Research Article

The Influence of Dosing Modes of Coagulate on Arsenic Removal

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Three different dosing modes, including one single dosing mode and two sequential dosing modes, were applied in high-arsenic contaminated water treatment. The results illustrated that the As (V) soluble and the As (V) nonspecifically sorbed were the insignificant species from Fe-As (V) samples in the sequential dosing mode, while they were higher in the single dosing mode. However, it could be further concluded that the mobility of the Fe-As (V) in sequential dosing mode was greater than that in single dosing mode. Besides, the main arsenic speciation governing the arsenic-borne coagulates was the As (V) associated with poorly crystalline hydrous oxides of Fe in sequential or single dosing mode. Moreover, the particle size distribution analysis indicated that the sequential dosing mode was more prevalent in neutralizing and adsorbing the As (V) compared with the single dosing mode. In the FT-IR spectra, the presence of arsenic was highlighted by a well resolved band at 825–829 cm$^{-1}$. The positions of the As–O stretching vibration bands were shifted gradually as the dosing mode changed from the single to the sequential. This result could be related to the distribution of arsenic speciation in different dosing modes.

1. Introduction

Arsenic is a common element found in naturally contaminated groundwater and surface water in many countries [1]. It is one of the most dangerous pollutants, owing to the toxicity, odorlessness, and nearly tastelessness [2–4]. The chronic and acute poisoning of As is related positively to the exposure to elevated concentrations, threatening groundwater safety, agriculture irrigation, and aquatic ecosystems [5, 6].

In the natural environment, arsenic exists in different oxidation states and various forms, for example, +V (arsenate), +III (arsenite), 0 (arsenic), and −III (arsine) [7]. It has been determined that the arsenic toxicity depended on the speciation [8]. Generally, inorganic arsenic species are more toxic than organic ones, while, among the inorganic arsenic species, arsenite (As (III)) is usually more toxic than arsenate (As (V)) [9]. Since As (III) species show greater mobility than those of As (V), they are more harmful to human health [10, 11]. Considering the high toxicity, the World Health Organization (WHO) has decreased the maximum contaminant level of arsenic in drinking water from 50 to 10 μg/L [12].

It has been widely acknowledged that arsenic pollution associated with the geochemical environment such as volcanic deposits, geothermal sources, and arsenic-containing rocks [13–15]. Besides, anthropogenic activities, such as mining, fossil fuels burning, ores smelting, chemical wood preservatives, and arsenical pesticides, also release high concentrations of arsenic to the environment directly, which have attracted attentions worldwide [16–18].

In high-arsenic aquatic system, the partition and release of arsenic are of serious concern owing to the reaction on water–mineral interfaces [1]. Conventionally, there have been several methods for arsenic removals, including coagulation (precipitation) [19, 20], adsorption [21–23], ion exchange [24], membrane filtration [25], bioremediation [26], and electrochemical treatments [27, 28]. Of all these methods, coagulation and flocculation were the most cost-effective ways for high-arsenic water [29]. In the coagulation process, arsenic ions (arsenate or arsenite) attach on the coagulants and precipitate with added ferric or aluminum ions [30, 31]. Then, the coagulants are separated through filtration, eliminating arsenic from arsenic-polluted water [32]. Although most researchers deduced that the coagulation efficiency was
Influenced by various parameters, fewer reported the effect of the dosing mode. In addition, little about the forms of arsenic in arsenic-borne coagulates was investigated, which could assist in elucidating the coagulation mechanism.

The objectives of this study were as follows.

1. Investigate the arsenic removal efficiency with ferric chloride dosed in different modes.
2. Determine the mechanisms of ferric chloride interacting with arsenate in different sequential dosing modes.
3. Investigate the surface complex formed on ferric chloride in different sequential dosing modes with Fourier transform infrared (FT-IR) spectroscopy.

2. Materials and Methods

2.1. Materials. All solutions were prepared with double-deionized water. The high-arsenic water (100 mg/L) was prepared by dissolving disodium hydrogen arsenate heptahydrate (Na$_2$HAsO$_4$·7H$_2$O purity > 98.5%) in Milli-Q water. Besides, all vessels were cleaned with detergent, soaked in 10% HNO$_3$ for 24 h, and rinsed three times with double-deionized water. The pH electrode was calibrated with either sodium hydroxide or hydrochloric acid. All chemicals used in the experiments were of reagent grade.

