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Nabeel Khan Niazi
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# Global Arsenic Hazard

## Ecotoxicology and Remediation

Springer

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Nabeel Khan Niazi · Irshad Bibi · Tariq Aftab
Editors

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# Contents

1 **Global Arsenic Hazard and Sustainable Development** . . . . . . . . . . . 1
Nabeel Khan Niazi

2 **Global Arsenic Contamination of Groundwater, Soil and Food Crops and Health Impacts** . . . . . . . . . . . 13
Sana Khalid, Muhammad Shahid, Irshad Bibi, Natasha, Behzad Murtaza, Tasveer Zahra Tariq, Rabia Naz, Muhammad Shahzad, Muhammad Mahroz Hussain, and Nabeel Khan Niazi

3 **Arsenic Contamination in Rice and the Possible Mitigation Options** . . . . . . . . . . . 35
Sudip Sengupta, Tarit Roychowdhury, Amit Phonglosa, and Jajati Mandal

4 **Arsenic in Gold Mining Wastes: An Environmental and Human Health Threat in Ghana** . . . . . . . . . . . 49
Albert Kobina Mensah, Bernd Marschner, Kenneth Joseph Bansah, Eric Stemn, Sabry M. Shaheen, and Jörg Rinklebe

5 **Arsenic Contamination in Karst Regions** . . . . . . . . . . . 85
Yafei Sun, Nabeel Khan Niazi, and Jianxu Wang

6 **Arsenic Dynamics in Paddy Rice Ecosystems and Human Exposure** . . . . . . . . . . . 99
Indika Herath, Chuxia Lin, and Jochen Bundschuh

7 **Interaction of Arsenic with Biochar in Water and Soil: Principles, Applications, and Prospects** . . . . . . . . . . . 129
Pabasari A. Koliyabandara, Udayagee Kumarasinghe, Danushika C. Manatunga, Randika Jayasinghe, Rohan S. Dassanayake, and Meththika Vithanage

**8 Accumulation and Translocation of Arsenic in Rice with Its Distributional Flow During Cooking: A Study in West Bengal, India** . . . . . 159
Antara Das, Nilanjana Roy Chowdhury, Deepanjan Mridha, Madhurima Joardar, Ayan De, Sharmistha Majumder, and Tarit Roychowdhury

**9 An Overview of Arsenic Contamination in Water Resources of Pakistan, Risk Assessment and Remediation Strategies** . . . . . 179
Saqib Bashir, Sanaullah Yasin, Safdar Bashir, Zubair Aslam, Waseem Hassan, Saadullah Khan Leghari, and Nabeel Khan Niazi

**10 Approaches for Stochastic Modelling of Toxic Ion Adsorption at Crystal-Water Interfaces: A Case Study of Arsenic** . . . . . 201
Inna Kurganskaya

**11 A Comparison of Technologies for Remediation of Arsenic-Bearing Water: The Significance of Constructed Wetlands** . . . . . 223
Aimen Ali, Muhammad Mahroz Hussain, Nabeel Khan Niazi, Fazila Younas, Zia Ur Rahman Farooqi, Nukshab Zeeshan, Muhammad Tariq Javed, Muhammad Shahid, and Irshad Bibi

**12 Application of Nanotechnology in Mitigating Arsenic Stress and Accumulation in Crops: Where We Are and Where We Are Moving Towards** . . . . . 247
Debojyoti Moulick, Swati Hazra, Arkabanee Mukherjee, Sapana Sinha, Subrata Mahanta, Anupam Das, Bedabrata Saha, Nabeel Khan Niazi, and Jayanta Kumar Biswas

**13 Nano-Enabled Remediation of Arsenic-Bearing Water and Wastewater** . . . . . 271
Rabia Ashraf, Irshad Bibi, Muhammad Mahroz Hussain, Tariq Aftab, and Nabeel Khan Niazi

**14 Molecular Aspects of Arsenic Responsive Microbes in Soil-Plant-Aqueous Triphasic Systems** . . . . . 291
Arnab Majumdar, Fathima Afsal, Saurav Pathak, Munish Kumar Upadhayay, Tarit Roychowdhury, and Sudhakar Srivastava

**15 Phosphate-Induced Phytoextraction by *Pteris vittata* Reduced Arsenic Uptake by Rice** . . . . . 313
Asit Mandal, Tapan J. Purakayastha, Ashok K. Patra, and Binoy Sarkar

16 Modified Biosorbents as Potential Biomaterials for Arsenic Removal from Contaminated Water ... 335
Shazma Muzammal, Asma Akram, Muhammad Bilal Shakoor, Asim Jilani, Sajid Rashid Ahmad, Mujahid Farid, and Nabeel Khan Niazi

17 Phytoremedial Potential of Perennial Woody Vegetation Under Arsenic Contaminated Conditions in Diverse Environments ... 355
Farah Ejaz, Muhammad Talha Bin Yousaf, Muhammad Farrakh Nawaz, Nabeel Khan Niazi, Sadaf Gul, Irfan Ahmed, Muhammad Asif, and Irshad Bibi

18 Bacterial Tolerance and Biotransformation of Arsenic in Soil and Aqueous Media ... 375
Etisam Mazhar, Tanvir Shahzad, Faisal Mahmood, Farrukh Azeem, Abid Mahmood, and Sabir Hussain

19 Arsenic Bioremediation of Soil and Water Systems—An Overview ... 407
Muhammad Shabaan, Kashiuf Asif, Qasim Ali, Hafiz Naeem Asghar, and Zahir Ahmad Zahir

20 Modern Aspects of Phytoremediation of Arsenic-Contaminated Soils ... 433
Tariq Mehmood, Anam Ashraf, Licheng Peng, Mehak Shaz, Shakeel Ahmad, Shakeel Ahmad, Ibadullah Khan, Muhammad Abid, Gajendra Kumar Gaurav, and Umair Riaz

21 Nanoparticulate Iron Oxide Minerals for Arsenic Removal from Contaminated Water ... 459
Hamna Bashir, Irshad Bibi, Muhammad Mahroz Hussain, Nabeel Khan Niazi, and Jibran Iqbal

22 Arsenic-Toxicity and Tolerance: Phytochelatin-Mediated Detoxification and Genetic Engineering-Based Remediation ... 481
Gouranga Upadhyaya and Aryadeep Roychoudhury

23 Distribution of Arsenic in Rice Grain from West Bengal, India: Its Relevance to Geographical Origin, Variety, Cultivars and Cultivation Season ... 509
Nilanjana Roy Chowdhury, Antara Das, Madhurima Joardar, Deepanjan Mridha, Ayan De, Sharmistha Majumder, Jajati Mandal, Arnab Majumdar, and Tarit Roychowdhury

24 Arsenic Contamination in Soil and Water Across South East Asia: Its Impact and Mitigation Strategies ... 533
Lalichetti Sagar, Sultan Singh, Meenakshi Attri, Sagar Maitra, Tanmoy Shankar, Masina Sairam, Tariq Aftab, and Akbar Hossain

**Correction to: Global Arsenic Hazard** . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . C1
Nabeel Khan Niazi, Irshad Bibi, and Tariq Aftab

# Chapter 1
# Global Arsenic Hazard and Sustainable Development

**Nabeel Khan Niazi**

**Abstract** Arsenic (As) is a highly toxic and non-essential element for all forms of life. Inorganic forms of As, arsenite and arsenate, are more toxic and mobile than the organic ones. Both geogenic and anthropogenic sources led to contamination of terrestrial and aquatic ecosystems with variable As concentrations in over 115 countries worldwide, posing health risk to ~ 250 million people. The pathways of As exposure to humans include drinking well water, irrigation water, food crops, exports and imports of food products (e.g., rice grain, baby food items). This chapter elaborates global As contamination issue in context of various Sustainable Development Goals (SDGs) of the United Nations. Hence it is crucial to address global As hazard to ensure water and food security, human health, SDGs, as well as improve the socio-economic situation of the communities in As-affected areas. The current chapter introduces key features of this book with twenty four chapters covering As contamination, ecotoxicology, remediation, risk assessment, environmental modeling of As etc. The introductory chapter also summarizes and provides key information about this book, which will be useful to successfully address global As problem for sustainable As mitigation on a global scale by 2030.

**Keywords** Global contamination · UN SDGs · Health · Water · Soil · Remediation

## 1.1 Introduction

Globally, terrestrial and aquatic ecosystems contamination with low to high arsenic (As) concentrations ($> 10$ to 1100 mg As $kg^{-1}$ soil and $> 10$ to 520 $\mu g\,L^{-1}$) is considered to be an alarming environmental, agricultural and public health issue because of the highly toxic nature of As and its many compounds (Smedley and Kinniburgh 2002; Niazi et al. 2015, 2022; Podgorski and Berg 2020). In the Agency for Toxic Substances and Disease Registry's Priority List of Hazardous Substances (ATSDR) of the USA, As ranks at number one because it has been classified as Class A human

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carcinogen by the International Agency for Research on Cancer (IARC) (WHO 2017; ATSDR 2020). Arsenic enters the food chain and affects humans primarily via As-contaminated food, drinking water, and in some case through air in the form of As-enriched particulate matter or gaseous As form, as well as direct As contact to skin from As-containing soil or water (Rahman et al. 2006; Ratnaike 2006; Natasha et al. 2020a, 2021, 2022).

Arsenic is released into soil and water systems both geogenically and anthropogenically, albeit geogenic sources represent one of the major pathway of As accumulation naturally in the ecosystem, impacting water-food-human systems (Naidu et al. 2006; Shahid et al. 2017; Shakoor et al. 2018; Bundschuh et al. 2022). Approximately, 250 million people have been reported at potential threat of As-induced poisoning in over 115 countries, notably because of ingestion of As-rich drinking well water, which is pumped through millions of hand-driven and electric pumps installed in alluvial sediments in many countries, especially in South and Southeast Asia and Latin America (Podgorski et al. 2017; Aullón Alcaine et al. 2020; Bundschuh et al. 2020; Ahmad and Bhattacharya 2021; Thakur et al. 2021).

In groundwater, soil and sediments, As mainly occurs in toxic inorganic species, arsenite ($As^{III}$) and arsenate ($As^{V}$), of which $As^{III}$ is 100-time more toxic and mobile than $As^{V}$. Arsenic toxicity to plants, microbes, animals and humans is mainly ascribed to absorption of $As^{III}$ or $As^{V}$ which are highly bioavailable/bioaccessible As forms in all life forms. In contrast, organic As species such as arsenobetaine, arsenocholine, and arsenosugars are non-toxic (Masscheleyn et al. 1991; Matschullat 2000; Rahman et al. 2009; Hussain et al. 2021a, b). Methylated and thiolated forms of As prevail mainly in the paddy (flooded) soils, wetlands, and in the sub-surface, near-surface sulfide rich environments where the abundance of microbial life and iron-sulfur cycling promote production of thiolated As species (Burton et al. 2013; Niazi and Burton 2016; Herath et al. 2018). In plant and human tissue, As associates with sulfur-bearing thiol groups and disrupts their normal functioning and cause toxicity. Intake of As by the people in its extremely toxic inorganic forms at high levels either via As-laced drinking well water, food (e.g., rice, vegetables), using As-containing water for cooking of food or by inhalation of tobacco smoke (Bundschuh et al. 2022). Exposure to inorganic As species, via drinking water or food, ultimately results in numerous type of health disorders, including skin lesions, cancers of skin, bladder, kidneys, hypertension (Hussain et al. 2019, 2021c).

## 1.2 Global Arsenic Problem—Developing and Developed World Concern

Arsenic contamination is not only a third world countries or developing nations problem because many developed world nations (e.g., USA, Australia, UK, France, China) have been exposed to As at elevated levels both from groundwater and soil As (Naidu et al. 2006; Brammer and Ravenscroft 2009; Bundschuh et al. 2022). Globally, new regions and countries are added every year, where previously contamination of As was not evident, hence As-affected peoples number is increasing and expanding worldwide (Fig. 1.1). For example, in Pakistan Shahid et al. (2018) estimated that around 47 million people are at stake of As poisoning from drinking well water (Fig. 1.2), especially in areas along the River Ravi, River Sutlej and River Chenab floodplains. Likewise, many areas in Bangladesh, China and in countries in Latin America have been reported with elevated As concentrations in groundwater and soil, although As issue is widely studied in groundwater (Fig. 1.2). There is a need of more strict regulations and their application in different sectors. Given extremely toxic nature of As and its spread globally, the World Health Organization (WHO) recommended that 10 μg/L As in drinking water and 100 in irrigation water are safe As limits to minimize its human exposure. In soil, there is a need to develop and set site specific guidelines for As contamination depending on land use, bioavailabilty and speciation of As (Niazi et al. 2011). The current US EPA guideline of As suggest that soil As concentration at 10 to 20 mg $kg^{-1}$ is considered to be safe for agriculture purpose. However, as mentioned before As risk in soil may vary with soil type, As species and plant species type and future research should be focused on region-, crop-, and soil-specific As safe limits.

In contrast to economically-rich communities, the depressed and poor nations remain at high risk of As-induced threat because they cannot easily afford clean and safe drinking water (UNESCO-WWAP 2003; UNDP 2004; FAO 2015). Hence, low- and low-middle income (developing) countries should be in focus of As mitigation programs at global scale. This is true that the problem of As contamination of well water also exist in developed regions, however, the health threat has been mitigated and resolved by application of appropriate, although costly, water treatment technologies. Despite of the fact, the problem of As is not completely solved in the

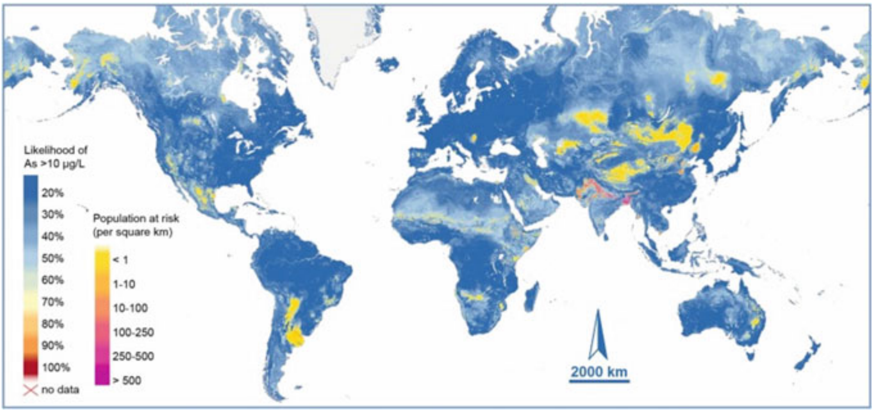

**Fig. 1.1** Probability of groundwater arsenic (As) distribution (with As safe level of WHO > 10 μg/L) based on the geostatistical model based prediction and the estimated risk of population from As [Reproduced with permission from the publisher—this is an open access paper (Bundschuh et al. 2022)]

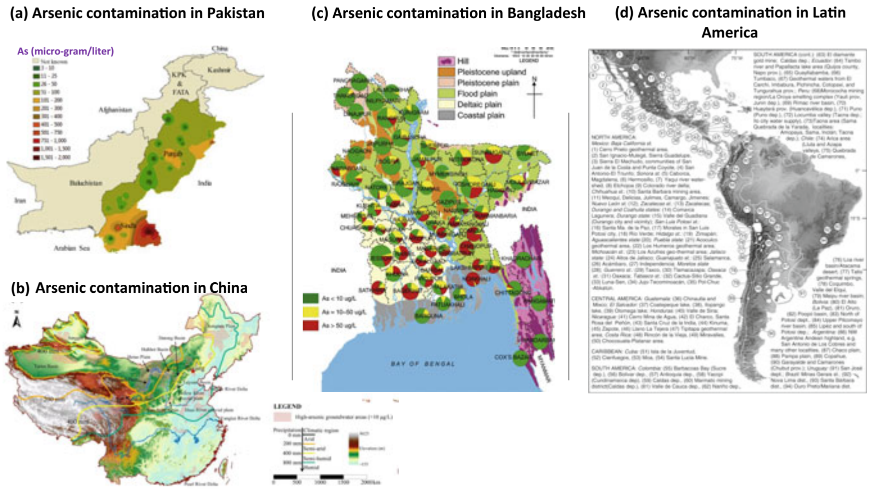

**Fig. 1.2** Distribution maps of groundwater arsenic (As) concentrations **a** Pakistan; **b** China (map is modified from He et al. (2020)); **c** Pakistan; and **d** various countries of Latin America [Reproduced with permission from the publisher (Bundschuh et al. 2010; Chakraborti et al. 2015; Shahid et al. 2018)]

developed countries (e.g., only in the USA, about 2 million people consume private well water for their drinking, which contains As concentrations above the safe limit of 10 $\mu$g/L (Schreiber 2021; Spaur et al. 2021).

Moreover, the presence of As in food products, especially rice grain and rice-related food products has been seen as a global issues spanning developing to developed people, thus it is not confined to the rice producing countries only where rice is cultivated using As-contaminated irrigation water or soil (Dittmar et al. 2007; Rahman et al. 2010; Segura et al. 2016; Upadhyay et al. 2020; Hussain et al. 2021a, b; Niazi et al. 2022). Due to the international trade of rice grain and rice-related food products (e.g., cereals, snacks from As-affected countries), As hazard is recognized as a worldwide health issue, especially for children (Jackson et al. 2012; Ashmore et al. 2019; Biswas et al. 2021; Rokonuzzaman et al. 2022). The situation is highly alarming and miserable in the case of children food items prepared from As-contaminated rice grain in several developed countries such as in the USA, Australia, UK (Signes-Pastor et al. 2009, 2017; Gu et al. 2020; US HoR 2021). Importantly, the inorganic $As^{III}$ or $As^{V}$ species predominate in rice grain or its derived food items, which have more toxic effects than the organic ones (Frankenberger and Arshad 2002; Meharg and Hartley-Whitaker 2002; Meharg and Jardine 2003; Meharg et al. 2014; Ashmore et al. 2019; Gu et al. 2020; Wang et al. 2021).

## 1.3 Global Arsenic Research to Seek Solution of the Problem

The research on various geochemical, environmental, geological, health, and and socio-economic aspects of As has seen significant progress, although further understanding and programs are needed to meet this challenge faced by humanity. There is a dearth of understanding required to understand various pathways of As hazard and create awareness among the people and other relevant stakeholders. Taking into account the developing countries, global management and mitigation integrated strategies must be devised and implemented in As endemic regions, which are poorly understood and explored. These As mitigation, remediation and awareness programs may involve the research on: effects of As exposure on humans through drinking water, food and air spanning low to high As levels, and (ii) evaluating the toxicity threshold of As species in various plant species and their transfer to humans (because inorganic As species are considered extremely toxic) (Meharg and Hartley-Whitaker 2002; Niazi et al. 2011, 2016; Ma et al. 2016; Ma et al. 2017; Abbas et al. 2018; Natasha et al. 2020b, 2021). As a result, it may lead to development of either too strict frameworks and mitigation strategies, which end up in unnecessarily high treatment costs, or too flexible options, thus causing high As exposure and consequently drastic health impacts and economic situation of people.

## 1.4 Arsenic and Sustainable Development Goals of the United Nations

Over the last 3–4 decades, a significant increase in research on As has been seen in various fields with a drastic increase in number of publications from 1999 to 2022 (Fig. 1.3a). In Fig. 1.3, for example, if we type key words ‘arsenic soil water plants’ in Web of Science database it yielded total 9422 publications (accessed on: 21-August-2022) in various fields including: Environmental Sciences Ecology (9088), Toxicology (6638), Agriculture (6196), Plant Sciences (6068), Water Resources (2994), Biochemistry Molecular Biology (2392). These data show the importance of As-mediated global hazard to environment, agriculture and human health and signifies its scope in multidisciplinary research fields. Given As related concerns to various forms of life, it is connected to many sustainable development goals of the United Nations. The United Nations General Assembly (UNGA) after passing the resolution (No. 70/1) set up 17 global goals, which are known as the ‘Sustainable Development Goals (SDGs)’ (UN 2015, 2020; Bundschuh et al. 2022). The problems associated with As are addressed in many SDGs including: (i) SDG 3 (ensure healthy lives and promote well-being for all at all ages); SDG 5 (gender equality); SDG 6 (ensure availability of safe water and sustainable management for all); SDG 10 (reduce inequality within and among countries), SDG 14 (conserve and sustainably use the oceans, seas and marine resources for sustainable development); and SDG 15

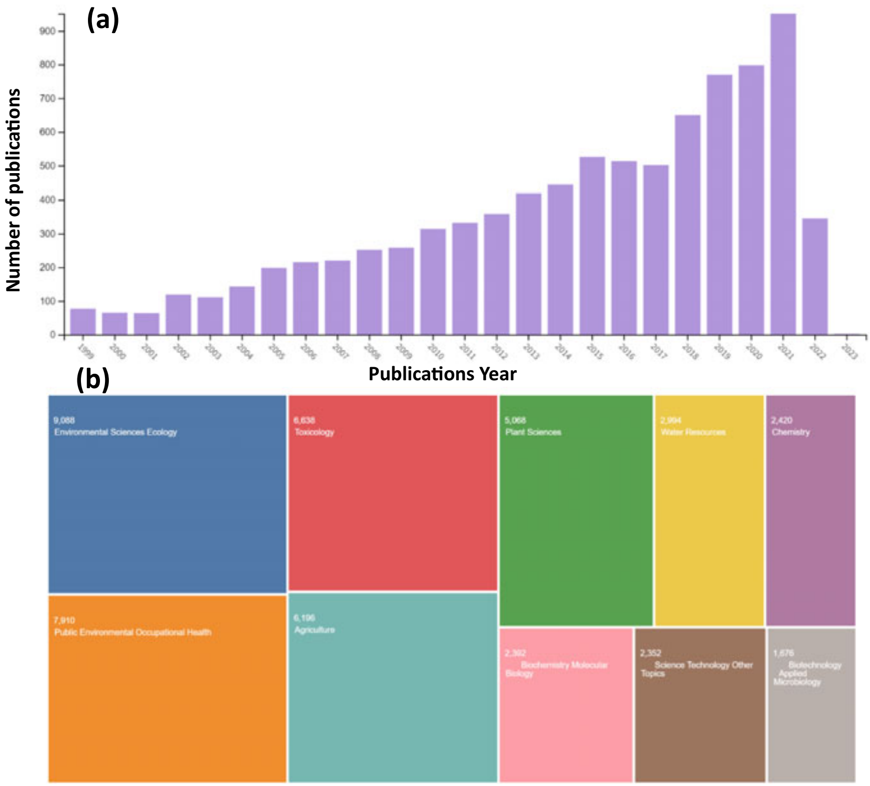

**Fig. 1.3** **a** The number of publications published on arsenic (As) research based on Web of Science data collected on 26th August 2022, and **b** number of articles on As in different disciplines

(protect, restore and promote sustainable use of terrestrial ecosystems, sustainably manage forests, combat desertification, and halt and reverse land degradation and halt biodiversity loss). Moreover, ensuring safe and As-free food underpins the SDG 1 (end poverty in all its forms everywhere) and eliminate hunger and threat to food security as a result of As-induced risk is associated with SDG 2 (end hunger, achieve food security and improved nutrition, and promote sustainable agriculture). And the SDG 13 (take urgent action to combat climate change and its impacts) links it with climate change induced changes in groundwater availability and quality, of which As is of major concern due to its release in aquifers under flooded (high rainfall) or drought (low rain fall) situations. The awareness programs to mitigate As related environmental, agricultural and health issues link it to the SDG 4 (ensure inclusive and equitable quality education and promote lifelong learning opportunities for all) (Bundschuh et al. 2022).

While As problem has not been directly linked to human rights in many resolutions of the UN, it should be embedded in basic human rights because of its association in water and sanitation. For instance, As-induced arsenicosis can cause complications in various human organs, and as such it has direct impact on the ability of work of male or female person. Because their work ability could be reduced and secondly poor health conditions will ultimately lead to poverty of that person and dependent family.

## 1.5 Important Contents of the Book

This book is divided into twenty-four chapters covering various crucial aspects on arsenic related research in water and wastewater, soil, plant, microbes and their connection to environmental, agricultural and human health consequences. The introductory part (Chap. 1) sets the scene on global arsenic contamination and its nexus with sustainable development goals of the UNs, highlighting priority areas of future research and policy framework. The global As contamination scenario in groundwater, soil and food crops has been summarized in Chap. 2 to provide an overview on As-mediated health risks in different regions. Arsenic contamination of food chain is directly linked with consumption of As-containing agricultural produce, of which rice crop is critical. Under paddy soil (flooded) conditions, irrigation to rice plants with As-contaminated well water or cultivation on As-contaminated paddy soils increase As accumulation in rice grain and is a major pathway of As contamination in food chain. Hence it is important to understand As transfer to rice grain either via cooking with As-contaminated water or As uptake by rice in paddy soil conditions (Chaps. 3, 6, 8, 12 and 23).

The book also covers water and soil As contamination routes, risk assessment and As distribution in different regions such as in Ghana, Pakistan, China (Chaps. 4, 5, 9). Considering the significance of robust stochastic modelling tools for prediction of toxic ions, it is important to develop new models for understanding As dynamics and biogeochemical behavior in diverse soil, sediment and environmental settings. This book provides new knowledge (Chap. 10) on designing and applying the Kinetic Montecarlo simulation models to assess As interactions at mineral-water interface.

Various innovative approaches have been developed for the remediation and restoration of As-contaminated soil and water/wastewater including biochar, biosorbents, nanomaterials, clay minerals, phytoremediation, constructed wetlands technology etc. There is growing interest in recent years to modify surface properties of adsorbents (e.g., biochar, nanoparticles) for improved removal of As from contaminated water. This critically-important topic on As remediation, with new interventions over the last decade, has been elaborated in multiple chapters (Chaps. 7, 11, 13, 15, 16, 17, 20 and 21), thus providing the readers an opportunity to gain key information and knowledge gaps on As remediation programs. Microbes play a key role in biotransformation and bioremediation of As in soil or water systems. Therefore, it is equally essential to develop understanding on the molecular aspects of microbes to control As transformation pathways in water-soil-plant ecosystem (Chap. 14).

In this book, Chaps. 18 and 19 describe the role of microbes in bioremediation of As-contaminated soil and sediments and how detoxification of As is associated with multiple transformation processes in microbe-soil-plant ecosystem. It is also essential to highlight the significance of genetic engineering-based As detoxification and remediation processes and provide insights on molecular aspects involved in plants to mitigate As stress (Chap. 22). The last chapter of this book presents an overview of As contamination status in soil and water in Southeast Asia, highlighting As-induced risk magnitude in these countries.

## 1.6 Future Outlooks

To cope with As related global hazard, it is paramount to focus on following key points:

- There is an urgent need to drive efforts on multidisciplinary and integrated research programs on As because of As contamination impact and link to agriculture, environment, human health, and socio-economic situations of the people. These aspects are primarily connected to majority of UN's SDGs that have been set up for limiting As exposure to people at elevated and toxic levels. Hence the supply of safe and As-free drinking water, irrigation water and food crops (mainly rice) would lead to protect the human life, soil, and water resources.
- We should focus on developing and improving in practice policies and regulations, as well as plan of actions, which must be based on sustainable approaches and consider integrated way forward for betterment of social and economic situation of the communities.
- There is a dire need to focus on community awareness programs to mitigate As issue by indigenous, sustainable, low-cost innovative techniques including: As removal from water; soil As retention and decreasing its bioavailability by integrated remediation approaches; screening for As tolerant crop varieties (e.g., As tolerant rice genotypes); applying As immobilizing agents to reduce As accumulation by crops; (iii) treating As-contaminated drinking water or wastewater from industries, and managed aquifer recharge programs in As-affected areas.
- Also, it is fundamentally-essential to establish strategic programs for capacity building of trained human resource, supporting the developing country institutions.
- Develop a global platform where data on As contamination in water, soil, food should be collected from the country wise case studies so that the results should be available free and widely.

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# Chapter 2
# Global Arsenic Contamination of Groundwater, Soil and Food Crops and Health Impacts

**Sana Khalid, Muhammad Shahid, Irshad Bibi, Natasha, Behzad Murtaza, Tasveer Zahra Tariq, Rabia Naz, Muhammad Shahzad, Muhammad Mahroz Hussain, and Nabeel Khan Niazi**

**Abstract** Arsenic (As) is an extremely toxic metalloid of global concern. Numerous health and environmental organizations have classified As being the "toxic and dangerous for the environment". Environmental and food chain contamination by As has been described globally, especially in Asia. Numerous reports have reported high As contents in the groundwater of South-Asian countries, especially India and Bangladesh. According to several reports, globally about > 200 million individuals are at severe risk of As-poisoning due to possible exposure to its toxic levels in drinking water, irrigation water, soil and edible plant tissues. Some recent reports in Pakistan have also revealed As levels > 10 mg/L in groundwater of the country. The groundwater is routinely consumed for drinking in many regions of Pakistan, especially Punjab and Sindh provinces. Hence there is a possibility of severe As-poisoning in different areas of Pakistan containing high As in groundwater. Moreover, soil/crop irrigation by As-containing groundwater has mediated As build-up in soils in different areas of the country and thereby a potential accumulation in food crops. Exposure to As, even at low levels, via any potential source can induce numerous As-mediated health issues, such as cancer. Hence, there is a need to assess the As environmental contamination level in the country. The purpose of this book chapter was to compile recent data regarding As status in groundwater, soils and food crops in Pakistan. The data compiled in this book chapter can be highly useful for future studies and policy making by regulatory authorities.

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## 2.1 Introduction

Globally, environmental contamination with an increasing toxic metal concentration is a serious concern (Bech 2022; Raju 2022). These toxic elements, when exist at elevated levels, not only target animals and plants but also affect humans through the food-chain contamination (Shahid et al. 2021a, b; Natasha et al. 2022). Therefore, numerous recent and past research reports have discussed the spatial distribution, environmental levels and associated health hazards of these toxic elements (Khan et al. 2021; Woolf 2022). Among these potentially toxic metals, arsenic (As) is recognized as an extremely toxic metalloid for both plants and animals/humans (Abbas et al. 2018; Raju 2022). Various geoganic and anthropogenic activities in the environment are the main reason of As pollution (Shakoor et al. 2018). Worldwide, As and its compounds have been found in the water and soils of various regions such as India, China, Bangladesh, France, Nicaragua, America, Brazil, Vietnam and others (Shakoor et al. 2015; Mawia et al. 2021; Bulka et al. 2022; Woolf 2022) (Table 2.1).

Arsenic naturally exists in the earth aquifer alone or in combination with other metals. Arsenic variable proportion is mainly present in various types of rocks (Natasha 2022; Nagra et al. 2022). Arsenic mainly exists in abundance (60%) as arsenate (AsV) form in the soil amongst 200 minerals, 20% are sulfides and sulfo-salts and other 20% are silicates, oxidase, elemental As, arsenites (AsIII) and arsenides (Shah et al. 2020). Igneous rocks such as basalt and granite constitute a major portion

**Table 2.1** Global arsenic contaminated regions

| Country/Region | As contaminated areas | References |
|---|---|---|
| America | USA, Chile, Alaska, Argentina, Peru, Honduras, Dominica, Nicaragua, El Salvador, Mexico | Sanjrani et al. (2019) |
| Pakistan | Lahore, Karachi, Vehari, Hasilpur, Multan, Rahim Yar Khan, Gujrat, Khairpur | Shakoor et al. (2015), Shahid et al. (2018), Shakoor et al. (2018) |
| Europe | Hungary, Romania, Croatia and Serbia, Greece, Spain, Romania, Hungary, Turkey, Croatia, Serbia, Italy | Katsoyiannis et al. (2015), Zuzolo et al. (2020) |
| African Country | Burkina Faso, Botswana, Ethiopia, Morocco, Ghana, Nigeria, Tanzania, South Africa, Zimbabwe, Togo | Medunić et al. (2020) |
| Canada | British Columbia, Alberta, Manitoba, Newfoundland, New Brunswick, Labrador, Quebec, Nova Scotia, Saskatchewan | McGuigan et al. (2010) |

of earth and contains high As contents. Arsenic is earth crust metalloid with 1.8 mg/kg by weight and associates with chlorine, sulphur and oxygen to form in-organic As compounds.

In the aquifers, rock water interactions are the major reason of As release and reason of groundwater quality deterioration (Javed et al. 2020). Generally, in groundwater, higher concentration of naturally present As were detected in aquifers particularly in unconsolidated sediments all around the world and associated to the numerous adverse health hazards (Niazi et al. 2018; Shakoor et al. 2018; Sarkar et al. 2022). High As levels in groundwater are seriously affecting almost > 500 million people all over the world (Shaji et al. 2021).

In addition to groundwater, numerous reports have reported high As contents in the soil at global scale. Both natural and anthropogenic sources induce soil As contamination (Khalid et al. 2022; Shah et al. 2022). Arsenic accumulation in soils either by weathering of rocks and using the As contaminated water used to irrigate crops that cause accumulation in the soil and subsequently As leaching in ground or surface water (Natasha 2022; Natasha et al. 2021a, b). The main human activities responsible of enhanced soil As contents include application of pesticides, mining, coal burning, and disposal of waste. Similarly, tannery sites which use animal hides to make leather show very high levels of As in soil.

Arsenic is the matter of concern owing to its health issues and environmental impacts. International Agency for Research on Cancer (IARC) has categorized As being the class-1 human carcinogen (Shahid et al. 2018). No significant metabolic role of As has been reported in the living organisms while due to its substantial toxicity, it may stimulate serious health issues even at low exposures (Ali et al. 2020). Continuous water As exposure, either via drinking As-contaminated water or consuming As-containing food, causes numerous health disorders such as ulceration, pigmentation, skin-cancer, hyperkeratosis and affects lungs, liver and kidney, and heart (Shakoor et al. 2015; Sarkar et al. 2022). High As contents naturally in the groundwater induce numerous human diseases and constitute key water quality issues especially in the Asian countries like Pakistan, Iran, India and Bangladesh (Natasha 2022; Sarkar et al. 2022). Generally it is known that As soil to plant transfer is a key human exposure pathway to As (Hussain et al. 2021a, b), mainly in the areas where groundwater As contents are less than WHO limit of 10 μg/L.

In this book chapter, we summarized the As level in groundwater aquifers, its sources and global aspects of As contamination. This chapter also highlight the brief summary of soil and plant contamination. This chapter compare the global As contamination trend with the contamination level in Pakistan.

## 2.2 Arsenic: An Environmental Contaminant of Global Concern

### 2.2.1 Groundwater Arsenic Contamination

Arsenic pollution due to the high As content in groundwater, soil and food is well-recognized as a foremost human health issue globally (Table 2.2). Arsenic pollution mainly in the drinking water has been found in nearly all regions of the world. Compared to other countries, South American and South Asian regions are the most As affected and reported areas (Shaji et al. 2021; Sarkar et al. 2022). The fate and As origin in groundwater have attained a higher consideration from the scientists after its identification in well water of the Bangladesh in the early 1990s (Woolf 2022).

Worldwide almost 150 million peoples are expected to be exposed to As, and the various As-contaminated regions are constantly reported around the world (Brammer

**Table 2.2** Source and arsenic levels in water (ug/L) and soil (mg/kg) of various regions in the world

| Country | Source | As in water | As in soil | References |
|---|---|---|---|---|
| Bangladesh | Well water | 436 | 14.75 | Saha and Ali (2007) |
| China | Saline well water | 238 | 21.1 | Neidhardt et al. (2012) |
| China | Groundwater | 42.88 | 16.52 | Ji et al. (2021) |
| China | Mine water | – | 173 | Qin et al. (2021) |
| India | Groundwater | 138 | 62.5 | Kumar et al. (2018) |
| South America | Groundwater | 120 | – | Machado et al. (2020) |
| Pakistan | Groundwater | 21 | 3 | Amir et al. (2021) |
| Pakistan | Wastewater | 64 | 20 | Shahid et al. (2021a, b) |
| Iraq | Groundwater | 1.06 | 5.32 | Sadee et al. (2016) |
| South America | Groundwater | 45.9 | – | Alcaine et al. (2020) |
| Japan | Groundwater | 2620 | – | Even et al. (2017) |
| India | Groundwater | 3880 | – | Bhowmick et al. (2018) |
| India | Pond water | 4.8 | – | Jaafar et al. (2021) |
| India | Groundwater | 94 | 26.6 | Jaafar et al. (2021) |
| India | Groundwater | 0.677 | 8.66 | Meena et al. (2020) |
| Finland | Groundwater | 980 | - | Nordstrom (2002) |
| India | Groundwater | 76 | 54 | Shrivastava et al. (2014) |
| Iran | Groundwater | 280 | 1500 | Zandsalimi et al. (2011) |
| Mexico | Well water | 740 | 30 | Rosas et al. (1999) |
| India | Well water | 825 | 390 | Patel et al. (2005) |
| Iran | Groundwater | 840 | 1775 | Khadem Moghadam Igdelou and Golchin (2019) |

and Ravenscroft 2009). High levels of groundwater As have been well documented in the Bangladesh, Chile, India, Vietnam, Iran, China, Mexico, Cambodia, Indonesia, Myanmar, Nepal, Philippines, Vietnam, Thailand and Taiwan (Shakoor et al. 2015; Shaji et al. 2021; Sarkar et al. 2022) (Fig. 2.2).

Extent of As pollution in groundwater is very high in deltaic and sedimentary aquifers of India and Bangladesh where millions of human population drink As-contaminated water (Sarkar et al. 2022). According to the study only in Bangladesh, annually approximately a total of 43,000 deaths (about 5.6% of total deaths) mainly occurred due to As poisoning (Flanagan et al. 2012). Recently, a study found that all around the world more than 230 million people are at higher risk due to As exposure, with the 180 million of them are included in the thirty one Asian kingdoms (Jakhrani et al. 2009).

Consequently, As contamination in drinking water globally is taken as a serious health and environmental issue owing to its high toxicity to public health. South and Southeast Asia are considered the most As-contaminated areas, including regions of Bangladesh and India (Natasha 2022; Sarkar et al. 2022). Recent study found that 220 million people have As contamination exposure and almost all people are residing in Asia Region (Podgorski and Berg 2020). However, normally As is not involved in the water quality testing parameters and is not found by human senses and also make it challenge to recognize the measure of the problem (Podgorski and Berg 2020). While since 1980s, the presence of As contamination in drinking or groundwater has been recognized and remains an understudied health concern in many countries.

### 2.2.2 *Sources of Arsenic in Groundwater*

Various factor effect groundwater quality such as invasion of salty water in coastal areas, topography, groundwater movement in rock type areas, climate human activities. Various anthropogenic activities, urbanization, agricultural practices, wastewater and fertilizer utilization may cause various types of pollutants production which negatively affect the quality of groundwater (Shahid et al. 2018). In the last few years, As groundwater contamination is a public health issue in several region around the globe.

Over the past decade, it was observed that almost all waterbodies like canals, rivers, oceans and groundwater reservoirs have high concentration of As ($> 10\ \mu g/L$) due to receiving contaminated effluents from households, municipals, urban runoffs, industries, agriculture and making water unfit for domestic use (Sardar et al. 2020a, b; Anwar et al. 2021). World Health Organization (WHO) has reported that around 0.14 billion people are consuming As-rich water ($As > 10\ \mu g/L$) through contaminated groundwater aquifers.

Being a natural component, As is present in over 200 minerals around the world (Khalid et al. 2017a, b) where FeAsS, $As_2S_3$ and AsS are the most common minerals (Amen et al. 2020). In groundwater systems, As is released by oxidative-reductive dissolution of Fe minerals, sorption mechanisms, and water–rock interaction (Hussain et al. 2020). Oxidative desorption is also considered as a major process of As release into aquifers along with changes in other physicochemical variables e.g., microbial and sulfate reduction, etc. (Natasha et al. 2020a, b).

Approximately, 12,000 tons of As and its compounds are naturally released to the environment every year (Pacyna and Pacyna 2001) while 50,000 tons of As are released directly or indirectly by anthropogenic activities to the environment (Bolan et al. 2014). Major sources of As on all continents as per characterization are sedimentary formations, particularly Holocene. In Asia, sedimentary rocks contribute 45%, volcanic rocks 5%, mining 30%, coal 10% and petroleum 10% in As release. The same pattern is also observed for Europe, America, Australia and Africa (Shaji et al. 2020).

### *2.2.3 Soil Arsenic Contamination*

Several factors cause As build up in soil (Table 2.2). However, these factors and their intensity of As contribution to soil vary in different regions. Almost every year 50,000 tons of arsenic is emitted by anthropogenic sources (Bolan et al. 2014). It is assessed that annually coal burning emitted about 45,000 tons of As and considerably contributed to the environmental pollution by As (Bolan et al. 2014). In Bangladesh, soil irrigated with As polluted water enhanced the soil As contents > 83 mg/kg (Abedin et al. 2002). Arsenic contents up to 1000 mg/kg have been found in numerous agriculture and mining areas of the United States and Australia (Niazi et al. 2015).

Arsenic soil pollution mainly occurs from both geogenic activities (mineralized regions of ore-deposits, denudation of bedrocks) and human-related activities (agrochemicals, industrial wastes, mining) (Shakoor et al. 2015). Primary sources of As are coal seams of geogenic sources and rocks bearing sulfide minerals in the Hindukush mountainous ranges and the Himalayas (Rahman et al. 2018). Weathering and mineral erosion ultimately cause their deposition to the low lying plains. Arsenic-bearing minerals release this metalloid and iron oxide into water in the reducing state (Shakoor et al. 2018) through microbial activities and the environmental factors.

Arsenic as well as its compounds have high application in metallurgy, agriculture, electronic, chemical warfare agents, livestock feed, medicine and electronics. Therefore, it is mined in great quantities every year to be used in above-mentioned and several other industrial activities. For example, according to the latest data of USGS (2022), about 32,000 metric tons of As was produced during 2020. China (24,000 metric tons), Morocco (5500 metric tons) and Russia (1500 metric tons) are the top three producers of As at global scale (USGS 2022).

Application of pesticides in agriculture land have been found the major As source (Cai et al. 2015). With the widespread use of pesticides in agriculture field to enhance the crop yield also effecting the soil and increase the As levels in soil. Soil contamination may occur because of industrial point sources such as multiple use of metal enriched fertilizers, pesticides, sludge, mining, dyestuffs, wood preservations, farm manuring and automotive emissions (He et al. 2005). Moreover, irrigation with groundwater containing high levels of As is considered a key factor of soil As contamination (Sardar et al. 2020a, b; Anwar et al. 2021).

### 2.2.4 Soil-Plant Transfer of Arsenic: Possible Buildup in Food Chain

Arsenic in soil may be metabolized and volatile by the microbes/microorganisms present in soil and uptake by plants from soil water system (Fig. 2.1). In the soil system, various chemical reactions affect the As in solid and solution phases which may also control As uptake by plants and its interaction mechanism in soil-plant systems (Shakoor et al. 2015; Anwar et al. 2021). Alterations in As behavior, such as the diversity of As species, precipitation, sorption oxidation-reduction, dilution, volatilization, adsorption, and development of As complex might be because of physical, chemical or biological processes taking place in the ecosystem (Abbas et al. 2018; Verbeeck et al. 2020).

From soil, As can be up-taken and accumulated in plants. Numerous reports have shown high As content build-up in plants grown on As-contaminated sites (Rehman et al. 2016; Anwar et al. 2021; Natasha et al. 2021a, b). Even some studies revealed As phytouptake and accumulation in edible plant parts of crops/vegetables (Sardar et al. 2020a, b; Anwar et al. 2021). However, the uptake and buildup of As in edible plant tissues vary with several factors related to soil and plant type. In fact, some crop/vegetable species accumulate low levels of As in their edible tissues. However, some crops/vegetables have capacity to accumulate high/toxic levels of As in their edible tissues (Khalid et al. 2017a, b) (Fig. 2.2).

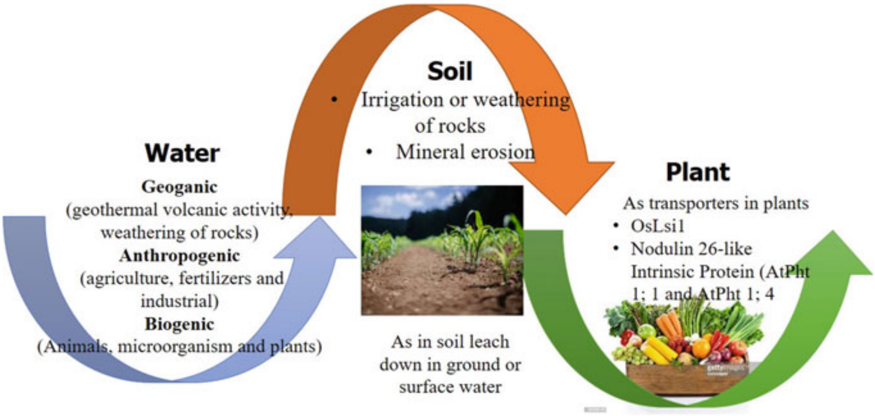

**Fig. 2.1** Arsenic movement from water to soil plant system

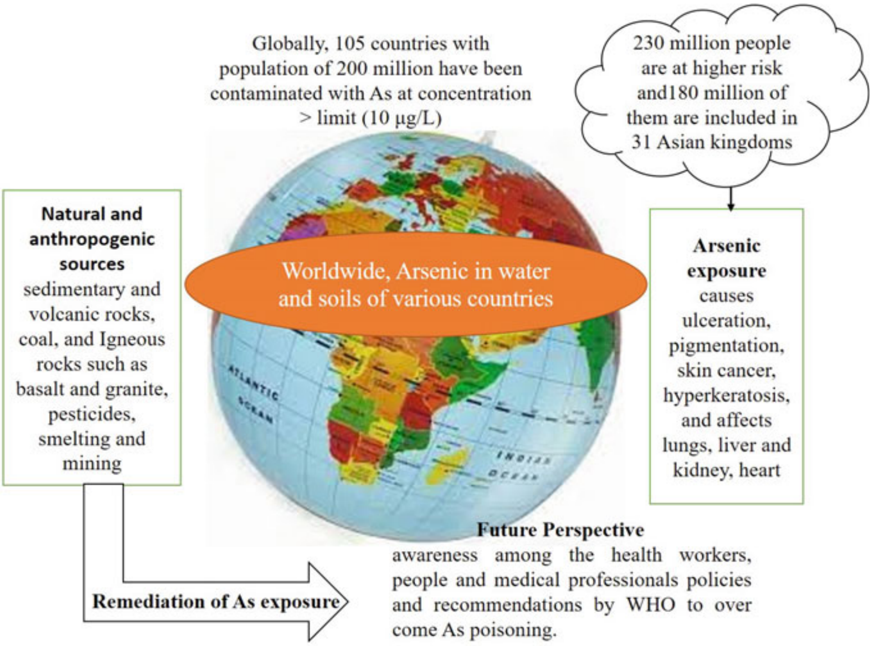

**Fig. 2.2** Global arsenic trend in environment

In addition to several other factors, the soil–plant transfer of As is controlled by the transporter proteins which mediate its absorption and root-shoot transfer (Abbas et al. 2018). Various studies reported that As(VI) has chemical structure analogs to the in-organic phosphate and uptake by plants via various transporters (Bakhat et al. 2017). Both these ions compete for transporters in plants for uptake. Nevertheless, phosphate transporters may exhibit greater affinity in plants for $PO_4$ than As(VI) (Abbas et al. 2018).

Arsenic intake through food has posed severe risk not only in the living organisms but also cause major threat to the food especially in the rice growing areas of the world. All the As contents in the soil are not plant-available, As plant absorption is dependent on its species and type, plant capacity to assimilate and translocate As, and the prevalent As species in the soil (Hussain et al. 2021a, b). Low As contents have positive impact on the plants growth but at higher As concentrations As is reported as a metabolic inhibitor that adversely affect plant growth (Abbas et al. 2018). The negative impacts of elevated level of As has been observed in plants such as; produces reactive oxygen species (ROS), causes necrosis, affects photosynthesis, inhibits germination, mineral nutrition, reduces root and shoot and growth, lowers yield thus causing major risk to agricultural production (Shahid et al. 2014; Shahid et al. 2017a, b; Abbas et al. 2018; Rafiq et al. 2018). The harmful impacts of As can be seen in human health likewise; various cancers, duration of exposure, obstetrics issues, neurological and cardiovascular diseases etc. all these depends upon the nutritional status and, the dosage of As (Bulka et al. 2022).

In the soil rhizosphere microorganisms produced methylated forms of As, which were also considered in greater concentrations in several plant parts. Rice grains, for example, acquired two times more methylated-As than inorganic form of As (Zheng et al. 2013). Due to similar characteristics in chemical structure with phosphates, As(V) is a main aerobic species in soil thus has capability to enter the root tissues (Abbas et al. 2018). This entrance of As(V) to plant roots is mostly via phosphate transporters. During this process various types of phosphate transporters participate in the As(V) uptake from the soil to roots. It has been reported that AtPht 1; 1 and AtPht 1; 4 are the two main phosphate transporters which mediate As(V) uptake in *Arabidopsis thaliana* (Khan et al. 2021). Moreover, the AtPht 1; 5 may absorb additional As from the source and transmit it to the sink (Khan et al. 2021). Inhibition or elimination of (AtPht1; 5) in mutant plants, on the other hand, greatly reduced As toxicity in As contaminated soils.

Moreover, the known transporters in Arabidopsis (AtPht 1; 7-9) considerably increased P and As phytouptake and boosted the As toxicity inside the plants (Khan et al. 2021). Arsenite (AsIII) is the most common type of As, and it's mainly found in anaerobic environments like submerged soils. Aquaporins and membrane channels, which mediate the transport of water and neutral molecules, respectively, have been discovered to have a major function in the absorption of As(III) in plant (Vats et al. 2021). Some studies reported that various sub-families of NIP (NIP1-7) actively play a part for transfer and uptake of As(III) in various plant types (Hans and Saxena 2022).

In addition, because As was detected in both exodermis and endodermis, the silicon-transporter (OsLsi1) in *Oryza sativa* was implicated in the As(III) absorption with roots. In addition to OsLsi2 and OsLsi3 have been found to be involved in As movement from *Oryza sativa* roots to xylem vessels and areal sections. (Mishra et al. 2014) reported that the maximum As has been accumulated in root vegetables like radish (2.5 mg/kg), fruit vegetables such as tomato (2.36 mg/kg DW) brinjal (1.32 mg/kg), bottle gourd (1.03 mg/kg) and lady finger (0.67 mg/kg). Caporale et al. (2013) revealed that As uptake in plant tissues enhanced while increasing As level from 1 to 3 mg/L in applied irrigation treatments. A similar data of increased As uptake and accumulation has been reported in cabbage when exposed to water containing As 0.08–0.14 mg/L (de Freitas-Silva et al. 2016).

Although most studies on As in vegetables have been carried out under increased As concentrations in soil and water, however the pertaining groundwater As levels in many countries are less than 10 g/L. However, in these countries the long-term and continuous use of water or wastewater for irrigation containing low levels of As can rise As accumulation in the soil (Anwar et al. 2021). This buildup of As in soil ultimately induce high As uptake by plants and thereby the possible food contamination. Inside plants, As mainly accumulates in the roots while small amount is transported to plant shoot, and in minor quantities to the grain/fruit (Anwar et al. 2021; Natasha et al. 2021a, b). There are numerous factors of high As build-up in plant roots, which vary with plant type. In fact, some plants have certain mechanisms (such as transporters) of high As build-up and transport to plant aerial parts (Khalid et al. 2017a, b). On the other hand, some plant species are not capable to either absorb or especially transfer high levels of As towards plant shoots (Khalid et al. 2017a, b). Another possible reason of high As accumulation in root tissues is that the plant roots are constantly exposed to As from soil. For example, it has been reported that by interacting with glutathione and phytochelatin in root tissues, As is compartmentalized, reducing its transfer to the aerial portions (Abbas et al. 2018). In the aerial part As transport is decreased because the sequestration by these complexes and anthocyanins, thus confirming that very little As reaches the fruits (Li et al. 2021).

## 2.3 Arsenic Contamination in Pakistan

### *2.3.1 Hydro-Geography and Climate of Pakistan*

Pakistan is located in South Asia. The population of the country is > 227 Million, and is ranked the 5th most populous nation in the world. The country has a total area of 881,913 km$^2$, and ranks 33rd largest nation globally. The country shares a border with China to the north-east, Iran to the south-west, India to the east, and Afghanistan to the west. The coastline spans about 1046 km along the Gulf of Oman and the Arabian Sea.

The physiography of the country is considered highly unique, which is distinctive of varied landscapes all over the country. The climate of entire country is highly distinct. Therefore, the physiography of the country is grouped into various soil classification. The main agricultural areas of Pakistan are situated in Punjab and Sindh provinces. The geology of plain areas of the country is categorized by quaternary loess and flood plain deposits (Iqbal et al. 2021). Sand and silt mainly constitute the loess deposits. The quaternary loess deposits constitute feldspars, mica, calcium carbonate and quartz. The latest Pleistocene alluvial-complexes contain unconsolidated sand, silt, gravel, and clay. In case of alluvial complexes, majority are comprised of fine-medium sand, silt, and clay (Shahid et al. 2017a, b; Iqbal et al. 2021). It is observed that in some areas, the siltstone and mudstone pebbles are found in silty or clayey sand. The water table depth in the country varies highly in different regions and ranges between 15 and 95 m (Iqbal et al. 2021).

### *2.3.2 Arsenic Groundwater Contamination in Pakistan*

Many local and international news agencies have reported groundwater As contamination as a growing issue particularly in South Asia including Pakistan. Significant groundwater contamination with As and its potential impacts on environmental components in Pakistan has drawn significant attention (Table 2.3). It is reported that around 50–60 billion of the population are consuming contaminated water near Indus Valley, Pakistan (BBC 2017). Likewise, a major percentage of Pakistan in Punjab and Sindh provinces (20% and 36% respectively) are using As contaminated groundwater (As > WHO threshold) for drinking purposes (Kumar and Singh 2020). The risk maps of As was developed with > 9882 groundwater samples from Pakistan (Shahid et al. 2018) and it showed that about 73% of the water samples exhibited As > 10 μg /L and about 41% had As > 50 μg /L and it was reported that about 0.047 billion people of Pakistan living in provinces Sindh and Punjab are facing serious As-contamination of the aquifers. The higher level of As is attributed to the oxidative dissolutions of the As-bearing mineral phases (Shahab et al. 2019).

Numerous recent studies have revealed a possible As groundwater contamination in different regions of Pakistan. For example, As level in groundwater has reached 1900 μg/L and 2400 μg/L in East Punjab (Farooqi et al. 2007a, b; Farooqi et al. 2007a, b) while about 91% samples exceed WHO safe limit. It is estimated that 20% population of Punjab and 36% in Sindh is at risk to As polluted groundwater (> 10 μg/L). It was even more threatening to report that about 3% population from Punjab and 16% population from Sindh was exposed to As concentration of over 50 μg/L (Ali et al. 2019a, b). In a joint project of United Nation's International Children Emergency Fund (UNICEF) and the PCRWR, approximately 8712 groundwater samples were collected from 1/3rd of the total districts in country i.e. (35/104) (PCRWR 2008). Drinking water wells have reported a significant percentage in Ahmedpur East (23%), Bahawalpur (24%), Rahim Yar Khan (21%), Multan City (71%), Hasilpur (8%), Jalalpur Pirwala (31%), Khairpur (5%), Sadiqabad (19%), Liaqatpur (18.5%), Shujaabad (43%) and Yazman (20%) areas of Punjab with arsenic levels exceeding WHO safe limit (Bhutta et al. 2008; Azizullah et al. 2011).

Some areas of Punjab Province, such as Bahawalpur, Multan, and Rahimyar Khan have reported higher As concentrations in drinking water of about 50 μg/L, whereas some areas of Sindh Province have reported even higher As concentrations, i.e. up to 4-folds higher than Punjab Province (Kahlown et al. 2002). Percentage of unsafe drinking water wells in Sindh Province that contain As concentrations greater than 10 μg/L is as under; Dadu (58%), Gambat (53%), Khairpur (13%), Johi (21%), Kotdiji (3%) and Sehwan (44%) (Azizullah et al. 2011).

Recently, Natasha et al. (2021a, b) explained hydrogeochemistry and distribution of As in five regions near Punjab floodplains. Bhakar and Kallur Kot were along Indus River, Jhelum along along Jhelum River and Hafizabad and Gujranwala near Chenab River. The groundwater As contamination in five area ranged between 0.1 and 121 μg/L. The study indicated that Fe oxide minerals phases play a significant role in As release into groundwater aquifers through sorption mechanisms. Furthermore, prevalence of Quaternary deposits in Punjab and Sindh is favored due to arid and semi-arid climate. The presence of As is therefore considered to be associated with the Quaternary period along with geo-sedimentation of alluvial and deltaic sediments (Shamsudduha and Uddin 2007). In the western sedimentary basin, these deposits promote oxidative environments and are widely distributed with less reduced conditions in these areas (Farooqi et al. 2007a, b; Shamsudduha and Uddin 2007).

**Table 2.3** Groundwater arsenic level (ug/L) in various areas of Pakistan

| City | As level | References |
|---|---|---|
| Punjab, Pakistan | 65 | Javed et al. (2021) |
| Indus plain, Pakistan | 386 | Malik et al. (2020) |
| Sewakht, Pakistan | 11 | Rehman et al. (2020) |
| Lahore, Pakistan | 78 | Ur Rehman et al. (2022) |
| Multan, Pakistan | 70 | Amir et al. (2021) |
| Gujrat, Pakistan | 15 | Masood et al. (2019a, b) |
| Punjab, Pakistan | 135 | Javed et al. (2020) |
| Larkana, Pakistan | 318 | Ali et al. (2019a, b) |
| Nagarparkar, Pakistan | 360–683 | Brahman et al. (2014) |
| Lahore | 111 | Waqas et al. (2017) |
| Karachi | 200 | Kori et al. (2018) |
| Islamabad | 4.03 | Abeer et al. (2020) |
| Nowshera | 17.58 | Khan et al. (2015) |
| Vehari | 41.5 | Shakoor et al. (2015) |
| Rahim yar Khan | 9.2 | Shakoor et al. (2015) |
| Chichawatni | 95 | Shakoor et al. (2015) |
| Sheikupura | 75 | Abbas and Cheema (2015) |
| Gujrat | 32 | Masood et al. (2019a, b) |
| Rahim yar Khan | 500 | Mahar et al. (2015) |
| Rahim yar Khan | 400 | Haque et al. (2008) |
| Muzffargarh | 900 | Nickson et al. (2005) |
| Khairpur | 315 | Jakhrani et al. (2009) |
| Punjab | 501 | Ali et al. (2019a, b) |
| Sindh | 81.1 | Ali et al. (2019a, b) |
| Larkana | 17 | Kori et al. (2018) |
| Tharparkar | 2580 | Brahman et al. (2013) |
| Jamshoro | 106 | Baig et al. (2010) |
| Khairpur | 98 | Baig et al. (2011) |
| Kasur | 548 | Mushtaq et al. (2018) |
| Mailsi | 750 | Rasool et al. (2016) |
| Kahror Pacca | 45.6 | Rasool et al. (2021) |
| Hasilpur | 100 | Tabassum et al. (2019a, b) |
| D.G Khan | 29 | Malana and Khosa (2011) |
| Bahawalnagar, Pakistan | 7.9 | Iqbal et al. (2022) |
| Hafizabad | 121.7 | Natasha et al. (2021a, b) |
| Health facilities, Vehari, Pakistan | 100 | Murtaza et al. (2020a, b) |

(continued)

**Table 2.3** (continued)

| City | As level | References |
|---|---|---|
| Schools, Vehari, Pakistan | 50 | Murtaza et al. (2020a, b) |
| Peri-urban, Vehari, Pakistan | 31.5 | Shah et al. (2020) |
| Hasilpur, Pakistan | 100 | Tabassum et al. (2019a, b) |
| Punjab, Pakistan | 206 | Shakoor et al. (2018) |
| Vehari, Pakistan | 123.8 | Shahid et al. (2017a, b) |
| Chichawatni, Pakistan | 201 | Shakoor et al. (2015) |

**Table 2.4** Soil arsenic level (mg/kg) reported in various areas of Pakistan

| As type | City | As level | References |
|---|---|---|---|
| As | Punjab, Pakistan | 50 | Javed et al. (2020) |
| As | Vehari, Pakistan | 1.4–19.6 | Natasha et al. (2021a, b) |
| As | Gujrat, Pakistan | 15 | Masood et al. (2019a, b) |
| As | Punjab/Sindh, Pakistan | 80 | Hashmi et al. (2020) |
| As | Sewakht, Pakistan | 3.28 | Rehman et al. (2020) |
| As | Nagarparkar, Pakistan | 110–266 | Brahman et al. (2014) |
| As | KPK, Pakistan | 3.0–3.9 | Rehman et al. (2016) |
| iAs | KPK, Pakistan | 1.2–2.6 | Rehman et al. (2016) |

### 2.3.3 Arsenic Soil Contamination in Pakistan

Pakistan is basically an agricultural country. There exists 22.1 million hectares cultivated land out of total (79.6 million hectares). In some regions, the researchers have reported soil contamination with As (Masood et al. 2019a, b; Hashmi et al. 2020; Javed et al. 2021). However, there are few studies indicating soil contamination by As in Pakistan. Table 2.4 summarizes the studies indicating As soil contamination in Pakistan. Majority of the studies indicating soil As contamination in Pakistan reported wastewater irrigation for crop irrigation as the key source of soil As contamination.

### 2.3.4 Food-Chain Contamination

Once the soil is polluted with As, it can transfer to plants and can buildup in edible tissues. Several studies in Pakistan has indicated As buildup in edible plant tissues (Table 2.5). Based on As contents in edible plant tissues, some studies have also reported possible health hazards associated with the consumption of As-contaminated vegetables (Rehman et al. 2020; Anwar et al. 2021; Javed et al. 2021). Keeping in view the As content in edible plant tissues and the associated health

**Table 2.5** Arsenic level (mg/kg) in different plant tissues reported in various areas of Pakistan

| City | Plant | Plant part | As level | References |
|---|---|---|---|---|
| Pakistan | Rice | Grain, oAs | 8.97 | Sarwar et al. (2021) |
| Pakistan | Rice | Grain, iAs | 35 | Sarwar et al. (2021) |
| Pakistan | Rice | Grain, AsIII | 27 | Sarwar et al. (2021) |
| Pakistan | Rice | Grain, AsV | 8.33 | Sarwar et al. (2021) |
| Multan, Pakistan | Brinjal | Edible | 0.84 | Amir et al. (2021) |
| KPK, Pakistan | Food | Edible | 1.25 | Muhammad et al. (2021) |
| Punjab, Pakistan | Rice | Grain | 0.28 | Javed et al. (2020) |
| Vehari | Vegetables | Whole plant | 6.5 | Natasha et al. (2021a, b) |
| Sewakht, Pakistan | Rice | Root | 0.93 | Rehman et al. (2020) |
| Sewakht, Pakistan | Rice | Straw | 0.35 | Rehman et al. (2020) |
| Sewakht, Pakistan | Rice | grain | 0.1 | Rehman et al. (2020) |
| UAF, Pakistan | Kainat | shoot | 3.1–28 | Hussain et al. (2021a, b) |
| UAF, Pakistan | Basmati-385 | shoot | 1.7–16 | Hussain et al. (2021a, b) |
| KPK, Pakistan | vegetable | Edible | 0.03–1.4 | Rehman et al. (2016) |
| Faisalabad, Pakistan | Rice (KSK-282) | grain | 0.034 | Niazi et al. (2022) |
| Faisalabad, Pakistan | Rice (KSK-434) | grain | 0.031 | Niazi et al. (2022) |
| Vehari, Pakistan | *Vigna radiata* | Shoot | 4.2 | Anwar et al. (2021) |
| Vehari, Pakistan | *Vigna radiata* | Root | 73.1 | Anwar et al. (2021) |
| Vehari, Pakistan | *Spinacia oleracea* | Shoot | 8.4 | Sardar et al. (2020a, b) |
| Vehari, Pakistan | *Spinacia oleracea* | Root | 13.3 | Sardar et al. (2020a, b) |

hazards, it is proposed to properly monitor the biogeochemical behavior of As in soil and plant systems.

## 2.4 Conclusions

Arsenic contamination in groundwater is a highly alarming issue globally. This chapter summarizes the latest data regarding groundwater As contamination worldwide and in Pakistan, it possible sources and soil-food contamination. Based on the pervious findings shows that various states of America, South Africa, Nepal, Bangladesh, Canada, China, India have an issue of As contamination in ground or drinking water. Also in Pakistan, many areas of the provinces are facing the As contamination problem. Based on the given data it is found that in Pakistan more than 47 million habitants are living the regions where the 50% groundwater containing As levels higher than the WHO limits. With the passage of time, As toxicity and its health issues are increasing and manmade activities are causing a global threat to food safety. Arsenic toxicity in soil negatively influenced the soil structure, properties and ultimately plant physiology, growth, and molecular mechanisms that accumulate As in the plants edible tissues and transported towards human through food-chain.

Prolonged intake of As-contaminated groundwater caused severe health problems. We suggest that with this increasing As contamination trend WHO should outlook the worldwide As contamination with top priority and create a global initiative for the monitoring and awareness among the health workers, people and medical doctors towards find the effective results. Overall logistic and financial assistance may be required by WHO to overcome the issue of As contamination and develop such policies and recommendations that can tackle the As poisoning.

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# Chapter 3
# Arsenic Contamination in Rice and the Possible Mitigation Options

**Sudip Sengupta, Tarit Roychowdhury, Amit Phonglosa, and Jajati Mandal**

**Abstract** Arsenic (As) in food poses a major threat to human health. Aside from drinking water, rice consumption is the principal route for As to enter the body. Due to the large population density in Asian countries, such as India, Bangladesh, Pakistan, and China, the problem requires more serious attention. The importance of studying the dynamics of the metalloid in the soil-plant system, as well as the rice plant's inherent ability to uptake, transport, and accumulate As in edible grains, necessitates a concentrated research effort. Several factors influence the chemistry of the metalloid, its occurrence, chemical species, and so on, in its natural environment, in soil. In rice, many transporters allow the contaminant to pass from the root to the shoot, and then the xylem and phloem mediate the As uptake in the grain. When irrigation water has elevated As levels, the high irrigation need of rice contributes to soil As build-up, hence a mitigation strategy should include both the sources (soil and irrigation water). The main goal of this chapter is to trace the As pathway in the soil-plant (rice) system, provide an overview of the status of As accumulation in rice grain, and consider possible mitigation strategies, such as modelling approaches for predicting the dietary risk associated with As consumption. A special emphasis is given to the soil-based calculative models and machine learning methodologies, that simulate the uptake of the metalloid in edible grains.

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## 3.1 Introduction

The presence of Arsenic (As), a naturally occurring toxic metalloid has created severe environmental concern due to its severe health hazard consequences (Bhattacharyya and Sengupta 2020; Kumari et al. 2021). The contaminant has crippled global human well-being through its widespread nature across parts of United States, China, Europe and mostly Southeast Asia (Srivastava et al. 2016). The severity of As toxicity is more pronounced in India and Bangladesh with As in groundwater several fold higher than WHO recommended limits of 0.01 $mgL^{-1}$ (Sanyal 2017). To have an overview nearly 200 million global population is subjected to the wrath of the grade 1 carcinogen, As, either straight from drinking of polluted groundwater or through consumption of As-laden food crops, especially edible cereal grain (Roy Chowdhury et al. 2020).

The cereal grains are considered as the richest source of energy, vitamins, minerals, carbohydrates, fats, oils, and proteins (Mandal et al. 2021; Sarwar et al. 2013). In the Asian countries rice is the principal dietary component which may be up to 0.5 kg (dry weight) (Zavala and Duxbury 2008). On an average 72.8% of the per capita daily calorie intake is shared from rice consumption in West Bengal, India and Bangladesh (Mondal and Polya 2008). Elevated levels of As in wheat and maize has already been reported (Mandal et al. 2019b; Bianucci et al. 2020) however rice in As-contaminated soils under anaerobic conditions has the incidence of highest As content in comparison to the others. The cultivation of rice occurs primarily under flooded soil in most Southeast Asian countries including the likes of Bangladesh, India, Pakistan and China. This cultivation practice promotes the redox transformation of more toxic, mobile and phytoavailable As(III) from comparatively less toxic As(V) forms (Suriyagoda et al. 2018). This phenomenon of reductive mobilization of As augments its bio- accumulation in rice grain and plant.

Arsenic has both inorganic and organic forms of which arsenite (AsIII) is the dominant species in rice field (63% of total arsenic), followed by the remaining forms as, arsenate (AsV, 36%), and methylated forms arsenic species (Abedin et al. 2002). Upon entry of specific As forms through specific transporter proteins, it interferes with the normal physiological process of the plants. In plant elevated levels of As affects phosphate metabolism, protein activity and catalytic functions. Apart from these visual physiological alterations of elevated As are reduced root extension, chlorosis in leaves, shrinking, and necrosis in aerial plant parts, severe curtailing of biomass accumulation, impaired fertility, yield, and grain production (Mitra et al. 2017). Further elevated As mediated stress condition may result in the plant to produce reactive oxygen species (ROS) that ultimately lead to membrane damage, non-specific protein and lipid oxidation and even DNA injuries (Awasthi et al. 2017).

## 3.2 Origin and Forms of Arsenic in Soil and Groundwater

In order to formulate the underlying reasons of the widespread groundwater As problem four main theories for As mobility in have been proposed (Bhattacharya et al. 2015) as follows: oxidation of pyrite, competitive ion exchange, reductive dissolution of iron oxyhydroxides, and reduction and re-oxidation. The alluvial plains of Eastern India and Bangladesh subjected to widespread contamination have pyrite oxidation as the major underlying process where excessive groundwater use for irrigation creates an oxidizing status of the aquifers (Chakraborty et al. 2015). The most important factor of As contamination in India and Bangladesh is based on the principle of reductive dissolution of metal oxides and Fe hydroxides, which results in the release of As. The fourth hypothesis behind the As menace deals with the reduction and re-oxidation theory (mobilization of As via Fe oxyhydroxides reduction followed by pyrite re-oxidation). This combination of processes although enables As immobilization yet a reduced environment restricts such process making As bioavailable (Bhattacharya et al. 2015; Shukla et al. 2020).

Arsenic exists in the environment in both inorganic and organic forms. Arsenate ($As^V$) is a predominant inorganic form of As that is phyto-available. It exists in four forms in aqueous solution based on pH: $H_3AsO_4$, $H_2AsO_4^-$, $HAsO_4^{2-}$ and $AsO_4^{3-}$. Similarly, As (III) exists in five forms: $H_4AsO_3^+$, $H_3AsO_3$, $H_2AsO_3^-$, $HAsO_3^{2-}$ and $AsO_3^{3-}$. With respect to the prevalence of the various forms As (V) dominate at pH $> 3$, and As (III) is neutral at pH $< 9$ and ionic at pH $> 9$. At pH 6 – 8, in most aquatic systems, both $H_2AsO_4^-$ and $HAsO_4^{2-}$ ions co-exists in considerable amounts in a oxidized environment (redox potential, Eh = 0.2 – 0.5 V), while for intense reduced condition, the aqueous acid, $H_3AsO_3$, is the predominant species (Eh = 0 – 0.1 V). The toxicity follows the order: arsine (-3) > organo-arsine compounds > arsenites ($As^{3+}$) and oxides ($As^{3+}$) > arsenate ($As^{5+}$) > arsonium metals (+1) > native arsenic metal (0) (Sanyal et al. 2015).

## 3.3 Arsenic in Soil as Influenced by Different Factors

In the natural systems, the availability of As to crops is intensely inclined by sorption to solid surfaces such as oxides of Mn, Al and Fe (Mukhopadhyay and Sanyal 2004). Among the different forms the adsorption of arsenate on amorphous Fe hydroxide, goethile, gibbrite, hematite, amorphous Al hydroxide, alumina, kaolinite, montmorillonite, and illite usually increased at a lower value of pH, exhibiting its maxima between pH range 3.0 to 7.0, and thereafter decreased at high pH (Goldberg 2002). The behavior of arsenite was also similar regarding adsorption on amorphous Fe hydroxide, amorphous Al-oxide, alumina where adsorption had an increase at lower pH, reached the peak at pH range 7.0 to 8.0, and decreased thereafter. However arsenate adsorption was greater than arsenite adsorption in all the surfaces (Goldberg 2002).

The transfer of As in its natural environment is governed by several factors, especially type of clays and soil organic matter. Upto pH 9.0 there was an increase in adsorption of arsenate on the clay mineral kaolinite, montmorillonite, and illite. Further soil type greatly influence the As toxicity as evident from Sheppard (1992) who opined inorganic arsenic to be atleast five times more toxic to plants in sandy soils (40 $\text{mgkg}^{-1}$) than in clayey soils with 200 $\mu$g $\text{Askg}^{-1}$. The grater toxicity in sandy soils may possibly be attributed to the low amount of Fe and Al oxides and clays (Bandyopadhyay et al. 2004).

As retention in soils is related to sorption and thus related to soil properties like pH, organic C, CEC, amorphous Fe content and amount of arsenic (Sanyal and Nasar 2002; Saha et al. 2005). The sorbed As content increases with an increase in the soil content of free iron oxides, magnesium oxide, aluminium oxide or clay. This can further be proved by soil treatment with oxalate which removes soil amorphous iron or aluminium and it reduces arsenic sorption competence of the soil (Livesey and Huang 1981). Further assessment of soil profile based As adsorption as in forest soil (Barry et al. 1995) revealed highest sorption of As at 30 cm soil depth (B2 horizon) rich in clay and oxyhydroxides of iron and aluminium. Carbonate bearing minerals play significant role in As sorption in case of calcareous soils especially at $\text{pH} > 9$. Calcium based adsorption of As in soil on the surface of kaolinite occurs through formation of Ca bridges, precipitation of calcium arsenates, or formation of soluble $Ca(H_2AsO_4)_2$, $CaAsO_4^-$, and $CaH_2AsO_4^+$ complexes. Through the calculations based on thermodynamics principle, iron arsenate in acidic, oxic and suboxic soils, and both iron arsenate and calcium arsenate in alkaline, acidic, oxic and suboxic soils limits soil solution phase As concentration.

For soils having pH 8.5 or more, arsenate adsorption decreases with increasing pH, whereas the reverse happens for arsenite. The adsorption maxima on FeOOH lie around pH 4.0 for arsenate, whereas the same for arsenite lie at 7.0–8.5 (Fitz and Wenzel 2002). Majumdar and Sanyal (2003) noted with increasing pH a reduction of arsenate adsorption, but only at low arsenate concentration, which got upturned at higher arsenate equilibrium concentrations possibly due to variations in the electrostatic potential of soil colloidal surfaces with pH.

The different studies based on chemical equilibrium of As in soil has also revealed that oxides of Iron (Fe), Aluminum (Al) and Manganese (Mn) invariably hold As in soils and sediments through inner-sphere complexes via ligand exchange mechanism (Majumdar and Sanyal 2003). Considering the surface of metal as M, the As sorption usually follows the steps as,

$$\begin{aligned}
&\mathrm{M{-}OH + H_2O \Leftrightarrow M{-}OH_2{}^+ + OH^-}\\
&\mathrm{M{-}OH_2{}^+ +\ H_2AsO_4{-}\ \Leftrightarrow M{-}OH_2{}^+ \ldots H_2AsO_4{}^-}
\end{aligned}$$

Or

$$\begin{aligned}
\mathrm{M{-}OH + H_2AsO_4{}^-} &\Leftrightarrow \left[\mathrm{M{-}O^+ - H \ldots H \ldots HAsO_2{}^{2-}}\right]\\
&\Leftrightarrow \mathrm{M{-}HAsO_4{}^- + H_2O}
\end{aligned}$$

The non-specific electrostatic mechanism-based adsorption is due to pH-dependent charged surfaces only especially at pH values below the point of zero charge (PZC) for a given adsorbent (Sanyal 2002). Through the above reaction scheme ligand exchange tends to augment negative charged surfaces on soil colloids and push the PZC to low pH (Ghosh et al. 2003).

Arsenic sorption is greatly influenced by redox potential of the soil as well. When the soil redox levels are higher (500–200 mV), solubility of As is low and mostly exists as As(V). At a redox potential of 0–100 mV (moderately reduced) dissolution of iron oxyhydroxides results in As bioavailability. At intense reduced condition of −200 mV, the soluble arsenic content is found to increase nearly 13 fold as compared to that at 500 Mv (Masscheleyn et al. 1991).

Several researchers have pointed out the phosphate concentration of soil influences arsenic adsorption. The chemical behavior of the anion $AsO_4^{3-}$ being similar to $PO_4^{3-}$, there exists a competitive relationship between them (Liu et al. 2001). Lin and Puls (2000) suggested that aging of the clay minerals affects the adsorption of As greatly with a possible understanding that long term aging results in stronger degree of bonding of As to the clay minerals as a result of arsenic diffusion at the soil water interface to internal pores of the clay aggregates.

Application of organic matter can impact the accessibility of As in the soil-plant system. Soil organic fractions that comprises of humic acid (HA) and fulvic acid (FA) behave as active accumulator of As through formations of metal-humate complexes of varying stability (Mandal et al. 2019a; Kumar et al. 2021). Soil microbial population also influences the microbial transformations of arsenic in soil through their arsenite oxidase enzyme activities. These results in alleviation of As stress and enables the growth of plant (Laha et al. 2021).

Soil moisture regimes also play a pivotal role in governing the availability of As in soil (Bandyopadhyay et al. 2004). In most of the studies the waterlogging results in increased As availability in rice plant rather than imposing water stress condition through adoption of intermittent wetting and drying.

## 3.4 Arsenic Uptake Mechanism in Rice Plant

Rice plants takes up As from the soil pore water into the root cells by two diverse mechanisms. In the first mechanism of uptake the phosphate ($PO_4^{3-}$) transport pathway plays the most important role (Catarecha et al. 2007; Bakhat et al. 2017). The phosphate transporters takes up As(V) from soil and thereafter transfer it to other parts of the plants (Wu et al. 2011). The second mechanism of As uptake in rice plant is mediated by aquaporin channels, the As species As (III) analogue of Silicic acid and also the methylated As species (Ma et al. 2008). The Si transporters favours the arsenite uptake in the rice root cells, owing to its resemblance with silicic acid; both having a high pKa (9.3 and 9.2 for silicic acid and arsenous acid, respectively) and also molecular structure (tetrahedral). Methylated As species like Monomethylarsonic acid (MMA) and Dimethylarsinic acid (DMA) are usually

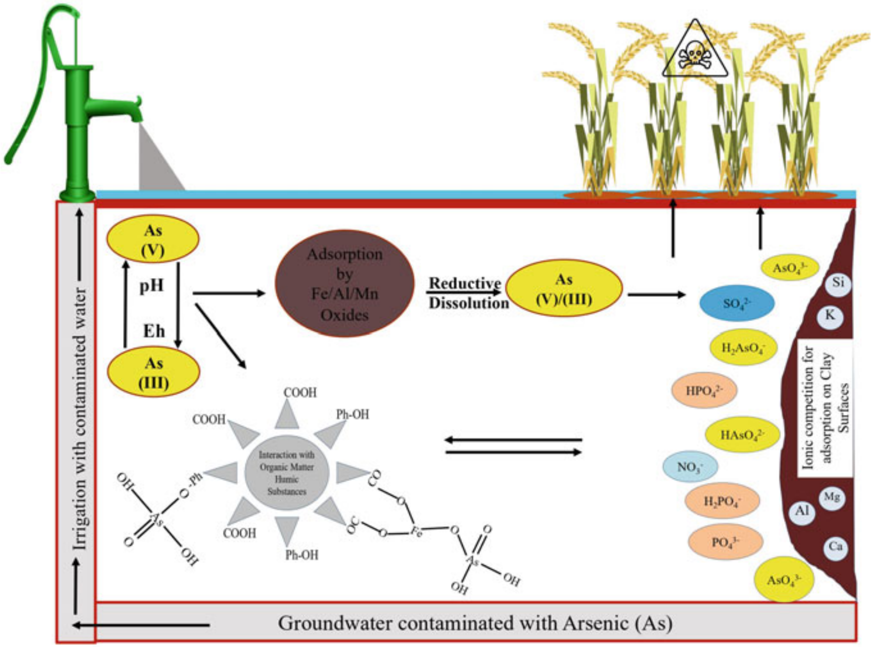

**Fig. 3.1** The arsenic (As) pathway in rice field

taken up by the plant through nodulin 26-like intrinsic protein and a high translocation follows from root to shoot rendering more phyto-toxicity In terms of toxicity it has been widely established that inorganic As are several orders higher than the pentavalent methylated As forms.

As(III) and DMA are the dominant species of As in rice grain. Studies have also revealed that the harmfulness of DMA is lower than inorganic As counterparts (Syu et al. 2015). Nodal phloem cells retain higher concentration of As through sequestration of As and thereby reduce As translocation to the grain. The phenomenon of vacuolar As sequestration and decreased As translocation into rice grains is characterized by the presence of a tonoplast transporter in phloem companion cells (Song et al. 2014). The transfer of As from irrigation water to soil and its interaction with the soil properties and subsequently its entry in to the rice grain can be observed from Fig. 3.1.

## 3.5 Mobilization of as Through Root-Shoot-Grain

An interesting perspective comes into purview if we tend to compare the uptake and translocation of As species. Inorganic As has greater uptake but lower translocation as compared to organic As showing the reverse trend (Zhao et al. 2013; Awasthi et al.

2017). Studies have also revealed that uptake rate of DMA (V) is only one-tenth of As(III); while the translocation for the same was 100 fold (Lomax et al. 2012). Thus in terms of mobility As species follows the trend of DMA(V) > MMA(V) > inorganic As.

After its uptake in the root tissues the mobility of As to above ground plant (shoot) occurs via transporters directly (no energy requirement) or through xylem sap by transporter mediated As loading (Suriyagoda et al. 2018). The loading As (V) occurs though Pi transporters while that of arsenite occurs by aquaporins (Verbruggen et al. 2009).

The phloem transporters in the upper stem nodes play an immense important role (Song et al. 2014; Chen et al. 2015) while the role of xylem is less conspicuous (Bauer and Hell 2006) as transpiration is limited here. Arsenite transporters for phloem are still not confirmed although often designated as inositol transporters (INT) (Duan et al. 2016; Kumarathilaka et al. 2018). In spite of the significant uptake of DMA(V) in the edible cereal grains, a possible silver lining exists regarding the fact that organic DMA is less toxic by several times as compared to inorganic forms and thus reduce some dietary mediated risk of the carcinogenic As (de Oliveira et al. 2020).

## 3.6 Strategies for Mitigating as Accumulation in Rice

### *3.6.1 Addition of Inorganic Amendments*

Iron (Fe) aids in the reduction of arsenic absorption in rice. Exogenic use of Fe causes the formation of oxides of Fe in form of Fe plaques surrounding rice plant roots, which reduces As uptake, increases co-precipitation of Fe and arsenic. Due to the presence of anaerobic condition during rice cultivation triggers the production of plaques (Fe) at the at the root surface. The plaque having high affinity for As(V) can sequester the arsenic, resulting in a decrease in As mobility from roots to shoots (Roy Chowdhury et al. 2020). Metallic Fe and Fe-oxide have been observed to decrease arsenic accumulation in rice by 51 and 47% (Matsumoto et al. 2015).

Phosphorus (P) contends with arsenate (AsV) for the same adsorption sites in soil and also on the plaques (Fe) mainly by ligand exchange which is a key characteristic in the rice field for bioavailability of arsenic and uptake by plants (Peryea and Kammereck 1995). Phosphate treatment in soil reduces As content in Fe-plaques (Smith et al. 2002; Bogdan and Schenk 2009). Phosphate ($PO_4^{3-}$), has an repressive influence at critical concentrations, where it contends with As(V) for the same transport channel during plasma membrane uptake (Meharg and Macnair 1992), and a rise in $PO_4^{3-}$ causes decrease in As(V) uptake (Pigna et al. 2010). Lee et al. (2016) proposed three key factors influencing arsenic mobility in soil and uptake in rice: (1) enmity between As and P for adsorption sites, (2) Antagonism between of inorganic P and As during transport in rice roots, and (3) role of P in As transfer from root to shoot.

For rice, silicon (Si) is an essential element. Plants utilize only mono silicic acid among the several soluble Si forms present in soil. As is taken up NIPs, the same transporter that takes silicon (Si) and transports it (Ma and Yamaji 2006). Because silicon competes with arsenite for uptake (Zhao et al. 2009), having a lot of silica in the soil lowers arsenite uptake by rice (Bogdan et al. 2008). Total As buildup in rice straw and grain was reduced by 78 and 16%, respectively, after Si was applied to the soil (Li et al. 2009a, b).

Sulfur (S) is a necessary component of plant growth, as well as a key player in minimizing arsenic buildup and translocation in plants. S application considerably lowers As in rice, according to (Hu et al. 2007) through three possible methods. (1) Sulphate ($SO_4^{2-}$) encourages the development of plaques (Fe) on the surface of the roots, lowering As levels in the soil; (2) $SO_4^{2-}$ may heighten the desorption of As(V) from the plaques; and (3) $SO_4^{2-}$ can hinder arsenate transport into cells at the membrane transport site. $SO_4^{2-}$ fertigation increased total S buildup and decreased As absorption and translocation in rice plants. In comparison to the treatment without S, the S treatment reduced As accumulation in rice grain by 50.1% as reported in a study by (Mridha et al. 2022). The percentage reduction of As in cooked parboiled and sunned rice compared to uncooked rice was 55.9–74% and 40.3–60.7%, respectively (Mridha et al. 2022). When rice is exposed to AsV, genes involved in $SO_4^{2-}$ absorption, transport, and metabolism are up-regulated (Srivastava et al. 2016). Another advantage of using $SO_4^{2-}$ in paddy soils is that under reducing conditions, $SO_4^{2-}$ has a great affinity for arsenic, causing it to precipitate as insoluble arsenic-sulfide (Signes-Pastor et al. 2007).

The importance of selenium (Se) as an essential trace mineral in human and animal health is well known. Though the effect of Se in plant species is still being researched, recent results suggest that adequate Se supplementation (at an early stage) benefits plants by improving photosynthesis and antioxidative reactions. Even when plants are grown in ideal or normal conditions, reactive oxygen species (ROS) (which develop in the chloroplast or mitochondria) occur (both invitro and invivo conditions). Recently (Moulick et al. 2016, 2017) reported on the benefits of priming rice seeds with Se boosting germination and seedling growth in non-soil and soil-based assays under both arsenate and arsenite stress conditions. When grown in As spiked soil, Se primed plants lowered As translocation from the root to shoot, as measured by the translocation factor (TF). Se primed plants have lower TF root to shoot (46.96%), TF root to husk (36.78–38.01%), and TF root to grain (39.63%) than unprimed plants maintained in same As stress (Moulick et al. 2018).

### *3.6.2 Organic Amendments and Water Management Practices*

One of the most efficient techniques for limiting As in the soil–plant system is water management in paddy fields (Somenahally et al. 2011). When irrigation water has high As levels, the high irrigation need of rice contributes to soil As build-up; consequently, a mitigation plan should include both sources. Alternate wetting and drying (AWD) involves drying wet soils occasionally to introduce periods of oxic conditions, which lowers the concentration of As(III) in the soil solution. Application of orgnics, on the other hand, diminish As bioavailability in soils (Sengupta et al. 2022) and therefore in plants, as hitherto showed for sesame (Sinha and Bhattacharyya 2011), wheat, and maize (Mandal et al. 2019b), and vegetables (Bhattacharyya et al. 2021). To investigate the efficacy of irrigation management (saturation and alternate soaking and drying) and organics (vermicompost, farmyard manure, and mustard cake) in decreasing As load an field experiment was conducted by (Sengupta et al. 2021). Vermicompost amendment combined with alternate wetting and drying resulted in the least amount of As accumulation in edible grains (0.318 mg $kg^{-1}$) with a 25% rise in grain yield. Water management measures alter soil redox status, checking the reduction of As(V) to As(III). The findings of (Talukder et al. 2011) complement previous findings that rice absorbs less arsenic (0.23–0.26 mg $kg^{-1}$) under aerobic water management measures than under anaerobic practices (0.60–0.67 mg $kg^{-1}$).

## 3.7 Developing Predictability Models

There are different models like Free Ion Activity Model (FIAM), Biotic Ligand Model (BLM) which are used for predictions of bioavailability or ecotoxicity, which assume that all chemical reaction in the medium external to the organisms are at equilibrium (Meyer 1999; Morel and Hering 1993; Slaveykova and Wilkinson 2005). The variation in Zn, Ni, and Cd content in wheat grain and Arsenic content in rice grain due to long term effect of sewage irrigation could be explain by FIAM (Meena et al. 2016). The use of censored regression model like Tobit Regression Model was used in determining the safe limit of As in soil and irrigation water by (Kumari et al. 2021). Use of Machine Learning (ML) algorithms like Logistic Regression (LR), Random Forest (RF), Decision Tree (DT), K-Nearest Neighbours (KNN), Neural Networks (NN) etc. can be effectively used in developing predictability models. The use of Random Forest (RF) for predicting grain Arsenic concentration in rice from hyperspectral data was reported by (Lv and Liu 2011). Sengupta et al. (2021) reported RF outperformed KNN and Generalized Regression Model in forecasting grain As concentration. As a result, if correctly calibrated and tested, the former can be a useful tool for estimating rice grain As concentration. With the use of DT and LR the maximum permissible total As concentration for rice soil of Asian countries was determined by Mandal et al. (2021). Similarly, Liu et al. (2011) applied generalized dynamic fuzzy neural network (GDFNN) to predict heavy metal concentration by integrating hyperspectral, environmental and heavy metal data (copper and cadmium). Shi et al. (2016) did a comparative study of arsenic in soil and rice plant to improve the prediction capability using genetic algorithm (GA) and partial least square regression model. Another study used RF, gradient boosted machine (GBM), and generalized linear (GLM) models were used and compared to determine BCF and identify potential controlling aspects in the transmission of heavy metals in soil-crop systems (Hu et al. 2020).

## 3.8 Conclusion

Arsenic buildup in rice is mainly governed by its bioavailability, which is influenced by a range of factors such as soil pH, OC, texture, the presence of other elements, and mineral composition such as Fe, P, S, and Si in soil, soil-rhizosphere-plant system; soil microbes and their behaviors, moisture content. Arsenic deposition in rice may be mitigated through changes in farming techniques and bioremediation procedures. Rainwater harvesting for agricultural irrigation, bioremediation with arsenic-resistant bacteria, natural arsenic chelators, genetically engineered rice plants, and aerobic paddy crop farming are all efficient ways to reduce arsenic pollution. Changes in farming practices, such as the use AWD, organic matter addition have been shown to reduce arsenic deposition in rice plants Although researchers are working on numerous genes in the rice plant that are involved in arsenic uptake, transport, and/or detoxification to create a more sustainable crop for human consumption, application in a range of field circumstances will be challenging.

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# Chapter 4

# Arsenic in Gold Mining Wastes: An Environmental and Human Health Threat in Ghana

**Albert Kobina Mensah, Bernd Marschner, Kenneth Joseph Bansah, Eric Stemn, Sabry M. Shaheen, and Jörg Rinklebe**

**Abstract** We provide an overview of arsenic (As) from gold mining spoils, tailings disposal sites, and mining degraded soils and propose sustainable soil remediation options to mitigate mobilization and human health impacts. In situating the As problem in a broader science, concepts related to As chemistry, As pollution, As mobilization, and As toxicity are discussed. Relying on empirical data from mine sites and nearby communities in southwestern Ghana and crucial scholarship and scientific literature, we report high concentration of As in six media comprising soil (tailings, farms, and mining sites), water (surface and groundwater), water sediments (rivers and streams), food (meat and fish), plants (vegetation and food crops/fruits), and human (urine and blood samples). Soil, water, and urine are the top three media

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that report the highest and most siginificant concentration of As with levels exceeding established recommended threshold limits. Additionally, we identify and discuss the gaps in As research in Ghana and provide recommendations on sustainable strategies for cleaning contaminated sites.

**Keywords** Buruli ulcer · Tailings · Safety · Environment · Human health · Remediation · Pollution

## 4.1 Introduction

In Ghana, gold mining is noted for environmental and social impacts in host communities (Mensah et al. 2015, 2021). These include, among others, the indiscriminate release of As from gold mining sites, which in turn affects accurate performance of ecological functions as reported by Armah et al. (2014). Tailings dam is one of the waste lands resulting from surface mining of minerals and an estimated 5–7 billion tons are created annually at the global scale (Edraki et al. 2014; Lu and Wang 2012). Surface gold mining affects surrounding areas through excavation of large quantities of earth materials and generation of mine wastes. Mine tailings comprise the residual fine (1–600 μm) material dumped after mineral extraction and processing, and it includes dissolved metals and other toxic elements (Edraki et al. 2014).

In many gold mining regions, As is associated with arsenopyrite (FeAsS) in gold mining spoils and tailings, making the spoils rich in As. Mobilisation of the gold ore (FeAsS) during mining and processing could significantly alter As biogeochemical cycle and consequently aid in its release into the surrounding ecosystem (Li et al. 2014). The released As can eventually get into rivers, get adsorbed unto its sediments, and the As-contaminated sediments can be carried over wide distances (Bundschuh et al. 2021). This can impact areas along river courses, the ocean, and the marine areas along coastlines. Consequently, these may pose potential health dangers to water, ecosystem, and humans in mining environments (Posada-Ayala et al. 2016; Bempah et al. 2013; Li et al. 2014; Mensah et al. 2020, 2021).

For instance, As contamination by mining at the upstream may cause pollution of irrigation water and may impact water quality of downstream users (Cagnin et al. 2017). At high concentrations, As is toxic to plants as reported by Shrivastava et al. (2015). Arsenate (AsV) is the principal form of As in soils and its chemical characteristics are like that of P; these properties enable As to compete with P in the plant system (Shrivastava et al. 2015). In addition, As hinders metabolic functions and impedes plant growth due to As-induced plant toxic effects. Also, microbial activity is inhibited significantly in As-contaminated soils as it reduces the activities and effectiveness of soil enzymes (Su et al. 2014; Gao et al. 2010). Furthermore, contact with As could cause many human health complications (Bortey-Sam et al. 2015; Chakraborti et al. 2013) as highlighted in Fig. 4.5. These may include dermal, respiratory, cardiovascular, neurological problems, reproductive, immunological, genotoxic, liver cancer and cutaneous lesions (Acosta et al. 2015; Rehman et al. 2021).

Early-life exposure to As may cause birth defects including shorter gestation period, low birth weight, and smaller new-borns were reported in Mexico by Laine et al. (2015). Further, Bundschuh et al. (2021) reported that accidental absorption of As-contaminated soil can harm the stomach, the kidney, the nervous system; and may cause death in chronic cases.

In line with mine sector sustainability, it is therefore imperative that As-contaminated mining spoils and tailings are progressively restored throughout the operational phase and during the decommissioning stage of the mine project life cycle. Additionally, sustainable approaches are required to repair the damage caused to the land during mineral extraction, to reduce release of As, to minimise runoff and mitigate As spillage from the mining site. Such measures are also needed to reclaim the degraded mine-sites to return the land to its pristine conditions and ensure safe re-use of the land post-mining. Eventually, such measures are needed to safeguard the integrity of the environment and hence to protect the health of humans and animals in mining areas. In this respect, Wuana and Okieimen (2011) reported that soil remediation measures are thus taken to prevent impacts on humans, plants, or animals, and to restore the lost function of soil to allow its safe use.

Various techniques are proposed for cleaning As-contaminated soils, which are broadly categorised into mobilisation and immobilisation techniques (Bolan et al. 2014). Mobilisation technique here will mean As is released to enter the soil solution and is subsequently removed with the aid of plant species. Immobilisation techniques involve complexing As from the soil solution through processes including adsorption, complexation, co-precipitation, and precipitation reactions. The benefits of using immobilisation options are that they lessen impacts caused to humans, animals, and plants in the surrounding environment; decrease their uptake into food crops; and they lessen leakage into surface and ground waters. Plant-based solutions, called phytoremediation, using green plants to clean up contaminated sites are also proposed in many studies (Antoniadis et al. 2017, 2021; Hou et al. 2020; Sheoran 2010, 2011; Wang et al. 2021).

The time duration of soil remediation is a limiting factor as it may take many years to clean the soil and to restore its functions to the pristine conditions. The alternative could be to employ immobilisation techniques that will consequently reduce environmental impacts on plants, the ecosystem, food chain, groundwater and subsequently limit its bioavailability into humans. Examples of amendments for As immobilisation comprise clay, cement, zeolites, minerals, compost, manure, and microbes (Gul et al. 2015; Bolan et al. 2014). Manufacturing deposits (e.g., red mud) (Zou et al. 2018), iron oxides (Wang et al. 2021) and biochar (Beesley et al. 2013) are also reported as having potential for immobilising As in mine contaminated spoils. The As-immobilisation potential of biochar, for instance, may be caused by its relatively high carbon content and presence of positive ions such as Al, Fe and Mn on the surfaces (Beesley et al. 2013).

Arsenic poses an environmental and human health threat to people in gold mining communities in Ghana. Over the years, limited studies have documented the sources and occurrence of As from gold mining spoils (Table 4.1), and these studies have mainly focused on the southwestern mining region of the country. These studies employed the total content method in assessing the risk and extent of contamination without employing advanced methodology such as X-ray absorption near edge spectroscopy (XANE) to investigate the species responsible for the pollution. In addition, these studies did not consider the influence of factors such as pH, dissolved organic carbon, phosphorus, oxides, sulphide, and redox potential that largely control the mobilisation and fate of transport of As. Similarly, these studies were quite silent on the human health implications of As. Furthermore, studies on As remediation using biochar, compost, or iron oxide alone or in combination with native green plants or introduced species are noticeably absent in the scientific literature. Therefore, any study that addresses the gaps in these previous research works will offer an interesting read to the global scientific community, inform the government's regulations and mining policies, and contribute to sustainable mining.

In this study, we provide an overview of the extent and distribution of As in gold mining spoils and propose sustainable soil remediation alternatives to repair the damage caused to the land during and after mineral extraction. This study also offers a path to mitigate the release of As from mine spoils and provides direction on reclamation for improved safety and sustainable post-mining land use. We introduce the problem and provide background to arsenic contamination in gold mining spoils, tailings disposal sites, and mining degraded soils in Ghana. Concepts related to As chemistry, pollution, and factors affecting mobilization and toxicity of As on environmental resources and human health are reviewed. Additionally, we identify and discuss the gaps in As research in Ghana, draw conclusions, and provide recommendations for policy actions and further studies. In this study, mining spoil refers to the wasteland that remains after extraction of the ore and mine tailings refers to the residue after gold extraction. However, these two terms are used interchangeably in this study.

### *4.1.1 Arsenic Chemistry, Characteristics and Forms in Soils and Sediments*

Arsenic has atomic number of 33 and a mass number of 75 atomic mass unit. It has chemical characteristics of metals and non-metals (metalloidic element); and it belongs to group 5A in the periodic table (Bissel and Frimmel 2003; Escobar et al. 2006). It consists of three allotropes: grey, yellow, and black. Natural As has one stable isotope, $^{75}$As (Audi, 2003), but other isotopes have been synthesized according to Shrivastava et al. (2015). Chemical characteristics of As are like that of P, as the two are in the same group in the periodic table, and they form compounds through covalent bonding (e.g. Escobar et al. 2006; Hussain et al. 2019; Pigna et al. 2009; Shrivastava et al. 2015). Arsenic occurs in two major oxidation states: arsenite with valency of three (AsIII); and arsenate with valency of five (AsV) (Bundschuh et al. 2021; Shrivastava et al., 2015); it is present in other oxidation states such as −3 in arsenides (arsine), and 0 in elemental As (Shrivastava et al. 2015). In a neutral

**Table 4.1** Selected studies reporting As contamination in environmental media from different gold mining regions in Ghana

| Number | Place/region | Environmental media affected | Arsenic concentration reported | Reference |
|---|---|---|---|---|
| 1 | Obuasi/Ashanti region | Soils from gold mine tailings | 542–1800 mg $kg^{-1}$ | Bempah et al. (2013) |
| 2 | Tarkwa/Western region | Surface and ground water sources | 4300–26,000 µg/L (surface water); 137–4343 µg/L (ground water) | Armah et al. (2014) |
| 3 | Tarkwa/Western region | River samples | <1.0–73 µg/L | Asante et al. (2007) |
| 4 | Obuasi/Ashanti region | Soils around mine tailings | 581–1711 mg/kg | Antwi-Agyei et al. (2009) |
| 5 | Obuasi/Ashanti region | Shallow wells and boreholes | 2–175µg$l^{-1}$ | Smedley (1996) |
| 6 | Obuasi and Kumasi/Ashanti region | Vegetation, food crops from farms and markets, cooked foods from homes, local fish and meats, soil, and water samples | 0.07–7.20 mg/kg for samples in Kumasi (non-gold mining town) and 0.12–70.50 mg/kg for samples in Obuasi (gold mining town) | Amonoo-Neizer and Amekor (1995) |
| 7 | Amansie West/Ashanti region | Streams, natural drainage systems, catchment basins, and farmlands | >15 mg/kg | Duker et al. (2005); Gyasi et al. (2012) |
| 8 | Konongo/Ashanti region | Water sources, untreated ore and tailing samples | 40 and 12,200 µg/L for water samples; 2978–4,628 mg/kg for ore samples; and 1776–1787 mg/kg was found for samples collected from tailing heaps | Boadu et al. (2001) |
| 9 | Tarkwa/Western region | Gizzard, liver, kidney, and muscle samples from chicken | Gizzard: 0.16 mg/kg<br>Liver: 0.21 mg/kg<br>Kidney: 0.37 mg/kg<br>Muscles: 0.13 mg/kg | Bortey-Sam et al. (2015) |

(continued)

**Table 4.1** (continued)

| Number | Place/region | Environmental media affected | Arsenic concentration reported | Reference |
|---|---|---|---|---|
| 10 | Prestea/Western region | Soil samples collected from active and abandoned gold mine tailings | 2000–8404 mg/kg | Mensah et al. (2020) |
| 11 | Mining areas | Water samples | 30 µg/L | Hadzi et al. (2018) |
| 12 | Prestea/western region | Water and sediments | Water samples:<br>8250 µg/L<br>Sediment:<br>942–10,200 mg/kg | Serfor-Armah et al. (2006) |
| 13 | Prestea/Western region | Water sediments | 15–325 µg/L | Obiri et al. (2016) |
| 14 | Jimi River Basin/Ashanti region | Sediments, water and fruits | 1746.5 mg/kg | Akabzaa et al. (2005) |
| 15 | Rural Ghana | Ghana's rural hand-dug wells and boreholes | >10 µg/L | Norman et al. (2006) |
| 16 | Prestea/western region | Soil and farms around a mine tailing | 3,144 mg/kg | Mensah et al. (2021) |
| 17 | Gambaga, Nalerigu, Nawchugu/south-eastern-northern Ghana | Soil and basin sediment samples | 22.68 mg/kg | Arhin et al. (2019) |
| 18 | Mining districts in southwestern Ghana including Obuasi | Soil samples in mining areas | 246 mg/kg | Kazapoe et al. (2021) |
| 19 | Mining towns in southwestern Ghana | Soil samples from gold mining areas | 246 mg/kg | Arhin et al. (2019) |
| 20 | Tarkwa/southwestern Ghana | Water (rivers and groundwater) and human urine samples | Groundwater:<br>0.1–4.0 µg/L<br>Rivers/streams:<br>0.5–8.0 µg/L<br>Urine samples:<br>34–700 µg/L | Asante et al. (2007) |
| 21 | Obuasi/Ashanti region | Soils from gold mine tailings | 8305 mg/kg | Ahmad and Carboo (2000) |
| 22 | Ankobra river/Western | River/water samples | 600 and 2200 µg/L | Irunde et al. (2022) |

(continued)

**Table 4.1** (continued)

| Number | Place/region | Environmental media affected | Arsenic concentration reported | Reference |
|---|---|---|---|---|
| 23 | Ankobra river/Western | Fish | 0.2–0.8 mg/kg | Gbogbo et al. (2017) |
| 24 | Accra/Greater Accra | Drinking water | 17 µg/L | Asante et al. (2012) |
| 25 | Eyinase/Western region | Water samples | 69.4 µg/L | Bhattacharya et al. (2012) |
| 26 | Damang-Tarkwa/Western | Soil | 40 mg/kg | Petelka et al. (2019) |
| 27 | Obuasi/Ashanti | Hair of mine workers at treatment plant<br>Hair of mine workers at shaft<br>Hair of non-mine workers | 336 mg/kg<br>26 mg/kg<br>39 mg/kg | Amasa (1975) |
| 28 | Ankobra/Western | River sediments | 183 mg/kg | Bannerman et al. (2003) |
| 29 | Western region | Hair samples | 0.052 mg/kg | Essuman et al. 2009 |
| 30 | Upper east region | Urine | 114.52 µg/L | Basu et al. (2011) |
| 31 | Upper east region | Urine | 14.75 µg/L | Abrefah et al. (2011) |
| 32 | Greater Accra region | Urine | 54.4 µg/L | Asante et al. (2012) |

pH, arsenite is present in solution principally as $H_3AsO_3$ and arsenate dominates as $H_2AsO_4^-$ and $HAsO_4^{2-}$ (Goldberg 2011). Arsenic exists in two kinds: inorganic and organic (Bundschuh et al. 2021; Escobar et al. 2006; Mandal et al. 2019). Inorganic As are reported to be more prevalent and of more interest than the organic ones due to its key role in the biogeochemical cycle (Mandal et al. 2019). Inorganic As principally consists of the mineral kinds in deposits, whereas organic As is dominant in plants and animals due to As absorption (Shrivastava et al. 2015). Content of As in non-contaminated soils range from 0.1 to 40 mg/kg (Kabata-Pendias 2010); total content threshold was earlier recommended to be less than 10 mg/kg (Fitz and Wenzel 2002) and the world soil average threshold is put at 6.83 mg/kg (Kabata-Pendias 2010).

#### 4.1.1.1 Inorganic Arsenic

Arsenic is mainly found in the soil in inorganic forms in more than 300 As-containing minerals (Bissen and Frimmel 2003; Kabata-Pendias 2010). Arsenic is greatly associated with deposits of many metals, often recognised as a good indicator in geochemical prospecting and hence it is mostly referred to as "pathfinder" (Kabata-Pendias 2010). Arsenate is the predominant inorganic As in the soil with 60% proportion; sulphides and sulphosalts—20%; oxides—10%; and arsenites, arsenides, elemental and metal alloys at 10% (Parshley and Bowell 2001; Drahota and Filippi 2009). They are mostly found in close relationships with cations such as Fe, Cu, Co, S, Ni, Cd, Pb, Ag, Sb and Au (Drewniak and Sklodowska 2013) and with other anions such as oxygen and chlorine (Bundschuh et al. 2021). Arsenopyrite (FeAsS) is the highest abundant As mineral, then pigment gold ($As_2S_3$), realgar ($As_4S_4$), and loellingite ($FeAs_2$) (Bundschuh et al. 2021). In acid mine drainage (AMD), arsenate and arsenite dominate ecosystems containing oxidized sulphur species (Cheng et al. 2009). Basic characteristic trait of mineral As is its unique strength when exposed to forces of weathering. The stability of sulphide As minerals is dependent on the following (Drewniak and Sklodowska 2013):

i. covalent bonding between As and S,
ii. coordination bonding between Fe and As or S, and
iii. van der Waals forces between molecules.

Weathering, exposure to atmospheric oxygen, surface and groundwaters and alteration of primary minerals yield secondary As minerals called the arsenites, which are mostly the oxides of As(III); and arsenates, principally consist of oxides of As(V). Arsenites such as arsenolite and claudetite are weathering products of AsS, nonetheless they can be produced as well through roasting of As-containing minerals. Common arsenic primary and secondary minerals are provided in Smedley and Kinniburgh (2002).

Scorodite is the most found As secondary mineral and is dominant in mining waste stockpiles and industrial deposits including mine tailings (Bempah et al. 2013; Mensah et al. 2020). Secondary As aggregates exhibit differences in water solubility and thus As availability. For instance, Ca-arsenates are water soluble, whereas Fe-arsenates are relatively insoluble (Drahota and Filipi 2009; Drewniak and Sklodowska 2013). The less soluble As-species are thus capable of precipitating and immobilizing As in contaminated mine spoils and consequently reducing their associated pollution of the environment.

##### Arsenic-Sulphides in Gold Mine Ores in Ghana

Arsenic sulphides include pyrite ($FeS_2$), arsenopyrite (FeAsS), pyrrhotite ($Fe_xS_{1-x}$), and marcasite ($FeS_2$). Arsenopyrite is a major pathfinder for gold exploration in Ghana. Arsenopyrite occurs naturally in well-developed crystallised forms with free compounds found to spread in the ores or assembled in groups and aggregates. The

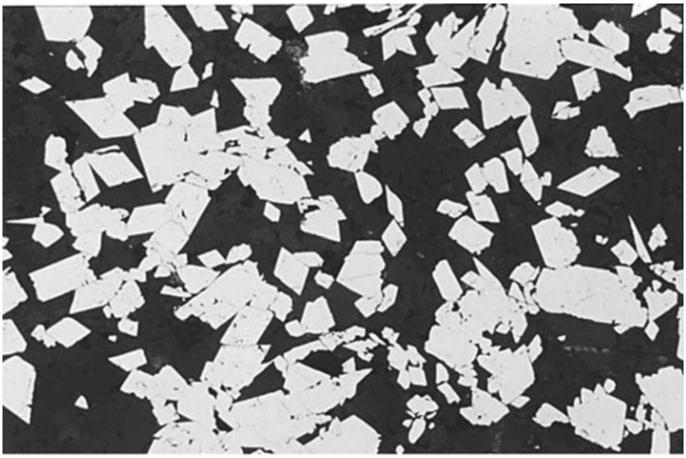

**Fig. 4.1** Photomicrograph showing well-developed crystallised form of arsenopyrite sulphide ore (white) of the Prestea gold mine. *Source* Oberthuer et al. (1997)

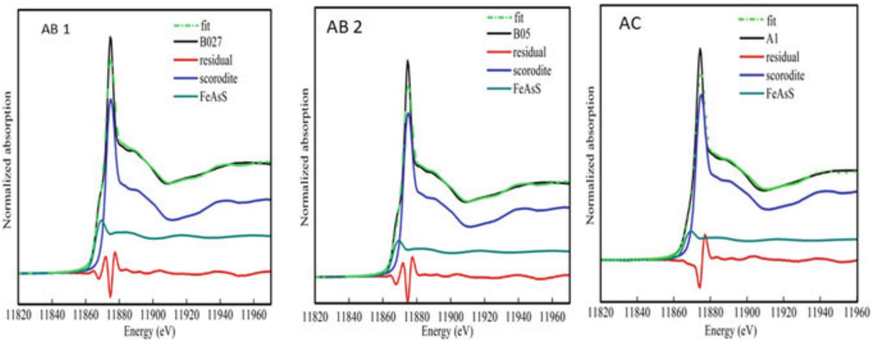

**Fig. 4.2** Arsenic K-edge XANES spectra of selected abandoned (AB) and active (AC) mine spoils and their linear combination fitting results (results are published and explained in detail in Mensah et al. 2020). The peaks are indications of dominant species (arsenopyrite and scorodite) in the mining spoils

crystals typically vary in length from 50 to 200 μm; however, they might also have lengths over the mm range (Fig. 4.1). Electron microprobe evaluation of arsenopyrite by Oberthür et al. (1994) indicated the following As-contents in arsenopyrite at some mining hotspots: Ashanti mine = 39.4−45.9 wt.%, Prestea and Bogoso mine = 41.4−47.4 wt.%, Ni = 2.02 wt.%, Co (1.17 wt.%, Sb contents = <0.2 wt.%. Synchrotron-based X-ray analysis by Mensah et al. (2020) also indicated that arsenopyrite accounted for 28–35% of total As in an abandoned mine tailing and 24% in an active mine tailing in Prestea. In the same study, scorodite accounted for 65–72% in the abandoned mining tailing, whilst it accounted for 76% in the active mine tailing (Fig. 4.2).

Pyrite, also known as “fool’s gold”, is another inorganic As-bearing iron sulphide found in gold mine ores. However, As content in pyrite is quite negligible, and pyrite oxidation causes acid mine drainage (AMD). The AMD process generates sulphuric acid and iron oxyhydroxides, and is responsible for contamination of streams, rivers, lakes, and reservoirs. Natural $FeS_2$ contains many other trace elements (e.g., Ag, As, Cd, Co, Cu, Hg, Pb, Sb, Se, and Zn), which are also of environmental concern because they are released into neighbouring waterways during oxidative dissolution. These elements exist as substitutions in the pyrite lattice or as inclusions (Murphy and Strongin, 2009). According to Oberthuer et al. (1997), larger varieties of $FeS_2$ including auriferous arsenian pyrite exist at the Bogoso and Prestea mines (up to wt. 5.5% As).

Pyrrhotite exists as a non-stoichiometric Fe–S point with constituents denoted as $Fe_xS_{1-x}$ (Murphy and Strongin 2009). Pyrrhotite occurs in 10–30 μm spherical to egg-shaped inclusions rarely coupled with chalcopyrite in arsenopyrite, or overgrowing arsenopyrite in unusual forms. Oberthuer et al. (1997) reported that there is the possibility of limited to complete substitution of pyrrhotite by marcasite and/or pyrite.

Marcasite has the capacity to replace pyrrhotite, and is less often intergrown with pyrite or pyrrhotite, or occurs as a separate crystal aggregate. Also, it occurs in two different forms of pyrite and has the $S_2$ pattern (Murphy and Strongin 2009). Free-milling gold is rare in the sulphide ores. Most gold grains observed microscopically are below 20 μm in diameter, and they display irregular shapes (Murphy and Strongin 2009).

#### 4.1.1.2 Organic Arsenic

Inorganic As becomes methylated when it gets absorbed by the food chain and it is then converted into less toxic ones. Organic As are thus the less toxic kinds of As and they include monomethylarsine (MMA), dimethylarsine (DMA), and trimethylarsine (TMA) (Shrivastava et al. 2015; Bissel and Frimmel 2003). Organic As, such as arsenobetaine or arsenocholine, are found in seafoods (Bissel and Frimmel 2003). Methylation according to Goldberg (2011) is either the addition or substitution of methyl groups ($CH_3$) to a substrate. Thus, in this case, $CH_3$ group is added or substituted into an inorganic As mineral to become a methylated or organic As. As(III) methylated compound species exhibit greater toxicity than the As(V) ones. This is because As(III) methylated species are more responsive near tissue biological molecules than As(V) counterparts (Kalman et al. 2014). Consequently, As toxicity is dependent on its speciation as: As(III) > As(V) > organoarsenicals (Fergusson 1990). Bundschuh et al. (2021) reiterated that mineral arsenite is sixty times extra toxic than arsenate, which is seventy times higher than the methylated As.

Microbes, such as bacteria, fungi, and algae in soils, can convert organic and inorganic As into a more volatile form called arsines ($AsH_3$). Organic arsines (methyl arsines) are monomethylarsine ($CH_3AsH_2$), dimethylarsine ($(CH_3)_2AsH$) and trimethylarsine($(CH_3)_2As$) (Goldberg 2011; Shrivastava et al. 2015). These arsine compounds are volatile, and they tend to escape into the atmosphere (Goldberg 2011). Arsine is a very lethal gassy As species (Chauhan et al. 2008), produced in high anaerobic fields (Kossoff and Hudson-Edwards 2012; Sharma 2009). A decrease in pH favours $AsH_3$ formation (Shrivastava et al. 2015). In reducing conditions, As is released from wet soils and damp surfaces accompanied by $CH_3AsH_2$, $(CH_3)_2AsH$, and $(CH_3)_2As$ (Kossoff and Hudson-Edwards 2012; Duker et al. 2005). Upon liberation into air through the action of microbes, these compounds may undergo oxidation in non-volatile forms and could be deposited back into the land (Bundschuh et al. 2021). The non-toxic forms of organic As are the arsenobetaine (AsB) and arsenocholine (AsC) (Kumaresan and Riyazuddin 2001). In summary, understanding As behaviour and speciation is key for designing empirical and appropriate remediation measures for mitigating As contamination problems in soils, sediments, and water and to eventually remove or reduce its human health-associated complications. Figure 4.3 summarises inorganic, organic, and biological forms of As including their empirical formulae and structure.

## *4.1.2 Natural and Anthropogenic Sources of As Contamination*

### 4.1.2.1 Natural Sources

The prevalent forms of As present in the environment are the natural ones (Sailo 2014; Smedley 2002), and they come from geological, hydrological and soil-forming biogeochemical processes (Escobar et al. 2006). Natural sources of As in soil and sediments are governed by the parent material, volcanic activity, history of weathering, sorption ability, activity of soil microbes and precipitation ability (Kabata-Pendias 2010). Arsenic concentration ranges between 1.7 and 400 mg/kg in alluvial rocks, and 1.3–3.0 mg/kg in igneous rocks (Escobar et al. 2006).

Natural sources may also come from atmospheric emissions or via the desorption and dissolution of As-rich minerals (Bhattacharyya et al. 2003). According to Matschullat (2000), 17,150 tons of As are emitted to the atmosphere by volcanoes and 27 tons by the oceans. Wind mobilization and deposition also contribute to As in the environments with suspended particles settling on the ground through a process called dry deposition or wet deposition.

### 4.1.2.2 Anthropogenic Sources

Areas with significant human activities can generate high contents of As via emissions from industrial processes to affect the ecosystem. For instance, Williams (2001) found high As concentrations (range: 5 µg/L–72 mg/L) in mining waters in seven countries of south-east Asia, Africa, and Latin America and attributed it to emissions

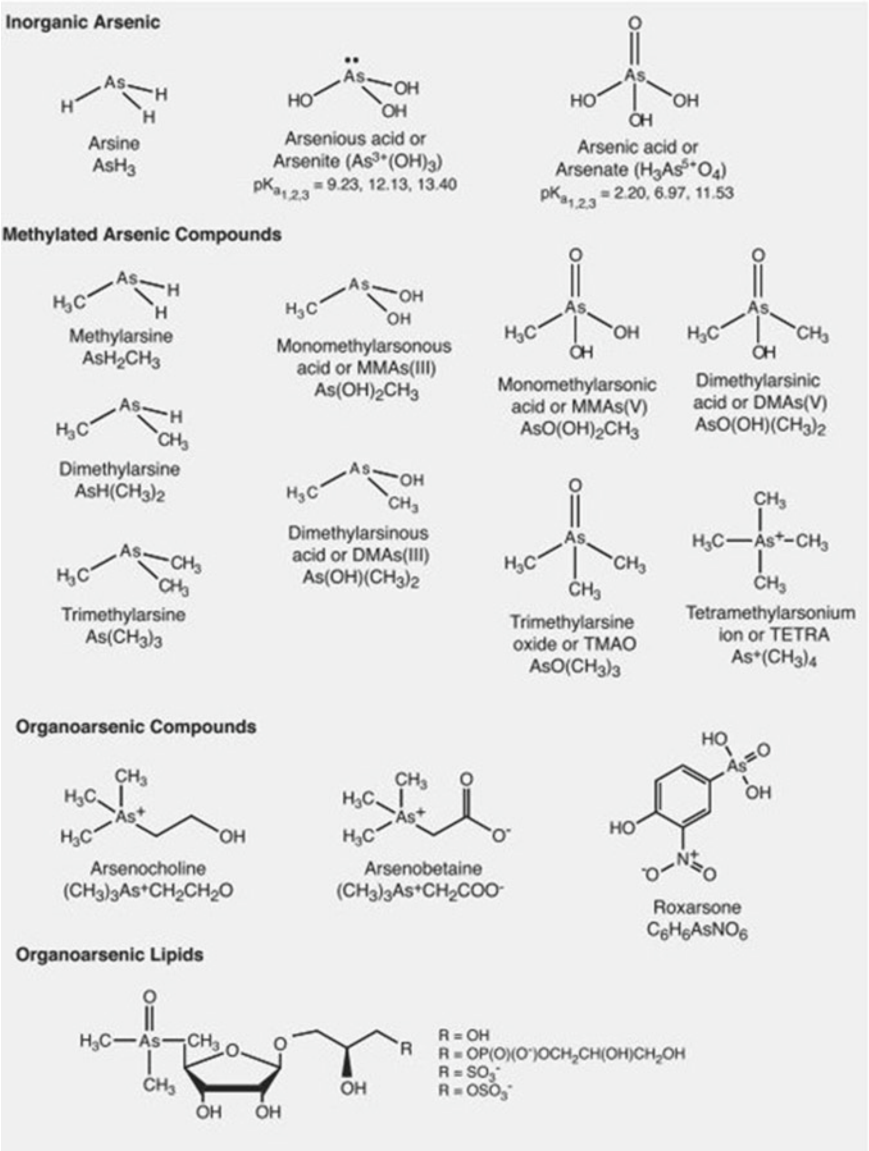

**Fig. 4.3** Inorganic, organic, and biological forms of As in the environment. Reproduced with permission from Elements magazine: O'Day, Peggy A. (2006). Chemistry and Mineralogy of Arsenic, Elements, Volume 2, Number 2, 77–83

from the mine processing plants. Burning of fossil fuels in households and power plants represents another anthropogenic source of As release (Bissel and Frimmel 2003).

For example, coal burning causes volatilisation of $As_4O_6$, leading to the discharge of As into the atmosphere (Matschullat et al. 2000). Fly ash from thermal power stations may also cause soil contamination (Bissel and Frimmel 2003). Additionally, arsenical fungicides, herbicides, and insecticides may constitute anthropogenic sources as indicated by Goldberg (2011). Residues of As in soils with continuing application of arsenical pesticides, herbicides, and insecticides are found with maximum total content of 2 g/kg (e.g., Sadler et al. 1994; Yan-Chu et al. 1994). Arsenic is also employed in the manufacture of lead-acid batteries, other electronic products (Ning 2002). These may constitute additional anthropogenic sources of As contamination to the soil, sediments, surface, and groundwater.

#### 4.1.2.3 Arsenic Contamination from Gold Mining

Gold mining and its activities constitute a major contributor to the release of high As content into the environment and mine surrounding areas (Drewniak and Sklodowska 2013). High concentration of As above recommended thresholds is reported in food crops, rivers, lakes, catchment basins and channels, natural drainage systems, river and basin sediments, soils, local fishes, and meats from homes, mine tailings, shallow and hand-dug wells, boreholes, groundwater, fruits, human blood and urine, local fishes, cooked food and water, and vegetation (Fig. 4.4). Extraction of As-rich sulphide ores means creation of waste lands that could release effluents from the mine site. Mine stockpiles and tailings can trigger discharge of As and other toxic elements into the environment. Concurrently, these can further be carried by running water or agents of erosion, and eventually pollute nearby ecosystems and various environmental media. In effect, As pollution from gold mining may either occur due to geogenic contamination (i.e., natural oxidation of parent material/the As-sulphide ore) or from anthropogenic sources (i.e., poor handling and/or management of mine wastes, etc.) (Bundschuh et al. 2021; Drewniak and Sklodowska 2013; Hussain et al. 2019; Martiñá-Prieto et al. 2018; Mensah et al. 2020, 2021; Posada-Ayala et al. 2016).

Figure 4.5 illustrates natural and anthropogenic causes of As contamination due to gold mining, pathways of contamination and the associated-environment, social and human health impacts. Again, natural contamination mainly comes from the oxidation of the gold mining ore- the FeAsS. In other instances, mine tailings can also contain other sulphides (e.g., pyrite ($FeS_2$)) that are capable of generating acidity and releasing As when they undergo oxidation (DeSisto et al. 2016, 2017). As a result, Posada-Ayala et al. (2016) recounted that sulphide-dominated mine tailings are a particularly rich source of As.

In other instances, As-rich tailings material may be carried by air or wind and may be deposited in the surrounding environment, posing threats to environmental and human health. Also, As may become mobilised during flooding (Mensah et al. 2021).

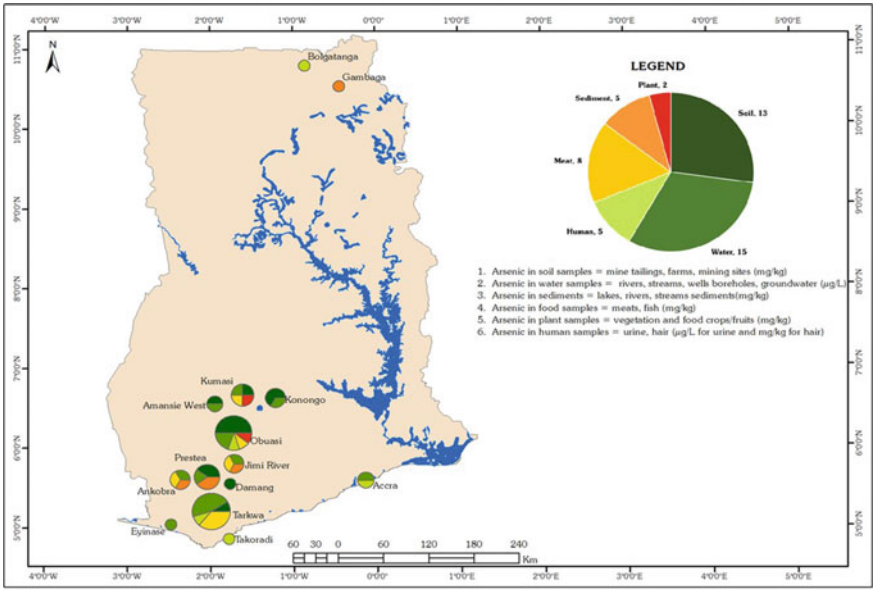

**Fig. 4.4** Map showing point distribution of As in various environmental media across Ghana

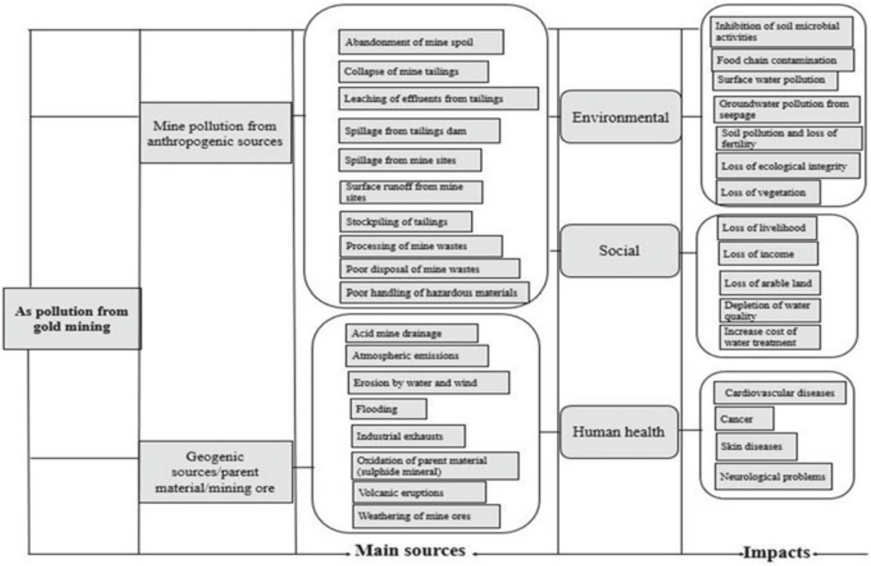

**Fig. 4.5** Diagram depicting As contamination from gold mining, sources of contamination and environmental, social, and human health impacts

Volcanic eruptions of such contaminated sites also have the capability of introducing and distributing As over a wide area. Besides, As can be generated through natural means from gold mining due to acid mine drainage. Acid mine drainage (AMD) is a spontaneous discharge of As when reactive sulphide minerals mainly pyrite and arsenopyrite are exposed to atmospheric oxygen, water and microbial action (Fosu et al. 2020).

In summary, AMD comes from the natural oxidation of the dominant gold mining sulphide minerals, FeAsS or the FeS in gold mining sites and spoils. Chemical, biological, and physical factors such as air (oxygen), water, microbial activity, and degree of metal sulphide exposure influence AMD generation. Acid mine drainage or acid rock drainage (ARD) waters remain a major ecological challenge confronted by gold mining industries; the occurrence of AMD or ARD happens through the following Eqs. 4.1 and 4.2 (Drewniak and Sklodowska 2013).

$$\begin{aligned} &\mathrm{FeAsS(s)} + 11/4\mathrm{O_2(aq)} + 3/2\mathrm{H_2O(aq)} \\ &\leftrightarrow \mathrm{Fe^{2+}(aq)} + \mathrm{SO_4^{2-}(aq)} + \mathrm{H_3AsO_3(aq)} \end{aligned} \tag{4.1}$$

$$\mathrm{H_3AsO_3} + 1/2\mathrm{O_2(aq)} \leftrightarrow \mathrm{H_2AsO_4^-} + \mathrm{H^+} \tag{4.2}$$

Anthropogenic sources of As contamination from gold mining may occur due to abandonment of mining spoils, collapse of mine tailings, leaching of effluents from mine tailings, spillage from tailing dams, spillage from mine sites, surface runoff from mine sites, stockpiling of mine wastes, processing of mine wastes, poor/indiscriminate disposal of mine wastes and poor handling of mine hazardous materials as illustrated in Fig. 4.5.

## *4.1.3 Soil and Biogeochemical Factors Influencing As Contamination and Mobilisation*

### 4.1.3.1 Soil pH

Soil pH is a major biogeochemical factor that affects sorption and desorption, oxidation state, solubility, mobility and thus toxicity of soil As species (Antoniadis et al. 2017; Bissen et al. 2003; Violante et al. 2010). In general, for cationic trace elements, lower pH results in higher mobility and availability, while higher pH results in increased mobility and availability for anionic species such as those of As (Antoniadis et al. 2017). For As, the explanation is that high pH reduces the electronegativity of silicate secondary compounds and hence facilitates their availability. Moreover, at high pH, positive charge on the surfaces of oxides diminishes, their activity and effectiveness for sorption decreases; and hence As retention reduces (Chen et al. 2012).

