fermentation process requires efficient conversion of cellulosic content into lactic acid with high yield.

It is reported that lactic acid yield is also enhanced in case of pretreatment of cellulosic substrate. Pretreatment results in effective hydrolysis of substrate which leads to efficient and increased productivity. Pretreatment with alkali dissolves lignin and hemicellulose which are present in natural agricultural wastes. In this way surface contact with enzymes are increased which results in better yield of lactic acid. It is investigated that pretreatment of vinasse with alkali or microwave method results in enhancement of lactic acid production i.e. 71% (Wang et al. 2010). There are reports that hydrothermal pretreatment of substrate with addition of $CaCO_3$ prior to fermentation increases the enzyme action which leads to increased production of glucose and lactic acid (Bretón-Toral et al. 2017).

8.4.2 Effect of Substrate Concentration on Yield of Glucose and Lactic Acid

Rate of enzymatic reaction also depends on the substrate concentration. The increase in substrate concentration in the fermentation reaction can decreases sugar yield, which may be caused because of poor stirring in the reaction. Enzyme may be inhibited by by-products of the reaction and it decreased synergistic action between cellulases enzymes (Idris and Suzana 2006).

Initial high substrate concentration could result in low productivity of glucose and lactic acid. In case of fed-batch process it is reported that lactic acid production is enhanced if low substrate concentration is maintained (Michelz Beitel et al. 2017).

8.4.3 Effect of Enzyme Concentration on Yield of Glucose and Lactic Acid

Enzyme concentration is important in determining the rate of an enzymatic reaction. For the production of glucose, enzyme concentration should be 10–80 FPU/g of palm date waste substrates. It is investigated that production of glucose from date palm waste is also dependent on the enzyme-substrate ratio. Maximum sugar production i.e. 71.03% and 31.57 mg/mL is achieved at 30 FPU/g substrate However, no effect on increase in glucose production is seen with increasing the enzyme concentration. Cellulase enzyme also affects the process of sugar production by its role in the transglycosylation reactions (Hofvendahl and Hahn–Hägerdal 2000).

It is investigated that addition of increased concentration of enzymes i.e. cellulose and pectinase can result in enhanced productivity and yield of lactic acid from alfalfa but it also increases the cost of production as well. Increased concentration of enzymes results in increased release of sugar for lactic acid production (Sreenath et al. 2001).

8.4.4 Effect of pH on Yield of Glucose and Lactic Acid

For the maximum activity of an enzyme, optimum pH for a chemical reaction is necessary. Production of sugar from date palm waste substrate is maximum achieved at pH 5.0. The pH conditions of a chemical reaction affects significantly on the enzymatic hydrolysis carried out by cellulase enzyme. For the action of enzyme, at optimum pH value, enzyme-substrate complex is formed for hydrolysis reaction. The effect of pH on hydrolysis as well as on adsorption is same and that occurs at around acidic pH 4.8 (Hofvendahl and Hahn–Hägerdal 2000).

During fermentation process, pH maintenance is very important. At the start of fermentation process, pH is maintained but due to production of acid in the process, pH is decreased. To control pH of the process, base titration method is used usually. Various studies have been carried out to check the effect of pH on the lactic acid yield. It is reported that maximum lactic acid production is achieved between pH 5–7 (Göksungur and Güvenç 1997). Lactic acid production yield was 79% at pH 6 which was optimum. When the pH is increased from 6 to 6.5, lactic acid production is decreased to 31.25%. Lactic acid production is also decreased to 16,55% when pH is lowered till 5.5 (Pailin 2010).

8.4.5 Effect of Temperature on Yield of Glucose and Lactic Acid

Optimum temperature is necessary for the maximum activity of any enzyme. If there is any increase or decrease in the temperature (which is ideal for activity of any enzyme) it may change and reduce the production of valuable products. For the production of glucose, complete enzymatic hydrolysis is achieved at 50 °C with glucose production of 71.23%. If temperature is increased from 50 to 55 °C, it results in decrease of glucose production i.e. 66.48% from 71.23% (Nancib et al. 2015).

Yield of lactic acid from cellulosic date palm waste is also affected by temperature which is one of the most important environmental factor. Investigations have been made to study the effect of temperature on the lactic acid yield and it is found that optimum temperature for the lactic acid production is 41–45 °C (Hofvendahl and Hahn–Hägerdal 2000). Lactic acid bacteria are mesophilic and their growth is optimum between 20 and 45 °C. Maximum lactic acid yield (79.8%) is reported at 40 °C (Pailin 2010). It is also observed that lactic acid productivity is decreases (35.30%) with a increase in temperature from 45 °C (Göksungur and Güvenç 1997).

8.5 Conclusion

The bioconversion of cellulosic wastes into valuable bio-products by fermentation processes is an important process that converts useless waste into very important products e.g. glucose and lactic acid. Development in the production of lactic acid from date palm is linked to the present general trends in biotechnology and its main factors include availability of date palm waste and progress in related scientific and technological areas. Date palm cellulosic waste represents an excellent starting material for its use in fermentation process for the production of glucose and lactic acid as it is cheap and it is easily available round the year. Production of glucose and lactic acid are significantly influenced by the substrate concentration, enzyme concentration, temperature and pH etc. Maximum glucose production is achieved at substrate concentration (4%) and enzyme concentration (30 FPU/g). Lactic acid production is affected by initial higher concentrations of substrate. Optimum temperature and pH for the production of glucose is 50 °C and 5 respectively, while

Lactic acid bacteria produce lactic acid at optimum condition of temperature 40 °C and pH 6. Cellulosic waste material i.e. date palm waste is an excellent alternative for the expensive raw material for industrial production of glucose and lactic acid through fermentation process. Such results are attractive and these suggest that date palm cellulosic material is an excellent and cheap source for glucose and lactic acid production enzymatically.

References

Agbor VB, Cicek N, Sparling R, Berlin A, Levin DB (2011) Biomass pretreatment: fundamentals toward application. Biotechnol Adv 29(6):675–685. https://doi.org/10.1016/j.biotechadv.2011.05.005

Agoudjil B, Benchabane A, Boudenne A, Ibos L, Fois M (2011) Renewable materials to reduce building heat loss: characterization of date palm wood. Energy Build 43(2–3):491–497. https://doi.org/10.1016/j.enbuild.2010.10.014

Åkerberg C, Hofvendahl K, Zacchi G, Hahn-Hägerdal B (1998) Modelling the influence of pH, temperature, glucose and lactic acid concentrations on the kinetics of lactic acid production by Lactococcus lactis ssp. lactis ATCC 19435 in whole-wheat flour. Appl Microbiol Biotechnol 49 (6):682–690. https://doi.org/10.1007/s002530051232

Al-Farsi* MA, Lee CY (2008) Nutritional and functional properties of dates: a review. Crit Rev Food Sci Nutr 48(10):877–887. https://doi.org/10.1080/10408390701724264

Alrumman SA (2016) Enzymatic saccharification and fermentation of cellulosic date palm wastes to glucose and lactic acid. Braz J Microbiol 47(1):110–119. https://doi.org/10.1016/j.bjm.2015.11.015

Al-Shahib W, Marshall RJ (2003) The fruit of the date palm: its possible use as the best food for the future? Int J Food Sci Nutr 54(4):247–259. https://doi.org/10.1080/09637480120091982

Altaf M, Naveena BJ, Reddy G (2005) Screening of inexpensive nitrogen sources for production of L (+) lactic acid from starch by amylolytic Lactobacillus amylophilus GV6 in single step fermentation. Food Technol Biotechnol 43(3):235–239. URI: https://hrcak.srce.hr/110538

Amrane A, Prigent Y (1998) Lactic acid production rates during the different growth phases of Lactobacillus helveticus cultivated on whey supplemented with yeast extract. Biotechnol Lett 20(4):379–383. https://doi.org/10.1023/A:1005331430943

Berry AR, Franco CM, Zhang W, Middelberg AP (1999) Growth and lactic acid production in batch culture of Lactobacillus rhamnosus in a defined medium. Biotechnol Lett 21(2):163–167. https://doi.org/10.1155/2015/501029

Bozoglu TF, Ray B (2013) Lactic acid bacteria: current advances in metabolism, genetics and applications. Springer, Berlin/Heidelberg. https://doi.org/10.1007/978-3-642-61462-0

Bretón-Toral A, Trejo-Estrada T, McDonald A (2017) Lactic acid production from potato peel waste, spent coffee grounds and almond shells with undefined mixed cultures isolated from coffee mucilage from Coatepec Mexico. Ferment Technol 6(139):2. https://doi.org/10.4172/2167-7972.1000139

Burgos-Rubio CN, Okos MR, Wankat PC (2000) Kinetic study of the conversion of different substrates to lactic acid using Lactobacillus bulgaricus. Biotechnol Prog 16(3):305–314. https://doi.org/10.1021/bp000022p

Bustos G, Moldes AB, Cruz JM, Domínguez JM (2004) Formulation of low-cost fermentative media for lactic acid production with Lactobacillus rhamnosus using vinification lees as nutrients. J Agric Food Chem 52(4):801–808. https://doi.org/10.1021/jf030429k

Büyükkileci AO, Harsa S (2004) Batch production of L (+) lactic acid from whey by Lactobacillus casei (NRRL B-441). J Chem Technol Biotechnol 79(9):1036–1040. https://doi.org/10.1002/jctb.1094

Carocho M, Morales P, Ferreira IC (2015) Natural food additives: Quo vadis. Trends Food Sci Technol 45(2):284–295. https://doi.org/10.1016/j.tifs.2015.06.007

Carrasco F, Pagès P, Gámez-Pérez J, Santana O, Maspoch ML (2010) Processing of poly (lactic acid): characterization of chemical structure, thermal stability and mechanical properties. Polym Degrad Stab 95(2):116–125. https://doi.org/10.1366/13-07176

Carroll A, Somerville C (2009) Cellulosic biofuels. Annu Rev Plant Biol 60:165–182. https://doi.org/10.1146/annurev.arplant.043008.092125

Chafran LS, Campos JM, Santos JS, Sales MJA, Dias SC, Dias JA (2016) Synthesis of poly (lactic acid) by heterogeneous acid catalysis from d, l-lactic acid. J Polym Res 23(6):107. https://doi.org/10.1021/bm101302t

Chandrasekaran M, Bahkali AH (2013) Valorization of date palm (Phoenix dactylifera) fruit processing by-products and wastes using bioprocess technology – review. Saudi J Biol Sci 20 (2):105–120. https://doi.org/10.1016/j.sjbs.2012.12.004

Chang D-E, Jung H-C, Rhee J-S, Pan J-G (1999) Homofermentative production of d-orl-lactate in metabolically engineered Escherichia coli RR1. Appl Environ Microbiol 65(4):1384–1389. https://doi.org/10.1186/1475-2859-12-57

Chao CT, Krueger RR (2007) The date palm (Phoenix dactylifera L.): overview of biology, uses, and cultivation. Hortscience 42(5):1077–1082. https://doi.org/10.1088/1757-899X/368/1/012009DOI

Datta R, Henry M (2006) Lactic acid: recent advances in products, processes and technologies—a review. J Chem Technol Biotechnol 81(7):1119–1129. https://doi.org/10.1002/jctb.1486

Datta R, Tsai S-P, Bonsignore P, Moon S-H, Frank JR (1995) Technological and economic potential of poly (lactic acid) and lactic acid derivatives. FEMS Microbiol Rev 16 (2–3):221–231. https://doi.org/10.1111/j.1574-6976.1995.tb00168.x

de Oliveira RA, Komesu A, Rossell CEV, Maciel Filho R (2018) Challenges and opportunities in lactic acid bioprocess design – from economic to production aspects. Biochem Eng J 133:219–239. https://doi.org/10.1016/j.bej.2018.03.003

Dien B, Cotta M, Jeffries T (2003) Bacteria engineered for fuel ethanol production: current status. Appl Microbiol Biotechnol 63(3):258–266. https://doi.org/10.1007/s00253-003-1444-y

Ding S, Tan T (2006) L-lactic acid production by Lactobacillus casei fermentation using different fed-batch feeding strategies. Process Biochem 41(6):1451–1454. https://doi.org/10.1002/biot.200600099

Eş I, Khaneghah AM, Barba FJ, Saraiva JA, Sant'Ana AS, Hashemi SMB (2018) Recent advancements in lactic acid production-a review. Food Res Int 107:763–770. https://doi.org/10.1018/10408398.2018.1477730

Friedman MR, Gaden EL (1970) Growth and acid production by Lactobacillus (L.) delbrueckii in a dialysis culture system. Biotechnol Bioeng 12(6):961–974. https://doi.org/10.1002/bit.260120608

Fu W, Mathews A (1999) Lactic acid production from lactose by Lactobacillus plantarum: kinetic model and effects of pH, substrate, and oxygen. Biochem Eng J 3(3):163–170. https://doi.org/10.1016/S1369-703X(99)00014-5

Garde A, Jonsson G, Schmidt AS, Ahring BK (2002) Lactic acid production from wheat straw hemicellulose hydrolysate by Lactobacillus pentosus and Lactobacillus brevis. Bioresour Technol 81(3):217–223. https://doi.org/10.17221/461/2017-CJFS

Göksungur Y, Güvenç U (1997) Batch and continuous production of lactic acid from beet molasses by Lactobacillus delbrueckii IFO 3202. J Chem Technol Biotechnol 69(4):399–404. https://doi.org/10.1002/(SICI)1097-4660(199708)69:4<399::AID-JCTB728>3.0.CO;2-Q

Goyal H, Seal D, Saxena R (2008) Bio-fuels from thermochemical conversion of renewable resources: a review. Renew Sust Energy Rev 12(2):504–517. https://doi.org/10.1016/j.rser.2006.07.014

Hamada J, Hashim I, Sharif F (2002) Preliminary analysis and potential uses of date pits in foods. Food Chem 76(2):135–137. https://doi.org/10.1016/S0308-8146(01)00253-9

Harding K, Harrison S (2016) Generic flowsheet model for early inventory estimates of industrial microbial processes. II. Downstream processing. South Afr J Chem Eng 22:23–33. https://doi.org/10.1016/j.ces.2017.07.008

Himmel ME, Xu Q, Luo Y, S-Y D, Lamed R, Bayer EA (2010) Microbial enzyme systems for biomass conversion: emerging paradigms. Biofuels 1(2):323–334. https://doi.org/10.4155/bfs.09.25

Hofvendahl K, Hahn-Hägerdal B (1997) L-lactic acid production from whole wheat flour hydrolysate using strains of Lactobacilli and Lactococci. Enzym Microb Technol 20(4):301–307. https://doi.org/10.1016/S0141-0229(97)83489-8

Hofvendahl K, Hahn–Hägerdal B (2000) Factors affecting the fermentative lactic acid production from renewable resources1. Enzym Microb Technol 26(2–4):87–107. https://doi.org/10.1016/S0141-0229(99)00155-6

Hujanen M, Linko S, Linko Y-Y, Leisola M (2001) Optimisation of media and cultivation conditions for L (+)(S)-lactic acid production by Lactobacillus casei NRRL B-441. Appl Microbiol Biotechnol 56(1–2):126–130. https://doi.org/10.1007/s002530000501

Idris A, Suzana W (2006) Effect of sodium alginate concentration, bead diameter, initial pH and temperature on lactic acid production from pineapple waste using immobilized Lactobacillus delbrueckii. Process Biochem 41(5):1117–1123. https://doi.org/10.1016/j.procbio.2005.12.002

John RP, Nampoothiri KM, Pandey A (2007) Fermentative production of lactic acid from biomass: an overview on process developments and future perspectives. Appl Microbiol Biotechnol 74(3):524–534. https://doi.org/10.1007/s00253-006-0779-6

Kailasapathy K (2013) Commercial sources of probiotic strains and their validated and potential health benefits-a review. Int J Ferment Foods 2(1):1. https://doi.org/10.3389/fmicb.2016.00578

Keller AK, Gerhardt P (1975) Continuous lactic acid fermentation of whey to produce a ruminant feed supplement high in crude protein. Biotechnol Bioeng 17(7):997–1018. https://doi.org/10.1002/bit.260170705

Khalid S, Ahmad A, Kaleem M (2017a) Antioxidant activity and phenolic contents of Ajwa date and their effect on lipo-protein profile. Funct Foods Health Dis 7(6):396–410. https://doi.org/10.7324/JAPS.2015.50826

Khalid S, Khalid N, Khan RS, Ahmed H, Ahmad A (2017b) A review on chemistry and pharmacology of Ajwa date fruit and pit. Trends Food Sci Technol 63:60–69. https://doi.org/10.1016/j.tifs.2017.02.009

Kimura Y, Misato I, Kojima H, Kanai Y, Seki Y, Aburai K, Kikuchi Y (2016) Glucose production method and glucose produced by said method. Google Patents. https://patents.google.com/patent/US20160090613A1/en

Kotzamanidis C, Roukas T, Skaracis G (2002) Optimization of lactic acid production from beet molasses by Lactobacillus delbrueckii NCIMB 8130. World J Microbiol Biotechnol 18(5):441–448. https://doi.org/10.1023/A:1015523126741

Kulozik U, Wilde J (1999) Rapid lactic acid production at high cell concentrations in whey ultrafiltrate by Lactobacillus helveticus. Enzym Microb Technol 24(5–6):297–302. https://doi.org/10.1016/s0141-0229(98)00122-7

Lim L-T, Auras R, Rubino M (2008) Processing technologies for poly (lactic acid). Prog Polym Sci 33(8):820–852. https://doi.org/10.1016/j.progpolymsci.2008.05.004

Linko Y-Y, Javanainen P (1996) Simultaneous liquefaction, saccharification, and lactic acid fermentation on barley starch. Enzym Microb Technol 19(2):118–123. https://doi.org/10.1016/0141-0229(95)00189-1

Martinez FAC, Balciunas EM, Salgado JM, González JMD, Converti A, de Souza Oliveira RP (2013) Lactic acid properties, applications and production: a review. Trends Food Sci Technol 30(1):70–83. https://doi.org/10.3390/app6120379

Martinez A, Rodríguez-Alegría ME, Fernandes MC, Gosset G, Vargas-Tah A (2017) Metabolic engineering of Escherichia coli for lactic acid production from renewable resources. In: Engineering of microorganisms for the production of chemicals and biofuels from renewable resources. Springer, Cham, pp 125–145. https://doi.org/10.1007/978-3-319-51729-2_5

Michelz Beitel S, Fontes Coelho L, Sass DC, Contiero J (2017) Environmentally friendly production of D (−) lactic acid by Sporolactobacillus nakayamae: investigation of fermentation parameters and fed-batch strategies. Int J Microbiol 2017:1–11. https://doi.org/10.1155/2017/4851612

Miura S, Arimura T, Itoda N, Dwiarti L, Feng JB, Bin CH, Okabe M (2004) Production of L-lactic acid from corncob. J Biosci Bioeng 97(3):153–157. https://doi.org/10.1016/S1389-1723(04)70184-X

Mohanty JN, Das PK, Nanda S, Nayak P, Pradhan P (2016) Comparative analysis of crude and pure lactic acid produced by Lactobacillus fermentum and its inhibitory effects on spoilage bacteria. Pharm Innov 3(11, Part A). https://doi.org/10.1155/2017/4851612

Moldes AB, Alonso JL, Parajo JC (2001) Strategies to improve the bioconversion of processed wood into lactic acid by simultaneous saccharification and fermentation. J Chem Technol Biotechnol 76(3):279–284. https://doi.org/10.1002/jctb.381

Naik SN, Goud VV, Rout PK, Dalai AK (2010) Production of first and second generation biofuels: a comprehensive review. Renew Sust Energ Rev 14(2):578–597. https://doi.org/10.1016/j.rser.2009.10.003

Nampoothiri KM, Nair NR, John RP (2010) An overview of the recent developments in polylactide (PLA) research. Bioresour Technol 101(22):8493–8501. https://doi.org/10.1016/j.biortech.2010.05.092

Nancib A, Nancib N, Boubendir A, Boudrant J (2015) The use of date waste for lactic acid production by a fed-batch culture using Lactobacillus casei subsp. rhamnosus. Braz J Microbiol 46(3):893–902. https://doi.org/10.1590/S1517-838246320131067

Nielsen J, Nikolajsen K, Benthin S, Villadsen J (1990) Application of flow-injection analysis in the on-line monitoring of sugars, lactic acid, protein and biomass during lactic acid fermentations. Anal Chim Acta 237:165–175. https://doi.org/10.1023/A:1016699701903

Oh H, Wee Y-J, Yun J-S, Ryu H-W (2003) Lactic acid production through cell-recycle repeated-batch bioreactor. In: Biotechnology for fuels and chemicals. Springer, Cham, pp 603–613. https://doi.org/10.1007/978-1-4612-0057-4_50

Pailin B (2010) Development of lactic acid production process from cassava by using lactic acid bacteria. https://doi.org/10.18178/IJCEA

Pandey A (2003) Solid-state fermentation. Biochem Eng J 13(2–3):81–84. https://doi.org/10.1016/S1369-703X(02)00121-3

Raman N (2010) Production of Glucose from Banana Stem Waste Using Strain A. UMP. ballistic model-based soft sensor to monitor lactic acid bacteria fermentations. Biochem Eng J 135:49–60. URI: http://umpir.ump.edu.my/id/eprint/3251

Richter K, Berthold C (1998) Biotechnological conversion of sugar and starchy crops into lactic acid. J Agric Eng Res 71(2):181–191. https://doi.org/10.1006/jaer.1998.0314

Rogers P, Chen J-S, Zidwick MJ (2006) Organic acid and solvent production. In: The prokaryotes. Springer, New York, pp 511–755. https://doi.org/10.1006/jaer.1998.0314

Roukas T, Kotzekidou P (1998) Lactic acid production from deproteinized whey by mixed cultures of free and coimmobilized Lactobacillus casei and Lactococcus lactis cells using fedbatch culture. Enzyme Microb Tech 22(3):199–204. https://doi.org/10.1016/S0141-0229(97)00167-1

Salas-Papayanopolos H, Morales-Cepeda AB, Sanchez S, Lafleur PG, Gomez I (2017) Synergistic effect of silver nanoparticle content on the optical and thermomechanical properties of poly (l-lactic acid)/glycerol triacetate blends. Polymer Bulletin 74(12):4799–4814. https://doi.org/10.1007/s00289-017-1992-4

San-Martín M, Pazos C, Coca J (1992) Reactive extraction of lactic acid with alamine 336 in the presence of salts and lactose. J Chem Technol Biotechnol 54(1):1. https://doi.org/10.1006/jaer.1998.03146

Saxena S (2015) Microbial enzymes and their industrial applications. In: Applied microbiology. Springer, pp 121–154. https://doi.org/10.1007/978-81-322-2259-0_9

Schepers AW, Thibault J, Lacroix C (2002) Lactobacillus helveticus growth and lactic acid production during pH-controlled batch cultures in whey permeate/yeast extract medium. Part I: Multiple factor kinetic analysis. Enzyme Microb Technol 30(2):176–186. https://doi.org/10.1016/S0141-0229(01)00465-3

Scully SM, Iloranta P, Myllymaki P, Orlygsson J (2015) Branched-chain alcohol formation by thermophilic bacteria within the genera of Thermoanaerobacter and Caldanaerobacter. Extremophiles 19(4):809–818. https://doi.org/10.1155/2015/410492

Shukla V, Zhou S, Yomano L, Shanmugam K, Preston J, Ingram L (2004) Production of d (−)-lactate from sucrose and molasses. Biotechnol Lett 26(9):689–693. https://doi.org/10.1023/B:BILE.0000024088.36803.4e

Södergård A, Stolt M (2002) Properties of lactic acid based polymers and their correlation with composition. Prog Polym Sci 27(6):1123–1163. https://doi.org/10.1016/S0079-6700(02)00012-6

Spann R, Roca C, Kold D, Lantz AE, Gernaey KV, Sin G (2018) A probabilistic model-based soft sensor to monitor lactic acid bacteria fermentations. Biochem Eng J 135:49–60. https://doi.org/10.1016/j.bej.2018.03.016

Sreenath HK, Moldes AB, Koegel RG, Straub RJ (2001) Lactic acid production from agriculture residues. Biotechnol Lett 23(3):179–184. https://doi.org/10.1023/A:1005651117831

Venkatesh K (1997) Simultaneous saccharification and fermentation of cellulose to lactic acid. Bioresour Technol 62(3):91–98. https://doi.org/10.1016/S0960-8524(97)00122-3

Vijayakumar J, Aravindan R, Viruthagiri T (2008) Recent trends in the production, purification and application of lactic acid. Chem Biochem Eng Q 22(2):2. https://doi.org/10.1016/j.jrras.2014.03.00245-264

Wang L, Zhao B, Liu B, Yu B, Ma C, Su F, Hua D, Li Q, Ma Y, Xu P (2010) Efficient production of L-lactic acid from corncob molasses, a waste by-product in xylitol production, by a newly isolated xylose utilizing Bacillus sp. strain. Bioresour Technol 101(20):7908–7915. https://doi.org/10.1016/j.biortech.2010.05.031

Wang Y, Tashiro Y, Sonomoto K (2015) Fermentative production of lactic acid from renewable materials: recent achievements, prospects, and limits. J Biosci Bioeng 119(1):10–18. https://doi.org/10.1016/j.jbiosc.2014.06.003

Wasewar KL, Yawalkar AA, Moulijn JA, Pangarkar VG (2004) Fermentation of glucose to lactic acid coupled with reactive extraction: a review. Ind Eng Chem Res 43(19):5969–5982. https://doi.org/10.1021/ie049963n

Wee Y-J, Yun J-S, Park D-H, Ryu H-W (2004) Biotechnological production of L (+)-lactic acid from wood hydrolyzate by batch fermentation of Enterococcus faecalis. Biotechnol Lett 26(1):71–74. https://doi.org/10.1023/B:BILE.0000009464.23026.e

Wee Y-J, Yun J-S, Lee YY, Zeng A-P, Ryu H-W (2005) Recovery of lactic acid by repeated batch electrodialysis and lactic acid production using electrodialysis wastewater. J Biosci Bioeng 99(2):104–108. https://doi.org/10.1263/jbb.99.104

Wee Y-J, Kim J-N, Ryu H-W (2006) Biotechnological production of lactic acid and its recent applications. Food Technol Biotechnol 44(2):163–172. https://doi.org/10.12691/wjoc-1-2-3

Xiaodong W, Xuan G, Rakshit S (1997) Direct fermentative production of lactic acid on cassava and other starch substrates. Biotechnol Lett 19(9):841–843. https://doi.org/10.1023/A:1018321200591

Yadav KS, Chuttani K, Mishra AK, Sawant KK (2011) Effect of size on the biodistribution and blood clearance of etoposide-loaded PLGA nanoparticles. PDA J Pharm Sci Technol 65(2):131–139. doi:tapraid4/zj5-pstj/zj5-pstj/zj500211/zj52228d11g

Yáñez R, Moldes AB, Alonso JL, Parajó JC (2003) Production of D (−)-lactic acid from cellulose by simultaneous saccharification and fermentation using Lactobacillus coryniformis subsp. torquens. Biotechnol Lett 25(14):1161–1164. https://doi.org/10.1007/s10529-012-1023-3

Yáñez R, Alonso JL, Parajó JC (2005) D-Lactic acid production from waste cardboard. J Chem Technol Biotechnol 80(1):76–84D. https://doi.org/10.1002/jctb.1160OI

Yun J-S, Wee Y-J, Kim J-N, Ryu H-W (2004) Fermentative production of dl-lactic acid from amylase-treated rice and wheat brans hydrolyzate by a novel lactic acid bacterium, Lactobacillus sp. Biotechnol Lett 26(20):1613–1616. https://doi.org/10.1023/B:BILE.0000045826.97010.82

Zamzam S, Nafiea ER, Al-Hadhromi HA (2018) Ali FA Utilization of Date Pits in the Production of Functional Chocolates. In: Qatar foundation annual research conference proceedings, 2018, vol 2. HBKU Press, Qatar, p HBPD415. https://doi.org/10.5339/qfarc.2018.HBPD348

Chapter 9
Application of Date-Palm Fibres for the Wastewater Treatment

Marija Nujic, Natalija Velic, and Mirna Habuda-Stanić

Abstract Many industries produce large quantities of wastewater. Effluents discharged from industries are often highly polluted and could be toxic to aquatic life. Recently, alternative methods for wastewater treatment have been extensively researched. Removal of different pollutants by adsorption on lignocellulosic materials proved to be a promising, cost-effective method. Large amounts of lignocellulosic materials are produced daily as waste materials of agri-food and wood industries, and large portion ends up on landfills. Such wastes are cheap and often available throughout the year, so their applications as adsorbents have multiple advantages: (i) waste decline and (ii) pollutant removal from wastewater.

This chapter explores the use of date-palm fibres as low-cost adsorbent in wastewater treatment processes. Studies have shown that date-palm based adsorbents have the capability to remove various pollutants such as dyes, heavy metal ions and phosphates. Furthermore, the review provides important information about the adsorption capacities and the utility of date-palm fibers used as adsorbent for pollutant removal from wastewater.

Keywords Adsorption · Date-palm fibres · Pollutants removal · Dyes · Heavy metals

9.1 Introduction

The protection of different ecosystems presents a huge challenge for scientists and engineers in times of intense technology development and population growth, especially in developing countries (Ahmad et al. 2012). As a result of their characteristics and the amounts released to the water bodies, pollutants can detrimentally affect human health, flora and fauna, biodiversity, as well as landscape diversity

M. Nujic (✉) · N. Velic · M. Habuda-Stanić
Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, Osijek, Croatia
e-mail: marija.nujic@ptfos.hr

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_9

(Naushad and Alothman 2015; Alqadami et al. 2016). Therefore, it is necessary to remove them from water bodies, or preferably remove them from wastewaters before the discharge to natural recipients. The increase in volume of industrial wastewater is evident in developing countries and can be related to the population growth (Gobi and Vadivelu 2013). Reports and statistics showed that 70% of freshwater consumption is related to food processing and irrigation. In addition, many pollutants can occur in groundwater and deteriorate its physical-chemical quality. In contrast, in developing countries over 70% of industrial waste is disposed without treatment, and about 90% of wastewaters enters rivers and lakes untreated (Wong et al. 2018).

The wastewater treatment is an integral part of water protection and, therefore, a subject of numerous researches with the collective aim to find new, effective and cost efficient treatment technologies (Awual et al. 2016; Naushad et al. 2016). Heavy metal ions and organic compounds in water for human consumption can cause different problems. For example, phenols can accelerate tumour formation, sulphates cause dehydration, and chromium can cause the formation of different carcinomas (Alshehri et al. 2014; Kumar et al. 2016). Dye loaded wastewaters can have a negative impact on the biota (Alghamdi 2016). There are a number of technologies available for water pollution control, such as filtration, oxidation, chemical precipitation, reduction, ion exchange, adsorption, membrane separation and many more (Ahmad et al. 2011). However, these methods have limitations such as oxidation by-products formation, sludge generation, regeneration of ion exchangers, membrane fouling, high energy cost etc. (Amin et al. 2017). Because of its simple operation, versatility and high efficiency, adsorption is often the method of choice for different pollutants removal from aqueous media.

Recently, researchers have shown an increased interest in alternative methods for pollutants removal from wastewater, including adsorption onto low-cost adsorbents, which are widely distributed, locally available and cheap (Belala et al. 2011). The applicability of waste lignocellulosic materials as adsorbents is achieved by the interaction of adsorbents with functional groups present in these materials (*e.g.* –OH and –COOH). These functional groups are mostly common to all lignocellulosic materials, but their number depends on the type of material. In order to modify the surface of the adsorbent, or to increase the number of functional groups available for adsorption processes, various modification methods of lignocellulosic waste material were investigated, such as modification with inorganic and organic acids (HCl, HNO_3, H_2SO_4, CH_3COOH, $CH_3CH(OH)COOH$, HCOOH), alkali and solutions (NaOH, $Ca(OH)_2$, $CaCl_2$, Na_2CO_3), and many other inorganic and organic compounds (formaldehyde, glutaraldehyde, methanol, epichlorohydrin) (Abdolali et al. 2014) (Fig. 9.1).

These adsorbents have been used for different water pollutants removal: metal ions, dyes, phenols, pesticides, polychlorinated biphenyls etc. (Ofomaja 2007). Various low-cost adsorbents (biosorbents) were investigated for dye removal, such as spent grain (Kezerle et al. 2018), cashew nut shell (Spagnoli et al. 2017), sunflower stalks (Sun and Xu 1997), wood sawdust (Suteu and Zaharia 2011), orange peel (Annadurai et al. 2002), palm-fruit bunch (Nassar et al. 1995), banana pith (Namasivayam et al. 1993), maize cobs (El-Geundi 1991), and others. Metal

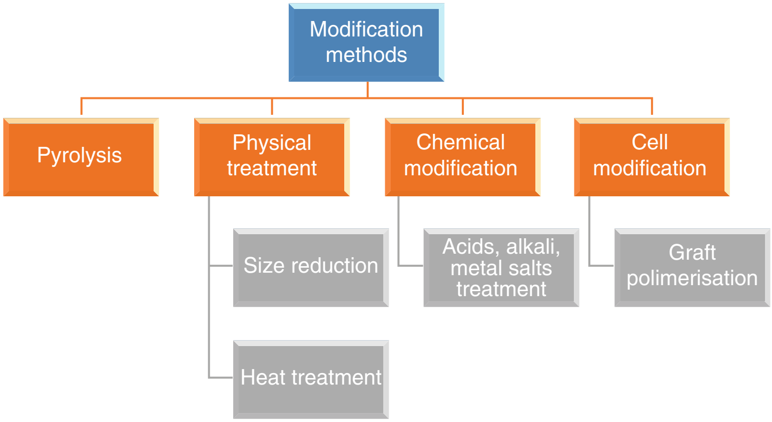


Fig. 9.1 Modification methods of waste lignocellulosic materials. (According to Nguyen et al. 2013)

ions adsorption onto biosorbents was also studied: spent grain (Li et al. 2012), brown seaweed (Uzunoğlu et al. 2014), okra, pumpkin, grape and squash seeds (Al Bsoul et al. 2014), lentil, wheat and rice shells (Aydin et al. 2008), etc. Date palm fibres (DPFs) have been investigated for the adsorptive removal of both, dyes and metal ions (Al-Haidary et al. 2011; Alshabanat et al. 2013), which is presented in this work.

9.2 Date Palm Fibres as Low-Cost Adsorbents

Low-cost lignocellulosic waste materials, offer some advantages for the removal of pollutants from water: porosity, high surface area and resistance to biological degradation. In addition, using waste materials as adsorbents and the development of technologies that incorporate raw materials is an important alternative for pollution control (Bryan and Daniella 2012; Kharat 2015; Alghamdi 2016).

Lignocellulosic materials consist of three polymers: cellulose, hemicellulose and lignin (Al-Kaabi et al. 2005). Besides these polymers, lignocellulosic wastes contain smaller amount of water, ash, cyclic carbohydrate and organic or inorganic extractives (Cagnon et al. 2009). Date-palm fibres (DPFs) have four types of fibres, namely, leaf fibres in the peduncle, baste fibres in the stem, wood fibres in the trunk and surface fibres around the trunk (Khidir et al. 2014; Alghamdi 2016) which make them potentially efficient adsorbents. So far, the research has been conducted using date-palm fibres for dye removal (crystal violet malachite green, Congo red, Rhodamine B6), metal ions removal (Cd, Pb, Cu, As) and phosphate removal.

Date-palm wastes as biosorbents are considered to be efficient for the removal of various pollutants from wastewater, but are particularly effective for the removal of heavy metal ions (Shafiq et al. 2018). Since large amounts of DPFs wastes are disposed unutilised, they have an economic and environmental potential to be valorised in wastewater treatment (Riahi et al. 2009a).

9.2.1 Removal of Synthetic Dyes from Wastewater Using Date Palm Fibres

Wastewaters containing high concentrations of dyes, are usually rich in organic content as well. Such wastewaters, after being discharged into the environment, can be harmful to aquatic life (Lee et al. 1999; Kadirvelu et al. 2001). Synthetic dyes are used in many industries. However, they are the most extensively used in textile, paper, leather and plastic industries, which are thus recognised as the main sources of dye-loaded effluents (Gouamid et al. 2013).

The adsorption of crystal violet (CV) on DPFs was studied by Alshabanat et al. (2013). DPFs were milled and sieved to obtain fine particles. About 0.25 g of adsorbent and 25 mL of CV model solution in concentration range of $0.9{\cdot}10^{-5}$–$7{\cdot}10^{-5}$ mol L^{-1} was used in the experiments. The impact of temperature and pH on adsorptive CV removal was also tested. All experiments were conducted at 25 °C and 100 rpm. The experimentally obtained data were fitted to Langmuir, Freundlich, Elovich and Temkin isotherm models. The results revealed that DPFs are a promising adsorbent for CV removal in a wide concentration range. Additionally, the adsorption of CV on DPFs was best described by Elovich model and the maximum adsorption capacity was equal to the experimental value. Higher removal percentage was achieved at lower temperatures and pH. Thermodynamic analysis showed that the interaction between CV and DPFs was exothermic and spontaneous, and the pseudo-second-order kinetic model gave a better fit with the experimentally obtained data. In another study, Alshabanat, Al-Mufarij, & Al-Senani (2016) examined the adsorption of malachite green (MG), an extensively used dye in textile industry, onto DPFs. The adsorption isotherms showed that the adsorption was more efficient with the increment of MG concentration in solution. The percent removal of dye increased (about 92–95.5%) with the increase of the dye solution pH (from 4 to 10). With the increase of temperature from 25 to 45 °C, the percent removal of dye decreased. Kinetic study revealed that the pseudo-second-order model showed a better fit than the pseudo-first-order model.

Belala et al. (2011) investigated the effect of contact time, temperature, and dye concentration on the adsorption process of methylene blue (MB) onto palm-trees waste. The recorded FTIR spectrum of the biosorbent indicated different functional groups (hydroxyl, carboxyl and carbonyl) that probably serve as the potential adsorption sites for MB. The effect of contact time was tested for the initial MB concentration of 100 mg L^{-1} and biosorbent concentration of 10 g L^{-1}. Results showed that the adsorption capacity increased with the increase of adsorption time and reached the equilibrium at 150 min. The adsorption was very rapid within the first 40 min and then slowed down until equilibrium was reached. In addition, the results showed that the adsorption improved with the increase of adsorption

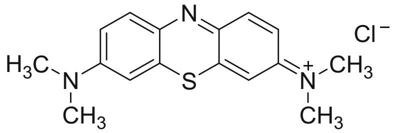


Fig. 9.2 Chemical structure of methylene blue

Table 9.1 Date palm biomass for dye removal from aqueous solutions

Adsorbent	Dye	q_{max}	References
Palm-trees waste	Methylene blue	39.5 mg g^{-1} (Langmuir)	Belala et al. (2011)
Date palm leaves	Methylene blue	58.14 mg g^{-1} (Langmuir)	Gouamid et al. (2013)
Date-palm fibre	Methylene blue	5.02 mg g^{-1} (Langmuir)	Mahmoud (2013)
Date-palm fibre	Crystal violet	12.02 mol g^{-1} (Temkin)	Alshabanat et al. (2013)
Date-palm fibre	Malachite green	0.21 mol g^{-1} (experimental)	Alshabanat et al. (2016)

temperature. The linearized Langmuir model was in a better agreement with experimentally obtained data, compared to linearized Freundlich and Temkin isotherm models, which suggests a monolayer coverage of the surface of adsorbent by MB (Belala et al. 2011). The structure of MB dye is given in Fig. 9.2.

There has been an attempt to remove MB from aqueous solution using date palm leaves. Gouamid et al. (2013) conducted the adsorption experiments in a batch process with adsorbent concentration of 1 g L^{-1} and MB solution of 200 mg L^{-1} at pH ranging from 2 to 8. Results revealed that the highest adsorption efficiency was achieved at pH 6.5. Four isotherms models have been used to analyse the experimentally obtained adsorption data: Langmuir, Freundlich, Temkin and Dubinin-Radushkevich. The Temkin isotherm proved to be the best. Kinetic studies revealed that MB is slowly transported via intraparticle diffusion into the particles and is finally retained in micropores.

