

Article

The Role of Naturally Occurring Fe(II) in Removing Arsenic from Groundwater: Batch Experiments and Field Studies

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Abstract: Higher levels of arsenic (As) and iron (Fe) in groundwater have been reported globally. This study aims to enhance our understanding of the role of naturally occurring dissolved Fe(II) in removing As from groundwater. Field experiments were conducted using five clay filters to investigate As and Fe removal from contaminated groundwater. The field results revealed a wide range of arsenic removal (7.3% to 80%) using the clay filters. The filter with the highest Fe concentration (14.5 mg/L) exhibited the highest As removal, while the lowest Fe concentration (2.2 mg/L) resulted in the lowest percentage of As removal. A direct correlation was observed between effluent As levels and the Fe/As molar ratio. An Fe/As molar ratio of 40 or more was identified as necessary to achieve effluent As concentrations below 50 µg/L. Laboratory batch experiments revealed that Fe(II) was more effective than Fe(III) in removing both As(III) and As(V) from contaminated groundwater. As(V) removal was consistently higher than As(III) removal, regardless of whether Fe(II) or Fe(III) was used. The results suggested that the oxidation of As(III) and the subsequent in situ formation of Fe(III) hydroxide were more efficient in As adsorption than direct Fe(III) treatment. The X-ray absorption fine structure (XAFS) analysis of the floc samples confirmed the dominant peaks of As(V), indicating that most of the As(III) oxidized to As(V) in the As(III)-Fe(II) system. The use of natural Fe(II) in groundwater, possibly supplemented with additional sources of Fe(II), is suggested as a promising, cost-effective, and efficient method for As(III) and As(V) removal.

Keywords: groundwater; arsenic; iron; water treatment; clay filter; pollutant removal; XAFS analysis



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1. Introduction

Arsenic contamination in drinking water is a significant global concern. This issue affects large segments of the global population and poses significant threats to human health. Notably, inorganic forms of As are acknowledged as potent human carcinogens [1,2]. The World Health Organization (WHO) has set a guideline value of 10 µg/L for arsenic in drinking water [3]. However, in certain developing countries with highly contaminated groundwater sources, the established limit for arsenic in drinking water is set at 50 µg/L due to practical considerations, economic constraints, or a lack of resources to meet lower standards [4]. The release of arsenic into groundwater from geologic alluvial sediment components originated from the redox reaction of arsenic-rich pyrites [5]. The mobility of

As in groundwater is significantly influenced by the pH of the water. The different oxidation states of arsenic predominate under different pH conditions, affecting its solubility and mobility [5].

Arsenic in groundwater exists in two main forms—arsenite (As(III): H_3AsO_3 or HAsO_2) and arsenate (As(V): H_2AsO_4^- or HAsO_4^{2-}). As(III) is more toxic than As(V), and it is often found in reduced groundwater conditions. As(III) removal is more challenging than As(V) removal using conventional treatment methods like adsorption/coprecipitation. The pre-oxidation of As(III) to As(V) using oxidation agents is a suggested strategy for enhancing the removal performance of As [6–8]. However, this process is complex and potentially cost-intensive.

To date, the conventional techniques for As removal include oxidation and precipitation [8,9]; adsorption with alum, iron, and other adsorbents [10,11]; ion exchange [12]; coagulation/flocculation with aluminum, iron, titanium, and zirconium [13,14]; microfiltration and ultrafiltration technologies [15]; electrodialysis [16]; and biological processes [17]. These methods have been widely applied as sustainable As mitigation strategies. Among these technologies, the adsorption process has been proven to be the most sustainable technique for As removal. This technology is highly effective in removing As from groundwater [18]. This process is comparatively simple and easy to operate [19]. It has low costs due to its energy-free operation [20] and low sludge production potential [21]. Nevertheless, the efficiency of As adsorption depends on water chemistry, including pH and redox conditions [18]. Moreover, if As(III) is the predominant species in the water, peroxidation steps may be required for effective removal [6–8]. Moreover, the presence of coexisting anions, such as phosphate and silicate, can hinder As adsorption [10]. Passive groundwater treatment utilizing native Fe(II) in groundwater to facilitate the oxidation and removal of As is one of the potential methods. This method involves the oxidation of Fe(II) and the coprecipitation of As with in situ-oxidized Fe(III) hydroxides [22–24]. This process enhances As(III) removal and is applied extensively. Thus, the use of dissolved ferrous iron (Fe(II)) is favored for As removal. The native Fe(II) in groundwater can serve as a source of Fe(II), minimizing the need for additional Fe(II) in the treatment process.

The elevated levels of arsenic in groundwater are often associated with higher levels of iron in many areas [25,26]. In Bangladesh, for example, groundwater was reported to have As concentrations ranging from 10 to 1660 $\mu\text{g}/\text{L}$ and Fe concentrations ranging from 0 to 20 mg/L [4]. In reduced groundwater conditions, both As and Fe exist as dissolved forms of As(III) and Fe(II), respectively. Therefore, the presence of dissolved Fe(II) in the groundwater may play a crucial role in the removal of As(III). Several Fe-based arsenic removal technologies, such as the SONO filter, the Kanchan arsenic filter (KAF), and the arsenic removal ceramic filter, have been successfully employed in arsenic-affected regions [26–28]. These technologies typically use Fe-amended sand filters or ceramic filters, where arsenic is removed through the formation of Fe(III) oxides in the water, facilitated by the corroding of metal iron, such as iron nets, iron nails, or iron fillings. These technologies may not fully account for the role of naturally present groundwater Fe(II) in the removal of As, especially As(III). As(III) is typically abundant in reduced groundwater and is less effectively adsorbed onto Fe(III) hydroxides, leading to potential miscalculations in the required Fe for the system. Therefore, understanding the interactions between As and Fe in their different oxidation states is crucial for optimizing As removal technologies. The consideration of existing groundwater conditions, As speciation, and the role of naturally occurring Fe(II) is essential in designing effective As removal systems.