The effects of pH on regulating As solubility and its availability are demonstrated in many previous studies.

Mensah et al. (2022) demonstrated the impact of pH on As solubility in a mine-contaminated soil from southwestern Ghana using the acid neutralisation capacity test (Fig. 4.5). Their results indicated that As solubility increases with increasing pH and there was a significant positive correlation between pH and soluble As ($r = 0.92$, $P < 0.01$). They further proposed three main assumptions to explain As release and mobilization at higher pH: (i) deprotonation of Al/Fe/Mn oxides, (ii) solubilisation of Fe/Mn oxides, and (iii) development of negative charges on the soil colloids.

Mamindy-Pajany et al. (2011) reported that studying the behaviour of As(V) onto mineral adsorbents containing Fe (e.g., hematite and goethite) as a function of pH aided to select the most suitable treatment for As stabilization in contaminated sediments. Moreover, Beiyuan et al. (2017) reported that pH is a key environmental factor that controls mobility of As in contaminated media; and that higher mobility of As occurs at lower redox potential and high pH. Further, batch leaching tests at different pH from Al Abed et al. (2007) showed a strong pH dependence on As and Fe leaching. This experiment focused on understanding the influence of pH on As availability and solubility; and to explain pH as a key factor of adsorption and mobility.

Violante et al. (2010) indicated that as the pH increases, the soil sorption capacity declines owing to a fall in positive charge of the inorganic material. Thus, increasing pH decreases sorption capacity of the soil for As species (Violante et al. 2010). Previous authors (e.g., Catalano et al. 2008; Martin et al. 2009; Violante et al. 2008) explained the sorption capacity of anions using the "inner-sphere sorption and outer-sphere sorption" phenomena. They reported that specifically-sorbed ions or molecules have the potential to substitute $OH^-$ found on the surfaces of variable charged-minerals. These reactions are encouraged at low pH, and they trigger $OH^-$ groups to take protons. "Inner-sphere sorption" is also termed as specific sorption (Violante et al. 2008). Arsenates and arsenite form inner-sphere complexes (Violante et al. 2010). Depending on pH of the medium and surface coverage, As(V) may form different surface complexation onto inorganic soil constituents (O'Reilly et al. 2001). For instance, in wide pH ranges, As(V) sorption will be more encouraged than that of As(III). However, arsenite sorption onto ferrihydrite will be facilitated relative to arsenate in basic pH medium (Violante et al. 2010).

The pH dependence of As species adsorption using the ionization capacities and surface charge phenomenon of adsorbates and adsorbents has been explained by Mamindy-Pajany et al. (2011). For instance, negatively charged arsenate species ($H_2AsO_4^-$, $HAsO_4^{2-}$, $AsO_4^{3-}$) are reported to dominate higher pH media (i.e., 2–12). The surface charge of adsorbents is thus governed by reactions involving transfer of hydrogen ions among the mixture or suspension and the mineral surface. The surfaces of the adsorbate (i.e., the mineral) can be positive, negative or zero; and they are dependent on the pH of the media. For instance, FeO are described by their point of zero charge which matches with the pH of the solution ($pH_{ZPC}$: pH at zero charge). At this point, the surface charge of FeO is zero because it has the same charge as the environmental media (the solution). In such scenario, Mamindy-Pajany et al. (2011) indicated that arsenate adsorption is promoted when surface charge of adsorbents is positive (e.g., when pH of FeO adsorbates is lower than $pH_{ZPC}$ of adsorbents). In conclusion, such phenomenon immobilises As in the environment and reduces its mobility and consequent ecological toxicity.

### 4.1.3.2 Soil Redox Potential

Water saturation in sediments and soils alters their chemical and biological properties, controls microbial populations, and regulates soil processes. In such scenarios, soils undergo a sequence of reducing and oxidising reactions, as soil's stage shifts from oxidising to reducing environments under flooding (Du Laing et al. 2009). Thus, concentration of As during flooding conditions is governed by the redox potential ($E_H$). This occurs either through direct changes in the soil $E_H$ due to created dynamics during wetting and drying regimes or via indirect $E_H$-induced changes in pH, DOC, and the chemical behaviour of Al, Fe, Mn, and S (Antoniadis et al. 2017; El-Naggar et al. 2019; Rinklebe et al. 2016a, b; Shaheen et al. 2014a, b). For instance, a decrease in $E_H$ during flooding and rainfall regimes could increase the pH, which in turn enhances As mobility and vice versa (Niazi et al. 2018; Rinklebe et al. 2016a, b). Also, redox potential could cause metal reduction during reducing periods (e.g., from $Al^{3+}$ to $Al^{2+}$, $Fe^{3+}$ to $Fe^{2+}$, and $Mn^{3+}$ to $Mn^{2+}$), and consequently trigger desorption and dissolution of As bound to Al/Fe/Mn oxides. The opposite occurs in oxidizing environments from long standing dry periods (Shaheen et al. 2014a, b).

Redox also influences As mobilisation through its indirect induced changes on the soil organic matter. Soil carbon is an effective carrier for As. This is because the surface of carbon is made up of many positive ions, which provide fertile sorption grounds for As and consequently reduce its mobility. Under redox conditions, organic matter influences As mobility in many ways. The following hypotheses are proposed: (i) organic matter dissolution, which causes the liberation of the bound-As; (ii) pH change associated with reduction reactions concerning organic matter desorption- causes desorption of held-As; (iii) creation of soluble organic matter from the presence and decay of microbial biomass; (iv) reductive dissolution of organic matter leading to release of Mn- and Fe-oxyhydroxides bound to organic matter and consequent release of bound-As (e.g., Grybos et al. 2007, 2009; Mensah et al. 2022).

Redox potential regulates environmental toxicity of As through its influence on the availability of potentially mobile As fractions. Potentially mobile fractions of As consist of the un-specifically bound As, As specifically-sorbed on mineral surfaces, those bound to the amorphous and low crystalline iron oxides, and As bound to crystalline iron oxides (Dybowska et al. 2005; Wenzel et al. 2001). These components may be available due to biogeochemical changes including for example, the soil pH and redox settings. For instance, during reducing conditions, As bound to the Fe oxide fractions could be released (Lemonte et al. 2017) and become available for environmental pollution and accumulation in the food chain contamination. Thus, flooding and its related activities as well as and the existing $E_H$ could influence the safety of food crops grown in As-contaminated mining areas.

Moreover, the effect of redox conditions equally plays a very critical role in controlling the fate of As transport by altering the oxidation states. This consequently affects their mobility and toxicity in aquatic environments and waterlogged soils (Rinklebe and Du Laing 2011). As earlier stated, As(III), for instance, is more mobile than that of As(V). This could be facilitated by the presence of reducing agents in soil, which can reduce As(V) to As(III). Thus, addition of organic matter or waterlogging fields could accelerate this reduction and consequently increase As availability (Rinklebe et al. 2016a, b; Shaheen et al. 2018). Since As(V) is strongly retained by inorganic soil components, microbial oxidation results in the immobilization of As. Arsenic in well drained conditions is present as As(V), and as As(III) in reduced soil conditions, together with elemental form As (As-0) and as arsine ($H_2As$) (Bolan et al. 2014).

#### 4.1.3.3 Metal Oxyhydroxides (Al/Fe/Mn)

Metal oxides (Al/Fe/Mn) perform critical functions regarding As pollution in soils and water systems (Bolan et al. 2014; Komárek et al. 2013; Wang et al. 2021). Oxides have significant, energetic surface areas and amphoteric nature, characteristics which provide suitable sites for remediation of As in contaminated soils. Soil remediation with oxides is made possible because of their high capacity to adsorb and immobilise As through processes such as specific sorption, coprecipitation, and by forming inner- and outer-sphere complexes (Bolan et al. 2014; Komárek et al. 2013). Thus, surfaces of FeO(OH) may perform a key task in retaining As. A positively charged surface, for instance, leads to binding of As, and vice versa.

Metal oxides (e.g., ferric oxides, manganese oxides, aluminium oxides, titanium oxides, magnesium oxides, and cerium oxides) are considered promising adsorbents for treatment of As because they have large surface areas (Hua et al. 2012; Koo et al. 2012). Mench (1998) reported decline in water extractable-As content, and lower uptake in plant tissues, when iron oxides were applied to As-contaminated garden soils. Similarly, Hartley and Lepp (2008) assessed the effectiveness of four Fe-bearing additives for reduction of As in three contaminated soils and found that goethite stood out as the most promising candidate for reducing uptake of As into the plant shoot.

#### 4.1.3.4 Soil Organic Matter

Soil carbon is basically a carrier of As and influences As (im)mobilisation via many means. For instance, there could be the formation of carbonates and carbon-As complexes; presence of surface functional groups; occurrence of positive and negative surface ions; indirect effects on the soil pH; and activation of microbes required for redox-controlled As solubility. For instance, a lower pH reduces the many negative charges on the surfaces of carbon and consequently increases its adsorption capacity for As and vice versa.

In calcareous soils and sediments, for instance, the presence of carbonates creates a valuable shield against a decline in their pH (Du Laing et al. 2009). Thus, carbonate production from soluble organic carbon, e.g., during liming of the soil, could concomitantly increase the presence of negative charges and may facilitate solubility and mobilisation of As.

Organic matter indirectly affects the fate of As transport and migration by providing a food source for microorganisms. Additionally, provision of C can arouse microbial population and activities. This may catalyse a sequence of redox reactions in the presence of electron acceptors (e.g., oxygen and iron) (Du Laing et al. 2009). These reactions largely affect solubility of As in contaminated mining spoils. For instance, addition of wastewater to soils could raise sources of C supply and nutrient contents. Consequently, populated microbes may enhance reduction of As into more reduced forms (Kunhikrishnan et al. 2017). More on redox impacts on As mobilisation is elaborated earlier in Sect. 4.1.4.2.

Other factors of interest that might influence As mobilisation increase its concomitant health threat include cation exchange capacity, soil particle distribution (e.g., presence of clay minerals), sulphide contents, anions presence (e.g., sulphates, chlorides, carbonates, fluoride, etc.), salinity and age of the mining spoil.

### *4.1.4 Toxicity of Arsenic*

Arsine gas ($AsH_3$) is reported as the most toxic compound (Kossoff 2012; Sharma 2009), and the fatal dose is 250 mg/m$^3$ at an exposure time of 30 min (Shrivastava et al. 2015). As earlier explained, As toxicity rests on their oxidation states and compound formulae (Nakamura 2011). Soil inorganic As, for instance, are accumulated in the food chain, they become toxic, and in turn tend to affect various life forms (Shrivastava et al. 2015). As discussed earlier, As(V) is relatively less toxic than that of As(III). Additionally, As(V) is commonly immobile and found in mineral forms, whilst As(III) easily becomes mobilised into aquatic and living organisms. Thus, the fatal dose ($LD_{50}$) of As(III) is less (15–42 mg/kg) than that of As(V), with 20–800 mg/kg (Kaise and Fukui 1992). Also, As(III) binds with sulfhydryl groups (also called the 'thiol' groups- RSH) of proteins, and consequently results in clinical manifestations (Shrivastava et al. 2015). In the organic groups, fatal dosages for MMA (1.8 g/kg) and DMA (1.2 g/kg) are much less than TMA (10 g/kg)'s (Nakamura et al. 2011).

#### 4.1.4.1 Plant Health

Plants growing in uncontaminated soil contain As < 3.6 mg/kg (Gebel et al. 1997), whilst Kabata-Pendias (2011) reported relatively specific value range (0–1.5 mg/kg). Plants can generally absorb As from the soil either through root uptake or dry deposition on its leaves (Shrivastava et al. 2015; Su et al. 2014). Plants can show signs of As phyto-toxicity through impeding germination of seed, decreasing the height of the plant and causing stunted growth, reducing growth of root, exhibiting necrosis in the leaves and reducing concentration of chlorophyll, lowering the yield of plants and they may be causing death of crops (e.g., Shrivastava et al. 2015; Su et al. 2014).

#### 4.1.4.2 Soil Microbial Activities

Arsenic contaminated soils have reduced and impeded activities of soil microbes and their activities (Su et al. 2014). For instance, Kandeler et al. (1997) found that there was reduced microbial biomass in an As-contaminated soil closer to a mine site compared to those located farer away from the mine site. Additionally, Fliebbach et al. (1994) stated that high As content above the threshold could decrease soil microbial biomass significantly. Further, soil enzymes have a key function to play in the decay of organic matter and in cycling of nutrients. Arsenic in the soil thus lessens the effectiveness of soil enzymes (e.g., Su et al. 2014; Gao et al. 2010). Consequently, Chander et al. (1995), found that enzyme activities in As-contaminated soils declined by ten to fifty times.

Gao et al. (2010) studied pollution effects of toxic elements on soil enzyme activities and their microbial community. They found that microbial populations were significantly lower under polluted sites than under control treatment, with soil bacteria decreasing most in population size than the other soil microbes such as fungi and actinomycetes. Further, elevated heavy metal concentrations and toxicant levels differently impacted on soil enzyme activities, with inhibition of phosphatase, urease, and dehydrogenase activity.

Furthermore, Koo et al. (2012) found that enzyme activities were negatively impacted due to high As contents in mine tailings. More particularly, the abundance and activities of soil enzymes were inversely proportional to the water-soluble fraction of As in the mining spoil. Thus, the soil enzymes activities were mainly affected by the As water-soluble fraction than by the other fractions. In the same study, the treatments that decreased the As water-soluble fraction enhanced the soil enzyme activities.

#### 4.1.4.3 Human Health

Arsenic is categorised as a Class-I human carcinogen (IARC 2012) and can cause many health complications (Ahoulé et al. 2015; Bortey-Sam et al. 2015). Some of these As-associated health complications are earlier highlighted in Fig. 4.5. Elevated

As contents are observed in food crops in gold mining areas in Ghana, which can subsequently impact the health of residents (e.g., Obiri et al. 2006, 2010). Chronic exposure to As also causes skin lesions (Su et al. 2014). Skin problems such as melanosis (hyperpigmentation), keratosis, and leukomelanosis (hypopigmentation) are reported in As-contaminated areas in India (e.g., Shrivastava et al. 2015; Su et al. 2014). Arsenic is further reported as a famous carcinogenic element and can cause cancer (e.g., that of the skin, the lung, the bladder, the liver, and the kidney) (IARC 2012; Khan et al. 2021). In Bangladesh, As poisoning in cattle resulted in difficulty in walking, diarrhoea, and death (Eisler 1988).

*Mycobacterium ulcerans,* the bacterium responsible for Buruli ulcer, thrives in As-contaminated areas (Duker et al. 2005). Interestingly, As has been found to pose a health threat to women and children in gold mining areas, with median As hazard index values ranging from 3000 to over 65,000 (Mensah et al. 2020). A further study by Mensah et al. (2021) of soils and farmlands near an abandoned gold mining spoil in southwestern Ghana indicated that As remained the highest contributor to metal/metalloid pollution in the mining fields. Particularly As contributed highest to the total pollution index and health risks (69–88%) in the mining sites (Fig. 4.6). The oxidation of As-dominated minerals, which usually happens in mine spoils, provides a medium for this ulcer causing bacterium, and more than 2000 cases of this ulcer have occurred in mining districts in Ghana (Duker et al. 2005). We speculate that women and children in the mining areas may be susceptible to As health-related problems. Women and children may thus be exposed to As-health threats such as that of Buruli ulcer, other skin diseases, genetic disorders, neurological problems, birth deformities in new-born babies and cognitive dysfunctions among children. In this regard, Duker et al. (2005) further observed that instances of Buruli ulcer were greater in As-enriched drainages and farmlands in mining districts in Ghana. Additionally, cases of bladder and lung cancers, reproductive outcomes, and declined cognitive function were reported among As-exposed populations in Latin America (e.g., Bundschuh et al. 2021; Khan et al. 2021).

In Burkina Faso, skin lesions, ulcer necrotic tumour and deaths found predominant among village patients were later linked to As-poisoning from drinking of As-contaminated-groundwater (Ouedraogo 2006; Smedley et al. 2007). The health implications of As in animal foods of livestock (e.g., gizzard, liver, kidney, and muscle) in mining contaminated regions in Ghana are provided in Bortey-Sam et al. (2015). The study detected As contents ranging from 52 to 100% in the animal foods consumed by people in the mining areas. The pollution was attributed to the oxidation of the gold bearing ores; processing of the ore, which produces arsenic trioxide ($As_2O_3$) into the environment; migration of As into topsoil and in watercourses; and As absorption into food crops.

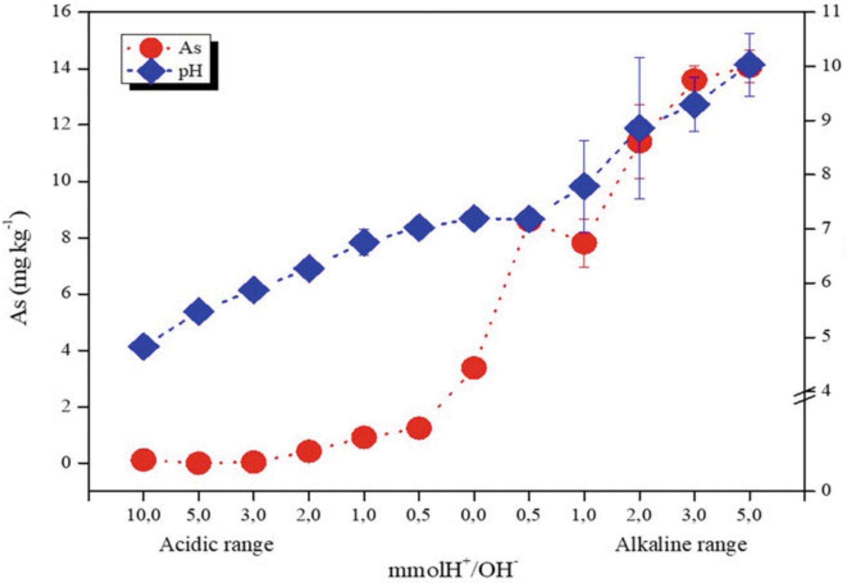

**Fig. 4.6** Dynamics of As solubility due to pH changes (impacts of pH changes on As solubility). Values are means of three replicates and error bars represent the standard deviations. *Source* Mensah et al. (2022)

### *4.1.5 Remediation of As-Contaminated Sites*

From the afore-discussed environmental and human health threats posed by mining spoils on residents in mining communities, it is thus imperative that gold mining is carried out in a sustainable manner. This includes remediation and restoration of mine contaminated and degraded sites. In this section, we present and discuss briefly various green and sustainable remediation options available for cleaning As and reducing its contamination in mine lands. Recent and detailed reviews of these green technologies and sustainable options are provided in Hou et al. (2020), Palansooriya et al. (2020), and Wang et al. (2021). Bolan et al. (2014) reviewed literature on remediation of metal and metalloid contaminated soils and categorised the techniques of remediation broadly into mobilization and immobilization methods; explained earlier in Sect. 4.1.1.

#### 4.1.5.1 Mobilisation Strategies for As Remediation

Use of Organic Amendments

Application of organic materials generally modifies the soil physico-chemical and biological properties. They thus improve the structure of the soil, improve the water retention ability of soils, control soil temperature and pH, improve nutrients and organic matter of the soil as well encourage microbial population and activities. Consequently, organic amendments enhance soil quality, boost plant growth, and increase crop yield. In other instances, organic soil amendments are added with the purpose of cleaning the soil and ameliorating presence of toxic elements in contaminated soil and water.

For instance, amendments like sewage sludge (biosolids), manure, biochar, compost can be added to As-contaminated soils to increase mobility for subsequent uptake by plants. In this regard, there were increases in leachable As in compost-amended soils (e.g., Redman et al. 2002). This was attributable to DOC competition with As for sorption sites. Shaheen et al. (2017) observed that soil irrigation with sewage effluent concomitantly increased their total As contents by 3.3 folds as compared to irrigation with clean water. Recently, Mensah et al. (2022) found that addition of the 0.5–5% of compost, manure, and biochar to a 3 kg-As contaminated soil respectively, increased the bioavailable fraction of As by 106–332%, 24–315%, and 28–47% as compared to control (Fig. 4.8).

Furthermore, under flooding conditions, Yang et al. (2022) found that pig prepared biochar enhanced solubility of As and subsequently increased its mobilisation and release. They gave two main reasons to explain this observation: i. 'anion exclusion' resulting from the electrostatic repulsive force between negatively charged pig biochar and the leading negative As species (e.g., $H_2AsO_4$, $H_2AsO_4^-$, $HAsO_4^{2-}$ and $AsO_4^{3-}$); and ii. production of soluble phosphate by the pig biochar which competed with As for binding sites on soil minerals.

### Application of Inorganic P-fertilizers and Liming Materials

Application of P fertilisers to As-contaminated soils can increase As availability and consequently heighten its environmental and human health threats. The role of P in As fate of transport and release has been extensively explained in previous sections. Thus, P fertilisers may be used to enhance the phytoextraction efficiency of hyperaccumulating plants for As. In this regard, Mensah et al. (2022) found that addition of inorganic fertiliser at 5 g/kg containing 15% $P_2O_5$ increased the readily bioavailable As in a mining spoil soil by 398% and the exchangeable/specific-sorbed As by 11% during a 28-day incubation study. These were further attributed to high contents of salinity and chloride associated with the inorganic fertilizer applied to the As-contaminated mining spoil soil. These high salinity and chloride contents encouraged production of negative ions, enhanced desorption of As anions from positively charged binding sites, and consequently facilitated its mobilisation (El-naggar et al. 2021a, b; Mensah et al. 2022). Moreover, the phosphate content would compete with As anions for available binding sites on the soil colloid, and the smaller ionic size of P makes it preferable (Yang et al. 2022). Ultimately, As sorbed on the exchange site could be displaced and its solubility and bioavailability will increase, and thereby exacerbating associated environmental and human health risks. For these reasons, Shaheen and Tsadilas (2015) cautioned against the use of P- fertilizers when

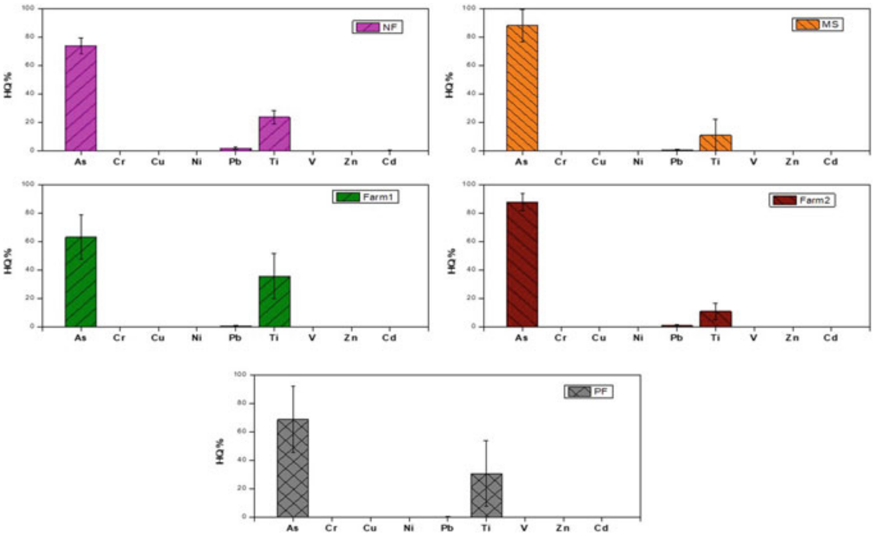

**Fig. 4.7** Mean percentage contributions of hazard quotients of studied PTEs to hazard index of the various mining affected sites. NF = Natural forest, MS = Mine surrounding, PF = Pueraria field. *Source* Mensah et al. (2021)

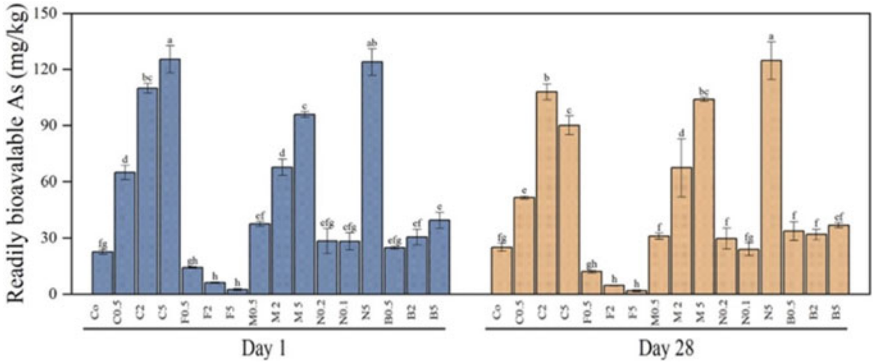

**Fig. 4.8** Changes in the mine spoil non-specifically (readily bioavailable) contents during the 1-day and 28-day incubation period following treatments with biochar-B, compost-C, iron oxide-F, manure-M, and inorganic fertiliser-N, at different dosages (Mensah et al. 2022)

they argued that although P addition seems to be highly effective, their excessive use could cause eutrophication of surface water and deplete groundwater quality. They therefore recommended the use of mixed treatments to improve effectiveness of inorganic P-fertilizers to reduce the possibility of As-food chain contamination (Fig. 4.7).

Liming can also be done to increase and enhance mobilisation strategies for As removal. Generally, liming is carried out to correct the soil pH, by decreasing the presence of protons and increasing the presence of hydroxyl ions on the soil colloids. Liming materials, e.g., carbonates, oxides, and hydroxides of alkali and alkali-earth metals (e.g., Ca, Mg and Na) could be used to increase the soil pH and lessen soil acidity. Also, eggshells, mussel shells, and oyster shells, biochar, red mud, and clay minerals have soil liming abilities (Palansooriya et al. 2020).

Applying higher amounts of MgO can cause mobilisation of metalloid PTEs including As, and restriction of trace elements (e.g., Fe, Mn, and Zn) (Holland et al. 2018); which may be beneficial either to support plant growth or aid remediation of toxic substances in the soil. Thus, deciding on the appropriate soil properties and forecasting anticipated soil pH are key things to consider prior to addition of lime (Palansooriya et al. 2020). Even so, combining liming materials with other amendments can amplify liming effectiveness and reduce the associated-ecological impacts. Higher pH, reduction in acidity, production of more negative ions and charges, and increased formation of total $CO_3{}^{2-}$ associated with liming are key reasons underpinning their influence on As mobility.

#### 4.1.5.2 Immobilisation Strategies for As Remediation

Immobilisation of As could also be accomplished chiefly through adsorption, precipitation, and complexation reactions. These mechanisms cause redistribution of elements from solution state to solid state, and consequently reduce the solubility and bioavailability of the toxic material. Examples include clay, cement, zeolites, minerals, phosphates, organic composts, and microbes (Bolan et al. 2014). Some studies (e.g., Hartley and Lepp 2008; Lebrun et al. 2020) have shown the remediation ability of residues (e.g., red mud and iron oxides) for treating As-contaminated sites and reducing their bioavailability. Others have used combination of treatments or modified red mud or iron-oxide with biochar in reducing the bioavailability and release of As into the surrounding (Zou et al. 2018). Immobilisation technologies may be carried out off-site (ex situ) or on-site (in situ). On-site strategies are favoured because of lesser labour and energy needs, but their implementation will be contingent on peculiar site situations (Wuana and Okieimen 2011). The strategy for solidification/stabilization treatment methods involves joining or inoculating agents for treatment into the polluted soil (Wuana and Okieimen 2011).

#### 4.1.5.3 Plant Techniques for As Remediation

This method of soil remediation uses green plants to facilitate removal of contaminants from the soil (Mensah et al. 2021; Reeves et al. 2018; Sheoran et al. 2010). According to Jiang et al. (2015), “phytoremediation, a green approach using plants to remediate toxic compounds, is a cost-effective, socially acceptable, and environmentally friendly technology for soil, and groundwater clean-up”. Reeves et al. (2018)

suggested that hyperaccumulator plants can be assisted with application of conventional fertilizers to enhance their removal of high amounts of toxic elements from the soil. Additionally, high biomass production capacity and high concentration of the desired element that can be extracted by the plants are two critical factors to be considered when selecting species for phytoremediation (Reeves et al. 2018). Other factors to consider in selecting suitable species for mine land remediation are provided in previous studies (e.g., Antoniadis et al. 2021; Mensah 2015, 2021). It is thus recommended that hyperaccumulation plants are those plant species that are capable of accumulating 1000 mg As/kg in the dry matter of the plant tissue (e.g., Baker et al. 2000; Mahar et al. 2016). Recently, Mensah et al. (2021) observed that *Chromolaena odorata*, an indigenous plant growing closer to a derelict mining tailing in Ghana could offer potential for cleaning As from mining sites (Fig. 4.9). In that study, *Chromolaena odorata* had an As translocation factor of 4.7, further implying its ability to accumulate As from the mining soils. Translocation factor, bioconcentration factor and bioaccumulation factors are other indices used to appraise the phytoremediation potential of plant species.

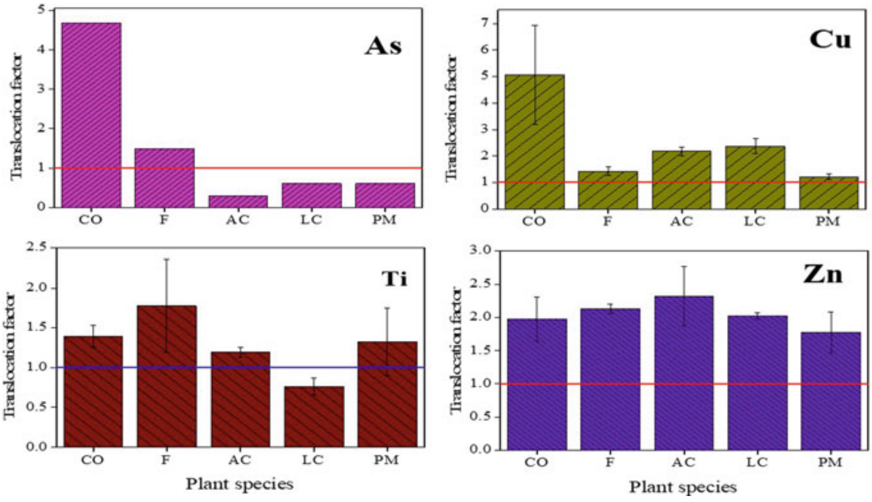

**Fig. 4.9** Root-to-shoot translocation factor (TF) of toxic elements (As, Cu, Ti, and Zn) into shoots by the five native plant species near the abandoned mine spoil. Added line indicates the threshold above which a plant is considered a phytoremediator. CO = *Chromolaena odorata*, F = fern, AC = *Alchornea cordifolia*, LC = *Lantana camara*, PM = *Pueraria montana*. *Source* Mensah et al. (2021)

## 4.2 Conclusions and Prospects for Future Research

We discussed the contamination and mobilisation of As and its associated environmental and human health risks in mining regions with a focus on mining areas in southwest Ghana and explored remediation options for contaminated mine spoils. Both active and abandoned mine sites reported significant concentrations with total As levels exceeding 8000 mg/kg in some instances. Arsenic was associated with the amorphous Fe oxide and the residual/sulphide components, suggesting that solubility of As in the contaminated sites is controlled by contents of amorphous iron oxides, sulphides, and As-bearing minerals. The dominant As species in the mining sites were mainly arsenopyrite (primary mineral) and scorodite (secondary mineral). Weathering, improper handling, and poor or lack of reclamation of arsenopyrite- and scorodite-containing ores could exacerbate ecosystem pollution with As. The high As contents and high presence of the dominant species demonstrate the ability to increase ecotoxicological implications on biota. The environmental and human health risks may increase under changing conditions of pH, redox potential, dissolved organic matter, sulphur, aluminium/iron/manganese and soluble anions such as chlorides, carbonates, phosphates, sulphates, and nitrates. For instance, chlorides and soluble anions (e.g., P) increase negative charges, reduce positive charges, and displace As from soil colloid and facilitate As availability. Remediation of degraded sites could reduce migration of As into watercourses, offer protection against pollution, improve soil quality, and mitigate human health concerns.

Phytoremediation using local plants can be considered to stabilise and/or clean As from mining spoils and polluted sites. Remediation efforts can make use of C, P-rich and alkaline materials to boost the As phytoremediation effectiveness of the plants. Also, Fe-rich materials can be employed to decrease the bioavailability of As, reduce losses and migration into surface and groundwater sources, and minimise potential environmental and human health risks. Such remediation efforts should take into consideration wet and dry conditions prevailing at the contaminated sites, limit anaerobic conditions and encourage aerobic conditions. This cautious plan will reduce the pH, raise the redox potential, and restrict As mobilisation from the mine spoil. Revegetation of mine sites could improve soil organic matter content, structure, and moisture, reduce surface runoff, and encourage soil microbial activities; thus, creating oxidising conditions and limiting As mobilisation and associated health risks.

This study offers opportunities for interesting research, and future works could consider the following:

i. Investigating the roles of biogeochemical parameters such as content of organic matter, Fe, Si and S in the mobilisation of As in mining sites.
ii. Investigating the mobilisation and dominant species of As in subsoils and exploring various remediation options and how they impact As mobilisation under different redox environments.

iii. Conducting a large-scale field remediation experiment involving the use of organic and inorganic materials to help better appraise the long-term applicability of such treatments on As mobilization.
iv. Employing synchrotron radiation X-ray spectroscopy to investigate the dominant species of As in abandoned mining spoils.
v. Gathering more evidence on the extent of As pollution in mining regions of Ghana.

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# Chapter 5
# Arsenic Contamination in Karst Regions

**Yafei Sun, Nabeel Khan Niazi, and Jianxu Wang**

**Abstract** Karst region is prone to being contaminated with arsenic (As) because alkaline pH favors As mobilization, and sinking streams and sinkholes provide a rapid route for contaminants from the land surface to the underlying aquifer. Here we presented a review on As contamination in soils, surface water, underground water, and plants in karst regions, as well as As speciation transformation process in the environment. We aimed to provide state-of-the-art knowledge on As distribution and contamination and the major biogeochemical process controlling As mobilization in karst regions. Results may be helpful for deepening the understanding of biogeochemical cycle of As, and enhancing the ability to manage As risks in karst regions in the world.

**Keywords** Karst region · Arsenic contamination · Biogeochemical transformation

## 5.1 Introduction

Arsenic (As) is a metalloid element that is widely distributed in the environment and its contamination is a major environmental concern in the world due to its carcinogenic effects on living organisms at excessive concentrations (Panagiotaras and Nikolopoulos 2015). Arsenic can enter the environments through natural geologic

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processes (i.e. weathering of rocks and sediments hydrothermal/geothermal activities), and anthropogenic activities (the use of insecticides, herbicides and phosphate fertilizers, semi-conductor industries, mining and smelting, industrial processes, coal combustion) (Singh et al. 2015). About 40% of global arsenic resources distributed in the southwestern (SE) part of China (Zhang et al. 2017). A coincidence is that SE region of China is also dominated by karst landscape.

The karst landscape takes its name from a region comprised between NE Italy and Slovenia dominated by outcrops of carbonate rocks. Karst environments are characterized by distinctive landforms related to dissolution of carbonates and evaporites and a dominant subsurface drainage (Gutierrez et al. 2014). As shown in Fig. 5.1, surface and subsurface rock dissolution largely overrules mechanical erosion, leading to a distinctive morphology and hydrology (Gutierrez et al. 2014). Karst distributes predominantly in southwestern part of China, southeastern Asia, the Mediterranean and north America (Wang et al. 2019) (Fig. 5.2), covering about 15% of the Earth's land surface area (22 million $km^2$). Among them, China has the largest karst area ($3.44 \times 10^6$ $km^2$), spanning in Guizhou, Guangxi, Yunnan, Chongqing, Sichuan, Hunan, Hubei, and Guangdong provinces (Fig. 5.2). Karst aquifers provide 25% of the world's drinking water (Ghasemizadeh et al. 2012).

Karst aquifer systems are extremely vulnerable, because rocky desertification, soil erosion and degeneration led to poor development of soil layer, and consequently resulting in limited filtration of pollutants for underground water (Zhang et al. 2014; Kacaroglu 1999). In addition, pollutants could easily enter the underground water through sinkholes, silos, and fissures. Therefore, karst aquifers were more vulnerable to being polluted than other aquifer types (i.e. porous media and fractured rock) (Kalhor et al. 2019). Many reviews on the geochemical behaviors of arsenic in non-karst areas had been reported (Panagiotaras and Nikolopoulos 2015; Hussain, et al. 2021). However, rare literatures have reported arsenic contamination in karstic regions (Zhang et al. 2017).

This chapter summarizes arsenic contamination in soils, plants, surface water, and underground water, and discusses its environmental fate of As in karst regions. We aim to provide essential knowledge for researchers to develop better strategies to manage the risks of As in karstic regions.

## 5.2 Arsenic Contamination in Karst Regions

### *5.2.1 Arsenic Contamination in Soils*

In karst regions, the background As level of carbonate rocks is high because high geological background, and the dissolution of carbonate by weathering results in the enrichment of As in soil (Zhang et al. 2021a). A close association of spatial distribution of As contamination in soil and carbonate rocks was observed. Wu et al. (2020) reported that the content of As in the carbonate bedrock in the upper stream of the

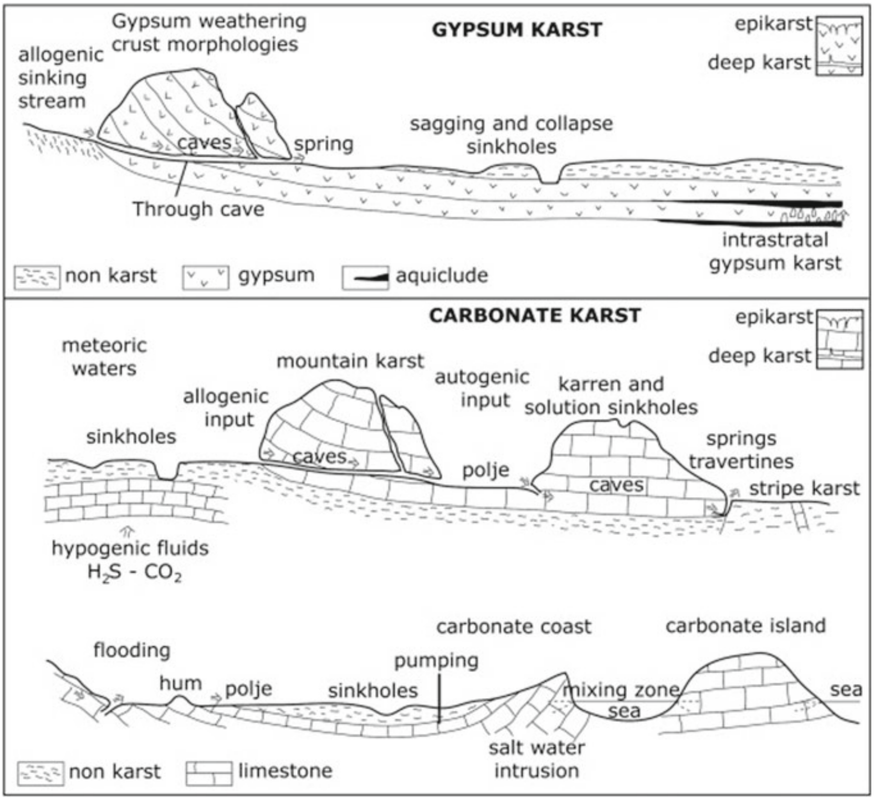

**Fig. 5.1** Simplified sketch of karst in gypsum and carbonate setting (Gutierrez et al. 2014)

Pearl River Basin was about 2–3 times higher than that of the upper continental crust (UCC). Wang et al. (2019) investigated As concentrations in soil profiles from a forest at a typical karst region in Guizhou province. Results showed that As concentrations were 27.74 mg/kg in surface soil, which was higher than the background value of As in soils in Guizhou province (20 mg/kg). Tang and Han (2017) investigated the contamination of As in soils under different land use in Puding county in Guizhou province in China. The concentrations of As ranged from 21.2 to 36.0 mg/kg, which was higher than the background values of As in soils in Guizhou province. Further, the mean concentration of As in soil samples in virgin forested site was higher than that in secondary forest, shrubbery, grassland, and farmland. Lixisol, a typical soil in Guizhou province, is characterized as high content of calcium and magnesium carbonate. He et al. (2020) reported that the content of As in Lixisol soil was up to 45.4 mg/kg, which was higher than the background value. Sun et al. (2020) studied As contamination in soils from different land use types in a karst plateau lakeshore wetland in Guizhou province. The results showed that the average concentration of As in the surface soil of farmland, grassland and wood land were 29.9, 32.57, and

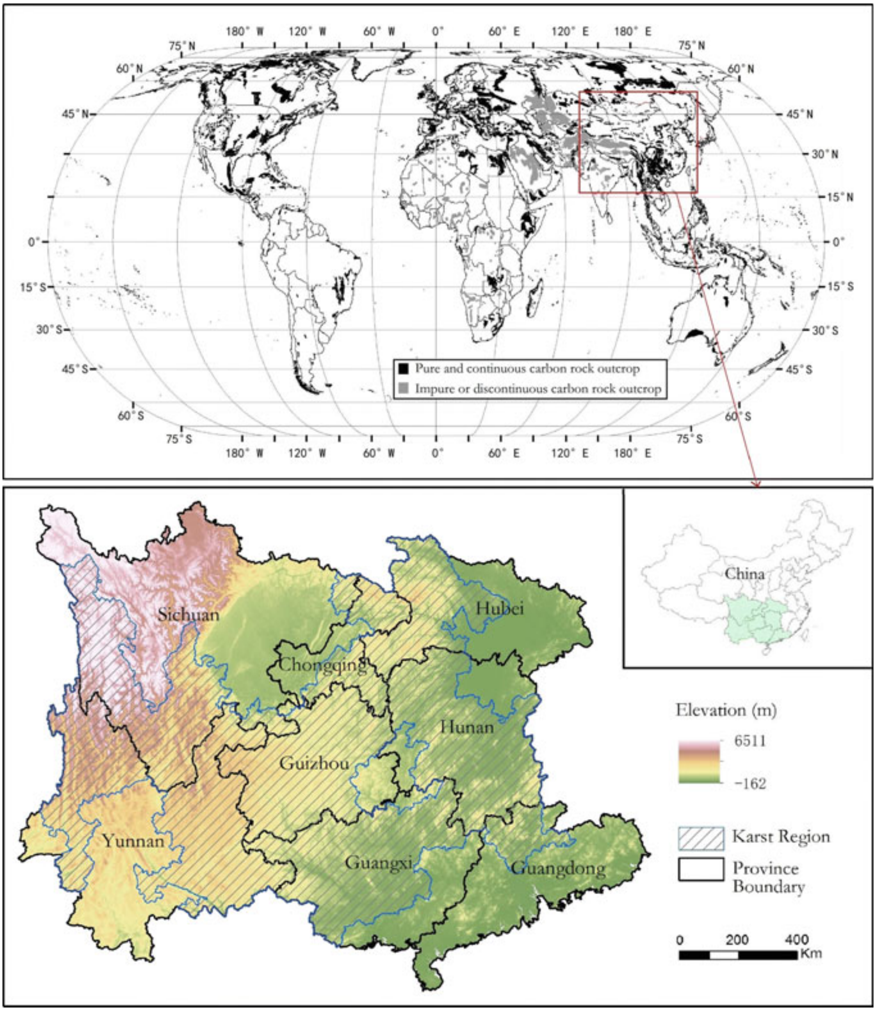

**Fig. 5.2** The spatial distribution of karst regions in the world and China (Wang et al. 2019)

36.92 mg/kg, respectively. These values were higher than the background values of As in soil in Guizhou province. In the karst region in Guangxi province in China, the concentration of As in paddy soil was recorded as 50 mg/kg (Zhang et al. 2021b), which was higher than the background values of As (20.5 mg/kg) in soils in Guangxi province. Also, Jia et al. (2020) reported that soils derived from carbonate rock had As concentrations over other soils. A number of studies have reported the elevated As concentrations in the soils and sediments collected from karst region in Guangxi province in China (Zhang et al. 2021a; Xiao et al. 2019; Yang et al. 2021; Wang et al. 2010).

The intensive anthropogenic activities further polluted soils at karst regions. Due to the widespread of sulfide deposit in SW, China, acid mine drainage (AMD) containing As was produced. The leaching of AMD resulted in the pollution of soil (Chen et al. 2022). Zhang et al. (2013) surveyed the pollution of As in paddy fields affected by AMD in the Xingyi region, southwest China. The results showed that average arsenic content in the surface soil ranged from 82.88 to 121.03 mg/kg, which was significantly higher than the average value of 47.36 mg/kg of control soil collected from nearby sites. He et al. (2021) investigated the distribution of As in soils around an antimony smelter at Qinglong county, Guizhou Province. The total concentrations of As in soils ranged from 23 to 539 mg/kg, which was higher than the corresponding control soils. Zhang et al. (2022) studied As pollution in sediment in Lengshuigou reservoir in Guizhou province affected by Sb mining activities. The concentration of As in sediments ranged from 65.15 to 98.27 mg/kg. The concentrations of As in soils from karst regions in China are summarized in Table 5.1.

Alexakis et al. (2021) studied the spatial distribution of As in soils from the Ioannina karstic basin in Epirus in the Northwestern part of Greece. The median As content of topsoil in the agricultural, urban, and wetland area was 16.0, 18.7 and 28 mg/kg, respectively, which was higher than that of the corresponding background values given by Salminen et al. (2005). Du Preez et al. (2016) evaluated As contamination in sediment in the Cave of the Witwatersrand Basin, South Africa. Results showed the concentration of As in sediments ranged from 3.77 to 41.00 mg/kg. Intamo et al. (2015) investigated the As concentrations in soils affected by Pb–Zn mining activities from a karst region in the Western part of Thailand. The concentration of As in soils ranged from 17 to 71 mg/kg, which was higher than the soil quality standards (3.7 mg/kg) for habitat and agriculture in Thailand.

### 5.2.2 *Arsenic Contamination in Surface and Underground Water*

According to WHO (the World Health Organization) guidelines, the maximum allowable As concentration in drinking water and underground water was 10 μg/L. A number of water samples in karst regions were contaminated with As. Concentrations of As in the Lihu subterranean stream water collected from the northwestern Guangxi province ranged from 12.5 to 126.2 μg/L, with the average value of 37.0 ± 31.8 μg/L (Zhang et al. 2014). Fang et al. (2021) investigated the spatial and temporal variations of As of the karst aquifer in the northern part of the Xikuangshan mine, Hunan province, China. Concentration of As in groundwater had a wide range, from 0.5 μg/L to 3 mg/L. Furthermore, As concentrations had a significant seasonal effect with higher As concentration in water presented in winter and lower As concentration in water in summer. Qin et al. (2019) studied the concentrations of As in surface and underground water samples collected from the Guilin-Yangshuo Basin

**Table 5.1** The concentrations of arsenic in soils from karst regions in China

| Region | Soil As concentration (mg/kg) | References |
|---|---|---|
| Libo County, Guizhou province | 27.74 | Wang et al. (2019) |
| Puding, Guizhou province | 21.2–36.0 | Tang and Han (2017) |
| Guizhou province | Lixisol: 45.4 | He et al. (2020) |
| Suohuangcang National Wetland Park, Guizhou province | 29.9–36.92 | Sun et al. (2020) |
| Hengxian County, Guangxi province | 47.8–50.0 | Zhang et al. (2021b), Jia et al. (2020) |
| The Diaojiang River, Guangxi province | 2–206 | Zhang et al. (2021a) |
| Guangxi province | Paddy soils: 26.3 | Yang et al. (2021) |
| Huixian wetland, Guangxi province | 21.45 | Xiao et al. (2019) |
| Yangzonghai Lake, Yunnan province | 32.87–62.99 | Wang et al. (2010) |
| Xingyi region, Guizhou province | 82.88–121.03 | Zhang et al. (2013) |
| Qinglong, Guizhou province | 23–539 | He et al. (2021) |
| Coal mine, Guizhou province | 31.9–105.1 | Chen et al. (2022) |
| Lengshuigou reservoir, Guizhou province | 65.15–98.27 | Zhang et al. (2022) |
| The Pearl River Basin | up to 991 | Wu et al. (2020) |
| Guilin, Guangxi province | 61.88 | Kong et al. (2018) |
| Guizhou province[5.1] | 20 | |
| Guangxi province[5.1] | 20.5 | |

[5.1] Background values of As in soil in Guizhou and Guangxi province

in the southwestern part of China, and these samples were affected by Pb–Zn mine activities. About 91% of downstream surface water samples and 67% of groundwater samples collected during the dry season exceeded the maximum allowable As concentration (10 μg/L) in the drinking water set by the Chinese government. Sun et al. (2013) studied As pollution in epikarst water affected by AMD at a coalfield basin, Xingren, Guizhou province. Concentration of As in the epikarst water was in the range of 2.90 to 2680 μg/L in the dry season and from 2.33 to 1666 μg/L in the wet season. Li et al. (2018a) investigated As concentrations in water samples from mining-impacted karstic environments in Nandan, Guangxi province. All studied water samples, including adit waters, flotation drainage, leaching waters, and river waters, and contained high concentrations of As, reaching up to 1877 μg/L. The

**Table 5.2** The concentrations of arsenic in surface and underground water in karst regions

| Region | As concentration (µg/L) | References |
|---|---|---|
| Lihu subterranean stream, Guangxi province | Underground water: 12.5–126.2 | Zhang et al. (2014) |
| Xikuangshan mine, Hunan province | Underground water: 0.5–3000 | Fang et al. (2021) |
| Xingren, Guizhou province | Surface water: 2.33–2680 | Sun et al. (2013) |
| Yangzonghai Lake, Yunnan province | Lake water: 147.3–176.9 | Wang et al. (2010) |
| Nandan, Guangxi province | Surface water: up to 1877 | Li et al. (2018a) |

concentration of As in surface and underground water in karst regions is summarized in Table 5.2.

### 5.2.3 *Arsenic Contamination in Plants*

In rice samples collected from a typical karst basin affected by AMD in the Xingyi county, southwest China, the concentration of As in the root was 20.58 mg/kg, straw was 3.76 mg/kg, and grain was 0.83 mg/kg (Zhang et al. 2013). In this case study, the As concentration in the grain was higher than the values reported by other studies (Zhu et al. 2008), and exceeded the maximum allowable As concentration (0.15 mg/kg) in the rice grain defined by the Chinese government. Also, in rice samples collected from karst region in Guangxi province, the concentration of As in rice grain was 0.21 mg/kg (Zhang et al. 2021a). Tang et al. (2021) investigated the contents of As in rice grains and sugarcanes in Liujiang karst regions, Guangxi province, and found that the average content of As in rice grain and sugarcane was 0.11 mg/kg and 0.006 mg/kg, respectively. Rice grains exhibited greater capacity to accumulate As than sugarcanes.

## 5.3 Environmental Fate of Arsenic in Karst Regions

### 5.3.1 *Arsenic Mobilization in the Environment*

Arsenic can be released by natural processes (weathering of carbonate rocks, and biological activities), and anthropogenic activities. During the weathering and pedogenesis of carbonate rocks in karst regions, trace elements were absorbed by clay minerals or iron (Fe) and manganese (Mn) oxides or entrapment into the crystal lattices of these oxides (He et al. 2021; Zhan et al. 2021; Wen et al. 2020) (Fig. 5.3). Arsenic mobility is poor in karst soils. Anthropogenic activities can affect As mobilization in the environment. For example, the incorporation of rice straw into

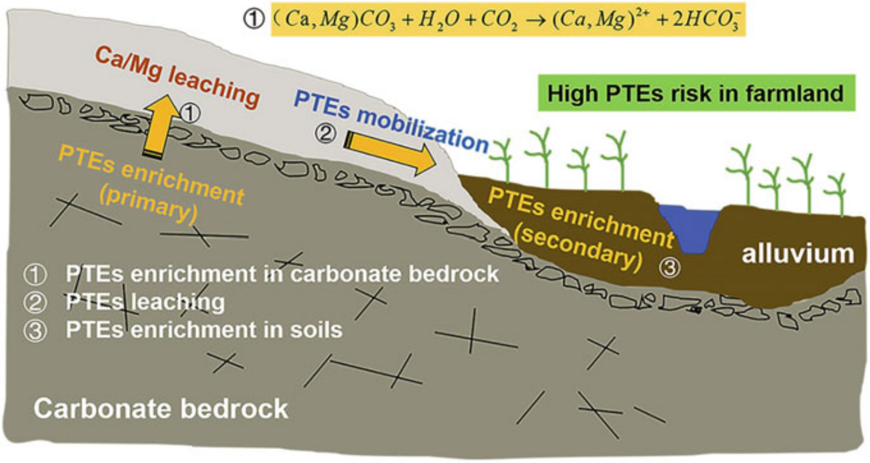

**Fig. 5.3** The processes of enrichment of potentially toxic elements in karst soils (Zhan et al. 2021)

As contaminated paddy fields significantly enhanced As mobilization in rhizosphere through enhancing microbial-mediated reduction of iron minerals and As(V) reduction to As(III) (Yang et al. 2018).

## *5.3.2 Factors Controlling Arsenic Speciation and Mobilization in Karst Regions*

### 5.3.2.1 The Effect of pH and Redox Potential

Redox potential ($E_h$) and pH are important factors affecting arsenic speciation and mobilization in the environment (Fig. 5.4). The underground rivers, fractures, conduits, caves, karst windows and swallow holes are sufficiently developed in karst regions. This causes a close association of subterranean stream with the atmosphere, precipitation and surface water. Zhang et al. (2014) reported that the redox environment in karst aquifers were different from either the strong reducing environment in closed basin groundwater ($E_h$ is −153 to +98 mV, with an average of −33 mV) (Yang et al. 2008), or the oxidation environment of surface water ($E_h$ is +200 to +400 mV) (Mandal and Suzuki 2002). Karst groundwater has characterized as weak reducing, with $E_h$ value ranging from −120 to +168 mV. The reduced form of As(III) in the underground water of karst region (51%) was lower than non-karst region in Hetao plain in China (79%), which might be due to stronger reducing condition of underground water in non-karst region than karst region. Further, pH of water is alkaline in karst regions (Zhang et al. 2014; Sun et al. 2013), which might be favorable for the mobilization of As (Ren et al. 2021).

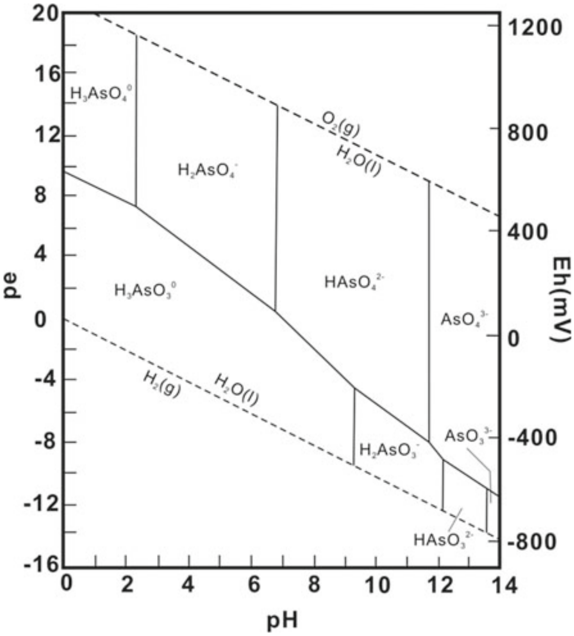

**Fig. 5.4** pH-pe-Eh diagram of arsenic species in water at 25°C (Zhang et al. 2017)

#### 5.3.2.2 The Role of Fe (Oxy) Hydroxides and Calcium Carbonate

Iron (Fe) oxides were the dominant adsorbents for As(V) in soils in the karst region. Iron oxides in soil can be classified as amorphous Fe oxides, crystalline Fe oxides and residual Fe by sequential extraction procedure (Wenzel et al. 2001). Arsenic can be operationally defined as nonspecifically sorbed fraction (F1), specifically sorbed fraction (F2), the fraction associated with amorphous and poorly crystalline oxides (F3), the fraction associated with well-crystallized oxides (F4), and the residual fraction (F5), respectively. Zhang et al. (2021b) reported that amorphous Fe oxides associated As accounted for 82% of total As in a paddy soil. The $CaCO_3$ can significantly affect the behavior of heavy metals in soils. According to a previous study (Hashimoto et al. 2009), heavy metals formed hydrated hydroxides and were closely associated with carbonates in alkaline and $CaCO_3$-enriched soils. The buffer capacity of calcareous soil was higher than that of non-calcareous soils (Liu and Shang 2001). In addition, $CaCO_3$ is an important component of soil micro-aggregates. It can bind with soil organic matter to increase the surface area and negative charge of soil (Kuzel et al. 2010). He et al. (2020) evaluated the ability of $CaCO_3$ and clay to adsorb heavy metals in topsoil sample collected from Guizhou province. The results showed that the mobility of As decreased with increasing of $CaCO_3$ content in soil samples, because Ca formed stale insoluble precipitation with As. This fact had been demonstrated by Zhong et al. (2015), that the exchangeable As content in soils decreased significantly by the addition of $CaCO_3$.

A recent study showed that the elevated carbonate could facilitate the enrichment of chemolithoautotrophs in karstic soils (Li et al. 2018b). Fe(II)-oxidizing bacteria could mediate the formation of iron minerals (mainly poorly crystalline Fe(III) (oxyhydr)oxides), which could immobilize As(Sowers et al. 2017). Tong et al. (Tong et al. 2021) cultivated microaerophilic Fe(II)-oxidizing bacteria from karstic paddy soils containing abundant iron oxides, and investigated their capacities for Fe(II) oxidation, and As sequestration. The results showed that Fe content in Fe(III) (oxyhydr)oxides layer increased, and concomitantly, the dissolved As concentration decreased. Besides, As(III) was oxidized to As(V) by Fe(II)-oxidizing bacteria, resulting in the adsorption of more As(V) by Fe(III) (oxyhydr)oxides. Bia et al. (2021) studied the interaction of geogenic As with carbonate minerals. As(V) could be adsorbed onto calcite and Fe(oxyhydr)oxides, and the low concentration of Fe(oxyhydr)oxides was favorable for the reaction between arsenate and calcite (Bardelli et al. 2011; Costagliola et al. 2013; Winkel et al. 2013). Alexandratos et al. (2007) found that arsenate was retained at the calcium carbonate mineral surface by adsorption in the presence of low arsenate concentration (10–100 $\mu$M) in solutions, while arsenate was incorporated within the calcite lattice in the presence of high arsenate concentration (e.g., 200 $\mu$M).

#### 5.3.2.3 The Interactions of As with Organic Matter

Zhong et al. (2018) studied the distribution of As and organic matter in soil profiles collected from a typical karst mining area in Guangxi province, and found a similar geochemical association between As content and organic matter, indicating that organic matter played an important role in affecting the mobilization of As. In soils and sediments, organic matter bound with iron oxide minerals to form Fe-OM aggregates (Lalonde et al. 2012), which could affect the mobilization of As. Calcium could strongly affect the structure of Fe-OM aggregates, and the extent of this effect depended on Ca concentration (Beauvois et al. 2020). In the presence of high concentration of Ca (i.e. Ca/OC $\geq$ 0.026), the coating of the Fe phases by OM decreased and thus the availability of Fe binding sites for As increased (Beauvois et al. 2021).

#### 5.3.2.4 Concentration of Co-existing Ions

The cations and anions like $Ca^{2+}$, $Mg^{2+}$, $Fe^{3+}$, $Al^{3+}$, $Mn^{2+}$ and $HCO_3^-$, can inhibit or facilitate the adsorption of As. Zhang et al. (2014) studied the contamination of As of underground rivers in Lihu Lake in Guangxi province and found that Fe, Al, Mg had positive correlations with As in sediments. The Ca and Mg contents in soils developed from carbonate rocks were high (Chen et al. 1993). The presence of high concentration of Ca could interact with As to form complexes, which could be subsequently adsorbed onto sediment surfaces. Zhang et al. (2014) also found that Ca was closely related to arsenic in the sediment. Besides, Jian et al. (2010) found the Ca–As in the sediment from Lihu subterranean stream, and the proportion of Ca–As was higher than that of other As forms, which was different from the results observed in fluvial sediment in non-karst regions. It should be noted that the fast erosion process of carbonate rock in karst regions causes high $HCO_3^-$ concentrations in water (Zhang et al. 2014). The anions such as $SO_4^{2-}$, $HCO_3^-$, $H_2PO_4^-$ and $SiO_3^-$ could compete with As for adsorption sites (Nguyen et al. 2021). In karst regions, the alkaline environment was unfavorable for As adsorption. Meanwhile, Ca and $HCO_3^-$ could chelate with adsorption sites on the surface of ferrihydrite, leading to the desorption of As (Saalfield and Bostick 2010).

## 5.4 Human Health Risks of Arsenic in Karst Regions

Human exposure to As was through the consumption of As-contaminated drinking water and/or As-contaminated foods (Singh et al. 2015). As-contaminated rice was the major source of daily human intake of inorganic As (Tang et al. 2021). According to US Environmental Protection Agency, the tolerance value of inorganic As was 0.3 μg/kg body weight/day (equivalent to 0.018 mg/day for a 60 kg adult). The target hazard quotient (THQ) was used to evaluate the potential risk of health effects. The THQ value less than 1 indicates no appreciable effect on human health. Tang et al. (2021) evaluated the human health risk by rice consumption in Liujiang District in China. The result showed that THQ values of As for both males and females were all greater than 1 (males: 2.61; females: 3.01), suggesting that local residents suffered from As exposure risk through the long term consumption of As-contaminated rice. Zhang et al. (2013) found that consumption of rice affected the health of people in Xingren county, Guizhou province. They estimated that the daily intake of total As and inorganic As for a 60 kg adult through rice consumption were above 4.2 μg/kg body weight/day and above 0.144 mg/day, respectively. These values obviously exceeded the human tolerable intake limit. Peng et al. (2022) studied the quality of groundwater in the exposed karst region (EKR) and buried karst region (BKR) in Bama, a typical karst region in the southwestern part of China. About 4.3% of the water samples had significant health risks (hazard index (HI) >1) due to the high As and other metals concentrations in the underground water.

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# Chapter 6
# Arsenic Dynamics in Paddy Rice Ecosystems and Human Exposure

**Indika Herath, Chuxia Lin, and Jochen Bundschuh**

**Abstract** Rice is the staple diet for more than 3.5 billion people around the world. Elevation of arsenic (As) in paddy rice ecosystems has become an environmental, economic, and public concern due to its adverse consequences on global rice production, food safety, and human health. Mining exploitation, weathering of As-bearing minerals, dissolution of aquifer sediments, and As-contaminated groundwater irrigation have extensively contributed to the contamination of paddy soil by As in high levels. Speciation, mobility and sequestration of As in paddy soil–water interfaces are controlled by iron (Fe) plaque formation, redox sensitive mineral surfaces (Fe and Mn), organic matter and competing substances ($PO_4^{3-}$ and $Si(OH)_4$). During flooding season, paddy soil porewater is contaminated with high concentrations of inorganic As species, particularly by more toxic arsenite (As(III)) as result of arsenate (As(V)) reduction under anaerobic conditions. Microorganisms play a crucial role in As speciation dynamics promoting redox transformation, methylation and volatilization processes. Various metabolic pathways, including As(V) reduction, As(III) efflux, and As(III)-thiol complexation govern As uptake, translocation, and loading into rice grains. The translocation of As from rice root to shoot leads to the accumulation of toxic As species in grains affecting rice quality and yield. The worst scenario of grain As is associated with the human exposure to high amounts of As via consumption of As-contaminated rice and related food products. Hence, this chapter provides an overview of (i) As speciation and transformation dynamics, (ii) As uptake mechanisms from root to shoot, (iii) As metabolic pathways over

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root, shoot and grain loading, and (iv) recommendations for future research. Such a widespread understanding of As dynamics in paddy rice ecosystems is crucial to develop sustainable As mitigation strategies and alleviate adverse impacts on global food safety and human health.

**Keywords** Arsenic speciation · Rice rhizosphere · Iron plaque · Methylation · Genotypes · Human health

## 6.1 Introduction

Rice (*Oryza sativa* L.) is the stable food for over 3.5 billion people around the world, predominantly Southeast Asians with an average daily intake of 500–600 g (Jia et al. 2015a, b; Herath et al. 2020b). Nearly 115 countries worldwide produce paddy rice for the global market, among which South Asian countries are the leading rice growers (Kumarathilaka et al. 2018a, b). Both geogenic and anthropogenic activities lead to the contamination of paddy soil–water systems by arsenic (As) at elevated levels. Weathering of As-bearing minerals and dissolution of alluvial deposits are the most common naturally occurring sources, whereas anthropogenic activities include mining exploitation, industrial discharges, and use of fertilizers and pesticides. Irrigation practices based on groundwater that is contaminated with As derived from geogenic sources, have become a significant threat for the rice production in major rice growing countries, such as Bangladesh, India, China and Vietnam (Dittmar et al. 2007; Kumarathilaka et al. 2018a, b). The mobility and bioavailability of As species, particularly more toxic arsenite (As(III)) become elevated during the flooded stage, and rice plants can readily take up, translocate and accumulate such toxic As species in rice grain (Liu et al. 2022a, b). The mobilization of As from solid to liquid phase across the paddy soil–water interface is of particular concern in terms of rice production, grain quality and human health risks. Therefore, extensive understanding of As dynamics in speciation, mobility, translocation and accumulation in paddy rice ecosystems is crucial in order to mitigate its adverse impacts on global food safety and human health.

Speciation, mobility, and transformation of As in paddy soil–water interfaces are governed by physiochemical and biological factors, including pH, redox potential (Eh), organic matter, redox sensitive elements (Mn, Fe, S, etc.) and microorganisms in the rice rhizosphere (Kumarathilaka et al. 2018a, b; Mishra et al. 2021a, b). Arsenic mobility in paddy soil is closely related with redox sensitive oxides of iron (Fe) and manganese (Mn). Under flooded conditions, As tends to release upon paddy soil porewater from adjacent As-bound solid phases through reductive dissolution of Fe oxides which is promoted by dissimilatory Fe reducing bacteria (Halim et al. 2015; Xie et al. 2015). Inorganic As(III) becomes prevalent in paddy porewater as it possesses much weaker adsorption capacities compared to arsenate (As(V)) on soil mineral surfaces which makes As(III) to be more mobile in the rice rhizosphere (Zheng et al. 2013; Wang et al. 2014; Yuan et al. 2021). The sequestration of As species through the rice rhizosphere is controlled by the formation of Fe plaque and microbes mediated biotransformation processes. Meantime, active and passive transport mechanisms involve in the uptake and translocation of As species in rice plants. The translocation of As from rice root to shoot leads to the accumulation of As species in rice grains affecting grain quality and production. The localization and accumulation of As species over plant tissues are governed by various metabolic pathways, including As(V) reduction, As(III) efflux and As(III)-thiol complexation (Geng et al. 2017; Limmer et al. 2022). Thus, it is clear that the loading of As species into rice grain is associated with environmental, biogeochemical, agronomic and plant genetic factors during rice cultivation.

The worst scenario of As accumulation in grains is directly associated with the human exposure to high levels of As through the consumption of As-contaminated rice and related food products, such as cereals, cakes, noodles and biscuits. For example, the lifetime cancer risk in West Bengal, India is reported to be $7.62 \times 10^{-4}$ which exceeds the threshold value of ($10^{-4}$–$10^{-6}$) recommended by the United States Environmental Protection Agency (USEPA) (Mondal et al. 2008). It is predicted that the total amount of As in rice grain produced in Bangladesh may upsurge from 0.15 to a range of 0.25–0.58 mg $kg^{-1}$ by 2050 because of current irrigation practices with As-contaminated groundwater (Dittmar et al. 2010). The export of rice from such As-vulnerable countries to safe regions around the world has become an overwhelming threat on the global food safety and human health. Environmental, economic and public concerns associated with As contaminated paddy ecosystems are therefore relatively significant compared to dryland agriculture practices. Hence, this chapter presents a holistic overview of (i) As speciation and mobility dynamics in the rice rhizosphere, (ii) mechanisms of As uptake from root to shoot, (iii) metabolism of As in rice plants, and (iv) recommendations for future research. Figure 6.1 illustrates the basic outline of the contents in this chapter. Such a widespread understanding of As dynamics in different compartments of paddy rice ecosystems, including soil, water, rice plants and grains is of paramount importance to develop sustainable As mitigation approaches in the global rice agronomy.

## 6.2 Arsenic as a Global Dilemma in Rice Cultivation

Figure 6.1 depicts the big picture of As problem in global paddy rice agronomy. Both anthropogenic and geogenic activities contribute to the release of toxic As species into paddy soil and water systems. Main sources of As contamination in paddy soil include natural geogenic sources, irrigation by As-contaminated groundwater, industrial wastewater discharges and mining activities. Table 6.1 summarizes major sources of As pollution in paddy ecosystems along with total As levels in paddy soil based on recently published research articles. The use of As-contaminated groundwater for irrigation has become a significant threat in the global rice production over the present decade. Rice grown in major rice cultivation countries such as Bangladesh, India, China and Vietnam, contains high concentrations of As because of elevated

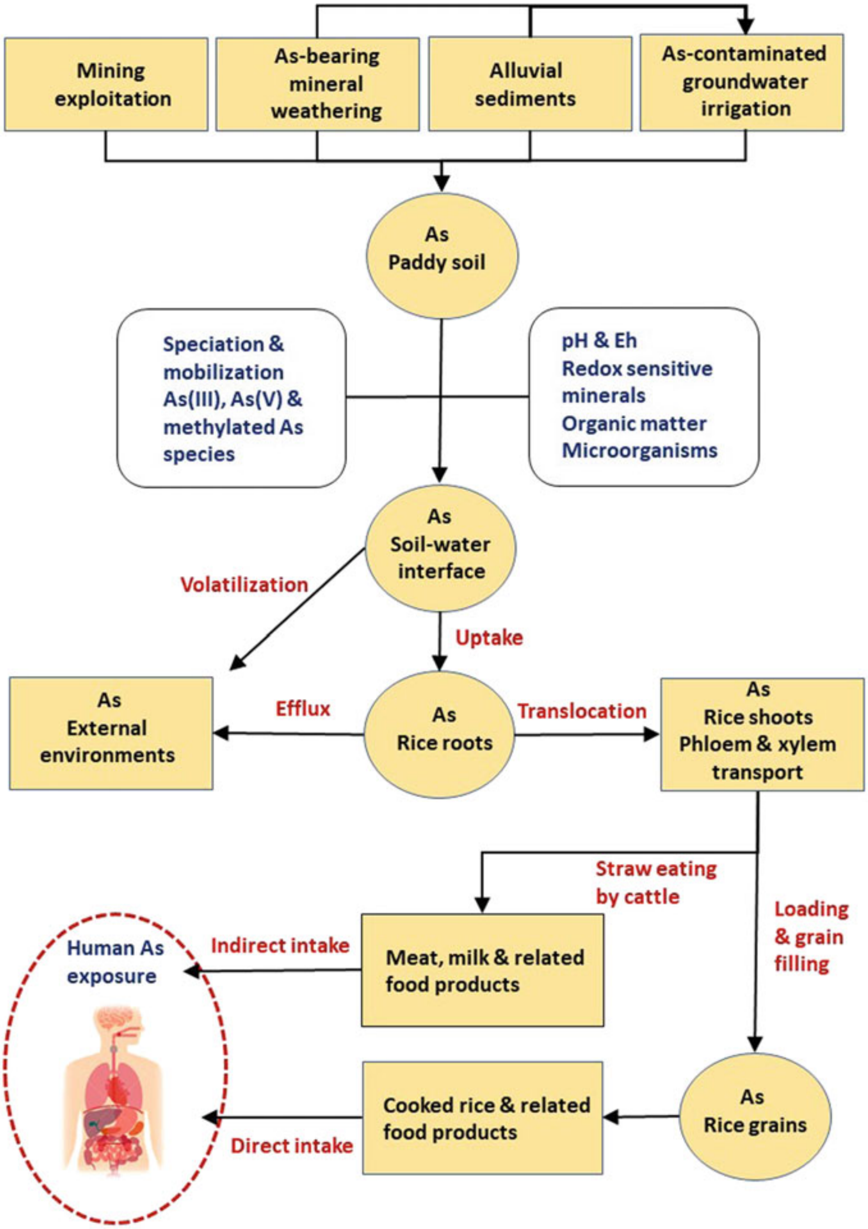

**Fig. 6.1** Outline of the chapter showing main contents associated with subtopics

**Table 6.1** Major sources of As contamination and the extent of As levels in paddy soil in various rice growing regions around the world

| Country/region | Source of As contamination | Concentration of As in paddy soil (mg kg$^{-1}$) | References |
|---|---|---|---|
| China | Mine tailings<br>Exploiting of tungsten ore<br>Mining activities<br>Mining activities<br>Mining activities<br>Geologic mineralization<br>Industrial wastewater | 141.3<br>46.6<br>141.3<br>36.0<br>140.4<br>89.0<br>34.0 | Yang et al. (2022a; b)<br>Zhang et al. (2022)<br>Yang et al. (2022a; b)<br>Yan et al. (2022)<br>Chen et al. (2022a; b)<br>Liu et al. (2022a; b)<br>Li et al. (2019) |
| Bangladesh | Groundwater irrigation<br>Mining activities | 99.0<br>4.5–68.0<br>224.0<br>56<br>14.8–41.9 | Rahman et al. (2022)<br>Rahman et al. (2010)<br>Hossain et al. (2008)<br>Panaullah et al. (2009)<br>Halim et al. (2015) |
| India | Groundwater irrigation<br>Geogenic origin | 51.5<br>4.6–9.7<br>2.4–14.1<br>13.9–24.1 | Shrivastava et al. (2017)<br>Bhattacharya et al. (2010a; b)<br>Biswas et al. (2014)<br>Chandrashekhar et al. (2016) |
| Vietnam | Groundwater irrigation<br>Surface water | 6–20<br>9.5–11.0 | Huang et al. (2016) |
| Taiwan | Groundwater irrigation | 11.8–112.0 | Hsu et al. (2012) |
| Nepal | Groundwater irrigation | 5.6–12.5 | Dahal et al. (2008) |
| USA | Geogenic origin | 4–7 | Williams et al. (2007) |

geogenic As contamination through ground- and surface-water that are used for irrigation. The concentration of total As in irrigation water should be under 100 $\mu$g L$^{-1}$ as recommended by the Food and Agricultural Organization (FAO). The risk assessment value of As in paddy soil is 30 mg kg$^{-1}$ (5.5–6.5 pH) based on guidelines of the Soil Environmental Quality Risk Control Standard for Soil Contamination of Agricultural Land (Li et al. 2019).

Rock weathering and alluvial deposits are considered as main geogenic sources of As in paddy soil. In countries including India, the weathering of As-bearing minerals such as bearsite ($Be_2(AsO_4)(OH)0.8H_2O$), wallisite ($(Cu,Ag)TlPbAs_2S_5$), and claudetite ($As_2O_3$) leads to the releasee As into paddy soil to a significant extent (Yuan et al. 2021). Therefore, primary and secondary As-bearing minerals contribute mostly to the pollution of adjacent paddy fields at elevated As levels. The mobilization of As from point sources to floodplain paddy fields occurs through alluvial deposition of sediments (Hundal et al. 2013). Moreover, paddy soil tends to be readily polluted by As when mining activities are active in close proximity to paddy fields (Table 6.1). China is the largest rice producer in the world to date, and As-contaminated paddy fields can be extensively found in China due to mining activities. Tailings and waste rocks, acid mine drainage and wet and dry deposition of dust from high rainfall and strong winds are responsible for As accumulation in paddy fields in the vicinity of mining areas (Yun et al. 2016). Therefore, As levels in paddy soil–water systems located along floodplains and near As-bearing mineral deposits are required to monitor regularly for controlling As distribution and accumulation in rice plants.

Rice cultivation in dry periods is largely dependent on irrigation water supplies. Ground- and surface-water are extensively used for irrigation in many rice growing regions in the world. Total As concentration in groundwater systems of some rice growing countries such as Bangladesh, India, Vietnam and Nepal is generally high due to As-bearing aquifer sediments (Herath et al. 2016). The flow velocity shows a close relationship with the elevation of As levels in irrigation water along the irrigation channel. At a slower flow velocity, aggregation and subsequent settling of As-bearing colloids occur due to the long residence time which promotes natural adsorption processes on adjacent soil mineral phases. Therefore, slower flow velocity results in a gradual decrease in total As concentrations along the irrigation channel (Roberts et al. 2007a, b). When the flow velocity is fast, the short residence time of water floor restricts the aggregation and subsequent settling down of As-bearing colloids along the irrigation channels. As a result, total As concentrations in irrigation water over the irrigation channel remains unchanged at higher operating flow velocities (Dittmar et al. 2007; Roberts et al. 2007a, b).

## 6.3 Arsenic Dynamics Across Paddy Soil–water Interfaces

Speciation and transformation of As in paddy soil depend on physicochemical and biological factors including, redox potential (Eh), redox sensitive minerals of iron (Fe), manganese (Mn), sulfur (S), and organic matter. In addition, naturally occurring competing substances such as phosphate ($PO_4^{3-}$) and silicic acid ($Si(OH)_4$) affect the mobility and phytoavailability of arsenic species in the rice rhizosphere.

### *6.3.1 Effects of Soil pH and Eh*

Soil pH and Eh play a vital role in arsenic speciation, mobility and transport across paddy soil–water-plant ecosystems (Herath et al. 2020a, b). Mobility of As in paddy ecosystems is mainly associated with different chemical forms of As, particularly As(V) and As(III) species depending on pH and redox potential. Generally, pH of paddy soil porewater acquires between 6 and 7.5 pH at which oxyanion of

As(III); $H_3AsO_3$ becomes the prevailing inorganic arsenic species. Flooded conditions generate reducing redox potentials ranging −400 to −800 mV in paddy soil, which promote more toxic As(III) species, including $H_2AsO_3^-$ (2 - 6 pH) and $HAsO_3^{2-}$ (12 pH<) to be dominant in the soil–water interface (Yuan et al. 2021). Under oxidizing conditions, As(V) exists in the form of $H_3AsO_4$ at low pH (<2 pH), and its deprotonated forms such as $H_2AsO_4^-$ and $HAsO_4^{2-}$ exist over a range of pH (2–11 pH) (Kumarathilaka et al. 2018a, b). In addition, organic As(V) species such as monomethylarsonic acid (MMA(V)) and dimethylarsinic acid (DMA(V)) are usually present at lower levels in paddy porewater (Huang et al. 2012). It has also been revealed that inorganic and methylated thioarsenate species can occur below 7 pH as a result of interactions between As and sulfur (S) under reducing conditions in paddy soil (Wang et al. 2020a, b). In the presence of As in paddy soil porewater at elevated concentrations, the accumulation of As in rice grains gets positively correlated with soil pH as reported by (Ahmed et al. 2011). Moreover, redox dependence of the formation of thioarsenate compounds in paddy soil and rice rhizosphere has been recently reported (Wang et al. 2020a, b). This study revealed that maximum thiolation of inorganic oxyarsenic species accounts for nearly 57% at a redox potential of −130 mV, whereas thiolation of mono- and dimethylated oxyarsenates is approximately 70 and 100%, respectively, below 0 mV.

### *6.3.2 Effects of Redox Sensitive Minerals*

Redox sensitive mineral phases based on Fe, Mn and S play a vital role in determining As speciation, transformation and mobility in paddy soil. Therefore, proper understanding of As mobilization and immobilization processes associated with such naturally occurring minerals is crucial to examine the fate of As in paddy ecosystems.

#### 6.3.2.1 Iron Bearing Minerals

Iron bearing minerals, such as ferrihydrite, goethite and hematite play a significant role in the speciation of arsenic and its mobility in paddy soil (Pan et al. 2014). Reductive dissolution of iron oxyhydroxides (FeOOH) is the most prominent mechanism which triggers the release of As from As-bearing minerals, including pyrite ($FeS_2$) and arsenopyrite (FeAsS)) into groundwater (Eqs. 6.1–6.3) (Xie et al. 2015; Sun et al. 2016). The reduction of Fe(III) is stimulated by dissimilatory iron reducing bacteria such as *Geobacter* sp. and organic matter that are present in soil (Lentini et al. 2012; Liu et al. 2022a, b). Such naturally occurring processes tend to dissolve As from As-bearing mineral phases into adjacent aquifer sediments and groundwater. Ultimately, when As-contaminated groundwater is used for irrigation, paddy fields get exposed to As at elevated levels as observed in some rice growing countries such as Bangladesh. Thus, geogenic processes together with human practices are directly associated with the contamination of paddy rice ecosystems with toxic As species.

$$2FeS_{2(s)} + O_{2(g)} + 2H_2O_{(l)} \rightarrow 2Fe^{2+}_{(aq)} + 4SO^{2-}_{4(aq)} + 4H^{+}_{(aq)} \tag{6.1}$$

$$4FeAsS_{(s)} + 11O_{2(g)} + 6H_2O_{(l)} \rightarrow 4Fe^{2+}_{(aq)} + 4H_3AsO_{3(aq)} + 4SO^{2-}_{4(aq)} \tag{6.2}$$

$$FeOAs(OH)_{2(s)} \rightarrow Fe^{2+}_{(aq)} + AsO^{3-}_{3(aq)} + 2H^{+}_{(aq)} \tag{6.3}$$

Moreover, Fe is responsible for the formation of root plaque which leads to the sequestration of As species from paddy soil–water interface into rice plants. Ferrihydrite, goethite, and lepidocrocite mainly contribute to the formation of Fe plaques in the rice rhizosphere. Radial oxygen loss (ROL) is the phenomenon that governs $O_2$ release into the rhizosphere through the root aerenchyma, thereby forming the Fe plaque (Eq. 6.4) (Colmer 2002). The total Fe contents in paddy soil, rice genotypes and ROL determine the amount of Fe plaque in the rhizosphere (Mei et al. 2009).

$$4Fe^{2+}_{(aq)} + 3O_{2(g)} + 6H_2O_{(l)} \rightarrow 4Fe(OH)_{3(s)} \tag{6.4}$$

The Fe plaque possesses great affinity towards As immobilizing both As(III) and As(V) in the rhizosphere, thereby decreasing their uptake and accumulation in rice shoots and grains (Herath et al. 2020a, b). Therefore, the formation of Fe plaque is an interesting naturally occurring phenomenon to reduce As mobility in the rice rhizosphere while decreasing As uptake by rice plants. However, high density plaque formation may limit the diffusion of $O_2$ into rhizosphere. It could also increase the Fe precipitation restricting the uptake of nutrients by rice roots (Suda et al. 2016). Thus, comprehensive research approaches are required to further understand the role of Fe plaque on the immobilization of As species in the rice rhizosphere.

#### 6.3.2.2 Manganese Bearing Minerals

There are strong interactions between Mn-oxide mineral phases and As species because oxide surfaces act as electron accepters in the oxidation of As(III) to As(V). The oxidation of more toxic As(III) to As(V) is an important redox transformation to decrease As mobility in paddy soil as As(V) tends to readily adsorb on the mineral surface (Eqs. 6.5 and 6.6) (Lafferty et al. 2011).

$$MnO_{2(s)} + H_3AsO_{3(aq)} + 2H^{+}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + H_3AsO_{4(aq)} + H_2O_{(l)} \tag{6.5}$$

$$2(MnOOH)_{(s)} + H_3AsO_{4(aq)} \rightarrow (MnO_2)AsOOH_{(s)} + 2H_2O_{(l)} \tag{6.6}$$

Reactive phyllomanganates are naturally occurring layered Mn-oxides with birnessite-type structures which also can oxidize As(III) to As(V), and subsequently adsorb on available active sites of the surface. Biogenic Mn-oxides formed by a manganese oxide-depositing fungus strain (KR21-2) have shown excellent affinity towards As(III) catalysing its oxidation to As(V) (Tani et al. 2004). Manganese also contributes to the formation of root plaque, thereby controlling As mobility in the rice rhizosphere. It has been reported that the accumulation of As in rice plant tissues is correlated with the concentration of Mn in paddy soil (Hossain et al. 2008; Zhou et al. 2022). However, the formation of Mn-plaque in the rhizosphere is still not fully understood due to the complexity of mineralogy in diverse soil systems.

#### 6.3.2.3 Sulfur–Arsenic Interactions

Sulfur compounds including sulfate ($SO_4^{2-}$) also play a vital role in determining As speciation and mobility in paddy soil. Under flooded conditions, $SO_4^{2-}$ gets reduced to sulfide ($S^{2-}$) decreasing the redox potential from −120 to −180 mV (Kumarathilaka et al. 2018a, b). Sulfate reduction in paddy soil is often encouraged by sulfate-reducing bacteria such as *Desulfovibrio, Desulfotomaculum, Desulfobulbus*, and *Desulfobotulus* (Wind et al. 1995; Jia et al. 2015). It has been revealed that the reduction of $SO_4^{2-}$ to $S^{2-}$ leads to the immobilization As(III) species via precipitation as arsenic sulfide, iron sulfide and mackinawite minerals in paddy soil (Burton et al. 2014). Moreover, sulfer-As interactions and formation of toxic thioarsenic compounds in paddy soil and rice grain have recently been investigated (Wang et al. 2020a, b; Chen et al. 2021; Dai et al. 2021).

Chen et al. (2021) have recently found that sulfur-As interaction result in the formation of thio-methylated As species in paddy soil when the redox potential decreased from 0 to −100 mV. This study further demonstrated that the incorporation of $SO_4^{2-}$ in paddy soil can increase the abundance of dissimilatory sulfite reductase β-subunit (*dsrB*) genes and arsenite S-adenosylmethionine methyltransferase genes (*arsM*), inducing the formation of dimethylarsinic acid (DMA), dimethylated monothioarsenate (DMMTA) and dimethylated dithioarsenate (DMDTA). In another recent study, more toxic DMMTA was detected in both paddy porewater and rice grains at concentrations ranging 0.2–36.2 $\mu gL^{-1}$ and 0.4–10.1 $\mu gkg^{-1}$, respectively under flooded conditions (Dai et al. 2021). The addition of sulfur containing fertilizers has further increased the amount of DMMTA accumulated in rice grains (Dai et al. 2021). Therefore, there is strong relationship between sulfur bearing compounds and As speciation dynamics in paddy rice ecosystems.

### 6.3.3 *Effects of Organic Carbon*

Dissolved organic carbon (DOC) generated from decomposed plant and animal matter under flooded conditions plays a key role in As speciation and mobility across the soil–water interface (Li et al. 2018). The DOC in paddy soil directly contributes to As cycling and labile fractions which control As uptake and accumulation in rice grains. Organic matter is therefore mixed with paddy soil as a form of manure in traditional rice cultivation. Further, rice stubble and roots are added back to paddy fields after being harvested rice grains (Said-Pullicino et al. 2016). It has been reported that the fraction of DOC in paddy soil is one of important soil parameters which determines arsenic solid-aqueous phase partitioning, while governing As release from Fe-bearing minerals (Williams et al. 2011). Incorporation of organic matter through poultry manure, lathyrus and vermicompost in As-contaminated paddy soil has decreased As levels in rice tissues (Rahaman et al. 2011). Fu et al. (2011) found that the concentration of As in rice grain is positively correlated with soil organic matter. On the other hand, soil DOC can enhance the mobility of As(III) and As(V) species, thereby encouraging their bioavailability (Mladenov et al. 2015). This is due to ligand exchange with active sites on As-bound Fe(III) (hydro)oxides (FeOOH), and subsequently the desorption of adsorbed As species. It has been revealed that DOC tends to stimulate Fe(III) reducing bacteria, promoting reductive dissolution of As bearing Fe minerals which results in the release of toxic As(III) into soil Chen et al. (2016a).

### *6.3.4 Role of Soil Microorganisms*

Both aerobic and anaerobic bacteria involve in the speciation of As via oxidation and reduction processes in paddy soil (Zhang et al. 2015). Figure 6.2 shows a graphical representation of As speciation and transformation pathways catalysed by microorganisms in the rice rhizosphere.

Herath et al. (2020a; b) have recently investigated the diversity of microbial communities in the rice rhizosphere based on the abundance of *16S rRNA* and As functional genes. In this study, sequencing bacterial data was characteristic with a total of 38 phyla including *Acidobacteria, Bacteroidetes, Chloroflexi, Firmicutes, Tenericutes* and *Proteobacteria* as the dominant phyla in the rhizosphere. Arsenic oxidation, reduction, and methylation processes are governed by different bacteria species having unique functional genes, such as arsenite oxidation gene (*aioA*), respiratory reducing gene (*arrA*), reductase gene (arsC) and arsenite methyltransferase (*arsM*) (Gu et al. 2017). Microbe mediated oxidation of As(III) to As(V) can be considered as a naturally occurring As detoxification mechanism which is catalysed by *aioA* gene related bacteria (Fig. 6.2) (Herath et al. 2020a, b). *Paracoccus* species can oxidize As(III) under both aerobic and anaerobic conditions in paddy soil in the presence of $O_2$ and $NO_3^-$ as electron acceptor (Zhang et al. 2015). Interestingly, microbe mediated As(III) oxidation becomes dominant in non-flooded paddy soil when the abiotic oxidation of As(III) gets hindered as a result of a passivation of reactive sites on soil mineral surfaces (Dong et al. 2014). In addition, As(III) oxidizing bacteria can improve plant growth promoting (PGP) substances such as siderophores, indole-3-acetic acid (IAA) and 1-aminocyclopropane-1-carboxylate (Das et al. 2016). For instance, *Bacillus flexus ASO-6* that is a gram-positive bacterium isolated from rice the rhizosphere has increased the rate of As(III) oxidation with a maximum velocity of 34 $\mu$M min$^{-1}$ 10$^{-7}$ cell (Das et al. 2016). Hence, it is clear that

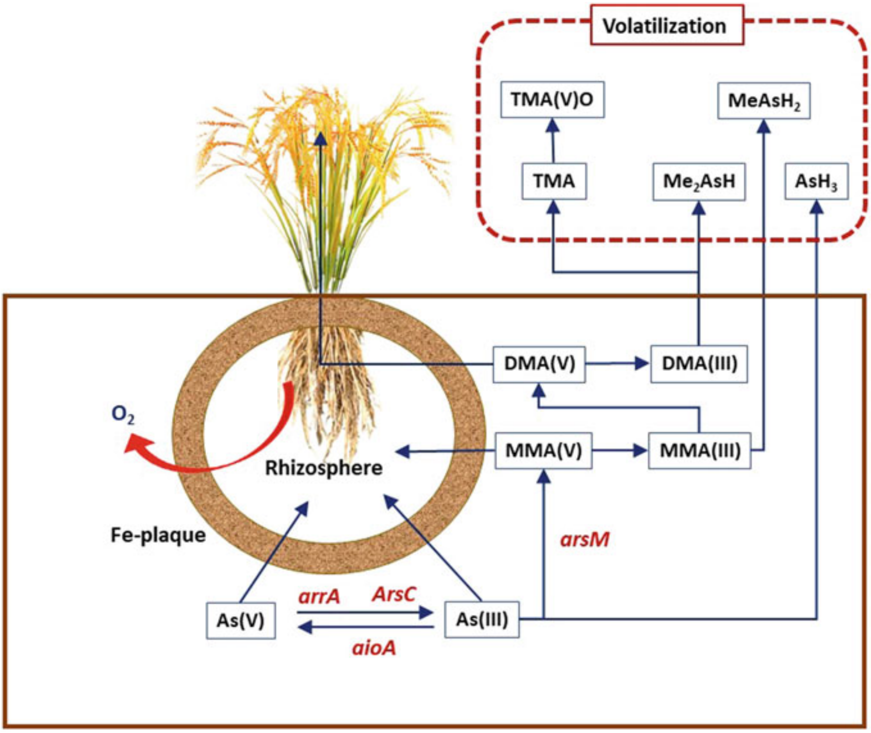

**Fig. 6.2** Influence of microorganisms on the speciation and transformation of As in the rice rhizosphere

bacteria species related to As(III) oxidization are beneficial for both As detoxification in soil and the growth of rice plants.

Bacteria species related to *arsC and arrA* genes are responsible for the reduction of As(V) to As(III) under flooded anaerobic conditions in paddy soil (Villegas-Torres et al. 2011). However, it has been found that phylogenetically originated As-resistant bacteria can reduce As(V) to As(III) even under aerobic conditions in soil (Bachate et al. 2009). It is noteworthy to mention that microbial reduction of As(V) to more toxic As(III) tend to promote As mobility in soil–water interfaces, thereby increasing its phytoavailability in paddy rice ecosystems.

Microorganisms bearing *arsM* genes code the transformation of inorganic As into methylated As species, including monomethyl arsenate (MMA(V)), dimethyl arsenate (DMA(V)), monomethylarsonous acid (MMA(III)), and dimethylarsinous acid (DMA(III)), in the rice rhizosphere (Fig. 6.2) (Wang et al. 2014). Various factors, such as the abundance and diversity of anaerobic microorganisms, extent of flooded conditions and adjacent As-bearing mineral phases influence on the methylation of As in paddy soil. Methylated As species detected in rice grains may come through microbial methylation in the rhizosphere as plant tissues cannot methylate inorganic

As in vivo (Zhao et al. 2013a, b). The As uptake transporters in rice roots, such as phosphate and aquaglyceroporins, assimilate both inorganic As(III) and As(V) as dimethyl arsenate (DMA(V)) and monomethyl arsenate (MMA(V)) from the rice rhizosphere (Kumarathilaka et al. 2018a, b).

Volatilization of As from paddy ecosystems directly contributes to emit more volatile As species into the atmosphere and it accounts for nearly 0.9–2.6% of global As emissions (Mestrot et al. 2011a, b). Paddy soil contributes to the emission of volatile As into the atmosphere ranging from 419 to 1252 tons annually, which is approximately 15–45 and 3—tenfold greater than that of from sea spray and forest fires, respectively (Mestrot et al. 2011a, b; Zheng et al. 2013). Microorganisms involve in volatilizing inorganic As to several As species, including trimethylarsines [TMAs ($(CH_3)_3As$)], arsine ($AsH_3$), monomethylarsine [$MeAsH_2((CH_3)AsH_2)$], and dimethylarsine [$Me_2AsH$ ($(CH_3)_2AsH$)] (Fig. 6.2) (Jia et al. 2012). It has been found that TMAs undergoes rapid oxidation by atmospheric $O_2$ producing trimethylarsine oxide (TMAs(V)O) (Bhattacharya et al. 2007). The rate and efficacy of As volatilization can be induced through biostimulation and bioaugmentation processes. Biostimulation is the process which stimulates the catalysis of microbial activities, whereas bioaugmentation promotes the inoculation of microbes (Chen et al. 2017a, b). Previous studies have demonstrated that total As concentration in paddy porewater is positively correlated with the extent of arsine emission (Mestrot et al. 2011a, b; Jia et al. 2012). Mestrot et al. (2011a; b) have found that the application of MMA(V) and DMA(V) in paddy soil can increase the rate of arsine volatilization by 3.5%.

## 6.4 Arsenic Metabolism in Rice Plants

Arsenic speciation, mobility, and phytoavailability in paddy soil are directly associated with As-bearing minerals phases, reductive dissolution of FeOOH minerals, formation of Fe plaque and microbe mediated biotransformation processes as discussed in the above chapters. Phytoaccessible fraction of As in the rice rhizosphere is responsible for the uptake of As species by rice plants, and ultimately accumulation in rice grains. Under flooded (reducing) conditions, As(V) present in paddy soil–water interface is converted to As(III) which is more mobile than As(V) species. As a result, the As(III)/As(V) ratio becomes high in paddy porewater encouraging more As(III) to be taken up by rice roots (Yamaguchi et al. 2014). However, Fe-plaque plays a vital role on the sequestration of As(III) and As(V) species in the rhizosphere. High ratio of As/Fe in Fe-plaque in the rice rhizosphere indicates its great capacity for the immobilization of As in the rhizosphere (Wu et al. 2011). Understanding of As metabolism mechanisms in rice plant tissues is vital for evaluating the uptake of As species through rice roots, and their translocation and accumulation in rice grains. Various types of genes are responsible for the metabolism of As in different parts of rice. Mechanisms of As metabolism mainly involve the reduction of As(V), efflux of As(III), translocation, complexation and localization. Table 6.2

provides an overview of different gene types which are responsible for As uptake, translocation, and loading into rice grains.

**Table 6.2** Different types of gene expressions which are responsible for As uptake, translocation and accumulation in rice plants

| Metabolic pathway | Function | Type of gene | Gene name | Reference |
|---|---|---|---|---|
| Reduction of As(V) | Conversion of As(III) to As(V) in root tissues | *As(V) reductase* | *OsHAC1;1*<br>*OsHAC1;2*<br>*OsHAC4* | Shi et al. (2016), Xu et al. (2017) |
| As(III) uptake by roots | Translocation of As(III) from rhizosphere to rice roots | Nodulin 26-like intrinsic proteins (NIPs | *OsNIP2;1 (Lsi1)*<br>*OsNIP2;2 (Lsi2)*<br>*OsNIP1;1*<br>*OsNIP3;1*<br>*OsNIP3;2*<br>*OsNIP3;3* | Ma et al. (2008) |
| Loading of As(III) into xylem | Translocation of As(III) from roots to shoot | Natural resistance-associated macrophage protein (*NRAMP*) | *OsNRAMP1* | Tiwari et al. (2014) |
| As(III) efflux | Extrude to surrounding environments | Nodulin 26-like intrinsic proteins (NIPs) | *OsNIP2;2 (Lsi2)* | Xu et al. (2017) |
| As(III) complexation in root and phloem | Sequestering it in the vacuoles of phloem companion cells | ATP-binding cassette transporter | *OsABCC1* | Song et al. (2014) |
| Loading of As(V) into xylem and phloem | As(V) uptake by roots, translocation and accumulation rice grains | Phosphate transporters | *OsPHT1;8 (OsPT8)*<br>*OsPHT1;1* | Kamiya et al. (2013a; b), Wang et al. (2016) |
| DMA(V) and MMA(V) uptake by roots | Methylation of As(III) and translocation into rice roots | NIPs | *OsNIP2;1 (Lsi1)* | Li et al. (2009) |
| Loading of DMA(V) into xylem and phloem | Translocation into rice leaves and accumulation in rice grains | Putative peptide transporter | *OsPTR7* | Tang et al. (2017a; b) |

### *6.4.1 Uptake Pathways of As(III)*

Inorganic As(III) is the most dominant inorganic As species under reducing conditions in flooded paddy soil–water systems. The nodulin 26-like intrinsic proteins (*NIPs*) which are generally known as aquaporin channels can metabolize As(III) in rice roots (Fig. 6.3) (Ma et al. 2008). Uptake of As(III) through Si competing mechanisms is governed by *OsNIP2;1* (*Lsi1*) gene which is present in the distal side of the plasma membranes of the exodermis and endodermis cells (Fig. 6.3). Silica (Si) transporters, such as *Lsi1* can trigger the influx of both As(III) in the form of arsenous acid ($As(OH)_3$) and silicic acid ($Si(OH)_4$) into rice roots (Fleck et al. 2013; Pan et al. 2022). This is probably due to similar size of both $Si(OH)_4$ and $As(OH)_3$ with tetrahedral orientation along with more or less similar dissociation constants ($pK_a$) (9.2 and 9.3, respectively) (Teasley et al. 2017).

In contrast to Lsi1, aquaporin channel *OsNIP2;2* (*Lsi2*) gene contributes to the efflux of ($Si(OH)_4$) leading to the release of Si back into the surrounding environments. The presence of both efflux (Lsi2) and influx (Lsi1) transporters in plasma membrane cells of rice roots tends to inhibit the transport of more As(III), thereby extruding available As(III) to external ecosystems (Zhao et al. 2010). In addition, a

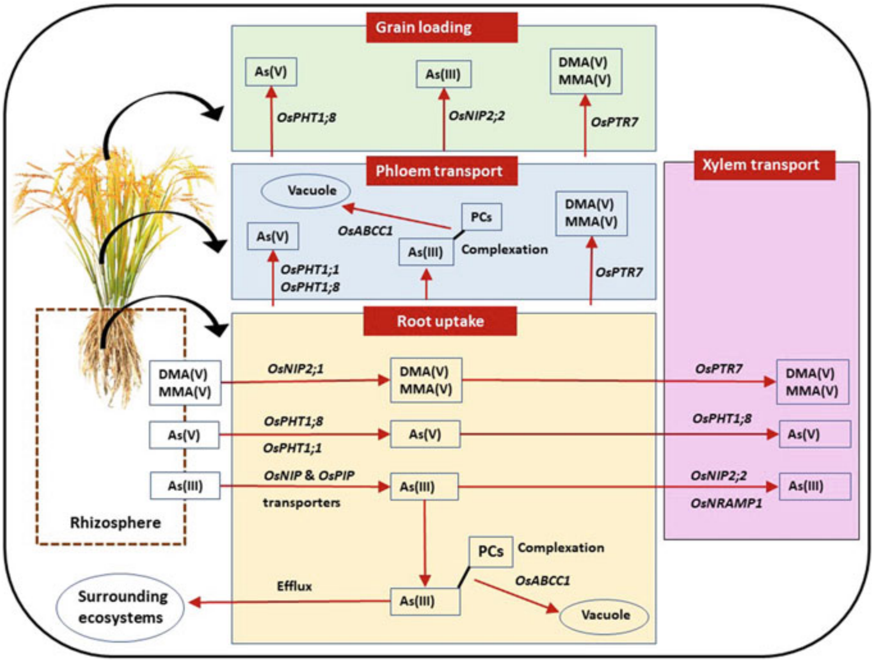

**Fig. 6.3** Graphical representation of main metabolic pathways involved in As uptake, translocation and grain loading

novel type of As(V) reductase gene called *OsHAC₄* has been identified as an excellent gene expression in rice roots to induce the efflux of As(III) into surrounding environments. The efflux of As(III) from the rice root system causes to decrease the translocation and accumulation As in plant tissues. Therefore, the addition of Si-based fertilizers into As-contaminated paddy soil has been a promising strategy to minimize As(III) uptake by rice plants (Guo et al. 2009). Furthermore, *OsNIP1;1* and *OsNIP3;1* genes can stimulate As(III) uptake via an oocytes-mediate metabolic pathway (Ma et al. 2008). Other NIPs such as OsNIP3;3 and OsNIP3;2 present in the lateral roots and stele region of the primary also can actively stimulate As(III) uptake by rice roots (Chen et al. 2017a). Moreover, the uptake of As(III) through rice roots is governed by plasma membrane intrinsic proteins (PIPs), including *OsPIP2;4, OsPIP2;6 and OsPIP2;7* genes (Mosa et al. 2012). Hence, understanding the role of different gene expressions for As(III) metabolism in rice plant tissues is crucial for assessing the translocation and accumulation of As in different parts of the rice plant, including grain filling.

### *6.4.2 Uptake Pathways of As(V)*

Arsenic in the form of As(V) becomes more prevalent under non-flooded conditions in paddy soil–water systems. Generally, As(V) and $PO_4^{3-}$ share similar uptake pathways in rice roots. The *OsPHT1;8 (OsPT8)* gene is the most common phosphate transporter which involves in As(V) uptake pathways in rice plants (Zhao et al. 2009). It has been found that the overexpression of *OsPT8* has increased the maximum influx of As(V) into rice roots (Wang et al. 2016). The OsPHT1;1 gene also can induce As(V) uptake metabolism in rice roots (Kamiya et al. 2013a, b). In addition, (Ye et al. 2017a, b) have found that As(V) uptake rate in *OsPT4*-overexpressing rice plants and grains can be increased up to a maximum of 66 and 30%, respectively, indicating its strong affinity towards As(V) uptake and transport metabolisms in rice plants.

The As(V) reductase enzymes such as *OsHAC1;1* and *OsHAC1;2* involve in controlling the reduction of As(V) to As(III) in rice roots (Xu et al. 2007; Shi et al. 2016). The *OsHAC1;1* is rich in the epidermis, root hairs, and pericycle cells of rice roots, whereas *OsHAC1;2* is abundant in outer layers of cortex and endodermis cells. Although As(V) reduction can elevate As(III) concentration in rice roots, As(III) tends to be released back to the surroundings of the rhizosphere through As(III) efflux mechanisms or complexation with thiol (S–H) groups. The As(III) efflux mechanisms in rice roots are induced by As(V) reductase genes, including *OsHAC4*, As(V) tolerance *QTL1* (*ATQ1*) and High Arsenic Content 1 (*HAC1*) (Chao et al. 2014). Interestingly, such naturally occurring As metabolic mechanisms lead to decrease As(III) levels in rice roots to a significant extent, thereby minimizing As(III) transport and accumulation in upper parts of the rice plant. Therefore, the application of $PO_4^{3-}$ based soil amendments in paddy cultivation has decreased As accumulation in rice grains (Abedin et al. 2002; Lihong et al. 2009).

### *6.4.3 Uptake of Methylated As Species*

Methylation of inorganic As does not commonly take place in rice plants in vivo. Organic As species; DMA(V) and MMA(V) detected in rice root, shoot and grain possibly originate from the rhizosphere due to microbe mediate methylation processes (Zhao et al. 2013a, b). Specific mechanisms for organic As uptake and metabolism in rice roots are still not fully understood. It has been suggested that the aquaporin *Lsi1* gene is capable of mediating the uptake of MMA(V) and DMA(V) in rice plants (Fig. 6.3) (Li et al. 2009). Lomax et al. (2012) reported that axenically grown rice can take up MMA(V) or DMA(V) from the rhizosphere while inducing redox transformation from MMA(V) to MMA(III). This study identified methylated As species in rice shoots and grains due to the methylation of inorganic As by *arsM* gene related bacteria in the rhizosphere. A recent study by (Chen et al. 2022a, b) demonstrated that the demethylation of DMA(V) and dimethyl monothioarsenate (DMMTA) in paddy soil is coupled to the methanogenesis with *Methanomassiliicoccus* and *Methanosarcina* species, and the suppression of methanogenesis process results in increased DMA(V) accumulation in rice grains.

### *6.4.4 Translocation of As Species from Root to Shoot*

Loading of As(III) into plant xylem is mediated by *Lsi2* and the Natural Resistance-Associated Macrophage Protein (NRAMP) transporter (*OsNRAMP1*) (Fig. 6.3). Various metabolic pathways such as efflux of As(III) into adjacent environments and formation of thiolated As complexes may limit the transport of As(III) from rice root to shoot as discussed in the above sections. The As(III) possesses a great affinity towards thiol-rich peptides, such as glutathione (GSH) and phytochelatins (PCs) (Kumarathilaka et al. 2018a, b). It has been revealed that the overexpression of PCs results in elevated concentrations of As in roots, but lower accumulation in rice grains of transgenic rice plants (Shri et al. 2014). This is due to the formation of As(III)-PC complexes, and subsequently transport into vacuoles for the sequestration by C-type ATP-binding cassette transporter (*OsABCC1*) which exists in the exodermis and pericle (Fig. 6.3) (Zhao et al. 2009; Yan et al. 2021a, b). Thus, the sequestration of As(III)-PC complexes in vacuoles is a crucial process to control As translocation through the rice shoot.

The efficacy of organic As translocation from root to shoot is significantly higher than that of inorganic As species (Raab et al. 2007; Kumar et al. 2022). This is because cytoplasmic pH conditions promote the dissociation of MMA(V) and DMA(V) in root cells (Raab et al. 2007). Certain fraction of MMA(V) gets reduced to MMA(III) and the remaining MMA(V) is readily transported through rice shoots (Li et al. 2009). Further, the formation of DMA(V)-PC complexes is scarce, so that more DMA(V) is highly available to translocate from root to shoot (Zhao et al. 2013a, b). The translocation of organic As species from root to grain is also stimulated by the *OsPTR7* gene known as the putative peptide transporter in rice (Tang et al. 2017a, b). The *OsPTR7* gene is prevalent in leaves, nodes, and roots during the flowering and grain filling stages, whereas it is more abundant in shoots and roots at the seedling stage. High-resolution synchrotron X-ray fluorescence studies have confirmed the translocation of DMA(V) through rice shoots and its localization in rice grains (Limmer et al. 2022).

### *6.4.5 Arsenic Loading to Rice Grain*

Accumulation of As in rice grain is the most threatening consequence of As contamination in paddy ecosystems as it directly links to the rice production, grain quality and human health. Phloem- and xylem-based transportation pathways are mainly responsible for the translocation of As from root to shoot and grain. The phloem is the primary route for the transportation both inorganic and organic As species. However, organic As species are more mobile compared to inorganic As species in the rice phloem according to previous investigations (Carey et al. 2010; Ye et al. 2017a, b). The highest translocation efficiency in rice plants acquires by DMA(V) followed by MMA(V) and inorganic As species (Geng et al. 2017). In a study reported by (Ye et al. 2017a, b), the phloem transportation has contributed to the accumulation of As(III), As(V), MMA(V) and DMA(V) in rice grains by 54, 56, 100, 89%, respectively. Inositol transporters (INT), such as *AtINT2* and *AtINT4* are responsible for loading As(III) to the phloem in some plants such as *Arabidopsis thaliana* (Duan et al. 2015). Nevertheless, information regarding transporters that are associated with phloem loading of As species in rice plants is scarce. Distribution of As species over different parts of the rice plant can be visualized by modern advancements in X-ray synchrotron technology such as synchrotron μX-ray fluorescence (μ-XRF) mapping (Chen et al. 2015). Mapping images obtained from the μ-XRF have revealed that the As (III) loading in the phloem is associated with different vascular bundles in the top node and internode (Chen et al. 2015). Therefore, the sequestration of As(III) through the phloem, top node, and internode may result in a decreased As(III) accumulation in rice grain.

The xylem transportation of As in rice plants depends on water management practices in rice cultivation. The As(V) was detected as the dominant As species ranging from 64 to 88% in the xylem sap under non-flooded conditions, while flooded conditions resulted in As(III) as the prevailing species (26–77%) followed by As(V) (12–54%) and DMA(V) (11–20%) in the xylem sap (Ye et al. 2015). A highly expressed Si pathway in rice plants may cause more loading of As(III) into the xylem during the flooded period in rice cultivation. However, only a few research can be found on studying As translocation pathways through the xylem in rice plants.

## 6.5 Grain Arsenic and Human Exposure

Translocation and accumulation of As in rice shoot highly affect the yield of rice causing adverse consequences on global rice production and food security. It has been found that high yielding rice cultivars have a great capacity to accumulate As in rice grain compared to low yielding rice cultivars (Bhattacharya et al. 2010a, b). Accumulated amount of total As in different parts of rice varies typically in the order of root > shoot > straw > husk > grain. Table 6.3 summarizes the concentration of As species and total As detected in different plant parts based on greenhouse and field scale studies. Herath et al. (2020a; b) have recently quantified the amount of As in rice obtained from market baskets in different rice growing countries, including South Asian regions and Australia. This study reported that inorganic As(III) is the dominant As species in rice grain ranging from 53 to 99% of the total As concentrations in all the rice varieties tested by using an ultra-high performance liquid chromatography coupled with inductively coupled plasma mass spectrometry (UHPLC-ICP-MS).

### *6.5.1 Arsenic Toxicity on Rice Quality*

Accumulation of As in rice plants causes severe plant diseases, such as straighthead which weakens grain filling and sterility of florates producing reduced grain yield (Rahman et al. 2008; Chen et al. 2022a; Limmer et al. 2022). The straighthead is a physiological disorder characterized by the sterility of florets with distorted lemma and palea (Chhabra et al. 2021). Rice plants exposed to high concentrations of As (>50 mg kg$^{-1}$) in paddy soil have shown remarkable severity of straighthead resulting in reduced plant height, panicle length and grain yield (Rahman et al. 2008). High As levels can also decrease the amount of chlorophyll a and b in rice leaves negatively affecting the photosynthesis process (Rahman et al. 2007). It has been demonstrated that DMA(V) accumulated in filial tissues such as embryo, endosperm, and aleurone leads to decrease the seed setting rate (spikelet sterility), and thereby losing grain yield to a significant extent.

In addition, exposure of rice seedlings to As(III) and As(V) tends to promote the formation of reactive oxygen species (ROS) which may involve in damaging the cell membrane and macromolecules in plant tissues (Murugaiyan et al. 2021). The As (III) that is entered the plant cell through NIPs and aquaglyceroporins, can react with the thiol (-SH) group of macromolecules while disturbing the protein structure. As a result, the membrane structure gets damaged causing aberration in cellular processes (Zhao et al. 2010; Mishra et al. 2021a, b). Cellular electrolytes tend to escape through a damaged cell membrane, which interrupts membrane integrity. For example, the accumulated As in plants can induce oxidative damage of the cell membrane due to high levels of malondialdehyde produced from the peroxidation of membrane lipids (Singh et al. 2018). The uptake of As(V) is mediated by phosphate transporters as discussed in the above sections. Such metabolic processes can replace

**Table 6.3** Concentration of inorganic and organic As species in straw, root and grain of different rice genotypes

| Rice genotype | Nature of the study | Plant part | Total As (a = μg kg$^{-1}$)<br>(b = mg kg$^{1-}$) | Concentration of As species (a = μg kg$^{-1}$)<br>(b = % of total As) | | | | | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | | | | As(III) | As(V) | DMA(V) | MMA(V) | DMMTA | |
| NR | Market basket (Asia, South Europe, North America and Australia) | Grain | 143a | 97.6a | ND | 29.4a | ND | 10.4a | Dai et al. (2022) |
| NR | Paddy field survey (China) | Grain<br>Bran | 12.5–492a<br>148–1581 | 6.1–328a<br>136–1306a | NR | 1.6–88.2<br>4.2–88.7 | NR | 2.1–34.8a<br>5.2–39.7 | Dai et al. (2022) |
| 16 different genotypes | Market basket (Asia and Australia) | Grain | 30 – 183a | 29–162a | ND | 20 – 72a | ND | NR | Herath et al. (2020a; b) |
| Shengyou 957 (Indica) | Greenhouse | Grain<br>Straw | 290a<br>750a | NR | NR | NR | NR | NR | Herath et al. (2020a; b) |
| Liangyou 8106 | Greenhouse | Shoot<br>Root | 19–20b<br>950–1000b | 98–99b<br>95–99b | NR | NR | NR | NR | Yan et al. (2021a; b) |
| Jiahua | Soil culture media | Shoot<br>Root | NR | 4.39b<br>83.9b | 1.29b<br>105.2b | 2.6b<br>2.6b | 0.22b<br>0.22b | NR | Jia et al. (2012) |
| M-206 | Greenhouse | Bran | NR | - | 69–88b | 12–31b | NR | NR | Seyfferth et al. (2011) |
| Koshihikari | Greenhouse | Grain | 25–487a | 31–431a | NR | 2–79a | NR | NR | Naito et al. (2015) |
| T116 | Greenhouse | Grain<br>Shoot<br>Root | NR | 0.83b<br>0.7b<br>4.25b | ND<br>0.56b<br>0.55b | 0.98b<br>1.08b<br>0.16b | 0.42b<br>1.30b<br>1.95b | NR | Geng et al. (2017) |

(continued)

**Table 6.3** (continued)

| Rice genotype | Nature of the study | Plant part | Total As (a = µg $kg^{-1}$)<br>(b = mg $kg^{1-}$) | Concentration of As species (a = µg $kg^{-1}$) (b = % of total As) | | | | | Reference |
|---|---|---|---|---|---|---|---|---|---|
| | | | | As(III) | As(V) | DMA(V) | MMA(V) | DMMTA | |
| Different genotypes | Market basket (Taiwan) | grain | 116.6a | 61.6a | 4.3a | 12.1a | 2.7a | NR | Chen et al. (2016a; b) |
| Different genotypes | Field survey | Grain | 129.4a | 107.1a | 4.7a | 9.6a | 0.3a | NR | Ma et al. (2016) |

*ND—Not detected; NR—Not reported

the inorganic phosphate ions through the phosphorylation, and thereby interfering with the ATP synthesis in plant cells (Mishra et al. 2021a, b). Therefore, As toxicity causes both membrane damage and cellular disorders resulting in reduced rice yield and low-quality grains.

### *6.5.2 Human Exposure to Arsenic by Rice*

Rice is the staple food in many parts of the world. Human exposure to As through As-contaminated rice and related food products has become a serious problem in terms of global rice production and demand. Direct and indirect pathways contribute to carrying As from rice grain to human body. For example, rice grown in paddy fields that are contaminated by As at elevated levels contributes to expose individuals to As via direct consumption. On the other hand, As-containing rice husks that are used as cattle feed in some countries (e.g., Bangladesh and China) is as an indirect pathway of As exposure to humans through food chains. People living in As endemic areas, particularly in Asia get exposed to high levels of As through the intake of As-contaminated rice due to the use of As-contaminated groundwater for both irrigation and cooking. This has also led to limit the global rice exportation from such As endemic countries adversely affecting their economy.

Health impacts of rice intake depend on the rice genotype, variety (i.e., brown, white, organic), processing method (i.e., polish or non-polish), and cooking conditions (i.e., purity of water, washing time and method). For instance, high levels of As localized in rice brans may cause severe health risks, so that removing the bran layer by polishing could be an effective way to get rid of the most As contents. Sequential washing practices prior to cooking have removed As in rice by 13–30% depending on the rice variety (Horner et al. 2013; Jitaru et al. 2016). Nevertheless, the use of As-contaminated water for washing and cooking in global As endemic areas has significantly contributed to increase As levels in cooked rice (Ackerman et al. 2005). For instance, communities living in As endemic areas, such as Prey Veng (Cambodia) intake inorganic As up to 24 times more than the previous provisional tolerable daily intake value (PTDI) of 2.1 $\mu g\ kg^{-1}$ of body weight per day (Kumarathilaka et al. 2019). Further, the As content in cooked rice has become doubled with the use of As-contaminated cooking water (0.001–0.200 mg $L^{-1}$) in the Murshidabad and Naida districts in India (Roychowdhury 2008). It has also been investigated that the cooking step involves changes of As speciation in cooked rice. For example, cooking rice had converted As(V) and DMA(V) into more toxic As(III) species (Horner et al. 2013). Furthermore, high As content in rice may reduce trace mineral nutrition, including metal ions (e.g., Zn, Se, Ni), amino acids and antioxidants producing poor quality grains (Dwivedi et al. 2010).

The consumption of As-containing grains through cooked rice and other rice-based food products (e.g., cakes, cereals, crackers, and noodle) leads to severe health risks in human body. Intake of inorganic As is a well-known cause of cancers (i.e., skin, lungs, breast and bladder), respiratory, cardiovascular, neurological, and metabolic diseases (Khan et al. 2020). Children exposure to As via As-contaminated cereal food is a worldwide problem at present, and hence the European Union (EU) has recommended a maximum level of 100 μg kg$^{-1}$ for inorganic As in rice related products intended for babies and young children (Petursdottir et al. 2015). The permissible level of inorganic As in polished rice grains for adults is 200 μg kg$^{-1}$ as recommended by the World Health Organization (WHO) (WHO 2014). Urinary As level is also a key indication of As exposure in humans (Lee et al. 2022). Toxic consequences of As-contaminated rice grain are also associated with bioaccessibility of As species. The bioaccessibility of As in humans reflects to the fraction of dissolved As due to the gastrointestinal digestion (Althobiti et al. 2018). A certain As species ingested through rice can be further converted to highly bio-accessible As species during the gastro-intestinal digestion using the hydrochloric acid in gastric juice. Even the saliva may initiate the changes in the chemical form of As in the mouth as it is the first step in the gastro-intestinal digestion process. Therefore, assessing the bio-accessible fraction of As after ingestion is crucial for realistic risk assessment of As-contaminated rice in human body.

## 6.6 Remarks and Future Recommendations

This chapter provided a comprehensive overview of As dynamics in paddy rice ecosystems with an emphasis on arsenic speciation, mobility, translocation, metabolism and loading into grains. Since the total As levels in paddy soil–water interface does not reflect a measurement from a single point, an understanding on veracity of spatial and temporal distribution of As species over global paddy rice cultivation is crucial. More importantly, the contribution of geogenic sources such as weathering of As-bearing mineral phases and aquifer sediments for the contamination of paddy soil with toxic arsenic As species, including thiolated-As complexes needs to be further studied. This can be accompanied by detailed investigation of soil minerology in As endemic areas associated with rice cultivation. Further, naturally occurring perturbed environmental conditions, such as flooding, acid rain and global warming may affect As dynamics in the paddy soil–water systems to a significant extent. Therefore, influence of unpredictable environmental conditions on As speciation, mobility and translocation rice ecosystems needs to be further researched and reported on a global scale.

The translocation and sequestration of toxic arsenic species, including As(III) and thiolated As compounds from paddy soil to plant tissues are associated with geochemical processes, microbe mediated biotransformation and plant genetic factors. Based on the studies carried out so far, high As contamination in rice grains produced in As vulnerable regions is mainly due to the use of As-contaminated groundwater for irrigation as well as mining activities. Thus, there is an urgent necessity to establish more As mitigation measures in As-prone areas around the world in order to alleviate As loading into rice grains.

- Firstly, implementation of modern agronomical, physiochemical, and biological approaches could be effective to reduce the mobility and bioavailability of As in soil–water interfaces. For example, the addition of mineral supplements containing Fe, Mn and S as soil amendments and fertilizers can be a promising strategy to immobilize As in paddy soil due to the promotion of root plaque formation, complexation, and precipitation processes. Similarly, $PO_4^{3-}$ and $Si(OH)_4$) based amendments may reduce As uptake by rice roots.
- Biostimulation via favourable microbe species may detoxify toxic As species in paddy soil–water interface through oxidation, methylation, efflux, and volatilization.
- Novel breeding practices and use of rice cultivars that can decrease the accumulation of As in rice grain would be another option to enhance grain quality. Localization of As species in different plant parts including the grain bran can be decreased by changing the expressions of transporter genes associated with As uptake, efflux, translocation, and sequestration.
- Alternative water management practices such as use of As-free water sources such as rainwater harvesting systems play a vital role in controlling As contamination in cooked rice. Rainwater harvesting systems can be implemented in As endemic regions for cooking purposes which is the most practical strategy to minimize As content in cooked rice.

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# Chapter 7
# Interaction of Arsenic with Biochar in Water and Soil: Principles, Applications, and Prospects

**Pabasari A. Koliyabandara, Udayagee Kumarasinghe, Danushika C. Manatunga, Randika Jayasinghe, Rohan S. Dassanayake, and Meththika Vithanage**

**Abstract** Arsenic (As) is known as an extremely toxic metalloid available in the environment due to both anthropogenic and geogenic activities. Even though adsorption has shown promising results in remediating As, the speciation of As poses a challenge. Bioavailability and mobility of As can be potentially improved with the addition of biochar to contaminated soil systems. Further, biochar modification can also aid in better As removal. Biochar, prepared via pyrolysis of organic materials is characterized with unique properties namely large surface area, elevated sorption capacity, ion exchange capacity, micro porosity, significant mineral, and carbon contents which are highly beneficial in water and soil remediation. The conditions of pyrolysis and the type of feedstock are two key factors that directly affect the characteristics of biochar. The abundant availability of feedstock, cost effectiveness and favorable physiochemical parameters of biochar aid in remediating metalloids like As in the environment. This chapter focuses on the principles, interactions, application of biochar in As remediation in soil and water and future perspectives.

**Keywords** Arsenic · Biochar · Feedstock · Pyrolysis · Sorption

## 7.1 Introduction

Known for its extreme toxicity arsenic is the 20th most abundant element in geosphere. Both organic and inorganic species ($AsO_3^{3-}$ and $AsO_4^{3-}$) of arsenic

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has been identified for its toxicity in aqueous systems. The concentration of arsenic could vary from μg/kg levels to elevated concentrations as 250,000 mg/kg (Mahimairaja et al. 2005). A wide array of environmental and health effects is linked with the different forms of appearance of arsenic. Life threatening effects could also be raised due to soil contamination, drinking water and irrigation water poisoning of this element. Among the different forms of As, inorganic As is known to cause disorders in skin, vascular and nervous system (Li et al. 2020). One of the major exposure routes of inorganic As is via intake of food and drinking ground water. Varied types of cancers too can be caused by the intake of inorganic As (Podgorski and Berg 2020). Well water having As concentrations with 10 mg/L creates risk to human and in Bangladesh the As related death rate is 1 in every 18 adult deaths. Similarly, it has been recorded that birth complications, neurodevelopmental issues can also be occurred even by exposure even to concentrations below 50 mg/L at early stages of life (Zeng et al. 2020). Challenges raised from As contamination have led to the development of standard permissible levels to the environment namely the World Health Organization (WHO) has set the arsenic Maximum Contamination Level (MCL) of 10 mg/L whereas in other countries the limit has been set as 50 mg/L without updated sources (Alka et al. 2021; Zeng et al. 2020). Arsenic is also regarded as one of the most significant carcinogens. Inorganic arsenic forms are associated with cardiovascular effects, endocrine disorders, negatives impact on reproductive health, genotoxicity, immunological disorders etc. (Chen et al. 2019). Geographical sources, biological activities along with the anthropogenic activities can be marked as the sources of As. Arsenic can be found in nature combined with Fe, oxygen, and sulfur. Mobility of As is linked with anthropogenic activities under anaerobic environments mainly in soil and groundwater environments. Its mobility in aqueous systems depends on organic contents, aquifer characteristics, adsorption desorption mechanisms, oxidation reduction processes, pH, amount of total and free Fe contents in sediments and etc. (Polya and Middleton 2017).

## 7.2 Different Technologies Used for Arsenic Removal in Water and Soil Systems

Different methods have been tested for the treatment of arsenic in water and wastewater, and in soil systems namely adsorption, reverse osmosis, chemical oxidation, phytoremediation, electrokinetic methods and etc. pH of the solution can pose a significant challenge in As treatment due to its speciation. The choice of a treatment method is specified to the requirement, regulations of the country and the cost associated.

The mechanism in adsorption is the use of the solid material in removing pollutants from gaseous of aqueous solutions. Flexibility in handling, low cost, efficient removal, and ease of operation can be stated as the advantages of adsorption (Alka et al. 2021; Vithanage et al. 2017). Adsorbents like ion oxide granules, agricultural waste, biochar, magnetite nanoparticles, have been tested for specific usage considering the type of pollutant and its speciation. Use of activated carbon too has gained attention in especially water treatment. It is majorly because of its high performance, large surface area and favorable properties (Mohan et al. 2006). The dosage of adsorbent, temperature, period of exposure, the concentration of arsenic are significant factors affecting the efficacy of adsorption (Sarkar and Paul 2016). The process of ion exchange has also been tested for the removal of arsenic. Arsenate with its negative charge is removed with the technique. The total dissolved solids in aqueous systems can reduce the efficiency of ion exchange (Jadhav et al. 2015). Another technique that is used for remediating As contaminated environment is phytoremediation. Plants with considerable root systems, tolerance have the potential to remove arsenic (Manoj et al. 2020). Phytoremediation is an environmentally friendly method which is also inexpensive. At the same time the disadvantage of utilizing the method is due to its time-consuming process, production of additional toxic materials by microbes and the negative effect on the growth of certain plants. Combining nanoparticles with phytoremediation too aids in arsenic removal and it is known as the nano phytoremediation (Jesitha and Harikumar 2018). The technique chemical precipitation too is used for arsenic removal mainly in aqueous environments. Separable solid substances are formed in the technique by the addition of varied chemicals namely calcium and magnesium salts, sulfides and ferric salts (Alka et al. 2021). High costs and formation of silts can be identified as drawbacks of the method.

Water and soil contaminated with arsenic can be treated with electrokinetic remediation which is cost effective way in removing heavy metals. It can be only act on a limited amount of soil at a time which can be a disadvantage. This method is considered as an in-situ technique which can be used in arsenic removal with coupling to another technique because the dissolved arsenic is a challenge to be treated (Li et al. 2020). Membrane technology has produced promising results as it has recorded around 96% potential reduction of arsenic in groundwater (Alka et al. 2021). The non-chemical usage, dissolving arsenic without assembling it, the low energy consumption, desirable efficiency and effective filtration performance are advantages of this system (Zakhar et al. 2018). Nano filtration and reverse osmosis have been noted as the most promising technologies in selective removal of arsenic, but the limitations occur as of its high cost. Biochar due to its low production and operational cost and efficiency in arsenic removal has caught the attention of research nowadays.

## 7.3 Biochar

The first biochar, “Terra preta” has been used thousands of years ago by the Amazonian civilization to rehabilitate poor forest soils. It’s time to use the traditional knowledge in sustainable resource management. The biochar, “super-charcoal” is made of burning biomass and found as a method of carbon sequestration. The burning of biomass under limited oxygen results in pure carbon- it is approximately 40% of carbon initially contained in the biomass. This pure carbon will remain in the soil for thousands of years while conditioning soil and empowering soil biota to promote a healthy ecosystem.

