

As(III) removal by Fe(III)-amidoximated PAN in the presence of H₂O₂ through simultaneous oxidation and adsorption

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ABSTRACT

This study explored the efficient removal of As(III) by Fe(III)-amidoximated PAN (Fe(III) AO PAN) in the presence of H₂O₂ through simultaneous oxidation and adsorption. It presented that As(III) could be oxidized to As(V) efficiently in the pH range 3–9 within a short time. At the same time, the oxidized As(V) was adsorbed by Fe(III)-AO PAN. The effect of pH value, H₂O₂ concentration, Fe(III)-AO PAN amount, and coexisting anions on the As(III) oxidation and removal were investigated in detail. Dynamic adsorption on fixed column was also studied. Arsenic removal efficiency including As(III) and As(V) could be achieved (95.2%) by the simultaneous oxidation and adsorption process at the following optimal conditions: pH = 6.5, dosage of Fe(III)-AO PAN = 2.5 g/L, H₂O₂ = 100 mg/L, initial concentration of As(III) = 5 mg/L. Dynamic adsorption on fixed column demonstrated that As(III) in simulated groundwater could be efficiently removed from 500 µg/L to <10 µg/L within 130 bed volumes (BV).

Key words | adsorption, arsenite, Fe(III)-loaded amidoximated polyacrylonitrile, H₂O₂, oxidation

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INTRODUCTION

Arsenic contamination in natural water has been considered as a great threat to human beings and other living organisms (Smedley & Kinniburgh 2002; Choong *et al.* 2007). The International Agency for Research on Cancer (IARC) recognizes arsenic and arsenic compounds as group 1 carcinogens, and the EU lists arsenic trioxide, arsenic pentoxide, and arsenate salts as category 1 carcinogens (Straif *et al.* 2009). Therefore, many countries have issued stringent restrictions on the arsenic concentration of drinking water. For example, the maximum permitted total arsenic concentration is 10 µg/L in the United States and European Union (Mondal *et al.* 2006).

Usually, the predominant forms of As in natural water are the inorganic species, including arsenate [As(V)] and arsenite [As(III)]. Between the two main arsenic species,

As(III) is more toxic, highly mobile, and difficult to remove because of its poor affinity for absorbents and coagulants (Choong *et al.* 2007). Therefore, the pre-oxidation of As(III) to As(V) is a very necessary process for enhancing arsenic removal efficiency. Various oxidants such as Fenton reagent (Krishna *et al.* 2001; Katsoyiannis *et al.* 2008), MnO₂ (Manning *et al.* 2002), UV/TiO₂ (Ferguson *et al.* 2005), UV/H₂O₂ (Lescano *et al.* 2012), TiO₂/H₂O₂ (Kim *et al.* 2015), and iron (hydro)oxides/H₂O₂ (Wang *et al.* 2013) have been extensively studied for the oxidation and removal of As(III). Among these, the strategy based on hydrogen peroxide (H₂O₂) is one of the promising methods for the oxidation and removal of As(III) (Podgoršek *et al.* 2009). Thus, a lot of metal oxides including iron (Bokare & Choi 2014), aluminium (Önnby *et al.* 2014), and

titanium (Kim *et al.* 2015) have been attempted to remove As(III) in the presence of H₂O₂. But the practical use of the above-mentioned systems for As(III) oxidation is limited by the strong pH dependence and slow oxidation kinetics (Kim *et al.* 2015). In addition, another drawback is the relatively low removal efficiency because of the poor adsorption affinity of the above-mentioned metal oxides for arsenic. So, it is still a challenge to develop a new arsenic removal process for simultaneous oxidation and removal of As(III).

