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Heavy metal toxicity, sources, and remediation techniques for contaminated water and soil



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ABSTRACT

Arsenic is a highly toxic metalloid that is extensively distributed in soils and water bodies, resulting in a variety of toxicity mechanisms and harmful effects on humans and environmental health. This paper comprehensively reviews the technological development in arsenic (As) removal from wastewater and contaminated soil, and provides insights into the challenges in effective arsenic removal from the environmental compartments. The arsenic removal efficiency of the available technologies is also discussed in terms of their principle of operation, efficiency, advantages, and shortcomings. Many of the existing technologies are not found economically feasible for the regions of interest or are not applicable at the community level. Some of the techniques are often responsible for producing toxic by-products. Overall, the adsorption technique demonstrated high efficiency of almost 100% and a maximum of 95% in removing arsenic from water and soil, respectively. Novel methods such as the application of nanotechnology and polymeric ligand exchangers have also been gaining traction but also seem to possess limitations similar to conventional and non-conventional techniques.

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1. Introduction

Heavy metals are generally known as naturally occurring metals possessing elemental densities more than 5 g cm^{-3} and atomic numbers more than 20 (Ali and Khan, 2018). Rapid industrialization and unplanned urbanization have introduced heavy metals into the environment through improper dumping of industrial wastes directly on land and into water bodies (Dixit et al., 2015). As a result, environmental contamination by heavy metals has emerged as a major concern (Hashem et al., 2017) and is associated with environmental pollution and bio-toxicity issues attributed to their ability

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to inhibit biodegradation activities (Masindi and Muedi, 2018). One of the heavy metals is Arsenic which are extensively dispersed across soils and water bodies. As the twentieth most plentiful element on Earth, arsenic is present as either an oxide, sulphides, or metal salt (Nicomel et al., 2015). It is often detected at very low concentrations in virtually all environments. Arsenic enters into the environment through natural processes, for example, weathering of rocks, volcanic eruptions, biological activities, and geochemical reactions, where soil leaching and erosion alone mobilize 2380×10^8 g and 612×10^8 g arsenic per year respectively (Siddiqui and Chaudhry, 2017). The extent of its mobility is determined by its parent mineral form, mobilization processes, and oxidation state. Arsenic can exist as four species in the environment: Arsenite (As^{3+}), arsenate (As^{5+}), arsenic (As), and arsine (As^{-3}). The inorganic arsenate and Arsenite are the utmost prevalent species and are more commonly found in water (Pous et al., 2015). While both species can exist in oxidized environments because of the transformations of slow redox, arsenic predominantly exists as Arsenite in anoxic waters and as arsenate in toxic environments (Nicomel et al., 2016a). Arsenic may also exist in different organic forms as methylated metabolites, namely, trimethylarsine oxide, dimethylarsinic acid, and monomethylarsonic acid.

Arsenic has adverse impacts on the health of various lifeforms (Singh et al., 2015). It has been ranked as the highest priority pollutant in the environment and has also been identified as a group 1 carcinogenic substance by the World Health Organization (WHO) (Nicomel et al., 2015). Arsenic has widespread commercial, agricultural, and medicinal uses (World Health Organization, 2011). Therefore, while most of the issues caused by arsenic are a consequence of the natural mobilization of the metal, anthropogenic activities have been attributed to causing further harm to environmental health. Commercially, arsenic is utilized in the manufacture of transistors, semiconductors, paper, dyes, pigments, wood, and glass, and in hide tanning processes and pharmaceuticals (Nidheesh and Singh, 2017a,b). Arsenic-based compounds are also used in pesticides, herbicides, fungicides, algicides, crop desiccants, and as additives to livestock feed in agriculture (Singh et al., 2015). In veterinary medicine, arsenic has been used in the elimination of tapeworms in dairy animals, and in the treatment of parasitic infections, including filariasis in dogs and blackhead in poultry (Tchounwou et al., 2012). In public health, the contribution of arsenic-based drugs includes the treatment of tropical diseases as well as serving as an anticancer agent. Therefore, the extensive industrial applications of arsenic, as well as its ubiquity in the environment, also expose populations to its adverse effects.

Many epidemiological researches have confirmed a strong link between arsenic acquaintance and increased incidences of both systemic and carcinogenic health effects on people who are chronically exposed to inorganic arsenic through drinking water at concentrations above $50 \mu\text{g/L}$ (Singh et al., 2015). People residing in areas vulnerable to arsenic contamination have been reported to be afflicted with hearing loss, cardiovascular diseases, diabetes, developmental anomalies, neurobehavioural and neurologic disorders, reproductive and pregnancy abnormalities, diseases of respiratory and gastrointestinal systems, haematologic disorders (leukopenia, anaemia, and eosinophilia), carcinoma, and cancers (Mohammed Abdul et al., 2015; Chakraborti et al., 2017; Rahman et al., 2018; Shahid et al., 2018a,b). The analysis of the toxic impacts of arsenic is challenging as its toxicity is heavily dependent on its oxidation solubility and state, and other factors such as exposure dose, biological species, duration and frequency, and the demographic, genetic, and nutritional factors of the people affected. However, it is established that inorganic arsenic species are more harmful than organic ones, where toxicity increases in the sequence of $\text{DMA} < \text{MMA} < \text{arsenate} < \text{Arsenite}$. In addition, As (III) is found to be more mobile, soluble, genotoxic, and cytotoxic, making it more detrimental to human health by increasing risks of developing arsenic-induced diseases (Singh et al., 2015).

Exposure to arsenic can be caused through ingestion (oral route), the parenteral route, inhalation, and skin contact to some point. Even though exposure from water, air, and soil is generally small, it may become an important environmental health issue in arsenic contamination. The concentration of arsenic may vary across different environments. In isolated locations away from human activities, arsenic concentrations in the air may vary from $1\text{--}3 \text{ ng/m}^3$ to concentrations from $20\text{--}100 \text{ ng/m}^3$ in urban areas (Tchounwou et al., 2012). Unless the sources occur near mining sites and mineral deposits, the concentration of arsenic in water is usually less than $10 \mu\text{g/L}$, which is the maximum level of contaminant approved by the WHO (World Health Organization, 2011). Exposure through drinking water is the primary contributor of human arsenic toxicity, and there have been reports of harmful arsenic concentrations in drinking water sources in Chile, the USA, Bangladesh, China, Taiwan, Argentina, Mexico, Canada, Poland, New Zealand, Hungary, India, and Japan, in areas where groundwater is the main source of drinking water (Mondal et al., 2013). Arsenic contamination in groundwater is caused by geothermal activity, burning of fossil fuels, mining, mineral dissolution (such as pyrite oxidation), use of arsenic-based compounds in wood and agriculture preservatives, and reductive dissolution and desorption (Smedley and Kinniburgh, 2013). Where arsenic contamination of drinking water is not significant, human arsenic toxicity occurs through food harvested in contaminated soils or soils irrigated with arsenic-contaminated water (Singh et al., 2015). Normally, arsenic in soil ranges from $1\text{--}40 \text{ mg/kg}$, but the use of arsenic compounds in farming or disposal of arsenic-containing waste may generate higher concentrations (Tchounwou et al., 2012).

The health problems caused by exposure to arsenic-contaminated water and soil (and consequently food) have led arsenic contamination to be a major concern in public health. Thus, the elimination of arsenic from contaminated soil and water has been a persistent subject of research interest. Many kinds of technologies have been advanced for arsenic removal from soil and water, and the performance of these technologies is affected by the physical and chemical properties of the arsenic compounds in the environment. Arsenic removal technologies from water utilize physicochemical techniques such as adsorption, membrane technologies, oxidation, ion exchange, and coagulation and flocculation (Mohanty, 2017; Ghosh Nath et al., 2019; Sarkar and Paul, 2016; Ungureanu et al., 2015; Nicomel et al.,

2015; Singh et al., 2015; Nidheesh and Singh, 2017a,b). In recent years, however, there has been a growing focus on novel methods like adsorption via nano-adsorbents and biosorbents, and remediation by microbes (Amen et al., 2020; Hayat et al., 2017; Lata and Samadder, 2016; Siddiqui and Chaudhry, 2017; Yang et al., 2017). On the other hand, the primary method for the removal of arsenic from soil is bioremediation (da Silva et al., 2018; Prum et al., 2018; Ma et al., 2018). The potential for extraction and recovery using chemicals has also been explored (Nguyen Van et al., 2017; Choi et al., 2016). Considering how issues of arsenic contamination and toxicity are particularly pronounced in developing nations and rural communities where energy and other resources are limited, an assessment of available treatment options is needed for the selection of the most appropriate technology for a given environmental compartment and the socio-economic context of the contaminated region. The limitations of some of the existing technologies in bringing the arsenic level below the maximum contaminant level (MCL) due to the complex nature of arsenic species' interactions in various environments also need to be addressed.

In recent years, many effective and novel arsenic removal technologies have emerged. However, the availability of information on the treatment performance of current state-of-art technologies for arsenic removal is severely limited. Thus, by first comprehensively elucidating on the sources, distribution, toxicity mechanism, and the chemistry and characterization of arsenic and its impact on human and environmental health, this paper aims to critically review the technological development that has occurred over the last few years in arsenic removal from wastewater and contaminated soil. Then, it provides insights into the challenges involved in the effective removal of arsenic from the environmental compartments with a focus on defining areas for improvement based on past and present practice. This paper then concludes by providing future direction for research and advancement in the processes for enhanced arsenic removal from the environment. With arsenic toxicity causing widespread morbidities across various nations, this paper will disseminate essential information and provide perspectives on future directions to relevant stakeholders working in the field of public and environmental health.

2. Source and distribution of arsenic in water

2.1. Sources of arsenic

Arsenic is an odourless and almost tasteless toxic metallic element found in the environment. Arsenic has four common valences including As (0), As (III), As (V) and it has three common forms including inorganic salt, organic salt, and gaseous form (Timalsina et al., 2021a,b). In general, arsenic exists in the form of two oxidation states, namely arsenate and Arsenite, both in the pH range of 6–9 (Shankar et al., 2014). The occurrence of arsenic in water under the ground results from many factors, including anthropogenic activity, geochemical reactions, and biological action. The man-made release of arsenic through various industrial and agricultural activities could also contaminate the soil and drinking water (Singh et al., 2021).

The sources of arsenic are classified as geogenic, biogenic, and anthropogenic. The major anthropogenic sources for arsenic contamination in groundwater are mining, use of arsenic herbicides, fossil fuels, fungicides and pesticides, wood preservatives, crop dedication, and animal arsenic additives. Geogenic sources include volcanic eruption and weathering of minerals and rocks. It has been reported that arsenic in arsenic-rich minerals and rocks is dissolved and dissolution under an oxygenated and reducing condition which then primarily contaminates the groundwater and soil (Ahmad and Bhattacharya, 2019). Every year, 12,000 tons of arsenic is exposed to the environment or is dissolved into it where an approximate 3 billion metric tons are produced by the European Union's 27-member states (Pacyna and Pacyna, 2001). In order to determine the presence of arsenic and arsenic species in water, a variety of chemical approaches, ranging from classical to modern analytical techniques, are applied. The contemporary methods include atomic spectrometry, ICP techniques, nuclear techniques and electrochemistry (Shahid et al., 2018a).

