



Background species effect on aqueous arsenic removal by nano zero-valent iron using fractional factorial design

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ABSTRACT

This study describes the removal of arsenic species in groundwater by nano zero-valent iron process, including As(III) and As(V). Since the background species may inhibit or promote arsenic removal. The influence of several common ions such as phosphate (PO_4^{3-}), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), calcium (Ca^{2+}), chloride (Cl^-), and humic acid (HA) were selected to evaluate their effects on arsenic removal. In particular, a 2^{6-2} fractional factorial design (FFD) was employed to identify major or interacting factors, which affect arsenic removal in a significant way. As a result of FFD evaluation, PO_4^{3-} and HA play the role of inhibiting arsenic removal, while Ca^{2+} was observed to play the promoting one. As for HCO_3^- and Cl^- , the former one inhibits As(III) removal, whereas the later one enhances its removal; on the other hand, As(V) removal was affected only slightly in the presence of HCO_3^- or Cl^- . Hence, it was suggested that the arsenic removal by the nanoiron process can be improved through pretreatment of PO_4^{3-} and HA. In addition, for the groundwater with high hardness, the nanoiron process can be an advantageous option because of enhancing characteristics of Ca^{2+} .

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1. Introduction

High arsenic-contaminated groundwater has become a world-wide issue of concern because of its toxicity and carcinogenicity [1]. Based on the literature review, there were regions which show relatively high arsenic concentrations such as Taiwan (~34–558 ppb [2]; 10–1820 ppb [3]) and Vietnam (~3050 ppb in rural groundwater samples [4]). The USEPA changed the maximum contaminant level (MCL) for arsenic from 50 $\mu\text{g}/\text{L}$ in 1974 to 10 $\mu\text{g}/\text{L}$ in 2001 due to its long-term health effect [5]. Arsenic is stable in several oxidation states, of which the arsenite, As(III), and arsenate, As(V), are the most common forms in natural waters. The dominant species of arsenic depend greatly on its surrounding environment. The As(V) is stable in oxidizing environment, whereas the As(III) is mainly found in reducing one [3]. Arsenic is typically associated with iron oxide under oxic environment, and pyrite minerals under anoxic one [6]. Furthermore, the arsenic may be released into water environments from both natural sources and anthropogenic activities [7,8].

According to the literature, the zero-valent iron (ZVI), which involves both adsorption and redox mechanisms, was a promising alternative for arsenic removal. The ZVI was firstly used for

arsenic removal by Lackovic et al. [9]; they reported that ZVI can be used to remove both As(III) and As(V) simultaneously, with the remediation capacities of As(III) and As(V), 298 $\mu\text{g}/\text{g}$ ZVI and 669 $\mu\text{g}/\text{g}$ ZVI, respectively. Based on the method of nano-scale ZVI (NZVI) synthesis developed by Glavee et al. [10], the NZVI possesses much higher capacity for arsenic removal than micro-scale ZVI [11,12]. However, there still remains need of investigation on background species effect on arsenic removal by this ZVI process, prior to field application. The phosphate (PO_4^{3-}), and bicarbonate (HCO_3^-) were reported that both can reduce performance of arsenic removal due to their competition for active sites on the adsorbent surface [13–15]. The silicate (SiO_3^{2-}) was reported to inhibit the performance of arsenic removal, due to the formation of surface complexes between silicate and iron (oxy)hydroxides and electrostatic repulsion [16]. Whereas, sulfate (SO_4^{2-}) can play both inhibiting and enhancing roles for arsenic removal, depending on its concentration level and experimental conditions [17,18]. It was reported that hardness (Ca^{2+}) plays an enhancing role for arsenic removal because it increases the positive surface charges of adsorbent, which favor adsorption for anionic arsenic species [16]. In addition, the humic acid (HA) was reported to result in significant reduction in arsenic removal, due to its high tendency of being adsorbed onto the surface of iron (hydr)oxides [12,19,20].

Currently, there still remains lack of information regarding the influence of mixture of background species on the arsenic removal by NZVI. In order to evaluate the performance of arsenic removal in

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the presence of background species of multi-components, experiments were designed by using two-level fractional factorial design (FFD). Note that the FFD, widely and commonly adopted in industry, is an efficient tool for evaluating a large number of variables with a reasonable number of experimental runs [21]. The FFD can help elucidate the effects of single and multiple factors on the problem of concern. In this study, the factors investigated are the major background species in groundwater, and the goal was set to explore the performance of arsenic removal in the presence of different background species. Hsu et al. [22] applied FFD to study the effect of multiple-ions competition in the adsorption of As(V) onto iron-oxide coated sands. Their results show that the competitive effects of the multi-ion species on As(V) removal was in the order of $\text{PO}_4^{3-} > \text{SiO}_3^{2-} > \text{HA} > \text{HCO}_3^- > \text{Cl}^-$. Additional advantage of the FFD is that no complicated calculations are needed to analyze the produced result [23]. The FFD is generally represented in the form of 2^{k-p} , where k is the number of factors and $1/2^p$ represents the fraction of the full factorial 2^k [24]. In this study, six species were selected and investigated for their effects on arsenic removal, including SO_4^{2-} , PO_4^{3-} , HCO_3^- , Ca^{2+} , Cl^- , and HA. Based on the FFD methodology, both individual and combined influences of background species on arsenic removal were observed when the proposed NZVI process was employed.