Recently, heterogeneous catalysts for Fenton-like reactions through immobilizing metal ions onto the polymer substrates have attracted great attention in the field of environmental pollution control. For example, Nafion membrane has been used for immobilizing Fe ions to form a Fe/Nafion catalyst for the degradation of organic pollutants (Matsunaga *et al.* 1996; Muñoz *et al.* 2002). Dong *et al.* have prepared Fe(III)-amidoximated PAN fiber and investigated its performance in oxidative degradation of azo dye under visible light irradiation (Dambies *et al.* 2000; Balaji *et al.* 2005). These Fenton-like heterogeneous oxidations can efficiently avoid the drawbacks of the classical Fenton reaction, such as the formation of Fe(III)-iron sludge and the acidic adjustment at the end of treatment (Cai *et al.* 2017; Gao *et al.* 2018; Cai *et al.* 2019). It is very interesting that the metal-loaded polymer substrates have earned much attention due to their higher adsorption capacity and selectivity for arsenic. Various metal ions such as Fe(III) (Suzuki *et al.* 1997; Tao *et al.* 2011), Zr(IV) (Fernandez *et al.* 1998), Mo(III) (Dhananjeyan *et al.* 2001), La(III) (Dong *et al.* 2010), and Cu(II) (Han *et al.* 2011) have been loaded onto chelating resin to remove arsenic. Just recently, Fe(III)-loaded amidoximated polyacrylonitrile (Fe(III)-AO PAN) with higher adsorption capacities for As(V) has been prepared in our previous study (Ji *et al.* 2016). Therefore, we expect that if Fe(III)-AO PAN and hydrogen peroxide are used for removing As(III), we can not only oxidize As(III) to As(V) through the Fenton-like reaction, but also simultaneously remove As(V) by using the excellent adsorption performance of Fe(III)-AO PAN. As a consequence, in this paper we plan to use Fe(III)-AO PAN as both a heterogeneous catalyst and adsorbent for the removal of As(III) in the presence of hydrogen peroxide, which will support the future practical application of Fe(III)-AO PAN for the contamination of As(III) in natural water.

EXPERIMENTAL

Chemicals and materials

Fe(III)-AO PAN was used as a raw material. The synthesis and characterization are described in our previous work (Ji *et al.* 2016). All other chemicals including NaCl, NaNO₃, Na₂SO₄, NaHCO₃, NaH₂PO₄, and Na₂SiO₃ were of analytical grade and did not require further purification. NaAsO₂ and Na₂HAsO₄·7H₂O (Sigma-Aldrich Co.) were used to prepare As(III) and As(V) stock solutions (1,000 mg/L), respectively. Deionized water was used in the whole experimental process.

Analytical methods

A pH meter (Mettler-Toledo, LE438 pH, China) was used for the measurement of pH value.

The total arsenic (As(III) + As(V)) concentration (denoted as As(T)) was measured using a double channel atomic fluorescence spectrometer (AFS-920, China). Prior to analysis, the samples were mixed with concentrated HCl and a reducing agent (1% thiocarbamide). The mixed liquid was kept under static conditions for 1 h. To selectively determine As(III), a pH 5 citrate buffer was used instead of concentrated HCl. Only As(III) is converted to AsH₃ under these conditions (Yamamoto *et al.* 1981). The concentration of As(V) and arsenic removal were calculated according to Equations (1) and (2), respectively.

$$C_{\text{As(V)}} = C_{\text{As(T)}} - C_{\text{As(III)}} \quad (1)$$

$$\text{Removal (\%)} = \frac{C_0 - C}{C_0} \times 100\% \quad (2)$$

where C_0 and C are the initial concentration and the concentration of arsenic in solution when the contact time is t , respectively (mg/mL).

Batch experiments

Kinetic experiments of arsenic oxidation and adsorption were carried out as follows: 0.050 g of Fe(III)-AO PAN were added into a 100 mL polyethylene bottle with a stopper

containing mixed with 50 mL solution. The concentration of As(III) and H₂O₂ in this solution were kept at 500 µg/L and 100 mg/L, respectively. Solution pH was adjusted to 6.5 ± 0.5. The mixture was shaken continuously in a thermostat-cum-shaking assembly at 25 °C. Half a milliliter of solution was sampled at various time intervals for the concentration analysis of As(III) and As(T). The experiments were conducted in triplicate and the average values are reported.