### *7.3.1 Production of Biochar*

Biochar is produced via different processes namely pyrolysis, gasification, torrefaction, flash carbonization, and hydrothermal carbonization (Verheijen et al. 2015; Suarez-Riera et al. 2020). Pyrolysis is the commonly practiced method in biochar production where different time–temperature combinations are used depending on the feedstock type in the absence of oxygen. There are two major pyrolysis processes depending on the heating rate and residence time, called slow pyrolysis and fast pyrolysis. Slow pyrolysis takes several hours to complete the process and produce biochar as a major product it's also known as conventional pyrolysis, where biomass is heated at a temperature in the range of 300–600 °C with a heating rate of 5–7 °C $\text{min}^{-1}$. This slow pyrolysis yields biochar, bio-oil, and syngas, by percentages of 35–45%, 25–35%, and 20–30% respectively (Pudełko et al. 2021). Fast pyrolysis is a high temperature (>500 °C with a heating rate of more than 300 °C $\text{min}^{-1}$) method in contrast slow pyrolysis. It can aid in high product recovery and low retention time. Bio oil and syn gas are the other two major products other than biochar which is generated from the method. In terms of gasification, it is a thermo-chemical conversion of biomass at high temperatures (>700 °C) under controlled amounts of oxygen resulting in the production of combustible gases called syngas or producer gas. In hydrothermal carbonization, the high moisture-containing feedstocks such as sewage, sludge, animal waste, and compost are converted into biochar with the help of the hydrothermal carbonization (HTC) method. It is generally accepted that typical biochar yields obtained by fast pyrolysis and gasification processes are significantly lower than that of slow pyrolysis and hydrothermal carbonization (Pudełko et al. 2021). The physiochemical characteristic of the produced biochar heavily depends on the feedstock characteristics (surface area, available functional groups, sorption abilities, cation exchange capacity, carbon sequestration capacity etc.), temperature, and duration of pyrolysis (Alka et al. 2021; Vithanage et al. 2017). Agricultural biomass and solid waste materials are generally used as feedstock for biochar. Materials namely, wood chips (Hagemann et al. 2020), organic portion of municipal solid waste (Beckinghausen et al. 2020) and animal manures (Rehman et al. 2020) are widely used as feedstock. Seaweeds which are considered as a nuisance too has been tried in the producing biochar and its alternative usage is beneficial for communities (Katakula et al. 2020).

### *7.3.2 Biochar as a Candidate for As Removal*

Biochar got the utmost attention in multidisciplinary sectors and seems no end of use due to its extraordinary characteristics. Biochar can be introduced as a healing agent for polluted environments, and it enhances the physiochemical properties of ecosystems. The biochar with large pore volume, surface area, and functional group has demonstrated to have excellent sorption capacity for heavy metals and other organic or inorganic metal pollutants. Recent researchers suggest that biochar amendment is a promising approach to mitigate soil/water contamination via immobilizing heavy metals and organic pollutants. At present, researchers are mainly focused on the remediation of heavy metals such as As, Pb, Cd, Zn, Cr, Cu, and Hg. Unlike organic pollutants, heavy metals are hard to be biologically degraded, which increases the difficulty of separation (Rajapaksha et al. 2014) Biochar may reduce the mobility of biochar of heavy metals in contaminated soil that rendering the risk of taking up by plants. Electrostatic sorption, ion exchange, and surface complexation of biochar enhance the sorption while soil pH elevation, the addition of carbonates ($CO_3{}^{2-}$) and phosphates ($PO_4{}^{3-}$) to the soil by biochar results in the removal of pollutants in soil by chemical precipitation. The purifying capacity (Heavy metal removal capability) of biochar varies on different factors such as type of the biomass, pyrolysis conditions, activation methods, which directly influence the chemical nature of biochar such as pH value, particle size fraction, CEC (Cation Exchange Capacity. Ion exchange and adsorption of cationic function mechanism, co-precipitation, complexation, and electrostatic absorption are the dominant mechanisms in metal sorption by biochar (Khalil et al. 2020). Efficient removal of As by contaminated soil and water has been proved by many studies. The negatively charged acidic functional groups on the biochar surface play a major role in the transformation of As(V) into As(III) (Linhoss et al. 2019).

## 7.4 Application of Biochar for As Remediation in Water

Biochar is produced from various plants and other bio sources such as pine (Jang et al. 2018), oak (Wang et al. 2015b), rice husks (Herath et al. 2016; Mayakaduwa et al. 2017), tea waste (Rajapaksha et al. 2014; Mayakaduwa et al. 2017; Keerthanan et al. 2020), date palm (Usman et al. 2016), coconut shell (Paranavithana et al. 2016), soybean (Vithanage et al. 2015), biosolids (Kimbell et al. 2018), animal manure (Idrees et al. 2018) and solid waste (Ashiq et al. 2019). It has been efficiently used for water remediation. Among these numerous materials, As removal has been followed using some specific materials such as, hard wood (Ayaz et al. 2022), sewage sludge (Agrafioti et al. 2014), rice husk (Babazad et al. 2021), municipal solid waste (Jin et al. 2014), pine (wood, bark, cone) (Mohan et al. 2007; Wang et al. 2015a) and paper mill sludge (Yoon et al. 2017).

However, the use of unmodified biochar has been found to be ineffective in removing As in many instances as the As removal is solely dependent on the surface charge of biochar. Biochar could mount both positive or negative charges on its' surface depending on the pH and the influence coming from the point of zero charge ($pH_{PZC}$). In situations where the pH is less than the $pH_{PZC}$, the protonation of the functional groups in biochar would lead to a net positive charge, whereas when the pH is greater than the $pH_{PZC}$ the surface of the biochar would become negatively charged. It highlights the that $pH_{PZC}$ plays a major role in determining the surface charge of biochar that leads to the adsorption of As in aqueous media.

However, as the charge of the biochar surface hugely affects the As adsorption pattern, it has been observed that the adsorption capacities of biochar can be improved by altering the surface charge subjecting the material to physical or chemical modifications thereby leading to the activation of biochar.

### *7.4.1 Use of Non-Activated- Biochar for As Removal in Water*

Out of many biochar materials used for As removal, Japanese oak wood has been a promising source in producing biochar for the purpose of As removal from drinking well water. In this regard, researchers have utilized Japanese oak wood biochar (OW-BC), to develop an adsorbent material for As removal where they have specifically investigated the As removal along with the fate of As using integrated spectroscopic and microscopic techniques (Fig. 7.1) (Niazi et al. 2018a). The results of Arsenic K-edge X-ray absorption near edge structure (XANES) spectroscopy have indicated a redox transformation of arsenite into arsenate on the OW-BC whereas the FT-IR results have further confirmed that the presence of the functional groups (–OH, –COOH, –C–O– and $–CH_3$) in OW-BC would trigger the complexation of arsenite or arsenate on to OW-BC surface. Furthermore, it has been observed that this OW-BC is capable of removing As from As- contaminated well water having As concentration of 27–144 $\mu g\ L^{-1}$ with a removal efficiency of 92–100% even in the presence of competing anions and cations. Sorption data further suggested that OW-BC follows Langmuir adsorption isotherm model over the As adsorption giving a higher sorption capacity for As(V) compared to As(III) highlighting its' possibility for monolayer sorption that arises due to the favorable surface interactions of As species and OW-BC surface (Niazi et al. 2018a).

Biochar of three origins which include biochar from rice husks (RH), organic solid wastes (SW) and sewage sludge (SS) have been prepared for the arsenic removal from water has been tested (Agrafioti et al. 2014). Out of the three biochar materials developed it has been noticed that the sewage sludge (SS) derived biochar has an excellent ability over As(V) removal than the biochar originated from other two materials, due to the fact that the sewage sludge would contain more of $Fe_2O_3$ which will allow the favorable interactions with arsenate species. Similar studies have also been conducted by other groups of researchers (Babazad et al. 2021).

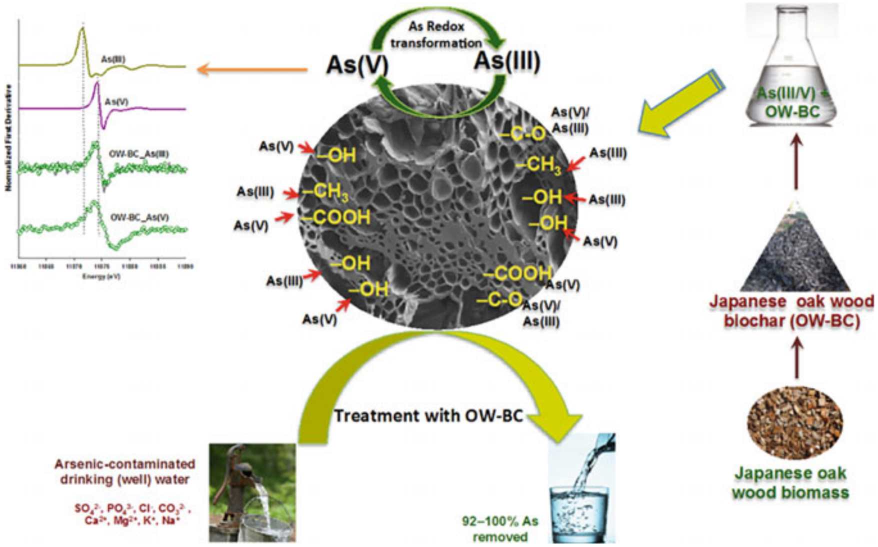


**Fig. 7.1** Use of Japanese oak wood biochar (OW-BC), to develop an adsorbent material for As removal in water bodies (Reprinted with permission from Niazi et al. (2018a), Copyright 2017 Elsevier Ltd.)

The use of medicinal or food plant waste materials for biochar generation and use them for remediation of As-contaminated water has also gained some attention as a cost-effective, sustainable way of removing As. In a study conducted by Niazi et al., perilla lead derived biochars have been employed to remove As(III) and As (V) from natural groundwaters. Two types of biochars (i.e. biochar of 300 (BC300) and biochar of 700 (BC700)) have been produced in this study by subjecting the leafy waste to two temperature treatments (300 °C and 700 °C) out of which BC700 has performed well in removing the As(III) and As(V) in the preferable pH range of 7–10. It has been explored that the high surface area, surface functional groups and the increased aromaticity of BC700 has outranged the performance of BC300 on As (III) and As (V) removal by accounting for a $Q_L$ of 11.01 $mgg^{-1}$ and $Q_D$ of 3.06 $mgg^{-1}$ by being best fitted to the Langmuir and Dubinin-Radushkevich models (Niazi et al. 2018b).

Treatment of acid mine drainage contaminated with As has been exploited by some researchers where they have used paper mill sludge (PMS) derived biochar. Paper mill sludge is created in the paper industry, where the sludge is enriched with Ca and Fe species due to the chemical treatments that have taken place in the industrial setting. In this work, PMS derived biochar has been produced by subjecting the PMS to pyrolysis under a $CO_2$ atmosphere which was later used for As (V) removal under strong acidic conditions. Physicochemical properties of as synthesized biochar confirmed that they have a complex aggregated structure augmented with FeO, $Fe_3O_4$ and $CaCO_3$ and graphitic carbon leading to an alkaline structure, leading to a maximum adsorption capacity of 22.8 mg/g for As(V) (Yoon

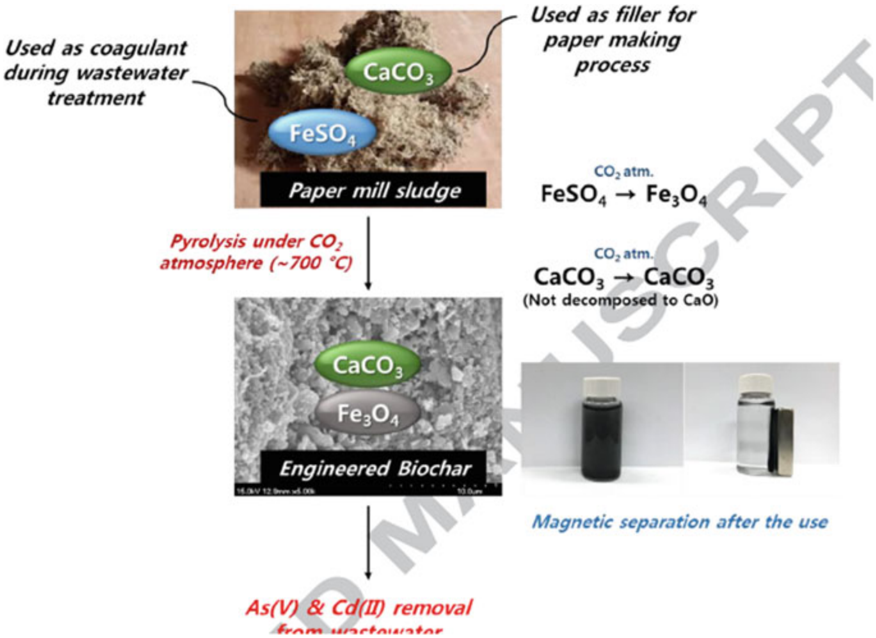


**Fig. 7.2** Activity of PMS derived biochar performing its' As removal ability (Reprinted with the permission of Yoon et al. (2017), Copyright 2017 Elsevier Ltd)

et al. 2017). More importantly, these structures have been magnetically responsive, which could be magnetically separable after use (Fig. 7.2).

Some current work has also gained attention on developing efficient and lucrative biochar using green marine algal blooms for the remediation of As contaminated water bodies. In the study conducted by Senthilkumar and co-workers (Year) have used green seaweed (*Ulva reticulata*) for the generation of a reusable biochar material. The results of the adsorption studies conducted with As(V) over the optimum pH of 4.0 revealed that this algae-based biochar material could lead to a maximum sorption capacity of 7.67 mg/g over As(V). Furthermore, a rapid removal trend over As(V) is further observed, approaching a maximum removal percentage within 30 min of incubation, which could possibly arise due to the favourable electrostatic interactions that establish between the As(V) species and the biochar surface functional groups. Further, this study provides evidence that the adsorbed As(V) could be easily desorbed, particularly under alkaline conditions, which allow the regeneration of the biochar column (Senthilkumar et al. 2020).

In another very recent study, lignocellulosic materials such as *Eucalyptus* wood has been employed to produce biochar for arsenic and fluoride removal in aqueous water. In here specifically, three types of biochar materials have been fabricated, of which the SEM images are depicted in Fig. 7.3, given the name as, laboratory-based (B1), barrel-based (B2), and brick kiln-biochar (B3), which have also outperformed at pH 10 for the effective removal of As in 96%, 94% and 93% respectively. The presence of carbonyl groups and alkene groups on the surface of the biochar proven with the FT-IR results has further highlighted the possible interactions between As species and biochar surface. Adsorption removal has been well explained by the Langmuir isotherm model (Ayaz et al. 2022).

### 7.4.2 Use of Activated Biochar for As Removal

Similarly, Fan et al., in their work, have produced biochar from corn straw impregnated with iron for the As(V) removal from aqueous systems (Fan et al. 2018). This biochar composite, accounting for 24.17% of iron and 27.76% of oxygen, has led to the highest adsorption capacity of 14.77 mg/g while showing a better performance in the pH range of 2–8. It is believed that iron oxides such as magnetite, natrojarosite as well as amorphous iron oxyhydroxides act as the adsorption sites for the As (V) (Fan et al. 2018).

Magnetic biochar is another widely investigated activated biochar material for the removal of As from aqueous solutions. To produce the biochar, various plant resources such as cotton wood (Zhang et al. 2013), pine wood (Wang et al. 2015a), bamboo culms (Alchouron et al. 2021) and waste wood (Chen et al. 2021) have been utilized.

$FeCl_3$ treated biomass has been subjected to thermal pyrolysis to prepare magnetic biochar out of cotton wood, which has led to the generation of $\gamma$-$Fe_2O_3$ (maghemite) being embedded in the porous biochar matrix. Prepared biochar composite has exhibited exceptional ferromagnetic property as well as a better sorption ability over As(V), accounting for a sorption capacity of 3.147 mg/g. More importantly, As(V) bound biochar was easily separable at the end of the sorption process from the water bodies (Zhang et al. 2013). Another source for magnetic biochar production is pine wood. In work carried out by Wang et al., pinewood biomass has been subjected to pyrolysis in the presence of $\alpha$-$Fe_2O_3$ (hematite) which has also generated a strong magnetic biochar material that has a profound ability to absorb As(V) over the unmodified biochar material. This ability is justified to be originated from the $\alpha$-$Fe_2O_3$ particles acting as serving as As chelating sites on the carbon surface (Wang et al. 2015a).

In some situations, As concentrations can reach a value of 2000 μg/L, which is way higher than the WHO safe drinking limit of 10 μg/L. This scenario is commonly observed in Latin American drinking waters. The use of biochar generated from readily available bamboo species (BC), has been a promising option for the removal of As(V) in such situations in a cost-effective manner. More importantly, the use of $Fe_3O_4$ impregnated bamboo biochar (BC-Fe) has been very much effective for the column sorption of As(V), accounting for a sorption capacity of 8.2–7.5 mg/g in the pH range of 5–9 and safe drinking water (Alchouron et al. 2021). Figure 7.4 illustrates the mechanism of interaction of arsenate with the BC and BC-Fe surfaces in the presence of competing ions. It has been observed that the effect of the interactions of the competing ions such as sulfate, phosphate, chloride, acetate, dichromate, carbonate, fluoride, selenate, and molybdate with very low concentrations (0.01 M)

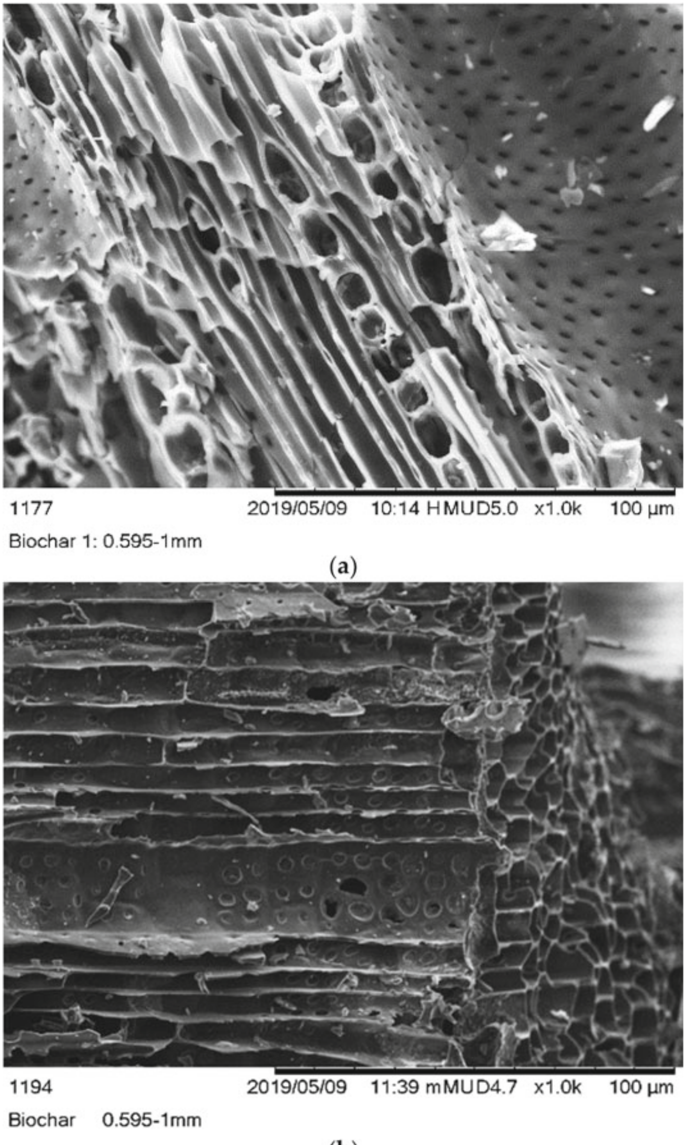
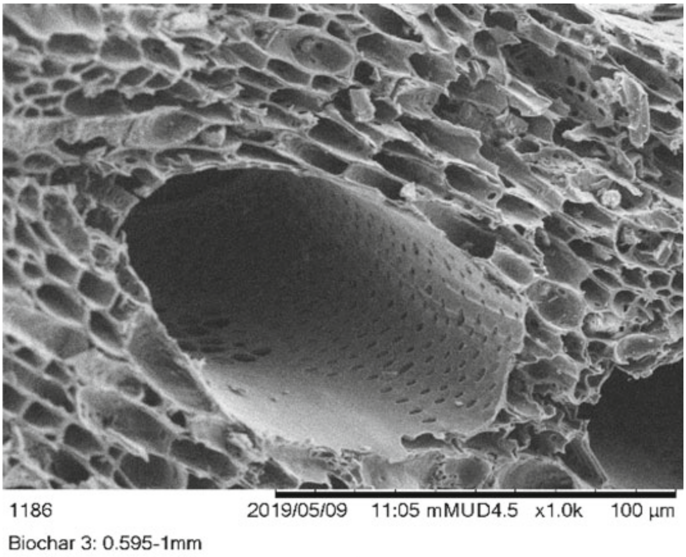


**Fig. 7.3** SEM images of **a** laboratory-based (B1), **b** barrel-based (B2), and **c** brick kiln-biochar (B3) (Reprinted with the permission of Ayaz et al. (2022) Copyright Creative Commons Attribution (CC BY) license)



(c)

**Fig. 7.3** (continued)

has provided a negligible effect on the adsorption of As(V) on to BC-Fe (Alchouron et al. 2021).

In addition to the magnetic biochar composites, some work has been also conducted on the generation of environmentally friendly inexpensive biochar containing MnO and CuO metal oxides for the batch scale removal of As in contaminated water. Sesbani is a supportive crop with a higher economic value grown in subcontinents and the stems are regarded as a waste after the harvesting period.

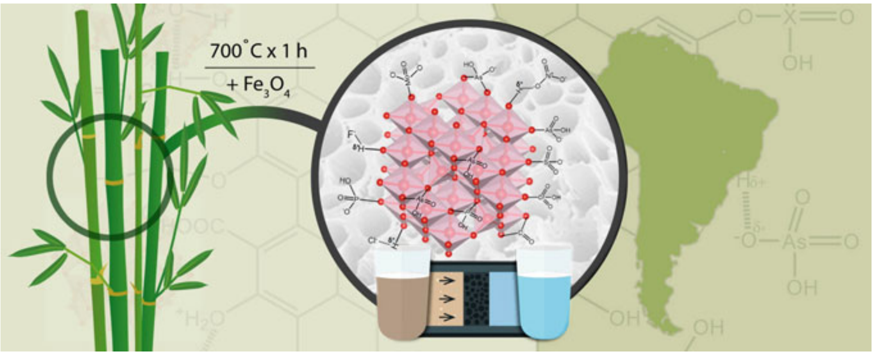


**Fig. 7.4** Schematic representation of possible interactions of arsenate and competitive contaminants ions on BC and iron oxide phases of BC-Fe (Reprinted with the permission from Alchouron et al. (2021), Copyright 2020 Elsevier Ltd)

Chen et al., has attempted to generate a novel nanobiochar composite by ligating *Sesbania bispinosa* biochar (SBC) with CuO (SBC/CuO) and MnO(SBC/MnO). Out of three materials SBC, SBC/CuO and SBC/MnO, the results of the adsorption studies revealed that SBC/CuO highest adsorption capacity over As(V) which is 12.47 mg/g provided with an optimum pH of 4. Furthermore the remarkable stability of SBC/CuO over four adsorption/desorption cycles has further highlighted the ability to use SBC/CuO biochar as an efficient adsorbent for As(V) removal from water bodies (Imran et al. 2021) (Table 7.1).

## 7.5 Application of Biochar for Remediation of As Contaminated Soil

Biochar is now considered a, a sustainable option opening the pathway for soil remediation of heavy metals and organics. Further, it is also considered an economical means of value addition to agricultural and industrial waste products. In addition, biochar is also known to play a major role in improving soil quality, enhancing microbial activity and nutrient content leading to improved crop yield (Cheng et al. 2020; Yuan et al. 2019).

The various feedstock of different origins has been used for the generation of biochar. Widely used biochar for soil remediation include; wood chips/branches, agricultural wastes, woody biomass, animal manure, sewage sludge, algal blooms (Wang et al. 2015a, 2018; Cruz et al. 2020; Liang et al. 2021; Guo et al. 2020; Taraqqi-A-kamal et al. 2021).

Biochar has favourable physio-chemical surface characteristics, especially the sensitivity to pH, the presence of functional groups that trigger the complexation, reduction, cation exchange, electrostatic attraction and precipitation of arsenic species. With the extensive availability of feedstock for biochar production, biochar has also been a very good material for As decontamination in soil (Cheng et al. 2020; Vithanage et al. 2017). However, it has been observed that surface modification is essential to improve the As decontamination from the soil using biochar (Vithanage et al. 2017). Various approaches such as alkali and acid treatment, amination, functionalization using surfactants, mineral incorporation, magnetic modification have been used for this purpose (Rajapaksha et al. 2016).

### *7.5.1 Use of Non-Activated Biochar for As Removal in Soil*

Soils contaminated with multiple metals (co-contaminated sites) and metalloids are found to be extremely difficult to decontaminate as each metal component will require different treatment strategies. However, in some studies, the use of stinging nettles (*Urtica dioica L.*) derived biochar which is known to have a high metal sorption

**Table 7.1** Different feedstock used for the generation of biochar targteing their application in As removal in aqeuous solutions

| Source | pH | As (III) removal mg/g | As (V) removal mg/g | Mechanism of removal | References |
|---|---|---|---|---|---|
| Japanese Oak wood | 7 and 6 | 0.041–1.81 | 0.045–1.99 | Langmuir isotherm model via surface adsorption (complex redox transformation and strong interaction with surface functional groups) | Niazi et al. (2018a) |
| *Eucalyptus* wood | 10 | 0.1086 | 0.1086 | Homogeneous (monolayer) adsorption explained by Langmuir isotherm model | Ayaz et al. (2022) |
| Sewage sluge derived biochar (SS) | 6.7–7 | – | 0.00425 | Interactions of arsenate anion with the oxidesand higher ash content in biochar solid matrix, sorption isotherms being fitted to Freundlich model | Agrafioti et al. (2014) |
| Rice husk derived biochar (RH) | 6.7–7 | – | 0.00259 | | |
| Solid waste derived biochar (SW) | 6.7–7 | – | 0.00354 | | |
| Perilla leaf | 7–10 | 4.71 ± 1.04 (BC300)<br>11.01 ± 1.51 (BC700) | 3.85 ± 0.58 (BC300)<br>7.21 ± 0.80 (BC700) | Surface complexation/precipitation dominated As removal where the sorption can be explained by Langmuir and Dubininin-Redushkevich models | Niazi et al. (2018b) |
| Municipal solid waste derived biochar | 2.5–7 | – | 24.49 (pristine biochar)<br>30.98 (2 M KOH activated biochar) | Functional groups such as carboxylic and phenolic groups on the surface of activated biochars enhancing the As (V) removal, of which the removal pattern is explained by the Langmuir model | Jin et al. (2014) |

(continued)

**Table 7.1** (continued)

| Source | pH | As (III) removal mg/g | As (V) removal mg/g | Mechanism of removal | References |
|---|---|---|---|---|---|
| Paper Mill Sludge derived biochar | 6.2 | – | 22.8 | Arsenate ions tend to adsorb via electrostatic attraction via the formation of a ternary cation–anion-surface complex and co-precipitation, especially in the presence of $Fe_3O_4$ | Yoon et al. (2017) |
| Oak bark, pine bark, oak wood, and pine wood chars | 3–4 | 7.40<br>12.15<br>5.85<br>1.20 | – | Calcium together with other light metals takes part in ion exchange reactions resulting in higher adsorption capacity | Mohan et al. (2007) |
| Green seaweed (*Ulva reticulata*) derived biochar | 4.0 | – | 7.67 | Occurrence of protonated functional groups on surface of biochar due to the accumulation of surplus of $H^+$ ions thereby increasing electrostatic attraction with the arsenate ions where the sorption isotherms have been explained via Toth, Redlich–Peterson, Langmuir and Freundlich isotherm models | Senthilkumar et al. (2020) |

(continued)

**Table 7.1** (continued)

| Source | pH | As (III) removal mg/g | As (V) removal mg/g | Mechanism of removal | References |
|---|---|---|---|---|---|
| Waste date palm leaves derived Fe-modified biochar (Fe-BC) | 5 | – | 0.962 | Electrostatic interaction between the positively charged surface of Fe-BC-500 and anionic As species of which the sorption isotherms are explained well by Freundlich model | Kirmizakis et al. (2022) |
| Corn cob and coffee husk derived ZnO impregnated biochar (CC-ZnO) | 5.8–6.8 | – | 25.9 | Adsorption of arsenate ions via the attraction forces between the positive charge of CC-ZnO and the negatively charged arsenate where the adsorption isotherms are explained by Langmuir, Freundlich, Redlich-Peterson and Dubinnin-Raduskevich models | Cruz et al. (2020) |
| Corn straw derived biochar impregnated with iron | 2–8 | – | 14.77 | Adsorption of arsenate to the biochar surface, strong inner-sphere surface complexing with amorphous iron oxyhydroxide, and partial embedment of arsenate into the crystalline Fe oxides or carbonized phase where the adsorption isotherms are explained by Langmuir model | Fan et al. (2018) |

(continued)

**Table 7.1** (continued)

| Source | pH | As (III) removal mg/g | As (V) removal mg/g | Mechanism of removal | References |
|---|---|---|---|---|---|
| Cotton wood derived magentic biochar | Not mentioned | | 3.147 | Monodentate or bidentate adsorption of As(V) to metal oxide surfaces through surface complexation reactions where the monolayer adsorption could be described with Langmuir model | Zhang et al. (2013) |
| Pine wood derived magnetic biochar (HPB) and pine wood biochar (PB) | 7 | – | 0. 4287 (HPB)<br>0. 2652 (PB) | $HAsO_4^{2-}$ interacts with the positively charged functional groups on both PB and HPB surfaces through electrostatic attractions. Furthermore, the surface functional groups of α-$Fe_2O_3$ will also allow the As(V) interactions | Wang et al. (2015a) |
| Bamboo derived magentic biochar (BC-Fe) | 5<br>7<br>9 | – | 7.5<br>8.2<br>8.4 | Electrostatic interactions, hydrogen bonding and weak chemisorption to phenolic compounds in BC | Alchouron et al. (2021) |

(continued)

**Table 7.1** (continued)

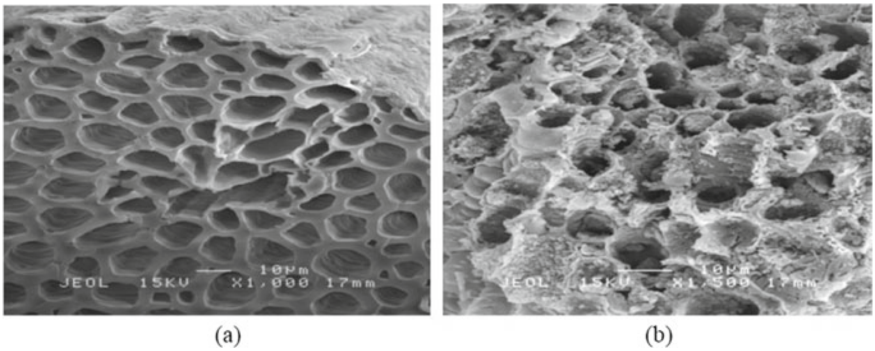
| Source | pH | As (III) removal mg/g | As (V) removal mg/g | Mechanism of removal | References |
|---|---|---|---|---|---|
| Magnetic biochar from waste wood pristine biochar (PB) modifed biochar (1FeC) and 1Fe2MnC | 9–11<br>11<br>3 | 0.18<br>1.0<br>0.90 | – | Physical interaction of As(III) with the pores in the biochar, hydrogen bonding with biochar surface, and modified biochar has major elements such as Mn oxidizing As(III) to As(V) and Fe triggering the bridging of As (III) to biochar surface where the sorption characteristics are explained by Langmuir model | Chen et al. (2021) |
| Sesbania bispinosa biochar (SBC) with CuO (SBC/CuO) and MnO (SBC/MnO | 4 | | 7.33<br>12.47<br>7.34 | Adsorbent surface is becoming positively charged at pH 4 which favors the attachment of As ions by electrostatic attraction of which the sorption mechanism is explained by Freundlich isotherm model | Imran et al. (2021) |

capacity, along with iron filling, has given rise to reduced Cu and As leaching in to the soil while degrading the organic contaminants, re-vegetating the soil and triggering the sunflower growth in the same site (Sneath et al. 2013).

Among different feedstocks for biochar generation, empty fruit bunches (EFB) have been the ideal source for biochar production. EFB has been effectively used for the cost-effective, eco-friendly removal of As species from the soil environments (Sari et al. 2014). In these studies, analyzing the physical and chemical properties of biochar produced from EFBs has received a great deal of interest as they solely define the performance of the biochar. Morphologically, EFBs have a rigid porous structure with more mesopores (Fig. 7.5). Chemically they were enriched with high carbon content compared to the biochar derived from rice husks (RHs). In addition, to higher carbon content, both were found to be alkaline, while elemental composition analysis indicated the presence of N, P, K, Ca and Mg in trace amounts. Both EFB and RH biochar have numerous surface functional groups, while RHs derived biochar was rich with higher silica content. Authors claim that due to these beneficial physicochemical factors, both EFB and RH derived biochar have exhibited excellent As and Cd adsorption capacities (values given in Table 7.2), making them ideal adsorbents in removing heavy metals in contaminated soil (Sari et al. 2014).

In another study, orchard prune residues combusted biochar has been used to increase the As concentration in pore water (500–2000 $\mu$g $L^{-1}$), increasing the solubility and mobility of As while reducing the plant uptake which has been studied using a pot experiment of tomato (*Solanum lycopersicum L.*) plantlets (Beesley et al. 2013).

Jun et al., in their study, has attempted to use lychee biochar for the remediation of a cocktail of metal ions such as Pb, Cd, As, and Zn from soil using sunflower (*Helianthus annuus*). In here, various percentages of lychee biochar (2.5%, 5% and 10%) have been applied to reduce the As accumulation in the soil of the Shuikoushan mining area, Hunan Province, China. More importantly, these biochar has triggered



(a) (b)

**Fig. 7.5** SEM images of **a** EFB biochar and **b** RH biochar exhibiting mesoporous structure which have been utilized for As removal in soil. (Reprinted with the permission from Sari et al. (2014), Copyright creative commons attribution (CC BY) license))

**Table 7.2** Different feedstock used for the generation of biochar targeting its' application in As remediation in soil

| Source | pH | As removal ability | Soil remediation mechanism | References |
|---|---|---|---|---|
| Empty fruit bunch (EFB) and rice husk (RH) derived biochar | 9.47<br>10.24 | 0.4240 mg/g<br>0.3522 mg/g | The alkaline properties of biochars led to the increase of the solution pH, which in turn has induced metal immobilization through metal precipitation while decreasing the metal solubility in the soil<br>The formation of functional groups Especially COOH and aromatic—OH during oxidation has triggered the complexation of arsenates with the biochar surfaces | Sari et al. (2014) |
| Biochar derived from lychee branches | 4.38 | Reducing the As content by 4.35% in the rhizosphere | Large specific surface area and strong adsorption capacity of Lychee biochar triggering the bioaccumulation of As specifically in the leaf and receptacle of sun flower plants (acting as a soil amendment) and stimulating the sunflower plant growth | Keerthanan et al. (2020) |
| Manure waste derived biochar | 8.10 | Initial soil contained As concentration of 180 mg/kg which has been reduced to 108 ± 6 mg/kg | Increase the phytoextraction of As by *Brassica napus* by triggering its' growth due to the higher surface area, porous nature of the biochar | Gascó et al. (2019) |

(continued)

**Table 7.2** (continued)

| Source | pH | As removal ability | Soil remediation mechanism | References |
|---|---|---|---|---|
| Palm (iron modified) biochar | 4–5 | The Fe-BC treatment significantly decreased concentrations of extractable As by 15.7% to 25.8% | As: 22.6 mg/kg Increased the soil pH; decreased available As and available Cd in the soil; reduced the accumulation of As and Cd in rice grains | Pan et al. (2019) |
| Rice straw derived biochar modified with Fe-oxyhydroxy sulfate (Biochar-FeOS), $FeCl_3$ (Biochar-$FeCl_3$), and zero-valent iron (Biochar-Fe) | 6–7 | 122.4 mg/kg was the initial As concentration in the field and the addition of Biochar-FeOS, Biochar-$FeCl_3$, and Biochar-Fe, decreased the extractable As in soils by 13.95–30.35%, 10.97–28.39%, and 17.98–35.18%, respectively | Amorphous and poorly crystalline hydrous oxides of Fe improves the As binding as well as ferrous materials increase the specific adsorption sites and facilitate the electrostatic interactions between As and the adsorbent surface | Wu et al. (2018) |
| Corn stalks derived iron (Fe), manganese (Mn), cerium (Ce) modified biochar | 9.72 | 138.0 ± 2.4 mg/Kg 33.0 ± 0.31 mg/Kg was the range of As in highly and low contaminated soils being reduced to residual As by 10.23% | Enhancing the redox potential of the soil, also to trap As as specifically or non-specifically bound forms of into amorphous hydrous oxide and crystalline hydrous oxides | Zhang et al. (2020) |
| Iron (Fe)-modified biochar (FeBC) derived from *Platanus orientalis* Linn branches | 6–7 | FeBC significantly decreased the As concentration concentration of As in the soil by 41.7 and 38.8%, under continuously flooded (CF) and alternatively wet and dry (AWD) conditions. Further the As concentration in rice straw and brown rice by 61.5% and 73.2% respectively under AWD conditions | Immobilization of As by Fe compounds, via the formation of amorphous Fe (III)-arsenate compounds | Wen et al. (2021) |

(continued)

**Table 7.2** (continued)

| Source | pH | As removal ability | Soil remediation mechanism | References |
|---|---|---|---|---|
| Calcium-based magnetic biochar (Ca-MBC) derived from rice straw | 6–7 | Lowering the extractable As by 26% | Ca-MBC could transform the unstable fraction of As into a stable fraction through the elevation of pH and cation exchange capacity as well as through the formation of bi-dentate chelate and ternary surface complexes on the surface of iron oxide, in addition porous biochar structure also enhances the adsorption of As further triggering the the bacterial colonization and thereby the stabilization of As | Wu et al. (2020) |
| Wheat straw derived goethite-modified biochar (GB) | 7.99 | As (1.57 mg $kg^{-1}$) sequestration has been taken place due to 1.5% GB, Further it has abridged the As content in the rice roots and shoots by 32.2% and 46.6% respectively compared to the control | Fe-plaque formation boosting the As sequestration and minimizing the accumulation of As in rice roots and shoots<br>High surface area, alkaline nature, and high cation exchange capacity (CEC) of biochar has further favored metal precipitation, decrease metal solubility and promote metal adsorption on the surface. This has been further triggered by the surface functional groups of goethite | Irshad et al. (2020) |

(continued)

**Table 7.2** (continued)

| Source | pH | As removal ability | Soil remediation mechanism | References |
|---|---|---|---|---|
| Corncob derived organic and inorganic modified biochar | 7–8 | The leaching concentration of As in biochar treated soil was reduced from 162.5 to 45.45 µg/L (72.03%) within 30 days | After biochar addition, elements such as Ca, Mg, and K found on biochar adsorption sites can be released and replaced with heavy metals such as As. Further the oxygen-containing functional groups and average pore size of biochar has also triggered the As adsroption | Luo et al. (2020) |

the bioaccumulation of As up to 67.9–110% in leaves and receptacles of sunflower plants while reducing the As content by 4.35% in the rhizosphere (Keerthanan et al. 2020).

In another study, manure waste-derived biochar has been employed for As remediation of mining soil in Riotinto- Spain. Here the researchers have utilized rabbit manure for the preparation of biochar by subjecting it to two temperature treatments at 450 °C (BM450) and 600 °C (BM600). These biochar in 10% weight has been then incubated for 60 days in the presence of and absence of *Brassica napus* aiming to trigger the phytoremediation. The obtained results have then confirmed that the combination of BM450 or BM600 with *Brassica napus* decreased the amount of As and other coexisting heavy metals in the soil (Gascó et al. 2019).

Acidic agricultural soils contaminated with As have also been attempted to decontaminate and neutralize using biochar derived from buffalo weed *A. trifida L. var. trifida*. Since these biochar materials have been very much alkaline in nature, their addition to soils has led to the recovery of soil quality, also suggests a decrease of 50% of bioaccumulation of As into the plants. The formation of As-Ca and As-carbonate complexes was found to be the driving mechanism in the precipitation of As in soil making buffalo weed derived biochar an excellent soil amendment (Koh et al. 2016).

### 7.5.2 Use of Activated Biochar for As Removal in Soil

The activation process of biochar would generally lead to the increased performance of biochar in soil remediation purposes as well as would provide environmental benefits (Rajapaksha et al. 2016). Among different biochar composites, Pan et al., in their work, have utilized palm thread derived Fe blended biochar to reduce the simultaneous mobility of As and Cd in the soil. Generally, it is believed that under flood conditions, the mobility of Cd is decreased while that of As is increased. However, in this study the combinational application of biochar along with zero-valent Fe (Fe-BC) and silica sol have hugely contributed to reducing the accumulation of As and Cd in rice grains which has been verified by conducting a 2-year field trial (Pan et al. 2019). Compared with other crops, paddy rice (*Oryza sativa L.*) has a higher prevalence of Cd and As uptake and translocation, encouraging a significant proportion of heavy metals being transferred from soil to grain, leading to an accumulation that could ultimately provide a public health threat (Yin et al. 2017). Similar studies have also been conducted in many research groups to minimize the translocation of As from contaminated soil (Yin et al. 2017).

Apart from the use of zero-valent iron, several other studies have also focused on the use of iron-based composite biochar materials for the remediation of As contaminated paddy soils and to reduce its' accumulation via food chains. The use of Fe-oxyhydroxy sulfate biochar (Biochar-FeOS), $FeCl_3$ bound biochar (Biochar-$FeCl_3$) are some of them (Wu et al. 2018).

In another study conducted by Zhang et al., biochar generated from corn stalks has been modified with iron (Fe), manganese (Mn), cerium (Ce) to produce a biochar composite (FMCBCs) to reduce the bioavailability of As in paddy soil. In here, researchers have focused more on exploring the oxidation–reduction status of the soil affecting the oxidation state of As, its effect on the microbial activity, and the soil enzyme activity. The results have indicated that this biochar composite could alter the redox potential of the soil, making the As (III) to get oxidized into As(V) via enhancing the redox potential of the soil, also trapping As as specifically or non-specifically bound forms into amorphous hydrous oxide and crystalline hydrous oxides. Furthermore, it has been also observed that the treatment of contaminated soil with FMCBCs would lead to increased urease, catalase, alkaline phosphatase and peroxidase like soil enzymes while triggering the abundance of soil microbacteria and making a suitable environment for microbial growth (Zhang et al. 2020).

Similar studies have also been conducted for the purpose of simultaneous removal of arsenic, cadmium, and lead from soil by iron-modified magnetic biochar (Qiao et al. 2018; Wan et al. 2020; Li et al. 2021; Wen et al. 2021; Wu et al. 2020; Irshad et al. 2020).

Apart from the use of iron modified biochar for As remediation, some research groups have also attempted to utilize corncob derived acrylonitrile and nano $TiO_2$ modified biochar to reduce the As contamination in yellow soil and cinnamon soil. As depicted in Fig. 7.6, these biochar materials have been produced by treating raw corn cobs at 350 °C, and 550 °C with devoid of oxygen which has been later on treated with acrylonitrile and nano$TiO_2$. The larger surface area, higher porosity, and abundant organic matter have led to the successful immobilization of As from the soil (Luo et al. 2020).

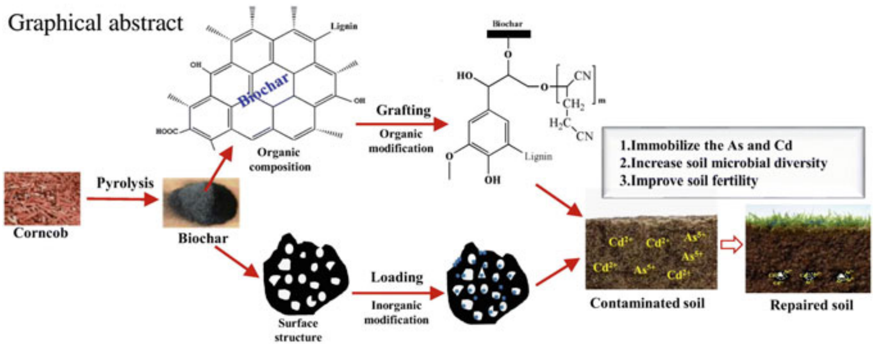


**Fig. 7.6** Production of corncob derived organic and inorganic modified biochar for As remediation in Beijing Cinnamon soil and Guiyang yellow soil (Reprinted with the permission from Luo et al. (2020), Copyright 2020 Elsevier Ltd)

## 7.6 Limitations

The adsorption capacity of pristine or unmodified biochar for As removal is usually low because of the negative charge on its surface. Therefore, pre-treatment of biochar is essential to develop modified biochars with high As removal ability. Various reagents can be used for the acid activation of biochar. However, using hazardous reagents, such as sulfuric acid and nitric acid, can be problematic (Amen et al. 2020). Using a more environmentally friendly acid such as Phosphoric acid may be more beneficial than using hazardous chemicals.

Several different factors affect the efficiency of As removal by biochar-based sorbents. The use of biochar in optimal doses is an important factor for maximum removal of As from water. Increasing the biochar dose above the optimum limit could reduce its sorption efficiency. According to Verma and Singh (2019), when adsorbent doses increase above the optimal level, the adsorption capacities of biochar decrease. This could be attributed to the reduction of active functional sites on the surface of the adsorbent.

The pyrolysis process greatly affects the quality of biochar. The process and process parameters, such as temperature and furnace residence time, are critical parameters that determine the quality of the final product. The process and process conditions also depend on the feedstock type in determining the nature of the product (Sohi et al. 2009). These factors could influence the properties of biochar, limiting the potential use of biochar in environmental remediation.

Biochar experiments are usually carried out in a controlled setup at a laboratory. In real life environmental remediation activities, various other elements may compete with As for sorption on the surface of biochar (Amen et al. 2020). These factors should be considered when carrying out real-life environmental remediation of As contaminated water using biochar-based sorbents. A number of studies have also been conducted on the harmful substances in biochar and their potential negative impact on the environment. The toxic effect of biochar is determined by the type of biochar (especially the feedstock used and pyrolysis temperature) and contaminants. The pH, electrical conductivity, polycyclic aromatic hydrocarbons and heavy metals are the main factors responsible for biochar toxicity (Godlewska et al. 2021). However, more systematic environmental risk assessments are needed to evaluate the effect of potentially harmful chemical contaminants associated with pyrolysis and toxic substances within feedstocks to assess the risk of biochar applications. Given the stability of biochar, safe rates of applications need to be determined for different environmental media to avoid possible detrimental effects on soil and water (Sohi et al. 2009).

The regeneration capacity for a certain number of sorption/ desorption cycles and reuse ability is essential for the economic viability of biochar applications. However the regenerated biochar based sorbents may not remove As as efficiently as before due to the loss of effective functional groups or impregnated particles from the surface of biochars (Zhu et al. 2020). Moreover, retrieval of As from biochar is still a challenge and should be thoroughly assessed before applying biochar as a viable sorbent for treating wastewater. Finally, after the product reaches the end of its lifecycle, it is important to develop sustainable methods for the management and safe disposal of the spent biochar (Amen et al. 2020).

## 7.7 Conclusions

Researchers have reported different strategies to remove As from contaminated environmental media. Adsorption is probably the most effective and promising method for remediating polluted soil and water ecosystems and removing As. Different adsorbents such as activated charcoal/carbon, activated alumina, zeolites, clay materials, metal oxides, carbon nanotubes, graphene-based materials, biochar, etc., have been successfully used to remove As species.

Biochar is a renewable carbon material. It can be used as an economically viable sustainable solution to remove As species with excellent adsorption capacities. Various types of feedstocks, such as rice husk, solid waste, perilla leaves, pinewood, Japanese oak wood, sewage sludge and paper mill sludge, can be used for biochar production. The use of medicinal or food plant waste materials for biochar generation and use of them for remediation of As-contaminated water has also gained some attention as a cost-effective, sustainable way of removing As. Magnetic biochar is another widely investigated activated biochar material for the removal of As from aqueous solutions.

Biochar has favorable physio-chemical surface characteristics, especially the sensitivity to pH, the presence of functional groups that trigger the complexation, reduction, cation exchange, electrostatic attraction and precipitation of arsenic species. Further, there is an extensive availability of feedstock for biochar production. However, surface modification is essential to improve the As decontamination from the soil using biochar. Various approaches such as alkali and acid treatment, amination, functionalization using surfactants, mineral incorporation, magnetic modification have been used for surface modification.

Biochar experiments are, in most cases, carried out on a laboratory scale. In real-life environmental conditions, various other elements may compete with As for sorption on the surface of biochar. These factors should be considered when carrying out environmental remediation of As contaminated water using biochar-based sorbents. Further, attention needs to be given to the potentially harmful substances such as polycyclic aromatic hydrocarbons and heavy metals in biochar and their negative impact on the environment. More systematic environmental risk assessments are needed to evaluate the effect of potentially harmful contaminants associated with pyrolysis and toxic substances within feedstocks to assess the risk of biochar applications. The regeneration capacity of biochar is also important for the material circularity and sustainability of the application. Finally, sustainable methods for the management and safe disposal of the spent biochar need to be developed.

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# Chapter 8
# Accumulation and Translocation of Arsenic in Rice with Its Distributional Flow During Cooking: A Study in West Bengal, India

**Antara Das, Nilanjana Roy Chowdhury, Deepanjan Mridha, Madhurima Joardar, Ayan De, Sharmistha Majumder, and Tarit Roychowdhury**

**Abstract** Rice is a staple food in most of the Asian countries and arsenic contamination in rice grain as well as cooked rice is one of the most distressing subjects in recent times. Arsenic translocates in rice plants in a descending manner from root to stem followed by leaf and grain. The present study finds the same descending translocation pattern in paddy grains of a single pedicel of paddy plants in both the arsenic exposed and control sites. The distribution of arsenic gets reduced with height, i.e. paddy grains located in the top part of a pedicel accumulates lowest amount of arsenic. Average arsenic concentration is found to be highest in the rice grains of lower part of the pedicels (272, 205 and 162 μg/kg) followed by middle (257, 176 and 156 μg/kg) and top (220, 162 and 115 μg/kg), respectively in exposed fields (Teghoria and Madhusudankathi) and control field (Pingla). The average decrease percentage of arsenic in whole paddy grains of a single pedicel from lower part to top is found to be 17.6% which is less than the control site (34%). The present study also showed the distribution variation of arsenic concentration and content among different parts of a whole paddy grain. The ratio of average arsenic concentration between rice grain and rice husk (1.15) is observed to be higher compared to the ratio of their average arsenic content (0.26). Interaction of micronutrients (zinc and selenium) present in rice grain has also been studied in comparison to arsenic. This study is also important for understanding the degree of arsenic exposure through consumption of cooked rice. Cooked rice arsenic concentration is governed by several factors where cooking water arsenic concentration plays a major role determining the flow of arsenic between rice and water. The present study observed that arsenic released from cooked rice to water during cooking with five differently arsenic concentrated waters; however, the rate of arsenic discharge percentage got decreased with increasing water arsenic concentration. The reduction percentage of arsenic from cooked rice to water was also found to be variety and cultivar dependent. Therefore, at domestic level, it

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is recommended to cook rice with arsenic safe water with proper and regular water quality monitoring.

**Keywords** Arsenic · Distribution · Rice grain · Cooked rice · Micronutrients

## 8.1 Introduction

Arsenic is a toxic metalloid and scientifically known as a Group 1 carcinogen (ATSDR 2007; IARC 2012). Arsenic contamination in drinking water is a prolonged health threat in India, Bangladesh and many other East-Asian countries (Chakraborti et al. 2013, 2018; Smedley 2005). In West Bengal, millions of people covering the districts Malda, Murshidabad, Nadia, North 24 Parganas and South 24 Parganas are affected with arsenic toxicity (Das et al. 2021a; Joardar et al. 2021a; Santra et al. 2013). Arsenic enters into groundwater due to its natural release from arsenic enriched sedimented aquifers (Chakraborty et al. 2015; Polya and Charlet 2009). As a consequence, arsenic poisons the entire crop cultivation system through contaminated irrigational water (Chowdhury et al. 2018a; Das et al. 2021a). Studies showed that irrigational water contains huge amount of arsenic in paddy fields like (<3–990 μg/l) in Raninagar-II block, Murshidabad; (74–301 μg/l) in Deganga block, North 24 Parganas; and (171–493 μg/l) in Gaighata block, North 24 Parganas districts (Chowdhury et al. 2018a; 2020a; Das et al. 2021a). A recent study showed that about 12.5 tonnes of arsenic is withdrawn annually through irrigational water from Raninagar-II block located in Murshidabad district (Das et al. 2021a). The direct effect of deposited arsenic on soil as well as groundwater showed that bio-accumulation of arsenic in rice grain (1.78), which is higher than the hyper-accumulation factor (Das et al. 2021a).Therefore, both the arsenic contaminated drinking water and foodstuffs cause adverse health effects to the inhabitants of the arsenic exposed areas (Joardar et al. 2021a; Mondal et al. 2021; Roychowdhury 2008). Arsenic in rice grain varies with cultivation season, background water and soil characteristics, rice cultivars etc. (Chowdhury et al. 2018a; 2020a). A maximum arsenic concentration of 200 μg/kg has been suggested for inorganic arsenic in polished rice by Codex Alimentarius, a body made by the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO) (Codex Alimentarius Commission 2014). Although, Meharget al. (2006) briefed that rice with inorganic arsenic concentrationover100 μg/kg starts to impose cancer risk in arsenic affected countries. Being a staple crop, maximum population from the Eastern-Asian countries, especially Bengal delta, relies on rice and rice based foods (Chowdhury et al. 2018b; Islam et al. 2017; Rahman et al. 2008). Arsenic accumulation in cooked rice is also a matter of concern where arsenic concentration depends on cooking water, cooking method, rice variety and rice-water ratio etc. (Chowdhury et al. 2020b; Mandal et al. 2019; Ohno et al. 2009; Rahman and Hasegawa 2011). Even, the domestic livestock in the rural Bengal are also fed with arsenic contaminated crushed rice grain, rice husk and gruel of cooked rice which results into deterioration of their health quality

(Das et al. 2021b). Consequently, arsenic pollutes the entire ecosystem starting from animal based food products to human to environment.

Bioavailability of arsenic in rice is highly reliant on arsenic species (Juhasz et al. 2006). Among the different arsenic species in rice varieties, it is proved that inorganic arsenic is more dominating in content than the organic one (DMA, MMA etc.) (Roychowdhury 2008; Williams et al. 2005) and arsenite (As III) prevails over arsenate (AsV) (Sinha and Bhattacharyya 2014). Dietary intake of arsenic contaminated rice grain on a regular basis in the arsenic exposed areas gives rise to high health risk (Chowdhury et al. 2020b; Joardar et al. 2021a). Even, significant amount of cancer and non-cancer risk is present in adults and children from rice grain in those populations who consume safe drinking water (Biswas et al. 2019; Joardar et al. 2021a, b).

Rice grain arsenic contamination followed by human exposure through consumption of arsenic contaminated cooked rice is a worldwide health concern. The translocation of arsenic is in descending order from root to stem and leaf to edible parts. Rice grain accumulates least amount of arsenic in comparison to all the other parts of the paddy plant. However, distribution and translocation of arsenic in paddy grains from a single paddy plant and different parts of paddy grain are topics of research interest. The present study has been focused on the accumulation and translocation pattern of arsenic in different paddy grains located in single pedicel height wise (low, mid and top positions). The study further investigates the distribution of arsenic concentration and content among different parts of a whole paddy grain like whole grain, rice grain and rice husk. Interaction of different micronutrients like zinc and selenium with variable arsenic concentration in rice grain has been elucidated. This study has of immense importance to understand the degree of arsenic exposure through consumption of cooked rice.

## 8.2 Materials and Methods

### *8.2.1 Study Area*

Paddy fields located in Teghoria (22°54′24.53″N, 88°47′47.26″E) and Madhusudankati (22°54′14.51″N, 88°46′25.36″E) village of Gaighata block, North 24 Parganas district of West Bengal have been selected for the arsenic exposed sites whereas paddy fields in Madhyabar village (22°14′47.76″ N, 87°32′50.83″ E) of Pingla block, West Medinipur district has been chosen for control sitein the present study according to the arsenic concentration in groundwater (Chakraborti et al. 2013; Chowdhury et al. 2020a). Gaighata has earlier been reported as one of the severely arsenic affected block out of the 107 arsenic-affected blocks in West Bengal (Roychowdhury 2010).

### 8.2.2 *Sample Collection, Preparation and Preservation*

Rice grain samples were collected from the farmers of the selected paddy fields in the above mentioned districts. Whole paddy grain samples were collected directly from the paddy fields. For the study of translocation of arsenic in pedicels, paddy grains were manually divided into three different parts according to height. Cooked rice and gruel (discarded water from cooked rice) samples were collected from the local families during their time of cooking. During sample collection, information about the samples has been gathered locally e.g. source, type of grain, cultivar, variety etc. The rice grain and cooked rice samples were brought to the laboratory in individual polyethylene zip-locks. Each water samples used for rice cooking were collected in sterile polyethylene containers and preserved by adding 0.1% (v/v) concentrated nitric acid (appx. 7.0 M) and stored at 4 °C until analysis. Gruel samples were also collected separately in clean polyethylene containers and stored for analysis. Details of sample collection, preservation, and sample preparation process were described in our previous publications (Chowdhury et al. 2018a, 2020a).

### 8.2.3 *Chemicals and Reagents*

Concentrated nitric acid ($HNO_3$, 69%) and hydrogen peroxide ($H_2O_2$, 30% v/v) were used for digestion of the solid samples. 10% of potassium iodide (aqueous KI) solution and 8% of concentrated hydrochloric acid (HCl) solution were added during sample preparation (5–10 ml) and the mixed solution was kept 45 min for settling down before analysis of arsenic. About 0.6% sodium borohydride ($NaBH_4$) (in 0.5% NaOH) and 5–10 M HCl were used (both from Merck, Mumbai, India) for estimation of total arsenic concentration. All the chemicals and reagents used in this study were of analytical grade. Double distilled water was used throughout the analytical work.

### 8.2.4 *Digestion and Estimation of Arsenic*

Approximately 0.2 g of the solid (rice grain and cooked rice) samples were digested with a mixture solution of concentrated $HNO_3$ and $H_2O_2$ solution in 2:1 in Teflon bomb at 120 °C for 6 h inside hot air oven. The volume of the digested solution was reduced through evaporation by placing it on the hot plate at about 90 °C for 1 h. The evaporated samples were made up to a volume of 2 to 5 ml with double distilled water and filtered through a suction filter of diameter 0.45 $\mu$m. The filtrate solutions were then preserved at room temperature to analyze total arsenic concentration. Detailed information of the digestion methodology has been described elsewhere (Chowdhury et al. 2018a, b). The semi-liquid gruel samples were also processed in the same way for digestion. No digestion process was followed for water samples. Arsenic estimation of the procured samples was done by Hydride Generation Atomic Absorption Spectrophotometer (Varian AA140, USA) coupled with Vapor Generation Accessory (VGA-77, Agilent Technologies, Malaysia) with software version 5.1. Detailed information of the instrumentation of the HG-AAS system has been described in our previous publications (Chowdhury et al. 2020a, b; Das et al. 2021a, b).

### 8.2.5 *Micronutrient Analysis*

Micronutrients like selenium and zinc in digested rice grain samples were analyzed by using Perkin Elmer Elan-DRC-e Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) at the Central Environmental Science and Engineering Laboratory (CESEL), Nanyang Technological University, Singapore.

### 8.2.6 *Quality Control and Quality Assurance*

Quality control and quality assurance of the analytical work was maintained through digestion of 30% of the samples on hot plate using concentrated nitric acid ($HNO_3$, 69%) and hydrogen peroxide ($H_2O_2$, 30% v/v) in 2:1. Analytical results have been validated through estimation of standard reference material (SRM) i.e. Rice Flour 1568a (NIST, Gaithersburg, MD, USA) by both the methods of digestion. Analysis of arsenic in the SRM sample showed 94–96% and 80–84% recovery through Teflon bomb and hot plate digestion methods, respectively against its certified value of 0.29 μg/g. Quality assurance of the study was also checked through proper standardization, blank and spiked sample estimation and duplicate sample analysis (Chowdhury et al. 2018a, 2020a, b).

## 8.3 Results and Discussion

### 8.3.1 *Accumulation and Translocation of Arsenic in Different Parts of Whole Paddy Grain Located in Single Pedicel (Height Wise)*

Usually, rice is cultivated in two seasons throughout the Bengal delta; Boro cultivation (pre-monsoon) which occurs with natural groundwater and monsoon or Aman cultivation involving groundwater due to insufficient rainfall. West Bengal owns 5.8 million hectare area under rice cultivation which covers both irrigated and the rain-fed areas, with an average productivity of 2.6 tonnes/ha (https://www.thehindubusinessline.com/economy/agri-business/west-bengals-paddy-output-seen-higher-on-optimum-rains/article32416297.ece). The majority area under paddy cultivation in West Bengal is arsenic affected which results into the entry of arsenic in plant system from contaminated irrigational water and soil (Chowdhury et al. 2018a, b; Das et al. 2021a). Arsenic causes phyto-toxicity in paddy plants by accumulating in plant parts like root, shoot, grain etc. through translocation from the rhizosphere (Liu et al. 2006). Accumulation of arsenic in rice varies with growing area as well as cultivars and rice can absorb arsenic up to 10 times more than other crops (Williams et al. 2007). The average translocation factor for arsenic is approximately 0.8, higher than the other crops like barley (0.2) and wheat (0.1) (Kalita et al. 2018). It is established in many studies that translocation of arsenic follows a specific trend in paddy plant system, i.e. root > stem > leaf > pedicel > grain (Abedin et al. 2002; Roychowdhury 2008); however, the exact reason is still a subject of interest. The rule of translocation has been established using radioactive $As^{73}$ tracer where it is found that only about 3% of arsenic is accumulated in grains from roots (Zhao et al. 2012). Throughout our previous researches, in both arsenic contaminated and non-contaminated area, it is observed that arsenic is able to translocate from the roots to the grains, with concentrations decreasing by several orders of magnitude (Chowdhury et al. 2018a, 2020b). The present study investigates the accumulation and translocation pattern of arsenic in rice grains in a single pedicel of a paddy plant. Arsenic accumulation follows the exact trend from lower grains to the apex ones in both the arsenic exposed sites and control site (Fig. 8.1a). Rice grain arsenic concentration is apparently highest in Teghoria field (mean: 249 μg/kg, range: 169–407 μg/kg) than Madhusudankati (mean: 181 μg/kg, range: 130–244 μg/kg). Average concentration of arsenic is observed to be highest in rice grains from the lower part of the pedicels (272, 205 and 162 μg/kg) followed by middle (257, 176 and 156 μg/kg) and top part (220, 162 and 115 μg/kg), respectively in Teghoria, Madhusudankathi and Pingla fields (Fig. 8.1a). The translocation theory is also maintained for rice husk and whole paddy grains where husk contain more arsenic than whole paddy grains and rice grains. In the lower part of the pedicel, whole grain and rice husk average arsenic concentrations in the three consecutive fields are 307 and 888 μg/kg (range: 190–446 μg/kg and 469–1642 μg/kg), 230 and 570 μg/kg (range: 213–276 μg/kg and 470–779 μg/kg), and 176 and 390 μg/kg (range: 98.6–241 μg/kg and 301–508 μg/kg), respectively.

The decrease percentage of arsenic in paddy from lower part of the pedicel to the upper part is found to be higher in control sites compared to the exposed fields (Fig. 8.1b). In paddy fields from exposed area, the average linear decrease (−) of arsenic in whole paddy grains of a single pedicel from low to top is observed as 17.6% which is lower than control site fields (34%). The arsenic decline percentage from lower pedicel to top in rice grain and rice husk are 20.1%, 30.2% and 29%, 36% in exposed and control site, respectively (Fig. 8.1b). Similar findings were also observed by Chowdhury et al. (2020b) where arsenic translocation percentage from root to grain in final ripening phase was lower in exposed fields (0.0027%) compared

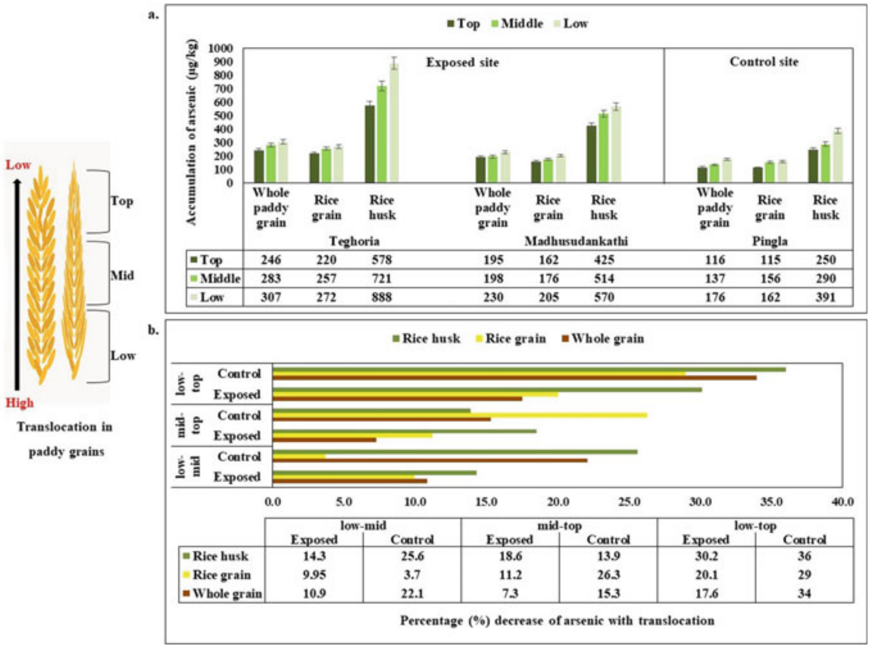

**Fig. 8.1** Translocation of arsenic in different parts of whole paddy grain located in single pedicel (height wise) and percentage (%) decrease of arsenic with translocation

to control fields (0.0215%). This might be due to the fact that rate of translocation is lower in exposed sites due to arsenic stress.

### *8.3.2 Arsenic Localization in Single Paddy Grain*

Variation of rice grain arsenic contamination with respect to cultivars and background water-soil concentration is already discussed in many researches (Chowdhury et al. 2018a, 2020b; Das et al. 2021b). Following the translocation theory, rice grain accumulates lowest amount of arsenic in a paddy plant, i.e. arsenic concentration in the rice system follows in the order of husk > whole grain > grain (Chowdhury et al. 2018b; Das et al. 2021a). Beside estimating human health risk from arsenic contaminated rice grain, evaluation of toxicity in livestock from arsenic contaminated rice husk is necessary too as it is a primary part of the living ecosystem (Das et al. 2021a). Analysis of seven cultivars of paddy grains collected from endemic site of West Bengal (North 24 Parganas district) also showed similar trend of metal accumulation (Fig. 8.2a) among which Ranjit cultivar showed highest accumulation in rice grain (649 µg/kg) and Masuri showed least accumulation (278 µg/kg). However, all

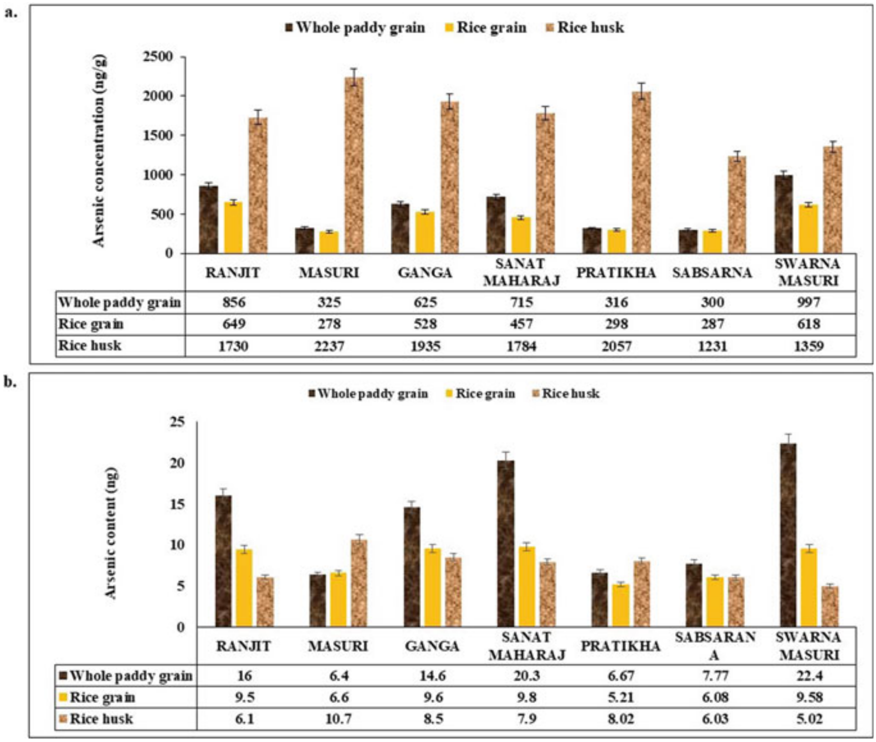

**Fig. 8.2** Variation of arsenic concentration and content in different parts of paddy grain

the cultivars accumulate higher level of arsenic than the maximum tolerable concentration of inorganic arsenic in rice (100 μg/kg) for human consumption in arsenic affected countries (Meharg et al. 2006).

Contrastingly when individual grains are counted, most of the cases, rice grains hold more arsenic content compared to husk. Ranjit, Ganga, Sanat Maharaj, Sabsarna and Swarnamasuri cultivars show that arsenic content is in the order of whole paddy grain > rice grain > rice husk (Fig. 8.2b). Individual whole paddy grain, its respective rice grain and rice husk contribute average dry weight of 0.0223 g, 0.0196 g and 0.0044 g, respectively which depicts that metal content assimilation is directly proportional to weight of the subject. While summative dry weights of a single rice grain and rice husk almost equal to that of a single whole paddy grain, whereas arsenic content scenario is not the same. The range ofdifference of the arsenic content between a whole paddy grain and a rice grain along with its husk is measured to be (−) 10.9 to (+) 7.8 ng (Fig. 8.2b). The ratio of arsenic concentration between rice grain and rice husk (average: 1.15, range: 0.61–1.90) is found to be more than that of the ratio of their arsenic content (average: 0.26, range: 0.13–0.45). However, regression analysis shows that both content and concentration between rice grain and husk are well coordinated; $R^2$ values are 0.87 and 0.83, respectively ($p < 0.05$). Significant correlation coefficient has also been observed between rice grain and its husk in both Boro ($r = 0.959$) and Aman rice ($r = 0.923$) (Bhattacharya et al. 2010). Arsenic is therefore localized more towards the inner side of a grain and the outer husk contains arsenic through surface adsorption. However, another report showed that arsenic is dispersed throughout the grain in white rice, the bulk of which comprises the endosperm and it is found to be selectively localized at the grain surface of brown rice analogous to the pericarp and aleurone layer (Meharg et al. 2008). XRF images of the study proved that arsenic was mainly located in the surface of the rice grains. Although, Lombi et al. (2009) showed high concentration of arsenic present in the aleurone and outer parts of the endosperm near the ovular vascular trace in rice grains. Arsenic localization study also reveals that brown rice contains more arsenic than white or polished rice which is the metal accumulation capacity of rice bran. Rice bran is reported with 10–20 fold higher arsenic concentration than found in bulk grain (Sun et al. 2008). Rahman et al. (2007) showed maximum arsenic concentrations in rice hull followed by bran-polish, brown rice, raw rice and polished rice. They showed that unpolished rice grains contain more arsenic than polished ones. Arsenic concentration was also higher in brown rice containing the outer layer of rice than white rice, shown by Yim et al. (2017). Kramar et al. (2017) also showed that polished rice available in the market contains lower arsenic concentration than the full grain because rice embryo has the highest arsenic concentration (upto 13,000 μg/kg).

### *8.3.3 Selenium and Zinc Along with Arsenic Distribution in Rice Grain*

Studies have been carried out to elucidate the interaction of different micronutrients along with variable arsenic concentration in rice grain. The present work on different variety of rice grain shows diversified arsenic changing patterns along with different micronutrient status. Therefore, the importance of Selenium (Se) and Zinc (Zn) concentration in the sunned and parboiled rice grains is discussed elaborately in this study. A significant regression of initial rice grain arsenic against initial rice grain Se and Zn was found in case of sunned rice grain ($n = 5$). The correlation between Se and Zn were slightly correlated with arsenic concentration of rice grain, which was examined by Pearson's test at the 95% level of confidence. Moreover, Pearson correlation analysis showed that the concentrations of Se ($r = -0.86$, $p < 0.05$)and Zn ($r = -0.21$, $p < 0.05$)in the sunned rice grain were significantly negatively correlated with arsenic concentrations. In the case of parboiled rice grain, both As and Se ($r = -0.76$) shows p value $< 0.05$ at 95% confidence level which clearly signifies a strong negative correlation. However, at the time of arsenic and Zn concentration, the relationship reciprocates an ambiguity ($r = 0.38$). The parboiled rice grain shows an abrupt asymmetrical ambiguous nature in arsenic and other element concentration. Previously it has been mentioned that parboiled rice grain obtained from sunned rice grain after two way boiling process, which include random application of contaminated water in arsenic exposed area, leads to huge arsenic deposition in rice grain (Chowdhury et al. 2018b) and it might be a reason for loss of different elements.

For most of the population, the chief source of Se is cereals. The staple cereal for Bengal delta is rice grain, which can accumulate Se from soil and integrate them into their tissue protein. Selenium status can vary from area to area according to its enrichment pattern globally (Duan et al. 2013). Surprisingly, the Se deficient regions usually overlap with arsenic contaminated site. In Bangladesh, a field survey propagated that Se concentration decreases with the increase of arsenic concentration and reciprocates an inversely proportional relationship between arsenic and Se (Malik et al. 2012). Selenium plays an antagonistic behavior in plant systems against a wide range of heavy metals like arsenic, cadmium, chromium, mercury etc. by inhibiting their translocation. For Asian population, rice is the primary source of Zn. Zinc concentration may vary with soil Zn concentration (Hels et al. 2003). In Bangladesh, surveys showed that Zn content is significantly decreased with increasing arsenic content in rice grains (Williams et al. 2009). The reported data deciphers that paddy soil arsenic concentration exacerbates entire soil-Zn deficiency in paddy plant. In contrast the Zn concentration interferes with arsenic detoxification by reducing arsenic methylation ability. Consequently, application of Zn in paddy soil, significantly reduce the soil arsenic level (Steinmaus et al. 2005).

### 8.3.4 Interpretation of Arsenic Flow at the Time of Cooked Rice Preparation

Arsenic toxicity is magnified through the consumption of contaminated cooked rice. The flow dynamics between arsenic contaminated rice grain and cooking water is a complex process. Accumulation of arsenic in cooked rice depends on several factors like rice cultivar, variety, arsenic concentration in raw rice grain and cooking water, cooking practice, cooking utensils etc. (Halder et al. 2012, 2014; Sengupta et al. 2006; Rahman and Hasegawa 2011). Presence of micronutrients or other minerals may also influence arsenic concentration in cooked rice or distribution of arsenic species (Batista et al. 2011; Chowdhury et al. 2020a; Mwale et al. 2018). Chowdhury et al. (2020a) showed that when rice is cooked with low (<3 μg/l) to moderately arsenic contaminated water (36–58 μg/l), arsenic releases from cooked rice grain to water; however, when cooked with higher than 80 μg/Lof arsenic concentrated water, arsenic is added in cooked rice from contaminated water (Fig. 8.3a). This study reported that maintaining an optimum arsenic concentration in cooking water is always necessary to determine the flow of arsenic between rice and water. However, no definite rule was followed in arsenic flow percentage for different varieties of rice grain (sunned and parboiled). Moreover, some rice cultivar like Nayanmoni, Saatswarna and Minikit showed higher threshold value of water arsenic accumulation during cooking (Chowdhury et al. 2020a).

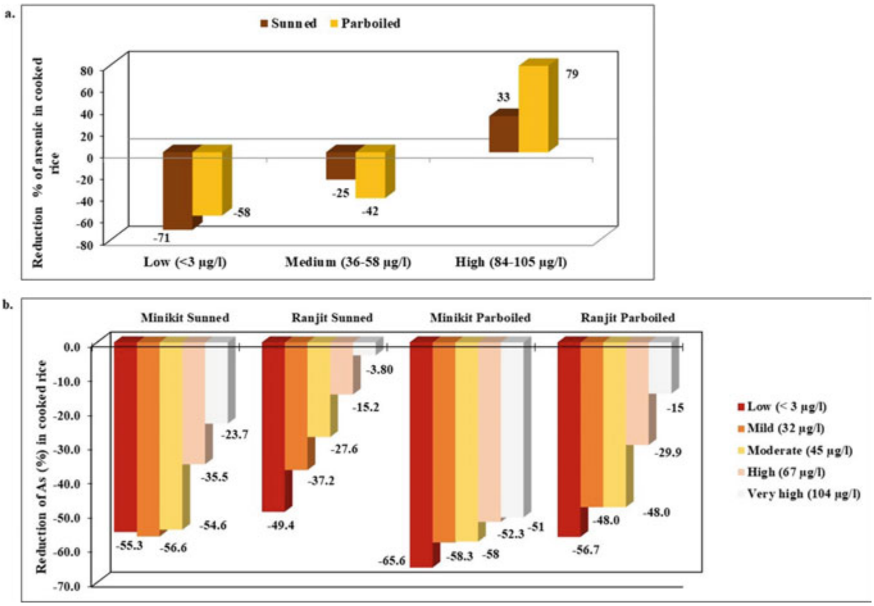

**Fig. 8.3** Flow of arsenic between rice grain and water: **a** Threshold value of water arsenic accumulation during cooking according to Chowdhury et al. (2020a), **b** Release of arsenic from cooked rice (with respect to cultivar and variety) during cooking with five different arsenic-concentrated water

In this context, the present study investigated the flow of arsenic during cooking depending on specific rice variety and cultivar. Both the sunned and parboiled varieties of rice grain of Minikit and Ranjit cultivars were cooked with five different arsenic concentrated water (<3, 32, 45, 67, and 104 µg/L). The study results showed that during cooking with the differently arsenic concentrated water, arsenic released from cooked rice to water; although the rate of release percentage got decreased with increasing water arsenic concentration (Fig. 8.3b). In each case, it was observed that highest percentage of arsenic was released from raw grain to cooked rice (55.3, 49.4, 65.6 and 56.7%) when cooked with < 3 µg/L of water arsenic concentration and lowest percentage of arsenic (23.7, 3.80, 51 and 15%) was released when cooked with 104 µg/L of water arsenic concentration in Minikit sunned, Ranjit sunned, Minikit parboiled and Ranjit parboiled, respectively. Therefore, the cooking water arsenic concentration and arsenic reduction percentage in cooked rice seems to be inversely proportional. During cooking, the average release capacity of arsenic in Minikit cultivar were 60.4, 57.5, 56.3, 43.9, and 37.4%, respectively which was comparatively higher than the Ranjit cultivar (53, 42.6, 37.8, 22.6, and 9.4%) for sunned and parboiled cooked rice. Similarly, arsenic (average) release potential was higher in parboiled varieties of cooked rice (61.2, 53.2, 53.1, 41.1, and 33%) than the cooked sunned variety of rice (52.3, 46.9, 41.1, 25.4, and 13.7%) for Minikit and Ranjit cultivars. It can be explained through the fact that the raw rice grain accumulates arsenic during a two-step boiling process of parboiling (Chowdhury et al. 2018b) which may be loosely bound around the outer part of rice and easily released during cooking. Cumulatively, Minikit parboiled rice grains showed maximum arsenic release potential during cooking with different arsenic concentrated water in the range of < 3–104 μg/l. This study also observed higher arsenic reduction percentage with higher arsenic concentration in raw rice grains. Arsenic release percentage from respective cooked rice was 45, 57, 26.6 and 39.5% in Minikit sunned, Minikit parboiled, Ranjit sunned and Ranjit parboiled rice while the initial arsenic concentration in these raw rice grains were 152, 384, 79 and 127 μg/kg, respectively (Fig. 8.4a). However, Chowdhury et al. (2020a) found that with higher initial arsenic concentration in raw rice, the percent increase of arsenic in cooked rice got lower even if the rice is cooked with contaminated water. The present study also observed the fact that the arsenic concentration in the gruel or discarded water increased with increasing cooking water arsenic concentration (Fig. 8.4b). Highest arsenic concentration was found in each of the rice grain's gruel (95, 182, 68.6 and 96 μg/kg) when cooked with 104 μg/l water arsenic. The study clearly revealed that water arsenic concentration has a significant effect on cooked rice arsenic concentration as well as the gruel arsenic concentration.

### *8.3.5 Arsenic Species Distribution in Rice Grain*

Arsenic is primarily speciated in rice grain as an inorganic form along with methylated species like dimethyl-arsinic acid (DMA) in a variable amount and little portion of monomethyl-arsonic acid (MMA) (Norton et al. 2009; Williams et al. 2005, 2006). Researches on arsenic metabolism and speciation study within the plant body, special reference to rice grain is still flourishing (Zhao et al. 2009). Abedin et al. (2002) reported that the accumulation rate of inorganic arsenic in paddy plant is much higher compared to methylated species like DMA or MMA. In the paddy root system, As (V) is converted into As (III) and translocated to paddy grain by xylem tissue through arsenite effluxer (Ma et al. 2008; Xu et al. 2008; Zhao et al. 2009). Other part of the research study says that arsenite might be detoxified by the formation of a complex with thiol rich peptides, includes phytochelatins (PCs) and glutathione into the vacuoles (Zhao et al. 2009). Methylated species of arsenic have much slower influx than the inorganic one in root system; however, they emerge in plant body more proficiently compared to others (Raab et al. 2007a). Raab et al. (2007b) postulated that this happens during translocation due to the lesser amount of complex formation of MMA and DMA along with their lower retardation capacity. Rice grain arsenic speciation is subjugated by inorganic arsenic and DMA (Williams et al. 2005). However, translocation of DMA was heavier in rice grain compared to inorganic arsenic as reported by Carey et al. (2010). By pursuing an arsenic speciation study on rice grain, Williams et al. 2005 reported that inorganic arsenic was predominantly found with a range of 64–81% in the samples of Europe, Bangladesh and India, where DMA was present as remnants. Several of our studies reported that inorganic arsenic (mainly arsenite and arsenate) contributed approximately 90% of

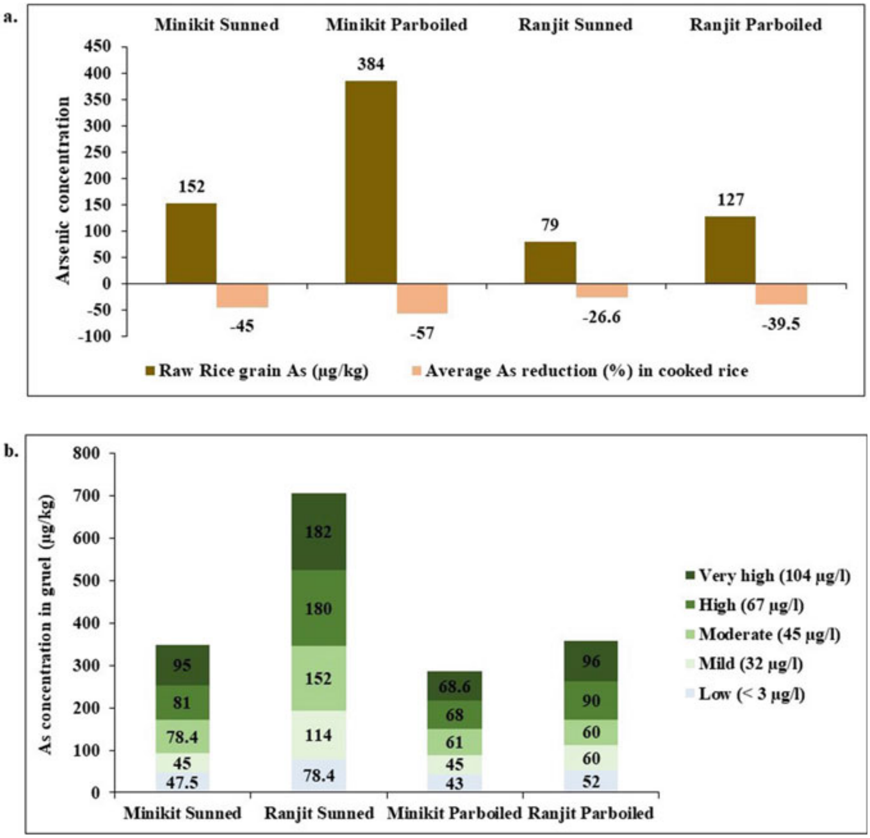

**Fig. 8.4** Flow of arsenic during cooking with respect to: **a** raw rice grain arsenic concentration, **b** gruel arsenic concentration

the total content of arsenic in rice grain and remaining was contributed by DMA (Biswas et al. 2019; Joardar et al. 2021b; Roychowdhury 2008). In another of our recent study, inorganic As contributed 100% and 93.8% in raw rice and respective cooked rice, when cooked with < 3 µg/L of arsenic contaminated water, whereas DMA contributed 6.2% in cooked rice (Chowdhury et al. 2020a). Whole plant study depicts that a lower concentration of DMA was found in rice shoots; however, astonishingly rice grain exhibits much higher amount of DMA (Abedin et al. 2002). Paddy plant has a remarkable role of unloading DMA into grain, because DMA is much transportable than inorganic arsenic via xylem and/or phloem. (Lombi et al. 2009; Tanaka et al. 2007).

## 8.4 Mitigation Strategies to Reduce Rice Grain Arsenic and Conclusive Remarks

The presence of inorganic arsenic species (arsenite or arsenate) in soil and water causes a phytotoxic effect when enters into the plant (Mridha et al. 2021). Management of irrigation water and different inorganic, organic amendments, nanoparticles and bio-chars were applied to mitigate the arsenic toxicity in soil–plant system. Priming of rice seed with K-humate and Se, significantly reduced As-mediated phyto-toxicity and enhanced plant growth under arsenic stress (Mridha et al. 2021). Under stress levels of 50 M arsenate and 50 M arsenite, the germination percentages in un primed seedlings were 65 and 58.3%, respectively. However, under arsenate and arsenite stress, germination percentages in K-humate primed seeds were 75 and 68.3%, correspondingly. Over the last decade, the impacts of various physicochemical and biological techniques on the work of arsenic reduction in rice grains have been widely explored. Alternative water management methods such as intermittent and aerobic irrigation regimes have been shown to reduce arsenic availability in the water-soil-rice system (Mukherjee et al. 2017; Rahaman and Sinha 2013). Different amendments (such as Fe and Mn) and nutrients (such as Si, $PO_4^{3-}$, S, and N) were applied to arsenic contaminated paddy soils to reduce arsenic accumulation in rice grains and the findings showed a significant reduction of arsenic in rice grains (Farrow et al. 2015; Li et al. 2019; Seyfferth et al. 2016). Apart from this, microbe inoculation and transgenic biological methods were also utilised to reduce arsenic accumulation in rice grains (Gustave et al. 2018; Li et al. 2016; Meng et al. 2011). Different metal oxide nanoparticles (CuO, ZnO, $MnO_2$ and $SiO_2$) were also used to reduce arsenic toxicity in rice plants (Liu et al. 2018; Ma et al. 2001). Furthermore, investigations have shown that Fe and/or Mn-modified bio-char enhances the development of root plaques, which increased the arsenic retention capacity in root plaques. In this way, biochar composites (i.e. impregnated with both Fe and/or Mn) significantly decrease arsenic accumulation in rice tissues (Yim et al. 2017).

Rice grain arsenic contamination is one of the most perturbing topics in recent times. To reduce arsenic concentration in rice, it is needed to remove arsenic from the source which is quite challenging. Irrigation water and soil arsenic concentration should be reduced first. Therefore, in arsenic exposed environment, cultivation practices should be switched over to rain water harvesting system along with surface water. Soil arsenic concentration can be decreased using large scale bio-remediation or phyto-chelation procedures. Arsenic resistant microbes and arsenic chelators can help us by reducing arsenic at the soil root system. Anaerobic paddy cultivation practices need to be modified and aerobic cultivation should be practised more. Paddy cultivation should be increased using drip irrigation or sprinkler irrigation method as well as low arsenic accumulating rice cultivars needs to be grown extensively. Therefore, making farmers aware about the correct irrigation and cultivation exercises is the prime call for the hour. Moreover, at the village level, people are advised to cook rice with arsenic safe water, for which regular monitoring of water quality is required. Conclusively, arsenic free drinking water and quality based diet are required for healthy living.

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# Chapter 9
# An Overview of Arsenic Contamination in Water Resources of Pakistan, Risk Assessment and Remediation Strategies

**Saqib Bashir, Sanaullah Yasin, Safdar Bashir, Zubair Aslam, Waseem Hassan, Saadullah Khan Leghari, and Nabeel Khan Niazi**

**Abstract** Water resources of Pakistan are seriously depleting due to mismanagement. One of the major issues in the depletion of water resources in Pakistan which makes water not assessable to use is its contamination. The issue of arsenic contamination has emerged as a serious health concern in Pakistan. Pakistani population is exposed not only to toxic but poisonous levels of arsenic contamination. Only in Punjab province more than 20% population is exposed to arsenic levels of more than 10 ppb out of which 3% are exposed to more than 50 ppb levels of arsenic contamination. Various studies have shown the arsenic contamination in both shallow and deep aquifers. This chapter will give a comprehensive overview of arsenic contamination in water resources of Pakistan, their associated health risks, and possible remediation strategies to reduce exposure of arsenic contamination in Pakistani population.

**Keywords** Contamination · Arsenic · Water resources · Health · Diseases

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## 9.1 Introduction

Human's exploration for the healthier future mainly depends on the various progressions in the systematic and scientific investigations. However, modernization and urbanization has caused new threats for the sustainable environment, in terms to keep it clean, green and healthy. Humans impact on natural ecosystem is increasing undoubtedly because of constant increase in population and industrializations. This resulted the contamination of various number of potential toxic elements including heavy metals, pesticides residues and hydrocarbons, etc., in the ecosystem, is growing day by day. The presence of potential toxic elements e.g., metal(loid)s in soil and water are emerging threat for the sustainable ecosystem (Shahid et al. 2021; Masuda 2018). Among all the pollutants, Arsenic (As) contaminated ecosystem is a serious matter of concern for the scientists. Arsenic (As) is a crystal-like lethal metalloid because of its intermediate physical and chemical properties that is commonly existing in ecological premises (Suzuki and Katoh 2020). It is present at Group VA of the Periodic Table having 33, atomic weight and 74.92 atomic mass. It exists in the natural ecosystem with four oxidation states, e.g., (arsine −3), (arsenic 0), (Arsenite +3), and (arsenate +5), among all these states arsenate is the most stable form (Gupta et al. 2012). Whereas (Arsenite +3) is considered the dominant form of reducing environment. Similarly, aerobic condition supports the (arsenate +5), formation (Srivastava et al. 2012). It is known as the 20th most abundant mineral on the earth crust and accounts 4.01 × 1013 metric tons in the crust (Suzuki and Katoh 2020) (Table 9.1).

Water is necessary in every aspect of our lives (Kılıc 2020). Water may contain a range of physical, biological, and chemical pollutants as a result of technological progress. Pollutants are transported from one location to another by nutrients and microbes (Prescott et al. 2002). Water becomes polluted when dangerous chemicals and germs from industrial and domestic waste come into touch with water bodies, flow off, or leak into ground water or freshwater resources (Arora 2007). Water pollution is a physical process that occurs in a variety of water resources such as lakes, groundwater, and rivers as a result of anthropogenic activities (Agarwal 2002). Highly toxic metal(loid) levels in soil and water are important contaminants. Agricultural and industrial operations like mining, smelting, refining, and manufacturing processes cause them (Shukla and Srivastava 2017). The water sanitation system and drainage pipes in Pakistan run in parallel, resulting in leaks and intermixing, lowering water quality (Patoli et al. 2010). The untreated discharge of hazardous chemicals into water bodies from urban areas and industries degrades water quality and has negative human health consequences.

Arsenic (As) is a hazardous metalloid found in soil and groundwater in many parts of the world, especially in Southeast Asian countries. It's a naturally occurring, extremely deadly, and poisonous metalloid that's found all throughout the Earth's crust and hydrosphere (Emilie et al. 2017). As pollution is caused by both natural biogeochemical processes and human acts (Podgorski et al. 2017). Anthropogenic arsenic is thought to account for roughly 60% of arsenic in the environment (Loska

**Table 9.1** Extent of Arsenic in Pakistan and their health impacts

| Metal | Exposure pathway | Major sources | Health impacts | | Concentrations of heavy metals in Pakistan | | |
|---|---|---|---|---|---|---|---|
| | | | | Province | City | Concentration (µg/L) | References |
| Arsenic (As) | Drinking water, food, smoking | Agricultural pesticides, fossil fuel burning, smelting, industrial wastes (Hughes et al. 2011) | Carcinogenesis, lung cancer, hypertension, cardiovascular disease risk, carotid atherosclerosis and diabetes mellitus, decreased mental performance | Punjab | Islamabad | 0.1–0.9 | Arshad and Imran (2017) |
| | | | | | Rawalpindi | 0–2.0 | |
| | | | | | Bhawalpur | 0.8–90 | |
| | | | | | Vehari | 32.2–123.4 | Shahid et al. (2018b)<br>Tariq et al. (2019) |
| | | | | | Faisalabad | 1.0–6.376 | Khattak et al. (2016) |
| | | | | | Mailsi | 11–828 | Rasool et al. (2016) |
| | | | | | Bhakhar | 1.62–55.37 | Rehman et al. (2020) |
| | | | | | Lahore | 2–111 | Bibi et al. (2015) |
| | | | | | Sheikhupura | 40–65 | Abbas and Cheema (2015) |
| | | | | | Jehlum | 0.50–100 | Ullah et al. (2022) |
| | | | | | Hasilpur | 0–100 | Tabassum et al. (2018) |
| | | | | | Multan | 1.2–206 | Shakoor et al. (2018) |
| | | | | | D. G. Khan | 0–29 | Malana and Khosa (2011) |
| | | | | Sindh | Karachi | 10–250 | Ahmad and Bhattacharya (2018) |
| | | | | | Khairpur sub-districts | 1.09–27.6 | Rabbani et al. (2017) |
| | | | | | Hyderabad | 0–0.181 | Khattak et al. (2016) |
| | | | | | Sakrand | 0–10 | Baloch et al. (2021) |
| | | | | | Nagarparkar | 360–683 | Brahman et al. (2014) |
| | | | | | Tharparkar | 9.98–2350 | Brahman et al. (2016) |

(continued)

**Table 9.1** (continued)

| Metal | Exposure pathway | Major sources | Health impacts | Concentrations of heavy metals in Pakistan | | | |
|---|---|---|---|---|---|---|---|
| | | | | Province | City | Concentration (μg/L) | References |
| | | | | | Jamshoro | 3–106 | Baig et al. (2009) |
| | | | | | Abbottabad | 0–2.980 | Khattak et al. (2016) |
| | | | | | Peshawar | 0–8.642 | |
| | | | | | Mardan | 0–9.0 | |
| | | | | | D. I. Khan | 0–7.932 | |
| | | | | Baluchistan | Q uetta | 1.306–9.307 | Khattak et. al. (2016) |
| | | | | | Jaffarabad | 0–0.0537 | |
| | | | | | Turbat | 0–0.0310 | |
| | | | | | Zhob | 0–0.0996 | |
| | | | | All Pakistan | Sindh, Punjab, Baluchistan, KPK (No. of samples 1184) | 0–500 | Podgorski et al. (2017) |

et al. 2003). When arsenic combines with other elements, it can form both inorganic and organic arsenic compounds. Inorganic arsenic compound is found in the presence of oxygen, sodium, potassium, copper, chlorine, iron, and sulphur. Arsenic combines with carbon and hydrogen in plants and animals to form organic arsenic. Organic arsenic compounds found in food are non-toxic and pass through the body quickly. Inorganic arsenic is more hazardous, with localized or systemic acute, subacute, and chronic effects. It is highly harmful when arsenic is present in high proportions in drinking water and food. Arsenic toxicity can damage humans in both acute and chronic forms. Arsenic trioxide is a known toxin, and even 0.1 g can be lethal to the environment. Excessive arsenic concentrations in the natural geochemical environment have been a substantial issue in recent years due to the potential for adverse human repercussions (Thornton 2016). Surface and groundwater, as well as fruits and vegetables, are contaminated with As, and continuous exposure to As through contaminated water and food poses major health risks (Muhammad et al. 2010). Humans can be exposed to this metal in a variety of ways, including inhaling dust particles from the atmosphere, consumption of polluted water or soil, or eating contaminated food (Tchounwou and Centeno 2008).

The continuous use of wastewater contains As for irrigation purpose not only leads to As accumulation in soils and thereby compromises the food safety because of As translocation into leafy vegetables and rice especially. In addition, pumping of ground water for irrigation purpose from the As contaminated sites could led to enhance its transfer rate from the As-accumulated crop species to human beings (Sarkar and

Paul 2016). Skin, lung, and leukaemia cancer, as well as melanosis, leucomelanosis, keratosis, hyperkeratosis, dorsum, non-petting edoema, and gangrene, can all be caused by inorganic arsenic ingestion, while inhalation can induce respiratory tract cancer (Karim 2000; Kotoky et al. 2008). A few cases of As(III) and As(V)-affected skin cancer patients have been discovered in several studies (Hsueh et al. 1995). Long-term inorganic arsenic exposure damages the respiratory, digestive, circulatory, endocrine, hematopoietic, renal, and reproductive systems, finally leading to metastasis (Maharjan et al. 2005; Mandal et al. 1996).

Arsenicosis is a long-term health effect of drinking water contaminated with high levels of arsenic (>0.05 mg/L) that causes skin disorders, skin cancers, internal cancers (bladder, kidney, lung), blackfoot disease, diabetes, high blood pressure, and reproductive problems (WHO 2013). Arsenic has been acknowledged as a global concern to the environment (Bundschuh et al. 2012; Chakraborti et al. 2010; Naujokas et al. 2013; Sohel et al. 2009).

### Arsenic Contamination in Pakistan Water Resources

Recently, in Pakistan arsenic risk becomes much serious than expectation. Pakistan's ground & surface water has been found alarmingly high level of As (PSQCA (2017). The permissible limits of As in groundwater has been devised to 10 µg/L by the US Environmental Protection Agency (USEPA) and the World Health Organization (WHO) (Hassan et al. 2016). In many developing countries, however, the permissible limits of As are similarly suggested at 50 µg/L. (Nickson et al. 2005).

The main causes of waterborne infections in Pakistan include the addition of urban sewage and industrial wastewater at various points in the water distribution network, as well as a lack of water disinfection and water quality monitoring at treatment plants. More than 50 million people in Pakistan are at risk of arsenic poisoning, according to Podgorski et al., because 95% of Pakistan's population lives in the Indus valley (Fig. 9.1) and drinks groundwater that exceeds the WHO permissible level (Tariq et al. 1996). In the early 2000s, Pakistan launched a systematic screening of groundwater for arsenic contamination, and multiple cities were found to have the highest levels of arsenic (Waseem et al. 2014). In Pakistan, substantial quantities of arsenic were discovered in surface and ground water, primarily in the Punjab and Sindh provinces. In Punjab and Sindh, respectively, 3% and 16% of water resources have an As contamination level of above 50 µg/L, whereas 20% and 36% of water resources have an arsenic contamination level of over 10 µg/L. According to the Pakistan Council of Research in Water Resources (PCRWR) and UNICEF's groundwater monitoring programme, in some regions of Punjab province, arsenic concentrations range from 10 to 200 µg/L, while 16–36% of residents in Sindh province are exposed to high arsenic (>10 µg/L) in the groundwater.

Arsenic levels were found to be high in surface and ground water in Pakistan, primarily in the Punjab and Sindh provinces. In Punjab and Sindh, respectively, 3% and 16% of water resources have an As contamination level of over 50 µg/L, whereas 20% and 36% of water resources in Punjab and Sindh have an arsenic contamination level of over 10 g/L. The Pakistan Council of Research in Water Resources (PCRWR) and the UNICEF groundwater monitoring programme reported As concentrations

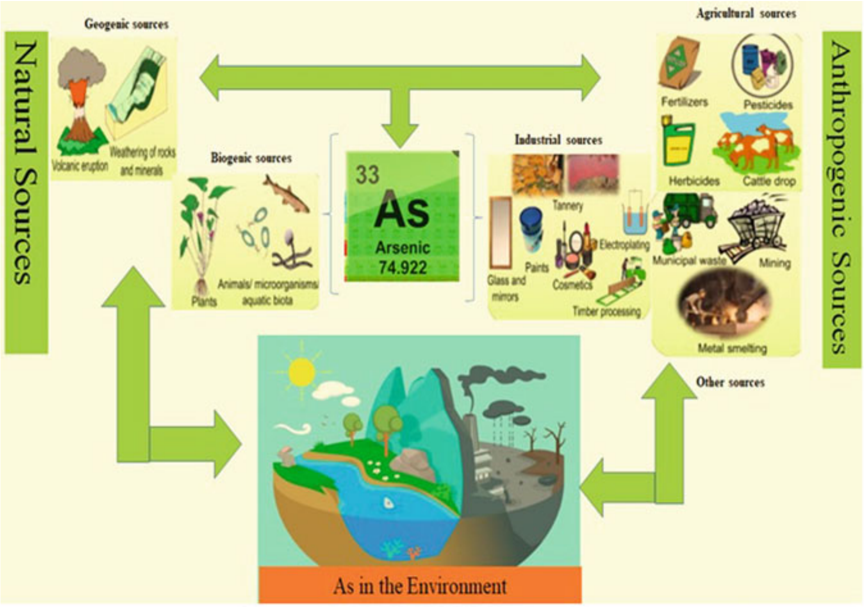

**Fig. 9.1** Sources of Arsenic, fate, and transportation between environmental compartments

of 10 to 200 µg/L in some parts of the Punjab province, and 16–36% of people in the Sindh province are exposed to high arsenic (>10 µg/L) in the groundwater Ahmad et al. (2004) due to very high concentration in the Indus alluvial plain (Shahab et al. 2016). Sindh province's water resources are very vulnerable to contamination (Shahab et al. 2018a). Heavy metal contamination has also been found in other parts of Pakistan, including Lahore, Kasur, and D. G. Khan (Punjab) (Nickson et al. 2005; Farooqi and Firdous 2007; Malana and Khosa 2011), Muzaffargarh District (Nickson et al. 2005), Peshawar Basin (Shah and Tariq 2007), and the Kohistan region (Shah and Tari (Muhammad et al. 2010). PCRWR has selected six districts in Punjab province as the most susceptible locations due to high concentrations of heavy metals: Lahore, Kasur, Multan, Sheikhupura, Bahawalpur, Vehari, and Gujranwala (PCRWR 2005). Jamshoro, Tharparkar, Matyari, and Manchar Lake districts (Baig et al. 2009; Arain et al. 2009; Kazi et al. 2009; Brahman et al. 2013), Nagar Parkar (Naseem et al. 2010), and Jaccobabad (Shahab et al. 2018b) in Sindh province are more contaminated with arsenic. In 2004, about 40 people died in the Hyderabad district as a result of drinking water contaminated with arsenic and other harmful components (Arain et al. 2008).

All of the districts mentioned above are alluvial deposits along the Indus River. Surprisingly, places closest to the Indus River system exhibited higher arsenic levels than areas further away from the river system within a same district. For example, all of the districts were found to have high levels of arsenic pollution (i.e. Multan,

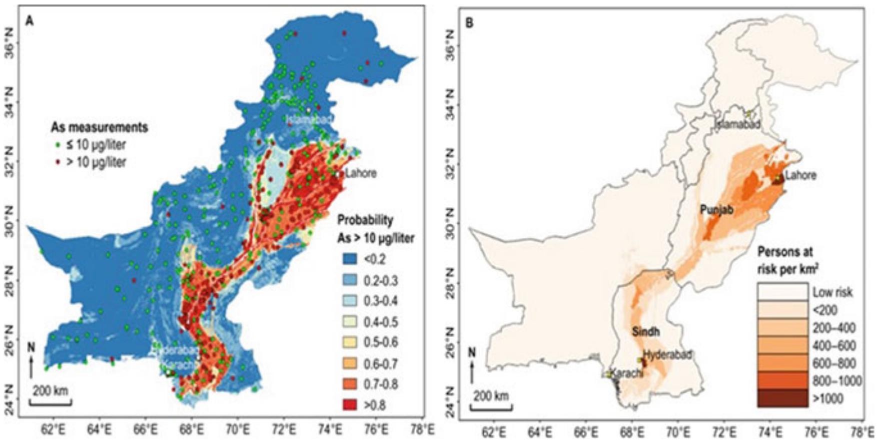

**Fig. 9.2** Arsenic prediction and risk models. **a** Probability (hazard) map of the occurrence of arsenic concentrations in groundwater exceeding the WHO as guideline of 10 µg/litre along with the aggregated arsenic data points used in modelling ($n = 743$). **b** Density of population at risk of high levels of arsenic in groundwater using the WHO As guideline of 10 µg/litre. Reproduced from Podgorski et al. (2017) with permission of American association for the advancement of science (AAAS). © Podgorski et al. (2017), some rights reserved; exclusive licensee AAAS. Distributed under a creative commons attribution non-commercial license 4.0 (CC BY-NC) http://creativecommons.org/licenses/by-nc/4.0

Bahwalpur, Rahim Yar Khan in Punjab province, and Khairpur, and Dadu in Sindh province) (Fig. 9.2).

## 9.2 Extent of Arsenic Contamination in Pakistan

Industrial effluents, solid wastes, and agricultural runoff are the main sources of water contamination in Pakistan. According to Mustafa and Cherry (2013), around 90% of household and industrial garbage is dumped directly into bodies of water, where it can eventually leach into groundwater. Furthermore, around 92% of untreated sewage and approximately 50% of human excreta are dumped directly into aquatic bodies in metropolitan areas. Untreated sewage effluents not only pollute the environment with harmful chemicals, but also cause widespread disease epidemics. Pakistan's agriculture industry contributes to pollution in water bodies. The most prevalent agricultural contaminants are sediments, pesticides, fertilizers, nitrates, phosphorus, and heavy metals.

Arsenic has become a big issue in Pakistan since many areas have high arsenic concentrations that surpass the World Health Organization's recommended safe limit of 10 µg/L. (WHO). Shahid et al. (2018a) reported that 73% of 43 published studies in Pakistan had mean arsenic levels above the WHO guideline, and 41% were higher than Pakistan's significantly less stringent 50 mg/L standard. Shakoor et al. looked into 123 wells in Punjab in 2018 from five different locations: Multan, Bahawalpur, Rahim Yar Khan, Vehari, and Chichawatni. As levels ranged from 1.2 to 206 g/L in Chichawatni, Multan, Bahawalpur, Vehari, and Rahim Yar Khan, with mean As concentrations in the following order: $120 < 72 < 53 < 22 < 9$ μg/L respectively (Fig. 9.2). About 75% of groundwater samples showed As concentrations that above WHO safe drinking water criteria, while 41% of wells had As values that exceeded Pakistan National Environmental Quality Standards (NEQS).

## 9.3 Health Impacts of Arsenic Toxicity in Pakistan

As is one of the most toxic and cancer-causing metalloids on the planet in terms of human health. Arsenic is a recognized human carcinogen that causes skin, bladder, and lung cancer, according to the International Agency for Research on Cancer (IARO) (Memon et al. 2014). Drinking As-contaminated water on a regular basis has both acute and chronic health implications. As visible in the lungs and gastrointestinal tract, about 80–100% was ingested and inhaled (Shemirani et al. 2005). Arsenic-induced lung cancers have different genetic and epigenetic mutations. Inorganic arsenic, as well as compounds generated during arsenic metabolism, have a role in the molecular alterations associated with arsenic-induced malignancies (Hubaux et al. 2013). Lung cancer caused by drinking arsenic-contaminated water is expected to have a greater death rate than lung, bladder, and kidney cancers, as well as cardiovascular diseases (Smith and Steinmaus 2009).

Due to significant intravascular hemolysis, arsine (AsH3) intoxication can cause anemia. The initial indicators of erythrocyte dysfunction are changes in salt and potassium levels (Chabowska et al. 2002). According to Tchounwou et al. 2003, arsenic-induced apoptosis is caused by overexpression of the BCR-ABL gene in human lymphoblast cells. Arsenic is a tumor-causing chemical that specifically triggers apoptosis in promyelocytic leukaemia, and this induced apoptosis causes alterations in other signaling pathways.

Arsenic has been recognized as the first chemical agent in humans, capable of causing liver damage. Long-term exposure damages the hepatic system by causing a buildup in the liver (Clarkon et al. 1991). Consumption of arsenic alters hormonal and mucosal immunological responses, resulting in hyperkeratosis, hyperpigmentation, and respiratory issues (Luqueno et al. 2013). Chronic arsenic exposure produces skin depigmentation and leukomelanosis, white patches on the skin (Singh and Kumar 2012). In Pakistan's Bobak hamlet, near Manchar Lake, 30–40% of residents were affected by major skin diseases and sores (Arain et al. 2009). High levels of arsenic in drinking water induced liver cancer in young children under the age of 20 (RR = 10.6, 95% CI 2.9–39.2, $p < 0.001$) and made them a target of death (Tantry et al. 2015). Arsenic replaces phosphate ions and thiol groups in cells in its ionic forms, arsenate and arsenite, interrupting normal cell activity (Shahid et al. 2015). If arsenic breaches the placental barrier, it can cause miscarriages, low-birth-weight babies, and neonatal and postnatal mortality (Lubin et al. 2007). Arsenic poisoning is more common in youngsters since the symptoms are difficult to detect early (Bhatia et al. 2014).

Arsenic can impact internal organs, disrupting their regular functioning without causing obvious external symptoms, making it difficult to identify. Arsenic poisoning can be identified in the hair, nails, urine, and blood before the outward manifestations (Petrusevski et al. 2007). The use of As-contaminated water on a daily basis reduces the production of white and red blood cells and damages blood vessels, causing a "pins and needles" sensation in the exposed person's hands and feet (Abernathy et al. 2003). Furthermore, Kazi et al. (2009) discovered that As-mediated chronic toxicity manifests itself in the form of keratosis and melanosis in 61–73% of residents in the Manchar Lake area of Sindh Pakistan (Fig. 9.2).

## 9.4 Remediation Strategies to Reduce Arsenic Contamination

Water contamination with arsenic is a severe concern all over the world, providing a serious hazard to a huge population, particularly in Asian countries. People's conditions would deteriorate as a result of this issue. If sufficient and efficient treatment technologies are not being adopted, then the water contamination will be worsening day by day. Humans can be affected by arsenic in a variety of ways. According to World Health Organization (WHO), the threshold level of As pollution in drinking water is 10 μg/L or 10 ppb (Duarte et al. 2009). While, This limit was revised by the United States in 2006 and adopted the standard for drinking water ranging from 50 μg/L to 10 μg/L. As a result, numerous strategies for As cleanup have been investigated. Keeping in view the above information, several attempts have been made to create sustainable bio-strategies for As removal from water sources that are both ecologically acceptable and simple to implement in polluted sites. Mostly, ecofriendly and cost-effective remediation approaches including (physical, chemical, and biological) have been applied for the decontamination of As from polluted water and soil. It is important to select those options which should meet all basic criteria without any other side effect on the environment, having the capacity to sustain the supply of water for long time (Duarte et al. 2009). Currently, biological techniques including bacteria, fungi, and plants also have the potential for the removal of As by various mechanisms (Su et al. 2010).

Particularly, excessive use of water in homes and industrial activities not only increase the water scarcity, but also poses a health risk, especially because of hazardous effects (after consumption). In wastewater, there are organic and inorganic chemicals, bacteria, and total solids (TS) which could contribute to pollute the water cycle (Ahmed et al. 2021a). As a result of recent development in the treatment of wastewater by using innovative and cost effective approaches is become a hot topic which got much attention around the globe. This section discusses new methods and strategies for removing arsenic from wastewater.

## 9.5 Chemical Strategies for Arsenic Remediation

### *9.5.1 Adsorption*

Adsorption is recognized as one of the most prominent approaches for removing arsenic and associated heavy metals from wastewater. A process that depends on the presence of active sites. It is one of the most successful wastewater treatment strategies that especially depends on the active sites and the specific surface area of the adsorbents (Ahmed et al. 2021b). Recently, researchers have developed various innovative methodological alteration to eliminate As content from wastewater using various organic and inorganic adsorbents because of their cost-effectiveness, flexibility, and are easy to apply. In this technique liquid and solid substances holds gaseous, solid, or solute particles on their surfaces of a solid or liquid through physical adsorption also known as (van der Waal's adsorption) and chemical adsorption. As presence in different species can be easily adsorbed on the upper layer of the adsorbent though van der Waal force. There are some key factors which could influence the As adsorption on the adsorbent includes, As initial concentration, dose of adsorbent, solution pH, temperature, contact time, and As solubilization in water (Lal et al. 2020). Additionally, As removal efficiency varied with the variation of affinity between adsorbing substance and As species (Trivalent and pentavalent). For example, smelting waste can be used as adsorbate for As removal from wastewater. According to the method, As (III) is oxidized before adsorption, which increases the affinity between the adsorbent and the oxidised form As (V) (Lal et al. 2020).

Lorenzen et al. (1997) described that addition of carbon based material showed the prominent efficiency for the removal of As from wastewater and drinking water. The maximum removal was recorded by 2.4, 4.53 and 4.09 mg $g^{-1}$ when Coconut-shell carbon, Coconut-shell carbon pretreated with Fe(III) and Coal-based carbon materials were incorporated respectively. The previous study reported by Chen et al. (2007) explained that addition of Iron-modified activated carbon exhibited the greater As adsorption capacity 51.3 mg $g^{-1}$ and 38.8 mg $g^{-1}$ As(V) and As(III) respectively. In another study, granular titanium dioxide was used for the removal of As from ground water. The maximum removal was noticed by 32.4 and 41.4 mg $g^{-1}$ for As(III) As(V) respectively (Bang et al. 2005).

### *9.5.2 Coagulation-Filtration Techniques*

Another prominent method for removing arsenic from wastewater is coagulation (Anjum 2017). This method relies on the use of chemical compounds (coagulants such as ferric iron) to catalyze the conversion process of soluble As to insoluble As (Fig. 9.3). The As-containing coagulation products are detached using gravity or sand filtration. Coagulation can be combined with the microfiltration (MF) technique to effectively reduce the amount of As in the water which can be used for treatments.

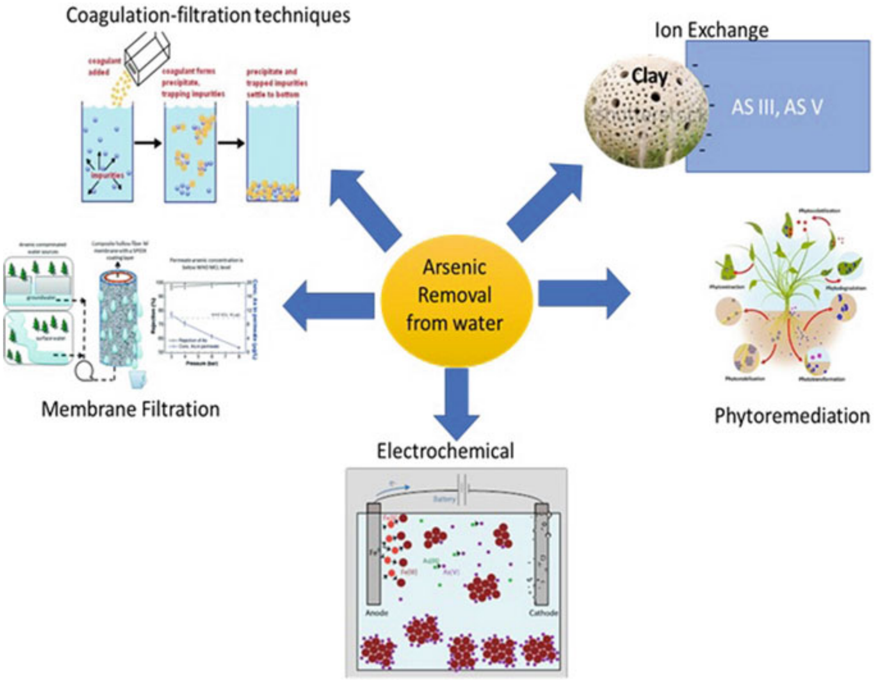

**Fig. 9.3** Summary of Arsenic remediation methods

As (V) adsorption onto coagulated flocs is considered the efficient approach relative to the filtration method for As removal (Song et al. 2006).

Arsenic may be eliminated using limonite which could precipitate As and develop scorodite in *In- situ* remediation strategy because of low iron super saturation (Li et al. 2021a, b). The development of scorodite mineral is a good way to remove As, especially via hydrometallurgical processes (Otgon et al. 2019; Ma et al. 2019). In this process, electronegative charged ions play vital role for adsorption through complexation of arsenite onto precipitated flocs and thereby removed from the wastewater. Another strategy for As mitigation has been described to improve the efficacy of the removal process by applying the electric current driven precipitation (electrocoagulation). This approach is suitable candidate for As removal from aqueous solutions due to its cost-effectiveness. The electrocoagulation technique, which uses anodes made of metals like aluminium, iron, and magnesium, has showed the promising effect for the treatment of As-contaminated water. Most notably, electrocoagulation is significantly more efficient than synthetic compound-assisted coagulation for As removal (Gandhimathi et al. 2015; Bandaru et al. 2020).

The removal of arsenic is mainly depending on the solution pH. If the solution pH is below than 7.6 then $Al_2(SO_4)_3$ and $FeCl_3$ have equally contributed for removal. The coagulant material type, dose level and the range of pH could affect the efficacy of this process. The pH plays a key role in As removal while, coagulation by iron needs the pH range from 6.0 to 8.5 (Feistel et al. 2016; Thakur and Mondal 2017). It has been demonstrated that addition of $FeCl_3$ at 30 mg/L showed the prominent reduction in As(III) and As(V) by 45% and 75%, respectively. Therefore, it was established that the maximum As reduction was occurred when the dose of $FeCl_3$ was increased. Similarly, Sun et al. (2013) suggested that addition of Ferric Sulfate showed effective reduction in As(III). The maximum removal was observed by 80% when $Fe_2(SO_4)_3$ was applied at 25 mg/L dosage level.

### 9.5.3 *Chemical Precipitation*

Chemical precipitation is well known approach for As removal from acidic nature effluents of smelting industry. Particularly, the salts of iron ($Fe_2(SO_4)_3{\cdot}7H_2O$ and $FeCl_3$) and aluminium as [$Al_2(SO_4)_3{\cdot}18H_2O$] could be used as the coagulants for the removal As. In this technique, chemicals have potential to transform the soluble form of As into stable (insoluble). Moreover, solid hydroxides might have great contribution to adsorb soluble form of As and further provides sites for the precipitation with other chemical compounds (Ungureanu et al. 2015). For example, pyrite sulphide also has potential to precipitate As (III) ions and promote the formation of $As_2S_3$ (Li et al. 2020a, b). The chemical process converts F(II) and As (III) to Fe(III) and As (V), respectively, resulting in the formation of crystalline scorodite, which removes 99.4% of the arsenic from the effluents discharged from smelting industry (Li et al. 2021b). The other chemical agents in oxidized form (chlorine, chlorine dioxide, ozone, hydrogen peroxide, chloramine, permanganate, air, and pure oxygen), acid, and caustic soda could also contribute for this technique. The primary goal of oxidation is to convert soluble As (III) to As (V), which is subsequently precipitated as As (V). As a result, compared to other arsenic removal procedures such as precipitation and adsorption, this approach is time-consuming and energy-intensive. In addition, high pH would increase the redox potential of the process, preventing the precipitation of trivalent arsenic ions. (Kim and Baek 2019).

### 9.5.4 *Ion Exchange*

It is recognized as a physicochemical process which involves the substitution of an anion from the solid complex phase with an ion in the industrial effluents. The solid phase generally consists of three-dimensional elastic hydrocarbon network with a surface of electronegative ionizable functional groups which promote the ionization electrostatically (Fig. 9.3). These surface groups can be replaced in solution with the ions of similar charge that have a higher exchange affinity (i.e. selectivity) for the resin. Another common way for removing arsenic and hazardous metal ions from industrial effluents (typically through precipitation) is the ion exchange process.

Under ultra-violet light, for example, As (V) was efficiently removed using phosphorus penta sulfide ($P_2S_5$) (Peng et al. 2018). In this approach, $H_3PO_4$ (rather than cations) is used to assist in the reusing of As and acid at low pH effluents.

However, such a process would not be appropriate or efficient for non-acidic contaminated water, and it takes longer in general. Secondly, this technique cannot be used in bioprocessing since the microbial activity would be greatly reduced under the requisite of strong acidic conditions. Furthermore, another effective strategy has been adopted for the application of hydrogen sulphide (HS) as a adsorbate for the removal of As (from industrial effluents). The effectiveness of ion exchange method is upgraded by the pre-oxidation of As (III) to As (V), its important to remove the additional oxidant in order to avoid the loss of complex resins. Moreover, its efficacy mainly depends on the pH of solution, the concentration of competing ions (sulfates and nitrates, resin type and alkalinity) (Pal 2015).

### *9.5.5 Membrane*

Membrane filtration is known as one of the most important technique which is made of the synthetic materials containing billions of microscopic pores and C–S BF nanoparticles, which plays key role as a barrier for the pollutants (Fig. 9.3). Thus, the structural characteristics of the membrane allows some residents to flow through the membrane, while others are prohibited (Rekik et al. 2017). The movement of toxic compounds across the membrane is required the pressure as a driving force along the both sides of the membrane. It is less cost effective than other As removal techniques and creates massive residual volumes. This processes can be classified into four classes with varying pore size: (a) microfiltration (MF) 0.1 micron; (b) ultrafiltration (UF) ranging from 0.0003 to 0.1 microns; (c) nanofiltration (NF) 0.001 to 0.003 microns (d) and reverse osmosis (RO) 0.0005 microns. The separation by these processes depends on the pore size of the membrane. Membrane filters contains bio-functionalized matrix which have great contribution for the removal of Arsenic (As) and Selenium (Se) ions from the wastewater (Zeeshan et al. 2020).

Moreover, this technology has potential to remove all dissolved chemicals including As from the wastewater and also prevent the entrance of microbial species when flow through the membrane and thereby minimizing the chances of diseases caused by water pollution. The study conducted by Sato et al. (2003) it was recorded that As(V) was elimination by 85% for all studied membranes. However, As(III) removal was recorded in minimum level. Misra et al. (2015) conducted a lab study in which 100 $\mu$g/L of As concentration was used for the adsorption study. The findings of current study showed the significant reduction was by 90% when membrane was used.

### 9.5.6 Arsenic Removal Through Biological Techniques

Biological (bioremediation) is an attractive environmentally valuable strategy that uses living species for the removal of both organic and inorganic contaminants. Bioremediation works by utilizing the microorganisms or plants to degrade, convert, stabilize, or volatilize contaminants at their source. In situ bioremediation is commonly employed to clean up contaminated places, especially if As is prevalent as contaminant across the large areas. These changes affect the transport and bioavailability of As in a variety of settings (Kumar et al. 2020). Arsenic remediation can be accomplished using living species either microbes (bacteria, algae, and fungi) Raj et al. (2013), as well as their products and plants (phytoremediation), and their combination can be used very successfully in a specific environment to detoxify the harmful compounds, and thereby cleaning the water ecosystem (Singh et al. 2021).

Potential toxic substances cannot be easily degraded, but they can be changed from their solubilize form to immobile or inaccessible form (Stucker et al. 2013). Arsenic detoxification involves a number of microbiological activities, including membrane protein transport, significant reduction in mobilization, methylation-induced volatile form formation, surface adsorption and complexation, and redox reactions. The mobility of As in an environment is prominently influenced by the microbial activity produced by organic substantial manganese, Sulphur and iron, which can be grouped into ferrous oxidizing, manganese oxidizing, sulfate reducing, and As resistant type. Furthermore, As can be respired by a variety of microorganisms in numerous anaerobic reactions (Singh et al. 2021).

### 9.5.7 Microbial Bioremediation

Microorganisms are abundantly present in the soil ecosystem including surface, subsurface and in the groundwater which have great contribution to minimize the biological activity of arsenic. It has been established that microbial species contains several functions and insight mechanisms for the detoxification of As from highly mobile to stable form. Thus, we may be able to clean up the places that have been contaminated by arsenic. Several previous studies Marwa et al. (2019); Pratush et al. (2018) and Wan et al. (2020) explained that immobilization of As can be accomplished by the chemical reactions (oxidation and reduction, pH changes, co-precipitation, co-dissolution), biological alteration (biosorption, bioaccumulation, biomethylation) and the formation of organic metallic complexes. It has been demonstrated that As can be immobilized by bacteria either directly or indirectly. Rhizospheric fungus (*Aspergillus flavus*) has the potential to bio-transform the solubilize form of As into the immobile form of As, and thus lessen the phytoavailability (Afzal et al. 2019). However, indirect stabilization of As includes the addition of ureolytic bacteria that has potential to produce urease, which could enhance the precipitation rat and thereby promote the stabilization of As through calcite precipitation (Achal et al. 2012).

Dey et al. (2016) demonstrated that two rod-shaped Gram-positive bacteria, (Bacillus sp. and Aneurinibacillus aneurinilyticus) were isolated from the As deteriorated groundwater. It was concluded that these isolated bacteria have potential to sustain the concentration of As(III) and As(V) by 4500 and 550 ppm and remove As from the groundwater by 51.4–51.9% As(III) and 50.3–53.0% As(V). Thus, it has been established that these isolated bacterial species can be used as a As resistant candidate for the bioremediation process. Similarly, microalgae such as (*Chlamydomonas Reinhardtii and Scenedesmus obliquus*) and fungus *Aspergillus niger* can be used for the removal of As from the contaminated sites especially As polluted water because of their highest tolerant nature and bioaccumulation ability (Kumar et al. 2020).

### *9.5.8 Phytoremediation: A Sustainable Strategy*

Phytoremediation is derived from two words Greek "phyto" (plants) and Latin "remedium," which involves the green technology (plants) to remove and extract the contaminants or elevating their bioavailability (Greipsson 2011). The use of plants species in phytoremediation should hold some key abilities e.g., speedy growth, maximum biomass, dense root system, adaption to root system and resistance to As toxicity as well as potential to uptake maximum amount (de Souza et al. 2018). Thus, such type of plants species is known as hyperaccumulator which efficiently absorbs PTEs from the polluted soil. Additionally, few plants species are naturally existing in the environment that have potential to uptake excessive quantity of As for polluted ecosystem restoration.

### *9.5.9 Microbial and Plants Assisted As Bioremediation (Phytobial Remediation)*

Phytobial remediation is the combination of plants and microbial special for the removal of As from the polluted ecosystem. Microbes-plants interactions showed the various vital roles in the environment, involving in their biogeochemical cycles and also assists for plant growth. Microbial species are present in the rhizosphere and form a mutualistic association with the plants as the endophytes, symbiosis and as a free-living (Hassan et al. 2020). The injection of microbial species along with hyperaccumulator plants efficiently transform As from arsenate to arsenite and enhance arsenite accumulation in plants aerial parts. It is accomplished by the significant reduction in ethylene levels after the production of phytohormone which could facilitate the plant species to withstand with As toxicity. According to the findings of Franchi et al. (2017) established that *Brassica juncea* and *Lupinus albus* have the potential to uptake As 41.1 mg/kg from the contaminated site when these plants were assisted by plant growth promoting bacteria (PGPB) including Actinomycetales (Gordonia alkanivorans, Microbacterium paraoxydans), Bacilli and Betaproteobacteria, has a promoting effect for plant biomass and phytoextraction of As. It is interesting to mention that the phytobial remediation strategy is suitable approach to overcome the all constraints in the bioremediation field, because of less expensive and less time-taking approach for the stabilization/removal of As from the polluted environment.

## 9.6 Conclusions and Future Perspectives

A brief overview of Arsenic contamination in Pakistan is discussed in this chapter and issue of Arsenic contamination is increasing at alarming rates in Pakistan. Therefore, there is a dire need of developing sustainable remediation technologies which may help to reduce the impact of Arsenic contamination to humans. Specifically, low cost arsenic remediation technologies for developing countries like Pakistan can be suitable option to choose. We also summarize the possible technologies which may help to reduce Arsenic contamination to safe limits. Most of these technologies are at experimental stages and there is an urgent need to enhance their application on large scales. Sorption technologies can be best option to reduce toxic levels of Arsenic contamination. Therefore, more research is needed to develop advanced functional materials for example carbon nanotubes, graphite oxides and biochar of natural wastes materials for example water melon rind can be more effective remediation technologies to apply on large scales. The research on developing hybrid remediation technologies can be of real importance in future as the efficiency and cost of the material are most important limiting factor for decision maker to adopt any technology.

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# Chapter 10
# Approaches for Stochastic Modelling of Toxic Ion Adsorption at Crystal-Water Interfaces: A Case Study of Arsenic

**Inna Kurganskaya**

**Abstract** Adsorption and fate of toxic ions in natural environments are complex phenomena involving a multitude of possible reactions at solid–fluid interfaces. Modelling of these reactions at realistic conditions defined by complex chemistry of natural waters can be a non-trivial task. Stochastic modelling approaches, such as Kinetic Monte Carlo (KMC), and the tools of statistical mechanics, can treat issues of system complexity by generation of possible system's configurations and time-dependent system's transitions. We present here basic theoretical background for these modelling approaches for beginners in this field. In particular, we show how KMC modelling can be applied to study adsorption of arsenic (V) on iron oxide nanocrystals. We begin this chapter with a description of molecular and microscopic structure of crystal-fluid interfaces as a necessary prerequisite for formulation of stochastic models. Stochastic modelling approach can be greatly beneficial for addressing phenomenon of toxic ion adsorption in natural water-containing systems. The application of this approach is in its embryonic state and requires a thorough and systematic development.

