Review

Arsenic Contamination in Groundwater: Geochemical Basis of Treatment Technologies

Sushil R. Kanel,* Tonoy K. Das, Rajender S. Varma, Sudarshan Kurwadkar, Sudip Chakraborty, Tista Prasai Joshi, Achintya N. Bezbaruah, and Mallikarjuna N. Nadagouda*

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ABSTRACT: Arsenic (As) is abundant in the environment and can be found in both organic (e.g., methylated) and inorganic (e.g., arsenate and arsenite) forms. The source of As in the environment is attributed to both natural reactions and anthropogenic activities. As can also be released naturally to groundwater through As-bearing minerals including arsenopyrites, realgar, and orpiment. Similarly, agricultural and industrial activities have elevated As levels in groundwater. High levels of As in groundwater pose serious health risks and have been regulated in many developed and developing countries. In particular, the presence of inorganic forms of As in drinking water sources gained widespread attention due to their cellular and enzyme disruption activities. The research community has primarily focused on reviewing the natural occurrence and mobilization of As. Yet, As originating from anthropogenic activities, its mobility, and potential treatment techniques have not been covered. This review summarizes the origin, geochemistry, occurrence, mobilization, microbial interaction of natural and anthropogenic-As, and common remediation technologies for As removal from groundwater. In addition, As remediation methods are critically evaluated in terms of practical applicability at drinking water treatment plants, knowledge gaps, and future research needs. Finally, perspectives on As removal technologies and associated implementation limitations in developing countries and small communities are discussed.

KEYWORDS: Arsenic, Groundwater, Geochemistry, Occurrence, Mobilization, Remediation, Physiochemical Treatment, Biological Treatment, Passive Treatment
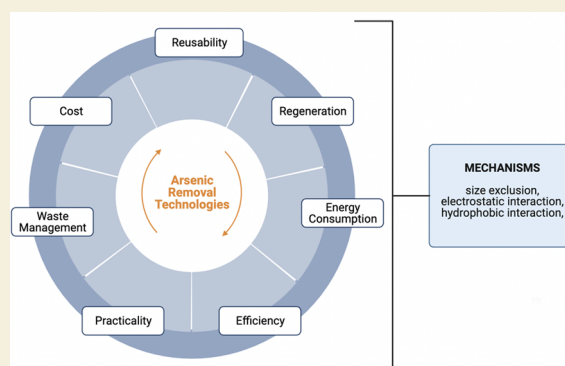
1. INTRODUCTION

Arsenic (As) has been widely used in medicinal and industrial applications. Yet, the health risks associated with arsenic exposure have not been recognized until the 20th century.[1] As present in various environmental matrices (i.e., water, soil, and air) and food can be attributed to both natural and anthropogenic sources.[2] More importantly, arsenic is the most toxic naturally occurring groundwater contaminant.[3,4] In fact, arsenic, particularly in its inorganic form, has been reported as a carcinogen and identified as highly problematic in drinking water.[5,6] It has been estimated that at least 150 million people globally drink water with elevated levels of arsenic.[7,8] Yet, according to the International Agency for Research on Cancer (IARC), arsenic is a Group 1 human carcinogen.[9,10] The U.S. Environmental Protection Agency (U.S. EPA), the U.S. National Toxicology Program, and the American Conference of Industrial Hygienists have also classified arsenic in their list of cancer-causing agents.[11] Aside from lung and skin cancer,[12,13] arsenic exposure also leads to ailments of the stomach, intestine, skin, respiratory system, kidney, and central nervous system.[14]

To protect human health, the World Health Organization (WHO) and the U.S. EPA have set a maximum contaminant level (MCL) of 10 μg/L for inorganic arsenic in drinking water.[15,16] To date, elevated arsenic levels in drinking water sources have been reported in more than 50 countries, affecting well over 200 million people.[17,18] Many aquifers worldwide have been identified with arsenic concentrations greater than 10 μg/L,[19−24] and these aquifer hotspots include Argentina, Bangladesh, Cambodia, China, India, Mexico, Nepal, and many parts of the U.S. (Figure 1).[22,25−27] In many of these countries, groundwater was promoted as safe for

Figure 1. Distribution and occurrence of arsenic in major aquifers with a specific focus on arsenic contamination due to mining and geothermal sources. (Reprinted with permission from Smedley et al.[22] Copyright 2002 Elsevier).

drinking given the reduced likelihood of microbial contamination.[28] Even though microbial contamination was not present, groundwater sources in these countries were contaminated with naturally occurring subsurface arsenic. Further, arsenic is odorless, tasteless, and colorless, making arsenic detection in contaminated water a challenge even when present at high concentrations.[29]

Several techniques have been proposed to remove arsenic from groundwater including precipitation, coagulation/filtration, adsorption, ion exchange, lime treatment, oxidation, and membrane filtration.[8] However, the broader implementation of these technologies is challenged by cost and complex operation and maintenance, making them less desirable for remote and challenged communities. Yet, significant research efforts have been spent on identifying appropriate aqueous arsenic removal technologies that are cost-effective, easily operated, and require minimal experience, while having high arsenic removal rates. This paper reviews the geo-chemistry, occurrence, mobilization, and microbial interaction of arsenic in the aquifer. Various technologies potentially appropriate for small, challenged, rural, and remote communities are discussed, and the pros and cons of some of the technologies are highlighted. Finally, research gaps and potential research and development opportunities are discussed.

1.1. Occurrence of Arsenic

The source of As-contaminated groundwater is predominately subsurface geologic formations containing arsenic. While As may find its way to the environment because of anthropogenic reasons, the significant contribution to water contamination comes from arsenic-bearing minerals in the subsurface of the earth.[22,30−32] Even though the earth's crust only contains 0.0001% As, As is also found in virtually all rocks and sediments.[22,33] However, most geogenic As in contaminated groundwater comes from relatively recently deposited alluvial sediments.[27] The release of As depends on the redox and pH conditions, where under anoxic conditions, As leaches due to the dissolution of As-bearing iron minerals in the aquifer. As is released from iron and aluminum hydroxides under oxidizing and high-pH conditions.[19,27,34,35] In addition, low hydraulic gradient aquifers tend to have higher residence time leading to high concentrations of dissolved arsenic in groundwater.[27] Moreover, arsenic buildup in waters can be attributed to the

release of arsenic from arsenic-bearing sulfide minerals (via oxidation)-enriched geothermal deposits.[27]

In nature, As is present in organic, inorganic, and gaseous forms, but the inorganic form is relevant for immediate public safety. Inorganic arsenic can be present in the environment in four oxidation states (−3, 0, +3, +5) depending on the pH and redox conditions (Figure 2).[8,20] As(V) or arsenate ($H_3AsO_4^0$,

Figure 2. Effect of pH on the distribution of As (III), As(V), monomethylarsonic acid (MMA), and dismethylarsinic acid (DMA) at 25 °C. (Reprinted with permission from Sharma et al.[43] Copyright 2009 Elsevier).

$H_2AsO_4^-$, $HAsO_4^{2-}$, AsO_4^{3-}) is the dominant species in aqueous aerobic environments, while As(III) or arsenite ($H_3AsO_3^0$, $H_2AsO_3^-$, $HAsO_3^{2-}$) is prevalent in anoxic environments.[20,36−38]

Above a pH of 9, As(III) exists as an uncharged neutral molecule (H_3AsO_3), whereas As(V) occurs as an anionic molecule ($H_2AsO_4^-$, $HAsO_4^{2-}$) above pH 2 (Figure 3).[22,39,40] The transition from As(III) to As(V) involves a thermodynamically favorable process, but the transformation period can range from days to years, depending on the specific

Figure 3. Activity of electrons (E_h) as a function of pH for arsenic species in the aqueous system As−O₂-H₂O at the following conditions (25 °C and 1 bar). (Reprinted with permission from Smedley et al.[22] Copyright 2002 Elsevier).

environmental conditions. For example, environmental parameters including strong acidity and alkalinity as well as higher temperatures can enhance the oxidation process.[20] Low groundwater redox potential favors the formation of As(III) species. On the other hand, As(V) is the most thermodynamically stable state of arsenic in oxidizing environments (redox potential above 100 mV).[41] Recently, Huq et al. reported that the high levels of arsenic in the shallow Holocene alluvial aquifers in Bangladesh are attributed to mobilized arsenic due to strong reducing and moderate alkalinity conditions.[42]

1.2. Mobilization of Arsenic in Groundwater

A recent review paper reported that arsenic naturally leaches from sources including: (i) volcanic rocks, where emissions can reach miles from the source, (ii) metallic mineral deposits that can contaminate drinking water or the food chain, and (iii) deep geothermal reservoirs containing As-rich geothermal fluids contaminating freshwater sources.[44]

Oremland and Stolz (2003) have proposed four possible ways for the mobilization of subsurface arsenic:[37] (i) arsenic oxidation in pyrites that contain As, (ii) the release of As(V) from iron oxide reduction by autochthonous organic matters (e.g., peat leading to the release of As(V)), (iii) iron oxides reduction by allochthonous organic matters present in, for example, recharging waters, and (iv) displacement of As(V) by chemical analogue phosphate (PO_4^{3-}) present in fertilizers. Kurz et al. also reported that the arsenic mobilization in Vietnam's groundwater is attributed to both oxidation and adsorption reactions, where arsenic is immobilized onto freshly formed iron hydroxides due to oxygen.[45] As mobilization has also been reported in the upper Jhelum basin, located in the western Himalayas, and is attributed to the reduction of Fe and Mn oxy/hydroxides.[46]

