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Removal of As(III) from Water by Fenton Oxidation Coupled with Flocculation

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As the deterioration of arsenic pollution problem, the experimental research on removal of As(III) from water by Fenton oxidation coupled with flocculation were studied. 0.5 mg/L arsenite [As(III)] water was treated by Fenton oxidation-flocculation coupled process and single flocculation process respectively. Various influence factors of Fenton method on arsenic removal were studied. The results show that Fenton method for removal of arsenic(III) is superior to single flocculation. The removal of arsenic(III) is mainly attributed to Fenton reagent reaction directly. The optimum conditions of removal of arsenic(III) from water was pH 3, H_2O_2 10 mg/L, Fe^{2+}/H_2O_2 (n/n) 0.2, reaction time 10 min, As(III) removal reached to 95.17 %. And Fenton oxidation-flocculation method is used for drinking water treatment, the residual concentration of arsenic in water after treated group is lower than "drinking water health standards" (GB5749-2006) in the standard of 0.01 mg/L.

Keywords: Fenton reagent, Oxidation, As(III), Flocculation.

INTRODUCTION

In recent years, with the rapid development of industry, wastewater emissions which contains a lot of heavy metals also gradually increased and has been reported the presence of As(III) among them. Having recognized the enormous health implications, the Department of Health, P.R. China lowered the provisional guideline value for arsenic in drinking water from 0.05 to 0.01 mg/L in July 2006 [1], along with the standard of drinking water strictly, the arsenic content in many areas of groundwater out of specification [2]. Many parts of the world have been reported the presence of As(III) in ground water, arsenic(III) pollution has become a common concern on the world at present [3-5]. So, the removal of As(III) from water by a treatment technology with high efficiency, economy and applicability should be studied.

Arsenic is an element poisonous to every other living creature in the planet except for a few specialized microscopic creatures, of which As(III) is more mobile and toxic than As(V) [6,7]. Several treatment methods such as chemical precipitation [8], oxidation [9], ions exchange [10] and adsorption [11] have been developed for the removal of As(III) from water. However, Fenton oxidation still remains an attractive and promising technology because of its simplicity, ease of operation, reaction speed and mild reaction conditions and environmentally friendly. The removal of arsenic(III) from water by Fenton oxidation coupled with flocculation, hydrogen peroxide (H_2O_2) can oxidize part of As(III) to As(V), then removal the arsenic under the effective flocculation of Fe^{2+}. Currently, Fenton oxidation process is applied to the arsenic removal is not widespread [12].

The experiment about removal of arsenic(III) from water by Fenton oxidation coupled with flocculation was studied in this study. Experiment with the As(III) simulated wastewater, compares the single flocculation and Fenton oxidation-flocculation of removing arsenic in water and investigate the factors affecting on the effects of arsenic removal.

EXPERIMENTAL

Experimental object was 0.5 mg/L arsenite [As(III)] water which configurate by arsenic standard solution and arsenic standard solution is 1 mL [As(III), 1 g/L], obtained from Iron & Steel Research Institute of P.R. China, was placed to a 1000 mL volumetric flask. Compared with the effective removal of As(III) in water by single flocculation and Fenton oxidation-flocculation process.

Single flocculation process: Measured 100 mL [As(III), 0.5 mg/L] in the taper bottle of 250 mL, add flocculants ($FeSO_4 \cdot 7H_2O$), adjusted pH = 7, made the flocculants exert its effect. The flocculants ($FeSO_4 \cdot 7H_2O$) and 0.5 mg/L As(III) simulated water was agitated on a gyratory shaker for 30 min. Then the suspension of the liquid was decanted and filtered through a 0.45 μm cellulose acetate filter and the supernatant was examined to check the concentration of As(III) using an inductively coupled plasma-atomic emission spectrometer (Intrepid II XSP).

Fenton oxidation-flocculation process: Measured 100 mL [As(III), 0.5 mg/L] in the taper bottle of 250 mL and adjusted pH about 3, then add flocculants ($FeSO_4{\cdot}7H_2O$) and add oxidizing agent (mass fraction 30 % H_2O_2) under agitated on a gyratory shaker, made the oxidizing agent exert its effect. The mixture of each reagent and 0.5 mg/L As(III) simulated water was agitated on a gyratory shaker for 10 min. Then adjusted the reaction of the liquid pH = 7, made the flocculants exert its effect, reaction of the liquid was agitated on a gyratory shaker for 20 min. Then the suspension of the liquid was decanted and filtered through a 0.45 µm cellulose acetate filter and the supernatant was examined to check the concentration of As(III) using an inductively coupled plasma-atomic emission spectro-meter (Intrepid II XSP).

