Arsenite removal from water by zero-valent iron/activated carbon galvanic couples

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1. Introduction

The occurrence of arsenic (As) in groundwater has long been a great concern due to the toxicity of As and the potential for chronic exposure [1]. To challenge this problem, a range of expensive iron-based technologies have been focused in recent years [2–5]. Among these technologies, the use of Fe$_0$ for As removal has attracted increasing attention due to its effectiveness and applicability under different geochemical conditions, operational simplicity and low-cost [2,3,6]. Critical reviews and in-depth investigations of Fe$_0$ removal have been made by Noubactep et al. [7–11]. In field applications, permeable reactive barriers (PRBs) were installed through placement of Fe$_0$ as a reactive material for immobilization and removal of multiple contaminants including halogenated organic solvents, heavy metals, radionuclides and As [3,12,13]. Although most of PRBs in field installation have worked well, three major issues including loss of Fe$_0$ media, reduction in permeability and design flaws were still concerned. The reactivity loss, rather than the permeability reduction, was considered to limit the longevity of PRBs [12].

1.1. Galvanic couples

Galvanic couples composed of zero-valent iron and activated carbon (Fe$_0$/AC) were investigated for As(V) removal from water. The effects of Fe$_0$ to AC mass ratio (FCR), solution pH, ionic strength and co-existing anions (phosphate, carbonate, silicate, nitrate, chloride and sulfate) and humic acid (HA) on As(V) removal were evaluated. The results showed that the optimum mass ratio was 1:1, and Fe$_0$/AC with this ratio was more effective for As(V) removal than Fe$_0$ and AC alone at pH 7 and ion strength of 0.03 M NaCl. The enhanced performance for As(V) removal was fulfilled through an accelerated corrosion process of Fe$_0$, which meant more corrosion products for efficient As(V) removal. The As(V) removal followed a pseudo-first order reaction. The rate constants (k) for 1:1 Fe$_0$/AC and Fe$_0$ alone were 0.802 and 0.330 h$^{-1}$, respectively. Potentiodynamic polarization scans further confirmed that Fe$_0$ corrosion was promoted when Fe$_0$ was coupled with AC. Except silicates, other co-existing anions promoted As(V) removal. No reduction form of (As(III) or As(0)) could be detected on iron corrosion products (ICPs) and in solutions. Identified ICPs included poorly crystallized lepidocrocite ($\gamma$-FeOOH) and magnetite/maghemite (Fe$_3$O$_4$/y-Fe$_2$O$_3$) for both of Fe$_0$/AC and Fe$_0$ systems. In conclusion, the Fe$_0$/AC couple exhibited higher As removal performance than that of Fe$_0$ alone from water.

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To accelerate the corrosion of Fe0, a range of methods have been reported, such as using bimetals, ultrasound, manganese oxides and activated carbon to combine with Fe0 [9,22]. Among which activated carbon was cheap and commonly used as adsorbent. Recently, the iron-carbon internal electrolysis reaction has been investigated in the treatment of pesticide, pharmacy and dye wastewater [23,24], and activated sludge [25]. In such a reaction, numerous microscopic galvanic couples were spontaneously formed between Fe0 and carbon, and Fe(II), hydroxyl and atomic hydrogen were released from the galvanic corrosion reaction, which had high activities in the decomposition of organic contaminants. However, the galvanic corrosion process of Fe0/activated carbon (Fe0/AC) for As removal was not investigated up to date.

In the present study, Fe0 and AC were coupled as galvanic couples for the removal of As(V) from water. The objectives of this study were: (1) to investigate the effects of FCR, pH of the solution, ion strength and co-existing anions on As(V) removal by Fe0/AC couples; (2) to determine the corrosion rate of Fe0/AC by using potentiodynamic polarization analyses; (3) to understand the removal process of As(V) by examining the redox transformation of As and identifying the composites of the ICPs.

2. Materials and methods

2.1. Materials

All chemicals were of analytical grade (AR) except for those used in the HPLC–HG–AFS analyses, which were of reagent grade (GR). The Fe0 powders (80–120 mesh) and AC powders (80–120 mesh) were obtained from the Sinopharm Chemical Reagent Beijing Co., Ltd. XRD analysis showed that the Fe0 powder was composed of pure iron.