**Keywords** Adsorption · Modelling · Stochastic algorithms · Monte Carlo · Statistical mechanics · Nanoparticle design

## 10.1 Introduction

Presence of toxic ions in natural environments imposes serious ecological problems and threats to human health. Understanding of toxic ion fate in various geochemical systems has crucial importance for mitigation of environmental hazards. Toxic ions may adsorb to surfaces of minerals and man-made crystals and become immobilized for transport in groundwaters, sediments, and soils. Desorption is another process complementary to adsorption that may contaminate natural waters. Process of crystal growth and dissolution widely occurring in nature at ambient conditions can modify

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adsorption properties of solid materials or destroy them. Therefore, understanding of the multitude of possible processes taking place on surfaces capable of toxic ion adsorption is necessary for prediction of toxic ion behavior in natural environments.

The adsorption phenomena coupled with growth and dissolution processes can be studied by means of field studies, laboratory experiments, theoretical modelling, and computer simulations. Theoretical modelling of the adsorption phenomena is difficult due to complexity and large degree of uncertainty of natural geochemical systems. Computer simulations can help us to overcome the issue of system's complexity. Modern computers are capable of handling solutions for quite large and complex numerical models. Stochastic modelling approaches can be especially beneficial for understanding and predicting behavior of such systems. Stochastic models are based on probabilistic formulations of complex systems and processes, thus substantially simplifying numerical models and simulation algorithms. In this chapter we introduce the basic theoretical background for Kinetic Monte Carlo (KMC) simulations and crystal-fluid interface structure. We show how KMC method was used to model adsorption of arsenate ions on iron oxide (hematite) nanocrystals. The chapter is aimed at beginners in modelling with minimal theoretical background in this field, so anyone who needs to construct such models can find a first guidance. We complement introduction into KMC with brief description of statistical mechanics approaches that can be potentially applied to the studies of surface adsorption.

## 10.2 Crystal-Fluid Interface Structure

The molecular structure of solid–fluid interfaces at natural conditions can be very complex. The coordination of surface atoms is different from their coordination in the bulk crystalline lattice because some of the bonds need to be broken in order to form a surface. This difference in coordination may influence geometric arrangements of surface atoms, thus generating so-called "surface relaxation effect". Surfaces in contact with water adsorb hydroxyls $\left(OH^-\right)$ and protons $\left(H^+\right)$ to maintain electric neutrality. Water molecules also get adsorbed at the surface and may form structured layers. Charged surface sites appearing due to protonation and deprotonation reactions electrostatically attract aqueous ions which also contribute to the overall surface charge. Hydrated aqueous ions form outer-sphere complexes that are mobile and exchange with the ions in the fluid. Outer-sphere complexes may become inner-sphere complexes if a chemical reaction happens at some surface sites. For example, an ion may lose water molecules from its shell and form chemical bonds with the surface oxygen atoms.

The interface can be roughly partitioned into three primary constituting parts: (1) surface atoms of a solid; (2) adsorbed water, protons, and hydroxyls, as well as inner-sphere adsorbed complexes (Fig. 10.1a); (3) outer-shell complexes in the Stern layer attached by electrostatic or Van der Waals forces; (4) loosely attached counter-ions (Fig. 10.1b). Geometry and bonding for atoms at the surface and in crystalline bulk lattice can be different due to the surface relaxation effects. Presence

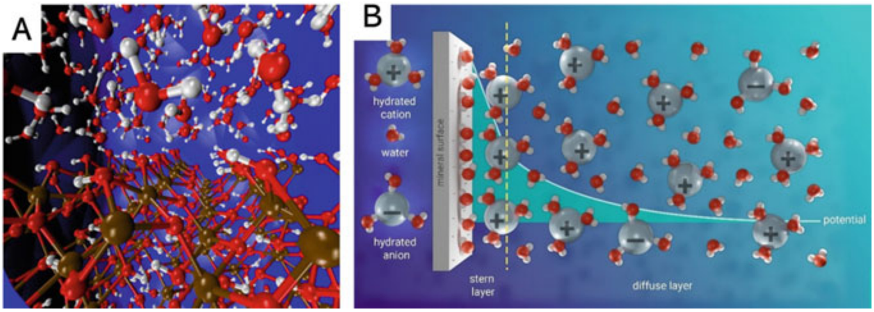

**Fig. 10.1** Structure of crystal-water interfaces. **a** Molecular model of the goethite (100) face in contact with water (Chen et al. 2017), from *Chen, Y., Bylaska, E.J., Weare, J.H., 2017. Weakly bound water structure, bond valence saturation and water dynamics at the goethite (100) surface/aqueous interface:* ab initio *dynamical simulations. Creative Commons Attribution 4.0 International License, Copyright (2017), The authors, Springer Nature*; **b** The schematic structure of the electric double layer (EDL). The white curve shows the magnitude of the electrostatic potential. The Stern layer is the first layer with strongly adsorbed ions via outer sphere adsorption mechanism. The image is taken from (Backus et al. 2021): *Backus, E.H.G., Schaefer, J., Bonn, M., 2021. Probing the Mineral–Water Interface with Nonlinear Optical Spectroscopy. Angewandte Chemie International Edition 60, 10,482–10,501, Copyright (2020); The authors, John Wiley and Sons, Creative Commons CC BY license*

of water may substantially influence onto the geometry of molecules at the interface: protons and water molecules adsorb on the surface and interact with the dynamic fluid (Fig. 10.1a).

Surfaces of natural crystals are rarely represented by atomically flat planes. The sites on a surface can be classified as terrace, ledge, kink sites, and adatoms, depending on the number of coordinating neighbors (Fig. 10.2a). There are three different mechanisms or *regimes* of crystal growth: growth of a rough surface (Fig. 10.2b), 2D nucleation (Fig. 10.2c), and spiral growth (2D). While the first two mechanisms are commonly realized at elevated concentrations of dissolved species in the mother phase or at elevated temperatures, the third mechanism realizes at close-to-equilibrium conditions commonly occurring in nature.

Minerals typically grow in chemically complex environments which contain impurity ions. Impurity ions may adsorb on a surface and facilitate the growth via spiral mechanism (Fig. 10.2d), where lattice sites are continuously misplaced to generate an atomic step which becomes an active place for attachment of atoms and crystal growth. A region where lattice sites are misplaced from their original lattice positions is called a hollow core of a screw dislocation. Misplaced atoms along a hollow core generate lattice strain which weakens chemical bonds. These distorted bonds possess extra lattice energy commonly called as *strain energy,* which makes surface sites at hollow cores primary candidates for dissolution (Blum and Lasaga 1987). Dissolution from these sites generates so-called stepwaves (Fig. 10.2e–f) on surfaces, which are concentric enclosed atomic steps of finite length moving out from their source (hollow cores) (Fig. 10.2e). The stepwaves grow in size and coalesce

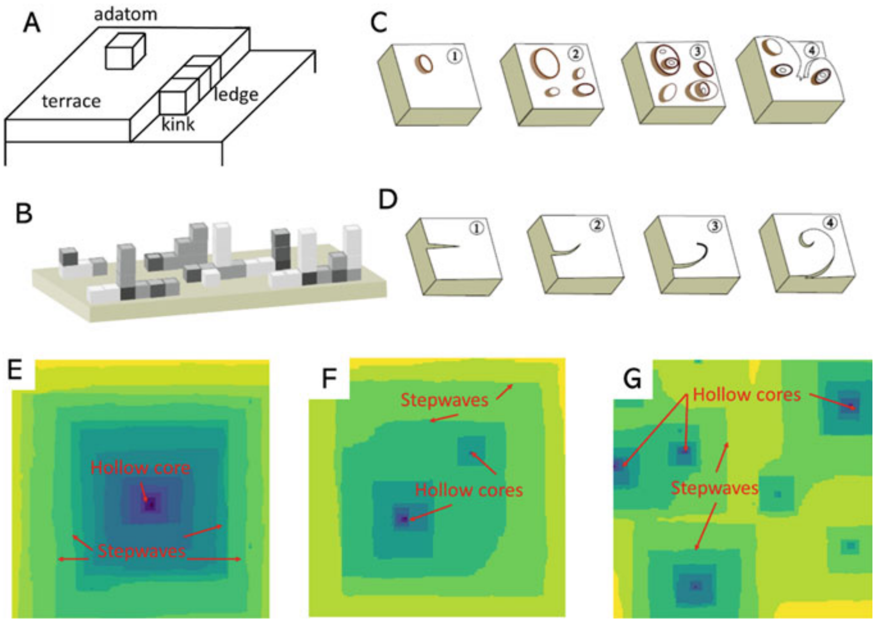

**Fig. 10.2** Microscopic structure of crystal-fluid interfaces. **a** Terrace-ledge-kink model of a surface; **b** Growth of a rough surface; **c** Crystal growth via 2D nucleation mechanism; **d** Crystal growth via spiral mechanism. **b**–**d**: Reprinted from *Li, J., Tilbury, C.J., Kim, S.H., Doherty, M.F., 2016. A design aid for crystal growth engineering. Progress in Materials Science 82, 1–38, Copyright (2016), with permission from Elsevier.* **e**–**f**: Dissolution mechanisms. Hollow cores serve as sources of stepwaves. **e**: Single etch pit; **f**: two interacting etch pits; **g**: interaction of multiple etch pits

to each other forming larger stepwaves travelling across the surface (Fig. 10.2f–g), so the surface retreats normal to itself. Areas of depression formed around hollow cores are essentially etch pits which become detectable by using modern microscopic techniques, such as Atomic Force Microscopy (AFM), Vertical Scanning Interferometry (VSI), and Secondary Emission Microscopy (SEM) (Kurganskaya et al. 2009). Defect assisted growth and dissolution processes are primary mechanisms of phase transitions in mineral–water systems at ambient conditions. Even at chemical equilibrium, some local process of surface reconstruction with local dissolution and growth may happen. Studies of crystal growth and dissolution as processes taking place at crystal-fluid interfaces have a great importance for understanding of ion adsorption and retention mechanisms at natural environmental conditions. Presence of active growth spirals and etch pits on realistic surfaces may potentially influence adsorption properties due to the variety of possible factors: change in the surface area active with respect to adsorption, appearance, or disappearance of crystallographic faces with different adsorption properties, changes in populations of adsorption sites.

Incorporation of foreign ions into growing crystals is a quite common process resulting in formation of solid solutions, e.g., (Ca, Mg, Mn, Fe, Pb,..) $CO_3$, or (Ba, Sr, Ra,..) $SO_4$. Such process is called *mineralogical sequestration* of toxic or radioactive ions. This way of toxic ion retention is fundamentally different from surface adsorption and desorption processes which retention capacity is limited by populations of active adsorption sites on surfaces. However, even mineralogically sequestered ions can remobilize if host minerals dissolve at changing environmental conditions. Studies of crystal growth and dissolution kinetics at various environmental conditions thus have critical importance for predicting fate of toxic ions. Complementary studies of surface charge and electric double layer structure have importance for not only understanding of adsorption processes, but also understanding kinetics of crystal growth and dissolution reactions at the atomistic and microscopic scales.

## 10.3 Kinetic Monte Carlo Modelling

### *10.3.1 Mathematical Foundations of the Method*

Kinetic Monte Carlo (KMC) method is a common approach to simulate temporal evolution of some systems or processes. The KMC method became widely known after a seminal work of Gillespie (1977), who simulated an ensemble of gas-phase chemical reactions. The idea of a KMC model is simple yet powerful: conversion of reaction rates into *probabilities of reactive events*. In this way, the problem of a complex reactive system evolution is solved by means of probabilistic modelling.

Let's consider a system with $N$ chemical species and $M$ possible chemical reactions between those species. In general, it may be difficult to establish which one of those $k$ reactions will happen next time in a particular point of space. The only information available is the reaction rates constants $k_i$, $i = 1, 2, \ldots M$. Such system seems to be too complex to predict its evolution precisely. Moreover, there can be more than one possible way of system's temporal evolution. The stochastic formulation of this problem makes it easily solvable: let's assume that *reactive events* happen randomly in time and space. The critical question is to quantify this randomness. Since we still need to reproduce reaction rates correctly, we should relate probabilities of reaction with their rates. Therefore, we establish that probability of an event is proportional to its rate on average:

$$P_i \sim k_i \tag{10.1}$$

Probabilities should follow definition of a probability space (Wentzel 1969; Rozanov 2013), which is in general defined as a mathematical structure equipped with three elements $(\Omega, F, P)$:

(1) a sample space $\Omega$ which consists of all possible outcomes. For example, getting "6" after throwing dice is an outcome;

(2) an event space $F$, which contains events, where event is a set of outcomes. For example, getting "6, 1, 3" after rolling dice three times is an event;

(3) A probability function $P$ that assigns to each event a probability, a number between 0 and 1.

Some important properties of probability spaces:

(1) the sum of all probabilities over the entire space $\Omega$ is equal to 1: $P(\Omega) = 1$. This condition imposes a critical restriction onto definition of a probability function $P$.

(2) Probability of a union of all elements from the event space $F$, $A_i \in F$ which form a countable collection of pairwise disjoint sets $\{A_i\}_{t=1}^{\infty} \subseteq F$, equals to the sum of all elements:

$$P\left(\bigcup_{i=1}^{\infty} A_i\right) = \sum_{i=1}^{\infty} P(A_i) \tag{10.2}$$

A probabilistic model must be defined in accord to the correct structure of a probability space in order to ensure collection of quantitatively meaningful results from simulations, as well as to have a predictive power.

In general, a system can be described in terms of its *states*, or *system configurations*. For example, if we have a surface with lattice sites $\{n, m\}$ where certain sites $\{n_k, m_k\}$ are occupied by adsorbed atoms, it can be considered as a system configuration. Desorption of an atom from a site $(n_l, m_l)$ results in a new system configuration (Fig. 10.3a). Similar analogues can be done for gas phase molecular reactions, surface reactions, crystal dissolution, and growth.

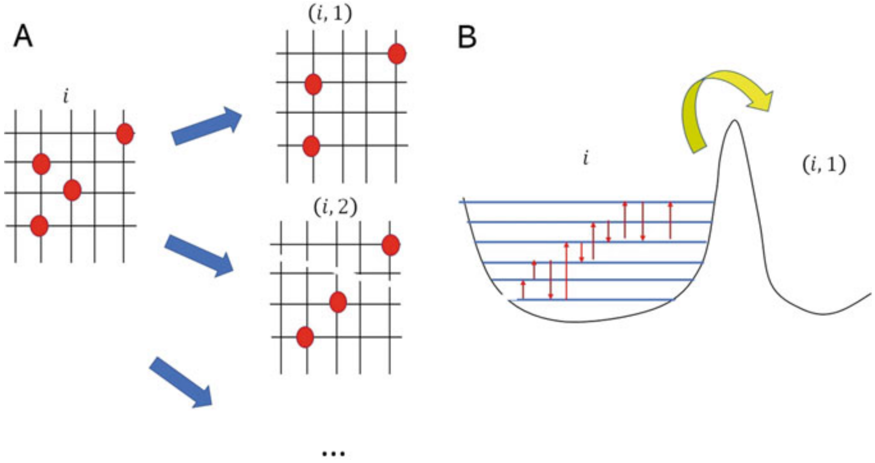

**Fig. 10.3** Schematic drawings for transitions in a system simulated by the Kinetic Monte Carlo method. **a**. Adsorbate atoms on a rectangular lattice. The system may change from the state configuration $i$ into configurations $(i, 1)$, $(i, 2)$ and so on. **b**. A system spends a substantial time in a potential well before making a transition over a potential energy barrier from a state $i$ into one of possible states $(i, 1)$

An important feature of systems simulated by KMC algorithms is discrete and sudden transitions between the *states*, such that system is in general memoryless and transition probabilities depend only on the current system configuration (Fig. 10.3a). This situation is common for many reactive systems, where most of the time a system spends in vibrational and rotational motion of atoms before a reactive jump over a potential barrier is made (Fig. 10.3b, for more detailed explanations see (Voter 2007)).

Probabilities of events in a system characterized by $k_{ij}$ transition rates between states $i$ and $j$ are defined in the following way (Voter 2007):

$$P_{ij} = \frac{k_{ij}}{\sum_{j=1}^{M} k_{ij}} = \frac{k_{ij}}{k_{tot}} \tag{10.3}$$

An event here is an occurrence of a reaction characterized by its rate constant $k_{ij}$. One event consisting of a one outcome (one of the $j$th reactions) is chosen at a time, and probability of all transitions equals to the sum of individual transition probabilities. The sum of all probabilities is 1. Therefore, the two properties of probability spaces mentioned above are satisfied.

Treatment of time propagation between reactive events is explained in (Voter 2007). We provide here his derivations and explanations because they form important theoretical prerequisite for construction of KMC models.

The rate of probability change for staying in a state $i$ is negatively proportional to the waiting time, $t$:

$$\frac{dP_{stay}(t)}{dt} = -k_{tot}t \tag{10.4}$$

The Eq. (10.4) refers to the so-called “mean first passage time problem”, where an average of all times required to overcome some barrier needs to be calculated. The Eq. (10.4) can be integrated to yield:

$$P_{stay}(t) = e^{-k_{tot}t} \tag{10.5}$$

The probability density $p(t)$ of a first passage time $t$ can be obtained if we integrate $p(t)$ over a time interval $t'$ and equate the result to the $1 - P_{stay}\left(t'\right)$:

$$\int_0^{t'} p(t)dt = 1 - P_{stay}\left(t'\right) \tag{10.6}$$

The physical meaning of this equation is the probability to escape the state during the time $t'$. $p(t)$ can be obtained from the Eq. (10.6) if we differentiate left and right hand sides:

$$p(t) = \frac{d\left(1 - P_{stay}\left(t'\right)\right)}{dt} = k_{tot}e^{-k_{tot}t} \tag{10.7}$$

The Eq. (10.7) is used to calculate the time interval between two transition events. A uniformly distributed random number $r \in (0, 1]$ is generated first, then time is calculated as follows:

$$t = -\frac{1}{k_{tot}} \ln(r). \tag{10.8}$$

This equation provides first passage times distributed over a probability density $p(t)$. This probability density can be used to calculate the mean first passage time $\tau$ for escaping the state $i$:

$$\tau = \int_0^{t'} p(t)dt = \frac{1}{k_{tot}}. \tag{10.9}$$

The Eq. (10.9) ensures proper statistical conversion of a kinetic model into a probabilistic model, where transition or reaction rates will be reproduced on average.

### *10.3.2 Description of a System Modeled*

In general, KMC models of adsorption at the surface require description of surface sites in terms of their location and reactive properties, as well as description of possible adsorption reactions characterized by their rates. There can be a large variety of different surface sites, as well as possible adsorbates and reaction rates depending on site and adsorbate type. A common approach in modelling of adsorption is representation of a surface as a planar lattice of adsorption sites, that may be either occupied or unoccupied, lateral interactions with adsorbate atoms can be included or excluded, as well as multi-layer adsorption can be enabled or disabled (Burghaus 2006). Realistic surfaces may differ from planar lattice geometries as they contain atomic steps, etch pits, microfacets, growth spirals, and other growth or dissolution defects. Defect sites, such as step and kink sites, may influence onto mechanisms of adsorption because their coordination differs from coordination of terrace sites. Geometric arrangement of atoms at atomically flat faces, their coordination, and adsorption properties also depend on the orientation of a crystallographic plane parallel to a surface of interest. Since natural crystals, micro-, and nanoparticles exhibit a variety of different energetically stable crystallographic faces, a natural variety of their adsorption properties can be expected.

Adsorption of ions from aqueous environment can be a complex process characterized by electrostatic or Van der Waals outer sphere adsorption, and possible dehydration of an ion and formation of inner sphere adsorption complexes. Desorption reactions for these complexes involve bond hydrolysis by water molecules. These reactions commonly have an energetic barrier because they involve formation and breaking of chemical bonds. As a result, inner sphere adsorption and desorption may happen much slower in comparison to the outer sphere adsorption events. Inner sphere adsorption complexes represent a particular interest for the problem of toxic ion sequestration because they are chemically attached to the surface and are less mobile. Modelling of adsorption for these complexes requires proper identification of surface sites where ion attachment and dehydration most likely occur.

Since realistic surfaces can be very complex and there can be a large number of possible adsorption reactions in a system of interest, a proper model reduction can be required. For example, if adsorption mostly occurs at defect sites, terrace sites can be ignored, or *vise versa*, if adsorption predominantly occurs at terrace sites, defect sites can be ignored if their contribution to the total population of adsorption sites is negligible. Ions or other species, that adsorb in statistically insignificant amount and desorb quickly without affecting the overall chemical balance, also can be excluded from consideration.

## *10.3.3 Adsorption Kinetics*

Once surface sites where adsorption of specific atoms, ions, or aqueous complexes may occur are established, a kinetic description of adsorption events is required in terms of their rates. If adsorption is reversible, complementary desorption reactions must be included into event lists. In general, forward, and backward adsorption reactions are related via an equilibrium constant $K_{eq}$ according to the following equations:

$$> S + A \leftrightarrow SA \tag{10.10}$$

$$K_{eq}^{A} = \frac{[> SA]_{eq}}{[> S][A]_{eq}}, \tag{10.11}$$

where $> S$ represents unoccupied adsorption sites, $SA$ adsorbed species, $A$ species in the aqueous solution, square brackets denote their concentrations, the index “eq” is attributed to equilibrium conditions.

Please note, that the Eqs. (10.10) and (10.11) refer to the equilibrium conditions and concentrations. In general, not all systems are at equilibrium. Equilibrium conditions require a system to be closed with regard to the material exchange with the surrounding environment. Even in this case, some adsorption or desorption reactions can be very slow and kinetically limited, so some time is required to achieve equilibrium conditions. This is especially important for strongly binding ions with large activation barriers for adsorption and desorption reactions. According to the Langmuir adsorption model (Langmuir 1918), the rate of adsorption reaction depends on the number of unoccupied sites and concentration of $A$ in the aqueous solution:

$$R_{ad} = k_{ad}[> S][A], \tag{10.12}$$

where $k_a$ is the adsorption rate constant for a single adsorption reaction. The rate of desorption is calculated in a similar way:

$$R_d = k_d[> SA], \tag{10.13}$$

where $k_d$ is the desorption rate. Adsorption and desorption rates are related via a Langmuir equilibrium constant $K_{eq}^A$:

$$K_{eq}^A = \frac{k_{ad}}{k_d}. \tag{10.14}$$

The $K_{eq}^A$ constant has units of L/mole because the Eq. (10.11) contains units of volume concentrations.

The Langmuir kinetics described by the Eqs. (10.10)–(10.14) can be easily converted into a KMC algorithm. The KMC method is widely used to simulate adsorption on catalytic surfaces and catalytic surface reactions (e.gBurghaus 2006; Exner et al. 2015; Hess et al. 2020)), although its use for adsorption from aqueous solutions is surprisingly limited. Probabilistic formulation for this model is as follows (Kurganskaya et al. 2021):

$$P_{ad} = \frac{k_{ad}[A][> S]S_a V N_a}{k_d[> SA]S_a + k_{ad}[A][> S]S_a V N_a}, \tag{10.15}$$

$$P_d = \frac{k_d[> SA]S_a}{k_d[> SA]S_a + k_{ad}[A][> S]S_a V}, \tag{10.16}$$

where $P_{ad}$, $P_d$ are probabilities for adsorption and desorption reactions, $S_a$ is the surface area, $V$ is the fluid volume, $N_a$ is the Avogadro's number.

If we our system is closed, then we can calculate the concentration of aqueous ions as follows:

$$C_{aq} = \frac{N_0 - N_{occ}}{V N_a}, \tag{10.17}$$

where $N_0$ is the initial number of aqueous ions before adsorption, $N_{occ}$ is the number of ions adsorbed on a surface (Kurganskaya et al. 2021).

## *10.3.4 Monte Carlo Algorithms*

The family of Monte Carlo simulations is a class of computational algorithms used to solve a physical or mathematical problem by random sampling. An easy to comprehend example of a random sampling solution is calculation of the π number (e.g., as it is explained in (Burghaus 2006)). Let's consider a circle of a radius $r$ inscribed

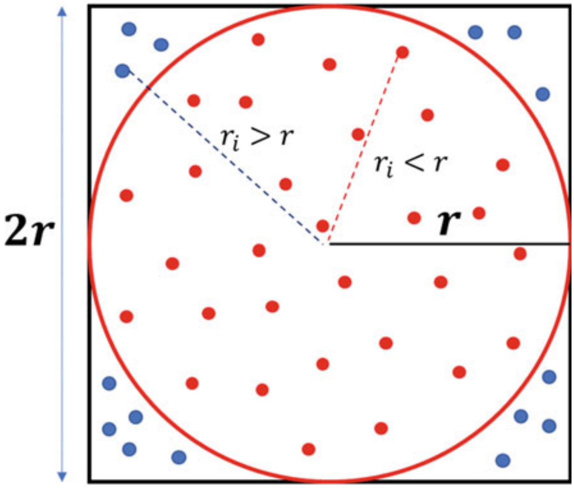

**Fig. 10.4** An illustration to calculation of the π number by using the Monte Carlo method. A circle of a radius $r$ inscribed into a square of a length $2r$. Points with radial coordinates $r_i$ are randomly generated. A simple comparison of their coordinates with the radius $r$ provides the ratio between the number of points lying within and outside the circle. This ratio is the ratio between corresponding areas, which provide an estimate of the π number

into a square of a length $2r$ (Fig. 10.4). Then let's generate a large number of points with radial coordinates $r_i = \sqrt{x_i^2 + y_i^2}$. A comparison whether $r_i < r$ provides a status $N_c$ to a point and $N_o$ otherwise. The number $N_c$ provides a relative estimate of the circle's area, while the number $N_o + N_c$ provide a relative estimate of the square area, such that

$$\frac{A_{circle}}{A_{square}} = \frac{N_c}{N_c + N_o} = \frac{\pi r^2}{4r^2} = \frac{\pi}{4}. \tag{10.18}$$

As we can see from the Eq. (10.17), the π number is the calculated $\frac{N_c}{N_c+N_o}$ ratio multiplied by 4 (Fig. 10.4). The growing number of random trials would also increase the accuracy of the π number estimation.

Algorithmic realization of the probabilistic model described in 3.1–3.3 requires a description of rules for sampling the event space and producing *system evolution trajectories*. A *trajectory* is sequence of events realized in time. Each trajectory is essentially stochastic and represents one of the possible evolution scenarios under provided kinetic constraints. This stochasticity is an intrinsic property of the KMC algorithm and its ultimate power. The KMC algorithm does not only provide a simple way to produce system's dynamics but also provides an approach to construct possible microscopic configurations that may arise in a system of interest. For adsorption of atoms on a lattice each microscopic configuration corresponds to a specific geometric arrangement of adsorbed atoms, e.g., as it is shown on the Fig. 10.3a. A trajectory for this system would be a sequence of different adsorbate numbers and geometric arrangements.

The key idea behind kinetic Monte Carlo algorithms is the direct relationship between probability distributions of events and time, as it has been shown in the 3.1. There are two major types of kinetic Monte Carlo algorithms: rejection KMC (rKMC) and rejection-free KMC (rfKMC). In the rejection algorithm a uniformly distributed random number $rn$ between 0 and 1 is generated and then compared with the probability of a suggested event $P_n$. If $rn < P_n$, then the event is accepted, otherwise is it rejected. The time is propagated at each iteration step by some constant value. Another, more commonly used algorithm for KMC simulations, is the rejection-free, or BKL algorithm (Bortz et al. 1975), where a reactive event is performed at each iteration step. According to this algorithm a reactive event is performed at each iteration step. The event is selected by construction of the "running sums", or sequential sums of all probabilities:

$$S_n = \sum_{j=1}^{n} P_{ij};\ S_{n+1} = \sum_{j=1}^{n+1} P_{ij}. \tag{10.19}$$

An $n^{th}$ event is selected if a uniformly distributed random number $rn$ between 0 and 1 satisfies to the following criterion:

$$S_n > rn > S_{n+1}. \tag{10.20}$$

Generation of the event sequence is directly related to the propagation of time according to the Eq. (10.8), so the time step is estimated according to this formula. Once an event is generated, the system is updated accordingly and a new iteration step with a new random number is launched again. A schematic description of this algorithm is shown on the Fig. 10.5. A KMC program first reads all the input information necessary to generate a surface. Surface atoms can be provided directly as $\{x_i, y_i, z_i\}$ coordinates, or a surface can be constructed by a program if crystallographic data are supplied in the form of unit cell parameters, (hkl) crystallographic indexes and type of surface termination, periodic boundary conditions in case of planar systems or sets of (hkl) indexes for nanocrystals/nanoparticles. In a case of nanocrystals/nanoparticles a truncation algorithm for bulk crystal lattice is required. The system size and the number of iteration steps are also provided as input parameters. A program then generates surface sites described by their geometric and reactive parameters (e.g., location, coordination, and adsorption properties). Initial aqueous ion concentration and reaction probabilities are calculated. The program then iterates over a loop by generating random numbers to choose an event (adsorption or desorption), and an appropriate site (occupied or unoccupied) to perform a reaction. Sites of identical types are selected by using another uniformly distributed random number because reaction probabilities for identical sites are the same. After making a decision event, the time is updated according to the Eq. (10.8), an adsorbate ion are added or removed from a selected site, concentration of ions in the fluid is recalculated, and the entire sequence is repeated at the next iteration cycle. A number $N_{out}$ is required as an input parameter to produce output data at a certain fraction of iteration steps. Output data are surfaces with adsorbed ions, populations of adsorbed sites, and aqueous ion concentrations.

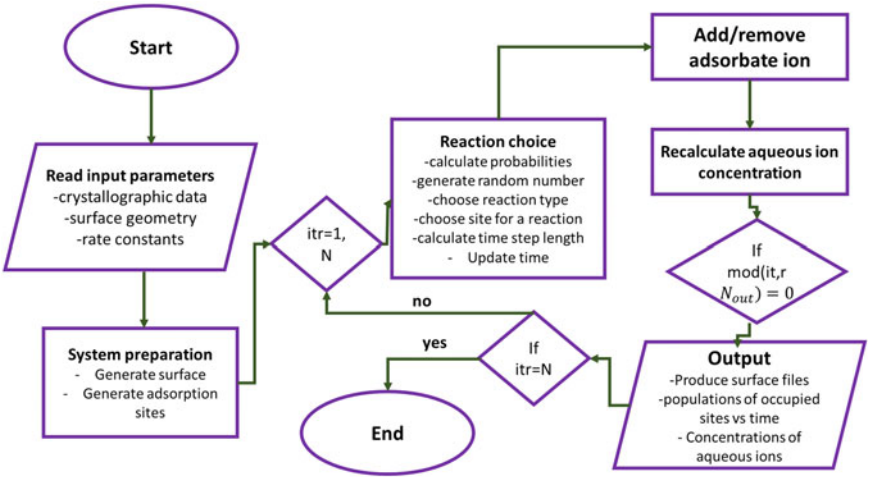

**Fig. 10.5** A workflow chart for the kinetic Monte Carlo algorithm applied to surface adsorption of aqueous ions

The algorithm presented here is generic and can be applied to any type of a surface and adsorbate ions, surface sites can be classified as having different adsorption probabilities and rates with respect to a variate of adsorbate ions. If there are any lateral interactions between the adsorbates which are likely to occur due to, for example, electrostatic Coulomb repulsion, then local coordination of adsorbate ions and their influence onto site adsorption probabilities should be incorporated. Presence of different ions in the fluid can induce *competitive adsorption*, as it is the case, for example, for arsenate and phosphate ions (Han et al. 2020) due to the similarity of their geometry and an ability to occupy the same surface sites.

### 10.3.5 Adsorption of As(V) on Hematite Nanocrystals

Iron oxides possess a unique property to adsorb aqueous arsenic ions (Aredes et al. 2012; Polowczyk et al. 2018; Chiavola et al. 2019; Usman et al. 2020). Its efficiency in adsorption stems from the positive charge of the surface which electrostatically attracts negatively charged arsenate (As(V)) and arsenite(As(III)) ions. Hematite ($Fe_2O_3$) is a naturally occurring iron oxide mineral that can be also synthesized at laboratory conditions. Its adsorption properties stem not only from the surface charge, but also from the specific geometry of surface sites where distances between the surface oxygen atoms are similar to the distances between oxygen atoms in the tetrahedral forms of As ions. This distance criterion was employed in construction of a KMC model for As(V) adsorption in the form of bidentate binuclear and bidentate mononuclear complexes on the surfaces of hematite nanocrystals (Kurganskaya et al. 2021). The following (hkl) crystallographic faces were considered: prism (110) (Fig. 10.6a), rhombohedral (101) (Fig. 10.6b), (104) (Fig. 10.6c), (012) (Fig. 10.6d), as well as basal (001) face in two possible terminations (Fig. 10.6e, f).

Crystallographic faces shown on the Fig. 10.6 have drastically different geometric arrangements of surface Fe and O atoms represented by $FeO_6$ octahedra forming face-specific structures. Corner-sharing octahedra have only one common Oxygen atom, while edge-sharing octahedra have two common Oxygen atoms. Vertices belonging only to single Fe atoms represent dangling Fe–O bonds which are primary binding sites that can compete with the oxygen atoms in $AsO_4{}^{3-}$ ions. Two dangling bonds at a distance comparable to the distance between Oxygen atoms in $AsO_4{}^{3-}$ ions are considered as most probable candidates for formation of bidentate binuclear surface complexes on the prism face (Fig. 10.6a) and rhombohedral faces (Fig. 10.6b–d). Since desorption of these complexes would require breaking of two chemical bonds, they are expected to be most stable on the surface. Bidentate mononuclear complexes also may form at the edges of $FeO_6$ octahedra (Fig. 10.6e). The other

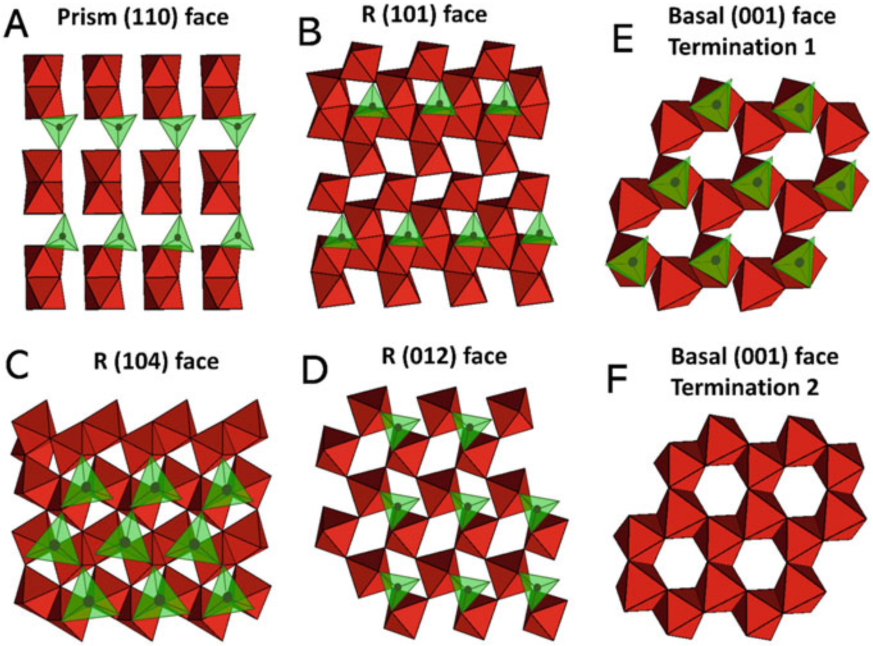

**Fig. 10.6** Geometry of sorption sites on different faces of hematite surface considered in the Kinetic Monte Carlo model. **a**–**d**: inner sphere bidentate binuclear (IS-B-B) adsorption sites, **e**: inner sphere bidentate mononuclear IS-B-M2 adsorption sites. $FeO_6$ surface groups are shown as red octahedrons. $AsO_4{}^{3-}$ anions are shown as green transparent tetrahedrons. **a**: prism (110) face; **b**: Rhombohedral (101) face; **c**: Rhombohedral (104) face; **d**: Rhombohedral (012) face; **e**: Basal (001) face termination 1; **f**: Basal (001) face termination 2. *Reprinted from Kurganskaya, I., Niazi, N.K., Luttge, A., 2021. Journal of Hazardous Materials 417, 126005, Copyright (2021), with permission from Elsevier*

types of complexes, e.g., outer sphere or monodentate complexes, that may form at hematite surface, were excluded from consideration as less stable. The reason behind their exclusion from this model is sensitivity of the surface charge to changing environmental conditions in terms of pH and concentration of different ions. Change in surface charge may trigger desorption of electrostatically adsorbed outer-sphere complexes. Monodentate complexes are chemically adsorbed and are more stable than outer-sphere complexes. However, they still possess some degrees of freedom in terms of their vibrational and rotational motion, so one bond can be broken or formed easier than two bonds of bidentate complexes. In any case, the other types of adsorption complexes can be incorporated into a KMC model of adsorption, it would only require the knowledge of adsorption–desorption constants for surface sites of relevant geometries.

The probabilistic KMC model was formulated according to the Eq. (10.10)–(10.17). The systems modeled were series of nanocrystals of different shapes placed into enclosed volumes of As(V) contaminated fluid characterized by different initial concentrations [C(t0)]. Over time concentrations in the fluid dropped, and chemical equilibria were established (Fig. 10.7a). The quantitative relationships between the equilibrium concentrations and fractions (concentrations) of occupied surface sites can be predicted from the Langmuir equation:

$$C_{eq} = \frac{\theta_{eq}}{1 - \theta_{eq}} \times \frac{1}{K_{eq}}. \tag{10.21}$$

Equilibrium pair values $\{\theta_{eq}, C_{eq}\}$ can be obtained from the KMC simulations at different initial concentrations [C(t0)]. Plot of data points from this set show that they follow the Langmuir Eq. (10.21) (Fig. 10.7b). This result is expected because reaction probabilities were derived from the Langmuir model. The Langmuir adsorption

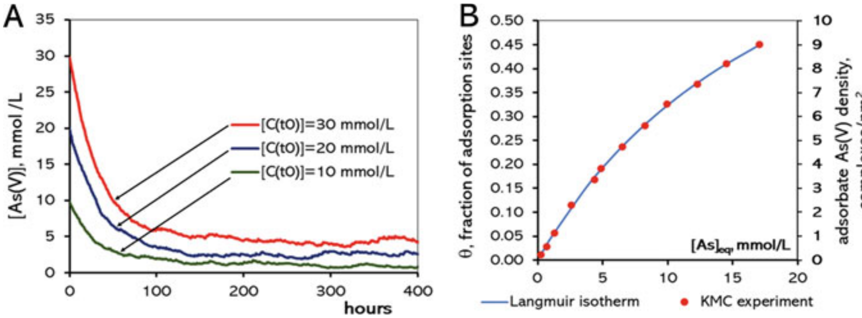

**Fig. 10.7** **a**: Concentration of As(V) in the solution phase vs. time at three different initial [C(t0)] concentrations of aqueous ions in a KMC simulation on a hematite nanoparticle. **b**. Langmuir isotherm (calculated from Eq. (10.21)) and Kinetic Monte Carlo relationships between the equilibrium As(V) concentration and the fraction of occupied sites. *Reprinted from Kurganskaya, I., Niazi, N.K., Luttge, A., 2021. Journal of Hazardous Materials 417, 126005, Copyright (2021), with permission from Elsevier*

model is one of the models commonly used to interpret macroscopic adsorption data. This result illustrates the convergence of a microscopic (KMC) model to a one-site one-adsorbate type macroscopic model (Langmuir). The KMC approach thus can be used to confirm a work hypothesis regarding microscopic reaction mechanisms suggested upon analysis of macroscopic experimental data.

Nanoparticles and nanocrystals can occur naturally, or they can be synthesized at laboratory conditions. Their shape and size can be designed to fulfill some target property. The shape of synthetic hematite nanocrystals can be quite well-controlled by using chemical additives and varying their concentrations in mother phase solutions (Wheeler et al. 2012; Fouad et al. 2019). Some variety of naturally occurring hematite crystal shapes is expected in the natural environment (Guo et al. 2013). There is a certain interest in designing nanoparticles or nanocrystals with the most optimal adsorption capacity possible. A KMC model as presented above can be used to test nanocrystals with regard to their adsorption efficiency (Fig. 10.8). The model which is based on the strongly binding bidentate adsorption complexes showed that elongated prismatic nanocrystals possess the highest adsorption capacity (Fig. 10.8). Flat platy hexagonal crystals commonly occurring in nature possess the lowest adsorption efficiency. Nanocrystals of rhombohedral morphologies are quite efficient adsorbents according to this KMC model. More detailed KMC models considering effects of Coulomb interactions between the adsorbed ions are required for more detailed information regarding their adsorption capacity.

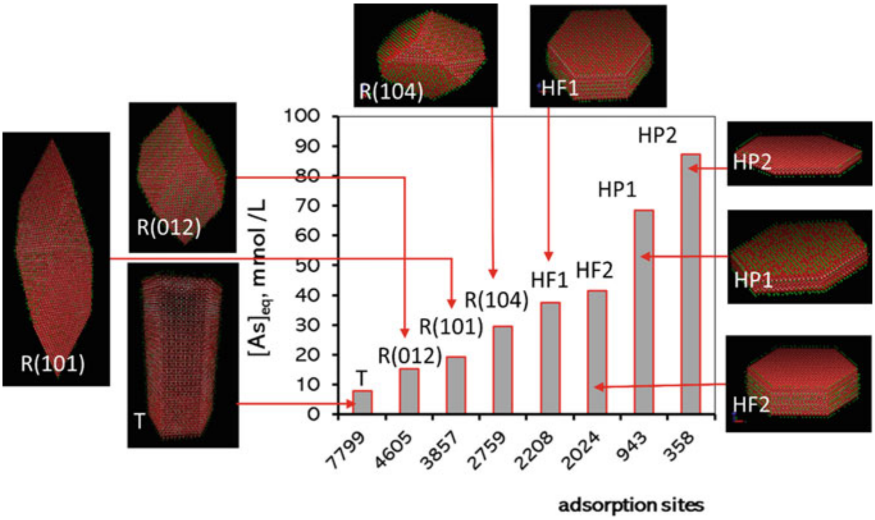

**Fig. 10.8** Equilibrium concentrations of As(V) ions for hematite nanocrystals of different morphologies, the diameter of all nanocrystals is 15 nm. The number of sorption sites for each nanocrystal's type is shown on the X-axis. *Reprinted from Kurganskaya, I., Niazi, N.K., Luttge, A., 2021. Journal of Hazardous Materials 417, 126005, Copyright (2021), with permission from Elsevier*

The ultimate power of the KMC approach to model adsorption is a possibility to use it as a heuristic tool for testing mechanistic hypotheses regarding process-controlling reactions, their rates, and proper identification of adsorption sites. The model formulated above showed a good qualitative agreement with the experimental tests for adsorption efficiency of nanoparticles possessing different shapes (Yan et al. 2020). Realistic quantitative predictions require more detailed formulation of a KMC model, including surface charge effects, protonation-deprotonation, as well as adsorption and desorption of all possible complexes and their electrostatic interactions. Since nanoparticles commonly form aggregate materials due to the surface charge, an appropriate modelling of aggregated charge material can improve simulation results. KMC type of models require input parameters formulated as reaction/event rates, probabilities, and locations of events. These data cannot be obtained from a KMC model which is a pure parameterized mathematical technique powered by mechanistic hypotheses regarding the physical chemistry of a process modelled. Therefore, alternative modelling approaches are required, such as Quantum Mechanical calculations (e.g., Density Functional Theory) and/or Molecular Dynamics simulations, to obtain rate parameters and understand molecular reaction mechanisms. The methods of statistical mechanics, such as Canonical and Grand Canonical Monte Carlo simulation approaches, can be successfully utilized to model surface charge, interaction of aqueous ions in the bulk fluid, and non-reactive electrostatic interaction between ions and charged surface, i.e., outer-sphere adsorption. We briefly delineate the essence and applications of the Grand Canonical Monte Carlo method for the studies of crystal-fluid interfaces.

## 10.4 Statistical Mechanics Approaches

Crystal-fluid interfaces at the molecular scale are very complex chemical systems with many degrees of freedom. Macroscopic behavior of the interfaces is the integrate result of processes at the microscopic and atomistic scales. There can be a large number of possible processes and surface reactions at the microscopic scale which may or may not lead to the identical macroscopic behavior. The connection between microscopic and macroscopic behavior of a chemical system is provided by a field of theoretical physics called *statistical mechanics* (Reif 2009; Allen and Tildesley 2017). A central idea is that a thermodynamic system can be described in terms of constant thermodynamic state parameters, constituting a *macrostate*, which can be obtained from probabilistic distributions of corresponding *microstates.* A microstate is a point in a *phase space*, defined by coordinates and momenta of particles. Statistical mechanics is thus constructed upon two key concepts: *probabilities* and *ensembles.* Ensemble is a collection of all possible microstates of a system with some fixed macroscopic parameters, e.g., energy (E), volume (V), temperature (T), chemical potential ($\mu$), or number of particles (N). Constant macroscopic parameters define the type of an ensemble: microcanonical (N, V, E), canonical (N, V, T), grand canonical ($\mu$, V, T), Gibbs (isobaric-isothermal) (N, P, T), or isoenthalpic-isobaric

(N, P, H). Probabilities of states with different energies depend on the type of an ensemble, but they are all proportional to the exponents of system's energy and other parameters as $\propto e^{f(E,\ldots)/kT}$. Probabilistic formulation of the statistical mechanics laws enables a possibility to employ stochastic modelling approaches. Metropolis Monte Carlo (MMC) approach is widely used in statistical mechanics for simulations of systems at equilibrium. The Metropolis algorithm produces a random sequence of system's configurations based on the probability distributions provided by the laws of the statistical mechanics, e.g., Boltzmann distributions. The algorithm is very simple: (1) generate a candidate system's configuration and calculate its probability of occurrence; (2) draw a random number; (3) accept a candidate if the number is less or equal to the probability, reject otherwise.

The MMC approach can be applied to a large variety of systems and problems. In particular, it can be used to simulate charged surface and ions in the bulk fluid interacting with each other (Labbez and Jönsson 2006). The Grand Canonical Monte Carlo (GCMC) approach is developed for grand canonical ensembles suitable for simulations of systems defined by fixed concentrations of ions represented by their chemical potentials $\mu$. Reactions of protonation and deprotonation of surface sites defined by their acidity constants, $K_a$, can be incorporated into the simulation algorithms (Labbez et al. 2006; Labbez and Jönsson 2006). This type of models employs so-called primitive electrolyte model where ions are represented by hard spheres of certain ionic radii with Coulomb charges placed into the centers of these spheres (Stokes 1972; Valleau and Cohen 1980). Since electrostatic attraction of hydrated ions to the charged surface sites is in fact outer-sphere adsorption, the GCMC approach can be used to simulate this type of adsorption. The power of the GCMC approach to simulate charged ionic systems is in its ability to capture the electrostatic correlations between the adsorbed ions and their influence onto the protonation and deprotonation reactions (Labbez et al. 2006, 2009; Porus et al. 2011). As a consequence, realistic "effective" acidity constants of surface sites can be calculated (Churakov et al. 2014).

The GCMC models of surfaces interacting with ions via Coulomb forces can be very useful for development and improvement of KMC models. Since KMC models require description of possible reactions and their probabilities, GCMC can be used to obtain statistics for protonated and deprotonated surface sites and populations of sites with adsorbed ions. This information regarding populations of charged sites can be directly incorporated into a KMC model of dissolution, growth, or adsorption. Charged sites typically have different rates for reactions of atomic attachments to the surfaces and detachment from the surfaces (i.e., as it was shown for silicate minerals, (Xiao and Lasaga 1994, 1996; Criscenti et al. 2006; Morrow et al. 2009)). Presence of adsorbed ions may also influence onto the dissolution rates (Kubicki et al. 2012; Zhang and Liu 2014). Example of such coupled KMC + GCMC approach is a microkinetic models of calcium carbonate dissolution as a function on pH conditions (Kurganskaya and Churakov 2018). The GCMC model was constructed as NaCl solution with $CaCO_3$ surfaces containing etch pits with atomic steps and kink sites subject to protonation and deprotonation reactions:

$$CO_3^{2-} + H^+ \leftrightarrow HCO_3^- \tag{10.22}$$

$$HCO_3^- + H^+ \leftrightarrow H_2CO_3 \rightarrow H_2O + CO_2^g \uparrow \tag{10.23}$$

$$Ca - OH_2 \leftrightarrow Ca - OH^- + H^+ \tag{10.24}$$

$$Ca - OH^- \leftrightarrow CaO^{2-} + H^+ \tag{10.25}$$

Carbonate kink sites showed the strongest affinity for protonation reactions in comparison to the other sites, step sites showed intermediate affinity, and terrace sites showed least affinity. Presence of the background electrolyte (NaCl) substantially enhanced protonation of the surface due to the adsorption of $Cl^-$ ions which attracted protons. Protonated sites are more reactive than electroneutral sites, so the populations of the protonated sites were incorporated into the KMC algorithm to obtain pH-dependence of dissolution rate.

The approaches of statistical mechanics have a great potential for applications to the studies of surface adsorption processes at natural environments. These methods can address atomistic details and molecular scale mechanisms altogether with complexity of possible system's configurations, thus providing a robust and meaningful approaches to study the solid–fluid interaction phenomena. Correct statistical description of the system should lead to correct predictions of its macroscopic behavior. The stochastic Monte Carlo approach enables a possibility to directly sample system's configuration space and acquire statistical data at the atomistic scale for larger scale models.

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# Chapter 11
# A Comparison of Technologies for Remediation of Arsenic-Bearing Water: The Significance of Constructed Wetlands

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**Abstract** Arsenic (As) contamination of aquatic and terrestrial systems is an emerging environmental and human health issue threating more than 200 million people globally at risk of As toxicity. Arsenic contamination has been reported in more than 115 countries worldwide especially in Asian and Southeast Asian countries, including in Bangladesh, China, Pakistan, India. In contrast to conventional and some advanced techniques (e.g., ion exchange, nanotechnology), constructed wetlands (CWs) can provide a sustainable, low-cost and nature-based solution for arsenic-contaminated water and wastewater. Although there is limited research available on implications of CWs for As remediation in water, this chapter describes sources of As contamination in aquatic environments; hazardous effects of As on the environmental and human health; provides comparative information and understanding of various As remediation technologies, and how the significance of CWs in remediation of As-contaminated water.

**Keywords** Wetlands · Groundwater · Health risk · Remediation technologies · Sustainability

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## 11.1 Introduction

Arsenic (As)-contaminated groundwater and surface water has become a major concern worldwide due to its highly toxic nature and classification as Class-I human carcinogen (Antoniadis et al. 2017; Shahid et al. 2017). The World Health Organization (WHO) has laid down the permissible limit of 10 μg As $L^{-1}$ for drinking water (WHO 2011). In the aquatic environments, As exists in organic and inorganic forms, while organic forms are 100-time less toxic compared to inorganic forms, mainly arsenite (As(III) and arsenate (As(V)) (Kumarathilaka et al. 2018; Smedley and Kinniburgh 2002). Ingestion of As-laced groundwater that is pumped from the millions of wells installed in the alluvium sediments contaminated with As acts as major pathway of As entrance to human food chain (Khalid et al. 2017). However, the intake of As via As-contaminated drinking water or via irrigation of food crops (e.g., rice) receiving As-rich groundwater or wastewater, may cause severe health issues such as: feet and hand related disease, decrease of white and red blood cells and damages blood vessels (Kazi et al. 2009).

Arsenic contamination has been reported to affect about 200 million people globally with over 100 million at As toxicity risk in Pakistan, Bangladesh and India (Abbas et al. 2018; Bakhat et al. 2017; Moyé et al. 2017). To remediate As-contaminated water, various physico-chemical and biological approaches have been used over the last few decades that have their own limitations and efficiencies (Back et al. 2018; Lata and Samadder 2016; Niazi and Burton 2016; Shaheen et al. 2019; Shakoor et al. 2016a). However, these conventional technologies have many drawbacks including sludge production, laborious, costly with a threat to emerge as an new noxious issue for the environment and human health (Shakoor et al. 2017). As a result, it is critical to use the low-cost, efficient, and sustainable technology to remediate As-contaminated water. Arsenic removal using phytoremediation and sorption has been promising way to remediate in water from wells and acid mine drainage (Corroto et al. 2019; Javed et al. 2019).

Compared to conventional or some highly advanced and expansive (e.g., membrane filtration, nanotechnology) technologies, constructed wetlands (CWs) has emerged as a cost-effective, environmentally-friendly and sustainable technology for treating As-contaminated water at small- to large-scale in recent years (Ashraf et al. 2016; Wang et al. 2020). This technique has certain advantages and its efficiency can be enhanced by using different bedding media, microorganisms and wetland plants to treat water. Arsenic remediation potential using CWs has been reported using micro- and meso-cosm experiments (Marchand et al. 2010; Rahman et al. 2014). The CWs had already been shown to effectively remove As and other potentially toxic elements from aqueous solutions in previous studies (Afzal et al. 2019; Corroto et al. 2019; Lizama-Allende et al. 2018; Olmos-Márquez et al. 2012; Valles-Aragón and Alarcón-Herrera 2014; Wu et al. 2019; Younas et al. 2022b).

Constructed wetlands application in remediation of the contaminated environments is considered to be the most effective, cost-effective and sustainable way. This chapter describes sources with threat of As contamination; hydrogeochemical As behavior and occurrence of As in water systems; and a comparative evaluation of various As treating technologies is given with a specific focus on the application of CWs with its future potential and research challenges.

## 11.2 Sources of Arsenic and Its Speciation

Arsenic (As) is the 20th most abundant element in the Earth's crust that is released into the soil and water environments by geogenic and anthropogenic sources. Anthropogenic sources include As-based agrochemicals, smelting and mining, coal combustion, cosmetics, wood treatment and dyes (Hussain et al. 2020; Mohan and Pittman 2007). Also, increased As concentration in water is ascribed to geogenic As release into groundwater (Arain et al. 2009; Baig et al. 2009; Shah et al. 2009). Natural sources of As release are parent material weathering, hot springs and volcanic eruptions (Hussain et al. 2021b). During weathering processes, ores containing sulfides release highly mobile form of As which may dissolve into dust particles and after rain it becomes the part of aqueous environment (Maity et al. 2011). However, in nature there are more than 200 As minerals of which 20% are sulfides, 60% arsenate and 20% arsenite, arsenide, oxide and silicates (Mushtaq et al. 2018). The presence of As in most of mineral phases, soils and water systems is directly related to different As species such as arsenite (As(III)) and arsenate (As(V)) species in groundwater, of which former is 60-time more toxic than the later (Herath et al. 2016).

Under aerobic conditions in thermodynamic equilibrium, As is controlled by As(V)-oxyanion. The neutral As(III) species predominate when reduced conditions exist. The redox kinetics may be significantly accelerated by the activity of microbes which are associated with the oxidation of As(III) and the reduction of As(V) that may govern the hydrogeochemical changes in As cycling (Hussain et al. 2021d, 2020; Smedley 2008). At low pH the rate of oxidation is slower that can employ the presence of As-sulfur minerals reduction with high dissolved As concentration due to high sulfide contents in aquatic medium (Hussain et al. 2019; Smedley 2008). Aqueous solutions of As(III) are the dominant medium over a wide range of pH under strongly reducing conditions associated with Fe (Hussain et al. 2020, 2021b; Smedley 2008).

## 11.3 Hazardous Effects of Arsenic on the Human Health

Various studies have revealed that As exposure to human body via different sources can cause cancers of various body organs (Table 11.1). Some studies have shown that chronic As exposure have serious neurological effects and lead to endocrine disruptors (Abdul et al. 2015; Ali et al. 2018; Biswas et al. 2020; Sun et al. 2016) and skin lesions, heart conditions, physiological also impacting gastrointestinal tract disorders (Chakraborti et al. 2017). Prolonged exposure of low As concentration may pose toxicity risk and cause oxidative stress, interference with neurotransmitters and effects on the hematopoietic system (Andrade et al. 2015). Arsenic exposure to humans has many biological effects which favor oxidative stress, DNA damage, and production of reactive oxygen species (Table 11.1) (Rao et al. 2017).

## 11.4 Challenges in Technologies to Remediate Arsenic-Contaminated Water and Wastewater

Arsenic-contaminated well water or wastewater is major threat to humans either via direct consumption of drinking water or through ingestion of As-contaminated food crops receiving As-contaminated groundwater or wastewater (Natasha et al. 2021, 2022). Therefore, it is imperative to minimize As mediated health risk by adopting suitable and effective remediation measures. Various techniques have been used for As removal from contaminated water such as: ion exchange, coagulation/flocculation, membrane filtration, oxidation/reduction, biochar, biosorbents, clay minerals, metal oxides.

## 11.5 Oxidation Techniques for Arsenic Separation from Water

### *11.5.1 Oxidation and Filtration*

Oxidation is referred to the transformation of As(III) to As(V) and as such As(V) is precipitated by using suitable materials under aerobic conditions. At neutral pH, As(III) species becomes predominant and mobile in the aquatic environment because As(III) is more mobile and toxic in water than As(V) species due to reduced conditions. Because of mobile nature of arsenite, it has low affinity for mineral surfaces while As(V) is readily adsorbed on mineral surfaces. Therefore, the oxidation coupled precipitation technique is very effective to remove As from water. Arsenite is oxidized to As(V) by conventional chemical oxidants such as chlorine, hydrogen peroxide, chloramine, permanganate, ozone and ferrate (Ahmad et al. 2019; Li et al. 2019; Ma et al. 2017; Sharma and Sohn 2009; Wei et al. 2019).

### *11.5.2 Photo-Chemical Oxidation*

The conversion of organic As species to inorganic ones is facilitated by photo-oxidation. While As(III) species cannot be photo-oxidized directly, light-absorbing chemicals such as Fe(III), $H_2O_2$, and $NO_3/NO_2$ can be used to oxidize As(III) in

**Table 11.1** Effect of elevated arsenic concentrations on human and plants

| As effects | | | | | References |
|---|---|---|---|---|---|
| Humans | | | | Plants | |
| Acute | Reference | Chronic | Reference | | |
| Headache | Mohan et al. (2017) | Human carcinogen | Zhou and Xi (2018)<br>Cardoso et al. (2018) | Disturb enzyme function | Mishra et al. (2016) |
| Malaise | Pathak and Pathak (2018) | Skin cancer | Hoque et al. (2016) | Loss of turgor | Chandrakar et al. (2018) |
| Abdominal pain | Zhu et al. (2017) | Lung cancer | Doll (2017) | Wilting | Jasrotia et al. (2017) |
| Nausea | Tan et al. (2015) | Bladder cancer | Koutros et al. (2018) | Alteration in membrane integrity | Kharroubi et al. (2017) |
| Vomiting | Tan et al. (2015) | Liver cancer | Sadaf et al. (2018) | Membrane degradation | Boehme et al. (2016) |
| Acute hemolysis | Guo et al. (2019) | Prostate cancer | Wang et al. (2017a) | Chlorosis | Wang et al. (2018) |
| Thickening of the skin | Tanga et al. (2016) | Diabetes | Muñoz et al. (2018) | Affects phosphorylation | Li (2017) |
| Dark skin | Mohammed et al. (2017) | Neurological disorders | Brown and Sen (2017) | Defoliation | Kofroňová et al. (2018) |
| Abdominal pain | Mohan et al. (2017) | Cardiac disorders | Emi (2017) | Guard cells, tissue death and fruit drop off | Xue and Yi (2017) |
| Numbness | Sharma et al. (2016) | Reproductive organs failure | Khatun et al. (2018) | Reduced yield | Iqbal et al. (2016) |
| >200 Enzymes inactivation | Ratnaike (2003) | Eyes burning | Bhattacharya et al. (2016) | Stunted growth | Ali et al. (2016) |
| Muscle cramping | Zhang (2016) | Cough | Ergün et al. (2017) | Necrosis | Gonçalves et al. (2017) |
| Weakness | Sharma et al. (2016) | Heamoptysis | Patir et al. (2016) | Inhibit phosphatase enzymes | Chen et al. (2016) |
| dizziness | Ishii et al. (2018) | Dyspnoea | Sanchez et al. (2018) | Affects metabolic processes | Xiao et al. (2016) |
| Muscle and bone pain | Mohan et al. (2017) | Paresthesia | Mohan et al. (2017) | Cause oxidative damage | Singh et al. (2018a) |
| Insomnia | Niño et al. (2018) | Leukopenia | Ally et al. (2016) | Sterility of the florates/spikelets in rice | |

(continued)

**Table 11.1** (continued)

| As effects | | | | | References |
|---|---|---|---|---|---|
| Humans | | | | Plants | |
| Acute | Reference | Chronic | Reference | | |
| Rigors | Haghi et al. (2018) | Proteinuria | Cheng et al. (2017) | Damages the chloroplast membrane | Gupta et al. (2015) |
| Loss of appetite | Hasanato and Almomen (2015) | Inflammation of respiratory mucosa | Torjussen (2017) | Disorganizes the functions of integral photosynthetic process | Chandrakar et al. (2016) |
| Skin lesions | Niedzwiecki et al. (2018) | Short term memory | Hasanato and Almomen (2015) | Decrease in pigment synthesis | Anjum et al. (2017) |
| Slurred speech capability | Kühn et al. (2016) | Tremors | | Oxidative stress | Singh et al. (2018a) |

irradiation solution (Kim et al. 2014; Vione et al. 2014; Wang et al. 2012). These agents produce high energy transient species which have ability to oxidize As(III) (Bhandari et al. 2011; Talebi et al. 2019). The chemical oxidant that is used mostly is Fe-based, which assists in the UV/photochemical-induced oxidation of As(III). Ultra-visible radiation has the ability to increase As(III) oxidation rate in groundwater with high $O_2$ levels. Sunlight/UV promotes the production of hydroxyl (–OH) radicals that helps in the photolysis of Fe(III). Moreover, oxidation rate becomes fast in the presence of both –OH radicals and $O_2$ (Sharma et al. 2007; Yoon and Lee 2005). There are many studies which revealed processes and mechanisms related to oxidation of As(III) by photons/UV radiation. In the perchlorate/perchloric acid solution having a pH range of 0.5–2.5, Fe(III) was added to As-contaminated groundwater with UV/sunlight exposure to increase As remediation process (Amyot et al. 2021; Hong et al. 2022).

Citrate-Fe(III) complex produces a large amount of reactive oxygen species (ROS) when photolyzed with high quantum yield. This solar oxidation and removal of As (SORAS) technology was able to remove As from contaminated groundwater (Wang et al. 2021). Addition of some drops of lime or juice of lemon (citrate) to the groundwater can also help promote the photochemical oxidation of As(III) to As(V). The cyclical reaction of juice of lemon juice or citrate with highly oxidative free radicals create more affinity by generating free radicals in high amount which have a negative effect due to the high removal rate (Bissen and Frimmel 2003). Recently, the As(III) oxidation was achieved via radiation with a vacuum based UV-lamp having a wavelength of 185 nm and 254 nm (Yoon et al. 2008).

A strong UV source with a potassium per-oxodisulfate was used to attain efficient oxidation of As(III). Effective oxidation of As(III) to As(V) can be attained by photocatalytic oxidation (PCO). Photochemical oxidation of As(III) was reported using adsorption of As on $TiO_2$. Photochemical oxidation of As(III) in the suspension with low $TiO_2$ loading and subsequent adsorption of As(V) to the surface of $TiO_2$ in a weakly acid medium reduces the As water concentration below the 10 $\mu g\ L^{-1}$ As permissible limit (Samad et al. 2016; Shumlas et al. 2016).

### *11.5.3 Biological Arsenic Oxidation*

Biological treatment of As-contaminated water is the use of biological or natural processes that favor most of the plants and microorganisms to assist in remediation of As in soil or water/groundwater (Hameed et al. 2021; Yadollahi et al. 2021; Younas et al. 2021). Arsenic in water is reduced and contains naturally high concentrations of dissolved Fe and Mn. In this method, the reaction sequence is given as follows: (i) Mn(II) is oxidized to Mn(IV) while Fe(II) to Fe(III), (ii) As(III) is oxidized to As(V), (iii) $MnO_2$ precipitation, (iv) abiotic oxidation of As(III) by $MnO_2$, (v) As(V) adsorption by $MnO_2$, where reaction (i) and (ii) are biological while reaction (iii), (iv) and (v) are not biological (Ahamad et al. 2021; Rodrigues et al. 2021).

Singh et al. (2018b) reported that microbes such as *Gallionella ferruginea* and *Leptothrix ochracea* species supported oxidation of Fe(II) and mediated oxidation of As(III) to As(V), which was then adsorbed on Fe(III) oxides upto 95% of total As. In another study, Katsoyiannis and Zouboulis (2006) revealed that using Fe and Mn oxidizing bacteria to remove Fe, Mn, and As could be more effective than Mn-oxidizing bacteria and faster than physico-chemical oxidation, indicating the role of bacterial catalysis during As removal (Fernandez-Rojo et al. 2017; Hameed et al. 2021; Kamei-Ishikawa et al. 2017; Liu and Qu 2021).

## 11.6 Phytoremediation

It is an eco-friendly approach to remediate As-containing water and soil (Fig. 11.1). Phytoremediation involves the hyperaccumulator plants, most of which are As-hyperaccumulating ferns like *Pteris vittata* (Chinese brake fern). These ferns are resistant to As and remediate by accumulating high As contents in arial parts (Han et al. 2016; Liu et al. 2018). *Pteris vittata* has the capability to accumulate up to 27,000 mg $kg^{-1}$ As dry weight basis when their cultivation is done in water-culture ponds (Hussain et al. 2021a; Qadir et al. 2021; Wang et al. 2002). It has been reported that there are many genes in plants which can help in reducing As concentration by improving the phytoremediation efficiency (Hameed et al. 2021; Hussain et al. 2021c). In addition, phytofiltration can also be used for remediation

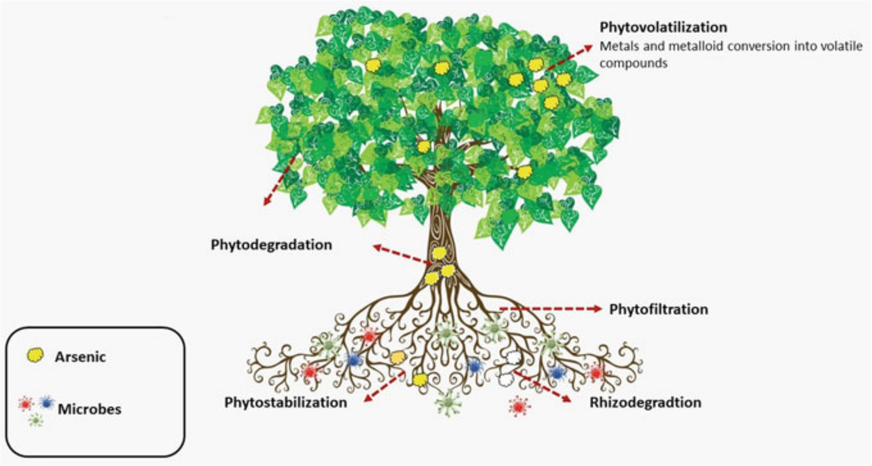

**Fig. 11.1** Conventional treatment technologies to remove arsenic (As) from As-contaminated water

of As-contaminated groundwater, where plant roots act as natural filtration medium to remove As ions in water (Fig. 11.1).

It involves several steps like selection of the most capable plants which can remove As from water. These plants accumulate As in roots and shoots. Some studies have reported that various wetland plants can be used to treat As-contaminated water such as *Eichhornia crassipes, Lemna minor, Lessonia nigrescens* and *Spyrogira spp.* (Javed et al. 2013). It has also been reported that biomass (fish scales, coconut fibers, dried roots of water hyacinth plants, Moringa seed powder, eggshell powder, human hair, rice hulls, and rice flour) can be used to remove As from contaminated water (Hussain et al. 2022; Hussain et al. 2021b; Qadir et al. 2021). For example, biomass from *Acacia nilotica* species was used to remove As from As-contaminated groundwater (Huang et al. 2016; Jasrotia et al. 2017).

### *11.6.1 Adsorption*

It is a technique to remediate As-contaminated water using various materials (adsorbents). This process is commonly used due to its high efficiency for contaminant removal, easy to execute and handling, cost-effective and it does not produce sludge. Recently, researchers have focused on the development of different types of carbon-based materials which could be used as adsorbents to remove As from groundwater (Hussain et al. 2022; Islam et al. 2021; Mohanta and Ahmaruzzaman 2018; Shakoor et al. 2020, 2016b, 2019, 2018; Yee et al. 2019). Process of adsorption usually involves interaction between sorbent and compound in which penetrated molecule retained in matrix of sorbent with the help of weak van der Walls forces (Endo and Koelmans 2016) Arsenic has the ability to adsorb on a variety of adsorbents. Capacity of adsorption can be influenced by pH, adsorbent dosage, ionic strength and competing ions (Luo et al. 2020; Wu et al. 2018).

## 11.7 Co-precipitation

It is referred to the addition of solids into As-contaminated water and then precipitation of As on that solid material. Both the processes take place at the same time in the water. For example, this process may include capturing or absorbing cement or other particulates inside the precipitated compound (Henke and Hutchison 2009). It has been reported that co-removal of As with Fe from groundwater through oxidation is effective only if As concentration in groundwater is $< 50\ \mu g\ L^{-1}$ (Gude et al. 2018). Similarly, Xu et al. (2019) examined that soil microbes also reduce sulfate to sulfide ($S^{2-}$) that further reduced pore water Fe(III) to Fe(II) and As could make stable precipitates As-$S^{2-}$ or FeS-As like precipitates.

## 11.8 Constructed Wetlands Technology for Arsenic-Contaminated Water Treatment

Traditional techniques for remediating As in water and wastewater have some constraints to implement due to the use of large quantities of chemicals and generation of the hazardous sludge, as well as high energy and operational cost requirements (Younas et al. 2022b). As mentioned above, As removal techniques include electroplating, filtration, ion exchange, chemical precipitation, reverse osmosis, co-precipitation, and adsorption with some major limitations to be noneconomic, laborious, and involvement of chemicals (Saba et al. 2019). But these methods may not be feasible due to production of highly toxic secondary sludge, inefficiency in natural condition, high operational and labor cost (Chowdhury et al. 2017). Therefore, inexpensive processes must be used to remediate As-contaminated water (Table 11.2).

Because of their great effectiveness, constructed wetlands (CWs) have been used as a sustainable, cost-effective, and ecologically-acceptable technology for wastewater treatment, although research on As-contaminated water treatment has see less progress (Chowdhury 2017; Kataki et al. 2021; Roy et al. 2015; Shahid et al. 2020). This technique has been shown to be effective in the treatment of both non-conventional and conventional contaminants such as hydrocarbons and hazardous metal(loids) like As, chromium, lead, nutrients, organic matter, (Kadlec and Wallace 2008). The use of CWs is linked to the concepts of phytoremediation and bioremediation, as well as the adsorption process using various bedding media to remove As from contaminated water (Castillo-Valenzuela et al. 2017; Younas et al.

**Table 11.2** Role of different wetlands plants, bedding media types and CWs to explore the potential for arsenic remediation

| Plants | CWs type | Wastewater type | Porous media | HRT (days) | Removal efficiency (%) | References |
|---|---|---|---|---|---|---|
| Phragmites australis | Subsurface vertical flow wetlands | Synthetic wastewater | Cocopeat, zeolite, limestone | – | > 98 | Allende et al. (2011) |
| Phragmites australis | Horizontal subsurface flow wetlands (HSSFs) | Acidic wastewater | Zeolite<br>Limestone/cocopeat | 11 | 99.9<br>99.8 | Allende et al. (2014) |
| Zantedeschia aethiopica<br>Anemopsis californica | Subsurface flow constructed wetland | Arsenic contaminated groundwater | Tezontle | 5 | 75.2 ± 7.1<br>77.8 ± 7.1 | Zurita et al. (2012) |
| Colocasia esculenta L. schott | Pilot-scale constructed wetlands | Synthetic solution | Literate soil | – | 89 | Thathong et al. (2019) |
| Phragmites australis | Horizontal subsurface flow constructed wetlands | Acidic synthetic water | Zeolite<br>Limestone | – | > 96 | Lizama-Allende et al. (2021) |
| Phragmites australis | Vertical flow constructed wetlands | Synthetic solution | gravel | – | 52.9 ± 21.3 | Fan et al. (2021) |
| Iris pseudacorus L | Hybrid constructed wetland | Synthetic wastewater | Soil<br>Coal cinder<br>Pebbles | – | 90 | Lu et al. (2019) |
| Phragmites australis | Vertical flow wetlands | Acidic wastewater | Limestone<br>Zeolite<br>Gravel<br>Cocopeat | – | 99<br>92<br>43<br>9 | Allende et al. (2012) |
| Phragmites australis | Horizontal subsurface flow | Mining wastewater | Limestone<br>laterite | 2 | 75.1<br>86 | Nguyen et al. (2019) |

(continued)

**Table 11.2** (continued)

| Plants | CWs type | Wastewater type | Porous media | HRT (days) | Removal efficiency (%) | References |
|---|---|---|---|---|---|---|
| Phragmites australis | Surface flow<br>Horizontal subsurface flow | Iron mine drainage sludge | Soil<br>Limestone | 2 | 80.5<br>83.1 | Ha and Anh (2017) |
| Vetiver grasses | Pilot scale subsurface flow constructed wetlands | Synthetic wastewater | Sand<br>Gravel | 6<br>9<br>12 | 52.9<br>59.2<br>72.1 | Singhakant et al. (2009b) |
| Eleocharis macrostachya | Subsurface flow constructed wetland | Synthetic water | Silty sand, rough gravel | – | 87–90 | Olmos-Márquez et al. (2012) |

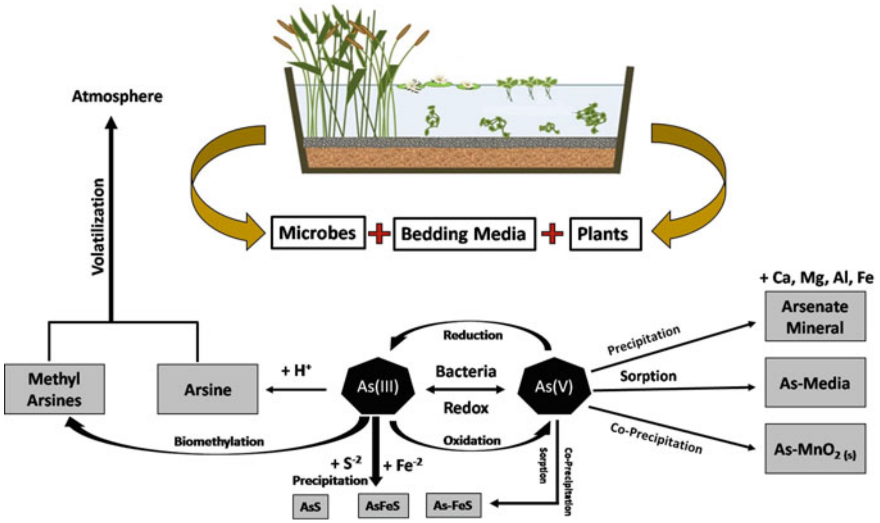

**Fig. 11.2** Constructed wetlands (CWs) treatment technology to remediate As-contaminated water

2022a). Constructed wetlands are highly efficient bio-hydro-geochemical system for the remediation of As-contaminated water (Wang et al. 2017b).

In all the remediation techniques, the behavior of As differs because each As removal procedure is distinct (Fig. 11.2). Copper and Zn, for example, precipitate at an alkaline pH, whereas As species necessitate more specific environmental factors (Lizama et al. 2011; Singhakant et al. 2009a).

### *11.8.1 Adsorption Media in Constructed Wetlands*

In CWs, it has been found that the main surfaces for adsorption of As contain: a bedding medium (or a matrix), mineral particles or colloids, and organic material (Fig. 11.2). Gravel is the most commonly used carrier for the removal of As from contaminated water (Buddhawong et al. 2005; Fan et al. 2021; Kröpfelová et al. 2009; Singhakant et al. 2009a). Furthermore, Buddhawong et al. (2005) found that adsorption capacity of gravel is low ($4.3\ \mu g\ kg^{-1}$), however, it is likely that additional processes such as Fe concentration present in the gravel media are used to reduce As in water. Therefore, the type and chemical composition of the carrier medium should be focused to improve the efficacy of metal exclusion in CWs (Ji et al. 2022; Ye et al. 2003). Some current reports have shown that the removal of As in CWs using suitable or specific adsorption media is an important aspect (Zurita et al. 2012).

Arsenic sorption onto metal oxides especially Fe oxy(hydr)oxides has been reported by many researchers (Kneebone et al. 2002; Lizama et al. 2011; Pastén et al. 2006) Arsenic removal capacity of CWs enhanced when Fe/Mn-(hydro)oxides were present in bedding media of CWs (Sjöblom 2003) In CWs, presence of organic material also enhances As removal from water by adsorption process (Wang and Mulligan 2006). Organic material may also contest with As for adsorption sites of metal oxides (Redman et al. 2002). In addition, As(V) can be reduced to As(III) during organic mineralization because organic material act as an electron acceptor (Ackermann et al. 2008). Therefore, the organic substance may increase As mobility in contaminated groundwater of organic substrates are used for treatment. In CWs, organic substances such as humic acid and fulvic acid may enhance CWs adsorption capacity for As (Singhakant et al. 2009a, b), although As binding ability of organic matter is controversial and depends on many other factors. Dissolved organic matter (DOM) tend to mobilize As while particulate organic matter tend to immobilize As. Because sorption is a complex process, it can take place on different CWs surfaces and is affected by various factors such as pH, redox potential, Fe/Mn oxides and organic matter. Sorption to Fe oxide is facilitated by oxidative conditions and a near neutral to acidic pH. Therefore, its need to work on various adsorbents to remove As from As-contaminated water in CWs.

### *11.8.2 Methylation of Arsenic in Constructed Wetlands*

Volatilization after methylation of As is a well-known process occurring in aquifers (Kosolapov et al. 2004; Mehdi et al. 2021). Under hypoxic conditions, As can be transformed into gaseous arsine ($AsH_3$), which is a highly toxic gaseous As compound (Frankenberger and Arshad 2002). Volatile As includes $AsH_3$, methyl-arsine ($CH_3(AsH_2)$), dimethyl-arsine ($(CH_3)_2AsH$) and trimethyl-arsine ($(CH_3)_3As$), which are highly toxic. King et al. (2002) reported that Hg methylation of sulfate-reducing bacteria in CWs, but there is no report of As methylation of sulfate-reducing bacteria, although these bacteria have been found to methylate in other environments (Chen et al. 2019).

## 11.9 Conclusions and Future Outlook

Arsenic contamination of groundwater, in particular, and wastewater is an alarming issue worldwide. This chapter highlights the current scientific scenario on water contamination and different As remediation comparative evaluation with a particular focus on CWs technology. which the major As removal techniques include coagulation/flocculation, nanoparticles, adsorbents of different types (e.g., biochar, biosorbents, clay minerals, metal oxides), membrane filtration. However, previous literature indicates that the implication of CWs to treat As-rich groundwater is in its infancy and major focus has been on the treatment of industrial wastewater. In the CWs, As methylation and plant uptake play a minor role. Microorganisms such as sulfate-reducing bacteria, Fe-oxidizing bacteria, As(III)-oxidizing bacteria and

As(V)-reducing bacteria can mediate mainly through oxidation/reduction reactions and subsequent precipitation, adsorption under ambient conditions. Future research is warranted on treatment of As-contaminated groundwater on small scale CWs units for household purpose or at large scale for industrial wastewater As treatment. Various parameters such as bedding media composition, identification of new indigenous plant species for As accumulation and some design aspects of CWs are some important research questions which can be explored.

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## Chapter 12

# Application of Nanotechnology in Mitigating Arsenic Stress and Accumulation in Crops: Where We Are and Where We Are Moving Towards

**Debojyoti Moulick, Swati Hazra, Arkabanee Mukherjee, Sapana Sinha, Subrata Mahanta, Anupam Das, Bedabrata Saha, Nabeel Khan Niazi, and Jayanta Kumar Biswas**

**Abstract** In recent past, nanoparticles (NPs) have fetched significant attention as possible applications in the agro-environment, especially in soils. Application of NPs to effectively lessen the toxic heavy metals (HMs) contents in agrosystem are showing encouraging outputs. Arsenic contamination and its subsequent impact on crop productivity as well as on human health is undoubtedly a global challenge.

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Numerous studies have described that the use of NPs in HMs-contaminated soils, which minimize phyto-availablity of toxic HMs concentration soils. Though, the efficiency of NPs to control the HMs content in long run is still under consideration. Here, we try to summarize the details about the current scenario of NPs to regulate activity of toxic HMs to agro-environmental systems. In conclusion, we present the mode of action and possible route of HMs-toxicity mitigation in crop plants by the applications of NPs and assessment on the future prospects also.

**Keywords** Arsenic · Agroecosystem · Crops · Nanoparticles · Nanoremediation

## 12.1 Introduction

Wide number of biotic (weeds) and/or abiotic stressors are usually present in different scales i.e. occurrence of excess salt, limitation of phytoavailable water and wide range of different elements are found in agro-environment from moderate to higher levels (Ghosh et al. 2020a, b, 2021, 2022a, b; Moulick et al. 2020; Hossain et al. 2021b). Arsenic (As) is the chemical element having the properties of a metalloid, i.e. intermediate between metals and non-metals. Though there are few reports on arsenic having medicinal applications at very low doses, chronic exposure to the element causes moderate to severe health hazards in humans and animals (Choong et al. 2007; Tseng 2007; Singh et al. 2015). Therefore, arsenic is considered as one of the most abundant toxic elements in the environment (Bowell et al. 2014). Metalloid with silver-grey chroma, atomic weight (74.9 $\text{gmol}^{-1}$), boiling point (614 °C) and melting point (817 °C) mainly exists in four oxidation states: – 3, 0, + 3, and + 5, and arsenite (trivalent) and arsenate (pentavalent) possess predominant presence in anaerobic and aerobic-oxygen rich environment, respectively (WHO 2001; IARC 2004; Alka et al. 2021). Due to more than one oxidation state, As plays redox reactions. This exhibits pivotal role in sorption–desorption reactions that determine the bioavailability of As (Caporale and Violante 2016).

Arsenic is widely distributed in the environment—in groundwater, soil biomass or near aquifers. It has no beneficial role in metabolic functions but only causes deleterious impact on humans if exceeded the limit ($10\ \mu\text{g L}^{-1}$) as exemplified by the non-melanoma skin, lung and bladder cancer; cardiovascular, pulmonary, immunological and reproductive health effects; endocrine and neurological disorders, liver disease, gastrointestinal disturbances, genotoxicity, arsenicosis, and dermal infections. Such *Myriad Carcinogenic Arsenic* generated by anthropogenic routes fascinates the interest of researchers to develop certain cost-effective and easy-to-handle methods with high efficiency for the biodegradation or detoxification of the arsenic from the soil and water systems with the help of nanotechnology (Moulick et al. 2021;

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Mukhopadhyay et al. 2020; Li and Chen 2016; Dodson et al. 2018; Chowdhury et al. 2000).

The element occurs naturally in several minerals of the earth's crust. Many industries, such as refineries of metal ores, battery manufacturing, and micro-electronics, play a role in the mobilization of As (Wang et al. 2019). Thus, anthropogenic activities have a great contribution towards As contamination which is a major concern for current and future generations. The metals and metalloids like As in agricultural soil have become a serious concern due to their adverse ecological impacts (Moulick et al. 2022; Chowardhara et al. 2019a, b). Arsenic present in the ecosystem can enter the food chain either through the As-contaminated drinking water or by consumption of foods grown in As-rich soil. The concentration of As in groundwater, which is the major source of drinking and irrigation water, is beyond the permissible limit (10 ppb as set by World Health Organization and US Environmental Protection Agency) in nearly 108 countries of the world. The problem is severe in the sedimentary and delta plains of mostly Asian and European continents with fewer reports from Africa, North America, South America, and Australia (Moulick et al. 2019a; Shaji et al. 2021). Moreover, agronomic practices i.e. hysterical nitrogen fertilization, water management can also influence the bio-/phyto-availability of respective HMs/As in agricultural soil while impacting their bioaccumulation in numerous crop plants and subsequently transmission into the food chain with significant impact in qualitative aspects also (Moulick et al. 2016b, 2018d, 2019a, 2022; Saha et al. 2019).

### *12.1.1 As Contamination in Soils*

Arsenic is abundant in the minerals of lithosphere and can be released in the environment (pedosphere, hydrosphere, biosphere and atmosphere) through a number of natural processes (biogeochemical, geothermal, and volcanic processes) and anthropogenic activities (Bowell et al. 2014; Zhu et al. 2014; Singh et al. 2015). The element can be present in the soil in both inorganic and organic forms, the former being the dominant one (Shrivastava et al. 2015). Because of its chalcophile behaviour, the inorganic form of As is mostly concentrated in the sulfide minerals and often adsorbed or co-precipitated with iron minerals, clays, and organic matter in the soil (Bowell et al. 2014; Shaheen et al. 2017). Mining is a major anthropogenic source of As contamination in soil and water. Source of comparatively less toxic organic forms [monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA)] of As in soil (Zhao et al. 2010) is the living organisms after consumption and bioaccumulation of As into their bodies. Arsenic can occur in several oxidation states in the environment. In the aerobic environment, the element is generally present in the oxysalt or oxyanion forms whereas the sulfur-bound forms of As are prevalent under the anaerobic conditions. Therefore, arsenite, i.e. the trivalent state [As(III)] dominates the contaminated aerobic sediments and soils whereas pentavalent arsenate [As(V)] is the predominant species in anaerobic sediments and soils (Campbell and Nordstrom

2014). Both these forms are also abundant in the groundwater reserves (aquifers) of the arsenic affected regions of the world.

### *12.1.2 Adverse Impact of As Contamination on Plant Productivity*

Globally, rice consumption is 55% of the total crops annually and due to the rice growth in surface water via irrigation, pesticides, soil contamination by industry enhances the possibility of arsenic accommodation through mucilage and exudates attached with roots translocated further to leaves with a capacity of ten times more than the other grain crops (Dittmar et al. 2010). So, rice as an important crop is affected by the arsenic contaminant and it is an important issue to protect or detoxify the highest consuming crop globally from the toxic arsenic stress by the help of most effective iron oxide nanoparticles (Khan et al. 2022).

Arsenic in the contaminated soil and irrigation water, finds its way into the plant body and may get accumulated in the food grains (e.g., rice) and edible shoots (e.g. leafy vegetables). Arsenate, which acts as a phosphate analogue, can enter the plant system through the phosphate transporters whereas arsenite along with some other methylated As species are taken up through the nodulin 26–like intrinsic aqaporin channels (Sharma 2012). Arsenic is capable of inducing the generation and accumulation of reactive oxygen species (ROS) which causes lipid peroxidation and damages to the cellular membranes, and thus inhibits plant growth (Zhang et al. 2021). Additionally, As can cause several physiological disorders, such as inhibition of gaseous exchange in leaves, phytases activity, protein and chlorophyll synthesis, and thus reduce photosynthesis efficiency and carbon assimilation of plants (Stoeva et al. 2005; Sharma 2012). Therefore, several phytotoxic symptoms, such as reduction in plant height, leaf number, root length (Ahmed et al. 2006), biomass of both roots and shoots (Carbonell-Barrachina et al. 1997; Miteva 2002) and yield (Jiang and Singh 1994; Cozzolino et al. 2010) might appear along with the changes in morphology (Shaibur et al. 2008; Srivastava et al. 2009) due to exposure to As. At higher concentrations, As can even cause death of plants (Jiang and Singh 1994).

### *12.1.3 Arsenic Accumulation and Transportation in Plant*

Both geogenic and anthropogenic sources of arsenic (As) in the agroecosystem are well established. The industrial discharge releases the same into the soil, but agricultural practices use contaminated water tables as the source. Accumulation of As from irrigation water and soil into the plant system mainly depends on the species of As available in the environment. Naturally As exists as ions in + 5 ($H_2AsO_4$, AsV) and + 3 ($H_2AsO_3$, As III) oxidation states. Soil factors like redox potential, pH, EC, presence of Fe, Mn influence the concentration of bio-available arsenic (Mahimairaja et al. 2005) as organic (Mono/ Dimethyl arsenic acid, Tri methyl arsine oxides, arsenobetaine, arseno sugar) and inorganic compounds (in majorly As V and As III salts). Abundancy in nature and toxic potential is reported to be on the higher side in the case of inorganic species (Rakhunde et al. 2012). Structurally, As V acts as analogous to the inorganic phosphate (Pi) salts due to similar pKa value and thermochemical radii between these two (Elias et al. 2012), and enters the plant root system using the phosphate transporter. The phosphate transporter (PHT1) is the protein situated in the plasma membrane, which is the dedicated transporter (PHT 1 through 9) for Pi accumulation from soil. Genes encode PHT 1 transporter protein (osPT1–osPT13) in rice. Escalation and deduction in the phosphate uptake by rice is an expression of osPT8 gene, which regulates arsenate uptake as well (Jia et al. 2011). A recent study on the effect of As V accumulation pattern in different levels of P sensitive plants *Hakea rostrata* (highly P sensitive), *Banksia seminuda* (moderately P sensitive), *Cucumis sativus L.* (lowly P sensitive) reported higher arsenic uptake in case of high and moderate P sensitive varieties along with visible chlorosis, necrosis, and low nutrient concentration in case of prolonged As V exposure (Abbasi et al. 2021). High and moderate affinity towards P was identified as the major transporter for arsenate by Catarecha et al. (2007) also. Due to the maximum use of irrigation water susceptibility towards arsenic accumulation is several folds higher in the case of rice. Upon As acquaintance, crop plants get severely impacted by producing reactive oxygen species (ROS) which used to modify in biomolecules, gene expression gets altered at transcriptional level, modulates cell division and differentiation, and ultimately leads to oxidative stress (Hossain et al. 2021a; Choudhury et al. 2022). Aforementioned visible symptoms of deterioration in plant health result in poor yield per plant, which can drive the worldwide population towards a malnourished future generation. The waterlogged situation in the early stages of rice cultivation predominates anaerobic condition in the root zone, thus arsenic in the root zone atmosphere transforms mostly into the $+ 3$ oxidation state. Higher water solubility elevates its uptake through a passive pathway commonly known as the aquaporins or nodule-like intrinsic proteins (NIPs). The membrane proteins for this channel consists of 3 amino acids, Alanine, Proline, and Asparagine, and have been labelled as the channel to pass solutes and ions from soil to the plant system. Arsenate (As V) is reduced to arsenite (As III) by oxidation of enzyme glutathione present in the root (Verbruggen et al. 2009) followed by its transportation in the aerial parts of the plants in reduced form. The xylem transportation of total arsenic reported 97% of total As is As III species (Bianucci et al. 2020), but the mode of transportation for the edible parts of the plant is phloem (Carey et al. 2010, 2011). Post accumulation fate of arsenic varies among the crops, stored in vacuoles, transported in the aerial parts of the plant, and released in the root zone due to root efflux (Allevato et al. 2019; Farooq et al. 2016). Chelation of the metalloids acts as an efficient detoxification mechanism, as the presence of Fe, Mn in soil forms ferromanganese chelate which binds arsenic on the root surface and forms a visible plaque (Lee et al. 2013). Similarly, chelation within the plant system by lightweight protein molecules, thiol group, and polypeptides to bind and store As in the vacuoles is a viable detoxification mechanism (Allevato et al.

2019). In the case of higher arsenic accumulating crops reduction of the total arsenic accumulated through roots requires an active detoxification mechanism to lower its concentration in edible parts. In the case of rice and wheat irrespective of genotypes, the arsenic concentration magnitude follows a similar pattern: root $\gg$ shoot > leaves > husk > kernel, grain (Mukherjee et al. 2017; Kamrozzaman et al. 2016). Another detoxifying mechanism is the methylation of arsenic within the plant system which is reported to reduce 4% total arsenic load to reach the edible parts (Xu et al. 2007). Crops like wheat, and maize remain less affected even as high as 50 mg $kg^{-1}$ arsenic exposure (Requejo and Tena 2014). As accumulation mechanism remains the same among all plants but the concentration magnitude and species component percentage differ along with irrigation practices, soil characteristics, and edible parts of the plant (root, shoot, grain/fruit).

### 12.1.4 Arsenic Exposure in Humans Through Dietary Sources and Health Hazards

Arsenic has already been identified and labelled as a class I carcinogen by International Agency for Research Cancer (IARC 1987). Though drinking water arsenic concentration was the prime source of human exposure, arsenic in the food chain has been a threat to half of the world's population (Biswas et al. 2020). According to FAO/WHO tolerable daily intake (TDI) of arsenic is 2.1 μg/kg of body weight for an adult (WHO 2000). Food being a diffused source of exposure, the population situated far away from the arsenic-contaminated areas can also be exposed equally to the crops cultivated with contaminated irrigation water. Apart from the direct exposure through crops, indirect sources of arsenic in the food chain majorly are cattle. Residuals from major staples (rice, wheat, maize) are used as cattle feed, hence the increased arsenic concentration evidently in the concerned products of livestock (egg, meat, milk) and are considered a source of health hazard in both human and cattle. Commonly, a higher concentration value attracts our attention, but in the case of toxicity bioavailability and species partition available in total arsenic load are the major deciding factors. Exposure level varies greatly among adults and children, lower body weight causes 3 folds consumption rate of food in children over adults (Signes-Pastor et al. 2017a, b; Moulick et al. 2021). Rice is identified as the major source of arsenic among all the staples in 60% of the total concentration in inorganic form (González et al. 2020; Halder et al. 2014; Rahman et al. 2014; Lin et al. 2015). In a study by González et al. (2020) on available rice from a different country of origin, in a market basket survey in Catalonia, Spain showed total arsenic concentration in white rice ranged between 78 and 169 μg/kg, the same for brown rice is much higher (162–229 μg/kg). In both scenarios, rice originating from Spain was recorded with the maximum concentration much higher over Asian countries. The iAs among all these observed data occupied 50% of the total arsenic load. Apart from direct rice other rice products like rice cake, and baby foods are issues of serious concern. European Union, Asian countries, Codex Alimentarius Commission fixed the standard for iAs in baby food items to reduce the exposure in infants as 0.1 μg/kg and the same for the adults as 0.2 μg/kg (FAO 2017).

Arsenic exposure through the food chain leads to threatening toxicity in the human body, which has already been reported for a few decades in different countries all over the world, such as Latin America (Khan et al. 2020), Pakistan (Shah et al. 2020a, b), Bangladesh (Rahman et al. 2018), India (Joardar et al. 2021), China (Jiang et al. 2015) and Taiwan (Chen et al. 2005), etc. The mechanism of arsenic in the human system starts with inhalation, penetration through skin mucous membrane, and ingestion. Approximately 80% of the total ingested iAs gets absorbed by the gastrointestinal tract and released into the circulatory system of the body, finally to reach different organs (liver, kidney, bladder, lungs, etc.) (Watanabe et al. 2013). Apart from the available species of arsenic in the environment, biotransformation activities within the body can spike toxicity by a substantial magnitude. The liver is the key organ that metabolizes accumulated arsenic within the human body using two pathways oxidation/reduction and methylation. The oxidation/reduction processes interchange between As III and As V species, whereas, methylation transforms inorganic As III species into monomethylarsonic acid (MMA), dimethylarsinic acid (DMA) and trimethylarsinic acid (TMA). The methylated species varies in toxicity and biogeochemical properties (Campbell et al. 2014). Though $MMA^{III}$ is an organic species, but the level of toxicity it possesses is higher even over iAs (Stýblo et al. 2002; Valenzuela et al. 2005). But estimation of the same in the body is a difficult task due to its transformation into + 5 form during elimination from the body by urine (Kalman et al. 2014). Speciation of the fresh urine samples recorded a major percentage of $DMA^{III}$ followed by $DMA^{V}$ (Valenzuela et al. 2005), and speciation component percentage differs considering level and duration of exposure. In the case of $TMA^{III}$ exhalation is another way of elimination due to its high volatility, which affects the epithelial tissues of the lungs (ATSDR 2019). Exposure to higher arsenic for a prolonged period causes uncontrolled cell proliferation which is also known as malignancy. Cancerous growth in the liver, lung, urinary bladder, skin, kidney, and prostate are already reported by multiple researchers. Even as low as 0.008–0.04 mg As/kg results AKT and mTOR symptoms in human lungs (Carpenter et al. 2011; Liu et al. 2011). Evident skin carcinoma cases increase in contaminated areas, squamous carcinoma being the predominating one in this case (Martínez et al. 2011). Arsenic concentrations between 10 and 300 ppb in drinking water can be responsible for neurological disorders, and renal dysfunctions (Chen et al. 2011). Among all other possible factors causing arsenic-induced bladder malignancy percentage is ranked ninth worldwide and is a serious threat to human health (Narayan et al. 2018). At the DNA level oxidative stress induced by arsenic due to ROS and other superoxides ($HO_2$, $O_2^-$, $H_2O_2$) released in the cellular environment can damage the cell repairing mechanisms along with the DNA damage identification system (Holcomb et al. 2017; Wu et al. 2017).

Arsenic contamination, both geogenic and anthropogenic is well distributed worldwide. Irrigated crops contributed to its transportation from soil to plate in both direct (through staples, pulses, vegetables, fruits, and fish) and indirect (milk, meat, egg) pathways. Among staples accumulation and uptake are much higher in rice, being majorly consumed by the maximum population worldwide, rice possesses a serious threat in all its different consumables forms (raw, parboiled, brown, baby food, rice milk, rice cake, etc.) cultivated under contaminated environment. Pulses and vegetables containing arsenic also contribute a significant percentage magnitude based on the exposure and daily intake quantity and frequency. Identified as a class I carcinogen significant health hazards following long-term exposure to As is inevitable. Skin, liver, bladder, lung carcinoma along with DNA alteration and methylation forwarding to the next generation are major threats caused by arsenic. Exposure in infants and children is severe compared to that of an adult.

## 12.2 Glimpses of Remediation Techniques Employed So Far

Various chemical and biological remediation strategies have been adopted by the researchers to manage the As contamination in soil and water (Fig. 12.1). Suitable techniques are selected depending on the forms, composition, and chemistry of As and the environment of the contaminated sources (Singh et al. 2015). Most of the chemical methods, such as ion exchange, membrane technologies, electrokinetics are particularly effective in the removal of As from groundwater. In situ immobilization of soil As can also be achieved by amending the soil with naturally occurring Fe, Mn, and Al oxides, such as iron grit and beringite (Mench et al. 2006). Exogenous application of phenolic compound (Salicylic acid or SA) which has been researched as a plant hormone in recent decades. SA can positively add biotic/pathogen resistance value to the crop plant species while also impart tolerance to wide range of abiotic stressors (Choudhury et al. 2021a, b; Mazumder et al. 2021). In recent past, literature suggests that supplementation of Se using seed priming technology could be a cost-effective, farmer-friendly strategy to minimize As accumulation in rice plant. Seed priming technology is independent of varietal difference can perform in both soil less and soil based medium (Moulick et al. 2016a, 2017, 2018a, b, c, 2019b). During the course of seed priming a certain amount of Se gets accumulated in the seeds, later during As exposure, majority of As were trapped into the root and thus reduce the above ground translocation of As in rice plant. Apart from exploring the potential of various remediation techniques for heavy metal/metalloid induced stress and subsequent accumulation in various crops, for past few years emerging areas like omics, utilities of wild relatives have also been evaluated (Hossain et al. 2022, 2021a, b, c; Choudhury et al. 2021a, b; Sahoo et al. 2019).

Biochemical transformation of active forms of As into comparatively less toxic, methylated or oxidized forms as mediated by microbes (bacteria and fungi) could be another good remediation option for both As-contaminated soil and water (Shaji et al. 2021). Plant-mediated (phytoremediation) processes, such as phytostabilization, phytoextraction, and phytovolatilization, are the eco-friendly ways to remove

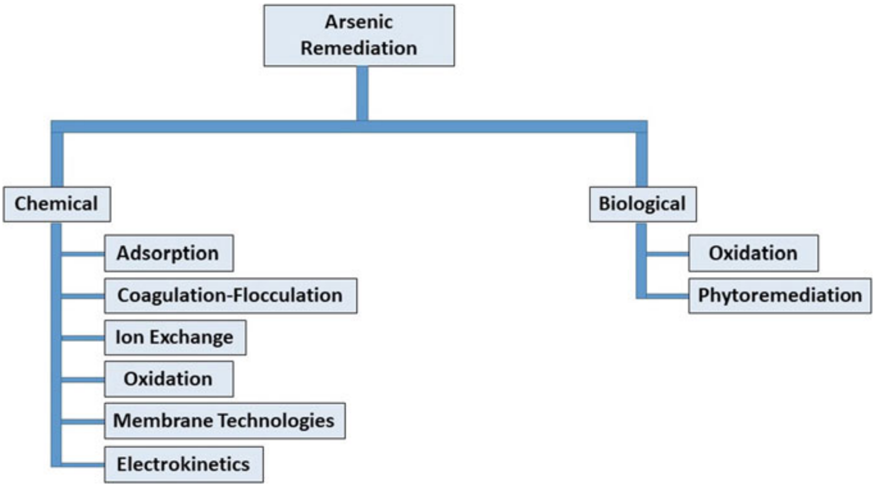

**Fig. 12.1** Various methodologies employed for arsenic remediation from water and soil

As from contaminated sites. Plants belonging to both higher (*Moringa oleifera*, *Momordica charantia*, *Acacia nilotica*, *Eichhornia crassipes*) and lower (*Spyrogira* sp., *Pteris vittata*) groups, growing in the terrestrial or aquatic environment, are capable of removing As from soil and accumulating it in the fronds at quite high concentration (Du et al. 2005; Tripathi et al. 2007; Singh et al. 2015). However, proper disposal of the plant biomass is essential after the phytoextraction of As from contaminated sites.

### 12.2.1 *Need for Nanoparticles for Managing As Contamination in Soil*

A commendable advancement has been made in the field of nanoscience and nanotechnology over the past two decades and the potential applications of nanoparticles are being thoroughly investigated in every possible fields including the environmental remediation technology. Management of As-contaminated groundwater and soil can be done by most of the chemical techniques only under ex situ condition which incurs high cost and disturbances in the natural environment. On the other hand, nanomaterials have been proved to be useful for in situ soil remediation to get rid of the toxic heavy metal contaminants including As which otherwise persists for a long time without any degradation (Linley and Thomson 2021). Nanoremediation of soil-As is primarily based on the enhanced reactivity and adsorption properties of the nanoparticles due to their very large surface area. Nanoscale zeolites, metal oxides, carbon nanotubes and fibers, enzymes, various noble metals, titanium dioxide, nanoscale zero-valent iron etc. have a good potential in detoxification of the environment from the hazardous pollutants like arsenic, organochlorine pesticides etc. Recently, graphene-based nanomaterials have come under the limelight because of their very high adsorption capacity of As(III) and As(V) through complex-forming and electrostatic interactions, respectively (Foti et al. 2020).

Various technologies have been applied or studied upon to reduce the toxic effects of arsenic (As) present in soil or water on plants. These technologies involve use of more tolerant varieties in contaminated soil, seed priming, exogenous treatments with ameliorating agents when the plants are in different stages of growth (Moulick et al. 2021). In recent years, nanoparticles or nanomaterials (size $< 100$ nm) have emerged to play vital role in phyto-research to enhance plant growth or to render protection from biotic/abiotic stressors. Nanoparticles are assumed to adsorb toxic metal ions and alters its bioavailability in organisms and/or restrict them inside organisms by reducing their metabolic availability. This can be done in two ways either the contaminated atmosphere of the organism is treated before the organism comes to life or the organism is treated after it comes to life to reduce the toxicity symptoms.

Focused observation of colloidal gold solution by Michael Faraday in 1856 during the preparation, an exceptionally pink color appearance originated that the nanoparticle or nanomaterial as the one which possesses at least one dimension in the range of 1–100 nm synthesized via either bottom-up approach or top-down approach (Tweney 2006). High permeability of the surrounding by easy exposure and enhancing the rate of the reactions, due to its small particle size and high surface to volume ratio, shows usable change in novel versatile properties like thermal, mechanical, optical, chemical and electrical which are the new weapons in treatment of unsolved problems with efficacy and safety in various forms in different fields. These includes in temperature and smoke sensors (Starr 2014), sensors in aerospace (Prosser 1993) and accelerometers (Madou 2018), pressure sensors (Ren et al. 2019), night vision systems (Bannur et al. 2019), improving production of food crops (seed germination treatment, plant growth, toxic agrochemical used for pathogens detection), self-cleaning building coatings (Storozhenko et al. 2019a, b), nano pigments (Serhat and Türker 2020), quantum dot laser (Zhou and Coleman 2016), hyperthermia cancer therapy (Beik et al. 2016), drug controlled release (Sowinska et al. 2017a, b), food packaging (Peelman et al. 2013). Here we will focus our discussion on the extraordinary application of nanoparticles in alleviating the impact of Arsenic contaminant under biotic or abiotic stress from the key role played by the plants or essential crops of the ecosystem.

### *12.2.2 Nano-Materials in Soil–Water-Plant Interfaces*

Soil contains numerous kinds of inorganic and organic particles; those are having one dimension in the nanoscale ($< 100$ nm). The most common forms are clay minerals, metal hydroxides, humic substances, whereas volcanic soils have abundance of allophane and imogolite in nano-scale dimension. Most of the nanoparticles in soil occur in associated form like inorganic constituents makes a coating onto the mineral surface. This affection among the nanoparticles augments their low extraction yield.

The great efficacy of nanoparticles lies with their surface properties that reflect by their macroscopic (bulk) counterparts. Major reactivity of any chemical substances depends on their solubility. It was found that particle size below ~ 10 nm steeply enhances the solubility (Banfield and Zhang 2001; Hochella 2002). Surface area is also dependent on the particle size. A spheroidal allophane material having diameter 3.5–5.0 nm possesses surface area as high as 900 $m^2g^{-1}$ depending on measurement method (Wada 1990). Another beauty of the soil nanoparticles was that the large proportion of their structural atoms and ions are exposed on their broken end surface where coordination requirements are mostly unsatisfied. This is the reason behind the reactivity of mineral nanoparticles towards nutrient ions and organic species (Hochella et al. 2008). All these structural peculiarities of the soil nanoparticles control the movement, fate, and bioavailability of environmental contaminants.

There are about 2000 naturally occurring minerals containing As at varied concentrations. Oxides and hydroxides of iron, aluminum, and manganese are the naturally occurring minerals existing ubiquitously in soil and aquatic environment, where they play significant role in adsorption and detoxification of As in soil. The metal oxide surface adsorbs As ion either as cation or anion through physical or chemical process. This is an environment friendly detoxification of As caused by the metal oxide in soil and water bodies. Nanoparticles of these metal oxides characterised with high surface area-to-volume ratio, high density of reactive sites make the metal oxide nanoparticles helpful in clean up of As contamination (Fig. 12.2). Among the metal oxides, iron oxides nanoparticles having much potential for arsenic decontamination because of their magnetic character, large surface area and higher active sites. The major derivatives of iron oxides are magnetite, hematite, maghemite, ferrihydrite, goethite etc., which are used for As(III) and As(V) remediation (Johnston et al. 2016; Siddiqui and Chaudhry 2017). Iron oxides interact with the As and/or other contaminants through one of the reactions mentioned in Fig. 12.2. The complex formation and its stability is totally depending on the $H^+/OH^-$ release stoichiometry. Moreover, zinc amendment (1–100 $\mu$M Zn) enhances the As adsorption onto magnetite nanoparticle (Yang et al. 2010). This could be the environmentally friendly magnetite nanoparticle-based arsenic decontamination technology.

## 12.3 NPs in As Stress Mitigation

We will discuss the role of metal oxides ($TiO_2$, ZnO, $Al_2O_3$, $Fe_2O_3$, $Fe_3O_4$, $CeO_2$, etc.) nanoparticles and carbon nanotube both single walled carbon nanotube (SWCNT) and multiwalled carbon nanotube (MWCNT) in minimizing As content.

According to *Langmuir adsorption isotherm,* 90 nm of $Fe_3O_4$ is the best size to remove maximum arsenic content and it was found that an increase in the $Fe_3O_4$ nanoparticle size in the solution containing arsenic implies low permeability inside the plant cell lowering the toxicity and improving plant growth (Praveen et al. 2018).

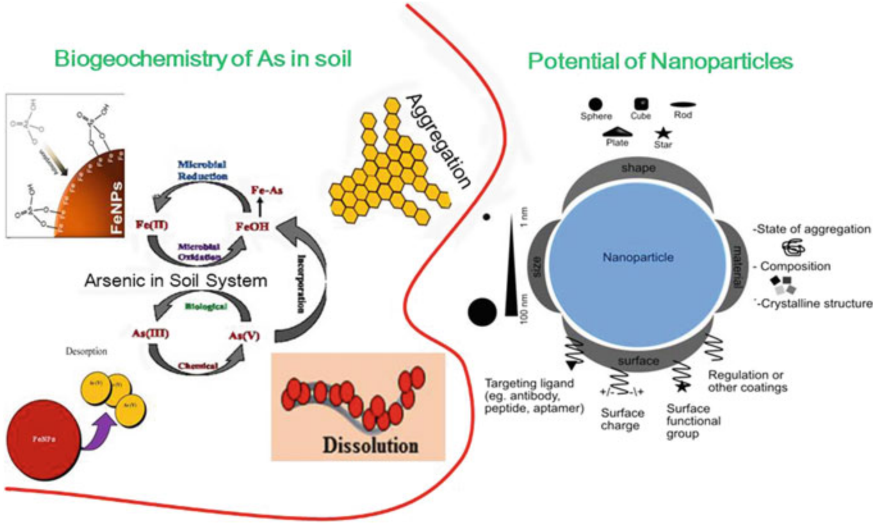

**Fig. 12.2** Geochemistry of metalloid in soil

In the recent past, research outputs showed prolific capacity of diverse nanoparticles in arsenic toxicity mitigation. Use of silicon as stress ameliorant is well documented (Saha et al. 2019) whereas silica in its nano form is a much better ameliorant (Tripathi et al. 2016). In maize plants under As stress silica nanoparticles were found to be more efficient in maintaining the redox homeostasis then silica. Silica nanoparticles synthesized by combustion of corn cub were found to be efficient As adsorbent, and hence can be applied to rice fields to prevent the uptake of toxic As ions by plants (Balasubramaniam et al. 2020). Silica nanoparticles mitigated As toxicity in tomato plants by preventing the translocation of As which resulted in better photosynthesis and maintenance of redox homeostasis (González-Moscoso et al. 2022). Titanium nanoparticles when applied to *Vigna radiata* plants exposed to As stress was found to drastically amend growth indices, membrane permeability and redox status when compared to control plants under As (Katiyar et al. 2020). Titanium oxide nanoparticles significantly decreased the bioaccumulation of As in rice plants, thereby reducing oxidative stress. Nano-$TiO_2$ with both anatase and rutile structures were used, where nanoparticles with rutile structure were found to perform better (Wu et al. 2021). A comparative study of both titanium and silica nanoparticles were conducted, though both the nanoparticles acted towards improving the activity of antioxidant enzymes, protecting the photosynthetic apparatus, sequestration of As in vacuoles; silicon nanoparticles at a dose of 100 mg/L performed better in rice plants (Kiany et al. 2022). Iron oxide nanoparticles acts as nano-adsorbents and prevent damage to mustard plants. Here also photosynthetic apparatus and antioxidant enzymes depicted better functioning when compared to plants subjected to As stress without any iron oxide nanoparticle dosage (Praveen et al. 2018).

Biosynthesized iron oxide nanoparticles from *Bacillus subtilis* reduced As toxicity in rice seedlings. The rice plants showed better germination percentage and biomass when checked for performance at seedling stage (Khan et al. 2020). Even iron oxide nanoparticles in synergism with the application of *Bacillus subtilis* S4 (a plant growth promoting bacteria) in *Cucurbita moschata* seedlings depicted improved performance under As stress. The synergistically treated plants had higher content of stress mitigating polyamines like, spermidine and putrescine, better rate of photosynthesis and gas exchange parameters (Mushtaq et al. 2020). Different nano materials which involved graphene, hydroxyapatite and iron; were checked for ameliorating potential in two rice cultivars, T705 and X24 for As stress. All the nanomaterials amended As stress according to their individual potentialities but the iron nanomaterials performed better with respect to plant biomass, antioxidant enzyme activity, and arsenic accumulation (Huang et al. 2018).

Melatonin and selenium when applied exogenously or even with seed priming has been found to ameliorate heavy metal stress in plants (Saha et al. 2019; Moulick et al. 2016a, b, 2018a, b, c, d). Application of melatonin and selenium nanoparticles to *Brassica napus* plants effected with As toxicity increased photosynthetic efficiency, biomass accumulation and reduced excessive ROS accumulation. Even the synergistic effect of both the nanoparticles outperformed the effect of melatonin and serotonin in its macro form (Farooq et al. 2022).

Iron oxide ($Fe_2O_3$, $Fe_3O_4$) nanoparticles dependent on the size and solubility in aqueous medium leading to the interaction with different sub-cellular compartments of cells mitigates the arsenic toxicity by increasing the retention time in solution and by decreasing the arsenic mobility acting as a strong adsorptive capacitor (Praveen et al.). On excessive intake of Arsenic through root plasma membrane in the plant cells access the binding of free sulphydryl groups, macromolecules which try to interfere in homeostasis (necessary for maintaining intracellular arsenic level) impacts the plant growth and increases toxicity. In ceriodaphnia dubia the nano-$Al_2O_3$/$Fe_2O_3$ enhances the toxicity and accumulation of As compounds (Hu et al.). In spinach, nano-$TiO_2$ promotes the growth through increasing the photosynthetic rate and nitrogen metabolism (Praveen et al. 2018).

Upon incorporation of As concentration ranging 0.8–4.0 mg $L^{-1}$, two tested genotypes (X24 than T705) showed varied responses. Authors attributed to greater retention time by rice roots in As-spiked solution than the shoots. Later, exposure of iron oxide-NPs, decreases with variation in As concentration along with an increase in the biomass in the absence of As contaminant can be observed (Huang et al. 2018). Modulation in CAT activity in presence of As tells us that plants can protect them from heavy metals while with increase in POD activity; it oxidizes and decomposes peroxides for performing the biological metabolisms in rice plants (Huang et al. 2018; Converso et al. 2000).

During flood, soils have Fe-reducing bacteria activity, creating unavailability of ferric (hydro) oxide or iron content, hence enhancing both As (V) and As (III) which indicates the increment of arsenic content in the crops grown in waters. And phosphorus is an important macronutrient for the rice plant that is the reason why rice plants show easy assimilation of arsenic contaminant as an analogous of phosphorus, and arsenic interrupts the mechanisms (ATP, phosphorylation) done by phosphorus indirectly increases the oxidative stress (Qian et al. 2022). In plants NPs carried by protein and ion channels to plasma membrane and cell respectively. Stomatal openings and trichomes decide the NPs permeability as in conventional cotton plants, they aggregate in the epidermis while in transgenic cotton, they enter following endocytosis. Any concentration of CuO NPs inhibits root and shoot growth in Indian mustard plant and maize while more than 10 $mgL^{-1}$ inhibits transgenic or conventional cotton growth (Ma et al. 2013a, b).

ZnO, CuO NPs causes the phytotoxicity while $MnO_2$, nano-$Fe_2O_3$, nano-$Al_2O_3$ alleviate the phytotoxicity of As. Zinc deficiency lightens a need as an important micronutrient in rice, maize and wheat plants recovered due to the ZnO NPs in combination with Arsenic stress. ZnO NPs are used as nano-fertilizers which increases mungbean and cotton growth and adsorption of As from water (Ma et al. 2013a, b).

By using 20.0 $mgL^{-1}$ of ZnO NPs, 40% higher chlorophyll content was seen in plant with As stress of 2.0 $mgL^{-1}$ but if the concentration of zinc increases from magnesium then it will compete with it, and decreases the photosynthesis content and damages the chloroplast (Regni et al. 2022). SOD converts super oxide into hydrogen peroxide which is less toxic and removed by CAT enzymes but on MDA induction the SOD and CAT content decreases leading to oxidative damage. At low zinc concentration SOD and CAT content increases while MDA content decreases. Optimal ZnO NPs for protecting from phytotoxicity is 100.0 mg $L^{-1}$ (Wang et al. 2018). Zinc oxide nanoparticles were also applied synergistically to *Luffa acutangula* grown in As contaminated soil, along with As tolerant plant growth promoting bacteria, *Providencia vermicola* and oxalic acid. The synergistic effect of all the three acting together amending As toxicity outperformed the effect of each ameliorant acting singularly. The plants depicted better oxidative stress management, less physiological damage, and improved level of nutrients (Tanveer et al. 2022). Zinc oxide nanoparticles in soyabean plant has been reported to reduce As toxicity by modulating ascorbate–glutathione cycle and glyoxalase system (Ahmad et al. 2020). Like other nanoparticles described above zinc oxide nanoparticles are also reported to reduce accumulation of As in plant tissues as evident from experiments conducted in rice. The zinc oxide nanoparticles reduced accumulation by upregulating phytochelatin content in roots (Yan et al. 2021).

On hydroponic experiment, tomato cultured with Hoagland solution having arsenic stress in presence of nanomagnetite and nanomagnetite-zeolite (hydrated alumino- silicates framework) composite decreases the plant growth by 45% and 22% accompanied with the increment in MDA levels respectively. Nowadays, iron oxide-NPs (goethite, hematite, maghemite and magnetite) acts as nanofertilizer, herbicide nanoemulsions that removes As but due to complexation of Fe(III) with phosphate a decrement of it from the nutrient and in photosynthetic pigments marks negative impact on plant growth (Pizarro et al. 2021).

Zeolite due to having negative surface charge occupation varies the adsorption of arsenic with pH and at pH below the isoelectric point have the positively charged surface which attracts the negatively charged oxyanion arsenic species. Nanomagnetite removes arsenic extensively with an obstruction of channels carrying nutrients to different parts of plants thus increasing oxidative damage with high levels of MDA and very less plant growth although the zeolite support for nanomagnetite removes very less arsenic with large iron content and less oxidative damage (Chandra et al. 2010). Thus, an efficient arsenic adsorbent order with maintained plant growth is from high to low as nanomagnetite- zeolite composite, nanomagnetite and just zeolite. If the NPs of primary diameter less than 36 nm, in between 36 and 140 nm and greater than 140.0 nm then translocation via roots to all parts, remained at roots only and not taken up even by roots in wheat plant respectively.

Different metal oxide nanoparticles are useful for plants under abiotic stress (salinity, drought, and flood) with enzymatic behavior ($CeO_2$, y-$Fe_3O_4$, $Mn_3O_4$) and non-enzymatic behavior ($TiO_2$, $SiO_2$, and ZnO) called nano-regulators or under biotic stress (bacteria, fungi, virus, and parasites) called nano-pesticides. $CeO_2$ NPs have an importance of concentration on the plant growth was found. At low concentration of 5 μM $CeO_2$, ROS scavenging due to the large alternative vacancies created between two oxidation states $Ce^{+3}$ and $Ce^{+4}$ as well chloroplast protection while at 10.0 mg $L^{-1}$ $CeCl_3$ exhibits a negative effect on radish plant. Poly acrylic acid coated $CeO_2$ NPs increased the stability due to hindrance for aggregation as well foliar sprayed $CeO_2$ is used in drought for sorghum plant for reducing the oxidative stress. In Brassica plant under salinity maintenance in plant growth is done by enhancing biomass, chlorophyll, and photosynthetic activity via sodium ion transportation at shoots more than at roots. Y-$Fe_2O_3$ NPs reduces the MDA or $H_2O_2$ levels for alleviating the oxidative stress in *Brassica* plants (Praveen et al. 2018). $Mn_3O_4$ NPs avail micronutrient for plants. $TiO_2$ NPs enhances the antioxidant enzyme activity directing towards ROS scavenging as well the osmotic balance by increasing the cellular content of sugar and proline. Both $TiO_2$ and $SiO_2$ NPs show better growth of cotton plants during drought circumstance. Due to salinity the GPX or SOD decreases but $SiO_2$ NPs not only maintains the antioxidants levels but also enhance the photosynthetic and biomass content in Cucurbita, tomato and rice plants. ZnO NPs impedant protein content as well enzyme activity under salinity. Under drought condition, by restoration and translocation of Nitrogen content in soil grown sorghum plant alleviated the oxidative stress (Zhao et al. 2020).

By the privilege of the nutrients induction done for the stress tolerance by NPs are called nano-fertilizers ($Al_2O_3$, CuO, FeO, MnO, NiO and ZnO) plays a critical role in the plant growth. FeOx NPs cultivates the lettuce (*Lactuca sativa*) and maize seedling by increasing the shoot length and germination rate respectively, in soyabean and peanut plant by increasing chlorophyll content and in legumes by increasing an embryonic root length (Praveen et al. 2018). ZnO NPs enhances mungbean and maize (*Vigna radiata*) seedlings growth. Even at 2000 mg $L^{-1}$ ZnO NPs do not inhibit seed germination unlike $ZnSO_4$ NPs. MgO NPs show an obvious enhancement of chlorophyll as well it also enhances the SOD and POD activity which directs the suppressing of *Ralstonia solanacearum* bacteria responsible for healthy growth of tobacco plant. MnO NPs enhance the defense systems in tomato plant from the diseases, and $Mn_3O_4$ acts as just ROS scavengers. Silica NPs provide the nutrient in tomato, wheat and Lupin plants by translocating the NPs from roots to chloroplast for indirect increment in photosynthesis and mesoporous silica (MSNs) NPs at 2000 mg

$L^{-1}$ do not show any oxidative damage in plants. $SiO_2$ NPs enhance the growth and yield in strawberry plants (Zhao et al. 2020).

Single walled carbon nanotubes are advantageous due to its adverse effects on agro-bacterium that damages the plant just for the correction of genetic disorders in plants that is fulfilled by SWCNT via transportation of genetic material as well SWCNT due to their self-fluorescence quality acts as a sensor for trafficking $H_2O_2$ or nitric oxide molecules. It is found that due to certain metabolic functions like respiration and photosynthesis, ROS production at low concentration signifies the molecules involved in growth and defense systems while at high concentration, only damages related to protein, DNA, cells can be observed which fascinates the need for ROS scavenging generally done by enzymatic way (SOD, CAT, POD, APX, GR, GPX) or non-enzymatic way (Vitamin C) (Murphy et al. 2011).

Biochar, which has been shown to contain raw carbon nanoparticles (Saxena et al. 2014) have been extensively been used for the adsorption of As from water (Amen et al. 2020). Biochar has been engineered or modified in diverse ways to amplify its adsorption capacity; mangenese oxide biochar, bismuth impregnated biochar, magnetic biochar, iron oxide nanoneedle array-decorated biochar, just to name a few (Yu et al. 2015; Zhang et al. 2013; Zhu et al 2016; Wei et al 2019). Engineered nanomaterials has also been on the forefront of adsorption of As from contaminated land or soil. The structure of the nano materials synthesized is an important criterion for its functioning. For example, in case of carbon nanotubes features that should be taken care of are: nanotubes' outer and inner surface, grooves present in the area of contact, interstitial channels in bundled tubes (Bassyouni et al. 2020). Iron oxide nanoparticles impregnated into carbon nanotubes have been successfully used to adsorb As from water (Tawabini et al. 2011). Plant bioremediation has long been used to detoxify soil from contaminating heavy metals including As; but plants and engineered nanostructures acting in synergy to amend soil is a new concept. Multi walled carbon nanotube have been reported to enhance remediation capacity of *Solanum nigrum* in soil contaminated with arsenic and cadmium (Chen et al. 2021).

Nanomaterials can also be used to adsorb harmful/toxic metal ions be it of As or any other metal, from soil or water before plants are grown on it, or before irrigation. In this direction very few studies have been conducted for the sustainable development of engineered nano-materials which can efficiently reduce As from soil or water. Starch functionalized maghemite nano-adsorbents has been displayed to adsorb even low quantities of As from water. Both starch functionalized and non-functionalized nanomaterials were tried upon with best response from starch functionalized maghemite nano-adsorbents (Siddiqui et al. 2020). Due to the reuse, regeneration and desorption capacity of copper oxide NPs, an advantageous solution to waste sludge and disposal production is employed towards the easy adsorption of As (III) which varies from 62 to 83% with pH (6–11). While, As (V) is independent of pH which adsorbs 90–97% on copper oxide-NPs in which As (III) oxidizes to As (V) and As (III) reduces to As (II) under acidic conditions. Copper expresses stress in plant through ROS generation and seedling growth inhibition which is improved by the nanotechnology. In water systems, stability maintained by dissolution, sedimentation (zeta potential variation with pH) determines the transformation and toxicity of CuO-NPs in the environment. At (0.03–0.15) M, the CuO NPs increases aggregation with the strong ionic strength of water. CuO-NPs by adsorbing natural organic matter decrement in positive charge increases the aggregation via electrostatic assimilation. When the surface charge on CuO-NPs shifts from positive to negative ions starts interacting showing an effect on toxicity. As (V) has strong affinity for iron, aluminium and manganese hydroxides adsorbed at pH 8.5, hence, decreasing its mobility although As (III) moves freely due to negligible affinity (Liu et al. 2018).

Apart from abiotic stresses, biotic stress is also reported to be controlled by the SWCNT, MWCNT and $CeO_2$ NPs which acts as an anti-fungal especially for *Fusarium graminearum* and *Fusarium poae* induces plasmolysis by inhibiting water uptake (Zhao et al. 2020). $TiO_2$ NPs with antimicrobial property shows a disadvantage by creating spot diseases in tomato plants due to high photocatalytic activity while MgO NPs initial treatment on tomato plant due to up regulation of salicylic acid-inducible PR1, jasmonic acid inducible LoxA, ethylene inducible osm suppresses it. Mesoporous silica NPs inhibit the Fusarium wilt in watermelon (Rizwan et al. 2019).

## 12.4 Merit and Demerits of Nanoparticles in Soil–Water-Plant System and Scope of Work

Nanoremediation can be performed in situ, there is no need to pump out the ground water or transport the soil for the treatment (Karn et al. 2009). However, indiscriminate release of nanoparticles in the soil–water-plant systems can lead to further hazards until and unless the full information is available in relation to the reactivity, mobility, toxicity, bioavailability, and stability of the particular nanomaterial (Nowack 2008). Therefore, thorough ecotoxicological studies on the potential impact of nanoparticles on the environment and human health are necessary before employing them to detoxify the natural systems. Till date, surprisingly no well recognized body working in "*Local–Regional-Global*" frame work has concentrated their attention to (i) conduct monitoring, (ii) issuing maximum permissible limits, (iii) legal doctrine to mention on product description (food, cosmetics etc.) or even (iv) conducting life cycle assessment (LCA) for NPs. If the trends continue without imposing regulations, we might welcome another ticking time bomb waiting to explode.

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# Chapter 13
# Nano-Enabled Remediation of Arsenic-Bearing Water and Wastewater

**Rabia Ashraf, Irshad Bibi, Muhammad Mahroz Hussain, Tariq Aftab, and Nabeel Khan Niazi**

**Abstract** Arsenic (As) is a toxic metalloid risking the health of millions of people globally due to drinking of As-contaminated water or through ingestion of As-contaminated food crops. Although numerous conventional techniques have been introduced to remove As from drinking water and wastewater, sorption is considered one of the most promising approach. Here, we provided emphasis on the potential of nano-enabled As remediation using various nanomaterials (e.g., nano- zero valent iron (nZVI), carbon nanotubes (CNTs), and nano-biomaterial based nanocomposites) for the removal of As from water. In this chapter, advancements in research on nano-enabled technologies are elucidated that has been used for removal of As from contaminated water. The utilization of raw and engineered nanoparticles (NPs) such as CNPs, graphene-based NPs, copper oxide, titanium oxide-based NPs, and bi-metal oxide-based NPs has also been discussed. Also, different techniques for the physicochemical characterization of NPs, including XRD, XPS, SEM, FTIR spectroscopy have been briefly explained for better understanding of the mechanisms for As removal. Moreover, some key parameters that influence on As adsorption capacity of NPs such as pH, particle size, initial As concentration and competing ions.

**Keywords** Nanoparticles · Remediation · Groundwater · Health · UN SDGs

## 13.1 Introduction

Water on the earth is an essential component for survival of life, earth comprise (75%) of water resources in which only 2.5% is freshwater resources and 30% of the

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groundwater resources, which mainly used for drinking, industrial and agricultural use globally (Raza et al. 2017). However, unplanned industrial growth and rapid urbanization have posed a serious threat to the safety of groundwater. Various sources of pollution are described in Fig. 13.1 highlighting that groundwater arsenic (As) pollution is mainly associated with geogenic As. Arsenic contamination is known as one of the considerable public health and environmental concern around the world (Amen et al. 2020; Raza et al. 2017; Shahid et al. 2018). According to the Agency for Toxic Substances and Disease Registry (ASTDR), As is ranked among the top 20 most hazardous substances (Jegadeesan et al. 2010; Pietrzak et al. 2021).

Arsenic is present in the reduced water environment mainly as arsenite (As(III)) that is 60 times more toxic than arsenate (As(V)), whereas organic As-species (dimethylarsinic acid (DMA) and mono-methylarsonic acid (MMA)) are 100-time less harmful than inorganic As (Amen et al. 2021; Niazi and Burton 2016). The main cause of As accumulation in the human body is via ingestion of As-containing well water which is used for drinking. Arsenic threshold level is 10 $\mu g\ L^{-1}$ laid down by the World Health Organization (WHO). Arsenic toxicity can cause serious diseases such as arsenicosis, cardiovascular, hyper-keratosis, hyper-tension diabetes, cancer, lower respiratory diseases, diarrhea, and mutagenic disorders (Amen et al. 2020; Kumar et al. 2019; Sanjrani et al. 2019).

