



Review

Natural attenuation processes for remediation of arsenic contaminated soils and groundwater

Suiling Wang, Catherine N. Mulligan*

Department of Building, Civil and Environmental Engineering, Concordia University, 1455 de Maisonneuve Boulevard W.,
EV6.187, Montreal, Quebec, Canada H3G 1M8

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Abstract

Arsenic (As) contamination presents a hazard in many countries. Natural attenuation (NA) of As-contaminated soils and groundwater may be a cost-effective *in situ* remedial option. It relies on the site intrinsic assimilative capacity and allows in-place cleanup. Sorption to solid phases is the principal mechanism immobilizing As in soils and removing it from groundwater. Hydroxides of iron, aluminum and manganese, clay and sulfide minerals, and natural organic matter are commonly associated with soils and aquifer sediments, and have been shown to be significant As adsorbents. The extent of sorption is influenced by As speciation and the site geochemical conditions such as pH, redox potential, and the co-occurring ions. Microbial activity may catalyze the transformation of As species, or mediate redox reactions thus influencing As mobility. Plants that are capable of hyperaccumulating As may translocate As from contaminated soils and groundwater to their tissues, providing the basis for phytoremediation. However, NA is subject to hydrological changes and may take substantial periods of time, thus requiring long-term monitoring. The current understanding of As NA processes remains limited. Sufficient site characterization is critical to the success of NA. Further research is required to develop conceptual and mathematical models to predict the fate and transport of As and to evaluate the site NA capacity. Engineering enhanced NA using environmentally benign products may be an effective alternative.

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Keywords: Arsenic; Biotransformation; Enhanced natural attenuation; Hyperaccumulation; Immobilization; *In situ* remediation

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* Corresponding author. Tel.: +1 514 848 2424x7925; fax: +1 514 848 7965.
E-mail address: mulligan@civil.concordia.ca (C.N. Mulligan).

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1. Introduction

Arsenic (As) occurs naturally and is widely distributed in natural systems. Release from As-enriched minerals is the primary source of As in the environment [1,2]. The main anthropogenic sources include mining and smelting, industrial processes, and agricultural practices [1,2]. The World Health Organization (WHO) guideline value for As in drinking water is 10 $\mu\text{g/L}$ [3]. Elevated As concentrations in soils and groundwater have been reported worldwide. There has been increasing concern on the toxicity of As to humans and other living organisms. It is a proven carcinogen causing skin cancer and other internal cancers [3]. It is also phytotoxic and may accumulate in plants [2,11].

Due to the high toxicity of As, remediation of As-contaminated soils and groundwater, therefore, is necessary to protect the environment and the public health. Natural attenuation (NA) is an environmentally compatible and cost-effective *in situ* remedial method that relies on the site intrinsic assimilative capacity. Regulatory definitions of NA generally include all types of processes that can reduce the concentration or minimize the toxicity of a contaminant [4]. The naturally occurring physicochemical and biological processes give light to the use of NA processes to remediate As-contaminated soils and groundwater. The NA of As mainly involves processes such as immobilization by sorption to solid phases such as (hydro)oxides of iron (Fe), aluminum (Al) and manganese (Mn), organic matter, and clay minerals, the intra-conversion between As(III) and As(V) induced by the Fe and Mn (hydro)oxides and clay phases or natural organic matter (NOM), biotransformation, and hyperaccumulation of As in plants.

The chemical forms and oxidation states in which As exists may play an important role in the NA processes, since they are closely correlated to the physiological and toxicological effects of As, and also have effects on its sorption behavior and consequentially its mobility and bioavailability [2]. As exists essentially in four oxidation states (i.e., -III, 0, +III, and +V). Depending on pH and redox conditions (Eh), As(V) and As(III) are widely present in soils and groundwater (Fig. 1) [4]. Methylated As compounds, such as monomethylarsonous acid [MMAA(III)], monomethylarsonic acid [MMAA(V)], dimethylarsinous acid [DMAA(III)], and dimethylarsinic acid [DMAA(V)], can be formed through biomethylation under favorable conditions [1,6]. Arsenobetaine (AsB) is a common organoarsenic species in marine mammals, while arsenosugars are the major As species found in plants like algae. In sulfide-concentrated solutions, the dissolved thioarsenic species such

as $\text{H}_2\text{AsOS}_2^-$ and H_2AsS_3^- can be formed under near-neutral to alkaline conditions [7]. Generally, inorganic As species are more toxic and mobile than organoarsenic species, and As(III) is more toxic and mobile than As(V).

The objective of this paper therefore is to analyze and evaluate the geophysical, chemical and biological processes that govern the mobility, transformation, and toxicity behavior of As in soils and groundwater, and exploit their implications on NA for remediating As-contaminated soils and groundwater.

2. As immobilization by sorption

Sorption of As to solid phases has been proposed as a principal control on its mobility (Table 1), which can transfer soluble or mobile As to particulate phases, thus immobilizing it. The knowledge of As sorption behavior therefore is helpful to understanding As NA through the immobilization mechanism. Especially, (hydro)oxides of Fe, Al and Mn are ubiquitous in soils and sediments, either as discrete particles or as coatings on other mineral solids, and are potentially the most important As adsorbents. Spectroscopic studies have confirmed that both As(III) and As(V) may form inner-sphere complexes on the surfaces of the (hydro)oxides and clay minerals through ligand exchange

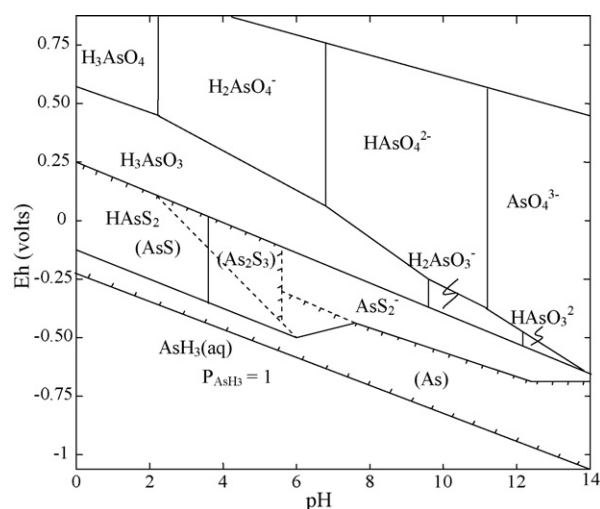


Fig. 1. Eh–pH diagram for As at 25 °C and 101.3 kPa with total concentration of As of 10^{-5} mol/L and total concentration of sulfur of 10^{-3} mol/L. Solid species with solubilities less than $10^{-5.3}$ mol/L are enclosed in parentheses in the cross-hatched area. The dotted line indicates the lower boundary between the As sulfides and As metal due to a decrease in sulfide activity (after Ferguson and Gavis [5]).