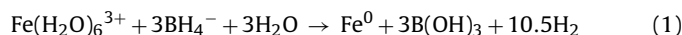
2. Materials and method

2.1. Chemicals

The chemicals of reagent grade used for NZVI synthesis in this study include $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (99%), and NaBH_4 (>96%), (Merck). The As(III) and As(V) stock solution were prepared from NaAsO_2 (Fluka) and $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (J.T. Baker), respectively. The selected species for test were prepared from Na_2SO_4 (Merck), $\text{CaCl}_2 \cdot 7\text{H}_2\text{O}$ (Merck), NaHCO_3 (Merck), $\text{Na}_2\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (Merck), NaCl (Merck), and HA (Acros organics). All chemical solutions were prepared with deionized water (18.2 M Ω Mill-Q).

2.2. NZVI synthesis

The NZVI was synthesized according to Glavee et al. [10]. 0.25 M of NaBH_4 was added into 0.045 M of aqueous FeCl_3 solution, and the mixture was agitated by a revolving propeller. The ferric iron was reduced by the borohydride, according to Reaction (1):



At the end of reaction, the NZVI particles were separated from liquid solution by a magnet. The dried NZVI was characterized first by TEM (JEL-2010, Japan) for its particle size. The solution pH with zero point charge, denoted as pH_{pzc} , was determined by using zeta-meter system 3.0+ (Meditop Co., Thailand). As a result, Fig. 1 shows the physicochemical properties of the NZVI, including its particle size distribution histogram and zeta potential versus pH. The average particle size and the pH_{pzc} were 56 nm and 7.8, respectively.

2.3. Batch test

2.3.1. Single species system

The NZVI (0.023 g/L) synthesized was added into a batch reactor with a volume of 4.4 L for the treatment of arsenic. The initial arsenic concentration was prepared at a level as high as 1000 $\mu\text{g/L}$. Two levels of low and high concentrations for each selected species were listed as follows: SO_4^{2-} : 10, 100 mg/L; HCO_3^- : 50, 500 mg/L; PO_4^{3-} : 1, 5 mg/L; HA: 0.5, 5 mg/L; Ca^{2+} : 50, 500 mg/L; Cl^- : 50, 500 mg/L. The solution pH was adjusted at the beginning of the experiment to 7.90 ± 0.1 . The solution pH was measured by pH meter (Suntex TS1),

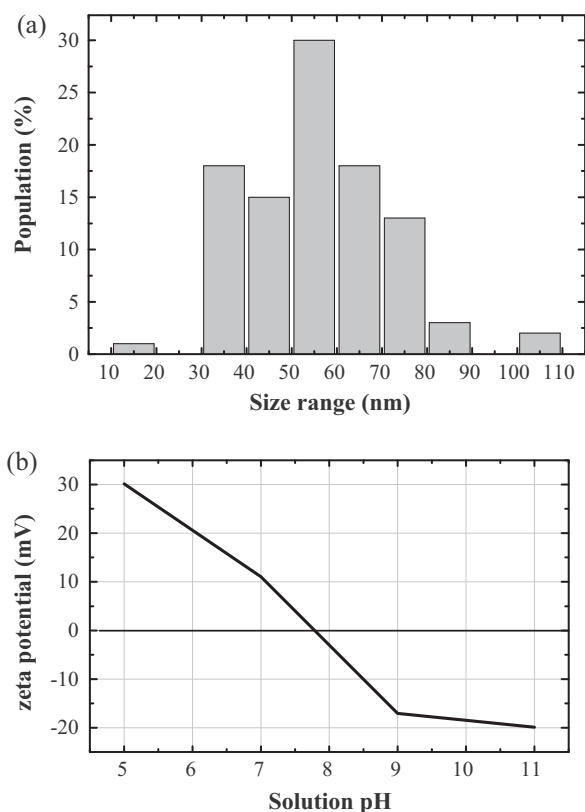


Fig. 1. Characterization of NZVI synthesized: (a) particle size distribution histogram and (b) zeta potential versus pH.

while the residual arsenic was determined by inductively coupled argon plasma (ICP) using Thermo Scientific Model iCAP 6000 series.

2.3.2. Multiple species system

In this part, the experiments were performed via a 2^{6-2} FFD with resolution IV to identify factors which impose significant effects on arsenic removal. Using a resolution IV design guarantees that no main effects are confounded with two-factor interactions or other main effects, and two-factor interactions are confounded with other two-factor interactions [21]. The basic assumption of the experimental design employed was that the interactions higher than two factors could be considered as insignificant [25]. The design matrix of FFD of each stated species were given in Table 1. The low (–) and high (+) levels of each factor in this FFD were determined by following the same concentration ranges of single species system. It is noticed here that the confounding factor was found by considering the variables E and F as the generators: $E = A \times B \times C$ and $F = B \times C \times D$. In Table 1, the generator employment for each run was shown in the third row. For instance, for Run #1, the variables A , B , and C have minus sign (–), the variable E ($A \times B \times C$) will then have minus sign (–) as well, resulting from a simple product of three minus signs. The same procedure is applied to determine the sign of variable F ($B \times C \times D$) [26]. All experiments with replicate were conducted to ensure data quality in terms of experimental reproducibility and reliability.