Analytical method: The removal efficiency of As(III)in solution was calculated by eqn. 1:

$$Q\,(\%) = \frac{C_o - C_e}{C_o} \times 100 \qquad (1)$$

where Q is the removal efficiency of As(III), C_o is the initial arsenic concentrations (mg L^{-1}) and C_e is the equilibrium arsenic concentrations (mg L^{-1}).

RESULTS AND DISCUSSION

Effect of single flocculation and Fenton oxidation-flocculationon As(III) removal: The mole ratio of Fe^{2+}/H_2O_2 controlled at 0.3, dosing amount of H_2O_2 was 20 mg/L. According to the experimental method steps in **2**. The result is shown in Fig. 1. Fig. 1 shows that single flocculation on total arsenic removal rate is about 80 % and the removal rate of arsenic in water by Fenton oxidation-flocculation can reach more than 95 %, it was higher than single flocculation. The Fenton oxidation-flocculation than single flocculation have absolute advantages, it was mainly based on strong oxidation of Fenton reagent, part of As(III) will be oxide As(V) and the solubility of As(III) compounds was easy dissolution than As(V) compounds, adverse to flocculation adsorption precipitation [13], so the removal efficiency of arsenic in water by Fenton oxidation-flocculation was higher than single flocculation.

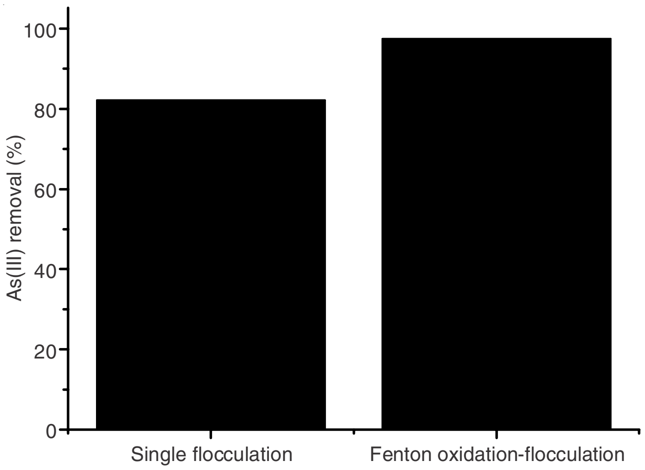

Fig. 1. Effect of single flocculation and Fenton oxidation-flocculation on removal of As(III)

Further research involved to investigate the factors affecting on the effects of removal of arsenic.

Effect of H_2O_2 on As(III) removal: The mole ratio of Fe^{2+}/H_2O_2 controlled at 0.3, the dosage of H_2O_2 were 5, 10, 20, 30, 50, 70 mg/L, respectively. The initial pH of As(III) water was about 6, then according to the experimental method steps of Fenton oxidation-flocculation process in **2** (Fig. 2).

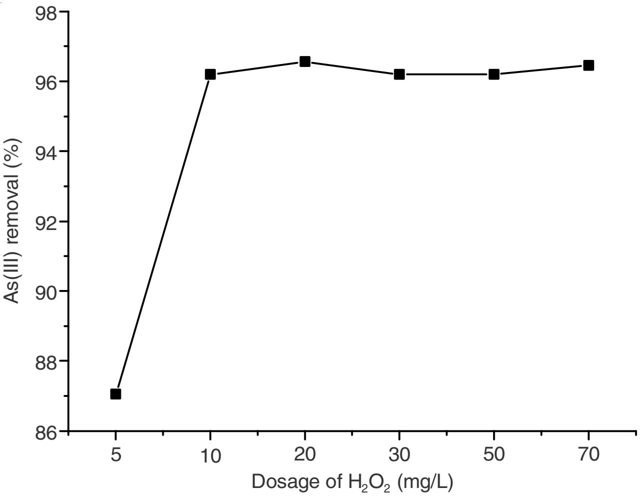

Fig. 2. Effect of H_2O_2 on removal of As(III)