2.2. Batch Tests. All batch tests were performed at constant temperature (25 ± 1°C). Conventional jar-test apparatus (MY3000-6M, Wuhan, China), equipped with 1.0 L plexiglass beakers, was used for the coagulation study. Certain amounts of ferric chloride (FC: FeCl$_3$·6H$_2$O) were dosed in three different dosing modes as shown in Figure I.

Mode A (single dosing): 500 mg of FC was added during rapid mixing (300 rpm for 1 min), followed by slow stirring at 100 rpm for 19 min, and further slow stirring at 50 rpm for 10 min.

Mode B (two-step sequential dosing): 400 mg of FC was dosed in the first step under the same coagulation process in mode A, while 100 mg of FC was used in the supernatant in the second step with the same coagulation process in mode A.

Mode C (three-step sequential dosing): under the same coagulation process, 300 mg of FC was used in the first step, 100 mg of FC was added in the supernatant of the first step in the second step, and 100 mg of FC was dosed in the supernatant of the second step in the last step. The coagulation processes of the last steps were same as those of mode A.

The pH of the solution was stabilized at desired values by adding 0.01 mol/L HCl and NaOH standard solutions. 10 mL of supernatant at 3 cm below the surface after sedimentation was sampled for the following batch experiments. All the supernatant samples were filtered through 0.22 μm PTFE membranes (Millipore, US) for total arsenic determination with flame atomic absorption spectroscopy (AAS). The arsenic removal efficiency (E) was calculated with

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E = \frac{C_0 - C}{C_0} \times 100\%,
\]

where $C_0$ and $C$ were initial arsenic concentration and effluent, respectively. The Fe-As (V) samples (sediment) were centrifuged at 8000 rpm for 10 min and filtered through 0.22 μm PTFE membranes (Millipore, US) for liquid/solid separation. Each sample was conducted in triplicate and mean values were reported.

2.3. Sequential Extraction. 2.0 g of Fe-As (V) samples was sampled from the batch experiments, following the methods of Daus et al. and Gao et al. [33, 34]. The binding information between arsenate and FC was investigated with a sequential extraction procedure [35]. Table I shows the details of the five-step extraction procedure.
All supernatant samples were taken at 3 cm below the surface of the settled mixture and filtered through 0.22 μm PTFE membranes (Millipore, US) before total arsenic by flame determination with atomic absorption spectroscopy (Perkin Elmer AAnalyst A300, Beijing, China). Each test was triplicate to guarantee the analysis quality.

2.4. Particle Size Distribution. Malvern Mastersizer 2000 (Malvern Co., Worcester, England) was used to analyze the size distribution of coagulant particles. The Malvern Mastersizer 2000 consisted of a 2 mW He-Ne laser (λ = 632.8 nm) as the light source, optic lens, and photo-sensitive detectors. Each measurement was triplicate to guarantee the analysis quality.

2.5. FT-IR Spectroscopy. To investigate the interaction between As (V) and FC, Fourier transformed infrared (FT-IR) spectroscopy was used to characterize arsenic-borne coagulates sorption in different dosing modes. All the samples were prepared under the following method: the sediment samples from the coagulation experiments were dried to solids at 40°C and stored in a desiccator filled with silica gel at room temperature; the dried samples were mixed with 200 mg of KBr and heated in an oven (130°C) for at least 24 h; the pellets for FT-IR analysis were made of 90 mg of this mixture. The FT-IR spectra were recorded with a Bruker IFS55 spectrophotometer at room temperature within the range of 4000–400 cm⁻¹ with 200 scans collected at 4 cm⁻¹ resolution [1, 33, 34].

3. Results and Discussion

3.1. The Effect of Dosing Modes on Arsenic Removal. The influence of pH on coagulation has been well investigated [36]. Previous studies have given the optimum pH range (4.5–8.0) for high-arsenic water ferric coagulations [29].

The distribution of As (V) hydroxide species as a function of pH demonstrated that H₂AsO₄⁻ and HAsO₄²⁻ are the dominant species at neutral pH. This implied that both could be major existing forms of As in these batch experiments [37, 38].

Figure 2 shows the arsenic removal efficiencies in different dosing modes in the following order: the sequential dosing mode (Mode C > Mode B) > the single dosing mode (Mode A). The arsenic removal preferred the sequential dosing mode to the single dosing mode.

3.2. Speciation Analysis. The arsenic-borne coagulates were treated following the sequential extraction method to study
the arsenic removal mechanisms in different dosing modes [35].