The effect of solution pH on As(III) oxidation and removal was determined by adding 0.05 g of Fe(III)-AO PAN into a 100 mL polyethylene bottle with a stopper containing 100 mL of solution. The concentration of As(III) and H₂O₂ was 5 and 100 mg/L, respectively. Solution pH was adjusted to a desired value with 0.10 M HCl and NaOH. The other experiments concerning the effect of H₂O₂ concentration, Fe(III)-AO PAN amount, and coexisting anions on As(III) oxidation and removal were performed according to a similar procedure as described above.

In the recycling experiments, NaOH (1 M) solution was chosen to regenerate the used Fe(III)-AO PAN. After being shaken with NaOH (1 M) solution, washed with deionized water, and dried at 50 °C, Fe(III)-AO PAN was reused for additional use cycles.

Fixed-bed column experiments

Dynamic adsorption experiments were conducted with a glass column (11 mm in diameter and 200 mm in length), in which 2 mL of Fe(III)-AO PAN were added. The volume of Fe(III)-AO PAN filled in the glass column was called the total volume of the resin bed (BV). Simulated As(III)-containing wastewater was introduced into the fixed-bed in a down-flow mode. A peristaltic pump (HL-2, China) was employed to assure a constant flow rate (6 BV/h). A definite volume of effluents was collected. The concentrations of As(III) and As(T) in the effluents were measured by a double channel atomic fluorescence spectrometer. The main components of the feeding solution were composed of 500 µg/L As(III), 100 mg/L H₂O₂, 60 mg/L Cl⁻, 80 mg/L SO₄²⁻, 25 mg/L SiO₃²⁻, 1 mg/L H₂PO₄⁻, which were obtained by mixing the above-mentioned components with definite amounts.

RESULTS AND DISCUSSION

Kinetics of As(III) oxidation and removal

To reveal the synergetic effects between Fe(III)-AO PAN and H₂O₂ on As(III) oxidation and removal, kinetics of As(III) oxidation and removal of three kinds of systems including H₂O₂, Fe(III)-AO PAN, and Fe(III)-AO PAN-H₂O₂ were investigated and the results are presented in Figure 1. As shown in Figure 1(a), the oxidation rate of As(III) in the presence of H₂O₂ is very low. Only about 23.2% of As(III) is oxidized into As(V) within 180 min ($C = 384.6$ µg/L), although H₂O₂ has strong oxidation activity (Pettine *et al.* 1999). In case of As(T) (shown in Figure 1(b)), no changes in concentration of As(T) are observed. In fact, H₂O₂ has no adsorption ability for arsenic at all. When used for arsenic removal and the contact time was 180 min, the removal rates of As(III) and As(T) are 83.5 and 78.8%, respectively. These results indicate that, because most of the arsenic removal adsorbents including Fe(III)-AO PAN involved in this paper have low adsorption capacity for As(III) compared with As(V) (Choong *et al.* 2007). Thus, it is difficult to effectively remove arsenic only through the adsorption of Fe(III)-AO PAN. As for the system of Fe(III)-AO PAN-H₂O₂, when the contact time was 60 min, the removal rates of As(III) and As(T) were 98.4%, and 98.9%, respectively. Obviously, significant increases in the arsenic removal are observed in the system of -H₂O₂. The above experimental results suggest that Fe(III)-AO PAN might catalyze the oxidation of As(III) to As(V) by H₂O₂, which is beneficial for Fe(III)-AO PAN to more effectively remove arsenic from aqueous solution (Pettine & Millero 2000).

To further elucidate the oxidation rate of As(III) in the H₂O₂ and Fe(III)-AO PAN-H₂O₂ systems, the kinetic data in Figure 1(a) were analyzed using the Langmuir-Hinshelwood pseudo-first-order kinetics model (Equation (3)) (Zhang *et al.* 2010).

$$\ln(C_0/C) = kt \quad (3)$$

where C_0 (µg/L) is the initial concentration of As(III), C (µg/L) is the residual concentration of As(III) at time t (min), and