2.2. Global scenario of arsenic contamination in water

Arsenic exists either as a dissolved or particulate form in water. Traditionally, the mobilization of arsenic into groundwater systems can affect a huge number of people. In different areas of the globe, the levels of arsenic in groundwater systems vary according to climate and geology. When groundwater is contaminated, the contamination tends to be localized and arsenic levels can be measured in the range of dozens of mg/L. Thus, a better understanding of global groundwater arsenic concentrations would aid in alleviating the problems with arsenic. Recently, a few new areas of arsenic-contaminated groundwater aquifers have been discovered around the world (Shakoor et al., 2018). Before the year 2000, there were four sites with significant arsenic groundwater contamination in Asia, including Bangladesh, West Bengal, China, and India. Since 2000, arsenic-polluted groundwater has been discovered in several additional Asian countries, namely Mongolia, Nepal, Cambodia, Myanmar, Afghanistan, Korea, Pakistan, and Western Iran (Rathi et al., 2021; Timalsina et al., 2021a,b).

Several countries have confirmed the arsenic in their groundwater, and it has been stated that arsenic is found in the water in more than 105 countries around the world (Chakraborti et al., 2018). There are over 200 million people exposed to an arsenic concentration that is greater than the threshold considered safe by the WHO. Arsenic is considered to be one of the highly toxic elements on the planet. Conducting toxicology research on arsenic is daunting because of

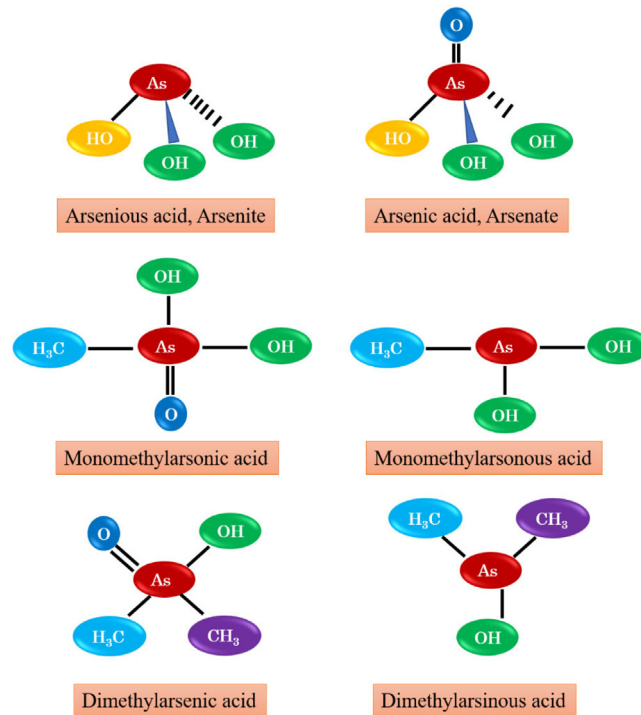


Fig. 1. Structure of some arsenic compounds.

its state of oxidation and solubility. There are additional factors such as extrinsic and intrinsic aspects that can further affect toxicity. Several investigations have found that arsenic exposure varies according to dose, frequency, and duration, as well as genetic and nutritional susceptibility. Inorganic arsenic has been the major source of most toxic exposures to humans. In terms of toxicity, inorganic As (III) is approximately 2 to 10 times more toxic than As (V) (Hong et al., 2014). Arsenic binds to sulfhydryl or thiol groups on proteins and impairs about 200 enzymes. This is likely why arsenic has such broad-ranging effects on different organs.

2.3. Chemistry and characteristics of arsenic

Arsenic is a metallic element which has an atomic mass of 74.92 amu, an atomic number of 33, and a density of 5.72 g/cm³ (Nidheesh and Singh, 2017a,b). Arsenic presents mostly in the earth's crust, soil, sediment, and water. About 1.5 mg/L of this metalloid is found in the earth, 3 ng/m³ in the air, and 10 mg/L in fresh water (Rieuwert, 2017). Arsenic exists in four oxidation states including As (V), As (0), As (-III), and As (III), but the two most prevalent in nature are As (V) and As (-III) (World Health Organization, 2011). Both As (V) and As (-III) are soluble in water but As (V) has higher solubility and toxicity than As (-III). As (V) is a low tricotric acid which tends to more precipitate from the solution by adding metal cations compared to As (-III). As (V) usually precipitates in Mn (AsO₄)m·H₂O form. Precipitation stability depends on the cation used in the precipitation and the conditions under which it is kept. Arsenic's mobility depends on the level of arsenic and other species, the pH, and Eh of the environment (Nazari et al., 2017). Arsenic pollution is a big concern because of its dynamic topology across a wide pH and Eh range. Arsenic is found as the fifty-third in the crust of the earth, the twelfth in humans, and the fourteenth in seawater (Nicomel et al., 2016a). In water, the Eh and pH are primarily responsible for arsenic evolution. Fig. 1 depicts the structure of some arsenic compounds and Table 1 tabulates the characteristics of elemental arsenic.

3. Impact of arsenic on human and environmental health

3.1. Impact of arsenic on human health

Arsenic is a prevalent environmental element and toxic to human health. Its elemental toxicity has been a major concern from both human and environmental health perspectives (Chatterjee et al., 2017). Arsenic in the inorganic form is carcinogenic and globally one of the remarkable chemical contaminants found in drinking water. Arsenic compounds

Table 1
The characteristics of elemental arsenic (Nazari et al., 2017).

Properties	Unit	Value
Atomic number	–	33
Density	g/cm ³	5.72
Atomic weight	g	74.92
Melting point (@3.7 MPa)	°C	817
Heat of fusion	kJ/kg	370.3
Boiling point (@0.1 MPa)	°C	613
Heat of vaporization	kJ/kg	426.77
Linear coefficient of thermal expansion	1/K	5.6×10^{-6}
Specific heat (@25 °C)	J/kg K	328
Electrical resistivity (@0 °C)	Ω cm	26×10^{-6}

present in water are inorganic and have increased toxicity and pose serious threats to human health (Shankar and Shanker, 2014). On the other hand, arsenic compounds in seafood are organic and have a lesser effect on human health. In 2010, when arsenic impacts on humans were evaluated, it was deduced by the Joint WHO/FAO Expert Committee on Food Additives (JECFA) that confirmation of adverse health effects was observed in particular regions of the world where the drinking water has inorganic arsenic concentrations exceeding 50–100 $\mu\text{g/L}$ (Kippler et al., 2016). Areas of 10–50 $\mu\text{g/L}$ arsenic concentration, demonstrated the possibility of unpleasant health effects but the incidence was lower and difficult to detect in epidemiological studies (WHO, 2018). Arsenic has also been classified by WHO as one of the 10 chemicals that are of public health concern because a significant number of individuals worldwide suffer from exposure to high arsenic concentrations, 100 $\mu\text{g/L}$ or higher which is more than the standard (WHO, 2018). The prime public health challenge is to limit arsenic exposure to these people by allowing them access to arsenic-free drinking water.

3.1.1. Arsenic exposure and cancer

Epidemiological studies and reports by the Environmental Protection Agency in the United States have illustrated the association of an escalated level of risk of skin, bladder, lung, kidney, and liver cancer due to the ingestion of drinking water containing arsenic. In addition, studies have also shown that drinking water containing arsenic could possibly have a prolonged dormancy period compared to most carcinogens. Evidence showed increased cases of cancers in the lung, kidney, and bladder even 40 years after being exposed to high arsenic concentration (Smith et al., 2018).

3.1.1.1 Lung cancer Arsenic was known to be the first chemical to have shown carcinogenic properties in 1879 with increased lung cancer rates among the miners who were reported to have inhaled this chemical contaminant. Generally, lung cancer has been suggested as the most frequent cause of arsenic related mortality by most studies (Ferdosi et al., 2016). Studies have also established that consumption of drinking water exceeding 100 $\mu\text{g/L}$ of arsenic is correlated with a high risk of lung cancer (Rahman et al., 2018). In addition, regardless of the exposure route, i.e. inhaling or consuming, the risk of lung cancer is strongly associated with prolonged arsenic exposure. Studies have been conducted using mouse models to observe the effect of arsenic compounds on lung cancer. Even inhaling reduced doses of about 0.05–0.07 mg/m^3 of arsenic was reported to cause lung cancer (Briffa et al., 2020). Other studies performed with animal utero-exposure to arsenic have demonstrated arsenic as an absolute transplacental carcinogen. When oral arsenic treatment was introduced to pregnant mice, the lung tissue of the offspring were diagnosed with dose-dependent tumours which resulted in malignant tumours in the further stages of the lifecycle, even in relatively low doses (Wei et al., 2019).

3.1.1.2 Bladder and kidney cancer Besides affecting the lungs, the carcinogenic effect of arsenic is also evident in other organs such as the bladder when exposed to drinking water with an arsenic concentration $>600 \mu\text{g/L}$ for an extended period, possibly longer than 40 years (Rahman et al., 2018). Fernández et al. (2020) investigated a comparative study of patients suffering from bladder cancer in both arsenic and non-arsenic exposed regions. The investigation demonstrated the presence of a higher proportion of progressive and top-grade tumours among patients from arsenic exposed sites. A multivariate analysis also established that the single significant predictor of an increased proportion of advanced tumours was arsenic exposure, with an adjusted odds ratio of 5.10 (95% CI: 2.03–12.77). Convincing evidence has also been provided by epidemiological studies in forming a correlation between exposure to environmental arsenic and an escalated risk of carcinoma in renal cells. Krajewski et al. (2021) observed a positive connection between exposure to arsenic and three types of cancers. Kidney cancer showed association with an adjusted odds ratio of 1.69 (95% CI: 1.37–2.09), colorectal cancer [1.64 (95% CI: 1.33–2.01)] and bladder cancer [1.89 (95% CI: 1.53–2.35)].

3.1.1.3 Skin cancer The common route of arsenic exposure in humans is through dermal contact followed by distribution in the body. Chronic arsenic exposure leads to some well-known skin issues like hyperpigmentation and hyperkeratosis. However, with an increased concentration of arsenic and a longer exposure period, the relative risk of skin cancer or carcinoma in the basal cells is inevitable (Yadav et al., 2021). Matthews et al. (2019) performed a systematic review with the available epidemiological studies to investigate how the exposure of trace elements like arsenic, zinc, chromium, selenium, and others are associated with the risk of non-melanoma (keratinocyte carcinoma) and melanoma skin cancer in humans. A review of the available literature on arsenic exposure suggests an increased risk of non-melanoma skin

cancer. There are too few studies exploring the connection between arsenic exposure and melanoma skin cancer to draw any conclusions.

3.1.2 Non-carcinogenic effects of arsenic

Besides the carcinogenic effects of arsenic, there are also reports of arsenic showing some non-carcinogenic symptoms such as irritation of the mucous and dermatitis membrane. In addition, other important effects reported include skin lesions, neurotoxicity, cardiovascular issues, respiratory diseases, and hormonal effects (Zhang et al., 2019). Certain studies have illustrated the effect of arsenic on animal models such as mice. Arsenic has an increased effect on some vital organs and reduces the resistance of mice to particular viral infections.