Fig. 2 shows the removal rate was increased with the increase dosage of H_2O_2. When dosage of H_2O_2 was 10 mg/L, As(III) removal reached 96 %, it was about 10 % higher than dosage was 5 mg/L, then As(III) removal basically remain unchanged with further increase of the dosage of H_2O_2. This is because with the increase of dosage of H_2O_2 (H_2O_2 concentration increases), the capture ability of hydrogen peroxide to hydroxyl radicals ($^{\bullet}OH$) will increase, so it consumed a part of hydroxyl radicals [14], this lead to reduce the availability of H_2O_2, as shown in eqn. 2.

$$^{\bullet}OH + H_2O_2 \longrightarrow {}^{\bullet}HO_2 + H_2O \qquad (2)$$

The oxidation ability of $^{\bullet}HO_2$ was inferior than hydroxyl radicals ($^{\bullet}OH$) [15,16]. Thus, we choosed dosage of H_2O_2 10 mg/L in the follow-up experimental.

Effect of Fe^{2+} on As(III) removal: The dosage of H_2O_2 was 10 mg/L, the mole ratio of Fe^{2+}/H_2O_2 controlled at 0.1, 0.2, 0.3, 0.4, 0.5, 0.8, respectively. According to the experimental method steps of Fenton oxidation-flocculation process in **2** (Fig. 3) shows the removal rate was increased with the increased of mole ratio (Fe^{2+}/H_2O_2), but not satisfactorily. When mole ratio 0.1, arsenic removal reached 90 %, removal rate over 95 % when mole ratio of Fe^{2+}/H_2O_2 was 0.2, then As(III) removal basically remain unchanged while still increased the mole ratio of Fe^{2+}/H_2O_2. So, we controlled the mole ratio of Fe^{2+}/H_2O_2 at 0.2 in the follow-up experimental.

Considered the flocculation effect of Fe^{2+}, in order to judged the direct causes was Fenton reagent reaction or Fe^{2+} flocculation, we need to add a set of test: measured 100 mL [As(III), 0.5 mg/L] in the taper bottle of 250 mL, adjusted pH about 3, then add flocculants ($FeSO_4{\cdot}7H_2O$), then add oxidizing agent (mass fraction 30 % H_2O_2) under agitated on a gyratory shaker, made the oxidizing agent exert its effect. The mixture

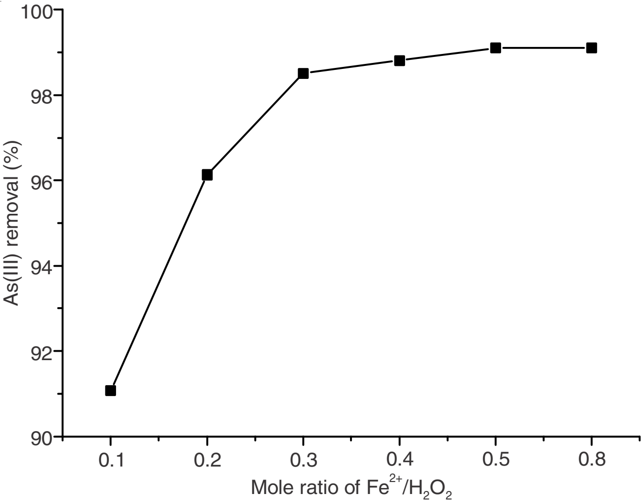

Fig. 3. Effect of Fe^{2+} on removal of As(III)

of each reagent and 0.5 mg/L As(III) simulated water was agitated on a gyratory shaker for 10 min, then adjusted one reaction liquid pH = 7, another unadjusted. Then the suspension of the liquid was decanted and filtered through a 0.45 µm cellulose acetate filter and the supernatant was examined to check the concentration of As(III) using an inductively coupled plasma-atomic emission spectrometer (Intrepid II XSP) (Table-1).

TABLE-1
REMOVAL EFFICIENCY OF ADJUST THE REACTION SOLUTION pH ON As(III)

	Adjusted one reaction liquid pH = 7	Another unadjusted
As(III) removal (%)	96.13	93.57

From the data in Table-1, the arsenic removal by Fenton oxidation-flocculation process reached 93.57 %, it was higher than single flocculation (82.29 %). This showed that arsenic removal was mainly caused by Fenton reagent reaction directly. The arsenic removal was 96.13 % which adjusted reaction liquid pH = 7, it was slightly higher than unadjusted, this was because the reaction after adjusted pH = 7 can promoted the flocculation sedimentation of iron salts, made the arsenic acid salt flocculating settling faster from water. In conclusion, the flocculating effect of Fe^{2+} can act on arsenic removal, but the main effect was caused by Fenton reagent reaction directly.