The present study aims to enhance our understanding of the role of naturally occurring Fe(II) in the removal of As from groundwater. The specific objectives are to (i) study the efficiency of As removal using a clay filter under real-field conditions; (ii) study the mechanisms involved in the removal of both As(III) and As(V) using Fe(II) and Fe(III) in laboratory batch experiments; and (iii) reveal the As removal mechanism through X-ray absorption fine structure (XAFS) analysis.

2. Materials and Methods

2.1. Clay Filters and Field Experiments

The clay filters were obtained from Mollahat Bazar, a local market in the Bagerhat district of Bangladesh. Each filter costs BDTK 700, equivalent to USD 10. The clay filter consists of a filtration bucket made of concrete. The filtration bucket has an approximate diameter of 25 cm and a height of 35 cm, providing a capacity of 17 L (Figure 1a). Two clay filter candles are fixed at the bottom of the bucket using cement mortar (Figure 1b,c). The detailed structure of the clay filter and its schematic are shown in Figure 1b. According to the seller, the clay filter candles are made of rice straw and clay soil.

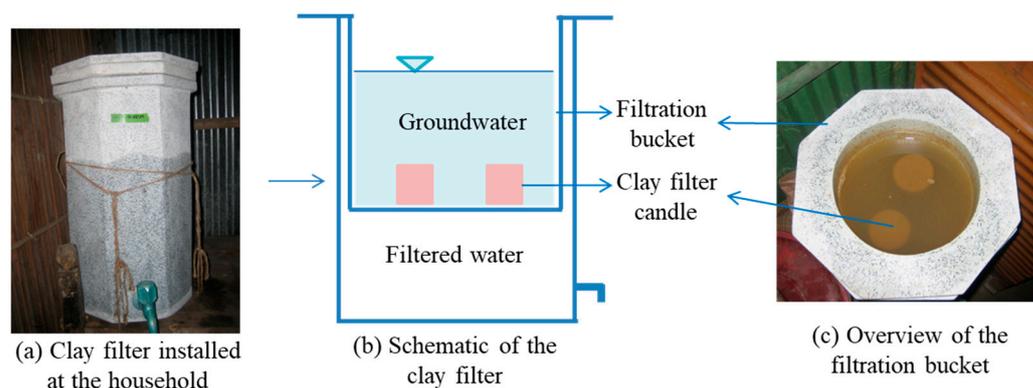


Figure 1. (a) Clay filters in the field, (b) schematic of the clay filter, and (c) top view of the filtration bucket.

While the detailed mineralogical compositions of the clay used in the filters are not known, the soil typically used for clay-based filters is primarily composed of clay, silt, and sand [28]. The exact pore size of the filter was unknown, but it was noted that the pore size was small enough to trap Fe hydroxide flocs. The filtration bucket was hung inside a storage bucket, as depicted in Figure 1b.

Five clay filters were distributed to local households in the Mollahat subdistrict (Figure 2), and they were instructed to operate the clay filters on a daily basis. The groundwater from the adjacent tubewell of each household was used as the raw water source for each clay filter. Filter operation included the simple process of pumping groundwater from a tubewell and pouring it into the filtration bucket. The filtration process was gravitational, meaning no external energy was required for the filters to function. Both groundwater (influent) and effluent samples were collected from each filter consecutively for three days. After collection, the samples were transported back to the laboratory and analyzed for various water quality parameters.

2.2. Reagents and Synthetic Groundwater

All chemicals for this study were obtained from Wako, Japan, and Nacalai Tesque Inc., Kyoto, Japan. As(III) and As(V) stock solutions (100 mg/L) were prepared using As_2O_3 and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ powder, respectively. A stock solution of Fe(II) was prepared using $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ immediately before starting experiments. Fe(III) solution with a concentration of 5 mg/L was prepared by dissolving 14.3 mg of FeCl_3 powder in 1 L of deionized water. Synthetic groundwater, simulating the natural groundwater of Bangladesh, was prepared in the laboratory. Concentrations of common water quality parameters for the synthetic groundwater are provided in Table 1.

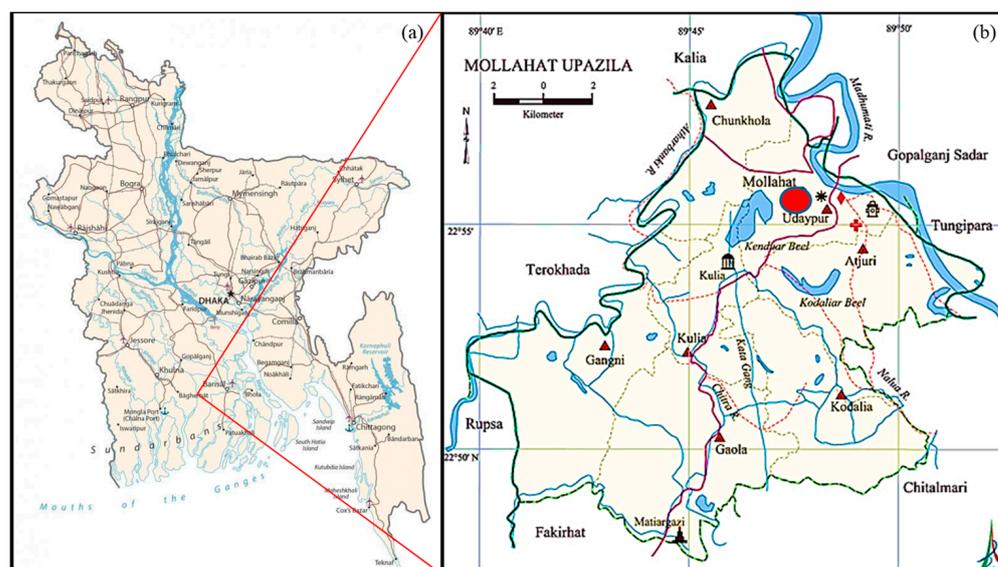


Figure 2. (a) Map of Bangladesh along with (b) map of Mollahat subdistrict (study area) (source: Banglapedia, https://en.banglapedia.org/index.php/Mollahat_Upazila (accessed on 2 November 2023)).