The study on MB adsorption on DPF was conducted by Mahmoud (2013) with the initial MB concentration from 50 to 150 mg L^{-1}. The results revealed that the amount of MB adsorbed increased from 4.82 to 12.25 mg g^{-1} at solution pH 7.5 and 30 °C. The percent removal of MB was in the range from 94% to 98% at temperatures from 30 to 60 °C and at pH from 6 to 8. The effect of particle size was also assessed: the adsorption of MB increased with the decrease in particle size. In addition, the Langmuir isotherm model fitted best (q_{max} = 5.02 mg g^{-1} at 60 °C) with initial MB concentration of 50 mg L^{-1} A comparison of the adsorption capacities using date palm biomass for dye removal are presented in (Table 9.1).

9.2.2 Removal of Metal Ions from Wastewater Using Date Palm Fibres

Different process parameters affect the adsorption of heavy metal ions: contact time, pH, dose and size of adsorbent, initial metal ion concentration, modification of adsorbent, *etc*.

The adsorption of copper, lead and arsenic on DPFs was examined by Amin et al. 2017). The DPFs were immersed in water and then separated into individual fibres (0.2–0.8 mm diameter). After that, the DPFs were washed with distilled water for 30 min and filtered, dried at 105 °C for 24 h and then crushed in a crushing machine. Kinetic experiments were conducted at following conditions: initial metal concentration of 20 mg L^{-1}, pH 5, adsorbent concentration of 0.5 g L^{-1} and particle size of 152 μm. The results showed that high adsorption capacities were achieved within first 90 min, while the slower metal uptake occurred for the next 30 min of 120 min contact time for all three metal ions (Cu, Pb and As). The adsorption data showed a linear increase in metal removal capacities with increasing DPFs concentration from 0.1 to 2 g L^{-1}. With increase of initial metal ion concentration from 20 to 80 mg L^{-1}, the removal percentage decreased 30–40% due to saturation of sorption sites on the surface of DPFs.

Amin et al. (2016) investigated the use of date-palm trunk fibres as biosorbent for copper ions removal from aqueous solution. The copper adsorption was dependant on the adsorbent particle size, where the highest adsorption capacity of 34 mg g^{-1} was achieved when 75 μm adsorbent particle was used. Furthermore, with the increase of Cu^{2+} concentration from 20 to 100 mg L^{-1}, the adsorption capacity also increased from 6 to 23 mg g^{-1}. The behaviour and nature of copper ions adsorption was analysed with Langmuir, Freundlich, Harkins-Jura and Dubinin-Radushkevich isotherm models. The experimental adsorption data were analysed using the appropriated isotherm models that fitted the data in the following order: Langmuir > Harkins-Jura > Freundlich > Dubinin-Radushkevich. The results indicate the monolayer copper adsorption. The experimental kinetic data were best described with the pseudo-second-order kinetic model, suggesting that surface modifications could improve the adsorption characteristics of date-palm trunk fibres as biosorbent (Amin et al. 2016).

Based on the results of their investigation, Yadav et al. (2015) concluded that date-palm trunk fibres could remove up to 99.95% of Cr (VI) from a 100 mg L^{-1} solution using only 1.2 g L^{-1} adsorbent. In a case of Pb(II) removal, the adsorption was quick and equilibrium established within 120 min (Yadav et al. 2013).

DPFs as adsorbents for lead removal from water were tested by Hikmat et al. (2014). This research also investigated the removal of lead ions using leaf base (petiol) waste. The results revealed that the adsorption equilibrium time was 30 and 40 min for Pb(II) by leaf and DPFs, respectively. In addition, an increase of lead uptake was observed in a pH range of 6.5–7 with adsorbent dose of 0.5 g. The thermodynamic parameters showed exothermic and spontaneous adsorption process. The removal percentage was 98.4% (q_{max} = 21.83 mg g^{-1}) and 96.5%

(q_{max} = 22.98 mg g^{-1}) by leaf and fibre, respectively. Thus, it was concluded that the tested waste materials can be successfully used for lead ions removal.

Al-Haidary et al. (2011) tested DPFs and petiole for Pb(II) removal from wastewater. The results of batch adsorption experiments showed that the adsorption capacity increased as the contact time increased. The adsorption capacity was higher at pH 4.5 than in alkali media, which can be attributed to the lower competition between protons and Pb(II) ions at higher pH. In addition, the adsorption of Pb (II) onto used biosorbents proved to be dependent on adsorbent concentration and particle size, as well as on ionic strength (NaCl solution). Three isotherm models (Langmuir, Freundlich and Dubinin-Radushkevich) were found to be applicable. The kinetics followed the pseudo-second-order model.

The removal of chromium using acid treated DPFs (0.1 M HCl, 8 h) was investigated by Hossini et al. (2016). A several parameters were investigated: the influence of pH, initial chromium concentration and biosorbent concentration. It has been shown that maximum chromium removal of 95% was achieved at pH 3.3, initial chromium concentration of 180 mg L^{-1} and biosorbent concentration of 0.8% (w/v) (particle size between 200 and 300 mesh size). The sorption kinetics showed good fit with pseudo-second-order model with tendency of fast adsorption. According to Langmuir isotherm model, the monolayer adsorption was suggested.

The adsorption of Cr(VI) onto DPFs (leaf) was investigated by (Haleem and Abdulgafoor 2010). The results revealed that the adsorption was pH dependent, with an optimum at pH 7. Also, at lower initial Cr(VI) concentrations, the removal percentage was higher. The adsorption data could be interpreted in terms of Langmuir isotherm model (adsorption capacity of 12.25 mg g^{-1}).

Rahmana et al. (2017) compared DPFs to commercially available adsorbents for chromium removal from aqueous solutions, and found DPFs to be better. The highest removal percentage was obtained at pH 2 (19.55 mg g^{-1}). The adsorption capacity increased with the increase of initial chromium concentration from 100 to 500 mg L^{-1} (from 9.84 to 57.26 mg g^{-1}), while the percent removal decreased from 98.44% to 57.26%. Furthermore, the increase of adsorbent concentration had also positively affected the chromium ions removal. The Langmuir isotherm model fitted the experimental adsorption data better than other models, thus confirming the monolayer adsorption. Table 9.2 shows the adsorption capacities of date palm biomass for metal ions removal.

The removal of Ni and Cd from wastewater with palm fibres powder has been studies by Boudaoud et al. (2017). The adsorption was pH dependent and the highest percent removal was achieved at initial metal ions concentration of 100 mg L^{-1}, 1 g of adsorbent, 20 °C and pH 5 (Ni) and 6.5 (Cd). The maximum adsorption capacities were 6.81 mg g^{-1} for cadmium at 60 min and 4.42 mg g^{-1} for nickel at 45 min. When these results are compared to adsorption capacities obtained using date palm seeds activated carbon for cadmium removal (0.0019 mg g^{-1}) (Nwakonobi et al. 2018), they proved to be much higher. The experimentally obtained data showed slightly better fit with Freundlich isotherm model. The $1/n$ values indicate that the adsorption process for both tested metal ions on the prepared adsorbent is a physical process. The pseudo-second-order model suggests that the adsorption is controlled

Table 9.2 Date palm biomass for metal ions removal from aqueous solutions

Adsorbent	Metal ion	q_{max}/mg g^{-1}	References
Date-palm fibre	As(V)	32.05 (Langmuir)	Amin et al. (2017)
Date-palm fibre	Pb(II)	18.416 (Langmuir)	Al-Haidary et al. (2011)
Date-palm fibre	Pb(II)	22.99 (Langmuir)	Hikmat et al. (2014)
Date-palm fibre	Cr(VI)	62.5 (Langmuir)	Rahmana et al. (2017)
Acid treateddate-palm fibre	Cr(VI)	34.12 (Langmuir)	Hossini et al. (2016)
Date-palm trunk fibre	Cu(II)	25.25 (Langmuir)	Amin et al. (2016)
Date-palm trunk fibre	Cr(VI)	129.87 (Langmuir)	Yadav et al. (2015)
Date-palm trunk fibre	Pb(II)	53.48 (Langmuir)	Yadav et al. (2013)
Date-palm fibre (leef)	Cr(VI)	12.25 (Langmuir)	Haleem and Abdulgafoor (2010)
Palm fibres powder	Ni(II)	4.42 (Langmuir)	Boudaoud et al. (2017)
Palm fibres powder	Cd(II)	6.81 (Langmuir)	Boudaoud et al. (2017)

by chemical process. The experimentally obtained adsorption capacities at equilibrium (6.486 mg g^{-1}) were in agreement with those calculated using the pseudo-second-order kinetic model (6.430 mg g^{-1}).

In the research performed by Ahmed (2010), wastes of date palm tree were used to remove heavy metal cations – Cu(II), Cd(II) and Zn(II) from wastewater by batch adsorption. The removal efficiencies were about 90% for Cu(II), 58% for Cd(II) and 38% for Zn(II) within 60 min of contact time and with adsorbent concentration of 30 g L^{-1}. The removal efficiency was lower in binary cation solutions.

9.2.3 Date-Palm Fibres as Filter Media

The application of DPFs as an efficient filter media for phosphorus, organic matter, turbidity and helminth eggs removal was investigated by Riahi et al. (2009a). Column experiments were performed under different experimental conditions such as flow rate, filter depth and diameter of the fibres. The results showed that the fibre diameter had a significant impact on the removal percentage. The filtration trough DPFs led to approximately 55% turbidity decrease, as well as 81% organic matter (as chemical oxygen demand – COD), 58% phosphorus and 98% of helminth eggs removal. The results showed that this technique has a potential to be used as economically feasible and environmentally friendly method for tertiary wastewater treatment.

DPFs as a laboratory filtration setup was employed for lead Pb(II) removal by Alghamdi (2016). It was observed that the breakthrough point was achieved after 3 min, which can be explained by the fact that the saturation rate of DPFs with lead ions was very quick. The recorded FTIR spectra showed that the adsorption of lead ions on DPFs was achieved by chemisorption in which mostly –OH groups were involved. The optimal flow rate was found to be 10 mL min^{-1} and initial Pb (II) concentration of 135 mg L^{-1}.

Ghazy et al. (2016) evaluated the performance of biofilters with various agricultural waste materials (rice straw, date-palm fibre, orange tree wood chips) for municipal wastewater treatment. Column experiments were performed under different operational conditions: hydraulic rates of 4.8, 6, 8 and 12 $m^3/m^2/d$ and medium size of fibres of 2, 4, 6 and 8 cm. The raw wastewater was pumped into the upper end of reactor and the effluent flowed out at the bottom of the reactor. The percent removal of the biological oxygen demand (BOD_5) was 81.5, 88.3 and 66.7% for rice straw, DPFs and orange tree wood chips, respectively. The results for chemical oxygen demand (COD) removal were 79.7% for rice straw, 88.3% for DPFsand 64.6% for orange tree wood chips. Total suspended solids (TSS), total nitrogen and total phosphorous were also determined. The investigation of the effect of the wood chip sizes of the used wastes as biofilters on the tested wastewater parameters showed that the smallest size was the most effective for all biofilter media, because it showed the best removal efficiency for wastewater contaminants (BOD, COD and TSS), while the largest size showed the lowest efficiencies for the tested parameters. The effect of column depth was also investigated. Four different depths were applied (20, 40, 60 and 80 cm), and it was shown that the highest removal percentage of BOD, COD and TSS was achieved at the depth of 80 cm, probably due to the increase in the total surface area and contact time between constituents and filter bed media. When comparing the hydraulic rates, the results showed that the lowest flow rate (4.8 $m^3/m^2/d$) showed the highest treatment efficiencies. In conclusion, the results showed that DPFs found to be the most efficient biofilter of all the tested materials, because it showed the best removal efficiencies for all tested parameters.

9.2.4 Removal of Other Pollutants from Wastewater Using Date Palm Fibres

Phosphates are often present in surface waters and wastewaters as organic phosphate, inorganic phosphate, oligophosphates and polyphosphates. They are extensively used in agriculture, as they are important nutrients for plants. However, excess concentrations in surface waters can have harmful effects to the environment, primarily eutrophication. Eutrophication of water bodies occurs if nutrients (nitrogen and phosphorus) are present in large amounts.

Riahi et al. (2009b) conducted a batch test to remove phosphates from aqueous solutions using DPFs. It was shown that the phosphate uptake increased with the increase of initial phosphate concentration and decreased with the increase of pH. The increase in adsorbent concentration also had a positive effect on phosphate removal. At pH 6.8, adsorbent concentration of 6 g L^{-1}, initial phosphate concentration of 50 mg L^{-1} and 18 °C, the adsorption capacity of phosphates was

4.35 mg g^{-1}, which makes this adsorbent potentially attractive for phosphate removal from water.

As it is already mentioned, phosphates in water are undesirable because they deteriorate the water quality. Granular date stones and palm surface fibres was used as biosorbents for phosphate removal from water by Ismail (2012). The percent removal of phosphates at initial phosphate concentration of 50 mg L^{-1} was 87% and 85% for granular date stones and palm surface fibres, respectively. The removal efficiency increased from 25% to 85% for palm surface fibres with the increase of biosorbent concentration from 1 to 10 g L^{-1}.

9.3 Conclusions

In this review, the use of date-palm fibre based biosorbents for the removal of different pollutants from aqueous solutions and/or wastewater have been reviewed. To date the literature on the use of this waste material as biosorbent is scarce. However, the existing data suggests that the date-palm fibres could be successfully employed as low-cost adsorbent for the removal of various pollutants from wastewater, such as synthetic dyes, heavy metals, organic matter and nutrients (phosphorus). Thus, date-palm fibers could present a good alternative to costly conventional adsorbents for water treatment, such as activated carbon. However, further research is needed to determine date-palm fibers feasibility as adsorbent on industrial scale. In addition, cost analysis needs to be performed, as well as the investigation of possible disposal methods of pollutant-loaded biosorbent left after adsorption removal process.

References

Abdolali A, Guo WS, Ngo HH, Chen SS, Nguyen NC, Tung KL (2014) Typical lignocellulosic wastes and by-products for biosorption process in water and wastewater treatment: a critical review. Bioresour Technol 160:57–66. https://doi.org/10.1016/j.biortech.2013.12.037

Ahmad T, Rafatullah M, Ghazali A, Sulaiman O, Hashim R (2011) Oil palm biomass-based adsorbents for the removal of water pollutantsa review. J Environ Sci Health Part C Environ Carcinog Ecotoxicol Rev 29:177–222. https://doi.org/10.1080/10590501.2011.601847

Ahmad T, Danish M, Rafatullah M, Ghazali A, Sulaiman O, Hashim R, Ibrahim MNM (2012) The use of date palm as a potential adsorbent for wastewater treatment: a review. Environ Sci Pollut Res 19:1464–1484. https://doi.org/10.1007/s11356-011-0709-8

Ahmed LAA (2010) Removal of heavy metals from waste water by date palm tree wastes. Eng Tech J 28:119–125

Al Bsoul A, Zeatoun L, Abdelhay A, Chiha M (2014) Adsorption of copper ions from water by different types of natural seed materials. Desalin Water Treat 52:5876–5882. https://doi.org/10.1080/19443994.2013.808593

Alghamdi AA (2016) An investigation on the use of date palm fibers and coir pith as adsorbents for Pb(II) ions from its aqueous solution. Desalin Water Treat 57:12216–12226. https://doi.org/10.1080/19443994.2015.1048743

Al-Haidary AMA, Zanganah FHH, Al-Azawi SRF, Khalili FI, Al-Dujaili AH (2011) A study on using date palm fibers and leaf base of palm as adsorbents for Pb(II) ions from its aqueous solution. Water Air Soil Pollut 214:73–82. https://doi.org/10.1007/s11270-010-0405-1

Al-Kaabi K, Al-Khanbashi A, Hammami A (2005) Date palm fibers as polymeric matrix reinforcement: DPF/polyester composite properties. Polym Compos 26:604–613. https://doi.org/10.1002/pc.20130

Alqadami AA, Naushad M, Abdalla MA et al (2016) Synthesis and characterization of Fe 3 O 4 @TSC nanocomposite: highly efficient removal of toxic metal ions from aqueous medium. RSC Adv 6:22679–22689. https://doi.org/10.1039/C5RA27525C

Alshabanat M, Alsenani G, Almufarij R (2013) Removal of crystal violet dye from aqueous solutions onto date palm fiber by adsorption technique. J Chem 2013:1–6. https://doi.org/10.1155/2013/210239

Alshabanat M, Al-Mufarij RS, Al-Senani GM (2016) Study on adsorption of malachite green by date palm fiber. Orient J Chem 32:3139–3144. https://doi.org/10.13005/ojc/320636

Alshehri SM, Naushad M, Ahamad T et al (2014) Synthesis, characterization of curcumin based ecofriendly antimicrobial bio-adsorbent for the removal of phenol from aqueous medium. Chem Eng J 254:181–189. https://doi.org/10.1016/j.cej.2014.05.100

Amin MT, Alazba AA, Shafiq M (2016) Adsorption of copper (Cu^{2+}) from aqueous solution using date palm trunk fibre: isotherms and kinetics. Desalin Water Treat 57:22454–22466. https://doi.org/10.1080/19443994.2015.1131635

Amin M, Alazba A, Amin M (2017) Absorption behaviours of copper, lead, and arsenic in aqueous solution using date palm fibres and orange peel: kinetics and thermodynamics. Pol J Environ Stud 26:543–557. https://doi.org/10.15244/pjoes/66963

Annadurai G, Juang RS, Lee DJ (2002) Use of cellulose-based wastes for adsorption of dyes from aqueous solutions. J Hazard Mater 92:263–274. https://doi.org/10.1016/S0304-3894(02)00017-1

Awual MR, Hasan MM, Eldesoky GE et al (2016) Facile mercury detection and removal from aqueous media involving ligand impregnated conjugate nanomaterials. Chem Eng J 290:243–251. https://doi.org/10.1016/j.cej.2016.01.038

Aydin H, Bulut Y, Yerlikaya Ç (2008) Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents. J Environ Manag 87:37–45. https://doi.org/10.1016/j.jenvman.2007.01.005

Belala Z, Jeguirim M, Belhachemi M, Addoun F, Trouvé G (2011) Biosorption of basic dye from aqueous solutions by date stones and palm-trees waste: kinetic, equilibrium and thermodynamic studies. Desalination 271:80–87. https://doi.org/10.1016/j.desal.2010.12.009

Boudaoud A, Djedid M, Benalia M, Ad C, Bouzar N, Elmsellem H (2017) Removal of nickel (II) and cadmium (II) ions from wastewater by palm fibers. Sci Study Res 18:391–406.

Bryan LSS, Daniella RM (2012) Study of the potential use of royal palm fibers in Hdpe Matrix. In: Proceedings of ECCM15 – 15th European conference on composite materials, pp 1–6

Cagnon B, Py X, Guillot A, Stoeckli F, Chambat G (2009) Contributions of hemicellulose, cellulose and lignin to the mass and the porous properties of chars and steam activated carbons from various lignocellulosic precursors. Bioresour Technol 100:292–298. https://doi.org/10.1016/j.biortech.2008.06.009

El-Geundi MS (1991) Colour removal from textile effluents by adsorption techniques. Water Res 25:271–273. https://doi.org/10.1016/0043-1354(91)90006-C

Ghazy M, Basiouny M, Badawy M (2016) Performance of agricultural wastes as a biofilter media for low-cost wastewater treatment technology. Adv Res 7:1–13. https://doi.org/10.9734/AIR/2016/27926

Gobi K, Vadivelu VM (2013) By-products of palm oil mill effluent treatment plant – a step towards sustainability. Renew Sust Energ Rev 28:788–803. https://doi.org/10.1016/j.rser.2013.08.049

Gouamid M, Ouahrani MR, Bensaci MB (2013) Adsorption equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using date palm Leaves. Energy Procedia 36:898–907. https://doi.org/10.1016/j.egypro.2013.07.103

Haleem AM, Abdulgafoor EA (2010) The biosorption of Cr (VI) from aqueous solution using date palm fibers (Leef). Al-Khwarizmi Eng J 6:31–36

Hikmat NA, Qassim BB, Khethi MT (2014) Thermodynamic and kinetic studies of lead adsorption from aquesous solution onto petiole and fiber of palm tree. Am J Chem 4:116–124. https://doi.org/10.5923/j.chemistry.20140404.02

Hossini H, Esmaeili Taheri H, Arab Markadeh A, Rezaee A, Rastegar SO (2016) Optimization of effective parameters in the biosorption of Cr(VI) using acid treated date palm fiber from aqueous solution. Desalin Water Treat 57:4994–5003. https://doi.org/10.1080/19443994.2014.995716

Ismail ZZ (2012) Kinetic study for phosphate removal from water by recycled date-palm wastes as agricultural by-products. Int J Environ Stud 69(1):135–149

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. Bioresour Technol 76:63–65. https://doi.org/10.1016/S0960-8524(00)00072-9

Kezerle A, Velić N, Hasenay D, Kovačević D (2018) Lignocellulosic materials as dye adsorbents: adsorption of methylene blue and Congo red on brewers' spent grain. Croat Chem Acta 91:1–12. https://doi.org/10.5562/cca3289

Kharat DS (2015) Preparing agricultural residue based adsorbents for removal of dyes from effluents – a review. Braz J Chem Eng 32:1–12. https://doi.org/10.1590/0104-6632.20150321s00003020

Khidir EA, Abdullah N, Mohamed N, Jailani M, Nor M, Faizal M, Tahir M, Zulkifli R, Nuawi MZ (2014) Effect of density on the sound absorption of date palm fibers. Appl Mech Mater 663:437–441. https://doi.org/10.4028/www.scientific.net/AMM.663.437

Kumar A, Guo C, Sharma G et al (2016) Magnetically recoverable ZrO2/Fe3O4/chitosan nanomaterials for enhanced sunlight driven photoreduction of carcinogenic Cr(VI) and dechlorination & mineralization of 4-chlorophenol from simulated waste water. RSC Adv 6:13251–13263. https://doi.org/10.1039/C5RA23372K

Lee CK, Low KS, Gan PY (1999) Removal of some organic dyes by acid-treated spent bleaching earth. Environ Technol (UK) 20:99–104. https://doi.org/10.1080/09593332008616798

Li Q, Chai L, Qin W (2012) Cadmium(II) adsorption on esterified spent grain: equilibrium modeling and possible mechanisms. Chem Eng J 197:173–180. https://doi.org/10.1016/j.cej.2012.04.102

Mahmoud MA (2013) Kinetics and thermodynamics of date palm fibers (DPF) as agricultural waste materials. J Chromatogr Sep Tech 4(7). https://doi.org/10.4172/2157-7064.1000194

Namasivayam C, Kanchana N, Yamuna RT (1993) Waste banana pith as adsorbent for the removal of rhodamine-B from aqueous solutions. Waste Manag 13:89–95. https://doi.org/10.1016/0956-053X(93)90038-X

Nassar MM, Hamoda MF, Radwan GH (1995) Adsorption equilibria of basic dyestuff onto palm-fruit bunch particles. Water Sci Technol 32:27–32. https://doi.org/10.1016/0273-1223(96)00114-X

Naushad M, Alothman ZA (2015) Separation of toxic Pb2+ metal from aqueous solution using strongly acidic cation-exchange resin: analytical applications for the removal of metal ions from pharmaceutical formulation. Desalin Water Treat 53:2158–2166. https://doi.org/10.1080/19443994.2013.862744

Naushad M, Abdullah Alothman Z, Rabiul Awual M et al (2016) Adsorption of rose Bengal dye from aqueous solution by amberlite Ira-938 resin: kinetics, isotherms, and thermodynamic studies. Desalin Water Treat 57:13527–13533. https://doi.org/10.1080/19443994.2015.1060169

Nguyen TAH, Ngo HH, Guo WS, Zhang J, Liang S, Yue QY, Li Q, Nguyen TV (2013) Applicability of agricultural waste and by-products for adsorptive removal of heavy metals from wastewater. Bioresour Technol 148:574–585. https://doi.org/10.1016/j.biortech.2013.08.124

Nwakonobi TU, Onoja SB, Ogbaje H (2018) Removal of certain heavy metals from brewery wastewater using date palm seeds activated carbon. Appl Eng Agric 34:233–238. https://doi.org/10.13031/aea.11875233

Ofomaja AE (2007) Kinetics and mechanism of methylene blue sorption onto palm kernel fibre. Process Biochem 42:16–24. https://doi.org/10.1016/j.procbio.2006.07.005

Rahmana M, Alia M, Sahaa I, Al Raihana M, Moniruzzamanb M, Alam MJ, Deb A, Khan MMR (2017) Date palm fiber as a potential low-cost adsorbent to uptake chromium (VI) from industrial wastewater. Desalin Water Treat 88:169–178. https://doi.org/10.5004/dwt.2017.21402

Riahi K, Ben Mammou A, Ben Thayer B (2009a) Date-palm fibers media filters as a potential technology for tertiary domestic wastewater treatment. J Hazard Mater 161(2–3):608–613. https://doi.org/10.1016/j.jhazmat.2008.04.013

Riahi K, Ben Thayer B, Ben Mammou A, Ben Ammar A, Jaafoura MH (2009b) Biosorption characteristics of phosphates from aqueous solution onto Phoenix dactylifera L. date palm fibers. J Hazard Mater 170:511–519. https://doi.org/10.1016/j.jhazmat.2009.05.004

Shafiq M, Alazba A, Amin M (2018) Removal of heavy metals from wastewater using date palm as a biosorbent: a comparative review. Sains Malaysiana 47:35–49. https://doi.org/10.17576/jsm-2018-4701-05

Spagnoli AA, Giannakoudakis DA, Bashkova S (2017) Adsorption of methylene blue on cashew nut shell based carbons activated with zinc chloride: the role of surface and structural parameters. J Mol Liq 229:465–471. https://doi.org/10.1016/j.molliq.2016.12.106

Sun G, Xu X (1997) Sunflower stalks as adsorbents for color removal from textile wastewater. Ind Eng Chem Res 36:808–812. https://doi.org/10.1021/ie9603833

Suteu D, Zaharia C (2011) Sawdust as biosorbent for removal of dyes from wastewaters. Kinetic and thermodynamic study. Chem Bull "Politechnica" Univ 56:85–88

Uzunoğlu D, Gürel N, Özkaya N, Özer A (2014) The single batch biosorption of copper(II) ions on Sargassum acinarum. Desalin Water Treat 52:1514–1523. https://doi.org/10.1080/19443994.2013.789403

Wong S, Ngadi N, Inuwa IM, Hassan O (2018) Recent advances in applications of activated carbon from biowaste for wastewater treatment: a short review. J Clean Prod 175:361–375. https://doi.org/10.1016/j.jclepro.2017.12.059

Yadav SK, Singh DK, Sinha S (2013) Adsorption study of lead(II) onto xanthated date palm trunk: kinetics, isotherm and mechanism. Desalin Water Treat 51:6798–6807. https://doi.org/10.1080/19443994.2013.792142

Yadav SK, Sinha S, Singh DK (2015) Chromium(VI) removal from aqueous solution and industrial wastewater by modified date palm trunk. Environ Prog Sustain Energy 34:452–460. https://doi.org/10.1002/ep.12014

Chapter 10
Recent Updates on Heavy Metal Remediation Using Date Stones (*Phoenix dactylifera L.*) – Date Fruit Processing Industry Waste

N. Sivarajasekar, J. Prakashmaran, Mu. Naushad, Bader Z. ALFarhan, S. Poornima, S. Sivapriya, V. Gayathri, T. Pradeepika, V. Raghu, S. Sivamani, Swapnil Dharaskar, and Nirajan Dhakal

Abstract *Phoenix dactylifera L.* date palm fruits are consumed largely worldwide. The date stone wastes from the date processing industries are huge and needs attention due to their high lignocellulose content. It is one of the good precursors for activated carbon and can be utilized for heavy metal remediation from wastewaters. Therefore, this chapter reports the metal ions adsorption by activated carbons prepared from date stone considering recent works of literature. This review elaborates the activation methods employed for activated carbon preparation, characterization strategies, parameters affecting the adsorption experiments and adsorption efficiency of the prepared carbons.

N. Sivarajasekar (✉) · S. Poornima · S. Sivapriya · V. Gayathri · T. Pradeepika · V. Raghu
Laboratory for Bioremediation Research, Unit Operations Lab, Department of Biotechnology, Kumaraguru College of Technology, Coimbatore, Tamil Nadu, India
e-mail: sivarajasekar@gmail.com

J. Prakashmaran
Department of Food Science and Nutrition, Periyar University, Salem, Tamil Nadu, India

M. Naushad
Department of Chemistry, College of Science, King Saud University, Riyadh, Saudi Arabia

B. Z. ALFarhan
King Abdulaziz City for Science and Technology, Riyadh, Saudi Arabia

S. Sivamani
Chemical Engineering Section, Salalah College of Technology, Salalah, Sultanate of Oman

S. Dharaskar
Department of Chemical Engineering, School of Technology, Pandit Deendayal Petroleum University, Gandhinagar, Gujarat, India

N. Dhakal
Environmental Engineering and Water Technology Department, IHE Delft Institute for Water Education, Delft, The Netherlands

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_10

Keywords Heavy metals · Toxic · Remediation · Lignocellulosic · Phoenix dactylifera stones

10.1 Introduction

Lignocellulosic content, renewability, and cheap-cost of the agricultural/food industry by-products qualify them as hopeful precursors for cost-effective adsorbent preparation (Sivarajasekar 2014; Chayid and Ahmed 2015; Gupta et al. 2015; Kenawy et al. 2017; Sivarajasekar et al. 2018a; Sivarajasekar and Baskar 2018). Specifically, Fruit stones and seeds from fruit processing industries are one of the agricultural by-products that are capable to produce hardest and porous activated carbons (Heschel and Klose 1995; Mechati et al. 2015). Peach stones (Uysal et al. 2014; Torrellas et al. 2015), apricot stones (Depci et al. 2014; Djilani et al. 2015) olive stones (Obregón-Valencia and del Rosario Sun-Kou 2014; Hazzaa and Hussein 2015), cherry stones (Nowicki et al. 2015; Olivares-Marín et al. 2012), grape stones (Okman et al. 2014; Jimenez-Cordero et al. 2014), and date pits/seeds/stones (Sekirifa et al. 2013; Yamina et al. 2013), have been evaluated for their efficiency for the production of adsorbents by many researchers.

Date palm's ((Phoenix dactylifera L.) fruit stones from date processing industry especially in Mediterranean countries are the candidate of interest (Amor and Ismail 2015). Nearly 21 million date palm trees are cultivated in Iraq, which is the world largest date producers, and its annual production is around 400,000 tons of the date fruits. The increasing worldly demand of dates (around 10 million per annum) is met by the top ten date cultivating countries such as United Arab Emirates, Saudi Arabia, Egypt, Algeria, Iran, Pakistan, Sudan, Oman, Tunisia, and Libya (Bhansali 2010). Notably 14% of the total weight of these date fruits are rejected as unwanted solid wastes in the form of stones/seeds, which is approximately 1.4 million tons (Briones et al. 2011; El-Naas et al. 2010). The date stone contains hemicellulose 23%, lignin 15%, and cellulose 57%, crude fibres 10–20%, oil 7–10%, protein 5–7%, moisture 5–10%, and ash 1–2% (Ahmed and Theydan 2014). Hence, the chemical ingredients of the date stone qualify it for converting it into effective adsorbents.

The presence of heavy metals in the water bodies are a potential hazard for human and aquatic biota which should be addressed with concern (Naushad 2014; Naushad et al. 2015, 2016; Alqadami et al. 2017a, b). Some of the pollutants including heavy metals could cause severe poisoning, malignancy, and brain impairment when consumed beyond the acceptance level (Naushad et al. 2017; Sivarajasekar 2007). Various methods such as adsorption, phytoremediation, exchange, coagulation, biodegradation, solvent extraction, oxidation, and electrolysis techniques have been reported for heavy metal remediation in water (AlOthman and Inamuddin 2011; AlOthman et al. 2013; Ahmed 2016; Muthusaravanan et al. 2018). Adsorption is an proven efficient strategy among other methods due to its simple design, versatile operation conditions, cheap, eco-friendly and suitability for a variety of pollutants (Sivarajasekar et al. 2017a, b, c, d, e; Sivarajasekar et al. 2018; Karthik et al. 2018; Sivarajasekar and Balasubraman 2018; Paramasivan et al. 2019). Therefore, activated carbon prepared from date fruit stones have been efficiently exploited and reported for adsorption of heavy metals. Ahmed (2016) discussed a detailed review in research of activated carbon preparation from date industry wastes and its usage for wastewater purification.

Therefore, this chapter summarises the appropriate available data with some of the up-to-date essential results in the past decade. The objective of the paper is to brief the preparation, adsorption experimentation and the comparison of the prepared adsorbents for different heavy metal removal.

10.2 Methods for the Activation of Date Stones

Activated carbon is mostly obtained from carbonaceous source materials, and further activated either by physical activation or by chemical activation, sometime combination of both activation methods.

10.2.1 Physical Activation

The fractional gasification of the precursor is carried out through steam and carbon dioxide at the high temperature range of 750 to 1100 °C. Date stone was carbonized at 900 °C for 3 h and activated using carbon dioxide. The prepared carbon was utilised for trivalent aluminum adsorption from aqueous solutions (Al-Muhtaseb et al. 2008; Awwad et al. 2013). Banat et al. (2002) dried the date stones at 105 °C, crushed and thermally activated them at 500 °C. He has also prepared activated carbon by carbon dioxide activation at 700 °C from date stones and compared their adsorption efficiency for Zn(II) and Cu(II) uptake. Banat et al. (2003) prepared activated carbon from date stones by carbon dioxide activation at 500 °C and 900 °C to evaluate its suitability for Cd(II) adsorption. Saad et al. (2008) used date stones for the adsorption of U(VI) ions. The Saudi Arabian date pits were roasted at 130 °C for 4 h, grinded to powder and then utilised as an adsorbent to eliminate Co (II) from wastewater.

10.2.2 Chemical Activation

Strong dehydrating agents like phosphoric acid or zinc chloride were used to dehydrate the lignocellulosic precursors initially and then pyrolysed at around 400 °C to 800 °C. High porosity with a large surface area is the resulting activated carbon. However, these activated carbons could not be used in food and

Table 10.1 Date stone activated carbon preparation by using different activation methods

Activation method	Activating agent	Adsorbate	References
Physical activation	Steam	Zn(II) and Cu(II)	Banat et al. (2002)
Physical activation	Carbon dioxide	Cd(II)	Banat et al. (2003)
Physical activation	Carbon dioxide	Al (III)	Al-Muhtaseb et al. (2008)
Physical activation	Steam	Cd(II) and Pb(II)	El-Hendawy (2009)
Physical activation	Microwave	Ni(II) and Cu(II)	Mahdi et al. (2018)
Chemical activation	Phosphoric acid	Pb(II)	Abdulkarim and Al-Rub (2004)
Chemical activation	Sulphuric acid	Cr(VI)	El Nemr et al. (2008)
Chemical activation	Carbon dioxide	U(VI)	Saad et al. (2008)
Chemical activation	Phosphoric acid	Cd(II)	Babakhouya et al. (2010)
Chemical activation	Calcium acetate	Co(II), Fe(III), Pb(II) and Zn(II)	Awwad et al. (2013)
Chemical activation	Phosphoric acid	Cd(II) and Pb(II)	El-Hendawy (2009)
Chemical activation	Nitric acid	Cd(II) and Pb(II)	El-Hendawy (2009)
Chemical activation	Phosphoric acid	Cd(II) and Cu(II)	Hilal et al. (2012)
Chemical activation	Sodium hydroxide	Cd(II) and Cu(II)	Ameh (2013)
Chemical activation	Phosphoric acid	Cd(II)	Chaouch et al. (2013)

pharmaceutical industries. El Nemr et al. (2008) reported that concentrated fuming sulphuric acid was used for the preparation of activated carbon from date seeds for 20 h. This carbon has been used for the removal of chromium (VI). Awwad et al. (2013) manufactured activated carbon from date stone by calcium acetate impregnation followed by thermal activation at 700 °C after passing through nitrogen gas. Abdulkarim and Al-Rub (2004) prepared activated carbon by phosphoric acid impregnation at 160 °C followed by activation at 215 °C. Babakhouya et al. (2010) utilised phosphoric acid activation at 160 °C to synthesize the date stone activated carbon and used it for Cd(II) removal (Table 10.1).

10.3 Characterization of Date Stone Activated Carbons

The adsorbents prepared for the metal ions elimination were characterized by several methods. The BET analysis was carried out by many researches to analyse the specific surface area of the prepared adsorbent (Banat et al. 2002; Abdulkarim and Al-Rub 2004). The Proximate and ultimate analyses were attempted to understand the residue, moisture, fixed carbon and volatile matter as well as the carbon oxygen and hydrogen respectively (Banat et al. 2003; El-Hendawy 2009). Fourier transform infrared spectra (FTIR) was utilised to identify the functional groups developed on the date stone carbon surface and to recognize the functional accountable for metal ions' binding (Mahdi et al. 2018; Chaouch et al. 2013; Al-Ghouti et al. 2010). Scanning electron microscope (SEM) was exploited to apprehend the morphology of date stone carbons surface like pores growth and pore structure (Awwad et al. 2013; Mahdi et al. 2018). Thermo gravimetric analysis and derivative of thermo gravimetric (DTG) studies were showed to apprehend the thermal strength of the date stone carbons (El Nemr et al. 2008; Hilal et al. 2012). The Fig. 10.1 shows the FTIR and SEM micrographs of the date stone carbons reported by the different researchers.

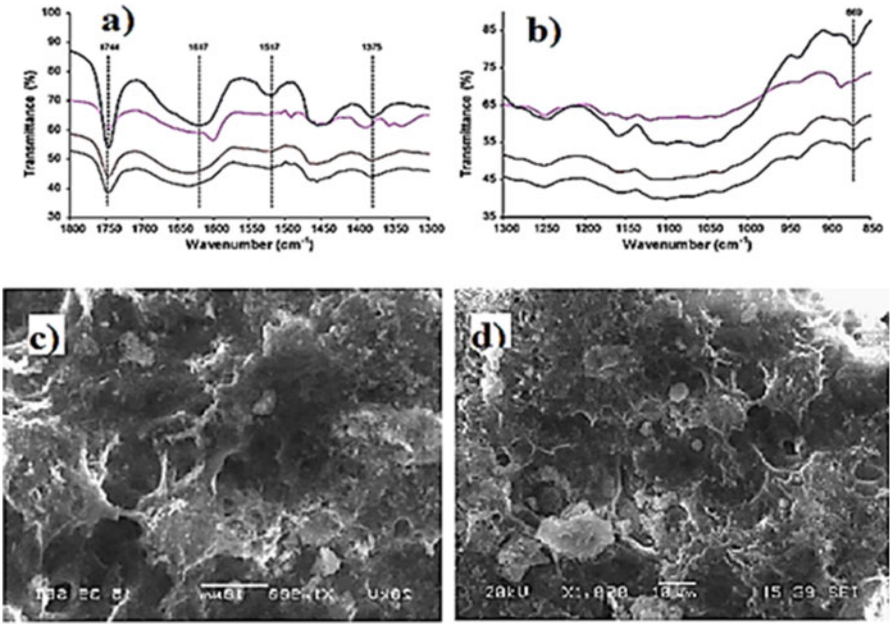


Fig. 10.1 FTIR spectra of raw date stones (**a**) loaded with Cu(II) and (**b**) loaded with Cd (II) (Al-Ghouti et al. 2010); (**c**) SEM image of pyrolysed Date stones at 700 °C (**d**) SEM image of pyrolysed Date stones at 700 °C with calcium acetate (Awwad et al. 2013)

10.4 Adsorption Studies of Heavy Metals onto Date Stone Activated Carbon

It's essential to explore the effects of adsorption process parameters for the metal ions adsorption. Further, the isotherm and kinetics were important to recognise the adsorption mechanism. Thermodynamic studies reveal the spontaneity of the adsorption process. Therefore, date stone has been explored as adsorbent for the sequestration of various metal ions from aqueous solutions.