The overall mobility of As in the aquifer is primarily driven by the adsorption and oxidation reactions of arsenic at the mineral water interface.[47] While As(V) is prevalent in the aqueous aerobic environment, an anoxic environment favors the presence of As(III). Adsorption, desorption, and biological transformation influence arsenic mobility in an aquifer. As(V) has affinity for some common elements and is easily bounded (adsorbed) to ferrihydrite and alumina.[37] In anoxic aquifer, As(III) is stable and dissolves in water as iron and manganese complexes.[48] A recent study reported that manganese (Mn) can impact iron and arsenic solubility in rice paddy soil.[49] As(III) often exists as neutral (uncharged) H_3AsO_3 species at environmentally relevant pHs (pK_a for H_3AsO_3 is 9.2). For typical groundwater pH (i.e., pH lower than 9.2), As(III) is less likely to interact with mineral surfaces, making it more mobile in the environment and of concern. Additionally, any arsenic otherwise coprecipitated and sorbed onto metal oxides (iron or manganese) may be reintroduced to the aqueous phase when the metal oxides are dissolved. However, in anoxic zones and in the presence of sulfide, As(III) is immobilized due to the formation of orpiment, realgar, or arsenopyrite or is coprecipitated with iron pyrite.[50]

Oremland and Stolz (2003, 2005) reported that certain prokaryotes use oxyanions of arsenic for their energy generation via As(III) oxidation or As(V) reduction.[37,51] These phylogenetically diverse microorganisms can mobilize aquifer arsenic from the solid to the aqueous phase (Figure 4). These researchers advocated that the chemical and biological arsenic mobilization and speciation processes may be simultaneous. These microorganisms play important roles in
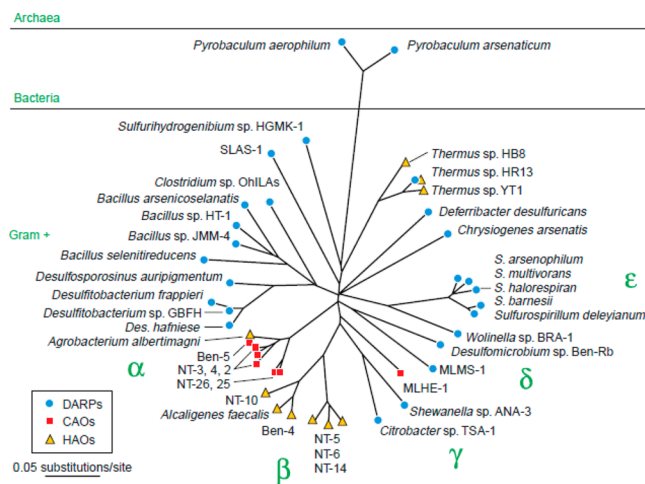
Figure 4. Arsenic-metabolizing prokaryotes present in waters. The D's represent dissimilatory arsenate-respiring prokaryotes (DARPs), the H's represent heterotrophic arsenite oxidizers (HOAs), and the C's represent chemoautotrophic arsenite oxidizers (CAOs). (Adapted with permission from Oremland et al.[51] Copyright 2005 Elsevier).

the oxidation and reduction of not only arsenic but also iron mineral present in the aquifers. A conceptual model for the arsenic problem in Bangladesh aquifers has also been proposed.[37,51] It is important to note that aquifers in Bangladesh are considered highly contaminated with arsenic and more than one-quarter (40 million+) of its total population is exposed to arsenic-contaminated drinking water. The conceptual model developed for Bangladesh aquifers proposed that chemoautotrophic arsenite oxidizers (CAOs) and heterotrophic arsenite oxidizers (HAOs) first oxidized As(III)-containing minerals (e.g., arsenopyrite) leading to deposition (adsorption) of As(V) on the oxidized minerals (e.g., ferrihydrite). The overpumping of an aquifer to meet drinking and irrigation needs resulted in lowering of the groundwater tables and has led to the further oxidation of As(III) by oxidants (e.g., molecular oxygen and (agricultural) nitrate). Over time, the buildup of organic matter and biomass causes the aquifers to become anoxic. Such organics and forms of peats can lead to the dissimilatory reduction of earlier converted As(V) and dissolution of arsenic adsorbents like ferrihydrite, where dissimilatory arsenate-respiring prokaryotes (DARPs) participate. Thus, arsenic is released to the aqueous phase (Figure 4).

Das et al. (2004) also proposed oxidation of arsenic-rich pyrite as one of the mechanisms that explain arsenic mobilization in the aquifer.[52] The reduction of iron oxyhydroxides and adsorption competition on the surface of iron oxides are other reasons for arsenic mobilization.[34,53,54] Liao et al. examined the relevant microbial community in arsenic-contaminated aquifers and indicated that a relatively diverse community of microorganisms can biotransform arsenic in the aquifer,[55] via detoxification and energy conservation reactions.[56] Most studies have identified methylation, demethylation, oxidation, and reduction as the primary microbial processes involved in arsenic transformation and mobilization.[37,57]
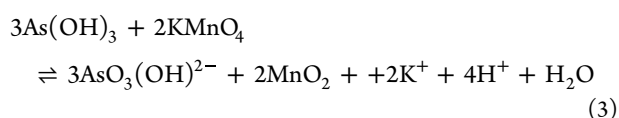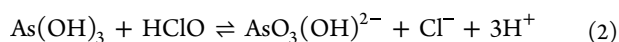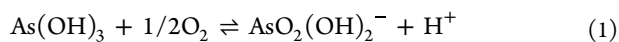
2. TECHNOLOGIES FOR ARSENIC REMOVAL FROM DRINKING WATER

The conventional arsenic removal processes include chemical-aided sedimentation, coagulation and flocculation, adsorption, ion exchange, and membrane processes.[57−59] The advantages and limitations of these existing technologies have been previously reported in detail.[60] In fact, high arsenic removal rates can be achieved with these process (80−100%). While these processes work well for municipal water utilities and resourceful communities, they may be cost-prohibitive when implemented at a small scale for rural communities. Furthermore, these practices are only efficient in removing As(V), and sometimes a pretreatment step (i.e., peroxidation unit process) is needed to oxidize As(III) to As(V) for effective arsenic removal.[58] As for the bench scale, the laboratory-based arsenic removal techniques include arsenic precipitation with Fe/Mn, lime softening, electrodialysis, ion exchange, adsorption on activated alumina/carbon, and others.[61] In the next section, the state-of-the-art methods for the removal of arsenic from water are discussed based on their relevance for potential use in small and remote communities as well as potential sustainability aspects.

2.1. Oxidation

Arsenic may be mainly present in groundwater as As(III) and/ or As(V) depending on solution pH and redox conditions.[22] As(III) is generally more mobile than As(V), so arsenic immobilization can be facilitated by As(III) oxidation to As(V).[20,62] The selection of appropriate oxidant materials for the oxidation of As is important and must consider the potential residuals of the oxidant used, oxidation byproducts, oxidation of other present water constituents, and the amount of the oxidant required (i.e., economics, worker safety, and storage requirement).

To date, the most feasible and common oxidants for As(III) are chlorine, potassium permanganate, ozone, manganese dioxide, hydrogen peroxide (in Fenton's reagent and involving Fenton-like reactions), and persulfate.[63] UV oxidizes As(III) to As(V) very quickly, generally within seconds, and UV irradiation can be achieved using high-pressure mercury arc discharge lamps with a 190−254 nm emission spectrum. Similarly, ozone-based oxidation is very fast and often used in surface water treatment for oxidation and disinfection.[64] When used for arsenic oxidation (Figure 5), ozone reportedly achieved more than 96% oxidation of As(III) to As(V) within 10 min. Both UV and ozone require high-energy inputs, which may not be cost-effective for small-scale water treatment plants. Given their abundance, oxygen, chloride, and permanganate deserve additional discussion (eqs 1−3).

$$As(OH)_3 + 1/2O_2 \rightleftharpoons AsO_2(OH)_2^- + H^+ \tag{1}$$

$$As(OH)_3 + HClO \rightleftharpoons AsO_3(OH)^{2-} + Cl^- + 3H^+ \tag{2}$$

$$3As(OH)_3 + 2KMnO_4$$
$$\rightleftharpoons 3AsO_3(OH)^{2-} + 2MnO_2 + +2K^+ + 4H^+ + H_2O \tag{3}$$

While As(III) can be oxidized into As(V) by atmospheric oxygen (eq 1), the process is very slow and can take weeks.[65] When pure oxygen was used, a maximum oxidation of 57% occurred in 5 days.[66] Chlorine is a widely deployed disinfectant in most water systems across the globe and can oxidize arsenite
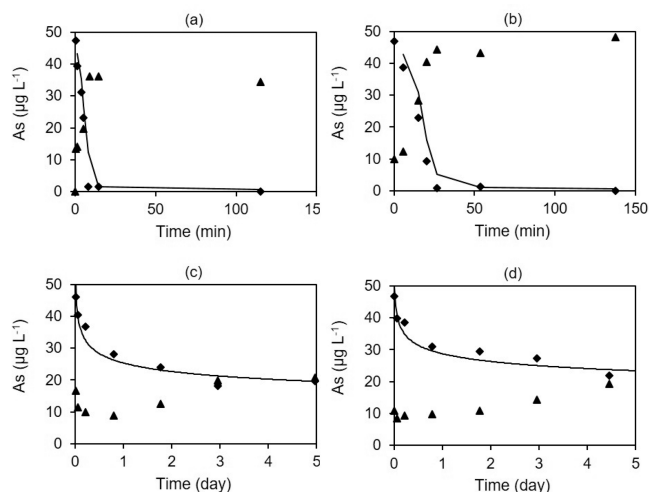
Figure 5. Concentration of arsenic in groundwater over time during oxidation: As(III) (◆) and As(V) (▲). (a) Sectoral Information System (SIS) (ozone), (b) S2S ozone, (c) S1S (oxygen), and (d) S1S (air). (Reprinted with permission from Kim et al.[64] Copyright 2000 Elsevier).