Table 1. Concentrations of common water quality parameters for the synthetic groundwater and the natural groundwater of the five clay filters.

Parameters	Unit	Concentrations	
		* Synthetic Groundwater	Groundwater Used for Five Clay Filters
pH	-	7.1–7.2	6.9–7.5
Eh	mV	138	90–141
DO	mg/L	6.0–6.5	2.5–2.9
As	µg/L	500	110–220
Fe	mg/L	5–20	2.2–14.5
Si	mg/L	20	16.9–24.1
Mn	mg/L	0.45	0.09–0.23
Ca+	mg/L	100	112–170
Mg+	mg/L	40	39–47
PO ₄ -P	mg/L	1.0	1.2–2.3
SO ₄ ⁻	mg/L	200	-
Hardness (as HCO ₃ ⁻)	mg/L	350	400–450

Note: * Synthetic groundwater was prepared based on the groundwater data from BGS and DPHE [4].

2.3. Batch Experiments

A series of batch experiments were conducted to investigate the removal of As(III) and As(V) using Fe(II) and Fe(III). Five batch experiments were conducted to understand the individual effects of adding Fe(II) and Fe(III) on the removal of As(III) or As(V) (Table 2). Synthetic groundwater was used for each series of experiments. The initial concentrations were set at 5 mg/L for Fe(II) or Fe(III) and 500 µg/L for As(III) or As(V), representing the average concentrations in Bangladesh groundwater (Table 2). For all experiments, synthetic groundwater was continuously mixed at 30 rpm for 5 h in a glass beaker using a Jar test apparatus. The pH was maintained between 7.0 and 7.2, and dissolved oxygen (DO) levels were kept at 6.0–6.5 mg/L to ensure oxic conditions. The samples were collected at intervals of 0.5, 1.0, 2.0, and 5.0 h. After collection, each sample was filtered using Advantec No. 5C filter paper and analyzed the residual As and Fe. After 5 h of batch experiments, the

oxidized hydrous ferric oxide (HFO) flocs were collected for analyzing the oxidation state of As using X-ray absorption fine structure (XAFS) analysis.

Table 2. Details of laboratory batch experiments.

Exp. Name	As(III) ($\mu\text{g/L}$)	As(V) ($\mu\text{g/L}$)	Fe(II) (mg/L)	Fe(III) (mg/L)
As(III)-control	500	-	-	-
As(III)-Fe(III)	500	-	-	5.0
As(V)-Fe(III)	-	500	-	5.0
As(III)-Fe(II)	500	-	5.0	-
As(V)-Fe(II)	-	500	5.0	-

2.4. Analytical Methods

The water quality parameters of the influent and effluent samples were measured using the methods specified in Table 3. Selected parameters, such as pH, redox potential (Eh), electrical conductivity (EC), dissolved oxygen (DO), and hardness, were directly measured on-field using standard probes or test strips. For measuring other parameters in the laboratory, namely As, Fe, Mn, Ca, Mg, Si, and $\text{PO}_4\text{-P}$, water samples were collected and stored in polypropylene bottles and preserved via acidification with a diluted HCl solution. The laboratory analyses were conducted in the Environmental Engineering Laboratory of Ritsumeikan University, Shiga, Japan.

Table 3. Details of laboratory analytical procedure.

Parameters	Equipment Used
pH, Eh, and EC	HORIBA-D-54S pH meter, HORIBA, Osaka, Japan
Dissolved oxygen (DO)	HACH-HQ30d DO meter, HACH, Tokyo, Japan
Hardness (as HCO_3^-)	AQUACHECK-ECO test strips, AQUACHECK, Loveland, CO, USA
As *	Inductively coupled plasma mass spectrometry (ICP-MS), Yokogawa, HP 4500, Hewlett-Packard, Tokyo, Japan
Fe *, Mn *, Ca *, Mg *, and Si *	ICP spectrometry (ICP-AES), Seiko SPS 4000, Tokyo, Japan
Sulfate, SO_4^{2-} *	HQ 30d UV spectrophotometer, Shimadzu, Kyoto, Japan
Phosphorus as $\text{PO}_4\text{-P}$ *	HQ 30d UV spectrophotometer, Shimadzu, Kyoto, Japan

Note: * Measured according to the standard method of APHA [29].

2.5. X-ray Absorption Fine Structure (XAFS) Analysis

X-ray absorption fine structure (XAFS) is a spectroscopic technique utilized to gather information about the local structure of a material. In this study, the XAFS As L3 absorption edge spectroscope was employed to detect the oxidation state of HFO flocs obtained from batch experiments. The analysis was performed at the BL-10 beam line in the Synchronized Radiation (SR) Center of Ritsumeikan University, Japan. Two chemical species, As_2O_3 and NaAsO_2 , were utilized as standards to determine the spectrum for As(III), while $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ and KH_2AsO_4 were used as standards for As(V). The spectrum peak of the HFO samples was compared and analyzed with standard samples. Comparing the spectrum peak of the HFO samples against the standard samples allowed for the identification and analysis of the oxidation states.