Several conventional As treatment approaches have been described in Table 13.1. These include physical (filtration, sedimentation and membrane separation), chemical (coagulation, flocculation, membrane technology and ion exchange), biological (microbial remediation) and electrochemical methods to remove As from As-bearing water and wastewater (Amen et al. 2020; Lata and Samadder 2016; Tabassum et al. 2019). However, these methods may have high costs and energy requirements, excessive secondary waste production, maintenance and operating costs, and inadequate

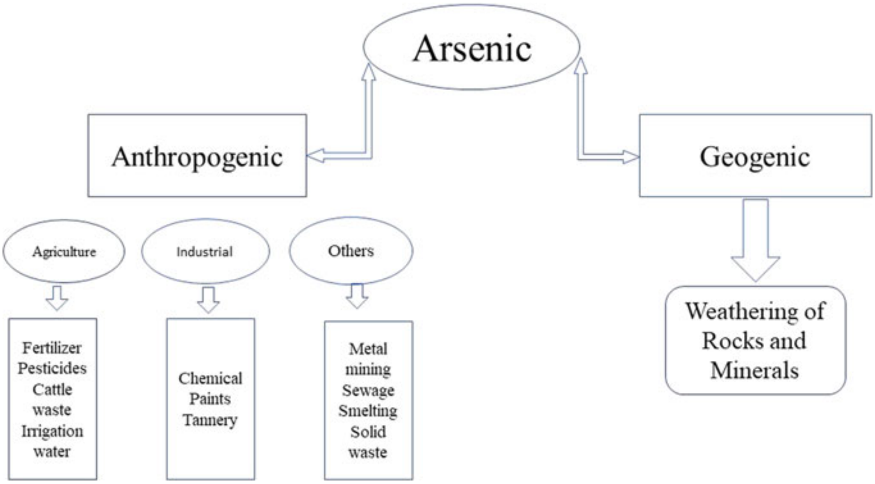

**Fig. 13.1** A schematic diagram showing various sources of arsenic in the environment

**Table 13.1** A summary of various conventional methods for water and wastewater treatment

| Others method | Advantages | Disadvantages |
|---|---|---|
| **Physical methods**<br>1. Adsorption<br>2. Filtration<br>3. Sedimentation<br>4. Membrane Separation | • Economical feasible<br>• Ecofriendly in nature<br>• High removal capacity | • Additional operational cost to disposal of huge sludge<br>• High maintenance required<br>• Time taking process |
| **Chemical methods**<br>1. Oxidation<br>2. Coagulation and flocculation<br>3. Membrane technology<br>a. Microfiltration<br>b. Ultrafiltration<br>c. Reverse osmosis<br>4. Ion exchange | • Simple operational cost<br>• Ecofriendly<br>• Applicable at large scale<br>• High selectivity | • Required high maintenance cost due to membrane fouling<br>• Produce toxic byproducts<br>• Highly pH sensitive |
| **Biological methods**<br>1. Microbial remediation | • High separation selectivity<br>• Cost effective<br>• Ecofriendly | • pH sensitive<br>• Continuous monitoring required<br>• Time taking process<br>• Well defined growth condition required |
| **Electrochemical methods**<br>1. Electrochemical Arsenic remediation (ECAR) | • Treating against large variety of contaminants<br>• Energy production | • Use at small scale level<br>• Cost intensive process |
| **Phytoremediation**<br>1. Phytostabilization<br>2. Immobilization<br>3. Rhizofiltration<br>4. Phytoextraction<br>5. Phytovolatilization | • Applicable at low and high level of contaminants<br>• High public acceptance<br>• Cost effective<br>• Ecofriendly | • Slower than other conventional methods<br>• Phytotoxicity of pollutants<br>• Not applicable at large scale<br>• Slower than physical, chemical processes<br>• Contaminant's fate might be anonymous |

As removal. Among these methods, adsorption especially using the nano-enabled adsorbents is recognized as the most desired technique because of its stability, effectiveness, high surface area, reusability, no toxic by-products and low-cost (Amen et al. 2021; Siddiqui et al. 2020).

Various categories of adsorbents previously used for sorption process such as mineral-based sorbents, metallic-based products, and non-metallic based materials (Raval and Kumar 2021). Nano-enabled adsorbents could have several unique properties that include rapid fragmentation, high number of active sites, strong reactivity, catalytic strength, and a small size of nanoparticles (NPs) that helps to remove As more effectively rather than other adsorbents. (Lata and Samadder 2016). Well-designed nano-composites include bi-metal oxides, polymers and nano-carbon where they are formed as a perspective adsorbent for the treatment As from water (Bhateria and Singh 2019; Qu et al. 2013a). Other metal oxide NPs include zinc, cerium, and titanium-based NPs because when these NPs reduced to a nanoscale, they show high surface area, stability and removal ability. In addition, carbon nanotubes (CNTs) are also being considered to determine their facility to extract As and other toxic ions from water and wastewater (Gangupomu et al. 2014; Tian et al. 2012). This chapter briefly describes classification and types of nanoadsorbents, influence of various environmental factors (e.g., pH, initial concentration) on As removal, characterization methods and regeneration ability of nanoadsorbents.

## 13.2 Nanoadsorbents Classification and Applications

The nano-enabled adsorbents or nanoparticles (NPs) exist in numerous forms like quantum dots, nanowires, particles, nanotubes, which have been produced with wide applications in various fields. Application of NPs for As removal has been described in detail in Table 13.2 (El-Sayed 2020).

### *13.2.1 Types of Nanoparticles Used for Arsenic Removal*

#### 13.2.1.1 Carbonaceous-Based Nanoparticles

The most efficient carbonaceous-based NPs are carbon nanotubes (CNTs) having distinctive attributes, for example, structural, physical, chemical, mechanical and electrical characteristics for their remediation potential. Carbon nanotubes are categorized to single-walled or multi-walled nanotubes with high surface chemistry, adsorption sites and high surface area important for the removal of As from water and wastewater (Li et al. 2012; Ma et al. 2013). In the adsorption process, functional groups produce electrostatic interaction between the surface of CNTs and As ions i.e., As(III) and As(V) (Lal et al. 2020). Recently, glycerol ($C_3H_8O_3$) and N,N-diethyl ethanol ammonium chloride ($(C_2H_5)_2NCH_2CH_2OH{*}NH_4CI$) belong to eutectic solvent that were used to functionalize the CNTs for remediation of As(III) contaminated water (Peng et al. 2005; Siddiqui et al. 2020). However, many aspects of its surface chemistry and mechanism of sorption yet need to be explored and open new research areas.

#### 13.2.1.2 Graphene-Based NPs

The carbon-based graphene materials have high adsorption ability to remediate As in water. Graphene-based NPs are two dimensional(2D) materials in which carbon particles are settled in a honeycomb lattice with hexagonal structure (Zhao et al. 2011; Zhu et al. 2012). Graphene is very cost-effective for wastewater treatment and simply produce by graphite. Graphene can be grouped into two major forms,

**Table 13.2** Nanoparticles (NPs)/nanoadsorbents properties and efficiency for the removal of arsenic (As) in contaminated water and wastewater

| Adsorbents | Preparation | Temperature | pH | Time (min) | Size range (nm) | Surface area ($m^2/g$) | Adsorbate | Adsorption capacity (mg/g) | References |
|---|---|---|---|---|---|---|---|---|---|
| Starch functionalized nanoparticles | Co-precipitation | 35 | – | – | – | – | As(III) | 8.90 | Siddiqui et al. (2020) |
| Ascorbic acid coated $Fe_3O_4$ NP | Hydrothermal process | RT | 2.7 | 30 | < 10 | 179 | As(III) | 40.06 | Feng et al. (2012) |
| Iron-doped titania NP on glass beads | Liquid impregnation method | – | 7 | – | 30–40 | – | As(III) | 0.59 | Danish et al. (2013) |
| Cerium oxide NP | Precipitation process | 298 K | 3.0–11.0 | 30 | 4 | 198 | As(III) | 170 | Li et al. (2012) |
| Magnesium oxide nanoflakes | Hydrothermal process | – | – | 360 | > 100 | 115.9 | As(III) | 506.6 | Li et al. (2012) |
| CuO NP | Thermal refluxing technique | 298 K | 8 | 300 | – | 52.11 | As | 1.0862 | Goswami et al. (2012) |
| Zirconium oxide NP | Hydrothermal process | 303 K | 5 | 720 | 5 | 327.1 | As(III) | 83 | Cui et al. (2012) |
| Multiwall carbon nanotube-zirconia nanohybride | Microwave accelerated reaction | – | 6 | 360 | – | – | As(V) | 5 | Ntim and Mitra (2012) |
| Chitosin-Fe3O4 NP | Sol–gel method | – | – | – | – | 52.48 | As(V) | 79.49 | Raza et al. (2020) |
| Oak leaves FeO NP |  | – | – | 20 | – | – | As(V) | 32.05 | Kamath et al. (2020) |

(continued)

**Table 13.2** (continued)

| Adsorbents | Preparation | Temperature | pH | Time (min) | Size range (nm) | Surface area ($m^2/g$) | Adsorbate | Adsorption capacity (mg/g) | References |
|---|---|---|---|---|---|---|---|---|---|
| Black tea FeO Np | – | – | – | 20 | 60–70 | 18.33 | As(V) | 18.98 | Kamath et al. (2020) |
| Green tea FeO NP | – | – | – | 20 | 30–40 | 3.26 | As(V) | 13.70 | Kamath et al. (2020) |
| Eucalyptus Leaves FeO NP | – | – | – | 40 | 35–50 | 22.57 | As(V) | 39.84 | Kamath et al. (2020) |

reduced graphene oxide (RGO) and oxidized form, graphene oxide (GO); the later shows capability for remediation of several environmental pollutants (Zhu et al. 2012).

However, it has been observed that after adsorption of As it becomes relatively difficult to remove or isolate graphene from wastewater, which is important to avoid the contamination and nanotoxicity of graphene in water thus creating a space for new pollutant in the aqueous environment (Zhao et al. 2011). To enhance efficiency of graphene, it is characterized into various functional groups. These functional groups may include epoxide, hydroxyl (–OH), carboxyl (–COOH), and carbonyl on the surface of GO and reduced graphene oxide (RGO) act as the active sites for As removal from water (Gao 2015). Graphene and RGO-based materials have been considered to show characteristics for toxic ions removal from water and wastewater (Hu & Mi 2013).

The preparation of magnetite-RGO (M-RGO) to remove As from water and wastewater was found to be highly efficient. (Chandra et al. 2010a) reported that the Langmuir isothermal model showed maximum adsorption capacity for M-RGO (13.1 mg/g for As(III) and 5.83 mg/g for As(V)). The magnetite iron oxide (MIO) produced by using 51% of Fe, which express high adsorption capability for both As (III) and As(V) with ratio of 54.18 mg/g and 26.76 mg/g (Sharma et al. 2015). The $Fe_3O_4$-enabled aerogels graphene was fabricated for removal of As-bearing wastewater (Yu et al. 2015). The aerogel had significantly high capability for As(V) adsorption from wastewater (40.04 mg/g).

Nanohybrid of magnetic manganese ferrite ($MnFe_2O_3$)-enabled single layered GO showed great potential to sorb As (III) (54.18 mg/g) and As (V) (26.76 mg/g) in wastewater (Kumar et al. 2014). Also, the conversion of As(III) to As (V) was another important property of $MnFe_2O_3$-enabled single layered GO supporting in the adsorption of As. Two new hybrid nano-enabled materials were prepared—the first one was titania nanotube-manganese ferrite (TMF) and second was GO-manganese ferrite (GMF). Both NPs were synthesized and identified for As removal from wastewater, with high adsorption capacity for As(III) (80 mg/g) and As(V) (102 mg/g) (Shahrin et al. 2018).

## *13.2.2 Metallic-Based Nanoparticles*

### 13.2.2.1 Alumina Nanoparticles

The alumina NPs in chitosan-graft-polyacrylamide (CTG-PA) are used as nano-enabled remediation of As-bearing wastewater (Saha and Sarkar 2012). The alteration of NPs by merging new functional groups showed a change in range of pH for As sorption, (b) sorption site density enhancement (c) increase sorption site uptake mechanism for the removal of As (Khodadadi Darban et al. 2013; Lata and Samadder 2016).

#### 13.2.2.2 Copper Oxide Nanoparticles

The cupric oxide (CuO) NPs are considered effective for remediation of As-bearing water and wastewater. This is because pH had negligible effect on As. These NPs are simple to reuse and for As bearing water remediation (Amen et al. 2021; Lata and Samadder 2016).

#### 13.2.2.3 Titanium Dioxide Nanoparticles

The titanium dioxide ($TiO_2$) NPs have various properties such as chemically stable, high affinity for As sorption, simple synthesis, cost efficient, nontoxic and low corrosivity (Hung et al. 2007) having redox selectivity and strong oxidizing power for As removal. Numerous studies used titanium as a titanium dioxide and nano-porous titania for As removal. In nano-adsorption, surface complexation process helps to describe the properties of nano-porous titania adsorbents (NTAs). Hence surface complexation model recognized category of surface species which contributed in effective As removal at a specific pH (Han et al. 2010). Titanium dioxide monodentate surface complexes were more effective for As(III) adsorption at broad range of pH, while for As(V) adsorption was dominated with formation of bi-dentate surface complexation process at pH 8 (Han et al. 2010; Lata and Samadder 2016).

The composites of magnetic-polyaniline (Mag-PANI) and strontium-titanium (MP-$SrTiO_3$) were fabricated using an organic polymer. Combination of collected magnetic nano-enabled particles and $SrTiO_3$ with coating of polyaniline increased surface area for As adsorption. As such the fabricated composite helps to remove As(III) upto 95%. The presence of two groups (imine-N and amine-N) produced electrostatic interactions among positively charged nanocomposites results to remove As.

#### 13.2.2.4 Zinc Oxide Nanoparticles

Iron oxide and carbon-based nano-sorbents has shown higher affinity to remove As from As bearing water. Furthermore zinc oxide (ZnO) is a very stable, effective and non-hazardous material. The ZnO NPs can remove As from water at the pH range between 5.8 and 6.8 efficiently (Lata and Samadder 2016; Singh et al. 2013). Arsenic removal efficiency of the cellulose acetate-ZnO NPs mixed matrix membrane was determined in a batch study having sorbent dose of 1 g/L and at pH 6.8, where the maximum As (58.77%) was removed from aqueous medium. Compared with the cellulose acetate membrane without built-in NPs, the membrane with embedded NPs showed higher As removal efficiency.

### *13.2.3 Bi-Metal Oxides Nanoparticles*

The composite usage of more than two metals yields parental oxides and express synergetic result of relatively more adsorption capacity for As than the single metal oxides. Several composites of metal oxides have been used to remove As from water and wastewater such as Fe/Mn, magnetite-GO (Chandra et al. 2010a), Fe/Ti (Gupta and Ghosh 2009), Mn-Co (Zhang et al. 2010 and Fe-Cu (Zhang et al. 2013). The $MnFe_3O$ and $Mn_3O_4$ nano-enabled particles showed relatively enhanced adsorption capacity among the studied metal oxide composites (Zhang et al. 2010). The $Fe_3O_4$, $Mn_3O_4$, and $MnFe_2O_4$ nanocomposites showed high high adsorption capacity for As among the bimetal oxides. Magnetic NPs of $MnFe_2O_4$ and $CoFe_2O_4$ were synthesized by chemical co-precipitation. These magnetic NPs have paramagnetic nature because they are easy to separate from solution after adsorption (Chandra et al. 2010a). The composites of M-RGO removed As (III) and As (V) by surface complexation and electrostatic attraction. In the case of As(III), increase in As sorption was observed on the surface of M-RGO at $pH > pH_{pzc}$ (point of zero charge) mainly due to less effect of negatively charged surface on neutral $H_3AsO_3$ species. However, in the case of As(V) at pH < pH zpc high positively charged surface promoted sorption of negatively charged As(V) species (Chandra et al. 2010b).

## 13.3 Adsorption Process of Nanoparticles

The adsorption process takes place in a single or multiple steps such as surface diffusion, external distribution, pores diffusion and adsorption on pore surface (Gulipalli et al. 2011). It was further explained that the adsorption of As(III) and As(V) on the sorbent contains three steps: (i) migration or transfer to the sorption surface, (ii) deprotonation/dissolution of complexed aqueous As(III) or As(V) and (iii) surface complexation (Kong et al. 2014a; Zhu et al. 2009).

Typical adsorption process methods are described in Fig. 13.2. In the process of adsorption, all existing sites are involved in both physical sorption or chemisorption and adsorption behavior depends upon electrostatic attraction and complexation between adsorbate and adsorbent (Saha and Sarkar 2012). It has been stated that As adsorption on alumina-coated polymer beads is regulated by two processes that is complexation reaction and electrostatic adsorption. Adsorption kinetics speeds up small particles that represent in the Fick's second law of distribution i.e., adsorption rates are in reverse proportion to particle size or area. Zeolite small size crystals have higher surface area for adsorption with faster rate than large size crystals of zeolite. In zeolite, small-size particles provides better and faster adsorption rate (Kong et al. 2014a; Lata and Samadder 2016).

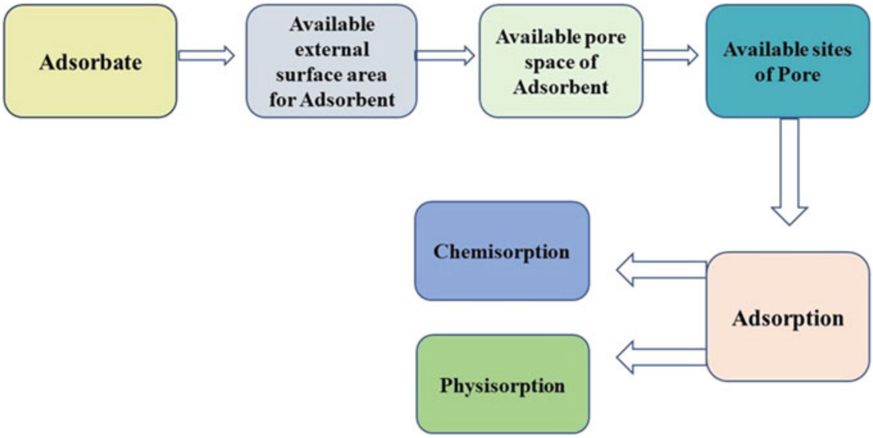

**Fig. 13.2** A flow-chart scheme of different pathways involved in arsenic adsorption by nanoparticles

## 13.4 Characterization of Nanoparticles

Characterization of NPs is important to identify their functional properties, physicochemical properties and mechanism of As removal. Various analytical techniques are being used to identify NPs including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Fourier transform infrared (FTIR) spectroscopy (Amen et al. 2021).

X-ray diffraction can be used for the characterization of nano-enabled materials. It provides information on the crystalline structure of nanoadsorbents. Purity and structure of silica and $Fe_3O_4$ quantum dots (QDs) silica compounds was examined using powdered samples on XRD (Rakibuddin and Kim 2020). Amorphous silica represented distinct features at 20.5° angle. Similarly, the nature of fabricated $Fe_3O_4$ NPs was found to be completely free of impurity. The typical size of $Fe_3O_4$ QDs crystals was 5 nm. Powdered XRD therefore supports $Fe_3O_4$ in composites in the presence of mesoporous silica (Rakibuddin and Kim 2020).

Magnetic NPs were formed using $FeC1_2$ and magnetite ore for bacterial amalgamation by *Fusarium oxysporum* (Balakrishnan et al. 2020; Saif et al. 2022). Characterization of magnetic NPs by XRD showed the sphere-shaped pure structure. The typical size of magnetic NPs, that were prepared using microbes, was 39.52 and 31.29 nm (Balakrishnan et al. 2020; Zeng et al. 2020).

X-ray photoelectron spectroscopy (XPS) has been employed for characterizing the surface of various nanoadsorbents with or without As- and other trace elements loading on NPs, which provides key knowledge about the multi-elemental species and also helps in their percentage quantification (Wang et al. 2015; Wu et al. 2012). The XPS is an excellent approach to detect alterations in the aromatic C percentages of fresh and aged biochars, as well as distribution of As species on NPs surface (Singh et al. 2014). This technique is used to analyze surface chemistry of nano-adsorbents and provide significant data of elemental composition along with chemical and electronic state of nano-enabled material. Specially, XPS technique analyze to recognize the As accumulation on the surface of nano-enabled material (Xi et al. 2020). Moreover it identifies the change in chemical structure of cellulose nano-crystals (CNCs), CNC-DW-Fe(II), fabricated polyethyleneimine (CNC-PEI-Fe(III))/Fe(II) CNC-PEI-Fe(III) by using XPS. XPS spectrum showed saturation of Fe and fabricated polyethyleneimine (PEI) compared to CNC peak of C1s which was transformed into single large peak instead of two sharp peaks. Also, the Fe saturation with Fe-modified CNCs is completed by the sharp peaks in O1s region. Due to binding effect of Fe ions, the results of XPS spectrum showed bond between PEI and CNC (Xi et al. 2020). For example, Fig. 13.3 shows that XPS spectra of As(III) and As(V) sorption by hydrous ceria oxide (HCO) NPs in water system (Li et al. 2012).

The scanning electron microscopy (SEM) helps to determine micro- to macro-scale morphology of NPs like shape, size, pore volume of nanoadsorbents. The SEM use electron as source rather than light to determine morphology of NPs (Balakrishnan et al. 2020). It requires high-resolution power to examine NPs morphology. For example, recently it was reviewed that the assembly of magnetic NPs was observed to be circular and spherical shape magnets and sometimes irregular with a minimum diameter between 27.54 and 81.22 nm under SEM. Similarly, the morphology of carbon nano-cone of polyethyleneimine with Fe(II)/(III) and it was observed using the SEM; the high polymerization rate was found for CNC-PEI-Fe(III), while low polymerization was observed for CNC-SW-Fe(III). Hence it was observed that the presence of PEI led to a stable and high degree of polymerization (Amen et al. 2021; Xi et al. 2020).

The surface functional groups can be identified using FTIR spectroscopy of different sorbents including nanoadsorbents. The FTIR spectroscopy is used to determine change in spectral peaks before and after As sorption. For example, the FTIR spectra of carboxylate MWCNTs (MWCNTs-$OCH_2CO_2H$) and pristine MWCNT indicated the presence of carboxylic group in MWCNTs-$OCH_2CO_2H$ with bands at 1603 and 1765 $cm^{-1}$ (Wang et al. 2022; Xi et al. 2020).

The $Fe_3O_4$ poly (p-phenylenediamine) composite with $TiO_2$ ($Fe_3O_4$, PpPDA, $TiO_2$) shells are the core NPs for As adsorption. In p-phenylenediamine two peaks at 1502 $cm^{-1}$ and at 1569 $cm^{-1}$ were observed which were ascribed to the structure of C=C and C=N bonding (Xi et al. 2020).

## 13.5 Regeneration of Nanoparticles

Regeneration of nanoparticles in the water and wastewater treatment process helps to regulate the reuse efficiency and economy of water treatment technologies. After completion of several adsorption cycles, NPs can be reused to remove As because they have ability to continue their adsorption process (Saha and Sarkar 2012). The pH-based solvents play a significant role in the reproduction of NPs. Compared to

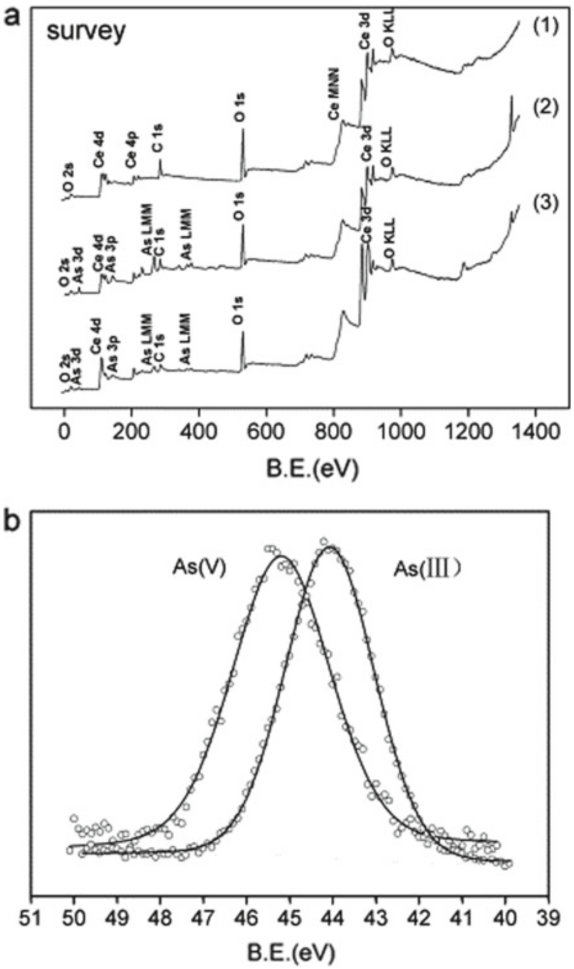

**Fig. 13.3** **a** The X-ray photoelectron spectroscopy (XPS) spectra of (1) hydrous cerium oxide nanoparticles (HCO), (2) As(III)–HCO, and (3) As(V)–HCO nanoparticles. **b** High-resolution XPS scans on As 3d peak of As(III)–HCO and As(V)–HCO nanoparticles [Reproduced with permission of the publisher, Li et al. (2012)]

polymer membranes, the ceramic membrane are always advantageous as they are more UV resistant (Qu et al. 2013b). Pretreatment of raw water is considered as significant in reducing turbidity during treatment process; then, the suspended particles retain in membrane and reduce the effectiveness of the treatment by clogging. Magnetic-separation is another process for the separation of Mg-NPs. Nano-enabled material coated in the treatment system area is re-injected in a quick and complete way. According to the previous studies, NPs can be recycled and reused to treat water, making them an economically active and effective (Kunduru et al. 2017). It has been reported previously that the pH sensitive NPs (NC-PEI/GA) have ability to continue their As adsorption process after completion of eight cycles (Chai et al. 2020).

## 13.6 Influence of Different Parameters on NPs

### 13.6.1 *Effect of pH*

Many NPs, for example, nano-size activated carbon, nano-akageneite, nZVI, iron doped activated nano-carbon (Fe-ANC) particles, mesoporous silica media, Al2$O_3$/Fe $(OH)_3$ ascorbic acid coated nano-$Fe_3O_4$, nano alumina powder and alumina nanoparticles graft chitosan polyacrylamide have been used to remove As from water with specific range of pH (6.5–8.5). Some other nano-adsorbents like $TiO_2$, maghemites (Deedar and Aslam 2009), MNPs layered zeolite (Salem Attia et al. 2014) were found to have high ability to adsorb As at low pH range. Although most of the MMO nanoparticles have great potential to remove both types of As species, As(III) and As(V), from drinking water at pH range of pH 6–9 (Lata and Samadder 2016). For example, Fig. 13.4 shows the effect of pH on As removal percentage by hydrous ceria oxide (HCO) NPs in aqueous phase, which decreases as pH increased, although trend is different for As(III) and As(V) (Li et al. 2012).

### 13.6.2 *Effect of Synthesis Method*

The integration of nZVI is typically performed by reduction method (Chandra et al. 2010a; Rahmani et al. 2011). Some nanoadsorbents are produced by several methods such as hydrothermal method, sol gel method (Deedar and Aslam 2009; Önnby et al. 2012; Savina et al. 2011), sonication method (Salem Attia et al. 2014), chemical precipitation (Basu and Ghosh 2011; Chandra et al. 2010a; Khodadadi Darban et al. 2013; Türk and Alp 2014; Zhang et al. 2013), and polymerization (Önnby et al. 2012; Savina et al. 2011; Sharma et al. 2010). Aluminum oxide and copper oxide NPs were prepared by different methods such as reverse micro-emulsion (Saha and Sarkar 2012) or the microwave irradiation method (Martinson and Reddy 2009), wet impregnation method (Jang et al. 2003), and thermal refluxing methods (Goswami et al. 2012) (Lata and Samadder 2016; Sharma et al. 2010).

### 13.6.3 *Effect of Initial Arsenic Concentration*

Previous research shows that initially low to high As concentrations decreased As adsorption on nanoadsorbents (nanoscale Fe-Mn binary oxides loaded on zeolite and nanostructured Fe(III)-Cu(II) binary oxide). For example, at an initial concentration of 2 mg/L and pH 7 adsorption capacities of nanoscale Fe-Mn binary oxides loaded on zeolite for As(III) and As(V) were 296 and 201 mg/g, respectively (Kong et al.

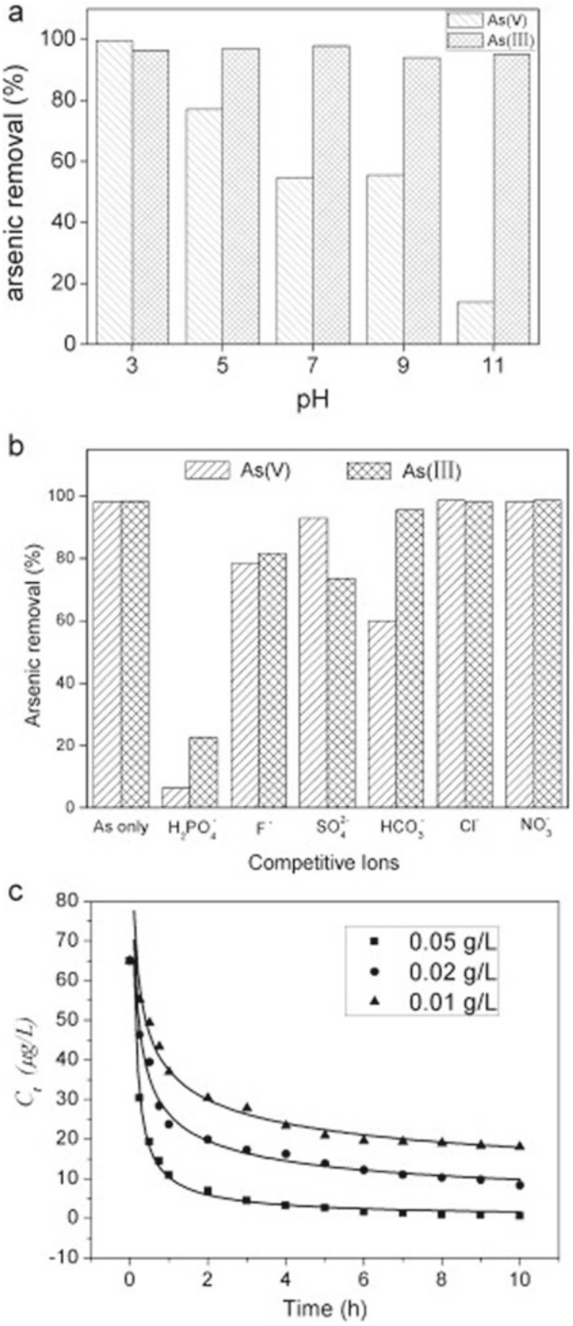

**Fig. 13.4** **a** The solution pH effect, and **b** influence of various competing ions on the sorption of arsenite (As(III)) and arsenate (As(V)) on hydrous cerium oxide (HCO) nanoparticles; **c** Arsenic (As) sorption kinetics in a natural water sample from Lake Yangzonghai on HCO nanoparticles [Reproduced with permission of the publisher, Li et al. (2012)]

2014b). Likewise, in another study adsorption capacity of nanostructured Fe(III)-Cu(II) binary oxide for As(III) was 122.3 mg/g and for As(V) it was 82.7 mg/g at an initial concentration of 10 mg/L and at pH 7 (Zhang et al. 2013).

### 13.6.4 *Effect of Nanoparticle Size*

Normally the adsorption of NPs may increase with decrease in particle size. For instance, zeolite small size crystals have high surface area for As adsorption with a fast rate than that of large size crystals of zeolite (Rouquerol et al. 2013). The adsorption kinetics of As on NPs may speed up where small size NPs are present that represent the Fick's second law of distribution, i.e., adsorption rates are in inversely proportion to particle size or the surface area. Nano-aluminum fixed Mn/Cu-ferrite polymer ($Mn_xCu_{1\text{-}x}Fe_2O_4$) was used as an adsorbent for As removal from water and the data showed that small size NPs showed higher As removal from water compared to relatively large size NPs (Malana et al. 2011).

### 13.6.5 *Effect of Competing Ions*

To determine the impact of interfering agents on As removal using nZVI, six ionic species were studies including: $SO_4^{2-}$, $PO_4^{3-}$, $HCO_3^-$, $Ca^{2+}$, $Cl^-$, and humic acid (HA); it was observed that HA, $PO_4$ and $SO_4$ had dominant suppressive effects on As sorption, but $Ca^{2+}$ led to increase in As removal (Tanboonchuy et al. 2012). Presence of $HCO_3^-$ had inhibitory effect on the removal of both As(III) and As(V) species (Savina et al. 2011). Increased $Ca^{2+}$ concentration and decreased $PO_4^3$ and HA concentrations were found ideal for effective removal of both As(III) and As(V) in water systems (Lata and Samadder 2016; Martinson and Reddy 2009). For instance, Li et al (2012)reported that among various ions in solution phosphate decreased substantially As sorption by HCO NPs in water (see Fig. 13.4).

## 13.7 Conclusions and Future Perspectives

Several \treatment techniques have been employed so far for As treatment in water and wastewater, although the nanoenabled technologies are found to be the most advanced, efficient, desirable and sustainable techniques. Nanoadsorption has the ability to remove As(III) and As(V) species in water without producing toxic sludge, and therefore, it is considered to be environmentally-friendly approach. Nano-enabled technologies have variation in adsorption of As that depends on surface area, pH, point of zero charge of NPs, functional groups on NPs surface, presence of competing ions and the time required for removal process. Future research work is warranted to explore the potential of functionalized nanoadsorbents to enhance their As adsorption efficiency in the presence of competing ions and for small to large scale application in water treatment programs. Also, pilot scale studies are required to unveil the mechanisms and pathways of As removal from water to determine their ultimate fate in the aquatic environment. Various advanced integrated spectroscopic and microscopic techniques could be employed to examine the redoc transformation and ultimate fate of As on NPs surface such as XPS, X-ray absorption spectroscopy, SEM-EDX, X-ray fluorescence spectroscopy. Moreover, research is required to explore the effect of different carrier materials (such as sand or biomaterials) to develop NPs coated carrier materials and explore their long term sustainability in As removal process. The studies must be focused on using advanced new kinetic Monte Carlo simulation models to predict sorption pattern of As species on the surface of different NPs under varying environmental conditions existing in natural water systems.

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# Chapter 14
# Molecular Aspects of Arsenic Responsive Microbes in Soil-Plant-Aqueous Triphasic Systems

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**Abstract** Arsenic (As) resistance is a primordial activity in microbes since millions of years, although, only in recent decades, the major scientific elucidations are made. Molecular mechanisms which are involved in As-resistance and tolerance are attributed to three domains- genomics, transcriptomics and proteomics. From the deep underground aquifers, As is released due to microbial activities to the surface soil where other microbial communities tackle this contamination by either cellular sequestrations or by safe transportation and passage extracellularly via transporter proteins. This whole scenario involves several gene operons, up/down regulated gene clusters and protein families. Genes involved in the redox changes of As intracellularly while co-transports other elemental ions in the course of metabolism and tolerance will be discussed here. Transcriptomics studies can specifically and accurately correlate with the findings of genomics data of As resistance in microbes. Further and more recent proteomics studies depict the relation of these microbial participations with their surrounding plant systems. Associations with plants can influence the microbial community profiling along with their ability to tolerate As

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effectively. This chapter will discuss briefly all the molecular aspects of As toxicity in microbes in the soil-plant-water triphasic environment with their involved machineries for remediation capacity.

**Keywords** Arsenic toxicity · Microbial resistance · Genomics-transcriptomics-proteomics · Environmental distributions · Remediation potential

## 14.1 Introduction

Arsenic (As) is a natural element that is distributed variably in the soil-sediment, aquifer-surface water bodies, plants-microbiomes and the fate of this natural pollutant depends upon the release mechanisms due to variable geochemical influences or microbes mediated dissolution, chelation or sorption. There is no distinct As uptake pathway in microbes as this element is not an essential or required nutrition or metabolically desired to the cell cycle (Tsai et al. 2009). The distribution of As in soil-water-plants has been closely studied by a different group of researchers and in every aspect, the microbial intervention has been reported profusely. Microbes are known to have differential gene operons to deal with the As translocation and transformation (Huang 2014; Majumdar et al. 2021). Microbial cell surface can adsorb As due to electrostatic interactions with hydroxyl, amide and amino groups attached to the cell surface which further led to the As redox transformation or translocation to the cell cytoplasm (Giri et al. 2013; Prasad et al. 2011). Although several decades of research have revealed the genomics and molecular findings that how microbes from diverse environmental systems are able to deal with the As toxicity and minimize the stress while associated with any plant, more research is needed to address the advanced knowledge gap of As and microbial protein interactions. This chapter briefly describes the microbial role in As biogeochemistry from the molecular point of view.

## 14.2 Arsenic Distribution in Soil-water-Plant-Microbiome

Arsenic distribution in the environment seems to be a simple yet extremely complicated natural process affecting and involving soil-water-plant systems with indissociable microbial communities. Microbes play role in both distribution and restriction management of As in these surrounding systems. It is also important to know such type of elemental distribution in nature, soil-sediments-wetlands or freshwater-marine water or arid-semi arid-tropical-agricultural plants where microbes are actively performing diversified metabolism (Majumdar et al. 2020a).

### *14.2.1 Arsenic Release from Aquifers and Contamination of Soil-Sediments*

Arsenic release occurs from different As-bearing minerals like arsenopyrite (FeAsS), arsenolite ($As_2O_3$), cobaltite (CoAsS), olivenite ($Cu_2OHAsO_4$) and Proustite ($Ag_3AsS_3$) to the deep aquifer or to the confined soil system from where indigenous microbes can start their role (Francesconi and Kuehnelt 2001). Dissolution of As from these minerals from unconsolidated sediments are dependent on the particle size fractions (Majumdar et al. 2019; Sarkar et al. 2017), having greater confinement within mud and clay soils. Under reducing conditions, As content has been found to be greater at nearshore and continental deposits with a gradual increase from the top horizon to the deeper layer (Majumdar and Bose 2017; Smedley and Kinniburgh 2002). Aquifers retain a neutral to mildly acidic pH (6.5–7.5) with a mild oxidative to the strong reductive environment which alters the solubilization of different S-minerals and Fe–Mn complexes which further can be assessed considering several hydrogeochemical modeling and stratigraphy measurements (Ahmed et al. 2004; Sracek et al. 2004). From the Eh–pH curve analysis of soil-aqueous As speciation, $H_2As(V)O_4^-$ is the predominant form within pH 2.5 to 7, $HAs(V)O_4^{2-}$ is the predominant form within pH 7 to 12 and $H_3As(III)O_3^0$ is predominant under the pH range 9. Microbes were experimentally proven to be associated in the dissolution of the Fe-minerals and concomitant release of As to the aquifer system. Anaerobic microbes mainly play the role while different electron mediators control the microbial metabolism of As release (Islam et al. 2004). Another report showed that the microbial community might exchange the As responsive genes through horizontal gene transfer and hence, arsenite oxidase, arsenate reductase and other As efflux pump proteins are profusely found in sub-surface microbes with a certain ability to metabolize As with a chance of release further (Sarkar et al. 2014). In sediments, primarily, metal oxides contribute to the As adsorption and due to further physicochemical changes in the sediments, As gets released (Majumdar et al. 2020b). It has been clear that the soil-aqueous phase, a retained flooded condition or anoxic soil status releases As frequently increasing the chance for plant uptake (Shrivastava et al. 2020). Reports showed that the reduction and dissolution of ferric arsenate complex under altered redox conditions releases As to the soil-solution phase and a rapid influx of pore water trigger this dissolution process (Barla et al. 2017; Majumdar et al. 2018). The soil mineralogy and geochemistry of inter elemental relationship with As and bioavailability depends on the soil pH, redox potential, electrical conductivity, total dissolved solids, and organic matter (Kabata-Pendiasa and Szteke 2015). Earlier reports have shown evidence that the soil As content can be suppressed by increasing competitive concentrations of Si and phosphate (Majumdar et al. 2019; Majumdar and Bose 2018). A consecutive over-extraction of As-rich groundwater has been marked to be one of the main reasons for As contamination to the soil and thereafter to the plant tissues (Chowdhury et al. 2018; Das et al. 2021a; Upadhyay et al. 2019).

### *14.2.2 Arsenic Stress Response in Plants and Microbial Involvement*

Due to the global distribution of As, most of the crops, vegetables and fodder plants contain low to a high degree of As concentration indicating a continuum of health risks to the consumers (Biswas et al. 2019; Das et al. 2021b; Upadhyay et al. 2020). Arsenic contamination in cereals, specifically in rice, wheat and maize has been widely researched to decipher the translocation mechanisms and toxicity effects (Majumdar and Bose 2017; Srivastava et al. 2021; Upadhyay et al. 2022). Several transporter proteins are discovered to have a role in As translocation to the plant tissues which creates intra-cellular stress to the plant tissues (Gupta et al. 2022) and plant-associated microbes are potential enough to modulate this As stress at the molecular level (Awasthi et al. 2021). Such stresses can cause intracellular generation of reactive oxygen species (ROS) which in turn results in damage to the cellular lipids, carbohydrates and other cell components (Majumdar et al. 2021; Mridha et al. 2021, 2022; Upadhyay et al. 2021). Soil rhizosphere microbes are found to play role in As content modulation which helps in minimizing the As load to the crop tissues and grains (Majumdar et al. 2021). Reports have elucidated the microbial efficacy in chelation of As by releasing organo complexes like phytochelatins or organic acids to chelate or precipitate As content which reduces the bioavailability to the crop plants (Tiwari and Lata 2018). Some of these microbes are termed as plant growth-promoting bacteria as they can induce plant growth factors and nutrient availability while minimizing the As stress by releasing siderophores and other microbial metabolites (Rajkumar et al. 2010).

## 14.3 Development of As Resistance Mechanism in Microbes

Out of the four forms of the metalloid, As is majorly present in the soil as arsenate (As(V)) and arsenite (As(III)). Although As is only the 20th most abundant element on the Earth today, it is believed to have been abundant and played roles in energy generation in the primordial Earth (Oremland et al. 2009). The exposure of soil microbes to elevated As concentration paved the way to the development of detoxification (utilization) mechanisms within their cellular networks to combat As toxicity. The As resistance was earlier thought to be a trait associated with environments inherently containing high concentrations of As such as geotherms and As-contaminated environments such as the Bengal basin. However, the presence of As resistant microbes in As-free soils (<7.7 mg As/kg soil) substantiates the role As resistant microbes play in natural As cycling in soils (Jackson et al. 2005). The toxicity, as well as the resistance developed by microbes, depend greatly on the chemical species of As. The oxidized form, As(V) became abundant following oxygen evolution and currently is responsible for the majority of As resistant mechanisms (Páez-Espino et al. 2009) Belonging to the pentavalent Group 15 elements, As(V) exhibits similarity with phosphate (P) and thus can replace P in cellular components, forming unstable compounds. On the other hand, As(III) can interact with sulfhydryl groups in proteins, thereby interfering with protein and enzymatic functions. Since As(III) is also mobile, it poses a larger threat to microbial cells. One of the first pieces of microbial evidence of As resistance genes arose from a study that looked at R factors in *Staphylococcus aureus* (Ghosh et al. 2015). Several studies followed this, and today it is known that a universal group of operons named the As-resistance system (*ars*) is responsible for microbial detoxification of As (Feikh et al. 2018). Some microbes can sequester As outside the cell and chelate As after they enter the cells to limit their interactions with cytoplasmic components (Pandey et al. 2015). However, the majority of microbes uptake As into their cells and take part in the detoxification process using a network of enzymes, as discussed below. Figure 14.1 depicts a brief schematic of As tolerance modes in microbes with general molecular structures of some common proteins involved.

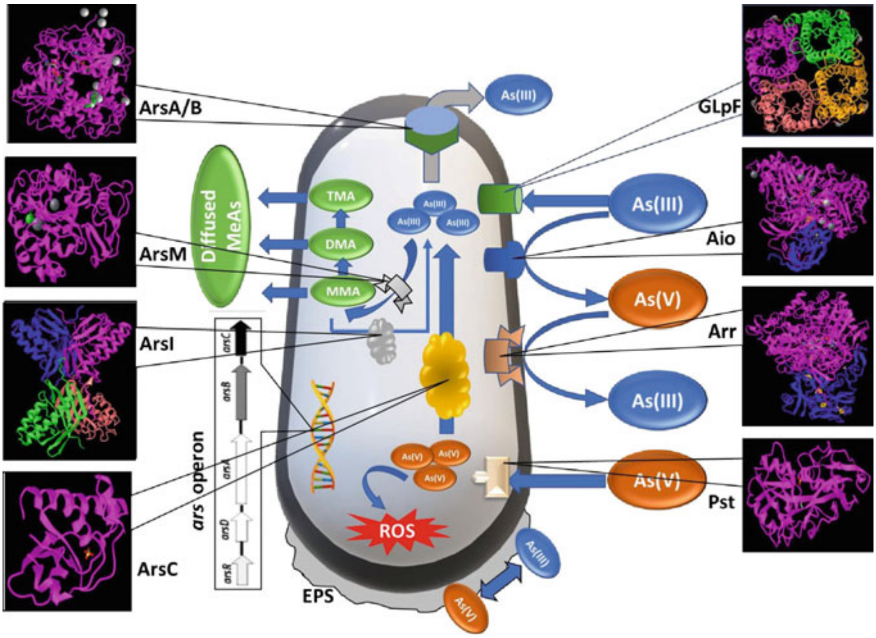

**Fig. 14.1** Arsenic tolerance modes in microbes and responsible proteins identified. Short forms used for: AS(III)-specific exporter (ArsB), associated ATPase (ArsA), As(V) reductase (ArsC), S-adenoisine methyltransferase (ArsM), nonheme iron-dependent dioxygenase with C·As lyase activity (ArsI), glycerol facilitator (GLpF), dissimilatory arseate reductase (Arr), aerobic arsenite oxidase (Aio), phosphate-specific transporter (Pst), extracellular polymeric substances (EPS), reactive oxygen species (ROS), monomethyl arsonite (MMA), dimethylarsinite (DMA), trimethylarsine oxide (TMA). Microbial EPS plays differently than the respective intracellular proteins in As transformation

## 14.4 Microbial Detoxification Mechanisms for Arsenicals in the Environment

### *14.4.1 The Entry of As into the Microbial Cells*

Although cells have As detoxification mechanisms and As plays the role of electron acceptor/donor in some microbes, it does not yet been found to play a metabolic/nutritional role inside the cells. In addition, it is also possible that the cells aim to remove the cellular As while limiting its uptake. Therefore, cells utilize the existing uptake systems to import As because of its similarity with other chemical species (Páez-Espino et al. 2009). As(V) is imported into the cell via the phosphate (Pi) transporters (*Pit* and *Pst*). It was observed that the presence of As(V) increases the expression of Pi transporters to compete with Pi for As(V) uptake (Ghosh et al. 2015). Once As(V) enters the cells, the *ars* operon can reduce As(V) and release out (AsIII). But eventually, the extracellular concentration of As(III) increases, and cells would need mechanisms to import As(III) to oxidize arsenite to maintain the equilibrium. The aquaglyceroporin transporters were initially identified to play roles in glycerol transport. However, due to the similarity of the polyol form of As(III) oxyanion to glycerol, aquaglyceroporins can import As(III) into the cells (Feikh et al. 2018). In addition to Pi transporters and aquaglyceroporins, there could also be other import systems that transport As (Páez-Espino et al. 2009). Once As enters the cells, *ars* operons play a role in carrying out oxidation and reduction reactions. Besides, biomethylation of As is also a key phenomenon to volatilize As.

### *14.4.2 Reduction of As(V)*

The microbial cells carry out the reduction of As(V) for either of the two reasons—(i) to carry out the detoxification of As alone (*arsRBC* and *arsRDABC*) or (ii) to utilize As as a final electron acceptor for respiration (*arrAB* and *arrABC*) Although the majority of bacteria and algae utilize the former mechanism, certain bacteria and archaea have been found to utilize the latter (Pandey et al. 2015). The microbes may express both the *ars* and *arr* system of operons differentially. It was observed that the *arr* system in *Shewanella* sp. strain ANA-3 is highly sensitive to lower concentrations of As(III) as compared to the amount required to activate *arsC* system (Saltikov et al. 2005). The two major operons responsible for the reduction of As(V) are *arsRBC* and *arsRDABC*. It is considered that the two-component operon *arsRB* might have been the initially developed system on the Earth, before oxygen evolution. The inducer (As) dependent operon transcriptional repressor *ArsR* and the efflux pump *ArsB* might have been helping the microbes to detoxify As (Feikh et al. 2018). The third gene, *arsC* responsible for the reduction of As(V) might have been added to the operon system later, thereby creating the *arsRBC* operon that is most commonly seen today in microbial cells. While the *arsRBC* is commonly found in Gram-positive cells and bacterial chromosomes, the operon possesses two additional genes in some of the Gram-negative cells. These two components that form the *arsRDABC* operon system are the (i) As(III)-stimulated ATPase *ArsA* that works with the efflux pump *ArsB*; and the (ii) weak transcriptional repressor *ArsD* (Pandey et al. 2015). In addition, *ArsD* is a metallochaperone that helps in the transfer of As(III) to the *ArsA*-*ArsB* efflux pump system (Lin et al. 2006). Over the years, this mechanism of As(V) reduction has remained mostly conserved in bacterial cells. However genetic alterations and environmental conditions have brought in several variations such as multiple copies of the operon for differential expression, different types of *arsC* genes, the presence of Acr3 instead of *ArsB* for transportation especially in eukaryotes, additional genes in the operon, and the formation of As gene islands (Pandey et al. 2015; Feikh et al. 2018; Freel et al. 2015). The second mechanism of As(V) reduction that occurs in certain bacteria and archaea is encoded by *arrAB* and *arrABC* operon systems. These microbes respire As(V) under anaerobic conditions to oxidize an electron donor to provide energy for bacterial cells. Most microbes have the *arrAB* system that consists of the heterodimer enzyme with the small subunit *ArrB* to transfer the electrons to the larger subunit *ArrA* where the reduction happens. Some of the bacteria have been found to encode a third gene, *arrC* upstream to *arrAB*, and is believed to help in anchoring *ArrAB* (Andres and Bertin 2016). Additional studies are required to characterize the enzymes.

### *14.4.3 Oxidation of As(III)*

Although As(V) has become abundant post-oxygen evolution, the continuous reduction of As(V) and mobility-induced toxicity of As(III) has led microbes to develop detoxification mechanisms to oxidize As(III). However, most of the microbes oxidize As(III) as part of their energy metabolism. The As(III) can be utilized for heterotrophic/chemoautotrophic growth, or for carrying out anoxygenic photosynthesis (Huang et al. 2012; Kruger et al. 2013; Kulp et al. 2008). The arsenite oxidation operon mainly consists of a larger subunit and a smaller subunit. The elucidation of the crystal structure of arsenite oxidizing genes revealed that the larger subunit resembles the dimethylsulfoxide (DMSO) reductase family of molybdenum enzymes, while the smaller subunit is similar to the Rieske [2Fe-2S] protein domain (Ellis et al. 2001). The *AoxA* enzyme carries an N-terminal twin-arginine translocation signal peptide sequence that might be helping its translocation to the periplasm (Muller et al. 2003). The inconsistency in the naming of homologous As(III) oxidase genes discovered in different microbes makes it most of the time difficult in their identification and comparison. The operons involved in arsenite oxidation found in different microbes are *aoxA/aoxB, asoB/asoA, and aroB/aroA* (Kashyap et al. 2006; Stolz et al. 2006; Santini and vanden Hoven 2004). When the As(III) oxidation operon was discovered, the smaller and larger subunits were named *aoxA* and *aoxB* respectively. But later, for all the names, ‘A’ and ‘B’ were interchangeably used. This is according to the biochemistry nomenclature to describe the molybdopterin as ‘a for alpha’ and the smaller subunit as ‘b for beta’ (Muller et al. 2003; Lett et al. 2012). However, the difference between the operons is mainly in terms of the presence of additional genetic elements such as regulatory genes. Therefore, a new nomenclature has been proposed to designate the smaller subunit as *aioB* (replacing *aoxA*, *aroB*, and *asoB*), and the larger subunit as *aioA* (replacing *aoxB*, *aroA*, and *asoA*), thereby referring it to as *AioBA* enzyme system (Lett et al. 2012). Another operon system that has been discovered to carry out As(III) oxidation act as a link between the *arr* and *aio* systems. It was discovered for the first time in the arsenite oxidizer *Ectothiorhodospira* sp. strain PHS-1 that lacked *aoxB*-type As(III) oxidase, but instead carried an oxidase similar to *arrA* gene (Kulp et al. 2008). The arsenate reductase arsenite oxidase (*arxA*) gene was also later discovered in *Alkalilimnicola ehrlichii* (Richey et al. 2009). Because of the ability of *ArxA* enzyme to oxidize arsenite in-vivo, its similarity to the *ArrA* enzyme, and the potential to carry out both arsenite oxidation and arsenate reduction in-vivo, the possibility of *arxA* being the phylogenetic link between *arrA* and *aoxB* cannot be ignored (Zargar et al. 2010). However, the order of emergence of these three genes remains debatable as new studies emerge. It was recently found using phylogenetic and experimental approaches that *Aio* might have been the ancient arsenite oxidase and that the *Arx* system had emerged recently (Szyttenholm et al. 2020).

### *14.4.4 Methylation of As(III)*

The methylation of As(III) is one of the most important processes involved in the As biogeocycle to help release As back to the atmosphere via volatile organoarsenicals. The study of biomethylation of metalloids began with the discovery of toxic methylated As species produced by fungi in the nineteenth century. Biomethylation now is a major detoxification process and produces several volatile (monomethylarsine (MMA), dimethylarsine (DMA), and trimethylarsine (TMA) and non-volatile (methylarsonate and dimethylarsinate) As species. The key enzyme involved in As(III) methylation is *ArsM* (most often found with the operon regulator gene *arsR*), which is an S-adenosylmethionine methyltransferase that forms trimethylarsenite [TMAs(III)] as the end product via the intermediates- monomethylarsenite [MMA(III)] and dimethylarsenite [DMA(III)] (Qin et al. 2006). Although the intermediates are toxic and potent carcinogens, their subsequent conversion to the non-toxic TMA diminishes the toxicity of the process. The TMA gets volatilized from the cells, thereby completing the process. (Chen et al. 2015). The trivalent methylarsenicals can also be exported out of the cells. Described as a part of the *ars* operon system, *ArsP* is a permease that is different from *arsB* or acr3 and provides greater protection than *ArsH* by transporting the trivalent methylarsenicals out of the cell (Feikh et al. 2018; Wang et al. 2009). The efflux efficiency of *ArsP* might be enhanced by its association with *ArsA* ATPase which also energizes the two arsenite other transporters-*ArsB* and Acr3 (Castillo and Saier 2010). In addition, the trivalent methylarsenicals can also undergo further transformations inside the cells. A new gene acting on the methylated forms of arsenite was found amongst the As resistance genes found in the virulence plasmid pYV of *Yersinia enterocolitica.* Named as *arsH*, the gene produce encodes an organoarsenical oxidase that can in the presence of oxygen, convert the biomethylated trivalent intermediates to their less-toxic pentavalent forms (methylarsonic acid [MAs(V)], dimethylarsenic acid [DMAs(V)], and trimethylarsenic oxide [TMAsO(V)] (Chen et al. 2015). Another additional source of pentavalent organoarsenicals is the human activity by the wide use of herbicides that has increased the exposure to bacteria (Zhu et al. 2014; Yan et al. 2019). It has been proposed that these pentavalent organoarsenicals can be biotransformed by a two-step pathway-first, the conversion to their trivalent forms by an unknown enzyme, followed by their demethylation to form inorganic As(III) by the enzyme *ArsI* (Yan et al. 2019; Yang and Rosen 2016). In addition to these genes, several other genes also have been proposed to take place in the methylation-demethylation process. The accumulation of As(V) in the cells in the presence of GAPDH can form the unstable organoarsenical compound 1-arseno3-phosphoglycerate (1As3PGA) which can be transported out of the cell by *ArsJ*, where it may dissociate into As(V) and 3-phosphoglycerate (Chen et al. 2016). While *ArsO* (homologous to flavin-binding monooxygenases) and *ArsT* (putative thioredoxin reductase gene) have been discovered, their functional mechanisms remain yet to be elucidated (Wang et al. 2006). Besides, the possibilities of *ArsM* independent methylation cannot be ignored although it has not yet been shown (Feikh et al. 2018). Most of the studies have focussed on prokaryotes, but algae are also incredible organisms with properties to metabolize As. Besides, multiple methylation strategies might also be present in a single organism-conversion of the abundant As(III)–As(V) followed by its uptake, or As(III) methylation. In a geo-thermal environment with high levels of methylated As, an extremophilic algae Cyanidioschyzon sp. has been found to carry out As(III) oxidation, As(V) reduction, and methylation (Qin et al. 2009).

## 14.5 Factors Influencing As Biotransformation

Several biotransformation mechanisms for As have already been described in this manuscript in detail. However, they can be modulated by several external factors. First and foremost, the presence of specific chemical species of As is the important determinant that selects for As resistance in microbes. The oxidants and reductants present in the environment such as nitrate can immobilize As(V) thereby reducing microbial uptake. The physical stress parameters for the microbial cells such as temperature and pH can also affect As detoxification (Goswami et al. 2014). There exists also a relationship between Fe and As oxidation. Fe containing Rieske subunits are required for the activation of As(III) oxidase. Siderophores are iron-chelating agents released by plants in soil that help in solubilizing Fe for plant uptake. However, several reports show the ability of siderophores to interact with other metals and metalloids to affect their mobility (Afsal et al. 2020). Thus siderophores can increase the mobility of As(III) and also help activate As(III) oxidase by increasing the availability of Fe for microbes (Afsal et al. 2020; Ghosh et al. 2015). The presence of different types of organic substrates can also modulate the expression of As detoxifying genes. The As(III) oxidase genes have been found to express several folds higher in microbes from multiple genres under carbon starvation conditions because of possible cross-protection (Nandre et al. 2017). Another study observed that the higher concentration of glycerol (>20 mM) prevented the entry of As(III) into the cell by competing for glycerol transport (Min et al. 2021).

## 14.6 Arsenomics

Culture-dependent methods exhibit great plate anomaly—not all the organisms being culturable due to the requirement of specific conditions, or growth-related constraints such as dormancy and adaptation to laboratory conditions. Moreover, culture-independent methods such as transcriptomics, and proteomics have a good capability to complement culture-dependent techniques to correlate the microbial genomic data for As resistance (Altowayti et al. 2020). These tools are also required to expand our knowledge about As transformation mechanisms by discovering different genes that may be playing roles in various microbes. 'Arsenomics' is thus the name proposed for the approach to utilize transcriptomic, metabolomic and proteomic tools to study the responses of organisms to As exposure (Tripathi et al. 2012). The contributions made by transcriptomics and proteomics in understanding microbial As detoxification mechanisms will be looked at briefly below.

### *14.6.1 Microbial Arsenic Resistance and Transcriptomics Studies*

Transcriptomics is a globalized approach to decipher the cellular pathways and modifications taking place inside microbial cells during their exposure to As. Although there are multiple pathways characterized by As detoxification, it is possible that different microbes differentially make use of these mechanisms. Besides transcriptomics studies have helped identify the effect of external factors such as Silica fertilizers in helping microbial As resistance (Das et al. 2021a, b, c). It has also been confirmed that rhizobia provide added protection to the leguminous plants by utilizing microbial As detoxification mechanisms (Lafuente et al. 2015). Transcriptomics of *aioA* and *arrA* genes isolated from the haloarchaea found in high altitude Andean Lake revealed that *arrA* was not expressed under aerobic conditions, thereby establishing the possibility of using *ArrA* as a marker for As(V) anaerobic respiration (Ordoñez et al. 2018). Microbes belonging to the same kingdom, and even the same genera may exhibit different protection mechanisms against As. A combined transcriptomics and metabolomics approach was used to study the As response-adaption strategies in the algae *Coccomyxa* sp Carn. It was observed that the algae increased the expression of an efflux system homologous to Acr3 while at the same time repressing the expression of phosphate transporters. Besides preventing As accumulation inside the cells, the algae also expressed high amounts of the antioxidant GSH. It did not show an accumulation of DMA or changes in motility unlike its algal counterparts *Euglena gracilis* which utilizes increased methylation and *Euglena mutabilis* which depend on increased gliding motility as part of their As resistance mechanisms (Koechler et al. 2016; Halter et al. 2012). On the other hand, the microbial responses to As can also be time-dependent. The microarray analysis carried out in the bacteria *Herminiimonas arsenicoxydans* revealed a two-stage response to As toxicity. The early-stage consisted of general stress responses such as the expression of genes for sulfur metabolism, oxidative stress, and chaperon synthesis while the late stage consisted of effects on phosphate transport and mobility (Cleiss-Arnold et al. 2010). Such transcriptomic-kinetic analysis help throw light on the details of As detoxification mechanisms existing in the microbes.

### *14.6.2 Microbial Proteomics of Arsenic Responsive Strategies*

Although transcriptomics helps to identify the varying levels of transcripts in response to changes, it is not necessary that all the transcripts get translated to functional proteins. Hence proteomics is the alternate technique that can be used to get a broader perspective about the functional end products of genes that carry out As detoxification in the microbial cells. Temporal protein profiling carried out in *Anabaena* sp. PCC7120 threw light into different proteins that helped the microbe adapt and respond to As stress (Pandey et al. 2012). Although some studies utilize a combination of transcriptomic and proteomic approaches, some studies used the proteomic approach alone and discovered the presence of more than one *ars* operon along with other cellular responses generated during As stress (Li et al. 2010; Sher and Rehman 2021). Proteomics also helps obtain a mechanistic understanding of As detoxification, as was done for the extremophilic strain isolated from the environment with very high As concentrations (Belfiore et al. 2013). This approach can also be used in algae to identify the tolerance exhibited by them towards acute As(V) stress (Ge et al. 2016). Another interesting area where proteomics has been employed is to study the mechanism of plant growth promotion provided by microbes free-living in the soil/ as endophytes in the plant hosts during As stress. Inoculation of microbes with plants exposed to As stress can improve plant resistance due to underlying plant–microbe signaling methods (Alka et al. 2021). The plant–microbe interactions are further enhanced when the microbes are endophytic, leading to bacteria-mediated regulation of protein expression in the plants, as shown by proteomic profiling (Alcántara-Martínez et al. 2018). So far, although transcriptomics has been widely employed for microbes, proteomics has been only majorly employed in plants and animals. Therefore, in the future the addition of proteomics to As studies would provide added advantage to deciphering the As detoxification mechanisms in microbes. Arsenomics thus as a whole can expand our knowledge and fill in the gaps in understanding the role played by the operons.

## 14.7 Plant Growth Enhancement by Microbial Amelioration

The interaction between plants and pathogens in heavy metal-laden soils plays an important role in a healthy plant environment (Ma et al. 2016). Rhizobactor is well known to directly or indirectly reduce heavy metal toxicity in plants and promote plant growth (Awasthi et al. 2018). These microorganisms control the phytohormones responsible for plant growth such as abscisic acid, ethylene and auxin and also facilitate the availability of nutrients needed for growth. Microorganisms that convert toxic inorganic forms into fewer toxic organics are found in arsenic-contaminated environments. Algae have hydroxyl, phosphoryl, sulfuryl, amine, cand arboxylic bonding groups on the cell surface (Awasthi et al. 2021). Algae have a high ability to absorb heavy metals or reduce their bioavailability by bioabsorption and detoxification in their cell wall. It is possible that these micromolecules have the property of reducing the toxicity of arsenic and increasing the growth of plants. Bacterial associations and algae have been used to reduce arsenic effects. Some micro-organisms also work to protect plants from harmful pathogens for plants. Micro-organisms have been found to reduce the availability of arsenic to plants in the soil through various mechanisms such as precipitation, dissolution, pH, chelation, etc. (Srivastava et al. 2018; Tang et al. 2021). Therefore, the detection of these microbes from the soil, their use for plant growth and stress conditions can help in plant survival (Awasthi et al. 2021; Kumar and Oommen 2012).

Rhizobacter is a well-known strategy in heavy metal biodegradation techniques. Kaur et al. (2020) identified 3 yeast strains *Candida tropicalis* (NBRI-B3.4), *Debaryomyces hansenii* (NBRI-Sh2.11) and *Candida dubliniensis* (NBRI-3.5) that have been shown to be helpful in reducing the arsenic stress environment in rice. Among these three strains, *D. hansenii* had higher arsenic removal efficiency than the other two. The cation transporter with the responsive gene *arsR* is one of the possible mechanisms of detoxification of arsenic. Responsive genes along with *arsR*, cation transporter and improved membrane stability are among the possible mechanisms of arsenic detoxification. Many micro-organisms such as *Deinocox*, *Pseudomonas*, *Aeromonas*, *Exiguobacterium*, *Acinetobacter*, *Bacillus*, *Acidithiobacillus* and *Desulfitobacterium* etc., belonging to different genera, have shown potential growth in heavy metal contaminated soil and aquatic environment (Rehman et al. 2010; Srivastava et al. 2018). In this way, these bacteria have developed special genetic components to maintain their existence by dealing with adverse conditions. Microbes with special genetic properties have arsenic-resistant operons. In this operon *arsA* and *arsB* are encoded as transmembrane efflux and *arsC* arsenate reductase. The *arsD* and *arsR* were the regulators of the operon (Kaur et al. 2020).

Hence, a simple, easy and cost-effective method of reducing arsenic uptake using arsenic tolerant microbes has proven to be effective as compared to other strategies (Fendorf et al. 2010; Lee 2013; Zhang et al. 2017). Currently, the important role of rhizospheric bacterial communities in arsenic immobilization, metal transformation, the bioavailability of toxicants and plant growth has been proven by geomicrobiological studies (Khanam et al. 2020). It has been proved by many studies that microorganisms (PGPR) are a suitable alternative in promoting plant growth aids such as mineral dissolution, better soil quality, hormone production, disease resistance, nitrogen and phosphorus availability.

## 14.8 Microbial Applicability as Engineered Bioagent

Phytoremediation and bioremediation are the emerging methods of controlling the contamination of toxic metals from soil because of the interaction between plants and microbes. Along with this, a positive role has been seen in the context of agricultural ecosystems such as the growth and yield of crops. PGPR, mycorrhiza, endophytes, fungi etc. are also associated with plants and they also play an important role in their sustainable development. Genetic engineering has shown great influence in the control of various types of pollutants and the efficiency of plant growth regulation. Contaminated industrial wastewater is being treated using microbial methods like bio-absorption, bio-evaporation, bio-accumulation, metal precipitation through mobilization, adsorption, decomposition reduction, co-precipitation methylation and adsorption (Paul et al. 2015; Roy et al. 2015). In addition, emerging microbial methods of wastewater treatment, especially for arsenic treatment include the production of metal chelators and biosurfactants, metal–organic complexation, extracellular sequestration, and metal efflux pumps (Gardner et al. 2015; Shakya et al. 2016; Weitzman 2015). Many microbes reduce arsenite to arsenate in an oxidizing environment, some microbes oxidize the arsenic content to replenish their energy, so arsenic levels have been observed to below. Arsenic is also well known as an electron donor in some cases. The *Australonuphis parateres* species (a marine polychaete) could accumulate up to about 2739 mg $kg^{-1}$ dry weight of As. According to Takeuchi et al., up to 2290 mg $kg^{-1}$ of arsenic can accumulate in the cells of *Marinomonas communis*. Microbial biomass is helpful for the biosorption of arsenic and participates in the removal of arsenic from groundwater. *Gallinonella furruginea* and *Leptothrix ochracea* are capable of reducing metal concentration by the bioaccumulation method (Katsoyiannis and Zouboulis 2004; Singh et al. 2015). The conversion of arsenic in the environment is mainly biological. The biological oxidation rate of Thermus aquaticus and Thermus thermophiles is about 100 times higher than that of abiotic oxidation (Gihring et al. 2001).

## 14.9 Microbial Environmental Clean-Up and Restoration

Various species of algae have been found in the marine ecosystem. These algae require fewer nutrients for nutrition. Algae make their own food and produce a lot of biomass (Abbas et al. 2014). The remediation by algae is also known by the term phycoremediation. Of the three groups of algae, brown (phaeophyta), green (rodophyta and chlorophyta), brown algae have the best bio-absorption tendency. The chemical composition, charge and chemical composition of the outer wall of algae affect the bioabsorption capacity of metal ions (Brinza et al. 2007; Oyedepo 2011). Various algae, alive or dead, have been used alone or in combination in batch and column in situ treatment methods. The Hydroxyl, amine, phosphate, and sulfate were potentially active metal-binding sites present in proteins found in the outer wall of algae for heavy metal remediation (Abbas et al. 2014; Romera et al. 2007). These ionic groups form complexes with metal ions. Similarly, by ion exchange, the calcium, magnesium and sodium ions present in the wall are replaced by heavy metals.

Bacteria of various sizes like coccus, bacillus, rod shape, filamentous and spiral were universally present in the environment. This bacterial mass is made up of living or non-living cells. Bio-absorption by bacteria is an efficient and inexpensive method of biodegradation of toxic pollutants spread in the form of heavy metals. Various species of bacteria have adapted it to survive in metal ions stress conditions (Mustapha and Halimoon 2015). Bioremediation by bacterial agents has become the subject of extensive research in the research field (Hassan et al. 2009; Akhtar et al. 2007; Kao et al. 2008). The rapid removal of Cu, Cr, Zn and Pb occurs by bacterial biomass (Ozer and Ozer 2003). The efficiency of biosorption depends on the cellular composition of the bacterium and the ionic tendency of the heavy metal (Hassan et al. 2010). Metal ions are primarily exposed to and attached to the outer cell wall of bacterial biomass. The amine, carboxyl, hydroxyl, phosphate, sulfate and teichoic acids, peptidoglycan and teichuronic acid anionic functional groups in the cell wall of Gram-positive and Gram-negative bacteria, respectively, are responsible for the binding of the metal (Sherbet 1978). All these functional groups were responsible for the interaction between the metal and the cell wall of the bacterium (Doyle et al. 1980; Vander Wal et al. 1997). Chromium binds with amino groups while Cadmium forms chelates with carboxylic groups by electrostatic interaction (Yee and Fein 2001). A minimum concentration of pollutants is required for enzymatic expression in bacteria (Adenipekun and Lawal 2012). *Geobactor*, *Pseudomonas*, *Bacillus* and *Desulfovibrio* species have proven useful for bioremediation.

Fungi present in the natural environment are known for their prevalence and are extensively exploited in industrial applications (Abdi and Kazemi 2015). Fungi are responsible for the nutrient cycle and decomposition in the ecosystem (Archana and Jaitly 2015). The structure and metabolic process of fungi adapt according to the environment. The fungus survives under various unfavorable conditions such as moisture, pH, availability of nutrients etc. Mycoremediation is the process of removal of different pollutants by fungi from different areas of the environment (Hamba and

Tamiru 2016; Esterhuizen-Londt et al. 2016). Mycoremediation does not leave any waste residue behind and is a less expensive method of degradation of pollutants. Hence it offers a complete solution to the mineralization of toxic pollutants present in the environment (Thenmozhi et al. 2013). Appropriate selection of fungal species for targeted heavy metals or other contaminants enables the mycoremediation process to be successful. Fungi reduce heavy metal concentrations or make them unavailable. It has an efficient ability to store heavy metals in its fruiting body. The availability of heavy metals or other contaminants in the media or environment depends on the presence of suitable fungal species and the chemical behavior of the elements. Sequestration of up to 65–70% of Cd and Pb has been recorded by *Saccharomyces* from polluted soils. The cell wall of fungi is made up of chitin, proteins, lipids, and polysaccharides which participate in metal chelation. The hydroxyl, amine, carboxylic, and phosphate group present in the cell wall interacts with the metal and is responsible for the biosorption process. In addition, fungi secrete some extracellular polymeric substances (EPSs) that provide tolerance to the environment and also act as heavy metal degradation. The anionic products of EPSs and positively charged heavy metals are bonded by electrostatic interaction. (Guibaud et al. 2005). EPSs have acidic nature due to the presence of hydroxyl, amine, carboxylic, uronic acid, sulfhydryl, and phenolic groups. Due to its acidic nature, positive interactions were formed with heavy metals. Among the most powerful representatives of the fungus, are those known for their ability to remove heavy metals by the process of biosorption *Penicillium chrysosporium* and *Penicillium simplicissimum* with 98% arsenic and chromium removal capacity of 92% respectively (Chen et al. 2019; Shah et al. 2018). Removal of aurum (95%), chromium (98.86%) and uranium (96%) can also be achieved with sorption properties of *Aspergillus* sp., *A. niger*, and *Geotrichum* sp., Respectively. Many studies have been carried out with the aim of repairing soil contaminated with heavy metals, and among them, Ascomycota (70%) is an important fungal group.

## 14.10 Concluding Remarks and Future Aspects

Arsenic distribution is one of the world's greatest threats to human health and it compromises not only the soil quality but also the crop yield and nutritional values. Soil microbiota is the most crucial factor which needs to be researched thoroughly and their potential for environmental restoration should be harnessed appropriately. Microbial genomics and transcriptomic studies revealed the mechanisms of As resistance and tolerance in microbial groups depending on the metabolism, habitat and environmental influences. It has been established that the beneficial microbes, either naturally potent or engineered, can be used for the As translocation to the plant and minimize the toxicity. But studies related to microbial protein synthesis and interaction with As are still not well understood. The proteomics studies with combined transcriptomics and further direct association analysis should be practiced more to get a clear idea of how the microbially derived metabolic products can be used for such environmental contamination management.

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# Chapter 15
# Phosphate-Induced Phytoextraction by *Pteris vittata* Reduced Arsenic Uptake by Rice

**Asit Mandal, Tapan J. Purakayastha, Ashok K. Patra, and Binoy Sarkar**

**Abstract** The phytoextraction with hyperaccumulator plant species has been found as a novel approach for cleaning up of arsenic (As)-contaminated soils. However, proper management strategy should be developed to enhance the phytoextraction potential of hyperaccumulator and minimize the bioavailability and As contamination to agricultural crops. A greenhouse study was evaluated to assess the effectiveness of phosphatic fertilisers viz. di-ammonium phosphate (DAP) and single superphosphate (SSP) with successive two growing cycles on As removal by Chinese brake fern (*Pteris vittata* L.) from the contaminated *Typic Haplustepts* soils of West Bengal, India. Present study evaluated the influence of phytoextraction by the fern (*P. vittata*) on redistribution of As in different fraction (water soluble, exchangeable, aluminium, iron and calcium bound) in soil as well as total and Olsen's extractable fraction in soil and its subsequent impact on rice crop. Among the five fractions, water soluble fraction and Fe-bound As was found in higher magnitude than the other As bound fractions viz. Al-bound, Ca-bound and exchangeable fraction. This fern was grown in As contaminated soils in successive two growing cycles (four months each), and the total As removal from the soil were measured. The removal values of As varied from 6.4 to 13.5% after the first growing cycle and from 10.6 to 23.9% after the second growing cycle. The phytoextracted soils were reused for rice cultivation to reveal the effect of phytoextraction on As accumulation in rice. In this enhanced process of phytoextraction by *P. vittata*, the phosphatic fertilizers, DAP was contributed greater than SSP in enhancing the more As uptake by the fern as confirmed by our previous study and followed by a significant decrease in available fraction of As in soil and reduced availability for accumulation in rice. Combining the process of two successive cycles phytoextraction with phosphate (DAP) management strategy leads to reduced bio-available fraction in the soil may serve better for soil with medium

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levels of As contamination. However, these cycles phytoextraction could be prolong with adjustable soil amendments for high As contaminated soil to attain safe limits of As in the soil and reduced the risk of rice consumption in the arsenic affected areas.

**Keywords** Arsenic fractions · Phosphates · Phytoextraction · *Pteris vittata* · Rice

## 15.1 Introduction

Arsenic (As) contamination of the environment is considered as a critical issue in worldwide. The contamination of As has caused several health related problems to humans and animals, and severely impacted the functionality of soil biota (Abdul et al. 2015; Turpeinen et al. 2004; Mandal 2017). Arsenic has been unequivocally treated as both toxic and carcinogenic to the humans and animals (Gamboa-Loira et al. 2017). The contamination of surface and underground waters with As across the world, especially in the developing countries, has become a serious sociopolitical issue. The issue has been extensively demonstrated in Asian countries where millions of people in Bangladesh and parts of India are severely affected (Chakraborti et al. 2017; Rasool et al. 2016, Naidu et al. 2006, Smith et al. 2000; Sanyal et al. 2020). A prolong exposure of As-contaminated aquifer and food to humans often show typical symptom of poisoning such as arsenical lesions, arsenicosis and potential cancer risks (Rahman et al. 2015).

Vast areas of agricultural soils being contaminated by an alarming rate of As through the application of As-laden irrigation water mostly in Bangladesh and India. There is a pressing need to control the transfer of the toxic element from contaminated soils to the human food chain via agricultural produces. It was illustrated extensively that the Chinese brake fern (*P. vittata* L.) can extract As from polluted soils and provide a viable approach for remediating the hazardous element. Therefore, cultivation of agricultural crops following phytoextraction of As from soils by growing the fern might render a viable alternative to grow crops safely in the contaminated regions. However, how many growing cycles of the fern and what management practices are needed to achieve a safe As level (that does not transfer unsafe level of As to the agricultural produce) in a contaminated soil might significantly vary from site to site. For example, it was reported that the frequency and distribution amount of phosphate fertilization during growing of the fern can become a critical factor that influences the plant availability of As in soils (Mandal et al. 2012a, b, 2018). Our earlier studies reported that cultivation of the fern over two successive repeated harvests and fertilization with di-ammonium phosphate (DAP) delivered a better As amelioration strategy in contaminated soil from West Bengal, India, than growing a single cycle of the fern and applying single super phosphate (SSP) (Mandal et al. 2018). Similarly, Williams et al. (2003) reported that among the various factors such as pH, pore water velocity and phosphorus fertilization, the later one held the greatest impact on the mobility of As(V) in soils down to the sub-surface profile.

Since arsenate/arsenite and phosphate occupy similar sorption sites in soil matrix, application of the later releases more As in the soil solution thereby increase its uptake by the As-hyper accumulating fern (Lessl et al., 2014; Liao et al., 2008). Not only phosphate fertilizers (SSP, DAP), but also slow-release rock phosphate application was shown to enhance As uptake by the fern from contaminated soils (Fayiga and Ma 2005; Mandal et al. 2012a). However, since plants take up As and P using a common transport system, phosphate might also compete with As for plant accumulation and uptake (Meharg and Hartley-Whitaker 2002), especially when both the elements are available in the soil solution in easily available forms. For example, Tu et al. (2004) reported that P addition to a hydroponic system reduced As removal by the fern significantly. Similarly, young fern feeding with initial low P or split-P was found more efficient in As removal from water than using older fern supplied with higher initial P or single P application (Santos et al. 2008). Wang et al. (2002) reported that the maximum net As-influx in P-starved plants increased by 2.5 times than P-supplied plants because plants did not encounter any uptake competition in the former situation. Therefore, in the context of phytoremediation, uptake of As by the fern would be largely dependent on the relative fractions (e.g., water soluble, exchangeable, and compound-bound) of the element in the contaminated soil, which warrants further research interest.

Arsenic contaminated soils of Bangladesh and the West Bengal state of India are mainly dominated by intensive cultivation of rice (*Oryza sativa* L.) which is the staple food of people in this south Asian region. Excessive use of As-contaminated ground water for irrigating summer rice not only lead to a buildup of As in the upper layer of soil but also caused increased As accumulation in rice grains indicating the potential risk of As exposure into the food chain (Khan et al. 2009). The cancer risk was reported due to daily exposure of arsenic in the drinking water and food consumption (Chakraborti et al. 2017; Joseph et al. 2015; Okoye et al. 2022).There are evidences of elevated levels of As in rice grain in the region where rice cultivation involves stagnation of As-rich irrigation water in the field (Rahman et al. 2007; Duxbury et al. 2003; Williams et al. 2005; Islam et al. 2004). Even a moderate level of As irrigation (0–8 mg of As $L^{-1}$) in soil could raise the risk of As concentration in rice grains to a toxic level (Abedin et al. 2002a). Due to the water stagnation behavior of rice soils would have their unique chemistry and elemental (As and P) fractionation which was not extensively studied earlier in a phyto-remediation scenario using the fern.

Reports suggested that As uptake by rice was reduced by application of phosphates in the soil (Abedin et al. 2002b) and organic amendments (Nahar 2022). To alleviate As toxicity, plants must take up sufficient amount of phosphate to balance excessive As (Carbonell-Barrachina et al. 1998). Very limited number of studies however investigated the redistribution of As in soils after phosphate mediated enhanced phytoextraction process by the fern and consequent As accumulation patterns in rice plants. Our previous studies demonstrated that phosphate application increased As phytoextraction by the fern from naturally contaminated soils and reduced As uptake by the rice (Mandal et al. 2012b). Since in our previous study the level of available As was not high, the interaction of phosphate and arsenate under limited As scenario might be different from an arsenate-abundant scenario. Through this experiment we wanted to study the influence of phosphate on mobilization of arsenate under As non-limiting condition which might be prevailing in the future of soil As contamination in the state of West Bengal, India. In the present study we aimed at highlighting the As redistribution patterns (different fractions such as total, Olsen's extractable, water soluble, exchangeable, Al-bound, Fe-bound and Ca-bound) following repeated phytoextractions by the fern from a highly As contaminated soil (>100 mg As kg$^{-1}$ soil), and subsequent effect on As accumulation in the edible parts of rice (grain) grown in the phytoremediated soil.

## 15.2 Materials and Methods

### *15.2.1 Soil Sampling and Characterization*

Soil samples (Total As = 2.7 mg As kg$^{-1}$, 0–0.15 m) were collected from the Nadia district in West Bengal that was same region as of naturally contaminated soils (Total As = 23.4 mg kg$^{-1}$ soil, Mandal et al. 2012a) as used in our previous study. The collected soil was- used for spiking with arsenic (As). However, the current study focused on these soils following artificially elevating the As concentration through spiking with As @100 mg kg$^{-1}$ with sodium arsenate ($Na_2HAsO_4$). This represented a high As-contaminated condition which might be prevailing in the state of West Bengal, India, in the future. The air-dried (<2 mm sieved) soils were analyzed for physicochemical properties (Table 15.1) such as soil pH, cation exchange capacity (CEC), organic carbon (OC) content, reactive Fe and reactive Al (McKeague and Day 1966), available N (Subbiah and Ashija 1956), available P (Olsen et al. 1954), available K and soil texture (Day 1965). The soils belong to *Typic Haplustept* classification. The spiking procedure was done by spreading the soil uniformly on a plastic sheet with a tray and the As solution (2000 mg L$^{-1}$) was sprayed evenly. The soil was then turned over 50 times to make a homogenous mixture. The spiked soil was then transferred to plastic pots with 4 kg soil and aged for 30 days prior to the fern growth experiment.

### *15.2.2 Green House Study and Rice Cultivation*

A greenhouse experiment was conducted at the National Phytotron Facility (NPF) of Indian Agricultural Research Institute (IARI), New Delhi, to evaluate the effectiveness of different phosphatic fertilisers (60 mg P kg$^{-1}$ through di-ammonium phosphate (DAP) and single superphosphate (SSP)) and growing cycles (one or two) on As removal by the fern from the spiked soils. Ferns were grown in 4 kg soil in plastic pots. After completion of two successive growing cycles of the fern, the same soil was used for growing rice during the rainy season (July to September) in a net

**Table 15.1** Physio-chemical characteristics of the experimental soil

| Parameters | Uncontaminated soil |
|---|---|
| pH | 6.9 |
| Organic carbon (%) | 0.59 |
| CEC [cmol ($p^+$) $kg^{-1}$] | 13.8 |
| Exchangeable Ca (meq $Ca^{2+}$ per 100 g soil) | 6.9 |
| Reactive Fe (%) | 0.25 |
| Reactive Al (%) | 0.23 |
| Available N (kg $ha^{-1}$) | 202 |
| Available P (kg $ha^{-1}$) | 20.5 |
| Available K (kg $ha^{-1}$) | 184.8 |
| Total N (g $kg^{-1}$) | 0.77 |
| Total P (g $kg^{-1}$) | 0.53 |
| Total K (g $kg^{-1}$) | 8.2 |
| Total As (mg $kg^{-1}$) | 2.71 |
| Sand (%) | 12.8 |
| Silt (%) | 62.1 |
| Clay (%) | 25.1 |
| Texture | Silty clay loam |
| Soil type | *TypicHaplustept* |

house of the Division of Soil Science and Agricultural Chemistry, IARI, New Delhi. Before rice transplantation (four weeks old seedlings), the pots were submerged with water for two weeks, and mixed with spatula. Drainage was allowed in the pots, but the leachate collected in base holder trays was added back to the soil to avoid any loss of As. Nitrogen and potassium were applied @120 and 60 mg $kg^{-1}$ soil in the form of urea and muriate of potash, respectively, in each pot and mixed with the soil. A popular variety of rice (*Oryza sativa* L., cv. *Swarna Dhan* MTU-7029) cultivated in the Nadia district of West Bengal was grown in As contaminated soils up to the maturity (110 days after transplanting).

### 15.2.3 Sequential Fractionation of Soil As and Available As Analysis

Sequential extraction of soil inorganic As fractions was carried out following harvest of the rice crop. The water soluble, exchangeable, Al-bound, Fe-bound and Ca-bound fractions of soil As were extracted with double-distilled water, 1 M $NH_4Cl$, 0.5 M $NH_4F$, 0.1 M NaOH and 0.5 M $H_2SO_4$, respectively (Onken and Adriano 1997). Available As in the contaminated soil was determined by Olsen’s reagent i.e. 0.5 M

$NaHCO_3$ at pH 8.5 (Olsen and Sommers 1982) as it was reported to be an effective reagent for extracting available form of As in neutral to slightly alkaline soil pH (Ghosh et al. 2003). Concentrations of As in the extracts were analysed on a ZEEnit 700 Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS, Analytik Jena, Germany).

### 15.2.4 Sample Digestion and Analysis

Arsenic accumulation and uptake in the biomass of the fern as well in rice crop was assessed. The representative dried fern biomass, and straw, grain and root samples of rice (dried at 70 °C for 48 h) were ground into powder using a Wiley Mill, and passed through a 1-mm mesh screen. It was digested in tri-acid mixture ($HNO_3$:$HClO_4$:$H_2SO_4$::10:4:1) following soaking overnight in 10 mL of concentrated $HNO_3$ (Jackson 1973). Following passing through 0.22 μm filters, the digests were diluted enough to determine the As concentration in $\mu g\ L^{-1}$ level by a ZEEnit 700 Graphite Furnace Atomic Absorption Spectrophotometer (GFAAS, Analytik Jena, Germany) (Mandal et al., 2018).

### 15.2.5 Human Health Risk Assessment

To evaluate the impact of rice grain consumption with high levels of arsenic on human health, a risk assessment was performed. The Health Risk Index (HRI) was calculated as the ratio of estimated exposure of rice and reference oral dose (RfD) ($\mu g\ kg^{-1}\ day^{-1}$). Estimated exposure is obtained by dividing the estimated daily intake (EDI) of heavy metals by their safe limits. An index value >1 is considered unsafe for human health (USEPA 2002). EDI was calculated by the following equation:

$$\text{EDI}\ (Estimated\,daily\,intake) = \frac{\text{C} \times \text{Con} \times \text{EF} \times \text{ED}}{\text{Bw} \times \text{AT}},$$

where C (in mg/kg) is the concentration of arsenic in the rice, Con (in g/person/day) is the daily average consumption of rice in the region, Bw (in kg/ person) represents body weight, EF is exposure frequency (365 days/year), ED is exposure duration (70 years, equivalent to the average lifespan), and AT is average time (365 days/year number of exposure years, assuming 70 years in this study). The average daily rice intake of adults and children was considered to be 389.2 and 198.4 g/person/day, respectively (Zheng et al. 2007). Average adult and child bodyweights were taken to be 55.9 and 32.7 kg, respectively, as used in many previous studies (Hang et al. 2009). The health risk for adult and children is considered separately since the contact pathway with each exposure way changes with age. The health index (HI) is calculated to evaluate the potential risk of adverse health effects from a mixture of chemical constituents in rice. The HI was calculated through daily average consumption of rice for a human being (adults and children) and is as follows:

$$\mathrm{HI} = \sum_{i=1}^{n} \mathrm{HRI}$$

Target hazard quotient (THQ) and health risk index (HRI) that could be derived according to standard EPA methods, the risk of non-carcinogenic effects is expressed as the ratio of the dose resulting from exposure to site media compared to a dose that is believed to be without risk of effects, even in sensitive individuals (Zheng et al. 2007). This ratio is referred to as the target hazard quotient (THQ). The THQ for the locals through consumption of contaminated rice can therefore be assessed based on the food chain and the reference oral dose (RfD) for each potentially toxic elements. The applied RfD for As was 50 $\mu$g kg$^{-1}$ day$^{-1}$, respectively. Oral reference doses were obtained from the Integrated Risk Information System (US-EPA 2008), with the exception of Pb, Hg, and As for which they have used the formula RfD = PTWI/7, where PTWI is the provisional tolerable weekly intake ($\mu$g kg$^{-1}$ day$^{-1}$) by the Joint FAO/WHO Expert Committee on Food Additives (JECFA) (FAO/WHO 1997; UNEP/FAO/WHO 1992). The THQ is determined by THQ = EDI/ RfD; If the value of THQ is less than one it is assumed to be safe for risk of non-carcinogenic effects. If it exceeds one it is believed that there is a chance of non carcinogenic effects, with an increasing probability as the value of THQ increases (Zheng et al. 2007; Tore et al. 2021).

Carcinogenic risk
A carcinogenic risk represents an incremental probability of developing cancer in an individual lifetime due to potential exposure of carcinogen (Lemke and Bahrou 2009). The carcinogenic risk was calculated using following formula,

$$\text{Cancer risk} = \mathrm{EDI} \times \mathrm{SF}$$

where EDI (mg kg$^{-1}$ day$^{-1}$) is the estimated daily intake of carcinogenic element, and the SF (mg kg day) is the slope factor of the carcinogenic element.

### *15.2.6 Statistical Analysis*

Data were subjected to a two-factor (phosphate source and growing cycle of the fern) Completely Randomized Design (CRD) analysis with Duncan's Multiple Range Test (DMRT) at 5% level of significance in order to separate the means. The analysis of variance (ANOVA) is based on three replicate pots per treatment. Statistical analysis was performed by DOS based MSTAT-C version C program developed by S. P. Eisensmith.

## 15.3 Results

### 15.3.1 Biomass Yield of the Fern

The frond dry matter production of the fern not significantly influenced by the factors growing cycle of fern and phosphate sources however, the root dry matter yield was significantly ($p < 0.05$) affected by these factors with an evident of decrement of dry matter production in the successive growing cycle of the fern. It was also speculated that the total dry matter yield of fern was found significantly ($p < 0.05$) more is first growing cycle than second growing cycle and also found higher with the application in order of DAP > SSP > control (Table 15.2).

### 15.3.2 Arsenic Uptake by the Fern

Irrespective of the growing cycles of the fern, total uptake (frond + root) of As by the fern was significantly ($p < 0.05$) influenced by phosphate application in the order of DAP > SSP > control. The As uptake by roots of the fern was much lower than that by the accumulated As in the frond. Total As uptake by the fern ranged from 19.4 to 44.5 mg pot$^{-1}$ in the first growing cycle, and from 10.4 to 32.1 mg pot$^{-1}$ in the second growing cycle. In successive two growing cycles, the fern removed 10.6 to 23.9% As, whereas one cycle removed only 6.4–13.5% of total soil As (Table 15.2). Phosphate fertilization with special reference to DAP as compared to SSP significantly ($p < 0.05$) enhanced the phytoextraction process and thereby removed the highest amount of As from the soil. The extent of total removal of As by DAP was 31% and 50% higher than that by SSP at the first, and first + second growing cycles, respectively. Therefore, the magnitude of As removal by the fern was higher in the first growing cycle than the second cycle. Overall, two successive growing cycles of the fern with DAP fertilization was the most effective treatment in decreasing As load in the contaminated soil.

### 15.3.3 Changes in Soil As Fractions

Arsenic distributions in the water soluble, exchangeable, Al, Fe and Ca-bound fractions before and after fern growth were affected by both phosphate application and growing cycles of the fern (Table 15.3). In general, the application of DAP and SSP significantly increased the water soluble, exchangeable, Fe- and Al- bound As in soils, whereas Ca-bound fraction remained unaffected under the no-fern treatment. Growing of the fern led to subsequent depletion of As from the Ca-bound fraction also from the soil. After the first growing cycle of the fern, application of SSP and DAP significantly ($p < 0.05$) decreased all the fractions of As except Ca-bound As;

**Table 15.2** Effect phosphates and growing cycles on biomass yield and arsenic accumulation in fern in arsenic contaminated soil

| Treatment | Biomass yield (g $pot^{-1}$) | | | | | | Arsenic uptake (mg $pot^{-1}$) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Frond | | Root | | Total[a] | | Frond | | Root | | Total§ | |
| | Growing cycle 1 | Growing cycle 2 | Growing cycle 1 | Growing cycle 2 | Growing cycle 1 | Growing cycle 2 | Growing cycle 1 | Growing cycle 2 | Growing cycle 1 | Growing cycle 2 | Growing cycle 1 | Growing cycle 2 |
| Control | 6.57a[b] | 4.47a | 1.63a | 1.27d | 8.17e | 5.73f | 18.9e | 10.1f | 0.48d | 0.30d | 19.4e | 10.4f |
| SSP | 8.40a | 6.60a | 2.17a | 1.60c | 10.57c | 8.20d | 33.2b | 20.9d | 0.83c | 0.54c | 34.0b | 21.4d |
| DAP | 9.60a | 8.17a | 2.73a | 2.73b | 12.33a | 10.90b | 43.2a | 31.1c | 1.29a | 1.02b | 44.5a | 32.1c |

[a] Summation of uptake by frond and root

[b] The mean data points with different small letters within a row and column for a particular measurement is significantly different according to Duncan's multiple range test at $p < 0.05$

the effect was more pronounced in DAP than in SSP treatment. After the second growing cycle of the fern, only the water soluble-, exchangeable- and Al-bound As was significantly ($p < 0.05$) reduced. Irrespective of the treatments, all the fractions of As were depleted due to repeated harvests of the fern. The phytoextraction with repeated growing cycles with phosphates led to depletion of various fraction of As in the order DAP > SSP > control, and had a significant ($p < 0.05$) influence due to the second growing cycle than the first. The contribution of different fractions for the depletion was: Fe-bound (56.3–60.6%) and Al-bound (32.4–62.6%) > exchangeable (30.5–38.9%) > Ca-bound (24.0–45.4%) > water soluble (21.8–35.2%) (Table 15.3). The phosphatic fertilizer (DAP and SSP)-treated pots significantly ($p < 0.05$) increased the extent of As removal in all these five fractions.

Olsen's extractable As, which is considered as available pool of As, constituted a major fraction of total As in the soil. In no-fern condition, the application of DAP significantly ($p < 0.05$) increased the available As contents compared to the control, but the effect did not differ significantly from SSP. The application of DAP significantly decreased the available As contents in soil after harvest of the fern at first growing cycle, while at second growing cycle, the available As was unaffected due to phosphatic fertilization. Irrespective of phosphatic fertilizer sources, the available As concentration in soil after the second growing cycle was significantly lower than that in either first growing cycle or without the fern (Fig. 15.1).

The effect of phytoextraction was more prominent when total As concentration in rhizosphere soil was measured at the end of the cropping. The application of DAP showed maximum removal of total soil As followed by SSP (Fig. 15.2). As compared to the initial level of As, its content in soil decreased significantly ($p < 0.05$) after first growing cycle of the fern which was further decreased after second growing cycle. The extent of decrease in As load with SSP and DAP after first growing cycle of the fern was comparable with that of control treatment of second growing cycle. The removal of total As contents were 6.4, 10.2, 13.5% in control, SSP and DAP treated soils, respectively after first growing cycle and after second growing cycle, the corresponding values were 10.6, 18.1, 23.9%.

### *15.3.4 Rice Yield and As Content in Rice*

The interaction effect of phosphates and growing cycles of *P. vittata* did not had significant influence on grain, straw or root biomass yields of rice whereas the main effect of phosphate sources and growing cycle of the fern has significant ($p < 0.05$) impact on biomass yield of rice (Figs. 15.3 and 15.4). The effect of phosphates application observed that grain yield of rice in DAP treated pot was significantly ($p < 0.05$) higher over SSP treated pot. The effect of growing cycle revealed that phytoextraction with *P. vittata* for two successive growing cycles produced significantly ($p <$ 0.05) higher grain yield of rice than either no-fern or one growing cycle of fern.

Application of phosphatic fertilizer and growing cycles of the fern had significant ($p < 0.05$) effects on As content in rice grains and root. The application of SSP and

**Table 15.3** Effect phosphates and growing cycles of the fern on distribution of arsenic in different fractions in arsenic contaminated soil

| Treatment | Water soluble-As (mg kg$^{-1}$) | | | Exchangeable-As (mg kg$^{-1}$) | | | Aluminium bound-As (mg kg$^{-1}$) | | | Iron bound-As (mg kg$^{-1}$) | | | Calcium bound-As (mg kg$^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | No-plant | Growing cycle 1 | Growing cycle 2 | No-plant | Growing cycle 1 | Growing cycle 2 | No-plant | Growing cycle 1 | Growing cycle 2 | No-plant | Growing cycle 1 | Growing cycle 2 | No-plant | Growing cycle 1 | Growing cycle 2 |
| Control | 22.07c[a] | 20.22c | 17.25f | 11.39b | 9.25c | 7.91e | 13.46a | 10.54c | 9.10d | 19.13a | 11.02d | 8.35f | 12.76a | 11.01a | 9.7a |
| SSP | 24.57b | 19.82de | 15.72g | 12.00b | 8.59d | 7.17f | 12.06b | 8.66d | 6.75e | 18.15b | 9.49e | 7.87f | 11.25a | 8.71a | 8.37a |
| DAP | 26.47a | 18.82e | 14.29h | 13.19a | 8.48de | 6.96f | 11.08c | 7.16e | 5.03f | 17.05c | 8.37f | 7.54f | 10.41a | 8.44a | 6.97a |

[a] The data points mean with different small letters within a row and column for a particular measurement is significantly different according to Duncan's Multiple Range Test (DMRT) at $p = 0.05$

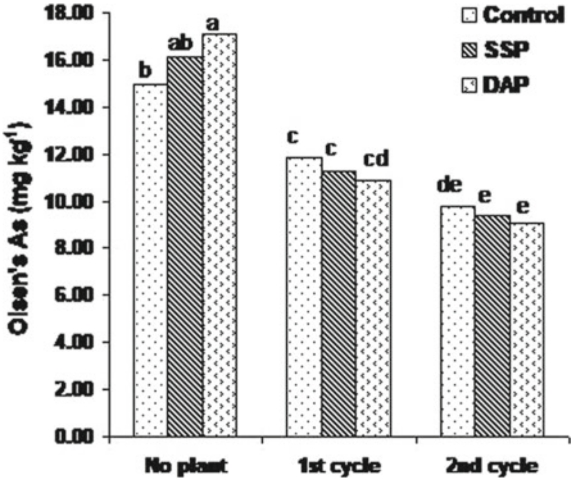

**Fig. 15.1** Effect of growing cycle of brake fern and phosphates on Olsen's arsenic content in arsenic contaminated soil after fern harvest bars; with different lower-case letters in a particular growing cycle is significant according to Duncan's Multiple Range Test at $p = 0.05$

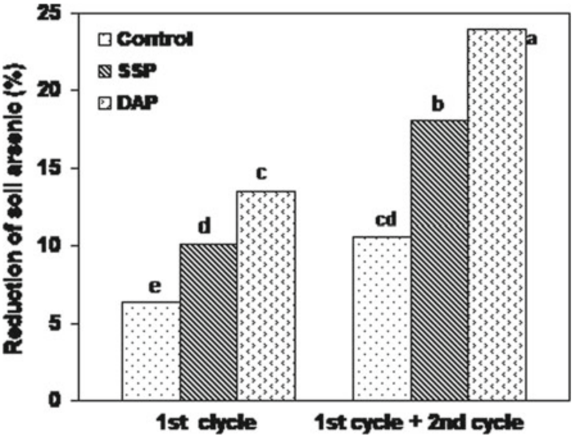

**Fig. 15.2** Effect of P source and growing cycles of brake fern on removal of arsenic from contaminated soil; bars with different lower-case letters in a particular growing cycle is significant according to Duncan's Multiple Range Test at $p = 0.05$

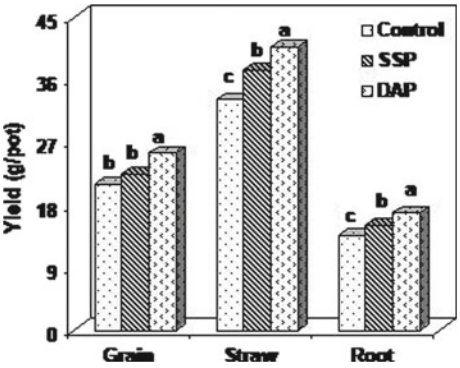

**Fig. 15.3** Effect of phosphate source used in phytoextraction by the fern on grain, straw and root biomass yield of rice grown in arsenic contaminated soil; bars with different lower case letters in a particular plant parts are significantly different according to Duncan's Multiple Range Test (DMRT) at $p = 0.05$

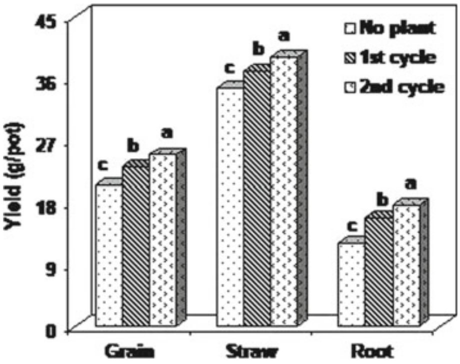

**Fig. 15.4** Effect of growing cycles of the fern used in phytoextraction on grain, straw and root biomass yield of rice grown in arsenic contaminated soil; bars with different lower case letters in a particular plant parts are significantly different according to Duncan's Multiple Range Test (DMRT) at $p = 0.05$

DAP during phytoextraction with the fern significantly ($p < 0.05$) decreased the As content in grain and straw. The extent of decrement of As content in rice grain and root was greater in DAP than SSP, and further it was more pronounced by the second growing cycles than either first growing cycle or no-fern condition. The As content in straw was not affected by either phosphatic fertilizer or growing cycle. Arsenic content in rice grain varied from 2.82 to 4.10 mg kg$^{-1}$ without phytoextraction, 1.44–2.83 mg kg$^{-1}$ after one growing cycle of phytoextraction and 0.71–1.75 mg kg$^{-1}$ after two growing cycles of the fern (Table 15.4). The As content in rice root was found manyfold higher than grain and which was varied from 33.8 to 44.0 mg kg$^{-1}$ in non phytoextracted soil and it varied from 26.1 to 33.7 mg kg$^{-1}$ and 23.2 to 30.6 mg kg$^{-1}$ after first and second growing cycles, respectively (Table 15.4).

**Table 15.4** Arsenic content in grain, straw and roots of rice grown in arsenic contaminated soil

| P source | As content in grain (mg kg$^{-1}$) | | | As content in straw (mg kg$^{-1}$) | | | As content in root (mg kg$^{-1}$) | | |
|---|---|---|---|---|---|---|---|---|---|
| | Growing cycles of the fern | | | | | | | | |
| | No plant | 1st cycle | 2nd cycle | No plant | 1st cycle | 2nd cycle | No plant | 1st cycle | 2nd cycle |
| Control | 4.10a[a] | 2.83c | 1.75e | 23.63a | 20.10a | 16.57a | 44.0a | 33.7c | 30.6d |
| SSP | 3.49b | 1.99d | 0.99g | 17.73a | 15.77a | 13.07a | 39.0b | 30.0d | 24.6ef |
| DAP | 2.82c | 1.44f | 0.71h | 16.47a | 13.70a | 12.10a | 33.8c | 26.1e | 23.2f |

[a] The data with different small letters within a row and column for a particular measurement is significantly different according to Duncan's multiple range test at $p < 0.05$

### 15.3.5 *Arsenic Uptake by Rice Grain*

The quantity of As uptake (content × biomass) was significantly affected by the repeated growing cycles with the aid of the fern and phosphate sources. Phytoextraction by the fern for repeated growing cycle significantly decreased the As uptake by rice followed by one growing cycle and without phytoextraction condition. Among phosphate sources, DAP decreased the As content dramatically in rice grain especially after phytoextraction of soil by the fern for two growing cycles (Table 15.5). The As uptake by rice straw was 6 to 8 times higher than that of uptake by grain (data not shown). Similar to rice grain, the As uptake by rice straw and root decreased significantly over phytoextraction with successive growing cycles. Application of phosphatic fertilizer during phytoextraction with the fern *significantly* ($p < 0.05$) reduced the As uptake by the succeeding rice crop. The DAP was found superior over SSP in reducing the As uptake by rice grown in the soil with one growing cycle of the fern. However, in no plant and second growing cycle, treatment DAP was statistically at par with SSP with respect to As uptake by grain. Growing of phytoremediating fern for two successive growing cycles showed lowest As uptake by rice. The As uptake by rice grain varied from 66.96 to 75.78 $\mu$g pot$^{-1}$ in without phytoextracted soil and it varied from 36.87 to 59.70 $\mu$g pot$^{-1}$ and 19.42 to 41.03 $\mu$g pot$^{-1}$ after one and two growing cycle, respectively (Table 15.5). As a consequences of arsenic contaminated rice consumption may leads to various kind of toxicity and human health risk issues. The human health risk assessment model used for the evaluations of intake exposure to arsenic in the contaminated rice grain was estimated by calculating a daily intake and health risk index.

#### 15.3.5.1 Exposure Risk Assessment and Cancer Risk in the Affected Areas

The human health risk assessment model derived by US-EPA (USEPA-IRIS 1998) was used to evaluate the toxic effects of arsenic present in drinking water on human health. The same model could be used for the assessment of intake exposure to

**Table 15.5** Arsenic uptake by grain of rice grown in arsenic contaminated soil

| P source | As uptake by grain ($\mu$g pot$^{-1}$) | | |
|---|---|---|---|
| | Growing cycles of the fern | | |
| | No plant | 1st cycle | 2nd cycle |
| Control | 75.8a[a] | 59.7c | 41.0e |
| SSP | 70.0b | 45.7d | 23.4f |
| DAP | 67.0b | 36.9e | 19.4f |

[a] The data with different small letters within a row and column for a particular measurement is significantly different according to Duncan's multiple range test at $p < 0.05$

arsenic in the contaminated rice grain was estimated by calculating a daily intake using the following equation-

$$\mathrm{DIA} = \frac{\mathrm{C} \times \mathrm{DI}}{\mathrm{BW}} \times \frac{\mathrm{EF} \times \mathrm{ED}}{\mathrm{AT}}$$

Assume:
C = 4.1 mg As $\mathrm{kg}^{-1}$ rice (without phyto-extraction in control condition).
DI = 0.389 kg.
BW = 55.9 kg (Adult).
EF = 365 days.
ED = 70 years.
AT = 25,550 days.

Then, DIA = 28.54 and CR = (DIA * SF) = 28.54 * 1500 = 42,810; where, DIA represents daily intake of arsenic (mg/kg day), C is the concentration of arsenic in contaminated rice grain (mg/kg); DI is the average daily intake rate (kg/day); BW is body weight (kg); EF is the exposure frequency (d/year), ED is the exposure duration (year), AT is the averaging time (d).

### *15.3.6 Lifetime Cancer Risk (CR) Associated with Ingestion Exposure was Calculated Using*

CR = DIA × SF; where, SF is the slope factor of arsenic (mg/kg/d). SF values employed in this study were 1.5 (mg/kg/d), obtained from the USEPA (IRIS 2013). In this study, the daily intake of arsenic from rice consumption is 28.54 μg per kg bw and the cancer risk is estimated as 42,810 * $10^6$. The average daily rice intake of adults and children was considered to be 389.2 and 198.4 g/person/day, respectively (Zheng et al. 2007).

## 15.4 Discussion

In this present study it is clearly understood that phosphorus had a tremendous capacity to improve the phytoextraction efficiency by enhancing bio-avaialability of As to the fern. Nevertheless, multiple harvests are necessary to lowering down the soil As contamination to an acceptable level (Fayiga and Ma 2005) in case of elevated soil As concentration (50 mg $\mathrm{kg}^{-1}$ soil). Tu et al. (2002) reported that the addition of 50 mg $\mathrm{kg}^{-1}$ arsenate to sandy soil increased the fern biomass by 107%. The present study of spiking with As (100 mg $\mathrm{kg}^{-1}$ soil) speculated that there was decline in biomass yield of the fern and repeated phytorextraction also deplete the As phytoextraction capacity of fern (Gonzaga et al. 2008; Tu and Ma 2002).

The phytoextraction capacity depends on the As bioavailability that could be derived from the bioavailability actor (BAF) and translocation factor (TF). The bioavailability factor increased by 41–42% and 71–72% due to application of SSP and DAP fertilizer, respectively in both the growing cycles. As compared to SSP, DAP was found as a most effective in enhancing the BAF by 20–22% (Mandal et al. 2018).Total As concentration is not a good predictor of As bioavailability, because only As dissolved in water can be transported to the roots and taken up by plants (Ritchie and Sposito 1995). Plants tend to first take up the most available fraction of As from the soils and as this pool becomes smaller, some of the As from other fractions will be slowly transformed to water-soluble fraction to re-establish their equilibrium (McGrath et al. 2000). Various fractions of As may changes due to phytoextraction of As contaminated soil. Total metal concentrations in soil seemed to be associated with soil amorphous Fe and Al minerals (Bhattacharyya et al. 2008). Das et al. (2011) reported that As affected soils were endowed with internally held surfaces of soil aggregates As followed by Fe and Al chemisorbed As and Ca-bound As. It was reported that As binds preferentially to Fe oxides and to a lesser extent to Al oxides while showing a secondary preference to $H_2SO_4$-extractable Ca (Akins and Lewis 1976; Wauchope 1975). Ghosh et al. (2003) who worked on the same soil had reported the inorganic fractions of As in the decreasing order of Fe-As > Ca–As > Al-As > Water soluble. Based on As fractionation in As-contaminated soils, most of the As was associated with the fraction bound with hydrous oxides Fe and Al minerals. regardless of the sources of As contamination (Smith et al. 1998; Wenzel et al. 2001). A pilot scale study reported that coupling in-situ phytoremediation by the fern with soil flushing with phosphate ($KH_2PO_4$) in liquid form is more efficient for removing total As contamination in soil (Yan et al. 2017). Changes in bioavailable fractions may be takes place as a result of phytoremediation of As contaminated soil. Metal concentrations in the two most labile fractions (i.e., water soluble and exchangeable fractions) were generally low (Bhattacharyya et al. 2008). The superiority of DAP over SSP was reported to be better in enhancing yield of rice and wheat from Bangladesh (Nizam et al. 2008) and green gram from India (Luikham et al. 2005). The superiority of DAP over SSP might be due to lesser precipitation of phosphates released from the former as Fe- and Al-phosphates than the latter source (Nizam et al. 2008). As a P analog, As is taken up by plants via the P transport system (Meharg and Hartley-Whitaker 2002) with a competitive uptake by the fern. The difference in As concentration between first and second harvest was narrow in the present study was used fresh planting in each harvest, while Gonzaga et al. (2008) used cutting and regeneration method of repeated harvests.

In this study revealed that overall phytoextraction by *P. vittata* for successive two growing cycles with DAP as the phosphatic fertilizer showed significant impact on the yield of rice. This was may be due to more As removal from soil by this treatment. This clearly showed that successive two growing cycles of *vittata* removed more As from soil which was responsible for enhancing rice yield and decrease As content in rice. In this present study it was observed that the translocation of As from root to the above ground plant parts (straw and grain) of rice was less, therefore, the probability of contamination of rice grain was less. This study revealed that the pattern of As accumulation was in the order of root > straw > grain. But it is also true that As at elevated level in soil enhanced its accumulation in grain as observed in several studies. The estimated daily intake of rice via consumption may accumulate significant amount of arsenic to human body which may leads to risk of carcinogencity to human being (Satpathy et al. 2014; Niazi et al. 2022).

Two successive growing cycles of *P. vitttata* with DAP fertilization proved to be promising as it removed significantly higher As from the As contaminated soil. Rice can be grown safely in As contaminated soil if rice grain attains the As accumulation below 1 ppm standard as per WHO is concern. However, in case of elevated levels of arsenic (>100 mg As $kg^{-1}$ soil) contaminated soil repeated harvests of the fern is has significant impact on the As accumulation by the rice. The elevated levels of As accumulation in the in various parts of rice crop could be restricted by the enhanced phytoextraction process with phosphatic fertilizer has enormous significance to reduce the risk of food chain contamination. However phytoextraction potential of the fern was influenced by the bioavailable fraction of As and type of amendments and local climatic condition in the rice growing belt. Furthermore, the preferential uptake of phosphorus by the rice in a As contaminated soil also has great significance to reduce the As uptake by the rice plants. The uptake rate in rice at 0.05 mM of arsenate decreased significantly with increasing phosphate concentration present in the incubating solution. The moderate levels of As contamination as reported might contaminate the rice crop (Abedin et al. 2002b; Suriyagoda et al. 2022).

Nonetheless, an elevated level of As in soil varied differential distribution of As in the soil was also responsible for varied As concentration in the rice edible grain. In this connection, Marin et al. (1993) reported that most indigenous As taken up by the plants remained in the root. In general, increasing the amount of soil phosphorus reduces As accumulation by plants, and vice versa (Marin et al. 1992).Two successive harvests with DAP as the phosphatic fertilizer emerged as the most important management strategy for accelerating the phytoremediation efficiency in As contaminated soil. In elevated As concentration (>100 mg As $kg^{-1}$), this study proved the phosphate mediated phytoextraction by *P. vittata,* attained maximum removal of soil As level by 38%. However, before popularization of the above technology among the farmers of As contaminated areas of West Bengal, India, it should be tested in the field level as a confirmatory trial. It is also essential to evolve sustainable methodology for successful disposal of As contaminated fronds of *P. vittata.* Phytoextraction of As from the contaminated soil by the fern for two repeated harvests along with DAP as the phosphatic fertilizer could be a promising option for cleaning up of As contaminated soil as it greatly reduced the transfer of As to rice crop grown on such soil.

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# Chapter 16

# Modified Biosorbents as Potential Biomaterials for Arsenic Removal from Contaminated Water

**Shazma Muzammal, Asma Akram, Muhammad Bilal Shakoor, Asim Jilani, Sajid Rashid Ahmad, Mujahid Farid, and Nabeel Khan Niazi**

**Abstract** Arsenic in water bodies has been a major concern around the world due to its carcinogenic properties. Among various methods of arsenic removal, biosorption using modified biosorbents is considered as one of the potential strategy to deal with arsenic pollution in water. Modified biosorbents proved to be cost-effective, stable and highly porous biological materials which possess numerous surface functional groups. Novel modification/treatment methods are needed to develop biosorbents with enhanced adsorption capacity for arsenic. The characterization of modified biosorbents using different advanced such as XPS, FTIR, SEM-EDX etc. should be studied for thorough understanding of biosorption process. Moreover, exploring the performance of modified biosorbents under varying environmental conditions could provide significant information about their properties as well as arsenic removal mechanism. Here we discussed various modification methods to prepare modified biosorbents for arsenic abetment in water. Finally, important future prospects as well as industrial/commercial-scale application of biosorbents have been emphasized. This book chapter will provide broad scientific opportunities for thorough understanding of applying modified biosorbents as a low-cost and environmentally sustainable material for the treatment of arsenic containing wastewater.

**Keywords** Arsenic · Biosorbents · Modification · Novel materials

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## 16.1 Introduction

Water is a fundamental source and reserve for the human beings on the earth having a financial, communal, health, and environmental impact, all around the globe (Sanakousar et al. 2021). In recent times, it has been stated that clean water is not accessible to 1.2 billion people for drinking. Every day, nearly 2 million tons of agriculture and industrial wastes are being released into the water bodies which contaminate them, in consequence causing the casualty of some 14,000 people per day (Bolisetty et al. 2019). Heavy metal/metalloid ions, being lethal for humans as well as aquatic life, have become the main pollutants in water and cause severe threats to the environment (Sanakousar et al. 2021).

Contamination of groundwater due to arsenic has been detected in more than 70 countries, including both developing and developed states. Pakistan, India, West Bengal, Myanmar, Vietnam, Bangladesh, Nepal, Cambodia, United States and China are the most affected countries due to As contamination. By utilizing contaminated water nearly 200 million people are exposed to extreme As concentration. Water reservoirs are being depleted by both natural and anthropogenic activities i.e. natural phenomenon includes rocks weathering, volcanic emissions, and several other human practices are arsenic-rich pesticides usage, food preservatives, fertilizers, pharmaceuticals and tanneries. Aquatic ecosystem is in distress due to release of the untreated effluents of industries in water bodies and nearby streams. These effluents include heavy metals such as cadmium, mercury, copper, zinc and metalloids including arsenic, antimony and silicon (Hao et al. 2018; Mahmood et al. 2018).

Intake of huge quantity of arsenic possibly will direct to the problem of digestive tract, instability of heart and brain systems, and lastly death (Islam et al. 2017). Near the beginning, awareness on the potential health effects of arsenic compounds emerged in ancient Asian civilization, though before, realgar commonly named as arsenic sulphide was customarily applied, mutually as a medication as well as a toxin (Bolt 2012). Moreover, in earlier period, compounds of arsenic such as monosodium methyl arsenate (MSMA), disodium methyl arsenate (DSMA) are used in the manufacturing of pesticides for use in agriculture and chromated copper arsenate (CCA) was used for wood protection. The use of arsenic has been outdated for the treatment of certain diseases such as such as chorea, asthma, malaria, leukemia, syphilis, skin and breast cancer (Basu et al. 2014). Consequently, limit for As in drinking water has been set by the World Health Organization (WHO) i.e. 0.01 mg/L. As a result, researches were done for developing reasonable and proficient practices to remove As from drinking, as it is essential for human health and eco-friendly environment. Various technologies are used to decontaminate water including coagulation–flocculation, ion exchange, adsorption, membrane technologies, osmosis electrochemical conversion and photo catalysis. Though, nearly all of the above mentioned techniques call for much preliminary and maintenance expenses along with trained labor force (Akram et al. 2022). At the present time, the most appropriate As removing technology that has been acknowledged is adsorption, due to its undemanding procedure, probable for restoration, and much lesser sludge production. The use of adsorption technique is easily reachable by the developing states and is highly appreciated because of lesser investment and no environmental effects. The biosorbents used in this adsorption technique can also be chemically modified just to enhance the removal efficiency (Asere et al. 2019). Enhancement of the binding capacity, environmental strength and reusability can be achieved by the modification in structure of biosorbent.

To treat As contaminated water, current researches have been exposed to an innovative reach for the advancement of modified biosorbents. Prior to their use, biosorbents are treated with variety of acid and bases solutions i.e. sodium hydroxide, sulphuric acid or hydrochloric acid. Furthermore, saturation can also be done by using oxides of iron i.e. magnetite and ferrihydrite; it can improve the strength and firmness, thus enhancing the removal capacity of metal ions. Additionally, biosorbents treated with acids or base could lessen the problem of coloration as well as discharge in water of different organic substances subsequent to treatment (Shakoor et al. 2016). These modified biosorbents not only remove arsenic from the aqueous solution but also fulfill the objective of waste reprocessing and recycling (Poudel et al. 2021).In recent times, agricultural wastes are used as potential materials intended for the refinement of different metals from the water. Here we have reviewed various modification methods for enhanced removal of arsenic as well as factors influencing the performance of modified biosorbents.

## 16.2 Environmental Factors Influencing Arsenic Sorption

### *16.2.1 Effect of pH*

Amongst the several environmental factors that are affecting the sorption capacity of arsenic, few of the most significant features are; pH, contact time, sorbent dose and arsenic ion concentration (Akram et al. 2022). The pH is considered to be one of the topmost parameter which influences the sorption process. According to a group of researchers, most effective arsenic removal using different biosorbents was recorded at acidic pH i.e., below 7 (Shakoor et al. 2019). Minor increase or decrease in this parameter can have a huge impact on the whole sorption process. Acidic pH helps in the availability of certain active sorption sites and also with the help of positive and negative ions' neutralization, the sorption process works incredibly efficiently for the removal of heavy metals like arsenic (Shakoor et al. 2017). However, it may vary for different biosorbents. On the contrary, alkaline pH most of the times has proved to be very less proficient due to the onset of an unhealthy competition between heavy metals and hydroxyl ions. This competition ultimately results in the non-availability of active sites for the binding of heavy metals (Shakoor et al. 2016; Akram et al. 2022).

### *16.2.2 Effect of Contact Time*

Another factor that shows the significant effect on the removal capability of sorption methods is termed as contact time. Appropriate contact time is deemed to be very vital for the efficient removal of toxic heavy metals. Hundreds of different carbon-based biosorbents have been in use so that the most suitable and eco-friendly biosorbents can be selected which should have many benefits like cost effectiveness, no sludge production, no toxic emissions of different chemicals, etc. (Shakoor et al. 2019). Contact time varies for almost every biosorbent such as in a research that was conducted using egg shell biochar, up to 96% of arsenate As(V) removal was seen with the contact time of 2 h. Further increase or decrease in it showed very less removal of arsenate ions because, when the contact time reached to 2 h, there was an enhancement noticed in the uptake of arsenate ions by egg shell biochar. This enhancement was due to accessibility of sorption sites for binding metals ions from the given solution (Shakoor et al. 2016; Akram et al. 2022). That is how its range differs for different biochar or biosorbents.

### *16.2.3 Effect of Arsenic Ions Concentration*

In-addition to that, arsenic ion concentration also influences the sorption capacity of biosorbents. The experimentation is usually performed by keeping one parameter variable and all other parameters like pH, contact time, sorbent dose etc. remain constant (Shakoor et al. 2019). The true arsenic ion concentration can be attained possibly by varying the concentration between different suitable values. For example, in case of arsenic removal using peanut shell biochar (PSB), 5 mg/L was the most suitable arsenic ion concentration recorded for the appropriate removal of arsenic ions from the aqueous media (Sattar et al. 2019).

### *16.2.4 Effect of Sorbent Dose*

Similarly an increase or decrease in the concentration of sorbent dose also has an extremely dominant impact on the sorption process. This involves the phenomenon of availability of certain sites that are exchangeable for the uptake of heavy metals or metalloids (Das et al. 2013; Akram et al. 2022).

### 16.2.5 *Effect of Anions*

Moreover, the presence of multiple anions like nitrates, phosphates, sulphates etc. also interrupts the sorption procedure and increases the risk of replacing arsenic ions during the uptake by different biosorbents (Pehlivan et al. 2013).

## 16.3 Mechanism of Arsenic Sorption

Different mechanisms such as complexation, physical sorption, precipitation, ion-exchange and chemisorption are being used for the sorption of heavy metals onto biosorbents from the solution stage (Fig. 16.1).

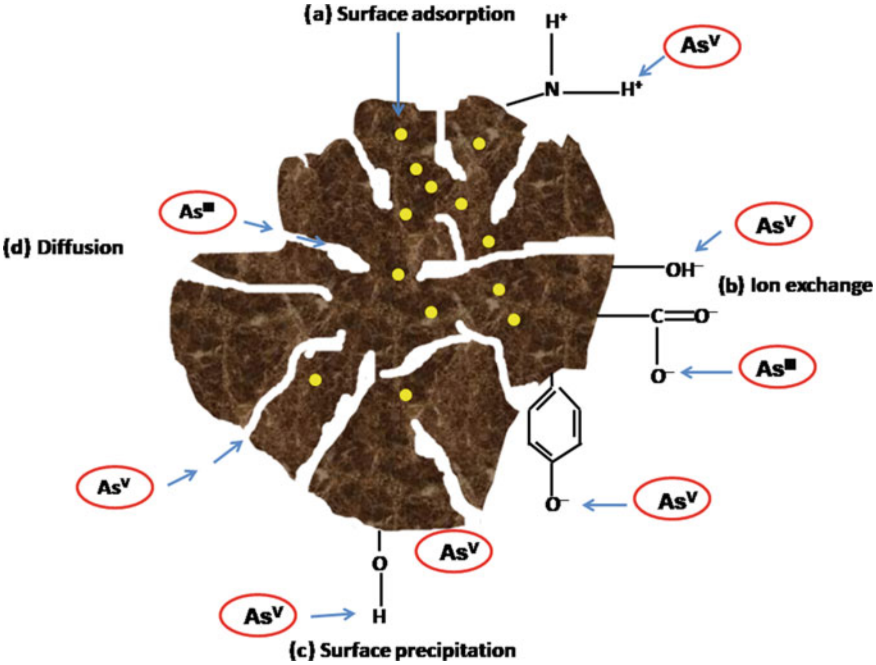

**Fig. 16.1** Arsenic sorption mechanism by biosorbents (reproduced with the permission from Shakoor et al. 2016)

### 16.3.1 Physical Sorption

In physical sorption, association of metal ions through diffusion all the way through the pores of specific sorbent is explained by the surface attachment of heavy metals onto biosorbents. In this sort of sorption, chemical bonds are not formed.

### 16.3.2 Ion Exchange

Moreover, ion exchange is interchange of positive ions on the biochar surface with the charged heavy metal ions in the solution phase. Efficacy and strength of ion exchange mechanism in sorption of heavy metals onto biochar depend on conditions such as heavy metal size and surface area of biosorbents (Zhao et al. 2017).

### 16.3.3 Complexation

In complexation, composites are formed on the biosorbents surface between the metals and ligands. Complexes formed are may be inner or outer sphere. This mechanism of sorption is primarily used for transition metals as they have much attraction for ligands due to partly filled d-orbitals.

### 16.3.4 Chemisorption

Chemisorption, also known as electrostatic interactions is the mechanism in which electrostatic reactions occur between the metal and biosorbent surface that is charged either positively or negatively. Point of zero charge (PZC) of biochar and pH of water mainly conclude the effectiveness of this mechanism (Dong et al. 2013). Graphene like structure of biochar usually formed at prominent temperature is dependable for metal sorption by chemisorption (Keiluweit and Kleber 2009).

### 16.3.5 Precipitation

Precipitation is well thought-out as an imperative mechanism for the exclusion of heavy metals. In this mechanism, for the sorption of heavy metals from the solution phase, usually solids are formed on the surface of biosorbent. Some metals having temperate ionizing potential such as zinc, copper and lead make supplementary precipitates on biosorbent surface.

## 16.4 Modification Methods

### *16.4.1 Polyethylenimine (PEI) Modified Zea Mays*

For the removal of arsenic from the contaminated water modified *Zea Mays* are used as an effective and proficient biosorbent. Maize mainly is an extensively cropped yearly cereal that cultivated rapidly and can produce abundant seeds enduring unfavorable conditions (Jadia and Fulekar 2009; Zhang et al. 2010). Raj et al. studied the efficient removal of arsenic by using *Zea Mays* cob powder (ZMCP), following doing structural and chemical modification with polyethylenimine (PEI) as it strengthen the functional groups present in *Zea Mays*, following the production of novel and effective biosorbents. Batch experiments of biosorption on ZMCP were performed using usual practices as function biosorbent dosage, pH, contact time and arsenic concentration. After complete experiment, the solution is filtered by using Whatman 42 filter paper. For the characterization of gathered filtrates, atomic absorption spectroscopy (SEM) is used. As a result, with the use of modified ZMCP with PEI, the removal efficiency has been increased from 70 to 80.57% for Arsenite As(III) and 85 to 97.45% for Arsenate As (V).

### *16.4.2 Aluminium Modified Guava Seeds*

It is well thought that seeds of Guava (*Psidium guajava*) can be used as a low-priced resource of biomass as it is generated in immense quantities. Major content of cellulose, lignin and protein are the foremost structural properties of guava seeds that present them as appropriate source of biosorbent. At most, it can be used for the removal of different anionic contaminants present in water due to presence of various functional groups such as carbonyl, alkanes, hydroxyl, carboxyl etc. on its surface. These functional groups take part in the sorption of fluoride as well as in the development of diverse sort of exchanges with metals such as As and Cr. Determination of the kinetic and equilibrium factors were done for adsorption, additionally the effect of adsorbent dose and pH was also studied. Scanning electron microscope (SEM) and infrared spectroscopy (FTIR) is used for the characterization of the adsorbent to conclude the morphology and functional groups currently present in the material. Modification of the guava seeds surface by using aluminium is of great significance as the fluoride ions and arsenate form complexes on the adsorbent surface with the help of aluminium. The removal efficiency of arsenate is to some extent quicker as compared to fluoride. It was noted that the time attained by Arsenate As(V) i.e. 90 min is lower than for F-removal i.e.150 min (Ramos-Vargas et al. 2018).