Banat et al. (2002) reported a relative study of Zn(II) and Cu(II) removal from aqueous solution onto carbon dioxide activated date stones and compared it with raw date stones. Raw date stones performed better than carbon dioxide activated date stones for Zn(II) and Cu(II) removal. It was reported that the functional groups which were essential for Zn(II) and Cu(II) ions removal were destroyed due to heat treatment given during activation. The removal efficiency of Cu(II) ions by both the adsorbents were better than the Zn(II) ions due to the molecular structure of Zn (II) ion, pore structure and the functional groups responsible for adsorption. The removal efficiency of both metal ions followed the increasing trend in the pH range (3.5–5.0) because of ion exchange mechanism. The removal efficiency was increased with decreasing the temperature from 50 °C to 25 °C where the active site dissociation responsible for the metal ion adsorption. The Gibbs free energy change values indicated that Cu(II) ion ($-\Delta G$) was more favorable than the Zn (II) ions ($+\Delta G$) and relatively quicker than the Zn(II) ion. The equilibrium data expressed that the metal adsorption was multilayer on raw date stones.

Banat et al. (2003) reported the Cd(II) ion adsorption by date stone activated carbon. It was conveyed that raw date stones adsorption capacity was multiple times larger than the carbonized date stones. This study reported the properties of process conditions like solution pH, date stone loading and the initial Cd(II) concentration. Increasing trend noted for Cd(II) adsorption at higher pH and Cd(II) concentration. The Langmuir and Freundlich isotherms were well correlated with batch adsorption and the pseudo-second-order kinetics was appropriate for raw date stones.

Abdulkarim and Al-Rub (2004) described the preparation of date stone activated carbon and hydroxyquinoline modified date stone activated carbon for Pb (II) adsorption from aqueous solutions. Both the prepared carbon equally performed well, however, the chemical modification did not show any effect on the Pb (II) significantly. Change in initial pH increased the Pb(II) ion adsorption. The addition of salts like sodium chloride and citric acid decreased the adsorption of Pb(II) ions sequestration. The adsorption data conformed pseudo-second-order kinetics and correlated good to both Langmuir and Freundlich isotherms.

Saad et al. (2008) investigated the retention of U(VI) as Uranyl ions from aqueous medium using date stones as an efficient and cheap solid extractor for the removal of Uranyl (II) ion from wastewater samples. The adsorption of Uranyl ions was quick and fit to the pseudo-first-order kinetics. The equilibrium data was fit to Freundlich isotherm and revealed the dual mode mechanism of surface adsorption.

Thermodynamic parameters showed that the adsorption of Uranyl ions was endothermic and spontaneous in nature.

El Nemr et al. (2008) developed an date stone activated carbon through sulphuric acid activation for Cr(VI) ions sequestration from aqueous solution. A sturdy dependence of the removal percentage was illustrious and removal efficiency augmented with rising pH. The Cr(VI) removal was spontaneous and higher update of Cr(VI) was reported as 120.48 mg/g by date stone activated carbon. The elovich isotherm and pseudo-second-order kinetics delivered a decent association for the equilibrium data. Physisorption mechanism of adsorption was explained by Dubinin–Raduskovich isotherm.

Al-Muhtaseb et al. (2008) reported the aluminum removal onto carbon dioxide activated date stones. The initial concentration positively affected the aluminum adsorption and maximum adsorption was found at pH 4. Different isotherm models such as Freundlich, Langmuir, Sips, and Dubinin–Radushkevich isotherms were inspected and inferred that Sips isotherm was suitable for the aluminium adsorption data. Maximum monolayer uptake of 5.831 mg/g was stated at 22 °C and pH 4 rendering to the Langmuir isotherm.

El-Hendawy (2009) considered the adsorption of Cd(II) and Pb(II) ions from their aqueous solutions on date stone activated carbons. Date stone was chemically activated using phosphoric acid at different temperatures (300–700 °C) for 3 h. Physically activated date stone carbon was prepared by steam activation at 700 °C. Batch adsorption data for Cd(II) and Pb(II) ions were evaluated for various isotherms at pH 3 and 5.9. As the solution pH was changed from 3 to 5.9, the adsorption was significantly increased for both Cd(II) and Pb(II) ions. Further treatment with nitric acid, the prepared carbons showed increased uptake for both ions. The prepared activated carbon showed greater adsorption capacity for Cd(II) and Pb(II) ions than the raw date stones. The equilibrium data for Cd(II) and Pb(II) ions followed Langmuir isotherm. Langmuir model fitting of the Cd(II) and Pb(II) ions are presented in Fig. 10.2.

Al-Ghouti et al. (2010) studied the adsorption of Cd(II) and Cu(II) ions from aqueous solutions using raw date stone as an adsorbent. The pH played a notable role that the elimination of these metal ions amplified with increasing pH due to surface ion complex formation and ion exchange reaction. The adsorption data of Cd(II) and Cu(II) ions were investigated with Langmuir and Freundlich isotherms. The isotherm data indicated that the metal ions and adsorbent interacted with heterogeneous surface binding. The mechanism followed for Cu(II) ions was bringing two cellulose/lignin elements together on the adsorbent surface. For Cd(II) ions, the most foreseen tool was attachment of Cd(II) using hydroxyl ions in the cellulose/lignin units.

Belala et al. (2011) discussed the adsorption of Cu(II) ions onto palm trees waste and date stones from aqueous solutions. The adsorptive removal of Cu(II) was quick and showed high adsorption capacity within 20 min. The Cu(II) ions adsorption obeyed pseudo-second-order kinetics and the isotherm study exposed that physical interaction between Cu(II) ions and the adsorbent was involved. The thermodynamic

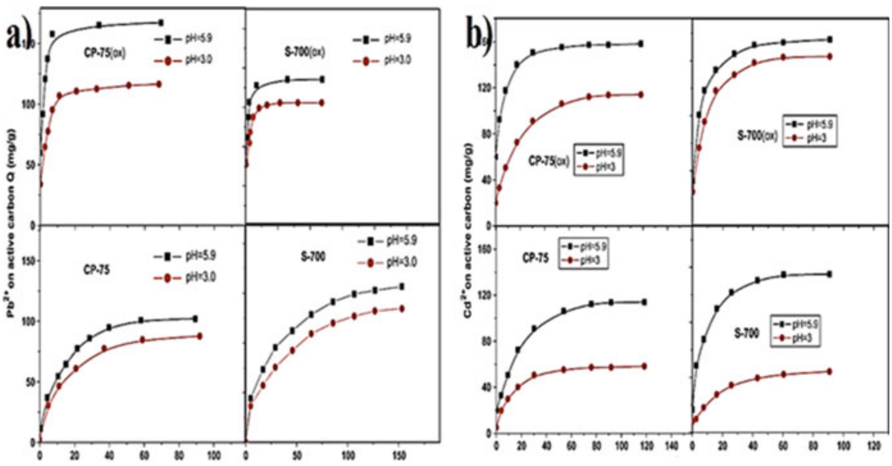


Fig. 10.2 Langmuir fit for (**a**) Pb(II) ions for variety of date stone carbons; (**b**) Cd (II) ions for variety of date stone carbons where CP – phosphoric acid activated date stone, CS – steam activated date stone, S-700 – steam activated carbon pyrolysis at 700 °C (El-Hendawy 2009)

investigation inferred that the adsorption was spontaneous and endothermic for Cu (II) ion adsorption.

El-Dars et al. (2011) reported the adsorption of Ni(II) from liquid solutions onto carbonized date stones and rice husks. The process parameters like initial pH, contact time, temperature, adsorbent dose and nickel initial concentration were examined in the batch mode. It was inferred that date stone followed pseudo-first-order model and correlation to Langmuir isotherm expressed physical nature of adsorption. The thermodynamic variables showed that nickel adsorption was endothermic and spontaneous.

Hilal et al. (2012) investigated the adsorption of Cu(II) and Cd(II) ions onto raw date stones and phosphoric acid activated carbon prepared from date stones. The optimum pH essential for maximum metal adsorption was noted to be 5.8. The phosphoric acid activation increased the maximum metal uptake of date stones. Langmuir model was followed by the phosphoric acid activated date stones whereas Freundlich model was obeyed by raw date stones respectively for both metal ions.

Bouhamed et al. (2012) reported the activated carbon preparation from Tunisian date stones through phosphoric acid activation. The Cu(II) ions adsorption was investigated onto chemically activated date stones and the parameters influence have been studied. Maximum adsorption capacity was found at pH 5 and pseudo-second-order kinetics was obeyed. The Langmuir and Dubinin–Radushkevich isotherm models were correlated well to the equilibrium data.

Ameh (2013) studied the adsorption behaviour of Cd(II) and Cu (II) onto NaOH modified Iraqi palm date activated carbon. It was seen that the adsorption of Cd (II) and Cu (II) could described well by Langmuir isotherm and the maximum monolayer capacities were evaluated as 118.06 and 88.42 mg/g, respectively. The adsorption process variables affected adsorption of both metals in the order: carbon dose > metal initial concentration > solution pH. The increase in dosage from 0.4 to

0.8 g/l improved uptake from 3.25 to 5 mg/g and 4.5 to 6.5 mg/g for Cd and Cu, then diminished to 3.75 and 6.0 mg/g, respectively at 1.4 g/l. The capability reduction beyond 0.8 g/l was due to the overlay of adsorption sites as an effect of overfilling of adsorbent particles.

Chaouch et al. (2013) activated the date stone using phosphoric acid at 450°C and its efficiency was performed to adsorb Cd(II) ions from aqueous solution. Various parameters like initial pH, contact time, initial Cd(II) concentration, and solution temperature were examined. The initial pH variation showed the increasing trend with increasing pH. The isotherm studies revealed the physisorption of Cd(II) ions onto prepared adsorbent and followed the Langmuir isotherm.

Awwad et al. (2013) reported the preparation of date stone activated carbon by physical and chemical activation. Physical activation was carried out using steam activation at 700 °C and the chemical activation was done by using 10% calcium acetate at 700 °C. The synthesized date stone carbons were examined for Co(II), Fe (III), Zn(II) and Pb(II) ions adsorption from synthetic aqueous as well as real water samples and found 100% removal for all selected metal ions.

Hamouche et al. (2015) investigated the Cr(IV) adsorption onto activated carbon produced from the mixture of olive stone and date stones. The influence of contact time, pH and initial Cr(IV) concentration were assessed for batch adsorption studies. The equilibrium time was found as 120 min and lower pH favored the Cr (IV) adsorption. Equilibrium data correlated the Langmuir isotherm and the pseudo second-order kinetics.

Mahdi et al. (2018) examined the Cu(II) and Ni(II) adsorption onto date-seed derivative biochar. The date stone biochar was obtained at various temperatures (350–550 °C). Biochar prepared at 550 °C showed good adsorption for both metal ions. The optimal pH was found at 6 and adsorption mechanism was ion-exchange type. The adsorption data was fitted well to the Sips isotherm model and the pseudo-second-order kinetic models. Packed-bed metal ions adsorption obeyed the Adam-Bohart model for break-through modelling.

10.5 Maximum Uptake Capacity of the Date Stone Adsorbents

The specific surface area is the key parameter for any solid adsorbent as it is directly related to the adsorptive capacity of the adsorbent (Bouhamed et al. 2012). The natural precursors such as date stone, that is abundantly available, possesses large surface area and high adsorption capacity. Therefore, a larger specific surface area effects in a superior adsorption capacity. The adsorption capacity of date stone based activated carbons was based on the pore size distribution developed during the activation methods (Hamouche et al. 2015). The structure of the pores such as macro- or micro-porosity connected with the mass transfer of the metal ions into the pore inner surfaces. Therefore, the idea of maximum adsorption capacity of the

Table 10.2 The maximum adsorption capacity of the date stone carbons for various metal ions

Adsorbate	Maximum adsorption capacity (mg/g)	References
Cr(IV) ions	53.42	Hamouche et al. (2015)
Pb(II) ions	1260	Awwad et al. (2013)
Cd(II) ions	1310	Awwad et al. (2013)
Zn(II) ions	1594	Awwad et al. (2013)
Cr(IV) ions	120.5	El Nemr et al. (2008)
Cu(II) ions	88.42	Ameh (2013)
Cd(II) ions	118.1	Ameh (2013)
Cu(II) ions	31.25	Bouhamed et al. (2012)
Cd(II) ions	127	El-Hendawy (2009)
Pb(II) ions	139	El-Hendawy (2009)
Al(III) ions	5.83	Al-Muhtaseb et al. (2008)
Cd(II) ions	4.29	Chaouch et al. (2013)
Pb(II) ions	220	Abdulkarim and Al-Rub (2004)
Cd(II) ions	6.5	Banat et al. (2003)
Cu(II) ions	0.421	Mahdi et al. (2018)
Ni(II) ions	0.333	Mahdi et al. (2018)

prepared activated carbons are very essential to understand the pore development, mass transfer and the explicit surface area accessible for the metal ions. Table 10.2 illustrates the maximum adsorption capacity of the various date stone based carbons for various metal ions.

10.6 Conclusion

In this book chapter, the recent literatures about the metal ions adsorption using date stones based activated carbons have been discussed elaborately. Raw date stones were used as adsorbents directly or synthesized into activated carbons. Many researchers mostly followed physical activation or chemical activation to develop the activated carbons from date stones. The metal ion adsorption by these carbons was mainly carried out by batch experiments and the influencing parameters were examined to understand the adsorption mechanism. The solution pH was found one of the key parameter in those batch experiments. The higher adsorption uptake of the different date stone activated carbon was also compared in order to understand the effect of activation procedures. It is found that only very few articles reporting the fixed-bed adsorption of metal ions onto date stone activated carbon at one side. On the other side, the new methods like microwave irradiation and biochar preparation are the unexplored areas with date stones. Hence, there are many research opportunities available in this research area.

References

Abdulkarim M, Al-Rub FA (2004) Adsorption of lead ions from aqueous solution onto activated carbon and chemically-modified activated carbon prepared from date pits. Adsorpt Sci Technol 22(2):119–134. https://doi.org/10.1260/026361704323150908

Ahmed MJ (2016) Preparation of activated carbons from date (Phoenix dactylifera L.) palm stones and application for wastewater treatments. Process Saf Environ Prot 102:168–182. https://doi.org/10.1016/j.psep.2016.03.010

Ahmed MJ, Theydan SK (2014) Fluoroquinolones antibiotics adsorption onto microporous activated carbon from lignocellulosic biomass by microwave pyrolysis. J Taiwan Inst Chem Eng 45 (1):219–226. https://doi.org/10.1016/j.jtice.2013.05.014

Al-Ghouti MA, Li J, Salamh Y, Al-Laqtah N, Walker G, Ahmad MN (2010) Adsorption mechanisms of removing heavy metals and dyes from aqueous solution using date pits solid adsorbent. J Hazard Mater 176:510–520. https://doi.org/10.1016/j.jhazmat.2009.11.059

Al-Muhtaseb SA, El-Naas MH, Abdallah S (2008) Removal of aluminum from aqueous solutions by adsorption on date-pit and BDH activated carbons. J Hazard Mater 158:300–307. https://doi.org/10.1016/j.jhazmat.2008.01.080

AlOthman ZA, Inamuddin NM (2011) Determination of ion-exchange kinetic parameters for the poly- o -methoxyaniline Zr (IV) molybdate composite. Chem Eng J 166:639–645. https://doi.org/10.1016/j.cej.2010.11.036

AlOthman ZA, Alam MM, Naushad M (2013) Heavy toxic metal ion exchange kinetics: validation of ion exchange process on composite cation exchanger nylon 6,6 Zr(IV) phosphate. J Ind Eng Chem 19:956–960

Alqadami AA, Naushad M, Abdalla MA, Ahamad T, AlOthman ZA, Alshehri SM, Ghfar AA (2017a) Efficient removal of toxic metal ions from wastewater using a recyclable nanocomposite: a study of adsorption parameters and interaction mechanism. J Clean Prod 156:426–436. https://doi.org/10.1016/j.jclepro.2017.04.085

Alqadami AA, Naushad M, Alothman ZA, Ghfar AA (2017b) Novel metal–organic framework (MOF) based composite material for the sequestration of U (VI) and Th (IV) metal ions from aqueous environment. ACS Appl Mater Interfaces 9(41):36026–36037. https://doi.org/10.1021/acsami.7b10768

Ameh PO (2013) Modelling of the adsorption of Cu(II) and Cd(II) from aqueous solution by Iraqi palm-date activated carbon (IPDAC). Int J Mod Chem 5:136–144

Amor HB, Ismail M (2015) Adsorption of chromium (VI) on activated carbon prepared by acid activation of date stones. Int J Sci Res 4:309–314

Awwad NS, El-Zahhar AA, Fouda AM, Ibrahium HA (2013) Removal of heavy metal ions from ground and surface water samples using carbons derived from date pits. J Environ Chem Eng 1 (3):416–423. https://doi.org/10.1016/j.jece.2013.06.006

Babakhouya N, Boughrara S, Abad F (2010) Kinetics and thermodynamics of Cd (II) ions sorption on mixed sorbents prepared from olive stone and date pit from aqueous solution. Am J Environ Sci 6(5):470–476

Banat F, Al-Asheh S, Al-Rousan D (2002) A comparative study of copper and zinc ion adsorption on to activated and non-activated date-pits. Adsorpt Sci Technol 20(4):319–335. https://doi.org/10.1260/02636170260295515

Banat F, Al-Asheh S, Al-Makhadmeh L (2003) Kinetics and equilibrium study of cadmium ion sorption onto date pits – an agricultural waste. Adsorpt Sci Technol 21(3):245–260. https://doi.org/10.1260/026361703322404395

Belala Z, Jeguirim M, Belhachemi M, Addoun F, Trouvé G (2011) Biosorption of copper from aqueous solutions by date stones and palm-trees waste. Environ Chem Lett 9(1):65–69. https://doi.org/10.1007/s10311-009-0247-5

Bhansali RR (2010) Date palm cultivation in the changing scenario of Indian arid zones: challenges and prospects. In: Desert plants. Springer, Berlin/Heidelberg, pp 423–459. https://doi.org/10.1007/978-3-642-02550-1_20

Bouhamed F, Elouear Z, Bouzid J (2012) Adsorptive removal of copper (II) from aqueous solutions on activated carbon prepared from Tunisian date stones: equilibrium, kinetics and thermodynamics. J Taiwan Inst Chem Eng 43(5):741–749. https://doi.org/10.1016/j.jtice.2012.02.011

Briones R, Serrano L, Younes RB, Mondragon I, Labidi J (2011) Polyol production by chemical modification of date seeds. Ind Crop Prod 34(1):1035–1040. https://doi.org/10.1016/j.indcrop.2011.03.012

Chaouch N, Ouahrani MR, Chaouch GN (2013) Adsorption of cadmium (II) from aqueous solutions by activated carbon produced from Algerian dates stones of Phoenix dactylifera by H3PO4 activation. Desalin Water Treat 51:2087–2092. https://doi.org/10.1080/19443994.2013.734558

Chayid MA, Ahmed MJ (2015) Amoxicillin adsorption on microwave prepared activated carbon from Arundo donax Linn: isotherms, kinetics, and thermodynamics studies. J Environ Chem Eng 3(3):1592–1601. https://doi.org/10.1016/j.jece.2015.05.021

Depci T, Onal Y, Prisbrey KA (2014) Apricot stone activated carbons adsorption of cyanide as revealed from computational chemistry analysis and experimental study. J Taiwan Inst Chem Eng 45(5):2511–2517. https://doi.org/10.1016/j.jtice.2014.05.015

Djilani C, Zaghdoudi R, Djazi F, Bouchekima B, Lallam A, Modarressi A, Rogalsk M (2015) Adsorption of dyes on activated carbon prepared from apricot stones and commercial activated carbon. J Taiwan Inst Chem Eng 53:112–121. https://doi.org/10.1016/j.jtice.2015.02.025

El Nemr A, Khaled A, Abdelwahab O, El-Sikaily A (2008) Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed. J Hazard Mater 152(1):263–275. https://doi.org/10.1016/j.jhazmat.2007.06.091

El-Dars FMSE, Sayed AO, Salah BA, Shalabi MEH (2011) Removal of Nickel (II) from aqueous solution via carbonized date pits and carbonized rice husks. Eurasian Chem Technol J 13:267–277

El-Hendawy ANA (2009) The role of surface chemistry and solution pH on the removal of Pb^{2+} and Cd^{2+} ions via effective adsorbents from low-cost biomass. J Hazard Mater 167:260–267. https://doi.org/10.1016/j.jhazmat.2008.12.118

El-Naas MH, Al-Zuhair S, Alhaija MA (2010) Removal of phenol from petroleum refinery wastewater through adsorption on date-pit activated carbon. Chem Eng J 162(3):997–1005. https://doi.org/10.1016/j.cej.2010.07.007

Gupta VK, Nayak A, Bhushan B, Agarwal S (2015) A critical analysis on the efficiency of activated carbons from low-cost precursors for heavy metals remediation. Crit Rev Environ Sci Technol 45(6):613–668

Hamouche A, Zine BM, Krim L (2015) Kinetics and thermodynamics of Cr ions sorption on mixed sorbents prepared from olive stone and date pit from aqueous solution. Int J Food Biosyst Eng 1(1):1–8

Hazzaa R, Hussein M (2015) Adsorption of cationic dye from aqueous solution onto activated carbon prepared from olive stones. Environ Technol Innov 4:36–51. https://doi.org/10.1016/j.eti.2015.04.002

Heschel W, Klose E (1995) On the suitability of agricultural by-products for the manufacture of granular activated carbon. Fuel 74(12):1786–1791. https://doi.org/10.1016/0016-2361(95)80009-7

Hilal NM, Ahmed IA, El-Sayed RE (2012) Activated and nonactivated date pits adsorbents for the removal of Copper (II) and Cadmium (II) from aqueous solutions. ISRN Phys Chem 2012. https://doi.org/10.5402/2012/985853

Jimenez-Cordero D, Heras F, Alonso-Morales N, Gilarranz MA, Rodríguez JJ (2014) Preparation of granular activated carbons from grape seeds by cycles of liquid phase oxidation and thermal desorption. Fuel Process Technol 118:148–155. https://doi.org/10.1016/j.fuproc.2013.08.019

Karthik V, Sivarajasekar N, Padmanaban VC, Nakkeeran E, Selvaraju N (2018) Biosorption of xenobiotic Reactive Black B onto metabolically inactive T. harzianum biomass: optimization and equilibrium studies. Int J Environ Sci Technol 1–12 (in press). https://doi.org/10.1007/s13762-018-1841-5

Kenawy ER, Ghfar AA, Naushad M, ALOthman ZA, Habila MA, Albadarin AB (2017) Efficient removal of Co (II) metal ion from aqueous solution using cost-effective oxidized activated carbon: kinetic and isotherm studies. Desalin Water Treat 70:220–226. https://doi.org/10.5004/dwt.2017.20534

Mahdi Z, Yu QJ, El Hanandeh A (2018) Investigation of the kinetics and mechanisms of nickel and copper ions adsorption from aqueous solutions by date seed derived biochar. J Environ Chem Eng 6:1171–1181. https://doi.org/10.1016/j.jece.2018.01.021

Mechati F, Bouchelta C, Medjram MS, Benrabaa R, Ammouchi N (2015) Effect of hard and soft structure of different biomasses on the porosity development of activated carbon prepared under N_2/microwave radiations. J Environ Chem Eng 3(3):1928–1938. https://doi.org/10.1016/j.jece.2015.07.007

Muthusaravanan S, Sivarajasekar N, Vivek JS (2018) Phytoremediation of heavy metals: mechanisms, methods and enhancements. Environ Chem Lett 16:1339–1359. https://doi.org/10.1007/s10311-018-0762-3

Naushad M (2014) Surfactant assisted nano-composite cation exchanger: development, characterization and applications for the removal of toxic Pb^{2+} from aqueous medium. Chem Eng J 235:100–108. https://doi.org/10.1016/j.cej.2013.09.013

Naushad M, Mittal A, Rathore M, Gupta V (2015) Ion-exchange kinetic studies for Cd (II), Co (II), Cu (II), and Pb (II) metal ions over a composite cation exchanger. Desalin Water Treat 54 (10):2883–2890. https://doi.org/10.1080/19443994.2014.904823

Naushad M, Vasudevan S, Sharma G, Kumar A, ALOthman ZA (2016) Adsorption kinetics, isotherms, and thermodynamic studies for Hg^{2+} adsorption from aqueous medium using alizarin red-S-loaded amberlite IRA-400 resin. Desalin Water Treat 57(39):18551–18559. https://doi.org/10.1080/19443994.2015.1090914

Naushad M, Ahamad T, Al-Maswari BM, Alqadami AA, Alshehri SM (2017) Nickel ferrite bearing nitrogen-doped mesoporous carbon as efficient adsorbent for the removal of highly toxic metal ion from aqueous medium. Chem Eng J 330:1351–1360. https://doi.org/10.1016/j.cej.2017.08.079

Nowicki P, Kazmierczak J, Pietrzak R (2015) Comparison of physicochemical and sorption properties of activated carbons prepared by physical and chemical activation of cherry stones. Powder Technol 269:312–319. https://doi.org/10.1016/j.powtec.2014.09.023

Obregón-Valencia D, del Rosario Sun-Kou M (2014) Comparative cadmium adsorption study on activated carbon prepared from aguaje (Mauritia flexuosa) and olive fruit stones (Olea europaea L.). J Environ Chem Eng 2(4):2280–2288. https://doi.org/10.1016/j.jece.2014.10.004

Okman I, Karagöz S, Tay T, Erdem M (2014) Activated carbons from grape seeds by chemical activation with potassium carbonate and potassium hydroxide. Appl Surf Sci 293:138–142. https://doi.org/10.1016/j.apsusc.2013.12.117

Olivares-Marín M, Fernández-González C, Macías-García A, Gómez-Serrano V (2012) Preparation of activated carbon from cherry stones by physical activation in air. Influence of the chemical carbonisation with H2SO4. J Anal Appl Pyrolysis 94:131–137. https://doi.org/10.1016/j.jaap.2011.11.019

Paramasivan T, Sivarajasekar N, Muthusaravanan S, Subashini R, Prakashmaran J, Sivamani S, Koya PA (2019) Graphene family materials for the removal of pesticides from water. In: A new generation material graphene: applications in water technology. Springer, Cham, pp 309–327. https://doi.org/10.1007/978-3-319-75484-0_13

Saad EM, Mansour RA, El-Asmy A, El-Shahawi MS (2008) Sorption profile and chromatographic separation of uranium (VI) ions from aqueous solutions onto date pits solid sorbent. Talanta 76 (5):1041–1046. https://doi.org/10.1016/j.talanta.2008.04.065

Sekirifa ML, Hadj-Mahammed M, Pallier S, Baameur L, Richard D, Al-Dujaili AH (2013) Preparation and characterization of an activated carbon from a date stones variety by physical activation with carbon dioxide. J Anal Appl Pyrolysis 99:155–160. https://doi.org/10.1016/j.jaap.2012.10.007

Sivarajasekar N (2007) Hevea brasiliensis-a biosorbent for the adsorption of Cu (II) from aqueous solutions. Carbon Lett 8(3):199–206. https://doi.org/10.5714/CL.2007.8.3.199

Sivarajasekar N (2014) Biosorption of cationic dyes using waste cotton seeds. Doctoral dissertation, Ph. D thesis. Anna University Chennai

Sivarajasekar N, Balasubramani K, Mohanraj N, Maran JP, Sivamani S, Koya PA, Karthik V (2017a) Fixed-bed adsorption of atrazine onto microwave irradiated Aegle marmelos Correa fruit shell: statistical optimization, process design and breakthrough modeling. J Mol Liq 241:823–830. https://doi.org/10.1016/j.molliq.2017.06.064

Sivarajasekar N, Mohanraj N, Balasubramani K, Prakash Maran J, Ganesh Moorthy I, Karthik V, Karthikeyan K (2017b) Optimization, equilibrium and kinetic studies on ibuprofen removal onto microwave assisted—activated Aegle marmelos correa fruit shell. Desalin Water Treat 84:48–58. https://doi.org/10.5004/dwt.2017.21107

Sivarajasekar N, Mohanraj N, Sivamani S, Moorthy GI (2017c) Response surface methodology approach for optimization of lead (II) adsorptive removal by Spirogyra sp. biomass. J Environ Biotechnol Res 6(1):88–95

Sivarajasekar N, Mohanraj N, Sivamani S, Moorthy IG, Kothandan R, Muthusaravanan S (2017d) Comparative modeling of fluoride biosorption onto waste Gossypium hirsutum seed microwave-bichar using response surface methodology and artificial neural networks. In: Intelligent Computing, Instrumentation and Control Technologies (ICICICT), 2017 international conference on, pp 1631–1635

Sivarajasekar N, Paramasivan T, Subashini R, Kandasamy S, Prakash Maran J (2017e) Central composite design optimization of fluoride removal by spirogyra biomass. Asian J Microbiol Biotechnol Environ Sci 19:S130–S137

Sivarajasekar N, Balasubramani K (2018) A short account on petrochemical industry effluent treatment. Int J Petrochem Sci Eng 3(1):12–13. https://doi.org/10.15406/ipcse.2018.03.00070

Sivarajasekar N, Baskar R (2018) Optimization, equilibrium and kinetic studies of basic red 2 removal onto waste Gossypium hirsutum seeds. Iran J Chem Chem Eng (IJCCE) 37(2):157–169. https://doi.org/1021-9986/2018/2/157-169

Sivarajasekar N, Balasubramani K, Baskar R, Sivamani S, Ganesh Moorthy I (2018a) Eco-friendly acetaminophen sequestration using waste cotton seeds: equilibrium, optimization and validation studies. J Water Chem Technol 40(6):334–342. https://doi.org/10.3103/S1063455X18060048

Sivarajasekar N, Mohanraj N, Sivamani S, Prakash Maran J, Ganesh Moorthy I, Balasubramani K (2018b) Statistical optimization studies on adsorption of ibuprofen onto Albizialebbeck seed pods activated carbon prepared using microwave irradiation. Mater Today Proc 5:7264–7274

Torrellas SÁ, Lovera RG, Escalona N, Sepúlveda C, Sotelo JL, García J (2015) Chemical-activated carbons from peach stones for the adsorption of emerging contaminants in aqueous solutions. Chem Eng J 279:788–798. https://doi.org/10.1016/j.cej.2015.05.104

Uysal T, Duman G, Onal Y, Yash I, Yanik J (2014) Production of activated carbon and fungicidal oil from peach stone by two-stage process. J Anal Appl Pyrolysis 108:47–55. https://doi.org/10.1016/j.jaap.2014.05.017

Yamina G, Abdeltif A, Youcef T, Mahfoud HM, Fatiha G (2013) A comparative study of the addition effect of activated carbon obtained from date stones on the biological filtration efficiency using sand dune bed. Energy Procedia 36:1175–1183. https://doi.org/10.1016/j.egypro.2013.07.133

Chapter 11
Removal of Toxins from the Environment Using Date Palm Seeds

Basma Al-Najar, Mohamed Bououdina, J. Judith Vijaya, Radhika R. Nair, and Tetiana Tatarchuk

Abstract Seeds of date palm trees are becoming one of the nature solutions for pollution as their interesting adsorption properties can compete with other conventional adsorbents such as activated carbons. In the Middle East, where massive amounts of palm pits are being disposed daily, researchers are interested in exploit these waste in beneficial applications such as water treatment from toxins. This chapter is reviewing the latest research that investigates the possible routes of extracting useful substances from palm dates including oil, cellulose and phenol. It also focuses on the chemical composition, surface morphology and microstructure of the treated palm seeds. Such remarkable properties reflect the outstanding behavior of the extracts during adsorption experiments. It is discussed here, how palm seeds can be effectively applied in heavy metal (Cu, Pb, Zn, Cr, Au, Br and Ni) removal from aqueous solution. Degradation of dyes (Rhodamine B (RhB), Methylene blue (MB), Congo red (CR) and Crystal violet (CV)) and other pollutants are also considered under different experimental conditions.

Keywords Date palm seeds · Toxins · Activated carbon · Adsorption

B. Al-Najar (✉) · M. Bououdina
Department of Physics, College of Science, University of Bahrain, Sakheer, Kingdom of Bahrain
e-mail: balnajar85@gmail.com; mboudina@gmail.com

J. Judith Vijaya · R. R. Nair
Catalysis and Nanomaterials Research Laboratory, Department of Chemistry, Loyola College, Chennai, India
e-mail: jjvijaya78@gmail.com; radhikatojo@gmail.com

T. Tatarchuk
Department of Chemistry, Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine

Educational and Scientific Center of Material Science and Nanotechnology, Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine
e-mail: tatarchuk.tetyana@gmail.com

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_11

11.1 Introduction

Clean water scarcity has been a global environmental issue due to the different and massive amounts of pollutants that residue daily as a product of industrial activities (Natarajan et al. 2018; Naushad et al. 2015a). Such pollutants include heavy metals (Kobielska et al. 2018; Shahat et al. 2015), dyes (Abbas and Ahmed 2016; Javadian et al. 2014), acids (Salman and Al-saad 2012) and also microbes (Li et al. 2018). Research studies have focused on the removal techniques of these un-degradable pollutants through several chemical and physical methods such as adsorption (Danish et al. 2012; Rajamohan et al. 2014), catalysis (Zhou et al. 2018) and filtration (Barnaby et al. 2017). Adsorption has been one of the effective routes to get rid of these pollutants and it depends mainly of the applied adsorbent which has to own certain chemical and physical properties (Ahsaine et al. 2018; Mittal et al. 2016) as well as being safe to environment (Banerjee et al. 2018). Activated carbon (Ac) (Farooq et al. 2017) nanoparticles (Khosravi et al. 2018) and biosorbents (Wen et al. 2018) are well known adsorbents for the removal of pollutants from aqueous solutions. Biological, green or echo-friendly materials has emerged to be efficient adsorbers to pollutants beside their low cost, easy preparation and environmental friendly (Amiri et al. 2017; Naushad et al. 2015b) such as walnut shell (Banerjee et al. 2018) coconut (Johari et al. 2016; Etim et al. 2016) and tea (Shen et al. 2017). Among these bio-adsorbents and in particular regions of the word (Middle East and North Africa) (Al-Mutairi 2010), the seeds of palm dates fruit have shown a great potential to be an excellent catalyst for adsorption procedures (Ahmed 2016). Due to the high consumption of dates in various regions, millions of tons of date pits are produced daily. Aside with their applications in biodiesel production (Al-Muhtaseb et al. 2016), in batteries (Izanzar et al. 2018) and other environmental applications (Jamil et al. 2016; Naushad et al. 2015c), it has been reported that date pits can be an excellent alternative to activated carbon which is used excessively for pollutants removal procedure (Al-Mutairi 2010). Palm dates have shown to possesses interesting properties such as high porosity and high surface area that makes it low cost and clean adsorber after undergoing extraction and pre-treatment stage (Ahmed 2016). Several research works focused on the applications of palm dates for water treatment and in particular for the removal of metals (Mahdi et al. 2018), dyes (Daoud et al. 2017) and others through adsorption. Physical and chemical treatment is very essential as it could dramatically affect the adsorption process as well as it alters the morphology of the adsorbent and the grain size and hence the surface area which is the key factor of the adsorption process (Gueu et al. 2006). This chapter provides an over view of the extraction characteristics of palm dates as well as a particular focus on its applications in the removal of metals, dyes and other from water.

11.2 Extraction Procedures and Synthesis Methods of Date Palm Seeds

Dates are the fruit of the palm tree. It has a very important nutritional value. It has been considered an important food in the past. Dates contain a large proportion of important minerals for the human body in its construction and protect it from many of the disease (Farsi et al. 2007). Date seed has also many benefits for human and animals and it is an important part of date represented the steel body, and is rectangular in shape, and pointed at both ends, and occupies the center of the fruit, and weighing between 0.5 and 4 g with length of 12–20 mm and usually the length of the seed is equal to three times the width. Date seeds represent 10–20% of the total weight of the fruit and contain protein, carbon hydrate, fiber, foodstuff, ash, fat water and oil (Barreveld 1993). It also contains many of important elements such as sodium, Potassium, Calcium, Iron, Copper, Magnesium, Manganese, Zinc and phosphorus. The common names are, date seeds, dates pits, date kernels, date stones, date pips (Ali et al. 2015). The different ripening stages of date palm according to days post pollination (DPP) shown in Fig. 11.1 (Ghnimi et al. 2017).

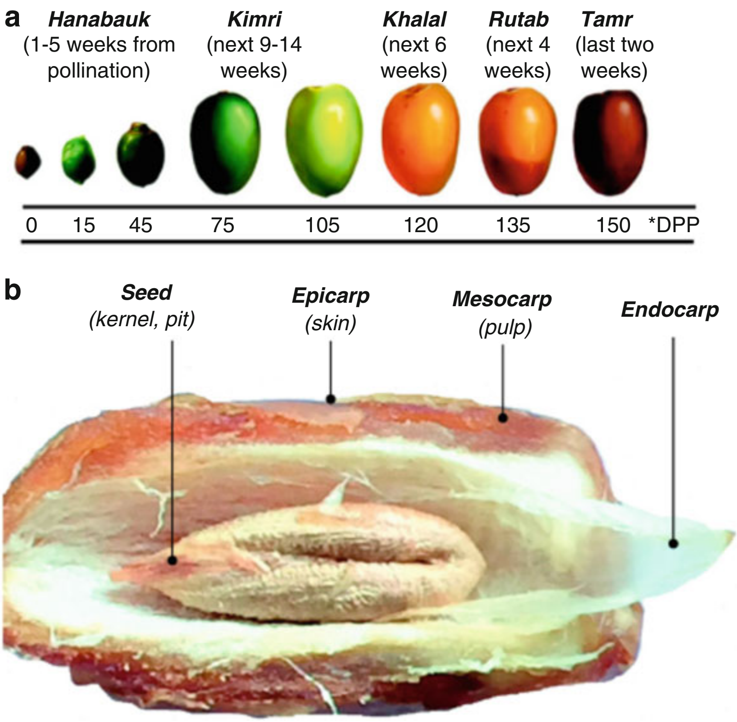


Fig. 11.1 Schematic diagram of different ripening stages of date palm according to days post pollination (DPP). (Ghnimi et al. 2017)

Bio-fuel production from date palm seed oil (Pheonix Canariensis) is a new trend, and solvent extraction is one of the traditional technique used for this purpose. This is a cheapest method and it is applied to produce oil such as Jojoba oil, soybean oil, palm oil and jatropha oil from oil seeds (Devshony et al. 1992). Many factors which affect the solid liquid extraction, like particle size, physical and chemical properties of the solvent solubility, temperature and solvent agitation. The extraction equipment also requires safety considerations such as, environmental factors, solvent and dust loadings and working environment. The main application of this procedure includes the extraction of oil from oil seeds and metal salts fro their ores (Rahman et al. 2007). Rate of extraction of oil from date seed depends on type of solvent, partial size of date seed, time of extraction and temperature (Mohsen et al. 1995).

The aim of this work is to produce bio-oil from date palm seeds by conventional Soxhlet apparatus method. The yield of this production is optimized with respect to grain size of the crushed seeds, extraction time and choice of the solvents used (Abd-Alla and El-Enany 2012). The obtained bio-oil were charcterized using Fourier Transform Infrared Spectroscopy (FT-IR) for the identification of functional groups and Gas Chromatography – Mass Spectrum for the identification of fatty acids composition, iodine value, saponification value and kinetics value are determined by this method (Abd-Alla and El-Enany 2012).