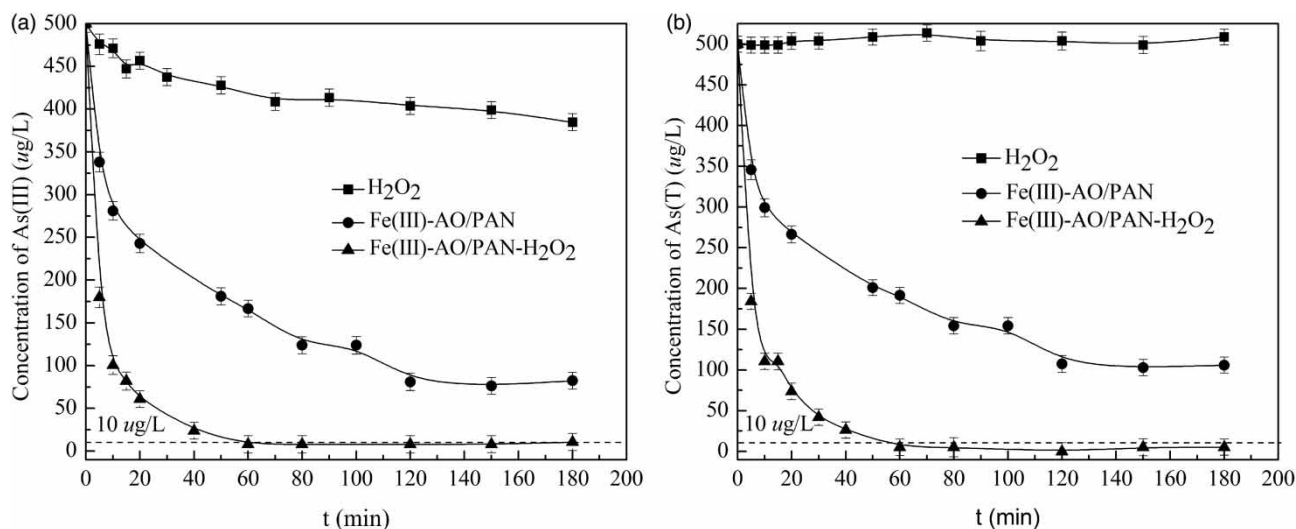


Figure 1 | Time profiles of As(III) oxidation (a) and total arsenic removal (b) in the systems of H₂O₂, Fe(III)-AO PAN and Fe(III)-AO PAN-H₂O₂ (Fe(III)-AO PAN 2.5 g/L; As(III) 500 µg/L; H₂O₂ 100 mg/L; pH 6.5).

k is the oxidation rate constant. From the linear time dependences of $\ln(C_0/C)$ versus t , the first-order rate constant k could be obtained (as shown in Figure 2).

As presented in Figure 2, the oxidation rate constants of two systems of Fe(III)-AO PAN-H₂O₂ and H₂O₂ were 0.001 and 0.053, respectively, which imply that the oxidation rate of the former is 53 times higher than that of the latter. These results indicate that, compared with using hydrogen peroxide alone, the oxidation of As(III) to As(V) can be strengthened in the system of Fe(III)-AO PAN-H₂O₂. This phenomenon has been reported in previous literature

(Voegelin & Hug 2003). More detailed studies about the possible active species and mechanism are under way.

Based on the high oxidation rate and removal of Fe(III)-AO PAN-H₂O₂ for As(III), the influence factors such as a solution pH, H₂O₂ concentration, Fe(III)-AO PAN amount, and competing ions were examined in the following study. In addition, dynamic adsorption experiments were also investigated.

Effect of influence factors on As(III) oxidation and removal

Solution pH

Figure 3(a) shows the effect of solution pH on As(III) oxidation and removal. Obviously, the solution pH in the range of 3–8.5 investigated in this study has little effect on the oxidation of As(III), meaning that Fe(III)-AO PAN-H₂O₂ can be used for As(III) oxidation in a wide pH range. However, the As(T) removal decreases with the increase of solution pH (Figure 3(b)), which can be ascribed to the lower adsorption property between Fe(III)-AO PAN and As(V) deriving from the competition from OH⁻ in aqueous solution (Anirudhan et al. 2011). Considering the pH value for most natural water falls in the range 6.0–8.0 and facile treatment process, the subsequent experiments were conducted at pH 6.5.