3. Results and discussion

3.1. Preliminary study

As a preliminary study, the NZVI was tested for the removal of arsenic in both deionized water and groundwater. The groundwater was taken from the monitoring well at Chia Nan University of

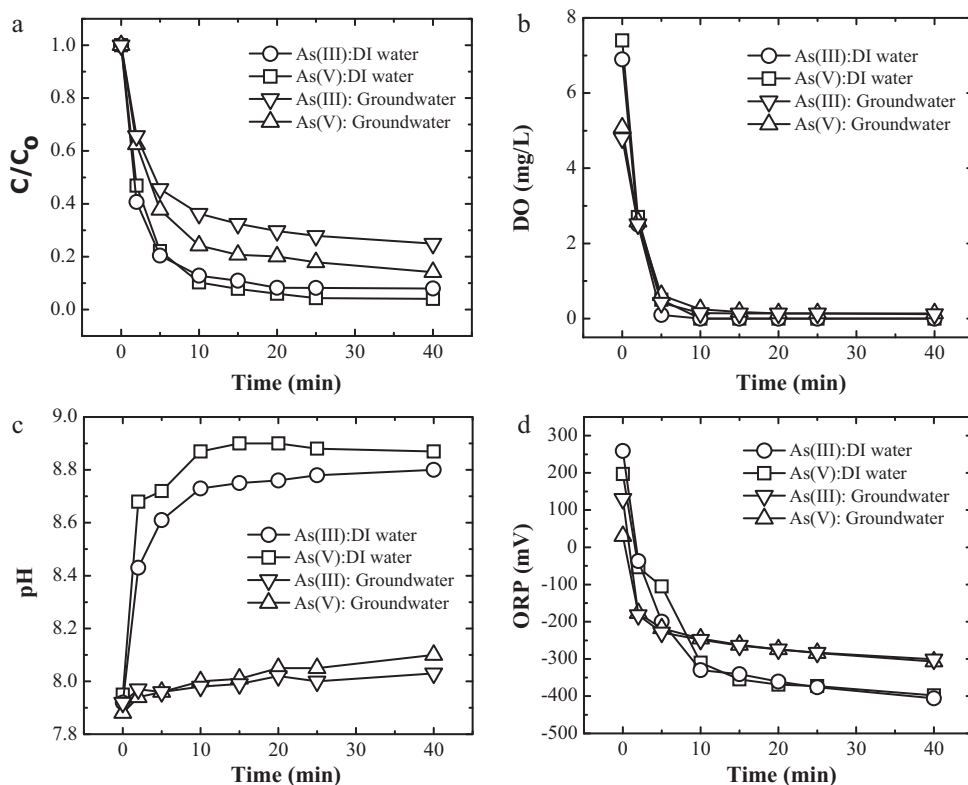


Fig. 2. Behavior of arsenic removal by NZVI in the deionized water and groundwater systems: (a) normalized residual arsenic concentration, (b) DO, (c) pH, and (d) ORP. [As] = 1000 ppb, NZVI dosage = 0.023 g/L, initial pH (DI water system) = 7.9 ± 0.1.

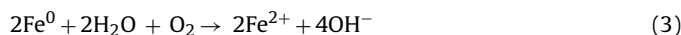
Table 1
Design matrix of the 2⁶⁻² FFD with resolution IV.

Run no.	Factors and codes					
	HA A	PO ₄ ³⁻ B	HCO ₃ ⁻ C	SO ₄ ²⁻ D	Ca ²⁺ E = ABC	Cl ⁻ F = BCD
1	-	-	-	+	-	+
2	+	+	-	-	-	+
3	+	+	+	-	+	-
4	-	+	-	+	+	-
5	-	-	+	-	+	+
6	+	-	+	-	+	+
7	+	+	+	+	+	+
8	+	-	-	+	+	+
9	-	+	+	+	-	+
10	+	+	-	+	-	-
11	-	+	+	-	-	-
12	+	-	-	-	+	-
13	-	+	-	-	+	+
14	+	-	+	+	-	-
15	-	-	+	+	+	-
16	-	-	-	-	-	-

Note: (1) The plus (+) and minus (-) signs indicate the high and low levels of the factors, respectively. (2) The test levels (low, high) in mg/L of codes A through F are as follows: A(0.5, 5), B(1, 5), C(50, 500), D(10, 100), E(50, 500), and F(50, 500).