Table 1
Effects of the main adsorbents on As immobilization and transformation

Adsorbents	Main affecting mechanism	References
Fe hydroxides	As(V), $\text{CH}_3\text{AsO}_2(\text{OH})^-$ and $(\text{CH}_3)_2\text{AsOOH}$ adsorption at pH 4–7, maximized around pH 4 As(III) adsorption at pH 7–10, maximized around pH 7 Desorption when pH increases Amorphous phases of a higher adsorption capacity than crystalline phases Releasing sorbed As during chemical and microbial reductive dissolution As(III) oxidization, catalyzed by light or H_2O_2 in alkaline pH	[8,19–21,23,24,27,28]
Al hydroxides	As(V), $\text{CH}_3\text{AsO}(\text{OH})_2$, and $(\text{CH}_3)_2\text{AsOOH}$ adsorption up to pH 7 and decreases significantly at higher pH As(III) adsorption at pH 6–9.5 and decreases at higher pH Amorphous phases of a higher adsorption capacity than crystalline phases	[24,30]
Mn hydroxides	Negligible As(V) adsorption, but increased in the presence of other divalent cations Slightly greater As(III) oxidation at low pH (pH 4) Poorly crystalline phases with high surface areas are more efficient	[17,31,32]
Clay	As(V) adsorption up to pH 7 and decreases with pH increases Low As(III) adsorption at low pH and increases with pH Clays with high surface areas showing a higher adsorption capacity As(III) oxidation in the presence of trace amounts of impurities such as Fe or Mn oxides, iodide, or TiO_2	[34,35]
Sulfides	As substitution for S in sulfides, forming of As sulfide precipitates in the reduced environment Releasing As during chemical and microbial oxidation of As-bearing sulfides	[7,36,37]
NOM	Enhancing As release mainly through competition for active adsorption sites, forming aqueous complexes, and changing the redox chemistry of site surfaces and As species Inhibiting As mobility by serving as a binding agent and/or by forming insoluble complexes, especially when saturated with metal cations	[2]
Anions	Competition for active adsorption sites, influenced by pH and concentration ratios between anion and As	[29,39,41]
Cations	Enhancing As sorption by increasing the amount of positive charge on the oxide surfaces and/or forming a positively charged surface	[30,38,39]

with OH and OH_2^+ surface functional groups. As(III) may also form outer-sphere complexes by simple coulombic (electrostatic) interactions on the surface of amorphous Al hydroxides and sulfide minerals [9]. Inner-sphere complex bonds are much stronger than outer-sphere complex bonds, resulting in a stronger adsorption, which makes the immobilization more permanent.

2.1. As sorption to Fe, Al and Mn (hydro)oxides

Fe hydroxides, such as goethite ($\alpha\text{-FeOOH}$), ferrihydrite ($\beta\text{-FeOOH}$), and lepidocrocite ($\gamma\text{-FeOOH}$), have high isoelectric points of about 8.6 and possess net positive charges in most geological environments, showing high affinities for As species. Excavation and sorption studies have revealed that As in soils is associated primarily with Fe hydroxides [9]. Both As(III) and As(V) are strongly chemisorbed. Adsorption affinity is higher for As(V) at lower pH values and for As(III) at higher pH values. Pierce and Moore [8] reported that As(V) is preferentially sorbed to Fe hydroxides between pH 4 and 7 with an optimal adsorption pH of about 4, whereas As(III) is preferentially sorbed onto Fe hydroxides between pH 7 and 10 with an optimal adsorption pH of about 7. Methylated As(V) species, $\text{CH}_3\text{AsO}_2(\text{OH})^-$ and $(\text{CH}_3)_2\text{AsO}(\text{OH})$, behave similarly to As(V) on adsorption to ferrihydrite [24]. Spectroscopic studies generally agreed that both As(III) and As(V) are specifically sorbed, forming inner-

sphere complexes [9]. The sorption of As(III) and As(V) to Fe (hydro)oxides contributes to As immobilization in soils. Under neutral or mildly acidic conditions, As sorption to Fe hydroxides and the formation of ferric arsenate precipitates may effectively decrease As concentrations in mining affected waters [26], which is a principal NA process to remove As from contaminated groundwater.

Al (hydro)oxides are ubiquitous in acidic soils and aquatic environments. Amorphous $\text{Al}(\text{OH})_3$ has an isoelectric point of 8.5, and thus is an extremely efficient adsorbent to immobilize As. Previous studies indicated that As(III) and As(V) adsorption on an Al oxide ($\gamma\text{-Al}_2\text{O}_3$) and gibbsite ($\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$) formed inner-sphere complexes [9]. Outer-spherical As(III) complexes have also been observed. It has been reported that the adsorption of As(V), $\text{CH}_3\text{AsO}(\text{OH})_2$, and $(\text{CH}_3)_2\text{AsOOH}$ increases up to pH 7 by amorphous $\text{Al}(\text{OH})_3$, crystalline $\text{Al}(\text{OH})_3$ (gibbsite), $\alpha\text{-Al}_2\text{O}_3$, and $\gamma\text{-Al}_2\text{O}_3$, and decreases significantly at higher pH values [24,30]. Although As(III) can be strongly adsorbed from pH 6 to 9.5, this decreases at higher pH values [30].

Mn (hydro)oxides in soils are often of poor crystallinity and mixed oxidation states. Mn hydroxides have an isoelectric point about 2.3, and therefore carry a net negative charge at the common natural pH range of 3–9, which suggests that they would not adsorb As anions. It was observed that the negatively-charged As(V) species, H_2AsO_4^- , was adsorbed negligibly

onto the negatively-charged birnessite surface at a pH range of 4–7 [31]. However, Mn hydroxides have the capacity to oxidize As(III) into As(V) [16–18], which may cause a surface alternation, creating fresh adsorption sites for As(V) on the oxide surface. Moreover, adsorption of other divalent cations may change the surface charge, resulting in a decrease in the negative surface charge followed by a positive surface charge, enabling the hydroxides to adsorb As(V) and As(III). EXAFS analyses showed that As(V) formed inner-sphere complexes on synthetic birnessite (MnO_2), synthetic vernadite ($\delta\text{-MnO}_2$), and K-birnessite ($\text{K}_4\text{Mn}_{14}\text{O}_{27}\cdot 9\text{H}_2\text{O}$) [9]. As(III) sorption by birnessite at pH 7 was observed [16,31]. As(III) adsorption by manganite ($\gamma\text{-MnOOH}$) decreased by 30% from pH 4.0 to 6.3 [32].