3.1.2.1 Neurobehavioral effects Acute arsenic exposure has shown significant brain impairment in infants, particularly affecting the peripheral sensory fibres compared to motor fibres (Mochizuki, 2019). However, none, or only minimal, neurobehavioral effects on adults were reported due to arsenic exposure. Silva-Adaya et al. (2020) discussed the relationship between oral doses of arsenic and its neurotoxic effects to understand the degree of impairment on the central nervous system. Reduced memory, confusions, mood effects, and hallucinations were some of the symptoms depending on mild or severe doses. Also, peripheral neuropathy development showed a strong association with prolonged inorganic arsenic exposure. Mochizuki (2019) evaluated the arsenic effects on human health based solely on the participant's medical history. This does not justify the results thoroughly as other essential factors including arsenic quantity, the volume of water consumption per individual, and the exposure route are interconnected and any of these may significantly influence the findings. In addition, the observed effects of arsenic causing neurotoxic symptoms are mostly very general, therefore, connecting them to arsenic exposure alone cannot be considered a robust claim in the absence of a multifaceted process.

3.1.2.2 Respiratory diseases The carcinogenic effect of arsenic is well known and has been studied for many years now. Recent studies have also established the relationship between arsenic exposure greater than 100 µg/L and its non-cancerous respiratory effects, which include some respiratory symptoms like severe infections in the respiratory tract, non-cancerous respiratory illness, and lung disease leading to a worsening of the lung function (Powers et al., 2019). Arsenic exposure was also observed to be linked with reduced forced expiratory volume and vital capacity in a meta-analysis study which could potentially be associated with absolute lung disease (Sanchez et al., 2018). Powers et al. (2019) also identified the correlation of low to average arsenic level with increased emphysema (self-reported), obstruction of airflow, spirometry pattern, and pausing for breath while walking. However, they also reported the effect of smoking and its toxicity to be a possible influencing factor masking the effect of arsenic, creating a loophole in their study.

3.1.2.3 Effect on hormonal and the reproductive system The toxic effect of arsenic on hormonal and reproductive development has been suggested by many epidemiological studies. Drinking water containing arsenic can be reportedly responsible to cause some dysfunction in the male reproductive system such as reducing the testis weight, sperm motility and viability, and the level of gonadotropins and testosterone (Renu et al., 2018). Zubair et al. (2017) reported changes in the follicle-stimulating hormone, luteinizing hormone, and testosterone level with a huge declination in germ cell numbers. To understand the reproductive and hormonal effect of arsenic, an investigation was also conducted using normal and diabetic rat models (Souza et al., 2019). When the alterations in the rats were examined after arsenic exposure, normal rats were shown to experience a reduced concentration of testosterone, and for diabetic rats, the reduction worsened. Additionally, in both types of rats, there was also reduced spermatozoon and sperm production. The bioaccumulation of arsenic in the rat models is thought to be responsible for causing an imbalance in the enzymatic activity of both groups of rats, with increased alterations in the diabetic one. The concluding remark stated that the combined consequence of diabetes and arsenic exposure contributed to an abnormal morphology in the animal models.

3.2 Impact of arsenic on environmental health

In most South Asian countries, arsenic toxicity is alarming and can be disastrous to environmental health. A huge quantity of waste containing arsenic is produced through most treatment methods which require reuse or safe disposal into the environment. Groundwater contamination by arsenic is an additional issue due to the possibility of arsenic entering the food chain through crops which might have come into contact with arsenic-contaminated water during irrigation. There is no doubt that arsenic-contaminated water, grasses, and rice plants are consumed by livestock daily. Additionally, organic waste produced by these livestock populations is an essential biomarker that pollutes the environment. However, for livestock, there are still few reports of clinical arsenic contamination though the crops they consume are grown with the same contaminated water used for drinking (Mandal, 2017). Plants exposed to arsenic also experience adverse effects which influence, through process inhibition, their ability to photosynthesize, biomass accumulation, and growth and development.

Arsenic is also responsible for interfering with a variety of metabolic processes in plants by directly acting as a competitive inhibitor or by hindering the activity of other key enzymes involved in metabolism. Certain processes like germination, growth of shoots/root, seedling development, and its earlier stages are also slowed down or inhibited due to the effect of arsenic in the plant. Interestingly, plants have also developed methods like synthesizing arsenic binding

proteins and accumulating compatible solutes to deal with arsenic's toxic effects (Abbas et al., 2018). Increased arsenic exposure is also a prime concern for the freshwater ecosystem. Some freshwater invertebrates and algae typically act as the producer or the base of aquatic food webs. Globally, the solubility of arsenic has reached beyond the acceptable limit of 0.010 mg/L due to the unrestrained use of arsenic in pesticides, mining activities, and industrial operations. The constant arsenic exposure to the freshwater environment, including various kinds of algae, fish, and aquatic organisms, is responsible for bioaccumulation in the vital organs of these organisms. This results in consequences such as prolonged and acute toxicity, hyperglycaemia, altered enzymatic functions and reduced immunity (Kumari et al., 2017). Significant reduction in the algae composition and herbivores due to arsenic toxicity is a major concern to the stability and health of the ecosystem (Chen et al., 2015). Any change due to arsenic contamination in these organisms can bring huge variation in the function and structure of the freshwater ecosystem.

Arsenic assimilation by organisms at each trophic level acts as a pathway for arsenic to be transferred along the food chain and eventually through food webs. Air is a significant source of arsenic where the presence of arsenic is in the mixed form of arsenate and Arsenite. The existence of arsenic in the air is mainly due to the increasing number of vehicle and industrial emissions which unfortunately poses a serious threat to the environment as air pollution. It was confirmed by an earlier investigation that a small constituent of air in the industrial, suburban and urban areas contain a methylated form of arsenic (Chung et al., 2014). The presence of this arsenic component is also responsible for arsenic exposure to humans in low concentrations. A reduced arsenic concentration is generally available in the air within a range of 0.4–30 ng/m³ and is responsible for exposing arsenic to living organisms. However, each day the approximate concentration of arsenic being inhaled by an individual in a polluted area is 40–90 ng (Chung et al., 2014). This draws a connection between arsenic's impact on environmental and human health. The presence of arsenic in the environment will affect human health and other living organisms with no doubt if the arsenic concentration in the environment is not limited in the first place.

4 Techniques for removing arsenic from contaminated water and soil

4.1 Arsenic removal techniques from wastewater

Water pollution from a plethora of domestic and industrial activities not only exacerbates water scarcity but threatens human health, particularly due to carcinogenic effects (after consumption). Organic and inorganic substances, microorganisms, and total solids (TS) can be found in wastewater (Ahmed et al., 2021a). Therefore, the development of both novel and improvised technologies for treating wastewater is a vital topic to address and have attracted great interest. This section reports on recent methodologies and techniques to remove arsenic content from wastewater.

4.1.1 Adsorption

Adsorption (Fig. 2), a phenomenon depending on the availability of active sites, is one of the most popular methodologies to remove arsenic and associated heavy metals from wastewater. Because of the extremely specific surface area of the adsorbents, adsorption is one of the most effective wastewater treatment techniques (Ahmed et al., 2021b). Being cost-effective and having design flexibility and ease of application, researchers have developed various innovative methodological changes to using adsorbents to remove arsenic content from wastewater (Nguyen et al., 2019). For example, using smelting wastes requires relatively few resources in the treatment of wastewater. Ligand exchange reactions leading to complexes are the main principle of adsorption. Consisting of various affinities between the adsorbent types and different forms of arsenic, removal efficiencies significantly vary and often require optimization. Depending on the pH and redox potential present in an aqueous solution, trivalent and pentavalent arsenic ions are the common forms. Methodologically, As (III) is oxidized before proceeding towards adsorption, enhancing the affinity between the adsorbent and the oxidized arsenic form, As (V), and increasing the removal efficiency of the contaminant (Lal et al., 2020). This section reviews the prominent techniques developed to treat arsenic in contaminated water via adsorption.

4.1.1.1 Electrosorption and electrochemical adsorption Electrosorption is popularly used for removing heavy metal ions, directing charged ions to migrate towards oppositely charged (carbon) electrode surfaces, operating under an electric field (Fan et al., 2016). The method adsorbs As (V) as inner-sphere complexes on ferrous oxides and manganese, present in wastewaters. The electrochemical redox reaction of Birnessite, investigated by Liu et al. demonstrated the adsorption of total As and trivalent arsenic ions under 1.2 V, subsequently decreasing Mn²⁺ concentration in wastewater (Liu et al., 2019). Importantly, prior to desorption and electrochemical adsorption (after multiple cycles), the Birnessite electrode ensured high arsenic removal. However, whether the iron oxide and manganese concentration in wastewater significantly affect the adsorption process could be further investigated. Provided that such research findings are yet being tested and analysed, electrochemical adsorption techniques using Birnessite electrodes require more investigation before mounting industrial-scale applications for wastewater treatment.

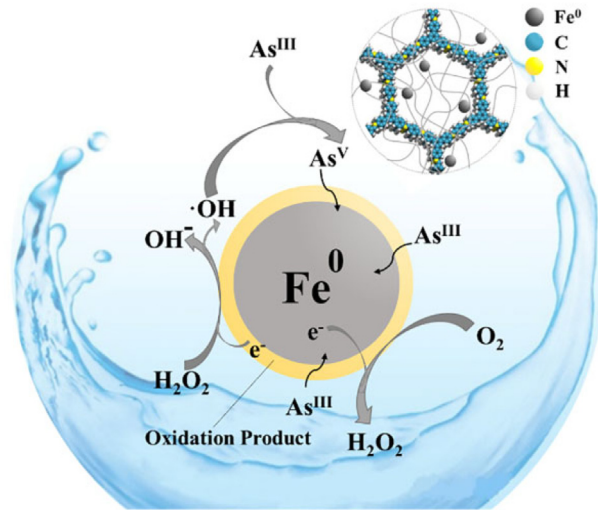


Fig. 2. Schematic of redox reactions on the surface of Fe⁰ during adsorption processes of As (III), reprinted with the permission of Elsevier from (Liu et al., 2020).

4.1.1.2 Adsorption mechanism using biochar/activated carbon A large number of sorbents have already been investigated for their ability to remove arsenic. Activated carbon, coal, red mud, fly ash, chicken feathers, kaolinite, montmorillonite, goethite, zeolites, activated alumina, titanium dioxide, iron hydroxide, zero-valent iron, chitosan, and cation-exchange resins are some of the materials that can be used in this process. Activated carbon, although expensive, is a common adsorbent used to treat water from heavy metal contaminants (Saleem et al., 2019), particularly because of its removal performance and availability. However, most of these adsorbents do not readily separate from the aqueous media after treatment. Biochar alone, such as rice husk, has a relatively low removal efficiency of heavy metal contaminants but when rice husk biochar is modified with synthesized hydrogel-biochar composite, it acts as an efficient sorbent for the sorption of arsenic, as demonstrated by Sanyang et al. (2016). The hydrogel sorbents are crosslinked polymeric networks with hydrophilic groups that remove toxic metal ions, working as complexing agents (El Halah et al., 2018). With high removal efficiency, improved hydrophilicity, favourable functional groups, preferable stability, and separation quality after treatment, rice husk biochar embedded into acrylamide-hydrogel (AAM-hydrogel) matrix was observed to have increased sorption capacity (Sanyang et al., 2016). However, when compared to ion imprinted polymers, better selectivity was observed for biochar adsorption technology in addition to high removal efficiency (Mafu et al., 2016).