Phoenix canariensis (Date palm) is mainly found in the Canary Islands and in countries like Australia and California. The Canary Island Date Palm, a very large palm grown for its rounded crown and its massive trunk, is mainly used in parks and gardens for avenue planting. The norm of chemical parameters of Phoenix canariensis are shown in Table 11.1 (Nehdi et al. 2010). For its growth, it requires a well-drained fertile moist, organic rich and loamy soil. It has a longer life span up to 150 years with less water requirement. The different methods used, for the extraction and synthesis are discussed below. The date palm seeds vary in amount of their oil, starch and other components. The seed is usually obtained from a small embryo and hard endosperm made up of cellulose.

Date palm seed weigh approximately 5.6–14.2%, in that 6.46% I moisture, 5.22% protein, 16.2% fiber, 8.49% fat, 62.51% carbohydrate and 1.12% ash. It contain several minerals like potassium, magnesium, calcium, phosphorous, sodium, iron and several acids like, fatty acids, oleic acid and lauric acid. The chemical composition, physical and chemical properties of Phoenix canariensis shown in Table 11.2 (Nehdi et al. 2010).

Table 11.1 Norm of chemical parameters of Pheonix canariensis (Nehdi et al. 2010)

Parameter	Norm
Saponification value	ISO 3657
Para-anisidine value	ISO 6885
Peroxyde value	ISO 3960
Acid value	ISO 660
Unsaponifiable matter	ISO 3961
Iodine value	ISO 3596

Table 11.2 Chemical composition, physical and chemical properties of Pheonix canariensis date palm seed (Nehdi et al. 2010)

Component	
Chemical composition of seeds	
Moisture content (%)	10.20 ± 0.25
Oil - dry matter (%)	10.36 ± 0.29
Ash - dry matter (%)	1.18 ± 0.02
Protein	5.67 ± 0.15
Carbohydrate	72.59 ± 0.28
Potassium	255.43 ± 0.02
Magnesium	62.78 ± 0.18
Calcium	48.56 ± 0.56
Phosphorous	41.33 ± 0.66
Sodium	8.77 ± 0.22
Iron	3.21 ± 0.34
Properties of seed oil	
Saponification number	191.28 ± 0.50
Iodine number	76.66 ± 0.28
Free fatty acids	0.59 ± 0.02
p-Anisidine value	3.67 ± 0.18
Peroxide value	3.62 ± 0.56
Unsaponifiable matter	1.79 ± 0.22
Index of refraction	1.456 ± 0.01
β – Carotene	5.51 + 0.03
Chlorophyll	0.10 + 0.02
Physical state at room temperature	Liquid

11.2.1 Solvent Extraction Using Soxhlet Apparatus for Protein Fraction from Date Palm Seeds

The seeds are manually isolated, soaked in water and washed to remove any remaining dirt. The flesh of the date is air dried for a week, and further dried overnight at 40 °C. The seeds are ground into a fine powder and defatted by extraction with hexane using a Soxhlet apparatus. The defatted powder is then dried to form a date seed powder (DSP). The Fig. 11.2 shows schematic diagram of conventional Soxhlet apparatus used in the laboratory and the outline diagram of the apparatus (Luque de Castro and Priego-Capote 2010).

The preparation of oil from date palm seed is carried out by placing 15 g of dried DPSP into an extraction thimble and sealed with a piece of cotton wool. The thimble is then inserted in a Soxhlet extraction flask. Anti-bumping agent granules are added before adding 300 ml of hexane to a cleaned dried and weighed round bottom flask. The extraction unit is then placed over an electric heating mantle. The temperature of the heater is adjusted to boil the hexane.

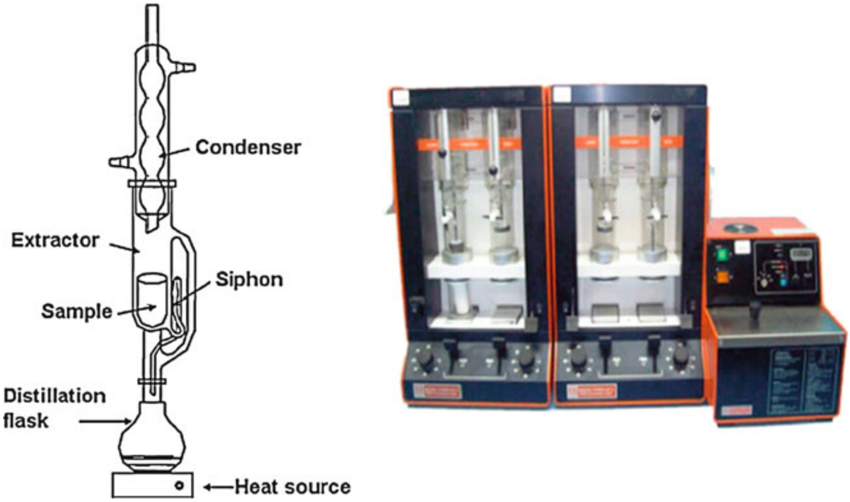


Fig. 11.2 Schematic diagram of conventional Soxhlet apparatus. (Luque de Castro and Priego-Capote 2010)

When the solvent starts to boil, some amount of hexane drips out from the condenser into the sample chamber where it extracts the oil from the DPSP. The extraction is continued for 10 h or until the solvent in the sample chamber becomes colorless which indicates that it was free from oil and that all the oil had been extracted (Ibrahim et al. 2012). At this point, the heat source is switched off. The sample is removed from the thimble and left overnight to dry at room temperature. The defatted date palm seed powder (DDPSP) is kept in plastic container at −20 °C until further use.

11.2.2 Extraction of Cellulose from Date Palm Seeds by Van Soest Analysis Method

The seeds of date palm are collected and directly isolated from date fruit, which are fully ripped. The obtained sample is washed with distilled water to remove any adhering date flesh, then air-dried and preserved at −20 °C. The as-dried date seeds are ground into powder with a microphyte disintegrator FZ10 in order to pass a 495 μm sieve. The size of the samples must be small to make sure the reaction reagent and fibers are optimum during the extraction process. Powdered date seeds (20 g) are sequentially subjected to Soxhlet extraction with water and petroleum for 8 h. each and followed by alkaline extraction: consistency (5%); NaOH (2%); temperature (70 °C) and treatment time (160 min) (Al-Hooti et al. 1998). The

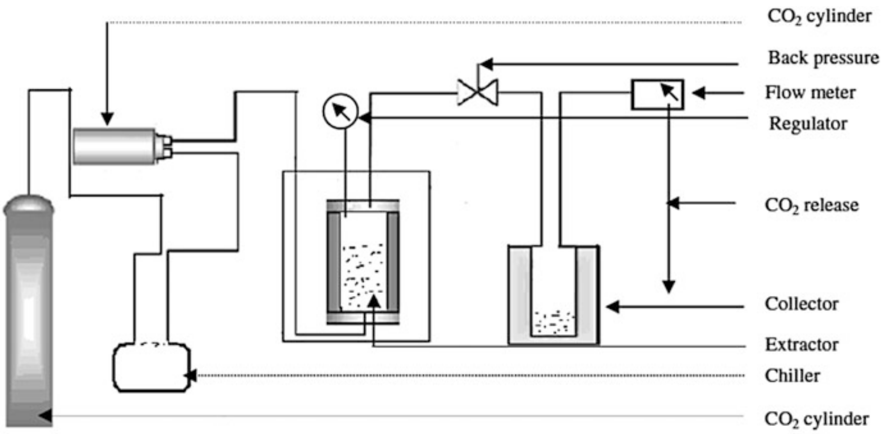


Fig. 11.3 Schematic diagram of supercritical CO_2 apparatus. (Pradhan et al. 2009)

bleaching step is carried out with acidified sodium chlorite (1.7%). The cellulose is extracted from holo cellulose with 10% KOH, containing 1% H_3BO_3 for 10 h at room temperature with a solid-to-liquor ratio of 1/25.

11.2.3 Extraction of Date Palm Seed Oil by Supercritical Carbon Dioxide Method

The collected date palm is usually preserved in a refrigerator. The flesh is separated from the seed manually and washed to eliminate any traces of impurities. Pure carbon dioxide (99.99%) which is equipped with supercritical fluid extractor is used throughout the experiment. 10 g of sample and size 2 mm of maximum dimension is weighed accurately in a glass dish that has been dried previously in an oven and set to operate at 103 ± 2 °C for 4 h (Hosam and Wissam 2011). The dish is weighed after cooling in the desiccators. The ground date seeds are sieved using plates of 0.5, 0.4, 0.3 and 0.2 mm pore size. Supercritical Carbon Dioxide (SC-CO_2) extraction is conducted at constant temperature and pressure, 40 °C and 30 MPa for different particle size. The schematic diagram of supercritical carbondioxide (SC-CO_2) apparatus shown in Fig. 11.3 (Pradhan et al. 2009).

SC-CO_2 extraction of date's fruit seed is carried out using laboratory-scale supercritical fluid extraction system. In this method a continuous flow of CO_2 gas with 99.9% purity is passed into the extractor with a flow rate of 24 mL/min and a temperature range of 40, 50, 60, 70 and 80 °C and a pressure range of 27.6, 34.5 and 41.4 MPa were used. An approximate amount of fine date palm powder were placed in an extraction vessel and extraction is set to be 40 min. The extracted oil is collected by placing a vial at the outlet of the restrictor (Crabbe et al. 2001).

11.2.4 Extraction Method for the Identification of Biomedical Protein from Date Palm Seed and Flesh

The seeds are manually removed from the fruits and washed to remove any remained date flesh. The seeds are air dried at room temperature and the flesh is cut into small pieces. Date seed and flesh are ground into powder using a precooled mortar in the presence of liquid nitrogen. The powder is further ground into fine powder by using a blender. All date samples are then kept at −80 °C until further use (Ambigaipalan and Shahidi 2015).

11.2.4.1 TCA-Acetone (TCA-A) Extraction Method

1.5 g of seed (2.0 g of flesh) powder issuspended in 12 mL of ice-cold extraction buffer [50 mMTris-HCl (pH 8.5), 5 mM EDTA (pH 8.5), 100 mMKCl, 2% v/v 2-mercaptoethanol] and vortexed for 15 min at 4 °C. After centrifugation (15,000 g, 10 min, 4 °C), the supernatant is collected and precipitated overnight with four to five volumes of acetone containing 10% w/v TCA at – 20 °C.

The supernatant is removed after centrifugation (15,000 g, 30 min, 4 °C) and the pellet is washed twice in ice-cold acetone/0.2% DTT. The pellet is incubated for 1 h between the two rinsing steps at −20 °C. After centrifugation at 10,000 g for 5 min at 4 °C, the supernatant is removed and the pellet is air-dried. The pellet is then resuspended in 400-μL resolubilisation buffer (7 M urea, 2 M thiourea, 4% w/v CHAPS) and vortexed for 1 hr. at room temperature. After centrifugation (10,000 g, 10 min, 4 °C), the supernatant is collected (Carpentier et al. 2005).

11.2.4.2 (Phe) Extraction Method

In Phe extraction method, 1.5 g of seed (2.0 g for flesh) powder is suspended in 10 mL of ice-cold extraction buffer [50 mMTris-HCl (pH 8.5), 5 mM EDTA (pH 8.5), 100 mMKCl, 2% v/v 2-mercaptoethanol, 30% w/v sucrose] and vortexed for 30 s Ice-cold Tris-buffered phenol (pH 8.0, 10 mL) is then added to the sample and vortexed for 15 min at 4 °C. After centrifugation (15,000 g, 10 min, 4 °C) the phenolic phase is collected and re-extracted with the same volume of extraction buffer and vortexed for 30 s. After centrifugation (15,000 g, 10 min, 4 °C) the phenolic phase is collected and precipitated overnight with 5 volumes of 100 mM ammonium acetate in methanol at −20 °C (Saravanan and Rose 2004). The supernatant is then removed after centrifugation (15,000 g, 30 min, 4 °C) and the pellet is washed twice in ice-cold acetone/0.2% DTT. It is then centrifuged and suspended in buffer.

11.2.4.3 TCA-Acetone-Phenol (TCA-A-Phe) Extraction Method

In this TCA-A-Phe extraction method, 1.5 g of seed (2.0 g for flesh) powder of is suspended in 10 mL of 10% w/v TCA in acetone and vortexed for 30 s. After centrifugation (15,000 g, 10 min, 4 °C) the supernatant is removed and then 10 mL of 100 mM ammonium acetate in methanol at −20 °C was added, vortexed for 30 s and centrifuged (15,000 g, 10 min, 4 °C). The supernatant is removed after centrifugation and washing steps were repeated twice with 10 mL of ice cold acetone at −20 °C. After centrifugation (15,000 g, 10 min, 4 °C), the supernatant is removed and the resultant pellet is air dried at room temperature to remove residual acetone (Wang et al. 2006). The following steps (Phe extraction, methanol/ammonium acetate precipitation, and pellet resolubilisation) are performed in the same way as in Phe extraction method.

11.2.5 Preparation and Extraction of Date Palm Nanoparticle by Agar Well Diffusion Method

Date seeds are soaked in water to remove any adhering date flesh, air-dried, then further dried in an air oven at 60 °C. The dried date palm seeds are ground and passed through 1–2 mm screens to produce date palm seeds flour or date-pits powder. The powder is then kept in the freezer at −20 °C (Saleh and Otaibi 2013). About 5 g of date palm seed powder is weighed and poured into a flask including 20–50 mL of 38% hydrochloric acid solution. The flask is then kept under stirring at a speed of 1000 rpm at a temperature of 30 + 2 °C. The date palm seed nanoparticles were filtered through a Millipore filter having a pore size of 220 nm. Alternately, the solution was centrifuged at about 9000 rpm for about 15 min to isolate the date palm seed nanoparticles.

11.2.6 Preparation and Extraction of Date Palm by Acid Hydrolysis

Date palm seeds are extracted with ether for 11 h and with aqueous methanol (70%) for 18 h in a continuous extraction apparatus (Soxhlet) until exhaustion. The aqueous extract is concentrated to a small volume and partitioned successively with chloroform and *n*-butanol. The *n*-butanol extract is then fractionated on a silica gel 60 (63–200 mesh) column chromatography and eluted with chloroform followed by step-wise addition of methanol to afford four fractions (Nagwa et al. 2009). Each fraction is subjected to sephadex and eluted with a mixture of methanol and water. All separation processes were performed using Whatman No. 1 paper with (S1) *n*-butanol-HOAc-H_2O (4:1:5, top layer) and 15% aqueous HOAc. The solution of each compound in 6% aqueous HCl is refluxed for 2 h. The reaction mixture is diluted with water and extracted with ether.

11.2.7 Preparation and Extraction of Date Palm by FRAP (Ferric Reducing Antioxidant Power Assay) Method

The date palm samples were packed in polyethylene bags, sealed and stored at 2–8 °C. The pits were removed from the flesh, washed to get rid of any adhering date flesh, and air-dried. Then, they were further dried at about 50 °C for 4 h. Date pits of each variety were separately milled up to 1–2 mm and then preserved at 2–8 °C.

About 0.02 g of powdered date seeds was shaked with 5 mL of solvent in a glass tube at room temperature, two times for 30 min and then centrifuged. Water, methanol:water (50:50, v/v), methanol, DMSO and water:methanol:acetone: formic acid (20:40:40:0.1) (3) were used as solvents. The extraction was carried out using these solvents to compare the antioxidant activities and the total phenolic contents of each extract.

In ferric reducing antioxidant power assay method, reduction of a ferric-tripyridyltriazine complex to its colored ferrous form in the presence of antioxidants. The FRAP reagent contained 5 mL of 10 mmol/L solution of TPTZ (2,4,6-tripyridyl-s-triazine) in 40 mmol/L HCl, 5 mL of a 20 mmol/L solution of $FeCl_3$and 50 mL of a 0.3 mol/L acetate buffer solution, pH 3.6 was maintained and warmed at 37 °C. The date palm seed extract of 50 μL was mixed with 1.5 mL FRAP reagent and after incubation at 37 °C for 10 min, the absorbance of the reaction mixture was measured at 593 nm (Benzie and Strain 1996).

11.2.8 Preparation and Extraction Date Palm Seed by Aqueous and Ethanolic Method

Palm date was collected at the initial growth stage and stored in a refrigerator at 4 °C, then removed the flesh of date from the pits. The pits were dried and crushed to fine powder. Fruits and seeds were defatted by using n-hexane then extracted three times with 500 ml methanol at room temperature for 24 h by a magnetic stirrer. To obtain crude methanol, the extracts were filtered and centrifuged at 6000 radius centrifugation force for 30 min at 3 °C (Pujari et al. 2011), then the supernatant was concentrated under low pressure at 40 °C for 1 to 2 h using a rotary evaporator. These extracts were stored in dark glass bottles at −4 °C. Also, the dry date palm

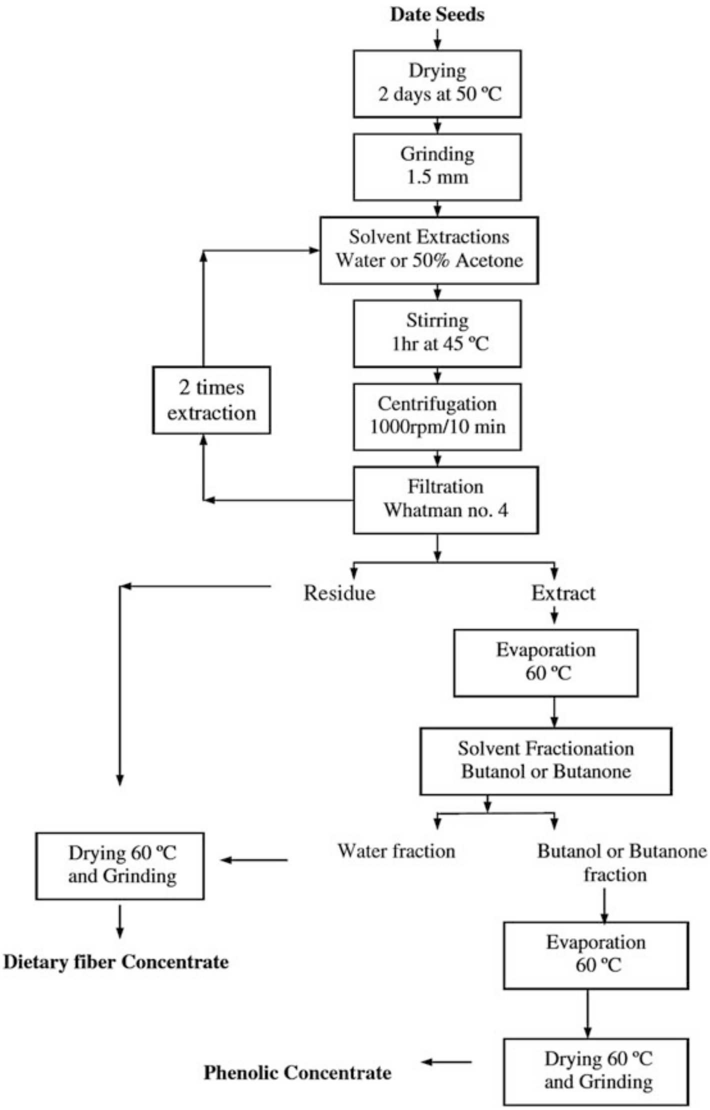


Fig. 11.4 Flowchart for the extraction procedure for Ethanolic and aqueous method. (Al-Farsi and Lee 2008)

seeds were soaked in water (1:5 w/v) at 40 °C then stirred for 24 h at a temperature of 4 °C. This mixture was centrifuged at 6000 RCF for 20 min and the precipitate was discarded and the supernatant liquid was stored at 4 °C. The flowchart for the procedure of Ethanolic and aqueous extraction was shown in Fig. 11.4 (Al-Farsi and Lee 2008).

11.2.8.1 Ethanolic Extract

100 g of the fresh blended date palm seed were extracted exhaustively with 1 L of ethanol and the mixture sieved, then the remaining ethanol in the extract was evaporated to obtain the concentrated extract, which was reconstituted in distilled water at a concentration of 1 mg/ ml and stored in the refrigerator (Amani et al. 2016).

11.2.8.2 Aqueous Extract

100 g of the fresh blended date palm seed were extracted exhaustively with 1 L of water and the mixture sieved, then the remaining methanol in the extract was evaporated to obtain the concentrated extract, which was reconstituted in distilled water at a concentration of 1 mg/ ml and stored in the refrigerator.

11.2.9 Preparation and Extraction of Date Palm Seed by Isoelectric Precipitation Method

The date palm seeds were soaked in water, washed to remove any adhering date flesh, and then air-dried. The fine powdered samples were collected, stored and then further dried at 50 °C. Date pits, of each variety, were separately milled up to 1–2 mm and then preserved at −20 °C. Lipid extraction was carried out with a SER 148 solvent extractor equipped with six Soxhlet posts. The extraction was carried out for 30 min, with thimbles immersed in boiling petroleum ether, and 60 min of reflux washing (Besbes et al. 2009). After removing solvent, using a rotavapour apparatus, the obtained defatted date seeds were used for preparation of fibro-protein extract.

The fibro-protein extract from defatted date seed was prepared according to the isoelectric precipitation method. The defatted date seed flower was mixed with distilled water (1:10 w/v), adjusted to pH 10 with NaOH and after stirring for at least 40 min, was centrifuged at 6500 g for 20 min at 4 °C. Then, the residue was mixed with distilled water (1:5 w/v), readjusted to pH 10 and centrifuged following the same process. The supernatant liquid of both centrifugations were blended and used as mother solution for DSFPE production (Tsaliki et al. 2002). This solution was adjusted at pH 4.5 with 0.1 HCl, centrifuged, freeze and lyophilized to obtain the DSFPE.

11.2.10 Preparation and Extraction of Date Palm Seed by Aqueous Ethanolic Method

In this method, date palms and flesh and pits were separated. Palm seeds were washed to remove adherent fruit material. After washing and drying, seeds were roasted and grounded to obtain fine date seeds powder, which was stored in plastic jars at ambient temperature. The solvent extraction was carried out using aqueous ethanol followed by extraction. In this method, 50 g of date seeds powder was added in 149 mL of aqueous ethanol in 250 mL conical flask, 1 mL of acetic acid and 40 mL of distilled water were added into flask. The mixture of solvent and date seeds powder was placed in orbital shaker for 3–4 h at 280 rpm with controlled temperature of 20 °C. The mixture was filtered through Whatmann filter paper No. 2. The solvent was evaporated using rotary evaporator under reduced pressure at 40 °C. The final extract was stored at – 40 °C (Farsi et al. 2005).

11.2.11 Different Method for the Preparation and Extraction of Anti – oxidant from Date Palm Seeds

11.2.11.1 Decoction Method

The date palm seeds powder is boiled in a process called decoction method in order to obtain a thick liquid solution which is rich in antioxidants. 5 g of sample is mixed with 100 ml deionized water and boiled at 100 °C for 30 min in water bath. Then, the mixture is centrifuged at 10000 rpm for 10 min. The liquid portion is filtered using muslin cloth, and the filtrate is used to determine the antioxidants (Lee et al. 2008).

11.2.11.2 Hydro-alcoholic Method

Antioxidants can be extracted from date palm seeds by the hydro-alcoholic cold separation method. In this method, 10 g sample is mixed with petroleum ether ethanol 90% at a ratio of 1:1 (v/v) in flask capped by cotton wool and shaken on a rotary shaker for 24 h. The solution is centrifuged at 10000 rpm for 10 min and filtered using eight layers of muslin cloth. The combined filtrate is concentrated in a rotary evaporator at 60 °C under reduced pressure to evaporate the petroleum ether and yield a thick solution. The hydro-alcoholic method achieved higher amount of total phenols and flavanones than methanolic and aqueous method. It is found that higher yield of antioxidants was achieved by the decoction method compared to the hydro-alcoholic method (Milovanovic et al. 2007).

11.2.11.3 Ultrasound Method

In this method, in a 25 ml flask, 2.5 g powdered date palm seeds were mixed with 20 ml methanol and the mixture is sonicated at 20 khz for 30 min at a temperature of 23 °C filtered using eight layers of muslin cloth. The combined filtrate is concentrated in a rotary evaporator at 60 °C under reduced pressure to evaporate the methanol. This method shows better yield and reduced time, and the effect of ultrasound mainly depends on the nature of the solvent used for extraction. The solvent in the ratio of 3:1 i.e. acetone: water with chloroform yields a high amount of phenol from date palm seeds (Pan et al. 2011).

11.2.11.4 Solvents Method

In this 1 g of fine form of date palm seeds were mixed with suitable solvents such as acetone, DMF, methanol, ethyl acetate and ethanol. Then the solution kept in a water bath for 60 °C for 4 h and then centrifuged at 10000 rpm for 10 min and filtered using muslin cloths. Then the obtained filtrate was concentrated using a rotary evaporator at 60 °C under reduced pressure. It was found that, the antioxidant extraction yield is influenced by the nature of the different solvents used and its concentration. For the extraction of anthocyanins, acid such as methanol or ethanol is used, DMF used as a solvent to extract polyphenol from tea than acetone (Paniwnyk et al. 2001).

11.2.12 Determination of Phenolic Content from Date Palm Seed by Folin-Ciocalteu Method

The date palms were purchased; pits removed and were stored in a refrigerator at 4 °C until used. The extraction procedure was carried out on the date seed powder. In a 125 mL Erlenmeyer flask, 1 g of date palm seed fine powder were mixed with 20 ml de-ionised water (20:1 ratio). The flask then placed in a water bath for 25 °C for 1 h, then the obtained solution was centrifuged at 1000 rpm for 10 min and then filtered. The solvent was evaporated by using a rotary evaporator at 60 °C (Hong et al. 2006).

Finally, the sample was analyzed for total antioxidants (TA), total phenolic (TP) and total flavonoid (TF) using a spectrophotometer. The same procedure was followed with all the solvents.

11.2.13 Extraction and Preparation of Silver Nanoparticle from Date Palm Seeds by Microwave Assisted Green Synthesis

In this extraction method, date palm seeds were dried, powdered, sieved and stored in the form of fine powder. From this, 0.3 g of date palm fine powder was mixed with 25 ml of double distilled water and exposed to microwave at 300 W. After cooling, the obtained reddish brown extract was filtered and stored at 5 °C. Similar procedure was followed for the synthesis of silver nanoparticle, 1 ml date palm extract mixed with 10 ml silver nitate solution and then irradiation at 300 W for 30 s in microwave. After cooling, this mixture was mixed with 0.1 ml 4-nitrophenol solution and 1.85 ml sodium brohydride solution (Aitenneite et al. 2016).

11.2.14 Extraction Method for the Identification Protein from Date Palm Seed by HPLC – PDA Analysis

The pits separated from the flesh of date palm, crushed into fine powder and around 100 g are taken in a flask. The fine powder was equally separated in individual flasks, immersed and extracted three times with 500 ml of n-hexane. The flask was shaken for 24 h with 3 h interval using a magnetic stirrer, and then filtered with Whatman filter paper. The solvent was removed under reduced pressure at 40 °C using a rotary evaporator to obtain hexane crude extracts.

The immersed seeds were separately extracted three times with methanol (500 ml) at room temperature for 24 h using a magnetic stirrer. The methanolic extracts were filtered and then centrifuges at 6000 for 30 min at 3 °C. The supernatant liquid was concentrated under reduced pressure at 40 °C for 1–2 h using a rotary evaporator to obtain methanol crude extracts. The n-hexane and methanol extracts were kept in dark glass bottles at −4 °C. Also, the dry date palm fruits were soaked in water (1:5 w/v) at 40 °C then stirred for 24 h at 4 °C (Wang et al. 2004). The mixture was centrifuged at 6000 RCF for 20 min to discard the precipitate and the supernatant was stored at 4 °C.

11.2.15 Extraction of Date Palm Seed by Ultrasonication Assisted Extraction

Dried date palm seeds were powdered to a uniform particle size. Sample-to-solvent ratio was kept constant for all the procedure. Extraction carried out in ultrasonic bathat 35KHz. Samples (2 g) were powdered and placed into Erlenmeyer flasks (250 mL) Samples were exhaustively extracted with different proportions of ethanol-water (from 0% to 100%) at different extraction time (from 5 to 45 min), in different ratios of aqueous ethanol to raw material (from 10 to 70 mL/g) and at extraction temperature varying from ambient temperature to 65 °C. Absolute methanol and 50% ethanol were used for extraction. Mostly, ethanol was selected as extraction solvent due to its low toxicity (Vijay et al. 2012). The mixtures were centrifuged at 2000 × g for 20 min at 4 °C and the supernatants were collected for the antioxidant activity determination. Figure 11.5 shows the experimental set up design for the ultrasonication assisted extraction method (Luque de Castro and Priego-Capote 2010).

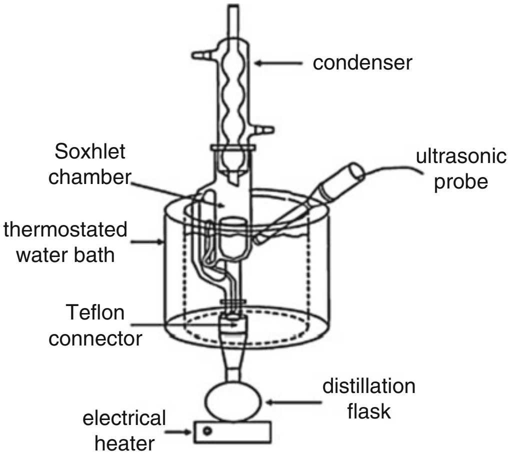


Fig. 11.5 Schematic diagram for the experimental set up for ultrasonication assisted extraction method. (Luque de Castro and Priego-Capote 2010)

11.2.16 Estimation of Flavonoid Content in Date Palm Seed by Aluminum Chloride Colorimetric Method

Date palm seeds were collected and dried into powder with uniform particle size. In this method, sample-to-solvent ratio was kept constant for all the procedure, i.e. 1 g seed powder in 50 ml solvent. Absolute methanol (Merck, Mumbai) and 50% ethanol were used for the extraction.

Aluminum chloride ($AlCl_3$) colorimetric method was used for flavonoids determination. 0.5 mL of each plant extract was separately mixed with 1.5 mL of methanol, 0.1 mL of 10% aluminum chloride, 0.1 mL of 1 M potassium acetate and 2.8 mL of distilled water. The reaction mixture was allowed to stand at room temperature for 30 min and then further analyses were conducted (Dobias et al. 2010).

11.3 Physico–Chemical Characteristics of Date Palm Seeds

11.3.1 Date Palm Seeds as a Precursor for Porous Carbon

There are many reports about using of date palm seeds as low-cost sorbent in the adsorption process for the purification of removal wastewater from pollutants. This approach has few options: the use of ***non-activated date pits*** as solid adsorbent and the use of ***activated date palm seeds carbons (biochar)*** obtained from date palm seeds as adsorbent for hazardous dyes and heavy metals from wastewater (Fig. 11.6).

Activated carbons can be prepared from date palm seeds by using two steps:

Step 1 – carbonization: means thermal treatment (pyrolysis) of the carbon precursors under inert gas atmosphere and high temperatures (600–700 °C) to obtain

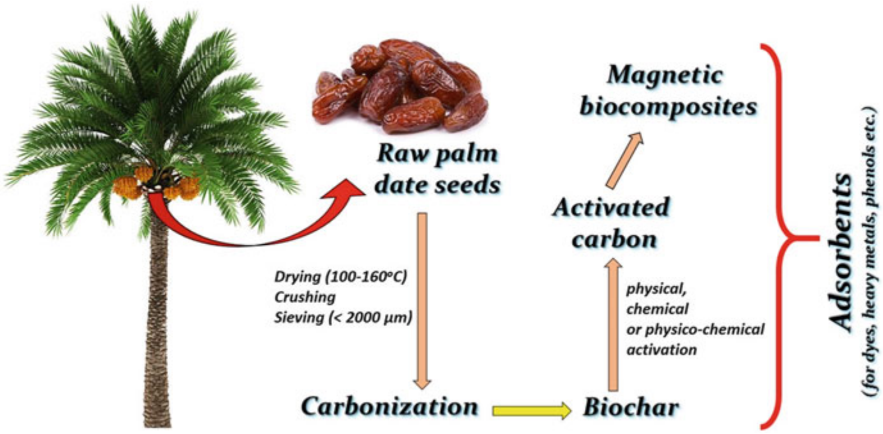


Fig. 11.6 Activated carbon preparation from date palm seeds

a ***biochar*** – a stable solid rich in carbon; but very often the obtained biochar shows low adsorption capacity and needs an activation step to increase its pore volume, porosity and surface area;

Step 2 – activation:

- ***physical activation***: using of CO_2 atmosphere or steam at temperatures above 700 °C; the high level of internal carbon mass is undesirable so it must to be removed to obtain a carbon with well-developed structure (Ahmadpour and Do 1996; Belhachemi et al. 2009);
- ***chemical activation***: the carbonization of the palm date pits precursor in the presence of chemical activators such as KOH, K_2CO_3, NaOH, Na_2CO_3, $AlCl_3$, $FeCl_3$, $ZnCl_2$, H_3PO_4 H_2SO_4 at temperatures lower compared to the physical activation (400–800 °C) and for shorter periods of time; these conditions help to get activated carbons with high surface area and porosity (Ao et al. 2018);
- ***physico-chemical activation***: simultaneous combination of physical and chemical activations after carbonization process in the temperature range 600–850 °C with using the potassium hydroxide, zinc chloride or orthophosphoric acid (as dehydrating agents) and CO_2 or steam (as oxidizing agents) leading to obtain a high porous structure (Ahmed 2016).

A wide number of studies have reported the preparation of activated carbon from date palm seeds by application physical or chemical activation. Ogungbenro et al. (2017) reported about activated carbon prepared from palm date seeds by physical activation for CO_2 capture applications. It was shown, that the optimal temperature for thermal treatment is 800 °C, while activated carbon obtained at 900 °C had the highest CO_2 adsorption capacity equal 141.14 mg/g. Md. A. Islam et al. (2015) prepared mesoporous activated carbon from palm date seed by alkaline activation of hydrochar. The activated carbon had high BET surface area equal 1282.49 m^2/g and the maximum adsorption capacity in regarding to methylene blue dye 612.1 mg/g. A. El Nemr et al. (2008) prepared activated carbon from date palm seed by dehydrating methods using boiling for 20 h with concentrated sulfuric acid (98%, 2.0 l). Its capacity to remove toxic chromium from different aqueous solutions was evaluated, reaching a maximum adsorption capacity 120.48 $mg.g^{-1}$ (for Cr (VI) concentration is 75 $mg.l^{-1}$ and carbon adsorbent concentration is 4 $g.l^{-1}$).

Magnetic biocomposite was fabricated by (M. Gazi et al. 2017) through the co-precipitation of palm seed-based biochar in the presence of magnetite particles (Fig. 11.7). Such magnetically separable palm seed-based biochar was investigated for the removal of Ni^{2+} ions. The as-prepared biocomposite has a surface area of 135 $m^2.g^{-1}$ and a saturation magnetization of 65.8 $Am^2.kg^{-1}$, with the Ni (II) removal ability reaching 87% (28 $mg.g^{-1}$) at pH 3. It was shown that the magnetic biocomposite can be regenerated without loss of its activity.

11.3.2 Chemical Composition, Surface Morphology and Microstructure

The different techniques used for physico-chemical characterization includes surface morphology, microtexture and element composition of date palm seeds biomass, such as FTIR, SEM, BET, TG-DTA-DTG etc. Approximate analysis have shown that the *chemical composition* of palm date seeds is follow: 4.9% moisture, 76.6% volatile matter, 10.8% ash, 7.7% fixed carbon (Hani H. Sait et al. 2012).

Scanning electron microscopy (SEM) observations usually reveal a porous microstructure of activated carbon. From Fig. 11.8a it is clearly seen that crushed raw date seeds have non-porous microstructure. After thermal treatment (for example, at 900 °C) the porosity increases and large pores clearly seen on the activated carbon texture (Fig. 11.8b), which leads for increasing of adsorption capacity in regarding to CO_2 (A. E. Ogungbenro et al. 2018).

Fourier-transform infrared spectroscopy (FTIR) helps to obtain information about the lignocellulosic composition of palm date seeds and the presence of different surface functional groups (alkene, ester, aromatic, alkanone, alcohol, hydroxyl, ether and carboxyl) (A. E. Ogungbenro et al. 2018). Usually the FTIR spectra of palm date seeds and activated carbon consists of several main adsorption peaks (Table 11.3). The broad adsorption peak at 3500–3500 cm^{-1} corresponds to free hydroxyl groups on the palm date seeds surface. The peak around ~2900 cm^{-1} related to asymmetric and symmetric stretching modes of the C–H bond of $–CH_2$ group. The peak around 1700 cm^{-1} corresponds to the stretching vibration of carboxyl group (–COOH, $–COOCH_3$) and carboxylic acids or their esters. The peaks at 1500, 1380, and 1100–1150 cm^{-1} are related C–C and C–O bonds

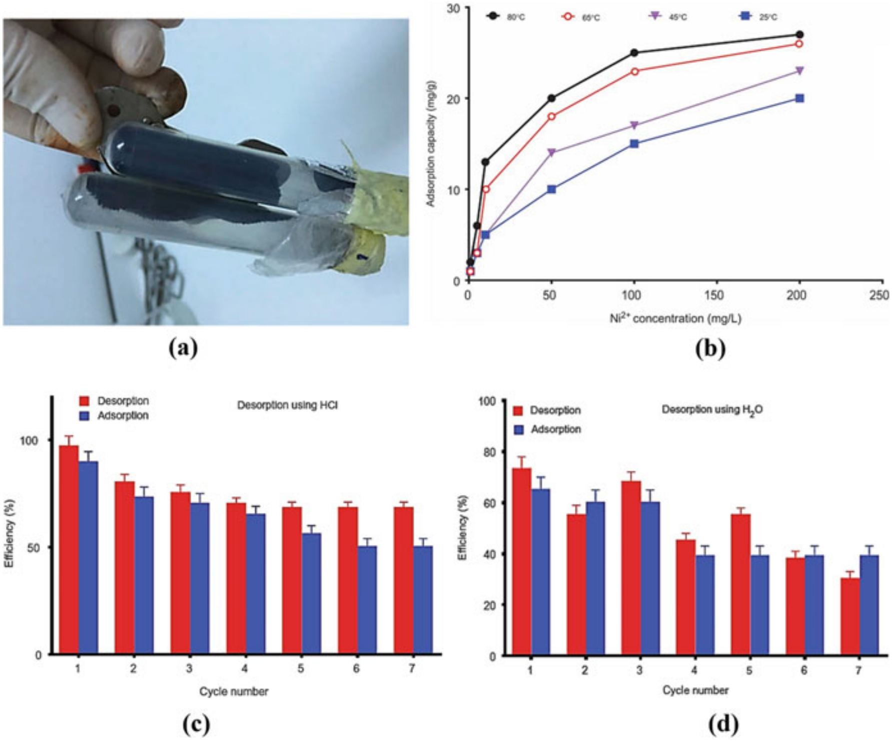


Fig. 11.7 Magnetic palm seed-based biochar and it's activity in nickel removal (**a**) magnetically separable palm seed-based biochar; (**b**) adsorption isotherms for magnetic biochar at different temperatures; (**c**, **d**) adsorption-desorption cycles using HCl (**c**) and H_2O (**d**) regenerants). (Reprinted from M. Gazi et al. (2017), Copyright (2017), with permission from Elsevier)

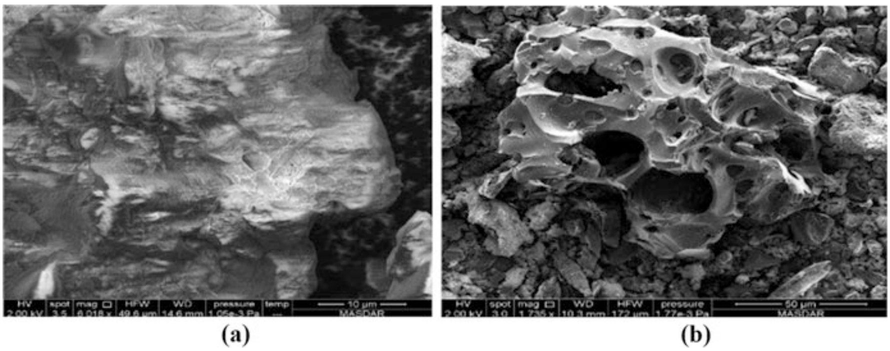


Fig. 11.8 SEM of crushed raw date seeds (**a**) and carbon samples after physical activation (**b**) with enhance adsorption capacity for CO_2 capture. (Reprinted from A. E. Ogungbenro et al. (2018), Copyright (2018), with permission from Elsevier)

Table 11.3 The main absorption peaks and corresponding functional groups in palm date seeds

Wavenumber (cm^{-1})	Functional groups of raw date seeds/activated carbon from palm data seeds
~3500–3300	O–H (existence of water, phenols, alcohols, carboxylic acids)
~2900–2950	C–H (CH_2 and CH_3 stretching vibrations)
~1700–1600	C=O (stretching vibration of carboxyl groups (–COOH, –$COOCH_3$)
~1530	Aromatic ring
~ 1390–1450	C–C (presence of alkanes)
~ 1100–1150	C–O (existence of alcohols, esters, ethers, carboxylic acids)

(Table 11.3) (D. Pathania et al. 2016). As pyrolysis occurs, infrared peaks become less intense due to fragmentation of correspondent functional groups. The bands around 3500 and 2900 cm^{-1} disappear due to decrease in moisture amount and aliphatic compounds in the seeds. The physical and chemical activation leads to stretching of the carbonyl group C=O (observed in the peak at ~1700–1600 cm^{-1}) (Ogungbenro et al. 2018).