to arsenate. Hypochlorite is a popular source for chlorine that oxidizes As(III) to negatively charged As(V) (eq 2). The use of chloramine and chlorine dioxide has also been reported.[67] Similarly, KMnO$_4$ (α-MnO$_2$) can oxidize As(III) to As(V) (eq 3). Manganese dioxide has also been used by some small drinking water systems for As(III) oxidation.[68]

The Fenton's reagent process has also been studied for oxidation of arsenic. The ferric ions formed in the process lead to precipitation of As(V). However, the residual hydrogen peroxide should not exceed the maximum permissible limit of hydrogen peroxide (i.e., 1 mg/L) to avoid potential toxicity for the consumers. Krishna et al. reported that adding 100 μL of H$_2$O$_2$ and 100 mg/L of Fe(II) (as ferrous ammonium sulfate) followed by adsorption (medium: zerovalent iron (ZVI)), with a contact time of 10 min, is capable of reducing As(III) from 2 mg/L to below 10 μg/L (Figure 6).[69]

Some researchers have demonstrated that reactive oxidizing species (e.g., hydroxyl radical, ·OH) can be produced during the photolysis of nitrite (NO$_2^-$) or nitrate (NO$_3^-$) and can convert As(III) to arsenate As(V). UV photolysis of NO$_2^-$ and NO$_3^-$ promotes the breakage of the O−N bonds producing
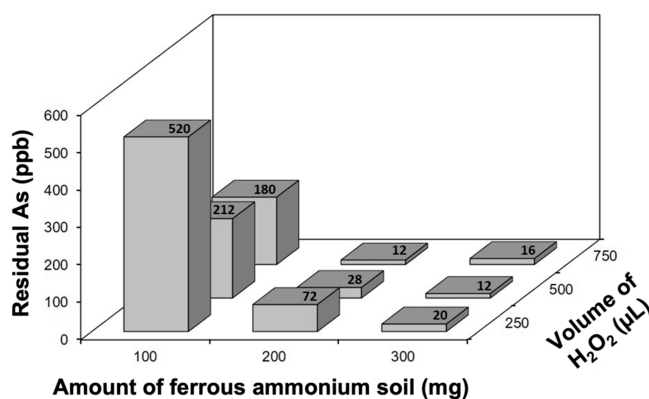

Figure 6. Residual arsenic after treating groundwater with Fenton's reagent. (Adapted with permission from Krishna et al.[69] Copyright 2001 Elsevier).

intermediate products that can serve a dual purpose: photochemically transform contaminants in an aqueous medium and oxidize chemical and microbial contaminants in water. The main reactions involved in this UV/As(III)/(NO$_2^-$) or (NO$_3^-$) system have been described in detail by Kim et al.[70] Briefly, the photolysis of NO$_2^-$ or NO$_3^-$ mainly generates nitrogen oxide radical and oxide radical anion, which in turn undergoes protonation to form ·OH. Even though As(III) was not directly oxidized via UV photolysis, adding 20 or 200 μM nitrite promoted the oxidation of As(III) under UV irradiation (λ > 295 nm), making NO$_2^-$ a photosensitizer for As(III) oxidation.[70] Another study reported the use of glow discharge plasma (GDP) to simultaneously oxidize and immobilize organoarsenic. The results showed that Roxarsone (ROX) (an organoarsenic compound) can be effectively oxidized to inorganic arsenic, but the process was energy-intensive. The addition of Fe(II) significantly enhanced the oxidation of ROX, mainly due to the additional ·OH generated via Fenton reaction in GDP coupled with simultaneous arsenic immobilization. The immobilization of arsenic was favorably obtained at a pH range of 4−6 and a 500−1000 μM Fe(II) concentration range.[71]

Future oxidation−reduction studies should focus on providing additional information about the rates of arsenic reactions and determining their specific rate constants.

2.2. Coagulation−Precipitation Process

2.2.1. Alum and Iron Precipitation. Coagulation is commonly used in drinking water treatment to destabilize dissolved and suspended solids allowing their aggregation to form flocs, which are subsequently removed via sedimentation.[72] The process can be described in three steps: (i) coagulant addition and colloid destabilization (rapid mix), (ii) interparticle collisions and colloid agglomeration (coagulation), and (iii) colloid removal via floc sedimentation (last phase of coagulation and then settling). To treat arsenic-laden water, coagulants are added, which, in turn, form arsenic-containing flocs of low solubility, which then settle and are removed by sedimentation. While calcium salts[73] and lanthanum salts[74] have been used in the water treatment industry, alum (aluminum sulfate),[75−77] ferric chloride, and ferric sulfate are the most widely used coagulants for arsenic removal (eqs 4−6).[78−83] Alum is the preferred choice by many water treatment units.

alum dissolution:
$$Al_2(SO_4)_3 \cdot 18H_2O \rightleftharpoons 2Al^{3+} + 3SO_4^{2+} + 18H_2O \quad (4)$$
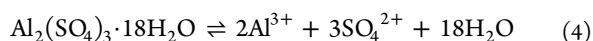
aluminium precipitation (acidic):
$$2Al^{3+} + 6H_2O \rightleftharpoons 2Al(OH)_3 + 6H^+ \quad (5)$$
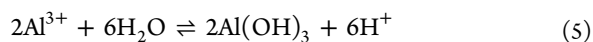
co-precipitation: $\quad H_2AsO_4^- + Al(OH)_3 \rightleftharpoons Al-As$
$$\text{(complex)} + \text{other products} \quad (6)$$

The possible reactions of arsenate with hydrous iron oxide ($\equiv$FeOH^0 represents the oxide surface site)[84] are listed below (eqs 7−9).

$$Fe(OH)_3(s) + AsO(OH)_3 \rightarrow FeAsO_4 \cdot 2H_2O + H_2O \quad (7)$$

$$\equiv FeOH^0 + AsO_4^{3-} + 3H^+ \rightarrow \equiv FeH_2AsO_4 + H_2O \quad (8)$$

$$\equiv FeOH^0 + AsO_4^{3-} + 2H^+ \rightarrow \equiv FeHAsO_4^- + H_2O \quad (9)$$
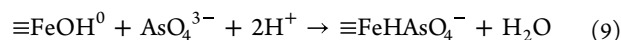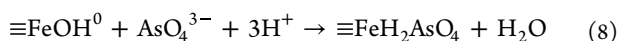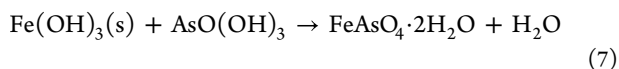
Immobilization of arsenic by hydrous iron oxide is another process of interest (eqs 7−9) that is highly influenced by the pH of the solution.[72] In one study, using a high dosage of FeCl$_3$ (i.e., 300 mg/L), arsenic was highly reduced to less than 5 μg As/L in the coagulated water.[85] Using the same coagulant, only 50−60% As(III) removal was achieved.[86,87] Under pH 5−6, As(V) adsorption onto hydrous iron oxide and goethite was higher than that of As(III), whereas, above pH 7−8, As(III) adsorption was more favorable to these adsorbents.[88] In fact, in mineral processing effluents, lime neutralization and coprecipitation of arsenate with iron has been implemented for the removal and immobilization of arsenic.[89] Arsenic coagulation with iron, aluminum, and zirconium salts has also been reported.[90]

A recent study reported an efficient and fast arsenic removal technology known as air cathode assisted iron electro-coagulation (ACAIE) enabled with in situ generation of hydrogen peroxide. During ACAIE operation, Fe(II) is readily oxidized and As(III) was completely removed. These authors demonstrated that within a short time frame (30 s), and at a charge dosage rate of 1200 Coulomb/L/min, ACAIE consistently outperformed iron electrocoagulation (FeEC) by reducing arsenic levels to below the 10 μg/L WHO level (Figure 7).[91]
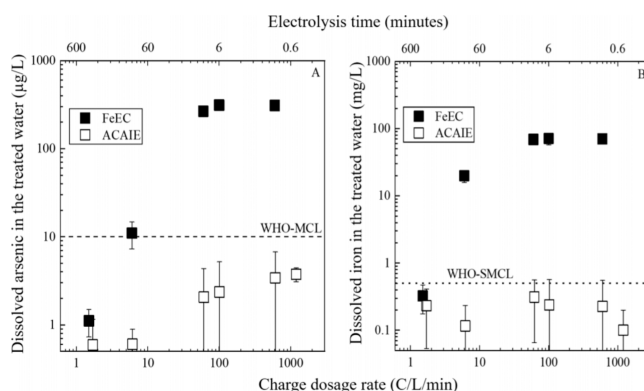
Figure 7. Dissolved arsenic (A) and iron (B) effluent concentrations after electrolysis as a function of carbon dioxide removal (CDR) in the FeEC (■) and ACAIE (□) systems. Total charge dosage of 600 C/L and initial As(III) concentration of 1464 ± 83 μg/L). (Reprinted with permission from Bandaru et al.[91] Copyright 2020 American Chemical Society).