3. Results and Discussion

3.1. Groundwater Quality

The analysis of the groundwater quality for the filters is presented in Table 1. pH values ranging from 6.9 to 7.5 indicate slightly alkaline conditions in groundwater aquifers. The pH of groundwater is crucial for controlling the chemical and biological parameters and the toxicity of various compounds [30]. The measured Eh values fell in the range of 90–141 mV, indicating reduced conditions in the groundwater. Dissolved oxygen (DO)

values were relatively low, ranging from 2.5 to 2.9. The Eh-pH and DO profiles of the five groundwater samples indicate that the groundwater in the area is in a reduced condition. As and Fe concentrations were found to be very high in the studied area. As concentrations were measured at 110–220 $\mu\text{g/L}$, significantly higher than the WHO standard limit of 10 $\mu\text{g/L}$. Fe concentrations ranged from 2.5 to 14.5 mg/L , exceeding the WHO standard limit of 0.3 mg/L . Under reduced groundwater conditions, indicated by the Eh-pH profile (Figure 3), As primarily exists as arsenite (As(III): H_3AsO_3 or HAsO_2), and Fe exists as dissolved Fe(II) [11,31]. Arsenic contamination may be attributed to the oxidation of arsenical pyrites originating from the Himalayas [32,33]. Mn concentrations ranged from 0.09 to 0.23 mg/L , exceeding the secondary maximum contaminant level [34]. Calcium (Ca^+) concentrations ranged from 112 to 170 mg/L , and magnesium (Mg^+) concentrations ranged from 39 to 47 mg/L , indicating hard water. Higher Ca^+ concentrations could originate from the dissolution of carbonate rocks, such as limestone and dolomites, or agricultural fertilizers [35]. The decomposition of dolomite and ferromagnesian minerals contributes to Mg^+ concentration [35]. Si concentrations ranged from 16.9 to 24.1 mg/L , suggesting that silica results from the weathering of silicate minerals in groundwater. Phosphate ($\text{PO}_4\text{-P}$) concentrations were relatively high, ranging from 1.2 to 2.3 mg/L . Phosphate is known to be the competitor for the iron-based adsorption site with As [23,24,36]. Therefore, high levels of phosphate can compete with arsenic for iron-based adsorption sites, potentially reducing the efficiency of arsenic removal in treatment processes. This comprehensive analysis of the groundwater quality suggests that monitoring and appropriate treatment processes are essential for mitigating the impact of As and Fe contamination on public health and the environment.

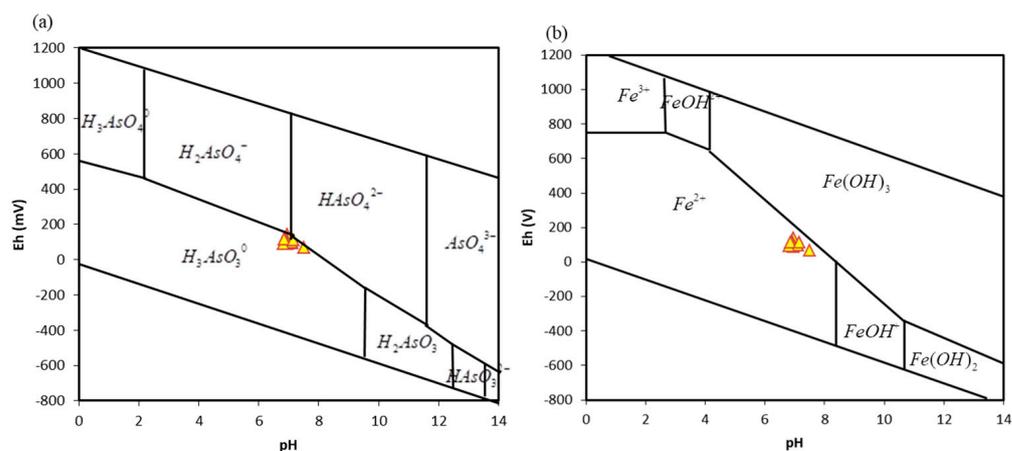


Figure 3. Eh-pH plots for (a) As and (b) Fe of collected groundwater samples. Triangle markers represent the redox conditions of the measured groundwater samples.

3.2. As and Fe Removal Using Clay Filters

In this study, an assessment of water quality in five groundwater sources revealed significant levels of arsenic (As) and iron (Fe) contamination. Therefore, the removal of these two elements from the groundwater is crucial and needs to be investigated. The field study results also indicate that the elevated level of As is correlated with the Fe concentrations in the groundwater (Table 1). Table 4 and Figure 4 present data on influent and effluent concentrations, as well as the percentage removal of As and Fe for the five clay filters. As removal varied among the filters, ranging from 7.3% to 80%, with the highest removal observed for Filter #1. The removal achieved with Filter #1 was substantial, resulting in a reduction of 156 $\mu\text{g/L}$. Interestingly, Filter #1, which exhibited the highest As removal, also had the highest Fe concentration at 14.5 mg/L . In contrast, Filter #4 showed the lowest As removal at 8 $\mu\text{g/L}$, corresponding to the lowest Fe concentration of 2.2 mg/L among all filters.

Table 4. Removal %, influent, and effluent As and Fe of the 5 clay filters.

	As ($\mu\text{g/L}$)			Fe (mg/L)			Fe/As (mol/mol)	
	Influent	Effluent	Removal %	Removal	Influent	Effluent		Removal %
Filter #1	220	64	70.9	156	14.45	0.21	98.5	49.0
Filter #2	160	85	46.9	75	4.4	0.25	94.3	20.5
Filter #3	140	38	72.9	102	10.35	0.13	98.7	55.2
Filter #4	110	102	7.3	8	2.28	0.11	95.2	15.5
Filter #5	125	25	80.0	100	6.5	0.11	98.3	38.8