2.2. Batch tests

Kinetic experiments were performed to evaluate the FCR on the removal rate of As(V). A given volume of As(V) stock solution was added to five 500 mL glass vessels containing 300 mL 0.03 M NaCl solution, to make a concentration of 5 mg/L of As(V). After the solution pH in each vessel was adjusted to 7.0 by adding 0.05 M HCl or NaOH solutions, 0.15 g Fe0 and AC at mass ratios ranging from 10:1, 2:1, 1:1, 1:2 to 1:10 were added. The glass vessels were shaken at 180 rpm, 25 ± 1°C, and the pH was maintained at 7.0 ± 0.2 throughout the experiment. The maximal volume of NaOH (or HCl) for pH adjustment was 3.4 mL, which did not affect the ion strength perceptibly. Approximately 4 mL aliquots were taken from the suspensions at intervals of 30 min during the 3 h reaction period. The samples were filtered through 0.45 μm membranes and acidified, and the residual As in the treated samples was analyzed using AFS. Fe0 alone and AC alone at a dosage of 0.5 g/L for As(V) removal were also evaluated under similar conditions. In addition to the original pH condition of 7.0 ± 0.2, we also evaluated the effect of pH 6.0 ± 0.2 and 8.0 ± 0.2 on the Fe0/AC couple with a FCR of 1:1 (1:1 Fe0/AC). Also, 1:1 Fe0/AC was tested without background electrolyte as well as in the presence of 0.01, 0.05 and 0.1 M NaCl, in addition to the initial 0.03 M concentration. In these tests, all other conditions were maintained as described, with the pH fixed at 7.0 ± 0.2.

The effect of co-existing anions (phosphate, carbonate, silicate, nitrate, chloride and sulfate) and humic acid (HA) on As(V) removal by 1:1 Fe0/AC was evaluated, with the Fe0 and AC dosage both at 0.5 g/L. The concentration of As(V) was fixed at 5 mg/L (66.7 μM). According to typical concentration ranges of common constituents in natural groundwaters [26], carbonate (40 and 400 mg/L), nitrate (41 and 411 mg/L) and sulfate (64 and 640 mg/L), in two molar ratios of 10:1 and 100:1 relative to As(V) (66.7 μM) were evaluated. Phosphate (6.3 and 63 mg/L) and silicate (6.1 and 61 mg/L) were present of 1:1 and 10:1, and HA was present at a concentration of 5 and 20 mg/L.

The soluble iron in the treated samples was tested for Fe0 alone and 1:1 Fe0/AC treatments using AAS after filtration and acidification. Speciation of aqueous As was determined using HPLC–AFS and the separated paste was collected and freeze-dried for further spectroscopic analyses.

2.3. Analytical methods

Total As and As speciation concentrations in the solutions were determined by a high performance liquid chromatography–hydride generation–atom fluorescence spectrometer (HPLC–HG–AFS, AF-610D2, Beijing Rayleigh Analytic Instrument Corporation, China), using published methods [27]. Acidified iron samples were determined by an atomic absorption spectrophotometer (AA-6300, Shimadzu, Japan).

The morphology of the freeze-dried products from Fe0 alone and 1:1 Fe0/AC was observed by high-resolution transmission electron microscopy (HRTEM, JEM 2010, JEOL, Japan). The phase compositions of the ICPs were determined by X-ray diffraction (XRD, X’Pert PRO MPD, PANalytical, the Netherlands). The valence states of As and iron on the ICPs were analyzed by X-ray photoelectron spectroscopy (XPS, Quantera, PHI, USA).

The corrosion rate of iron correlated positively with its corrosion current (i corr) [20]. The effect of corrosion current (i corr) and free corrosion potential (Ecorr) on the rate of electrochemical reactions involving a corroded iron electrode, was described by the Butler–Volmer equation [20,28]. The value of i corr was obtained from potentiodynamic polarization curves of the iron electrode [20,28]. Thus potentiodynamic polarization analyses could be used to assess the effect of the iron corrosion rate on the removal rate of As(V). In the first instance, Fe0 and AC powder were equally wrapped in two pieces of foam nickel (size 1 cm × 1 cm) and pressed at 30 kPa for 5 min to obtain plate shaped electrodes. Secondly, the Fe0 plate electrode as the working electrode was immersed in 5 mg/L As(V) solution at pH 7.0. To evaluate the effect of iron strength on the corrosion rate of Fe0, the concentrations of NaCl ranged from 0 to 0.1 M. The AC plate electrode or platinum plate electrode functioned as the counter electrode and Ag/AgCl electrode was used as the reference electrode. The Fe0 plate was parallel and opposite to the AC or platinum plate electrode at a distance of 1 cm. Polarization experiments were performed using a scanning potentiostat and software (660C, CHI, USA). The values of i corr were measured by analyses of the potentiodynamic polarization curves produced by polarizing the electrodes ±150 mV with respect to their open circuit potentials at a scan rate of 5 mV/s.