### *16.4.3 Sodium Bicarbonate Modified Wheat Straw*

Agricultural cellulose is one of those adsorbents that have high capability for metal sorption in aqueous solution. The beneficial components of agricultural cellulose are extractives, lignin, lipids, protein, simple sugars, hemicellulose, water hydrocarbons and starch surrounded by range of different functional groups to facilitate the progress of metal complexation which aids for the impounding of heavy metals (Shakoor et al. 2015). This seems to be economical, practicable and environmental friendly adsorbent for the removal of metals from contaminated.

Ebrahimi et al. (2013) considered that minor amount of arsenic can be removed from aqueous solution by using wheat straw modified by sodium bicarbonate ($NaHCO_3$) as an efficient adsorbent. Wheat straw, a crop residue, is a rich natural material easily all around the globe. It is full of 40–60% of hemicellulose and natural cellulose. As a result, it can be used as for efficient metal removal, as it can offer a cost-effective basis because no complex and vast preparation is needed while being used. The working parameters that include adsorbate concentration, modifier concentration, pH of the solution, contact time are effectual for assessing the adsorption efficiency of arsenate. Though, It is accomplished that adsorption by utilizing modified wheat straw is a proficient and effective technique for As(V) exclusion from aqueous solutions.

### *16.4.4 Citric Acid Treated Water Melon Rind*

Water melon, available in various South and South-east Asian countries, counting Pakistan is one of the plentiful and also in expensive fruit. According a report, annual production of water melon is 3,50,000 tons (FAO 2013). A common agricultural by-product, water melon rind (WMR) is an ordinary as well as rich source of several non-essential amino acids. These amino acids include cellulose, proteins, pectin and carotenoids compounds all along citrulline. Further adding, different functional groups such as –COOH, –OH, $-NH_2$ are present in these kind of biopolymers. These groups can easily bind and substitute arsenic from the contaminated water without any difficulty (Niazi et al. 2018a, b).

To increase the sorption capacity of rice husk, citric acid has also been used as a modifying mean which led to Pb sorption of greater than 5 mg $g^{-1}$ from contaminated water (Guo et al. 2016). When rice straw is used with citric acid, the –COOH groups can increase on the surface of biosorbents, that ultimately results to augment sequestration of the particular metal.

Shakoor et al. (2018) considered the efficiency of water melon rind (WMR) modified with citric acid, to remove the arsenic from aqueous solutions and thus calculated the effect of sorbent dose, contact time, pH, initial As(III) and As(V) concentration and pH on As sorption (Fig. 16.2). It was examined though that the capability of natural water melon rind to remove arsenite and arsenate was enhanced

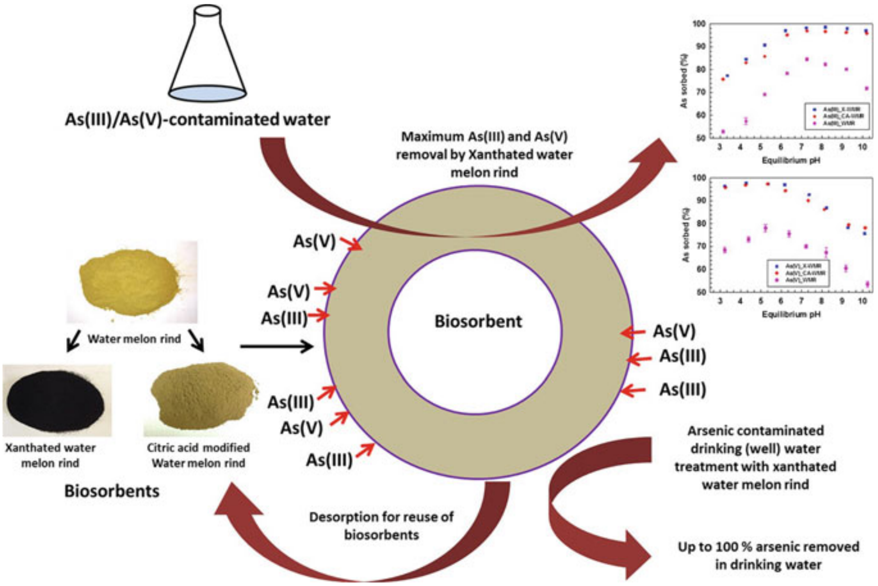

**Fig. 16.2** Treatment of As contaminated water by using citric acid modified water melon rind (WMR) (reproduced with the permission from Shakoor et al. 2018)

after citric acid modification. Results confirmed that modified WMR exposed that arsenite As(III) and arsenate As(V) removal percentage, i.e., 99% and 98% was highest, respectively.

### 16.4.5 *Fe(III) Oxyhydroxide Modified Sawdust of Spruce*

Studies have also been done on efficiency of chemically modified sawdust of spruce with Fe(III) to get rid of arsenic from the contaminated water. Adsorbent prepared by chemical modification of spruce by using Fe(III) oxyhydroxide demonstrated much higher affinity for arsenate As(V). Much promising results were shown by using this sawdust of spruce from contaminated water. The utmost adsorption capability of Fe(III) modified sawdust was 9.259 mg/g (Urik et al. 2009).

### 16.4.6 *Modified $TiO_2$ Pomegrante Peel*

Arsenite (As(III)) removal can also be made by exploiting $TiO_2$saturated pomegranate peel as a probable adsorbent (Poundel et al. 2020).For the removal of toxic metals and other organic impurities from the aqueous solution, pomegranate peel (PP) has been implied as a biosorbent (Bhatnagar and Minocha 2010). There is much lesser study on the effectiveness of Pomegranate peel as biosorbent for removing toxic contaminants from the aqueous solutions and contaminated water. The pomegranate peel (PP) comprises of up to 30% of the fruit's entire weight. Till now, it is generally discarded as a waste remains and is simply accessible at very low cost (Ben-Ali 2021). Due to presence of cellulose/hemicellulose, lignin and pectin, it can be used as an effectual biosorbent, in addition providing adequate functional groups i.e. carbonyl, carboxyl and hydroxyl for modification. Moreover, It includes nearly 10–15% of pectin, resulting it as a well-off resource of natural pectin (Yang et al. 2018).

Moreover, (Zirconium) Zr(IV) modified adsorbents are not that toxic to human health with a benefit that is low leaching rate (Rahman et al. 2021). Under these kind of conditions, modifier Zr(IV) is used treat pomegranate peel to boost As(V) adsorption performance. To get saponified pomegranate peel (SPP), PP is treated with an alkali, prior to Zr(IV) loading. This process of saponification will be advantageous because it will result in the breakage of ester bonds. In addition, it will also increase the carboxyl and hydroxyl groups for Zr(IV) loading and by this means the capability to uptake the As(V) will be enhanced (Ghimire et al. 2003). On another hand, total inorganic arsenic from groundwater contaminated samples were successfully remediated by using the Saponified Pomegranate peel (SPP). Therefore, this can be reported and practiced a proficient, eco-friendly, economical, and capable anion exchanger used for removing arsenate from polluted water.

### *16.4.7 Polyethylenimine (PEI) Leucaena Leucocephala (Subabul) Seed Powder*

A tropical wild plant, Leucaena leucocephala (subabul), is which does not need man-made irrigation and in large quantities offered all around the year. Patil and Shrivastava (2010) reported that the seeds of subabul plant are considered as agricultural waste because they are produced in bulk quantities. Though, current researches presents that sorption potential can be increased of L. leucocephala seed powder (LLSP) for As(III) and As(V) from contaminated water bodies. PEI modification can improve the capability of LLSP by absorption of positively charged amino groups for negatively charged species. As a result, improvement in % sorption of As (III) from 81.88 to 85% and As (V) from 92.61 to 99% was observed. Nevertheless, this projected technique does not remove arsenic compounds to the safe limit prescribed as 0.01 mg/L. It brings in a less costly and eco-friendly pretreatment green method former to high-tech chemical treatments. So, L. leucocephala seed powder (LLSP) can be predicted as a novel, effervescent, economical biosorbent for arsenic cleaning procedures.

### 16.4.8 2-Mercaptoethanol Modified Sugarcane Bagasse

Moreover, arsenic contaminated water can also be treated by waste product of sugarcane which is green, low-priced, easily accessible, and economical, exhibits probable capacity for efficient removal of arsenite and arsenate from aqueous solution in a short span of time by means of an undemanding procedure. Sugarcane Bagasse when chemically modified with 2-mercaptoethanol, can efficiently remove As(III) and As(V) by forming complex with Arsenate and arsenite (Gupta et al. 2014). The adaptability of the sorbent has been confirmed in diverse experiments by its application to total inorganic arsenic removal from arsenic contaminated water.

### 16.4.9 Modified Chicken Feathers by Diverse Doping Agents

It is predictable that more than 65 million tonnes of feather waste are generated all around the Globe. About 90% of protein (Keratin) is choked in the poultry feathers; they are inexpensive and mere supply of protein fibers. In industrial processes, there is little or no use of feathers. In recent times, researchers engaged chicken feathers to eliminate dyes and ions of heavy metals from wastewaters just because of several properties such as high surface area and frequent reactive functional groups. Furthermore, consequences of adsorption shows that modified form of chicken feathers as a biosorbent have more sorption potential of As ion than unmodified form. Structural alteration throughout modification and entirely extended the use of modified CF by designing arsenic removal filters. Chemically, numerous modifications of CF were caused by handling and treating with diverse doping agents. The degree of modification of the filter including material can be assessed by different characterization techniques such as SEM and FTIR and the adsorption effectiveness was estimated by means of kinetic and isothermal studies of the biosorption (Khosa et al. 2013).

### 16.4.10 Agricultural-Based Biowaste (Orange Peel, Banana Peel and Rice Husk)

Amongst the above mentioned biosorption techniques for arsenic removal, another method which has been considered as the most viable and eco-friendly practice is the use of agricultural based biosorbents or biochar to get rid of toxic heavy metal i.e., arsenic from any aqueous solution (Table 16.1). Several researchers carried out batch experiments to evaluate the proficiency of different biosorbents which were derived from agricultural biowaste (Tabassum et al. 2019a, b). The selected biosorbents were the peels of bananas and oranges and rice husk due to their unlimited benefits such as they have extremely stable physico-chemical properties, non-hazardous nature, higher ability of metal adsorption, and generate eco-friendly residues (Shakoor et al.

**Table 16.1** Different biosorbents and their efficacy in the arsenic removal

| Type of biosorbent | Parameters involved | Removal efficiency (%) | References |
|---|---|---|---|
| Japanese oak biochar | pH | 84 | (Niazi et al. 2017) |
| Peels of potato | pH and contact time | 99 | (Bibi et al. 2017) |
| Charged orange peel | pH | 98 | (Abid et al. 2016) |
| Blue pine | pH and contact time | 97 | (Saqib et al. 2013) |
| Rice husk | pH, flow rate and contact time | 100 | (Amin et al. 2006) |
| Meliaazedarach | pH and contact time | 98 | (Sarwar et al. 2015) |
| Pinusroxburghii's bark | pH and contact time | 95 | (Shah et al. 2016) |
| Iron chitosan spacer granules | pH and reaction time | 22.47 ($As^{+5}$) | (Gupta and Sankararamakrishnan 2010) |
| Cellulose-g-GMA-bTEPA | pH and reaction time | 75.13 ($As^{+5}$) | (Yu et al. 2013) |

2016; Niazi et al. 2017; Tabassum et al. 2019a, b). For the experimentation, arsenic contaminated (laboratory prepared) samples were taken with known As concentration, along with some groundwater samples from the area of South Punjab, Pakistan that too contained different concentration of arsenic i.e. 5, 10 and 50 μg/L respectively. The above mentioned biosorbents were washed off thoroughly and then after drying in oven they were grinded and sieved to be used for further procedure. Plexiglas columns of different dimensions with layers of saturated fine sand and gravel were used and 3 cm thick layer of biosorbent was placed in the center. Along with that, two peristaltic pumps (pumps with wide-ranging flow rate) were used at the inlet and outflow sides and after the last case of arsenic removal, no flushing of columns was done with acids like HCL unlike during the attainment of equilibrium stage and biosorbent which was then loaded with arsenic collected for further analysis on FTIR (Bibi et al. 2017; Tabassum et al. 2019a, b).

Fourier Transform Infrared Spectroscopy (FTIR), a well-known instrument used for metal analysis, obtained the spectra of biosorbents at resolution of 4 $cm^{-1}$ and wavenumber ranging from 400 to 4000 $cm^{-1}$.The basic purpose was to find out the functional groups present on biosorbents using FTIR (Tabassum et al. 2019a, b). Three different parameters; (contact time, As concentration and type of biosorbent) were taken during the demonstration of results. Ultimately, complete 100% removal of arsenic was observed from all the contaminated water samples in the time duration of 2 h except for the one that contained 100 μg/L of arsenic concentration in which efficacy of removal was reduced to some extent due to high metal load. The results showed that agricultural-derived biosorbents (orange peel, banana peel and rice husk) when combined with FTIR are proved to be very effective and environmental friendly method to get rid of carcinogenic heavy metal (arsenic) from any drinking, surface or groundwater (Tabassum et al. 2019a, b). Moreover, application of rice husk as a biosorbent, is considered to be one of the best bio techniques for the removal of arsenic and this removal proficiency is by far supported by several researchers (Asif and Chen 2017; Amin et al. 2006).

### *16.4.11 Perilla Leaf Biochar with Modified Spectroscopic and Macroscopic Investigation*

Another method has proven to be very suitable for the arsenic removal in which biochar made up of perilla leaf was used extensively accompanied by different isotherm models (Niazi et al. 2017). The cultivation of perilla is noticed to be very common in countries like Thailand, Japan, Korea and several Asian regions. As a result of its harvesting on a larger scale, huge amount of waste containing perilla leaves was generated (Igarashi and Miyazaki 2013). In-addition to several feedstock based biochar such as biochar prepared from fruit bark, pine and oak bark, rice husk, biosolids etc., Perilla leaf biochar was also considered as a worthy and sustainable biosorbent for the removal of arsenic (Wang et al. 2015; Mohan et al. 2007; Zama et al. 2017; Niazi et al. 2017). While performing batch experiments after proper washing and drying, two different temperatures were used for the pyrolysis of resultant biochar derived from perilla leaves i.e. 300 °C and 700 °C respectively. They both were then referred to as BC300 and BC700 and categorized on the basis of their numerous physical and chemical properties (moisture content, ash content, pH, polarity index, elemental composition, pyrolysis temperature etc.) (Niazi et al. 2017). Initial arsenic (both As(III) and As(V)) concentration was taken in the range i.e. 0.05–7 mg/L and the other foremost parameter pH were set between 3 and 10. After the sorption isotherm experimentation in which usually modified methods like centrifugation, filtration and analysis on atomic absorption spectrometer were done, detailed investigation to find out the removal efficiency and structural features of arsenic containing biochar and without arsenic loaded biochar, scanning electron microscopy in accompany with energy dispersive X-ray spectroscopy was used (SEM-EDX) (Niazi et al. 2017).

BC700 biochar was recorded to be the best biosorbent as compared to BC300 for arsenite removal (up to 90%) at pH ranging from 7 to 9. Amongst that, spectroscopic results in coordination with macroscopic results, again BC700 biochar had proved to be very competent in the removal of arsenite (As(III)) from aqueous solution and when examined in groundwater samples, removal proficiency of even up to 100% was achieved for arsenite using BC700 biochar (Niazi et al. 2017).

This research showed that perilla leaf biochar is a must option as compared to the other conventional techniques for the removal of inorganic arsenic particularly from drinking water sources.

### 16.4.12 HPEI Modified Biosorbent Based on Cellulose Fiber

The process of adsorption is taking much attention due to its several advantages as compared to the other removal approaches for arsenic species. Another modified biosorbent was introduced to combat with arsenic pollution in water sources. Cellulose fiber which is an enriched biopolymer natural sorbent was selected based on its multiple positive aspects like it can withstand high thermal conditions, eco-friendly, cost-effective, can be recycled etc. (Habibi et al. 2010; Tsioptsias et al. 2008). The use of cellulose fiber without any modification was observed not to be that much effective but with the addition of certain modifier, addition of different functional groups like amino, carboxyl etc. on the sorbent sites can enhance its ability to increase the sorption process for different heavy metals particularly for inorganic arsenic (Zhu et al. 2015). Ma et al. (2014), reported in their research that the addition of Hyper branched Polyethylenimine (HPEI), to any sorbent (biosorbent usually) can increase its capability to adsorb heavy metals sturdily due to presence of amine group on it. It moreover, ensures the effective adsorption of both $As^{+3}$ and $As^{+5}$through strong electrostatic bond (Ma et al. 2014). However, one more important modification is the use of microwave irradiation (MW) which assists in the uniform dissipation of energy when its electromagnetic heat is absorbed by the particles which eventually results in the less consumption of cost and energy (Deng et al. 2015).

Hence by using HPEI modified cellulose fiber, the removal efficiencies turned out to be pretty good. Temperature was considered as the most significant factor while carrying out batch experiments. The maximum arsenite ($As^{+3}$) removal efficiency noted in this experiment was 97.3% at about 90 °C and on the contrary at the same temperature about 99.2% of arsenate ($As^{+5}$) removal was observed comprehensively. Removal efficiency is somehow directly proportional to the temperature in the range of 40–100 °C (Deng et al. 2016). Other than that, at pH 4, maximum adsorption of arsenite and arsenate was observed by using modified cellulose fiber (Deng et al. 2016).

### 16.4.13 Date Seeds Husk Modified with Lemon Juice and Microwave Provision

The addition of raw and modified date seed husk to other organic biosorbents for arsenic removal has showed the great removal efficacy which is quite commendable. The plus point of all these organic biosorbents is that they are extremely cost effective and have non-toxic nature towards the living organisms and environment (Khan et al. 2019; Raj et al. 2013a, b). Due to the stable production of dates all over the world, a group of scientists, discovered that date seeds husk can be used for the removal of deadly arsenic from drinking water particularly (Khan et al. 2019). For this experiment, date seeds (*Phoenix Dactylifera*) were utilized in two ways; one was raw date seeds husk (RDS) without adding any chemical or activator and other one was modified raw date seeds husk by using lemon juice which was aided by microwave. In microwave assisted lemon juice modified date seed husk (LMDS), lemon juice which is a very eco-friendly activator, activated more carboxylic functional group (–COOH) on the adsorption sites of modified date seeds husk and thus helps in the arsenic removal more efficiently (Khan et al. 2019).

Different batch, kinetic and isotherm studies were conducted to check the ability of RDS and LMDS. The speed of shaking influenced the adsorption capacity greatly such as for RDS, the highest adsorption rate recorded was 60.50% at 250 rpm and on the other hand, LMDS showed maximum adsorption (90.25%) at a moderate speed of 150 rpm (Khan et al. 2019). Other factors like contact time, pH, adsorbent dose and temperature also affected the rates of arsenic removal or adsorption using RDS and LMDS. In case of contact time, LMDS showed maximum removal in shorter time period (90.59% in 30 min) than RDS in which removal percentage was about 82.25% in the time span of about 45 min. However, pH also contributed in the removal of arsenite ($As^{+3}$) especially. Maximum removal was at pH 4 for RDS i.e. 84.625% and at pH 5 (89.75%) for LMDS respectively. 293.0 K was the best fitted temperature recorded at which maximum $As^{+3}$ removal percentage was obtained for both RDS (90.16%) and LMDS (93.53%). Above this temperature, due to poor coordination between adsorbate and the sorption site, there was less or no removal. The commercial importance of this biosorbent is that it can also be used to treat other heavy metals on industrial level with very little cost and no sludge production (Khan et al. 2019).

### *16.4.14 Removal of Arsenic with the Use of Tamarind Bark*

Despite of using several agricultural-based biosorbents, there is still a room for many biowaste derived biosorbents to remove heavy metals from any polluted aqueous media. Tamarind is a commonly cultivated plant and produces tons of biowaste. In this study, two researchers carried out batch experiments to check out the capacity of tamarind bark for the adsorption of arsenic present in industrial wastewater (Bangaraiah and Kumar 2019). Different factors were used during the experimentation to evaluate the efficiency of cost-effective tamarind bark as a biosorbent. Those parameters were; pH, arsenic ion concentration, contact time and dosage (Xue and Peng 2014; Bangaraiah and Kumar 2019). After the proper cleaning of tamarind bark, it was grinded and sieved to get a uniform sized fine powder and stock solution was prepared using sodium arsenate hydrate solution (Sivaprakash and Rajamohan 2011).

When sorption capacity of tamarind bark for the best contact time was observed, it came out to be between 50 and 60 min because of the availability of large number of sorbent sites needed for removal (Jaafarzadeh et al. 2015). However, as far as pH was concerned, about 65% of arsenic was removed when pH was increased from 2 to 4. Further increase in pH caused the precipitation process to reach at much higher stage which is not considered appropriate for the proficient sorption of arsenic and when it is reduced to the value that was less than 4, so in that case due to the abundance of H+ ions, no competent removal was occurred using tamarind bark (Ramos-Vargas et al. 2018). Sorbent dose which showed about 62% removal was 0.8 g, because of great number of biosorption sites that were available for the adsorption of arsenic (Cernansky et al. 2007). 0.1 g/L deemed to be the perfect metal ion concentration for the removal of arsenic loaded polluted water (Yamani et al. 2012). Langmuir and Freundlich models were also used simultaneously to analyze the values obtained during the conduction of this experiment. Consequently, by considering all the above mentioned parameters, the maximum arsenic sorption witnessed was 68% (Bangaraiah and Kumar 2019). Although this agricultural based biosorbent did not show efficient removal as compared to the other above mentioned biowaste derived biosorbents, but still it is far better than other physical and chemical techniques used for arsenic sorption in which usually encounter several problems like cost, emission of noxious gases, sludge production, a lot of energy consumption etc.

### *16.4.15 Chemically Modified Fungal Biomass*

Several researches supported the idea of using fungal biomass for the sorption of arsenic. In this finding, arsenate removal was carried out by using different types of biomasses based on fungus (Cardenas-Gonzalez et al. 2017). The fungal biomasses utilized were; Aspergillus fumigatus I-II, Cladosporium sp, Aspergillus flavus III, IV and V, Mucor sp-1 and 2 and Paecilomyces sp (Cardenas-Gonzalez et al. 2017).

Utilization of fungal biomasses when experimented with the coating of iron-oxide, the homogenized mixture was proved to be more effective in the arsenate removal (Pokhrel and Viraraghavan 2006). Likewise other bioremoval techniques, certain parameters like incubation time, temperature, initial arsenic and biomass concentration etc. can cause variations in the removal capacity. In the demonstration of results, it was observed that for Paecilomyces sp based fungal biomass coated with iron at 6.0 pH showed maximum arsenate removal (89%). pH value greater than 6 did not deem suitable because of beginning of competition between arsenate ions and hydroxyl ions in the solution (Raje and Swain 2002). The other parameter i.e. suitable incubation time helps in the accessibility of sorption sites and iron-coated fungal biomass species recorded greater removal up to 90% at 24 h (Chen et al. 2007; Pokhrel and Viraraghavan 2006). 89% removal of arsenate was displayed by iron-coated Paecilomyces fungal biomass species at temperature 30 ± 1 °C (Pokhrel and Viraraghavan 2006; Cardenas-Gonzalez et al. 2017). However, based on different researches, increase in modified biomass concentration will enhance the sorption capacity and in this case improved sorption removal was observed at 5 g of biomass contained Paecilomyces fungal species and percentage removal was about 99.3% (Singh et al. 2014). After a series of experiments performed with each above mentioned fungal biomass species using same parameters, the ultimate results showed that Aspergillus flavus (IV) fungal biomass specie was the best fitted modified fungal biomass due to the certain amino and carboxyl groups present at the cell wall accompanied by the availability of essential elements, which removed the arsenate up to 97% (Bartnicki-Garcia 1968; Cardenas-Gonzalez et al. 2017). Hence, metal can be recovered easily by using this modified iron-coated fungal biomass due to its eco-friendly nature and economic feasibility (Cardenas-Gonzalez et al. 2017).

### *16.4.16 Chitosan-Coated Modified Biosorbent*

Arsenite being more toxic form of arsenic than arsenate is usually oxidized to As(V) so that this pretreatment will help in the removal process from contaminated water samples loaded with arsenite (Zhao et al. 1996). In this experiment, chitosan (a product of chitin), was selected for the sorption of arsenate because of its certain benefits like it is abundantly available in nature, comprises of special functional groups that enhance the adsorption capacity, have eco-friendly nature etc. (Bodduet al. 2008). Moreover, due to its soft texture, it helps in the aggregation of particles. On the contrary, due to the non-availability of sorption sites at most of the times and reduced porosity levels, it did not prove much effective for the removal of arsenic.

Later on, to enhance its capacity of sorption, scientists decided to modify its removal efficiency, chitosan was subjected to different physico-chemical processes (Guibal et al. 1995; Piron et al. 1997). The history of adsorption mechanisms using different biosorbents determines that the utilization of biowaste derived organic biosorbents has been done quite a long time ago. For the development of modified chitosan biosorbent, ceramic alumina was used as a coating agent and resultantly, a composite chitosan biosorbent was formed. This modification not only helped in the removal of As(V), but it can also recover As(III) species from polluted media (Dambies et al. 2000; Boddu et al. 2008). While carrying out experiments using modified chitosan, the basic objective was to ensure the evaluation of arsenite and arsenate removal under dynamic equilibrium conditions (Boddu et al. 2008). Likewise to the other bioremoval techniques of heavy metals, one most important factor i.e. pH, influenced the operability of the sorption process. Well, pH 4.0 was recorded to be perfect for the sorption process, and above that there was decline in the sorption capability (Boddu et al. 2008).However, the removal efficiency using chitosan-coated biochar was recorded 56.5 mg/g for arsenite and 96.5 mg/g for arsenate respectively (Boddu et al. 2008).

All these modified biosorbents centered procedures indicate that instead of using other non-eco-friendly methods, naturally derived biosorbents are proved to be very active and realistic for the removal of deadly heavy metals like arsenic. Arsenic levels in groundwater predominantly keeps on increasing day-by-day, which needs immediate attention and treatment and this only can be fixed with the utilization of several agricultural based biosorbents modified by different processes (Shakoor et al. 2015; Niazi et al. 2017).

## 16.5 Conclusion

Arsenic contamination of water bodies is a widespread issue nowadays. The removal of arsenic from polluted water using adsorption is considered to be a major step in controlling arsenic pollution in recent times. Various low-cost biomaterials have been used however; biosorbent modifications using various advanced techniques have proved to be highly effective. The arsenic sorption capacities of biosorbents is largely influenced by different environmental factors such as pH, arsenic concentration, sorbent dose and contact time. Therefore, to achieve maximum clean up of water, new modification methods are required and should be tested under various environmental conditions. Moreover, further research work is also required to develop low-cost and environmental friendly modification methods with real field application for arsenic contaminated water.

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# Chapter 17
# Phytoremedial Potential of Perennial Woody Vegetation Under Arsenic Contaminated Conditions in Diverse Environments

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**Abstract** Due to carcinogenic and toxicological nature of arsenic (As) groundwater contamination, major agricultural, environmental and health issues are seen in many industrialized countries. About 170 million people in the world are affected by long-term exposure to arsenic-contaminated groundwater. Exposure of plants to arsenic, even at low concentrations, causes many major morphological, physiological, and biochemical disturbances. The traditional membrane filtration method, reverse osmosis method, precipitation method, ion exchange method, coagulation and flocculation method are commonly used remediation methods for As-polluted water, but these are expensive. Using perennial woody vegetation to remediate and stabilize heavy metal pollution such as arsenic is an efficient, environmental friendly and sustainable method. This chapter will briefly describe the role of woody vegetation in phytoremediation and/or detoxification of the harmful effects of arsenic under different environmental conditions.

**Keywords** Agroforestry trees · Phytostabilization · Arsenic sources · Woody vegetation

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## 17.1 Introduction

Pollution cannot be wiped out of the Earth even if a single person lives on the Earth because the presence of man is the major cause of pollution. It refers to the entry of pollutants into the natural environment that can cause adverse and harmful effects. Pollution can be divided into two groups: point source pollution and diffuse source pollution. Identifiable and man-made source pollution discharged through discrete channels such as sewage treatment plants and pipelines is known as Point source pollution. Diffusion pollution also known as non-point source pollution is considered to be pollution from non-identified sources that is caused by multiple activities and multiple pathways (WHO 2017). Agriculture is a good example of diffuse source pollution. Industrial pollution is the main type of point source pollution and heavy metals are the main cause of animal, plant and human poisoning. Heavy metals can be toxic and can cause severe health hazards for human. A pollutant becomes toxic when it causes harm to humans, plants and animals. For example, metals present in high concentrations in the environment are not toxic until they are bioavailable (Rahman et al. 2005).

Overall, in the industrialized biosphere the major problems are the concentration of heavy metals in the soils which have the great toxic and negative effects on human and its atmosphere. The extraction of metals has historically served good purposes, but a serious problem arises when they are released into different environmental components (Kumari et al. 2003). In the race for development, metals are still widely mined and utilized, however, the improper disposal of liquid and solid waste beside or in water streams has resulted in water and soil contamination. Long-term low-dose exposure to heavy metals can cause serious environmental degradation and health problems. In a variety of situations, extreme exposure to heavy metals can lead to severe and lethal effects. Many environmental and human health threats are caused by heavy metals (Salokannel et al. 2013). Toxic heavy metals include aluminium, cadmium, uranium, lead, mercury, barium, chromium, arsenic, etc. Most environmental distresses are due to these heavy metals which have health hazards, toxic effects on animals, human and plants because of metals' high solubility in water (Abumiya et al. 2012).

It is estimated that diarrheal diseases alone kill more than 2.5 billion children each year in the world, accounting for one-third of all deaths (Wu et al. 2012). In Pakistan, about one-third of groundwater contributes to whole water resources which are available to the most cities (Wu et al. 2012). Along the coastal area of Karachi more than the 6000 different units of industries including, chemical, oil refineries, metal, petrochemical, pharmaceuticals, tanneries and textiles are present (Safarzadeh et al. 2014). More than 300 million gallons of domestic and industrial wastewater are discharged directly to coastal areas of Karachi every day (Harvey et al. 2002). The main causes of ground and surface water pollution are residues from many industries such as metals, textiles, fertilizers, dyeing chemicals, cement, pesticides, energy and electricity, petrochemicals, sugar processing, leather, steel, construction, food processing, Engineering, mining, etc. (Ito et al. 2012). Municipal sewage, industrial wastewater, and urban and agricultural waste are discharged into rivers through canals and drains, aggravating and amplifying water pollution (Twidwell et al. 2011). Industrial wastewater and sewage treatment is a major problem in Pakistan, so, it is often drained into farmland to grow crops such as vegetables and trees (Lemieux et al. 2014). In developing countries such as Pakistan, where mostly people may drink contaminated water (Wagner et al. 2014), approximately 20–40% of illnesses are attributed to drinking poor quality water (Wagner et al. 2014). It is estimated that in Pakistan only 30% of urban and 23.5% of rural population are provided with drinking clean water (Lemieux et al. 2014).

Arsenic (As) contamination in soil is a big problem globally due to its high lethality, formation of various harmful compounds, and widespread distribution in the earth's crust (Mandal and Suzuki 2002). About 200 mineral forms of As are found in the crust, among which arsenopyrite (FeAsS), realgar (AsS) and orpiment ($As_2S_3$) are the most abundant (Mandal and Suzuki 2002). Arsenic is mostly present in water, air, organisms, soil, plants and humans. According to abundance, arsenic (As) ranks 14th in seawater, 20th in the crust, and 12th in humans (Farnese et al. 2014). Arsenic is derived from Greek word "arsenikon" which means mighty. It has an atomic mass of 74.922 g $mol^{-1}$ and an atomic number of 33, therefore, the element As has 5 valence electrons, its concentration level does not exceed 99% of the earth's crust, and belongs to a group of trace elements (Graff and Sparks 2006). In 1250 AD, Albertus Magnus discovered arsenic when heating soap and male spices ($As_2S_3$) (Alloway 1990). Arsine ($AsH_3$) was discovered by the Swedish chemist Scheler. From 1850 to 1950, people were affected by arsenic in medicine, water, work, food and air, and during this period, the production of arsenic trioxide in the world expanded from 5000 tons in the first year to 60,000 tons. It belongs to V (A) group of periodic time which have both metallic and non-metallic characteristic. It has four type of oxidation states and it can exist in allotropic structures: hexagonal (black, β-As) and rhombohedral (yellow, α-As) crystal structures (Safarzadeh et al. 2014).

In ecosystems, increasing arsenic (As) concentration is a major problem affecting the environment and human health. Arsenic contamination of soil is usually due to anthropogenic activity and natural processes (Niazi et al. 2011). Manures, tannery wastewater and other industrial processes such as dyeing and pigment units are the important causes of arsenic contamination in cultivated soils (Sheik et al. 2012). In addition, soil arsenic contamination comes from alloy and metal manufacturing processes, refining of petroleum products, wood processing, treatment operations and the tanning industry, fossil fuel combustion and municipal waste (Sheik et al. 2012).

The accumulation of arsenic in plant tissues grown in arsenic-contaminated groundwater, especially, in edible crops and vegetables, has been widely reported (Hossain 2006). During photosynthesis, As prevents the pathway of pentose-phosphate which results in death. As concentrations are variable among different parts of plant. In plants, As accumulation can be determined by elemental concentration, chemical method and the presence of different particles in earth (Stolz et al.

2006). For crops, normal amount of As is 40 mg per kg and above that concentration it becomes toxic i.e. inhibits the metabolism and growth of plants. Accumulation of higher levels of As can results in its transfer to animal and human population. Arsenic poisoning is potentially harmful to animals and plants. In humans, low levels of As can cause bladder, skin, prostate and lung tumors while non-lethal effects of arsenic in humans include heart disease, anemia and diabetes (Zhang et al. 2002). Therefore, taking effective measures to treat arsenic-contaminated soil is crucial to reduce the toxicity of arsenic-contaminated soil. However, there is a lack of information in the literature on rational methods for decontamination of arsenic-contaminated areas.

The toxicity and bioavailability of arsenic varies by soil type (Hussain 2006). Studies have shown that soil chemical composition and soil quality are the main factors regulating the bioavailability of As to plants. Basically, the key factors for the availability of arsenic to plants are carbonates, Eh (Redox potential), organic matter, soil pH and texture and plant species (Sharma 2012). Reduction of heavy metals from contaminated soils is very complex and expensive; therefore, arsenic (As) contaminated soils are used as untreated soils. Plant immobilization and immobilization techniques are effective methods to remediate heavy metal-contaminated soils (Singh et al. 2021). Furthermore, phytoremediation by the use of woody vegetation has more advantages as compared to annual/perennial plants because of its higher yield, long term process, cost effectiveness and its greatest advantage of having low risk of contaminants entering the food chain (Yadava and Srivastava 2020). The selected trees have the ability to tolerate the resistance against the As contamination soil and produce maximum biomass in result. Therefore, in order to better recognize the acceptance and adsorption mechanism of heavy metals, one can try to utilize suitable tree species in situ (Nawaz et al. 2016).

## 17.2 Sources of Arsenic

The toxic metal As is a highly toxic substance and present in atmosphere, rocks, soils and water bodies in great amount which make it a great alarm to the environment and human being. The increased level of As metal is harmful to ecosystem and human due to its anthropogenic property. Mostly the As compounds are odourless and dissolve in water easily which make it highly toxic to human health. The As metal is present in the environment in a different oxidation forms such as (−3, 0, +3 and +5) both in liquid and solid phase (Wang and Mulligan 2006). It has different species which some work on lower pH and some higher. Different factors effect on oxidation and reduction of As (Smedley and Kinniburgh 2002).

### *17.2.1 Natural Sources*

In the natural environment, the natural sources of As are different types of rocks which include volcanic rocks, hydrothermal deposits, marine sedimentary rocks, volcanic ash and fossil fuels (Coal and oil) (Kumar et al. 2020).

Naturally, As is present in the soil as various inorganic compounds. Arsenopyrite (FeAsS), realgar (AsS) and orpiment ($As_2S_3$) are the maximum common arsenic-bearing crystals and they are often associated with sulfide ores or other metallic ores, and are the main starting point for arsenic entry into the atmosphere. The normal level of As concentration in the earth's crust is about 2–5 mg/kg, while in uncontaminated soil globally is 5–6 mg/kg. Many past studies have reported arsenic levels as high as 11 mg/kg in Canadian soils (Mazumdar and Das 2021).

The concentration of As metal in groundwater range from 50 to 3000 parts per mL is due to natural weathering of rocks and minerals. As is present in the soil due to biological activity, geothermal water and volcanic eruptions (Singh and Fulzele 2021). The results of massive groundwater pumping from the last fifty-year increase which lowers the level of water and increase As minerals level in groundwater (Mazumdar and Das 2021).In natural water bodies the concentration of As is associated with climate change, hydrogeology, geochemical, local geology and human activities. The concentrations of As in the groundwater is directly related to oxidation of As sulfides, iron, aluminum and manganese oxides. In Halifax, Nova Scotia area the level of As in the groundwater bodies is 0.037 mg/L (Baig et al. 2010).

The major sources of As is soil parent material which are present naturally. Certain kinds of parent materials, for example, sandstone, molten rock, shale, volcanic rock and coal contain substantial amounts that can produce as inorganic forms through weathering and in this way enter via infiltration of soil and surface runoff into Rivers and Lakes (Barbafieri and Giorgetti 2016) (Fig. 17.1).

### *17.2.2 Anthropogenic Sources*

In environment, the most common and major anthropogenic activities that may release arsenic include mining and smelting, wood preservation, fossil fuel processing and combustion, removal and incineration of municipal and industrial excess and production and application of pesticides (Parvez et al. 2021). The release of As toxic metal in the earth due to application of pesticides to the crops and industrial solid waste and these toxic substance also pollute the atmosphere and groundwater in large amounts. The most vital source of As toxic metal is industrial discharges which can pollute the air, soil and water resources. The main sources of As in Canada are smelter facilities and thermal power plants and it is estimated that the release of these unit is 310 tons in the atmosphere, 15 tons in liquid seepages and 770 tons in the form of solid per year (Mladenov et al. 2010). These amounts decreased during

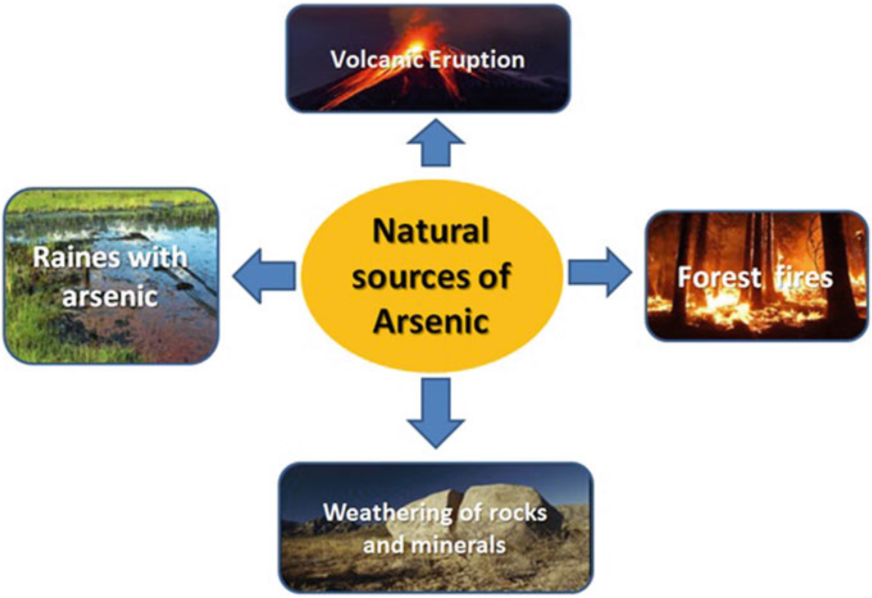

**Fig. 17.1** Natural sources of arsenic

the 2000 due to closing of gold mine but it was sharply increased during the 2002 (Zanin et al. 2017).

One of the major source of the As toxic metals are different type of pesticides including calcium, lead, magnesium, zinc arsenate and Paris green which were mostly used in agricultural land before DDT introduction in 1947 (Bissen and Frimmel 2003). Officially the lead arsenate was not recommended to use in apple orchards until 1975 in Ontario. It was reported that these pesticides applied to orchards have more concentrations of these toxic substance in the soil compared to other control orchards where no application of these pesticides. Hence, these pesticides are banned in Canada due to its toxic effects (Martin et al. 2012). It was stated that in the Annapolis Valley where these As pesticides were applied, higher concentrations of As (9.8–124 mg/kg) of topsoil were observed in twenty five orchards (Bissen and Frimmel 2003).

The As concentration is present in the coal which is released during the combustion and processing of coal. About 6000 mg per kg of As toxic metal was observed in Kimberley coals (Han et al. 2019). Near the steel mill in the Sydney, As concentration was recorded from 2 to 157 mg per kg (Lemonte et al. 2017). During 1970–80, the As metal pesticides were used about 70% which late decrease in use in many countries including Australia and New Zealand (Malakar et al. 2016) (Fig. 17.2).

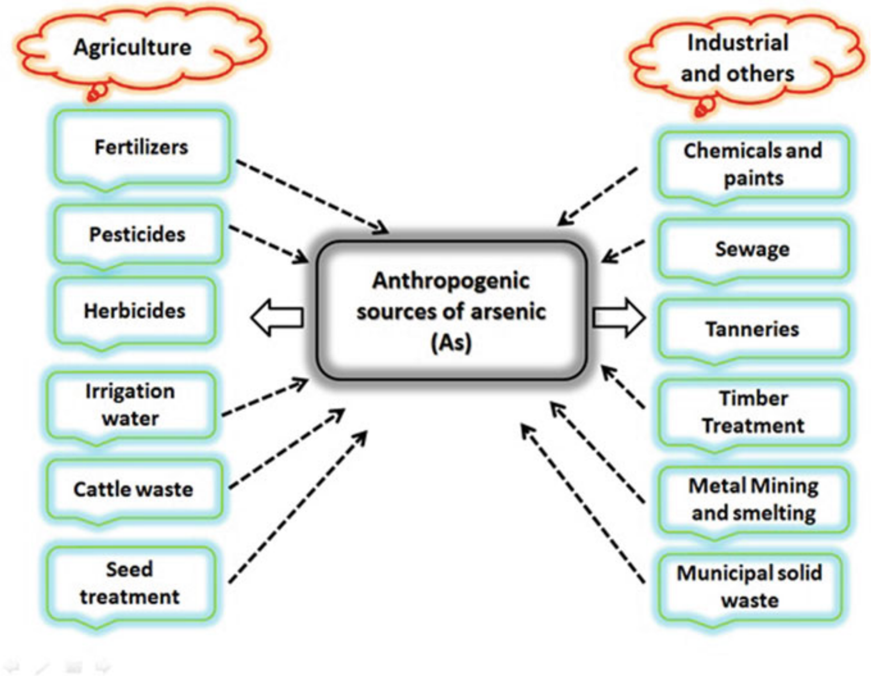

**Fig. 17.2** Anthropogenic sources of arsenic

## 17.3 Factor Affecting Arsenic Uptake by Trees

### *17.3.1 Soil Properties*

The bioavailability, solubility and speciation of As metal have precarious effects due to soil properties (Joardar et al. 2020).

#### 17.3.1.1 Redox Potential

Redox potential significantly affects As species and solubility in soil. In general, maximum redox potential of AsV was under aerobic condition and in AsIII the low redox potential was found under flood conditions. In +V state, As was less toxic and moveable compared to +III state. The solubility of As metal directly related to iron and manganese hydroxides/oxides, mean significant correlation was observed between As and Fe but flooding have no effect on their solubility (Ding et al. 2018).

#### 17.3.1.2 Soil pH

Main factor which effect the plant availability, movement and separate the chemical, solid and solution phase is soil pH (Shi et al. 2020). The concentration of As metals also associated with. Precipitation and adsorption of As was less with more pH of soil binding with different metal in the soil. It was observed that the solubility of As metal was 3 time higher at 8 pH compared to 5 pH because its reduction potential was high on higher pH. The solubility and movement of As metal in the soil has been directly linked with pH of soil i.e. movement of As in soil lower at 6.5–8.5 pH. The movement and solubility also increased by increasing pH of soil, $CaCo_3$, $FeO_2$ and level of carbon in the soil (Stojanović et al. 2016).

It has been studied that at higher pH of soil the co-precipitates of As metal with Ca and $SO_4$ (Boghi et al. 2018). Negative correlation is found between the metal availability and soil pH. Maximum adsorption of As V was recorded at 5 pH of soil. So, the soil pH has great effect on the adsorption and movement of As in the soil (Amaral et al. 2017).

#### 17.3.1.3 Root Exudates and Microbial Interaction (Arsenic Methylation)

The inorganic As have been studied from last 30 years but the As biomethylation has been reviewed from the 100 years. During the study of As in 1930, it was found that As metal concentration found in drinking water and comprehensive research showed that As have chemical aspects and their methylation process (Caporale, et al. 2013). The toxicity and availability of As metal is directly related with its from, soil, microorganism and plant type. Different studies showed that As can be explain by its oxidation and reduction process. Methylated species have also been found in different soil environment and plants (Yuan et al. 2015). However, little is known about microbial catalysis of these important steps in the arsenic cycle in soil.

### *17.3.2 Soil Types (Sand, Silt and Clay Interaction)*

The bioavailability of arsenic in soil varies significantly by source and type. The studies showed that the As content in plants was more closely related to the water-soluble As content than that in soil. The level of As in the soil was increased and its toxicity and solubility only related with soil property (Rahman and Hasegawa 2011). The factors which effect the As availability in the soil are Fe, Mg, phosphorus, microorganism, pH and flooding (Romero et al. 2014).

## 17.4 Impact of Various Geo-Environmental Factors on Phytoremediation of Arsenic-Contaminated Soils

Due to arsenic concentrations, inorganic and organic arsenic contaminants and their degradation in soil ecosystems are often associated with human activities such as the Industrial Revolution, the application of agrochemicals in farmland, energy production and fuel processing, mining and steelmaking activities as well as waste disposal that is harmful to various forms of life (Wu et al. 2012).

Hyperaccumulators are plants that are able to absorb and concentrate more than 0.1% of a specific element in their tissues. Metal hyperaccumulation is a rare phenomenon in terrestrial higher plants. To date, approximately 400 plant species have been identified as metal hyperaccumulators, representing less than 0.2% of all angiosperms (Baig et al. 2010). About two-thirds of known super-accumulators are Ni accumulators. This is due to the widespread presence of nickel-rich ultramafic (serpentine) soils and the long history of ultramafic flora studies. There are far fewer plant species capable of excessive accumulation of Cd, Co, Cu, Pb, Zn and As (Safarzadeh et al. 2014).

The definition of metal hyperaccumulation takes into account not only the metal content in aboveground biomass, but also the metal content in soil. When evaluating whether a particular plant is a metal hyperaccumulator, both bioaccumulation factors (BF) and transport factors (TF) must be considered (Tu and Ma 2002). The term BF, defined as the ratio of metal concentration in plant biomass to metal concentration in soil, has been used to determine the effectiveness of plants in removing metals from soil. The term TF is defined as the ratio of metal concentrations in plant shoots to root metal concentrations and is used to determine the effectiveness of plants in transporting metals from roots to shoots (Tu and Ma 2002). Therefore, arsenic hyperaccumulator plants should have BF > 1 and TF > 1, and > 1000 mg kg$^{-1}$ total accumulation in plant biomass.

While some plants can survive in environments with extremely high concentrations of metals, they may not exhibit a high ability to accumulate metals. For example, thorn grass grown in soils with up to 26,500 mg kg$^{-1}$ of arsenic has 3470 mg kg$^{-1}$ of arsenic. Although the concentration of arsenic in plants is high, it cannot be defined as arsenic hyperaccumulation because its bioconcentration factor (BF) and transport factor (TF) are both less than 1.

## 17.5 Phytoremediation of Arsenic Through Woody Vegetation

Phytoremediation is a method to extract heavy metals from polluted soil through trees and accumulate heavy metals into plant portioning such as in roots, stems, and branches to decontaminate the polluted sites. Logically, repeated planting and harvesting of trees in the same places that uptake heavy metals will ultimately minimize the toxic metal concentration in the soil to levels acceptable for other uses. Perennial woody vegetation such as trees has more benefits over grasses and other small plants due to deeper root systems; as a result, they are used to ameliorate the soils more deeply. Furthermore, some special organic compounds produced through tree roots form a rhizosphere zone that is more susceptible to microorganisms that detoxify the pollutants. Greenhouse studies have shown that mangium and aliculiformis accumulate significant amounts of As, Pb, Cd, and Hg from sludge-treated tailings (Guo et al. 2012). In this regard, studies have found that a stand improves the severe microclimate of a polluted site and also recovers its soil properties. Planting woody species for phytoremediation has the added benefit of producing wood at the end of the rotation. Numerous studies in temperate regions have shown that tree species are used as bioaccumulates to eliminate metals pollutants containing (Cd, Cu, Ni, Pb, and Zn) (Camacho et al. 2011). This designates that woody species have great prospective to extract heavy metals from contaminated sites. However, this cost-effective approach has some limitations, as contaminated sites are often unfavourable for establishing plants.

Phytoremediation is defined as a collection of different technologies that deal with the use of plants to remediate polluted sites. This word is derived from two words (Phyto) means plants and (Remediation) means to eliminate and eradicate. Soil remediation is defined as the restoration of soil to an ecologically stable condition while establishing the plant community it supports to adapt to the conditions earlier to disruption (Ali et al. 2016). For the last 300 years, the capability of plants to eliminate environmental contaminants has been renowned and applied to fields such as land utilization. Over time, the use of these trees has been established to deal with the structure of wetlands and even planting trees to neutralize air pollution. Recently, there has also been interest in finding technologies to address residual pollution, including phytoremediation. The processes of application and extraction of metals by numerous plants depend on the concentrations and accessibility of metals in soil, sequence of dissolution, and the species of plants growing on these soils (Upadhyay et al. 2019) (Fig. 17.3).

### *17.5.1 Phytostablization*

Phytostablization refers to using certain tree to stabilize contaminants in polluted soil (Singh et al. 2020). It is recycled to decrease the movement and bioavailability of toxins in the atmosphere, thereby stopping their leaching into groundwater. Trees can uptake heavy metals through root adsorption and recombination (Singh et al. 2020).

Metals containing diverse valences have numerous toxic elements by releasing specialized oxidoreductases, trees have the ability to convert these toxic metals into comparatively less toxic states and ultimately reduce possible metal stress and damaging effects. Trees restrict the addition of heavy metals in the biota and

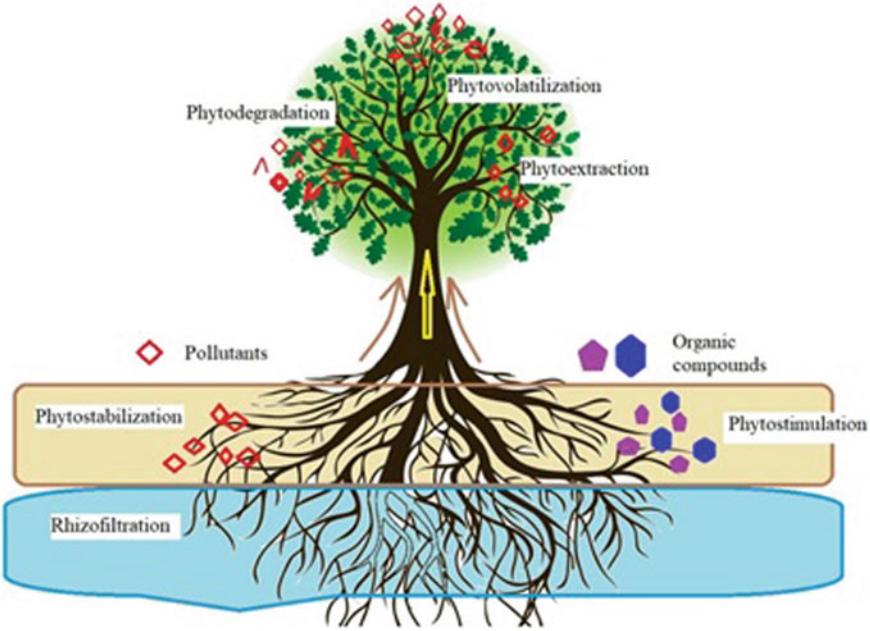

**Fig. 17.3** Different approaches to phytoremediation/bioremediation

reduces the potential for heavy metals to leach down into deeper soil horizons and underground water.

Primarily trees are used for sediments, soil, and slurry remediation and depend on the capability of the root system to edge the flow and bioavailability of pollutants in the soil media. Stabilization of vegetation can be attained by complexation, adsorption, precipitation, or reducing the metal valency. Deep and extensive root system binds the soil particles and limits soil disintegration (Camacho et al. 2011).

### 17.5.2 *Phytoextraction*

Also known as phytoabsorption it deals with the extractor uptake of pollutants from soil depth or water bodies by tree roots and then their transfer to above-ground biomass into different plant portioning. The uptake and movement of metals concentration from roots to shoots or leaves above ground using metal-accumulating trees is also known as phytoaccumulation. Several compounds such as organic acids have been used to enhance the ability to extract metals from soil horizon due to their ability to make complexes with metals and increase their effectiveness (Bian et al. 2012).

Phytosiderophores is defined as a type of plant roots that produce the substance that mobilizes the metal in the root horizon region. The acidification and metal suspension can be increased by $H^+$ ions secreted by roots which also function as adsorption of heavy metals. It is also absorbed because root secretions affect the pH of the soil which lower 1–2 unit in the rhizosphere region ultimately boosting the heavy metal concentration (Sarma and Sunil 2010).

Moreover, rhizosphere microorganisms (mycorrhizal bacteria and fungi) may significantly improve the bioavailability of these poisonous metals in soil. The bioavailability of heavy metals in soil, soil assets, heavy metal structures, and tree species are the variables that influence proficiency of woody vegetation to remove heavy metals. The trees which are suitable for metal extraction should have the following desirable characteristics (Singh et al. 2019):

(1) Extra growth ratio.
(2) Producing additional aboveground biomass.
(3) Spreading and densely branched root system.
(4) The selective metals uptake efficiently from the soil horizon.
(5) Metals mobility from roots to shoot portion.
(6) Accept the toxicity of selective metal.
(7) More adaptability under unfavorable conditions at that time.
(8) Combat against diseases.
(9) Cultivation and harvesting should be easy.
(10) Protect from herbivores and avoid ecosystem imbalance.

The phytoextraction prospective of the vegetation is determined by the aboveground metal concentration and biomass (Li et al. 2012).

Factors that limit the extent of metal extraction by trees include the following:

1. Rhizosphere metal bioavailability.
2. The root uptake rate of metals.
3. Root metal “fixed” proportions.
4. The rate of xylem loading/transportation into shoots.
5. Cellular tolerance to toxic metals.

Metals mobility and bioavailability depend upon the soil’s chemical and adsorption properties, which is a key factor affecting the efficiency of tree extraction of target heavy metals. Generally, only a small fraction of metals in soil are available for uptake by trees. Regarding the bioavailability of heavy metals/metalloids in soil, it can be divided into three categories; easy bioavailability (As, Cd, Cu, Ni, Se, and Zn); moderate bioavailability (Co, Fe, and Mn), and Minimum bioavailability (Cr, Pb, and U) (Qurat-ul-Ain et al. 2017). However, woody vegetation have developed certain mechanisms to dissolve heavy metals in soil.

The best way to eliminate contamination, mainly by isolating it from the soil, deprived of destroying the soil structure and fertility which is known as phytoaccumulation. The trees absorb the pollutants and toxic metal through a shallow layer which presents very low concentrations and radionuclides from contaminated soils into biomass (Huang et al. 2011).

The discovery of hyper-accumulating tree species further advances the technology. For this technology to work, trees should be extracting more heavy metals from their roots and converting these metals into biomass. The eliminating metals can be restored from contaminated tree biomass. Few factors such as group selectivity, growth rate, disease resistance, and harvesting method are very valuable. Although slow growth, shallow root systems, and lower biomass, final disposal limits the consumption of hyperaccumulator species (Eid et al. 2021).

### *17.5.3 Phytodegradation*

It is described as the deprivation of pollutants by the trees with help of dehalogenases and oxygenases enzymes (Upadhyay et al. 2019). Trees are capable to extract heavy metals from contaminated settings and purify them. Due to this reason, green plants like trees can be seen as the "green liver" of the biosphere. Few limits are existing for phytodegradation the removal of heavy metals like they are not decomposable. Composite or complex organic compounds are converted into simple compounds or the association of these compounds with plant tissue (Tyagi et al. 2020). The pollutants are broken down after being absorbed by trees during this mechanism.

In phytoremediation of carbon-based material, trees metabolism decreases contaminants by altering, decomposing, alleviating, and volatilizing them from soil horizon and groundwater. Phytodegradation is a process in which the degradation of organic matter is absorbed by trees into simpler molecules and their assimilation into plant materials. In trees, various enzymes are present that break down and convert chlorinated solvents, ammunition waste such as trichloroethylene, and other herbicides. These enzymes are normally dehalogenases, oxygenases, and reductases (Chandra et al. 2018). The breakdown of organic matter in the soil by microbial activity in the root zone (rhizosphere) during daytime (sunlight) is known as solar degradation. It is much slower than plant degradation. Some microorganisms such as Yeast, Fungi, and Bacteria, consume and digest organic matter, such as firewood and thinners. All phytoremediation procedures are not unique and can be used simultaneously, but the removal of metals depends on their bioavailable ingredients in the soil.

### *17.5.4 Rhizodegradation*

The breakdown of heavy metals in the rhizosphere with the help of bacteria and other microorganisms is known as rhizodegradation. The rhizosphere extends around the root system normally 1 mm and is influenced by the vegetation (Paya and Bhatt 2010). The enhancement of the breakdown of contaminants in the rhizosphere may be leading to microbial records and metabolic actions.

Roots' secretions containing amino acids, carbohydrates, and flavonoids may enhance microbial action about ten to a hundred times in the rhizosphere. Roots' secretions also release nutrient-containing exudates that increase microbial activity in the root horizon by getting carbon and nitrogen sources for soil microbes and creating a nutrient-rich atmosphere. Furthermore releasing organic compound that enhances microbial growth and activity in the rhizosphere (Yadava and Srivastava 2020).

### *17.5.5 Rhizofiltration*

Rhizosphere filtration is the elimination of contaminants from polluted surface water or wastewater through tree roots (Mukhopadhyay and Maiti 2010). In fact, in rhizosphere filtration, the heavy metals are removed through trees including aquatic and terrestrial water bodies. It may capable of partially treating industrial discharge, acid mine wastewater, and agricultural runoff. It can also be used for zinc, lead, copper, arsenic, cadmium, nickel, and chromium, which are generally present in root horizons. Several benefits of rhizosphere filtration such as it can be useful in situ or ex-situ, and species other than hyperaccumulators can be used.

Plant filtration (using tree roots), floral filtration (using cut plant shoots; Latin caulis = shoot), or air filtration (using seedlings) is also known as rhizosphere filtration (Dong et al. 2016). During this plant filtration, pollutants are adsorbed or absorbed, so their flow to groundwater is decreased to a minimum.

### *17.5.6 Potential of Tree Species to Remediate Arsenic*

Trees have long been recognized as promising for arsenic phytoremediation, however, the most suitable tree species are still under examination. Though there are several arsenic tolerant plants, Chinese brake fern (*Pteris vittata* L.) is the first arsenic hyper-accumulator and the most widely studied (Faroog et al. 2016). Therefore, Budzyńska et al. 2019 was aimed to investigate the uptake and accumulation capabilities of As(III) by one-year-old trees from the three different tree species such as *Acer platanoides L., Betula pendula Roth., Quercus robur L., Ulmuslaevis* Pall using hydroponic culture. The highest accumulation of As(III) was detected in *A. platanoides* (BCF = 2.16) and *Q. robur* (BCF = 2.69). Another research was studied (Brahman et al. 2013) in a laboratory-conducted hydroponic system was employed to characterize phytofiltration for the uptake of arsenic and macronutrients by two arsenic hyperaccumulators, *Pteris cretica cv Mayii* (Moonlight fern) and *Pteris vittata* (Chinese brake fern). Arsenic was shown to preferentially accumulate in the leaves and stems of *P. cretica* cv Mayii compared to roots. Salix has the potential to effectively phytostabilize arsenic in Sweden as the tree crop is known to accumulate arsenic preferably/actively in its roots and belowground biomass which is a key feature of Phytostabilization. The experiment conducted at the Botanical Garden, University of the Punjab, Lahore, revealed that *Eucalyptus camaldulensis*, *Terminalia arjuna* and *Salix tetrasperma* showed varying adaptability to survive under the arsenic stress environment, suggesting them as strong candidates to be exploited for arsenic remediation (Ahmad et al. 2018). Trees showed tremendous results in phytoremediation of arsenic. This may be due to the activities of key antioxidant enzymes like it is reported that APX and CAT were significantly increased in root and shoot of *P. pinnata* under different As treatments (Kumar et al. 2017).Similar to this, enhanced levels of antioxidant enzymes under heavy metal stress in plants have been reported in earlier studies which suggest that this phenomenon might be a powerful strategy for the survival of metal accumulating plants (Tripathi et al. 2016).Moreover, arsenic also effects on nutrient elements distribution. Availability of mineral elements like calcium, magnesium, iron, zinc, potassium, sodium, sulfur and manganese were also reported to increase in the presence of arsenic (Kumar et al. 2017).

## 17.6 Conclusion

Arsenic is a toxic metal that is harmful to humans and the environment. However, various nitrogen-fixing tree species have the ability to enrich and reduce arsenic in arsenic-contaminated soil and groundwater. Removing arsenic from contaminated water may be the only effective option for reducing health hazards. Removal and mobilization of arsenic from contaminated soil and groundwater using phytoremediation techniques is an effective and economical approach to successfully degrade arsenic contamination in the environment.

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# Chapter 18
# Bacterial Tolerance and Biotransformation of Arsenic in Soil and Aqueous Media

**Etisam Mazhar, Tanvir Shahzad, Faisal Mahmood, Farrukh Azeem, Abid Mahmood, and Sabir Hussain**

**Abstract** Arsenic (As) is one of the most toxic metalloids present in soil and water resources. The presence of microorganisms in soil and aqueous media have a significant impact on the toxicity of arsenic because the microorganisms interact with it in different ways such as sorption, reduction, oxidation and methylation etc. This chapter covers the microbial processes which have the impact on the fate as well as mobility of As in the environment with a special focus on the role of bacteria in defining the fates of As. The dominant bacterial As biotransformations which define its mobility and toxic impacts in the environment include the arsenite [As(III)] oxidation, arsenate [As(V)] oxidation, methylation, demethylation and volatilization. However, the different biotransformations of As by bacterial are affected by the changes in pH, redox potential, nutrient availabilities and presence of different interacting substances such organic matter etc.

**Keywords** Arsenic · Bacterial tolerance · Biotransformations · Mobility · Toxicity

## 18.1 Introduction

Arsenic (As) is a hazardous metalloid which abundantly exists in soils, water resources and minerals (Singh et al. 2021). It makes its way into the environment mainly through natural weathering processes as well as different geothermal, biological, industrial and mining activities etc. and is considered as a global threat (Mallick et al. 2015; Singh et al. 2021). In earth crust, it is found in various sedimentary and igneous rocks (Darma et al. 2021). It is available in different organic and inorganic

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forms in the environment. Different organic forms of As existing in the environment include monomethylarsenate, dimethylarsenate, dimethylarsenite and dimethylarsenite etc. (Singh et al. 2021). In the environment, the most commonly prevalent forms of inorganic As include arsenate [As(V)] and arsenite [As(III)] (Singh et al. 2021). Arsenite is commonly present in reducing conditions, whereas, arsenate is commonly present in oxidizing conditions (Singh et al. 2021). Arsenite is considered to have more toxic impacts due to its attraction to bind with different functional groups of various biomolecules such as catalytic proteins (Krumova et al. 2008; Singh et al. 2021; Darma et al. 2021). Conversely, As(V) interferes with the natural phosphorylation processes and affects the cell metabolism through impersonation with phosphate (Tseng 2004; Singh et al. 2021). The existence of different forms of As as well as their movement in the soil relies on numerous environmental parameters including pH, redox potentials, presence of metal oxides, organic matter content and moisture etc. (Drahota and Filippi 2009; Darma et al. 2021). It has been reported that groundwater containing As is extensively used for domestic purposes including irrigation of agricultural crops in different regions of the world including China and United States (Brammer 2008; Banerjee et al. 2013). As a result of this irrigation, the level of As increases in the field and results into the entry of As in the food chain (Rahman et al. 2007a, b; 2008; Bhattacharya et al. 2009; Mallick et al. 2015).

Remediation of the soils contaminated with As is considered as a challenge because the existing physiochemical As removing techniques have the disadvantages of high cost as well as many reasons of inefficiencies (Mallick et al. 2015). Hence, there is an attractive focus on the environmentally friendly and inexpensive technologies for As removal (Alkorta and Garbisu 2001; Mallick et al. 2015). One of such ecofriendly and cost-effective technologies is bioremediation. Bioremediation of As is carried out by involvement of living organisms. For example, the microorganisms including bacteria and fungi have adapted a number of ways for resistance to survive under As stressful conditions (Stolz et al. 2002; Mallick et al. 2015; Singh et al. 2021). Such microbiota having the potentials for accumulating, degrading, reducing or oxidizing the As might be helpful and exploited for bioremediating the soils contaminated with this metalloid (Mallick et al. 2015; Darma et al. 2021). The potential of such microorganisms for As accumulation from the contaminated environments might also be improved by employing the genetic engineering strategies (Silver and Phung 1996; Mallick et al. 2015; Singh et al. 2021). In rhizosphere, bacterial remediation of As might be carried out by different ways. One group of the microorganisms might be helpful in relieving the stress due to As in the rhizosphere resulting into limiting As accumulation in plants (Cavalca et al. 2010; Pandey et al. 2013; Mallick et al. 2015). The other group of the microorganisms might be helpful in accumulating As in plants and thus promoting the As phytoremediation (Ghosh et al. 2011; Yang et al. 2012; Mallick et al. 2015). Although there are limited reports regarding applications of such rhizobacteria in agricultural fields, the microorganisms have been reported to have the potential not only for the resistance of As (Nriagu et al. 2007; Yan et al. 2019) but also for its different transformations including the reduction (Glasser et al. 2018; Singh et al. 2021), oxidation (Bahar et al. 2013a, b; Darma et al. 2021), methylation (Huang 2014; Singh et al. 2021) and volatilization

(Mallick et al. 2015). Ubiquitous existence of As in the earth and the existence of As-resistance and transformation potentials in microbiota has necessitated to explore the role of the micro biota for developing As bioremediation strategies. This book chapter primarily focuses on As resistance as well as transformation processes existing in bacteria and the application of such potential bacteria for As bioremediation in the environment.

## 18.2 Arsenic in the Environment: Sources and Toxicity

Although the abundance of As is relatively low in the earth crust (0.0001%), it is extensively present in the environment and is commonly found in association with different ores of metals such as copper and lead, etc. (Nriagu et al. 2007; Kruger et al. 2013). Arsenic comes from different natural sources such as volcanic eruptions, weathering of rocks and minerals, fossil fuels and different biological activities (Mallick et al. 2015; Darma et al. 2021). Despite that the most of the problems occur due to mobilization of As originating from the natural sources, it is also contributed through different human activities including mining, smelting, wood conservation, municipal and industrial waste, inorganic fertilizers, pesticides and electronics etc. (Dixit et al. 2015; Singh et al. 2021). The entry of As in the global cycling primarily takes place through interactions of the As containing bedrocks, sediments, and soils with the water bodies along with local depositions through atmosphere (Nriagu et al. 2007; Mallick et al. 2015). Arsenic is also reported to be extensively present in groundwater resources worldwide (Mallick et al. 2015; Rabbani et al. 2017; Shahid et al. 2018). The concentration of As in groundwater varies depending upon the physicochemical and environmental conditions of the water resources, sediments and the bedrocks (Nriagu et al. 2007; Mallick et al. 2015; Shahid et al. 2018). The major reason for the existence of As in groundwater resources is thought to be the solubilization of As rich iron oxyhydroxides in the groundwater (Smedley and Kinniburgh 2002; Mallick et al. 2015).

Arsenic is considered hazardous for all the living organisms because it is carcinogenic in nature and its compounds are ranked as a Group 1 human carcinogenic (Sheik et al. 2012; Shahid et al. 2013). Arsenic contamination results in the entry of As to food crops, fruits, vegetables, grains and fodder from where As gets entry into food chain and commercially used food products by human beings not only in contaminated regions but also to other part of world (Tripathi et al. 2007; Zavala and Duxbury 2008; Meharg et al. 2009; EFSA 2009; Zhao et al. 2010; Hare et al. 2017). Thanks to their more solubility, the inorganic forms of As such as arsenite [As(III)] and arsenate [As(V)] are considered to have more noxious impacts than the organic As forms (Mallick et al. 2015). Among the mentioned two forms, arsenite is considered as more soluble as well as toxic form of As as compared with arsenate which is relatively less soluble (Neff 1997; Mallick et al. 2015). The more toxicity of arsenite is considered due to its ability to inactivate the proteins of the living organisms by binding with sulfhydryl groups of cysteine residues (Mallick et al.

2015). Conversely, arsenate has the potential to hinder the oxidative phosphorylation process in living organisms due to its chemical analogy with phosphate (Ordóñez et al. 2005). Arsenic has been found to create the toxic impacts in human being as well as other living organisms acutely as well as chronically. The symptoms of acute As toxicity have been reported to comprise of anemia, diarrhea, and gastrointestinal discomfort in different regions of the word (Guha-Mazumder et al. 1992). However, chronically it affects the skin, respiratory system, digestive tract, cardiovascular system, nervous system, etc. (Mallick et al. 2015). Arsenic toxicity also affects the male reproductive system by reducing the production of testosterone and causing infertility in human beings (Meeker et al. 2010; Davila-Esqueda et al. 2012). It also shows negative impacts on infants resulting into loss of weight, severe issues of birth, premature delivery and sometimes mortality (Chakraborti et al. 2003; Milton et al. 2005; Rahman et al. 2007a, b).

## 18.3 As Remediation in the Environment

### *18.3.1 Conventional Methods for As Remediation and Their Disadvantages*

Arsenic from the contaminated water can be removed by numerous conventional treatment technologies such as chemical oxidation, coagulation/flocculation, ion exchange, adsorption and reverse osmosis (Bahar et al. 2013a, b). Different conventional emerging methods for removal of As at laboratory scale, from the small drinking water systems and applicable to dcenetralized rural and urban populations have been reviewed, summarized and discussed in detail by different researchers (Mondal et al. 2006; Katsoyiannis and Zouboulis 2006; Visoottiviseth and Ahmed 2009; Litter et al. 2010; Bahar et al. 2013a, b). Nevertheless, these techniques are more focused on in-situ treatment approaches such as chemical oxidation, multiphase extraction, coagulation/flocculation and adsorption methods etc. (Bahar et al. 2013a, b). However, the most of these techniques have different limitations including the impacts on microbial and geochemical processes, requirement of chemical oxidants, production of toxic solid wastes and bye products, limited efficiencies, pH adjustment requirements, regeneration of adsorbents and interference by suspended/dissolved solids (Simeonova et al. 2005; Litter et al. 2010; Bahar et al. 2013a, b). In view of the limitations of the conventional treatment technologies, there is a worldwide focus on exploring the bioremediation-based approach for removal of As impacts from the environment.

### *18.3.2 Bioremediation of Arsenic from the Environment*

Due to various risk factors associated with different conventional methods for treatment of As, there is a growing interest in bioremediation as a cost effective and environmentally compatible alternate (Vidali 2001; Bahar et al. 2013a, b). Bioremediation encompasses the detoxification of the pollutants by involvement of living organisms, mainly the microorganisms. Bioremediation of As is carried out by different types of microbial activities which might result into detoxification through various processes such as biotransformation, mobilization, immobilization, biomethylation, volatilization, sorption, and complexation (Wang and Zhao 2009; Yan et al. 2019; Singh et al. 2021; Darma et al. 2021). As the arsenite [As(III)] is comparatively more mobile and toxic form of As, one of the more convenient approach of bioremediation to deal with it is its microbial biotransformation into relatively less mobile and less toxic arsenate[As(V)] and it has been reported to be carried out by a number of microorganisms predominantly bacteria (Singh et al. 2021; Darma et al. 2021). During the recent years, a number of bacteria belonging to various genera have been described for bioremediation of As through different processes including biotransformation, oxidation, reduction, mobilization, immobilization, biomethylation, volatilization and sorption in the soil and aqueous media (Mallick et al. 2015; Singh et al. 2021; Darma et al. 2021). This book chapter comprehensively encompasses the interactions of bacteria with arsenic in the environment for its bioremediation and their possible applications for this purpose.

## 18.4 Arsenic Bacteria Interactions in the Environment

In the environment, interactions of the bacteria with different forms of As is an important factor which has a significance in the biogeochemical cycle of As as well as its toxicity. Bacteria have been found to harbor different mechanisms for As resistance which help them to survive in the As contaminated environment by involving in specific biochemical pathways for protection of the bacterial cells against As toxicity (Stolz et al. 2006; Mallick et al. 2015; Singh et al. 2021). Actually, the bacteria carry out different types of transformations of As which affect not only the movement and dispersal of different As forms but also their toxic impacts (Mateos et al. 2006; Inskeep et al. 2007; Mallick et al. 2015; Darma et al. 2021). These transformations of As resulting into bacterial resistance against As may include arsenite oxidation, arsenate reduction, volatilization and As methylation which have been discussed in detail in this section below.

### 18.4.1 Arsenic Resistance in Bacteria

Arsenic tolerance in bacteria is one of the main features which makes the bacteria capable of coping with the presence of As in the environment. There are several bacteria belonging to various genera including *Staphylococcus, Microbacterium, Thiomonas, Escherichia*, etc. which have been reported for the tolerance against the presence of As in the environment (Silver 1998; Achour-Rokbani et al. 2010; Kruger et al. 2013). Resistance of bacteria against the presence of As is usually facilitated by the presence of *ars* operon in the genetics of these bacteria (Rosen 2002; Kruger et al. 2013). However, the organization of *ars* operons significantly diverges in different bacteria (Kruger et al. 2013). A very simple gene set which results into a basic As resistance in bacteria comprises of three-gene operon *arsRBC* which has been discovered in different bacteria including *E. coli* as well as *Staphylococcus aureus* (Carlin et al. 1995; Silver 1998). In *Staphylococcus aureus*, this three-gene operon is located on the plasmid pI258 (Silver 1998). However, for imparting resistance to a high concentration of As, an extended five-gene operon *arsRDABC* was also revealed in *Escherichia coli* (Chen et al. 1986). In *E. coli*, this five-gene operon was located on plasmid R773 (Chen et al. 1986). Sometimes both of these operons might also be located within the same strain as already reported for a bacterial strain *Thiomonas arsenitoxidans* (Arsène-Ploetze et al. 2010). These operons might also be complemented by few other genes linked with As resistance such as *arsH* and *arsN* (Muller et al. 2007; Chauhan et al. 2009; Paez-Espino et al. 2009; Kruger et al. 2013).

As(III) is sometimes excluded out of the microbial cells by involvement of transmembrane transporter protein *ArsB*. Some bacteria harbor *arsA gene* whose gene product, an ATPase, increases As(III) resistance by coupling with *ArsB* (Rosen 2002; Kruger et al. 2013). Sometimes, *Acr3p* having homology with yeast As(III) extrusion protein has also been reported to be attached with *ArsA* especially under the situations when *ArsB* is not present (Castillo and Saier 2010). *ArsD* functions as an As(III) chaperone which activates *ArsA* subunit of the *ArsAB* complex by transferring As(III) from glutathione-bound complexes to *ArsA* (Lin et al. 2007; Yang et al. 2010; Kruger et al. 2013). The As resistance in AS(V) is extended by *arsC* through coding for a small cytoplasmic As(V) reductase. The bacterial As(V) reductases are distributed among two distinct families. The first family of the As(V) reductases comprises of homologues of the *arsC* harbored by plasmid R773 of *E. coli* which use glutaredoxin as well as glutathione as electron donors for As(V) reduction (Chen et al. 1986; Shi et al. 1999). However, the second family of the As(V) reductases comprises of the homologues of *arsC* harbored by the plasmid pI258 of *Staphylococcus aureus* which uses thioredoxin for As(V) reduction (Ji and Silver 1992; Ji et al. 1994; Kruger et al. 2013). The enzymes originating from this family are related to phosphatases (Zegers et al. 2001). However, As(III) resistance mechanisms under anoxic environment have been speculated to be evolved earlier as compared with As(V) resistance mechanisms which were evolved under oxic environment (Rosen 2002; Kruger et al. 2013). The evolution of As(III) and As(V) resistance mechanisms in this sequence is also supported by the fact that As(III) is easier to be recognized as compared with As(V) (Kruger et al. 2013). Furthermore, few other genes have also been identified in ars operon (Wang et al. 2009; Chauhan et al. 2009; Achour-Rokbani et al. 2010). For example, an *arsP* gene presumably coding for membrane permease having some homology with other As transporters has been identified in a bacterial strain *Campylobacter jejuni* (Wang et al. 2009). Similarly, a thioredoxine system encoding *arsTX* gene has been reported in a bacterial strain belonging to *Microbacterium* genus (Achour-Rokbani et al. 2010) and an acetyltransferase-like protein encoding *arsN* gene has been reported in *Escherichia coli* (Chauhan et al. 2009). Despite those few mechanisms of As resistance in bacteria are known, there is need to further elucidate the widespread As resistance processes existing in bacteria worldwide.

### 18.4.2 Arsinite [As(III)] Oxidation by Bacteria

One of the dominant interaction between As and bacteria in the environment is the oxidation of As(III) resulting into production of As(V) (Mallick et al. 2015; Singh et al. 2021; Darma et al. 2021). This oxidation occurs as a potential detoxification mechanisms along with serving as an electron donor for microbial respiration in combination with oxygen under oxic conditions and this phenomenon has been reported in a number of bacterial strains belonging to various genera including *Alcaligenes, Bordetella, Achromobacter, Ochrobactrum, Agrobacterium, Rhodococcus, Rhizobium, Bacillus and Ancylobacter* etc. (Li'evremont et al. 2003; Oremland and Stolz 2003; Branco et al. 2009; Andreoni et al. 2012; Bachate et al. 2012; Mallick et al. 2015; Pattanapipitpaisal et al. 2015; Wang et al. 2015; Watson et al. 2017; Kumari et al. 2019; Singh et al. 2021). Different As(III) oxidizing bacteria have been enlisted in Table 18.1. The microbial oxidation of As(III) to As(V) primarily results into a reduction in mobility of arsenic in the environment because As(V) has relatively more affinity towards the mineral solids in the environment (Dixit and Hering 2003; Huang 2014). Hence, the oxidation of As(III) to As(V) by the microorganisms is often reported as an approach for removal of As from the water resources (Ito et al. 2012; Cavalca et al. 2013; Huang 2014).

The most of the As(III) oxidizing bacterial strains have been reported to isolated from the environmental components contaminated with high levels of As, however, many such bacteria have also been reported to be isolated either from the fresh soils having no As contamination or from the soils with low As contamination indicating for a widespread of these bacteria (Bahar et al. 2013a, b). The efficacy of oxidizing As(III) in these bacteria varies from strain to strain due to their varying physiological traits and growth conditions. For example, Salmassi et al. (2002) reported the isolation of a bacterial strain AOL15 belonging to genus *Agrobacterium* which had the potential to oxidize 585 μM As(III) within 24 h. Similarly, Weeger et al. (1999) isolated a bacterial strainULPAs1 belonging to genus *Herminnimonas* which had a good tolerance against the presence of As(III). This strain exhibited almost equal

**Table 18.1** Bacterial strains involved in arsenite [As(III)] oxidation in soil and aqueous media

| Sr. # | Bacterial strains | Remarks/details | References |
|---|---|---|---|
| | *Rhizobium* NT-26 | This *aioA* and *aioB* harboring bacterial strain was isolated from a gold mine soil. This strain oxidized As (III) with the optimal oxidation at pH 5.5. This oxidation was catalyzed by periplasmic arsenite enzyme | Santini et al. (2004) |
| | *Azoarcus* sp. DAO1 | This facultative aerobic bacterial strain was isolated from As contaminated industrial soil. It carried out the oxidation of 5 mM As(III) within 7 days of incubation under denitrifying conditions | Rhine et al. (2006) |
| | *Sinorhizobium* sp. NT-4 | This *aioA* harboring bacterial strain was isolated from an arsenopyrite-containing rock. This strain grew in the presence of As(III) and had the potential to carry out the oxidation of 5 mM As(III) within 4–5 days | Inskeep et al. (2007) |
| | *Agrobacterium* sp. BEN5 | This *aioA* harboring bacterial strain was isolated from an As contaminated water in vicinity of a gold mine. It showed resistance to the presence of As(III) during its aerobic growth in minimal salt medium | Inskeep et al. (2007) |
| | *Sinorhizobium* sp. M14 | This bacterial strain was isolated from an As rich sediment of a gold mine. It showed the resistance to the presence of 250 mM of As(V) and 20 mM of As(III) during incubation study. It had the potential to oxidize As(III) through respiratory process | Drewniak et al. (2008) |
| | *Thiomonas* sp. 3As | This *aioA* and *aioB* harboring moderately acidophilic bacterial strain was isolated from an arsenite containing acid mine drainage water. It carried out the oxidation of A(III) at rate of 0.125 μM oxidation min − 1 (mg of protein) − 1 having a membrane fraction associated arsenite oxidase activity | Duquesne et al. (2008) |

(continued)

**Table 18.1** (continued)

| Sr. # | Bacterial strains | Remarks/details | References |
|---|---|---|---|
| | *Burkholderia cepacia* UC-2 | This *aioA* and *aioB* harboring bacterial strain was isolated from a biofilm on volcanic rocks. It carried out 90% oxidation of As(III) at rate of 9.3 $\mu$g mL$^{-1}$ h$^{-1}$. It resisted to the presence of more than 8 mM As(III) | Campos et al. (2009) |
| | *Alcaligenes* sp. strain RS-19 | This bacterial strain was isolated from an abandoned mine soil and could carry out the oxidation of 1 mM As(III) within 40 h. It could resist up to 26 mM As(III) in the medium | Yoon et al. (2009) |
| | *Pseudomonas stutzeri* GIST-BDan2 | This *aioA* harboring bacterial strain was isolated from constructed wetlands water. It carried out the complete oxidation of 1 mM As(III) within 30 h with an initial cell population of 107 cells mL$^{-1}$ | Chang et al. (2010) |
| | *Pseudomonas arsenicoxydans*. VC-1 | This bacterial strain was isolated from an As containing sediment. It showed the potential to tolerate the presence of 5 mM As(III) and carried out 100% oxidation of 500 mg L$^{-1}$ As(III) | Campos et al. (2010) |
| | *Pseudomonas lubricans* | This bacterial strain was isolated from an industrial wastewater. It resisted to the presence of 40 mM As(III) in the medium. The crude extract of its cells oxidized about 42, 78, and 95% of the initially added As(III) from the medium within 24, 48, and 72 h, respectively | Rehman et al. (2010) |
| | *Azospira* sp. strain ECC1-pb2 | This *aroA* harboring bacterial strain was found to carry out the oxidation of As(III) in the sludge samples as well as in pure cultures along with a linked reduction of chlorate | Sun et al. (2010a, b) |
| | *Dechloromonas* sp. strain ECC1-pb1 | This *aroA* harboring bacterial strain was found to carry out the oxidation of As(III) in incubation experiment with the sludge samples as well as in pure cultures along with a linked reduction of chlorate | Sun et al. (2010a, b) |

(continued)

**Table 18.1** (continued)

| Sr. # | Bacterial strains | Remarks/details | References |
|---|---|---|---|
| | *Achromobacter* sp. SPB-31 | This bacterial strain was isolated from a garden soil. It could resist 40 mM As(III). It had the potential to carry out oxidation of 5 mM As(III) only within 12 h with an initial $OD^{600}$ value of 0.65 | Bachate et al. (2012) |
| | *Bordetella* sp. SPB-24 | This arsenic resistant bacterial strain was isolated from a garden soil. It could resist 15 mM As(III). It had the potential to carry out oxidation of 5 mM As(III) within 12 h with an initial $OD^{600}$ value of 0.65 | Bachate et al. (2012) |
| | *Variovorax* sp. MM-1 | This bacterial strain was isolated from a heavy metal contaminated soil. It had the potential to tolerate 20 mM As(III) and 200 mM As(V) in the medium. Moreover, it carried out the oxidation of 500 μM As(III) within 3 h with an initial cell population of 107 cells $mL^{-1}$. It harbored *aioA* gene | Bahar et al. (2013a) |
| | *Stenotrophomonas* sp. MM-7 | This *aioA* harboring strain was isolated from a heavy metal contaminated soil. It carried out the oxidation of 500 μM As(III) within 12 h with an initial cell population of 107 cells $mL^{-1}$ | Bahar et al. (2012) |
| | *Brevibacillus* brevis S1 | This gram positive As(III) tolerant strain was isolated from an As contaminated soil. It carried out the bioaccumulation (50%) as well as biotransformation (50%) of As(III) at its initial concentration of 50 mg $L^{-1}$ within 24 h | Banerjee et al. (2013) |
| | *Herminiimonas arsenicoxydans* | This bacterial strain had the potential for the oxidation of As(III) in wastewater through immobilization on different adsorbents such as Ca-alginate and chabazite etc | Drewniak and Sklodowska (2013) |

(continued)

**Table 18.1** (continued)

| Sr. # | Bacterial strains | Remarks/details | References |
|---|---|---|---|
| | *Microbacterium lacticum* | This bacterial strain was isolated from a municipal sewage through an enrichment culture process. It had the potential to carry out the oxidation of 50 mM As(III) form the groundwater while being immobilized on brick pieces | Drewniak and Sklodowska (2013) |
| | *Arthrobacter* sp. Datong-1 | This gram positive bacterial strain was isolated from an As aquifer sediment and it showed a good growth dependent oxidation of As(III) in the medium even in the presence of As(V) | Duan et al. (2013) |
| | *Bacillus flexus* SSAI1 | This strain was isolated from an agro-industry waste. It resisted to the presence of 25 mM As in the mineral salt medium. It exhibited a rapid potential for As(III) oxidation by involvement of *aioAB* genes coding arsenite oxidase reductase | Mujawar et al. (2021) |

growth in the media without As(III) and the media containing 1.33 mM of As(III), and showed a good potential for oxidation (0.4 mM $h^{-1}$) of As(III). Bachate et al. (2012) reported two As(III) oxidizing strains, *Bordetella* sp. SPB-24 and *Archromobactor* sp. SPB-3, having 1166 and 1186 μM $h^{-1}$ values of the maximum oxidation rate of As(III). Yoon et al. (2009) reported the isolation of a bacterial strain RS-19 belonging to genus *Alcaligenes* from an As contaminated soil which had a good potential for oxidation (0.042 mM $min^{-1}$) of As(III) during heterotrophic growth. Liao et al. (2011) isolated a bacterial strain AR-11 belonging to genus *Bosea* from an As contaminated groundwater which had the potential for oxidation of 0.25 mM As(III) only within 12 h. *Stenotrophomonas* sp. strain MM-7 isolated from a low As containing soil had the potential to oxidize 500 μM As(III) within 12 h of incubation in minimal salts medium (Bahar et al. 2012). Biswas et al. (2019) reported the isolation of a facultative chemolithotrophic bacterium *Delfia* sp. BAs29 which had the potential not only to resist the presence of 70 mM As(III) in the medium but also to carry out the oxidation of As(III). Kumari et al. (2019) reported an As(III) biotransforming *Rhodococcus* sp. which had the potential to resist 12 mM As(III) in terms of minimum inhibitory concentration. This strain showed a potential to oxidize 48.34% of the initially added 500 μg $L^{-1}$ within 6 h and complete removal within 48 h. Recently, Sun et al. (2020) reported the isolation of a multifunctional bacterial strain *Roseomonas rhizosphaerae* which had not only the potential to oxidize As(III) but also to simultaneously oxidize As(III) and antimonite [Sb(III)]. This strain was found to harbor an As-resistance gene *aioAB* which encoded As(III) oxidase. Similarly, Bagade et al. (2020) reported the isolation and characterization of a hyper tolerant bacterial strain *Bacillus firmus* L-148. This strain had the potential to tolerate the presence of 3 M As in the medium and to oxidize 75 mM As(III) in the medium within 14 days even in the presence of other metal ions. The potential of this strain to oxidize As(III) was also tested in a microcosm study by using a synthetic As(III) contaminated wastewater.

Different studies have indicated that As(III) oxidation by bacteria is an enzymatic function and it is associated with the catalytic activity of arsenite oxidase (*aox*) enzyme (Bahar et al. 2013a, b; Mallick et al. 2015). The *aox* is a membrane-bound/periplasmic enzyme which comprises of two subunits. The larger unit of *aox* encompasses an Mo-protein and an iron protein (3Fe-4S) which is encoded by *aoxB*, whereas, the smaller sub-unit of *aox* comprises of Rieske active center which is encoded by *aoxA* (Mukhopadhyay et al. 2002; Silver and Phung 2005; Mallick et al. 2015). Sometimes, the *aox* gene is also designated as *aro* and *aso* and the large subunit *aoxB* is then designated as as *aroA* and *asoA*. However, a new nomenclature for the genes involved in As(III) oxidation was proposed by Lett et al. (2012). They proposed the term of *aio* for arsenite oxidase genes. Similarly, they proposed the terms of *aioA* and *aioB* for the genes encoding the larger subnut and the smaller subunit of arsenite oxidase, respectively. Anderson et al. (1992) reported the purification of *aio* from a bacterium *Alcaligenes faecalis* and Ellis et al. (2001) carried out its characterization.

### *18.4.3 Arsenate Reduction by Bacteria*

Reduction of arsenate [As(V)] in the environment is another prominent interaction of the bacteria with As (Bahar et al. 2013a, b; Mallick et al. 2015; Singh et al. 2021; Shen et al. 2022). Reduction of As(V) has been found to be carried out by several bacteria belonging to different phylogenetic groups including *Shewanella, Escherichia, Bacillus, Clostridium, Pentoea, Thermus, Exiguobacterium, Alkaliphilus, Desulfitobacterium*, etc. (Blum et al. 1998; Gihring and Banfield 2001; Stolz et al. 2006; Malasarn et al. 2008; Bahar et al. 2013a, b; Guo et al. 2015; Tian et al. 2015; Zhu et al. 2017; Badilla et al. 2018; Cai et al. 2020; Singh et al. 2021; Darma et al. 2021). Different bacterial strains involved in As(V) reduction have been summarized in Table 18.2. Several bacteria carryout the reduction of As(V) as a detoxification strategy which is facilitated by the cytoplasmic arsenate-reductase enzyme (Rosen 2002; Bahar et al. 2013a, b; Mallick et al. 2015). Another way for reducing the As(V) in bacteria is the dissimilatory anaerobic respiration in which they use it as a terminal electron acceptor (Lièvremont et al. 2009; Bahar et al. 2013a, b; Kruger et al. 2013; Zhu et al. 2017; Singh et al. 2021). For example, Tian et al. (2015) reported that two As(V) reducing bacterial strains belonging to *Pantoea* and *Alkaliphilus* genera had the potential to carry out complete reduction of As(V) only within 20 h. Similarly, Guo et al. (2015) reported that a bacterial strain *Bacillus* sp. M17-15 had the potential to significantly reduce the As(V) from the surface of goethite during an incubation period of 4 to 16 days resulting into an increase in potion of As(III). Recently, Cai et al. (2020) reported that an As(V) reducing bacterial strain *Desulfitobacterium* sp. DJ-3 had a good potential to reduce and release As(V) from an organic matter and iron complex resulting into release of notable amount of As(III). However, in the same study, *Exiguobacterium* sp. DJ-4 had the potential only for the reduction of free As(V) but did not show the potential to release As(V) from the complex.

Arsenate makes its entry into the bacterial cell through via phosphate transporters followed by a reduction to As(III) which is then either released out of the cell or seized within the cell either in free form or in conjugation with different components such as glutothione (Vahter 2002; Mallick et al. 2015). The microorganisms including bacteria carry out the reduction of As(V) by two mechanisms namely detoxification as well as dissimilatory reduction. The detoxification of As(V) is catalyzed by arsenate reductase *ArsC* which is often found in the cytoplasm of the organisms (Silver and Phung 2005; Mallick et al. 2015). The *ArsC* has the potential to reduce As(V) to As(III) and it is coded by genes found in *ars* operons present in bacteria and some archea. These operons present in bacteria are usually comprised of either three (*arsRBC*) genes or five (*arsRDABC*) genes which are often organize in a single transcriptional unit (Schafer et al. 1994; Mallick et al. 2015). The As(V) reducing system comprising of three genes (*arsRBC*) contains a transmembrane pump (*arsB)* as well as a transcriptional repressor (*arsR*) along with arsenate reductase (*arsC)* (Mukhopadhyay et al. 2002; Silver and Phung 2005; Mallick et al. 2015). The *arsRDABC* system contains an arsenite inducible repressor (*arsR*) and a negative regulatory protein (*ArsD*) along with ATPase and membrane- located arsenite efflux pumps named *ArsA* and ArsB, respectively, as well as an arsenate reductase (*ArsC*). This whole system was primarily found to be located on a plasmid harbored by the bacteria strain belonging to *Escherichia coli* (Chen et al. 1986). However, later on, this system was also reported in the plasmids born in the bacterial strains belonging to genus *Acidiphilium multivorum* (Suzuki et al. 1998). The dissimilatory As(V) reduction is often carried out either by strict anaerobic bacteria or facultative anaerobic bacteria which couple their growth with As(V) as the terminal electron acceptor (Malasarn et al. 2004). Despite those few mechanisms for As(V) reduction by bacteria have been explored, there is need to conduct further research in order to get a deep insight into these mechanisms.

### *18.4.4 Arsenic Adsorption by Bacteria*

One of the useful mechanisms for remediation of the metal ions including As form the environment is their adsorption through bacteria (Sudha and Abraham 2001; Say et al. 2003). There is relatively less possibility of adsorption of As by bacteria and other microorganisms due to the reason that normally As(V) and As(III) are found as negatively charged oxide ions and neutral oxide, respectively (Mallick et al. 2015). Therefore, in order to promote As adsorption by microorganisms, there is need of some pre-processing to modify their cell surface (Loukidou et al. 2003; Mallick et al. 2015). However, some adsorption may naturally be carried out by the

**Table 18.2** Bacterial strains involved in arsenate [As(V)] reduction and detoxification in soil and aqueous media

| Sr. # | Bacterial strains | Remarks/Details | References |
|---|---|---|---|
| | *Sulfospirillium barnesii* | This iron and As respiring bacterial strain had the potential to carry out the complete reduction of As(V) in a sand flow-through reactor experiment within 2 days resulting into the release of As(III) | Herbel and Fendorf (2006) |
| | *Shewanella putrefaciens* CN-32 | The As(V) and Fe(III) reducing bacterial strain was tested for reduction of As(V) in flow-through reactor experiments. It transformed the significant amount of As(V) into As(III) through its reduction resulting into a release of As(III) | Kocar et al. (2006) |
| | *Bacillus benzoevorans* HT-1 | This As(V) respiring bacterial strain had the potential to carry out significant reduction of As(V) in a sand flow-through reactor experiment within 1 days resulting into the release of As(III) | Herbel and Fendorf (2006) |
| | *Shewanella* sp. ANA-3 | This bacterial strain had the potential to reduce As(V) as well as Fe(III) during batch incubation. This strain had the potential to carry out the respiratory reduction of As(V) which was faster than its potential of detoxification As(V) reduction | Campbell et al. (2006) |
| | *Bacillus selenatarsenatis* SF-1 | This dissimilatory arsenate reducing bacterium was tested for remediation of an As contaminated soil through As(V) reduction in a microcosm experiment. The potential of this strain for As(V) reduction was enhanced in the presence of electron shuttle compound | Yamamura et al. (2008) |
| | *Desulfuribacillus alkaliarsenatis* | This gram-positive bacterial strain was isolated through enrichment process from a soda lake in Russia. This haloalkaliphilic bacterial strain had the potential for dissimilatory As(V) reduction using pyruvate and lactate as electron donor | Sorokin et al. (2012) |

(continued)

**Table 18.2** (continued)

| Sr. # | Bacterial strains | Remarks/Details | References |
|---|---|---|---|
| | *Anaeromyxobacter dehalogenans* strain PSR-1 | This As(V) reducing strain was isolated from the soil of a chemical plant and had the potential for reduction of As(V) not only in soil solution but also the As(V) adsorbed on soil minerals | Kudo et al. (2013) |
| | *Geobacter pelophilus* | This Fe(III) and As(V) reducing bacterium had the potential for reduction of As(V) in the soil used during an incubation study | Ohtsuka et al. (2013) |
| | *Geobacter* sp. OR-1 | This dissimilatory arsenate reducing bacterium was isolated from a paddy soil in Japan. It carried out the reduction of As(V) using Fe(III), nitrite and fumarate as electron acceptors | Ohtsuka et al. (2013) |
| | *Bacillus* sp. SXB | This *arsB* harboring As(V) reducing bacterial strain was isolated through enrichment from a soil in Shanxi Province. This strain showed more effective As(V) reduction under aerobic conditions. It carried out more than 90% reduction of As(V) in aerobic condition only within 36 h | Wu et al. (2013) |
| | *Pantoea* sp. IMH | This *arsB* harboring As(V) reducing bacterial strain was isolated through enrichment from a soil in Inner Mongolia. This was the first As(V) reducing bacterial strain belonging to Pantoea. strain showed more effective As(V) reduction under aerobic conditions | Wu et al. (2013) |
| | *Shewanella* sp. OM1<br>*Pseudomonas* sp. OM2<br>*Aeromonas* sp. OM4<br>*Serratia* sp. OM17 | These dissimilatory arsenate reducing bacteria were isolated form the microbial mats of a gold mine. These strains had the capability to grow in anaerobic condition and had the potential for As(V) reductive dissolution using it as a terminal electron acceptor | Lukasz et al. (2014) |

(continued)

**Table 18.2** (continued)

| Sr. # | Bacterial strains | Remarks/Details | References |
|---|---|---|---|
| | *Bacillus* sp. M17-15 | This dissimilatory arsenate reducing bacterium was isolated form an aquifer sediment from Hetao basin in Mongolia. It was resistant to both As(V) and As(III). This strain harbored both arr and ars genes and showed good As(V) reduction in the presence of organic carbon | Guo et al. (2015) |
| | *Alkaliphilus oremlandii* OhILAs | This *arrA* harboring As(V) reducing bacterial strain had the potential for reduction of the dissolved As(V) anaerobically | Tian et al. (2015) |
| | Pantoea sp. IMH | This *arsC* harboring As(V) reducing bacterial strain had the potential for 100% reduction of As(V) aerobically from the waste residues | Tian et al. (2015) |
| | *Desulfosporosinus* sp. | This dissimilatory arsenate reducing bacterium was obtained from pristine soils and it showed a considerable As(V) reduction in the presence of biogenic electron shuttles | Yamamura et al. (2018) |
| | *Staphylococcus* sp. As-3 | This bacterial strain was isolated from a sediment core. This strain showed good resistance up to 7.5 mM for As(III) and 200 mM for As(V). This strain significantly reduced As(V) under anoxic conditions | Rathod et al. (2019) |
| | *Desulfitobacterium* sp. DJ-3<br>*Exiguobacterium* sp. DJ-4 | The dissimilatory arsenate reducing bacterium *Desulfitobacterium* sp. DJ-3significantly reduced OM-Fe complexed As(V) in an incubation experiment. However, the strain DJ-4 had the potential to carry out the reduction of only free As(V). It did not reduce the complexed As(V) | Cai et al. (2020) |
| | *Shewanella putrefaciens* 81 CN-32 | This bacterial strain showed the potential for reduction of Fe(III) and As(V) while synthesizing the *arrA* genes during As(V) reduction | Shi et al. (2020) |

extracellular components existing on the surface of the microorganisms including bacteria (Miyatake and Hayashi 2009; Ahsan et al. 2011; Mallick et al. 2015).

### *18.4.5 Arsenic Methylation and Demethylation by Bacteria*

Methylation of As is also one of the prominent phenomena among the interactions of the bacteria with As in the environment (Kruger et al. 2013; Singh et al. 2021). Generally, methylation of As is considered as a mechanism of As detoxification despite the fact that some of the compounds of the methylation pathway have been reported to be even more toxic than the inorganic forms of As (Styblo et al. 2000; Kruger et al. 2013; Singh et al. 2021). Different methylated compounds of As are often found in the environment (Ali et al. 2021; Singh et al. 2021). Methylation of As(III) in bacteria is often carried out by an arsenic methyltransferase gene (*arsM*) resulting into production of monomethyl arsenite, dimethyl arsenite and trimethyl arsine as final product (Cullen and Bentley 2005; Kruger et al. 2013; Ali et al. 2021; Singh et al. 2021). All these methylated compounds are often volatilized after diffusion out of the cell (Kruger et al. 2013). The *arsM* gene is considered responsible not only in methylation of As but also results into a resistance of the strain against the As (Qin et al. 2006; Kruger et al. 2013; Singh et al. 2021). For example, Qin et al. (2006) carried out the cloning of an arsenic methyltransferase gene (*arsM*) from an As tolerant strain *R. palustris* into an As sensitive bacterium belonging to *Escherichia coli*. They observed that cloning of *arsM* gene in *E. coli* resulted into a significant increase in resistance of this strain against As and also resulted into the production of a gaseous methylated As compound namely trimethyl arsine. Despite that few methylated As intermediates might be even more toxic, however, their high volatility because of being in gaseous forms balances this toxicity (Kruger et al. 2013). Induction of As resistance in bacterial strains as a result of methylation due to involvement of *arsM* gene is also supported by the fact that *arsM* gene is often found in close affinity to *arsR* in many As resistant bacterial strains (Qin et al. 2006). The methylation of As(III) resulting into the production of trimethyl arsine is proposed to follow the same pathway as already reported for few fungi including *Scopulariopsis brevicaulis* (Qin et al. 2006; Stolz et al. 2006; Kruger et al. 2013). Previous studies indicate that As methylation can be carried out not only by aerobic as well as anaerobic bacterial strain by also by few photosynthetic organisms (Bentley and Chasteen 2002; Ye et al. 2012; Kruger et al. 2013).

Demethylation of the methylated As compounds is relatively a less explored process despite the fact that it is necessarily required for completion of geochemical As cycle (Kruger et al. 2013; Singh et al. 2021). Although the demethylation of methylated As compounds may happen under well oxygenated as well as anoxic conditions, however, well oxygenated environmental conditions are more preferred for a faster occurring of demthylation (Huang et al. 2007). Nevertheless, it has been observed that removal of organic functional groups including methyl group from the As compounds often results into increase of As toxicity but decrease in its mobility (Kruger et al. 2013; Singh et al. 2021). That is why it is considered less suitable for remediation purpose and draws relatively less interest. Although it is an evidenced mechanism, there is a relatively lesser characterization of microbial demethylation and the microbial communities involved this process (Khokiattiwong et al. 2001; Lehr et al. 2003; Maki et al. 2006; Sierra-Alvarez et al. 2006; Huang et al. 2007; Yoshinaga et al. 2011; Kruger et al. 2013). Some of the bacteria belonging to different genera involved in demethylation of the methylated As compounds have previously been reported to be characterized (Maki et al. 2006; Yoshinaga et al. 2011; Nadar et al. 2014; Singh et al. 2021). For example, *Mycobacterium neoaurum* was found to have the potential to demethylate some methylarsenicals (Lehr et al. 2003; Maki et al. 2006). Similarly, Yoshinaga et al. (2011) isolated and reported *Burkholderia* and *Streptomyces* species having the potential for demethylation of methylated As compounds. They found that demethylation of monomethylarsonic acid to arsenite was carried out in two steps and could only be completely performed by a mixed culture instead of a single strain (Yoshinge et al. 2011). They also observed that demethylation did not inevitably follow the reverse path of methylation. Few researchers have also reported the anaerobic demethylation of DMAs(V) (Sierra-Alvarez et al. 2006). However, there is need to further investigate this process to explore complete pathways as well as the factors at molecular level which might be playing their role in demethylation.

### *18.4.6 Arsenic Volatilization by Bacteria*

Arsenic biovolatilization might serve as an effective way for mitigation of the hazardous effects of As against the living organisms in aquatic and terrestrial environments (Wang et al. 2014). Few microbial strains including bacteria, fungi and algae were reported to produce the As species which move to the atmosphere from the soil and water resources through volatilization (Jakob et al. 2010; Yin et al. 2011; Wang et al. 2014). According to an estimate, about $2.1 \times 10^7$ kg of As on the land is volatilized per annum (Srivastava et al. 2011; Wang et al. 2014). Therefore, the application of the potential As volatilizing organisms in natural environment including soil might serve as cost-effective friendly method of As bioremediation through its volatilization (Wang and Zhao 2009; Wang et al. 2014). However, it has been reported to be less effective for bioremediation because the lifetime of the most of the volatile As compounds in the atmosphere is relatively shorter due to their quick oxidation into water soluble forms (Wang et al. 2014). However, it has been reported that trimethylarsine is relatively stable volatile form of As which can stay and travel over a long period in the atmosphere (Cullen 2005; Mestrot et al. 2011; Wang et al. 2014). Hence, there is need to further explore the As volatilization process in the environment in order to promote its bioremediation from the As-contaminated environments.

## 18.5 Environmental Factors Affecting the Biotranformations of Arsenic by Bacteria

The diversity and performance of the As biotransformation by the bacterial strains has been observed to be affected by a number of factors including the As concentration, the amount of organic matter, pH, redox potential, alkalinity, dissolved oxygen, temperature and presence of different nutrients such Sulphur, nitrogen and iron etc. (Lizama et al. 2011; Huang et al. 2012; Jia et al. 2013; Zhang et al. 2016, 2017). For example, Zhang et al. (2016) reported that the abundance as well as the diversity of the As biotransforming microbes and genes is correlated with the concentration of the As in the paddy soil. Similarly, Jia et al. (2013) reported that the abundance of the *arsM* in the soil solution of a paddy soil was positively correlated with the concentration of methylated As indicating that As methylation is linked with the amount of As in the soil. Like the concentration of As, the amount as well as the form of organic matter also plays a key role in defining the bacterial biotransformations of As in the soil and aqueous media (Huang et al. 2012; Zhang et al. 2017). Several experiments conducted in microcosms have indicated that the addition of the organic matter in the soil resulted into a promotion of the bacterial As(III) oxidation (Huang et al. 2012). For example, Jia et al. (2013) reported that application of rice straw in the rhizosphere of a soil resulted into an increase in the community diversity of As(III) oxidizing bacteria. Similarly, the activity of the As(III) methylating bacteria in the soil and paddy rhizosphere was also found to be enhanced as result of addition of different organic matters (Huang et al. 2012; Jia et al. 2013). Huang et al. (2012) also demonstrated that the addition of straw in the soil considerable enhances the abundance of As(V) reducers and stimulates the activity of the As(V) reducing bacteria. Similarly, Yang et al. (2020) also reported the impacts of straw and its biochar on the microbial biotransformation of As in a paddy soil. Recently, Shen et al. (2022) studied the impact of tetracycline on mobilization and biotransformation of As in flooded soils. They observed that As(V) reduction as well as the abundance of As reducing genes in the soils were increased due to the presence of tetracycline. The presence of sulphate ($SO_4^{2-}$) in the soil has also been found to affect not only the composition of the microbial community but also the As(III) oxidation and As(V) reduction activities (Zhang et al. 2016, 2017). One of the possible reasons for these impacts of $SO_4^{2-}$ might be the sharing of the microbial groups of sulfur oxidation and As redox (Zhang et al. 2016). Zhang et al. (2016) also reported that the available nitrate and ammonium nitrogen are also among the dominant factors affecting not only the microbial communities but also the bacteria carrying out As(III) methylation. Like sulphate, the composition of the microbial communities involved in As biotransformation is also affected by the iron concentrations (Cummings et al. 1999; Xu et al. 2008; Zhang et al. 2017). The impacts of the iron might be due to the absorption/desorption dynamics of iron/oxyhydroxides and As(V) which affect the concentration and species of bioavailable As (Cummings et al. 1999; Xu et al. 2008).

pH is an important factor which affects not only the overall microbial communities but also the activity of several functional microbial populations including the As biotransforming bacterial communities (Dastidar and Wang 2009; Hussain et al. 2015; Zhang et al. 2017). Arsenite oxidation by the bacterial strains has been found to be conducted over a diverse range of pH values depending on the forms of As. For example, few species of bacteria such as *Sulfolobus acidocaldarius* and *Thiomonas arsenivorans* were found to carry out the oxidation of As(III) at low pH ($\leq 4$) (Sehlin and Lindström 1992; Dastidar and Wang 2009). However, the most of the oxidizing bacteria carry out the oxidation of As(III) ranging near the neutral pH value (Suttigarn and Wang 2005; Zhang et al. 2017). For example, *Stenotrophomonas* sp. MM-7 was found to carry out the optimal As(III) oxidation at pH values ranging between 5 and 7 (Suttigarn and Wang 2005; Zhang et al. 2017). The optimal pH for oxidizing As(III) by the bacterial strain *Alcaligenes faecalis* strain O1201 was reported to be 7.0 (Suttigarn and Wang 2005). However, the optimal pH for oxidation of As(III) by the bacterial strain *T. arsenivorans* strain b6 was reported to be 6.0 (Dastidar and Wang 2009). Battaglia-Brunet et al. (2002) reported an autotrophic population CASO1 for oxidation of As(III) for carrying out substantial oxidation of As(III) between the pH values of 3.0–8.0. All these findings suggest that adjustment of pH is necessarily required to achieve the optimal biotransformations of As in the environment. Despite that many other factors such as redox potential, temperature and dissolved oxygen also affect the biotransformations of As in the environment, there is a lack of sufficient knowledge regarding the impacts of these factors (Lizama et al. 2011; Zhang et al. 2017). Hence there is need to conduct further studies with this focus.

## 18.6 Applications of Bacteria for Bioremediation of Arsenic in Soil and Water

Despite that several studies have been conducting for exploring the processes of biotranformations of As including methylation, demthylation, As(III) oxidation and As(V) reduction by the environmental bacterial strains, there are few studies reporting the applications of such functional bacterial strains for removal of As from the soil and water resources. Some of the applications of bacteria for removal of As from the soil and water resources have been summarized below.

### *18.6.1 Removal from Water*

There are different ways for removal of As from the water, however, many studies report As(III) oxidation through bacteria as an important step for enhancing the As adsorption from the water (Yamamura and Amachi 2014; Biswas et al. 2019). For example, Ike et al. (2008) reported that As adsorption by activated alumina from a water sample was significantly enhanced when it was inoculated with an As(III) oxidizing enrichment culture comprising of *Haemophilus* spp., *Micrococcus* spp. and *Bacillus* spp. Similarly, Andrianisa et al. (2008) indicated that the removal of As through coprecipitation by ferric hydroxide in an effluent sample was observed to be significantly enhanced when it was inoculated with an As(III) oxidizing activated sludge having the As(III) oxidizing bacteria. Likewise, Ito et al. (2012) used immobilized aerobic As(III)-oxidizing bacteria as a pretreatment in a continuous bioreactor in order to remove As from a groundwater sample. Like aerobic As(III) oxidizing bacteria, different anaerobic oxidizers have also been reported to be applied for oxidation of As(III) followed by its removal through adsorption. For example, Sun et al. (2010a, b) reported that adsorption and immobilization of As by activated alumina in continuous bioreactors was significantly enhanced as a result of As(III) oxidation by inoculated oxidizing denitrifying granular biofilms. Similarly, Sun et al. (2009) reported the concurrent oxidation of As(III) and Fe(II) associated with denitrification in a continuous flow sand columns which was inoculated with denitrifying sludge having the potential for oxidation of As(III) resulting into an enhanced As immobilization in the column. Recently, Biswas et al. (2019) reported the bioremediation of As from a ground water sample by employing an As(III) oxidizing strain followed by adsorption through a biosorbent of *Moringa oleifera.*

In addition to As(III) oxidation, As(V) reduction can also be employed for removal of As from the aqueous media but under more reducing conditions (Yamamura and Amachi 2014). It is preferred because As(III) can be precipitated with sulfide under the reducing conditions (Chung et al. 2006; Yamamura and Amachi 2014). For example, different studies focused on the bioreactors for As removal have indicated the production of As sulfides along with concurrent decrease in As levels as a result of As(V) and sulfate reduction by microbes including bacteria (Chung et al. 2006; Upadhyaya et al. 2010). Furthermore, Upadhyaya et al. (2010) reported the concurrent remediation of nitrate and As from a synthetic groundwater using a fixed-bed bioreactor system consisting of two consecutive columns. In this bioreactor system, removal of nitrate was mainly observed in the first column and As was mainly immobilized in the subsequent column through As sulfide precipitation and surface precipitation on iron sulfides.

### *18.6.2 Removal from Soil*

Like water resources, application of As biotransforming bacteria has also been reported for remediation of As from the soil resources (Zobrist et al. 2000; Islam et al. 2004; Yamamura et al. 2005, 2008; Lee et al. 2009; Soda et al. 2009; Kudo et al. 2013; Ohtsuka et al. 2013; Yamamura and Amachi 2014). In As contaminated soils, As often exists as As(V) (Cances et al. 2005). However, it is much sorbed on the soil solid surfaces (Yamamura and Amachi 2014). Therefore, one of the primary step required for the remediation of As contaminated soils is to reduce the As(V) into

As(III) resulting into the release of less adsorptive As(III) from the soil solid phase to soil aqueous phase (Yamamura and Amachi 2014). Hence, the As(V) reducing bacterial strains are often applied for this purpose in order to remediate As from the contaminated soils (Zobrist et al. 2000; Islam et al. 2004; Yamamura et al. 2005; Kudo et al. 2013; Ohtsuka et al. 2013; Yamamura and Amachi 2014). However, the applicability of microbial As mobilization to bioremediation is largely unknown because most studies conducted to date have focused on biogeochemical aspects. For example, Yamamura et al. (2008) reported the remediation of As from two contaminated soils through reductive dissolution of As(V) by a dissimilatory As(V) reducing bacterial strain *B. selenatarsenatis* SF-1. In parallel to As(V) reduction, this strain had also the potential to reduce Fe(III). In this study, about 56% and 40% of As was found to be removed from the soils having 250 and 2400 mg $kg^{-1}$ of As, respectively. Similarly, Soda et al. (2009) reported the application of a dissimilatory As(V) reducing bacterium for remediation of an As contaminated soil in a slurry bioreactor through reductive dissolution of As(V). They also developed a mathematical model for understanding and predicting As dissolution in soils.

Lee et al. (2009) reported that stimulation of the indigenous As(V) reducing bacteria by addition of organic carbon in an As contaminated soil resulted into the reductive dissolution of As in batch- and column-type bioleaching reactors. This reductive dissolution was followed by an electrokinetic treatment which resulted into an enhanced removal (67%) of As from a soil highly contaminated with As (>4023 mg $Kg^{-1}$ of As). As the soil replacement, containment, and solidification/stabilization have been previously reported to exist as the main mechanisms for remediation of As contaminated soils, therefore, the application of dissimilatory As(V) reducing bacterial for reductive dissolution of As in the soil might be exploited as a novel bioremediation strategy for As removal from soils.

## 18.7 Conclusions and Future Perspectives

The contents of this book chapter clearly indicate that the mobility as well as the toxicity of As in the environment including soil and aquatic resources is significantly influenced by the microbial biotransformation processes. Important role of several bacterial strains involved in various biotransformations of As along with the dominant mechanisms for these biotransformations has been described in this study. These mechanisms can be exploited to devise effective strategies for remediation of As from the soil and aquatic resources. An important role of Fe(III) reducing bacteria in reduction of As(V) has also been described in this study. The Fe(III) reducing and Fe(II) oxidizing potentials of bacteria for biotransformations of dominant As species can be exploited for mobilization and detoxification of As in aqueous as well as soil environment. However, there is need to conduct further studies to explore the potential of various functional As bio transforming bacterial strains by applying them in real water and soil resources in natural environment because the most of the findings have been reported on the basis of laboratory studies under controlled conditions.

There is also need to further explore the processes underlying the bacterial biotransformations of As by comprehensive molecular characterization through mapping the genes involved in As biotransformations. There is also need to deeply explore the impacts of different environmental factors as well as different other organic and inorganic components present in the environment on the bacterial biotransformations of As in the environment.

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# Chapter 19
# Arsenic Bioremediation of Soil and Water Systems—An Overview

**Muhammad Shabaan, Kashiuf Asif, Qasim Ali, Hafiz Naeem Asghar, and Zahir Ahmad Zahir**

**Abstract** Arsenic (As) contamination of ground water and soil has become a global issue by virtue of its carcinogenicity and toxicity to human and animal health, and is related to both geogenic and anthropogenic sources. Exposure to As occurs primarily by the consumption of contaminated drinking water or food. Its dissolution as a result of redox reactions leads to natural prevalence of As in ground water. Several countries have reported the presence of As in drinking water beyond threshold limits such as India, Bangladesh, Mexico, Thailand and Chile, etc. Its toxicity results in the prostate, lung and skin cancer, skin lesions, rhagades, mitochondrial damage, and may interrupt the DNA repair system. Conventional physicochemical techniques for As remediation are costly and generate toxic products. However, bioremediation technique involving the use of microorganisms, plants or genetically modified organisms, etc. can be efficiently opted as a sustainable and cost-effective technology. Microorganisms evolve several mechanisms such as As oxidation or reduction, methylation or intracellular bioaccumulation in stressed environments. This chapter reviews the possible roles offered by the microorganism in the effective remediation of As from soil–water systems. Moreover, various advancements in the field of bioremediation have been discussed. Different challenges to microorganism-based remediation technologies are also explained.

**Keywords** Arsenic · Physicochemical approaches · Bioremediation · Phytobial remediation · Phytosuction separation

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## 19.1 Introduction

Arsenic (As) pollution has been recognized as one of the most significant environmental contaminants because of multiple anthropogenic activities, and numerous institutions have reported regarding its toxicity and remediation including various industries, environmental groups as well as the general public (Alka et al. 2021). It is the 20th highest metalloid found naturally in the earth crust and is generally recognized for causing adversity on human and marine animals (Yin et al. 2017). Moreover, World Health Organization (WHO) has classified arsenic (As) as Class I carcinogen, as it is closely associated with the cancerization of numerous organs including skin, bladder, lung and kidney (Lindsay and Maathius 2017). Most of the As related concerns arise from anthropogenic activities and resultant contamination leads millions of individuals to life menacing situations by drinking the poisoned water as well as consuming the foods produced on As contaminated soils. Its contamination has been noted as the 21st century devastation by several researchers and scientific authorities (Hare et al. 2019; da Silva et al. 2019). Arsenic exists in nature in numerous oxidation states i.e., $3^-$, 0, $3^+$ and $5^+$ as well as in many organic and inorganic forms (Palma-Lara et al. 2020) due to different reasons i.e., human and microbial activities as well as volcanic eruption, rock weathering (Villaescusa and Bollinger 2008; Verma et al. 2018), mining, consumption of agrochemicals (fertilizers and pesticides) and fuel consumption. Its exposure to human beings occurs via numerous pathways including air, water, food and soil (Khan et al. 2020), the exposure pathways vary region wise, and depend highly on the geological compositions of the aquifers as well as activities of residents such as drinking groundwater (Liang et al. 2016; Alam et al. 2016) or ingesting the As contaminated fish and shellfish (Liang et al. 2011). Based on the recommendations given by the WHO, the permissible limit of As in drinking water is $10\ \mu g\ L^{-1}$ (Tariq et al. 2019; Zacarías-Estrada et al. 2020). Generally, people suffer from As contamination via food as well as drinking water (Lindberg et al. 2006; Kabiraj et al. 2022). Its accumulation in the soil and water leads to serious health hazards in humans (Verma et al. 2018; Abad-Valle et al. 2018). In recent times, health concerns related to As exposure have gained considerable attention in different countries (Singh et al. 2015a, b; Osuna-Martínez et al. 2020). Various epidemiological studies have reported the adverse impacts of chronic As exposure to different body systems e.g., reproductive system, respiratory system, circulatory system and immune system (Jain and Ali 2000). Nearly, 13 million people in Pakistan belonging to 27 major districts are susceptible to As contamination due to the consumption of contaminated water for drinking, and more threats are being observed by those populations residing along the Indus river (Rabbani et al. 2017; Ali et al. 2019). The As contamination may arise naturally or anthropogenically (Smedley 2008; Farooq et al. 2016). In Chakwal and Jhelum cities (Punjab province), geothermal sources and coal mining activities contribute towards As contamination whereas, in Tharparkar district (Sindh), complicated geological structure as well as arid climate result in As contamination in the ground water via favoring the reductive dissolution of minerals containing As (Brahman et al. 2013).

### *19.1.1 Arsenic (As) in Soil–Water System*

Various countries of the world, including China, Bangladesh, USA and India, have reported dangerous levels of As in drinking water and consequent human exposure (Hoover et al. 2017; Li et al. 2018; Wasserman et al. 2018; Chatterjee et al. 2018). On a global scale, reports about the natural contamination of drinking water with As are available for more than 70 countries, and majority of these countries lie in the South Asian to Southeast Asian regions (Ravenscroft et al. 2011). Several biogeochemical processes (adsorption/desorption, volatilization, methylation/demethylation, or precipitation) caused either microbially/algally or chemically, may accelerate As mobilisation, resulting in a massive increase in As content in water bodies (Drewniak and Sklodowska 2013). The concentration of As in water varies from one water to the next, as various researchers have discovered. Welch et al. (1988) found that the concentration of As in the ocean is between 0.15 and 6 g $L^{-1}$, but Chapell et al. (2001) found it to be between 1–2 g $L^{-1}$. The freshwater As concentrations can vary from 100–1000 μg $L^{-1}$ of water (Mandal and Suzuki 2002; Barringer and Reilly 2013). Similar to other countries, Pakistan is also facing the issue of water scarcity as well as contamination in the available water supply (Ali et al. 2019). Rehman et al. (2019) performed a systematic field study to investigate the drinking water for total As concentrations, its organic (monomethylarsonic acid and dimethylarsenic acid) and inorganic species (arsenate and arsenite) in the KPK province of Pakistan. They reported total As concentrations ranged from 1.2 to 23 times in 28% of samples collected from Dera Ismail Khan and Lakki Marwat, exceeding WHO standards for drinking water and inorganic As species. Most of the Pakistan's area is located in the arid to semi-arid climate where the average annual rainfall is below 200 mm and the availability of groundwater is scarce (Salma et al. 2012; Alamgir et al. 2016). Alarming levels of As in the ground as well as surface water resources of Pakistan have been found (PSQCA 2017). Major groundwater resources of Pakistan include the irrigated areas of Indus basin. Since most of the Pakistani people use ground water for drinking as well as other household purposes, As contamination of ground water renders more than 50 million people at higher risks of poisoning (Podgorski et al. 2017).

The mineralogical characteristics of the aquifer contribute greatly towards the concentration of As in ground water which can release As upon weathering. The extent of weathering is regulated by the physical and chemical characteristics of the groundwater as it is essential for aquifer weathering. Geothermal activity can sometimes contribute to As pollution in ground water because oxidized forms of As may be found in groundwater in many regions of the world, it is clear that the processes of As dissolution are not caused by the reduction of As-rich iron minerals, but rather by the oxidation of As-rich materials (Sarkar and Paul 2016). Because As comprises, alongside other elements such as antimony (Sb), boron (B), selenium (Se), lithium (Li) and mercury (Hg) comprises a distinct group that does not fit easily within the network of common rock minerals (Barringer and Reilly 2013). The As is the most problematic oxyanion forming element that is easily available over a broad range of redox circumstances without getting immobilized.

## 19.2 Remediation Measures

### *19.2.1 Physicochemical Methods*

Incessant consumption of As-rich ground water leads to various kinds of chronic diseases i.e., keratosis, pigmentation, black-foot disease, nausea and cancer as well where inorganic As compounds are relatively more lethal as compared to the inorganic compounds. Among the organic compounds, methylated arsenic acids are believed to have demonstrated carcinogenic effects in humans. In this regard, scientists as well as researchers are exploring new ways to alleviate this issue. Several measures have been undergone for treating the As contamination such as activated carbon (C), via chemicals, reverse osmosis as well as nanomaterials via adsorption, etc. (Sarkar and Paul 2016). The conventional As remedial measures are mainly the physicochemical techniques. Adsorption, coagulation-precipitation, membrane filtration, ion exchange, reverse osmosis, and permeable reactive techniques are only a few examples. Every treatment technique uses the adsorption, coagulation-precipitation and oxidation–reduction principles, followed by filtering. Prior to treating the aqueous As, a pre-oxidation process is generally preferred as As (III) species usually prevail at drinking water pH and cannot be easily removed as compared to the As (V) species (Malik et al. 2009) and for this purpose, different methods such as aeration, ozonation, oxidation is frequently carried by using potassium permanganate or hydrogen peroxide, UV rays or chlorination (Litter et al. 2010).

#### 19.2.1.1 Coagulation-Precipitation and Filtration

Coagulation followed by flocculation has been found useful for the effective extraction of As (particularly arsenite) from soil–water system (Ge et al. 2020). It does not require the comprehensive pre-treatment, preparation of the wastewater or use of non-manufactured chemicals (Cheng et al. 1994). Rather, the pre-requisite for the process include pre-oxidation and pH corrections. Transformation of dissolved As to globules occurs after adding the cationic coagulants, which nullify the negative charges present on the surface of colloidal particles. Resultantly, colloids accumulate into larger sized particles followed by their precipitation into flocs which are easily isolated by filtration. This method in turn, improves the quality of the water by allowing the separation of suspended particles, poisonous compounds along with As (Mohanty 2017; Wang et al. 2021a, 2021b, 2021c). Ferric chloride and alum have been long accepted as efficient chemical coagulants for removing As (Inam et al. 2021). It is a simple, straightforward, and successful approach for separating charged particles from liquids including the formation of a stable colloidal particle for floc accumulation and resultantly, extraction is preferred. Uniform incorporation of the coagulant into the As contaminated water is desirable for achieving maximum As extraction efficacy. Water insoluble As substances such as arsenate are removed by the resultant gelatinous precipitates (Mohindru et al. 2017). Important coagulants include titanium sulfate, zirconium (IV) chloride, titanium (III)/titanium (IV) chloride, titanium (IV) oxy-chloride and zirconium (IV) oxychloride etc.

#### 19.2.1.2 Adsorption

Adsorption is a useful process for decreasing the arsenic concentration from the environment (Gulledge and O'Connor 1993). Using the activated C is costly as there are recovery issues which limits its use in the developing nations (Ochedi et al. 2020; Rodríguez-Romero et al., 2020).Which has increased the demand for low cost efficient adsorbing materials, with greater adsorption abilities as well as commercial availability (Kumar et al. 2013; Subburaj and Kumar 2020; Sivaranjanee and Kumar 2021). Guan et al. (2012) reported the removal of natural as well as inorganic As by using the titanium dioxide ($TiO_2$) and related products. To date, photocatalytic oxidation of arsenite to arsenate as well as chemisorption of As (organic and inorganic) seems to be the focus of As extraction methods involving $TiO_2$. Moreover, Fe-based nanoparticles have shown higher potential for As adsorption particularly at pH close to neutral. Most fascinating attribute of the Fe based nanomaterials is the extent of ease in their magnetism-based removal from the faded medium (Nikić et al., 2020). Similarly, biochar is a safe, cost-limiting and long-lasting and has shown phenomenal potential to remove toxic substances from water including As. However, revival of biochar and As recovery from biochar are still a mystery which needs to be resolved before the extensive application of biochar for the remedial purpose. It is indeed very critical to implement the most suited technique for post adsorption processing of used biochar (Amen et al. 2020).

In contrast to the conventional sorbent materials, modern synthetic materials i.e., graphene oxide, organic metal frameworks, nanotubes and related materials have shown great tendency to replace traditional materials owing to their tremendous As removal potential as demonstrated by improved reuse and higher partitioning co-efficient (Liu et al. 2020a, 2020b). Similarly, another form of dual hydroxide, hydrotalcites, has proved to be an effective adsorbent material for the smooth recovery of As contaminated water. However, determination of remaining arsenite intensity in the optimum solution after using hydrotalcites still remains challenging and demands further attention (Dias and Fontes 2020).

#### 19.2.1.3 Membrane Based Remedial Methods

Membranes based methods for the extraction of arsenic has replaced other conventional techniques as they do not generate solid by-products unlike in other methods (Kartinen and Martin 1995). Membranes possess distinctive surface morphology such as permeability, pore size, harshness, hydrophobicity, width, segregation and harshness on account of their physicochemical attributes. They should reveal following properties (a) chemical and mechanical opposition, (b) long reliability, (c) high specificity and permeability and (d) low price. Moreover, all the membrane comprising technologies generate a concentrated stream from where, the ions are restored (Moreira et al. 2020). Membrane based procedures encompass several ways to reduce As. The As species are too small to pass through the membrane hence, ultrafiltration and microfiltration may not allow for the immediate removal. Govindappa et al. (2022) developed a novel polymer inclusion membrane (PIM) for the extraction of arsenic (As) from water. The PIM is among one of the best substituents to solvent extraction process with additional advantages such as considerably less solvent, extractant, economical and cost-effective even for large scale industrial processes. They concluded that the developed PIM permitted the transport of As (V) at higher concentrations for different natural waters spiked with 100 mg $L^{-1}$ As (V). Moreover, they confirmed that low-cost novel PIM device can be used in metal industries to extract arsenate from contaminated water with greater efficacy. Nano filtration membranes and Reverse osmosis (RO) have also been reported to separate As species from groundwater in numerous working conditions. Nanofiltration is typically used for removing the divalent cations however, it can also remove As (III) and As (V) species predominantly by size omission (Siddique et al., 2020; Worou et al., 2021).