4.1.2 Nanotechnology

With recent advancements and research in the field of nanotechnology and nanoparticles, various nano-inspired solutions have been studied and gradually used to remove arsenic and toxic metal ions from water. Over the past years, a plethora of carbonaceous nanomaterials has been investigated and developed to have favourable porosity, chemical inertness, and adsorption capacity (Lal et al., 2020), with remarkable modifiable physical-chemical properties and great adsorption quality. However, apart from being expensive, these nano-inspired adsorbents, including activated carbons, have limited recycle use. The research tried to diminish most disadvantages by developing carbon nanocomposites (loading carbon nanoparticles on natural mineral surfaces), by enhancing surface activity.

Unlike activated carbon, nano-dimensional graphene have oxygen-rich functional groups and a higher surface area encouraging homogeneous dispersion and interaction of the adsorbent and pollutants, via π - π interaction and static electricity (Wang et al., 2018). Pristine CNT has also demonstrated enhanced oxidation with NaOCl, HNO₃, or KMnO₄ (Wang et al., 2019). Additionally, Li et al. (2015) demonstrated that spray pyrolysis synthesized carbon nanospheres with a high surface area can efficiently absorb Se ions and As from water samples. Moreover, using waste onion sheathing, Venkateswarlu et al. (2016) modified graphene oxide with magnetite nanoparticles, removing trivalent arsenic ions from water. This method is an innovative approach that utilizes waste onions to aid the removal of toxic metal ions. More investigation on optimal pH, temperature, and cost-descending approach would make this methodology more promising. Further, Ge et al. utilized β -FeOOH nanorods with modified carbon foams (3D) to adsorb arsenic from contaminated water (Ge et al., 2017). Furthermore, zero-valent iron nanoparticles were also understood to capture arsenic ions, using porous organic frameworks (Liu et al., 2020). The techniques investigated by Liu et al. removed trivalent arsenic ions present in contaminated wastewater.

The solvothermal method employs morphological variances in carbon, (unique spherical, nanorod, and structures), inducing intrinsic adsorption qualities and nanostructures, that enhance the adsorption of arsenic in an aqueous solution. Islam et al. (2021) demonstrated carbon with nanorod morphology to have an 82% adsorption affinity for Arsenite at pH

3, along with better acid withstanding strength. Therefore, tailoring and exploring the structural morphology have been of recent interest to increase adsorption capacity (Tuzen et al., 2020; Yu et al., 2020; Yunus et al., 2020). Adsorption of pentavalent arsenic ions depended on the strength of the acidity and microstructure of the aqueous medium. However, since the investigation particularly focused on arsenic adsorption via structured carbon, further study on the efficiency to adsorb other heavy metals would be beneficial. Moreover, stable surface functionality and the ability to accomplish effective adsorption at low temperatures over a wide pH would be significant advancements.

Porous Fe₂O₃ nanocubes and graphene aerogel (PGA/PeFe₂O₃), investigated by Yu et al. (2019), has an adsorption equilibrium of 30 and 5 min, respectively. The rapid dispersion of arsenic is facilitated by the aerogel. Both adsorbents have a remarkable reusability, and an anti-interference shield over other adsorbents. The manganese oxides (recycled from spent batteries), consisting of alginate beads and being a bio-nano sorbent (CABs-MO), efficiently removed arsenic and cadmium from aqueous solutions. Although metal oxides can display good sorption ability, the particle size can affect the practicality of the mechanism. Thus, this approach requires more testing before mounting large-scale removal applications.

4.1.3 Bio-adsorbent

Biogenic and recycled materials, based on microbial, plant, animal polymers (by bacteria, fungi, algae, lignin), which are modified to have multi-surface functional groups, are better alternatives to remove contaminants (organic/inorganic) from wastewater as they are environmentally friendly and relatively cost-effective (Shim et al., 2019a,b; Mukherjee et al., 2016). Utilizing biosorption, heavy metal traces can be removed from a dilute aqueous medium. For example, fungi can act as an economic bio sorbent for arsenic removal. Another example includes the biofilm on Neem leaves by *Bacillus arsenicus*, along with MnFe₂O₄ composite, which scavenges trivalent and pentavalent arsenic ions (Podder and Majumder, 2016). Performing on film diffusion rather than intraparticle diffusion, the reaction reaches equilibrium by 30 °C, and is a comparatively eco-friendly arsenic removal technique (Podder and Majumder, 2016).

The innovative methods that use nanomaterial technology are still expensive (to manufacture and modify) and relatively difficult to separate after treatment compared to other adsorption mechanisms such as electro-sorption. Furthermore, efficient techniques to regenerate, reuse, and develop bio-based modifications are yet to be studied (Yang et al., 2019). More importantly, the biocompatibility of using carbon-based nanomaterials needs to be thoroughly understood, particularly to prevent unknown health hazards. Adsorption techniques can be reversible, depending on the methodology and adsorption substance. Therefore, combining adsorption with other techniques allows the removal of more than one type of metal ion. As demonstrated by Nguyen et al. modified iron-ore sludge together with horizontal-subsurface-flow wetland and *Phragmites australis*, adsorbs heavy metals, including arsenic from mining wastewater (Nguyen et al., 2019). However, apart from investigating the optimal environmental conditions needed to enhance best adsorption capacity, research is required to identify the potency of metal ions leaching from the adsorption surface, the concentration of metal ions present, and the hydraulic loading rate, including the type of wetland (surface-flow, horizontal/vertical subsurface flow). One of the most potent adsorption techniques, investigated by Qiu et al. (2019), is the simultaneous removal of As and Sb from mining wastewater via reusable granular TiO₂. This methodology not only removes two toxic metal ions but also enables the TiO₂ column to be reused again for adsorption, making the technique cost-effective and efficient compared to other adsorption removal methods. However, given the methodology is fairly new, further investigations on adsorption dynamics centred around various other reaction systems are necessary.

4.1.4 Coagulation/precipitation

Coagulation is another popular method to remove arsenic from wastewater (Anjum, 2017). In this method, the arsenic can be removed through the experiment of one bucket with filtration and two-bucket scheme as shown in Fig. 3. Limonite for instance donates iron, in situ, initiating a low iron supersaturation, precipitating arsenic and forming scorodite (Li et al., 2021d,c). Dissolved ferric Arsenite sulphate (tooeleite) induces 99% efficiency within a pH 1.8–4.5 range, with an initial As (III) concentration greater than 0.75 g/L at room temperature (Chai et al., 2016). The methodology significantly outperforms other arsenic-bearing slags, directly removing trivalent arsenic ions. The scorodite production is a good mechanism to remove arsenic, particularly via hydrometallurgical routes (Otgon et al., 2019; Ma et al., 2019). Another mechanism, a bioremediation route, involves the use of microbes, thermo-acidophilic Fe(II)-oxidizing archaea, to clean acid wastewater and enhance bio-crystallization (Zeng et al., 2021). Although other metal ions (such as Cu) or factors such as pH and temperature could inhibit/affect the microbial activity, environmental conditions need to be monitored strictly (Okibe et al., 2017).

4.1.5 Chemical precipitation

Chemical precipitation is an effective methodology to remove arsenic content from strong acidic wastewater, particularly in smelting industries. Sulphide ions from pyrite react with As (III) ions, forming a stable compound, As₂S₃ (Li et al., 2020a,b). As the reaction process oxidizes Fe(II) and As (III) to Fe(III) and As (V) respectively, crystalline scorodite is ultimately formed, which removes approximately 99.4% of the arsenic from copper smelting wastewaters (Li et al., 2021b). However, the efficiency of arsenic removal could vary depending on arsenic ion concentration in wastewater bodies. The reaction process operates for 12 h at low pH (acidic environment) under high temperature. Therefore, compared to other precipitation and adsorption techniques that remove arsenic, this process is comparatively time-consuming and requires a large amount of energy. Secondly, high pH would enhance the reaction's redox potential, inhibiting the precipitation

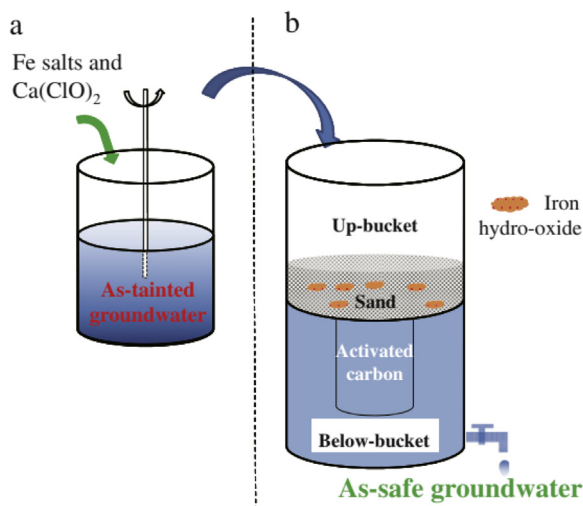


Fig. 3. Coagulation process of arsenic removal with (a) one-bucket test & filtration (b) with two-bucket scheme, reprinted with the permission of Elsevier from Cui et al. (2015).

of trivalent arsenic ions (Kim and Baek, 2019). For further arsenic removal from the system, deep purification for 3 h at 25 °C was performed (Li et al., 2021b). The treated water is usually recycled for smelting, so this method is considered to be cost-effective and environmentally friendly. However, with the energy needed for the reaction to run within the time frame for the complete process, precipitation of arsenic using pyrite seems to be expensive. Secondly, the chemical precipitation method for arsenic removal harbours a disposal dilemma – if the arsenic is not properly disposed of, it stands to be a pollutant and a potential health hazard.

Investigated by Liao et al. ultrasonic induced zerovalent lead, together with copper (II) sulphate, a diffusion-controlled process, removes trivalent arsenic ions from industrial wastewater (Liao et al., 2021). However, mass transfer efficiency for the method could be improved, alongside accelerating the arsenic removal rate. Nevertheless, the methodology required less temperature to operate, making it energy-efficient relative to other methods. However, the rate of arsenic removal needs to be further investigated, given that at a lower temperature, it is expected the reaction rate would be slow (even though external heat is not required for the process). Sulphide precipitation, followed by hydrothermal mineralization, precipitates 99.65% of arsenic under optimal conditions (Hu et al., 2019). The hydrothermal mineralization enhances the stability of the compound, As₂S₃. Overall, the methodology is a potent arsenic precipitator, requiring low volume substrates and is, therefore, a potential option for treating acidic wastewater.

4.1.6 Ion exchange

Another conventional technique to remove arsenic and toxic metal ions from wastewater (usually under the method of precipitation) relies on the mechanism of ion exchange as shown in Fig. 4. For instance, As (V) was efficiently removed using phosphorus pentasulfide (P₂S₅) under ultra-violet radiation (Peng et al., 2018). This methodology introduces H₃PO₄ (instead of cations) to aid the recycling of arsenic and acid in a low pH wastewater medium. However, such a methodology would not be suitable/efficient for non-acidic contaminated water and generally takes a longer time. Secondly, such a mechanism cannot be employed where bioprocessing is involved, since under the required strong acidic conditions, the microbial activity would be significantly inhibited.

The removal of arsenic (in acidic wastewater) using hydrogen sulphide (H₂S) is another efficient method. However, conventional sulphuration builds H₂S pollution, whereas the Kong et al. methodology immediately precipitated sulphides. The reaction efficiency increases by 2.5-fold with UV irradiation, operated in the dark, removing more than 99.9% of arsenic/heavy metals (Kong et al., 2020). Additionally, using formaldehyde wastewater and carbon resource, Zhao et al. (2016) prepared a biofloculate (MBF-79), which showed a better removal efficiency for arsenic at pH 7 compared to other flocculants. Although promising, maintaining neutral pH for wastewater would be difficult, which could potentially be a challenge for this mechanism.