3. Results and discussion

3.1. Batch experiment

3.1.1. Effect of Fe0 to AC mass ratio

Fe0 corrosion was enhanced by coupling with AC. Fe0 acted as a micro-anode and AC as a micro-cathode. Different FCR values, leading to various contact area ratios of anode to cathode, would significantly affect the corrosion rate and thus the As(V) removal rate. The effects of FCR on As(V) removal rate were presented in Fig. 1(a), which showed that when the FCR ranged from 10:1 to 2:1, the As(V) removal rate was significantly enhanced. By further increasing the ratio to 1:1, only a slight increase was observed. After a 2 h reaction period, a removal ratio of 98% was achieved and after 2.5 h, 100% was achieved. At a FCR of 1:1, the contact area of Fe0...
Fe\textsuperscript{0} alone and AC alone. We found that the kinetic process of Fe\textsuperscript{0} alone and 1:1 Fe\textsuperscript{0}/AC can be described by the pseudo-first order equation \( (d[As]/dt = -k[As]) \) with a correlation coefficient \( r > 0.953 \). Pseudo-first order rate constants \( (k) \) for Fe\textsuperscript{0} alone and 1:1 Fe\textsuperscript{0}/AC were 0.330 and 0.802 h\(^{-1}\) and their half life \( (t_{1/2}) \) were 2.10 and 0.86 h, respectively. These results show that galvanic corrosion by 1:1 Fe\textsuperscript{0}/AC significantly promoted the removal kinetics of As(V).

It has been reported that the corrosion rate of Fe\textsuperscript{0} in solutions can be estimated through the release of soluble iron [18]. In this study, the corrosive release of iron in the solutions for 1:1 Fe\textsuperscript{0}/AC and Fe\textsuperscript{0} alone was presented in Fig. 2. From the initiation to 1.5 h, the concentration of released iron increased to 1.35 mg/L for Fe\textsuperscript{0}/AC 1:1 at pH 7 and to 0.65 mg/L for Fe\textsuperscript{0} alone. The release of iron was slower for Fe\textsuperscript{0} alone than that for 1:1 Fe\textsuperscript{0}/AC over the same time period. A greater corrosive release of iron for 1:1 Fe\textsuperscript{0}/AC was indicative of a higher corrosion rate than for Fe\textsuperscript{0} alone. After 2 h, iron in the solution significantly decreased for 1:1 Fe\textsuperscript{0}/AC and Fe\textsuperscript{0} alone. After 3 h, the iron concentrations in both solutions quickly decreased almost to zero. It was thought that soluble iron was entirely transformed to Fe(III) oxyhydroxides through hydrolysis and precipitation.

Based on above results it was considered that Fe\textsuperscript{0}/AC could be used to remove high concentrations of As(V) with fast reaction kinetics, such as 0.1–5 mg/L of As occurred in areas of sulfide mineralization, and in geothermal groundwater [1,6]. Also high As can be unexpectedly confronted from accidently leaching from chemical plants, such as more than 5 mg/L of As was occurred in the serious contaminated reaches of Dasha river in Henan Province, China, in 2008.

3.1.2. Effect of pH on arsenate removal

The effect of pH on As(V) removal by 1:1 Fe\textsuperscript{0}/AC was demonstrated in Fig. 3. The removal of As(V) occurred rapidly at pH 6 and pH 7 and showed little difference between these two values. Almost 100% of As(V) was removed after a 2 h reaction period. However, the rate became relatively slow when the pH increased to 8 and only 61% of As(V) was removed after 2 h. The results showed the pH value had a distinct effect on As(V) removal by Fe\textsuperscript{0}, consistent with findings from previous studies [18,30].

The observed difference between pH 6 and 8 could be due to the pH-dependent As speciation and/or the surface charge on iron oxides from corrosion. With pH increasing from 6 to 8, the main species of As tend to be H\textsubscript{2}AsO\textsubscript{4}\textsuperscript{−} rather than H\textsubscript{3}AsO\textsubscript{4}\textsuperscript{2−} [4]. And since a pH of 8.0 was near or above pH\textsubscript{pzc} of iron oxides (e.g. lepi-
Fig. 3. Effect of pH on As(V) removal by 1:1 Fe⁰/AC (NaCl concentration, 0.03 M; initial As(V) concentration, 5 mg/L; Fe⁰ addition, 0.5 g/L).

docrocite, 7.7; maghemite, 6.5; magnetite, 8.0) identified in ICPs (Section 3.4) [31,32], the surface of iron oxides would be negatively charged or less positive, which might result in electrostatic repulsion between As(V) and iron oxide surface.