Figure 3 shows that, in Step I, less than 2% of the arsenic-borne coagulates were extracted for Mode C more than that for Mode B. For Mode A, this number was close to zero. In Step II, the percentage of arsenate extracted, associated with the relatively exchangeable fractions, such as As (V) bounded with outer-sphere complex, ascended from Mode A to Mode C. The numbers from Step III and Step IV were higher than 90% of the arsenate adsorbed for all three dosing modes, which represented the specifically sorbed As (V) and amorphous crystalline hydrous oxides of Fe, respectively.

Figure 3 showed that the order of the As (V) specifically sorbed was Mode A > Mode B > Mode C while the order of the As (V) associated with amorphous and poorly crystalline hydrous oxides of Fe was Mode C > Mode B > Mode A. Both As species would not be expected to be easily released under natural conditions. Besides, there was no fraction associated with well-crystallized hydrous oxides of Fe (Step V).

The five-step sequential extraction of As (V) from the Fe-As (V) materials sampled from each dosing step (A, B-I, B-II, C-I, C-II, and C-III) was given in Figure 4. In the three modes (A, B, and C), the As (V) was slightly soluble or physically exchangeable, once bound to the coagulant surface, and the As (V) specifically sorbed and associated with amorphous crystalline hydrous oxides of Fe were the dominant species (Steps III and IV). The main mechanism of arsenic removal with FC was a chemisorption process, involving the formation of inner-sphere surface complexes and low-solubility minerals (scorodite). The fact that the fractions of the As (V)

Figure 5: Variations of the size distribution with the Fe-As (V) samples in different dosing modes (pH<sub>Initial</sub> = 7.0).
soluble and nonspecifically sorbed in sequential dosing mode were higher than those in single dosing mode means that the arsenic-borne coagulates of the sequential dosing modes were more environmentally hazardous.

3.3. Particle Size Distribution Analysis. The adsorption rate mainly depended on the radius of particles [39]. Figure 5 displayed the size distribution of the arsenic-borne coagulates in the different dosing steps (A, B-I, B-II, C-I, C-II, and C-III). All of arsenic-borne coagulates were fine particles, ranging between 2.5 and 160 μm. The particles showed that the different average size in different dosing modes followed the following order: Mode A > Mode B (B-I > B-II) > Mode C (C-I > C-II > C-III). The As (V) nonspecifically sorbed and soluble of Mode C was approximately 3.0% lower than Mode B and Mode A. It is likely attributed to the changeable surface structure of the particles. Generally, the specific surface area increased with size decreasing and the smaller particles physically sorbed more As (V). Consequently, it could be concluded that the surface structure of the arsenic-borne coagulates favored the neutralization and adsorption of the As (V) and two sequential dosing modes were more prevalent than the single one.

3.4. FT-IR Spectra Analysis. FT-IR spectra of arsenate sorbed on the coagulant samples from three dosing modes
were showed in Figure 6. In the whole range scanning (400–4000 cm$^{-1}$), a strong band was present in the hydroxyl stretching region at 3400–3300 cm$^{-1}$, which is likely attributed to the presence of H$_2$O in the Fe-As (V) samples [40, 41]. In the spectra a band at 1630 cm$^{-1}$ was also found, resulting from the water O–H bending mode [42]. For all spectra, an adsorbed peak due to stretching vibrations of Fe–O bond was present approximately at 490 cm$^{-1}$ [41]. Additionally, there was one well resolved band, peaked at 825–829 cm$^{-1}$, owing to the As–O stretching vibration of the As–O–Fe coordination of the ferric arsenate (i.e., scorodite) and the surface complex (i.e., protonated FeO$_2$As(O)(OH)$^-$ and unprotonated FeO$_2$As(O)$_2$$^{5-}$ forms) on the precipitates [35]. This demonstrated that the main mechanism of the arsenic removal was a chemisorption process, which matched well with the speciation analysis.

4. Conclusion

The experimental results showed that arsenic removal efficiency of the sequential dosing mode was higher than the single dosing mode. The sequential extraction procedure, applied to Fe-As (V) samples exchanged with arsenate, showed that the As (V) specifically sorbed associated with amorphous crystalline hydroxides of Fe were the dominant species (over 90%) from the Fe-As (V) samples in different dosing modes. The main mechanism of the arsenic removal with FC was a chemisorption process, matching with the information obtained with FT-IR spectra analysis. The particle size distribution analysis illustrated that the surface structure of the arsenic-borne coagulates favored the neutralization and adsorption of As (V) and the sequential dosing mode was prevalent, compared with the single one.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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