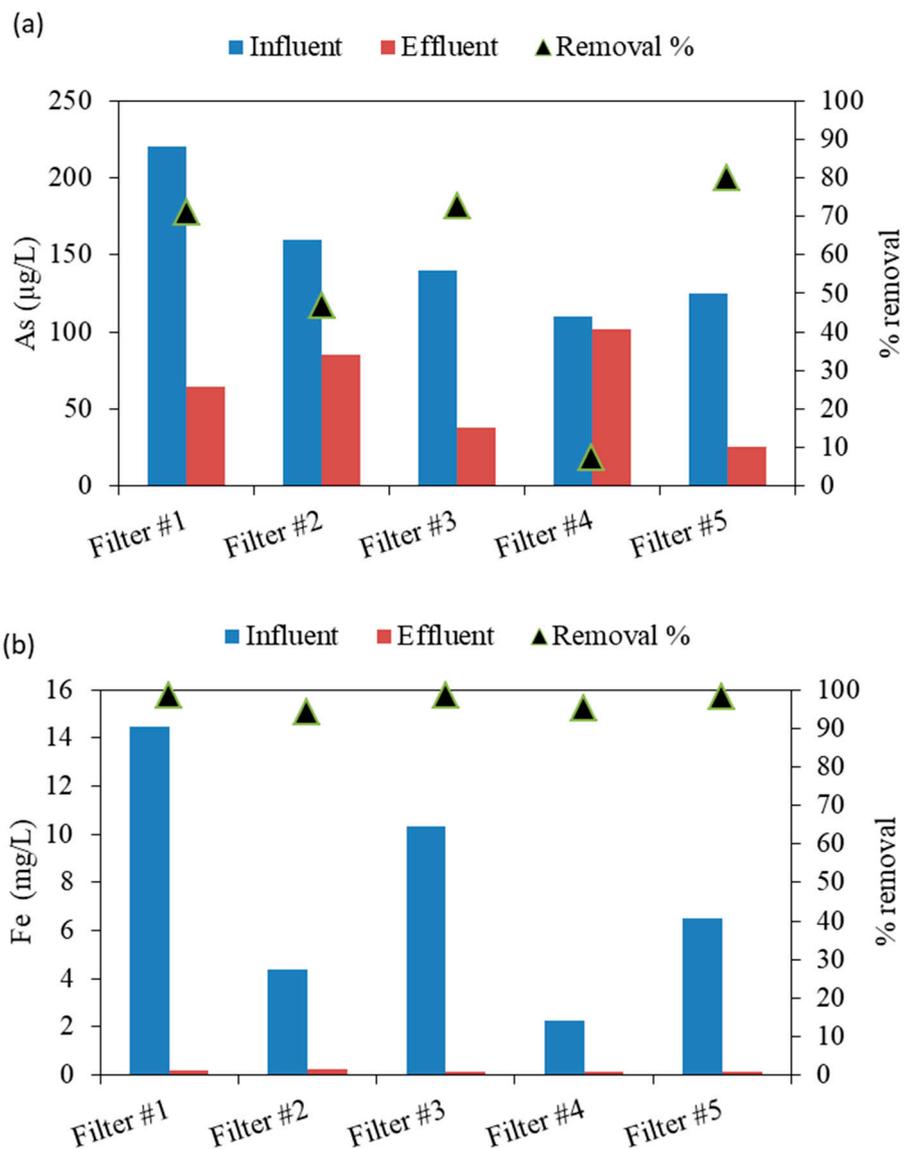


Figure 4. Removal %, influent, and effluent of (a) As and (b) Fe of the 5 clay filters.

Notably, Fe removal exceeded 94% for all filters, signifying the effectiveness of the filter in eliminating Fe contamination from the groundwater. The removal of Fe was attributed to the oxidation of dissolved Fe(II) to Fe(III) hydroxide, followed by filtration through the clay filter. Despite the reducing conditions in the groundwater (Eh 90–141 mV and DO 2.5–2.9 mg/L), the Eh and DO inside the filter (after pouring water) increased to 400–430 mV and 6.0–7.0 mg/L, respectively. The increased Eh and DO inside the filter

create a more oxidizing environment, facilitating the efficient oxidation of dissolved Fe(II). These findings also suggest that As removal with clay filters is significantly influenced by the natural Fe levels in the groundwater. Further analysis was performed to establish a relationship between effluent As and the Fe/As molar ratio in the groundwater. The results depicted in Figure 5 illustrate a direct correlation, indicating a decrease in effluent As with an increase in the Fe/As molar ratio. The effluent As was achieved below the Bangladesh standard limit of 50 µg/L when the Fe/As molar ratio reached 40 or more. A positive correlation coefficient ($R^2 = 0.598$) suggested a robust association between As removal and the Fe content in the groundwater. Consequently, it was inferred that As removal primarily occurred through the oxidation–coprecipitation process, emphasizing the role of Fe oxidation in facilitating As removal. The Fe/As molar ratio was identified as a key parameter for ensuring successful arsenic removal in the treated effluent. Controlled laboratory batch experiments were conducted to further comprehend the mechanism of simultaneous As and Fe removal from the groundwater. The results of the batch experiments are discussed in the following section.

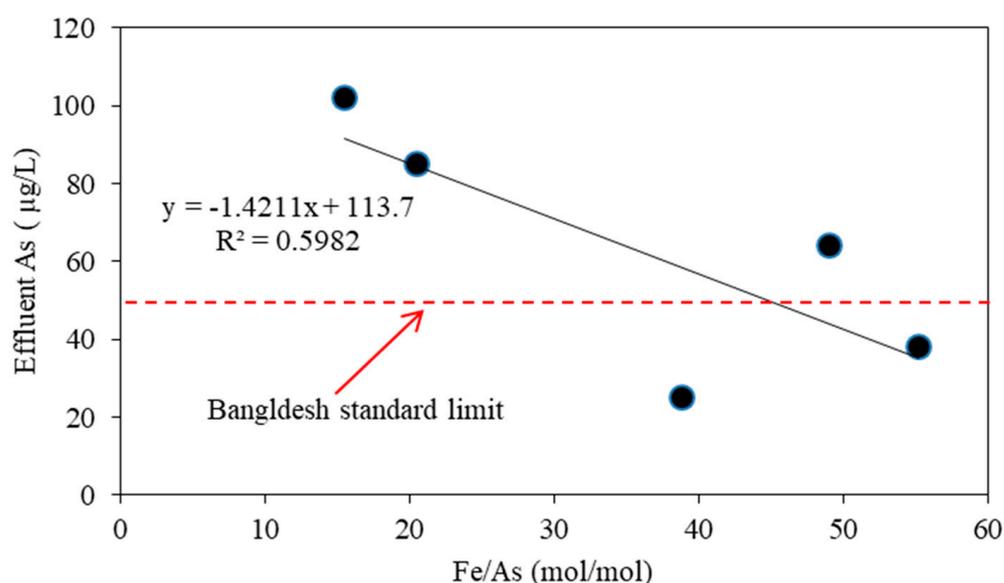


Figure 5. Correlation between the effluent As of the clay filter and the Fe/As molar ratio of groundwater.