3.1.3. Effect of ion strength on As(V) removal
Fe⁰ corrosion is influenced by the nature of the electrolyte. The effects of ion strength on As(V) removal by 1:1 Fe⁰/AC at pH 7 was illustrated in Fig. 4. The As(V) removal rate increased significantly in a solution of 0.03 M NaCl and reached 94% after 2 h and 100% after 2.5 h. However, in the solutions of 0.05 and 0.1 M NaCl, the removal rates decreased and were lower than that in a solution of 0.03 M NaCl over the time period 0–2.5 h. However, after 3 h, a 96% removal ratio was achieved in both the solutions of 0.05 and the 0.1 M NaCl.

When NaCl concentrations increased from 0.03 to 0.1 M, a decrease in As(V) removal rate might be due to the difference in phase and binding affinity of ICPs comparing to that in the presence of 0.03 M NaCl. Chemical simulations coupled with corrosion tests showed that akaganéite (β-FeOOH) rather than lepidocrocite were preferred to form when a large excess of dissolved Fe²⁺ and Cl⁻ (0.032–3.2 M) existed[33]. It was also reported that Cl⁻ could retard magnetite formation [34].

Fig. 4. Effects of ion strengths on As(V) removal by 1:1 Fe⁰/AC (pH, 7.0 ± 0.2; initial As(V) concentration, 5 mg/L; Fe⁰ addition, 0.5 g/L).

3.1.4. Effects of co-existing anions on As(V) removal
The effects of co-existing anions and HA in typical concentration ranges of nature groundwater on As(V) removal were shown in Fig. 5. Compared with the absence of anion, the presence of sulfate and nitrate significantly increased the removal rate of As(V), where sulfate was more effective than nitrate. Phosphate and carbonate showed a slight promotional effect on As(V) removal. HA had negligible effects, while silicate showed some inhibition. When considering the low and high concentrations of present anions on As(V) removal, minimum differences were found, with the exception of nitrate and silicate, where nitrate had an enhancing effect and silicate an inhibitory effect at relatively high concentration.

It was thought that in the presence of sulfate and nitrate, the ion strength of the solution would increase, so that Fe⁰ corrosion would be enhanced and at the same time, no competitive adsorption of As(V) with sulfate and nitrate on Fe(III) oxyhydroxides would occur. For phosphate and carbonate, competitive adsorption of As(V) with phosphate and carbonate on Fe(III) oxyhydroxides are often reported[35,36], and generally it was said that phosphate was inhibiting [37,38]. However, a slight promotion of As(V) removal was found in the presence of phosphate and carbonate. We considered that when AC was present, this promotional effect with increasing ion strength exceeded the effect of competitive adsorption. In addition, results of phosphate inhibiting were often reached where huge amounts (such as 100 mM) of phosphate ions were used to form a protective surface layer on Fe⁰ [37,38], while in this study, 0.067 and 0.67 mM of phosphate ions were used and maintained at neutral pH. For silicate, it was commonly used as corrosion inhibitor and has been found to reduce the iron corrosion rate [38,39]. In the present study, Fe⁰ corrosion sustained by AC was also inhibited and less corrosion meant less corrosion products for adsorption and co-precipitation [7,16]. In addition, competitive adsorption of silicate could significantly reduce As(V) adsorption by iron hydroxides [39]. Therefore, its distinctive suppressive effect was observed.

3.2. Electrochemical analysis
Fig. 6(a) showed an example of the potentiodynamic polarization curves used to determine the values of icorr for Fe⁰ alone and 1:1 Fe⁰/AC. The value of icorr was 363 μA for Fe⁰ alone and was 474 μA for 1:1 Fe⁰/AC. These results showed that icorr significantly
increased after coupling, and meant that the corrosion of Fe⁰ was significantly increased. The Fe⁰ alone and 1:1 Fe⁰/AC \( \bar{i}_{corr} \) values compared within a period of 3 h were showed in Fig. 6 (b). The values of \( \bar{i}_{corr} \) for both Fe⁰ alone and 1:1 Fe⁰/AC showed a slightly increase with time, and \( \bar{i}_{corr} \) of the latter was approximately 100 \( \mu \)A higher than that of the former during the whole testing period. This confirmed that Fe⁰ corrosion in the Fe⁰/AC couple was effectively enhanced.