4.1.7 Membrane

One of the most promising membrane techniques utilizes nanofiltration technology. A polyamide core-shell with a bio-functionalized matrix membrane, consisting of varying quantities of C-S BF nanoparticles, developed via dissolution casting methodology, efficiently removes both Arsenic (As) and Selenium (Se) ions. The novel mechanism filters pure water against As (III) and Se ions with a brilliant regeneration ability and filtration efficiency of 99% and 98% against As (III) and Se ions, respectively (with low-pressure drops) (Zeeshan et al., 2020). Compared to other membrane filtration techniques,

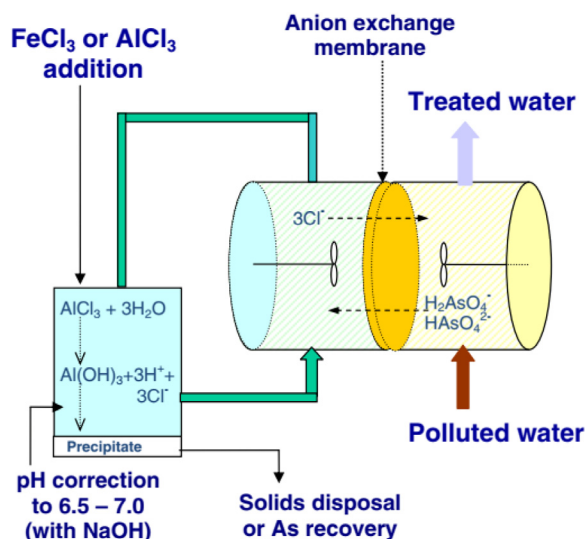


Fig. 4. Arsenate removal process through the Ion exchange system, reprinted with the permission of Elsevier from Oehmen et al. (2011).

the rejection efficiency of heavy metal ions is lower. Increased bio composite nanoparticles in membranes enhance the augmentation and increase the rejection efficiency of metal ions (Rekik et al., 2017). However, augmentation passing the optimum level and non-homogeneous dispersion of particles can potentially block pores, resulting in decreased functionality of the membrane and hence efficiency, particularly in the basic medium.

4.1.8 Oxidation

Biotechnology involving aerobic granular sludge, removes both arsenic and heavy metal(loid)s from wastewater, utilizing an oxidation mechanism (He et al., 2019). Biogenic scorodite synthesis, with the oxidation of As (III), catalyzed by granular activated carbon (GAC) showed significant arsenic removal efficiency and precipitated stable scorodite particles and thus, is a feasible approach to both crystallize scorodite and remove arsenic contaminants. The major technologies for arsenic removal from wastewater are summarized in Table 2. Vega-Hernandez et al. (2020a,b) also demonstrated the precipitation of Fe (III) with As (V), using microbial oxidation, which can inactivate GAC. However, more clarity on what happens to the GAC and whether it needs to be replaced (when inactivated), including how the removal efficiency is affected afterwards, would have been beneficial.

4.2 Arsenic removal techniques from contaminated soil

After water, soil is the environmental component most exposed to arsenic pollution. Inorganic forms of arsenic (AsIII and AsV) are mostly found in soil, but aerobic soil conditions often contain As (V) (da Silva et al., 2018). Usually, soil arsenic is the major means of arsenic contamination in plants. A significant amount of arsenic is also bioaccumulated in animals when they use these plants for various purposes. The arsenic accumulation in soil is regulated by the soil composition, presence of organic/inorganic chemicals in soil, and other external factors. Since both animals and plants are highly dependent on the multiple benefits produced through soil, it is necessary to assure efficient arsenic removal from soil. Unlike water, efficient arsenic removal from soil involves many complexities due to its solid structure, clogging possibilities in machinery, and the diversity of soil types. Therefore, efficient arsenic removal techniques should also be designed for specific soil contexts. This section of the paper discusses some of the most efficient soil arsenic removal techniques that include phytoremediation, washing methods, chemical treatment, electrical mechanisms, chemical treatment, and so on.

4.2.1 Bioremediation

Bioremediation refers to a living organism (i.e. bacteria, plants, fungus) mediated contaminant-removal mechanism. Such mechanisms are often applied in the case of arsenic removal from soil. Phytoremediation, fungal-remediation, and algal-remediation are the most common types.

4.2.1.1 Phytoremediation Phytoremediation refers to a plant-mediated treatment strategy commonly used for heavy metal treatment from water or soil. This process, shown in Fig. 5, is very promising since the growth characteristics of the plants and their corresponding removal efficiency has been found to be very suitable in the case of soil treatment (Yan et al., 2017). One of the most important aspects of this process over the other renowned As removal processes is that this is a culturally and socially accepted mechanism due to its intrinsic relationship with natural components (Alka et al.,

Table 2
Overview of the major arsenic removal technologies for wastewater treatment.

Method	Advantages	Disadvantages	Arsenic form removed	Removal rate	Optimal condition	Removal Efficiency	Ref.
Adsorption	Economical	Requires efficient control of pH, temperature	Arsenic content (bonded form)	99.8 wt.%	pH < 6	50%	Du et al. (2016)
	High reusability	pH needs to be maintained critically	As (V)	Rapid (not specified)	pH = 10	81 and 92%	Barakan and Aghazadeh (2019)
	Negligible leaching of binder	Operational range of pH is relatively narrow	As (III), As (V)		Arsenic solutions with an initial concentration of 1000 ppb	around 70%	Mangwandi et al. (2016)
	Negligibly affected by pH (works across a wide pH range)	The reaction mechanism does not remove As (III)	As (V)	>95%	pH = 2–11, 298 K, 300 min; adsorbent dosage e 0.1 g/50 mL; speed reached 180 rpm,	98.51%	Zheng et al. (2020)
	Tuneable physical–chemical properties	Unknown biological implication on human health/ecosystem	As (V), As (III)	As (V)92–98% As (III): 42%–65% (using iron impregnated activated charcoal)	A broad range of pH (based on adsorbent)	70%–90% (depending on the nanomaterial used)	Lal et al. (2020)
	Requires low-cost adsorbents (Rice husk); environmentally friendly	Sorption capacity decreases after 6 h; Strictly dependent on sorbent dosage, primary contaminant concentration, contact time, and solution pH	–	–	pH= 6; HBC-RH dosage:0.167 to 16.67 g/L	–	Sanyang et al. (2016)
	High adsorption of As	Reduced adsorption at high pH; suitable for acidic waste water; microstructure-dependent	As (V)	–	pH 3; 25 C	82%	Islam et al. (2021)
	Better selectivity	Varying conditions required for batch and column adsorption	As (III) and Se ions	–	pH 6–8	–	Mafu et al. (2016)
	Relies on locally available natural material; independent of pH (arsenic predicted to be present as oxyanion in alkaline medium)	Sorption of arsenic is minimal for wastewater bodies with high arsenic content due to finite adsorbent surface	–	–	pH > 10; 15 min of equilibration, 1 g of dosage; arsenic concentration 20 mg L ⁻¹	–	Masindi and Gitari (2016)
Outperforms metal oxides, biopolymers, and nanotubes in terms of cost and efficiency	Particle size could affect the practicality of the mechanism	As (III); Cd	6.5 mg g ⁻¹ after 12 h	pH (3–9), initial concentration: (30–300 mg L ⁻¹); adsorbent dosages: 0.1–2.0 g	As > 31%	Shim et al. (2019a,b)	

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Table 2 (continued).

Method	Advantages	Disadvantages	Arsenic form removed	Removal rate	Optimal condition	Removal Efficiency	Ref.
	Reusable TiO ₂ ; cost effective; Metal(loids), antimony (Sb) removed as well	Specific for a reaction system	As (III), As (V)	Batch column: < 100 µg/L Field column: As (0.378–0.534 mg/g)	600 g, 200 g of TiO ₂	–	Qiu et al. (2019)
	Deep removal, in bulk; fast diffusion	Requires high arsenic wastewater	As (III), As (V)	–	0.5 g L ⁻¹ of PGA/PeFe ₂ O ₃ ; pH:5; 298 K Humic acid: 10 mg L ⁻¹	Almost 100% As (III)	Yu et al. (2019)
	Arsenic (As) and heavy metals	Depended on the type of wet land	–	–	Influent Concentration: 0.1 mg/L; Hydraulic Loading Rate 5 m ³ /d; substrate: Limestone	75.1%	Nguyen et al. (2019)
	High removal efficiency, even after 4 cycles	Negative effect of coexisting anions	As (V)	Rapid (not specified)	pH > 9; room temperature	(more than 87%	Barakan and Aghazadeh (2020)
Chemical Precipitation	Allows the use of solid waste; low cost	Supersaturated iron ions can hinder the crystallization of scorodite	–	–	80 C; Fe/As molar ratio: 2.0;	97.86%	Li et al. (2020a,b)
	Feasible strategy and cost-effective	Works for only high arsenic concentrate wastewater	–	–	pH = 10	91.37%	Li et al. (2021a)
	Direct removal; high efficiency	Requires high-arsenic acid wastewater	As (III)	–	room temperature; pH 1.8–4.5; initial As (III) concentration greater than 0.75 g/L	99%,	Chai et al. (2016)
	Treats wastewater from arsenic-contaminated soil; ferrous oxalate phase acts as solid electrolyte; economically feasible	Arsenic precipitated was less;	–	pH 1.2; mild reducing conditions	–	0.67%	Kim and Baek (2019)
	Allowing a low iron supersaturation	Expensive; strict reaction conditions; high temperature required	–	–	pH of 1.5; 90 degree Celsius; Fe/As molar ratio of 4; As: 10 300 mg/L; Sulphuric acid: 72 500 mg/L	98.3% at a Fe/As molar ratio of 5 (389 mg/L-residual AS concentration)	Li et al. (2021d,c)

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2021). The environment-friendly nature of the process also makes it different from many other more effective As removal mechanisms. Despite being a very slow process to extract the highest proportion of As from soil compared to other methods, it is still preferred over other more complex remediation strategies due to its low-cost implementation and sustainable outcomes. Since the plant roots play the most important role for As isolation, the effectiveness of the process gradually reduces due to the gradual reduction of root exudates after a specific period of time ([da Silva et al., 2018](#)). The roots gradually reduce their biomass over time after a certain growth period, and thus lose their root exudates and the surface area for As extraction. Here, increased As content in the plant body also works as a contributing factor for a gradual reduction in As extraction efficiency. The process is compatible with biological absorption, as in many cases As molecules are absorbed through the plant's internal absorption mechanism mediated by the roots.

Table 2 (continued).