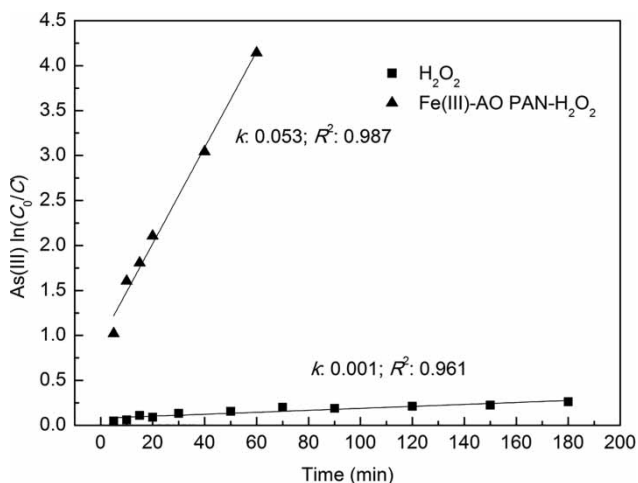


Figure 2 | Kinetic linear fitting curves of H₂O₂ and Fe(III)-AO PAN-H₂O₂.

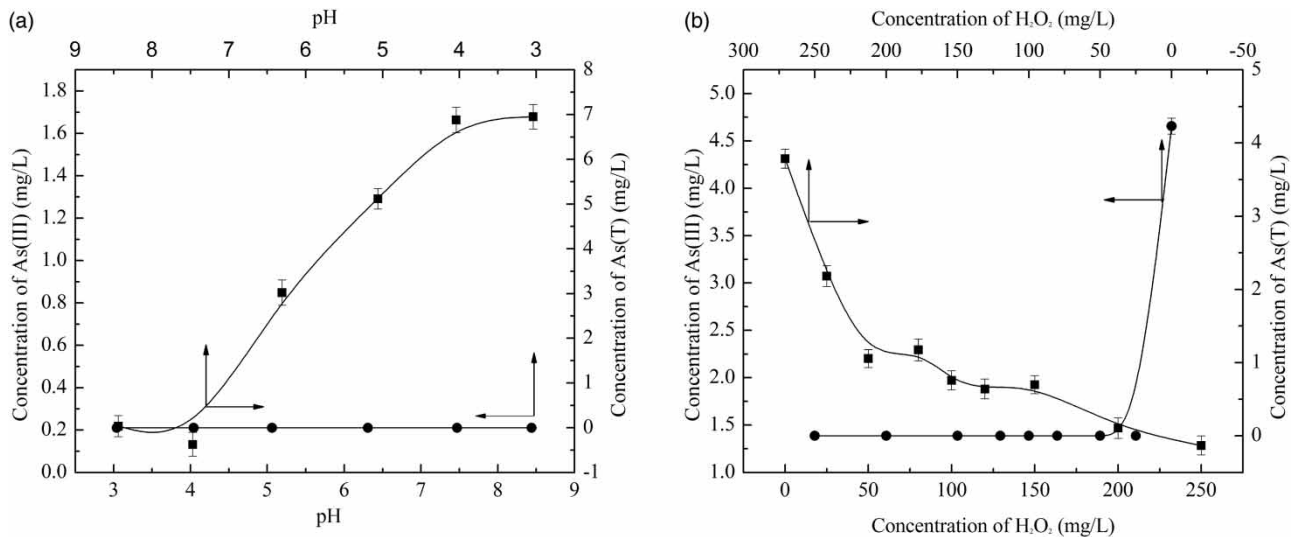


Figure 3 | (a) Effect of solution pH on arsenic removal (Fe(III)-AO/PAN: 0.5 g/L, As(III): 5 mg/L, H₂O₂: 100 mg/L, 25 °C) and (b) effect of H₂O₂ concentration on arsenic removal (Fe(III)-AO PAN 0.5 g/L; As(III) 5 mg/L; pH 6.5; 25 °C).