The degree of crystallinity and surface area of the (hydro)oxides have demonstrated significant effects on their sorption capacity. Generally, poorly crystalline hydroxides with a higher surface area show a higher As sorption capacity by providing more active sorption sites. For example, the adsorption of As(III) and As(V) was two or three times greater (on a surface area basis) on ferrihydrite than on goethite [23]. Adsorption of As(III), As(V), MMA, and DMA by hematite was about half as much as goethite which has a larger surface area [22]. Under comparable experimental conditions, amorphous $\text{Al}(\text{OH})_3$ adsorbed more As(V) per gram than crystalline $\gamma\text{-Al}_2\text{O}_3$ and gibbsite [30]. As adsorbed by cryptomelane ($\alpha\text{-MnO}_2$, $34.6\text{ hm}^2/\text{kg}$) was almost 20 times that adsorbed by pyrolusite ($\beta\text{-MnO}_2$, $0.8\text{ hm}^2/\text{kg}$) [16].

However, desorption and remobilization of the sorbed As from the (hydro)oxides may occur when the site biogeochemical conditions change with time. Significant As(V) remobilization from Fe hydroxides can occur at pH values of approximately pH 8 and higher, due to the increase of electrostatic repulsion on the negatively charged oxide surface, and the rate of As(V) desorption can be quite high [21]. Moreover, in reducing soils, As sorbed on Fe(III) hydroxides can be remobilized and released into groundwater as a result of the reduction of Fe(III) to Fe(II) and the reduction of As(V) to As(III) [27]. Therefore, engineering strategies may be required to control the site geophysicochemical conditions such as pH and Eh during the application of NA to prevent remobilization.

2.2. As sorption to clay minerals

Ubiquitous in the terrestrial environment, clay minerals largely consist of aluminosilicates with alternating layers of silica oxide and Al oxide. FTIR analyses indicated that the retention of As(V) by halloysite was likely due to the formation of hydroxy-As(V) interlayers in crystals. It was also reported that nearly all As(III) and As(V) were physisorbed to smectite, and only a portion of them was chemisorbed on kaolinite forming inner-sphere complexes [9]. As(V) adsorption to kaolinite, montmorillonite, illite, halloysite, and chlorite occurs up to pH 7, then decreases with a pH increase [34]. As(III) adsorption by the same clay minerals is minimal at low pH and increases with increasing pH. As(V) is adsorbed to a greater extent than As(III) on all clay minerals at a pH below 7. At higher pH val-

ues, adsorption of As(V) and As(III) are more comparable [34]. Moreover, the poorly crystallized clay minerals of larger surface area are of higher As sorption capacity, and the presence of mineral impurities such as Fe species may further enhance the sorption capacity [34].

2.3. Enhanced sorption by cations

Cations, such as Ca^{2+} and Fe^{2+} , may increase As adsorption by increasing the amount of positive charge on the oxide surface and/or forming a positively charged surface [30,38,39]. Ghosh and Teoh [30] observed that the adsorption of As(V) onto Al oxides was enhanced in the presence of Ca^{2+} at a pH above 8. Addition of Ca^{2+} also increased the As(V) adsorption onto ferrihydrite at pH 9 [38]. Meng et al. [39] reported that the addition of Ca^{2+} and Mg^{2+} to the suspension of ferrihydrite negated part of the competitive effect of silicate on As adsorption. The formation of CaCO_3 minerals can restrict the development of high pH, thus inhibiting the As(V) release from the oxides and clays. Moreover, the formation of $\text{Ca}_3(\text{AsO}_4)_2$ and CaHAsO_3 precipitates has been observed in contaminated soils [40], which contributes to As immobilization.

2.4. Competing sorption by anions

It has been demonstrated that phosphate can suppress the adsorption of both As(V) and As(III), while As(V) is much more strongly affected than As(III) [41]. Sulfate has essentially no effect on As(V) adsorption but may compete with As(III) adsorption when the pH is below 7 [38,39,41]. Generally, carbonate exhibits little effect on As(III) and As(V) adsorption [21,39], but the presence of bicarbonate (HCO_3^-) can facilitate As mobilization from As-containing sulfides such as orpiment in both oxic and anoxic environments [42]. As mobilization increases with increasing HCO_3^- concentrations and pH. Silicate reduces the adsorption of As(III) and As(V) on ferrihydrite at pH 6.8 [39]. Competitive adsorption between As(V) and molybdate was also observed [29]. The competing sorption between As and the anions can inhibit As sorption and then increase As mobility, which hinders As immobilization.

2.5. Effect of NOM on As sorption

NOM (e.g., humic and fulvic acids) is an inherently complex mixture of polyfunctional organic acids derived from the decomposition of terrestrial and aquatic animals and plants. Prevalent in subsurface, NOM is highly reactive toward both metals and surfaces, and therefore may play an important role in governing the mobility and bioavailability of As [2]. The formation of NOM–metal complexes may strongly bind As(III) and As(V) anions through metal-bridging mechanism [44], which contributes to As immobilization. As(V) adsorption on humic substances is maximal at pH 5.5 and at a much higher pH of 8.5 for As(III) [43]. However, both As(III) and As(V) can form aqueous complexes with humic and fulvic acids, but As(III) prefers aqueous complexation when compared to As(V) [2]. Complexes with fulvic acids generally are more soluble than those of humic

acids because of their lower molecular weights, higher oxygen contents, higher contents of acidic functional groups and higher acidity [2]. The formation of aqueous complexes may desorb As from solid phases, thus increasing its mobility and hindering the immobilization.

Under acidic and slightly acidic conditions, NOM sorbs to metal hydroxides mainly through ligand exchange surface complexation. Therefore, it tends to compete with As(III) and As(V) anions for active adsorption sites [2,23,43,44]. The formation of predominantly negatively charged surfaces due to the NOM adsorption can further inhibit the adsorption of As anions. Grafe et al. [23] observed that the inhibitory effect of a peat humic acid on As(V) adsorption onto goethite started at pH 9 and reached a maximum at pH 6.5. The inhibitory effect on As(III) adsorption started at pH 7 and increased when pH decreased. The inhibitory effects on As sorption may increase As mobility, thus interfering with As immobilization.