M.A. Al-Ghouti et al. (2010) investigated the adsorption mechanisms of methylene blue dye onto date palm seeds through FTIR spectroscopy (Fig. 11.4). The FTIR data indicated interactions of the methylene blue molecules with functional groups on the data palm seeds surface (Fig. 11.9a). The *hydrogen bonding* between the seed's surface hydroxyl groups and the nitrogen atoms of dye molecules and *electrostatic attraction* as two mechanisms of adsorption on the palm pits surface were observed (Fig. 11.9b and c).

11.4 Palm Seeds Applications in The Removal of Pollutants from Water

Treated palm dates stones is a potential bio-adsorber that has been used effectively to eliminate residuals and un-degradable materials such as metals (Danish et al. 2012), dyes (Daoud et al. 2017) and acids (Salman and Al-saad 2012) from aqueous solutions. Adsorption is well known as an efficient chemical approach that depends mainly in chemical bonding between adsorber and adsorbents (Ahmed 2016) and hence it is highly affected by the chemical and physical conditions of the medium such as pH (Mahdi et al. 2018), temperature (Danish et al. 2017), time (Al-Saidi 2016), string speed (Islam et al. 2015) and initial concentration of the adsorber and pollutants (Salman and Al-saad 2012). Table 11.4 illustrates the different pollutants used for adsorption procedures applying palm seeds stones.

Adsorption process would reach an equilibrium stage where no more pollutant can be adsorbed. The amount of the adsorbed pollutants at equilibrium and at any time can be calculated applying the following Eqs. (11.1–11.2)

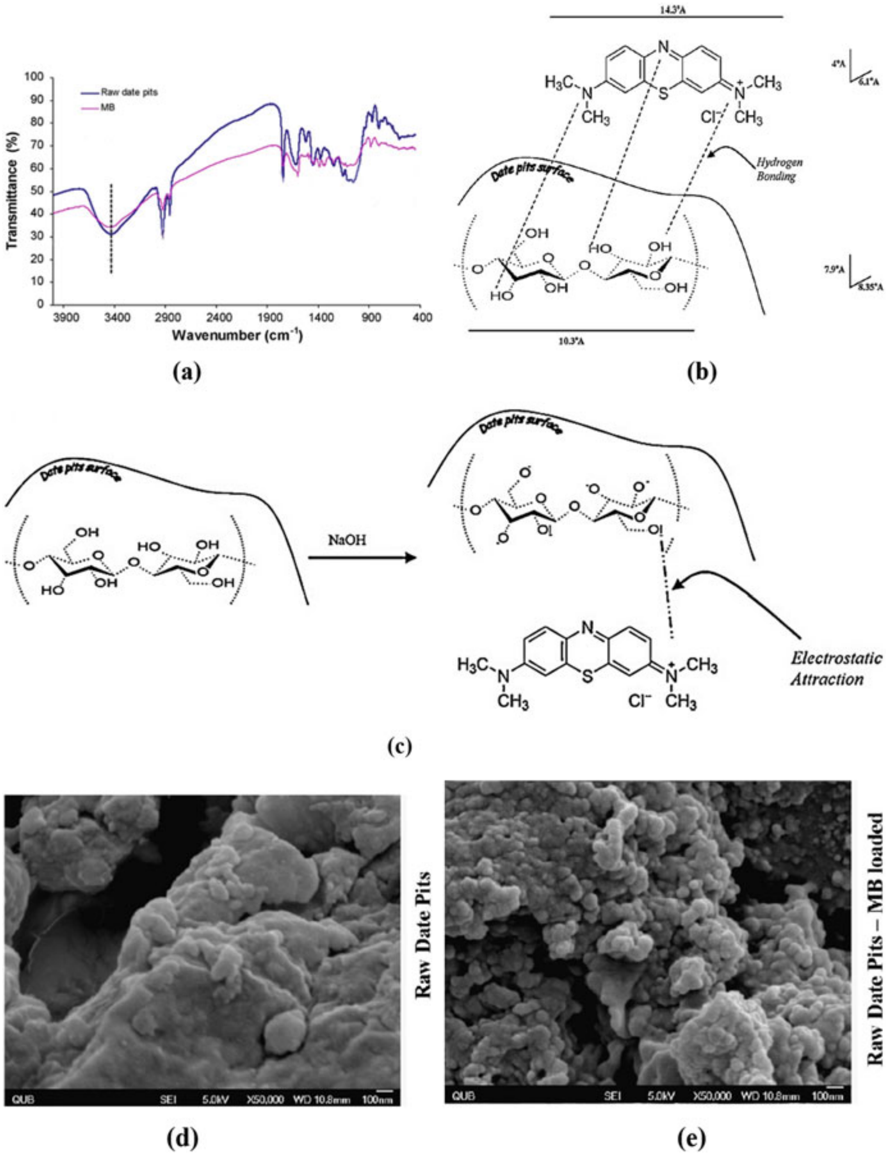


Fig. 11.9 Adsorption mechanisms of removing MB dye using date pits adsorbent: (**a**) FTIR spectra of the raw date pits and raw date pits-MB loaded samples respectively; (**b**) hydrogen bonding between methylene blue dye molecule and OH-groups on the seeds surface; (**c**) electrostatic attraction between dye molecule and the cellulose unit of the seeds surfaces; (**d**) SEM micrographs for the raw date pits and (**e**) raw date pits-MB loaded samples respectively. (Reprinted from M.A. Al-Ghouti et al. (2010), Copyright (2010), with permission from Elsevier)

Table 11.4 Examples of metals that can be removed applying palm seeds adsorbers

Heavy metal	Experimental conditions	Max obtained removal efficiency (%)	References
Copper (Cu)	Solution (50 mL) C_0: 300 mg.L^{-1}, pH = 4	44	Gueu et al. (2006)
Lead (Pb)	Solution (50 mL) C_0: 300 mg.L^{-1}, pH = 4	51	Gueu et al. (2006)
Zinc (Zn)	Solution (50 mL) C_0: 300 mg.L^{-1}, pH = 4	41	Gueu et al. (2006)
Chromium (Cr)	C_0: 125 mg.l^{-1}, pH 1.0, speed: 200 rpm, 27 °C	70	El Nemr et al. (2008)
Gold (Au)	Solution (100 mL), HCl (0.5 Mol.L^{-1}), speed (150 rpm), 25 ± 0.1 °C	90	Al-Saidi (2016)
Bromide (Br)	Solution (50 mL), $C_{0:}$ 200 mg L^{-1} pH = 4	57	Al-Ghouti et al. (2017)
Nickel (Ni)	Solution (10 g L^{-1}); C_o = 1.0 mM pH = 6, room temperature	80	Mahdi et al. (2018)

$$q_e = \frac{(C_i - C_e)V}{W} \tag{11.1}$$

$$q_t = \frac{(C_i - C_t)V}{W} \tag{11.2}$$

where C_i, C_e, and C_t (mg/L) are the liquid phase concentrations at initial, equilibrium, and time t (min), respectively, V is the solution volume (mL) and W is the adsorbent mass used (g) (Pathania et al. 2016). Hence the removal efficiency can be also determined from the equation:

$$R\% = \frac{(C_i - C_e)}{C_i} \times 100 \tag{11.3}$$

Different fitting models can be chosen to explain the behavior and mechanism of a certain removal procedure with consideration to the different parameters such as equilibrium, adsorption constants, adsorption energy, adsorbed solute and concentration solute. These models include Pseudo (Islam et al. 2015) Langmuir, Freundlich, Koble–Corrigan, Redlich–Peterson, Tempkin, Dubinin–Radushkevich and Generalized isotherm equations (El Nemr et al. 2008).

11.4.1 Heavy Metal Removal

The idea of heavy metal removal by applying extracts from palm seeds has been proposed since many years because of it low cost and availability (Gueu et al. 2006).

Activated carbon was extracted from the seed shell of palm trees and used to prepare an adsorbent (GA) for heavy metals (Cu, Pb and Zn). The catalyst was characterized in term of Ash content, acidity group and surface area (95 $m^2 g^{-1}$), which plays the major role in the adsorption process. Adsorption test was carried out with a metal solution of 300 mg/L for each Cu, Pb and Zn with three different adsorbent mass (2, 4 and 6 g). The results were compared with other adsorbent extracted from coconut shell. It was found that a considerable percentage of metal was adsorbed due to the precedence of GA adsorbent as the removal increases with GA amount. The process was shown to be more efficient with Pb metal as it reached 50.67% in 30 min. It was also seen that the adsorption percentage raised dramatically by changing the pH from 2 to 4 and then remains almost steadily from pH 4 to 10 (Gueu et al. 2006).

Activated Carbon from date palm seeds were also used for the adsorption of chromium Cr^{+6} from wastewater. Full adsorption kinetics were applied using different amount of Cr^{+6} (25, 50, 75, 125 mg^{-1}) in 100 mL of water. During a period of 180 min, a 100% of removal efficiency was achieved at 25 mg/L of Cr^{+6}. This efficiency decreased gradually with increasing the initial concentration until reaching 70% at 125 mg/L and pH 1 which was found to be the optimum acidity for the reaction. The removal efficiency was affected negatively by raising the pH level of the medium (from 1 to 8) (El Nemr et al. 2008).

Date pits have been involved in the removal of Nobel metals (Au) pollutants from water. Dried and crushed date pits of palm trees in KSA have been through several chemical treatments before applying it as an adsorbent. The characterization of the adsorber was investigated in term of morphology and chemical properties. Scanning electron microscopy observations showed a smooth surface that become rougher by the adsorption of Au particles (Fig. 11.10a–b). Batch adsorption procedure with 100 mL of aqueous solution and 10 mM of Au ions with presence of 0.5 molL-1 of HCl showed a remarkable percentage of removal efficiency. Figure 11.10c shows a maximum of 90% in 120 min where the reaction reached its equilibrium. It is shown that the first stage (40 min) experienced higher rate of adsorption due to the availability of adsorption sites that eventually will be filled with the Au particles which prevents further adsorption and the reaction reaches equilibrium. For further explanation of the Au attachment to the to the palm seed sdsorber, FTIR was applied before and after the adsorption process to investigate the difference in chemical bonding (Fig. 11.10d). A shift in the hydroxyal group was noticed after adsorption which indicates the formation of new hydrogen bond which cause the Au particles to interact with the adsorber. Also, several shifts to lower wavelengths were seen in other existing bonds. XRD analysis was also carried out to confirm the pure metallic Au formation on the surface of the adsorber (Al-Saidi 2016).

Date pits were applied to desalinated water to clear Bromide ions. It went through the conventional physical and chemical treatments to prepare two adsorbents (roasted and unroasted) that were compared with commercial activated carbon (Al-Ghouti et al. 2017). SEM images showed a narrow pore microstructure associated with both roasted and unroasted. However, the roasted adsorbent showed more

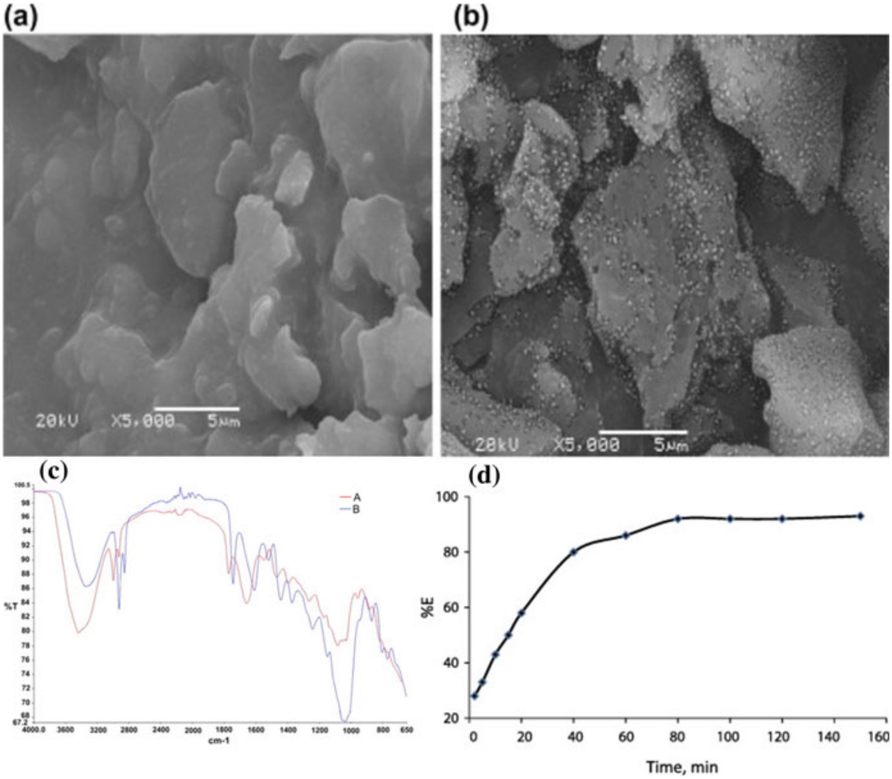


Fig. 11.10 SEM images of RDPs taken (**a**) before and (**b**) after adsorption of Au(III); (**c**) FT-IR spectra of RDPs (*A*) before and (*B*) after adsorption of Au(III); (**d**) the effect of time on removal percentage of Au(III) by RDPs. Conditions: test solution (100 mL), HCl (0.5 mol L^{-1}), RDP doze (0.1 ± 0.001 g), shaking speed (150 rpm), and temperature (25 ± 0.1 °C). (Al-Saidi 2016)

pure surface with less contaminations. The adsorption process was shown to be affected by the pH of the medium as pH 4 (weak acidic medium) showed the maximum adsorption of 57% of Br. This was explained as the higher values of pH (pH 8 and 11) might change the ionization and the charge on the adsorbent surface and hence affect the uptake of the negative Br- ions. In the other hand, the excess of the H+ in the weak acidic medium (pH = 4) changes the anion groups on the surface to cationic groups that assess the adsorption process. With further increase in acidity (pH = 2), the adsorption was found to be decreased because of the creation of chlorine ions that negatively affect the process (Al-Ghouti et al. 2017).

Two adsorption isotherm fittings (Freundlich and Langmuir) were applied to explain the mechanism of the process. It was indicated clearly that the non-linear model (Freundlich) fits well with the adsorption behavior (Fig. 11.11a). Kinetic models showed that the surface functional groups as well as the pore microstructure of the date pits adsorber highly influenced the efficiency of the adsorption. It was also shown that the grain size affects the kinetics of the removal as three different

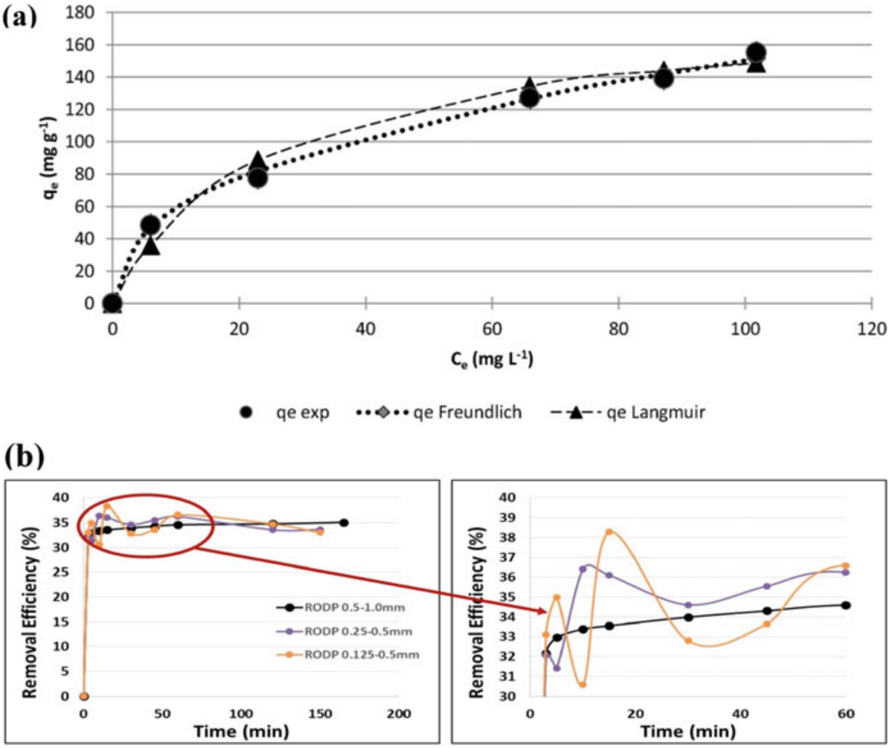


Fig. 11.11 (**a**) Adsorption isotherm fitting to experimental data using Freundlich and Langmuir isotherms for roasted date pits adsrorber; (**b**) effect of particle size on the removal efficiency of Br- with roasted palm date pits: mass 1.0 g, KBr initial concentration 200 mg L^{-1}, and pH 4, at particle size 0.5–1.0 mm, 0.25–0.5 mm, and 0.125–0.25 mm. (Al-Ghouti et al. 2017)

ranges of grain size were investigated (0.5–1, 0.25–0.5 and 0.125–0.25 mm). With larger range of grain size, more fluctuation was observed in the first 60 min of the adsorption process where all the sizes have the same behavior after reaching the saturation level (Fig. 11.11b). The effect of the initial concentration and the adsorbant mass were also reported (Al-Ghouti et al. 2017).

Moreover, Ni^{2+} and Cu^{2+} ions were shown to be effectively removed from aqueous solution by applying biochar samples prepared from palm dates pits using different calcinations temperatures (350, 450 and 550) and time periods (1, 2 and 3 h). adsorption procedures were carried out through Batch experiment (Fig. 11.12a) and all samples showed a considerable efficiency in the removal of Ni and Cu ions with the maximum rate for the sample with highest calcination temperature and time (550 °C at 3 h). Therefore, the latter sample was chosen for further experiments to investigate the effect of pH, particle size and contact time. It was shown that as pH increases from 2 to 6, the adsorption capacity increases too by 30% (Fig. 11.12b). The lower adsorption in lower pH medium referred to the creation of H+ ions that decrease the active adsorption sites in the adsorbent. It is well-known that the pH of a

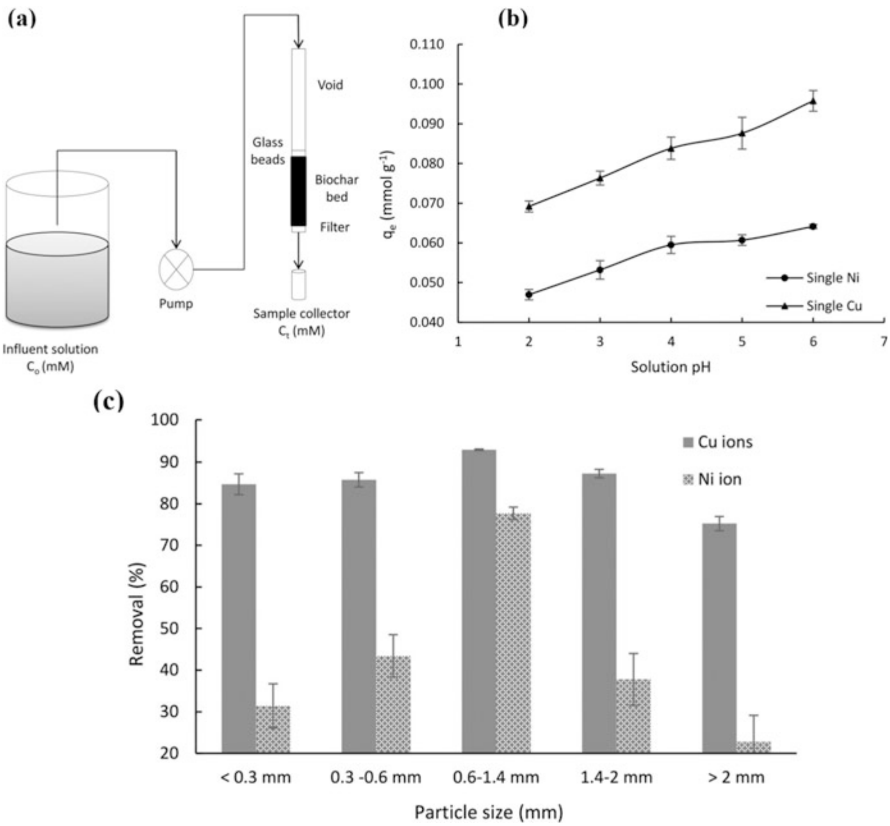


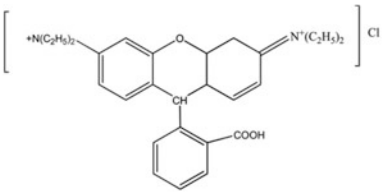
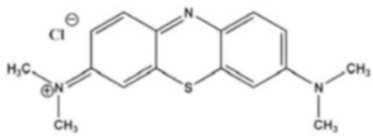
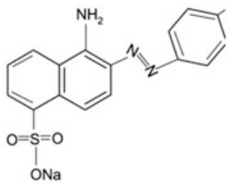
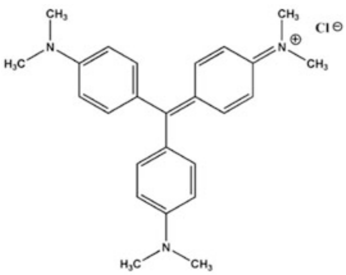
Fig. 11.12 (**a**) Fixed bed adsorption arrangement; (**b**) effect of pH on the adsorption of Cu^{2+} and Ni^{2+} onto biochar (room temperature; biochar: solution = 10 g L^{-1}; C_o = 1.0 mM); (**c**) effect of biochar particle size on the adsorption of Cu^{2+} and Ni^{2+} (room temperature; biochar: solution = 10 g L^{-1}; C_o = 0.5 mM). (Mahdi et al. 2018)

medium would highly affect the surface functional groups such as carboxyl (COOH), Amino (NH) and hydroxyal (OH hence strongly affect the adsorption process. Experiments also revealed that at a certain particle size range (0.6–1.4 mm) of the prepared adsorber, the removal efficiency reached its maximum. Lower and higher ranges of sizes caused lower rates of removal efficiencies. This was more noticeable in the case of Ni adsorption (Fig. 11.12c) (Mahdi et al. 2018).

11.4.2 Removal of Dyes

Dyes are one of the most found pollutants in water and most of them are organic and non-biodegradable, thereby they accumulate in water causing serious problems to

Table 11.5 Examples of dyes that can be removed using palm dates seed adsorber

Dye	Color	Chemical composition	Max obtained removal efficiency	References
Rhodamine B (RhB)			67%	Danish et al. (2017)
Methylene Blue (MB)			99%	El Messaoudi et al. (2016)
Congo Red (CR)			76%	Pathania et al. (2016)
Crystal Violet (CV)			99%	El Messaoudi et al. (2016)

environment habitat and human health (Ahsaine et al. 2018; Pathania et al. 2015). Date seeds were shown to have a considerable effect during the removal process of these dyes from water. Table 11.5 shows some of the dyes that can be adsorbed by treated date seeds adsorber.

Mesoporous activated carbon was produced from palm tree seeds and applied for the degradation of MB dye that reached its maximum (450 mg.g^{-1})) around 700 min (Islam et al. 2015). It was also shown that the amount of the dye removal depends on the amount of the palm seeds adsorbent (Fig. 11.13a). At a very low concentration (50 mg.L^{-1}), almost no removal achieved whereas by increasing the amount gradually to 100, 200, 300, 400 and 500 mg.L^{-1}, the removal efficiency started to increase too until it reached its maximum at the highest amount of adsorbent.

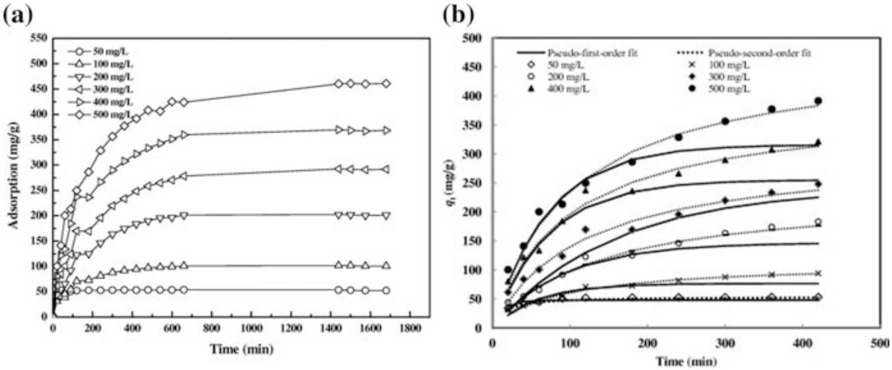


Fig. 11.13 (**a**) Effect of contact time and initial concentration on removal of MB onto HTC–PDS3 at 30 °C (**b**) Adsorption isotherm fitting to experimental data using Pseudo first and second order isotherms. (Islam et al. 2015)

Performing the adsorption experiment with different pH showed that the removal efficiency is better at higher pH (10 and 12). Adsorption isotherm studies showed that the Pseudo second order model has better fitting to the adsorption behavior (Fig. 11.13b) (Islam et al. 2015).

Also, activated carbon from date seeds has been applied efficiently for the removal of RhB dye (Danish et al. 2017). FESEM images taken before and after the adsorption process revealed the difference in the morphology of the adsorbent after attachment with the dye. Figure 11.14a showed lower porosity for the adsorbent after dye adsorption confirming that the dye molecules are attached to the adsorbent and significantly blocking the pores. EDS analysis showed changes in elemental composition of the adsorbent as a result of the dye attachment as the carbon weigh percent increased slightly due to the attachment with the organic dye that contains carbons in its chemical chain. The effect of pH and initial concentration were confirmed too showing the same trend of the previous studies. Intensive analysis was carried out to explain the behavior of the adsorption by applying various fitting models and Box-Behnken design experiment Fig. 11.14b where the number of parameters such as dosage, concentration, time, temperature and pH were taken into account simultaneously. Moreover, the process maintained its efficiency over four adsorption cycles (Fig. 11.14c) (Danish et al. 2017).

Furthermore, Congo Red (CR) dye was shown to be efficiently removed from aqueous solution by applying the palm seeds adsorber (Pathania et al. 2016). FTIR used to study the effect of the adsorption and to have more understanding to its mechanism, revealed several peaks shift into higher/lower wavelengths which indicates weakness/strength of the corresponding bonds. New peaks immerged as a result of the attachment between the dye and the adsorbent as well as the creation of new chemical bonds (Fig. 11.15a). Similar to other studies, the adsorption was influenced by pH and initial concentration. Moreover, the effect of temperature was examined too and higher temperature medium (55 °C) showed higher

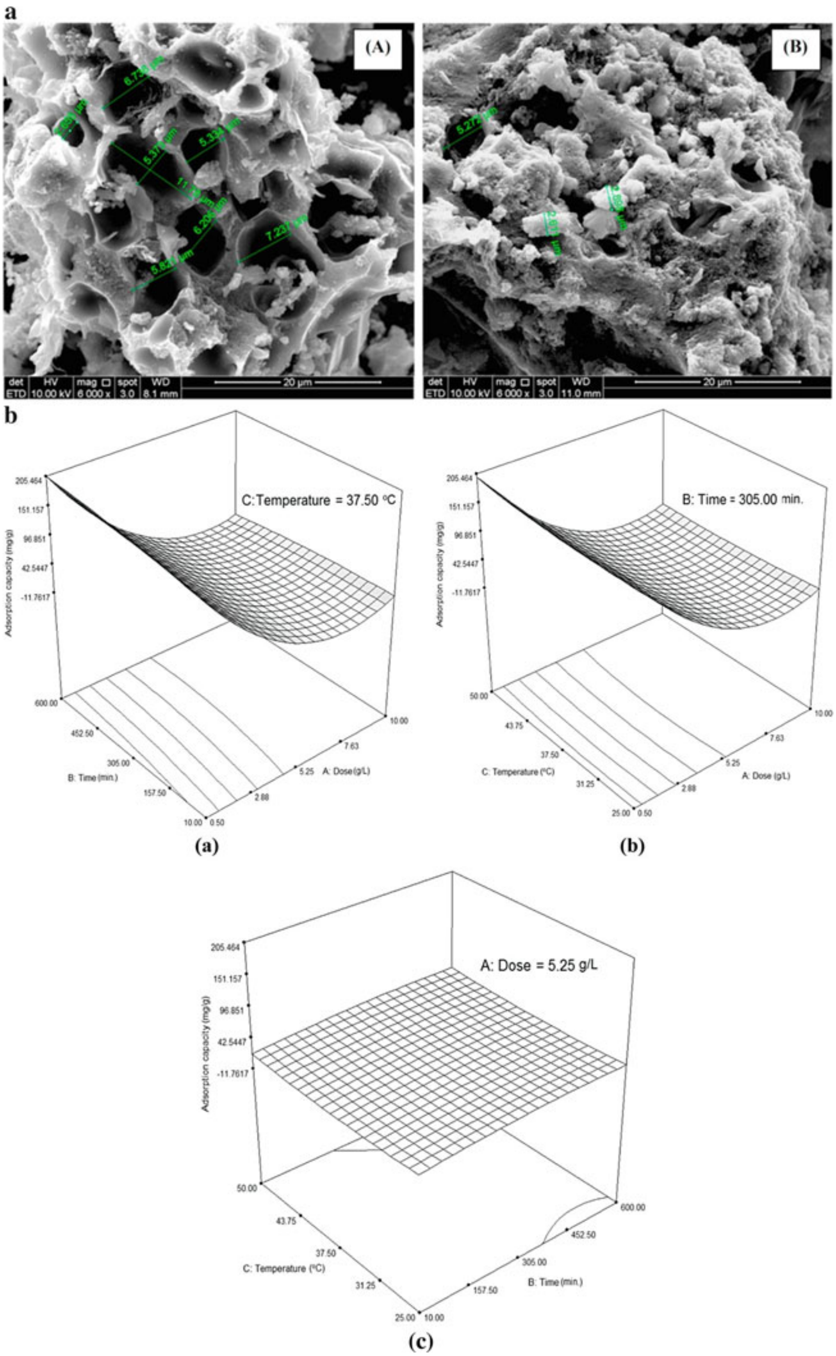


Fig. 11.14 FESEM images of activated carbon extracted from date seeds (*A*) before and (*B*) after RhB adsorption; (**b**) 3D response surface graph for adsorption capacity versus (**a**) time and adsorbent dose (**b**) temperature and adsorbent dose (**c**) temperature and time; (*c*) Adsorption efficiency and reusability of activated carbon from dates pits for RhB in various recycles. (Danish et al. 2017)

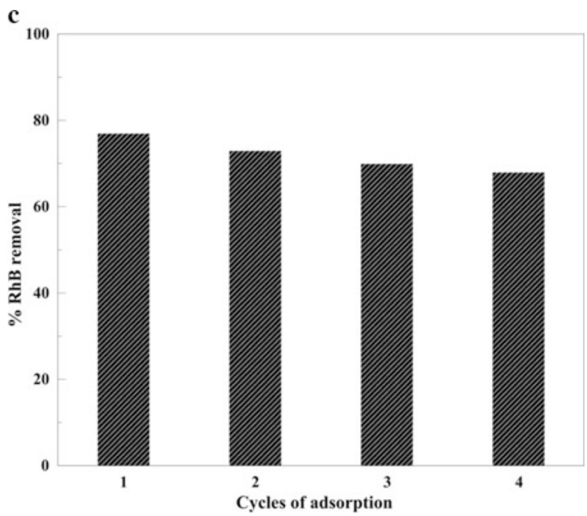


Fig. 11.14 (continued)

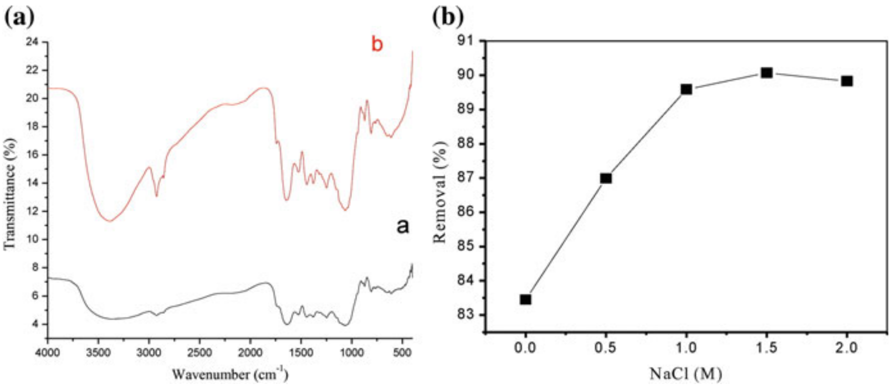


Fig. 11.15 (**a**) FTIR spectrum of the date pits adsorber before (**a**) and (**b**) after adsorption; (**b**) effect of ionic strength for CR dye adsorption onto date pits [dye concentration 20 mg/L, sorbent dosage 0.60 mg, pH 2.0, contact time 120 min, temperature 30 °C]. (Pathania et al. 2016)

adsorption capacity, due to the higher diffusion of the dye molecules into the adsorbent pores. The effect of the ionic strength of the medium (Fig. 11.15b) by adding different amount of NaCl salt from 0 to 1.5 M, indicated that the removal efficiency was positively enhancing from 83.45 to 89.83%, respectively. The presence of NaCl increases the dye agglomerates and hence causes better attachment to the adsorber (Pathania et al. 2016).

It is very essential to mention here that the influence of pH, temperature and initial concentration is different and the trend is changing form a study to another based on many reasons including the chemical reaction between the dye and the adsorbent as different dyes and different absorbents combination is not necessarily affected by experimental conditions in the same manner. Table 11.2 illustrates the chemical composition of different dyes.

Another study, investigated the efficiency of the treated palm seeds on the adsorption of the reactive dye (BEZAKTIV Red S-MAX) and compared with the commercial activated carbon. Three temperatures where applied for the adsorption experiment (298, 308 and 318 K) and the results was similar to previous studies as the maximum adsorption occurred at the highest temperature (Fig. 11.16a). However, for pH effect, the result was different than other reported studies. It was found that the optimum pH for the reaction is 8 while at pH 10 the adsorption decreased (Fig. 11.16b). This was related to the surface properties of the adsorbent and the degree of ionization of the dye (Daoud et al. 2017).

On the other hand, another study showed different effect of the initial concentration when Crystal violet (CV) dye was adsorbed by treated palm seeds

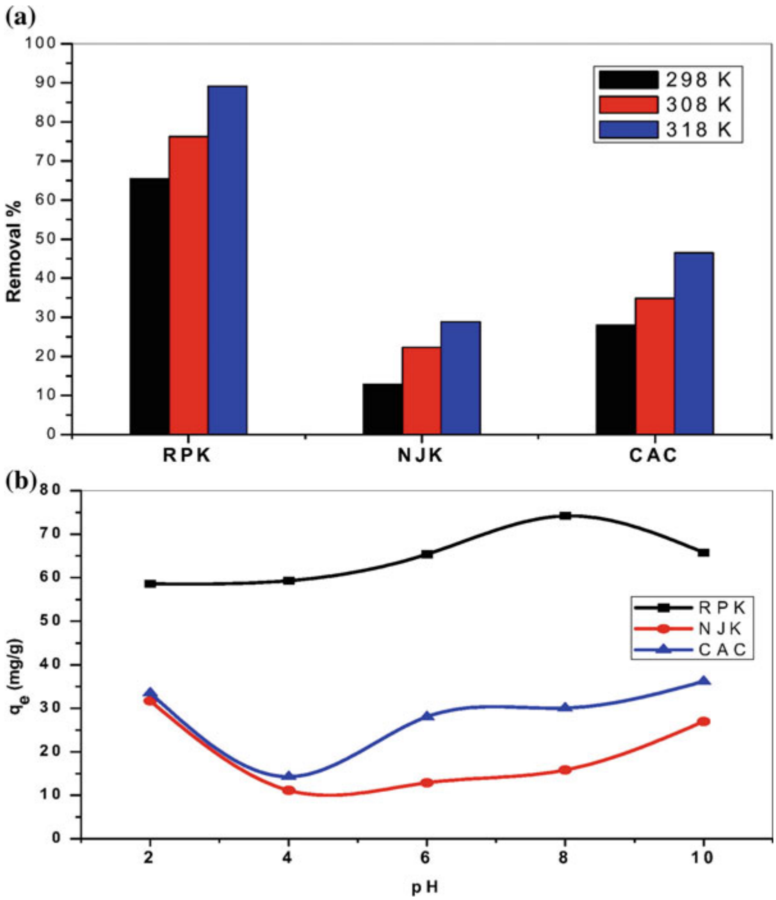


Fig. 11.16 (**a**) Effect of solution temperature on dye uptake on RPK (date pits), NJK (other adsorbers) and CAC (activated carbon); (**b**) The variation of the pH Effect on the adsorption of dye uptake on RPK (date pits), NJK (other adsorbers) and CAC (activated carbon). (Daoud et al. 2017)

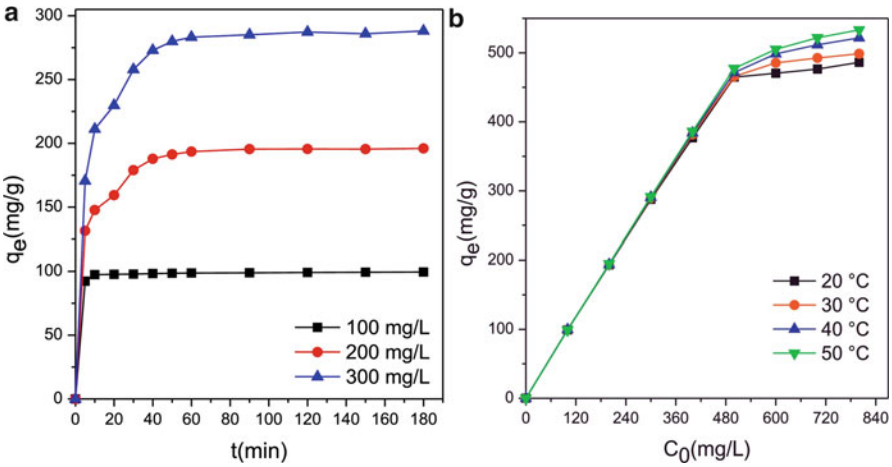


Fig. 11.17 Effect of (**a**) initial concentration of and (**b**) temperature in the adsorption of CV dye. (El Messaoudi et al. 2016)

(El Messaoudi et al. 2016) as the adsorption was found to increase with increasing the dye concentration (in other words with decreasing the actual amount relative amount of adsorbent to dye) (Fig. 11.17a). This was explained as the enhancement of mass transfer rate that increases the effective mass ratio of the dye/adsorbent. The same behavior was also seen with MB dye using the same adsorbent. The combined effect of temperature and dye concentration showed that the influence of temperature is almost unnoticeable until reaching a certain dye concentration of 480 $mg.L^{-1}$ where higher temperature causes a higher adsorption rate (Fig. 11.17b) (El Messaoudi et al. 2016).