Method	Advantages	Disadvantages	Arsenic form removed	Removal rate	Optimal condition	Removal Efficiency	Ref.
	Reaction temperature achieved by ultrasound; Copper (II) sulphate does not contribute to secondary pollution; industrial wastewater reusable after treatment	Arsenic removal reaction rate is slow	As (III)	1.44 mg/L	55 °C; Pb/As molar ratio 3, CuSO ₄ (1 g/L); ultrasonic power 90 W; 120 min	99.98%	Liao et al. (2021)
	Rapid reaction rates	Efficiency decreases when terminal pH increases up to 6; hydrothermal mineralization and stabilization process requires high energy	As (III)	-	25 °C; pH = 4, S ²⁻ /As molar ratio:3.0:1, 60 min.	99.65%	Hu et al. (2019)
Oxidation	Cost effective green methodology; facilitates solid-liquid separation	HRT optimization	As (III)	-	pH 1.2 and 70 °C	99% (oxidation efficiency)	Vega-Hernandez et al. (2020a,b)
	Remove As from organic wastewater.	Batch reactors required	As (III) oxidized to As (V)	-		(74.6%e82.6%	He et al. (2019)
Ion exchange	Minimal H ₂ S pollution; low cost; Removes Cu (II)	Requires acidic conditions	As (III)	-	UV Irradiation: 2.5-fold in the dark; thiosulphate: 2-24 mM; [H ⁺] = 1.86 M; As (III)] = 2 mM	99.9%	Kong et al. (2020)
	Disposed of environmentally friendly precipitates	Applicable for ferrous smelting wastewater only	As (III) to As (V)	-	Room-temperature; initial arsenic concentration: 8458 mg/ L	98.85%	Li et al. (2020a,b)
Ion exchange resin, Precipitation	pH independent; ion-specific resin remove As ions	Competing anion may have a strong impact	As (III)	-		99.4%	Li et al. (2021b)
Ion exchange, Adsorption, Redox reaction	Removes nitrate from wastewater that lacks organic matter, together with arsenic	Arsenic is not removed at high pH	-	-	pH < 6	Higher than 90%	Zhang et al. (2018)
Ion exchange, Electrochemical redox reactions, electrochemical adsorption	Better contact between birnessite and Arsenic ions, facilitating adsorption	Inner-sphere complex formation may hinder/slow desorption	As (V)	-	1.2 V	As (T) and As (III) removal ratio: 54.3%	Liu et al. (2019)

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There are several factors regulating the phytoremediation techniques in terms of As removal from soil. For instance, soil type is one of the major regulators of the phytoremediation process. Studies show that when multiple types of soils are treated under the same condition, result variations are found that correlate with the soil content. The efficiency of

Table 2 (continued).

Method	Advantages	Disadvantages	Arsenic form removed	Removal rate	Optimal condition	Removal Efficiency	Ref.
Precipitation, oxidation	Haematite used to make iron; recycling	Expensive	Cu-As; Fe-As	–	O ₂ injected at ~90 °C, atm pressure; pH of 0.7	Cu-As: 99% As: 95% (after 4 h)	Zeng et al. (2021)
Biogenic precipitation, oxidation	More stable scorodite particles	Maintenance cost particularly for microorganism culturing	A (III) oxidized	–	4 and 20 g/L of GAC	–	Vega-Hernandez et al. (2020a,b)
Bio-oxidation followed by filtration and adsorption	Heavy metals removed (<90%) along with arsenic; Bio-column can be regenerated	Gradual clogged of filter media	As (III) oxidized and As (V) precipitated	–	pH: 2.5; 1M H ₂ SO ₄ ; 30 °C-35 °C	–	Kamde et al. (2019)
Coagulation	Suspended solids (in waste water liquor) enhances Arsenic removal	Higher efficiency of As-removal for alum than ferric chloride	–	–	pH: 4 to 9; 5 µg/L of initial As (V) concentration	<30% of the As	Ge et al. (2020)
Ion exchange, coagulation (UV-Light promoted sulphuration)	Facilitates recycle and reuse of arsenic	Expensive	As (V), As(T. Zeng et al., 2021)(III)	Increased by 12-fold under UV radiation	As (III) = 6.67 mM; As (V) = 6.67 mM; [H ⁺] = 3.72 M; S/As ratio-3:5	99.2% (by P ₂ S ₅ in the Dark)	Peng et al. (2018)
Bioflocculation	MBF-79 positively associated with cell growth	Strict monitoring necessary for proper microbial growth	Arsenate; Arsenite	–	Inoculum size of 7.0%; Formaldehyde: 350 mg/L; pH of 6.0; at 30 C	Arsenate: 98.9%; Arsenite: 84.6%	Zhao et al. (2016)
Biosorption, bioaccumulation (film diffusion)	Comparatively eco-friendly	An extensive process requiring maintenance, under a neutral pH for bacterial growth	As (III), As (V)	–	240 min; 30 °C; biosorbent dose of 0.9 g/L; 120 rms	As (III):79.565% As (V): 86.385%	Podder and Majumder (2016)
Nanofiltration membrane	Brilliant regeneration performance; Removes Se ions as well	Augmentation and non-homogeneous dispersion can block pores; acidic medium effects As (III) rejection	As (III)	–	pH = 9; contact angle (46°)	99% and 98% As (III) and Se ions	Zeeshan et al. (2020)

As removal for a specific plant also relies on the As type present in the specific soil condition. For example, as per the study of Yan et al. (2017), labile arsenate (L-As) form has been found to be easily removable using *Pteris vittata*. Another study on the efficiency of the same species for soil As removal found that *Pteris vittata*-mediated As removal is highly cost-effective and easy to implement under extreme environments.

Among other plants to be chosen for As removal, Vetiver grass and water hyacinth have shown effective As removal from soil, with water hyacinth showing almost double the effectiveness over vetiver grass, under optimum conditions (Taleei et al., 2019). However, limitations of water hyacinth mediated As removal include the requirement of a flooding condition over the soil. Another plant with the capacity to remove As from soil slowly is *Colocasia esculenta* L. Schott. Despite this species very slow outcome, a pilot-scale study found its effectiveness under certain conditions (Thathong et al., 2019). Since this setup has not yet been executed on a large scale, there is the possibility of failure or the necessity to modify the approach for large-scale application. In all these different cases, the efficiency of the process is also dependent on the root constitution of the plants. Studies show that different zones of the roots cause a different rate of As extraction from soil.

Phytoremediation can also be coupled with other treatment strategies to enhance the efficiency of the process. For instance, when coupled with the flushing/washing method, phytoremediation using *Pteris vittata* shows an increased efficiency of at least 17% (Yan et al., 2017). In a similar study, instead of using a washing mechanism, external phosphate (Phosphate Rocks) was added to the system to increase efficiency. In this regard, added phosphate played role in process efficiency enhancement. The addition of 20%–28% iron-containing laterite soil has also been found to drastically improve the As removal potential (Thathong et al., 2019). Thus, the presence of different ingredients accelerates or

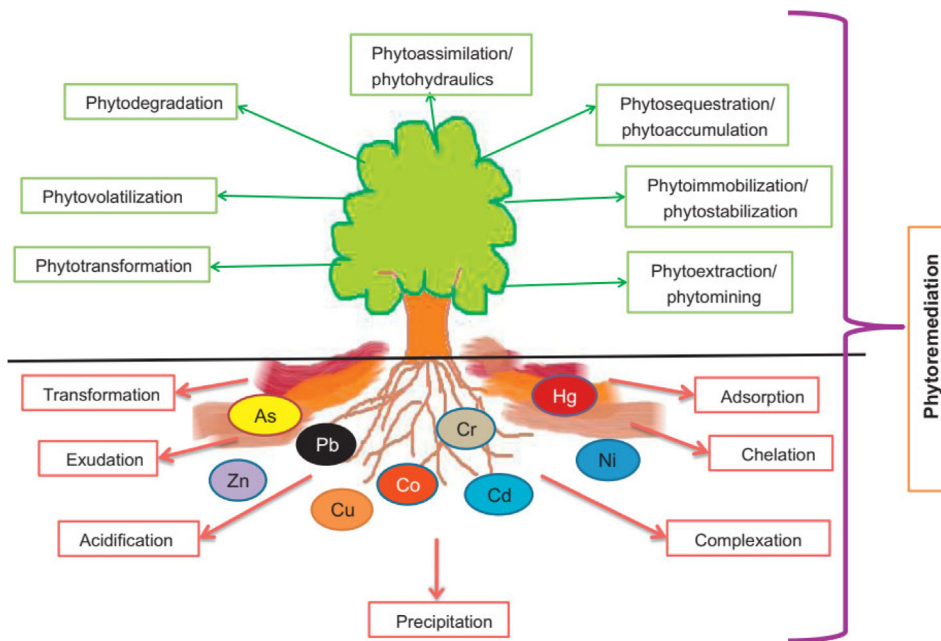


Fig. 5. Different steps during phytoremediation, reprinted with the permission of Elsevier from (Shukla and Srivastava, 2019).

improves the phytoremediation mechanism. However, in all these cases, such coupling does not promote remediation directly, e.g. the addition of laterite soil is a type of intermediate stage during phytoremediation which results in the development of iron-oxidizing bacteria. The introduction of such stages gradually achieves the expected efficiency and rate of phytoremediation. Thus, the limitations of the phytoremediation process can be overcome.

4.2.1.2 Fungal remediation Fungi-mediated As removal from soil has been observed and while only a few species have been found to be effective in removing As from the soil, some of them have shown significant potential. *Talaromyces* is one such example that is highly arsenic-tolerant and can remove As from media (Nam et al., 2019). However, unlike phytoremediation, fungal remediation can be applied in the aqueous media of As-contaminated soil. Another notable difference between phytoremediation and fungal remediation is that unlike the plants used in phytoremediation, fungi volatilize the absorbed As. This can also be hazardous, as the volatilized As will still accumulate in random places in the environment.

4.2.1.3 Algal remediation Not many algae have shown significant As removal potential, however algal remediation of As contaminants can be suitable for soil, especially for humid soil conditions. Chara Algae (*Chara Vulgaris*) is one of the few algae with algal remediation properties and in many cases, this alga is usually more effective than some phytoremediation methods (Taleei et al., 2019). However, unlike phytoremediation, effective algal remediation requires a comparatively higher amount of investment in soil processing, since the algal growth and sustainability is highly regulated by the corresponding soil components, moisture contents, temperature, and other variables. Therefore, processing techniques are yet to be designed for a highly effective As remediation.

4.2.2 Washing methods

The washing method, a reagent-based cleaning method, refers to the suitable extraction of contaminants from media. This process is already a very popular soil contaminant (especially heavy metals) removal mechanism; the potential reasons behind its popularity are its simple operation, uncomplicated regulations, practicality, abundantly available research, the broad scope for process upgradation, and so on (Bi et al., 2019). Unlike As removal from water, the washing method has been found more suitable for As removal from soil. From a technical point of view, this is due to its capacity to manipulate the soil's properties altering enzymatic reactive and fertility potentials (Yan et al., 2017). The major priority in this process of soil contaminant removal is the appropriate preparation of the washing agent. Additionally, washing conditions should also be carefully determined as they are dependent on the soil characteristics and the constitution of the reagents. Based on the significant amount of research into this area, this paper classifies washing methods into four broad categories depending on the type of reagents used in the process. This includes acid-based washing, soluble organic matter-mediated washing, coupling with other processes, and non-conventional processes.

4.2.2.1 Acid-based washing methods Acid-based medium is the most commonly used reagent in washing methods. A wide range of acidic media has already been identified in the literature that covers the use of multiple acids at different concentrations. Maintaining suitable ratio, concentration and optimum conditions are necessary for effective As removal without damaging soil properties, since strong acids often leach contaminants that alter the physical and chemical constitution of soil (Cho et al., 2020). Traditionally, two strong acids, phosphoric acid and sulphuric acid, are commonly used as soil washing agents at a suitable concentration. However, it was noted that their efficiency can be increased by altering their concentration in the medium which imposes certain conditions. In this regard, soil particle size is another important factor influencing the process. Such inorganic acids can be easily applied to large-scale soil As removal and, considering the economic, operational, and technical suitability, even a sophisticated set up of this mechanism can be useful for extreme ex-situ conditions.