A recent study investigated a mixture salt composed of cactus mucilage and ferric (Fe(III)) salt to remove arsenic from water. Mucilage treatment improved As removal compared to only Fe(III) treatment, where the system achieved an As removal efficiency of 75−96% within 30 min.[92]

2.3. Lime Softening

Arsenic can also be removed during lime softening processes using calcium hydroxide (Ca(OH)$_2$) and soda (Na$_2$CO$_3$). Similar to other processes, the arsenic removal efficiencies are enhanced if arsenic in the water is oxidized from As(III) to As(V). A recent survey on 516 full-scale water treatment plants[93] reported that hard water tends to have a higher concentration of arsenic compared to soft water. However, up to 90% of the soluble As(V) could be potentially removed if a high softening pH was used to precipitate magnesium. McNeill

and Edwards (1997) reported that 90% arsenic removal can be achieved via precipitation softening with iron.[94] pH and the presence of chlorine govern the removal of arsenic in the lime softening process. For example, only 15% arsenic removal was possible in nonchlorinated water containing 400 μg/L arsenic at a pH less than 10.5. However, when the pH was adjusted to 11, arsenic removal reached 80%.[95] Sorg and Logsdon (1978) also demonstrated that pH impacts the removal of arsenic during lime softening. Low As(III) and As(V) removal efficiencies were achieved at pH values less than 10, but As(V) and As(III) removal approached 100% and 75%, respectively, at pH values greater than 10.5.[96]

2.4. Adsorption

Activated carbon, activated alumina, zerovalent iron, iron oxides, and clay are among the adsorbents that have been deployed to remove arsenic from water. Rapid small-scale column testing (RSSCT) procedures for arsenic were developed similar to those used for adsorption of organic constituents by granular activated carbon (GAC). However, it is important to note that there are significant differences between adsorption of organics by GAC and adsorption of arsenic by metal oxides. The most prominent differences are the nature of the bonds and the internal pore structure of the adsorbents. Hydrophobic bonds are dominant between organic solutes and GAC, whereas arsenic adsorption onto metal oxide surfaces is initially attributed to electrostatic attraction. RSSCT allows full-scale results to be obtained in a short time with a fragment of the processed water and samples collected and analyzed.[97] Thomson et al. used RSSCT to investigate arsenic adsorption using activated alumina, ferric oxyhydroxides, and a proprietary medium developed by Sandia National Laboratories.[98]

Activated alumina (AA) or granular ferric oxides and hydroxides are the optimal adsorbents due to their abundance, high arsenic removal efficiency, and ease of operation.[99] Research studies have also evaluated industrial byproducts, montmorillonite clay, and other activated carbon-based adsorbents to remove arsenic from aqueous solutions, which exhibited low adsorption capacities. Low-cost natural adsorbents such as *Moringa oleifera* were investigated with favorable arsenic removal results (>60% removal of As(III) and >80% of As(V)) and regeneration potential.[100] Magnetic biochars prepared by chemical co-precipitation of Fe^{2+}/Fe^{3+} on a biomass (i.e., water hyacinth) followed by pyrolysis showed that it is a highly efficient adsorbent for aqueous As(V) removal.[101]

Prasai et al. studied the interactions of organoarsenic compounds with ferric and manganese binary oxide (FMBO) to elucidate the mechanism that governs adsorption, and the adsorption performance was compared to that of ferric oxide (FeOOH) and manganese oxide (MnO_2).[102] The maximum adsorption capacities (Q_{max}) of FMBO toward aromatic organoarsenic compounds including p-arsanilic acid (p-ASA) and roxarsone (ROX) were 0.52 and 0.25 mmol/g, respectively, at pH = 7.5, which were higher compared to those of FeOOH and MnO_2. The corresponding Q_{max} values of p-ASA were 0.40 and 0.33 mmol/g, and those for ROX were 0.08 and 0.07 mmol/g, respectively.[102]

2.4.1. Activated Alumina. Activated alumina (AA) is considered to be an adsorbent material even though ion exchange takes place.[103] A series of cerium oxide composites of AA have been prepared and employed as adsorbents for arsenic

removal from water. The adsorption capacity of these composites ($Al_2O_3-CeO_2$) depended on the preparation conditions. The highest adsorption capacity of arsenic was achieved when CeO_2 was deposited on powdered AA (6 g) at a 0.5 mol ratio of H_2O_2/Ce. More specifically, arsenic adsorption was optimal when the nanosize CeO_2 was deposited on the Al_2O_3 support, where a Langmuir adsorption isotherm model was followed with Q_{max} of 13.6 and 10.5 mg/g for arsenate and arsenite, respectively (Figure 8).[104]
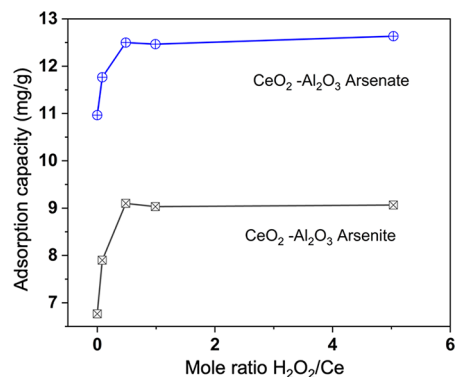

Figure 8. Impact of H_2O_2/Ce mole ratio on As adsorption capacity. Data obtained from Nakamoto et al.[104]

Regeneration of saturated alumina can be achieved by exposing the medium to a strong base (e.g., NaOH). Using pilot filters, Frank and Clifford (1986) demonstrated that As(III) is not removed by activated alumina but As(V) is adsorbed, and breakthrough may occur at 10 000−20 000 bed volumes (As initial concentration of 100 ppb and pH = 6).[105] Figure 8 shows the removal kinetics on alumina at a pH of 6. Giles et al. reported the use of iron and aluminum-based adsorbents for As removal and further discussed the oxidation of As(III) to As(V) using various oxidizing agents to facilitate As adsorption (see Section 2.1).[106]

2.4.2. Zero-Valent Iron and Iron Oxide. The adsorption of arsenic by iron oxides is a very important process because it occurs naturally in the environment and is highly favorable under oxidizing and slightly acidic conditions. It can also be engineered and configured as a removal mechanism during water treatment. Granular ferric oxide Bayoxide E33 and granular ferric hydroxide GFH are iron-based media frequently used as adsorptive media in small drinking water systems in the U.S.[107] Unlike activated alumina, iron-based media are not typically regenerated and require periodic media replacement. A recent high-resolution imaging analysis demonstrated that arsenic atoms diffuse preferably along the grain boundary of iron oxides explaining the surface sorption or surface complex formation of arsenate on ferric hydroxide (FeOOH).[108] Understanding the effectiveness of this removal technology across a wide range of environmental conditions can improve As removal in water treatment plants and provide an accurate prediction of As transport through soils and aquifers.

In situ chemical immobilization has been used to reduce arsenic contamination in soils by applying iron amendments to contaminated soils and, thus, reducing As mobility and bioavailability in the soil.[109] While there have been many studies focused on arsenic adsorption using iron oxides, the specific mechanisms that govern how adsorption changes with pH and redox conditions remain unclear.
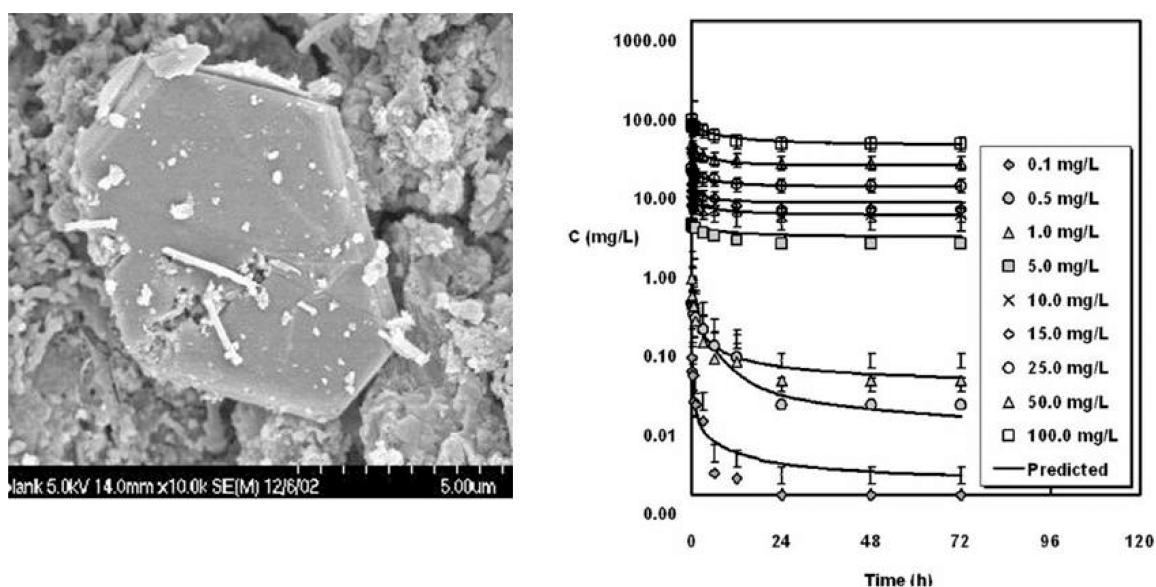
Figure 9. SEM image of blast furnace slag (left) and As adsorption change over time for a specific initial As(III) concentration; initial As(III): 0.01−100 mg/L, slag dose: 10 g/L, pH: 12 (right). (Reprinted with permission from Kanel et al.[118] Copyright 2006 American Chemical Society).