11.4.3 Other Pollutants

Palm dates seeds have also shown to be efficient in the removal of other pollutants such as Nitrophenols which is a highly toxic acid that comes from pesticides applications, refineries and manufacturing. A statistical analysis design was applied for the adsorption batch experiment depending on pH, time, concentration, temperature and speed of shaking with a comparison of activated carbon. It was found that the efficiency of the removal of the date pits is 15% higher than the activated carbon. Toxicity analysis were performed too (Al-Mutairi 2010).

Chemically and thermally treated date stone were applied to remove three types of Drin pesticides (aldrin, dieldrin and endrin) from aqueous solutions. Three particle size ranges of the adsorbent were prepared and the smaller sizes were associated with the highest removal efficiency due to their larger surface area and hence this size range was applied for further investigations. It was shown that each type of acids has different response to the palm date adsorber and the Aldrin showed the highest amount of adsorption with time before it reaches equilibrium (Fig. 11.18a). It is very essential to mention here that the treatment of the date stone highly influenced the adsorption process (Fig. 11.18b). The effect of temperature was examined too as the temperature of the medium was raised gradually from 10 to 40 °C (by 5 °C in each interval). For the three acids, it was found that the removal percentage was decreased with increasing temperature. This result was different than results reported in previous mentioned studies and it was related to

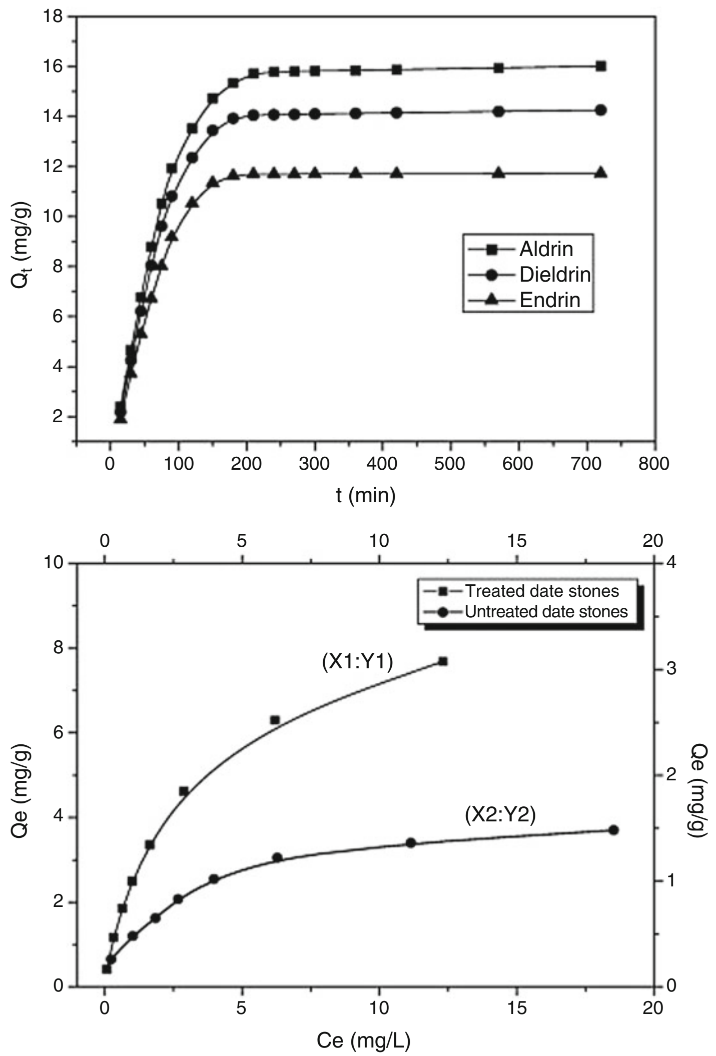


Fig. 11.18 (**a**) Adsorption kinetics of pesticides on acid-treated date stones (**b**) Adsorption isotherms of endrin on treated and untreated date stones determined at 25 °C. (El Bakouri et al. 2009)

the solubility of the pesticides as increasing temperature will make them more soluble and hence affect negatively their bonding with the palm seeds adsorber. (El Bakouri et al. 2009).

Palm seeds were found to be effective for the adsorption of other pollutants too. For examples acids, that undergo the same removal mechanisms of dyes and metals and the same fitting models can be applied (Salman and Al-saad 2012). Moreover, activated carbon was extracted from palm dates and used to remove 2,4-Dichlorophenoxyacetic acid. Three isotherms models were applied to fit the behavior of the removal (Lamgmuir, Freundlicn and Temkin) at three different temperatures 30, 40 and 50 °C. Here the effect of temperature is related to the chemical nature of the adsorbent. Endothermic nature materials tend to attach more with the adsorber in high temperatures whereas exothermic behaves in opposite way and its bonding with adsorber become weaker at higher temperatures (Salman and Al-saad 2012).

11.5 Conclusion

This chapter focused on the applications of date seeds in the removal of different pollutants from wastewater. Most of these pollutants are metals, dyes and acids which are very difficult to be biologically degraded in nature causing major hazard to the environment. It was shown that the stones of the palm dates represent a great potential adsorber for these different pollutants with a very high rate of removal that can be compared with other well-known adsobers such as activated carbon. Studies revealed that the extraction and treatment procedure of the date stones adsorber affect greatly the removal efficiency. This comes along with the adsorption experimental parameters mainly pH, temperature and initial concentration. Understanding the adsorption kinetics needs fitting with standard adsorption models that take into account all of these different factors. Therefore, it can be concluded that the palm date stones which is mostly considered as a food waste can be turned to an efficient adsorber of highly toxic pollutants. Such treated water can be reused in other domestic applications heading in the way of sustainable water resources and cleaner environment.

References

Abbas AF, Ahmed MJ (2016) Mesoporous activated carbon from date stones (Phoenix dactylifera L.) by one-step microwave assisted K_2CO_3 pyrolysis. J Water Process Eng 9:201–207. https://doi.org/10.1016/j.jwpe.2016.01.004

Abd-Alla MH, El-Enany AWE (2012) Production of acetone– butanol–ethanol from spoilage date palm (Phoenix dactylifera L.) fruits by mixed culture of Clostridium acetobutylicum and Bacillus subtilis. Biomass Bioenergy 42:172–178. https://doi.org/10.1016/j.biombioe.2012.03.006

Ahmadpour A, Do DD (1996) The preparation of active carbons from coal by chemical and physical activation. Carbon 34(4):471–479. https://doi.org/10.1016/0008-6223(95)00204-9

Ahmed MJ (2016) Preparation of activated carbons from date (Phoenix dactylifera L.) palm stones and application for wastewater treatments: review. Process Saf Environ Prot 102:168–182. https://doi.org/10.1016/j.psep.2016.03.010

Ahsaine HA, Zbair M, Anfar Z, Naciri Y, El Alem N (2018) Cationic dyes adsorption onto high surface area 'almond shell' activated carbon: kinetics, equilibrium isotherms and surface statistical modeling. Mater Today Chem 8:121–132. https://doi.org/10.1016/j.mtchem.2018.03.004

Aitenneite H, Abboud Y, Tanane O, Solhy A, Sebti S, Bouari A (2016) Rapid and green microwave-assisted synthesis of silver nanoparticles using aqueous phoenix dactylifera L. (date palm) leaf extract and their catalytic activity for 4-Nitrophenol reduction. J Mater Environ Sci 7:2335–2339. http://Document/vol7/vol7_N7/251-JMES

Al-Farsi MA, Lee CY (2008) Optimization of phenolics and dietary fibre extraction from date seeds. Food Chem 108:977–985. https://doi.org/10.1016/j.foodchem.2007.12.009

Al-Ghouti MA, Li J, Salamh Y, Al-Laqtah N, Walker G, Ahmad MNM (2010) Adsorption mechanisms of removing heavy metals and dyes from aqueous solution using date pits solid adsorbent. J Hazard Mater 176(1–3):510–520. https://doi.org/10.1016/j.jhazmat.2009.11.059

Al-Ghouti MA, Al Disi ZA, Nasser Al-Kaabi N, Khraisheh M (2017) Mechanistic insights into the remediation of bromide ions from desalinated water using roasted date pits. Chem Eng J 308:463–475. https://doi.org/10.1016/j.cej.2016.09.091

Al-Hooti S, Sidhu J, Qabazard H (1998) Chemical composition of date seed fruit cultivars of United Arab Emirates. J Food Sci Technol 35:44–46. https://doi.org/10.1016/0308-8146(95)00051-J

Ali MA, Al-Hattab TA, Al-Hydary IA (2015) Extraction of date palm seed oil (Phoenix Dactylifera) by Soxhlet apparatus. Int J Adv Eng Technol 8:261–271. http://ijaet.org/media/3I27-IJAET0827749-v8-iss3-261-271

Al-Muhtaseb AH, Jamil F, Al-Haj L, Al-Hinai MA, Baawain M, Myint MTZ, Rooney D (2016) Efficient utilization of waste date pits for the synthesis of green diesel and jet fuel fractions. Energy Convers Manag 127:226–232. https://doi.org/10.1016/j.enconman.2016.09.004

Al-Mutairi NZ (2010) 2,4-Dinitrophenol adsorption by date seeds: effect of physico-chemical environment and regeneration study. Desalination 250:892–901. https://doi.org/10.1016/j.desal.2008.10.035

Al-Saidi HM (2016) The fast recovery of gold(III) ions from aqueous solutions using raw date pits: kinetic, thermodynamic and equilibrium studies. J Saudi Chem Soc 20:615–624. https://doi.org/10.1016/j.jscs.2013.06.002

Amani MM, Abdel AH, Seham AM, Azza A, Gehan S (2016) Aqueous and methanolic extracts of palm date seeds and fruits (phoenix dactylifera) protects against diabetic nephropathy in type II diabetic rats. Biochem Physiol 5:2168–2177. https://doi.org/10.1080/10408398.2010.499824

Ambigaipalan P, Shahidi F (2015) Antioxidant potential of date (Phoenix dactylifera L.) seed protein hydrolysates and carnosine in food and biological systems. J Agric Food Chem 63:864–871. https://doi.org/10.1021/jf505327b

Amiri M, Salavati-Niasari M, Akbari A, Gholami T (2017) Removal of malachite green (a toxic dye) from water by cobalt ferrite silica magnetic nanocomposite: herbal and green sol-gel autocombustion synthesis. Int J Hydrog Energy 4:24846–24860. https://doi.org/10.1016/j.ijhydene.2017.08.077

Ao W, Fu J, Mao X, Kang Q, Ran C, Liu Y, Zhang H, Gao Z, Li J, Liu G, Dai J (2018) Microwave assisted preparation of activated carbon from biomass: a review. Renew Sust Energ Rev 92:958–979. https://doi.org/10.1016/j.rser.2018.04.051

Banerjee M, Basu RK, Das SK (2018) Cr(VI) adsorption by a green adsorbent walnut shell: adsorption studies, regeneration studies, scale-up design and economic feasibility. Process Saf Environ Prot 116:693–702. https://doi.org/10.1016/j.psep.2018.03.037

Barnaby R, Liefeld A, Jackson BP, Hampton TH, Stanton BA (2017) Effectiveness of table top water pitcher filters to remove arsenic from drinking water. Environ Res 158:610–615. https://doi.org/10.1016/j.envres.2017.07.018

Barreveld WH (1993) Date palm products: FAO agricultural services bulletin no. 101. Food and Agriculture Organization of the United Nations Rome. http://www.fao.org/docrep/t0681e/t0681e00.htm

Belhachemi M, Rios RVRA, Addoun F, Silvestre-Albero J, Sepúlveda-Escribano A, Rodríguez-Reinoso F (2009) Preparation of activated carbon from date pits: effect of the activation agent and liquid phase oxidation. J Anal Appl Pyrolysis 86(1):168–172. https://doi.org/10.1016/j.jaap.2009.05.004

Benzie IFF, Strain JJ (1996) The reducing ability of plasma as a measure of 'antioxidant power'- the FRAP assay. Anal Biochem 239:70–76. https://doi.org/10.1006/abio.1996.0292

Besbes S, Drira L, Blecker C, Deroanne C, Attia H (2009) Adding value to hard date (Phoenix dactylifera L.): compositional, functional and sensory characteristics of date jam. Food Chem 112:406–411. https://doi.org/10.1016/j.foodchem.2008.05.093

Carpentier SC, Witters E, Laukens K, Deckers P, Swennen R, Panis B (2005) Preparation of protein extracts from recalcitrant plant tissues: an evaluation of different methods for two-dimensional gel electrophoresis analysis. Proteomics 5:2497–2507. https://doi.org/10.1002/pmic.200401222

Crabbe E, Hipolito CN, Kobayashi G, Sonomoto K, Ishizaki A (2001) Biodiesel production from crude palm oil and evolution of butanol extraction and fuel properties. Process Biochem 37:65–71. https://doi.org/10.1016/S0032-9592(01)00178-9

Danish M, Hashim R, Ibrahim MN, Rafatullah M, Sulaiman O (2012) Surface characterization and comparative adsorption properties of Cr(VI) on pyrolysed adsorbents of Acacia Mangium wood and Phoenix dactylifera L. stone carbon. J Anal Appl Pyrolysis 97:19–28. https://doi.org/10.1016/j.jaap.2012.06.001

Danish M, Khanday WA, Hashim R, Binti Sulaiman NS, Akhtar MN, Nizami M (2017) Application of optimized large surface area date stone (Phoenix dactylifera) activated carbon for Rhodamin B removal from aqueous solution: box-Behnken design approach. Ecotoxicol Environ Saf 139:280–290. https://doi.org/10.1016/j.ecoenv.2017.02.001

Daoud M, Benturki O, Kecira Z, Girods P, Donnot A (2017) Removal of reactive dye (BEZAKTIV red S-MAX) from aqueous solution by adsorption onto activated carbons prepared from date palm rachis and jujube stones. J Mol Liq 243:799–809. https://doi.org/10.1016/j.molliq.2017.08.093

Devshony S, Ethesola A, Shani A (1992) Characterization and some potential application of date palm (Pheonix Dactylifera L) seeds and seed oil. J Am Oil Chem Soc 69:595–597. https://doi.org/10.1007/BF02636115

Dobias P, Pavlikova P, Adam M, Eisner A, Benova B, Venture K (2010) Comparison of pressurised fluid and ultrasonic extraction methods for analysis of plant antioxidants and their antioxidant capacity. Cent Eur J Chem 8:87–95. https://doi.org/10.2478/s11532-009-0125-9

El Bakouri H, Usero J, Morillo J, Rojas R, Ouassini A (2009) Drin pesticides removal from aqueous solutions using acid-treated date stones. Bioresour Technol 100:2676–2684. https://doi.org/10.1016/j.biortech.2008.12.051

El Messaoudi N, El Khomri M, Bentahar S, Dbik A, Lacherai A, Bakiz B (2016) Evaluation of performance of chemically treated date stones: application for the removal of cationic dyes from aqueous solutions. J Taiwan Inst Chem Eng 67:244–253. https://doi.org/10.1016/j.jtice.2016.07.024

El Nemr A, Khaled A, Abdelwahab O, El-Sikaily A (2008) Treatment of wastewater containing toxic chromium using new activated carbon developed from date palm seed. J Hazard Mater 152(1):263–275. https://doi.org/10.1016/j.jhazmat.2007.06.091

Etim UJ, Umoren SA, Eduok UM (2016) Coconut coir dust as a low cost adsorbent for the removal of cationic dye from aqueous solution. J Saud Chem Soc 20:S67–S76. https://doi.org/10.1016/j.jscs.2012.09.014

Farooq M, Bell AH, Almustapha MN, Andresen JM (2017) Bio-methane from an-aerobic digestion using activated carbon adsorption. Anaerobe 46:33–40. https://doi.org/10.1016/j.anaerobe.2017.05.003

Farsi MA, Alasalvar C, Morris A, Baron M, Shahidi F (2005) Comparison of antioxidant activity, anthocyanins, carotenoids, and phenolics of three native fresh and sun-dried date (Phoenix dactylifera L.) varieties grown in Oman. J Agric Food Chem 53:7592–7599. https://doi.org/10.1021/jf050579q

Farsi MA, Alasalvar C, Alabid M, Shoaily KA, Amry MA, AlRawah M (2007) Compositional and function characteristics of dates, syrups, and their by-products. Food Chem 104:943–947. https://doi.org/10.16966/2470-6086.108

Gazi M, Oladipo AA, Azalok KA (2017) Highly efficient and magnetically separable palm seed-based biochar for the removal of nickel. Sep Sci Technol 53(7):1124–1131. https://doi.org/10.1080/01496395.2017.1340955

Ghnimi S, Umer S, Karim A, Kamal-Eldin A (2017) Date fruit (*Pheonix dactylifera L*): an underutilized food seeking industrial valorization. NFS J 6:1–10. https://doi.org/10.1016/j.nfs.2016.12.001

Gueu S, Yao B, Adouby K, Ado G (2006) Heavy metals removal in aqueos solution by activated carbon prepared by coconut shell and seed shell of the palm tree. J Appl Sci 6(13):2789–2793. http://docsdrive.com/pdfs/ansinet/jas/2006/2789-2793.pdf

Hong Y, Tomas BF, Kader A, Mitchell A (2006) The flavonoid glycosides and procyanidin composition of Deglet Noor dates. J Agric Food Chem 54:2405–2411. https://doi.org/10.1021/jf0581776

Hosam MH, Wissam HI (2011) Nutritional quality of 18 date fruit varieties. Int J Food Sci Nutr 62:544–551. https://doi.org/10.3109/09637486.2011.558073

Ibrahim A, Akasha LC, Stephen RE (2012) Extraction and characterisation of protein fraction from date palm fruit seeds. Int J Food Eng 6:875–877. http://scholar.waset.org/1307-6892/3421

Islam MA, Tan IAW, Benhouria A, Asif M, Hameed BH (2015) Mesoporous and adsorptive properties of palm date seed activated carbon prepared via sequential hydrothermal carbonization and sodium hydroxide activation. Chem Eng J 270:187–195. https://doi.org/10.1016/j.cej.2015.01.058

Izanzar I, Dahbi M, Kiso M, Doubaji S, Komaba S (2018) Hard carbons issued from date palm as efficient anode materials for sodium-ion batteries. Carbon 137:165–173. https://doi.org/10.1016/j.carbon.2018.05.032

Jamil F, Al-Muhtaseb AH, Al-Haj L, Al-Hinai MA, Hellier P, Rashid U (2016) Optimization of oil extraction from waste “date pits” for biodiesel production. Energy Convers Manag 117:264–272. https://doi.org/10.1016/j.enconman.2016.03.025

Javadian H, Angaji MT, Naushad M (2014) Synthesis and characterization of polyaniline/γ-alumina nanocomposite: a comparative study for the adsorption of three different anionic dyes. J Ind Eng Chem 20:3890–3900. https://doi.org/10.1016/j.jiec.2013.12.095

Johari K, Saman N, Song ST (2016) Adsorption enhancement of elemental mercury by various surface modified coconut husk as eco-friendly low-cost adsorbents. Int Biodeter Biodegr 109:45–52. https://doi.org/10.1016/j.ibiod.2016.01.004

Khosravi R, Moussavi G, Ghaneian MT (2018) Chromium adsorption from aqueous solution using novel green nanocomposite: adsorbent characterization, isotherm, kinetic and thermodynamic investigation. J Mol Liq 256:163–174. https://doi.org/10.1016/j.molliq.2018.02.033

Kobielska PA, Howarth AJ, Farha OK, Nayak S (2018) Metal–organic frameworks for heavy metal removal from water. Coord Chem Rev 358:92–107. https://doi.org/10.1016/j.ccr.2017.12.010

Lee SU, Lee JH, Choi SH, Lee JS, Kameyama MO, Kozukue N, Levin CE, Friedman M (2008) Flavonoid content in fresh, home-processed, and light-exposed onions and in dehydrated commercial onion products. J Agric Food Chem 56:8541–8548. https://doi.org/10.1021/jf801009p

Li Q, Xinru C, Yuwen C, Yang X, Qiao W, YouLi Y, Wang X (2018) Strategies for the stable performance and rapid inhibition recovery of a thermophilic digester treating coffee wastes and the synergistic effects of microbes. Int Biodeter Biodegr. https://doi.org/10.1016/j.ibiod.2018.02.014

Luque de Castro MD, Priego-Capote F (2010) Soxhlet extraction: past and present panacea. J Chromatogr A 1217:2383–2389. https://doi.org/10.1016/j.chroma.2009.11.027

Mahdi Z, Yu QJ, El Hanandeh A (2018) Investigation of the kinetics and mechanisms of nickel and copper ions adsorption from aqueous solutions by date seed derived biochar. J Environ Chem Eng 6:1171–1181. https://doi.org/10.1016/j.jece.2018.01.021

Milovanovic V, Radulovic N, Todorovic Z, Stankovic M, Stojanovic G (2007) Antioxidant, antimicrobial and genotoxicity screening of hydro-alcoholic extracts of five Serbian Equisetum species. Plant Foods Hum Nutr 62:113–119. https://doi.org/10.1007/s11130-007-0050-z

Mittal A, Naushad M, Sharma G et al (2016) Fabrication of MWCNTs/ThO2 nanocomposite and its adsorption behavior for the removal of Pb(II) metal from aqueous medium. Desalin Water Treat 57:21863–21869. https://doi.org/10.1080/19443994.2015.1125805

Mohsen AE, Nezam M, Din EM (1995) Technological study on Dibis production from the Siwi date. Egypt J Food Sci 23:229–239. https://doi.org/10.1016/j.sjbs.2012.12.004

Nagwa MA, Lamia TA, Abou EK, Nabil ES, Lalita MC, Tom JM (2009) Flavonoid constituents and antimicrobial activity of date (phoenix dactylifera L.) seeds growing in Egypt. Med Aromat Plant Sci Biotechnol 49:719–721. https://doi.0906/MAPSB_3(SI1)/MAPSB_3(SI1)1-5o

Natarajan S, Hari CB, Tayade RJ (2018) Recent advances based on the synergetic effect of adsorption for removal of dyes from waste water using photocatalytic process. J Environ Sci 65:201–222. https://doi.org/10.1016/j.jes.2017.03.011

Naushad M, ALOthman ZA, Awual MR et al (2015a) Adsorption kinetics, isotherms, and thermodynamic studies for the adsorption of Pb2+ and Hg2+ metal ions from aqueous medium using Ti(IV) iodovanadate cation exchanger. Ionics (Kiel) 21:2237–2245. https://doi.org/10.1007/s11581-015-1401-7

Naushad M, Ahamad T, Alothman ZA et al (2015b) Synthesis, characterization and application of curcumin formaldehyde resin for the removal of Cd2+ from wastewater: kinetics, isotherms and thermodynamic studies. J Ind Eng Chem 29:78–86. https://doi.org/10.1016/j.jiec.2015.03.019

Naushad M, Khan MR, ALOthman ZA et al (2015c) Removal of BrO3− from drinking water samples using newly developed agricultural waste-based activated carbon and its determination by ultra-performance liquid chromatography-mass spectrometry. Environ Sci Pollut Res 22:15853–15865. https://doi.org/10.1007/s11356-015-4786-y

Nehdi I, Omri S, Khalil MI, Al-Resayes SI (2010) Characteristics and chemical composition of date palm (*Pheonix canariensis*) seeds and seed oil. Ind Crop Prod 32:360–365. https://doi.org/10.1016/j.indcrop.2010.05.016

Ogungbenro AE, Quang DV, Al-Ali K, Abu-Zahra MRM (2017) Activated carbon from date seeds for CO_2 capture applications. Energy Procedia 114:2313–2321. https://doi.org/10.1016/j.egypro.2017.03.1370

Ogungbenro AE, Quang DV, Al-Ali KA, Vega LF, Abu-Zahra MRM (2018) Physical synthesis and characterization of activated carbon from date seeds for CO_2 capture. J Environ Chem Eng 6 (4):4245–4252. https://doi.org/10.1016/j.jece.2018.06.030

Pan Z, Qu W, Ma H, Atungulu GG, McHugh TH (2011) Continuous and pulsed ultrasound-assisted extractions of antioxidants from pomegranate Peel. Ultrason Sonochem 18:1249–1257. https://doi.org/10.1016/j.ultsonch.2011.01.005

Paniwnyk L, Beaufoy E, Lorimer JP, Mason TJ (2001) The extraction of Rutin from flower buds of Sophora Japonica. Ultrason Sonochem 8:299–301. https://doi.org/10.1016/S1350-4177(00)00075-4

Pathania D, Sharma G, Kumar A et al (2015) Combined sorptional–photocatalytic remediation of dyes by polyaniline Zr(IV) selenotungstophosphate nanocomposite. Toxicol Environ Chem 97:526–537. https://doi.org/10.1080/02772248.2015.1050024

Pathania D, Sharma A, Siddiqi ZM (2016) Removal of Congo red dye from aqueous system using Phoenix dactylifera seeds. J Mol Liq 219:359–367. https://doi.org/10.1016/j.molliq.2016.03.020

Pradhan RC, Venkatesh M, Rout PK, Naik S, Dalai AK (2009) Supercritical CO_2 extraction of fatty oil from flaxseed and comparison with screw press expression and solvent extraction processes. J Food Eng 98:393–397. https://doi.org/10.1016/j.jfoodeng.2009.11.021

Pujari RR, Vyawahare NS, Kagathara VG (2011) Evaluation of antioxidant and neuroprotective effect of date palm (Phoenix dactylifera L.) against bilateral common carotid artery occlusion in rats. Ind J Exp Biol 49:627–633.http://nopr.niscair.res.in/handle/123456789/12528

Rahman MS, Kasapis S, Al-Kharusi NSZ, Al-Marhubi IM, Khan AJ (2007) Composition characterization and thermal transition of date pits powders. J Food Eng 80:1–10. https://doi.org/10.1016/j.jfoodeng.2006.04.030

Rajamohan N, Rajasimman M, Dilipkumar M (2014) Parametric and kinetic studies on biosorption of mercury using modified Phoenix dactylifera biomass. J Taiwan Inst Chem Eng 45:2622–2627. https://doi.org/10.1016/j.jtice.2014.07.004

Sait HH, Hussain A, Salema AA, Ani FN (2012) Pyrolysis and combustion kinetics of date palm biomass using thermogravimetric analysis. Bioresour Technol 118:382–389. https://doi.org/10.1016/j.biortech.2012.04.081

Saleh FA, Otaibi MM (2013) Antibacterial activity of date palm (PheonixDectyliferaL) fruit at different ripening stages. J Food Process Technol 4:285–290. https://doi.org/10.4172/2157-7110.1000285

Salman JM, Al-saad KA (2012) Adsorption of 2, 4-dichlorophenoxyacetic acid onto date seeds activated carbon: equilibrium, kinetic and thermodynamic studies. Int J Chem Sci 10 (2):677–690. http://www.tsijournals.com/abstract/adsorption-of-2-4dichlorophenoxyacetic-acid-onto-date-seeds-activated-carbon-equilibrium-kinetic-and-thermodynamic-studi-10635.html

Saravanan RS, Rose JKC (2004) A critical evaluation of sample extraction techniques for enhanced proteomic analysis of recalcitrant plant tissues. Proteomics 4:2522–2532. https://doi.org/10.1002/pmic.200300789

Shahat A, Awual MR, Khaleque MA et al (2015) Large-pore diameter nano-adsorbent and its application for rapid lead (II) detection and removal from aqueous media. Chem Eng J 273:286–295. https://doi.org/10.1016/j.cej.2015.03.073

Shen B, Tian L, Li F et al (2017) Elemental mercury removal by the modified bio-lchar from waste tea. Fuel 187:189–196. https://doi.org/10.1016/j.fuel.2016.09.059

Tsaliki E, Kechagia U, Doxastakis G (2002) Evaluation of the properties of cottonseed protein isolates. Food Hydrocoll 16:645–652. https://doi.org/10.1016/S0268-005X(02)00030-9

Vijay K, Ankit G, Madhu N (2012) Comparative study of various methods for extraction of antioxidant and antibacterial compounds from plant seeds. J Nat Remedies 12:162–173. https://Ankit_Gupta6/publication/235437071

Wang H, Johnson LA, Wang T (2004) Preparation of soy protein concentration and isolate from extruded-expel led soybean meals. J Am Oil Chem Soc 81:713–717. https://doi.org/10.1007/s11746-004-966-8

Wang W, Vignani R, Scali M, Cresti M (2006) A universal and rapid protocol for protein extraction from recalcitrant plant tissues for proteomic analysis. Electrophoresis 27:2782–2786. https://doi.org/10.1002/elps.200500722

Wen X, Du C, Zeng G, Huang D, Zhang J, Yin L, Tan S (2018) A novel biosorbent prepared by immobilized Bacillus licheniformis for lead removal from wastewater. Chemosphere 200:173–179. https://doi.org/10.1016/j.chemosphere.2018.02.078

Zhou Y, Jin C, Li Y, Shen W (2018) Dynamic behavior of metal nanoparticles for catalysis. NanoToday 20:101–120. https://doi.org/10.1016/j.nantod.2018.04.005

Chapter 12
Date Palm Based Activated Carbon for the Efficient Removal of Organic Dyes from Aqueous Environment

Shamik Chowdhury, Sharadwata Pan, Rajasekhar Balasubramanian, and Papita Das

Abstract Dyes are an important class of recalcitrant organic compounds, with a broad range of applications in the textiles and clothing industry. It is estimated that almost 2% of the dyes produced annually are discharged directly onto aqueous effluents through manufacturing and processing operations, and nearly 10% is subsequently lost during the coloration process. The presence of dyes in industrial wastewaters can create a host of environmental problems because of their potential cytotoxic, carcinogenic, and mutagenic effects on human health, as well as on general flora and fauna. Amongst the various physical, chemical, and biological techniques that are currently explored by the scientific community for the removal of dyes from aqueous medium, adsorption on activated carbon (AC) is widely considered as the most effective and promising option. However, commercially available ACs are fairly expensive and are often produced from non-renewable coal based resources, which make them economically undesirable and environmentally unsustainable. Consequently, there is a growing interest to synthesize ACs from renewable agricultural waste, which is conceived to be sufficiently abundant. Particularly, attributing to their high lignocellulosic composition and low ash content, date palm residues (such as fibers, seeds, rachis, fronds, etc.) as low cost precursors for manufacturing ACs are being intensively investigated in recent years. Compared to the commercial AC, the ACs derived from date palm byproducts exhibit superior textural characteristics, and, subsequently, greater adsorption capacity toward a plethora of dyes. Clearly, solicitations of date palm biomass, as a base feedstock for the mass production of AC, can not only solve the waste disposal crisis in date

S. Chowdhury (✉) · R. Balasubramanian
Department of Civil & Environmental Engineering, National University of Singapore, Singapore, Singapore
e-mail: shamikchowdhury04@gmail.com

S. Pan
School of Life Sciences Weihenstephan, Technical University of Munich, Freising, Germany

P. Das
Department of Chemical Engineering, Jadavpur University, Kolkata, India

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_12

palm growing countries, with a beneficial and enhanced revenue potential, but may also contribute in regulation of the unsustainable management of the waste byproduct. This chapter targets this aspect amongst others, with an objective to provide a systematic overview of the recent progress in the development and application of date palm based ACs for decolorizing textile effluents. Furthermore, it attempts to segregate and identify the key gaps in the specific domain knowledge, and lays out novel strategic research guidelines, for making further advances in this promising approach, to a hitherto sustainable development.

Keywords Dyes · Adsorption · Adsorbents · Activated carbon · Date palm

12.1 Introduction

It all started with a vivid purple dye, discovered serendipitously on April 28, 1856 during the Easter holidays. William H. Perkin (18) stumbled upon a technique to synthetically manufacture purple color, while attempting synthesizing the antimalarial drug 'quinine' from coal tar, which he promptly patented as 'mauveine'. Until then, pigments extracted from natural resources, i.e., plants, insects, animals, mineral deposits, and even semi-precious stones, prevailed as the only coloring technology (Merdan et al. 2017). Attributing to their lasting color pay-off, reproducibility in shades, and overall cost factor, synthetic colorants soon ostracized the solicitations of natural dyes (Shahid-ul-Islam and Mohammad 2017).

Today, more than 100,000 synthetic dye variants, for instance acid dyes, azoic dyes, basic dyes, chrome dyes, diazo dyes, direct dyes, disperse dyes, reactive dyes, sulfur dyes, and vat dyes, commercially exist with an annual global market in excess of 7×10^5 tons (Chowdhury and Saha 2010; Chowdhury et al. 2011). It is estimated that ~2% of the fabricated dyestuffs are discharged directly onto aqueous effluents, during manufacturing and subsequent processing operations (Singh and Arora 2011). Of the remaining 98%, approximately two thirds are employed by the textile industry, to dye natural and synthetic fiber or fabrics; about one sixth are utilized for coloring paper; and the rest are engaged predominantly in the production of organic pigments, and in the dyeing of leather and plastic. As the entire cohort of dye molecules do not bind to the substrate, an additional 10% is concomitantly lost during the dyeing process (Kausar et al. 2018). Depending on the type of dye, its loss in both the dyeing baths and the residual effluents, could vary from 2% for the basic dyes to as high as 50% for the reactive dyes (Singh et al. 2015). All these eventually manifest severe contaminations of surface and ground waters, in the vicinity of the dyeing industries.

Dyes, in general, are stable organic pollutants that persist in the environment due to their complex aromatic structures (Kodam and Kolekar 2015). The thin layer of discharged dyes, formed on the surface of the receiving water streams, can compromise the photosynthetic activity of aquatic flora by restricting sunlight penetration (Pereira and Alves 2012). This in turn decreases the dissolved oxygen levels, ultimately affecting the aquatic fauna (Sharma et al. 2015; Pathania et al. 2016a).

Furthermore, since synthetic dyes are derived from petrochemical sources, a vast majority of them act as toxic mutagens, potential carcinogens, and eye irritants (Merdan et al. 2017; Pathania et al. 2016b). The release of colored wastewaters into the ecosystem is, therefore, both unsafe and aesthetically unacceptable.

Consequently, a wide array of strategies have been extensively adopted and rigorously evaluated over the years, for the removal of color from textile wastewaters. These range from physical (adsorption, sedimentation, flotation, flocculation, coagulation, ultrafiltration, photoionization, incineration, and membrane separation) and chemical processes (neutralization, reduction, oxidation, electrolysis, ion-exchange, wet-air oxidation), to biological treatment methods (stabilization ponds, aerated lagoons, trickling filters, activated sludge, anaerobic digestion, and various types of microbial strains) (Crini 2006; Singh and Arora 2011). Amongst these, adsorption on solid media have garnered maximum scientific attention, attributing to its low capital investment as well as a multitude of competitive advantages: (i) flexibility and simplicity of design, (ii) ease of operation, (iii) insensitivity to toxic pollutants, (iv) lower sensitivity to diurnal variation, and (v) comprehensive removal of contaminants even from dilute solutions (Pereira and Alves 2012; Rafatullah et al. 2013; Yaqub et al. 2014). Additionally, adsorption cannot be linked with manifestation of objectionable and/or harmful byproducts (Rafatullah et al. 2013; Yaqub et al. 2014).

In light of the aforementioned merits, several diverse solid supports, such as zeolites, alumina, activated carbon, and silica gel, have been proposed and developed during recent years, to eliminate various categories of dyes from wastewaters (Gupta et al. 2009). Amongst them, activated carbon (AC) is the most widely studied adsorbent, because of its fundamental porous structure as well as many exciting properties: (i) high surface area (500–2000 $m^2 g^{-1}$), (ii) controllable pore structure, (iii) admirable thermostability, (iv) low acid/base reactivity, and (v) good biocompatibility (Crini 2006; Gupta et al. 2009; Rafatullah et al. 2013; Suhas et al. 2016). Indeed, the enormous internal surface area, along with numerous cracks, crevices and voids between the carbon layers, permit and facilitate the accumulation of a large number of contaminant molecules, often in excess of the weight of the material. In addition, adsorption on AC is not usually selective, as it occurs through weak attraction forces, such as electrostatic or van der Waals forces (physisorption) (Gupta et al. 2009). This tendency can be leveraged to eliminate a wide range of colorants from textile effluents.

Despite their proven potential in adsorption processes, most commercial ACs are manufactured from expensive and nonrenewable fossil fuel based resources, for instance petroleum coke and coal (Gao et al. 2017; Rashidi and Yusup 2017), which seriously hinder their practical utility, especially at the industrial scale. This has paved way for a growing research interest in the production of AC from renewable, abundantly available, and low cost precursors (Crini 2006). In this context, date palm fruits processing products and byproducts are particularly attractive, because of their high cellulose (40–50%), hemicellulose, (40–50%), and lignin (15–35%)

content (Ahmad et al. 2012; Alrumman 2016) and low ash load (5%) (Ahmed 2016; Lattieff 2016). Further, the date palm is one of the most cultivated fruit-bearing flora in the arid and semi-arid regions of the world (El may et al. 2012; Elmay et al. 2014). It is estimated that the number of date palms worldwide is about 105 million (Elmay et al. 2013; Ahmed 2016). Date fruit production yields several crop residues, including date palm leaves (fronds), fruitstalk prunings, and seeds (also known as stones or pits) during date fruit harvesting; and trunks, rachis, and spines during replanting activities (El May et al. 2012). At present, over 3.7 million tons of date byproducts are being generated annually (Almi et al. 2015). Much of the waste is either illegally burnt (Chandrasekaran and Bahkali 2013; Usman et al. 2015; Arevalo-Gallegos et al. 2017), thereby contributing to air pollution, or simply left to decay in dedicated landfills (Bekheet and El-Sharabasy 2015; Nasser et al. 2016), emitting methane, a more potent greenhouse gas compared to carbon dioxide (CO_2). Utilization of date palm byproducts, as a base feedstock for the mass production of AC, can mitigate the waste disposal crisis in date palm growing countries, with a potential revenue benefit option. Moreover, it may also assist in regulating unsustainable management of the waste byproduct. Compared to commercial AC, the AC prepared from date palm wastes, exhibit superior textural properties, and thus, greater adsorption capacity towards a multitude of dyes.

Therefore, the current chapter has been conceived to provide an overview of the latest development in valorization of date palm wastes for sustainable production of AC, including their potential as adsorbents for the removal of different types of synthetic colorants from wastewaters. Additionally, it makes an attempt to identify and segregate the fundamental lacunae in the domain, while laying out novel strategic research guidelines for making further advances in this promising waste valorization approach, with a clear mandate and focus on sustainable development.

12.2 Activated Carbon from Date Palm Residues for Dye Removal

Over the past few years, a wide spectrum of date palm residues, including seeds, rachis, fronds and fibers, have been investigated, as a sustainable and renewable feedstock for preparation of AC (see Table 12.1). The yield, textural characteristics and surface chemistry of the ACs are largely dependent on both the lignocellulosic composition of the precursor, and the manufacturing process. In general, there are two fundamental steps for the production of AC: (1) the carbonization of raw materials below 800 °C in the absence of oxygen, and (2) the activation of the carbonized product, using either physical or chemical activation methods. More recently, alternative manufacturing protocols with energy and chemical stashes, such as microwave heating, have also been successfully developed for the preparation of AC from date palm biomass.