Pharmacy and Science, Taiwan. The arsenic was spiked into this field groundwater sample to obtain its initial arsenic concentration of 1000 ppb. As shown in Fig. 2(a), the performance of both As(III) and As(V) removal in deionized water system was higher than that in groundwater system. The reason appears to be that competition for adsorptive sites exists between arsenic species and background species (e.g. SO₄²⁻, PO₄³⁻, HCO₃⁻) in field groundwater. Another reason might be due to a lesser content of initial DO in the field groundwater (Fig. 2(b)), which can oxidize the NZVI to generate iron (oxy)hydroxides for favorably adsorptive removal of arsenic [17].

As shown in Fig. 2(c), all solution pH profiles were observed to rise continuously throughout all reaction period, due to the build-up of OH⁻, according to Reactions (2) and (3). Such phenomenon was similar to earlier study with ZVI in micron scale [27]. However, the pH in the case of groundwater system increased quite slowly, possibly because of buffering capacity of carbonate alkalinity (680 ppm as CaCO₃) contained in the filed groundwater.



In brief, the preliminary study shows that the presence of background species in groundwater can affect greatly the performance of arsenic removal by the studied NZVI process.

3.2. Single species system

3.2.1. Humic acid (HA)

As shown in Fig. 3, the presence of HA in low concentration slightly decreased the removal performance of both As(III) and As(V). However, when the concentration of HA increases from 0.5 to 5 mg/L, the removal efficiencies of arsenic dramatically decrease from 91% to 61%, and 92% to 61% for As(III) and As(V), respectively. In the presence of HA, the Fe²⁺ produced during iron corrosion was oxidized into Fe³⁺. Then the Fe³⁺ reacted with HA to form Fe-humate complex [28], resulting in the increase of dissolved iron concentration. Because of such complex mechanism, the formation of the iron (oxy)hydroxides was hindered, and thus the arsenic removal through its sorption onto the (oxy)hydroxides decreased. Furthermore, the reduction in arsenic performance is due to that the HA, one kind of natural organic matter (NOM), can be adsorbed onto the surface of iron (oxy)hydroxides, resulting in less adsorptive surface of iron (oxy)hydroxides [20].

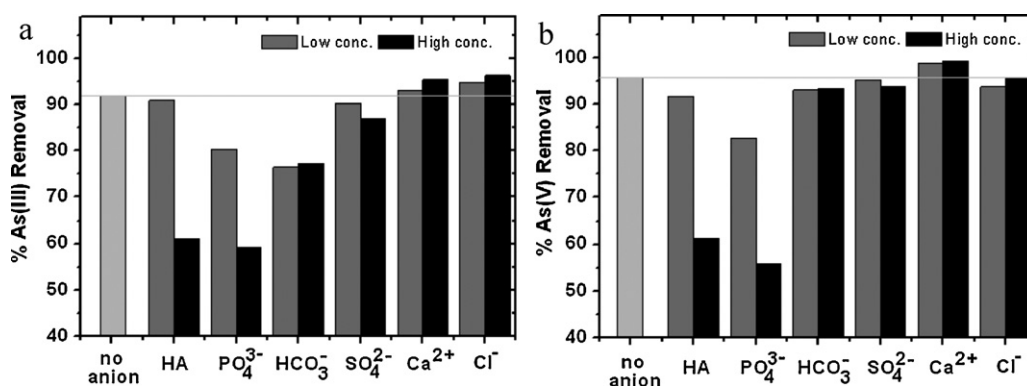


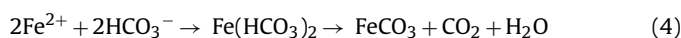
Fig. 3. Percentage of removal of (a) As(III) and (b) As(V) in the presence of low and high concentrations of selected species: [As] = 1000 µg/L, NZVI = 0.023 g/L, initial pH 7.9 ± 0.1.

3.2.2. Phosphate (PO₄³⁻)

The effect of PO₄³⁻ (1 and 5 mg/L) on arsenic removal was presented in Fig. 3. The presence of PO₄³⁻ inhibited the removal performance of arsenic, both As(III) and As(V), significantly. Table 2 depicts the pK_a values and predominant forms of arsenic and phosphate species, respectively. Such information indicates that the dominant dissociation species of phosphate and arsenic have similar chemistry, especially those of the phosphate and As(V). In other words, competition between arsenic species and phosphate for the same adsorption sites exists on the surface of iron (oxy)hydroxides [14]. Phosphate may be adsorbed onto iron (oxy)hydroxides through the formation of inner-sphere complexes with the hydroxyl groups [22]. In addition, the affinity of phosphate for iron (oxy)hydroxides was much stronger than arsenic species [6]. Therefore, the phosphate can retard the removal of arsenic significantly. In addition, Su and Puls reported that the inhibiting effect of PO₄³⁻ on As(V) removal was greater at high pH than at low pH; whereas the opposite trend was observed for As(III) [29].