3.3. Laboratory Batch Experiments

Figure 6 presents the results of controlled batch experiments investigating the removal of As(III) and As(V) using Fe(II) and Fe(III). Both As(III) and As(V) concentrations decreased from 500 µg/L to 405 µg/L and 276 µg/L, respectively, when using Fe(III) (As(III)-Fe(III) and As(V)-Fe(III) batch experiments). The removal percentages were calculated as 21% for As(III) and 44% for As(V), respectively. These results suggest that the adsorption of As(V) onto Fe(III) hydroxide is more dominant than that of As(III). It was also observed that most of the adsorption of As(III) and As(V) occurred within the first 30 min of the experiments. When using Fe(II), As(III) concentration was reduced to 245 µg/L, corresponding to a 51% removal rate. This is significantly higher than the removal achieved with Fe(III) (21%) (Figure 7). For As(V), Fe(II) was highly effective, allowing for the removal of up to 97% (Figure 7). In summary, these findings indicate that Fe(II) is more effective than Fe(III) in removing both As(III) and As(V) and that the adsorption behavior varies between these two As species. Thus, Fe(II) can be a valuable option for As removal in water treatment processes.

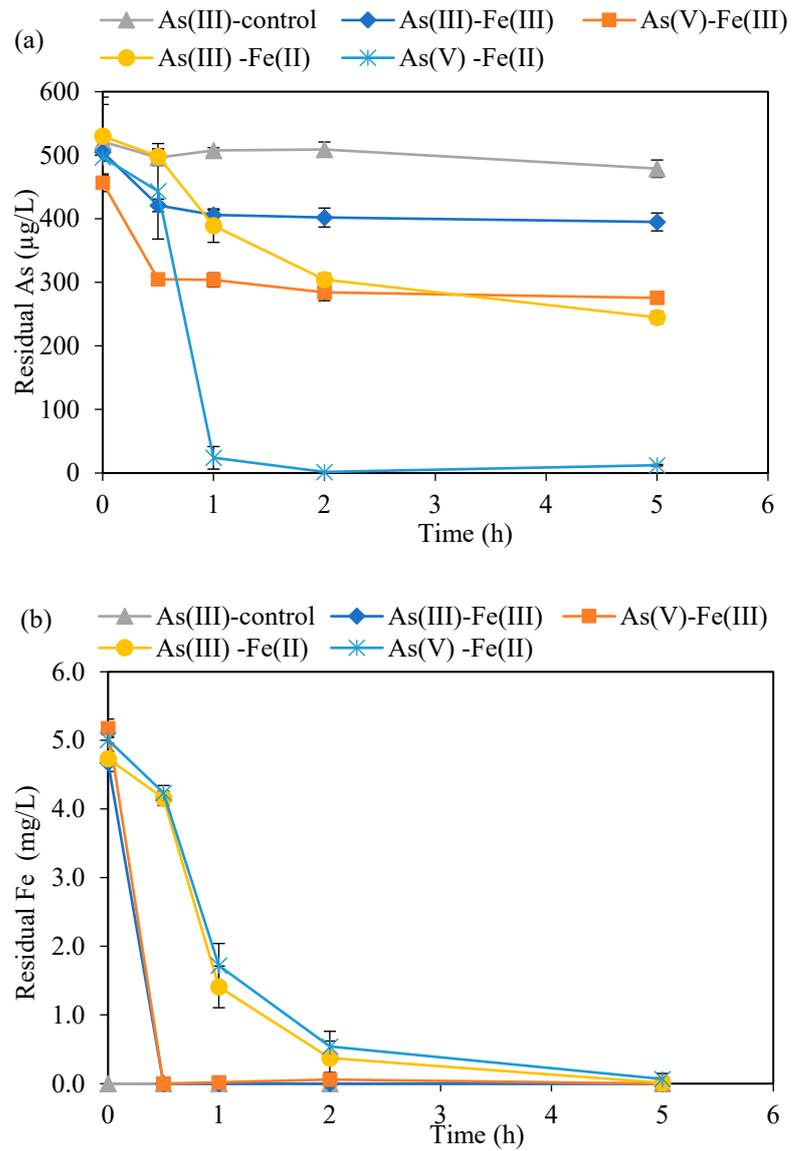


Figure 6. Removal of (a) As and (b) Fe under different experimental conditions.

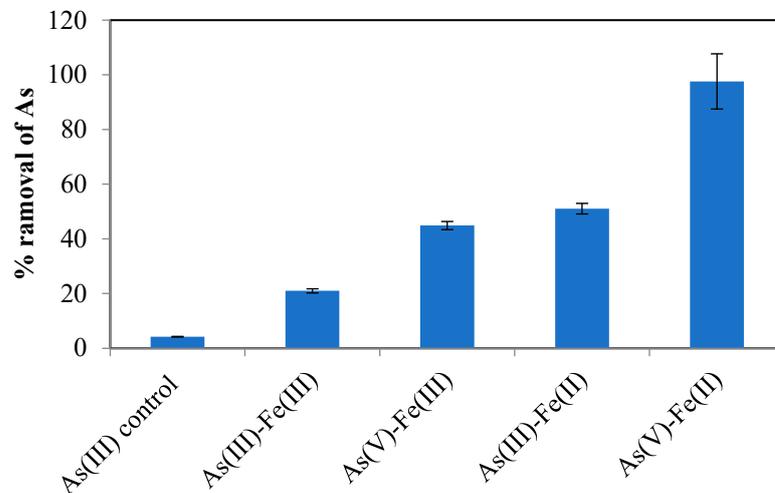


Figure 7. % Removal of As(III) and As(V) under different experimental conditions.