#### 19.2.1.4 Ion Exchange

Ions exchange phenomenon involves the active replacement of electrostatically held ions on the solid phase by the ions present in the solution phase having uniform charge (Katsoyiannis and Zouboulis 2006) and used to remove various pollutants including arsenic (As). It is used to lessen the hardness of water and to extract different contaminants i.e., chromate, selenite, arsenate and nitrite anions in the waste water. Regularly synthesized resins are used and waste water passes from them recycling and reinforcing the exchanges ions (Al-Jubouri and Holmes 2020). Ion exchange predominantly remove arsenate from the waste water owing to the presence of negative charge (Jadhav et al. 2015). Total dissolved solids (TDS) interfere with the efficacy of As removal during the exchange process (Jadhav et al. 2015). Specific ion exchange resins have been recommended by the U.S. Environmental Protection Agency (EPA) particularly chloride ions for As removal. Factors determining the efficiency of ion exchange resins induced As removal are type of resins, total dissolved salts (TDS), arsenic concentration, high sulfate salts and competing ions (Sarkar and Paul 2016). Limited reports exist in literature regarding the use of ion exchange for As removal (Dong 2019).

#### 19.2.1.5 Electrokinetic Technique

The Electrokinetic approach is a promising, effective and emerging technology for removing the free pollutants from soil (Li et al. 2020a, 2020b). It implies the removal mechanism comprising the movement as well as transport of various pollutants in the soil under the influence of an electric field such as electromigration, electrophoresis, electroosmotic flow and water electrolysis (Xu et al. 2019). Electrokinetic method for the removal of arsenic (As) has also been evaluated (Weng et al. 2009; Yang et al. 2016). The approach faces limitation during the As removal because it is difficult to be treated in its dissolved phase however, its efficiency can be remarkably enhanced and it can be made economically viable by coupling with other removal techniques (Li et al. 2020a, 2020b). Yuan and Chiang (2007) performed a study, where they used an electrokinetic process coupled with a permeable reaction barrier (PRB) in a soil matrix to remove As. Moreover, the efficacy of electrokinetic technique can also be significantly improved by combining with a permeable reactive barrier such as activated carbon (Zhao et al. 2016), hydrous ferric hydroxide (Yuan and Chiang 2007), carbon nanotubes, atomizing slag (Chung and Lee 2007). A brief summary of the As-remediation efficacy of different physiochemical approaches used by researchers has been illustrated in Table 19.1. The physicochemical methods have several limitations which hinder their excessive application on a larger scale such as generation of toxic sludge, high operational and maintenance cost, decreased efficiency under natural conditions and operational difficulties, etc. (Srivastava and Dwivedi 2015). In contrast to that, bioremediation does not involve such limitations and can be used for the efficient removal of As from the environment (Rahman and Singh 2020). Various researchers have reported the beneficial impacts of using various bioremediation approaches for As removal i.e., phytoremediation (Yang et al. 2018), remediation using bacterial species (Taran et al. 2019), phytobial remediation approach involving the application of biological agents (bacteria and plants) in integration with genetic engineering techniques (Irshad et al. 2020; Moens et al. 2020; Banerjee et al. 2020), fungal bioremediation (Tripathi et al. 2020), phytosuction separation approach (PS-S; Arita and Katoh 2018) and biosorption by using microbial cells (Podder and Majumder 2018), etc. Despite the ongoing extensive research, bioremediation of As is still limited to laboratory or pilot scale trials and its practical and field implications still require laborious and recurrent scientific researches.

### *19.2.2 Bioremediation Approaches*

#### 19.2.2.1 Phytoremediation

Phytoremediation has gained much importance as an important, promising, cost-effective and eco friendly technique for As clean up from the contaminated environments (Budzyńska et al. 2017; Lei et al. 2018). Many researchers have found that As hyperaccumulators provide most effective, eco-friendly and low-cost solution

**Table 19.1** Summary of various physicochemical techniques to remove arsenic from different medium

| Method | Types | Mechanisms | Removal efficiencies (%) | Medium | References |
|---|---|---|---|---|---|
| Ion exchange | Natural as well as synthetic resins | Exchange of ions from solid phase with those present in the solution phase | 97.9 | Water | Huang et al. 2015; Shakoor et al. 2017; Hu and Boyer 2018; Karakurt 2019 |
| Chemical precipitation | – | Forms separable solid precipitates from solution, precipitated materials get separated from solutions. For example, processed wastewater containing toxic substances | 95 | Water | Senn et al. 2018; Vega-Hernandez et al. 2019 |
| Surface adsorption | Biochar, activated carbon in granules form, magnetite nanoparticles, activated alumina, Iron coated sand | Using the solids to remove target contaminants from liquid or gaseous phase | 95 | Water and soil | Hao et al. 2018; Wang et al. 2018; Ghosal et al. 2018 |
| Electrokinetic process | – | Effective on contaminated soil (fine grained) | 90 | Water and soil | Yuan and Chiang 2008; Mao et al. 2016; Xu et al. 2019 |
| Electro-coagulation | Ferric sulfate (Fe $(SO_4)_3$),<br>ferric chloride ($FeCl_3$),<br>aluminum sulfate ($Al_2$ $(SO_4)_3$) | Application of current in between iron electrodes leads to the production of metal cations to liquify the soluble anodes in the treated waste<br>It is an alternative remedy to chemical precipitation technique | 99.9 | Water | Gomes et al. 2007; Song et al. 2017; Nidheesh and Singh 2017; Rosales et al. 2018; Gilhotra et al. 2018 |

(continued)

**Table 19.1** (continued)

| Method | Types | Mechanisms | Removal efficiencies (%) | Medium | References |
|---|---|---|---|---|---|
| Membrane based removal technology | Electrodialysis, reverse osmosis (RO), Nano-filtration, | Semi-permeable membrane only allows the movement of selective molecules via a driving force and generates large residual volume | 96 | Water | Ungureanu et al. 2015; Zakhar et al. 2018 |

for bioremediation via the bioaccumulation of As within the plant body (Kofroňová et al. 2019), phytovolatilization (Guarino et al. 2020) and phytoextraction (Lei et al. 2018). Phytoremediation is a green technology which employs plants for the cleaning process and is a cost-effective and environment friendly approach. There are two types of approaches which are commonly used for the remediation of contaminants from soils as well as wetlands i.e., natural and induced phytoremediation (Niazi et al. 2016). The use of genetically modified plants (GMOs) has also been proposed recently however, GMOs are currently facing the issue of restrictive legislation (Rahman et al. 2016). However, the phytoremediation process also bears some limitations in terms of climatic and geographic distributions as well as relative biomass content (Irshad et al. 2021). Moreover, different factors affect the efficiency of phytoremediation process. For example, pH is an important factor determining the solubility of different ions as well as their interactions. Similar is the case for As where increased soil pH lessens the solubility of arsenite and increases the solubility of arsenate. Hence, a reduction in pH will uplift the phytoavailability of arsenite (Fresno et al. 2016). Similarly, humic substances in the soil can adsorb arsenite on their surface, where maximum adsorption capacity is demonstrated at pH 5.5. The roots mediated oxidation and reduction of As owing to the pH alterations perform a keen part in As immobilization. So, the remediation of As is a multifactorial strategy where the optimization of each factor is inevitable to maximize the removal efficiency (Duan and Zhu 2018).

Another limitation of the phytoremediation is the sensitivity of the used plants towards soil chemical conditions as well as the level of As contamination (Yang et al. 2018). So, there is a need to explore an efficient, economical and practical solution. Moreover, the safe disposal of the harvested biomass after the completion of phytoremediation is also an issue (Irshad et al. 2021). In addition, there is a need to use the integrated approaches to enhance the phytoremediation efficiency such as microbe-assisted phytoremediation and phytosuction separation techniques. Various scientists have also emphasized on the combined application of microorganisms and plants to accelerate the phytoremediation process.

#### 19.2.2.2 Microbial Based Bioremediation

Bacteria

Bacteria use different mechanisms to mobilize, transform or bioremediate the As such as biosorption (Saba et al. 2019), redox reactions (Zhang et al. 2016; Bhakat et al. 2019), volatilization and methylation (Zhang et al. 2014), etc. Many As-resistant bacteria that can withstand elevated concentrations of As have been potentially used for the bioremediation of As from soil–water systems. Several systems exist in bacteria which aid in overcoming As toxicities such as arsenate (ars system), arsenite oxidation system (aio), anaerobic arsenate respiration system (arr) and arsenic methylation system (arsM). There could be multiple As resistance system operating in a single bacterium however, the most common is the ars system (Kumar et al. 2021). Saba et al. (2019) investigated the efficiency of extracellular polymeric substances (EPS) producing bacterial species for As bioremediation and correlated it with the EPS production potential of the bacteria. The EPS are complex high molecular weight substances that are released by microorganisms. They concluded that the presence of large number of polyanionic functional groups on the bacterial EPS can sequester As via covalent or electrostatic interactions. Bacterial mediated oxidation of As is mainly related to the catalytic activity of As (III) oxidase (periplasmic enzyme) and it is a major detoxification process usually carried out by the heterotrophic As-oxidizing bacteria (Rahman and Hassler 2014). Several prokaryotes have demonstrated the potential of As oxidation such as *Agrobacterium*, *Pseudomonas* and *Alcaligenes* (Ghosh et al. 2015). Biswas and Sarkar (2019) isolated two-gram positive bacteria from shallow aquifers and tested their As tolerance. One of the specie was found to be able to withstand 70 mM of arsenite and the other was tolerant against 1000 mM of arsenate. Both the strains exhibited tremendous potential to convert As (III) to less toxic As (V) from As enriched media. They reported that the As oxidizing bacteria can perform a keen role in the subsurface As transformation that can help in designing future bioremediation strategy. At the same time, some bacterial strains also cause the reduction of arsenic (Jebelli et al. 2017; Rios-Valenciana et al. 2020) and thereby, facilitate the transfer of As in the above-ground plant parts. The reduced form, As (III) predominates in the soil as compared to the oxidized form (As, V) as plant's ability to uptake As (III) depends on the competition with phosphate present in the soil which makes it difficult for the plant to remediate it (Alka et al. 2020).

Many bacterial species also use As (III) oxidase or As (V) reductase enzymes thereby, use As compounds as electron acceptors/donors and get their energy by metabolizing them (Rhine et al. 2007). Due to alarming increase in the As contamination, transgenic bacteria using genetic engineering techniques can also be used for ensuring As bioremediation. Various studies have evidenced regarding the effectiveness of using transgenic bacteria possessing the target genes responsible for increased As methylation as well as detoxification (Huang et al. 2015; Prum et al. 2018; Vezza et al. 2020). This strategy has also contributed towards decreased translocation followed by accumulation of As in food crops (Chen et al. 2013).

### Yeast and Fungi

Myco-remediation (using fungi to remediate contaminants) has emerged as one of the most promising and cost-effective approach for As detoxification (Tripathi et al. 2015) in plants and their beneficial role regarding the plant growth and survival under stressed conditions. Fungi have been extensively known for their widespread metabolic competence and the ability of their cell wall to bind metal (loid) ions owing to the presence of amino group and polysaccharides. Hence, isolation followed by enumeration of As tolerant fungal species from the contaminated sites could provide an inside into the fungal mediated As bioremediation (Singh et al. 2015a, b). Until now, numerous fungal species have been isolated from As contaminated sites such as *Trichoderma*, *Aspergillus*, *Fusarium* and *Penicillium* etc. (Caporale et al. 2014; Zeng et al. 2015; Govarthanan et al. 2018). The adaptation of fungi towards the contaminated sites might be due to their high surface area to volume ratio and different mechanisms of metal detoxification (Kapoor et al. 1999; Tripathi et al. 2020). Biomethylation of As by fungi via the enzyme based conversion of As into the volatile as well as non-volatile species and by using the S-adenosylmethionine and thiols offer a keen role in its biogeochemical cycling and detoxification. Govarthanan et al. (2019) examined the metal mineralization potential of calcite, microbially induced precipitate using *Trichoderma* in remediating the As contaminated soils. The fungus was found to tolerate 500 mg $L^{-1}$ of As. The effect of three different factors on the bio-mineralization of As was checked i.e., $CaCl_2$ concentration, urea concentration and the pH. Their results revealed the formation of metal-carbonates by the *Trichoderma* species and carbonate fraction of As was found to be uplifted by 46% in the bioremediated site as compared to the control (35.5%). The X-ray diffraction indicated the potential of calcite precipitate in bioremediating the As contaminated soil. They concluded that microbially induced calcite can have promising effects on the remediation of As from the contaminated sites.

Yeast is a unicellular fungus that can proliferate easily and are able to adapt to various environmental niches (Mukherjee and Sen 2015). They also exhibit the bioremediation capacity against certain contaminants (Khan et al. 2016; Ilyas and Rehman 2018). Bobrowicz et al. (1997) reported the presence of fragment of 4.2 kb on the chromosome XVI and its contribution in conferring resistance against sodium arsenate (7 mM). They further explained that in yeasts, three genes are present in a continuous manner ($ACR_1$, $ACR_2$ and $ACR_3$) which exhibit resistance against arsenic compounds. Two proteins are present in the As-ATPase efflux pump namely ArsA and ArsB, in which ArsA possesses the catalytic activity and ArsB has inner membrane protein (Rosen et al. 1988). Similarly, another protein, ArsC displays reductase activity and transforms As (V) to As (III), which is then, released to the outer environment through As efflux pump (Sher and Rehman 2019). Verma et al. (2019) assessed the potential application of yeast as a plant growth promoting agent to stimulate rice growth. Under As stress, the transgenic yeast species *Saccharomyces cerevisiae* harboring the *WaarsM* gene demonstrated an increased As methylation followed by volatilization activity under As stress. Moreover, the rice seedling coated with yeast showed high seedling vigor index in comparison with the control. They concluded that As volatilization form the contaminated sites is possible with the help of yeast and it could be effectively used as an instrumental agent for reducing As contents from the soil water system.

### Algal Bioremediation

Few reports are also available regarding the As methylation by algae (Jia et al. 2015) which uses several detoxification pathways for As (Upadhyay et al. 2018) and hence, convert As (III) into less toxic and mess mobile form As (V) (Jia et al. 2013). The cell wall of algae possesses several functional groups i.e., carbonyl, hydroxyl (-OH), carboxyl (-COOH), thiol (-SH) and amino which possess the tendency to adsorb metal(loid)s including the As oxyanions from water (Wang et al. 2015). Many algal species can cause a rapid absorption of As from the aqueous media and hence, plays a key role in its detoxification (Jiang et al. 2011). Among these species, red algae (*Gracilaria*, *Porphyra* and *Ceramium*), brown algae (*Dictyopteris*, *Eisenia* and *Cystoseira*), green algae (*Ulva* and *Caulerpa*) and seagrass (Zostera) have exhibited tremendous capacity to adsorb As with the maximum adsorption capacity (1.3 ± 0.1 mg $g^{-1}$) achieved by sea grass and red alga (Ceramium; Pennesi et al. 2012). In algae, the biotransformation of As starts with the uptake of As (V), which is then, reduced to As (III) followed by subsequent formation of methylated species (Wang et al. 2015). Earlier studies have reported about the phosphate independent uptake of As (V) by algae which further depicted that more As (V) uptake pathways prevail in algae in addition to As uptake via the phosphate channels (Duncan et al. 2014). The As transformation pathways in algae are influenced by different factors such as concentration and species of As, composition of the growth medium (Wurl et al. 2013), pH, temperature, Eh (Murray et al. 2003), duration of light exposure as well as intensity (Zhang et al. 2013) etc. Moreover, phosphate presence in water is of critical importance as it can also affect As uptake by algae. Algal mediated As sorption has a tremendous potential in As bioremediation in aquatic system due to its environment friendly nature and high removal efficiency (Hussain et al. 2021).

### Phytobial Remediation

This approach uses the plant microbe interactions and assists the phytoremediation process and thereby, plays a critical role in the plant survival, growth and development under contaminated sites. It helps the plants by conferring stress resistance, favoring nutrient acquisition and supplying different phytohormones (Kaur et al. 2018). Remediation by exploiting the plant–microbe interactions for As removal has been extensively reported in the literature (Liang et al. 2019; Irshad et al. 2020). Few reports are available where the As remediation by the plants was increased in presence of transgenic bacteria that were harboring As degradation genes. However, this treatment still faces certain limitations in lieu of the efficacious application of transgenic bacterial strains (Liu et al. 2019). Irshad et al. (2020) investigated the symbiotic relationship between indigenous *Bacillus* specie and As-hyperaccumulator named *Vallisneria denseserrulata* to remove As. They found that the native bacterial specie was able to excrete higher quantities of EPS, siderophore and indole acetic acid (IAA) and thereby, reduced As toxicity to the plants. The synergetic relationship exhibited more As uptake and removal potential. They further reported that the As detoxification was attributed to the presence of various carboxyl, amide, hydroxyl and thiol groups as well as the prevalence of an As metabolizing process in the plant leaves.

### Phytosuction Separation

Phytosuction separation (PS-S) is a relatively modern technique for reducing the heavy metals or metalloids concentration from the soil. Current method involves two soil types: a planting soil without any metal(loid) followed by a heavy metal(loid) contaminated base soil present in the bottom and these soils are separated by an immobilizing material. In the As remediation study, ferrihydrite has been used as an immobilization material. Plants are grown on the planted soil and irrigation water is applied as recommended. In response to the applied irrigation, plant roots suck the water which then take up the dissolved heavy metal(loid) present in the bottom soil due to water suction effect of the roots, and the contaminant is held by the above lying immobilization material (Katoh et al. 2016). Arita and Katoh (2018) used ferrihydrite as an immobilization material and applied in the As contaminated soil. They compared the efficiency of PS-S system with that of phytoextraction (PE). Their results indicated that PS-S system holds greater tendency to remove As than PE and its efficiency increases with an increase in the depth of the soil (even less than 0.5 cm soil layer), indicating the efficacy of PS-S system in the shallow soil layers. Nearly 38% of the As was removed from the soil which was observed to be 54% more than PE technique. Positive growth regulating microbes might improve the effectiveness of this technique by facilitating the supply of proper nutrients towards the plants. It has also been shown that the metal(loids) existing particularly in the form of oxyanions are more prone to be removed by the PS-S system as compared to those existing as cations. This technique has also shown promising results during the phytoremediation of lead (Pb) and antimony (Sb) with removal efficiencies ranging from 8–25 and 69–533 times respectively as compared to the phytoextraction process. Main factors during the smooth running of the OS-S system are mobility of the target metal(loids) under consideration.

### Arsenotrophy

Despite its toxicity, As is also used by several microbial species to harvest their metabolic energy needs rather then its detoxification. Their metabolic activities comprise As oxidation as well as reduction via electron transfer for using it as food or respiration (Amend et al. 2014). The process is termed as arsenotrophy (Oremlan et al.

2009) and the related microbes are termed as arsenotrophs (Stuckey et al. 2015) which are known for their tremendous role in the biogeochemical cycling of As. During the arsenotrophy process, microbes solubilize the As from sediments followed by the reductive transformation of As (V) to As (III). The exposition of microbial processes determines their effectiveness to remove As from the contaminated sites. They are known to stimulate the oxidation of different organic compounds such as lactate, acetate, malate, pyruvate, ethanol and glycerol by reducing As in anaerobic conditions (Stolz and Oremland 1999; Anand et al. 2022). Moreover, arsenotrophy has been termed as redox reactions of As related to the phototrophic or respiratory processes via the transfer of electrons to/from As for energy (Silver and Phung 2005). Three different types of enzymes are responsible for catalyzing this process in prokaryotes viz. AioA, ArxA and ArrA (Andres and Bertin 2016). Most of the arsenotrophic pathways have been identified in chemoautotrophs however, anoxygenic photosynthesis, a light dependent pathway involving As (III) as an electron donor was first identified in *Ectothiorhodospira* species (Budinoff and Hollibaugh 2008). Various researchers have reported regarding the microbially mediated arsenotrophic reactions of As transformation. Uhrynowski et al. (2017) used an indigenous arsenotrophic bacterium *Aeromonas* sp. and investigated its transformation potential for As. They reported that *Aeromonas* is a facultative anaerobe which can utilize arsenate as a substrate to carry out its respiration and lactate, citrate and acetate as electron donor. The introduced strain exhibited considerable resistance against As and other heavy metals and the As reduction was observed to be initiated after 24 h. The strain exhibited increased production of biofilm which was found to be responsible for the entrapment of dissolved arsenic species as well as other toxic elements. In addition, several studies have evidenced about the enrichment of As contaminated groundwater with numerous arsenotrophic bacteria (Sanyal et al. 2016) Table 19.2.

## 19.3 Concluding Remarks

The problem of arsenic contamination has dramatically increased in the recent times owing to the enhanced global pollution. Different limitations related to the conventional physicochemical approaches imply that in the present times, bioremediation approaches are the most widely accepted, eco-friendly and sustainable techniques to tackle As contamination. With advancements and further experimentations, more perfection and practical outcomes are expected. However, few things need to be addressed to proceed with clear understandings. More comprehensive knowledge is required to clearly understand the mechanisms of bacterial mediated As oxidation. Advancements in the use of transgenic organisms (plants or microbes) can discover new interventions in using As for the bio-energy systems and microbial fuel cells applications. Moreover, the fate of the harvested plants after the successful completion of phytoremediation (phytoextraction) process is still a challenge. Pyrolysis, bio-gasification and composting could assist in this regard. In addition, cost–benefit

**Table 19.2** Summary of different bioremediation techniques for As removal from soil–water system

| Method | Plant/microbial species | Results | Medium | References |
|---|---|---|---|---|
| Phytoremediation | *Lemna valdiviana* Phil | Plants were able to accumulate 1190 mg $kg^{-1}$ of As (dry weight) from aqueous media and reduce 82% of their initial concentration | Water | de Souza et al. 2019 |
| Phytobial remediation using fungi | AMF *Glomus mosseae* in *Medicago sativa* | Fungal colonization significantly increased the phosphorous (P) and arsenic (As) contents in plants with a concomitant increment in the plant growth attributes | Soil | Chen et al. 2007 |
| Phytobial bioremediation with bacteria | *Pseudomonas* sp. in *Glycine max* | Inoculation with the bacterial species resulted in a tremendous improvement in the soybean growth under $As^{3+}/As^{5+}$ treatment | Soil | Oller et al. 2020 |
| Phytoremediation | *Pteris vittata* | Presence of As-transporters such as PvACR3, PvACR3;1 and PvTIP4;1 along with As tolerance result in efficient removal of As from the medium | Soil | Vandana et al. 2020 |
| Bacterial biosorption | *Pseudomonas aeruginosa* | 98% removal efficiency of As from groundwater was observed | Water | Tariq et al. 2018 |
| Phytoremediation | *Neptunia oleracea* | The plant exhibited nearly 30 ppm tolerance against As with maximum As removal as well as accumulation was observed ranging from 30–60 ppm | Water | Atabaki et al. 2020 |
| Phytobial bioremediation with bacteria | *Pseudomonas monteilii* in *Pteris vittata* | Inoculation of *P. monteilii* in the plant led to As accumulation ($1.9 \pm 0.04$ g $kg^{-1}$) as well as bioconcentration factor ($16.3 \pm 0.35$) | Soil | Abou-Shanab et al. 2022 |

(continued)

**Table 19.2** (continued)

| Method | Plant/microbial species | Results | Medium | References |
|---|---|---|---|---|
| Phytobial bioremediation with fungi | *Humicola* sp. in *Bacopa monnieri* | Arsenic bio-volatilization (53.39 mg $kg^{-1}$ biomass) was observed after inoculation | Soil | Tripathi et al. 2020 |
| Phytoremediation | *Acacia mangium* | Plant utilized phytostabilization as a pre-dominant mechanism to accumulate As in plant tissues | Soil | Rosli et al. 2021 |
| Phytobial bioremediation using fungi | Arbuscular mycorrhizal fungi (AMF) in *Pteris vittata* L | Colonization of *Pteris vittata* with AMF improved the remediation process of As with a tremendous impact in the depth of 0–0.2 m | Soil | Cantamessa et al. 2020 |
| Bacterial biosorption | *Bacillus* sp. | Maximum biosorption capacity (92%) was obtained at room temperature where the bacterial strain acted as an admirable host to the arsenate | Water | Dadrasnia et al. 2019 |
| Algal bioremediation | *Synechocysis* sp. | As accumulation by *Synechocysis* sp. was observed to be as much as 1.0 and 0.9 g $kg^{-1}$ DW after exposure to 0.5 mM arsenate and arsenite for 14 days respectively | Water | Yin et al. 2012 |
| Phytosuction separation (PS-S) | *Megathyrsus maximus* plant | As removal ratio of PS-S system increased with a decrease in the soil depth where maximum ratio (192%) was found at the soil depth of 0.2 cm | Soil | Arita and Katoh 2018 |

analysis is a pre-requisite for the successful implementation of the bioremediation process on a larger scale.

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# Chapter 20
# Modern Aspects of Phytoremediation of Arsenic-Contaminated Soils

**Tariq Mehmood, Anam Ashraf, Licheng Peng, Mehak Shaz, Shakeel Ahmad, Shakeel Ahmad, Ibadullah Khan, Muhammad Abid, Gajendra Kumar Gaurav, and Umair Riaz**

**Abstract** Pollution from potentially toxic metalloids such as arsenic is becoming a major concern for living organisms all over the world. Arsenic (As) is a non-essential metalloid in plants that can build up to toxic levels. As-contaminated soil remediation ought to be sustainable, low-cost, and applicable in the most vulnerable

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The original version of this chapter was revised: The correction at section 20.4 first Para has been updated. The correction to this chapter is available at https://doi.org/10.1007/978-3-031-16360-9_25

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low-to-middle income countries. Phytoremediation is an aesthetically appreciable and successful approach that can be used for As decontamination using the best approach(es) and the most promising plant(s). On the other hand, Phytoremediation lacks the requisite speed, and the stress generated by As often can reduce plants' ability to remediate. To solve these faults, we need to supplement plants' potential with appropriate contemporary science means, such as microbial treatments and plant genetic modification, in order to reduce As stress and increase As accumulation in phytoremediator plants. According to the literature, integrated techniques like phytobial, constructed wetlands employing As-resistant microorganisms with vegetation activities have not been substantially researched. For As remediation, integrated phytoremediation techniques with practical application and reliability are seen to be the most promising. Further technology improvements would aid in exploring literature review gaps in various techniques, guiding us toward As phytoremediation sustainability and perfection. This chapter describes how arsenic concentrations, speciation, absorption, bioavailability, uptake, transport, phytotoxicity, and arsenic detoxification in plants may all be linked. This chapter aimed to provide insight into recent breakthroughs in phytoremediation technologies for overcoming arsenic poisoning in ecosystems. Aspects such as the current and future use of assisted phytoremediation approaches are also discussed.

**Keywords** Arsenic · Modern approaches · Phytotoxicity · Phytoremediation · Soil

## Abbreviations

| | |
|---|---|
| AC | Alternating current |
| Ag | Silver |
| As | Arsenic |
| As (III) | Arsenite |
| As (V) | Arsenate |
| AsS | Realgar |
| As2S3 | Orpiment |
| APX | Ascorbate peroxidise |
| BF | Bioaccunulation factor |
| CAT | Catalase |
| Ca | Calcium |
| Cd | Cadmium |
| DMA | Dimethyl arsine |
| DC | Direct current |
| ECS | Enrichment co-efficient of shoot |
| FeAsS | Arsenopyrite |
| Fe | Iron |
| GR | Gluthathione reductase |
| GMO | Genetically modified organisms |

| | |
|---|---|
| GSH | Glutathione |
| MMA | Monomethyl arsine |
| MTs | Metallothioneins |
| N | Nitrogen |
| NPs | Nanoparticles |
| NIPs | Nodulin intrinsic proteins |
| PvPht | *Pteris vittata* |
| PCs | Phytochelatins |
| Pb | Lead |
| ROS | Reactive oxygen species |
| S | Selenium |
| SOD | Superoxide dismutase |
| TMA | Trimethyl arsine |
| TF | Translocation factor |
| Zn | Zinc |

## 20.1 Introduction

Arsenic (As) is a ubiquitous heavy metalloid ranked as 20th most abundant element of the Earth's crust. Historically, it appears to be an abundantelement on the original Earth's surface, supplying energy to few early life forms but posing a metabolic challenge to others. As Earth cools, it absorbed heavy elements like iron, nickel, sulfur, and As, leaving barely traces on the surface that allowed life to flourish (Olsen et al. 1990; Roy et al. 2015). Later on, periodic volcanic eruptions and weathering from geogenic rock, brought it to the surface. On the other hand, fungicides, pesticides, and herbicides containing heavy metals like As and careless mining activities all contributed to the abnormally high proportion in soils (Masuda 2018). It's not unexpected that a vast range of living species, including bacteria and plants, have survived in the presence of this lethal As; rather, it's the result of millions of years of adaption, selection of nature, and evolution (Oremland et al. 2002). Owing to As toxic nature, it is classified as Class I category carcinogenic heavy metal by the International Agency of Research on Cancer (Cohen et al. 2019). Additionally, As is positioned at the top of the most hazardous substances (ATSDR 2019). According to Akinbile et al. (2012), 150 million people are exposed to As contamination throughout the world. Long-term exposure to sub-acute levels of As poisoning causes arsenicosis, which varies in severity from skin lesions to neurological disorders, cancer, and even mortality (Ozturk et al. 2021; Rahaman et al. 2021). Soil and water both contain very low amounts of arsenic which is responsible for As chronic exposure (Smedley et al. 2002), has evolved As tolerance or detoxifying systems in most, if not all, living species (Rosen 2002), including humans (Apata et al. 2020). Exposure to As has been exacerbated bythe use of contaminated groundwater to irrigate staple food crops like rice and wheat (Smedley et al. 2002, Rahman et al. 2011). Long-term irrigation with As-contaminated water causes As to build up in the soil (Gillispie et al. 2015). Abandoned mines also contaminate nearby agricultural soils with As (Kim et al. 2005; Susaya et al. 2010). Phytoremediation is cost-effective, socially acceptable, and environment friendly compared to conventional methods; that's way got the attention of researchers to be used as a potential method of As remediation and revegetation of As contaminated land (Ali et al. 2013; Chatterjee et al. 2013; Irfan et al. 2022).

## 20.2 Origin and Occurrence of Arsenic

Arsenic is considered the 20th most plentiful component in the amount of 5 mg/kg (Garelick et al. 2008) as well an undyed, inodorous and unflavoured toxic substance present in the lithosphere (Katsoyiannis et al. 2006). In nature, it exists in the combined form of minerals such as Realgar (AsS), Orpiment (As2S3), and Arsenopyrite (FeAsS) (Magalhaes 2002). After weathering process, particles of arsenic combine with rain droplets, and through this pathway, arsenic penetrates into aquifers. It is to be noted that aquifers of some Asian and American countries have ahigher amount of arsenic (Melkonian et al. 2011). As it exists naturally, but the elevated use of arsenic in human activities isthe major cause of increasing its concentration in nature (Taylor et al. 2003; Raj, 2019),which badly effecting flora and fauna in multiple ways (Smedley and Kinniburgh 2002; Irshad et al. 2021). Generally, arsenic is present in 4 major forms from which the amount of arsenic (0 oxidation state) and arsenide (-3 oxidation state) is not constant in the soil (Xie and Haung 1998). As they are very poisonous in nature, but when they penetrate the nutrient cycle and convert into low poisonous forms such as MMA (Monomethyl arsine) DMA (Dimethyl arsine) and TMA (Trimethyl arsine) (Edmonds and Francesconi 1988; Lee and Wen 2019). Arsenate is majorly present in areas with higher availability of free oxygen, but the elevated concentration of arsenite exists in an oxygen-deficient (free) environment (Abedin et al. 2002; SignesPastor et al. 2007).

## 20.3 Historical Usage of Arsenic

In 1250 CE, arsenic was primarily identified. In the past, it was used as a medication for dermatosis, embellishment (Shrivastava et al. 2015) and pest killer chemicals in crops (Smith et al. 2003). Due to the elevated dissolving capacity and arsenic's fast-poisoning ability, it has been utilized to form chemicals to kill rodents, insects, and herbs. In earlier times, the food of farm animals also contained arsenic as an additional supplement in their food, but after the twentieth century, its use was legally prohibited (Jones 2007). Among the duration of 55 years, from 1900–1955, arsenic was also utilized in tick management that affected cows and buffaloes (Rahman et al. 2019). In the past, arsenic was also considered as a source of causing impurities and pollutants in food stuff materials. The outbreak of Manchester in 1900 occurred by the utilization of beer that was poisoned by arsenic (Phillips and French 1998). Furthermore, the severe Japan epidemic of 1956 happened because of arsenic toxicity in soya sauce (Mizuta et al. 1956).

## 20.4 Arsenic Phytoremediation

Phytoremediation is one of its kind in green abetment technology. During the process of phytoremediation, soil fertility increases and replenishes soil microbes (Yan et al. 2020a, b). There are various kinds of phytoremediation, such as phytoextraction, phytostabilization, and phytovolatilization; which can be utilized for As removal from soil based on the ground condition, suitability of option, and the objective of the remediation (Guarino et al. 2020, Kowitwiwat and Sampanpanish 2020, Wei et al. 2020). Recent phytoremediation studies to treat As polluted soil are summarized in Table 20.1. These studies revealed that plant suitability for phytoremediation is highly dependent on translocation and bioaccumulation factors. Plants with translocation and bioaccumulation factors greater than one are considered ideal for phytoextraction because they can accumulate high concentrations of As in their above-ground parts (Mateoet al., 2019). Plants with less than one translocation and bioaccumulation factor, on the other hand, cannot uptake and store higher As concentrations in above-ground parts, making them inefficient for phytoextraction but potentially useful for phytostabilization (Shackira and Puthur 2019).

Using commercially viable plants in phytoremediation also makes it practical for farmers (Ali et al. 2013; Irfan et al. 2022). Plants having high biomass, fast growth rate, and high shoot As accumulation are suitable for phytoremediation (Ye-Tao et al. 2012). However, it has proven a challenge to discover all three traits in one plant for the scientists. Some plants with high As accumulation capacity in shoots areshort-lived and have poor biomass, whereas others have high biomass but low As accumulation efficiency (Chatterjee et al. 2013). Further, several economically beneficial plants having high biomass suffer from As toxicity and cannot develop to their full potential. To overcome such obstacles optimal combination of physicochemical and biological technologies for successful sustained rehabilitation of polluted regions. To address such issues, integrated approaches like microbe-assisted phytoremediation have been applied to boost plants' development and biomass and enhance plant As accumulation efficiency (Mesa et al. 2017). Nanoparticles have become an accepted strategy forthe reclamationof degraded ecosystems (Zuverza-Mena et al. 2017; Ranjan et al. 2021). The idea of nano-phytoremediation technology has been developed to remove toxins from soil/water, integrating nanotechnology and phytoremediation (Srivastav et al. 2018; Liu et al. 2020; Usman et al. 2020). As phytoremediation, there are numerous ways that may be applied strategically to cleanse polluted environments.

**Table 20.1** Recent research trends for As phytoremediation form polluted soil by using phytoremediation alone or in conjunction with other techniques

| Plant name | Amendments | Experimental conditions | Synthesis | Comments | References |
|---|---|---|---|---|---|
| Pteris vittata | | As (8885 mg/kg) in mining area soil | Accumulated 7215–11,110 mg/kg As | Hyperaccumulator | (Wei et al. 2020) |
| Landolita punctata | | As (V) (0.5–3.0 mg/L) | Concentration greater than 1 mg/L was toxic while lower wasn't | Hyperaccumulator | (Canatto et al. 2021) |
| Portulaca oleracea | | As (154 gm/kg) in soil | Accumulated 94.5 mg/kg As | High biomass production and in-situ | (Negi 2018) |
| Calatropisprosera | | As in Soil | Reduces As concentration by 30%—36% in 30 days in soil | High biomass production | (Singh et al. 2021) |
| Hydrilla verticillata | | As (V) (375 µg/L) | Total accumulated As was 197.2 µg/g DW | Economically viable | (Zhao et al. 2020) |
| Helianthus annus | | As (85.6 mg/kg) in farmland soil | As accumulated in above ground parts (49 mg/kg) | Economically viable | (Sahito et al. 2021) |
| Alfalfa | Ensifer sp. M14 | As (III) (10 mg/kg) in soil | 11% higher As accumulation in plant with added microbiota | Phytobial remediation | (Debiec-Andrzejewska et al. 2020) |
| Arundo donax | *Stenotrophomonas maltophilia* and *Agrobacterium* sp. | As (III) (20 mg/L) in soil | As phytovolatilization was 11.3 mg/kg | Phytovolatilization | (Guarino et al. 2020) |
| Lsatiscappadocica | Glutathione modified superparamagnetic iron oxide nanoparticles (nFe3O4@GSH) | 1000 µMAs + 200 mg/L | 56% higher As accumulation in plant shoots with added nanoparticles | Nano Phytoremediation | (Souri et al. 2020) |

(continued)

**Table 20.1** (continued)

| Plant name | Amendments | Experimental conditions | Synthesis | Comments | References |
|---|---|---|---|---|---|
| Nicotiana tabaccum | PvPht1;3 from P. vittata | As (V) (9.66 mg/kg) in soil | As accumulation increased in transgenic plants | Transgenic Phytoremediation | (Cao et al. 2019) |
| Saccharomyces cerevisiae | PvPht1; Pteris vittata L | As in Soil | As accumulation increased two-fold in transgenic plants | Transgenic Phytoremediation | (DiTusa et al. 2016) |
| Ballota hirsute Benth | | As (98–149 mg/kg) in soil | As accumulated in above ground mass (3.4 mg/kg) | Native plant | (Gabarrón et al. 2018) |
| Pityrogramma calomelanos(L.) Link | | As in Soil | As concentration in plant shoot 280.18 mg/kg | Hyperaccumulator and a Medicinal plant | (Ancheta et al. 2020) |
| Pteris vittata L | | As (85.4–1400 mg/kg) in soil | Phytoextracted As (1860 mg/kg) | Hyperaccumulator | (Ha et al. 2019) |
| *Pennisetum purpureum* cv. Mott | Biochar (Cow manure or acacia wood) | As in mine tailings soil | Biochar5% application reduced As accumulation (0.74 mg/kg) in above-ground plant parts after 120 days | Phtostabalization, stabilized by organic matter | (Kowitwiwat and Sampanpanish 2020) |

## *20.4.1 Phytoextraction*

It is the simplest and most appropriate method in which plants are used to eliminate the pollutants from soil and water samples. In this process, the roots of plants consume the pollutants and transfer them to the leaves, but a little proportion of the pollutants can eliminate from soil after reaping the crops. This process occurred in "hyperaccumulators" plants (Nedjimi 2021). The best features of hyperaccumulators include higher biomass content on the ground surface, a great production ratio, effective transportation of materials, and they are very simple to grow and reap. Generally, these plants assemble metals in tissues and donot generate poisonous circumstances, and the plants having deep roots become suitable for greater consumption of pollutants (Bhargava et al. 2012). Usually, arsenic is restricted to certain locations in plants such as epidermis, mesophyll, and vascular tissues (especially xylem) (Vithanage et al. 2012). The shoots of naturally occurring plants have a great influence on the rate of photosynthesis and also on the capability of producing flowers. Therefore, these natural plants accumulate metals in their root system and inhibit the movement of metals towards the shoot system. It is noticed that this feature is not present in hyperaccumulator plants. Therefore, they are considered suitable plants for phytoextraction. Some hyperaccumulators are *Hydrilla verticilata*, *Vallisnerlaneotropicals* (Chen et al. 2015; Li et al. 2018). Another difference is hyperaccumulator plants have no elevated biomass.

On the other hand, naturally occurring plants have elevated biomass. Yet they donot possess the higher accumulation of selected metal, but they are able to produce assuring consequences such as *Brassica juncea* (Niazi et al. 2017). When the pollutants are diminished in a definite range from the soil, harvesting starts. After harvesting, the plants are carefully discarded in the form of contaminated pollutants or get smelted to rehabilitate metals. By determining some components such as translocation factor (TF), enrichment co-efficient of the shoot (ECS), and bioaccumulation factor (BF) the transportation ability of the plant can evaluate. Furthermore, by determining the quantity of arsenic in shoots transferred from roots, the phytoremediation capability of plants can be determined (Rahman et al. 2011).

### 20.4.1.1 Translocation Factor (TF)

It evaluates the plant's capability to transfer the metals in shoots from roots. It is the proportion of the amount of component in the shoot (mg.g$^{-1}$) to the amount of identical component in the root (mg.g$^{-1}$). Hyperaccumulator plants have anelevated rate of translocation factor, but generally, the rate of translocation factor in normal plants is not greater than 1 (Francesconi et al. 2002).

#### 20.4.1.2 Enrichment Co-efficient of Shoot (ECS)

It can utilize to evaluate the consumption-ability of metals in plants Bienert. It is the proportion of the amount of metal in the shoot to the amount of the same metal in the soil. Once the value of ECS in the plant is higher than one, this exhibits the shifting capability of the plant to shift metals towards shoots, mainly in vacuoles (Elshamy et al. 2019).

#### 20.4.1.3 Bioaccumulation Factor (BF)

It can utilize to assess the consumption ability of heavy metals in roots from the soil. It is the amount of components accumulated in roots (mg.g-1) to the amount of identical components in the soil (mg.g$^{-1}$). Grasses such as barnyard grass (Sultana and Kobayashi 2011) and rice cutgrass (Klaber et al. 2014) are suggested for trees because they possess greater biomass and production ratio and are much more suitable for unfavorable conditions (Ali et al. 2013). It is necessary to adopt protective measures to inhibit the attack of consumers as they become the cause of the entrance of pollutants into the nutrient cycle.

### *20.4.2 Phytostabilization*

It is an effective controlling method in regions near mines. It maintains the pollutants also diminish the accessibility and motility of the pollutants. Therefore, it helps in diminishing ex-situ pollution (Shrivastava et al. 2015). Arsenate reductase is an enzyme excreted by plants that maintain the pollutant (arsenic) via sorption, complexation/metal valence reduction or precipitation it to low poisonous shape (Thakur et al. 2020). Therefore, that procedure is not indicated to produce insignificant debris, as it elevates soil productivity. There should be extended roots in plants that become suited for phytostabilization and give adequate vegetation to the soil, have resistance to the pollutants, and restricted the pollutant in roots and soil, diminishing accessibility of arsenic and erosion (Gonzaga et al. 2006).

Furthermore, there should be less contaminant assemblage capacity in shoots of plants thatare selected for phytostabilization, such as Eucalyptus and Arundo donax L. because if the pollutant assembles in the shoots of other plants then they penetrate nutrient cycle (Bolan et al. 2011; Mirza et al. 2011). The plants of the Eucalyptus family have wood;when they face the pollutant, these plants accumulate less concentration of metals than the other plants. Due to the presence of terpenes and phenolics in shoots of these plants, they are infrequently occupied by organisms and inhibit the entrance of pollutants in the nutrient cycle (King et al. 2008). It is also noticed that the motility of heavy metals is constricted in phytostabilization and is not considered an enduring solution tothat issue (Ali et al. 2013). Therefore, the location should be regularly observedto make sure that all the circumstances are controlled.

### 20.4.3 Phytofiltration

It is utilized to purify the water (the surface, below the surface, waste, etc.) having less pollutants (Garg et al. 2011; Shrivastava et al. 2015). This procedure shows that the pollutants are consumed by plants, lowering the quantity of contaminants in water, i.e., purifying heavy metals from water to roots (Mykolenko et al. 2013). That is why the plants with great absorbing capacity are selected. *Micranthemumumbrosum* is considered a powerful assembler of metals because it accumulates 1000 mg As g-1 in its shoot parts and lowers the quantity of arsenic in a solution of 10 folds (Islam et al. 2015). It has 3 kinds that depend on the components of the plant utilized for that method. Rhizofiltration (roots), blastofiltration (seedling) and caulofiltration (shoots) (Ali et al. 2013). The more productive plants, ineffective metal carriers (carry metal towards shoot, causing rhizofiltrationto become inefficient) and extended roots should be selected, such as Eucalyptus globules, *Faidherbia albida* etc. (Anawar et al. 2008). When the procedure reaches its end point, roots harvesting occurs and then desiccates. Metals can remove by acid analysis or ignite at unhealthy debris locations (Dushenkov et al. 1995). Therefore, this method is considered as a productive, environmentally sound procedure to decrease the pollution in naturally occurring marshlands and waterway zones. Because of the great metal assimilation capability in *Lemnagibba* is used to remove the contaminated metals from the water coming from mining areas (Anawar et al. 2008).

### 20.4.4 Phytovoltalization

This procedure exhibits the consumption of pollutants from the soil and its discharge in fewer amounts into the atmosphere in a gas form via transpiration (Ranjan et al. 2020). It is noticed that poisonous contaminants got weakened or probably transformed into a rarely poisonous type in the environment (Guarino et al. 2020). Direct and indirect are two kinds of this procedure. Direct includes vapourization from shoots or roots, but indirect has underground vapourization because of the actions of roots (Pandey et al. 2018). It is considered as acontentious type of phytoremediation. It exhibits the shifting movement from one form to another and can return back into its actual form. Therefore, it shows low or no command of the mobility of pollutants (Bolan et al. 2011). Another benefit of this procedure is that no physical work or stress is required to shift or eliminate plants' polluted components, andit needs low controlling effort (Heaton et al. 1998). Generally, arsenic is used in the shape of trimethylarsine in phytovolatilization, the concluding outcome of the methylation route where arsenic is passed from the methylation process and converted into dimethylarsenic acid then to trimethylarsenine oxide, which faces a reduction process and producesthe final product called trimethylarsine (Mirza et al. 2011). In phytovolatilization, *P. vittata*can be utilized to discharge heavy metals into the atmosphere (Sakakibara et al. 2007).

## 20.5 Consumption and Transportation of Arsenic in Plants

Generally, the roots of plants consume As. Mostly the accessibility of As in four major states in plants such as As (III), As (V), MMA and DMA. In the soil, these states are developed, and at the same time, their consumption occurs particularly by the roots through various routes and carriers. The consumption process shows involvement in the use of phosphate carriers required in the route of phosphate transportation. Due to the structural similarity of As (V) with phosphate, the entrance of As (V) becomes possible in roots.

### *20.5.1 Transportation of Arsenic in Plants by Phosphate Carriers*

Different scientists explained their work that phosphate carriers have great importance in promotingthe transportation and bearing capacity of arsenic in plants (Fig. 20.2). Cao et al. (2019) examined the role of the phosphate carrier named *Pteris vittata* phosphate transporter (PvPht1;3) in increasing the adaptation and transportation of arsenic in shoots of *Nicotiana tobaccum* (grow in both terrestrial and aquatic mediums). Research shows the proof of arsenic consumption and addition in Oryza sativa through phosphate carriers. Generally, OsPT1, OsPT4, and OsPT8 (genes) are used to increase response to the stimulus in rice plants' root and shoot system and showed strong attraction for As (V). Sun et al. (2019) examined the upregulation of PvPht1;4 decreased transportation and poisonous effects of arsenic in tobacco plants. The tobacco plants using that gene assimilated less arsenic concentration of arsenic upto 37–55% in shoots than other plants.

### *20.5.2 Transport of Arsenic by Aquaporins*

Aquaporins give definite functions in As acquirement of plants. The groups of aquaporin proteins determined the consumption of As (III) by plants. Kamiya et al. (2009) observed that nodulin 26-like intrinsic proteins (NIPs) belonged to aquaporin proteins and participated in the consumption of arsenic (III). NIPs are classified into three types due to their porous configuration. Ma et al. (2008) revealed the accessibility of NIP 1 protein to water, lactic acid, and glycerol. Mitani et al. (2008) showed the participation of NIP II proteins in the transportation of greater solutes such as formamide, boric acid, and urea due to their big porous structure. Still, NIP III proteins are accessible to silicic acid. Protein carriers related to NIP family showed involvement in assimilation and transportation of arsenic in *Oryza sativa* plants. Sun et al. (2018) recognized the overexpression of two NIP group carriers OsNIP1:1 and OsNIP3:3 decreased the amount and transportation of As (III) in shoots of rice

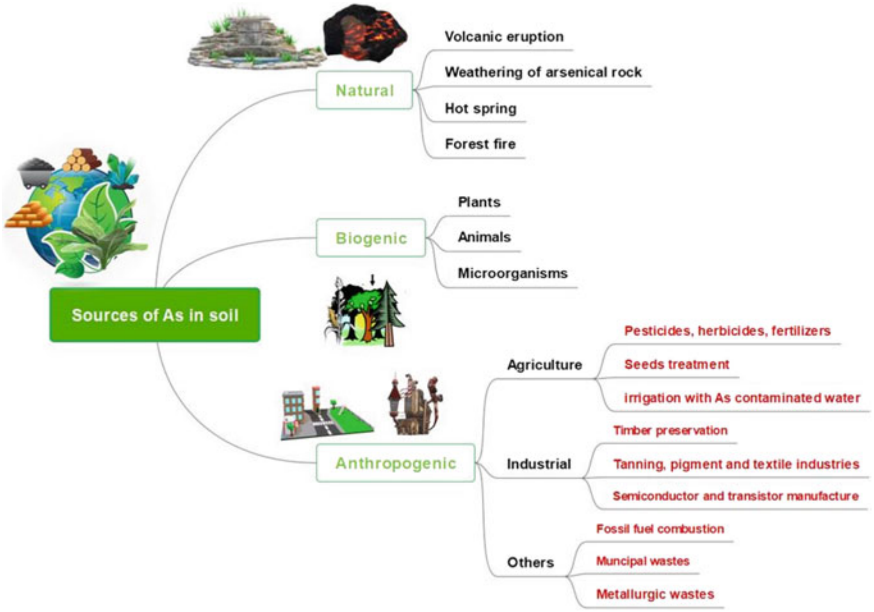

**Fig. 20.1** Sources of arsenic contamination in soil

plants. The upregulation of NIP genes caused the effluence of As (III) from the stele, constricted As' storage in vascular tissues (xylem) and its adaptation in rice plants. Xu et al. (2015) reported the analytical part given by 9 NIP group carriers in the accession and transportation of As in shoots from the roots of Arabidopsis thaliana. The overexpression of NIP3:1 in the roots of variants increased the consumption of As (III) in roots, and transfer to aerial components of plants showed powerful bearing capacity against the poisonous effect of As (III). Kamiya et al. (2009) observed the involvement of NIP1; 1 in the susceptibility of As (III) in plant tissues. He et al. (2016) carried out a study and developed a new protein PvT1P4; 1 from Pteris vittata showed significant As (III) consumption. It is a protein carrier restricted toplasma membrane.

### 20.5.3 *Involvement of Silicon Carriers in Transportation of Arsenic*

Two silicon carriers Lsi1 and Lsi2 of NIP III group, took part in the consumption and transportation of As III in plants. Lsi1 is present in the plasma membrane (roots) and participated in consuming As III in Oryza sativa. The overexpression of Lsi1 in Xenopus laevis oocytes increased the accession of As III (Yamaji et al. 2015). Ma

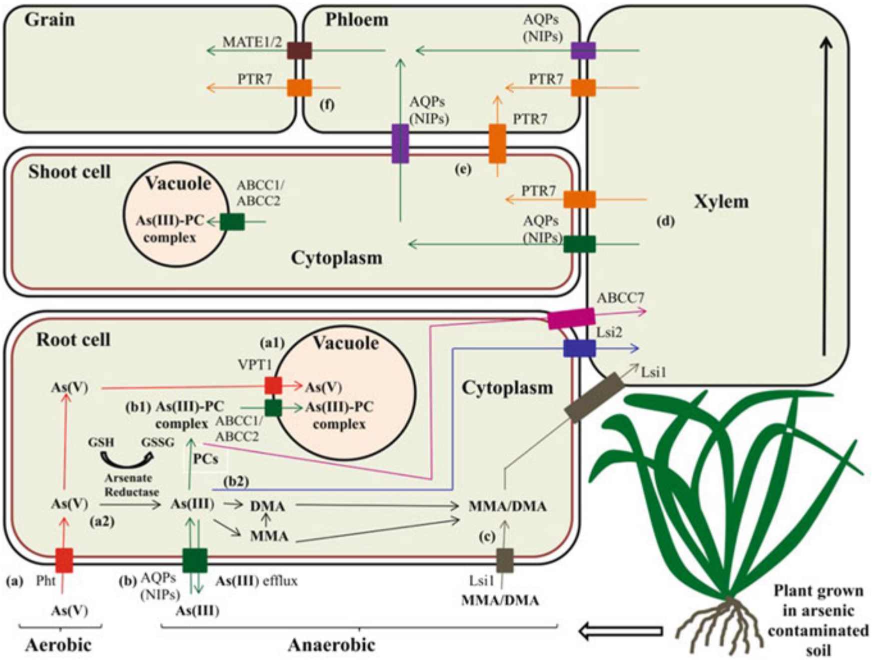

**Fig. 20.2** Schematic representation of transporter-assisted arsenic acquisition and transport in plant tissues. **a** Upregulation of phosphate (Pi) transporters (Pht1; 1, Pht1; 2, Pht1; 3) mediate As(V) uptake inside the roots cell under aerobic conditions. **a1** Vacuolar phosphate transporter (VPT1) contributes towards vacuolar phosphate sequestration and is associated with As(V) quenching inside the vacuole, hence confer plant tolerance towards arsenic toxicity. **a2** The cytoplasmic enzyme arsenate reductase reduces As(V) to As(III) and provides resistance to the plants against As(V) toxicity. **b** Overexpression of aquaporines (AQPs) like nodulin 26-like intrinsic proteins (NIPs) (Nip1; 1, Nip3; 1, Nip5; 1, Nip6; 1) induce As(III) uptake inside the root cell under anaerobic conditions. **b1** Two ATP binding cassette transporters (ABCC1/ABCC2) are involved in the transport of As(III)-PC complex inside the vacuole and a member of the same sub-family transporter ABCC7 mediate its transport to shoots via xylem. **b2** As(III) from root cell is exported to the xylem by the silicon transporter (Lsi2), resulting in root to shoot transport of As(III). **c** Organic species monometylarsonic acid (MMA) and dimethylarsinic acid (DMA) are taken up by plant roots via silicon transporter (Lsi1) and is transported to aerial parts via xylem. **d** Arsenic as MMA/DMA or As(III) is transported to shoots by expression of PTR7 and NIPs. **e** To phloem, arsenic is transported by PTR7 as DMA or As(III). **f** Arsenic transport as DMA or As(III) from phloem to the grain is mediated by (MATEs) MATE1/2 and a long-distance transporter PTR7. Copyright 2022 Elsevier. Reproduced from (Bali et al., 2022)

et al. (2008) observed that Lsi2 variants work more efficiently than Lsi1 variants in lowering accession and transportation of As III in rice plants.

### 20.5.4 *Consumption and Transportation of Methylated Arsenic Species in Plants*

The use of arsenic in chemicals for killing pests, herbs, and methylation arsenic by microorganisms has been mixed in minute amounts of As group such as MMA, DMA inthe soil (Chen et al. 2020; Rahman et al. 2019). In plants, anelevated amount of methylated arsenic has been identified. The plants consumed methylated arsenic slowly as compared to inorganic arsenic. However, DMA is wholly transferred to the sexual and above-ground components of the plants (Tang et al. 2016; Zhu et al. 2017). The carriers of organic compounds caused the transportation of DMA to sexual parts of the plants. It is observed that rice granules have an elevated amount of DMA than inorganic arsenic (Yan et al. 2020a, b). OsPTR7 is a putative peptide transporter in Oryza sativa. Successive variants of OsPTR7 considerably reduced the transportation of DMA in shoots from roots than the brown rice plants.

### 20.5.5 *Consumption and Transportation of Thioarsenate Species in Plants*

The structure of thioarsenates is related to As (V) and derived from As (III) in sulfate-reducing circumstances. In the case of monothioarsenates, μM arsenic is more poisonous than As (V) and becomes less poisonous than As (III). Planer-Friedrich et al. (2017) elevated the toxic effect and bearing capacity of arsenic is influenced by monothioarsenate in *Arabidopsis thalliana.* After studies, the writers discovered that adaptation of arsenic in the roots was less on adding monothioarsenate, possibly because of increased levels of As in roots. Inspite the As transportation in shoots from roots was higher for monothioarsenate than arsenate. Introduction to monothioarsenates brought comparatively elevated adaptation to phytochelatins in the ferocious variants (Col-o), thus presenting *Arabidopsis thaliana* to fight arsenic stimulated toxic effects (Planer-Friedrich et al. (2017). The latest research performed by Wang et al. (2020) shows that oxygen-deficient soil growth at various pHs caused thiolation of arsenic polluted soils. Soils with neutral sulphur (pH greater than 6.5) demonstrated the supremacy of thioarsenates. In addition, soils having methylated oxyarsenates (pH lower than 7.0) showed the existence of methyl thioarsenates. It is highlighted that arsenic thiolation and surplus sulphate in the soil exhibited the same results, but increased amounts of soluble Fe in the soil reduce arsenic thiolation (Wang et al. 2020). On the other hand, the translocation of inorganic and methylated thioarsenates interceded by carriers was not recognized until now. Future endeavors in this area are definitely approaching the scientists regarding the probable part of protein carriers in the attainment and uptake of thioarsenates in the plant tissues.

### *20.5.6 Process of Arsenic Decontamination in Plants*

The secure method forthe production of reactive oxygen species (ROS) because of the existence of arsenic is the generation of antioxidant enzymes such as superoxide dismutase (SOD), catalase (CAT), gluthathione reductase (GR) and ascorbate peroxidase (APX) to maintain radicals without charge. In plants the generation of some osmolites such as proline (Sayantan 2017), glyanebetaine and mannitol are noted below oxidation conditions because of conservation and durability (Abbas et al. 2018). The main route of antioxidant protection to clean $H_2O_2$ is the Ascorbate–Glutathione route. Four enzymes such as ascorbate peroxidise, monodehydroascorbate reductase, dehydroascorbate reductase, and gluththione reductase have a major part in cleaning ROS in that route and conserving the plant from numerous abiotic conditions (Hasanuzzaman et al. 2019). The other method involves the arsenic complexity with ligands. When arsenic penetrates the plant after the reduction process, As (V) converts into As (III) by using the arsenate reductase enzyme (Zhao et al. 2003). Arsenite is considered the causative agent affecting metabolism in the cytoplasm, so decontamination takes place. All of this is noted in plants such as H. Verticillata, Brassica juncea, tomato, and rice (Chen et al. 2015).

## 20.6 Integrated Approaches for Enhanced Phytoremediation

### *20.6.1 Phytobial Remediation*

Bioremediation and phytoremediation are combined in phytobial remediation techniques to abate pollution. The micro soil biota helps plants in numerous ways to improve health and productivity by regulating nutrients (Mehmood et al. 2021c; Glick 2012), enhancing the status of growth limiting factors such as nitrogen and phosphorus, and to improve soil enzyme activities (van der Heijden et al. 2008, Ullah et al. 2015). The microbiota in the rhizosphere helps increase the plant biomass and raise bioavailability of As to plant (Khan 2005; Alka et al. 2020; Srivastava et al. 2021). Therefore, it is essential to select such species of microbes that could enhance plant productivity andAs phytoremediation to achieve good results. The functions of the plant-bacteria symbiotic association are phytoimmobilization, rhizofiltration, phytostabilization, chelation, As solubilization, and phytoextraction. Several studies have shown that plants and their root communities work better together than plants or bacteria alone in soil and water systems with high levels (Mehmood et al. 2021a, 2022a; Irshad et al. 2021).

### *20.6.2 Transgenic Phyto and Phytobial Remediation*

Genetically modified organisms (GMO) based technology has the potential to augment the innate bioremediation capability of plants and microorganisms in such as a way to enhance symbiosis betweenplant and soil microbiota for better As bioremediation (Guarino et al. 2020). Transgenic plants are developed either with increased capacity to extract As from soil or stable food crops with increased ability to restrict As absorption from soil providing new hope for As phytoremediation. Genes encoding As absorption channels and transporters have been identified in As accumulator and hyperaccumulator plants (Roy et al. 2015). As a result, preventing the uptake of As(V)/As(III) via roots is possible by inactivating or deleting the genes encoding several phosphate transporter variants, NIP aquaporins, and Lsi2-like carrier proteins (Roy et al. 2015).

The detoxification process is indicated when ligands (glutathione (GSH), phytochelatins (PCs) or metallothioneins (MTs)) are integrated into complexes, they are sequestered or compartmentalized in trichomes or vacuoles which are dedicated tissues such for this task. Consequently, genetic engineering has increased the capacity of As accumulating plant to either sequester As in its roots via rhizofiltration or improved hyperaccumulation in shoots/fronds (phytoextraction) phytovolatilization pathways. Enhanced root surface area and plant biomass may be obtained by developing such phenotypes having more hairy roots (Eapen et al. 2003).

Metal tolerance could be promoted by activating oxidative stress-related genes. Targeting C synthesis and transporter genes may promote enhanced translocations into shoots and higher vacuole storage (Cherian et al. 2005). Genes involved in As methylation might possibly be a target. In transgenic rice plants, as has been methylated and volatilized. Novel biotechnological approaches, such as the development of transgenic plants, not only have the ability to phytoextract and accumulate large amounts of As but also possess toxin or conditional lethality genes which could be resisting Asa transfer to the food chain by distracting herbivores and resisting pest attack, can alleviate concerns about food chain contamination (Eapen et al. 2003; Zhao et al. 2009).

### *20.6.3 Phytoaugmentation (Addition of Abiotic Factors)*

Nature's attenuation process may be accelerated by introducing various biotic (microbes) and abiotic (addition of various chemicals; bioaugmentation). The As-immobilizing microbes and abiotic chemicals may be put into the soil to achieve phytoimmobilization. To achieve long-term As immobilization by solid-phase sorption, acidic and oxidizing conditions must be maintained (Adriano et al. 2004). The pH buffering agents should be used to improve and stabilize As sorption and inhibit As remobilization. If Fe salts, such as $FeCl_2$ and $FeSO_4$, are combined with $H_2O_2$, they may precipitate As from groundwater. The presence of $H_2O_2$ maintains as an oxidizing environment for As(V) sorption bypromoting the oxidation of As(III) species to As(V) species (Wang et al. 2006). It is feasible to use such oxidant types, ensuring that subterranean soil and water are adequately oxygenated. It is possible to increase Fe bioavailability by using naturally abundant soil organic compounds such as humic acids. (Adriano et al. 2004).

Researchers studied the impact of several soil amendments on the plant P. vittata (Cao et al. 2003; Paz-Ferreiro et al. 2014). Calcium (Ca2 + ), selenium (S), and nitrogen (N) have been demonstrated to increase *P. vittata*As accumulation (Liao et al. 2007; Paz-Ferreiro et al. 2014). According to Huang et al. (2012) adding organic matter to the soil of a rice field significantly boosted the methylation and volatilization of As from the soil. It has been shown that using various kinds of nutrients and microbial growth-enhancing agents, such as compost and biochar, lowers As stress in plants (Mehmood et al. 2017, 2021b; Irshad et al. 2021).

### *20.6.4 Nano Phytoremediation*

Nano-phytoremediation has recently emerged as a possible approach for improving plants' capacity to grow in a polluted and stressed environment while accumulating arsenic in plants (Fig. 20.3). The development of efficient and environmentally friendly nanoparticles for the successful treatment of widespread contamination by hazardous metalloids has gotten a lot of attention (Ganie et al. 2021). Nanoparticles (NPs) have the potential to improve plant stress tolerance to promote phytoremediation and minimize toxicity (Srivastava et al. 2021; Mehmood et al. 2022b). Nanophytoremediation, which treats contaminated soils and water using plants with high NPs/metal absorption efficiency, has the potential to be an efficient alternative to As phytoremediation (Gul et al. 2022).

Nanoparticles, according to studies, may be utilized to manage polluted agricultural areas and stimulate plant growth and development. Nanostructured silicon dioxide has been shown to be a feasible agent for enhancing the phytoremediation process and achieving the necessary results (Bao-Shan et al. 2004). Nanoparticles of aluminium oxide (n$Al_2O_3$) were shown to have no deleterious effects on Arabidopsis thaliana when tested at doses of up to 4000 mg/L (Lee et al. 2010). The inclusion of nanoscale zero-valent iron aided the phytoremediation process (Song et al. 2019). It was discovered that nano-TiO2 reduced As accumulation in rice by 40–90% when administered at a concentration of 1000 mg/L (Wu et al. 2021). Adding zinc oxide to rice seedlings improved rice seedling development, decreased As buildup in roots and shoots, and increased phytochelatin levels (Yan et al. 2021). Nano-phytoremediation advances have the potential to pave the way for the development of safe, economical, and environmentally sustainable As phytoremediation technologies for awide range of environmental settings (Zhou et al. 2020).

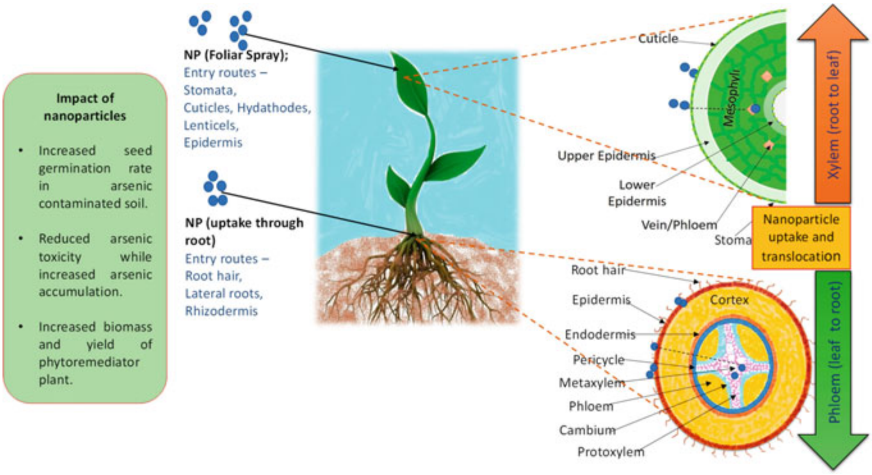

**Fig. 20.3** The use of nanoparticles through foliar spray and via roots can effectively enhance the tolerance of plants to arsenic. Copyright 2022 MDPI. Reproduced from (Srivastava et al. 2021)

### *20.6.5 Phytosuctionpartition*

Phytosuction partitioning is a newly designed and improved phytoremediation technology (Katoh et al. 2016a). According to several research investigations phytoremediation of hazardous metal and/or metalloid polluted soils is both cost-effective and environmentally acceptable (Ali et al. 2013; Chatterjee et al. 2013; Jha et al. 2022). However, the PE technique requires longer time periods, making it unworkable even with hyperaccumulators. This approach employs heavy metal(oid)-contaminated bottom soil and heavy metal-free planting soil. A layer of immobilisation material separates these two kinds of soils. Plants are cultivated by growing them in soil (devoid of heavy metals) (Kabiraj et al. 2022). Following this method involves spraying a chemical like ferrihydrite over contaminated soil and then growing plants on top of it, potentially immobilizing the target hazardous metal and/or metalloid. Roots sucking up water attract metals and metalloids, causing them to get immobilized. Arsenic may be removed from ferrihydrite-polluted soil using a novel technology that employs ferrihydrite's immobilizing agent. When the phytosuction partitioning approach was compared to classic PE, it was discovered that the phytosuction partitioning method produced superior ratios.

Furthermore, as compared to the PE approach, the removal ratios were greater at shallow soil levels of up to 0.25 cm (Arita and Katoh 2019). This approach has been shown to remove 8–25 times more lead (Pb) and 69–533 times more antimony (Sb) from the environment than PE (Katoh et al. 2016b). It takes less time than the PE technique since it does not need root systems to absorb metals or metalloids. According to our findings, one of the most important aspects influencing phytosuction efficiency is the mobility of the metal/metalloid under consideration.

### 20.6.6 Electrokinesis Assisted Phytoremediation

Electrokinetic remediation has sparked considerable interest as a method of boosting plant absorption of pollutants (inorganic and organic), whereas the majority of research which is focused on combining electrokinetics assisted phytoremediation has concentrated on improving phytoextraction of heavy metals (Gomes et al. 2012). The electric field makes contaminants mobile, thus increasing bioavailability, which is evident by improved plant growth (Cameselle et al. 2013). Low-intensity direct current is transferred between two electrodes implanted vertically into the soil without causing structural damage to the soil. Organic and inorganic molecules are separated using an electric current. Water and electromigration are two routes for heavy metal cations to reach the cathode. Electromigration transports anions and other small-charged particles towards the anode. Applied electric field to the soil regulates the movement of pore fluid, ions, and colloids via electroosmosis, electromigration and electrophoresis, respectively, allowing for higher metal buildup in the rhizosphere interstitial fluid and absorption by the plant (Chirakkara et al. 2016).

Electrokinetics and phytoremediation have shownpromising results in laboratory experiments for heavy metals such as Zn, Pb, Cd, and As (Cameselle et al. 2013). It is reported that the efficiency of phytoremediation may be increased if the soil is kept from becoming too acidic or basic by modulating the electric field. Soil with acidic or alkaline conditions hasa detrimental impact on the metabolism of plants, growth, and biomass yield. Keeping the electric current intensity low will limit the extent of the electrolysis of water and, as a result, the fast changes in pH in the region surrounding the electrodes. Two possible methods for reducing pH variations in soil include periodic polarity inversion in the case of DC or the application of AC current (Aboughalma et al. 2008). The other main issue of the application of electric field in phytoremediation is elevated exposure of heavy metals to the plants, which may exacerbate plant stress. To solve this issue, researchers have suggested to use plants that can withstand elevated metal concentrations (i.e., hyperaccumulator plants with short growth cycles) in electrokinetic assisted phytoremediation (Cameselle et al. 2013). Even yet, further large-scale testing is required to establish if this technology can be employed in the future as a low-cost remediation option. Combining many methods proved to be more successful than using just one.

### 20.6.7 Co-cultivation and Intercropping

In agriculture, intercropping is a typical approach for improving soil conditions for plant development and soil enzyme activity and nutrient availability by cultivating two different crops together to improve soil conditions (Srivastava et al. 2021). The reduction of As contamination in field and to reduce the stress of As on sensitive and non-accumulator plants Intercropping is utilized. The *P.vittata* (As hyperaccumulator) is cultivated with either As sensitive or a non-As accumulator plants. It is investigated that in the intercropping of two commercially important plants; *P.vittata* and Panax notoginseng the rhizospheric concentrations of As for Panax plants were lowered compared to Pteris (Lin et al. 2015). When *P.vittata* was intercropped with Morus alba; Pteris has accumulated As, leaving behind lower As levels for Morus alba plants (Wan et al. 2017).

The *P.vittata* intercropping with maize (Zea mays) plant is studied in coordinate and malposed intercropping settings. When the rate of As accumulation in *P.vittata* was compared in both settings, the As phytoextraction was more in malposed intercropping than in coordinate intercropping. Malposed intercropping had a 2.4-fold higher rate of As removal than coordinated intercropping. (Ma et al. 2018). Ma et al. (2018) also found that following malposed intercropping, maize grains indicated decreased As levels in grains, below the threshold maximum contamination limit. Therefore, intercropping Pteris could achieve promising results with other cash crops/economically essential crops. Intercropping has long been recognized as the ideal technique for remediating soil and using the land for economic advantage (Lin et al. 2015; Srivastava et al. 2021). The *P. vittata*cocultivation with rice has significantly reduced rice's As and DMA concentration (Ye et al. 2011).

## 20.7 Disposal of Plants After Remediation

The aim of phytoremediation cannot be encountered if plants utilized in this process are not accurately discarded or controlled after discharging metals in the atmosphere because of the deposition of metals in the biomass of plant (Ghosh et al. 2005). Phytoremediation becomes a much more environmentally safe method due to the recycling ability of final materials of this process. Composting is known as the secure discharging method of heavy metals. It helps in diminishing the amount of biomass and simple transportation (Mohanty 2016; Newete and Byrne 2016). The main disadvantage is the transportation of poisonous materials from one location to another (Ghosh et al. 2005).

The procedures lime can use to lower the leachability of heavy metals (Vocciante et al. 2019) are known as stabilization procedures. Plants that use such procedures are not able to discard at any place, but they discard in specific locations such as areas near mines. Generally, incineration and generated charcoal are other procedures thatare the causative agents of producing energy for cooking fires (Ghosh et al. 2005). It confirms that biomass is not utilized for producing chemicals forplant growth and food foranimals. As it can pollute the air, thus incineration is not suggested forexecution in uncovered areas. Pyrolysis is another substitute in which biomass is heated in the absence of oxygen between 350 and 650 °C (Vocciante et al. 2019).The final materials are pyrolytic fluid oil and coke (Newete and Byrne 2016). In biogasification, methanol (gas) and some liquids are generated, and they are used as an origin of fuel (Monanty 2016). The sorption of methylene blue (dye) can occur by producing biochar (Gong et al. 2018).

## 20.8 Conclusion and Future Perspective

The conventional As remediation technologies have evident limits, whereas phytoremediation is now a realistic, cost-effective, and trustworthy solution for abating As toxicity. Along with technological and scientific research development, phytoremediation will be made more sustainable and utilized in an excellent manner. To aid comprehension, the following options are stated:

(1) One of the most important criteria for the successful restoration of contaminated areas and polluted fields is proper plant selection. Plant variety and variability increased throughout time, providing a wide range of plant alternatives. Economic plant species that are not edible may be used for safe phytoremediation and revenue production.
(2) The use of plant growth-promoting microbes, nanoparticles, and other integrated approaches have tremendous potential to significantly reduce As pollution in plants and the environment. However, extensive study is needed to fully understand the potential of microbe/nano-assisted phytoremediation to purify As-contaminated soils.
(3) Although the number of microbes associated with plants is growing all the time, more research into the methods and roles of individual genomes and the enzymatic activities involved in Photobiol As cleaningis still needed. In addition, further focus on functional tests is necessary to determine if microbiota boosted with As stress improves the plant.
(4) For practical ramifications, a better knowledge of the processes involved in bacterial As oxidation is required. In addition, the use of genetic engineering in the utilization of As in bioenergy generation and microbial fuel cell applications might bring fresh insights.
(5) Phytoextraction of As by hyperaccumulators is one of the promising techniques, as shown by a number of practical implications. However, the fate of acquired biomass must be considered; composting, pyrolysis, or biogasification may all be viable options.
(6) Currently, no specific advice is available on the design criteria for establishing a big wetland for arsenic removal. Extensive lab, pilot, and field-scale research and geological modeling studies are necessary to develop a constructed wetland.
(7) The crucial need for a successful phytoremediation application is a cost–benefit analysis and computation of landowner economic advantages in the clean-up process.

More research is needed to improve phytoremediation technology, and new technology may be developed to separate heavy metalloids. For example, waste biomass and the reuse of safe biomass with a high quantity of stored carbon for biofuel or feed. Finally, we might claim that phytoremediation cleaning, either alone or in cooperation with others, represents a potential low-cost option. As a result of restoration throughout a large portion of As polluted soil and visually pleasing to the community.

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# Chapter 21
# Nanoparticulate Iron Oxide Minerals for Arsenic Removal from Contaminated Water

**Hamna Bashir, Irshad Bibi, Muhammad Mahroz Hussain,
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**Abstract** Groundwater contamination with arsenic (As) is a global environmental and human health problem affecting over 200 million people worldwide, with low to high concentrations of As via drinking well water. Therefore, remediation of As-contaminated water has been under discussion over the last 3 to 4 decades given its highly toxic and carcinogenic properties of As compounds, particularly inorganic arsenite and arsenate species. Several types of sorption techniques have been used to remove As from water such as clay minerals, biochars, metal oxides (e.g., iron oxide minerals), microbes and algae. This chapter provides: (1) insights on the significance of nanoparticulate iron (Fe) oxide minerals (such as nano-ferrihydrite, nano-goethite, nano-magnetite) for their efficiency in the removal of As from contaminated water; (2) develops critical understanding for several As removal methods, compares their potential for As remediation, and critically examines the properties and effectiveness of nanoparticulate Fe oxide minerals to remove As in drinking water or wastewater; and (3) implication of the nanotechnology in remediation of As-rich water. This chapter also elucidated the mechanism of As removal using Fe-oxide nanoparticles in detail.

**Keywords** Groundwater · Health · Nanoparticles · Remediation · Water treatment

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## 21.1 Introduction

Globally, arsenic (As) is recognized as one of the most toxic geogenic pollutant, which is released into groundwater and makes its pathway to humans through As-contaminated drinking water and food. Arsenic related health risks have been reported in more than 100 countries throughout the world, especially in the developing countries including Pakistan, Bangladesh and India (Hussain et al. 2021; Natasha et al. 2021). Natural processes including the weathering of parent material, geothermal waters and vulcanization and anthropogenic activities such as mining and smelting, metallurgy, fossil fuel burning, use of As-containing pesticides, herbicides, and crop desiccants have led to pollution of soil, groundwater, surface water with varying concentrations of As (Abbas et al. 2018; Bundschuh et al. 2022; Hussain et al. 2020a; Shaheen et al. 2022).

Chronic As exposure, particularly through drinking water, has been related to a number of detrimental health effects, including arsenocosis, cardiovascular and haematological effects, cancers of skin, bladder, kidneys and neurological problems (Aftabtalab et al. 2022; Shahid et al. 2017). Environmental and regulatory authorities have taken a serious stance on As in water due to its devastating effect on human health. The World Health Organization defined a maximum allowable limit for As in drinking water of 10 $\mu g\ L^{-1}$ (WHO 2011) and recently in the Netherlands a debate on setting a new limit of 1 $\mu g\ L^{-1}$ has been started for As in drinking water (Ahmad et al. 2020).

Several treatment technologies (e.g., chemical precipitation/flocculation, adsorption, ion exchange, reverse osmosis, and electrodialysis) have been evolved for removing As from contaminated water (Khan 2020; Natasha et al. 2021; Shaheen et al. 2022; Shakoor et al. 2018; Singh et al. 2022; Yadav et al. 2017). Membrane techniques such as nanofiltration and reverse osmosis, for remediating As in surface water and groundwater have been used over the past few decades (Amen et al. 2020; Basu et al. 2014b; Pan et al. 2021; Shaheen et al. 2022; Shakoor et al. 2016b). These techniques have some advantages such as high removal efficiency, convenience of use and reduced detrimental sludge buildup throughout the operation. The initial capital and running expenditures are high like extremely high pressure in membrane filtration to drive tainted water through the membrane requires energy and cost. Furthermore, in membrane processes concentrate discharge, membrane fouling, and flux reduction are unavoidable. Similarly, electrodialysis can eliminate As from water and other impurities, but it leads to a large amount of insoluble coagulant on the cathode (Sawood and Gupta 2018).

Because of its low cost, high efficiency and convenience of use, nanoadsorption may be one of the most promising technologies for eliminating As and other hazardous metal (liods) from contaminated water (Nazri and Sapawe 2020; Niazi and Burton 2016b; Pal et al. 2018; Patel et al. 2022b; Shaheen et al. 2022; Singh et al. 2022). Iron-based sorbents have been investigated and found to be effective in removing As from water (Ali et al. 2018; Shaheen et al. 2022). Granular ferric hydroxide (GFH) and nano zero-valent Fe are the two adsorbents that have been commercially produced on a significant scale with high As removal efficiency. However, most of these adsorbents are rarely used in practical field applications due to the existence of interfering ions in water despite the fact that they have high efficiency for removing As in water (Luo et al. 2018). Zero-valent iron is the most studied nanomaterial for water filtration. It is one of the most popular nanosorbents because it captures the broadest range of environmental pollutants such as halogenated organics, pesticides, arsenic, nitrates, and heavy metals (Table 21.1). Common anions such as chlorides, nitrates, and sulfates have little effect on As adsorption by the Fe-based sorbents because of the unique chemical interaction between As and Fe. Phosphate has been demonstrated to effectively compete with As, especially with arsenate (As(V)) for adsorption sites, thus decreasing adsorption capability of Fe oxides (Singh et al. 2015).

Similarly Rashid et al. (2020) reported that 99.57% of the As was removed with nZVI by adsorbing As species on the surface of Fe nanoparticles. Furthermore, Wu et al. (2019) found that As(V) adsorption was found to fit well with pseudo-first and pseudo-second order kinetic models, suggesting that removal of As(V)

**Table 21.1** Nanoparticulate iron oxide minerals, iron oxide minerals, and modified Fe oxide nanoparticles potential to remove arsenic (As) from As-contaminated water

| (Nano) iron oxide minerals | pH | Sorbent dose ($g\ L^{-1}$) | Arsenic (M) | Adsorption capacity (mg/g) | | References |
|---|---|---|---|---|---|---|
| | | | | As(III) | As(V) | |
| Ferrihydrite | 4.6, 9.2 | 2–40 | $2 \times 10^{-4}$–0.028 | 266 | 111 | (Baragaño et al. 2020; Gallegos-Garcia et al. 2012; Shaheen et al. 2022; Xu et al. 2022) |
| Ferrihydrite | 7 | 0.44 | 0–$2 \times 10^{-3}$ | – | 87 | |
| Goethite | 7 | 0.44 | 0–$5 \times 10^{-4}$ | – | 442 | |
| Goethite | 2–10 | 4 | $6.6 \times 10^{-6}$ | – | 0.50 | |
| Hematite | 2–10 | 4 | $6.6 \times 10^{-6}$ | – | 0.50 | |
| Goethite | 1.5–2.5 | 2.5 | $3 \times 10^{-5}$ to $1 \times 10^{-2}$ | – | 15 | |
| Goethite | 7.5 | 5 | $10^{-6}$, $10^{-3}$ | 0.374 | 0.449 | |
| Magnetite | 6.5 | 5 | $10^{-6}$, $10^{-3}$ | 0.206 | 0.253 | |
| Hematite | 7.3 | 5 | $10^{-6}$, $10^{-3}$ | 0.265 | 0.827 | |
| Granular ferric hydroxide (GFH) | 6.5–7.5 | – | 0.1 mg/L | – | 1.1 | (Sorlini et al. 2015) |
| β-FeOOH nanoparticles | 7.5 | – | 20 mg/L | – | 120 | (Sun et al. 2013) |
| Magnetite | 5.0 | – | 70 mg/L | 16.56 | 46.06 | (Feng et al. 2012) |
| Magnetite-maghemite ($Fe_3O_4$–γ-$Fe_2O_3$) | 2.0 | – | 1.5 mg/L | 3.69 | 3.71 | (Chowdhury et al. 2011) |
| Nano-Fe/oyster shell | 6.8 | – | 1.8 mg/L | 0.9 | – | (Fan et al. 2015) |
| $FeCl_3$ treated chestnut shell | 9.0 | – | 100 mg/L | 0.9 | – | (Targan and Tirtom 2015) |
| $Fe_3O_4$ coated wheat straw | 6–8 | – | 28 mg/L | 3.9 | 8.1 | (Sharma and Bhattacharya 2017) |

with Fe nanoparticles synthesized from eucalyptus involves a physical and chemical process adsorption. By promoting almost complete immobilization of As(V) species, Fe nanoparticles do not convert As(V) to the more toxic As(III) unless the Fe-material is exposed to a low pH and $E_h$ (Xu et al. 2022). After the diffusional surface adsorption and internal diffusional adsorption reach equilibrium, Fe(III) in the Fe nanoparticles is coordinated with As(V) to form monodentate chelating ligands and bidentate binuclear complexes (Table 21.1). Subsequently, co-precipitates form and accumulate into corrosion products on the surface of iron nanoparticles (Baragaño et al. 2020; Xu et al. 2022). So, keeping in view the importance and implications of Fe-oxide nanoparticles this chapter briefly reviews various As removal methods, compares their potential for As remediation, and critically examines the properties and effectiveness of nanoparticulate Fe oxide minerals for removing As from water.

## 21.2 Technologies for Arsenic Removal from Water

Arsenic removal technologies must meet a number of basic technical requirements, including robustness, environmental-sustainability, the ability to provide water supply systems all year, taking current climate change scenarios into account, and the required physicochemical and microbiological quality (Rahman et al. 2014). Main aim is to develop a conceptual framework for As removal that takes into account the presence of different As species such as As(III) and As(V) in the aquifers. If As removal is more critical and complex due to its hydrogeochemical behavior in water bodies, utilization of a membrane filtration procedure (reverse osmosis or nanofiltration) without an As(III) oxidation step (traditional or alternative approaches) can be employed (Seyfferth et al. 2010; Shakoor et al. 2016a).

## 21.3 Traditional Techniques

Physical exclusion is a method of eliminating dissolved As and other particulate components by passing them over synthetic membranes that are permeable to some, but not all dissolved substances. These membranes may remove dissolved As from the flowing water but this is an expensive method that involves high material and synthesis cost with high operation costs.

Coagulation filtration and lime softening are both inexpensive, but ineffective methods (~90%). Aluminum carbonate adsorption is one of the most efficient and cost-effective technologies (>95%) (Hoque et al. 2017). Under various experimental settings, many hybrid inorganic–organic adsorbents containing thiol groups were produced by altering activated alumina (AA) with mercaptopropyl-functionalized silica. The insertion of thiol groups improves the adsorption capability of the hybrid adsorbent for As(III), while maintaining the advantages of AA for As(V) adsorption (Postma et al. 2017).

### *21.3.1 Physicochemical Technologies for Arsenic Removal*

Although the above-mentioned traditional As removal techniques are well documented, some of them have recently gained popularity. New technologies for eliminating As are now being researched extensively. These methods concentrate on low-cost methods for improving the efficiency and cost-effectiveness of As removal in small water systems. Adsorption, for example, has been improved by introducing novel chemical oxidation processes and enhancing or employing new adsorption materials. The majority of these methods rely on As(III) oxidation followed by filtration through porous media to remove As via adsorption and coprecipitation (Mondal and Garg 2017).

### *21.3.2 Biological Methods for Arsenic Removal*

Many of the above chemical processes can be catalyzed by introducing bacteria to enhance bio-scavenging activity, but nothing is known about As bio-scavenging from water yet. Depending on the physicochemical state of the environment, some As compounds are extremely soluble. Arsenic species determines their toxicity and bioavailability, which is determined by microbial alterations such as reduction, oxidation, and methylation. Commercially viable and environmentally-friendly ways for removing As in water are chemical or adsorption based approaches. Understanding the metabolism of As in bacteria can aid in the prevention of As contamination in water bodies (Basu et al. 2014a; Hussain et al. 2021).

The majority of research, however, has been carried out at the pilot-scale and must be expanded and examined at large scale to determine their viability and potential for remediating As-contaminated waters. Various As remediation processes (such as oxidation/reduction, precipitation/dissolution, and adsorption/desorption) and biological mechanisms (oxidation, reduction, methylation, and thiolation of As species) (Hussain et al. 2019, 2020b). In certain reactions microbes play an important role in remediating As-contaminated water but the limitation of these process must be known that microbes can regulate the change in the $E_h$ and pH of the aquifers thus interfering the As hydrogeochemical cycling (Crognale et al. 2017).

## 21.4 Production of Nanoparticles and Their Implications

Nanoparticles are advanced materials in nanotechnology, and can be defined as the physical and chemical modification of substances to produce materials with specific features and properties that can be used for a variety of applications with a size of less than 100 nm (Badetti et al. 2021). Nanoparticles have features or functions that are distinct from bulk materials, such as thermal, electrical, chemical, optical, medicinal, and agricultural engineering, information, and communication (Khan 2020; Mushtaq et al. 2020). Traditional methods for synthesizing NPs, such as pyrolysis and abrasion, have a number of drawbacks, including surface creation flaws, limited productivity, high cost, and high energy demand (Table 21.2). The majority of the nanoparticles created are commonly used in photocatalytic dye removal techniques (de Souza Trigueiro et al. 2021). Toxic chemicals are frequently used in chemical syntheses such as sol–gel and chemical reduction processes, which result in harmful by-products and contamination of precursors.

As a result, it was discovered that developing ways to synthesis NPs results in nanoparticles that are clean, non-toxic, and ecologically benign (Siddiqui et al. 2019b). Green syntheses have been extensively documented in numerous publications for their adsorption capacity and effectiveness for pollutants removal such as As, Cr, and other PTEs when compared to other traditional approaches (Table 21.2). These green synthesized NPs do not include any dangerous chemicals and are made using non-toxic technologies to generate clean and environmentally friendly NPs on a wide scale (Sreeja et al. 2015). Biosynthesis components such as enzymes and microorganisms can act as capping or reducing agents, lowering the cost of the synthesis process and eliminating the need for significant energy consumption (energy saving). As previously stated, a great range of biological resources can be produced by synthesizing nanoparticles from microbes and plant extracts, such as Several authors have recently discovered methods based on microbial synthesis that mediate the biological creation of nanoparticles advantageous for the removal of contaminants, pharmaceuticals, product manufacturing, and other applications in their research and plants (Yan et al. 2015b; Yang et al. 2018).

Plant extracts can rapidly decrease metal ions, reducing the time required to synthesis NPs when compared to other biological sources. Depending on the plant variety and concentration of phytochemicals utilized, NPs might be created in minutes or hours. This benefit is clear when employing plants, as the synthesis of different nanoparticles takes time, but other natural sources create NPs quickly (de França Bettencourt et al. 2020). The disadvantage of microbes is a major issue while creating nanoparticles that require sterile settings. The costs of handling microorganisms, such as skilled personnel and cost scaling, are typically prohibitive (Dildar et al. 2022).

## 21.5 Technology for Nanoparticles Biosynthesis

Because of their numerous chemical and physical features, nanoparticles made by biological or known biosynthetic processes are becoming a popular synthesis approach. The necessity to generate environmentally-friendly nanoparticles in materials synthesis has drawn the attention of researchers all over the world to the integration of nano and biological technologies. The capabilities of this technique have been extensively researched, particularly in the synthesis of inorganic compounds (Table 21.2). Metal nanoparticles mediated by microorganisms and plants are the subject of

**Table 21.2** Iron NP synthesis techniques and their product morphology, advantages, and disadvantages

| Techniques | | Advantages | Nanoparticles morphological description | Disadvantages | References |
|---|---|---|---|---|---|
| Physical (8% of total nanoparticles production) | Electron beam lithography | Well-controlled interparticle spacing | Spheres and irregular spheres | Problematic in controlling the size of particle | (Soenen et al. 2009) |
| | Deposition of gas phase | Easy to execute | Spheres and rods | Requires expensive and highly complex machines | (Cuenya 2010) |
| Biological (2% of total nanoparticles production) | Microbial incubation | Small platelets, spherical or rod-like spheres, irregular spheres | Small platelets, spherical or rod-like spheres, irregular spheres | Slow and laborious | (Narayanan and Sakthivel 2010) |
| Chemical (90% of total nanoparticles production) | Oxidation | Narrow size distribution and uniform size | Irregular elongated and small spheres | Ferrite colloids of small size | (Lin and Samia 2006) |
| | Hydrothermal | Particle size and shapes are easily controllable | Elongated, compact rregular spheres, and numerous shapes | High pressure and reaction temperature | (Wu et al. 2008b) |
| | Sol–gel method | Aspect ratio, precisely controlled in size, and internal structure | Spheres, irregular spheres, porous and nonporous spheres, or spindles | High permeability, weak bonding, low wear resistance | (Laurent et al. 2008) |
| | Chemical co precipitation | Simple and effective | Spheres | Inappropriate for the synthesis of high untainted, precise stoichiometric phase | (Wu et al. 2011) |

ongoing research. The NPs are less harmful and environmentally-beneficial. Green chemistry can refer to a wide range of microorganisms, including bacteria, fungus, and plants (Niazi and Burton 2016a; Saunders et al. 2018; Yan et al. 2015a).

Nanoparticle creation requires three primary components that should be tailored to the green chemistry area, namely H solvents appropriate as synthesis media, a moderate reducing agent environment, and no harmful compounds are created. Synthetic methods have been shown to have major negative consequences for organic solvents, not only for the environment but also for individuals. Nanoparticles are safe for many manufacturing uses, thus research and development necessitate cross-sectoral usage of environmentally friendly and biocompatible processes to generate them (Singh et al. 2022). Microorganisms and plant extracts can thus produce nanoparticles that can be used as eco-friendly nano factories as building blocks and biomolecules.

## 21.6 Biocompatible Green Reagents Synthesis Biopolymers

Non-toxic synthetic biocompatible materials have been studied for the creation and stability of magnetic nanoparticle-polymer composites. Zhang et al. (2020) reported that water-soluble starch to stabilize bimetallic Fe/Pd nanoparticles in this experiment. Starch is a hydrophilic polymer made up of around 20% amylose that was discovered to be helpful in dispersing and stabilising iron nanoparticles in this study. Another work used a redox-based hydrothermal technique to make magnetite ($Fe_3O_4$) nanoparticles from the biopolymer sodium alginate utilising $FeCl_3.6H_2O$ and urea as starting ingredients. The sodium alginate nanoparticles had a homogeneous spherical shape with an average diameter of 27.2 nm. Ahmad and Mirza (2018) first created well-dispersed magnetite ($Fe_3O_4$) agar nanocomposites by co-precipitating Fe(III) and Fe(II) ions.

Further Patel et al. (2022a) reported on the creation of Fe nanoparticles utilizing ascorbic acid (vitamin C). Aqueous ascorbic acid (vitamin C), which lowers transition metal salts to their corresponding nanostructures, was used to make core–shell iron and copper nanoparticles. Similarly, Savasari et al. (2015) employed ascorbic acid to make stable zero-valent iron nanoparticles that self-assemble into chains, with individual particles measuring 20 to 75 nm in diameter. Furthermore, ascorbic acid has been employed as a nanoparticle functionalizer and stabiliser. In one work, superparamagnetic iron oxide nanoparticles were coated with ascorbic acid (vitamin C) and subsequently functionalized to generate stable dispersions for medical purposes. The coated nanoparticles revealed spherical particles with an average particle size of 5 nm in transmission electron microscopy (TEM) pictures (Sreeja et al. 2015).

***Amino acids***: Wet-chemical co-precipitation was used to prepare amine-functionalized magnetite nanoparticles, according to Krishna et al. (2012). Functionalization with L-lysine amino acids produced a highly crystalline magnetite phase (in situ). Similarly, the effect of pH on zero-valent iron production was studied using various amino acids such as L-glutamic acid, L-glutamine, L-arginine, and

L-cysteine. Hemoglobin and myoglobin are two different types of hemoglobin. Single-phase chemical reduction yields stable iron nanoparticles at room temperature, according to a study. The synthesized particles' size distribution ranged from 2 to 5 nm, and they were found to be crystalline. This method of making bioconjugate nanoparticles for biological applications could be a useful and important technical approach.

## 21.7 Arsenic Removal Using Nanoparticulate Iron Oxides

Nanopartichuate Fe oxides mineral-based sorbents have received significant attention because of their high As removal efficiency, eco-friendly nature, and ease of synthesis and availability (Table 21.2). The research was previously focused on the synthesis of new nano-Fe adsorbents with high As adsorption potential (Xu et al. 2022). Nanoadsorbents produced from (nano) Fe-oxide minerals, nano zero-valent Fe, Fe-based bimetallic oxides, and Fe-impregnated composite adsorbents has been explored for their application for As removal under different conditions (Aftabtalab et al. 2022; Baragaño et al. 2020; Rashid et al. 2020; Siddiqui et al. 2019b).

Environmental remediation employs certain metal nanoparticles (NPs) with adsorptive capacities such as $TiO_2$, ZnO, and Ag NPs (Zhu et al. 2019b). However, due to their potent photocatalytic properties, these metal nanoparticles are better suited for use in ceramics, optics, chemistry, biology, electronics, and other domains. Many other compounds have been reported as above to have a great affinity for As, but Fe oxyhydroxide has gotten the most attention because of its ease of usage (Saravanan et al. 2021). Ferrous and ferric salts, which are generated by hydrolysis and oxidation processes, can precipitate as akaganeite ($\gamma$-FeOOH), goethite ($\alpha$-FeOOH), ferrihydrite ($Fe_{10}O_{14}(OH)_2$), and patina as shown in Fig. 21.1 (Cantu et al. 2016).

## 21.8 Arsenic Removal Adsorption Process

### *21.8.1 Coagulation/Flocculation*

Colloidal solid particles in As-contaminated water initially coagulate because the ions appear as hydrolyzed species in the Stern layer of the colloidal particles ($Al_3$ or $Fe_3$ ions). Electrolytic coagulation has the similar mechanism of As removal as the addition of single coagulant (Mohamed Noor et al. 2021). Dissolved As ions react with hydrolyzed species in the stern layer to produce Fe-As(V) ($FeAsO_4$) or aluminum-As(V) ($AlAsO_4$), which is adsorbed on the coagulum. This phenomenon is referred to as precipitation or co-precipitation (Siddiqui et al. 2019b).

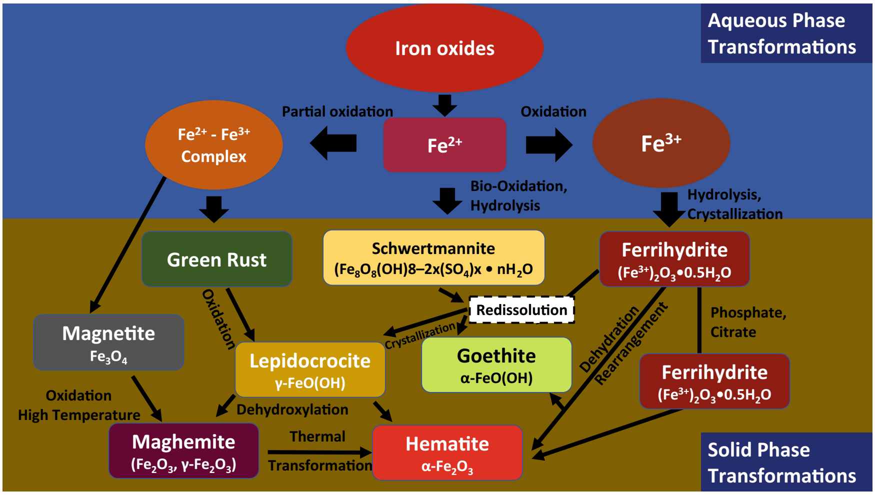

**Fig. 21.1** Different iron oxide minerals and their transformations pathways in aqueous and solid phase

## 21.8.2 Ion Exchange Method

Further advancement to coagulation method methods includes the exchange of ion between different species. Thus the addition of Fe-oxides and Al(OH) flakes, for example, exhibit a strong attraction for dissolved As. Arsenic is drawn to adsorption sites on the solid surface and remediated from the solution phase. Ion exchange is a one-of-a-kind form of adsorption, and it is frequently regarded as such. Ion exchange is the reversible displacement of adsorbed ions by dissolved As species on a solid surface. Other sorts of adsorptions result in stronger, reliable compounds that has more half-life with larger surface area that can be easily removed by using other coagulants. In the adsorption process, the adsorbent is the most significant factor. Adsorbents with a porous structure and a high surface-to-volume ratio are effective (Basu et al. 2014a; Singh et al. 2015).

To remove As from water, various adsorbents (natural and synthetic sources) have been developed, such as polymeric resins, activated carbon, ion exchange resins, and hydrous metal oxides, such as activated alumina, metal-supported coral limestone, hematite ore, and porous resins loaded with crystalline hydrated zirconia. The Fe oxide has a stronger ability to absorb As from water than activated alumina in fixed bed systems. Adsorption is commonly thought of as a method of removing As (Aftabtalab et al. 2022; Saravanan et al. 2021; Shaheen et al. 2022). It is influenced by pH, sorbent pretreatment, and the presence of other ions (sulfate, chlorides, etc.). Organic components in aqueous solutions can reduce As removal considerably. This could be explained by competing effects of coexisting solutes on adsorption, such as surface complexation processes, inner and outer layer complexes along with string affinity for As sorption sites. The phosphate ion is a frequent competitor in the As adsorption process due to chemical characteristics similar to As(V) (Mandal et al. 2018; Niazi et al. 2017).

## 21.9 Adsorption of Arsenic on Nano-Iron Enabled Minerals

### *21.9.1 Nano Iron Oxide Minerals for Arsenic Adsorption*

Iron oxide minerals such as goethite, hematite, limonite, ferrihydrite, and magnetite has been reported to be used as adsorbent for As removal (Table 21.1). Goethite (α-FeOOH) is a Fe oxide mineral formed of two FeO(OH) octahedral double bands sharing edges and corners to form a 2:1 octahedral tunnel partially connected by H-bonding (62.9%), Fe and $O_2$ (27%), 10.1% of O and $H_2O$ (Fig. 21.2). This sample contains acicular crystals with grooves and edges. Hematite ($Fe_2O_3$) is a mineral composed of 70% iron and 30% oxygen. The cations are octahedrally coordinated, and the structure is based on hexagonal oxygen atom closest packing (Nazri and Sapawe 2020). The most common and important iron ore is hematite, which can be found in rocks.

The ability of Fe oxide minerals to absorb As has been studied in a number of ways. Goethite is the best iron oxide mineral for adsorbing As in water. The adsorption of As(V) on goethite in water was studied by Mamindy-Pajany et al. (2009) as a function of pH and ionic strength. Goethite retains a maximum amount of As(V) in acidic pH conditions with adsorption of As(V) on the goethite surface is unaffected by ionic strength. Moreno-Jiménez et al. (2012) reported that similar results for As(III) and As(V) adsorption on goethite in water. Synthetic goethite has a capacity of 5 mg $g^{-1}$ of As adsorption at pH 5.0 (Chowdhury et al. 2016). To assess the As adsorption capacity, Siddiqui and Chaudhry (2017) reported that in a batch experiments with synthetic goethite at pH 1.5–2.5 and various ionic strengths (0.02–0.15 $mol^{-1}$ NaCl). A Langmuir isotherm was used to fit As adsorption to goethite. Ionic strength and pH have modest effects on adsorption capacity at lower pH values. Sulfate ions obstruct As removal from water by competing with As(V) for adsorption sites on the goethite surface. Hematite's potential to remove As(V) from aqueous settings has also been investigated. To fit the adsorption of As(V) on hematite, Langmuir isotherms were used (Siddiqui et al. 2019b; Singh et al. 2015).

Adsorption of As(V) is preferred electrostatically above hematite PZC (point of zero charge) (pH 7.1). Adsorption fell below pH 4.2 due to hematite breakdown and reduction in the number of adsorption sites between 3 and 11 on the pH. The adsorption and desorption behaviour of As(V) and As(III) on doublet ferrihydrite was studied by Liu et al. (2020) that showed As(V) and As(III) significantly adsorbed on Fe-oxide materials. The As(V) is thought to have a stronger affinity for Fe-oxide surfaces than As (III) (Xu et al. 2022).

Magnetite has been utilized as adsorbents to remove As from water in series of batch sorption experiment. However, the kinetics of As(V) adsorption on goethite

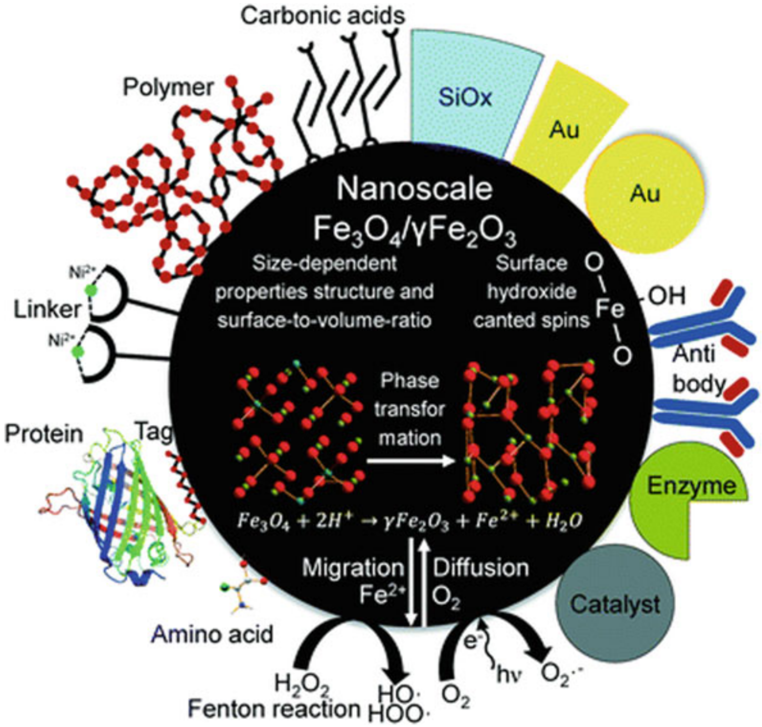

**Fig. 21.2** Sorption pathways for the iron oxide nanoparticulate minerals (Reproduced with permission from Publisher from Schwaminger et al. (2017). This article is licensed under a Creative Commons Attribution-NonCommercial 3.0 Unported Licence and open access to use material)

revealed two states (Yadav et al. 2017); (i) the first high rate of adsorption could be due to As(V) adsorption at more accessible spots on the goethite's outer surface, whereas (ii) the second low rate of adsorption could be due to As(V) slowly diffusing into the pores of the goethite particles due to goethite (Balint et al. 2020).

### *21.9.2 Arsenic Adsorption on Nanoparticulate Iron Oxide Minerals and Effect of Various Factors*

The speciation of As in solution is influenced by the pH of the solution. The pH-dependent distribution of As(V) and its hydrolyzed species. While As(V) species are only stable in the right pH range, for example, pH 2 for $H_3AsO_4$, pH 2–7 for $H_2AsO_4$, pH 7–11 for $HAsO_2$, pH > 12 for $AsO_3^{4-}$, At pH 9, As(III) is stable as $H_3AsO_3$, pH 9–12 in $H_2AsO^{3-}$, pH 12–13 in $HAsO_2^{3-}$, and pH > 13 in $AsO_3^{3-}$ (Xua and Lia 2020). Each species of As is known to have a particular affinity for the

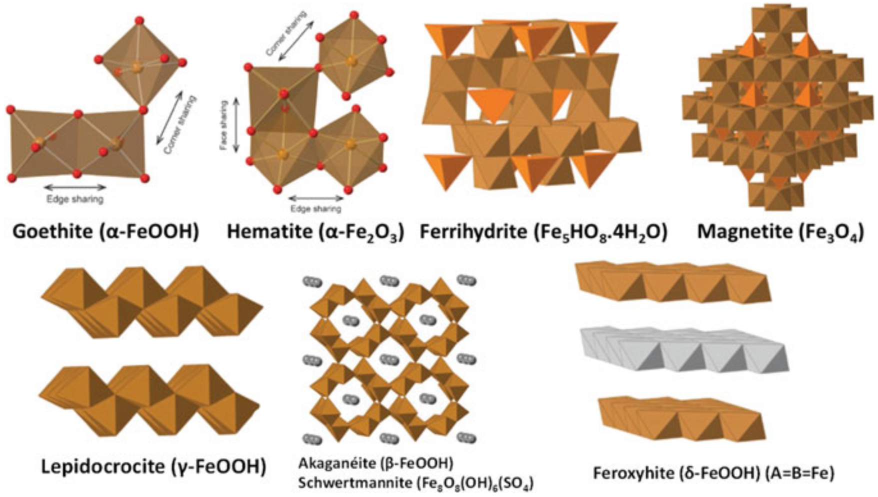

**Fig. 21.3** Structural demonstration of the different nanoparticulate iron oxide minerals (modified from Scheinost and Singh 2022)

surface of Fe-oxide minerals. As a result, the chemisorption capacity of As on Fe-oxide mineral surfaces changes depending on the As species and hence the pH of the solution altered (Fig. 21.3). The adsorption of As(V) by Fe-oxide minerals declines with increasing solution pH and peaks at very low pH values, whereas As(III) adsorbs at these pH values and peaks around pH 8.5. (Koomson and Asiam 2020). The pH of the solution has an impact on the surface charge on Fe-oxide mineral particles. The surface is negatively charged in the pH range above PZC (Khan 2020; Pan et al. 2021).

Because the charge of the adsorbent and the adsorbate have the same sign in the pH range above PZC, there is an electrostatic repulsion between the As species and the surface of the Fe-oxide material, that results in low sorption for As species (Adebayo et al. 2020). The amount of As adsorption onto Fe oxide minerals is reduced when competing anions are present. In the presence of phosphate ions, for example, As(V) and As(III) adsorption on goethite is greatly reduced, while some sites are far more selective for As(III) than for phosphate. Other anionic components, such as sulphates, chlorides, or natural organics, can impair the efficacy of As removal by adsorption utilizing Fe-oxide rocks as the adsorbent (Doherty et al. 2021). The conflicting effects of coexisting solutes on As adsorption, such as surface complexation processes, can explain this. Because of its molecular closeness to As(V) and its abundance in natural water, phosphate is a common competitor in the As adsorption process (Kobya et al. 2020).

### *21.9.3 Adsorption of Arsenic by Iron Oxide Minerals in Water*

Several Fe-oxide minerals have been investigated for their ability to adsorb As from contaminated water. A large percentage of As was removed. The elimination of arsenic is greatest at acidic pH and minimal at alkaline pH (Kamei-Ishikawa et al. 2017). At pH 3–6 and an As concentration of 13.35 mmol$^{-1}$, the greatest removal of As(V) using hematite as an adsorbent was almost 100% (Koomson and Asiam 2020). Rahim and Haris (2015) reported that the ability of natural hematite to remove As from drinking water using batch and column experiments. It has been discovered that as hematite grain size decreases, removal efficiency increases. Nitrate ions had little influence on As(V) uptake, however phosphate ions significantly slowed it down. Natural hematite, can be used as a sorbent to extract As from water, but it is more effective than hematite (Guo et al. 2014). The physical and chemical features of mineral powders, such as particle size, specific surface area, surface active sites, and microscopic surface morphology, are known to influence As adsorption on Fe oxide minerals.

## 21.10 Arsenic Adsorption Mechanisms on Nanoparticulate Iron Oxide Minerals

The extended X-ray absorption fine structure (EXAFS) spectroscopy was used to investigate As(V) adsorption on Fe-oxide minerals (Herath et al. 2020; Palansooriya et al. 2020). On the Fe-oxide surface, the As(V) complex in the form of the bidentate binuclear inner sphere was shown to be the thermodynamically most favorable and consequently most numerous species. However, there are some inconsistencies in the production of bidentate mononuclear and monodentate complexes, leaving As(V) adsorption on Fe-oxides unsolved. On dried samples, Fourier transform infrared (FTIR) spectroscopy was used to analyze development of bidentate binuclear complexes (Zama et al. 2018; Zhu et al. 2019a). The hydroxyl groups on the Fe-oxide surface generate the As complex, according to the findings. The hypothesized mechanism consists of two steps: (i) the creation of a monodentate surface inner sphere complex with a high adsorption rate, (ii) followed by slow ligand exchange and the formation of a bidentate inner sphere complex (Cui et al. 2018; Wu et al. 2018).

Covalent bonds between adsorbed ions and reactive surface functional groups are defined as inner sphere complexes (Pintor et al. 2020). In a 1:1 stoichiometric ratio, the complexes of the inner spherical surface can form monodentate complexes (e.g., -Fe-$OAsO_3H$) or bidentate complexes in a 1:2 stoichiometric ratio (Sobh et al. 2019). Most As(V) and As(III) oxanions replace the two separately coordinated -OH groups on the surface of Fe-oxide minerals, forming the Fe-O-AsO(OH)-O-Fe and Fe-O-As(OH)-O-Fe dinuclear bridging complexes (Dixit et al. 2016). Arsenite prefers two-coordinate surface OH groups, whereas As(V) prefers three-coordinate surface OH groups. The $HAsO_2^{2-}$ ion takes part in the ligand exchange reaction, displacing mono-coordinate surface hydroxyl groups and adsorbing as dinuclear species to iron oxide minerals (Zhu et al. 2020). The predominant binding mechanism for As(V) adsorption to goethite is still the bidentate binuclear complex. The age of the surface-covering oxides influences the three forms of As(V)-goethite surface complexes. The ligand exchange reaction of $H_2AsO_2^{4-}$ with surface OH groups create monodentate complexes with exceptionally low surface occupancy (Li et al. 2017; Zhao et al. 2021). After the second ligand exchange event, the production of bidentate surface complexes dominates the adsorption of As(V) at large surface loadings.

On goethite and ferrihydrite, As(V) forms intraspheric bidentate complexes. Monodentate complexes can form on crystalline goethite under these conditions, but only at very low surface coverage. The proportion of monodentate bonds diminishes as As(V) coverage of amorphous iron oxide crystals increases, and bidentate binuclear bridge complexes become the dominant adsorbed complexes. pH and As species have a big impact on how As interacts with iron oxide surfaces. On ferrihydrite, the largest As(V) adsorption occurred between pH 3.5–5.5, while the maximum As(III) adsorption occurred between pH 8 and 10. Variable charge characteristics and As species on the surface of Fe oxide minerals are blamed for these tendencies (Almeida et al. 2020). Electrostatic attraction and surface complexation between As species in solution and Fe(II) and/or Fe(III) hydroxides on minerals are thought to be involved, resulting to As adsorption on iron oxides via PZCs (Saravanan et al. 2021; Siddiqui et al. 2019a; Wu et al. 2011, 2008a; Xu et al. 2022).

The As adsorption of Fe oxide minerals has been studied using a variety of techniques including FTIR spectroscopy, X-ray absorption spectroscopy (XAS), and scanning electron microscopy coupled with energy dispersive spectroscopy (SEM–EDX). As a direct method for examining As adsorption processes on Fe oxide minerals, ATR-FTIR spectroscopy has been proposed. Anions displace $OH^-$ and/or $H_2O$ off the surface, resulting in differences in band intensity after and before adsorption, which can be detected by FTIR spectroscopy (Yu et al. 2018).

## 21.11 Conclusions and Future Perspectives

This chapter reviews some important As removal technologies with a particular emphasis on nanoparticulate Fe oxide minerals for As remediation in water because conventional or membrane-based techniques are complex, expensive, and cause secondary pollution in form of sludge production. As a result, selecting the most appropriate treatment plan is critical in order to meet increasingly stringent quality standards of various impurities and toxic ions, such as As in water. The decreasing number of water sources suitable for public supply, the increasingly stringent nature of drinking water quality standards, and the potential impacts of climate change on the quantities of potable water highlight the significance of alternative, sustainable, and low-cost As removal technologies.

Until now, the majority of previous research has been directed into developing new adsorbent materials with high adsorption capabilities. Furthermore, nanomaterials have been investigated for As adsorption in recent years although nanoparticles could agglomerate in water, reducing adsorption and removal efficiency. As a result, loading nanoparticles onto appropriate supporting bio- or geo-materials is becoming a viable technique, with the benefits of high reactivity and ease of water separation. Adsorbent-based technologies must be developed further to be utilized in the field in a sustainable manner. More research is needed to discover the local and frequently available resources to produce Fe nanoparticles to accomplish the sustainability of nanomaterial synthesis. Understanding the molecular mechanisms involved in Fe oxides nanoparticles efficiency to remove As is essential for determining the environmental fate of adsorbed As and its safe disposal. Further studies in the future should focus on green synthesis techniques to mediate Fe nanoparticles production at large scale. It is important to improve Fe oxides nanoparticles stability. Some previous studies have reported that the biosynthesized Fe nanoparticles are less hazardous than designed nanoparticles. Furthermore, a full risk evaluation of Fe oxides nanoparticles, green fabricated Fe NPs should be conducted considering their toxicity and fate, transport, dissolution, and kinetics in the environment. The green nanotechnology techniques discussed in this chapter could provide a powerful tool and solid foundation for the manufacturing of a wide range of biological or functionalized Fe oxide nanoparticles that can be used in the development of novel products for use in environmental remediation and restoration programs.

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# Chapter 22
# Arsenic-Toxicity and Tolerance: Phytochelatin-Mediated Detoxification and Genetic Engineering-Based Remediation

**Gouranga Upadhyaya and Aryadeep Roychoudhury**

**Abstract** Arsenic (As), a ubiquitous metalloid in the Earth's crust, is one of the most toxic soil constituents affecting the plants. Accumulating from geogenic and anthropogenic sources, As piles up through the trophic levels of the food chain, leading to human health risk. As-uptake through the roots occurs through the apoplast, enters into the cell cytoplasm by phosphate transporters or aquaporin channels and can be transported to the above-ground tissues also through xylem. As-led toxicity is mediated by oxidative stress, severely impacting the staple food crops worldwide, including rice, wheat, pulses, etc. Decreased germination and vitality index, chlorophyll content, biomass content, etc. massively reduce yield percentage. In response to As-stress, plants have evolved several defense mechanisms, such as the production of antioxidant enzymes, like superoxide dismutase, catalase, glutathione, etc., and induction of phytochelatin synthesis. Phytochelatin-triggered As-detoxification is regulated by the transport of As-phytochelatin complex to the vacuole, leading to metal ion sequestration. Hence, to resolve the adverse effects of As on the whole ecosystem, genetic engineering can be used to develop As-tolerant plants. Overexpression of *phytochelatin synthase* genes, either alone or together with $\gamma$-ECS can render tolerance to As-stress. Thus, significant research has been carried out in recent years concerning As-transport, speciation and detoxification. However, the gaps to be filled include the mechanism of As-compartmentalization in the vacuoles, transport through the xylem, and accumulation in grains. Therefore, studies of cellular mechanism of As-detoxification may open up new prospects to develop tolerant crop cultivars for sustainable As-free agriculture practice. The present book chapter focuses on As-toxicity and detoxification with special emphasis on phytochelatin regulation and genetic engineering approaches to enhance stress tolerance.

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## 22.1 Introduction: Why is Arsenic One of the Most Toxic Elements on Earth?

Arsenic (As), present in more than 200 different minerals in Earth's crust, is ranked as the 20th most omnipresent element in the environment. However, arsenic is categorized as one of the most toxic and carcinogenic elements in the list of world's potential toxic elements. Arsenic and its related compounds are labeled as Group 1 human carcinogen by the US Environmental Protection Agency (EPA) and the International Agency for Research on Cancer (IARC). Even, the Agency for Toxic Substances and Disease Registry (ATSDR) has ranked As among the top 20 priority hazardous substances. The incessant accumulation of As in the environment is contributed by both natural geogenic processes and anthropogenic activities; the geogenic processes include mineral or rock weathering, volcanic activity and hot spring discharges, while anthropogenic ones comprise multiple human activities like mining, smelting, excessive agricultural use of As-based fertilizers and pesticides or As-contaminated groundwater, etc. Owing to such chronic anthropogenic activities by human, the USEPA-recommended permissible soil As-concentration of 24 mg $kg^{-1}$ has been long outdone in case of majority of the countries across the world.

Arsenic is known to occur in four types of oxidation states: As (0), As(III), As (-III) and As(V). Although both organic and inorganic species of As exist, the inorganic form, especially arsenate [As(V)] and arsenite [As(III)] forms are the causes of concern owing to their high mobility and subsequent toxicity. As(III) can exist in reduced conditions, and As(V) majorly dominate under oxidized environment. Around 60% of total arsenic is found in arsenate form, 20% as sulfides and the rest 20% as arsenites/arsenides/silicates/oxides and elemental As. As-sulfides such as realgar ($As_4S_4$), arsenopyrite (FeAsS) and orpiment ($As_2S_3$) are among the most abundant As ore minerals (Farooq et al. 2016). Among all the inorganic forms as mentioned, As(III) has been hailed as the most toxic species owing to its higher solubility and mobility. It is around 60 times more toxic than As(V) because it can react with sulfhydryl (–SH) groups of proteins and enzymes, resulting in disruption of all the cellular metabolism and ultimately causing cell death (Abbas et al. 2018). However, dimethylarsenate (DMA), an organic As-species has been hailed more toxic than inorganic As [As(V)], in terms of reduced germination rates and grain yield in wheat (Duncan et al. 2017).

In addition to the groundwater contamination, soil contamination with As is a serious environmental hazard, particularly in agricultural areas. Despite the fact that As is a toxic non-essential metalloid, As is taken up by plants. Because As is so heavily abundant in soil, and accumulated through food chain, it affects other organisms of the ecosystem as well (Samanta and Roychoudhury 2021a). For example, in China's Hunan province, rice grains were found to harbor up to 723 $\mu g\ g^{-1}$ of

As, far exceeding the maximum allowance level of 150 μg $g^{-1}$ for inorganic As (Okkenhaug et al. 2012). Depending on the bioavailable concentration of As in soil and its speciation, As can be taken up by plants and even translocated to the different plant parts. Multitude of chemical reactions taking place under the soil could affect solution-and solid-phase speciation of As in soil which regulates As-uptake by plants (Martínez-Sánchez et al. 2011). Generally, As in its inorganic form, As(III) or As(V) is known to enter the plant roots with the help of transporter proteins, depending on the As-concentration gradient. Although not much transporters have been reported till date, As(V) has been reported to use the phosphate (Pi) transporters, while As(III) uses NIP channels to cross the plasma membrane of the root cell owing to structural analogy. Being taken up by plants, As exerts its toxicity in plants through morphological, physiological, biochemical and molecular alterations, eventually affecting the growth and productivity (Chandrakar et al. 2016; Begum et al. 2016). The most damaging biochemical effect of As at the subcellular level is the production of the reactive oxygen species (ROS), which can lead to irreparable damage to important macromolecules, including lipids, proteins, carbohydrate, and DNA. In response to As-stress, plants equip themselves with defense mechanisms for As-detoxification like increased cellular antioxidants and strategized vacuolar compartmentalization. Cellular antioxidants like enzymes, viz., superoxide dismutase (SOD), catalase (CAT), glutathione reductase (GR), ascorbate peroxidase (APX) and non-enzymatic antioxidants like glutathione (GSH), proline, etc. function to alleviate the As-induced ROS. Additionally, the vacuolar compartmentalization of As, complexed with certain ligands is a well-developed As-detoxification strategy adopted by plant cells. The thiol-reactive cysteine-rich peptides such as phytochelatins (PCs) can form complexes with As, rendering them non-toxic (Anjum et al. 2015). Since As-induced impairment of the growth, physiology and metabolism of plants is a cause of concern for the farmers worldwide, scientists have tried implementing several techniques to prevent or remediate this stress. Advancement in the present days is highlighting the use of genetic engineering techniques to develop As-tolerant plants. Overexpression of *phytochelatin synthase* (*PCS*) genes either alone or together with γ-ECS has been reported to help prevent As-translocation and accumulation in plants. Development of genetically modified crops could be a next-generation technology to mitigate As-stress. Hence, understanding of underlying mechanism of every step starting from As-uptake to As-sequestration can give us a clue for successful implementation of transgenic approach (Roychoudhury et al. 2012). Thus, not only the conventional PCS and γ-ECS, but also the other checkpoint genes of As-accumulation pathway could be targeted for fruitful engineering.

Although ample research has shed light on the mechanisms of As-transport, speciation, and detoxification mechanism in plants, certain knowledge gaps, specifically pertaining to As-compartmentalization in vacuoles, transport through the xylem, and accumulation in grains need immediate scientific limelight. Therefore, this book chapter attempts to comprehensively cover studies on biological impact of As-contamination on agricultural system across the world along with the mechanism of As-uptake, translocation, detoxification and As-mitigation strategies.

## 22.2 How is As Taken up by Plants and Translocated to Different Plant Parts?

Although As is generally hailed as extremely toxic element, minute concentration of As has been reported to improve plant growth (Gulz et al. 2005). Less than 0.1% As concentration (on DW basis) has been reported in different plant species, growing on As-contaminated soil (Austruy et al. 2013). As is taken up by the cells belonging to plant roots, then translocated through the tissues to xylem and phloem, from where it is transported to long distances to other tissues of the plant by active or passive mechanism.

### *22.2.1 Bioavailability and As Speciation in Soil*

The As-uptake by plants is dependent on the bioavailable concentration of As in the soil around the plant, which is dependent on the different speciation states of As. The speciation state is a more important factor than the total As-concentration in the soil; the total As present in stable minerals is usually not bioavailable, while the As present in adsorbed state on various organic and inorganic constituents is readily bioavailable (Li et al. 2015; Khalid et al. 2017). The two main inorganic forms of As available in nature are As(III) and As(V), usually in different forms. The most thermodynamically stable forms include $HAsO_4{}^{2-}$, $H_2AsO^{4-}$, and $H_3AsO_3$; $H_2AsO^{4-}$ in aerobic soil conditions. This inorganic speciation or biogeochemical behavior of As is dependent on the pH and redox potential of the surrounding soil environment. In an acidic soil environment, i.e., with a $pH < 5.5$, As is converted to a more soluble As(III), helping it gain mobility and penetrability to plant roots. Multiple studies have reported inter-conversion of As(III) and As(V) based on the change in soil pH (Abbas et al. 2018). Similarly, the redox potential of soil is also another important factor in charge of As-speciation. As the soil redox potential decreases, i.e., as the environment turns reducing, As(V) is converted to As(III) and vice-versa. Thus, under oxidizing soil state, As is usually more soluble and bioavailable. Another important factor regulating metal speciation and bioavailability in soil is the activity of soil microbe consortium (Abbas et al. 2018). Soil microorganisms indirectly or directly regulate the speciation and fate of a metal in the soil–plant system, like microorganism-dependent interconversion of As(III) and As(V) result in changes of adsorption/desorption, solubility, mobility, bioavailability and soil–plant translocation. Bacterial species such as *Thermus sp.*, *Crysiogenes arsenates*, *Bacillus arsenic oselenatis*, *Desulfutomaculum auripigmentu*, *Geospirillum barnesi*, and *Geospirillum arsenophilus* have been reported for their capacity to synthesize arsenite oxidase, helping in oxidiation of As(III) into As(V). Contrastingly, microorganisms like *Bacillus arsenicus*, *Geospirillum arsenophilus*, *Geospirillum barnesi*, *Crysiogenes arsenatis*, *Sulfurospirillum barnesii*, *Sulfurospirillum arsenophilum*, *Oselenatis*, and *Desulfutomaculum auripigmentu* can also reduce As(V) into As(III) via unrelated reduction by utilizing As(V) as a terminal electron acceptor for anaerobic respiration. Therefore, inoculation of microorganisms in soil can be used to control phyto-availability of As in soil (Mishra et al. 2017).

In addition to As(V) and As(III) species, several methylated species like MMA, DMA and trimethylarsine oxide (TMAsO) are also present in soil in varying proportions (Jia et al. 2012; Zavala et al. 2008). MMA and DMA were previously used as foliar contact herbicides and pesticides on a global scale which resulted in massive As build up in agricultural soil (Williams et al. 2007). However, As-methylation and its bioavailability in plants is not much studied and needs more scientific attention.

## *22.2.2 Arsenic Uptake and Translocation by Plants from Soil*

The usual As-species available in soil for uptake by plants include arsenate [As(V)], arsenite [As(III)] and methylated As (MMA and DMA). Although these forms exist simultaneously in soil, the transporters involved in the uptake pathways for each As form are often quite different, utilizing concentration gradient existing between the source and the sink as the major driving force (Fig. 22.1).

### 22.2.2.1 Arsenate [As(V)] Uptake and Translocation

Arsenate (V) is the most dominating species in aerobic soil conditions, and hence is the most easily bioavailable form for uptake by plants. Since As(V) is a structural chemical analog of phosphate, they are taken up by the cells in the plant root tissues via phosphate (Pi) transporters. This uptake mechanism involves co-transport of Pi or As(V) along with protons at a stoichiometry of a minimum of $2H^+$ for each $H_2PO_4^-$ or $H_2AsO_4^-$. For example, Shin et al. (2004) reported two genes encoding for high-affinity phosphate transporters, i.e., AtPht1;1 (Pi transporter 1;1) and AtPht1;4 that allow uptake of Pi and As(V) in *Arabidopsis thaliana* at both high and low phosphate level. This was also validated in rice mutants for a Pi transporter (OsPht1;8) which were unable to take up both Pi and arsenate. A study compared As(V) tolerance of Kasalath with Nipponbare rice; Kasalath variety was observed to be more tolerant to As(V) than Nipponbare, with approximately 2-3 fold higher expression of OsPT2 and OsPT8 (Wang et al. 2016). Supporting the notion, over-expression of the phosphate transporters in rice plants accelerated the uptake and translocation of Pi and As. Similarly, OsPht1;1 located in the plasma membrane of rice plants also showed high affinity for As(V) uptake (Wu et al. 2011; Jia et al. 2011). In *Arabidopsis thaliana*, two Pi transporter family members, AtPht1;1 and AtPht1;7, have been found to be hypersensitive to arsenate, but absolutely non-responsive to As(III) species (LeBlanc et al. 2013). DiTusa et al. (2016) characterized three Pht1 transporters in *P. vittata* wherein, PvPht1;3 and PvPht1;5 exhibited similar affinities for phosphate, but PvPht1;3 showed higher affinity for arsenate than phosphate. In addition, a dicarboxylate carrier localized in the inner mitochondrial membrane of

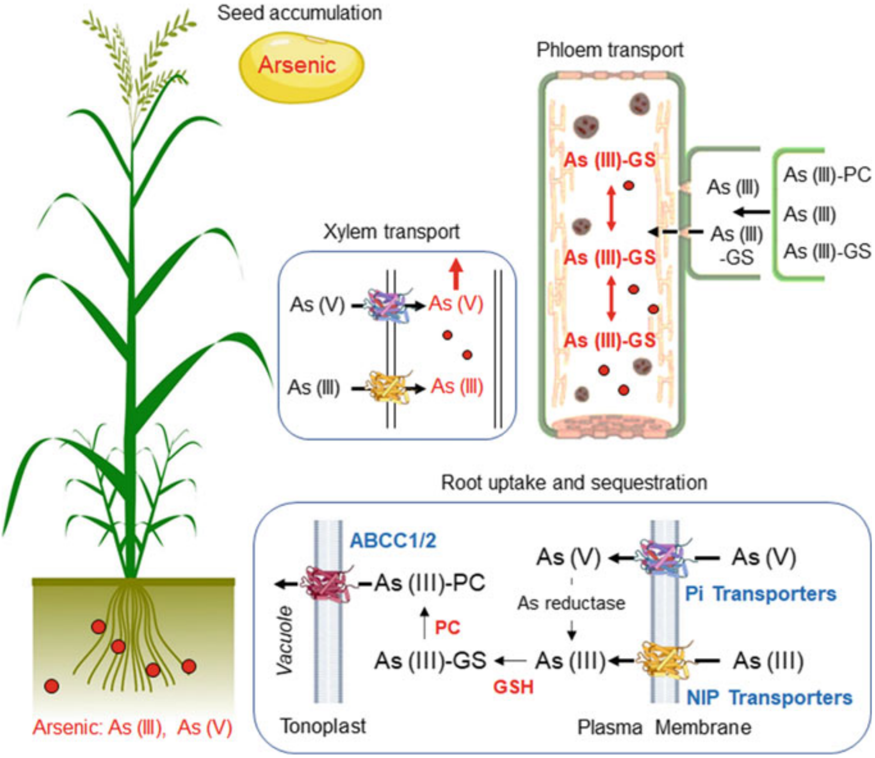

**Fig. 22.1** Arsenic uptake and translocation through plant system. Arsenic in the form of As(III), As(V) and others (not shown here) in the soil are taken up by root through different transporters as shown in the right lower panel. Nodulin 26-like intrinsic protein (NIP) transporters help in As(III) uptake, while Pi transporters take up As(V) in the root cells through the plasma membrane. Inside the cells, As(V) gets reduced to As(III), and both are able to be complexed with glutathione (GSH) and phytochelatins (PCs) helping in their vacuolar sequestration through transporters like ABCC1/2. For long distance transport, both xylem and phloem aid in the transport of As, either in free form or as complexes, through varying transporters, as shown in the middle left and right panel, respectively. Ultimately, As is found to be accumulated in seeds as shown in the uppermost illustration

the plants has been also identified for As(V) uptake by plants (Palmieri et al. 2008; Samanta and Roychoudhury 2021b). In case of flooded soil where the conditions are anaerobic in nature, As-uptake through the P pathway is a minor mechanism owing to As(III) dominance (Xu et al. 2008). Subsequently, the root-to-shoot transport of As(V) also occurs through different PHT proteins, like OsPHF1 (phosphate transporter traffic facilitator 1) and PHR2 (phosphate starvation response 2) (Awasthi et al. 2017).