Surface complexation and electrostatic models can predict the effectiveness of As removal using iron oxides. The accurate prediction of adsorption performance is difficult because of assumptions incorporated into various models. Different approaches can be taken to model the adsorption phenomena occurring at the sorbent surface including the diffuse double-layer model of Dzombak and Morel that predicts arsenic adsorption by iron oxides.[110] However, this model was derived for synthetic solutions and does not account for the competitive interactions found in real complex systems. More importantly, the database contains a limited amount of experimental data.[110] On the other hand, the CD-MUSIC model of Hiemstra and van Riemsdijk[111] is more promising but more complex. Additional work with model verification and validation is required to improve the output of these products.

The use of mineral oxides in small-scale water treatment systems may be feasible for arsenic removal, but additional studies are needed to evaluate their performance in treating highly concentrated arsenic-laden industrial effluents. Over the years, zerovalent iron (Fe^0) has been used as a permeable reactive barrier medium for the removal of various groundwater contaminants,[112] including various chlorinated hydrocarbon compounds through reductive dehalogenation.[113,114] Su et al. also reported that Fe^0 has been used to remove arsenic from groundwater and performance was impacted by reaction time, pH, and oxidation reduction potential.[112] In another study, Pierce et al. reported that using 4.45 mg/L of $Fe(OH)_3$ resulted in arsenite removal efficiency of at least 50%.[65] A ferric-based layered double hydroxide intercalated with alpha-alanine was synthesized by a coprecipitation method to remove As(III) from water.[115] Nanoscale iron–manganese binary oxides have also been tested in column experiments for the removal of both As(III) and As(V) from aqueous media.[116]

Zerovalent iron (ZVI) is one of the widely used adsorbents for the rapid removal of As(III) and As(V) in the subsurface environment.[117−120] The large size, lower surface area, and lack of mobility of ZVIs have limited their applications shallow groundwaters. To overcome these limitations, nanoscale zerovalent iron (nZVI) has been studied due to its high surface area and reactive properties.[121] nZVIs have shown great potential for As removal from groundwater sources.[122,118,123] Both As(III) and As(V) were removed from real water matrices containing dissolved natural organic matter.[118,123] As(III) may be adsorbed either onto nZVI or can be oxidized to As(V) and adsorbed on nZVI surface.[124−126] Ezzatahmadi et al. reviewed the adsorption performance of clay minerals, zerovalent iron materials, and clay-supported nZVI composites in removing various heavy metals including arsenic from aqueous solutions. Clay-supported nZVI composites achieved the highest removal efficiency for various contaminants including arsenic.[124]

Recently an iron-anode enhanced sand filter was employed to remove arsenic with initial concentration of 196−472 μg/L to below 10 μg/L from tube well water in the Jianghan Plain, central China. A current of 0.6 A and a flow rate of about 12 L/h were used, and the residual As was about 110 μg/L without electricity.[127]

2.4.3. Industrial Byproducts. Metal oxides and hydroxides of iron or alumina[128] have been widely studied for the removal of As from water and wastewater. However, there is an urgent need to develop cost-effective, efficient, and sustainable adsorbents that can be implemented in developing countries.[129] Several industrial byproducts including red mud,[129] neutralized red mud, fly ash, ferruginous manganese ore,[130] Fe(III)/Cr(III) hydroxide waste,[131] and steel slag[117] have been evaluated for the removal of arsenic from water. Steel slag (basic oxygen furnace slag (BOFS) and blast furnace slag (BFS)) are steel industrial byproducts, having FeO and CaO as their main components, and are considered one of the cheapest widely available materials.[132] More importantly, iron oxide and calcium oxide are important components, due to the strong bonding capacity and ability to stabilize sludge produced after As adsorption, making BOFS and BFS good candidates for As adsorption. From an environmental perspective, BOFS recovered from high temperature is safe since metals are well-stabilized and do not leach easily.[133] Figure 9 shows a scanning electron microscopy (SEM) image

of the steel slag and the As adsorption kinetics to steel slag, showing that total As can be effectively removed.[117]

2.4.4. Clay. In addition to As adsorption being influenced by the concentration of the arsenic, the chemical and physical properties of aquifer materials affect As adsorption. The clay fraction has been identified as a major sink for arsenic contamination. The composition of the clay is also one of the fundamental factors affecting the biological toxicity of As.[134] The pH and cation exchange capacity (CEC) of the subsurface material affect adsorption. The form of arsenic species impacts adsorption onto clay minerals as a function of pH. The maximum adsorption capacity of As(V) onto kaolinite and montmorillonite was found to be at pH 5, whereas the As(III) adsorption increased beyond this pH. For example, at pH = 8, more As(III) was adsorbed compared to As(V).[47,135,136] The effect of pH can also be observed with other adsorbents, where the As(III) adsorption onto alumina, bauxite, and carbon decreases at pH greater than 7.[137]

As(V) adsorption onto clay minerals has been studied using batch experiments as a function of pH and NaCl. Four clay minerals (i.e., illite, kaolinite, montmorillonite, and chlorite) were selected due to their abundance in sediments and their different crystalline structure. Increasing NaCl concentration enhanced As(V) adsorption, indicating that surface complexes were formed, in which Na^+ ions served as bridges between the clay surface and the As(V) anions.[138] In a different study, the effects of dissolved calcium (Ca^{2+}) and pH on As(V) reactivity and surface speciation were investigated using adsorption performance experiments and extended X-ray absorption fine-structure spectroscopy (EXAFS) analyses. EXAFS analysis revealed that As(V) tetrahedral molecules were coordinated on aluminum octahedral via bidentate binuclear bonding at pH 4.5−6.75.[139]

Sund et al. also studied the adsorption of arsenites with four different Indian soils with different CECs and pH values.[140] The adsorption of arsenic was impacted by the fraction of sesquioxide, clay, and the concentration of exchangeable Ca^{2+} and Mg^{2+} in the soils. The amount of arsenic sorbed to soils, including clayey brown, degraded chernozem, slightly gray, sod-alluvial carbonate, and carbonate meadow was influenced by the soil solution pH. Galba et al. indicated that, in strongly acidic soils, arsenic sorption was localized mainly on the surface of clay minerals, while in weakly acidic soils, colloidal sesquioxides participated in the arsenic sorption. In extremely alkaline environments (pH > 11), calcium arsenate complexes were found.[141] The quantity of arsenic adsorbed by soil increased with increasing initial concentration.[141]

Coexisting ions can impact arsenic sorption in the environment, as ions tend to compete for sorption sites or can form complexes with arsenic. Similar to arsenate, phosphate strongly competes for sorption sites on iron oxides, soils, and sediments, whereas anions including Cl^- and SO_4^{2-} have no or slight impact. On the other hand, organics can form complexes with arsenic, increasing its mobility and decreasing its sorption. Manning et al. reported the fractionation of added As(III) to three soils: Fallbrook, Panoche, and Indio.[142] Fallbrook and Panoche soils displayed greater adsorption and oxidation compared to Indio soil. Yet, for all three soils, the total recoverable As(III) consistently decreased for 48 h, due to the slow intraparticle diffusion of both As(III) and As(V). Following adsorption, oxidation of As(III) to As(V) occurred, which then partitioned between the solid and solution phases.

Soil can oxidize As(III) to As(V), which is very important in the cycling of arsenic species.[143]

2.4.5. Activated Carbon. Activated carbon has been widely deployed as a point-of-use treatment for waters containing metals.[144] Arsenic removal by chemically treated activated carbon at ambient pH[145] is more effective for As(V) removal than As(III) removal. A relatively large quantity of carbon is required to effectively remove As(V) from solution. Recently, arsenic removal from water by δ-MnO_2 modified activated carbon has been reported. Within the first 9 h, approximately 90.1% and 76.8% removal efficiencies of As(III) and As(V), respectively, were achieved, and adsorption equilibrium was achieved within 48 h.[146] The Q_{max} value of As(V) and As(III) at pH 4.0 was determined as 13.30 and 12.56 mg/g, respectively, using Langmuir adsorption isotherms.[146]

In a different study, Huang et al. studied arsenate adsorption by 15 different activated carbons[147] and found that arsenate adsorption depended on carbon type, pH, and arsenic concentration. Contaminant removal has been investigated using virgin activated carbon, chemically treated activated carbon, and activated carbon impregnated with ferric hydroxide.[148,149] High As adsorption capacity to chemically treated activated carbon has been recently reported.[150] Activated carbon prepared from coconut and rice husks has been investigated for the removal of arsenic from water. Lee et al. reported the effect of dosages on uptake using carbon from quaternized rice husks with an optimal As removal efficiency of 86% and solid phase concentration of 3 mg As/g quaternized carbon at pH = 7.5.[151] Manju et al. evaluated the performance of coconut husk carbon (CHC) and copper impregnated coconut husk carbon (CICHC) for the removal of As(III) from water and demonstrated significant removal with a 4 h reaction time.[152] The As(V) adsorption kinetic process was similar to that of As(III), consistent with the results generated with the adsorption isotherm profiles of As(V) and As(III) by the δ-MnO_2-modified activated carbon (Figure 10).