3.2.3. Bicarbonate (HCO₃⁻)

The effect of HCO₃⁻ on arsenic removal was shown in Fig. 3. The As(III) removal was inhibited dramatically in the presence of HCO₃⁻, whereas the As(V) removal was affected only slightly. The possible reasons may be due to competition for adsorptive sites between HCO₃⁻ and arsenic species since the HCO₃⁻ can form inner-sphere surface complexes with iron (oxy)hydroxides [18]. In addition, the NZVI can be rapidly oxidized into Fe²⁺, the primary product, as shown in Eqs. (2) and (3), and this Fe²⁺ can result in several forms of iron (oxy)hydroxides, which serve as good sites for arsenic adsorption. Furthermore, in the presence of HCO₃⁻, the generated Fe²⁺ may react with HCO₃⁻ to form iron carbonate (FeCO₃) [30] according to Eq. (4). Consequently, lower performance for arsenic adsorption was observed.



As reported in the literature, the release of arsenic from sandstone aquifer was found to be strongly and positively related to the HCO₃⁻ concentration in the leaching solution [31]. Also another report shows that HCO₃⁻ can promote iron dissolution

from hematite (α-Fe₂O₃) surface [32], leading to the increase of the dissolved arsenic in solution. In this study, both low and high HCO₃⁻ concentrations show comparable arsenic removal, indicating significant impact by alkalinity even less than 50 mg/L.

3.2.4. Sulfate (SO₄²⁻)

As presented in Fig. 3, the removals of both As(III) and As(V) were retarded slightly in the presence of low and high concentrations of SO₄²⁻, with the As(III) to a relatively higher degree. Wilkie and Hering reported that the decrease of sorption performance of arsenic on iron hydroxides fell within the range of pH 4–7 in the presence of SO₄²⁻ [33]. In the ZVI system, the pH was observed to go beyond pH 7, as shown in Fig. 2(c) with the case of DI water. Thus, the effect of SO₄²⁻ in this study became only slight significance under a pH condition higher than 7. Such phenomenon was reported due to the electrical repulsion between SO₄²⁻ and negatively charged arsenic species, according to Table 2 [29]. Another reason is that the SO₄²⁻ can replace iron (oxy)hydroxides, which were attached to the iron surface, leading to the decrease of adsorption sites available to arsenic [34].

3.2.5. Calcium (Ca²⁺)

As shown in Fig. 3, the efficiency of both As(III) and As(V) removal was enhanced slightly in the presence of Ca²⁺. The solution pH of this study was set at 7.9, higher than the pH_{pzc} of pristine NZVI. So the surface of NZVI was with positive charge. However, when the reaction was carried on, the solution pH increased and became even higher than the pH_{pzc} of iron (oxy)hydroxides, due to the OH⁻ being produced, according to Eqs. (2) and (3). This then resulted in negative charge on the surface of iron (oxy)hydroxides, with charge property identical to arsenic species [35]. Thus, the electrostatic repulsion force led to decreasing adsorption of arsenic. In the presence of Ca²⁺, it serves to neutralize the negative surface charge of iron (oxy)hydroxides, and thus reduces the electrostatic repulsion for negatively charged arsenic, allowing the arsenic to remain on the adsorption sites [36]. For the other explanation, the Ca²⁺ forms a complex with surface sites (SS) of iron (oxy)hydroxides, as depicted in Eqs. (5) and (6).

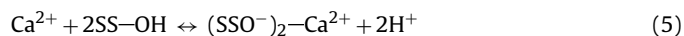


Table 2
pK_a values of arsenic species and phosphate.

Species	pK _a values		Predominant form at various			pH's	Reference
	pK ₁	pK ₂	pK ₃	<pK ₁	pK ₁ – pK ₂		
As(III)	9.22	12.13	12.7	H ₃ AsO ₃	H ₂ AsO ₃ ⁻	HAsO ₃ ²⁻	[29]
As(V)	2.2	6.97	11.53	H ₃ AsO ₄	H ₂ AsO ₄ ⁻	HAsO ₄ ²⁻	[29]
PO ₄ ³⁻	2.15	7.1	12.4	H ₃ PO ₄	H ₂ PO ₄ ⁻	HPO ₄ ²⁻	[41]

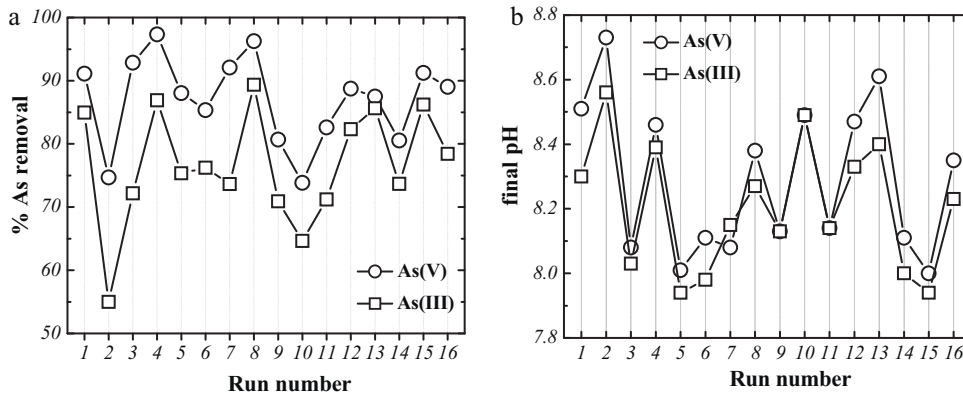
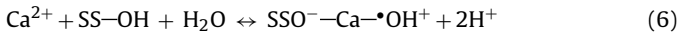


Fig. 4. Effect of six selected species with concentrations of different levels on (a) arsenic removal by NZVI, and (b) the final pH: [As] = 1000 µg/L, NZVI = 0.023 g/L, initial pH 7.9 ± 0.1.