H₂O₂ concentration

The effect of H₂O₂ concentration on As(III) oxidation was also studied and the results are shown in Figure 3(b). As shown in Figure 3(b), when there is no hydrogen peroxide in the system, the As(III) removal efficiency of Fe(III) AO PAN is only 15.4%, ascribing to the adsorption effect of Fe(III)-AO PAN alone toward As(III). After the addition of H₂O₂, the removal efficiencies of As(III) and As(T) are obviously improved. When the concentration of H₂O₂ increases to 25 mg/L, the removal efficiency of As(III) is sharply raised to 100%. In the case of As(T), the removal rate is increased with the increasing of the H₂O₂ concentration. These results may be ascribed to the decrease of solution pH with the increase in the H₂O₂ amount.

Fe(III)-AO PAN amount

The effect of Fe(III)-AO PAN amount on the As(III) oxidation and removal was also investigated and the results are shown in Figure 4. Obviously, the oxidation efficiency of As(III) increases from 86% to 100% when the Fe(III) AO PAN amount increases from 0.1 g/L to 0.25 g/L, implying the oxidation of As(III) in the Fe(III) AO PAN-H₂O₂ system is greatly effective. In addition, Figure 4 depicts

that As(T) removal increases with the increase in Fe(III) AO PAN dosage, which can be ascribed to the more active sites on the surface of Fe(III) AO PAN. When the amount of Fe(III) AO PAN is 2.5 g/L, the arsenic removal is above 95%. These results indicate that the simultaneous oxidation and removal of As(III) can be achieved in the system of Fe(III)-AO/PAN-H₂O₂. This strategy of arsenic removal is both environmentally friendly and efficient.

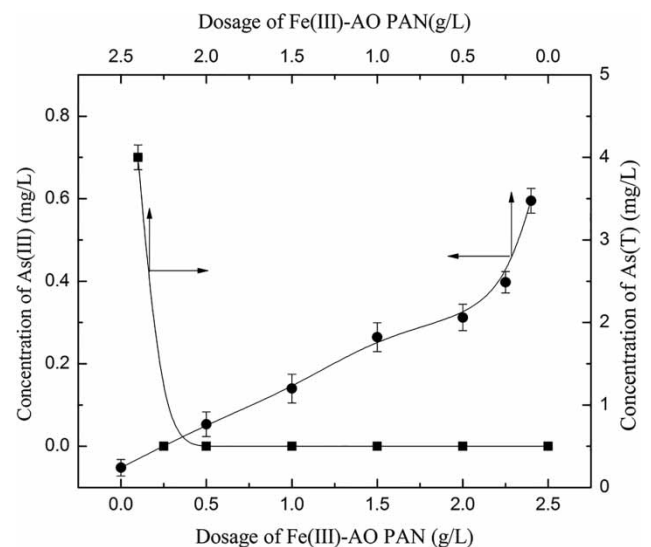


Figure 4 | Effect of Fe(III)-AO PAN amount on arsenic removal of in the presence of H₂O₂ (As(III) 5 mg/L; H₂O₂ 100 mg/L; pH 6.5; 25 °C).