3. Chemical oxidation and reduction processes

Redox-sensitive surfaces, such as those of Fe and Mn (hydro)oxides, clay minerals, and NOM have demonstrated an ability to oxidize As(III) to As(V) [16–19]. Since As(III) is more toxic and mobile than As(V), the oxidation of As(III) to As(V) is helpful to NA by alleviating the toxicity of As(III). The resulting As(V) is more strongly adsorbed and becomes relatively immobilized. In turn, the reduction of As(V) may occur under anaerobic reducing conditions in flooded soils or deep sediments or in aerobic environments, thus may remobilize the sorbed As and jeopardize the NA processes.

3.1. Oxidation of As(III) by Fe (hydro)oxides

The oxidation of As(III) by Fe hydroxides has been observed, and the reduction of As(V) to As(III) can be retarded in the presence of Fe(III) hydroxide (e.g., ferrihydrite) [19]. Lin and Puls [19] reported that 65–80% of the As(III) adsorbed on Fe hydroxides was oxidized. There is evidence showing that the oxidation reaction can be catalyzed by the presence of light [28] or hydrogen peroxide (H_2O_2) in alkaline environments [20]. DeVitre et al. [28] found that 83% of the added As(III) to Fe hydroxide was oxidized within 10 days in the presence of light, but only 9% was oxidized in the absence of light. Voegelin and Hug [20] reported that in natural environments with high H_2O_2 concentration (1–10 μM) and alkaline pH, the As(III) oxidation by Fe (hydro)oxides can be accelerated.

3.2. Oxidation of As(III) by Mn (hydro)oxides

Both Mn(IV) and Mn(III) are able to oxidize As(III). Solid MnO_2 , notably birnessite, assists in the oxidation of As(III) to As(V) while itself being partially reduced to Mn(II) [31]. The rate of oxidation depends on the surface area and surface charge of the MnO_2 and is slightly greater at low pH. Highly ordered, low surface area pyrolusite oxidized As(III) at a much lower rate than the poorly crystalline, high surface area birnessite and cryptomelane [16]. Chiu and Hering [32] measured three times more

As(III) oxidation by manganite at pH 4.0 than at pH 6.3, possibly due to the greater As(III) adsorption at the lower pH [17]. Moreover, reactions with birnessite at very high initial As(III) concentrations may lead to the formation of an insoluble mineral, krautite ($\text{MnHAsO}_4 \cdot \text{H}_2\text{O}$) on the birnessite surface [33], thus enhancing As immobilization.

3.3. Oxidation of As(III) by clay minerals

Oxidation of As(III) adsorbed by halloysite, kaolinite, illite, illite/montmorillonite and chlorite has been observed [34,35]. It was reported that the As(III) oxidation by clays ranged from 50 to 85% and increased with the reaction time and reached 100% after 75 days [19,34]. It is postulated that the oxidation was incurred by the presence of Fe and Mn oxides or trace amounts of impurities such as iodide in the clay minerals [19,34]. Titanium-containing clays have also been observed to be able to oxidize As(III) in the presence of light and oxygen [35].

3.4. Sulfide-related As redox reactions

Under very reducing conditions where SO_4^{2-} reduction to H_2S , As(V) can be rapidly reduced by H_2S and the reduction rate increases with decreasing pH [36]. It precipitates As in the form of secondary sulfides like orpiment, As_2S_3 , and/or As rich pyrite [7,36], which have low solubilities and are predicted to be stable. However, once they are exposed to oxidizing conditions, the sulfides become unstable, and the As will be released and become mobile again [9]. The minerals can be oxidized by O_2 and Fe^{3+} , causing As contamination in groundwaters in regions of active and historic mining as well as in non-mined areas [1,37].

3.5. NOM-induced As redox reactions

NOM is able to incur the reduction of Fe(III) and Mn(III or IV) hydroxides, leading to the release of sorbed As [2]. It may also catalyze the oxidation and reduction reaction between As(III) and As(V), in part by the quinone-mediated formation of free radicals [44]. They may serve as an electron shuttle between kinetically inert redox species or between microorganisms and As species. Metal (hydro)oxides may act as a surface catalyst or as an electron-transfer intermediate. As immobilization may be enhanced by the redox reactions between NOM, As and substrates resulting in the oxidation of As(III) to the less mobile As(V) form [2,44]. Additionally, the reduction of As(V) to As(III) by an Inangahua River NOM was also observed in aerobic environments [44]. Similarly, soil organic matter was reported to be able to mediate the reduction of As(V) to As(III) in aerobic CCA-contaminated soils [45], thus increasing As mobility.

4. As biotransformation

Although As is highly toxic, microorganisms have evolved various strategies for dealing with it. As(V) can be used as an electron acceptor for anaerobic respiration, or As(III)

Table 2
Main microorganisms and their role in influencing As transformation and mobility

Mechanisms	Microorganisms	References
As methylation and demethylation under favorable conditions	<i>Methanobacterium bryantii</i>	[49]
	<i>Achromobacter</i> sp., <i>Enterobacter</i> sp., <i>Aeromonas</i> sp., <i>Nocardia</i> sp.	[6]
	<i>Methanobacterium formicicum</i> , <i>Clostridium collagenovorans</i> , <i>Desulfovibrio vulgaris</i> , <i>Desulfovibrio gigas</i>	[50]
As(V) reduction under anaerobic conditions	<i>Escherichia coli</i> , <i>Staphylococcus aureus</i> , <i>Staphylococcus xylois</i>	[77]
	<i>Anabaena oscillaroides</i>	[55]
	<i>Sulfospirillum barnesii</i>	[47]
As(V) reduction under aerobic conditions	<i>Sphingomonas</i> , <i>Caulobacter</i> , <i>Rhizobium</i> , <i>Pseudomonas</i>	[58]
Both As(III) oxidation under aerobic conditions and As(V) reduction under anaerobic conditions	<i>Thermus</i> HR13	[80]
As(III) oxidization of As(III) under oxic conditions	<i>Pseudomonas arsenitoxidans</i> NT-26	[46]
	<i>Thermus aquaticus</i> , <i>Thermus thermophilus</i>	[60]
Fe oxidization and thus As precipitation	<i>Sphaerotilus</i> , <i>Leptothrix ochracea</i> , <i>Gallionella ferruginea</i>	[62]
As precipitation as ferric arsenate and arsenate-sulfate	<i>Thiobacillus acidophilus</i>	[26]
Reduction of Fe(III) to Fe(II) thus releasing As(V)	<i>Shewanella alga</i> (strain BrY)	[64]
As precipitation as ferric arsenate and arsenate-sulfate under acidic and high SO_4^{2-} conditions	<i>Acidithiobacillus ferrooxidans</i>	[26,63]
Oxidation of sulfides under oxic conditions thus releasing As	<i>Acidithiobacillus ferrooxidans</i> , <i>Leptospirillum ferrooxidans</i>	[37]

can be used as an electron donor to support chemoautotrophic fixation of carbon dioxide into cell carbon under aerobic conditions (Table 2) [46,47]. Microbially mediated methylation–demethylation and oxidation–reduction reactions produce a significant effect on As mobility and toxicity, providing a basis for the NA of As-contaminated soils and groundwater.