2.5. Ion Exchange

During the ion exchange process, a reversible interchange of ions occurs between the solid and the liquid phase. The arsenic
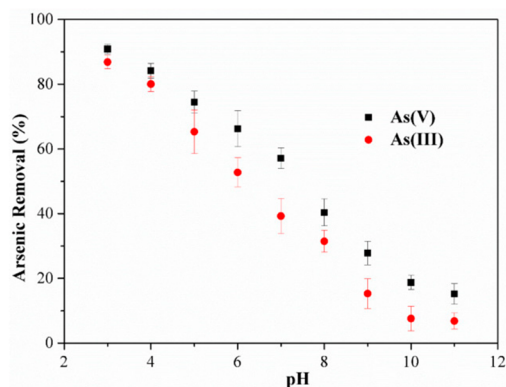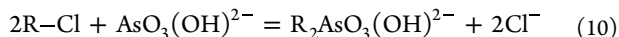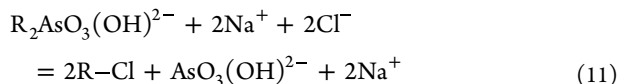
Figure 10. As(V) and As(III) adsorption profile on δ-MnO_2-modified activated carbon. Experimental conditions: adsorbent dose = 1.0 g/L, initial arsenic concentrations C_0 = 6.0 mg/L, and equilibration time of 48 h (Reprinted with permission from Wang et al.[146] Copyright 2020 Elsevier).

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exchange and regeneration with common salt can be represented by the following equations

Arsenic exchange:

$$2R-Cl + AsO_3(OH)^{2-} = R_2AsO_3(OH)^{2-} + 2Cl^- \quad (10)$$

Regeneration:.

$$R_2AsO_3(OH)^{2-} + 2Na^+ + 2Cl^-$$
$$= 2R-Cl + AsO_3(OH)^{2-} + 2Na^+ \quad (11)$$

where R = ion-exchange resin.

Recently, a tetrahedron ion-exchange resin filter assessed in Bangladesh has shown promise in removing arsenic from water. As expected, the bed volumes to arsenic breakthrough decreased as sulfate concentration increased from 0 to 150 mg/L . An additional increase in sulfate concentration (>150 mg/L) exhibited a slight increase in bed volumes to arsenic breakthrough.

The applicability of ion exchange (IX) has been well-studied along with competing water constituents (e.g., SO_4^{2-} for IX) and regeneration requirements.[153] Magnetically impregnated ion-exchange (MIEX) has also been used as a medium for arsenic removal via ion exchange. Incorporating iron into the matrix combines favorable iron−arsenic interactions with the ionic exchange mechanisms. As(V) was removed using an iron-impregnated ion exchange bed.[154] A new class of environmentally friendly starch-bridged magnetite nanoparticles was developed and evaluated for removal of arsenate from spent IX brine. 0.049% (w/w) of the low-cost, "green" starch was used as a stabilizer to prevent the agglomeration of nanoparticles while preserving their high arsenic adsorption capacity (Figure 11). When this adsorbent was used to treat a synthetic spent
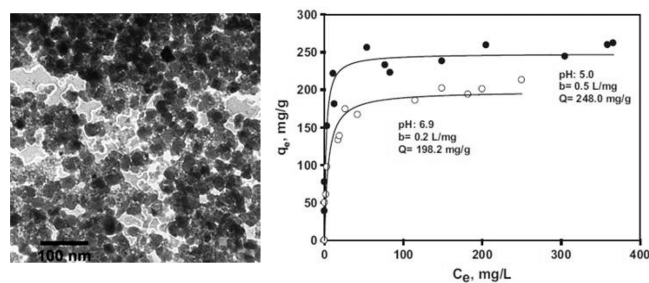
Figure 11. Starch-stabilized magnetite particle (left) and arsenate adsorption profile for starch-bridged magnetite particles at pH 5.0 and pH 6.9 (final pH) using a spent brine solution (Fitted using Langmuir model). Brine compositions: initial As (V): 17 mg/L, SO_4^{2-}: 600 mg/L, HCO_3: 305 mg/L, NaCl: 6 wt % (w/w). (Reprinted with permission from An et al.[156] Copyright 2011 Elsevier).

IX brine, complete arsenic removal was achieved within 1 h, compared to only 20% removal when bare magnetite particles were used. The Langmuir adsorption capacity was determined as 248 mg/g at pH 5. Increasing NaCl concentration from 0 to 10% (w/w) in the brine slightly impacted the adsorption capacity of arsenic.[155]

Recently, arsenic removal from geothermal water has been studied using a hybrid system consisting of novel 1JW, 2JW, and 2PTN resins along with Dowex XUS 43594.00 resin (Figure 12).
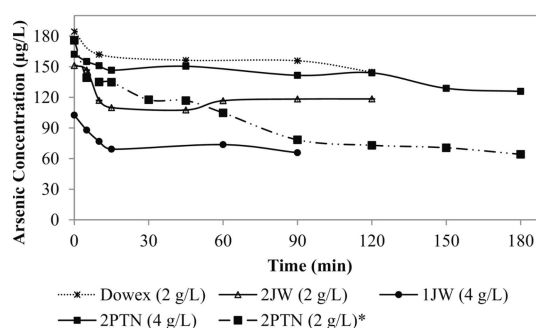

Figure 12. Arsenic concentration in permeate over time profiles for commercial and novel chelating resins. (Reprinted with permission from An et al.[156] Copyright 2011 Elsevier).

2.6. Membrane Techniques

Several membrane technologies have been used for the removal of arsenic from water (e.g., nanofiltration (NF), reverse osmosis (RO), and electrodialysis). Membrane separation offers several advantages including ease of operation, no addition of chemicals, and high performance, as many contaminants including bacteria, salts, and other heavy metals could be potentially removed. Clifford et al. found that reverse osmosis could effectively remove 98−99% of As(V), while As(III) was partially removed (46−75%) due to the neutral form of As(III) as H_3AsO_3.[157] Yet, the low water recovery rates, the high transmembrane pressure requirements, the relatively high capital and operating costs, and membrane fouling hamper the wide spread of membrane technologies.

Nanomaterials have been increasingly used in membrane technologies for arsenic treatment. Recently, a TiO_2-coated carbon nanotube (CNT) network membrane, prepared via a simple filtration−steam hydrolysis method, was evaluated for arsenic removal. The TiO_2 coating uniformly covered the CNT network surface with an ∼2-fold greater specific surface area than that of the bare CNT network. The TiO_2−CNT As sorption kinetics increased with increasing cell potential, as shown in Figure 13.[158]
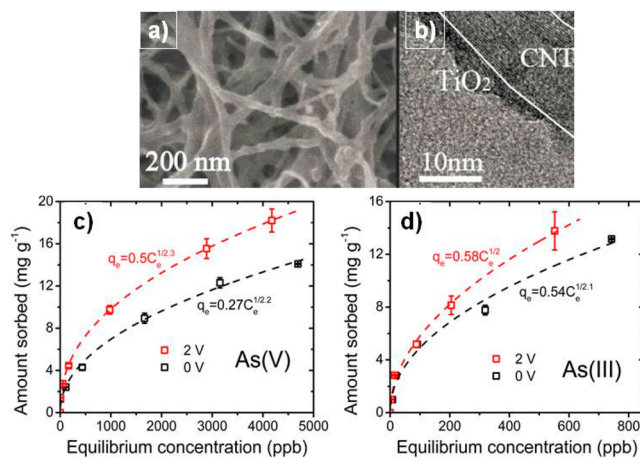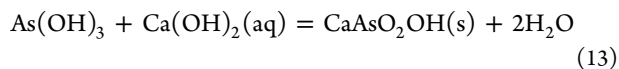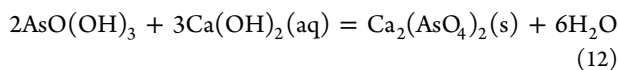

Figure 13. (a) SEM image of TiO_2 CNT, (b) TEM image of TiO_2 CNT, adsorption isotherms of (c) As(V) and (d) As(III) on TiO_2−CNT (Reprinted with permission from Liu et al.[158] Copyright 2014 American Chemical Society).

2.7. Stabilization of Arsenic-Bearing Waste Solids

In this procedure, arsenic waste (e.g., As-loaded or spent adsorbent) is stabilized by adding chemicals (e.g., cement, lime) to avoid costly disposal of hazardous waste. The stabilization of arsenic adsorbed by this process has been investigated by various researchers.[159−161] In one study, Comba et al. investigated arsenic removal from solution by forming mimetite, a lead arsenate chloride mineral (Pb$_5$ (AsO$_4$)$_3$ Cl).[162] Aqueous arsenic concentrations were reduced from several mg/L to 0.2 μg/L, and a phosphate/arsenate solid solution (phosphomimetite) was formed. Cement or cement lime has also been used to stabilize various arsenic-bearing materials,[163,164] calcium and iron arsenate contaminated soil, and ferric hydroxide precipitated soils in the presence of chloride and phosphate. In a different study, Diamadopoulos et al. studied As(V) removal from aqueous solution by fly ash and found that arsenic adsorption was almost irreversible with arsenic removal of more than 80% at a pH of 4.[165]

Cornwall et al. provided guidelines for disposing waste resulting from arsenic removal processes, which serve as a good reference for water utilities on how to dispose residuals containing elevated concentrations of arsenic.[166] Sullivan et al. also reviewed the disposal of water treatment As wastes, with a particular emphasis on solidification/stabilization (S/S) technologies.[167] As can be treated by Portland cement/lime mixes, oxidation of As(III) to As(V), and the formation of calcium−arsenic compounds using binders such as geo-polymers and activated alumina.[167] Arsenites can chemically bond with hydrated lime to form precipitates as follows.[168]

$$2AsO(OH)_3 + 3Ca(OH)_2(aq) = Ca_2(AsO_4)_2(s) + 6H_2O \tag{12}$$

$$As(OH)_3 + Ca(OH)_2(aq) = CaAsO_2OH(s) + 2H_2O \tag{13}$$

Dutre et al. also investigated S/S of arsenic-containing waste and the behavior of arsenic in leachate.[168] The mechanism that governs the S/S of As-contaminated soils including Portland cement (PC) and cement kiln dust (CKD) was explained using various analytical tools including X-ray powder diffraction (XRPD), X-ray absorption near edge structure (XANES), and extended X-ray absorption fine structure (EXAFS) spectros-copy. As immobilization after stabilization was evaluated using a 1 N HCl extraction according to the Korean Standard Test (KST). After 1 day and 7 days of treatment with 30 wt % PC and 50 wt % CKD, respectively, the level of As leaching from the amended soils was less than 3 mg L^{-1} (i.e., the Korean countermeasure standard).[169]