Figure 6b further clarifies the processes involved in the removal of As(III) and As(V) using Fe(II). The graph indicates that a significant portion of Fe(II) was oxidized and precipitated within the first 2 h of the As(III)-Fe(II) and As(V)-Fe(II) experiments. The experimental conditions, i.e., a pH level of 7.0–7.2, dissolved oxygen (DO) concentrations of 6.5–6.8 mg/L, and redox potential (Eh) of 300–400 mV, contributed to the accelerated oxidation of Fe(II) and the subsequent removal of As(III) and As(V). It is also worth noting that most of the As(III) and As(V) compounds were also removed within the first 2 h of the experiments. These results imply that the removal of As(III) and As(V) is predominantly dependent on the oxidation of Fe(II) and the coprecipitation process. The interaction between Fe(II) oxidation and the subsequent removal of both As species is crucial in this context. The efficiency ranking for the removal of As(III) and As(V) using different Fe species is provided as follows: As(V)-(Fe(II)) > As(III)-(Fe(II)) > As(V)-(Fe(III)) > As(III)-(Fe(III)). This suggests that using Fe(II) as an alternative to Fe(III) is more efficient in removing both As(III) and As(V).

3.4. Mechanisms of As(III) and As(V) Removal Using Fe(II)

The results of the laboratory experiments indicate higher removal percentages for both As(III) and As(V) when using Fe(II) compared to Fe(III) (Figure 7). Based on these results, two possible mechanisms may be involved in the process of As removal with Fe(II). During the oxidation of Fe(II), As(III) is oxidized, and the in situ formation of hydrous ferric hydroxide (HFO) occurs. This in situ-formed HFO is reported to be more efficiently adsorbed compared to direct Fe(III). Batch experiment results confirmed that Fe(II) is oxidized and subsequently coprecipitated with As. In the As(III)-Fe(II) system, intermediate reactive oxidants (OH, H₂O₂, and O₂) are produced during the oxidation of Fe(II). These reactive oxidants are very effective in the concurrent oxidation of As(III) to As(V) [22,37]. Hence, using Fe(II) instead of Fe(III) significantly improves the As removal efficiency, since the oxidized As(V) is more efficiently absorbed and coprecipitated with the in situ-formed hydrous ferric oxide (HFO) (Figure 7). Moreover, in situ-formed HFO flocs have a more active surface than direct Fe(III) oxides [38], which can effectively remove As from the aerated water. Therefore, in the natural system (field experiments with the clay filters), dissolved Fe(II) significantly contributes to the removal of As from the contaminated groundwater. Although the speciation of As(III) and As(V) was not measured in the groundwater samples for which the clay filters were used, it is reported that most As-enriched groundwater in similar settings exists in reduced conditions, with As(III) comprising more than 80% of the total As [39]. The measured parameters, including pH, ORP, and DO, support the assertion that the groundwater in the study area is in reducing/anoxic conditions, where As(III) and Fe(II) species are predominant. The oxidation and coprecipitation processes occurring in the clay filter are proposed to be responsible for the removal of As(III) and Fe(II) from the groundwater.

To gain further insights into the mechanisms of As(III) and As(V) removal using Fe(II) and Fe(III), the HFO flocs formed during the batch experiments were examined via XAFS L3-edge spectroscopy. XAFS spectroscopy, particularly at the L3 edge, is a powerful tool for the speciation of arsenic, distinguishing between As(III) and As(V) and providing valuable information about their local environments [40]. The XAFS L3-edge spectra of the standard solutions of As(III) and As(V), along with the four HFO floc samples from the batch experiments with As(III)-Fe(II), As(III)-Fe(III), As(V)-Fe(II), and As(V)-Fe(III), are illustrated in Figure 8a,b. Two distinct peaks at around 1331 eV and 1328 eV were identified for two As(V) standard samples, while a distinct peak for As(III) standard samples was identified at 1327 eV. The XAFS spectra of the standard solution were compared with those of the experimental samples. Both As(V)-Fe(II) and As(V)-Fe(III) samples showed two distinct peaks at 1331 and 1327 eV, similar to the two As(V) standard samples. As(III)-Fe(III) samples exhibited a shoulder/doublet left peak at 1326.5–1328 eV, suggesting the presence of both As(III) and As(V). This suggested that a portion of As(III) might have oxidized to As(V) in this sample. As(III)-Fe(II) samples displayed two distinguished peaks at 1331 and

1328 eV, similar to the As(V) standard samples. Nevertheless, a shoulder/doublet left peak at 1326.5–1328 eV indicates the existence of As(III) in the sample. These results suggest that, during the oxidation of Fe(II), most of As(III) was oxidized to As(V). Overall, the present study concludes that the oxidation and coprecipitation processes of As(III) are involved when using Fe(II) in the system. The findings are summarized in Figure 9, which illustrates the As(III) and As(V) removal process, emphasizing the role of Fe(II).