4.1. Methylation and demethylation

The methylation of As occurs via alternating reduction of pentavalent As to trivalent As and addition of a methyl group

(Fig. 2) [48]. The conversion of As(V) to small amounts of volatile methylarsines was first described in a pure culture of a methanogen, *Methanobacterium bryantii* [49]. Recently, several pure cultures of anaerobes, including a methanogen (*Methanobacterium formicicum*), a fermentative bacterium (*Clostridium collagenovorans*) and sulfate-reducing bacteria (*Desulfovibrio vulgaris* and *D. gigas*), were also implicated in the formation of methylarsines [50]. As(V) can be converted to monomethylarsine and dimethylarsine by *Achromobacter* sp. and *Enterobacter* sp., and to monomethylarsine, dimethylarsine and trimethylarsine by *Aeromonas* sp. and *Nocardia* sp. [6]. Anaerobic microcosms established from the sediments of

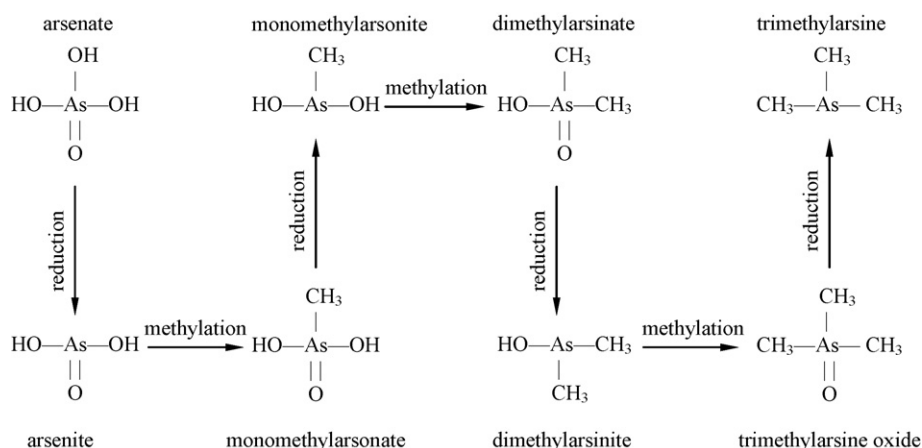


Fig. 2. Challenger mechanism for As methylation pathway (based on Challenger [48]).

a gold mine impacted lake were found to be able to methylate As(V) forming MMAA(V) and DMAA(V) [51]. On the other hand, the trivalent methylated intermediates such as MMAA(III) and DMAA(III) are found to be readily oxidized chemically and biologically [52,53]. Shariatpanahi et al. [53] reported that the rates of methylation and demethylation of monosodium methylarsenate at 10 and 100 mg/L of normal culture media by *Aeromonas*, *Nocardia*, *Enterobacter*, *Flavobacterium*, *Achromobacter*, *Pseudomonas*, and *Alcaligenes* species followed first order composite kinetics.

Methylation and demethylation may play a significant role in influencing the toxicity and mobility of As in soils and groundwater. As(III) and As(V) methylation may form volatile species leading to the escape of As from water and soil surfaces by volatilization. However, the contribution of volatilization to As NA is almost negligible. Though the methylated As species are generally considered less toxic than the inorganic species, the methylation processes do not necessarily contribute to the detoxification mechanism. Recent research has demonstrated that trivalent methylated As species are more effective in destroying DNA. The potency of the DNA damage decreases in the order DMAA(III) > MMAA(III) > [As(III), As(V)] > MMAA(V) > DMAA(V) > trimethylarsine oxide [TMAO(V)] [54]. Therefore, biomethylation is not beneficial for As NA due to the formation of more toxic products.

4.2. Microbially mediated As(V) reduction

Anaerobic microorganisms can potentially use As(V) as an electron acceptor for the oxidation of organic matter or H₂ gas, yielding energy to support their growth [55,56]. Microorganisms from 16 species of diverse taxonomy, referred to collectively as dissimilatory As(V) reducing prokaryotes (DARPs), have been isolated [56]. Additionally, many microorganisms, including bacteria, archaea and fungi, display resistance to As(V) toxicity. A common mechanism of resistance involves the reduction of intracellular As(V) to As(III) by As(V) reductases, since As(III) is the substrate of efflux pumps [56].

The reduction of As(V) to As(III) under anaerobic conditions has been reported to be mediated by a diverse population of anaerobic microorganisms, including methanogens, fermentative bacteria, and sulfate- and iron-reducers [57]. The electron donors can be organic matter such as buried peat in sediments, anthropogenic input organic contaminants such as the benzene, toluene, ethylbenzene, xylene (BTEX) group, or organic acids from landfill sites [2]. Microbially mediated reduction of As(V) can occur even when As is bound to Fe hydroxides [27]. Zobrist et al. [47] showed that the As(V) reduction can lead to As mobilization without dissolving the sorbent phase by anaerobically incubating As(V) co-precipitated with Al hydroxide in the presence *Sulforospirillum barnesii*. Moreover, the microbial reduction of As(V) to As(III) under aerobic conditions in As-contaminated soils may occur relatively fast, resulting in enhanced As mobilization and transport from contaminated soils to groundwater [58]. The biologically catalyzed reduction of As(V) to As(III), therefore, may hinder As NA by increasing its mobility.