#### 22.2.2.2 Arsenite [As(III)] Uptake and Translocation

As(III) uptake in plants have been reported to take place across the cell membranes of roots with the help of plant aquaporin channels, Nodulin 26-like intrinsic proteins (NIPs). Unlike the unidirectional Pi transporters, the bidirectional NIPs known for water conductance also aid in As(III) transport. Studies reported for As(III) permeation include NIP2;1, NIP3;3 (rice roots), NIP1;1, NIP1;2, NIP3;1, NIP5;1, NIP6;1 and NIP7;1 (Arabidopsis) and NIP5;1 and NIP6;1 (*Lotus japonicus*) (Bienert et al. 2008; Katsuhara et al. 2014; Kamiya et al. 2009; Xu et al. 2015). Further, silicon transporters are also being increasingly reported in As(III) uptake owing to the similar tetrahedral size and high pka value (9.2–9.3) of As(III) and Si, for example, Lsi1 silicon transporter (also called NIP2;1) promotes As(III) influx in rice roots (Ma et al. 2006, 2008). In addition to NIPs, plasma membrane intrinsic proteins like OsPIP2;4, OsPIP2;6 and OsPIP2;7 also contribute to As(III) adsorption in rice (Mosa et al. 2012). Overexpression of these transporter proteins in Arabidopsis tissues confirms the role of these proteins in As(III) tolerance. Other studies reported tonoplast intrinsic proteins (TIPs): PvTIP4;1 and NRAMP1 (Natural Resistance-Associated Macrophage Protein 1) in As(III) uptake (He et al. 2016; Tiwari et al. 2014). Another recent study by Duan et al. (2016) showed involvement of sugar alcohol, inositol transporter proteins, AtINT2 or AtINT4 which allowed As(III) loading into the phloem tissues. Such transporters are yet to be identified in rice plants. This study showed that As-translocation through phloem is probably the reason behind As-accumulation in seeds, and hence, genetic manipulation of such transporter genes might prevent As-accumulation in rice grains.

#### 22.2.2.3 Methylated As Species Uptake

Very minute amounts of methylated As-species (MMA, DMA, etc.) are also found to be taken up by plant roots at a low rate of efficiency (Li et al. 2009; Jia et al. 2012; Abedin et al. 2002). The transporters reported in the influx of methylated As-species till date include aquaporin Lsi1 in rice roots and OsNIP2;1 (Li et al. 2009). Rahman et al. (2011) showed that the transport of DMAA and MMAA in rice roots mainly occurs via MIPs/ aquaglyceroporins.

Although majority of the plants aim to restrict As-abundance in the roots, certain proportion of As is translocated to the shoot and other tissues of the plant, viz., As has been detected in leaves and grains, but the concentration decreases upwards gradually. Transport of As(III) and As(V) can be possibly mediated with the help of OsLsi1/2 and Pi transporters, respectively (Raab et al. 2005). A hydroponic survey of many plant species (Raab et al. 2007) showed that the root-uptake of As follows the order: As(III) > As(V) > MMA (V) > DMA (V), but the translocation to other plant parts is in the order DMA (V) > MMA (V) > As(V) $\geq$ As(III). Thus, DMA has been noted to be more mobile, allowing more efficient translocation from roots to shoots utilizing both xylem and phloem systems in plants such as rice and castor bean, wherein the phloem concentration was around 3.2 times that of xylem (Carey et al. 2011; Ye et al.

2010). On the other hand, As(III) mainly opts for the phloem translocation channel. Plant response to As accumulation occur at various levels, starting from sub-cellular changes to tissue alterations. These physiological responses also control As-uptake in plants as a part of their defense strategy.

## 22.3 What Effects As Induce on Plant Metabolism, Growth, Physiology and Yield?

Arsenic contaminated soil has been shown to affect crop physiology, resulting in substantial low quality and yield, which indirectly poses severe threat for human consumption as well. Although low As-concentration often show stimulatory effect on plant growth, higher concentrations are extremely detrimental, surpassing the beneficial effects. Although the mechanism for growth stimulatory role of As has not been studied yet, it was suggested by Tu and Ma (2005) that the plant growth gets benefitted owing to As-stimulated Pi uptake. Although both the inorganic forms, viz., As(V) and As(III) can be easily taken up by plant cells, plant tissues, viz., roots and shoots were found to contain about 90% of As in the form of As(III), the more toxic of the two forms, even when plants were specifically exposed to As(V) (Finnegan and Chen, 2012; Xu et al. 2007). Arsenate reduction can occur both enzymatically and non-enzymatically. In the non-enzymatic pathway, oxidation of two molecules of GSH is able to reduce As(V) to As(III) (Delnomdedieu et al. 1994). However, the enzymatic pathway is comparatively faster, wherein, As(V) to As(III) reduction by arsenate reductase have been reported in many species as a detoxification measure, like *AtACR2* (Arabidopsis), *OsACR2* (rice), *HlAsr* (*Holcus lanatus*) and *PvACR2* (*P. vittata*) (Duan et al. 2007; Dhankher et al. 2006; Ellis et al. 2006). An arsenate reductase *ATQ1* in Arabidopsis has been identified to catalyze As(V) to As(III) reduction in the outer cell layer of root which also helps in efflux of As(III) back into the soil (Sanchez-Bermejo et al. 2014; Chao et al. 2014). Many studies together point to the fact that in Arabidopsis and other similar plants, enzymes other than ACR2 also show As(V) reductase activity, like glyceraldehyde-3-phosphate dehydrogenase (GAPDH), polynucleotide phosphorylase, purine nucleoside phosphorylase (PNP), glycogen phosphorylase and the mitochondrial $F_1$ $F_0$ ATP synthase (Finnegan and Chen, 2012). These enzymes function by means of As(V) incorporation instead of Pi into biological molecules, which leads to the formation of an arsenoester and aid in the enzymatic reduction of As(V) to As(III). Additionally, plants can also reduce MMA (V) taken up by the roots to MMA (III), as proven by some studies in rice roots. Some detected around 15% of the aqueous As in the rice roots [treated with MMA (V)] that was in the form of MMA (III) (Li et al. 2009; Ye et al. 2010). Another study reported that 65% of As in rice roots occur as MMA (III) (Lomax et al. 2012). Interestingly, 9% of the As in the shoots of these rice plants was also in the form of MMA (III). Presence of MMA (III) in the plant cells can have severe implications in plant metabolism owing to its cytotoxicity, although not reported yet.

Roots are the first tissues to be exposed to As-stress, and as a result, root extension and proliferation are impaired. Subsequent translocation to shoot leads to disrupted plant growth and biomass with sufficient loss to the reproductive capacity of the plants and consequent yield and fruit quality. At higher toxic concentrations, As can interfere with critical metabolic and cellular processes leading to cell death. However, none of the As forms shows consistent phytotoxicity, which might be due to the fact that As interacts differently with differently available nutrients. In this regard, study of MMA (III) can be crucial as it showed around 18 times more cytotoxicity in animal cells than As(III), although phytotoxicity remains to be elucidated (Styblo et al. 2000; Naranmandura et al. 2011). Moreover, there may be other species of As as well, which are yet to be detected, since a few studies have reported that a significant percentage of As could not be recovered.

## *22.3.1 Cellular Effects of As-Toxicity*

At the cellular level, As can interfere with many critical processes, putting the fate of the plant cells at risk. Because of the structural analogy of As(V) and Pi, As can substitute for Pi in biochemical reactions, thereby harming vital cellular processes. On the other hand, As(III) is highly reactive toward thiol groups of proteins or enzyme co-factors, along with MMA (III) and DMA (III), which may alter or inhibit their activity and pose a severe threat. Oxidative stress induced by inevitable ROS production during As exposure has been hailed as the main driver of As-toxicity in plants.

### 22.3.1.1 As(V)-Mode of Action: Phosphate Replacement in Biochemical Reactions

Ability of As(V) to replace Pi in important cellular and biochemical reactions compromises significant metabolic processes of a cell, including glycolysis, oxidative phosphorylation, phospholipid metabolism, DNA/RNA metabolism, protein phosphorylation/ dephosphorylation, etc. Firstly, the Pi transporters (PHT1) in a plant root cell are targeted by As(V) for Pi substitution. Since Pi competes with As(V) for uptake, As(V) toxicity is lower under high Pi conditions, and vice-versa. Besides PHT1, other transporters that mistake As(V) for Pi include inner mitochondrial membrane Pi translocator, dicarboxylate carrier, PHT4 transporters in plastid and Golgi, etc.

Some significant cellular enzymes mistake As for Pi, like the mitochondrial $F_1$-$F_0$ ATP synthase, which instead of ATP, produces ADP-As(V) (Gresser, 1981). It might be similar for the plastid $F_1$-$F_0$ ATP synthase, although no direct evidence has been reported yet. Similarly, glyceraldehye-3-phosphate-dehydrogenase (GAPDH), aspartate-β-semialdehyde dehydrogenase, PNP enzymes also act in a similar fashion, incorporating As(V) instead of Pi with nearly same Km. These enzymes usually form

As-esters, which are extremely unstable and can undergo rapid hydrolysis to yield free As(V). This results in futile reaction cycles, and uncoupling of electron transport from ATP synthesis in the mitochondrial inner membrane and photosynthetic electron transport in chloroplast thylakoid membranes. This severely threatens the energy status of the cell. The glycolytic pathway also incorporates As(V) at many crucial steps: hexokinase can use ADP-As(V) to produce arsenolate glucose to glucose-6-As(V), which can be used by glucose-6-phosphate dehydrogenase during reductive pentose phosphate pathway, and also by phosphoglucomutase forming glucose-1-As(V) (Long and Ray, 1973). Thus, many significant cellular processes are totally disrupted owing to the presence of As(V).

#### 22.3.1.2 As(III)-Mode of Action: Binding Thiols

Quite different from As(V), As(III) exerts its greater toxicity as a thiol-reactive compound. As(III) can bind to three sulfhydryl groups, by virtue of which it can act as a cross-linker between three monothiol molecules, like the antioxidant GSH. However, As(III) can also bind to poly-thiol compounds like phytochelatin along with other thiol-containing proteins and co-factors such as dihydrolipoamide-co-factor associated with mitochondrial and plastid pyruvate dehydrogenase complexes, 2-oxoglutarate dehydrogenase complex, glyceraldehyde decarboxylase complex and branched-chain 2-oxoacid decarboxylase complex, etc. More the number of bonds, greater the stability of the complexes, i.e. As(III)-trithiol complexes are most stable, as supported by the finding that As(III) prefers binding to Zn finger proteins with three or more Cys-residues (Zhou et al. 2011). Many enzymes, transcription factors, signal transduction proteins, proteolytic proteins, and structural proteins have been reported to be affected by As(III) binding, since it can cause severe changes in protein folding.

Additionally, recent studies showed that methylated species of As(III) is more toxic as compared to As(III) alone, since MMA (III) is a more potent inhibitor of enzymes, like GSH reductase and thioredoxin reductase. Both MMA (III) and DMA (III) have been noted to be Zn-finger protein inhibitors. This thiol-binding nature of As(III) provides the main detoxification mechanism of both As(V) and As(III), as discussed in the next segment.

#### 22.3.1.3 Secondary Oxidative Stress

Most evidently, multiple scientific studies have documented the involvement of ROS production in response to As(III) and As(V) exposure to plants, including several types of ROS species like superoxide, hydroxyl radical, nitric oxide (NO) and $H_2O_2$ (Das and Roychoudhury 2014). Many plant species have been reported with elevated ROS production in response to As-stress, like *H. lanatus*, *T. pratense*, *V. radiata*, *O. sativa* etc. which showed extreme $H_2O_2$ production (Kostecka-Gugała and Latowski, 2018). Some studies showed that dimethylarsine [DMAH, $(CH_3)_2AsH$] react with oxygen to form DMA radicals and superoxide anions, thereby contributing towards ROS production in plants (Sharma 2012). Exposure to MMA (III) results in ROS production mainly in mitochondria, whereas DMA (III) affects ROS generation in other organelles as well along with the ability to damage the DNA. Consequently, As-stress has been found to produce significant damaging impact on proteins, amino acids, purines, nucleotides and nucleic acids along with membrane lipid peroxidation. Studies by Srivastava et al. (2005) and Singh et al. (2006) showed ROS production in As-hyperaccumulator plant, *P. vittata*, proving the fact that ROS generation is an evident generalized stress response. In addition to ROS, As-exposure may also lead to reactive nitrogen species (RNS) formation, including NO, $NO_2$, $N_2O_3$, $N_2O_4$, $ONOO-$ , S-nitrosoglutathione, and S-nitrosothiols, resulting in nitrosative stress, which can have consequences in many cellular processes like lipid nitration, S-nitrosylation, etc. (Sahay and Gupta 2017). As-stress can cause disruption of the redox state by combining decline in cellular antioxidants along with ROS up regulation, which can lead to cell death. Many antioxidants like SOD, catalase, GSH, phytochelatins, ascorbate, etc. have been found to be induced initially and then under extreme stress decline steeply. Role of these antioxidants in cellular defense strategy have been discussed later.

## *22.3.2 Metabolic Effects of As-Toxicity*

All the species of As, i.e., As(V), As(III), MMA, DMA, etc. can induce severe cellular consequences which culminate in impaired metabolic processes in plants. As(V) substitute Pi in biochemical reactions; As(III) binding to thiols and enzymes along with extreme oxidative stress build up and impede the carbon, nitrogen, sulfur and other significant metabolic processes in a plant, including photosynthesis, respiration, nitrogen fixation, etc.

### 22.3.2.1 Photosynthetic and Respiratory Impairment

All the toxic As-species taken up by plants have been reported to inhibit net photosynthesis by damaging the light harvesting complexes and photosystem II activity. As a consequence, As may reduce photosynthetic electron flow through the thylakoid membranes, obviously decreasing the production of ATP and NADPH, needed for carbon fixation reactions. Moreover, replacement of Pi by As(V) in photophosphorylation might lead to uncoupling of electron transport from ATP synthesis. In case of carbon-fixation stage or dark-reaction phase of photosynthesis, the RuBisCo large subunit was found to decrease with As(V) treatment in case of rice leaves (Ahsan et al. 2010).

Additionally, photorespiration is another carbon metabolism cycle which is curbed by As. Photorespiration involves the lipoamide-containing GDC enzyme, wherein the dithiol group of dihydrolipoamide acts as a target for As(III) binding. Arabidopsis plants with silenced mtLPD showed more sensitivity to As(V) stress (Finnegan and Chen 2012). Alternative pathways independent of GDC have been also shown to be involved in As-stress. For example, non-enzymatic oxidative decarboxylation of glyoxylate results in formate in the presence of $H_2O_2$, following which formate is further oxidized to $CO_2$ by $NAD^+$ formate dehydrogenase. The NADH thus produced contributes electrons to the electron transport chain and aids in ATP production. This has been proved by the accumulation of $NAD^+$ formate dehydrogenase protein in the leaves of rice plants exposed to As-stress (Ahsan et al. 2010). Lastly, As(III) has been found to inhibit the amylolytic activity resulting in decrease of maltose production from starch (Liu et al. 2005).

Moreover, even GAPDH protein required for both photosynthesis and glycolysis decreased in response to As-stress in the roots of rice plant, and interestingly increased in shoots (Ahsan et al. 2008, 2010). Since GAPDH can act as an arsenate reductase, As(V) may uncouple ATP synthesis from glycolysis. Even *alcohol dehydrogenase* (*ALDH*) transcripts increased in As(V)-treated Arabidopsis, showing an increase in fermentation and decrease of carbon flow from pyruvate to citric acid cycle (Abercrombie et al. 2008). Possibly, mtPDC containing both lipoamide and LPD gets blocked by As(III) binding in plants, as found in animals. Thus, another enzyme from citric acid cycle, OGDC containing lipoamide and LPD is also sensitive to As(III). Hence, As(V) to As(III) conversion leads to reduction in rate of respiration as well. Many steady-state glycolytic and citric acid cycle metabolite pools underwent major alterations in response to As-stress, such as increase in the succinyl-CoA synthetase $\alpha$ subunit and mitochondrial ATP synthase subunit in the maize roots and loss in malate dehydrogenase and ATP synthase $F_A$d subunit in maize shoots (Requejo and Tena, 2005, 2006). The major damage to respiration by As is the uncoupling of ATP synthesis from electron transport owing to the production of unstable ADP-As(V) intermediates. This would eventually lead to a sharp fall in ATP production of the cell.

The triose-phosphate/Pi translocator, working across the plastid inner membrane to transport Pi [and As(V)] in exchange for triose-phosphate was found to be transcriptionally up regulated in As(V)-treated rice seedlings (Chakrabarty et al. 2009). Moreover, dicarboxylate carrier 2 (DIC2), a mitochondrial substrate carrier protein was also found to be repressed in As(V)-treated Arabidopsis (Abercrombie et al. 2008). This may influence a negative impact on the cellular redox balance by inhibiting malate/oxaloacetate exchange.

### 22.3.2.2 Others: Nitrogen and Sulfur Metabolism

Other significant metabolic processes in a plant like symbiotic nitrogen fixation in alfalfa root systems are also critically affected, with almost less than half of the number of root nodules observed in response to As-stress, probably due to 90% less rhizobial infections (Carrasco et al. 2005; Pajuelo et al. 2008). Later, studies found out that As(III) caused disruption of gene expression involved in early nodule development (Lafuente et al. 2010). Moreover, in case of As(V) exposure, supply of inorganic N to the assimilation pathway has been found to be impacted. Transcripts for $NO_3^-$ transporter and $NH_4^+$ transporter were found to be greatly reduced (Norton et al. 2008; Chakrabarty et al. 2009). Nitrate reductase activity was also impaired (Chakrabarty et al. 2009). Arsenic-exposure even led to a massive blow to the entire amino acid pools, and consequently, the total protein content in different parts of plant also suffered a major reduction.

Even the sulfur metabolism suffered a major setback owing to the ability of As(III) to bind to the sulfhydryl groups in GSH and PC. Many sulfate transporters have been reported to be up regulated in rice, Arabidopsis, and *Brassica* to support the increased biosynthesis of GSH and PC for As-detoxification process. Even sulfate assimilation pathway was found to be induced in response to As(V) in plants and As(III) in yeast, proved by the up regulated transcript level of 5′-adenylylsulfate reductase gene. As-tolerant varieties showed induction in Cys synthase, Ser-acetyltransferase and γ-glutamyl cysteine synthetase activity along with an increase in Cys and GSH levels. Thus, increased sulfur metabolism possibly served as a viable mechanism for increasing As-tolerance in plants (Finnegan and Chen 2012).

## 22.4 How Do Plants Counter As-Induced Stress?

Plants majorly aim to restrict As-mobilization within the plant body in three ways: (i) restrict As-inflow from soil to the roots, (ii) As-efflux back to the soil, and (iii) restrict As-translocation from root to shoot through vacuolar sequestration.

Firstly, As-uptake restriction has been used as an adaptive measure by some plants growing in heavily As-contaminated soils, such as *Holcus lanatus* and *Cytisus striatus*. These plants show constitutive suppression of As(V) transport which leads to significant low As-uptake (Meharg and Macnair 1990; Bleeker et al. 2003). Since As(V) uptake is mediated by phosphate transporters, if the external soil phosphate concentration is high enough, phosphate will be taken up more effectively as compared to arsenate. In this regard, As-toxicity was found to be greatly reduced upon Pi exposure in *Oryza sativa* (Choudhury et al. 2011). Furthermore, accumulated As can be removed by volatilization into gaseous trimethylarsine with the help of S-adenosylmethionine-dependent methyltransferase, as seen in bacteria, fungi and mammals and evidences point towards the same mechanism in plants (Messens and Silver 2006). Secondly, efflux of As back into the soil can be another efficient strategy exerted by plants. Xu et al. (2007) showed that in *Lycopersicon esculentum* and *Oryza sativa*, As(V) was reduced to As(III) in roots and effluxed into the medium. Similar results were also demonstrated in *H. lanatus* (Logoteta et al. 2009). Moreover, since aquaporins are bidirectional transporters, Zhao et al. (2010) found that the rice silicon transporters, Lsi1 (OsNIP2;1), which is a major route for As(III) entry into rice roots, can also participate in As efflux. Lastly, the most efficient and organized defense strategy to combat As-stress is by means of synthesis of metal binding proteins, like PCs and elimination of these toxic ions either through efflux transporters or by vacuolar compartmentalization. Moreover, the cellular antioxidants, both enzymatic and non-enzymatic ones are also activated which can control the overproduced ROS to control the oxidative stress-mediated cellular damages. Compatible solutes or osmolytes like proline, glycine-betaine and mannitol may also play vital roles in As-detoxification, possibly by scavenging of the induced oxidative stress.

### *22.4.1 Arsenic-Sequestration Mediated Detoxification*

Synthesis of metal binding peptides like PCs and GSH has been observed in almost all plant species and has been widely reported for its immediate metal (As) detoxification activity. All the plant types, viz., non-tolerant, non-accumulator, hypertolerant and hyperaccumulator plants show substantial up regulation of PC synthesis. The complexation of As with GSH and PC renders the As species non-reactive, which has been experimentally demonstrated in various plants, including *Cicer arietinum*, *Rauvolfia serpentina*, *Holcus lanatus*, *Helianthus annuus*, and *Brassica juncea* (Gupta et al. 2011). In fact, As-tolerance in plants highly increased in transgenic plants overexpressing the genes of thiol (cysteine, GSH, or PC) biosynthetic pathway (as discussed in the next segment).

Phytochelatins (PCs) can be described as heavy metal-binding peptides derived from GSH with the general structure ($\gamma$-Glu-Cys)n-Gly (n = 2–11). Their biosynthesis is catalyzed by PC synthase carrying out transpeptidation of $\gamma$-glutamylcysteinyl dipeptides from GSH. PC synthase is activated by heavy metals (like As), leading to PC synthesis, which aid in complexation of the heavy-metal ions by thiolate coordination (Schmoger et al. 2000). For example, *OsPCS1* was identified to be a crucial factor, reducing As-accumulation in rice grains (Hayashi et al. 2017). Supported by inhibitor studies, biochemical studies and mutant analyses, it was clearly demonstrated how PCs, upon complexation with the metal-ions, rendered them immobile and non-reactive. Following that, plant vacuoles act as final detoxification stores for As. In rice, much of As was observed in the vacuoles of pericycle cells of roots and companion cells of the nodal phloem (Moore et al. 2011, 2014). Song et al. (2010) for the first time identified two ABC transporters in Arabidopsis, namely AtABCC1 and AtABCC2 as the responsible factors for active transport of PC-conjugated As(III) in plant vacuoles. Later, in 2014, the same group of authors identified OsABCC1 in rice as the As-detoxifying transporter which helps to reduce As accumulation in rice grains (Song et al. 2014). OsABCC1 in the upper nodes of rice plants have been demonstrated to restrict As-distribution in the grains by sequestering it within the vacuoles of the phloem companion cells of diffuse vascular bundles in the grain. In another study, wild-type plant roots showed 69% of As to exist as As(III)-PC4, As(III)-PC3, and As(III)-(PC2)2, while the GSH-deficient mutant *cad2-1* and the PC-deficient mutant *cad1-3* showed only 25 and 8% plants with As-complexes, respectively. The two mutants show enhanced As-mobility from root to shoot and higher As(III) efflux from roots to the medium. Validating from further use of inhibitors in the study, the authors suggested that complexation of As(III) with

PCs in Arabidopsis roots decreases both the efflux to the external medium and the translocation from root to shoot (Liu et al. 2010). Similar process has been observed for GSH-mediated sequestration and subsequent detoxification as well. As(III) and GSH have been found to form a (GS)3-arsenite complex with cysteinyl sulfhydryl group of GSH as the As(III) binding site. Even organic As-species like DMA can strongly bind to GSH.

### 22.4.2 Cellular Antioxidants-Mediated Scavenging of Generated Oxidative Stress

As discussed in the earlier segment, As-induced stress majorly exerts its toxicity by means of oxidative stress-induced damages. ROS overproduction in cells leads to severe impact in all the cellular constituents, proteins, lipids and nucleic acids. In order to relieve the cells from the oxidative stress-induced damages, the cellular antioxidants play a crucial role, including the well-known SOD, CAT, GR, APX, etc. The hyperaccumulator plants are well-suited to accumulate such high concentration of As and still limit the As-induced damages by means of up regulation of such cellular antioxidants against the generated high level of free radicals. Multiple studies as reviewed in Abbas et al. (2018) showed the production of different antioxidants in response to both As(V) and As(III) in variable plant species, including *O. sativa*, *S. melongena*, *P. sativum*, *L. sativa*, *B. juncea*, *N. tabacum*, *A. thaliana*, *P. vittata*, *G. max*, *H. annuus*, etc.

In addition to such antioxidants, proline, the well-known osmoprotectant, has been observed to accumulate in these metal-tolerant plants that possibly help in osmotic adjustment to cope with water deficit stress as documented in plants like *T. aestivum* and *O. sativa.* Proline aids in As-tolerance by: (i) changing the cell wall structure to protect the plasma membranes and reduce As-uptake, (ii) quenching As-induced ROS generation, (iii) increasing the activities of other cellular antioxidants, and (iv) regulating the stress-related gene expression (Abbas et al. 2018). Some others like nitrous oxide (NO) and salicylic acid (SA) have been also found to play roles in As-detoxification process. NO has been reported to aid in activating ABC transporters and down regulating *OsLsi1* and *OsLsi2* to reduce As-accumulation, up regulate sulfur carrier genes and activate PC synthesis, and scavenge the overproduced ROS. On the other hand, SA can help in membrane stabilization, enhance NO production, activate ABC transporters, reduce As-translocation from roots to shoots, stimulate antioxidants and maintain redox balance (Abbas et al. 2018).

## 22.5 How Can Genetic Engineering Help in As-Stress Alleviation?

In general, tolerance of heavy metal stress is not monogenic. In plant system, multiple genes participate in metal accumulation, while many other genes participate in sequestration of metal stress, i.e., enhancement in tolerance level. Therefore, mitigating metal stress is a matter of multigenic trait development through manipulation of multiple metal-responsive genes (Macnair et al. 1999; Bert et al. 2003). Many genes take part in several processes of metal deposition pathway: some help in uptake; some members participate in translocation and some of them are involved in sequestration. Thus, the choice of a particular mechanism as well as a particular gene to enhance metal tolerance level is very difficult. Till date, it has been found that genes that can be targeted for manipulation for metal tolerance can be categorized into three types; transporters, proteins involved in metal chelation, and metabolic enzymes involved in detoxification (Banerjee and Roychoudhury 2018). In most of the cases, genes were considered from micro-organisms where the mechanism of lower-accumulation of metal is well defined from previously studied model organism like *Arabidopsis thaliana*, which is a non-accumulator of toxic metals.

This section discusses about genes that encodes protein which were previously reported to function in metal detoxification upon overexpression. Phytoremediation is the widely used method to remove As-contaminant from soil and water. Therefore, understanding cellular mechanism of plants can lead to further implication in As-sensitive plants. One such major member of As-detoxification is the mechanism involved in the production of cysteine-rich thiol-reactive peptides, such as PCs. Phytochelatins (PCs) and glutathione are the main binding peptides involved in chelating heavy metal ions in plants (Guo et al. 2008). The PC was firstly discovered in tomato plant wherein PCs were found to show coordinated response exposed to As (Steffens et al. 1986). The enzyme PCS plays central role in synthesizing PC and reduced glutathione (GSH) is used as a substrate (Grill et al. 1989). $\gamma$-glutamylcysteine synthetase ($\gamma$-ECS) is the precursor enzyme for the synthesis of GSH (Foyer and Noctor, 2005). *PCS* gene was found to be present in almost all higher plants and most of the species have two copies of the gene (Clemens 2006).

Numerous studies reported that overexpression of gene encoding PC biosynthesis can result in increased tolerance to As. Similarly, genetic manipulation of GSH synthesis has been widely undertaken to supply adequate GSH for PC production. Table 22.1 enlists some potential *PCS* and $\gamma$*-ECS* genes isolated from various plants along with their function when used as a transgene.

However, biotechnological approaches to mitigate As-stress are not only restricted to ECS and PCS manipulation, but effort has been made to achieve it by targeting some other candidate genes. Several intermediate pathways have been targeted including As-transport to As-sequestration. Multiple classes of genes have been identified and characterized from different species developing for As tolerance. Therefore, genes that fall under the pathway of As-accumulation has been targeted and manipulated so that it can serve as a barrier. The core path that has been centrally

**Table 22.1** PCS and ECS transgenic approach to alleviate As-stress

| Gene | Isolated from | OE (∧)/ KO (∨) | Transgenic plant | Role | References |
|---|---|---|---|---|---|
| *PCS1* and *GSH1* | Garlic and baker's yeast | ∧ | *Arabidopsis thaliana* | Single transgenic line has higher As tolerance level than non-transformed; however, double transgenic/co-transformed plant has significantly higher As tolerance ability | Guo et al. (2008) |
| *PCS1* and *PCS2* | *Oryza sativa* | ∨ | – | Plants turned sensitive to As stress | Yamazaki et al. (2018) |
| *PCS1* | *Arabidopsis* | ∧ | *Brassica juncea* | Enhanced As tolerance | Gasic and Korban (2007) |
| *Grx_C7 and Grx_C2.1* | *Oryza sativa* | ∧ | *Arabidopsis* | Reduces intracellular Arsenic Accumulation and Increases Tolerance | Verma et al. (2016) |
| *PCS1* | *Arabidopsis* | ∧ | Arabidopsis | Enhanced arsenic tolerance and hypersensitivity | Li et al. (2004) |
| *PCS1* and *ABCC1* | *Arabidopsis* | ∧ | *Arabidopsis* | Resulted in plants exhibiting increased arsenic tolerance | Song et al. (2010) |
| $\gamma$-*ECS* | Bacterial | ∧ | *Arabidopsis* | Directs the long-distance transport of thiol-peptides to roots conferring tolerance to As | Li et al. (2006) |
| *PCS1* | *Ceratophyllum demersum* | ∧ | *Oryza sativa* | Leads to 58% lower As accumulation in grain | Shri et al. (2014) |
| *PCS1* | *Arabidopsis* | ∧ | *Arabidopsis* | Enhances phytochelatin levels, root As/Cd accumulation and pollutant detoxification | Zanella et al. (2016) |
| *PCS1* | *Oryza sativa* | ∧ | *Oryza sativa* | Plays a crucial role in reducing arsenic levels in rice grains | Hayashi et al. (2017) |
| *YCF1* and $\gamma$-*ECS* | *S. cerevisiae* and bacteria | ∧ | *Oryza sativa* | Reduced 70% As accumulation in grain | Deng et al. (2018) |
| *PCS1* | *Caenorhabditis elegans* | ∧ | *Nicotiana tabacum* | Enhanced As tolerance | Wojas et al. (2008) |
| $\gamma$-*ECS* | Bacterial | ∧ | Eastern cottonwood | Enhanced arsenic tolerance | LeBlanc et al. (2011) |

[*] OE represents overexpression and KO represents knockout

followed to gain As-tolerance is the inhibition of As-uptake by root. The alternate way is to inhibit the deposition of As in variable plant storage organ, especially grain. Details of such candidate genes from various literature are compiled in Table 22.2. Rice *HAC4* has high expression in root tissue and it helps to efflux As to the external environment (Xu et al. 2017). *Cyc07* gene from *Nicotiana* allowed increase in As-tolerance and ameliorate oxidative stress in yeast and tobacco (Kim et al. 2020). Upon overexpression of *Cyc07*, expression of endogenous plasma membrane exporter (*NIP1;1*, *PIP1;1*) was increased, but expression of importer (*NIP3;1*, *4;1*) was decreased. Previous findings on genes that encodes arsenic transporter (like phosphate transporters, *Pht*) from *Pteris vittata* (*PvPht1;4* and *PvPht1;3*), *Oryza sativa* (*OsPht1;1,1;4* and *1;8*) and *Arabidopsis thaliana* (*AtPh1;1*) correlates well with this observation. Their knockout mutant resulted in significant decrement in *As*-uptake in root (Kamiya et al. 2013; Cao et al. 2017; Wang et al. 2016; Shin et al. 2004). NIPs from rice and Arabidopsis have been found to lower the root to shoot As-translocation by limiting xylem loading (Sun et al. 2018; Chen et al. 2017b; Kamiya et al. 2009; Xu et al. 2015). Likewise, CRT-like transporter and WRKY family protein that contribute in As-translocation can reduce the As-transfer rate upon silencing (Yang et al. 2016; Wang et al. 2018). Loss of function of well-known arsenite transporter of *Saccharomyces cerevisiae*, *Pteris vittata* and *Ensifer medicae* can enhance As-transportation towards vacuole and its further sequestration in root vacuoles (Duan et al. 2012; Chen et al. 2017a, 2019; Pérez-Palacios et al. 2019). Gene involved in As-efflux (*Lsi*) and *arsenite S-adenosyl-methyltransferase* (*ArsM*) have depicted a significant role in As-detoxification. Their knockout/ectopic expression resulted in positive increment in As-tolerance and As-accumulation in organs.

## 22.6 Conclusion and Future Directions

Arsenic stress and its molecular mechanism from the uptake stage till its translocation to the grains have been widely studied and established. However, few critically important questions pertinent to As-induced alterations in plants still remain, and the more they are answered, more questions pop up regarding their molecular intricacies. Firstly, the reason behind the abundance of different As-species in different plants, or even in different varieties of the same plant species needs to be studied. Except for genotypic reason, difference in soil conditions and agricultural practices can also play a major role. If any molecular difference could be curved out, it could be utilised to ensure As-free rice grains (Kalita et al. 2018). Even the As-methylation ability of plants have not been dissected well, which if probed can provide interesting leads regarding plant defence measures. Bioavailability of these methylated species has also not been studied much. Furthermore, how low As-concentration leads to enhanced plant growth also remains a mystery till date, which can provide critical information regarding As-tolerance mechanism induced in plants. As-detoxification mechanisms are very interesting research areas, which have received sufficient attention. However, except for rice and Arabidopsis, the vacuolar transport proteins and

**Table 22.2** List of genetically engineered plants with lower arsenic uptake and accumulation

| Gene | Isolated from | OE (∧)/ KO (∨) | Transgenic plant | Role | References |
|---|---|---|---|---|---|
| *ACR2* | *Oryza sativa* | ∧ | *Oryza sativa* | Increased As tolerance | Duan et al. (2007) |
| *ABCC* | *Oryza sativa* | ∧ | *Oryza sativa* | Enhance As tolerance | Ma et al. (2008) |
| *PHF1* | *Oryza sativa* | ∨ | – | Loss in As-tolerance | Wu et al. (2011) |
| *CLT1* | *Oryza sativa* | ∧ | *Oryza sativa* | Required for glutathione homeostasis and As tolerance | Wang et al. (2016) |
| HAC4 | *Oryza sativa* | ∧ | *Oryza sativa* | Increased As tolerance | Xu et al. (2017) |
| *Cyc07* | *Nicotiana tabacum* | ∧ | *Nicotiana tabacum* | Higher Tolerance to and Lower Accumulation of Arsenite | Kim et al. (2020) |
| *MYB40* | *Arabidopsis* | ∧ | *Arabidopsis* | Act as a central regulator of As responses, enhance plant’s As tolerance and reduce As uptake | Chen et al. (2021) |
| *HSP23* | *Medicago sativa* | ∧ | *Nicotiana tabacum* | Confers enhanced tolerance to salinity and arsenic stress | Lee et al. (2012) |
| *PHTs* (1;1,1;4 and 1;8) | *Oryza sativa* | ∨ | – | Decreased 33–60% As accumulation in grain | Kamiya et al. (2013); Cao et al. (2017); Wang et al. (2016) |
| *Pht1, 4* | *Arabidopsis* | ∨ | – | Increased As tolerance | Shin et al. (2004) |

(continued)

**Table 22.2** (continued)

| Gene | Isolated from | OE (∧)/ KO (∨) | Transgenic plant | Role | References |
|---|---|---|---|---|---|
| *NIPs* (1,3) | *Oryza sativa* | ∨ and ∧ | – | Decreased As accumulation 16–22% in root, 41–56% in shoot and 36–53% in grain | Sun et al. (2018); Chen et al. (2017a, b) |
| *NIPs* (1, 3) | *Arabidopsis* | ∨ | – | Almost 44–70% relative As content | Kamiya et al. (2009); Xu et al. (2015) |
| *CLT1* | *Oryza sativa* | ∨ | – | Root can accumulate around 50% less As | Yang et al. (2016) |
| *WRKY28* | *Oryza sativa* | ∨ | – | 16–31% decrement in the As content | Wang et al. (2018) |
| *ACR3* | *Saccharomyces cerevisiae* | ∧ | *Oryza sativa* | Reduced As accumulation around 20% in grain and increased As efflux | Duan et al. (2012) |
| *ACR3* and *ACR3;1* | *Pteris vittata* | ∧ | *Arabidopsis*, *Nicotiana tabacum*, *Oryza sativa* | Increased As accumulation to root, decrease root to shoot As translocation and deposition in grain | Chen et al. (2017a, b); (2019) |
| *ACR1* | *Ensifer medicae* | ∧ | *Nicotiana tabacum* | Promote As efflux and reduce root deposition | Pérez-Palacios et al. (2019) |
| *Lsi2* | *Oryza sativa* | ∨ | – | Decrease As accumulation in grain | Ma et al. (2008) |
| *ArsM* | *Rhodopseudomonas palustris* and *Westerdykella urantiaca* | ∧ | *Nicotiana tabacum* | 25–50% decrease in As accumulation in grain | Meng et al. (2011); Verma et al. (2018) |

plasma membrane efflux proteins have not been studied in other plant species. Hence, studies in other species can open up new research prospects with the identification of many other transport proteins, and it can shed light on probably unidentified As-detoxification mechanisms of plant systems.

The study of molecular basis of As-tolerance is a complex mechanism. Though a lot of findings helped to understand the mechanism governed by a series of genes, further research is needed to dissect out the exact phenomenon that can be strategized to cope As-toxicity. To date, most of the biotechnologists have focused on overexpression of genes in model plant Arabidopsis, which need to be implemented in plants more prone to metal stress. Similarly, in most of the studies, authors have used CaMV35S promoter to constitutively express the targeted protein. However, this needs to be more fine-tuned and focused in such way so that it can be expressed in a particular tissue at a particular stage by sensing the metal level. Otherwise, it can have some cumulative negative effect on the plants like futile cycling of transporter genes in plasma membrane of all the cells. Therefore, novel promoter that can be induced during specific cellular conditions and can control the location of the transgene is a required condition. Hence, depending upon the nature of the metal, three major steps can be considered in targeting the uptake from soil to root, translocation of the metal from root to shoot and further detoxification at the storage vacuole.

Since As-contamination is a burning problem in the field of agriculture with a constant threat looming over the global food security, the research pertaining to As-alleviation need to be dealt with significant scientific attention. Detailed studies probing on As-tolerance and As-transport mechanisms definitely shall provide an efficient affordable solution to this global problem, rendering the globe arsenic-free.

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# Chapter 23
# Distribution of Arsenic in Rice Grain from West Bengal, India: Its Relevance to Geographical Origin, Variety, Cultivars and Cultivation Season

**Nilanjana Roy Chowdhury, Antara Das, Madhurima Joardar, Deepanjan Mridha, Ayan De, Sharmistha Majumder, Jajati Mandal, Arnab Majumdar, and Tarit Roychowdhury**

**Abstract** Groundwater arsenic contamination has been a staggering issue for the last 45 years. When the contaminated water is used for irrigational activities, the problem aggravates. Bengal delta is mainly reliant on rice as the staple diet and its cultivation often requires irrigation water during summer due to scarcity of fresh water and insufficient rainfall. Therefore, in arsenic exposed area, the use of contaminated groundwater can introduce arsenic into the soil–plant system. Astonishingly, rice grain accumulates up to 10 times more arsenic than other regularly harvested crops and its accumulation differs with geographical location, rice variety, cultivars and cultivation season. Importantly, arsenic concentration of paddy is highly dependent on the primordial arsenic concentration in irrigation water and soil. Geographical attributes of an area are the most significant factors of arsenic content in rice grains, as they are the chief influencer of soil arsenic concentration. In this study, the contamination quotient of rice grain arsenic is determined by the average values from four sampling sites namely North 24-Parganas, Nadia, Kolkata and West Medinipur districts of West Bengal, India and the values are 300, 215, 190, and 137 μg/kg, respectively. Apart from geographical origin, rice grain arsenic concentration also differs with cultivar. So here, rice grains are classified into three different categories according to their arsenic accumulation and assimilation capacity. The maximum amount of rice cultivars in the entire study area are medium accumulators; range of arsenic concentration is > 100–300 μg/kg (n = 45) with an average value of 178 ± 41 μg/kg. Simultaneously, arsenic concentration of rice grain depends on various

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factors; however, variety is one of the key players. Parboiling with arsenic contaminated water act as a “factor enhancer” during this process in arsenic exposed area. Our study found that sunned rice grains contain lower arsenic (188 µg/kg) compared to the parboiled one (268 µg/kg). Concurrently, the fourth factor is cultivation season. In Bengal delta, paddy cultivation is practiced in two seasons: pre-monsoonal and monsoonal season. The data depicts that monsoonal grain contains lesser amount (224 ± 63 µg/kg) of arsenic than pre-monsoonal (528 ± 434 µg/kg) grain. This can be interpreted by the theory of dilution, because in monsoon season, rainwater mixes with the waterlogged irrigation field and dilutes the initial arsenic concentration. Transport of arsenic-contaminated rice grain grown in arsenic endemic areas to the non-endemic sites and consequent dietary intakes leads to great threats for the local inhabitants.

**Keywords** Groundwater arsenic · Soil–plant system · Geographical attributes · Rice cultivars · Sunned rice · Parboiled rice · Cultivation season

## 23.1 Introduction

Groundwater arsenic contamination is a long standing concern in India, Bangladesh and many other East-Asian countries (Chakraborti et al. 2018; Phan et al. 2010; Smedley 2005). In West Bengal, millions of people are affected due to arsenic toxicity-directly or indirectly, and some of them have been suffering from several adverse chronic health hazards (Chakraborti et al. 2009, 2015; Mazumder and Dasgupta 2011; Roychowdhury 2010). Arsenic is reported as a Group 1 carcinogen by the International Agency for Research on Cancer and Agency for Toxic Substances and Disease Registry (ATSDR 2007; IARC 2012; Zavala and Duxbury 2008). It comes into groundwater due to its natural release from aquifer sediments (Majumdar and Bose 2018; Polya and Charlet 2009). According to the reports, anaerobic metal-reducing bacteria could be responsible for the dispersion of arsenic in sediments in the Bengal delta (Chakraborty et al. 2015; Islam et al. 2004; Afsal et al. 2020). Beside arsenic-contaminated drinking water, arsenic exposure elevates through contaminated irrigational water which is responsible for food chain contamination (Chowdhury et al. 2018a, 2020a; Roychowdhury et al. 2005).

In West Bengal, paddy is the largest irrigational crop with an approximate cultivation area of 5,900,000 ha (Signes et al. 2008). About 88,750 km$^2$ area of this state has been identified as significantly arsenic-contaminated including areas from Nadia, Murshidabad, North 24 Parganas, South 24 Parganas and Malda districts where rice cultivation is a regular practice (Santra et al. 2013). Rice cultivation needs huge amount of water, which is mainly met by arsenic contaminated groundwater in summer season in exposed areas (Chowdhury et al. 2018a; Majumdar et al. 2019; Roychowdhury 2008) and sometimes in monsoon, when rain is not sufficient (Chowdhury et al. 2020a). The exposure of paddy fields to arsenic through irrigational water leads to arsenic accumulation in rice grains at undesirable levels as well as it decreases the essential mineral nutrients in rice grain gradually (Chowdhury et al. 2020a; Dwivedi et al. 2010). Simultaneously, arsenic stress in paddy plants reduces grain yield which in turn affects food security (Duxbury et al. 2003; Meharg 2004; Mridha et al. 2021, 2022). The population of Bengal delta is mainly dependent on rice as a staple diet and surprisingly rice grain accumulates up to 10 times more arsenic than other regularly harvested crops e.g. wheat (Williams et al. 2007). Several researchers have shown that the prime source of dietary arsenic exposure in human is contaminated rice and rice based products in arsenic contaminated regions of South-East Asia (Chowdhury et al. 2018b; Islam et al. 2017; Meharg and Rahman 2003).

Accumulation of arsenic in rice grain radically differs with cultivation season (Chowdhury et al. 2018a, 2020a), rice variety, cultivar variation (Booth 2008; Chowdhury et al. 2018a), geographical location (Biswas et al. 2019; Chowdhury et al. 2020b; Meharg et al. 2009) and most importantly on the primordial arsenic concentration in irrigation water and soil where paddy cultivation takes place (Chowdhury et al. 2018a; Roychowdhury et al. 2002, 2005). Moreover, the post harvesting procedure of sunned rice grain into parboiled rice grain causes an additional arsenic burden in the arsenic endemic areas where the parboiled rice grain and the rice by-products are found with higher arsenic concentration (Chowdhury et al. 2018b, 2019). So, the present study will put forward a comprehensive idea on the insight of accumulation of arsenic in rice grain and its distribution with reference to its growing season, variety, cultivars, topographical variations etc. in West Bengal, India.

## 23.2 Materials and Methods

### *23.2.1 Study Area*

Different districts of West Bengal with different level of background arsenic exposure have been chosen for collection of rice grains like North 24 Parganas, Nadia, West Medinipur and Kolkata (Fig. 23.1). Nadia and North 24 Parganas are well evidenced with massive arsenic contamination in groundwater since many years and are termed as ‘highly affected’, situated on the eastern side of the Bhagirathi River (Chakraborti et al. 2009; Das et al. 2020; Roychowdhury et al. 1997; Santra 2017). Even though Kolkata may be called an apparently control site, the mega city is reported with 14.2% groundwater sample with arsenic contamination above permissible limit in drinking water (n = 4210) which comprises 77 wards out of total 144 (Chakraborti et al. 2017). West Medinipur district has been selected as an arsenic safe location according to its concentration in groundwater of the area (Chakraborti et al. 2013; Chowdhury et al. 2020a).

Fig. 23.1 Study area (*Source* Google)

### 23.2.2 Sample Collection, Preparation and Preservation

The entire rice grain sampling was done from four districts over five consecutive years (2015–2020). Samples were collected from farmers, rice mills, markets, shops and households of the mentioned study areas. Rice grains have been collected from Kolkata (n = 158), West Medinipur (n = 32), Nadia (n = 132) and North 24 Paraganas (n = 527) districts respectively. During sample collection, information regarding the samples has been garnered like the source, type of grain, cultivar, variety etc. The samples were stored in individual polyethylene zip-locks and stored at room temperature in laboratory until further processing for digestion and analysis. The overall collected number of samples according to their variety have been summed up in Table 23.1.

**Table 23.1** Sampling pattern of rice grains throughout the sampling site according to their variety

| Variety | Location | Sampling area | *n* |
|---|---|---|---|
| Sunned | Kolkata | North Kolkata Market | 4 |
| | | Manicktala Market | 4 |
| | | South Kolkata Market | 2 |
| | | Jadavpur Market | 6 |
| | *Total number of samples from Kolkata* (sunned variety) | | 16 |
| | North 24 Paraganas | From farmers, Gaighata | 9 |
| | | Post harvesting samples, Gaighata (Madhusudankati village) | 4 |
| | | Pedicel samples, Gaighata (Teghoria village) | 12 |
| | | Pedicel samples, Gaighata (Madhusudankati village) | 12 |
| | | Gaighata Market | 10 |
| | | Deganga Market | 8 |
| | | Post harvesting samples, Deganga | 10 |
| *Total number of samples from North 24 Parganas* (*sunned variety*) | | | 65 |
| *Total number of sunned variety* | | | 81 |
| Parboiled | Kolkata | North Kolkata Market | 6 |
| | | Kankurgachi Market | 9 |
| | | Manicktala Market | 12 |
| | | From the families of North Kolkata | 15 |
| | | South Kolkata Market | 6 |
| | | Jadavpur Market | 12 |
| | | From the families of South Kolkata, 2016 | 15 |
| | | From the families of South Kolkata, 2019 | 19 |
| | | Kolkata and its adjoining areas | 11 |
| | | Purba Kolkata Odia School | 37 |
| | *Total number of samples from Kolkata* (*parboiled variety*) | | 142 |
| | West Medinipur | From the farmers of Pingla | 11 |
| | | From the families of pingla | 21 |
| | *Total number of samples from West Medinipur* (*parboiled variety*) | | 32 |
| | Nadia | Ghetugachi Jaguli Junior Basic School, Chakdah* | 42 |
| | | Laupala Primary School, Haringhata* | 45 |
| | | Laupala High School, Haringhata* | 45 |
| | *Total number of samples from Nadia* (*parboiled variety*) | | 132 |
| | North 24 Parganas | Milling samples, Gaighata | 4 |
| | | Gaighata market | 10 |
| | | Madhusudankati free primary school, Gaighata* | 44 |

(continued)

**Table 23.1** (continued)

| Variety | Location | Sampling area | *n* |
|---|---|---|---|
| | | Math para village, Gaighata | 14 |
| | | Teghoria village, Gaighata | 15 |
| | | Jamdani village, Gaighata | 10 |
| | | Madhusudankati village, Gaighata | 16 |
| | | Post harvesting samples, Madhusudankati | 4 |
| | | Gobordanga municipality, Gaighata | 16 |
| | | Samples from the families, Gaighata | 20 |
| | | Chandalati village, Deganga | 28 |
| | | Sirajpur village, Deganga | 10 |
| | | Chharabagan village, Deganga | 11 |
| | | From the farmers of Deganga | 3 |
| | | Deganga Market | 19 |
| | | Post harvesting samples, Deganga | 10 |
| | | Chandpur vandulal madhyamik siksha kendra, Deganga* | 45 |
| | | Jhikara village, Deganga | 11 |
| | | Mudipara village, Deganga | 14 |
| | | Kaliyuga village, Deganga | 37 |
| | | Maulana Abul Kalam Ajad Free Primary Shool, Basirhat* | 21 |
| | | Merudandi Sluisgate S.S.K (School), Basirhat* | 50 |
| | | Chak Kamardanga Free Primary School, Basirhat* | 50 |
| | *Total number of samples from North 24 Parganas* (*parboiled variety*) | | 462 |
| *Total number of parboiled variety* | | | 768 |

* Collected from the school children at domestic level

### 23.2.3 Chemicals and Reagents for Arsenic Analysis

Concentrated nitric acid ($HNO_3$, 69%) and hydrogen peroxide ($H_2O_2$, 30% v/v) were used for digestion of the rice grain samples. During sample preparation, 10% of potassium iodide (aqueous KI) solution and 8% of concentrated hydrochloric acid (HCl) solution were added (5–10 ml), and the mixed solution was kept 45 min for settling down prior to estimation of arsenic. For the analysis of total arsenic concentration, 0.6% sodium borohydride ($NaBH_4$) (in 0.5% NaOH) and 5–10 M HCl were used (both from Merck, Mumbai, India). All the chemicals and reagents used in this study were of analytical grade. Double distilled water was used throughout the analytical work.

### 23.2.4 *Digestion*

Solid grain samples (approximately, 0.2 g) were digested with a mixture solution of concentrated $HNO_3$ and $H_2O_2$ in 2:1 in Teflon bomb at 120 °C for 6 h inside a hot air oven. The volume of acid digested solution was lessened through evaporation by placing it on the hot plate at about 90 °C for 1 h. The evaporated samples were made up to a volume of 2–5 ml with double distilled water and filtered through a suction filter (Millipore 0.45 μm) and the filtrate solutions were stored for estimation of total arsenic. Detailed information of the digestion methodology has been described in our previous publications (Chowdhury et al. 2020a, b).

### 23.2.5 *Arsenic Analysis*

Arsenic in digested rice grain samples was estimated by Hydride Generation Atomic Absorption Spectrophotometer (Varian AA140, USA) coupled with Vapor Generation Accessory (VGA-77, Agilent Technologies, Malaysia) with the software version 5.1. Detailed information of the instrumentation and methodology of the HG-AAS system has been described in our earlier publications (Chowdhury et al. 2020a, b; Das et al. 2021a, b).

### 23.2.6 *Quality Control and Quality Assurance*

Quality control and quality assurance study were performed to maintain the scientific quality of the entire work. Approximately, 30% of the samples were digested on hot plate using concentrated nitric acid ($HNO_3$, 69%) and hydrogen peroxide ($H_2O_2$, 30% v/v) in 2:1 ratio. Validation of the analytical results has been done through analysis of arsenic in standard reference material (SRM) i.e. Rice Flour 1568a (NIST, Gaithersburg, MD, USA) by both the methods of digestion correspondingly. Subsequent analysis of arsenic in the SRM sample showed 96 and 84% recovery through Teflon bomb and hot plate digestion methods, respectively against its certified value of 0.29 μg/g. Accuracy and precision of other analytical protocols were maintained through proper standardization, blank measurements, analyzing duplicates and spiked sample estimation (Chowdhury et al. 2018a, b, 2020a, b).

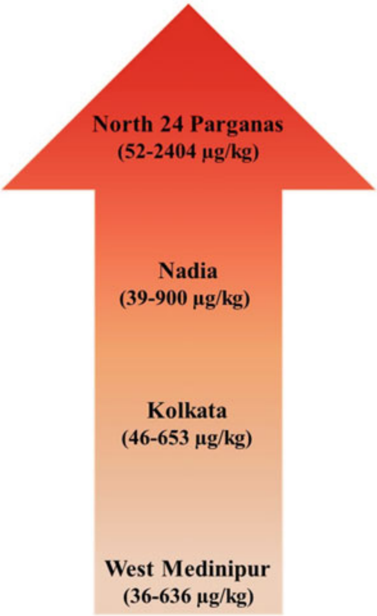
## 23.3 Results and Discussion

Rice grain arsenic contamination has enkindled serious health risk in the population of arsenic exposed and apparently unexposed areas irrespective of their ages and sex (Biswas et al. 2019; Joardar et al. 2021a, b). But, this study will be of immense importance to understand the degree of arsenic exposure and expansion in rice grain with respect to its cultivation areas, cultivar type, variety and cultivation season.

### *23.3.1 Contamination Quotient of Arsenic in Rice Grain with Respect to Its Different Cultivation Areas*

Geographical and geological locations are the most important background factors of arsenic content in rice grains, as they are the predominant influencer of soil arsenic concentration (Meharg et al. 2009). Carey et al. (2019) discussed in their report that low arsenic contaminated rice can be found in southern hemisphere (eastern latitudes) while the high arsenic containing rice is subjugated by South American and Mediterranean rice producing countries. Arsenic contamination in Ganga-Meghna-Brahmaputra (GMB) plain is a long standing concern for the last 40–42 years. This plain comprises many states in India, starting from Allahabad-Kanpur track, India and up to Bangladesh. West Bengal, in this study falls under the GMB plain which is well enriched with arsenic (Chakraborti et al. 2013; Sengupta et al. 2003). Therefore, over the years arsenic contaminated soil and groundwater both have stirred up arsenic contamination in rice by uptake through paddy plants (Bhattacharya et al. 2009; Farooq et al. 2010). Variation of arsenic concentration in rice grains collected from the different districts of West Bengal is shown in Fig. 23.2.

**Fig. 23.2** Variation of arsenic concentration in rice grains collected from the different districts of West Bengal



The heat map (Fig. 23.2) depicts that different types of rice grains (n = 527) collected from North 24 Parganas district have varied higher range (52–2404 µg/kg) of arsenic concentration with the average value of 300 µg/kg. North 24 Parganas has been previously reported to be among one of the rigorously arsenic contaminated zones in West Bengal due to its indigenous soil and groundwater arsenic concentration (Chowdhury et al. 2018a, b; Joardar et al. 2021b; Roychowdhury 2010). So, the arsenic concentration in rice grain of several blocks of North 24 Parganas district is a follow up of the impact of its food chain arsenic contamination from paddy soil to rice grain using arsenic contaminated irrigational water during cultivation. Rice grains (n = 132) were collected from the households of several blocks of Nadia district. This exhibits an average value of 215 µg/kg of arsenic with the range of 39–900 µg/kg. The second highest arsenic containing rice grain sample was found in Nadia district according to our data structure (Fig. 23.2). This is due to the in situ arsenic environment of the district. Das et al. (2020) showed that groundwater in all the 17 blocks of Nadia is arsenic contaminated while Rahman et al. (2014) stated the same with a fact that 51.4% of studied groundwater samples exhibit higher range of arsenic above the WHO recommended limit of 10 µg/L. Kolkata is a large metropolitan city where rice cultivation does not take place due to scarcity of irrigation land. However, being located near to the cultivation areas of other arsenic exposed districts, the rice grain arsenic concentration of the city is diffused compared to others. Arsenic concentration is found to be moderate in collected rice grains (n = 158) according to the average value of 190 µg/kg (Fig. 23.2). However, range (46–653 µg/kg) reciprocates to an unexpected ambiguous scenario when samples were studied cumulatively from households of Kolkata and during market basket survey. This is explained by the fact that the rice is transported to Kolkata district from the nearby endemic areas where rice is grown regularly (Biswas et al. 2019). Simultaneously, rice grain (n = 32) arsenic concentration was found in the range of 36–636 µg/kg with an average value of 137 µg/kg in West Medinipur district, where groundwater arsenic concentration is found to be safe (Chakraborti et al. 2009; Chowdhury et al. 2020a; De et al. 2022). Contamination quotient concludes through the average value of four sampling sites that, contamination might be higher to lower; however, not less than 100 µg/kg. Such results are observed since 100 µg/kg is considered to be the maximum tolerable concentration of inorganic arsenic in rice for human consumption predominantly in arsenic exposed area (Meharg et al. 2006).

### 23.3.2 *Appraisal of Arsenic Concentration in Rice Grain with Respect to Its Varied Range of Cultivars*

Rice grain arsenic concentration depends on rate of accumulation, assimilation and bioavailability to plants from irrigation water and soil arsenic concentrations; however, it differs intricately among cultivars (Biswas et al. 2014; Schmidt 2015). Therefore, rice grains can be classified into different categories according to their arsenic accumulation and assimilation capability. Previously, a study has been conducted in the GMB plain on the identification of low arsenic accumulating rice plants to find a solution from this natural hazard. It is reported that arsenic buildup in different cultivars of rice grain is governed by various environmental and genetic factors (Norton et al. 2009a, b). The present study of different rice grains from different sampling area has been categorized according to the available rice cultivars (n = 74) into three classes from low to high arsenic accumulation status (Table 23.2).

Arsenic accumulation capacity of rice cultivars has been shown in Fig. 23.3. From the Table 23.2 and Fig. 23.3, it is seen that the greatest amount (61%) of rice cultivars (n = 45) in the entire study area are medium arsenic accumulators (> 100–300 µg/kg), having range of arsenic concentration 102–261 µg/kg with an average value of 178 ± 41 µg/kg. A range of 58–98 µg/kg with an average value of 79 ± 14 µg/kg arsenic containing rice cultivars (n = 13) was also found in the same study area as a lower (50–100 µg/kg) arsenic accumulating rice grain. Along with this, a similar amount of rice cultivars (n = 16) with a higher (> 300–1000 µg/kg) arsenic accumulation tendency also sustain there with a range of 302–930 µg/kg with an average value of 403 ± 160 µg/kg. The lower and higher arsenic accumulating rice grains were found in the study area at an amount of 17 and 22%, respectively (Fig. 23.3).

The lowest arsenic accumulating rice cultivar among all the 74 cultivars is found to be Ranjan masuri (58 µg/kg) and the highest arsenic accumulating rice cultivar is Ganga Kaveri (930 µg/kg) (Table 23.2). It is pertinent to mention here that the WHO recommended suggested limit of arsenic in rice i.e. 1000 µg/kg (Bhattacharya et al. 2010; National Food Authority 1993) only for arsenic unaffected areas. Biswas et al. (2014) reported that Shatabdi as the highest arsenic accumulating rice cultivar (range: 690–780 µg/kg) collected from paddy fields of arsenic affected district Nadia. It is evident that soil has a pivotal role on accumulation of arsenic in rice grains, because it is observed that a same cultivar of rice grain holds almost 17 folds higher arsenic when grown in high arsenic containing soil than the low arsenic containing soil (Kuramata et al. 2011). Chowdhury et al. (2018a) observed that Minikit cultivar of whole paddy grain has a high accumulation capability of arsenic (mean = 1300 ± 246 µg/kg, n = 8), compared to the Jaya cultivar (mean = 370 µg/kg, n = 2) whilst, the present study has observed varied range of arsenic concentrations in different types of Minikit cultivar rice grains including Minikit dishi = 163 µg/kg; Red minikit = 168 µg/kg; Gosai minikit = 184 µg/kg, Minikit = 209 µg/kg, White minikit = 349 µg/kg and Shatabdi minikit = 353 µg/kg throughout the study area (Table 23.2). Jaya cultivar holds much lower range of arsenic concentration including Jaya musuri = 95 µg/kg, Jaya = 175 µg/kg as reported in Chowdhury et al. (2018a).

**Table 23.2** Classification of rice cultivars according to their arsenic (As) accumulation

| Low As accumulator | | | Medium As accumulator | | | | | | High As accumulator | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Range = 50–100 µg/kg; n = 13 | | | Range = > 100–300 µg/kg; n = 45 | | | | | | Range = > 300–1000 µg/kg; n = 16 | | |
| Sl no | Rice cultivar | As (µg/kg) | Sl no | Rice cultivar | As (µg/kg) | Sl no | Rice cultivar | As (µg/kg) | Sl no | Rice cultivar | As (µg/kg) |
| 1 | Ranjan masuri | 58 | 1 | Ratna atap | 102 | 24 | Gosai minikit | 184 | 1 | Netiya | 302 |
| 2 | Masuri atop | 59 | 2 | Dayar mashuri | 106 | 25 | Awam | 186 | 2 | Basumati | 311 |
| 3 | Kamini sur | 61 | 3 | Jeera Rice | 108 | 26 | Hybrid-sankar chem | 192 | 3 | IR 64 | 322 |
| 4 | Bilmota | 68 | 4 | Gangakaberi | 117 | 27 | Banskathi | 193 | 4 | PAN 802 | 322 |
| 5 | KRT royal | 74 | 5 | Bansmoti | 121 | 28 | Ranjit | 196 | 5 | Desi 36 | 338 |
| 6 | Deradun atop | 78 | 6 | Sanap atop | 125 | 29 | Kichmich | 198 | 6 | Kabiraj chem | 342 |
| 7 | Tulsivog | 81 | 7 | Swarnamasuri | 126 | 30 | Maharaj | 199 | 7 | White minikit | 349 |
| 8 | Laxmi vog | 83 | 8 | Swarna mota | 127 | 31 | Khitish | 201 | 8 | Shyamashree | 351 |
| 9 | Badshah vog | 88 | 9 | Deradun | 138 | 32 | Sp.13555 chem | 203 | 9 | 101 Najrul | 353 |
| 10 | Pahari atop | 93 | 10 | Bil mota | 142 | 33 | Dayar rice | 206 | 10 | Shatabdi minikit | 353 |
| 11 | Jaya masuri | 95 | 11 | Banskathi | 149 | 34 | Minikit | 209 | 11 | Black rice | 353 |
| 12 | Polish ranjan | 97 | 12 | Punjab Bansmoti | 150 | 35 | Jayanti | 210 | 12 | Chowmonmoni | 365 |
| 13 | Gobindovog | 98 | 13 | Vanilla chem | 152 | 36 | Gopal vog | 213 | 13 | Bansmoti premium | 380 |
| | | | 14 | PAN 802 chem | 155 | 37 | Badshahvog | 215 | 14 | Sp. 13,555 | 434 |
| | | | 15 | Galaxy | 157 | 38 | 101 Ratna | 215 | 15 | Sp. chaitali chem | 636 |
| | | | 16 | Rup shal | 161 | 39 | Deradun chem | 222 | 16 | Ganga kaveri | 930 |

(continued)

**Table 23.2** (continued)

| Low As accumulator | | | Medium As accumulator | | | | | | High As accumulator | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | 17 | Minikit dishi | 163 | 40 | Hybrid sankar | 231 | | | |
| | | | 18 | Shatabdi | 165 | 41 | IR64 organic | 232 | | | |
| | | | 19 | Red minikit | 168 | 42 | Saatswarna | 235 | | | |
| | | | 20 | Nayanmoni | 168 | 43 | Victoria | 243 | | | |
| | | | 21 | Masuri | 170 | 44 | Vanilla | 247 | | | |
| | | | 22 | Jaya | 175 | 45 | Ganga | 261 | | | |
| | | | 23 | Ratna | 184 | | | | | | |

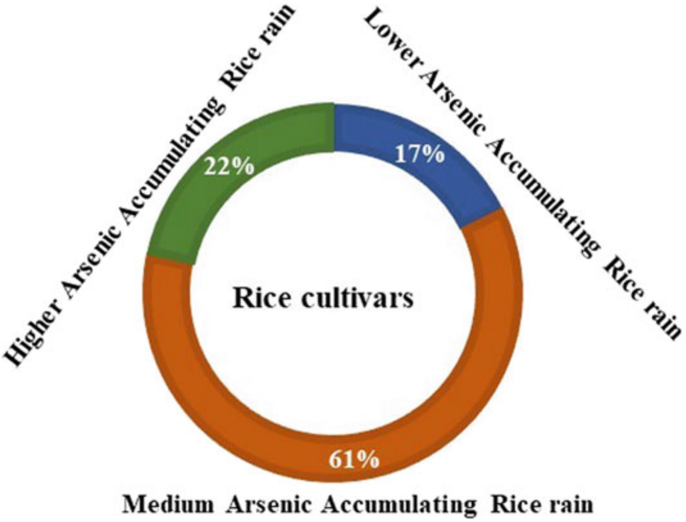


**Fig. 23.3** Percentage of rice cultivars according to their arsenic accumulation capacity

### 23.3.3 Rice Grain Arsenic Assimilation Scenario with Respect to Its Sunned or Parboiled Variety

Rice grain arsenic concentration depends on various factors; however, variety is one of the major contributors among all. Rice grain is always marketed either in non-parboiled (sunned) or parboiled state (Upadhyay et al. 2020). Sunned rice grain is prepared by mechanical de-husking of sunned whole grain after harvesting. Contrastingly, post-harvesting of paddy is a tedious two way boiling method in which the paddy whole grain (sunned) undergoes four distinct stages (sunned whole grain, half boiled whole grain, full boiled whole grain and parboiled whole grain) along with mechanical de-husking to obtain parboiled rice grain (Chowdhury et al. 2018b). Bae et al. (2002) reported during their on-site studies on rice grain that parboiled rice grain contains heavier amount of arsenic, compared to the sunned one. Arsenic concentration in parboiled rice grains is observed to be higher than the raw or sunned rice grains, when arsenic-contaminated groundwater is used during parboiling or post-harvesting procedure (Chowdhury et al. 2018b; Roy et al. 2011). Parboiling with arsenic contaminated water act as a “factor enhancer” during this process.

The present study deals with various kinds of rice grains; however, in this section we are mainly focusing on the variety as mentioned before. Both type of sunned and parboiled rice grains has been collected systematically from the study area, compared them throughout their post-harvesting processing along with their average arsenic concentration in rice grain collected from each sampling site (based on collected 81 and 768 rice grain samples from sunned and parboiled variety, respectively placed in Table 23.1) and shown in Fig. 23.4.

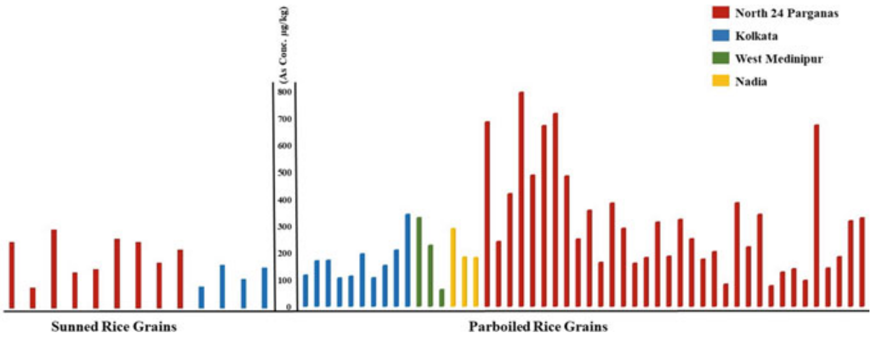


**Fig. 23.4** Variation of arsenic concentration in rice grain according to their variety in each sampling area

It corroborated the previous findings (Chowdhury et al. 2018b) that the sunned rice grains contain lower arsenic (mean: 188 μg/kg, range: 80–311 μg/kg, n = 81) compared to the parboiled one (mean: 268 μg/kg, range: 61–793 μg/kg, n = 768) (Table 23.1 and Fig. 23.4).

So, the findings (Fig. 23.4) indicated that additional arsenic can enter into parboiled rice grain in arsenic endemic region only with the use of arsenic contaminated water during post harvesting processing (Chowdhury et al. 2018b). Regions like Kolkata and Medinipur also possess higher amount of arsenic in parboiled rice grain, due to the transportation of rice grain from arsenic endemic to non-endemic region (Biswas et al. 2019).

The trace element and mineral composition of parboiled rice is found to be higher than sunned rice as loss of the nutrients is lessened during the absence of milling while parboiled rice was prepared (Doesthale et al. 1979). Moreover, the protein content of milled rice was found to be unchanged by parboiling; however, the solubility of protein decreases after parboiling (Rao and Juliano 1970). The riboflavin content also stays unaffected during parboiling of rice (Ocker et al. 1976). According to Heinemann et al. (2005), parboiled rice contains 18% higher mineral content due to sustainability of K and P. Parboiling procedure helps us by providing huge amounts of health benefits; however, this is a chief way to bring arsenic into our food chain during post harvesting, if prepared in an arsenic affected zone.

### *23.3.4 Cultivation Seasons and Its Impact on Rice Grain Arsenic Accumulation*

Paddy cultivation season may vary in different parts of the country, depending upon temperature, rainfall, soil types, water availability, climatic and topographic conditions. In the eastern region of India, paddy is cultivated throughout the year and has the highest intensity of rice cultivation. Mandal et al. (1996) stated that India and

Bangladesh pursue two types of cultivation practice according to their seasonal rainfall pattern. In West Bengal, paddy cultivation mainly occurs in two different seasons, pre-monsoon (February to April) and monsoon (July to September), respectively. In summer season, the huge need of rice grain in Bengal delta is satisfied by boro or pre-monsoon cultivation practice with the help of enormous withdrawal of groundwater (Chowdhury et al. 2018a). Boro cultivation practice along with the help of groundwater has been increased rapidly since 1970 (Harvey et al. 2005). On contrary, Aman or monsoon cultivation practice requires ample amount of groundwater due to insufficient downpour (Chowdhury et al. 2020a). When the groundwater and soil of exposed areas are arsenic contaminated, the arsenic causes phyto-toxicity to the plant and intrudes into paddy grain during translocation via its root system. However, the accumulation in grain is lesser than other parts of the paddy plant (Chowdhury et al. 2018a, 2020a). Arsenic movement, behavior, flow in different phases of paddy cultivation and assimilation in rice grain (edible part) varieties depend on various seasons (Chowdhury et al. 2018a, 2020a). According to Chowdhury et al. (2020a), pre-monsoonal rice grains (boro) contain approximately three times higher amount of arsenic than the monsoonal grains (aman), irrespective of the variety of cultivar and area of cultivation. The average accumulation and assimilation of arsenic in rice grains grown in two different seasons in the study area along with their type of cultivar or variety is described in Table 23.3.

Arsenic mobilization and its flux is dependent on the As-rich groundwater usage during the boro/winter-summer time and the study by Majumdar et al. (2021) showed how to quantify the arsenic concentration that is being fluxed in to the deeper soil or flushed out from the field. Depending on the irrigation pattern or seasonal water content in the field, two parametric equations are proposed which considers soil physico-chemical parameters, cultivation strategies and plant accumulation rates of arsenic to determine the total flux content. Boro season rice cultivars were found to accumulate more arsenic due to greater arsenic percolation to the rhizosphere soil. The study also showed a clear relation amongst seasonal variation, arsenic content and microbial community distribution in the paddy field. Microbial populations were found to be enhanced during boro season with moist soils and monsoonal season with semi-arid soils modulating the degree of arsenic availability to the bulk soil and hence, to the plant root systems. Due to the preferable growth conditions, microbes found to thrive well while producing all the As-responsive genes profusely to minimize the arsenic stress inside the cell and hence, further induce restriction and/or mobility of arsenic in the soil (Majumdar et al. 2020).

Apart from this, the assessment of arsenic accumulation in monsoonal and pre-monsoonal seasons along with different rice grain arsenic standards and previous study reports (Chowdhury et al. 2018a, 2020a) have been described in Fig. 23.5. It depicts from the earlier findings (Chowdhury et al. 2018a, 2020a) that, the monsoonal grain contains lesser amount (~30%) of arsenic than the pre-monsoonal (~70%) one. The average arsenic concentration of pre-monsoonal rice grain was found 528 ± 434 μg/kg; whereas, the arsenic concentration was 224 ± 63 μg/kg in monsoonal rice grain in the present study. The range of arsenic accumulation was found 149–1560 and 152–342 μg/kg in pre-monsoonal and monsoonal rice grain, respectively

**Table 23.3** Seasonal arsenic distribution in rice grains from different districts of the study area

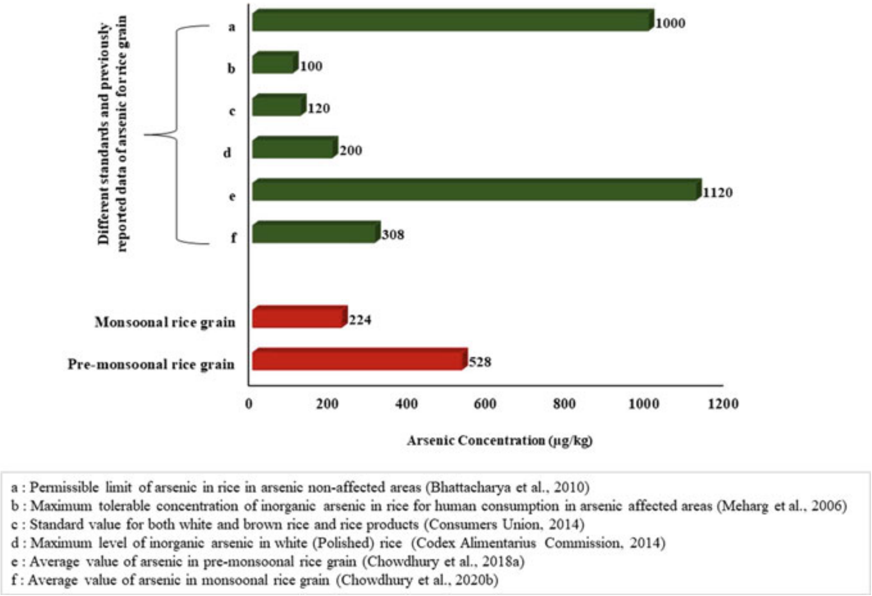
| Season of cultivation | Location | Sampling area | Available rice cultivar/variety | As in rice grain (µg/kg) | |
|---|---|---|---|---|---|
| Monsoonal | West Medinipur | Pingla | IR64 organic | Sunned | 232 |
| | | | IR 64 (double steamed) | Parboiled | 244 |
| | | | IR 64 (single steamed) | Parboiled | 242 |
| | | | PAN 802 chem | Parboiled | 155 |
| | | | Vanilla chem | Parboiled | 152 |
| | | | Deradun chem | Parboiled | 222 |
| | | | Kabiraj chem | Parboiled | 342 |
| | North 24 Paraganas | Madhusudankati, Gaighata | Sunned | | 154 |
| | | Teghoria, Gaighata | Sunned | | 275 |
| *Average* ± *SD* | | | | | 224 ± 63 |
| Pre-monsoonal | West Medinipur | Pingla | Sp. chaitali chem | Parboiled | 636 |
| | | | IR 64 chem | Parboiled | 322 |
| | | | Netiya shyamashree chem | Parboiled | 296 |
| | | | Sp.13555 Chem | Parboiled | 203 |
| | | | Hybrid sankar chem | Parboiled | 192 |
| | North 24 Paraganas | Deganga field | Sunned | | 1460 |
| | | | Sunned | | 370 |
| | | | Sunned | | 970 |
| | | | Sunned | | 1560 |
| | | | Sunned | | 360 |
| | | | Sunned | | 1560 |
| | | | Sunned | | 1270 |
| | | | Sunned | | 930 |
| | | | Sunned | | 1280 |
| | | | Sunned | | 1430 |
| | | Basirhat | Parboiled | | 369 |
| | | | Parboiled | | 329 |
| | | Post harvesting samples, Deganga | Sunned | | 314 |
| | | | Sunned | | 166 |

(continued)

**Table 23.3** (continued)

| Season of cultivation | Location | Sampling area | Available rice cultivar/variety | As in rice grain (μg/kg) |
|---|---|---|---|---|
| | | | Sunned | 268 |
| | | | Sunned | 338 |
| | | | Sunned | 247 |
| | | | Sunned | 374 |
| | | | Sunned | 274 |
| | | | Sunned | 165 |
| | | | Sunned | 287 |
| | | | Sunned | 218 |
| | | Post harvesting samples, Deganga | Parboiled | 323 |
| | | | Parboiled | 149 |
| | | | Parboiled | 328 |
| | | | Parboiled | 636 |
| | | | Parboiled | 362 |
| | | | Parboiled | 230 |
| | | | Parboiled | 286 |
| | | | Parboiled | 373 |
| | | | Parboiled | 250 |
| | | | Parboiled | 458 |
| | | | Parboiled | 465 |
| *Average ± SD* | | | | 528 ± 434 |

(Table 23.3 and Fig. 23.5). So, the pre-monsoonal rice grain is not at all in a non-toxic zone compared to the other standards, which is totally in line with our previous report (Chowdhury et al. 2020a). This can be interpreted by the fact that in monsoon, rainwater mixes in the waterlogged irrigation field and dilutes the initial arsenic concentration. Rainwater has a major effect on the paddy fields during monsoonal cultivation to decrease the original arsenic concentration in top soil due to seasonal flooding (Shrivastava et al. 2017). Lateral removal of thinning water, flood water arsenic diffusion and its movement to the deeper soil layer by infiltration causes less bio-availability of arsenic to the plant root (Chowdhury et al. 2020a; Sahoo and Kim 2013). Therefore, it can be inferred that rain fed or monsoonal cultivation of rice is much safer in arsenic endemic region too. It can act as a potential window for the future rice production of the country.



a : Permissible limit of arsenic in rice in arsenic non-affected areas (Bhattacharya et al., 2010)
b : Maximum tolerable concentration of inorganic arsenic in rice for human consumption in arsenic affected areas (Meharg et al., 2006)
c : Standard value for both white and brown rice and rice products (Consumers Union, 2014)
d : Maximum level of inorganic arsenic in white (Polished) rice (Codex Alimentarius Commission, 2014)
e : Average value of arsenic in pre-monsoonal rice grain (Chowdhury et al., 2018a)
f : Average value of arsenic in monsoonal rice grain (Chowdhury et al., 2020b)

**Fig. 23.5** Variation of seasonal arsenic concentration in rice grain with respect to standards

## 23.4 Conclusive Remarks and Future Remedial Aspects for Rice Grain Arsenic Contamination

Arsenic toxicity and its toxic impact on rice grain is a major public health concern. Arsenic is heavily distributed in rice grain in different manners according to their area of cultivation, cultivar type, variety and mostly the cultivation season. Arsenic is translocated to the plants through the phosphate or silicic acid transporter. Among the inorganic one, arsenite is much more toxic than the arsenate but methylated species are much safer than the inorganic one. Now the foremost priority is to reduce oncogenic arsenic from rice grain for human well-being. ‘Total arsenic concentration and its diverse species’ content differ mostly in paddy cultivable soil, different rice variety and its cultivars. Mitigation strategies need to be figured out to reduce arsenic content through detoxification and produce arsenic safe rice grain using techniques of molecular biology and cut down the arsenic flow at its initial level. Some sustainable strategies have to be taken to alleviate arsenic assimilation in rice grain from soil by agronomic bio remedial measures. To reduce arsenic content from irrigation water (groundwater), we should switch over to rain water harvesting procedure to cultivate paddy with stagnant water. Arsenic resistant microbes and arsenic chelators can help us by reducing arsenic at the soil root system (Majumder et al. 2013; Mridha et al. 2021, 2022; Tang et al. 2020; Zecchin et al. 2017). We are mainly practising anaerobic cultivation with the help of sluggish water in irrigation land; however, this practice needs modification by switching into aerobic cultivation practice for arsenic reduction. Genetically modified crops like paddy must be a meaningful approach towards the society with the help of advanced biotechnology. Sprinkler irrigation method is another fruitful method in our present agriculture science spectrum for lessening arsenic in rice grain, although scientists and researchers are equally hopeful on different genes, which are related to arsenic build up, accumulation, uptake, assimilation and mostly detoxification. Finally, arsenic free and quality based rice grain are the most essential issues in view of public health.

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# Chapter 24

# Arsenic Contamination in Soil and Water Across South East Asia: Its Impact and Mitigation Strategies

**Lalichetti Sagar, Sultan Singh, Meenakshi Attri, Sagar Maitra, Tanmoy Shankar, Masina Sairam, Tariq Aftab, and Akbar Hossain**

**Abstract** Globally, a continuous and swift increase in population raised the water demand. Due to scarcity in available freshwater resources, ground water turned out to be a key source of water for crop and human consumption. Recently, many groundwater aquifers across the world reported exceeding the limits of the prescribed arsenic level, in turn raising a serious concern on both environment and human health. Arsenic is a ubiquitous metalloid that exists in four different oxidation states inclusive of both metallic and non-metallic characteristics and occurs both in [arsenite ($As^{III}$) and arsenate ($As^{V}$)] and inorganic (monomethylarsonic acid (MMA) and dimethyl arsenic acid (DMA)) forms. The arsenite ($As^{III}$) form is comparatively more toxic than arsenate ($As^{V}$), MMA and DMA. Heavy accumulation of arsenite ($As^{III}$) form in the plant tissues stimulates the production of reactive oxygen species (ROS) which in turn affects the membrane stability, permeability, enzyme activity, electron transport chain, and ion homeostasis leading to poor seed germination, growth retardation and yield reduction in plants. In general, arsenite ($As^{III}$) form of arsenic predominates in reducing the environment that usually prevails in rice-growing tracts of the world. Rice is the staple food in South East Asian countries viz., Bangladesh, Cambodia, China, India, Myanmar, Nepal, Pakistan, Thailand, and Vietnam in turn has a growing concern about arsenic poisoning in the human food chain. In consideration of the associated damage due to arsenic accumulation, many mitigation strategies were

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devised by several researchers. This chapter focuses on appropriate strategies that could mitigate arsenic toxicity effectively and in a sustainable manner.

**Keywords** Arsenic toxicity · Bioremediation · ROS · Impacts · Crop · Productivity

## 24.1 Introduction

Arsenic is a highly noxious and omnipresent metalloid in the environment. Belonging to group VA of the periodic table, arsenic exists in four different oxidation states viz*.*, $-3, 0, +3$ and $+5$, respectively (Williams and Pillay 2011). In nature, arsenic occurs both in organic [arsenite ($As^{III}$) and arsenate ($As^{V}$)] and inorganic [monomethylarsonic acid (MMA) and dimethyl arsenic acid (DMA)] forms (Huang et al. 2008). Globally, due to improper checks on natural and man-made activities viz*.,* metal mining, smelting, use of arsenic-based inputs in agriculture and irrigation with water polluted with arsenic species from last few decades augmented to exceed arsenic levels of soil and groundwater beyond safe limit threshold level as prescribed by WHO (Shah et al. 2020). Further, crops raised in these polluted areas pose a serious hazard of arsenic accumulation to the plant. However, the rate of arsenic accumulation depends on the soil and plant characteristics, respectively (Lin et al. 2015).

Heavy accumulation of arsenic in the plant tissues stimulates the production of reactive oxygen species (ROS) which in turn affects the membrane stability, permeability, enzyme activity, electron transport chain, and ion homeostasis leading to a decrease in germination, growth, and yield of the plant (Nahar et al. 2022). In general, the root is the primary organ that accumulates the arsenic species from the soil and later this accumulated arsenic is translocated to shoot through specific transporters (Fayiga et al. 2005). Due to the prevailing anoxic and reduced soil environment in rice, the arsenite form ($As^{III}$) form of arsenic predominated in availability (Suriyagoda et al. 2018). In comparison, arsenite ($As^{III}$) form is highly toxic than arsenate ($As^{V}$) and methylated arsenic species (Coelho et al. 2020).

Recently, several studies evaluated ground water quality in different locations of the world in which it was found that many aquifers in South East Asia were not potable as arsenic concentration exceeded the limits recommended by WHO (Kim et al. 2011). Since this region is a predominant tract for rice cultivation, the creation of a reduced soil environment is often attributed to increased intake of highly toxic forms of arsenic from soil and irrigation water (Sandil et al. 2021). On the other hand, in dry land crops accumulate the $As^{V}$ form due to oxidation of arsenic under prevailing aerobic conditions (Mitra et al. 2017). The South East Asian countries viz*.,* Bangladesh, Cambodia, China, India, Thailand, and Vietnam depend on rice as their staple food crop which is highly susceptible to arsenic poisoning hence evoking a concern of gaining arsenic entry into the human food chain (Sankhla et al. 2018). Arsenic being carcinogenic in nature, direct exposure of humans to arsenic leads to several chronic ailments that harm the bladder, lungs, liver etc. and induces cancer (Kapaj et al. 2006).

In the light of the above facts, various approaches were developed for mitigating arsenic toxicity. The use of resistant microbes, hyper-accumulating plants, and the adoption of proper agronomic management practices has a marked role in detoxifying arsenic efficiently. This chapter sheds light on the present status of arsenic noxiousness in South East Asia, its impact on plants and mitigation.

## 24.2 Status of Arsenic Pollution in South East Asia

The use of groundwater for drinking and irrigation purposes are the major cause of exposure to arsenic intake to human beings and worldwide around 2.5 million people bank on groundwater for drinking purposes (Shaji et al. 2021). Presently, arsenic pollution in groundwater beyond the permissible limit has been noticed in more than 108 countries in the globe across several continents such as Africa, Asia, Australia, Europe, North America, and South America. However, out of 230 million people in the world, about 180 million affected persons by arsenic poisoning are from Asian countries. Moreover, South East Asian countries are severely affected (Table 24.1).

**Table 24.1** Distribution of arsenic toxicity in South East Asia

| Country | Location | Population exposed to arsenic poisoning | References |
|---|---|---|---|
| Bangladesh | Dhaka | 85 million | Huq et al. (2020) |
| Cambodia | Mekong delta at Prey Veng province | 2.4 million | Murphy et al. (2018) |
| China | Xinjiang Uygur | 19.6 million | Chen et al. (2017) |
| India | Ganges and Brahmaputra river basin | 50 million | Chakraborti et al. (2018) |
| Myanmar | Ayeyarwady region | 2.5 million | Phyu et al. (2019) |
| Nepal | Terai region | 3 million | Timalsina et al. (2021) |
| Pakistan | Punjab and Sindh | 13 million | Ali et al. (2019) |
| Thailand | Ron Phibun | 1000 people | Tiankao and Chotpantarat (2018) |
| Vietnam | Red river delta | 10 million | Bozack et al. (2019) |

### 24.2.1 Bangladesh

Bangladesh has been prone to severe arsenic toxicity due to the dependence of rural households on groundwater as a major source for drinking and domestic use (Flanagan et al. 2012; Safiuddin et al. 2022). Before the spread of tubewells in the country, people used to rely on surface water as a source of drinking water, but that water was microbiologically contaminated and people suffered in diarrheal diseases. On the other hand, groundwater lifted from shallow depth was well thought-out microbiologically safe; hence tubewells became popular in Bangladesh to supply drinking water for combatting diarrheal diseases (Khan et al. 1997). Such disease infection was brought down after the successful spread of tubewells; however, arsenic contamination in drinking water created another dimension to the health issues (Ahmed et al. 2018). This issue was unraveled in 1993, with the identification of a high concentration of arsenic above the safe threshold (>10 μg/L) in the tubewell water derived from Chapai Nawabganj district of Bangladesh by the Department of Public Health and Engineering (Flanagan et al. 2012). Further, studies indicated that 61 out of 64 districts of Bangladesh were adversely affected by arsenic toxicity (Rahaman et al. 2022).

The Ganges–Brahmaputra-Meghna River system covers the major geographical area of Bangladesh that comprises arsenic-containing sediments which leach into groundwater (Islam and Miah 2003; Safiuddin et al. 2022). In comparison, the shallow aquifers were more highly contaminated with arsenic than deep aquifers (Das and Mondal 2021). Therefore, drinking water from deep sources (>300 m) is safe to avoid arsenic contamination. However, shallow aquifers have been a major source of drinking water for the poor in turn intensifying the occurrence of arsenicosis among the poor (Inauen et al. 2013). To combat arsenic pollution, in 1998, Bangladesh started Arsenic Mitigation Water Supply Project (BAMWSP) which randomly screened the tubewells (Shafiquzzaman et al. 2009). Later in 2004, National Policy for Arsenic Mitigation (NPAM) was formulated. Also, the Implementation Plan for Arsenic Mitigation (IPAM) was initiated. However, it is a major health issue in Bangladesh that needs a multisectoral approach for a long-lasting solution (Ahmed et al. 2018). The issue of arsenic pollution of groundwater is a major challenge for the country, and therefore, multi-sectoral approaches have been implemented.

### 24.2.2 Cambodia

An investigation conducted by the Ministry of Rural Development of Cambodia in 1999 supported by WHO recorded the presence of elevated levels of arsenic in drinking water. Kandal province was the first detected locality where arsenic contamination was found in the country (Feldman and Rosenboom 2001; Sampson et al. 2008b, a). Recently, the ground water in Cambodia is reported to have concentrations above 10 μg/L leading to severe arsenic toxicity (Sovann and Polya 2014). The kingdom of Cambodia is categorized into five distinct regions based on its geographical location. Among these regions, the Mekong lowland of central plains situated along the Mekong River bank has been a dominant rice growing tract. The use of groundwater for agriculture and domestic purposes has been increased in recent years due to the availability of shallow alluvial aquifers in the Mekong plains (Hoan et al. 2022). Further, this is attributed to an increase in the number of tubewells across the country with a marked increase in Prey Veng province (Sugimoto et al. 2007). Other six provinces along the Mekong River where arsenic contamination is found in Cambodia are Kandal, Kampong Cham, Kratie, Kampong Thom, Kampong Chhnang, and Peri-urban of Phnom Penh. The severely contaminated province of Cambodia is Kandal (Ratha et al. 2017).

Presently, due to short duration exposure to arsenic-contaminated water could not report any visible arsenic toxicity symptoms in populations exposed to this toxicity (Sankhla et al. 2018). However, continuous dependence on arsenic-contaminated water for drinking and cultivation of rice might accumulate into the human food chain of the population residing around the banks of the Mekong River. According to an estimate more than 2.4 million people of Cambodia are subjected to Arsenic risk (Arslan et al. 2016). The main source of drinking water was tubewell that was exposed to arsenic contamination (Ratha et al. 2017).

### *24.2.3 China*

China is considered as a hotspot for arsenic poisoning attributed due to both natural and industrial effluents and estimated that more than 19.6 million people were affected directly or indirectly by arsenic pollution (Lin et al. 2015). Although arsenic poisoning is widespread all over China, but it is predominant in the northern province of the country (Sanjrani et al. 2019). The threshold level of arsenic in the ground water is 50 μg/L according to the Chinese standard and reported the first arsenicosis case in the Kuitan region, Xinjiang Uygur province, China in 1980 (Dey et al. 2014). Later in 1989, Inner Mongolia was recognized as an endemic locality of arsenic contamination (Sun 2004). The groundwater of the South of Yinshan mountain, northern plain of Yellow River and plain of Heihe River are rich in arsenic (Shaji et al. 2021). Recently, quaternary aquifers in parts of Shanxi, Mongolia, Ningxia, Liaoning and Jilin Provinces have been found to have arsenic concentrations up to 4,400 μg/L (Van Halem et al. 2009). A study indicated that the South and Northeastern regions of China were prevalent in arsenic toxicity with a medium concentration of 9.7 mg/kg in surface soils and the concentration was reduced with the soil depth (Zhou et al. 2018). In China also, the over-lifting of groundwater caused arsenic pollution (Maliva 2020). From 2001 to 2005, the Chinese government took the initiative to test groundwater pumped by the wells in risk-prone counties (Rodríguez-Lado et al. 2013).

### 24.2.4 India

Globally, the Ganga–Brahmaputra-Meghana basin is one of the important hotspots for arsenic contamination in India (Biswas et al. 2022). West Bengal of India reported high ground water arsenic concentration in the early 1980s (Mahmudur Rahman et al. 2005). The arsenic contamination in groundwater was first recognized in India in West Bengal in 1983 and afterwards, it was also noticed in neighbouring states such as Bihar, Jharkhand and the eastern part of Uttar Pradesh belonging to the flood plain of the Ganges. Further, the Brahmaputra flood plain regions of Assam and Manipur also faced the presence of higher arsenic concentration in the drinking water lifted from the tube wells. The alluvial terrain of Punjab and Haryana and the hard rock terrain of Karnataka and Chhattisgarh also witnessed arsenic contamination in groundwater (Bhattacharya and Lodh 2018). As per Radhapyari et al. (2017), in 19 districts of Assam, groundwater is contaminated by arsenic; however, Bordoloi (2012) claimed that 20 out of 24 districts in Assam were contaminated by the excess arsenic in groundnut. Other north-eastern states of India are Tripura (3 districts), Arunachal Pradesh (6 districts), Nagaland (2 districts) and Manipur (1 district) where arsenic-contaminated groundwater has been detected (Bordoloi 2012). The issue of excess arsenic contamination was noticed in Bihar in 2002 in the middle Ganges plain, the flood-prone area of the state with a multi-aquifer system with a spread in 15 districts affecting around 9 million people (CGWB and BARC 2009; Bhattacharya and Lodh 2018). In Chhattisgarh, a small patch of Rajnandgaon was observed, however, In Haryana, sporadically arsenic-contaminated regions covered by alluvial aquifers have been identified (Bhattacharya 2017; Bhattacharya and Lodh 2018).

Presently, the problems of arsenic poisoning were also perceived in all the quaternary aquifers present all along the Ganges basin. Predominant cultivation of rice and dependence on arsenic-contaminated ground water for irrigation was reported for the presence of arsenic in rice grains (Mitra et al. 2017) and thus, consumption of rice serves as a source of arsenic intake by human beings attributing to serious health issues. More than 50% of groundwater aquifers in West Bengal were contaminated with arsenic toxicity (Chakraborti et al. 2009). A study conducted in the West Bengal of India revealed that samples of rice analyzed in arsenic-contaminated areas reported arsenic concentrations within the threshold of 1.0 mg/kg (Upadhyay et al. 2019). However, in the near future, upon constant exposure might pose a serious health risk to the rice-consuming population.

### 24.2.5 Myanmar

In Myanmar, it is assessed that around 2.5 million people out of 51 million population are directly exposed to arsenic through drinking water. Ayeyarwady River delta region is a marked hotspot for arsenic contamination. The reducing environment coupled with arsenic desorption and microbial respiration favoured elevated levels of arsenic in the ground water of this region. Geen et al. (2014) carried out a study and observed that out of 55 samples analyzed for arsenic concentration only 17 were observed with elevated arsenic concentrations ranging between 50 to 630 μg/L. Similarly, another study conducted by Pincetti-Zúniga et al. (2020) revealed that 14% of groundwater in central and southern Myanmar was noted to exceed the threshold limit of 10 μg/L as prescribed by WHO.

### *24.2.6 Nepal*

The Terai region is found to be the hotspot for arsenic contamination in Nepal. This region is densely populated due to the availability of adequate drinking water and fertile lands for cultivation (Gwachha et al. 2020). Being a rice-grown tract, the occurrence of a reducing environment is prominent in this region. Recently, many studies reported high arsenic concentrations exceeding the levels prescribed by both WHO and National Steering Committee (NSSC). This risk was further aggravated because of the dependence of inhabitants of the Terai region on arsenic-polluted groundwater exclusively for both domestic and agricultural use (Pokhrel et al. 2009). Thakur et al. (2011) in a study carried out in 25 districts of Nepal found that 7.9% of ground water was polluted with arsenic concentrations ranging between 10 and 50 μg/L and in 2.3% samples, the arsenic concentration was recorded above 50 μg/L.

### *24.2.7 Pakistan*

The Indus River is the major source of surface water in Pakistan. In general, it is 3180 km in length and covers the most fertile provinces of the country viz., Punjab and Sindh (Sarkar et al. 2021). Due to adequate availability of water and fertile soils, these provinces reported the highest agricultural productivity in the country. Because of natural and anthropogenic sources, the arsenic concentration in the ground water of the Indus region was reported beyond the national threshold limit of 50 μg/L (Rasool et al. 2016). Altogether in the Indus region, there are nearly 27 districts with 40 million residents. Among them, several studies revealed that around 13 million people were prone to arsenic poisoning (Ali et al. 2019). Rabbani et al. (2017) noted an average arsenic concentration of 14.98 μg/L from 2517 ground water samples collected from Sindh province. Similarly, another study conducted in regions of Hyderabad and Lahore reported that 785 samples out of 1184 samples exceeded the safe limit threshold of WHO.

### *24.2.8 Thailand*

The alluvial mining in Thailand provoked the release of arsenic into the soil. Tin mining was very popular in the Ron Phibun region of Thailand which in turn resulted in the mobilization of arsenic from the organic substances into the soil (Visoottiviseth et al. 2002). A survey conducted in 1990 by the Department of Industry and Department of Mineral Resources of Thailand reported the soils of the southern part of Thailand were more highly contaminated with arsenic toxicity than other regions in comparison (Paul et al. 2015). The ground water samples were analyzed for the arsenic range between 1 to 4000 μg/L (Shankar and Shanker 2014). Further, constant intake of arsenic directly or indirectly posed serious health issues like skin cancer, reduction in IQ levels, impairment in speech and sensory receptors etc. (Kumar et al. 2019).

### *24.2.9 Vietnam*

The arsenic contamination has been widely spread in the deltaic alluvial tracts of the Red river and Mekong river (Shinkai et al. 2007). In Vietnam, more than 75% of the total ground water samples analyzed for arsenic concentration from these regions were reported to exceed the permissible limit of 10 μg/L (Huang et al. 2016). Ground water contamination with arsenic beyond the permissible limit was first tapped in Vietnam along the deltaic alluvial tracts of the Red River in the year 2001 (Postma et al. 2012). A study indicated that incessant exposure of organic-rich sediments in deltaic alluvial tracts of the Red river and Mekong river to anoxic conditions could be a prime cause of arsenic pollution in Vietnam (Kim et al. 2011; Stopelli et al. 2020). Further, these results were confirmed (Buschmann et al. 2008 and Wang et al. 2020). In the Red river delta, Holocene and Pleistocene aquifers are the prime sources of water for agriculture and domestic purposes. Both these aquifers were separated by water-permeable clay allowing the water to flow between them (Sankhla et al. 2018). In this region, arsenic is usually bound to iron oxy-hydroxides present in the naturally occurring organic matter (Ahmed et al. 2018). Rice being a predominant crop of this region, anoxic conditions in rice promote the reduction of iron oxides in turn resulting in arsenic contamination. Moreover, this increased arsenic was found to be accumulated in the human food chain through the consumption of arsenic-contaminated rice and drinking water (Mitra et al. 2017).

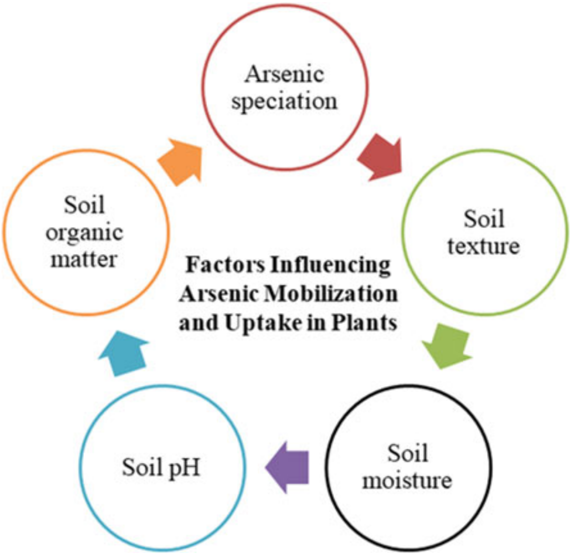
## 24.3 Factors Influencing Arsenic Mobilization and Uptake by Crops

The natural and anthropogenic causes of arsenic contamination in soil and water have been recognized; however, removal of arsenic by plants greatly depends on several factors (Fig. 24.1) which have been presented below.

### *24.3.1 Arsenic Speciation*

Arsenic species occur in both organic and inorganic forms. The inorganic forms exist as minerals and are more phytotoxic compared to organic forms of arsenic (Paul et al. 2015). There are more than 300 species of arsenic present in the soil as minerals (Pigna et al. 2015). Among them, sulfide and arsenate minerals are the most common and predominant soil bond minerals whereas other minerals form usually appear during weathering (Alam et al. 2014). Arsenite ($As^{III}$) and arsenate ($As^{V}$) are the predominant oxidation states of arsenic under anaerobic and aerobic conditions, respectively (Das and Barooah 2018). Due to the presence of lone pairs of electrons, the arsenite form is characterized by a pyramidal geometry while the arsenate form shows a tetrahedral geometry (Mukherjee et al. 2019). These inorganic forms after gaining their entry into living organisms undergo methylation and get transformed into less toxic organic form. Monomethylarsonic acid (MMA) and dimethyl arsenic acid (DMA) were the most commonly occurring forms of arsenic species (deCastro et al. 2014). The order of toxicity within commonly occurring arsenic species is $As^{III}$ >

**Fig. 24.1** Important factors influencing mobilization and uptake of arsenic in plants



$As^V$ > MMA > DMA (Komorowicz et al. 2019). Since the characteristics of arsenic were intermediate between both metal and no-metal hence complete oxidation of arsenic into carbon dioxide and water is not possible. Therefore, to reduce the impact of arsenic toxicity in the plant, highly toxic arsenic species are transformed into a less phytotoxic form either through oxidation or methylation.

### *24.3.2 Soil Organic Matter*

The sorption capacity of the soil was significantly influenced by the organic matter content in the soil. High organic matter percentage in the soil is ascribed to increase sorption capacities, binding energies at the sorption sites and ion exchange capacities, respectively (Durovic et al. 2009). Studies indicated increased arsenic mobility in the soil due to the competing ability of dissolved organic carbon for arsenic sorption sites (Pigna et al. 2015; Mladenov et al. 2015). Moreover, it was recorded a noteworthy reduction in arsenic solubility in soils rich in organic matter (Tarvainen et al. 2013). This occurs mainly due to the higher affinity of organic matter sorption sites for arsenic which in turn led to the formation of organo-arsenic complexes (Tuchowska et al. 2019). These built-up complexes impede the innate mobility of arsenic species and minimize the uptake and translocation of arsenic within the plants.

### *24.3.3 Soil pH*

The soil pH determines the predominance of arsenic species and its mobility in the soil in turn affecting solubility and availability of arsenic to plants. Both higher and lower soil pH had a marked impact on soil arsenic availability and uptake (Soti et al. 2015). In general, in neutral pH arsenic exists as an oxyanion resulting in the formation of complexes with different elements viz., calcium, manganese and aluminum (Inam et al. 2018). At very low pH the arsenic-based complexes become soluble resulting in enhanced arsenic poisoning of plants (Bhattacharya et al. 2012). Similar, negative relationships between arsenic concentration and soil pH were recorded by (Saldana-Robles et al. 2018 and Bustingorri et al. 2015). However, conversely, positive relationships between arsenic accumulation and soil pH were also narrated in various findings (Sushant and Ghosh 2010 and Ancheta et al. 2020). At alkaline pH, the affinity of arsenate for iron oxyhydroxide was found to be greater than other elements and with the increase in pH the sorption capacity of arsenate decreases while that of arsenite increases subsequently (Maitlo 2020). Under reducing environments, the negative charges on the soil surface were aggravated by high soil pH in turn facilitating arsenic desorption into free arsenic and accumulated in the rhizosphere region (Lin et al. 2020).

### *24.3.4 Soil Moisture*

The chemical form of arsenic is mainly determined by the presence of soil moisture in a given period of time (Pandey et al. 2018). The arsenate form has a high affinity to bond with iron hydroxides under aerobic conditions. However, in water-logged soils the sorption energy of iron oxyhydroxides was low and in turn, releases the adsorbed arsenic thus attributed to enhancing the bioavailability of arsenic in plants (Hartley et al. 2010). Moreover, with the increase in soil moisture the free oxygen in the soil pores gets exhausted and reducing conditions prevail (Dresemann et al. 2018). This reducing condition further ascribes to the reduction of arsenic species from arsenate ($As^{V}$) to arsenite ($As^{III}$), respectively (Kumari et al. 2017a, b).

### *24.3.5 Soil Texture*

Iron (III) oxide-hydroxide is one of the main sorbents for arsenite ($As^{III}$) and arsenate ($As^{IV}$), respectively (Druwe and Vaillancourt 2010). Among both the inorganic arsenic species arsenate form binds to iron oxyhydroxides strongly compared to the arsenite form (Wei et al. 2016). In comparison, Iron (III) oxide-hydroxide concentration is more in clay soils than in sandy soils (Stefanou and Papazafeiriou 2013). Henceforth, arsenic poisoning is more prominent in clay soils than sandy textured soils. However, reduction of the predominant inorganic arsenic species occurs without desorption from Iron (III) oxide-hydroxide under anoxic conditions whereas under aerobic conditions Iron (III) oxide-hydroxide was reported to be strongly insoluble with the lesser release of arsenic (Coles and Rohail 2020).

## 24.4 Impact of Arsenic Toxicity on Growth and Productivity of Plants

Roots are the plant organs that are prominently exposed to arsenic toxicity. The arsenic contaminated water absorbed by plants are translocated to different tissues in plants which ultimately influence on several physiological and metabolic processes. Moreover, arsenic toxicity disturbs the plant system at morphological and cellular levels (Fig. 24.2).

### *24.4.1 Seed Germination*

Germination percentage as influenced by the increase in arsenic concentration manifested a marked decline. In chickpea, a significant decrease in the germination

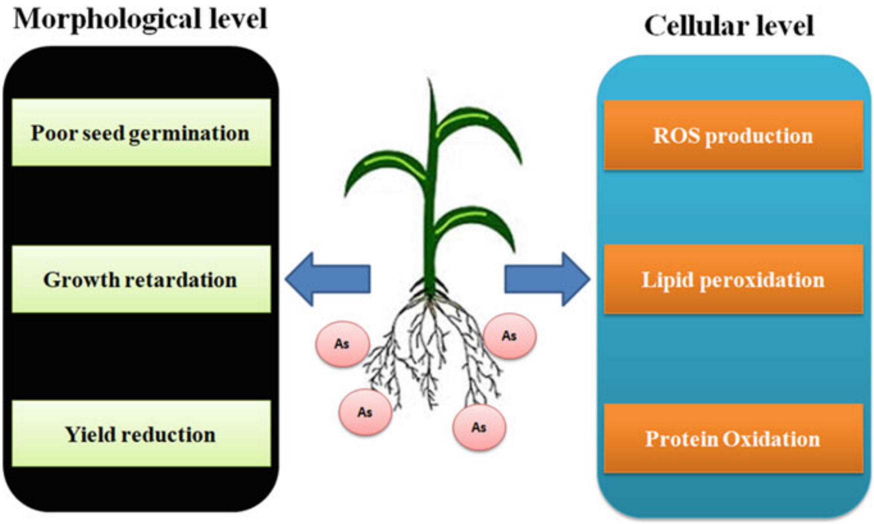


**Fig. 24.2** Impacts of arsenic contamination in plants

percentage of the seeds was noted with the increase in arsenic concentrations from 200 to 800 ppb when treated with arsenite and arsenate salts, respectively (Bhattacharya et al. 2012). The influence of arsenite salt on seed sprouting was comparatively more detrimental than arsenate salts. This might be attributed to the ability of trivalent forms of arsenic to cause phytotoxicity compared to its pentavalent form (Bhattacharya et al. 2012). Similarly, in rice, the seed germination percentage showed a steep decline of 46% with the increase in arsenic concentration from 50 to 100 μM/L while, a 62% decline was recorded with a further increase in arsenic concentration from 100 to 150 μM/L (Bag et al. 2019). In another trial, a decline in seed germination by 8, 4, 60, 4 and 4% was noted in black gram, maize, rice, tomato, and groundnut at an arsenic concentration of 40 mg/L, respectively. Moreover, with a further increase in arsenic concentration from 40 to 60 mg/L it was noticed that no other crop seeds were germinated except rice (Devi et al. 2022). This proves that CO 51 variety of rice is tolerant to arsenic concentrations upto 60 mg/L among all other crop varieties under comparison.

### *24.4.2 Growth*

A marked reduction in all the growth parameters was noted by the plants raised in an arsenical toxic environment. This influence of arsenic species on growth was mainly attributed to the interference of higher arsenic concentration on different plant metabolic functions (CI et al. 2012). Several studies indicated that the availability of arsenic in trace amounts had a stimulatory impact on plant growth, whereas the increase in arsenic concentration beyond its maximum threshold overshadowed its beneficial impact (Mishra et al. 2016). In tomato, when exposed to arsenic concentration beyond 5 ppm found to report a significant reduction in all the growth parameters viz., plant height, number of leaves, and fresh and dry biomass than control. This was mainly due to the partitioning of energy to withstanding the adverse effect of hyper-accumulated arsenic on the physiological functioning of the plant (Rai and Singh 2021). Similarly, a significant decrease in root and shoot length has been documented with an increase in arsenic concentration from 0 to 50 and 100 μM in black gram (Srivastava and Sharma 2013). In rice plants, plant height and dry matter accumulation in shoots were reduced markedly with enhanced concentrations of arsenic in soils. The highest number of tillers per pot was noted by arsenic control in BARI hybrid Dhan 1 and the lowest number of tillers was recorded when the crop was raised by 30 mg/kg soil arsenic concentration (Rahman et al. 2007). In another study, when mustard growth was evaluated under different concentrations of arsenic has shown a significant suppression in plant height (66%), leaf area (72%), number of leaves per plant (71%), shoot dry weight (72%) and root dry weight (69%) by 75 mg/kg arsenic concentration than control. However, in terms of growth parameters, the response of 50 mg/kg remained on par with 75 mg/kg arsenic concentration (Niazi et al. 2017).

### *24.4.3 Yield*

According to many studies, the yield of a crop was significantly influenced by arsenic concentration. In a study, different arsenic levels viz., 10, 20, 30 and 40 mg/kg of soil were applied to potatoes and compared with control. It revealed that with the small increase in arsenic level from control to 10 mg As/kg of soil and however with further increase in arsenic concentrations yield of potato was noted to decline subsequently. The maximum tuber yield was noted with control and the minimum tuber yield was noted with 40 mg arsenic per kilo gram of soil (Hussain et al. 2014). Similarly, when red Amaranthus was treated with 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 mg of arsenic through irrigation water the fresh leaf yield was not affected up to 15 mg arsenic dose and thereafter drastic reduction was observed with the increase in dosage beyond 15 mg. The highest yield reduction of 100% was noted when the red Amaranthus was supplied with 55 mg of arsenic and 50 mg arsenic concentration was reported to be the maximum threshold for yield reduction in red Amaranthus (Choudhury et al. 2008).

### *24.4.4 Oxidative Stress*

In general, plants produce reactive oxygen species (ROS) viz., superoxide, hydroxyl radical, peroxide and hydrogen peroxide when subjected to arsenic toxicity (Nahar et al. 2022). Further, with the increase in exposure to soil arsenic toxicity, the ROS production was subsequently amplified (Korany et al. 2019). At low concentrations, oxygen free radicals act as signaling molecules and help in initiating the stress signal transduction pathway (Vranova et al. 2002). However, over-production of reactive oxygen species causes an imbalance in homeostasis between pro-oxidant and antioxidant molecules leading to oxidative stress (Pisoschi and Pop 2015). This increased production of ROS in plants is characterized by the peroxidation of membrane lipids. Further, this surge in ROS production as influenced by the severity of arsenic toxicity leads to membrane instability and the death of cells at the cellular level (Karuppanapandian et al. 2011). Hasanuzzaman and Fujita (2013) reported that the increase in arsenic concentration from 0.25 to 0.5 mm in seedlings of wheat noted 41 and 95% increase in $H_2O_2$ content and on the other hand antioxidant-scavenging and the glyoxalase systems were also found to allay with the increase in severity of arsenic-induced oxidative stress. It is evident from another study the rice crop was more sensitive to arsenite than arsenate toxicity and found that the activity of ROS scavenger showed a declining trend with an increase in arsenic concentration than control (Gaikwad et al. 2020).

## 24.5 Strategies to Mitigate Arsenic Toxicity

### *24.5.1 Microbial Bioremediation of Arsenic*

Arsenic toxicity in rice fields is a growing concern across the world. Mitigation of arsenic toxicity using conventional practices is economically non-viable and technologically complex. In recent time, many studies recognized the ability of microbes in the reclamation of heavy metal contamination in soil (Paul et al. 2015; Maitra et al. 2022). Employing this innate potential of microorganisms in mitigating the arsenic toxicity of rice is likely to be the most effective and sustainable strategy (Table 24.2). In general, bioremediation of arsenic using microorganisms was mainly facilitated by efflux of metals from the cell, hyper accumulation of metals through specific transporter, enzymatic immobilization, and transformation of heavy metals into less toxic forms (Zango et al. 2020). Arsenic being a ubiquitous metalloid, it cannot be oxidized to carbon dioxide and water as other organic pollutants; whereas, instead it can be oxidized from a lower oxidized state to a higher oxidized stage (Yu et al. 2020).

In bacteria, the heavy metal arsenic usually enters its cell structure through aquaglyceroporins and phosphate transporters (Asati et al. 2016). The resistance of bacterial strains to arsenic exposure is mainly controlled by genes within *ars* operon (Kaur et al. 2011). Recently, Satyapal et al. (2018) recorded that AK1 and AK9 strains of *Pseudomonas*, collected from the middle Gangetic plain of Bihar, harbours the arsenic marker genes aoxR, aoxB and aoxC and conferred to arsenic bioremediation through the oxidation process. Similarly, in another study Das and Mondal (2021) indicated the potential of *Lysinibacillus* spp. and *Bacillus safensis*

**Table 24.2** Microbial bioremediation of arsenic

| Microorganisms | Types of Microorganism | Crops | References |
|---|---|---|---|
| *Bacillus vietnamensis* | Bacteria | *Oryza sativa* | Mallick et al. (2018) |
| *Acinetobacter lwoffii* (RJB-2) | Bacteria | *Vigna radiata* | Das and Sarkar (2018) |
| *Methylobacterium oryzae* | Bacteria | *Acacia farnesiana* | Alcantara-Martinez et al. (2018) |
| *Ralstonia eutropha, Rhizobium tropici, Exiguobacterium aurantiacum* | Bacteria | *Brassica rapa, Raphanus sativus* | Wang et al. (2017) |
| *Brevundimonas diminuta* | Bacteria | *Oryza sativa* | Singh et al. (2016) |
| *Bacillus flexus* | | *Oryza sativa* | Das et al. (2016) |
| *Rhizoglomus intraradices* and *Glomus etunicatum* | Arbuscular Mycorrhizal Fungi | *Triticum aestivum* | Sharma et al. (2017) |
| *Rhizophagus intraradices* | Arbuscular Mycorrhizal Fungi | *Glycin max* | Spagnoletti and Lavado (2015) |
| *Rhizophagus intraradices* | Arbuscular Mycorrhizal Fungi | *Oryza sativa* L | Li et al. (2016) |
| *Glomus geosporum, Glomus versiforme, Glomus mosseae* | Arbuscular Mycorrhizal Fungi | Isolated from *Pteris vittata*, and used for *Oryza sativa* | Wu et al. (2015) |
| *Chlamydospores of Trichoderma asperellum* | Rhizospheric Fungi | isolated from realgar mines and used for *Ipomoea aquatic* | Su et al. (2017) |
| *Trichoderma sp.* | Rhizospheric Fungi | *Helianthus annuus* | Govarthanan et al. (2018) |
| *Piriformospora indica* | Rhizospheric Fungi | *Oryza sativa* | Mohd et al. (2017) |
| *Chlorella vulgaris and Nannochloropsis sp.* | Algae | *Oryza sativa* | Upadhyay et al. (2016) |
| *Anabaena sp.* | Algae | *Oryza sativa* | Ranjan et al. (2018) |
| *Pseudomonas putida and Chlorella vulgaris consortium* | Algae | *Oryza sativa* | Awasthi et al. (2018) |

in transforming arsenic species present in arsenic polluted soils into simpler and non-toxic compounds.

In addition, some fungal species have the potential to accomplish a noteworthy role in the alleviation of arsenic stress. The role of fungus in arsenic tolerance and detoxification is attributed to the conjugation of arsenic with glutathione enzyme resulting in the formation of As $(GSH)_3$ which is further stored in the cell vacuoles

(Parker et al. 2017). In a recent investigation ectomycorrhizal fungus namely *Hebeloma cylindrosporum* has been widely gaining popularity in imparting resistance to the plants affected under arsenic stress (Naher et al. 2013). Arsenic resistance in plants by ectomycorrhizal fungi was mainly attributed to its influence on the glutathione biosynthesis mechanism (Mrnka et al. 2012).

### *24.5.2 Phytoremediation*

The ability of certain bacteria to unfetter arsenic species back into the soil environment and alter its toxicity when exposed to unfavourable conditions is one of the main backdrops of microbial bioremediation (Hadis et al. 2011). Therefore, the identification and adoption of efficient and sustainable alternatives have become imperative. Phytoremediation is one such sustainable bioremediation strategy that ameliorates the arsenic-contaminated areas efficiently using green algae and higher plants (Hassan et al. 2022). The phytoremediation of heavy metals in crop-growing areas is mainly facilitated through phytoextraction, phytostabilization, phytovolatilization and rhizo-filtration processes (Parmar and Singh 2015). Earlier research revealed that potential plant species could be chosen for phytoremediation (Table 24.3).

Many species of Chlamydomonas, Synechocysis and Chlorella were noted to be tolerant against high arsenic concentrations (Wang et al. 2015). Multiple mechanisms were reported for the detoxification of arsenic by microalgae. The prominent mechanisms that attribute to the role of micro-algae in the detoxification of arsenic were hyperaccumulation of arsenic through phosphate channels, adsorption on their cell wall, and methylation of toxic inorganic arsenic species into less toxic organic form and vacuolar sequestration (Briat 2010). Huq et al. (2020) observed that bioaccumulation of arsenic in micro-algae increased with the increase in arsenic contamination and time of exposure.

Recent studies discovered the exceptional ability of *Pteris vittata,* a predominant fern of both tropical and sub-tropical regions, in reclamation of arsenic contaminated soils and groundwater through hyperaccumulation of high concentrations of arsenic

**Table 24.3** Phytoremediation of arsenic

| Plant | Arsenic concentration accumulated | References |
|---|---|---|
| *Helianthus annus* | 84.85 mg/kg | Sahito et al. (2021) |
| *Azolla caroliniana* | 284 mg/kg | Rahman and Hasegawa, (2011) |
| *Portulaca oleracea* | As (154 mg/kg and 193 mg/kg at site-I and site-II) | Negi (2018) |
| *Leucaena esculenta* | 84.85 mg/kg | Sahito et al. (2021) |
| *Hydrilla verticillata* | 37 mg/kg | Talukdar (2013) |
| *Eichhornia crassipes* | 67.9 mg/kg | Islam et al. (2013) |
| *Echinochola crusgalli* | 27 mg/kg | Islam et al. (2013) |

(Derakhshan Nejad et al. 2017). Besides, higher plants like *Ecalyptus globules* were also observed to accumulate 8.19 and 8.91 mg of arsenic when exposed to 100 and 200 μg As/mL arsenic concentrations, respectively (Reboredo et al. 2021).

In a wetland ecosystem many plants like *Eichhornia crassipes, Azolla pinnata, Lemna minor* and some arsenic tolerant free-floating aquatic plants viz*., Alternanthera* spp., *Vetiveria* spp. are recently being recognized for their role in remediating arsenic contamination. However, the bioaccumulation capability of arsenic varies from one species to another. In comparison, the arsenic recovery efficiency of water hyacinth was reported to be higher than duckweed (Alvarado et al. 2008). Similarly, from a study, it was evident that algae viz*., Chlorodesmis* sp. and *Cladophora* sp. were more tolerant to arsenic toxicity than water hyacinth. Further, these algal species were reported to bring down the arsenic concentrations from 6 mg/L to 0.1 mg/L of ground water (Jasrotia et al. 2017).

### *24.5.3 Irrigation Management*

Water used for irrigation is the most prominent source of arsenic contamination in crops. Artificial application of water to supplement crop water needs is essential to achieve optimum crop productivity (Kumari et al. 2017a, b). However, the indiscriminate use of arsenic-contaminated ground water by farmers is mainly aggravating the arsenic bioaccumulation in the crops (Bhattacharya et al. 2010). According to an estimate, a 28% increase in arsenic content in irrigation water resulted in a 6% increase in arsenic content in rice grains (Mukherjee et al. 2019). Rice being the high requiring crop arsenic contamination is highly susceptible to arsenic poisoning. In traditional rice farming, water is stagnated during the major period of crop growth (Midya et al. 2021). Curtailed dependence on irrigation water in arsenic-contaminated areas could be a sound strategy to reduce the uptake and bioavailability of arsenic in the human food chain (Chung et al. 2014). Basu et al. (2015) examined three regimes of deficit irrigation, viz., intermittent ponding, saturation and aerobic conditions in contrast to continuous ponding and found that deficit irrigation can be resourcefully chosen to minimize the arsenic content in rice grain by 9 to 21%. However, this strategy does not fit in areas where a reduced supply of irrigation water has an adverse impact on crop growth and productivity. In this context, proper identification of the right source, right time, and right method to schedule irrigation water has become imperative to tackle this problem efficiently.

### *24.5.4 Fertilizer Management*

Recent studies indicated that the concentration of phosphorus, sulfur and iron plays a vital role in the mobility and gathering of arsenic in plants (Hasanuzzaman et al. 2015). Several studies reported that the increase in the concentration of phosphorus in the soil solution led to a significant decrease in arsenic uptake and this role of phosphorus was mainly attributed to the competition with arsenate for the same transporter protein (Strawn 2018). Similarly, sulfur helps in the formation of iron plaques in the rhizosphere which entails a decrease in soil arsenic concentration (Yang et al. 2020). Besides, sulfhydryl groups of glutathione and phytochelatins stimulated by the exposure of plants to an arsenic-rich environment subsequently helps in the detoxification of arsenic species by translocating them into the vacuoles (Kumar et al. 2020). In a recent study, the application of silicon in rice was found to reduce arsenic bioaccumulation into the rice grain by 16% and straw by 78%, respectively. Since the uptake of arsenite and silicon in rice usually occurs through a common transporter viz., nodulin 26 therefore, silicon competes with arsenic species during uptake and translocation (Ma et al. 2008).

### *24.5.5 Biochar*

Biochar is a carbon-rich material formed by pyrolysis of various feedstocks viz., rice husk, biosolids, animal products, and several solid wastes (Wang et al. 2020). The biochar application in the soil was reported to minimize the mobility and bioavailability of arsenic to the plants (Li et al. 2018). This was mainly ascribed to the physical property and structural complexity of biochar (Ayaz et al. 2022). Studies indicated that biochar produced at low temperatures was reported to be more stable as compared to biochar produced at high temperatures above 500 °C, respectively (Askeland et al. 2019). The mechanism of arsenic remediation by the application of biochar was ascribed to phytostabilization and transformation. The presence of a negative charge on the surface of biochar is responsible to trap arsenic species (Wu et al. 2020). Consequently, the application of biochar creates a favourable environment for rapid microbial multiplication in the soil resulting in arsenic species transformation from a highly toxic oxidation state to a less toxic oxidation state (Gregory et al. 2015).

## 24.6 Future Perspectives

The adverse impact of arsenic poisoning on soil, plants and humans in turn made it imperative to devise a sound strategy to mitigate the arsenic toxicity in biological systems. In recent times, due to increased awareness about arsenic chemistry and its possible routes to enter the food chain, many researchers were triggered to find out novel and efficient mitigation strategies and block their routes to enter the human food chain. Genetically, to impart resistance it is highly essential to have a clear understanding of the molecular base of hyperaccumulation in plants. However, this is highly questionable and unclear. Therefore, researchers should focus on developing resistant genotypes using advanced biotechnological tools. Further, the success of arsenic mitigation lies in the assessment of toxicity levels and the adoption of an appropriate strategy based on the prevailing conditions in that locality. This paves a need for location-specific research to devise the most appropriate arsenic mitigation strategies based on the surroundings. Advancement in nano-technology in recent times, the role of nano-particles in the remediation of arsenic toxicity should be explored and help to devise novel strategies to tolerate arsenic toxicity.

## 24.7 Conclusion

The chemical form of arsenic and soil properties are the main factors that influence the severity of arsenic toxicity. The waterlogged, clayey soils with high soil pH, associated with low soil organic carbon are responsible to aggravate the arsenic poisoning in plants. Consequently, when the arsenic concentration exceeds the safe limits as prescribed by WHO, both in soil and irrigation water were observed to impair seed germination, growth retardation and yield reduction. At cellular levels, increased arsenic concentration stimulates the production of reactive oxygen species (ROS) that further reduces the cell membrane stability through lipid peroxidation. Among various strategies, employing microbes to immobilize the toxic arsenic species by hyperaccumulation is found to be the most effective strategy. However, the resurgence of accumulated arsenic back into the soil environment after some time is one of the main backdrop of microbial bioremediation, hence phytoremediation is getting popularized. On the other hand, arsenic toxicity is mainly caused by the relative concentration of arsenite ($As^{III}$) compared to other species. Hence, reducing the dependence of arsenic polluted ground water for irrigation and adopting aerobic rice could be the most appropriate way to reduce the risk of exposure to arsenic toxicity. Moreover, the adoption of porous soil amendments like Biochar ascribed to increase sorption energies and helps to arrest the free movement of arsenic in the soil thus reducing arsenic toxicity. This chapter concludes that a detailed multidimensional study is essential to provide sustainable ways to mitigate arsenic polluted soil and crop that consequently, helps to minimize arsenic bioaccumulation in the economically sink of the crop.

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# Correction to: Global Arsenic Hazard

**Nabeel Khan Niazi, Irshad Bibi, and Tariq Aftab**

## Correction to:
## N. K. Niazi et al. (eds.), *Global Arsenic Hazard*, Environmental Science and Engineering, https://doi.org/10.1007/978-3-031-16360-9

The original version of the book was inadvertently published with the following corrections:

Chapter 14 The affiliation of authors "S. K. Pathak and S. Srivastava" has been changed as "Plant Stress Biology Laboratory, Institute of Environment & Sustainable Development, Banaras Hindu University, Varanasi 221005, India"

Chapter 20 The correction at section 20.4 first Para has been updated with given corrections.

The correction chapters and the book has been updated with the changes.

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