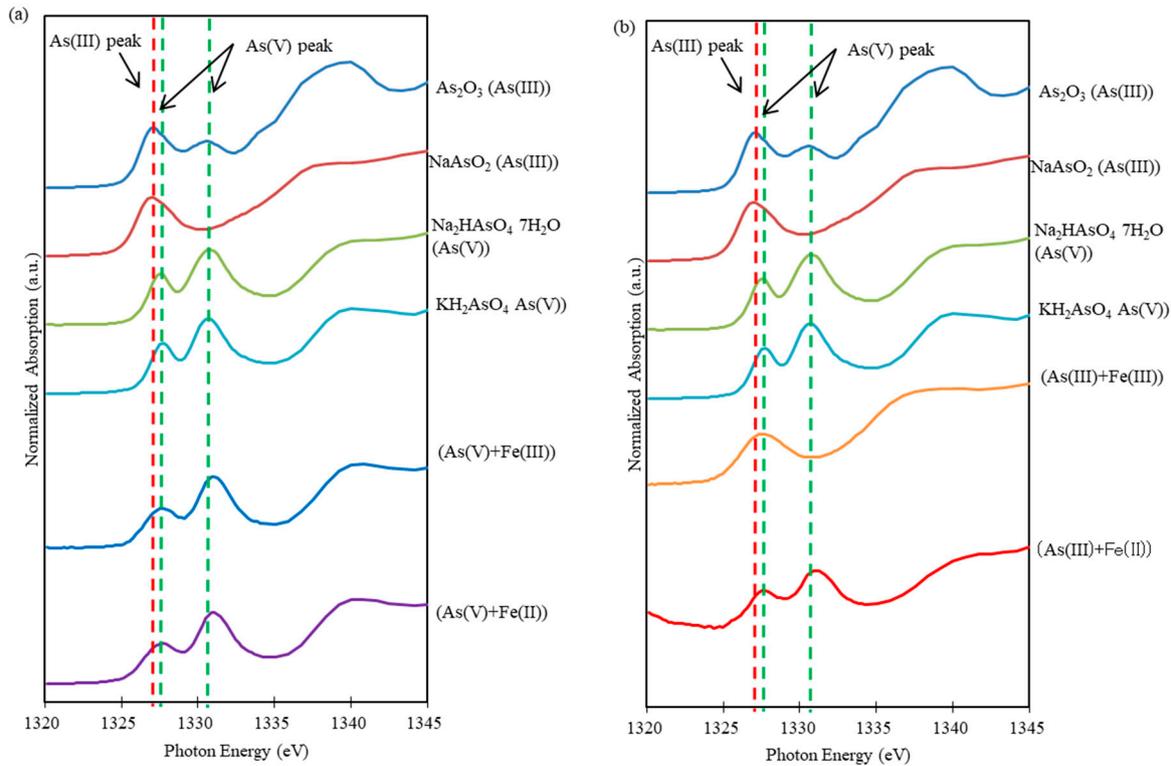


Figure 8. L3-edge spectra of XAFS of the HFO flocs (a) As(V)-Fe(III) and As(V)-Fe(II) batch experiments and (b) As(III)-Fe(III) and As(III)-Fe(II) batch experiments along with reference standards.

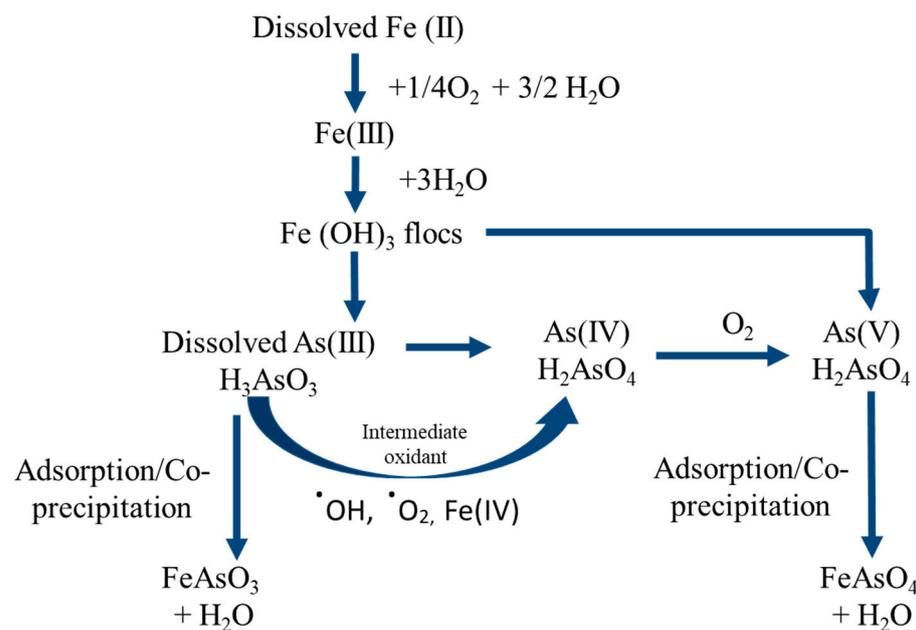


Figure 9. Possible mechanisms of As(III) and As(V) removal with Fe(II).

The comprehensive analysis of the XAFS spectra provides valuable insights into the complex processes involved in the removal of As(III) and As(V) during the formation of HFO flocs in the presence of Fe(II). The findings highlight the significance of the oxidation of As(III) in enhancing the removal of As. Overall, this study suggests that the elevated levels of naturally occurring Fe(II) in natural groundwater can contribute to and enhance the As removal from groundwater. Moreover, the results of this study show that dissolved Fe(II) is more efficient than direct Fe(III) in removing both As(III) and As(V). Therefore, the use of natural Fe(II) in groundwater with additional sources of Fe(II) can be a cost-effective and efficient method for As removal. Fe(0) (zerovalent iron) such as iron net or iron nail is a locally available source of Fe(II) that can be used [25,28].

4. Conclusions

This study provides insight into the specific role of naturally occurring Fe(II) in the removal of As from groundwater. The five clay filters demonstrated varying As removal efficiencies, ranging from 7.3% up to 80%. As removal was highly dependent on the concentration of Fe(II) in the groundwater. As removal was highest when the groundwater had higher concentrations of Fe and, conversely, the removal efficiency was lower when the Fe content in the groundwater was lower. An Fe/As molar ratio of 40 or more was identified as a critical parameter for achieving effluent arsenic concentrations below 50 µg/L. This molar ratio serves as a practical guideline for optimizing As removal efficiency, emphasizing the importance of the relative concentrations of Fe and As. Fe(II) was more efficient than Fe(III) in removing both As(III) and As(V) from the contaminated water. Regardless of whether Fe(II) or Fe(III) was used, the removal efficiency for As(V) was consistently higher than that for As(III). XAFS analysis revealed the dominant presence of As(V) in the HFO flocs. In this study, the concurrent oxidation of both Fe(II) and Fe(III), followed by precipitation, is identified as the primary mechanism for the effective removal of As from groundwater. The study highlights the importance of dissolved Fe(II) in oxidation processes, emphasizing its role in the oxidation of As(III) to As(V). Overall, the utilization of natural Fe(II), possibly in combination with other sources of Fe(II), presents a viable approach for the removal of As from groundwater, offering practical guidelines for optimizing the process.

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