4.3. Microbially mediated As(III) oxidation

Certain chemoautotrophs, such as *Pseudomonas arsenitoxidans* NT-26, can oxidize As(III) by using O₂, NO₃⁻, or Fe(III) as a terminal electron acceptor and CO₂ or HCO₃⁻ as the carbon source [46]. The As(III) oxidation process provides energy for the microbial growth. However, Gihring et al. [60] found that the ecological role of the As(III) oxidation to As(V) by *Thermus aquaticus* and *Thermus thermophilus* might be the detoxification of As. The oxidation of As(III) to As(V) by bacterial colonies attached to macrophytes occurs immediately when the geothermal fluid is exposed to oxygenated conditions. An estimated half-life was around 20 min for the oxidation of As(III) to As(V) in Hot Creek, Sierra Nevada Mountains of California [59]. Microbial As(III) oxidation was observed in the acid mine waters of the Matsuo sulfur-pyrite mine in Japan [61]. Since As(V) is less mobile and toxic than As(III), the bio-oxidation will contribute to As NA by enhancing As immobilization and alleviating As toxicity, especially when the water becomes much less acidic as a result of dilution from inflowing water and neutralization by the alkalinity of the environment.

4.4. Microbially mediated As mobility

Fe and Mn oxidizing bacteria, including sheaths (e.g., *Sphaerotilus*), *Leptothrix* group (e.g., *Leptothrix ochracea*), or spirally twisted stalks (e.g., *Gallionella ferruginea*), are able to accelerate Fe(II) oxidation, resulting in As precipitation with respective Fe oxides [10,28,62]. As can be immobilized through sorption due to the presence of a mixture of Fe oxides, organic material and microbial biomass following the biological oxidation of Fe. Katsoyiannis and Zouboulis [10] found that the biotic oxidation of Fe by microorganisms *G. ferruginea* and *Leptothrix ochracea* was effective in removing As from groundwater. As(III) was partially oxidized to As(V), which enabled high As immobilization as the oxidized form was much more strongly sorbed on the biogenic Fe oxides. Similarly, *Acidithiobacillus ferrooxidans* was found to be able to catalyze the oxidation from Fe(II) to Fe(III) and facilitate the formation of schwertmannite under acidic and high SO₄²⁻ conditions, which enhances As NA by immobilizing it through sorption [63].

However, other microbially induced redox reactions may remobilize sorbed As, thus jeopardizing the NA processes. Cummings et al. [64] reported that the dissimilatory Fe reducing bacterium *Shewanella alga* (strain BrY) enhanced As mobilization from a crystalline ferric arsenate (FeAsO₄·2H₂O) as well as from sorption sites within whole sediments. This oxidation of sulfide minerals catalyzed by microorganisms, such as *Acidithiobacillus ferrooxidans* and *Leptospirillum ferrooxidans*, will release As into surface and groundwaters [37].

5. As hyperaccumulation in plants

There is evidence that high concentrations of As can accumulate in microbes and plants [11–13,65,66]. It has been reported that the marine polychaeta accumulated As concentrations up to 2739 mg/kg (dry mass) [66]. However, As accumulation in

Table 3
Reported As-hyperaccumulating plants and their performance

Plants	Performance	References
<i>Jasione Montana</i> , <i>Calluna vulgaris</i>	Accumulated As up to 6640 and 4130 mg/kg (DW) on mine waste in UK	[68]
<i>Agrostis tenuis</i> , <i>Agrostis stolonifera</i>	Accumulated As up to 1% (DW) on smelter waste in southwest England	[67]
<i>Agrostis castellana</i>	Accumulated As up to 1900 mg/kg from gold mines in Portugal	[78]
<i>Paspalum racemosum</i>	Accumulated As up to 5280 mg As/kg in leaves from a copper mine in northern Peru	[79]
<i>Pteris vittata</i>	Rapidly accumulated As from contaminated soils into its fronds up to 22,000 mg/kg (DW)	[11]
<i>Pityrogramma calomelanos</i> , <i>Mimosa pudica</i> , <i>Melastoma malabathricum</i>	Accumulated As up to 8350 mg/kg (DW) from soils contaminated by mine tailings	[12]
<i>Pteris cretica</i> , <i>Pteris longifolia</i> , <i>Pteris umbrosa</i>	Accumulated up to 7600 mg As/mg (DW) in the fronds from contaminated soils	[13]
<i>Lemna gibba</i> L. (duckweed)	Accumulated As from tailing water up to 2000 mg/kg (DW)	[65]

microbes might not assist As NA since usually it is not easy to separate the microbes from soils. Conversely, As hyperaccumulation in plants may be an important NA mechanism to reduce As concentrations at the contaminated sites by translocating the As into plant tissues. As hyperaccumulators are those plants that have the ability to uptake As from soils and waters extraordinarily and transport and accumulate it in their shoots. The ratio of shoot As concentration to soil/water As concentration, defined as bioconcentration factor, should be greater than 10 [11,13,65,67]. A few plants have been reported to be able to hyperaccumulate As (Table 3).

The first reported As hyperaccumulator is the Chinese brake fern *Pteris vittata* [11]. It can accumulate 12–64 mg As/kg in its fronds from uncontaminated soils containing 0.5–7.5 mg As/kg, and up to 22,630 mg As/kg from a soil amended with 1500 mg As/kg [11]. Several other fern species, including *Pityrogramma calomelanos*, *Pteris cretica*, *Pteris longifolia* and *Pteris umbrosa*, have also been reported to be able to hyperaccumulate As [12,13]. Other plants, such as *Agrostis tenuis* and *A. stolonifera*, grew on smelter waste in southwest England and accumulated As up to 1% dry weight [67]. *A. tenuis* accumulated foliage As concentrations between 2080 and 3470 mg/kg [68]. These plants are tolerant of high concentrations of As(V) but not As(III). An accumulation of As up to 2000 mg/kg (dry mass) in *Lemna gibba* (duckweed) was observed in the tailings water of abandoned uranium mine sites in Saxony, Germany [65]. The authors suggested that *L. gibba* might be used as an indicator for As and for As transfer from contaminated waters to plants.

The uptake and accumulation of As in plants, however, are influenced by the soil properties and the presence of other ions. Phosphates have long been reported to suppress plant uptake of As(V) because As(V) uptake through phosphate uptake pathway. Significant reduction in As accumulation in *L. gibba* and Indian mustard (*Brassica juncea*) were observed with the addition of phosphate [65,69]. Warren and Alloway [70] found that the application of FeSO₄ together with ground agricultural lime lowered the lettuce As concentration by 84% due to the formation of precipitated Fe oxides, which decreased As bioavailability.

6. Engineering strategies to enhance NA

The biogeochemistry of As suggests that NA may provide a potential remedial option for As-contaminated sites. However, NA generally is subject to hydrological changes and may take substantial periods of time. It alone may not be sufficient for the remediation of contaminated sites in a reasonable time frame [14]. Engineering enhancement strategies may be incorporated to reduce risk and enhance attenuation rates [1].