Fig. 6(c) showed the values of \( \bar{i}_{corr} \) for 1:1 Fe⁰/AC exposed to electrolyte solutions ranging from 0 to 0.1 M NaCl for a 3 h period, with a fixed As(V) concentration of 5 mg/L. The values of \( \bar{i}_{corr} \) increased with increasing concentration of electrolytes and over time. That meant that the corrosion of 1:1 Fe⁰/AC changed incrementally with increased electrolyte concentration. This result contradicted the apparent effect of ion strength on As(V) removal (Section 3.1.3). We expected that high concentrations of chloride ions would not only accelerate Fe⁰ corrosion, but also affect the phase transformation and the stability of the ICPs from 1:1 Fe⁰/AC, where unstable phases might be changed to phases with low affinity for As(V).

3.3. Arsenic speciation analysis

The valence states of As and iron on the ICPs were identified from the characteristic As3d and Fe2p binding energy positions. The As3d spectra of 1:1 Fe⁰/AC and Fe⁰ alone when reacted with 5 mg/L As(V) for 3 h were collected as shown in Fig. 7(a). Both showed a single photoelectron peak at \( \sim 45.3 \) eV, corresponding to the characteristic peak position of As(V)\[18\]. No As(III) or As(0) peaks near 44.3 or 41.5 eV\[40,41\] were observed, indicating that As(V) was mainly present on the surface of the ICPs. The binding energy of Fe2p centered at 711.0 eV (Fig. S1), indicating that iron on the ICPs was mainly Fe(III)\[42\].

Arsenic speciation in the solutions after the reaction with Fe⁰/AC 1:1 and Fe⁰ alone were determined by HPLC–HG-AFS. The results indicate that no As(III) was detectable and only As(V) was present in the solutions. It was thought no reduction of As(V) was occurred within the 3 h reaction period for 1:1 Fe⁰/AC and Fe⁰ alone in this study.

In open batch reactors, no reduction of As(V) to As(III) was observed in the present study. Similar results were also reported in previous study in the case of open batch reactors\[20\]. On the other hand, conversion of As(V) to As(III) by iron filings\[40\] and nanoscale Fe⁰ \[41\] under anoxic conditions were observed in closed batch reactors. In all cases it was considered that As was removed mainly through adsorption and co-precipitation, and it was even possible that reduced As was co-precipitated\[7,16\]. The reported As(III) might be attributed to a slow reduction of As(V) by evolved Fe²⁺ or H₂/H within the matrix of the oxide layer on the surface of Fe⁰ \[7\].

AC is an absorbent for As(V) but equilibrium time is necessarily longer than the time of adsorption onto in-situ generated
iron hydrides. Accordingly, AC masked by Fe\(^0\) was reported, but adsorbed As(V) would readily be transferred to Fe(III) hydrides. With other words this result was also a hint for lack of reduction as the proliferation of galvanic cells sustained reduction.

3.4. Corrosion product analyses

Combined with TEM (Fig. S2) and XRD (Fig. S3) observations, the ICPs were identified and the main components included poorly crystallized lepidocrocite (γ-FeOOH) and magnetite/maghemite (Fe\(_2\)O\(_3\)/γ-Fe\(_2\)O\(_3\)). Detailed results and analyses were provided in Supplementary materials.

4. Conclusions

The current study aimed at evaluation the performance of Fe\(^0\)/AC galvanic couples for aqueous As(V) removal. The results showed that As(V) removal of Fe\(^0\)/AC was higher than that of Fe\(^0\). The removal process followed a pseudo-first order reaction. The kinetic constants indicated that the reaction rate of Fe\(^0\) with As(V) was accelerated in presence of AC. Fe\(^0\) corrosion was sustained and enhanced by AC yielding continuous production of nascent iron hydrides for As(V) removal. The enhancement of Fe\(^0\) corrosion by AC was further confirmed using potentialdynamic polarization scans. With the exception of silicate, promotional effects on As(V) removal by co-existing anions were found, especially sulfate and nitrate. As(V) was confirmed to be present on the ICPs and in residual solutions and no reduction form was detected. The identified phase in ICPs included lepidocrocites and magnetites/maghemites for both 1:1 Fe\(^0\)/AC and Fe\(^0\) alone.

Based on above results, it was considered that Fe\(^0\)/AC could be used to remove high (e.g. 5–10 mg/L in mining sites) concentrations of As(V) from water with fast reaction kinetics. Furthermore, it seems that Fe\(^0\)/AC was effective and applicable for As removal from water with co-existing anions excluding high concentration of silicate as high as 60 mg/L.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version,