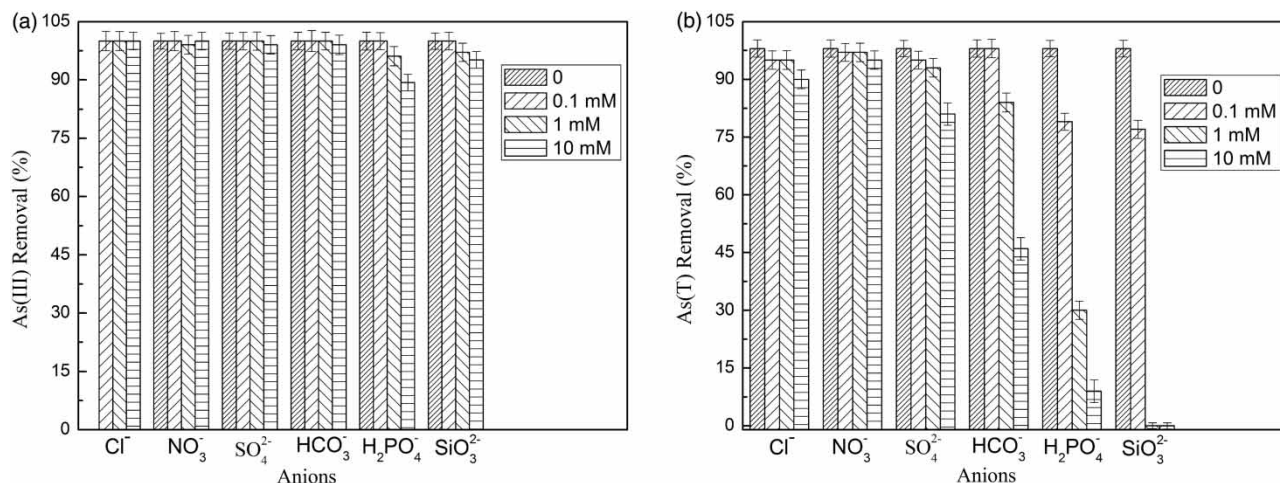


Figure 5 | Effect of competing anions on As(III) oxidation and removal by Fe(III)-AO PAN in the presence of H₂O₂ (a: As(III); b: As(T))/Fe(III)-AO PAN 2.5 g/L; As(III) 5 mg/L; H₂O₂ 100 mg/L; pH 6.5; 25 °C).

Coexisting anions

Generally, various anions such as chloride, sulfate, silicate and phosphate, which usually exist in natural water, might perform competitive adsorption with arsenic (Mohan & Pittman 2007). To assess the effects of coexisting anions on As(III) oxidation and removal, several kinds of anions such as Cl⁻, NO₃⁻, SO₄²⁻, HCO₃⁻, H₂PO₄⁻, and SiO₃²⁻ were chosen as competitive anions. Three concentration levels (e.g. 0.1, 1, and 10 mM) were selected in this article (Hang et al. 2011). As shown in Figure 5(a), the selected anions have little effect on the As(III) oxidation efficiency in the concentration ranges investigated in this study. Even if the concentration is as high as 10 mM, the As(III) oxidation efficiency still reached above 89%. However, the foreign anions have a definite negative effect on arsenic removal to some extent. Furthermore, as shown in Figure 5(b), the arsenic removal is seriously hindered by HCO₃⁻, H₂PO₄⁻ and SiO₃²⁻ compared to Cl⁻, NO₃⁻, and SO₄²⁻, indicating significant competition for adsorption with arsenic in the presence of HCO₃⁻, H₂PO₄⁻ and SiO₃²⁻. This can be explained by the chemical similarity between the two foreign ions and arsenic, which leads to a significant competition (Pan et al. 2014).

Desorption and reusability

To investigate the reusability of Fe(III) AO PAN in the presence of H₂O₂, five operating cycles were conducted. The

used Fe(III) AO PAN was regenerated by using 1 M NaOH solution as the eluent (Zhou et al. 2008). The As(III) oxidation and removal are depicted in Figure 6. It can be noted that the removal rates of As (III) and As(T) after five re-use cycles are 68% and 66%, respectively. This indicates that Fe(III) AO PAN can be regenerated with 1 M alkali solution and reused in eliminating the contamination of arsenic by simultaneous oxidation and adsorption.