Effect of pH on As(III) removal: The dosage of H_2O_2 was 10 mg/L, the mole ratio of Fe^{2+}/H_2O_2 controlled at 0.2, adjusted pH at 2, 3, 4, 5, 6, 7, respectively. According to the experimental method steps of Fenton oxidation-flocculation process in **2** (Fig. 4).

Fig. 4 shows the optimal pH of As(III) removal from water by Fenton oxidation coupled with flocculation was about 3. The removal of arsenic(III) was over 93 % when $2 \leq pH \leq 4$ and reached 97.8 % when pH = 3. The removal efficiency of arsenic(III) declined as the increased of pH value, its showed that arsenic removal efficiency unevenly under alkaline conditions. Alkaline conditions destroyed the stability of H_2O_2, stability decreases caused H_2O_2 break down into H_2O and O_2, this reduced the utilization of H_2O_2. In alkaline conditions, Fe^{2+} were generated hydroxide precipitation which is oxidized to ferric hydroxide, its greatly reduced the generation of hydroxyl radicals, led to utilization of H_2O_2 reduced. So, we controlled the pH = 3.

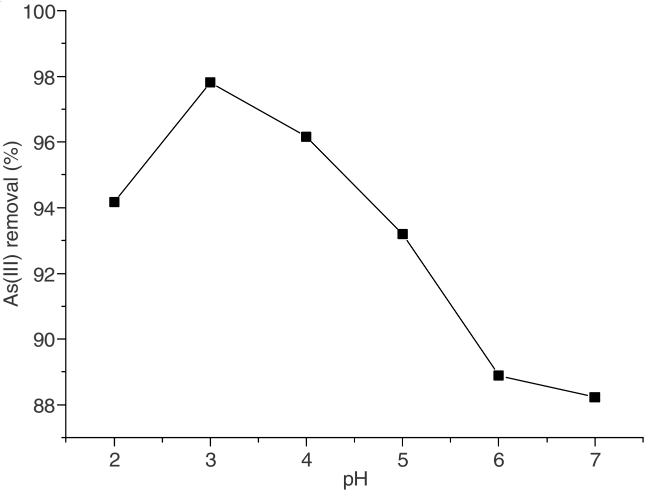

Fig. 4. Effect of pH on removal of As(III)

Effect of reaction time on As(III) removal: The dosage of H_2O_2 was 10 mg/L, the mole ratio of Fe^{2+}/H_2O_2 controlled at 0.2, adjusted pH = 3, respectively. Fenton reaction of oxidation time were 5, 10, 15, 20, 30, 40 (min), respectively and the flocculation time was 20 min (Fig. 5).

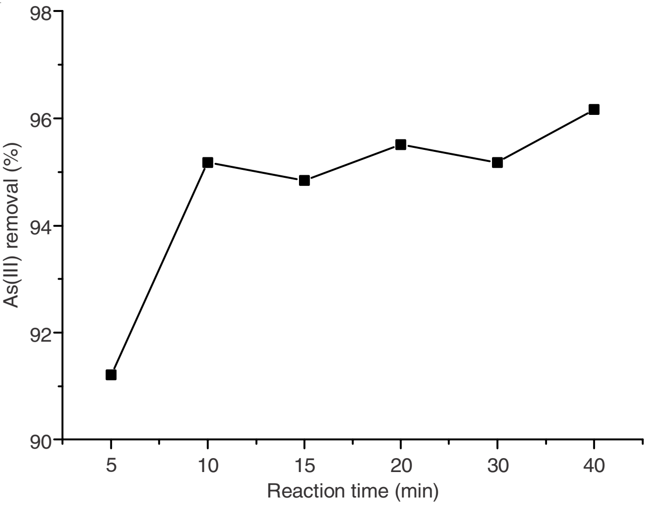

Fig. 5. Effect of reaction time on removal of As(III)

Fig. 5 shows the removal rate was changed little while the Fenton reaction of oxidation time increased. When reaction time was 10 min, arsenic removal was over 95 %, then the removal rate changed little while continued increase the reaction time. So, we controlled the Fenton reaction of oxidation time at 10 min.

Effect of the Fenton oxidation-flocculation on drinking water: In order to better illustrate the removal effeciency of arsenic(III) by Fenton oxidation-flocculation process, based on the best conditions of above experiment results. The experiment of Fenton oxidation-flocculation method treat drinking water was also studied. The quality of drinking water source as shown in Table-2.