Organic acids have also shown potential for effective soil As removal. This usually includes oxalic acid, citric acid, and ascorbic acid (Nguyen Van et al., 2017). Among them, oxalic acid is one of the most commonly used acids. However, using oxalic acid as a washing reagent is more expensive compared to the above-mentioned inorganic acids. In order to minimize the operational cost of the oxalic acid-based washing mechanism, other chemicals are added to it so that it becomes both economically feasible to implement and operationally effective for As removal. Therefore, a study found a POE (phosphoric acid, oxalic acid, and Na₂ EDTA (Ethylenediaminetetraacetic acid disodium salt dihydrate) respectively at 0.05M, 0.075M, and 0.075M concentration) combination that achieved a balance of operational cost and effectiveness. (Wei et al., 2016). Though all three of these agents are distinctly very effective washing agents, their combination makes the process more practical. Though such processes should be strictly regulated to avoid unintentional soil damage, successful industrial-scale implementation is still possible with some upgradation of available techniques. Another suitable process for minimizing the cost of the oxalic acid-mediated washing method is to extract valuable resources using a multi-staged reaction mechanism. By applying a two-staged reduction reaction mechanism (using sodium dithionite), the recovery of iron and oxalates can be assured while extracting soil As using an oxalic acid-mediated washing mechanism (Kim and Baek, 2019). This process is more applicable at an industrial scale since it produces ferrous oxalate which can be used in industry as useful resources. Therefore, this process might not be very useful for non-industrial applications.

4.2.2.2 Soluble organic matter mediated washing methods In this process of soil As removal, soluble organic matter is used to wash away the soil As from the contaminated soil. Such soluble organic matter can be of various types; however, abundant oxygen-containing functional groups are more effective. These humic substances (HS) are effective washing agents as they can effectively extract As from soil as a means of chemical treatment altering the chemical configuration of the corresponding functional groups. The removal efficiency is highly reliant on the soil type and the number of washing mechanism repetitions (Bi et al., 2019). There is another organic matter which in the dissolved form can assist induced As isolation from the soil. For instance, during bioremediation of As from soil using plants or useful bacteria, dissolved peptone or beef extract has been found to assist phytoremediation (Das and Das, 2020). However, using a suitably dissolved form of the organic matter is important since this assures enough penetration of these washing agents into the nooks and crannies between the soil particles.

4.2.2.3 Non-conventional washing methods In addition to the above-mentioned conventionally adopted As removal strategies, non-conventional strategies are often adopted in order to isolate soil As. This is an emerging area of application that requires significant modification before large-scale implementation is possible. The preference of these non-conventional washing methodologies lies in their suitability over conventional methods due to their less environmentally hazardous characteristics. Utilization of biodegradable chelator as washing agents during induced washing of As contaminated soil might be a potential alternative to conventional soil As removal mechanisms. The process is carried out by the formation of coordinate bonds in between the toxic elements and chelation agents that transform the solid form of the contaminants into a soluble and easily removable form. Though the process has already shown effective removal at a pilot scale, its large-scale implementation is still challenging due to the knowledge gap on the process mechanism (Wang et al., 2020a,b). More development of the process is required to assure a more suitable application of chelator-induced washing for As removal.

4.2.2.4 Washing methods coupled with other methods In some cases, many of the As removal processes do not result in the expected As removal efficiency. Therefore, the coupling of multiple processes is needed to achieve suitable efficiency. In these cases, washing agents are usually added to other processes. For example, when KH₂PO₄ is added to the phytoremediation mechanism, it enhances the efficiency by changing the soil composition and permeability coefficient (Yan et al., 2017). However, this process can be criticized because it adds chemicals to the soil. Added chemicals such as phosphate or nitrogen may cause eutrophication on small scale, causing degraded soil fertility. However, it is still useful for sophisticated As removal from soil. Another example of coupling washing methods with other As removal mechanisms is the incorporation of washing agents while sieving contaminated soil. In addition to this, washing methods are often coupled with sieving, flotation, or other physical As extraction techniques. The purpose of such coupling is to enhance the efficiency and rate. For instance, while the soil is sieved in the presence of washing agents, the process is enhanced by both of the individual efficiencies being coupled (Liao et al., 2016). This coupling of washing methods with physical As removal strategies might not be that effective at an industrial scale, however, it is still a good starting point to assure successful applications of more in-depth extraction. Thus, the addition of different reagents to other As extraction systems create more efficient removal.

4.2.3 Chemical treatment

The above-mentioned processes incorporate some evidence of chemical treatment mechanisms for As removal. However, chemical treatment of As contaminated soil is comparatively more difficult than As contaminated water, since processes incorporating soil systems cause difficulty for carrying, transportation, and other stages of the treatment mechanism. Considering the unique characteristics of a soil system, *chemical precipitation* might be a suitable technique for soil As removal. In this process, a solid substance is formed from a solution for which fine-grained soil shows more efficiency since they have a higher potential for forming more solid structures from the solution (Alka et al., 2021). The utilization of *Biochar* is also another suitable chemical agent for chemical treatment of As contaminated soil. Biochar refers to a carbon-rich solid structure.

Magnetic biochar, derived from iron oxides or zero-valent iron, has been found to assure efficient As removal from soil. Magnetic biochar immobilizes bonded or non-bonded forms of As in a wet environment by forming temporary bonds among the contaminants and biochar agents. Thus, it uses the contaminant's multivalent properties for the successful removal of the contaminant itself (Li et al., 2021d,c). The molecular magnetic properties of the available carbon present in the biochar assist in bond formation and bond breakage in this context (Wan et al., 2020). In addition to magnetic biochar, wheat straw biochar has also been found to be useful for sustainable chemical treatment of soil As. This biochar assures efficient As removal through a series of chemical processes, i.e. physisorption, chemisorption, diffusion, and ion exchange (Kumar and Bhattacharya, 2021). This is a type of biochemical remediation since living bodies have been utilized to promote chemical treatment. Whereas chemical treatments are found to be more useful for As removal from water, there are many other chemical components that can be used as examples of chemically mediated As removal from soil.

4.2.4 Electrical mechanism

Electrical mechanisms are often found useful for soil As removal through the application of different electricity-related principles. Applications of electrokinetic techniques and electro-dialytic processes are the most suitable process of soil As removal. Electro-dialysis is the process through which ions are transported through a highly selective semipermeable membrane that is designed as per the users' interests and necessity. Electro-dialysis helps to isolate As and other metallic contaminants using electric force in a semipermeable membrane system. In this process, suspended soil slurry (contaminated with As) is poured into an electric setup containing an ion exchange membrane that selectively takes away the As molecules from the soil slurry. The highest efficiency is achieved in the first few days and then reduces over time (Ferreira et al., 2019). The process is useful for small-scale As extraction from heavily contaminated soil, with large-scale implementation still a challenge.

Another electrical mechanism for soil As isolation is an electrokinetic system where electrokinetic force is used for As removal. It is an emerging, non-conventional and promising means of soil As removal. Its removal potential is limited to the removal of non-dissolved As from contaminated soil. The process, itself, refers to an electricity-mediated mechanism under which direct current is applied to mobilize the contaminants in the corresponding system. Coupling of the electrokinetic remediation with other remediation processes, e.g. bioremediation and chelation, helps to increase the removal efficiency drastically (Alka et al., 2021). However, as an emerging non-conventional mechanism, there are limitations and associated challenges with the process, i.e. the process is not yet capable of being applied at a large scale. Large soil particles do not act efficiently under this process of As removal. Therefore, there is a need to improve the application of the electro-kinetic mechanism for soil As removal. However, other electrical mechanisms, such as electrocoagulation, electrochemical processes, and others, might be suitable for As removal from water. However, these processes are not applicable for soil As removal. Therefore, knowledge of the above-mentioned two processes, electro-dialysis, and electro-kinetics, should be prioritized in terms of developing large-scale soil As removal setups that use electric force.

4.2.5 Physical treatment

Like many other treatment mechanisms, soil As removal is also able to incorporate many physical treatment strategies that include flotation, adsorption, and so on. Physical treatment is often preferred over other remediation strategies because it retains the soil's properties by not incorporating any chemical or biochemical change throughout the process. Unlike water As removal, soil As removal that uses physical treatment strategies needs to be carefully handled as not every physical treatment setup can be incorporated in a soil system. In this context, flotation, a physical separation system, is dependent on the density of the associated chemicals present in the flotation setup. Usually, soil As contaminants are present in a slightly ionic form for which a suitable flotation media might be oil agglomerates. Such nonpolar oil particles form nonpolar hydrocarbon bridges with the fine soil particles, mostly with SiO₂. In this way, polar As ions are removed from the nonpolar system created by the oil agglomerate (Choi et al., 2016). Based on the process steps described, flotation can also be considered as a physiochemical process.

Adsorption is another suitable physical treatment system for soil As removal. Adsorption refers to a physical treatment strategy that uses solid substances to isolate liquid or gaseous substances. This process is one of the oldest treatment strategies due to its very simple operational scheme. The utilization of sophisticated surfaces for adsorption ensures efficient contaminant isolation (Alka et al., 2021). However, the binding coefficient is the key influential factor that determines adsorption's removal efficiency. The process sometimes also incorporates some chemical properties making it a physiochemical process (Sodhi et al., 2019). The major soil arsenic removal technologies are summarized in Table 3.

Table 3
Overview of the major soil arsenic removal technologies.

Method	Advantages	Disadvantages	Arsenic form removed	Removal rate	Optimal condition	Removal Efficiency	Ref.
Phytoremediation	Less expensive environment friendly effective for a long period of time	Efficiency is not high if it is not coupled with flashing/other treatments. Less effective in heterogeneous soil	Arsenic content (bonded form with Oxygen, Calcium, Iron, Aluminium), As (V) and As (III)	Slow, increases while coupled with other treatment	Slightly alkaline soil pH Some plants are more effective in wetlands. Addition of laterite soil increase efficiency	54.04% (<i>Pteris vittata L. (P.v.)</i>) Around 50% (Water Hyacinth – <i>Hyacinthus orientalis</i>) 30% (Vetiver Grass – <i>Vetiveria zizanioides</i>) 89% (<i>Colocasia esculenta L. schott</i>)	da Silva et al. (2018), Yan et al. (2017), Taleei et al. (2019) and Thathong et al. (2019)
Fungal remediation	Cost-effective environment friendly sustainable works in extreme environment	Aqueous media needs to be created. Very slow process	As (V) and As (III)	Slow process (As (V) removal is 3 to 5-fold higher than As (III))	Aqueous media and pH 3.0 – 10.0	>70% (<i>Talaromyces</i>)	Nam et al. (2019)
Algal remediation	Effective process available resources	Requirement of soil processing to create a suitable environment for algal growth	As (III)	Slow (Highest efficiency is achieved after a month)	Humid soil	Around 40% (Chara Algae – <i>Chara Vulgaris</i>)	Taleei et al. (2019)
Native hygrophyte-mediated remediation	Environmentally sustainable inexpensive reduces bioavailable As	Cannot be fully extracted, instead bioavailability is reduced through bond creation with other agents	Non-bonded As	Slow	Nutrient-rich soil	22.9% removed. 76.7% bonded with atmospheric Fe	Huang et al. (2019)
Acid-based washing methods	Usually affordable (Though few acid-based systems are expensive) Easily operational Effective coupling capacity Multiple combinations of the acids might be designed for more effective washing agent designing	Inappropriate setup might be extremely hazardous. May cause acid mine drainage. Might be environmentally hazardous	As (V), As (III), and Bonded Arsenic	Fasters (highest efficiency can be achieved within hours)	Suitable combination leads to higher efficiency	35.81% (H ₂ SO ₄) 62.96% (H ₃ PO ₄) 70.5% (0.6M H ₂ SO ₄ + 0.6M H ₃ PO ₄ in 1:1 mixture solution) 41.9% (POE)	Nguyen Van et al. (2017), Cho et al. (2020) and Wei et al. (2016)
Sieving coupled with washing agents	Increased efficiency due to the combination of two methods	Might not be effective in all the contexts	As (III) and As (V)	Fast	Optimum pH depending on the agent's constitution	10.2–45.5% (Depending on the size of soil particles)	Liao et al. (2016)
Flotation coupled with washing agents	Increased efficiency due to the combination of two methods	Not much useful for very fine extraction	Bonded As, As (III) and As (V)	Fast		82–93%	Liao et al. (2016)

(continued on next page)

Table 3 (continued).