In situ S/S offers three main advantages including being a well-established, efficient, and cost-effective approach; requires no secondary treatment; and more importantly, poses no risk to site workers through As exposure.[170] Influence of the addition of fly ash on S/S performance is reported in Figure 14. It was found that addition of cement-stabilized arsenic waste stabilized the arsenic.[171]

2.8. Natural Attenuation

Natural attenuation of As can occur when the dissolved phase is trapped by precipitation of secondary As minerals, coprecipitation/sorption reaction with Fe, Mn, and Al oxyhydroxides, carbonates, clay minerals, or complexed by organic matter.[172] Redox reactions mediated by microorgan-isms play an important role in the fate of As, as the microbial oxidation of As (As(III) to As(V)) favors the stabilization of
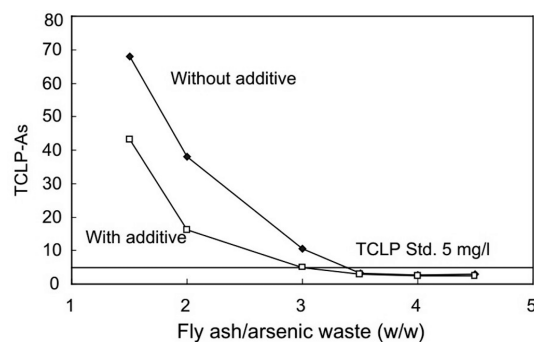
Figure 14. Impact of fly ash on S/S performance. The data is based on cement/sample weight ratio of 1 (Reprinted with permission from Shih et al.[171] Copyright 2003 Elsevier).

As in the solid phase.[173] Arsenic sorption onto aquifer sediments has been investigated in anaerobic bench- and pilot-scale experiments and analyzed by X-ray absorption spectroscopy (XAS).[174] Margarita et al. reported that arsenic in semiarid soils contaminated by wastes containing oxidized arsenic species is naturally stabilized.[175] For areas with high acetate loadings and under sulfate-reducing conditions, arsenic release was higher. Lab-scale experiments revealed that, in the presence of the reduced precursors arsenite and sulfide, multiple thioarsenic formed.[176] Iron hydroxide can bind better to arsenic, followed by clay minerals and then feldpars.[177] The methylation of arsenic occurs via alternating reduction of pentavalent As to trivalent As and addition of a methyl group (Figure 15).[178,179]
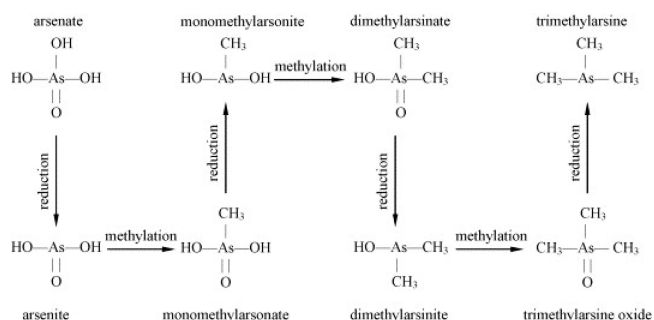
Figure 15. Challenger mechanism for arsenic methylation path-way.[178,179]

2.9. Low-Cost As Remediation Technologies

Natural attenuation can be a viable treatment technology for developing communities that lack resources to implement some of the previously discussed processes (e.g., metal-impregnated adsorbents, IEX, and fly ash incineration). Solar oxidation of As-laden waters is another low-cost remediation technology. A technology called SORAS—solar oxidation and removal of arsenic—has been shown to remove 75−90% of As[180] from waters containing both arsenic and iron, which have been photochemically pretreated with the addition of lemon juice. The citric acid induces the precipitation of ferric iron, where arsenic then adsorbs to the solid iron compounds and clean water is decanted off of the top.[180] Optimizing the process with the addition of steel wool to the source water, Cornejo et al. was able to reach a removal efficiency of at least 99.5% with final arsenic concentrations below 10 μg/L.[181] The optimal molar ratios for arsenic, citrate, and iron were

determined by Lara et al. to be 1:4.5:18.7, respectively, to achieve over 90% As removal efficiency after 4 h of irradiation.[182] SORAS was not significantly affected by pH, as increasing the pH from 5 to 9 had no negligible impact on aresenic removal.[183] Geroni et al. attributed that pH independency to at least 30 individual reactions and equilibria occurring simultaneously (many of which are competing), where at the end state, arsenic removal was mostly unaffected.[183] With this positive performance over a wide pH range, SORAS could be applied to arsenic contamination due to mining activities (mining waters usually have a wide pH range). SORAS requires behavior modification by the community in order to be effective. For example, treated water bottles need to be left overnight in the vertical position to allow arsenic—iron compounds to settle out.[184]

Unlike other treatment technologies, subsurface arsenic removal (SAR) does not generate waste (e.g., As-containing sludge, waste from the regenerated resin or the spent adsorbent, or brine with high As concentrations) that needs to be handled and disposed in a safe manner. In addition, SAR requires no electricity or chemical additives. SAR is not a new technology but is a modified form of subsurface iron removal (SIR). With SIR, the oxidation of iron species is prompted, which leads to iron precipitation, and the solid iron compounds stay in the ground as iron-free water is extracted. Fortuitously, if arsenic is present it will react and combine with iron and become trapped in a precipitated iron—arsenic complex. Similar to technologies described earlier, oxidizing As(III) to As(V) is preferable for optimal arsenic removal in situ. With SAR, water with dissolved oxygen concentrations of ∼8 mg/L is introduced into the anaerobic subsurface to accomplish the oxidation.[6] With such an oxygen concentration, the reaction is slow—on the order of hours to days—but the residence times in the subsurface are of the same order of magnitude, and therefore the viability of technology remains. The benefits to using the aerated water as the oxidant are cost and convenience; no additional chemicals are needed to convert arsenite to arsenate.

SAR requires a source of aerated water to introduce into the subsurface, which is typically accomplished with aboveground storage tanks that incorporate paddles, plates, bubbling, or a similar methodology to achieve aeration. The aerated water is then introduced into the subsurface aquifer by a handpump, which is widely available in developing countries including Bangladesh and Bengal Delta areas. A simple diagram of the one pump SAR design is included in Figure 16.
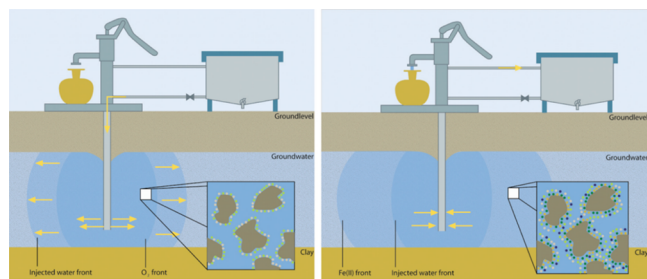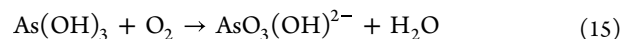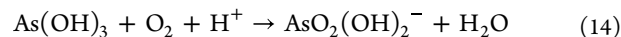

Figure 16. Single well design for subsurface arsenic removal (left: injection; right: extraction). (Reprinted with permission from Halem et al.[185] Copyright 2009 Elsevier).

The following section describes the chemical reactions during SAR. After the aerated water is introduced into the aquifer, arsenite is oxidized into arsenate as shown below.

Arsenite oxidixzing to arsenate:

$$As(OH)_3 + O_2 + H^+ \rightarrow AsO_2(OH)_2^- + H_2O \tag{14}$$

$$As(OH)_3 + O_2 \rightarrow AsO_3(OH)^{2-} + H_2O \tag{15}$$

For SAR to be effective, iron is a requirement where oxidation of ferrous iron to ferric iron takes place at the same time as arsenic oxidation. Ferric iron exists in different complexes (e.g., ferric hydroxide or hydrous ferric oxide (also referred to as ferrihydrite and HFO) or goethite (FeOOH), etc.), but the majority of these complexes are in solid form. eqs 16 and 17 demonstrate these processes.
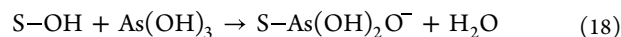
Ferrous oxidizing to Ferric:

$$4Fe^{2+} + 4H^+ + O^2 \rightarrow 4Fe^{3+} + 2H_2O \tag{16}$$
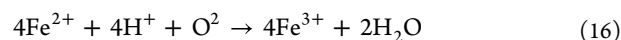
Ferric to Ferric Hydroxide (or to HFO (FeH_2O_4), or Fe_2O_3, $FeOH_2^+$, $Fe(OH)_2^+$, FeOOH, etc.):

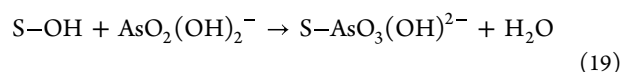$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \tag{17}$$
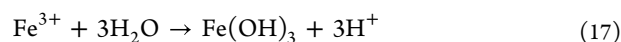
These solid forms of iron have relatively high surface areas and will sorb arsenate compounds out of solution. HFO has a surface area of 141 m^2/g, and goethite has reported surface areas of 39 and 103 m^2/g.[99] HFO and goethite, in particular, have demonstrated significant arsenic removal.[6] eqs 18 and 19 below show the arsenic adsorption to the solid iron oxides. The various iron oxides are represented with the "S−" notation to reflect the "solid" form of the compound.
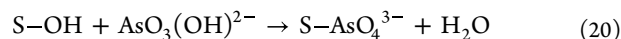
Arsenite adsorbs to iron oxides:

$$S-OH + As(OH)_3 \rightarrow S-As(OH)_2O^- + H_2O \tag{18}$$

Arsenate adsorbs to iron oxides:

$$S-OH + AsO_2(OH)_2^- \rightarrow S-AsO_3(OH)^{2-} + H_2O \tag{19}$$

Arsenate to iron oxides:

$$S-OH + AsO_3(OH)^{2-} \rightarrow S-AsO_4^{3-} + H_2O \tag{20}$$

Additionally, when (aerobic) water is extracted from the aquifer, ferrous iron in solution becomes adsorbed onto soil particles (eq 21). The adsorbed ferrous iron then undergoes oxidation to ferric iron by a pathway similar to eq 16 and thereby creates more sites that are available for arsenic adsorption during follow-on cycles of SAR aeration and extraction.