6.1. Additives to enhance immobilization

As may be immobilized in soils or removed from groundwaters by sorption to solid phases under favorable pH and redox conditions (Table 1). The retention of As in soils within a desired time scale therefore can be achieved by the addition of sorbing phases and complexing agents, inhibition of competing effects, and manipulation of pH and redox conditions. The sustainability of reducing and maintaining the reduced solubility conditions is the key to the long-term success of the treatment. The sorption or assimilative capacity of soil can be improved by increasing the fraction proportions of amorphous metal oxides and adding organic amendments in the form of compost or peat moss. Addition of adsorbents such as amorphous Fe hydroxides or Fe hydroxides coated sands may adsorb and coprecipitate dissolved As and thus reduce As concentrations in groundwater.

Adjustment of pH can be accomplished by adding pH buffers [4,15]. To increase and stabilize pH, calcium or calcium/magnesium-containing compounds such as calcium oxide (lime), calcium hydroxide, calcium carbonate, magnesium carbonate, and calcium silicate slags can be added. Acidification or the reduction of pH can be achieved through adding elemental S or S-containing compounds such as sulfuric acid, liquid ammonium polysulfide, and Al and Fe sulfates.

Oxidation of As(III) to As(V) may enhance the sorption and immobilization of As since the oxidized form As(V) adsorbs more strongly to solid phases than As(III). Addition of oxygen and other oxidants can be used to ensure the oxidation of As(III). Oxygen addition can be achieved by biosparging and the addition

of oxygen releasing compounds such as CaO₂ [15]. Chemical oxidants such as potassium permanganate, ozone, manganese oxides, and hydrogen peroxide can be added. Advanced oxidation methods using ultraviolet (UV) light and a photoabsorber (e.g., Fe salts and sulfite) can also be used.

Under comparable conditions, Fe (hydro)oxides demonstrated a higher sorption capacity than the Al and Mn (hydro)oxides and clay phases [28,29]. Manning and Goldberg [29] reported that gibbsite (45 m²/g) adsorbed about 17% less As(V) than goethite (44 m²/g) between pH 5 and 9 under identical conditions. Lin and Puls [19] reported that Fe hydroxides could adsorb two or more orders of magnitude of As than clays, and the As(V) adsorbed by clay minerals could be easily desorbed compared to that adsorbed by Fe hydroxides. Moreover, as discussed in Section 2.1, amorphous Fe (hydro)oxides demonstrate a higher sorption capacity to As than the crystalline Fe (hydro)oxides.

Therefore, the addition of amorphous Fe hydroxides or other Fe-rich materials to create amorphous Fe hydroxides *in situ* tends to be a promising method to enhance As NA. The presence of abundant Fe hydroxides may enhance the immobilization of As through sorption, coprecipitation and oxidation of As(III) to the less mobile As(V). As(V) can be immobilized by coprecipitation with Fe hydroxides, with the ultimate formation of scorodite (FeAsO₄·2H₂O) [25]. It was estimated that a Fe/As ratio of 3–4 is sufficient to efficiently retain As in polluted soils [9]. The mobility of As decreases when the Fe/As ratio increases. A higher Fe/As ratio may be necessary to eliminate the competition effects by other anions. The maintenance of an acidic and oxidizing environment is necessary to ensure the long-term immobilization of As. Addition of H₂O₂ and Fe salts (e.g., FeCl₂ and FeSO₄) together can be used to precipitate As from groundwaters. Addition of H₂O₂ can create Fe hydroxides *in situ*, catalyze the oxidation of As(III) to As(V), and provide an oxidizing environment to favor As(V) sorption. The optimal pH should be controlled in the range of 4–7 to enhance As sorption and prevent As remobilization. Moreover, zero-valent iron also has been demonstrated as an inexpensive, nontoxic and efficient adsorbent that can be used to remove arsenic from groundwater [81].

Various field trials have been performed to evaluate the feasibility of using steel shots and beringite to immobilize As [71,72]. The corrosion of the steel shots enhances the formation of Fe/Mn oxides while beringite affects the soil pH. Boisson et al. [71] reported that the amendment of soil with 1% steel shot and 5% beringite was very effective in reducing As mobility due to adsorption and precipitation with Fe oxides. But hydroxyapatite addition could enhance As mobility due to competition with phosphate. Mench et al. [72] evaluated the long-term sustainability of various amendments at a former gold mine including 5% compost with steel shot (CSS), 5% compost with 5% beringite and 1% steel shot (CBSS), 5% compost and others. The CBSS and CSS treatments were very successful in terms of revegetation and decreased leaching, compared to compost only. Addition of immobilizing agents that are insoluble such as hydroxyapatite, zeolites or illitic clays can be problematic, particularly to depths below 50 cm.

6.2. Bioaugmentation and biostimulation

Natural biological processes usually occur at a low rate. Substrates can become less bioavailable via interaction with negatively charged clay particles and organic matter. Bioavailability of electron acceptors can influence microbial activity. Solid Fe(III) must be available and in direct contact for the microorganisms. Bioaugmentation and biostimulation can be used to promote local microbial activity. Biostimulation is the process by which a stimulus to the microorganisms that already exist in the site is provided by adding nutrients and other growth substrates, together with electron donors and acceptors, while bioaugmentation is the process of introducing exogenous microorganisms into the site.

Biosurfactant foam technology can be used to deliver nutrients or microbial populations into the subsurface [73,74]. As by-products from bacteria and yeast, biosurfactants (e.g., rhamnolipid, surfactin, and sophorolipid) generally are environmentally benign due to their low toxicity and high biodegradability. The use of biosurfactants may increase the availability of Fe(III) and As to the microorganisms due to the decrease in interfacial tension and formation of micelles. An aerobic or anaerobic environment can be created by changing the foaming gas. Aerobic conditions can be created by using air or oxygen as foaming gas. Anaerobic biological processes can proceed with the addition of nitrates, Fe(III) oxides, Mn(IV) oxides, sulfate and CO₂. Addition of natural organic matter such as humic acids can provide electron acceptors since humic acids can chelate Fe. The presence of humic acids can significantly increase Fe bioavailability [4]. A preferred pH range can also be achieved with addition of different pH buffers.

Particularly, Fe-oxidizing bacteria, such as *G. ferruginea* and *Leptothrix ochracea*, are indigenous in most groundwaters [10]. These bacteria, in case of their absence, may be introduced into the groundwater. Nutrients can be added to stimulate the growth of the bacteria. These bacteria can catalyze the oxidation and subsequent precipitation of respective Fe oxides under specific pH (slightly over 7), dissolved oxygen (2–4 mg/L), and redox conditions (Eh = 100–600 mV) [10,28,62]. Soluble As then can be removed from groundwater by sorption to the produced biogenic Fe oxides. The oxidation of As(III) catalyzed by the bacteria can further enhance the NA efficiency [10].