Table 12.1 Carbonization and activation conditions of date palm residues, and the textural characteristics and dye adsorption capacities of the resulting activated carbons as reported in the literature

Raw Material	Carbonization condition	Activation condition	Activating agent	Remarks	S_{BET} ($m^2\ g^{-1}$) [a]	V_t ($cm^3\ g^{-1}$)[b]	Adsorbate	Conc. Range ($mg\ L^{-1}$)	Adsorption capacity ($mg\ g^{-1}$)	Reference
Date pits	600 °C/2 h	950 °C	CO_2	–	–	–	Methylene blue	50–2000	590	Abdulkarim et al. (2002)
Date pits	700 °C/2 h	900 °C/ 30 min	CO_2	–	–	–	Methylene blue	20–100	17.27	Banat et al. (2003a)
Date pits	600 °C/2 h	800 °C/1 h	CO_2	Pretreatment with KOH	870	0.51	Methylene blue	–	123.1	Banat et al. (2003b)
Date pits	600 °C/6 h	–	$ZnCl_2$	One step carbonization/ activation	713	0.396	Methylene blue	–	127.3	El-Sharkawy et al. (2007)
Date pits	900 °C	–	Steam	One step carbonization/ activation	1047	0.5797	Methylene blue	–	155.3	El-Sharkawy et al. (2007)
Date pits	600 °C/2 h	950 °C	Steam	–	1040	0.884	Methylene blue	10–100	244	Ashour (2010)
Date pits	600 °C/2 h	950 °C	Steam	–	1040	0.884	Remazol yellow	10–100	173	Ashour (2010)
Date pits	800 °C/1 h	971 °C/ 56 min	CO_2	–	666	0.41	Methylene blue	400–1200	110	Reddy et al. (2012)
Date pits	800 °C/1 h	400 °C/ 58 min	H_3PO_4	–	725	1.26	Methylene blue	400–1200	345	Reddy et al. (2012)
Date pits	700 °C/1 h	–	$FeCl_3$	One step carbonization/ activation	780	0.573	Methylene blue	50–450	259.25	Theydan and Ahmed (2012)
Date pits	400 °C/2 h	–	$ZnCl_2$		1380	0.91	Methylene blue	0–1000	434	Mahmoudi et al. (2015)

(continued)

Table 12.1 (continued)

Raw Material	Carbonization condition	Activation condition	Activating agent	Remarks	S_{BET} (m^2 g^{-1})[a]	V_t (cm^3 g^{-1})[b]	Adsorbate	Conc. Range (mg L^{-1})	Adsorption capacity (mg g^{-1})	Reference
				One step carbonization/ activation						
Date pits	400 °C/2 h	–	$ZnCl_2$	One step carbonization/ activation	1380	0.91	Methyl Orange	0–1000	455	Mahmoudi et al. (2015)
Date stones	500 °C/0.5 h	–	$ZnCl_2$	One step carbonization/ activation	–	–	Methylene blue	–	286.3	Alhamed (2006)
Date stones	700 °C	600 W/ 8 min	KOH	Microwave-assisted activation	856	0.468	Methylene blue	50–500	316.11	Foo and Hameed (2011)
Date stones	500 °C/1.25 h	–	$ZnCl_2$	One step carbonization/ activation	1046	0.641	Methylene blue	50–450	381.79	Ahmed and Theydan (2012)
Date stones	700 °C/1.25 h	–	$FeCl_3$	One step carbonization/ activation	780	0.573	Methylene blue	50–450	255.32	Ahmed and Theydan (2012)
Date stones	500 °C/1 h	–	$ZnCl_2$	One step carbonization/ activation	1046	–	Methylene blue	50–450	398.19	Ahmed and Dhedan (2012)
Date palm seeds	200 °C/5 h	600 °C/1 h	NaOH	–	1282	0.66	Methylene blue	50–500	612.1	Islam et al. (2015)
Date palm seeds	700 °C/1 h	–	H_3PO_4	One step carbonization/ activation	–	–	Methylene blue		199.4	Hussein et al. (2015)

Date palm rachis	800 °C/1 h	–	KOH	One step carbonization/ activation	1160	0.583	BEZAKTIV red S-MAX	10–100	128.21	Daoud et al. (2017)
Date palm fronds	700 °C/1 h	–	H_3PO_4	One step carbonization/ activation	–	–	Methylene blue		199.8	Hussein et al. (2015)
Date palm fibers	700 °C/1 h	–	H_3PO_4	One step carbonization/ activation	–	–	Methylene blue		198.8	Hussein et al. (2015)

[a]Brunauer–Emmett–Teller specific surface area. Values are rounded off to the nearest whole number wherever applicable.
[b]Total pore volume.

12.2.1 Physically Activated Carbon

The typical synthesis route for the preparation of AC *via* physical activation involves two consecutive steps. The first step is 'carbonization' of the raw materials, where the precursor is pyrolyzed in the temperature range 400–700 °C in an inert atmosphere (usually nitrogen or argon) (Menya et al. 2018). During this phase, a vast majority of the non-carbon species, such as oxygen and hydrogen, are expelled as volatile gases (Gaspard et al. 2014), resulting in the formation of a fixed carbon mass (called 'char') that has a rudimentary pore structure (Rashidi and Yusup 2017), and hence manifests a minimal adsorption capacity (Menya et al. 2018). The second step in the preparation of AC, by physical activation, involves a controlled 'gasification' of the char at high temperatures (600–1000 °C) in the presence of a suitable oxidizing gas, such as air, CO_2, steam, or their mixtures (Menya et al. 2018). When the carbonized raw material is subjected to partial gasification, majority of the reactive carbon atoms are selectively eliminated from the sample, thereby converting the char into a form that contains the utmost possible number of randomly distributed pores of various shapes and sizes (Gaspard et al. 2014). Indeed, the final activated carbon has a well-developed porosity and a correspondingly large surface area. A typical instance is that of Ashour (2010), who developed ACs with enormous specific surface area (1040 $m^2\ g^{-1}$), sufficiently large pore volume (0.884 $cm^3\ g^{-1}$), and a well-defined micro/mesoporous structure through steam activation of date pits. When tested as adsorbents employing a batch experimental set-up, the date pit-derived ACs showed remarkably high adsorption capacities towards both anionic (remazol yellow, 173 mg g^{-1}) and cationic (methylene blue, 244 mg g^{-1}) dyes, similar to commercial ACs.

The extent of pore formation and pore size distribution, and thus the adsorption potential, are, however, strongly dependent on the cellular structure of the original material, activation holding time, as well as the choice of the activation agent. For instance, Belhachemi et al. (2009) compared the influence of CO_2 and steam as activating agents, on the textural characteristics of ACs synthesized from date pits. It was found that, under analogous experimental conditions, the molecular size and reactivity of the activating agents played important roles in porosity development of the resulting ACs. Particularly, attributing to its smaller molecular size and faster diffusion rates, steam activation, in general, produced ACs with broader pore size distributions and greater surface area compared to CO_2 activation. However, additional improvement in porosity with increasing burn-off extent was more pronounced for CO_2 than steam (see Fig. 12.1). This trend can be ascribed to the way by which these agents react with the active sites of the pore structure. Precisely, steam attacks the active sites at the center and on the pore walls simultaneously. On the other hand, CO_2 primarily reacts with the active sites at the center of the pores (thus creating microporosity), and only attacks the pore walls when the activation time is too long. The latter results in significant broadening of the micropore diameter, ultimately yielding more mesoporous carbons (Gonźalez et al. 2009). Despite the clear dissimilarities between the pore size distributions obtained using

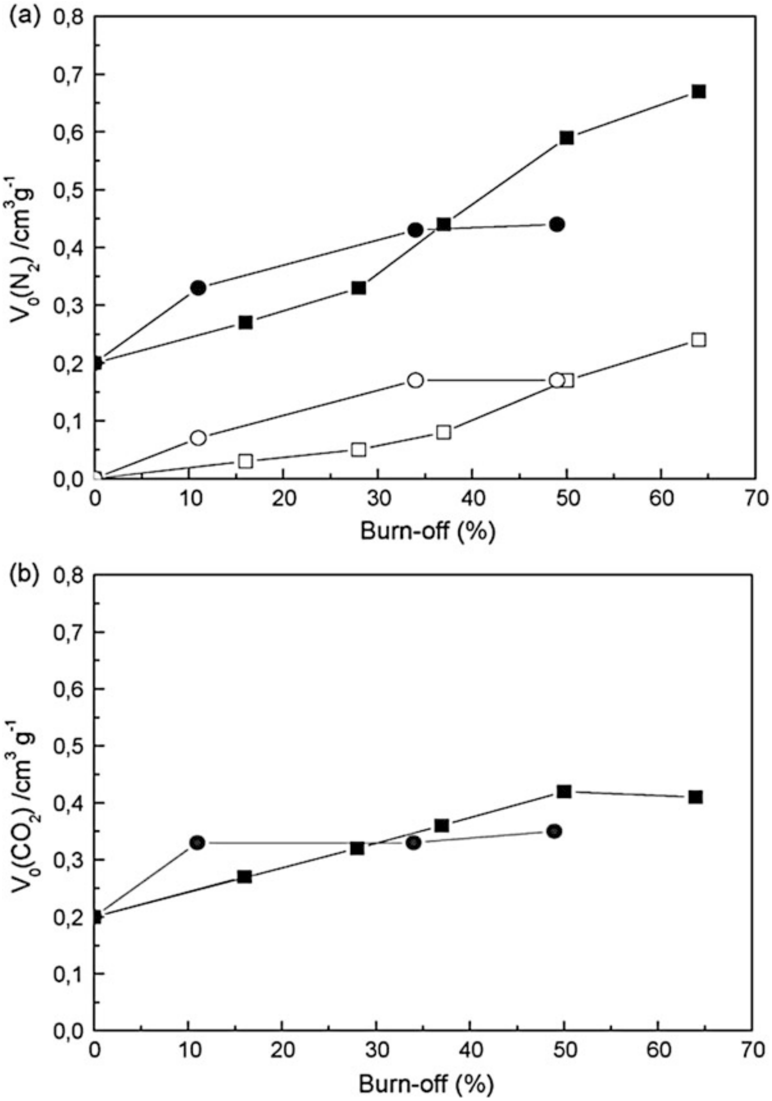


Fig. 12.1 Evolution of pore volume as a function of burn-off. (**a**) Micropore volume ($V0(N_2)$): ■ – CO_2 activated, ● – steam activated; Mesopore volume ($V_{0.95}$ – $V0(N_2)$): □ – CO_2 activated, ○ – steam activated. (**b**) Micropore volume ($V0(CO_2)$): ■ – CO_2 activated, ● – steam activated. Reproduced from Belhachemi et al. (2009), Copyright 2009, with permission of Elsevier

steam and CO_2 as activation agents, both steam and CO_2 have been widely used to produce ACs from date palm residues, with high adsorption capabilities towards several classes of dyes (Table 12.1).

In comparison to other activation approaches, several key merits of physical activation could be distinguished: (i) simplicity and ease of operation with no additional processing, such as washing of the end products; (ii) environmentally benign approach, since it avoids the use of toxic and harmful chemicals; (iii) scalability and low-cost (Ioannidou and Zabaniotou 2007; Sevilla and Mokaya 2014). Nevertheless, prolonged activation time associated with dual-stage processes, low carbon yield, and high power consumption, significantly limits the economic feasibility of the process (Rashidi and Yusup 2017).

12.2.2 Chemically Activated Carbon

As opposed to physical activation, chemical activation, in general, is a single stage process (Rashidi and Yusup 2017), implying that the transformation of the waste biomass into a carbonaceous residue and the generation of porosity take place concurrently. It usually involves impregnating the precursor with a chemical, followed by pyrolysis at relatively low temperatures of 400–700 °C (Menya et al. 2018). The most widely used chemical activating agents include alkalis such as potassium hydroxide (KOH) and sodium hydroxide (NaOH), acids such as phosphoric acid (H_3PO_4), and transition metal salts like zinc chloride ($ZnCl_2$) and ferric chloride ($FeCl_3$) (Rashidi and Yusup 2017). These chemicals act both as dehydrating agents and as oxidants, so that carbonization and activation processes occur simultaneously in a single step (Hsi et al. 2011). For instance, when H_3PO_4 is used as the chemical activating agent, it hydrolyses the glycosidic linkages in the polysaccharides (hemicellulose and cellulose) and cleaves the aryl ether bonds in lignin at low temperatures (Gaspard et al. 2014). This structural reconfiguration weakens the precursor structure and swells the carbon framework, allowing the cellulose microfibrils to separate. As the temperature increases, cyclisation and condensation reactions lead to aromatization of the carbon skeleton, and the altered microfibrils form an open porous structure (Gaspard et al. 2014). It is, therefore, conceivable that in the chemical activation process, the pore size distribution and the surface area are determined by the mass of chemical agent infused into the precursor and the impregnation duration (Rafatullah et al. 2013; Gaspard et al. 2014). Nevertheless, the flexibility to obtain different pore size distributions depends entirely on the reagent employed. Further, the carbon yield in chemical activation is usually higher compared to physical activation, since the chemical activating agents inhibit the formation of tar and curb the production of other volatile substances during pyrolysis, due to their inherent dehydrogenation properties (Gaspard et al. 2014). Consequentially, the chemical activation route has been more frequently exploited for the processing of date palm residues into ACs, for pollution control in the textile industry (Table 12.1), even though it requires meticulous washing to remove the residual chemicals, which may entail additional costs (Rashidi and Yusup 2017).

A notable example is that of Theydan and Ahmed (2012), who prepared ACs from date pits through chemical activation with $FeCl_3$. Textural parameters, evaluated from nitrogen (N_2) adsorption/desorption isotherms, revealed that the as-made ACs were predominantly microporous (0.468 $cm^3\ g^{-1}$), with micropores accounting for nearly 82% of the total porosity. Moreover, the AC samples had fairly large surface areas (780 $m^2\ g^{-1}$), and could, therefore, adsorb huge amount of dyes from aqueous media. Indeed, a removal efficiency in excess of 90% was recorded for methylene blue, with the maximum adsorption capacity peaking around 259 mg g^{-1} at 30 °C. A further improvement in the dye removal capacity (382 mg g^{-1}) was achieved upon activation with $ZnCl_2$ (Ahmed and Theydan 2012). This observation was attributed to the better capability of $ZnCl_2$ to eliminate volatile species from the precursor, as compared with $FeCl_3$, which resulted in ACs with increased surface areas (1046 $m^2\ g^{-1}$) and larger micropore volumes (0.512 $cm^3\ g^{-1}$) (Fig. 12.2) (Ahmed and Theydan 2012). Kinetic studies suggested that adsorption of methylene blue on the AC samples followed a pseudo-second-order rate equation, and the adsorption equilibrium data could be well represented by the Langmuir isotherm. Thermodynamic analysis indicated that the adsorption process was spontaneous and endothermic.

In another noteworthy study, Islam et al. (2015) devised a novel strategy to synthesize ACs from date seeds. Their approach involved hydrothermal carbonization of the waste biomass at 200 °C, followed by impregnation with NaOH, and heating under a N_2 flow at 600 °C for 1 h. The resulting carbon materials displayed a relatively higher specific surface area and a total pore volume of 1282 $m^2\ g^{-1}$ and 0.66 $cm^3\ g^{-1}$, respectively. Subsequently, they evaluated the adsorption potential of the date seed based ACs for methylene blue, by conducting batch adsorption tests. The adsorption equilibrium exhibited a perfect correlation with both the Langmuir and Freundlich isotherms with a monolayer uptake capacity of 612 mg g^{-1}, which is among the largest reported in the literature.

Impressively, employing H_3PO_4 as the activating agent, Hussein et al. (2015) produced a series of ACs from an array of byproducts, derived from processing of

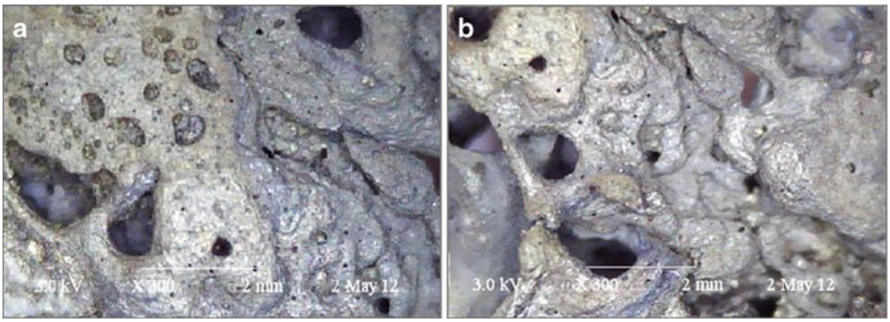


Fig. 12.2 Scanning electron microscopy (SEM) images of activated carbon prepared from date pits through chemical activation with (**a**) $FeCl_3$ and (**b**) $ZnCl_2$. Reproduced from Ahmed and Theydan (2012), Copyright 2012, with permission of Elsevier

the Iraqi Khestawy date palm: palm fronds (AC1), date palm seeds (AC2), and palm fiber (AC3). The sample AC1, due to its profound porosity, as inferred by estimating the moisture content, demonstrated the maximum adsorptive uptake of methylene blue compared with AC2 and AC3.

More recently, El-Shafey et al. (2016) explored Omani date palm leaflets as a precursor for AC *via* KOH activation. The as-prepared ACs were further oxidized and functionalized to produce basic and hydrophobic ACs. They were then tested for methylene blue adsorption from aqueous solutions. Depending on the surface chemistry, methylene blue interacted differently with the carbon sample under investigation. Interestingly, in spite of its relatively small surface area, the hydrophobic ACs showed the best dye removal performance.

12.2.3 Physiochemically Activated Carbon

It is evident from the breadth of aforementioned discussions that both physical and chemical activation methods are being actively pursued to obtain ACs from date palm biomass, for remediation of hazardous dye-bearing effluents. Nevertheless, in some cases, the activation step may involve longer processing times and require larger equipment. This results in highly non-uniform heating profiles, which in turn deteriorates the quality of the resulting ACs (Yuen and Hameed 2009). Additionally, there is a considerable risk of local overheating or even thermal runaway reaction, leading to the complete combustion of the char (Yuen and Hameed 2009). In an effort to overcome the aforementioned challenges, Foo and Hameed (2011) devised a rapid and facile physiochemical method for preparing ACs from date stone char, which involved KOH treatment and a short burst of direct microwave irradiation. The as-obtained ACs presented a well-developed and easily accessible porous structure (Fig. 12.3), with huge specific surface area (856 $m^2\ g^{-1}$) and large pore volume (0.468 $cm^3\ g^{-1}$). Consequently, these ACs could readily adsorb dyes from aqueous solutions, with a maximum monolayer uptake capacity of 316 mg g^{-1} for methylene blue.

Meanwhile, Banat et al. (2003b) investigated the adsorption of methylene blue onto ACs derived from date seeds through physiochemical activation, with KOH and CO_2 as the activating agents. The experimental equilibrium data conformed to the Langmuir isotherm, with maximum monolayer coverage of 123 mg g^{-1}. The latter could be attributed to the significantly high surface area (870 $m^2\ g^{-1}$) of the as-prepared AC samples.

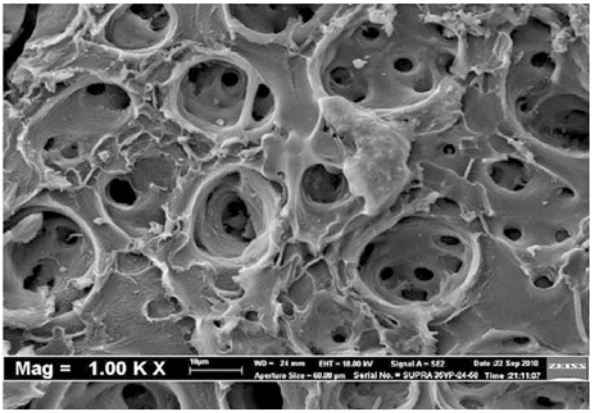


Fig. 12.3 SEM image of activated carbon derived from date stone char by microwave induced KOH activation. Reproduced from Foo and Hameed (2011), Copyright 2011, with permission of Elsevier

12.3 Summary and Outlook

It is apparent from the extensive literature review that exploiting date palm byproducts, as a base feedstock for the production of carbonaceous adsorbents, can resolve the waste disposal crisis in date palm growing countries, with a potential revenue benefit option. In addition, it may also aid in regulating the unsustainable management of the waste byproduct. Compared to commercial AC, the ACs prepared from date palm wastes exhibit superior textural properties, and thus, greater adsorption capacity towards a multitude of dyes. However, this field of investigation is still at a nascent stage. Several fundamental issues and technical bottlenecks need immediate attention, to make more significant advances in this exciting new research domain of topical interest. First, the assessment of the dye removal capability of date palm based ACs is strictly restricted to batch adsorption tests. There is hardly any report on the adsorption of dyes using fixed bed reactor set-up. Continuous column study is, therefore, highly recommended since it represents a more practical approach of exploring the actual process-level performance of an adsorbent. Second, the equilibrium adsorption data, without exception, have been empirically correlated with the conventional isotherm models (such as Langmuir, Freundlich, Temkin etc.). However, since these analytical isotherm models are incapable of predicting pH-dependent adsorption behavior in a consistent manner (Jeppu and Clement 2012), the well-established surface ionization/complexation model or the double layer retention model should be frequently applied to investigate the effect of pH or ionic strength on the adsorption process. Third, although the ease of regenerating the spent adsorbent dictates the techno-economic viability of an adsorption process, studies along this direction are currently unavailable and should be actively pursued in the immediate future. Last but not the least, since several different varieties of dyes could simultaneously co-exist in industrial effluents, future research efforts should, therefore, also focus on evaluating the adsorption potential of the date palm based ACs with simulated wastewater, in order to ascertain their practical use.

Beyond these considerations, a rigorous assessment of the engineering economics of the date palm derived carbonaceous adsorbents should be conducted, upon scaling up the materials, for large-scale industrial applications. Additionally, economic models must be identified to perform a life cycle assessment, in order to establish the feasibility and sustainability of the bulk production of ACs from different date palm residues.

References

Abdulkarim MA, Darwish NA, Magdy YM, Dwaidar A (2002) Adsorption of phenolic compounds and methylene blue onto activated carbon prepared from date fruit pits. Eng Life Sci 2:161–165. https://doi.org/10.1002/1618-2863(200206)2:6<161::AID-ELSC161>3.0.CO;2-2

Ahmad T, Danish M, Rafatullah M, Ghazali A, Sulaiman O, Hashim R, Ibrahim MNM (2012) The use of date palm as a potential adsorbent for wastewater treatment: a review. Environ Sci Pollut Res 19:1464–1484. https://doi.org/10.1007/s11356-011-0709-8

Ahmed MJ (2016) Preparation of activated carbons from date (*Phoenix dactylifera* L.) palm stones and application for wastewater treatments: review. Process Saf Environ Prot 102:168–182. https://doi.org/10.1016/j.psep.2016.03.010

Ahmed MJ, Dhedan SK (2012) Equilibrium isotherms and kinetics modeling of methylene blue adsorption on agricultural wastes-based activated carbons. Fluid Phase Equilib 317:9–14. https://doi.org/10.1016/j.fluid.2011.12.026

Ahmed MJ, Theydan SK (2012) Physical and chemical characteristics of activated carbon prepared by pyrolysis of chemically treated date stones and its ability to adsorb organics. Powder Technol 229:237–245. https://doi.org/10.1016/j.powtec.2012.06.043

Alhamed YA (2006) Activated carbon from dates' stone by $ZnCl_2$ activation. J King Abdulaziz Univ Eng Sci 17:75–100. https://doi.org/10.4197/Eng.17-2.4

Almi K, Lakel S, Benchabane A, Kriker A (2015) Characterization of date palm wood used as composites reinforcement. Acta Phys Pol A 127:1072–1074. https://doi.org/10.12693/APhysPolA.127.1072

Alrumman SA (2016) Enzymatic saccharification and fermentation of cellulosic date palm wastes to glucose and lactic acid. Braz J Microbiol 47:110–119. https://doi.org/10.1016/j.bjm.2015.11.015

Arevalo-Gallegos A, Ahmad Z, Asgher M, Parra-Saldivar R, Iqbal HMN (2017) Lignocellulose: a sustainable material to produce value-added products with a zero waste approach – a review. Int J Biol Macromol 99:308–318. https://doi.org/10.1016/j.ijbiomac.2017.02.097

Ashour SS (2010) Kinetic and equilibrium adsorption of methylene blue and remazol dyes onto steam-activated carbons developed from date pits. J Saudi Chem Soc 14:47–53. https://doi.org/10.1016/j.jscs.2009.12.008

Banat F, Al-Asheh S, Al-Makhadmeh L (2003a) Evaluation of the use of raw and activated date pits as potential adsorbents for dye containing waters. Process Chem 39:193–202. https://doi.org/10.1016/S0032-9592(03)00065-7

Banat F, Al-Asheh S, Al-Makhadmeh L (2003b) Preparation and examination of activated carbons from date pits impregnated with potassium hydroxide for the removal of methylene blue from aqueous solutions. Adsorp Sci Technol 21:597–606. https://doi.org/10.1260/026361703771953613

Bekheet SA, El-Sharabasy SF (2015) Date palm status and perspective in Egypt. In: Al-Khayri J, Jain S, Johnson D (eds) Date palm genetic resources and utilization. Springer, Dordrecht, pp 75–123. https://doi.org/10.1007/978-94-017-9694-1_3

Belhachemi M, Rios RVRA, Addoun F, Silvestre-Albero J, Sepúlveda-Escribano A, Rodríguez-Reinoso F (2009) Preparation of activated carbon from date pits: effect of the activation agent and liquid phase oxidation. J Anal Appl Pyrolysis 86:168–172. https://doi.org/10.1016/j.jaap.2009.05.004

Chandrasekaran M, Bahkali AH (2013) Valorization of date palm (*Phoenix dactylifera*) fruit processing by-products and wastes using bioprocess technology – review. Saudi J Biol Sci 20:105–120. https://doi.org/10.1016/j.sjbs.2012.12.004

Chowdhury S, Saha P (2010) Sea shell powder as a new adsorbent to remove basic green 4 (malachite green) from aqueous solutions: equilibrium, kinetic and thermodynamic studies. Chem Eng J 164:168–177. https://doi.org/10.1016/j.cej.2010.08.050

Chowdhury S, Mishra R, Saha P, Kushwaha P (2011) Adsorption thermodynamics, kinetics and isosteric heat of adsorption of malachite green onto chemically modified rice husk. Desalination 265:159–168. https://doi.org/10.1016/j.desal.2010.07.047

Crini G (2006) Non-conventional low-cost adsorbents for dye removal: a review. Bioresour Technol 97:1061–1085. https://doi.org/10.1016/j.biortech.2005.05.001

Daoud M, Benturki O, Kecira Z, Girods P, Donnot A (2017) Removal of reactive dye (BEZAKTIV red S-MAX) from aqueous solution by adsorption onto activated carbons prepared from date palm rachis and jujube stones. J Mol Liq 243:799–809. https://doi.org/10.1016/j.molliq.2017.08.093

El May Y, Jeguirim M, Dorge S, Trouvé G, Said R (2012) Study on the thermal behavior of different date palm residues: characterization and devolatization kinetics under inert and oxidative atmospheres. Energy 44:702–709. https://doi.org/10.1016/j.energy.2012.05.022

Elmay Y, Trouvé G, Jeguirim M, Said R (2013) Energy recovery of date palm residues in a domestic pellet boiler. Fuel Process Technol 112:12–18. https://doi.org/10.1016/j.fuproc.2013.02.015

Elmay Y, Jeguirim M, Dorge S, Trouvé G, Said R (2014) Evaluation of date palm residues combustion in fixed bed laboratory reactor: a comparison with sawdust behaviour. Renew Energ 62:209–215. https://doi.org/10.1016/j.renene.2013.07.007

El-Shafey EI, Ali SNF, Al-Busafi S, Al-Lawati HAJ (2016) Preparation and characterization of surface functionalized activated carbons from date palm leaflets and application for methylene blue removal. J Environ Chem Eng 4:2713–2724. https://doi.org/10.1016/j.jece.2016.05.015

El-Sharkawy EA, Soliman AY, Al-Amer KM (2007) Comparative study for the removal of methylene blue via adsorption and photocatalytic degradation. J Colloid Interface Sci 310:498–508. https://doi.org/10.1016/j.jcis.2007.02.013

Foo KY, Hameed BH (2011) Preparation of activated carbon from date stones by microwave induced chemical activation: application for methylene blue adsorption. Chem Eng J 170:338–341. https://doi.org/10.1016/j.cej.2011.02.068

Gao Z, Zhang Y, Song N, Li X (2017) Biomass-derived renewable carbon materials for electrochemical energy storage. Mater Res Lett 5:69–88. https://doi.org/10.1080/21663831.2016.1250834

Gaspard S, Passé-Coutrin N, Durimel A, Cesaire T, Jeanne-Rose V (2014) Activated carbon from biomass for water treatment. In: Gaspard S, Ncibi MC (eds) Biomass for sustainable applications: pollution remediation and energy. RSC Publishing, London, pp 46–105. https://doi.org/10.1039/9781849737142-00046

Gonźalez JF, Román S, Gonźalez-García CM, Valente Nabais JM, Ortiz AL (2009) Porosity development in activated carbons prepared from walnut shells by carbon dioxide or steam activation. Ind Eng Chem Res 48:7474–7481. https://doi.org/10.1021/ie801848x

Gupta VK, Carrott PJM, Ribeiro Carrott MML, Suhas (2009) Low-cost adsorbents: growing approach to wastewater treatment – a review. Crit Rev Environ Sci Technol 39:783–842. https://doi.org/10.1080/10643380801977610

Suhas, Gupta VK, Carrott PJM, Singh R, Chaudhary M, Kushwaha S (2016) Cellulose: a review as natural, modified and activated carbon adsorbent. Bioresour Technol 216:1066–1076. https://doi.org/10.1016/j.biortech.2016.05.106

Hsi H-C, Horng RS, Pan T-A, Lee S-K (2011) Preparation of activated carbons from raw and biotreated agricultural residues for removal of volatile organic compounds. J Air Waste Manag Assoc 61:543–551. https://doi.org/10.3155/1047-3289.61.5.543

Hussein FH, Halbus AF, Lafta AJ, Athab ZH (2015) Preparation and characterization of activated carbon from Iraqi Khestawy date palm. J Chem. https://doi.org/10.1155/2015/295748
Ioannidou O, Zabaniotou A (2007) Agricultural residues as precursors for activated carbon production – a review. Renew Sust Energ Rev 11:1966–2005. https://doi.org/10.1016/j.rser.2006.03.013
Islam M, Tan IAW, Benhouria A, Asif M, Hameed BH (2015) Mesoporous and adsorptive properties of palm date seed activated carbon prepared via sequential hydrothermal carbonization and sodium hydroxide activation. Chem Eng J 270:187–195. https://doi.org/10.1016/j.cej.2015.01.058
Jeppu GP, Clement TP (2012) A modified langmuir-freundlich isotherm model for simulating pH-dependent adsorption effects. J Contam Hydrol 129–130:46–53. https://doi.org/10.1016/j.jconhyd.2011.12.001
Kausar A, Iqbal M, Javed A, Aftab K, Nazli Z-i-H, Bhatti HN, Nouren S (2018) Dyes adsorption using clay and modified clay: a review. J Mol Liq 256:395–407. https://doi.org/10.1016/j.molliq.2018.02.034
Kodam KM, Kolekar YM (2015) Bacterial degradation of textile dyes. In: Singh SN (ed) Microbial degradation of synthetic dyes in wastewaters. Springer, Cham, pp 243–266. https://doi.org/10.1007/978-3-319-10942-8_11
Lattieff FA (2016) A study of biogas production from date palm fruit wastes. J Clean Prod 139:1191–1195. https://doi.org/10.1016/j.jclepro.2016.08.139
Mahmoudi K, Hosni K, Hamdi N, Srasra E (2015) Kinetics and equilibrium studies on removal of methylene blue and methyl orange by adsorption onto activated carbon prepared from date pits – a comparative study. Korean J Chem Eng 32:274–283. https://doi.org/10.1007/s11814-014-0216-y
Menya E, Olupot PW, Storz H, Lubwama M, Kiros Y (2018) Production and performance of activated carbon from rice husks for removal of natural organic matter from water: a review. Chem Eng Res Des 129:271–296. https://doi.org/10.1016/j.cherd.2017.11.008
Merdan N, Eyupoglu S, Duman MN (2017) Ecological and sustainable natural dyes. In: Muthu SS (ed) Textiles and clothing sustainability. Springer, Singapore, pp 1–42. https://doi.org/10.1007/978-981-10-2185-5_1
Shahid-ul-Islam, Mohammad F (2017) Anthraquinone-based natural colourants from insects. In: Muthu SS (ed) Textiles and clothing sustainability. Springer, Singapore, pp 81–98. https://doi.org/10.1007/978-981-10-2185-5_3
Nasser RA, Salem MZM, Hiziroglu S, Al-Mefarrej HA, Mohareb AS, Alam M, Aref IM (2016) Chemical analysis of different parts of date palm (*Phoenix dactylifera* L.) using ultimate, proximate and thermo-gravimetric techniques for energy production. Energies 9:374. https://doi.org/10.3390/en9050374
Pathania D, Gupta D, Al-Muhtaseb AH et al (2016a) Photocatalytic degradation of highly toxic dyes using chitosan-g-poly(acrylamide)/ZnS in presence of solar irradiation. J Photochem Photobiol A Chem 329:61–68. https://doi.org/10.1016/j.jphotochem.2016.06.019
Pathania D, Katwal R, Sharma G, Naushad M (2016b) Novel guar gum / Al2O3 nanocomposite as an effective photocatalyst for the degradation of malachite green dye. Int J Biol Macromol 87:366–374. https://doi.org/10.1016/j.ijbiomac.2016.02.073
Pereira L, Alves M (2012) Dyes – environmental impact and remediation. In: Malik A, Grohmann E (eds) Environmental protection strategies for sustainable development. Springer, Dordrecht, pp 111–162. https://doi.org/10.1007/978-94-007-1591-2_4
Rafatullah M, Ahmad T, Ghazali A, Sulaiman O, Danish M, Hashim R (2013) Oil palm biomass as a precursor of activated carbons: a review. Crit Rev Environ Sci Technol 43:1117–1161. https://doi.org/10.1080/10934529.2011.627039
Rashidi NA, Yusup S (2017) A review on recent technological advancement in the activated carbon production from oil palm wastes. Chem Eng J 314:277–290. https://doi.org/10.1016/j.cej.2016.11.059

Reddy KSK, Al Shoaibi A, Srinivasakannan C (2012) A comparison of microstructure and adsorption characteristics of activated carbons by CO_2 and H_3PO_4 activation from date palm pits. New Carbon Mater 27:344–351. https://doi.org/10.1016/S1872-5805(12)60020-1

Sevilla M, Mokaya R (2014) Energy storage applications of activated carbons: supercapacitors and hydrogen storage. Energy Environ Sci 7:1250–1280. https://doi.org/10.1039/C3EE43525C

Sharma G, Naushad M, Pathania D et al (2015) Modification of Hibiscus cannabinus fiber by graft copolymerization: application for dye removal. Desalin Water Treat 54:3114–3121. https://doi.org/10.1080/19443994.2014.904822

Singh K, Arora S (2011) Removal of synthetic textile dyes from wastewaters: a critical review on present treatment technologies. Crit Rev Environ Sci Technol 41:807–878. https://doi.org/10.1080/10643380903218376

Singh SN, Mishra S, Jauhari N (2015) Degradation of anthraquinone dyes stimulated by fungi. In: Singh SN (ed) Microbial degradation of synthetic dyes in wastewaters. Springer, Cham, pp 333–356. https://doi.org/10.1007/978-3-319-10942-8_15

Theydan SK, Ahmed MJ (2012) Adsorption of methylene blue onto biomass-based activated carbon by $FeCl_3$ activation: equilibrium, kinetics, and thermodynamic studies. J Anal Appl Pyrolysis 97:116–122. https://doi.org/10.1016/j.jaap.2012.05.008

Usman ARA, Abduljabbar A, Vithanage M, Ok YS, Ahmad M, Ahmad M, Elfaki J, Abdulazeem SS, Al-Wabel MI (2015) Biochar production from date palm waste: charring temperature induced changes in composition and surface chemistry. J Anal Appl Pyrolysis 115:392–400. https://doi.org/10.1016/j.jaap.2015.08.016

Yaqub MT, Sen TK, Afroze S, Ang HM (2014) Dye and its removal from aqueous solution by adsorption: a review. Adv Colloid Interf Sci 209:172–184. https://doi.org/10.1016/j.cis.2014.04.002

Yuen FK, Hameed BH (2009) Recent developments in the preparation and regeneration of activated carbons by microwaves. Adv Colloid Interf Sci 149:19–27. https://doi.org/10.1016/j.cis.2008.12.005

Chapter 13
Date Palm Assisted Nanocomposite Materials for the Removal of Nitrate and Phosphate from Aqueous Medium

Mirna Habuda-Stanić, Marija Nujic, Blanca Magdalena Gonzalez Silva, Sveinung Sægrov, Stein Wold Østerhus, and Mario Šiljeg

Abstract Nitrate and phosphate are naturally occurring nutrients in the environment, both essential for plants and animals. However, during the past decades, due to extended usage of fertilizers and detergents, as well as due to impropriate disposal of human and animal waste, the presence of nitrate and phosphate in the aquatic ecosystems became serious environmental and human health issues. Namely, the excessive loading of streams, rivers, lakes, bays and coastal waters with nitrate and phosphate can causes excessive algae growth, deteriorating water quality and severely reduce or eliminate oxygen in the water which, at the end, results with illnesses or death of large numbers of fish. Some algae also produce harmful toxins, which can be accumulated in fish and shellfish if they are grown at polluted aquatic environment. Numerous evidence also confirmed negative effect of elevated nitrate and phosphate concentrations in drinking water on human health. Ingested via drinking water, nitrates can cause life-threatening methemoglobinemia for infants. Some epidemiological studies also associated long-term exposure to high nitrate concentration in drinking water with the occurrence of diabetes, certain cancers and reproductive problems, while the chronical exposure to high phosphate concentration was related with incidence of renal disease, damage of blood vessels and induce of aging processes.

To prevent further environment loading with nitrate and phosphate compounds, as well to reduce the risk for population health, various techniques were used for their phosphate removal from drinking and wastewater. This review presents the

M. Habuda-Stanić (✉) · M. Nujic
Faculty of Food Technology Osijek, Josip Juraj Strossmayer University of Osijek, Osijek, Croatia
e-mail: mirna.habuda-stanic@ptfos.hr

B. M. G. Silva · S. Sægrov · S. W. Østerhus
Department of Civil and Environmental Engineering, Norwegian University of Science and Technology (NTNU), Trondheim, Norway

M. Šiljeg
Faculty of Geotechnical Engineering, University of Zagreb, Varaždin, Croatia

M. Naushad, E. Lichtfouse (eds.), *Sustainable Agriculture Reviews 34*,
Sustainable Agriculture Reviews 34, https://doi.org/10.1007/978-3-030-11345-2_13

results of studies which tested the possibility of nitrate and phosphate removal from aqueous solutions using the date palm assisted nanocomposite materials.

Keywords Date palm · Nanocomposite materials · Nitrate removal · Phosphate removal · Water

13.1 Introduction

Population growth, anthropogenic activities, industrialisation, urbanisation, climate change and global warming strongly affect natural water bodies worsening water quality in physical, chemical and microbiological aspects (Alam et al. 2013, 2014). The International Food Policy Research Institute (IFPRI) and Veolia recently published the results of global study on water quality and water quantity. Due to the results of that comprehensive study, the water quality in many countries is in rapid and incontinent decrease, and over 30% of world population will be exposed to a high risk of water pollution by 2050 (IFPRI and Veolia 2014). The IFPRI and Veolia study also emphasized that the main reason for such dramatic decrease of surface waters quality will be caused by increasing amounts of nitrogen and phosphorous in water bodies and increasing values of biochemical oxygen demand (BOD).