Method	Advantages	Disadvantages	Arsenic form removed	Removal rate	Optimal condition	Removal Efficiency	Ref.
Washing by humic substance	Effective, easily controllable process	May degrade the soil properties	Bonded As, As (III) and As (V)	Very fast due to chemical treatment	Neutral pH (=7)	93% (black soil) 74.5% (fluvo aquic soil) 74.3% (red soil)	Bi et al. (2019)
Biodegradable chelator-induced washing	Environmentally sustainable higher efficiency Transition from the age-old conventional mechanism	Lack of knowledge/research in terms of the process Blurry knowledge on the corresponding risks		Fast	pH = 5	>90% from farmland soil	Wang et al. (2020a,b)
Chemical Precipitation	Cost-effective and easy to implement	Cannot be implemented at a large scale		Medium	Works better on acidic medium	90%	Alka et al. (2021)
Magnetic biochar-mediated chemical treatment	Low cost, less complex, and efficient process	Not much suitable for wet soil condition	Both bonded and non-bonded As	Not that fast, significant removal is found after a day.	Soil moisture is needed	28%	Li et al. (2021d,c) and Wan et al. (2020)
Wheat-straw biochar-mediated chemical treatment	Low cost available ingredients for biochar production reduce both the straw waste and As contamination	Pyrolysis plant requires sophisticated regulations during highly stable biochar production.	Mostly As (III)	Medium	Extremely high temperature (700 °C) Suitable pH = 6.57 Suitable EC = 75 µS/cm	92% (at 700 °C)	Kumar and Bhattacharya (2021)
Electro-dialytic process	Very effective in terms of time and efficiency	High implementation cost large scale implementation is challenging	Ionized As found in soil slurry	Fast for the first 3 days, then the rate reduces	pH = 10	63% (after first 3 days) 80% (after 2 weeks)	Ferreira et al. (2019)
Electro-kinetic process	Very efficient and rapid process Low-cost implementation	Limited to only fine soil particle treatment as per existing knowledge, it is applicable only for the in-situ condition	Non-dissolved As	Very rapid process	Alkaline pH	90%	Alka et al. (2021)

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5 Challenges in removing arsenic from wastewater and contaminated soil

Arsenic removal from wastewater and contaminated soil is currently a challenge for the biophysical climate and living organisms. Arsenic contamination through both anthropogenic and natural routes has created great global concern about water and soil bodies (Masindi and Muedi, 2018). In most parts of the globe, the presence of arsenic in the environment exceeds recommended levels. Consequently, a very selective, efficient, and economical system is necessary to eliminate it from the environment, particularly from wastewater and contaminated soil which is quite challenging. Arsenic toxicity in humans can cause health issues including encephalopathy, abdominal pain, skin darkening and thickening, watery diarrhoea, numbness, and heart disease. Therefore, arsenic in a high concentration that enters the body can affect gut microflora, which in turn could contribute to metabolism problems, as well as many diseases including cancer (Choiniere and Wang, 2016).

Although there are several available techniques to remove arsenic from different sources, each technique has some limitations in its feasibility, efficiency, impact on the environment, and cost-effectiveness. For example, adsorption and chemical precipitation are the most commonly used arsenic removal methods (Salameh et al., 2015; Wang et al., 2015). However, these removal techniques still face a number of challenges, including high treatment costs, massive hazardous

Table 3 (continued).

Method	Advantages	Disadvantages	Arsenic form removed	Removal rate	Optimal condition	Removal Efficiency	Ref.
Flotation	Effective for soil properties reservation less expensive and less complexities of the process	Large soil particles are not suitable for this process. Floating media should be selected consciously for effective As extraction	As (III) and As (V)	Medium	pH = 4	50%	Choi et al. (2016)
Adsorption	Flexible and simplistic operation low cost	Sorbent surface should be carefully changed before reaching saturation. For extremely contaminated soil, the process is ineffective. Highly selective putting barrier to random adsorption	As (III) and As (V)	Fast	–	Up to 95%	Alka et al. (2021) and Sodhi et al. (2019)

waste production of arsenic, and environmental pollution. In light of the high toxicity and substantial discharges of the solid wastes generated by the processes, arsenic removal from contaminated soil and wastewater with a harmless process is essential to the long-term growth of industry and the general safety of the environment. Despite some merits, each arsenic removal technology faces a number of challenges as summarized in [Table 4](#).

6 Future perspectives

Advanced functional materials, namely graphite oxides, carbon nanotubes, metal–organic frameworks, and developing other innovative functional material forms are better alternatives in future improvement of arsenic removal techniques from water and contaminated soil. Any emerging removal technology should address the issues of efficiency, effectiveness, cost of operation and maintenance, the toxicity of by-products, and proper handling of post-remediation waste. Arsenic can be completely removed from contaminated soil and water using the most efficient methods under ideal conditions. Techniques that do not cause secondary environmental issues, consume less energy, and are cost-effective, are characterized as sustainable recycling technologies, however, they require additional attention to become a successful method of reducing arsenic contamination. As every single technology for arsenic removal has limitations, hybrid technologies should be explored and evaluated for various fundamental conditions. Cooperation between researchers, industries, and government bodies is also important in tackling the arsenic pollution issue and contamination in the environment.

7 Conclusion

Lowering the health and environmental risks from arsenic contamination can only be achieved by effective soil and water treatment techniques. Technologies such as coagulation and flocculation, adsorption, and membrane technologies are widely used. Other conventional methods primarily focus on Arsenite oxidation by introducing atmospheric oxygen, microbial metabolism, or chemical activities. Adsorption presents many advantages: stable and simple operation, compact facilities, easy waste handling and management, the lack of need for reagents, and the relatively lower operation cost. The state-of-the-art technologies for arsenic removal are, however, ridden with limitations. For example, coagulation–flocculation processes require manipulation of the size of soluble species, which is not always possible. The adsorption capacity of current techniques is low and the technologies do not allow regeneration or the reuse of components such as adsorbents. Most of the technologies are not effective enough in bringing the arsenic concentration under maximum contaminant level, as various factors like arsenic characterization and interaction with the environment compartment play a role in determining removal efficacy. Overall, and regardless of the limitations, the adsorption technique can remove arsenic from water and soil with high efficiency of nearly 100% and up to 95%, respectively.

Table 4
Challenges of arsenic removal from contaminated soil and wastewater using different treatment techniques.

Treatment	Challenges
Electrokinetic	Not effective unless the capacity of cation exchange and salinity is low Need sufficient soil moisture
Phytoremediation	Usually not efficient on contaminants which are strongly bound or insoluble to the soil particles In unfavourable climatic conditions, remediation may be slowed or lengthened, attempts to treat the soil may be hampered. Climate conditions can interfere with or impede plant development, slow the remediation process, or lengthen the treatment period
Screening	Not effective in removing the arsenic Efficiency depends on the movement of wastewater which is not easy to be controlled
Oxidation/precipitation	The process is quite slower Cannot remove arsenic on its own, it must be used in conjunction with other methods
Skimming	Skimmer cleaning is required frequently to ensure process efficiency.
Biological	Heating might be needed to continue the biological activity which involves noticeable cost Processing cost may be increased if an additional nutrient is required,
Aeration	Several cycles are required to effectively remove the arsenic Not enough efficient for arsenic removal without integration with other techniques
Coagulation - filtration	Generates toxic sludge Preoxidation might be necessary Low-efficient in removing As (III)
Adsorption	Operational range of pH is relatively narrow Regeneration/replacement is required Cyanotoxin accumulation in adsorbents Adsorption capacity mostly relies on the properties of activated carbon. Several activated carbons may be commercially available but they are quite expensive.
Nanomaterials-based adsorbents	Not sufficiently tested in ground conditions Possible adverse impact on the environment
Flotation	A more complicated and costly process, in comparison to other physical treatments High capital cost is involved Chemicals needed to maintain appropriate froth characteristics
Turnover-attenuation	High capital and maintenance costs Reduces the nutrient concentration in soil Difficulty in finding adequate clean soil sources
Resins of Ion-exchange	Competing anion may have a strong impact
Membrane-based technique	Difficult to regulate the selectivity of membranous system There could be fouling in the process Toxic wastewater is generated Important micronutrients needed for human health are rejected High capital, high operating and maintenance cost Water recovery rate is relatively low
Bioremediation	Implementation on a large scale is quite complex
Polymeric ligand exchanger	Low-efficient for As (III) removal Not adequately tested in ground conditions
Biofilters	It is required to replace the filter on a regular basis A surface with a large area is needed A high chance of blockage of being blocked
Nitrification-denitrification	Large difference in the conditions needed for denitrification and nitrification makes maintenance difficult
Anaerobic, Aerobic treatment	Maintenance is quite expensive High land space is required
Thermal oxidation	Requires initial capital costs High operating costs Effluent transportation and storage
Biosorption	It is necessary to clean adsorbents at a specific time interval
Membrane bioreactor	Membrane pollution as a result of regular membrane replacement Very costly
Microbial fuel cell	The mechanism is hindered by microbes' sluggish growth rate Not cost-effective as the process is highly expensive
Chemical precipitation	Much more ineffective in the removal of metal ions Consume chemicals such as lime, oxidants Necessitate an oxidation step

CRedit authorship contribution statement

Shams Forruque Ahmed: Conceptualization, Writing – review & editing, Data curation, Formal analysis. **P. Senthil Kumar:** Conceptualization, Validation, Supervision. **Mahtabain Rodela Rozbu:** Writing – review & editing, Data curation, Formal analysis, Visualization. **Anika Tasnim Chowdhury:** Writing – review & editing, Resources, Formal analysis, Visualization. **Samaha Nuzhat:** Writing – review & editing, Data curation, Formal analysis, Visualization. **Nazifa Rafa:** Writing – review & editing, Resources, Formal analysis, Visualization. **T.M.I. Mahlia:** Data curation, Formal analysis, Visualization. **Hwai Chyuan Ong:** Resources, Formal analysis, Visualization. **M. Mofijur:** Conceptualization, Validation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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