6.3. Hyperaccumulation in combination with phytoremediation

Hyperaccumulation transfers dissolved As from soils or waters into plant tissues. A combination of hyperaccumulation with phytoremediation can remove or contain As, offering an effective, environmentally nondestructive and cheap remediation method. It is critical to select proper hyperaccumulating plants. Plants that are suited for As hyperaccumulation should have wide distribution, high above-ground biomass, high bio-concentration factors, a short life cycle and high propagation rates. In the case of groundwater remediation, plants with deep roots are preferred. Site conditions must be analyzed and then necessary nutrients can be added to ensure the vigorous growth

of the plants. The availability of As to plants can be increased by using electrokinetic methods [75]. Genetic engineering strategies may be used to modify plants for As uptake, transport and sequestration, thus to increase the As hyperaccumulating capacity of plants. It has been demonstrated that the overexpression of proteins involved in intracellular As sequestration can increase the As-hyperaccumulating capacity significantly. Dhankher et al. [76] reported that the engineering tolerance and hyperaccumulating capacity of As in *Arabidopsis thaliana* plants was enhanced by combining As(V) reductase (ArsC) and γ -glutamylcysteine synthetase (ECS) expression. When grown on As, the transgenic plants accumulated 4- to 17-fold greater fresh shoot weight and accumulated 2- to 3-fold more As per gram of tissue than wild type or plants expressing γ -ECS or ArsC alone.

In general, planting of plants that are capable of hyperaccumulating high concentrations of As from soils and shallow groundwater within a short time period at the contaminated sites should be considered as a main engineering strategy for enhancement. Those plants (e.g., *P. vittata*, Table 3) that are capable of accumulating As concentrations more than 1000 mg/kg in tissues with a bioconcentration factor above 10 and able to uptake As from relatively unavailable pools should be considered as promising candidates. Addition of organic materials such as cow manure can be used to support the plant growth and may increase As mobility and availability to the plants. Plant harvest is absolutely required. After harvesting, the hyperaccumulating plants can be either disposed of as hazardous wastes or subjected to extracting processes to remove As for industrial use [1].

7. Conclusions and recommendations

NA of As occurs mainly through immobilization, biotransformation and hyperaccumulation. As can be retained in soils or removed from groundwater by sorption to Fe, Al and Mn

(hydro)oxides, clay mineral phases and NOM, forming insoluble solids. Chemical and microbially mediated oxidation and reduction reactions may produce less mobile As species and mixed solid phases capable of sorbing As, thus enhancing the immobilization processes. However, the immobilization processes by sorption is reversible and the remobilization of sorbed As may occur when the site biogeochemical conditions change with time. Biotransformation may contribute to As detoxification by forming less toxic species and volatilization occasionally by forming volatile species. Hyperaccumulation in plants can translocate As from soils and waters into plant tissues, reducing the in site As concentrations. Engineering strategies using environmentally benign products may be considered to enhance the remediation rates and efficiency.

NA of As contamination in soils and groundwater is a complicated function of the co-occurring physicochemical and biological processes (Fig. 3). As immobilization through sorption to solid phases currently is the best NA mechanism to retain As in soils and remove it from groundwater, and this process can be enhanced by microbial activities. Hyperaccumulation is another applicable choice to remove As from soils and shallow groundwater. However, NA is site specific and cannot be assumed to be operational at a given site. It will be effective only at sites with special environmental conditions conducive to the attenuation of As. Sufficient characterization of the site geology, hydrology, and microbiology is required to model the fate and transport of As in the contaminated soils or groundwater. Conceptual and mathematical models developed then will be useful to predict whether the desired reactions can take place to obtain effective and optimal immobilization of the contaminant with solid phases and transformations that will enhance the immobilization or reduce the toxicity. Detailed investigation and long-term continued monitoring are absolutely necessary to ensure that the NA processes really occur at an acceptable rate, to ensure that

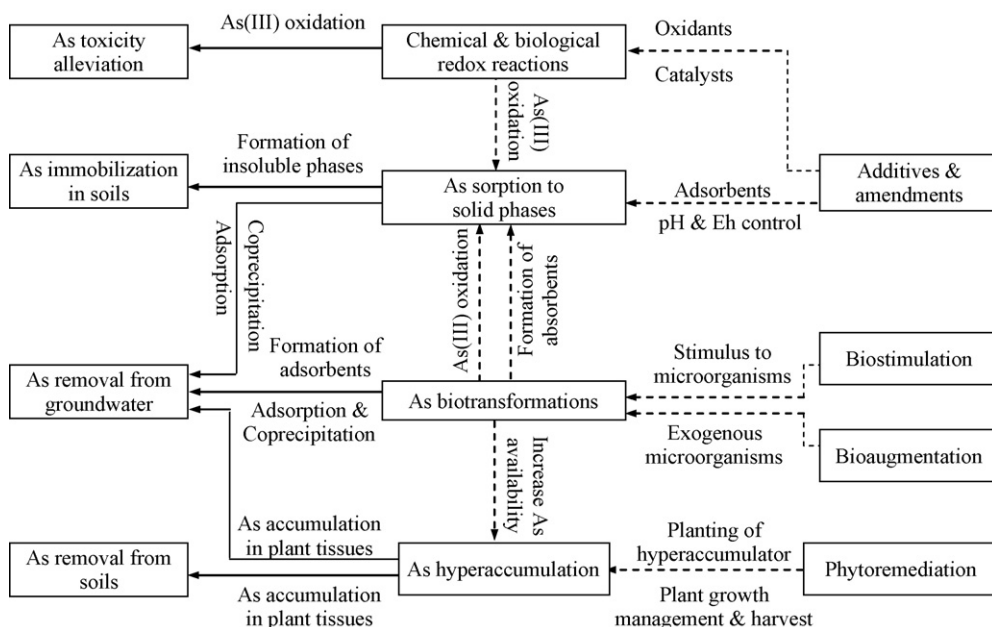


Fig. 3. Main As NA processes and engineering enhancement strategies.

conditions that do not favor NA occur, and to calibrate the models. Although various technical protocols have been established for NA, they are mainly adapted for organic contaminants in groundwater [14]. Further efforts are needed to verify whether they are applicable to As-contaminated soils and groundwater, or to develop applicable alternatives.

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