Dynamic adsorption on fixed column

To study the potential performance of the Fe(III)-AO PAN-H₂O₂ system in the potential applications, dynamic

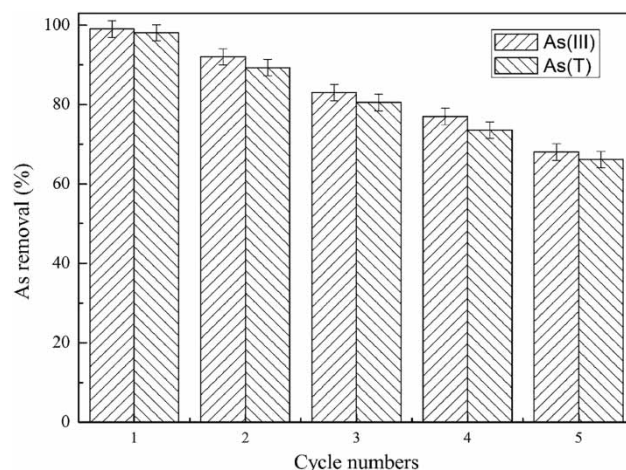


Figure 6 | Recycling of Fe(III)-AO PAN for As(III) oxidation and removal in the presence of H₂O₂ (As(III), 5 mg/L; Fe(III)-AO PAN, 50 mg; H₂O₂, 100 mg/L, pH 7.0, 25 °C).

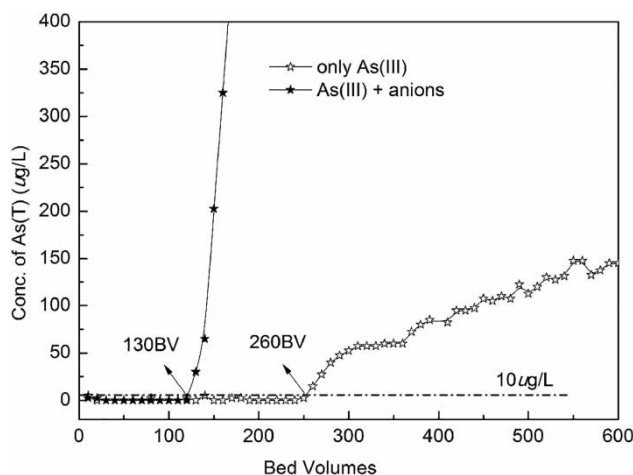


Figure 7 | Breakthrough curves of As(T) in the system of Fe(III) AO PAN-H₂O₂ (As(III), 500 µg/L; H₂O₂, 100 mg/L; Cl⁻, 60 mg/L; SO₄²⁻, 80 mg/L; SiO₃²⁻, 25 mg/L; H₂PO₄⁻, 1 mg/L; pH: 6.5 ± 0.5; 25 °C).

adsorption on fixed column was conducted with a single-component arsenate solution or a multicomponent feeding solution through two separate columns filled with 2 mL of Fe(III)-AO PAN, respectively. The breakthrough curves are presented in Figure 7. The breakthrough point is set as 10 µg/L (the horizontal dashed line in Figure 7), which is the maximum contaminant level for arsenic in drinking water promulgated by World Health Organization (WHO). As presented in Figure 7, arsenic removal from the multicomponent feeding solution onto Fe(III) AO PAN breaks through quickly, and the effective treatment volume is less than 130 bed volumes (BV), whereas that for the single-component arsenic solution is around 260 BV under otherwise identical conditions. The fixed column experiments show that Fe(III) AO PAN-H₂O₂ system is effective for As(III) removal from solution in practical application.

CONCLUSION

The Fe(III)-AO PAN-H₂O₂ system was first used for As(III) oxidation and removal in this paper. The results indicated that the Fe(III)-AO PAN-H₂O₂ system showed high removal efficiency towards both As(III) and As(V), which is attributed to the synergies gained from Fe(III) AO PAN and H₂O₂. The oxidation efficiency of As(III) was almost unaffected over a wide pH range. The results also revealed the

oxidation rate of Fe(III)-AO PAN-H₂O₂ increased with increasing concentration of H₂O₂, which was 53 times higher than that of the single H₂O₂ system. Dynamic adsorption on fixed column demonstrated that As(III) in simulated groundwater could be efficiently removed from 500 µg/L to <10 µg/L within 130 bed volumes (BV). Furthermore, Fe(III)-AO PAN-H₂O₂ may be a promising system for removing low concentration As(III) rapidly and effectively. Further research is underway to investigate the active species and mechanisms of Fe(III)-AO PAN-H₂O₂ for As(III) oxidation and removal.

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