Both reactions provide a bridge between surface of adsorbent and the negatively charged arsenic by increasing the positive surface charge of the adsorbent, which favors more negatively charged arsenic species adsorption [16].

3.2.6. Chloride (Cl⁻)

Fig. 3 indicates that the efficiency of As(V) removal decreased slightly in the presence of low Cl⁻ concentration, even when Cl⁻ concentration was high, no significant As(V) removal was observed. However, Cl⁻ was capable of enhancing the performance of As(III) removal. According to Choe et al. [37], they reported that Cl⁻ in solution induces pitting corrosion of the iron surface, which may increase the reactive area of iron for arsenic adsorption

3.3. Multiple species system

3.3.1. Arsenic removal with species concentrations of different levels

The profiles of arsenic removal by NZVI in the presence of six selected species with concentrations of different levels were shown in Fig. 4. It appears that higher arsenic removal was found in Runs # 4 and 8 for both As(III) and As(V). Both runs have the same concentration level of HCO₃⁻ (-), SO₄²⁻ (+), and Ca²⁺ (+). Thus, it is possible that HCO₃⁻ will play an inhibiting role for arsenic removal, whereas both the SO₄²⁻ and Ca²⁺ play an enhancing role. In contrast, Runs # 2 and 10, which involve HA and PO₄³⁻ with high concentration, gave lower efficiency of arsenic removal. Such results indicate that arsenic removal was retarded possibly by HA and PO₄³⁻. The analysis of effect of each species will be further discussed in detail by the FFD method. According to Fig. 4(b), all the final solution pH's were higher than the initial pH's, due to ZVI oxidation (Eqs. (2) and (3)). Additionally, Runs # 3, 5, 6, 7, 9, 11, 14, and 15 gave lower final pH's (<8.2) because of higher concentration of HCO₃⁻, which will provide higher buffering capacity for solution pH.

3.3.2. Effect of main species

The 2⁶⁻² FFD with resolution IV was chosen for the experimental design. Thus, average main effects were confounded with three-factor interaction, for instance, A = A + BCE + DEF, where the interactions higher than two factors could be assumed to be negligible. In this manner, all estimates of main effects were obtained [23]. The estimate of effect for each of the factors shown in Fig. 5 is the difference between the average response of high level (+) and the average response of low level (-) of that particular factor in design matrix of Table 1 [22]. Given the calculation for the estimate of effect of factor A on As(III) removal as an example,

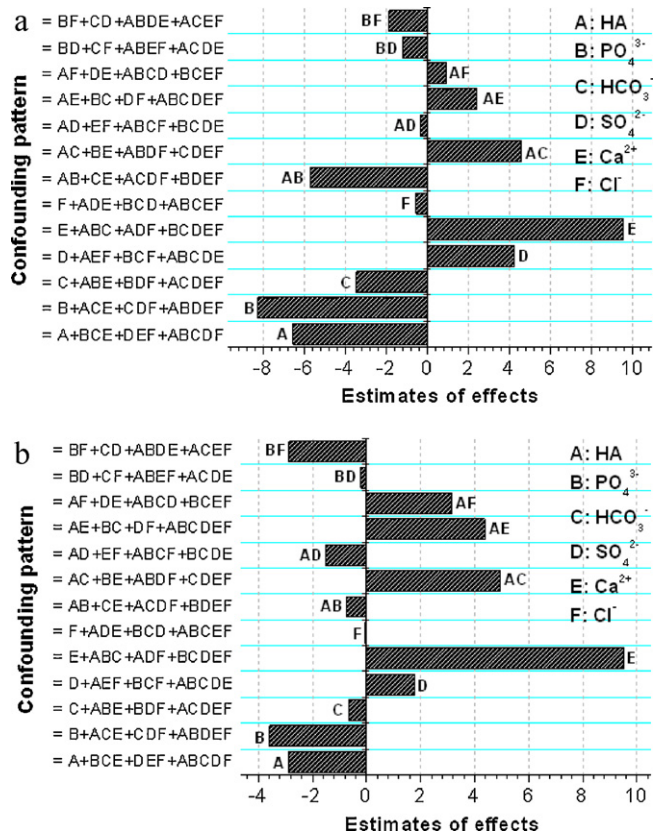


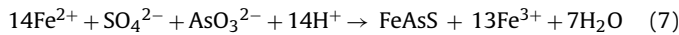
Fig. 5. Identification of main-effect and interacting factors on (a) As(III) and (b) As(V) removal by NZVI: [As] = 1000 µg/L, NZVI = 0.023 g/L, initial pH 7.9 ± 0.1.

the average responses of high level (+) and low level (-) are 73.37 (= (54.99 + 72.16 + 76.23 + 73.63 + 89.36 + 64.62 + 82.30 + 73.76)/8) and 79.94 (= (84.94 + 86.88 + 75.33 + 70.90 + 71.19 + 85.6486.21 + 78.42)/8), respectively. The difference between both levels is -6.57 (= 73.37 - 79.94), which is the value plotted in Fig. 5(a). Note that the data for average response calculation were taken from those plotted in Fig. 4.