TABLE-2
QUALITY OF THE DRINKING WATER SOURCE

Drinking water source	pH	As (mg/L)	Chromaticity
Content	5.93	0.08	2

Adjust the pH of drinking water source reaction liquid at 3, another unadjusted (5.93). The dosage of H_2O_2 was 10 mg/L, the mole ratio of Fe^{2+}/H_2O_2 controlled at 0.2, Fenton reaction of oxidation time were 10 min and the flocculation time was 20 min (Fig. 6).

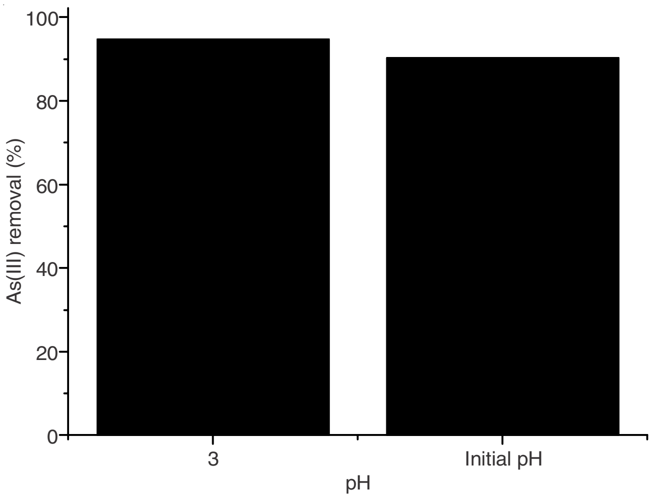

Fig. 6. Effect of the Fenton oxidation-flocculation on drinking water

Fig. 6 shows the arsenic removal rate by Fenton oxidation-flocculation reached 94.71 % when pH = 3 and the final residual concentration of arsenic in water was 0.0042 mg/L, which was lower than "drinking water health standards" (GB5749-2006) in the standard of 0.01 mg/L. However, the removal rate of another unadjusted (5.93) was 90.34 %, the residual concentration of arsenic in water is 0.0077 mg/L, also achieved the drinking water health standards "(GB5749-2006) in the standard of 0.01 mg/L.

From the test results we can be obtained, the optimum conditions on As(III) removal from water by Fenton oxidation coupled with flocculation will certain feasibility in practical engineering.

Mechanism on arsenic removal by Fenton oxidation-flocculation: The mechanism on arsenic removal by Fenton oxidation-flocculation was based on Fenton reaction intermediate (including H_2O_2, $^{\bullet}OH$, $O_2^{\bullet}$, $^{\bullet}HO_2$, *etc.*), these reaction intermediate can oxidize As(III), ultimately combined with Fe^{2+} flocculation as shown in eqn. 3:

$$\text{As(III)} + H_2O_2/^{\bullet}OH/O_2^{\bullet}/^{\bullet}HO_2 \longrightarrow \text{As(V)} \qquad (3)$$

The redox potential of hydroxyl radicals ($^{\bullet}OH$) is 2.080 V and redox potential of As(III) oxide into As(V) is 0.560 V. As the redox potential of As(III) oxide into As(V) was inferior to $^{\bullet}OH$ (2.080 V), so eqn. 3 could occur, then use flocculation of Fe^{2+}/Fe^{3+} with As(III)/As(V) produce coprecipitation, to achieve purpose.

Conclusions

The 0.5 mg/L arsenite [As(III)] water was treated by Fenton oxidation-flocculation coupled process and single flocculation process respectively. The removal efficiency of arsenic(III) in water by Fenton oxidation-flocculation was higher than single flocculation. The flocculating effect of Fe^{2+} can act on arsenic removal, but the main effect was caused by Fenton reagent reaction directly.

Various influence factors of Fenton method on arsenic removal were studied. The results show that Fenton method for arsenic removal is superior to single flocculation. Arsenic removal is mainly attributed to Fenton reagent reaction directly. The optimum conditions of As(III) removal from water was pH 3, H_2O_2 10 mg/L, Fe^{2+}/H_2O_2 (n/n) 0.2, reaction time 10 min, As(III) removal reached to 95.17 %. And Fenton oxidation-flocculation method is used for drinking water treatment, the residual concentration of arsenic in water after treated group is lower than "drinking water health standards" (GB5749-2006) in the standard of 0.01 mg/L.

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