Adsorbing Ferrous

$$S - OH + Fe^{2+} \rightarrow S - OFe(II) + +H^+ \tag{21}$$
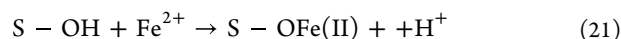
The oxidation zone formation and activation time is between 8 and 12 h, and, similar to SORAS, behavioral change is needed to allow for this time to completed before water is extracted from the well. Care and caution must also be exercised to avoid contamination of the injected aerated water from above-ground. Additional areas needing further research for optimization of SAR include determining the impact of the natural organic matter concentrations on the As removal efficiencies and further researching the remobilization of arsenic once fixed to the subsurface.[6]

3. COST ANALYSIS

According to an arsenic demonstration program,[186] capital costs are the main drivers of the cost of arsenic treatment technology. However, the cost of site improvements (buildings) and residual disposal (sewers, ponds) were not included in the cost analysis.

Based on arsenic demonstration studies ranging from 1 to 5 years in length, operation and maintenance (O&M) costs were very dependent on treatment technology with adsorptive media systems being higher than iron removal, coagulation/filtration, and ion exchange treatment technologies. The cost to replace adsorptive media accounted for around 80% of the operation and maintenance costs. As new media alternatives become commercially available, adsorptive media systems have reduced O&M costs by switching to lower-cost and higher-performance media products.[186] Chen et al. studied the feasibility of regenerating iron media products to reduce the operating cost.[107] A 4% caustic (NaOH) solution was able to achieve more than 80% removal of arsenic from iron-based exhausted media (e.g., E33 and ARM200) and restored some of its arsenic removal capability.[107]

4. DRINKING WATER TREATMENT DEMONSTRATIONS

The U.S. EPA completed demonstrations of arsenic removal technologies at 50 locations throughout the U.S.[186] The focus of the demonstrations was on commercially available technologies or engineering approaches for removal of arsenic from drinking water supplies. Major considerations included (1) arsenic treatment technology performance, (2) cost of media and media replacement, and (3) residuals management (typically disposal of backwash water). Examples of arsenic treatment effectiveness under the demonstration program are highlighted below.

Spring Brook Mobile Home Park, in Wales, Maine, tested three different media in their full-scale treatment plant with influent arsenic concentrations of 38 μg/L at pH 8.5 and found a 1.5-to-2-fold difference in the volume of water treated before exceeding the 10 μg/L arsenic maximum contaminant level (MCL).[187]

Chlorination can effectively oxidize As(III) and iron(II) as demonstrated by the Chateau Estates project in Springfield, OH, where arsenic-laden particles were formed that were filterable by AD-26 media. The AD-26 system decreased the total arsenic levels to less than 2.5 μg/L.[187]

The U.S. EPA also published information on demonstration projects on coagulation/filtration for arsenic removal from a park water supply in Conneaut Lake, PA; on adsorptive media for arsenic removal at Seely-Brown Village in Pomfret, CT;[188] and at Geneseo Hills Subdivision in Geneseo, IL.[189]

4.1. Residuals Management

Many arsenic removal technologies generate waste and require safe disposal of residuals that can significantly drive cost. Adsorptive technology generates exhausted media that can be regenerated on or off site or sent to a landfill. Backwash water with solids can be generated during treatment of arsenic using iron removal, coagulation/filtration, and adsorptive technologies. Backwash water with solids can be recycled or disposed into sewers, septic systems, and evaporating ponds. Ion exchange treatment residuals (i.e., regenerated brine) while reverse osmosis and nanofiltration residuals (i.e., reject water from the membrane treatment processes) can be sent to the sewer, septic system, or evaporated in holding ponds.[186] Local and state regulations should be consulted when developing such residual management practices.

5. CONCLUSIONS AND FUTURE RESEARCH NEEDS

Groundwater is the main drinking water source for more than 1.5 billion people. Therefore, it is essential to ensure the production of safe, potable water from this source is paramount. Arsenic concentrations greater than published maximum concentration levels have been identified globally, with high arsenic levels detected in Bangladesh, West Bengal-India, and the Western parts of the United States. Understanding this contaminant's source, fate, transport, and treatment options is a pressing environmental problem that poses human health risks.

Characterizing the subsurface geology is essential to understand the primary source of As. Nearby industrial activities and pesticide applications should be considered but, generally, to a lesser extent than the underlying geologic formation. In addition to the subsurface composition, environmental conditions (e.g., pH, ionic strength, competing ions) are important to consider when assessing the oxidation state of As and its fate. Several methods have been employed for arsenic treatment, including oxidation, coagulation-precipitation, lime softening, adsorption, ion exchange, membrane technologies, As-waste stabilization, and natural attenuation. The ultimate disposal of As waste generated by these treatment methodologies need to be considered. The optimal treatment technology depends on the specific field conditions (e.g., type of water or soil, pH, ionic strength), treatment objective, cost, and environmental regulations (i.e., discharge limits and hazardous waste disposal permits). Despite extensive efforts in the development of arsenic treatment technologies, environmentally friendly, cost-effective, scalable, and adaptable technologies that require minimal maintenance are needed.

Future research ought to focus on the stabilization of arsenic-loaded sorbents (i.e., spent sorbents). In developing countries, spent, arsenic-adsorbed materials are often disposed into the environment in an uncontrolled manner, resulting in As contamination in the backyard of the household and its release back into the groundwater supply. In developed countries, there is a greater need to develop in situ treatment technologies, rather than ex situ, so that As can be treated without excavation. Injection of nanomaterials may be one of the several new options for treatment of As-contaminated groundwater supplies. However, before their application, the health risks associated with the nanomaterials need to be determined. For instance, nZVI can be injected into As-contaminated groundwater because it transforms to iron oxides and hydroxides, which are nontoxic forms of iron.[123,190]

■ AUTHOR INFORMATION

Corresponding Authors

Sushil R. Kanel — *Department of Chemistry, Wright State University, Dayton, Ohio 45435, United States;* ⊙ orcid.org/0000-0002-3629-4528; Email: sushil.kanel@wright.edu

Mallikarjuna N. Nadagouda — *Office of Research & Development, Center for Environmental Solutions and Emergency Response (CESER), United States Environmental Protection Agency, Cincinnati, Ohio 45268, United States;*

orcid.org/0000-0002-4800-4436;
Email: Nadagouda.mallikarjuna@epa.gov

Authors

Tonoy K. Das − *Nanoenvirology Research Group, Department of Civil and Environmental Engineering, North Dakota State University, Fargo, North Dakota 58108, United States*

Rajender S. Varma − *Office of Research & Development, Center for Environmental Solutions and Emergency Response (CESER), United States Environmental Protection Agency, Cincinnati, Ohio 45268, United States;* orcid.org/0000-0001-9731-6228

Sudarshan Kurwadkar − *Department of Civil and Environmental Engineering, California State University, Fullerton, California 92831, United States*

Sudip Chakraborty − *Laboratory of Transport Phenomena & Biotechnology, Department of DIMES,, Universita della Calabria, Rende 87036 CS, Italy;* orcid.org/0000-0002-1752-4682

Tista Prasai Joshi − *Environment and Climate Study Laboratory, Faculty of Science, Nepal Academy of Science and Technology, Lalitpur 44700 Khumaltar, Nepal*

Achintya N. Bezbaruah − *Nanoenvirology Research Group, Department of Civil and Environmental Engineering, North Dakota State University, Fargo, North Dakota 58108, United States;* orcid.org/0000-0002-1911-0862

Complete contact information is available at:
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Author Contributions

CRediT: **Sushil R. Kanel** conceptualization (equal), formal analysis (equal), writing-original draft (equal); **Tonoy Das** conceptualization (equal), data curation (supporting), methodology (equal); **Rajender S. Varma** writing-review & editing (equal); **Sudarshan Kurwadkar** data curation (equal), methodology (equal), validation (equal); **Sudip Chakraborty** data curation (equal), methodology (equal), validation (equal); **Tista Prasai Joshi** writing-review & editing (equal); **Achintya N Bezbaruah** supervision (equal), writing-review & editing (equal); **Mallikarjuna N Nadagouda** conceptualization (equal), project administration (equal), supervision (equal), writing-review & editing (equal).

Notes

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