As shown in Fig. 5, the negative estimates of main effect of A (HA), B (PO₄³⁻), C (HCO₃⁻) were -6.57, -8.31, and -3.48 for As(III) and -2.9, -3.58, and -0.64 for As(V), implying that these main factors play an inhibiting role for arsenic removal. For example, increasing HA concentration from 0.5 to 5 mg/L results in the decrease of As(III) removal by 6.57% (the average response decreases from 79.94% to 73.37%, when HA concentration changes from low

(–) to high (+) level), and increasing PO_4^{3-} concentration from 1 to 5 mg/L leads to the decrease of As(III) removal by 8.31%. In other words, to improve the removal of arsenic by the proposed NZVI, pretreatment of HA, PO_4^{3-} , and HCO_3^- is strongly recommended.

On the other hand, the main factors D (SO_4^{2-}) and E (Ca^{2+}) were observed to enhance arsenic removal, the positive estimates of main effect of D (SO_4^{2-}) and E (Ca^{2+}) were 4.24, and 9.57 for As(III) and 1.79, and 9.51 for As(V). Interestingly, the role of HCO_3^- appears to be quite different from that of other factors, depending on the presence of the species of As(III) or As(V). This is to say that HCO_3^- inhibits As(III) removal, on the contrary, its impact becomes insignificant in the case of As(V). Such result agrees with that in the case of the single species system, which shows that As(III) removal decreased dramatically in the presence of HCO_3^- , whereas only slight decrease was observed in the removal of As(V). In regard to SO_4^{2-} , it plays an inhibiting role for the removal of both As(III) and As(V) in single species system, but its enhancing role was observed in the multiple species system. This might be due to the acceleration of precipitation of arsenopyrite, FeAsS , through the reaction of SO_4^{2-} with the Fe^{2+} , AsO_3^- and H^+ , according to Eq. (7) [38].



Another report pointed out that SO_4^{2-} can corrode the surface of iron (hydr)oxides, thereby increasing the reactive sites on the surface [34].

In summary, among the selected species, the estimates of the inhibiting effects on the removal of both As(III) and As(V) are in the order as follows: $\text{PO}_4^{3-} > \text{HA} > \text{HCO}_3^-$, while the estimates of enhancing effects are in the following order: $\text{Ca}^{2+} > \text{SO}_4^{2-}$. As for the Cl^- , it plays no significant role.

3.3.3. Effect of interaction factor

The effect of interaction factor was considered because of its large estimate of effect, as illustrated in Fig. 5. A significant two-factor interaction indicates antagonism or synergism between two factors: their combined effect is not the sum of their separate contributions [21]. Interactions are presented in the model matrix by cross-products, as depicted in Table 1. The interaction AB are products of A and B , for example, Run #1: $(-)(-)=(+)$, Run #2: $(+)(+)=(+)$, Run #4: $(-)(+)=(-)$, etc. [27]. According to Fig. 5(a), for instance, the estimate of effect of interaction AB , or $\text{HA} \times \text{PO}_4^{3-}$, was -5.73 , but this value did not only result from the interaction of A and B , but rather from the estimate of effect of interaction of C and E as well (see Fig. 5 for the confounding patterns, where the item higher than two factors could be considered as insignificant). This means that the interaction of $(\text{HA} \times \text{PO}_4^{3-})$ was confounded with $(\text{HCO}_3^- \times \text{SO}_4^{2-})$ and the relationship could be described as $(\text{HA} \times \text{PO}_4^{3-}) = (\text{HA} \times \text{PO}_4^{3-}) + (\text{HCO}_3^- \times \text{SO}_4^{2-})$.

Fig. 6 shows two-factor interaction plots for each two-factor interaction, in terms of the percentage of arsenic removal. The interactions between factors are strong for arsenic removal due to factors in x -axis when significant slope of each line within each cell is observed; on the other hand, when the distance between the two data points (black and red) in y -axis remains sufficiently long, the interactions due to factors in y -axis are significant [39]. For instance, for the cell AB in Fig. 6(a), factor B shows strong interaction effect on As(III) removal, when factor A remains at high concentration level (see the red line). On the other hand, when keeping factor A at low level, interaction effect of factor B still exists, yet to a lesser degree (see the black line with lower slope). If factor B remains at low level, factor A will impose no impact regardless of its being at high or low level; yet, at high level of factor B , increasing factor A from low to high level will lead to significant drop of As(III) removal.