Nitrogen and phosphorous are naturally occurring nutrients in the environment, but during the past decades their concentrations in water bodies significantly increased. Increase of nutrients in water bodies is primarily caused by human activities such as extensive usage of detergents, agricultural fertilizers and manure, livestock waste disposal, discharge of domestic and industrial wastewaters in the environment without appropriate wastewater treatment and leaching from sanitary landfills and garbage dumps. Elevated concentrations of nitrogen and phosphorous have been determined in numerous aquatic ecosystem all over the world causing its eutrophication (Kundu et al. 2015; Pandey and Yadav 2017; Álvarez et al. 2017).

Eutrophication (hypertrophication) is the process of excessive growth of plants and algae caused by elevated concentrations of nutrients (primarily nitrates and phosphates) in surface water bodies. Oxygen depletion, extensive increase of phytoplankton, and, overall, negative effects on biodiversity usually accompany this process. A natural processes or anthropogenic activities can cause eutrophication phenomenon. Natural eutrophication occurs due to ageing of water body and a slow accumulation of organic material, which cause increasing of nutrients during long period. Human-induced eutrophication occurrences more intensively as the result of frequent usage of fertilizers and discharge of nitrogen- and phosphorus-rich industrial and domestic waste waters into terrestrial, freshwater and marine ecosystems (Serrano et al. 2017; Ménesguen and Lacroix 2018).

Besides mentioned negative effect on ecosystem, elevated concentration of nitrates and phosphates can also have harmful effects to human health. Ingested via drinking water nitrates can cause methemoglobinemia (hemoglobin of the red blood cells forming methemoglobin unable to transmit oxygen in the body) in the case of acute exposure, or the occurrence of cancer in the case of chronical exposure, while the ingestion of phosphate can cause incidence of renal disease, damage of blood vessels and induce aging processes (Sadeq et al. 2008; Espejo-Herrera et al. 2015; Rojas Fabro et al. 2015; Zhai et al. 2017).

Having global negative trends in water quality and fragility of ecosystems, regulations and scientists' effort are generally focused on improvement of current drinking water and waste water technology efficiencies in order to reduce energy requirements and environmental impacts. Following those imperatives, the conception of water treatments is moving towards a circular economy approach and environmental sustainability. One of possibility to meet those criteria is usage of adsorption as easy-to-use, economically acceptable, flexible and efficient water purification technology (Sadeq et al. 2008). Adsorption was primarily used due to effective removal of organic compounds that are causing unwanted taste and odors of drinking water. But, with development of science and technology, over the last two decades, conventional adsorbents were modified and the numerous new porous materials were synthesized with aim of their effective application in various contaminants removal. Such adsorbents are nanocomposites (Figoli et al. 2017).

Nanocomposites are new generation, multiphase materials. They are usually produced as the solid base material with combination of a bulk matrix and nano-dimensional phase(s) by in situ polymerization, solvent-assisted methods, and, in the most cases, melt homogenization and tested for possible application in water purification processes (Singh et al. 2015). Nanocomposites can be also produced in the form of colloids, gels, or copolymers with structure characterized by nano-scale repeat distances between the different phases and dimensions of less than 100 nanometers. Since their structures contains various materials, properties of nanocomposites are defined by the same factors which characterize each nanocomposite component making the nanocomposite complex adsorbents with very large interfacial area and high adsorption capacities for different pollutants (Singh et al. 2015; Figoli et al. 2017). That makes nanocomposites the adsorbents with a high potential for application in drinking water and wastewater treatments.

In order to make nanocomposite adsorbent cheap and environmentally friendly, various types of organic materials i.e. agriculture waste were used as a base material for nanocomposites green synthesis. The agriculture waste is characterized by presence of variety functional groups and high amount of hemicellulose, hydrocarbons, proteins, lipids, lignin, simple sugars, water, and starch (Bhatnagar and Sillanpää 2010). Several studies reported successful nanocomposite synthesis using remains of wheat straw, chitosan as well as remains of *Imperata cylindrical*, *Moringa oleifera*, *Adansonia Digitata*, *Vitex trifolia*, and *Tabernaemontana divaricate, Callistemon viminalis, Calotropis gigantean* and *Theobroma cacao* (Rahimi et al. 2015; Dai et al. 2018; Ding et al. 2018). Several studies also reported good adsorption capacities of date palm-based nanocomposites (Bhatnagar et al. 2010; Ahmad et al. 2012; Yadav et al. 2014; Rahimi et al. 2015; Logam and Kumbahan 2018; Yulizar et al. 2018).

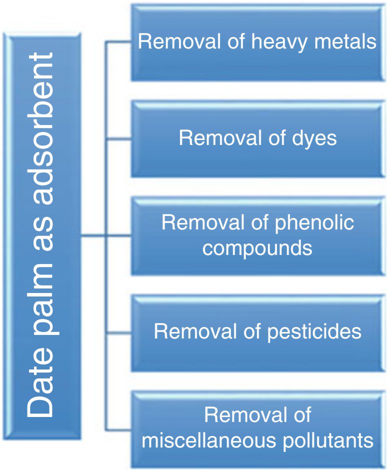


Fig. 13.1 Application of date palm as adsorbent. (According to Ahmad et al. 2012)

The date palm (*Phoenix dactylifera L.*) tree is dominant agricultural plant in East and North Africa grown for providing staple food for local population and basic material for production of palm oil. During exploitation of date palms, large amount of agricultural waste have been produced in the form of dry leaves, stems, pits and seeds. Those remains are usually transform into activated carbons which gained popularity over the last decades due to its separation performances in water purification processes and efficient removal of both organic and inorganic trace contaminants (Ahmad et al. 2012). Additionally, due to date-palm fibres, leaf fibres in the peduncle, baste fibres in the stem, wood fibres in the trunk and surface fibres around the trunk, date palm waste have been tested in raw form as adsorbent for removal of heavy metal ions, dyes, pesticides, miscellaneous pollutants and oils (Riahi et al. 2009a; Ahmad et al. 2012, Alghamdi 2016; Hussin et al. 2016; Abdelwahab et al. 2017; Ghazali et al. 2018; Logam and Kumbahan 2018). Figure 13.1 present main usage of date palm adsorbents.

This chapter present the overview of the studies conducted with the aim to remove of nitrate and phosphate from aqueous solutions using nanocomposite materials.

13.2 Nitrate Removal from Water by Palm Biomass–Based Adsorbents

Nitrogen as a major constituent, which is present in the biosphere as ammonia, nitrite and nitrate. Nitrate in environment is usually product of nitrogen denitrification and it is a highly soluble nutrient, essential for living beings. However, as the results of uncontrolled and excessive usage in various anthropogenic activities, nitrate concentrations in natural waters become a worldwide environmental problem and threat to human's health (Khan et al. 2016; Naushad et al. 2014). Due to high solubility and stability in water, conventional water treatment techniques as coagulation with flocculation and lime softening, bout followed by filtration, does not remove nitrate enough efficiently.

As efficient nitrate removal techniques following methods have been used: reverse osmosis, biological and chemical denitrification, electrodialysis, functionalized graphene nanostructured membrane, ion exchange and adsorption (Bhatnagar and Sillanpää 2011; Loganathan et al. 2013; Nur et al. 2015; Kalaruban et al. 2016a; Jahanshahi et al. 2018; Kalaruban et al. 2018). Among water treatments that efficiently removes nitrate, adsorption shows significant benefits: easy-to-use and easy-to-operate technique, cost-effective, low space requiring, high efficiency and easy upgrade water treatment. Various materials have been tested for nitrate removal showing good adsorption capacities: synthetic adsorbents, agricultural waste, fly ash, surfactant-modified zeolite, carbon nanotube, alunite and cement (Bhatnagar and Sillanpää 2011; Hu et al. 2015; Nur et al. 2015).

Tyagi et al. (2018) emphasized that efficient removal of nitrate imply its reduction to nitrogen gas and nitrogen monoxide. Following reagents shown good nitrate-reducing performances: active metals, ammonia, iron, hydrazine, borohydride, hydroxylamine, hydrogen, and formate, as well as so-called "energy methods" such as electrochemical, thermal, or photocatalytic reactions. Nitrate reduction also can be effective in the presence of powerful catalysts. Therefore, todays researches are focused on synthesis of new materials which should small surface area, high catalytic properties and excellent reducing potential, i.e. to enable nitrate reduction to ammonia (NH_3), nitrogen gas (N_2), nitrite (NO_2^-) or ammonium (NH_4^+), depending on used nanocomposite material (Tyagi et al. 2018).

Drinking water is generally produced from surface waters (river and lakes) or groundwaters. Occurrence of nitrogen in surface waters is mostly the result of excessive use of inorganic fertilizers and discharges of untreated wastewaters, while nitrate occurrence in groundwaters can be caused by the same reasons and geological composition of the aquifer (Singh et al. 2005; Bonometto et al. 2017).

Nitrate presence in drinking water is sensorially undetectable and present the health hazard. Namely, ingested by drinking water in heightened concentration, nitrate is transformed to nitrite. Transformation begin in the digestive system and nitrite enters the circulatory system where nitrite oxidizes the iron in the hemoglobin and form methemoglobin. Methemoglobin does not have the oxygen-carrying ability which causing an abrupt drop in blood oxygen and appearance of blue skin. The overall reduced ability of the red blood cell to release oxygen to tissues results with hypoxemia and the condition known as methemoglobinemia ("blue baby syndrome"). Most humans over 1 year of age have the ability to rapidly convert methemoglobin back to oxyhemoglobin, but methemoglobinemia can be fatal for infants under 6 months of age (Afzal 2006; Sadeq et al. 2008). Besides methemoglobinemia, transformation of nitrate ions from nitrite also causes a subsequent generation of carcinogenic nitrosamine (Meghdadi 2018). Therefore, the primer reason for nitrate removal from drinking water is public health.

Table 13.1 Agro-industrial waste materials for nitrate removal from aqueous solutions

Adsorbent	q_{max}	References
Chitin	200 mg g^{-1}	Morghi et al. (2015)
Wheat straw anion exchanger (WS-AE)	58.8 mg g^{-1}	Xu et al. (2010)
Coconut granular activated carbon	1.7 mg g^{-1}	Bhatnagar et al. (2008)
Red mud (unmodified)	1.859 mmol g^{-1}	Cengeloglu et al. (2006)
Red mud (modified)	5.858 mmol g^{-1}	Cengeloglu et al. (2006)
Quaternized Chinese reed	7.55 mg g^{-1}	Namasivayam and Sangeetha (2006)
Activated carom from coconut shells	$2.66 \cdot 10^{-1}$ mmol g^{-1}	Ohe et al. (2003)
Activated carbon from bamboo	$1.04 \cdot 10^{-1}$ mmol g^{-1}	Ohe et al. (2003)
Rice hull	1.32 mmol g^{-1}	Orlando et al. (2002)
Sugarcane bagasse	1.41 mmol g^{-1}	Orlando et al. (2002)
Pure alkaline lignin	1.8 mmol g^{-1}	Orlando et al. (2002)
Pure cellulose	1.34 mmol g^{-1}	Orlando et al. (2002)

Following materials have been tested as adsorbent for nitrate removal from drinking water: carbon-based materials (powder activated carbon, carbon cloth, carbon nanotubes, commercial activated carbon, $ZnCl_2$ treated granular activated carbon, iron oxide-dispersed activated carbon fibers), natural adsorbents (clay, zeolite, sepiolite) agriculture wastes (sugarcane bagasse, rice hull, coconut shells, wheat residues, almond shell, sugar beet pulp), industrial waste (fly ash, red mud, slag), biosorbents (chitosan, bamboo powder, Chinese reed) and miscellaneous adsorbents (layered-double hydroxides/hydrotalcite-like compounds/ hydroxyapetite, nano-alumina, mesoporous silica, cement paste), Nanoscale Zero Valent Iron (NZVI), nanotubes, nanofibres etc. (Bhatnagar and Sillanpää 2011; Olgun et al. 2013; Motamedi et al. 2014; Hu et al. 2015; Kalaruban et al. 2016a, b; Dai et al. 2018; He et al. 2018; Meghdadi 2018; Tyagi et al. 2018).

To obtain maximum adsorption capacities, various adsorbents demands various conditions and efficiency of adsorbent is mainly defined by adsorbent type, initial nitrate concentration in raw water, pH and temperature (Singh et al. 2018).

Due to its loose and porous structures, abundantly of functional groups such as the carboxyl- and hydroxyl- groups, renewability and low cost, various agriculture and industrial waste were tested as adsorbents for nitrate removal from water. Agro-industrial waste materials and their maximum capacities for nitrate adsorption are presented in Table 13.1.

Various palm biomass–based adsorbents were tested as potential low-cost adsorbents. Ohe et al. (2003) used coconut shells to prepare activated carbon for nitrate removal. Obtained activated carbon was ground up and sieved to obtain adsorbent with the size of particles in the range from 0.3 to 0.5 mm. Authors tested obtained adsorbents for nitrate removal as a function of contact time, pH, temperature and initial nitrate concentration. Prepared palm biomass–based adsorbents shown high selectivity for nitrate anions and inversely proportional of adsorption capacity and temperature. As highest capacity of coconut shells based activated carbon, authors reported 3.06 mmol g^{-1} noted at room temperature. They also emphasized that nitrate removal of 70% was obtained at pH 4 (Ohe et al. 2003).

Namasivayam and Sangeetha (2006) modified coir pith in order to produce $ZnCl_2$ loaded activated carbon as adsorbents for removal of nitrate and several other contaminants. Coir pith was dried in sunlight for 5 h and then zinc chloride activated coir pith carbon was prepared by adding the coir pith in a boiling solution of zinc chloride. After filtration and drying, adsorbent was carbonized at 700 °C. After cooling, carbonized material was sieved to 250–500 μm particle size and tested as adsorbent used for adsorption studies. Authors reported more than 90% removal of nitrate at pH 6.2 and adsorbent dose of 400 mg/50 ml (Namasivayam and Sangeetha 2006).

Kalaruban et al. (2016a, b) studied nitrate removal by chemically surface-modified coconut copra. Chemical surface modification implied incorporation of amine groups with the aim to increase the surface positive charges. Authors reported that maximum nitrate adsorption capacity of 59 mg/g was obtained by modified coconut copra at pH 6.5 (Kalaruban et al. 2016a, b).

Adebayo et al. (2016) tested palm kernel shell as nitrate removal material. Preparation of adsorbent implied soak of biosorbent in warm deionized water, washing with NaOH, and rinsing with deionized water. pH neutral adsorbent was further oven-dried, ground, and sieves to obtain particles size 53-74 μm. Adsorbent particles were put in a flask for 2 h for treatment with acid solution and heated reflux (95 °C). After 2 h, adsorbent was rinsed with deionized water until neutral pH. Palm biomass–based adsorbents was than dried at 60 °C, pulverized to 0.45 mm, heated for 2 h at 200 °C, and tested for nitrate removal. The adsorption capacitiy of the adsorbent was tested by 50 mL solutions with initial nitrate concentrations ranged from 50 to 500 mg L^{-1} and 0.2 g of the adsorbents. As maximum adsorption capacity 85.73 mg g^{-1} was reported (Adebayo et al. 2016).

Bashir et al. (2018) tested low-cost bioadsorbent obtained by chemical modification of palm kernel shells. Effect of initial nitrate concentration, pH and temperature on nitrate removal was tested. Authors reported the maximum adsorption capacity of 54.18 mg/g and removal efficiency of 79.6%. Palm biomass–based adsorbent removed effectively nitrate in a wide range of pH 4–8 and temperature (20–40 °C) (Bashir 2018).

13.3 Phosphate Removal from Water by Palm Biomass–Based Adsorbents

Phosphate is an inorganic compound, which is considered as a non-toxic for humans. The United States Food and Drug Administration (FDA) reported that inorganic phosphates, as food ingredients, are considers as “generally safe”. FDA also quoted that average phosphate levels found in a litre of drinking water are about 100 times lower than the average phosphate levels found in the average American diet.

Table 13.2 Agriculture and industrial waste materials for phosphate removal from aqueous solutions

Adsorbent	q_{max}/mg g^{-1}	References
Alkaline residue	2.2 mg g^{-1}	Yan et al. (2014)
Granular date stones	8.7 mg g^{-1}	Ismail (2012b)
Palm surface fibres	5.5 mg g^{-1}	Ismail (2012a)
Wheat straw	8.43 mg g^{-1}	Ma et al. (2011)
Wheat straw anion exchanger (WS-AE)	45.7 mg g^{-1}	Xu et al. (2010)
Date palm fibres	4.34 mg g^{-1}	Riahi et al. (2009a)
Red mud (raw)	0.23 mg g^{-1}	Huang et al. (2008)
Red mud (HCl treated)	0.58 mg g^{-1}	Huang et al. (2008)

Phosphate in water bodies is undesirable due to a worldwide problem of eutrophication. Phosphate in water resources mainly originates from fertilizers, detergents which contains sodium tripolyphosphates and untreated wastewater. But, nowadays, wastewater has been recognized as alternative source of phosphorus, and newest trends in wastewater treatments are now focused on phosphate recovery from wastewater as a potential respond to overcome the global challenge of phosphorus scarcity (Weiner et al. 2001; Length 2012).

Various physical, biological and chemical techniques have been tested for the phosphates removal from water and wastewaters including ion exchange, chemical precipitation/coagulation and adsorption (Length 2012). Among all mentioned methods, adsorption is widely accepted as efficient phosphate removal method.

Phosphate removal by adsorption is tested by decades and adsorption capacities of numerous unmodified and modified materials have been investigated such as: activated alumina, clay, fly ash, calcite, graphene, activated carbons, iron oxide, modified zeolite, dolomite, aluminum oxide, lanthanum hydroxide hybrid material, pumice powder, nanocomposite, brucite-periclase materials etc. (Onar et al. 1996; Prochaska and Zouboulis 2006; Islam et al. 2014; Nur et al. 2014; Mehrabi et al 2015; Andrés et al. 2018). Adsorbents obtained from agriculture and industrial waste were also tested and their maximum capacities for phosphate removal are presented in Table 13.2.

The palm biomass was in the focus of several adsorption studies for phosphate removal from aqueous solutions. Riahi et al. (2009a) studied the removal of phosphate ions from domestic wastewater by date palm fibers. Date-palm fibers filter media whit diameters 0.2–0.5, 0.5–0.8 and 0.8–1.2 mm were tested in glass column. Fixed-bed up-flow filter media was between 12 and 72 mL min^{-1}. Results shown that efficiency of adsorbent depend on initial phosphate concentration, pH, and adsorbent dosage. Amount of adsorbed phosphate increased with the increase of its initial concentration, while increasing pH values had negative effect on adsorption. The highest phosphate removal (cca 57%) was obtained when filter material with smallest particle size was used. Authors emphasized that tested date-palm fibers filter most suitable for small water supply systems (Riahi et al. 2009a).

The same year (2009b) Riahi et al. published result of similar study conducted with the aim to test natural fibers from the surface of *P. dactylifera* L. date palm for phosphate removal. Used date palm surface fibers had 0.2–0.8 mm diameter. Prior usage, date palm fibers were washed with distilled water and dried at 105 °C for 24 h. Adsorption tests were preformed with various initial phosphate concentrations and contact time at room temperature. Obtained results shown that pH, initial phosphate concentration and adsorbent dosage were key factor for effective removal.

With initial pH in range 5–8, about 4.35 mg of phosphate was adsorbed on 1 g of adsorbent (Riahi et al. 2009b).

In the year of 2017, Riahi et al. published the results of a kinetic modeling study of phosphate adsorption onto *Phoenix dactylifera* L. date palm fibers conducted in batch mode in order to define the mechanisms and kinetic model for phosphate sorption. Test were performed by the solutions with initial phosphate concentration in the range from 30 to 110 mg/L. Using seven statistical functions, authors estimated that Elovich equation and pseudo second-order equation provide the best fit to experimental data. Authors emphasized that adsorption in time dependent. They reported that over 88% of phosphate was adsorbed within 30 minutes in the test performed when solution with initial phosphate concentration of 110 mg/L was used (Riahi et al. 2017).

Ismail (2012) tested palm fibres and the granular date stones obtained from the trunk surface of a *Phoenix dactylifera* L. date palm for phosphate removal. The effects of contact time, initial phosphate concentrations, sorbent dosage and pH were examined. Author reported that increase of adsorbents dosages from 1 to 10 g L^{-1} increased efficiencies of phosphate removal from 25% to 85%, although maximum adsorption capacities were obtained after the adsorbent amount exceeded 5 g L^{-1}. Tested palm-based adsorbents untaken more phosphate with decreasing the pH. Ismail reported that maximum adsorption capacity of granular date stones were 8.70 mg P g^{-1}, and maximum adsorption capacity of palm surface fibres 8.50 mg P g^{-1} (Ismail 2012).

13.4 Conclusions

Industrialisation, population growth and agriculture activities are the main factors that significantly interrupted the quality of aquatic ecosystems during the last decades. Although various water bodies are characterized by different chemism, anthropogenic eutrophication driven by general increasing of phosphate and nitrate in surface water becomes global environmental and health issue. Therefore, significant efforts are daily given by many scientists all over the world for finding the most cost-benefit solutions for nitrates and phosphates removal from drinking water and wastewater in order to prevent further nitrate and phosphate loading of the environment.

One of the eco-friendly solution for nitrate and phosphate removals is water treatment by biosorbents i.e. adsorbents obtained from biomass which is, in the most cases, classified as agriculture waste. Using biosorbents for nitrate and phosphate removal contribute to achievement of circular economy goals. The other benefit of biosorbents usage is that after their saturation with nutrients they can be used organic fertilizers i.e. source of bioavailable nitrogen and phosphorous for crops.

The palm biomass-based adsorbents have been tested, with or without prior modification, as adsorbents for nitrate and phosphate removal from water. Authors of adsorption studies reported good performances and adsorption capacities of raw palm-based adsorbents which were additionally improved by chemical modifications of materials.

Effective removal of nitrate and phosphate, as well as guidelines for agriculture waste management are the main reasons which will keep palm biomass as attractive base material for further research and applications in water treatments.

References

Abdelwahab O, Nasr SM, Thabet WM (2017) Palm fibers and modified palm fibers adsorbents for different oils. Alex Eng J 56(4):749–755. https://doi.org/10.1016/j.aej.2016.11.020

Adebayo OL, Adaramodu AA, Ajayi MG, Olasehinde FE, Oyetunde JG (2016) Purification of nitrate contaminated aqueous solution using modified and unmodified palmkernel shell. Int Lett Chem Phys Astron 71:11–18. https://doi.org/10.18052/www.scipress.com/ILCPA.71.11

Afzal BM (2006) Drinking water and women's health. J Midwifery Women's Health 51(1):12–18. https://doi.org/10.1016/j.jmwh.2005.08.014

Ahmad T, Danish M, Rafatullah M, Ghazali A, Sulaiman O, Hashim R, Ibrahim MNM (2012) The use of date palm as a potential adsorbent for wastewater treatment: a review. Environ Sci Pollut Res 19(5):1464–1484. https://doi.org/10.1007/s11356-011-0709-8

Alam MM, ALOthman ZA, Naushad M (2013) Analytical and environmental applications of polyaniline Sn(IV) tungstoarsenate and polypyrrole polyantimonic acid composite cation-exchangers. J Ind Eng Chem 19:1973–1980. https://doi.org/10.1016/j.jiec.2013.03.006

Alam MM, ALOthman ZA, Naushad M, Aouak T (2014) Evaluation of heavy metal kinetics through pyridine based Th(IV) phosphate composite cation exchanger using particle diffusion controlled ion exchange phenomenon. J Ind Eng Chem 20:705–709. https://doi.org/10.1016/j.jiec.2013.05.036

Alghamdi AA (2016) An investigation on the use of date palm fibers and coir pith as adsorbents for Pb(II) ions from its aqueous solution. Desalin Water Treat 57(26):12216–12226. https://doi.org/10.1080/19443994.2015.1048743

Álvarez X, Valero E, Santos RMB, Varandas SGP, Sanches Fernandes LF, Pacheco FAL (2017) Anthropogenic nutrients and eutrophication in multiple land use watersheds: best management practices and policies for the protection of water resources. Land Use Policy 69(August):1–11. https://doi.org/10.1016/j.landusepol.2017.08.028

Andrés E, Araya F, Vera I, Pozo G, Vidal G (2018) Phosphate removal using zeolite in treatment wetlands under different oxidation-reduction potentials. Ecol Eng 117(March):18–27. https://doi.org/10.1016/j.ecoleng.2018.03.008

Bashir MT (2018) A sustainable approach of nitrate adsorption from water using palm oil agricultural waste. Asian J Microbiol Biotechnol Environ Sci 20(2):451–457

Bashir MT, Ali S, Azni I, Harun AR (2018) A sustainable approach of nitrate adsorption from water using palm oil agricultural waste. Asian J Microbiol Biotechnol Environ Sci 20(2):451–457

Bhatnagar A, Sillanpää M (2010) Utilization of agro-industrial and municipal waste materials as potential adsorbents for water treatment – a review. Chem Eng J 157:277–296. https://doi.org/10.1016/j.cej.2010.01.007

Bhatnagar A, Sillanpää M (2011) A review of emerging adsorbents for nitrate removal from water. Chem Eng J 168(3):493–504. https://doi.org/10.1016/j.cej.2011.01.103

Bhatnagar A, Ji M, Choi Y, Jung W, Lee S, Kim S et al (2008) Removal of nitrate from water by adsorption onto zinc chloride treated activated carbon. Sep Sci Technol 43(4):886–907. https://doi.org/10.1080/01496390701787461

Bhatnagar A, Vilar VJP, Botelho CMS, Boaventura RAR (2010) Coconut-based biosorbents for water treatment – a review of the recent literature. Adv Colloid Int Sci 160:1–15. https://doi.org/10.1016/j.cis.2010.06.011

Bonometto A, Giordani G, Ponis E, Facca C, Boscolo Brusà R, Sfriso A, Viaroli P (2017) Assessing eutrophication in transitional waters: a performance analysis of the Transitional Water Quality Index (TWQI) under seasonal fluctuations. Estuar Coast Shelf Sci. https://doi.org/10.1016/j.ecss.2017.08.008

Cengeloglu Y, Tor A, Ersoz M, Arslan G (2006) Removal of nitrate from aqueous solution by using red mud. Sep Purif Technol 51(3):374–378. https://doi.org/10.1016/j.seppur.2006.02.020

Dai Y, Sun Q, Wang W, Lu L, Liu M, Li J, . . . Zhang Y (2018) AC SC. https://doi.org/10.1016/j.chemosphere.2018.06.179

Ding J, Li Q, Xu X, Zhang X, Su Y, Yue Q, Gao B (2018) SC. Carbohydrate polymers. Elsevier. https://doi.org/10.1016/j.carbpol.2018.02.032

Espejo-Herrera N, Cantor KP, Malats N, Silverman DT (2015) Nitrate in drinking water and bladder cancer risk in Spain. Environ Res 137:299–307. https://doi.org/10.1016/j.envres.2014.10.034

Figoli A, Saeed M, Dorraji S, Amani-ghadim AR (2017) 4 – Application of nanotechnology in drinking water purification. Elsevier, New York. https://doi.org/10.1016/B978-0-12-804300-4/00004-6

Ghazali A, Shirani M, Semnani A, Zare-shahabadi V, Nekoeinia M (2018) Optimization of crystal violet adsorption onto Date palm leaves as a potent biosorbent from aqueous solutions using response surface methodology and ant colony. Biochem Pharmacol 6:3942–3950. https://doi.org/10.1016/j.jece.2018.05.043

He Y, Lin H, Dong Y, Li B, Wang L, Chu S et al (2018) Zeolite supported Fe/Ni bimetallic nanoparticles for simultaneous removal of nitrate and phosphate: synergistic effect and mechanism. Chem Eng J 347:669–681. https://doi.org/10.1016/j.cej.2018.04.088

Hu Q, Chen N, Feng C, Hu W (2015) Nitrate adsorption from aqueous solution using granular chitosan-Fe3+ complex. Appl Surf Sci 347:1–9. https://doi.org/10.1016/j.apsusc.2015.04.049

Huang W, Wang S, Zhu Z, Li L, Yao X, Rudolph V, Haghseresht F (2008) Phosphate removal from wastewater using red mud. J Hazard Mater 158(1):35–42. https://doi.org/10.1016/j.jhazmat.2008.01.061

Hussin MH, Aqilah N, Garba ZN, Kassim MJ, Abdul A, Brosse N et al (2016) International journal of biological macromolecules physicochemical of microcrystalline cellulose from oil palm fronds as potential methylene blue adsorbents. Int J Biol Macromol 92:11–19. https://doi.org/10.1016/j.ijbiomac.2016.06.094

International Food Policy Research Institute (IFPRI) and Veolia (2014) The murky future of global water quality. https://espas.secure.europarl.europa.eu/orbis/sites/default/files/generated/document/en/IFPRI_Veolia_H2OQual_WP.pdf

Islam M, Mishra S, Swain SK, Patel R, Dey RK, Naushad M (2014) Evaluation of phosphate removal efficiency from aqueous solution by polypyrrole/BOF Slag nanocomposite. Sep Sci Technol 49(13):2668–2680. https://doi.org/10.1080/01496395.2014.933981

Ismail ZZ (2012) Kinetic study for phosphate removal from water by recycled date-palm wastes as agricultural by-products. Int J Environ Stud 69(1):135–149. https://doi.org/10.1080/00207233.2012.656975

Jahanshahi D, Vahid B, Azamat J (2018) Computational study on the ability of functionalized graphene nanosheet for nitrate removal from water. Chem Phys 511:20–26. https://doi.org/10.1016/j.chemphys.2018.05.018

Kalaruban M, Loganathan P, Shim WG, Kandasamy J, Naidu G, Nguyen TV, Vigneswaran S (2016a) Removing nitrate from water using iron-modified Dowex 21K XLT ion exchange resin: batch and fluidised-bed adsorption studies. Sep Purif Technol 158:62–70. https://doi.org/10.1016/j.seppur.2015.12.022

Kalaruban M, Loganathan P, Shim WG, Kandasamy J, Ngo HH, Vigneswaran S (2016b) Science of the total environment enhanced removal of nitrate from water using amine-grafted agricultural wastes. Sci Total Environ 565:503–510. https://doi.org/10.1016/j.scitotenv.2016.04.194

Kalaruban M, Loganathan P, Shim WG, Kandasamy J (2018) Applied sciences mathematical modelling of nitrate removal from water using a submerged membrane adsorption hybrid system with four adsorbents. https://doi.org/10.3390/app8020194

Khan MR, Wabaidur SM, Alothman ZA et al (2016) Method for the fast determination of bromate, nitrate and nitrite by ultra performance liquid chromatography-mass spectrometry and their monitoring in Saudi Arabian drinking water with chemometric data treatment. Talanta 152:513–520. https://doi.org/10.1016/j.talanta.2016.02.036

Kundu S, Vassanda Coumar M, Rajendiran S, Ajay, Subba Rao A (2015) Phosphates from detergents and eutrophication of surface water ecosystem in India. Curr Sci 108(7):1320–1325

Length F (2012) Phosphate pollution control in waste waters using new, 4 April, 73–85. https://doi.org/10.5897/IJWREE11.132

Logam P, Kumbahan A (2018) Removal of heavy metals from wastewater using Date Palm as a biosorbent: a comparative review. Sains Malaysiana 47(1):35–49

Loganathan P, Vigneswaran S, Kandasamy J (2013) Enhanced removal of nitrate from water using surface modification of adsorbents – a review. J Environ Manag 131:363–374. https://doi.org/10.1016/j.jenvman.2013.09.034

Ma Z, Li Q, Yue Q, Gao B, Li W, Xu X, Zhong Q (2011) Adsorption removal of ammonium and phosphate from water by fertilizer controlled release agent prepared from wheat straw. Chem Eng J 171(3):1209–1217. https://doi.org/10.1016/j.cej.2011.05.027

Meghdadi A (2018) SC. Water Res. https://doi.org/10.1016/j.watres.2018.04.063

Mehrabi N, Soleimani M, Sharififard H, Yeganeh MM (2015) Optimization of phosphate removal from drinking water with activated carbon using response surface methodology (RSM), (September). Desalin Water Treat 57(33):15613–15618. https://doi.org/10.1080/19443994.2015.1070763

Ménesguen A, Lacroix G (2018) Modelling the marine eutrophication: a review. Sci Total Environ 636:339–354. https://doi.org/10.1016/j.scitotenv.2018.04.183

Morghi M, Abidar F, Soudani A, Zerbet M, Chiban M, Kabli H, Sinan F (2015) Removal of nitrate ions from aqueous solution using chitin as natural adsorbent. Int J Res Environ Stud 2:8–20

Motamedi E, Atouei MT, Kassaee MZ (2014) Comparison of nitrate removal from water via graphene oxide coated Fe, Ni and Co nanoparticles. Mater Res Bull 54:34–40

Namasivayam C, Sangeetha D (2006) Recycling of agricultural solid waste, coir pith: removal of anions, heavy metals, organics and dyes from water by adsorption onto ZnCl 2 activated coir pith carbon, vol 135, pp 449–452. https://doi.org/10.1016/j.jhazmat.2005.11.066

Naushad M, Khan MA, ALOthman ZA, Khan MR (2014) Adsorptive removal of nitrate from synthetic and commercially available bottled water samples using De-Acidite FF-IP resin. J Ind Eng Chem 20:3400–3407. https://doi.org/10.1016/j.jiec.2013.12.026

Nur T, Johir MAH, Loganathan P, Nguyen T, Vigneswaran S, Kandasamy J (2014) Journal of industrial and engineering chemistry phosphate removal from water using an iron oxide impregnated strong base anion exchange resin. J Ind Eng Chem 20:1301–1307

Nur T, Shim WG, Loganathan P, Vigneswaran S, Kandasamy J (2015) Nitrate removal using Purolite A520E ion exchange resin: batch and fixed-bed column adsorption modelling. Int J Environ Sci Technol 12:1311–1320. https://doi.org/10.1007/s13762-014-0510-6

Ohe K, Nagae Y, Nakamura S, Baba Y (2003) Removal of nitrate anion by carbonaceous materials prepared from bamboo and coconut shell. J Chem Eng Jpn 36(4):511–515. https://doi.org/10.1252/jcej.36.511

Olgun A, Atar N, Wang S (2013) Batch and column studies of phosphate and nitrate adsorption on waste solids containing boron impurity. Chem Eng J 222:108–119. https://doi.org/10.1016/j.cej.2013.02.029

Onar AN, Balkaya N, Akyüz T (1996) Phosphate removal by adsorption. Environ Technol 17 (May):207–213. https://doi.org/10.1080/09593331708616378

Orlando US, Baes AU, Nishijima W, Okada M (2002) A new procedure to produce lignocellulosic anion exchangers from agricultural waste materials. Bioresour Technol 83(3):195–198. https://doi.org/10.1016/S0960-8524(01)00220-6

Pandey J, Yadav A (2017) Alternative alert system for Ganga river eutrophication using alkaline phosphatase as a level determinant. Ecol Indic 82(January):327–343. https://doi.org/10.1016/j.ecolind.2017.06.061

Prochaska CA, Zouboulis AI (2006) Removal of phosphates by pilot vertical-flow constructed wetlands using a mixture of sand and dolomite as substrate. Ecol Eng 26:293–303. https://doi.org/10.1016/j.ecoleng.2005.10.009

Rahimi S, Moattari RM, Rajabi L, Derakhshan AA (2015) Optimization of lead removal from aqueous solution using goethite/chitosan nanocomposite by response surface methodology. Colloids Surf A Physicochem Eng Asp 484:216–225. https://doi.org/10.1016/j.colsurfa.2015.07.063

Riahi K, Mammou AB, Thayer BB (2009a) Date-palm fibers media filters as a potential technology for tertiary domestic wastewater treatment. J Hazard Mater 161(2–3):608–613. https://doi.org/10.1016/j.jhazmat.2008.04.013

Riahi K, Thayer BB, Mammou AB, Ammar AB, Jaafoura MH (2009b) Biosorption characteristics of phosphates from aqueous solution onto Phoenix dactylifera L. date palm fibers. J Hazard Mater 170(2–3):511–519. https://doi.org/10.1016/j.jhazmat.2009.05.004

Riahi K, Chaabane S, Thayer BB (2017) A kinetic modeling study of phosphate adsorption onto Phoenix dactylifera L. date palm fibers in batch mode. J Saudi Chem Soc 21(s1):s143–s152. https://doi.org/10.1016/j.jscs.2013.11.007

Rojas Fabro AY, Pacheco Ávila JG, Esteller Alberich MV, Cabrera Sansores SA, Camargo-Valero MA (2015) Spatial distribution of nitrate health risk associated with groundwater use as drinking water in Merida, Mexico. Appl Geogr 65:49–57. https://doi.org/10.1016/j.apgeog.2015.10.004

Sadeq M, Moe CL, Attarassi B, Cherkaoui I (2008) Drinking water nitrate and prevalence of methemoglobinemia among infants and children aged 1 – 7 years in Moroccan areas. Int J Hyg Environ Health 211:546–554. https://doi.org/10.1016/j.ijheh.2007.09.009

Serrano L, Reina M, Quintana XD, Romo S (2017) A new tool for the assessment of severe anthropogenic eutrophication in small shallow water bodies effect of hydroperiod on the specific richness of zooplankton view project shallow wetland lake functioning and restoration in a changing European environment view project. Ecol Indic 76:324–334. https://doi.org/10.1016/j.ecolind.2017.01.034

Singh KP, Malik A, Singh VK, Mohan D, Sinha S (2005) Chemometric analysis of groundwater quality data of alluvial aquifer of Gangetic plain, North India. Anal Chim Acta 550(1–2):82–91. https://doi.org/10.1016/j.aca.2005.06.056

Singh B, Chauhan S, Verma G (2015) Nanocomposites – a review. J Chem Cheml 5 (September):506–510

Singh NB, Nagpal G, Agrawal S (2018) Water purification by using adsorbents: a review. Environ Technol Innov 11:187–240. https://doi.org/10.1016/j.eti.2018.05.006

Tyagi S, Rawtani D, Khatri N, Tharmavaram M (2018) Journal of water process engineering strategies for nitrate removal from aqueous environment using nanotechnology: a review. J Water Process Eng 21(September 2017):84–95. https://doi.org/10.1016/j.jwpe.2017.12.005

Weiner ML, Salminen WF, Larson PR, Barter RA, Kranetz JL, Simon GS (2001) Toxicological review of inorganic phosphates. Food Chem Toxicol 39:759–786

Xu X, Gao BY, Yue QY, Zhong QQ (2010) Preparation of agricultural by-product based anion exchanger and its utilization for nitrate and phosphate removal. Bioresour Technol 101 (22):8558–8564. https://doi.org/10.1016/j.biortech.2010.06.060

Yadav SK, Sinha S, Singha DK (2014) Chromium(VI) removal from aqueous solution and industrial wastewater by modified date palm trunk. Environ Prog Sustain Energy 34(2):452–460. https://doi.org/10.1002/ep

Yan Y, Sun X, Ma F, Li J, Shen J, Han W et al (2014) Removal of phosphate from wastewater using alkaline residue. J Environ Sci (China) 26(5):970–980. https://doi.org/10.1016/S1001-0742(13)60537-9

Yulizar Y, Bakri R, Bagus Apriandanu DO, Hidayat T (2018) ZnO/CuO nanocomposite prepared in one-pot green synthesis using seed bark extract of *Theobroma cacao*. Nano-Structures & Nano-Objects 16:300–305. https://doi.org/10.1016/j.nanoso.2018.09.003

Zhai Y, Zhao X, Teng Y, Li X, Zhang J, Wu J, Zuo R (2017) Groundwater nitrate pollution and human health risk assessment by using HHRA model in an agricultural area, NE China. Ecotoxicol Environ Saf 137(December 2016):130–142. https://doi.org/10.1016/j.ecoenv.2016.11.010