Specifically, as described in single species system, factor B (PO_4^{3-}) and E (Ca^{2+}) were factors affecting removal; the previous one inhibits arsenic removal, whereas the latter one enhances its

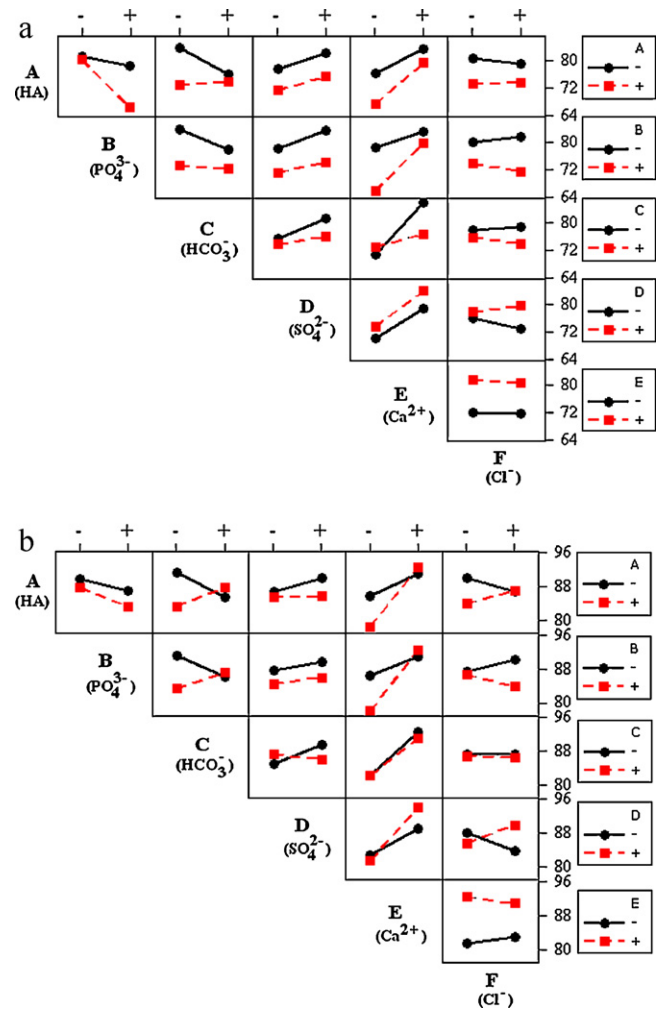


Fig. 6. Interacting effect plots in terms of (a) As(III) and (b) As(V) removal percentage.

removal. Concerning the interaction of BE ($\text{PO}_4^{3-} \times \text{Ca}^{2+}$), the percentage of arsenic removal drops dramatically (78–65% for As(III), and 87–78% for As(V)), when PO_4^{3-} changes its concentration from low to high level and Ca^{2+} remains at low concentration level. However, the PO_4^{3-} poses insignificant interaction effect on arsenic removal, when concentration of Ca^{2+} is high. In the other way around, at low PO_4^{3-} , the interaction effect of Ca^{2+} resulted in only slight increase of arsenic removal (78–83% for As(III), and 87–91% for As(V)); at high PO_4^{3-} , the increase in arsenic removal is relatively more significant (65–80% for As(III), and 78–92% for As(V)). According to this study, when background species were co-existing, the effect of which on arsenic removal was quite different from that when they exist alone [40].

In general, according to Fig. 6(a), among all cells of paired interaction factors, the red lines (high level) in Columns C and F show near zero slopes. In Column F , the black line (low level) is also observed to be horizontal. In addition, the overlapping data points (black and red) exist in the cells of AB (low B), AC (high C), CD (low D), CE (low E), CF (low F) and DF (low F). According to Fig. 6(b), the horizontal lines include those cells in Column D (the red lines), and cell CF (black and red); and the overlapping data points are those in cells AB (low B), AC (high C), AD (low D), AE (high E), AF (high F), BC (high C), BE (high E), BF (low F), CD (low D), CE (low and high E), CF (low and high F), DE (low E), and DF (low F). Based on the observation of both horizontal lines and overlapping data points, one may single out important factors for interaction within each cell.

4. Conclusions

In this study, the influence of six selected species on arsenic removal by NZVI, both single and multiple species systems, was investigated. The experiments for multiple species system were designed according to the 2^{6-2} FFD with resolution IV. As a result, in both systems, the important species which play a significant role in removing arsenic were HA, PO_4^{3-} , and Ca^{2+} , with the first two species imposing inhibiting effect and the last one enhancing effect. In particular, SO_4^{2-} plays an inhibiting role in single species system, but a promoting role in multiple species system. In the presence of HCO_3^- , in both systems it inhibited As(V) removal only slightly, but the inhibition became significant in As(III) removal. Based on the FFD, the performance of arsenic removal was determined not only by main factors but also by interaction factors. The results of this study suggest that increasing Ca^{2+} concentration but decreasing PO_4^{3-} and HA concentrations create the condition for the best removal of both As(III) and As(V).

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