Treatment of high arsenic content wastewater by a combined physical–chemical process

Hong-Jie Wang^{a,*}, Wen-Xin Gong^b, Rui-Ping Liu^b, Hui-Juan Liu^b, Jiu-Hui Qu^b

^a College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, China

^b State Key Laboratory of Environmental Aquatic Chemistry, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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ABSTRACT

The performance of a novel combined process, consisting of pre-oxidation, co-precipitation, adsorption and coagulation was investigated for treatment of high arsenic content industrial wastewater. KMnO_4 was used to oxidize As(III) to As(V) firstly, meanwhile the total arsenic concentration reduced about 9%. Then lime and ferrous co-precipitation was performed and the arsenic concentration decreased dramatically from 423 mg/L to 6.8 mg/L. Subsequent ferric and manganese binary oxide (FMBO) adsorption and polyaluminum chloride (PACl) coagulation process as a final treatment removed over 99.88% of the residual arsenic. About 5000 m³ of industrial wastewater, with average arsenic concentration of 465 mg/L, was safely treated and disposed by a combined pilot-scale system. The average effluent concentration of the system was 0.008 mg/L which meets the discharge limit of 0.05 mg/L, and the total removal efficiency was 99.998%. The pilot-scale results indicated that the combined process would be advantageous and practical in treating of high arsenic content wastewater, especially in treating emergency accident of arsenic pollution.

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1. Introduction

Most environmental arsenic problems were the result of mobilization under natural conditions. However, effluents from industries such as mining, smelting and petroleum processes had high arsenic content [1–3]. Previous literatures had provided general description of the toxicity of arsenic and health hazards, such as diseases of skin, neurological, and cardiovascular system, as well as cancer of the skin, bladder, kidney, skin, and lung, so arsenic poisoning had been an environment concern worldwide [4,5].

Many different techniques, such as ion exchange, membrane, coagulation, lime softening, precipitation and adsorption, had been developed for arsenic elimination from water [4–6]. In recent years, more attention has been paid on adsorption process for arsenic removal and a variety of adsorbent materials, such as biological materials, mineral oxides, activated carbons, or polymer resins, were developed worldwide and adsorption process was considered to be one of the most promising technologies [6]. While most of the adsorption techniques were effective for As(V) removal, but failed in case of As(III). The reason was that As(III) existed as neutral species with low affinity with conventional reagent and was more mobile. Recently, Fe–Mn–mineral materials, such as ferric and

manganese binary metal oxide (FMBO), had been investigated for oxidation of As(III) and adsorption of As(V) simultaneously [7,8]. However, for the wastewater with high concentration of arsenic (>400 mg/L), any single treatment method would be inadequate to make the effluent consistent with the discharge limits (less than 0.05 mg/L).

Pre-oxidation of As(III) was usually used to improve arsenic removal [9,10]. Precipitation was recognized as a useful technology for the treatment of high concentration of As(V). As long as the residual arsenic concentration was reduced to a certain level, the adsorption process would be very suitable for further treatment. Thus, a novel pilot-scale combined process, consisting of KMnO_4 pre-oxidation, lime and ferrous co-precipitation, FMBO adsorption and PACl coagulation, was conducted in this study to safely treat and dispose the high arsenic concentration industrial wastewater.

The research was divided into two experimental phases. The first phase was laboratory studies including the optimization of pre-oxidation, co-precipitation, adsorption and coagulation, which was conducted using a six-paddle stirrer. The effects of dosage of oxidant, precipitant, adsorbent and coagulant and reaction time on arsenic removal were investigated in detail. Based on the batch experimental results, in the second phase a pilot-scale system was constructed and applied for the treatment of about 5000 m³ of industrial wastewater, with average arsenic concentration of 465 mg/L.

* Corresponding author. Tel.: +86 10 6284 9160; fax: +86 10 6284 9160.
E-mail address: whj.99@hotmail.com (H.-J. Wang).

2. Materials and methods

2.1. Materials

Potassium permanganate (KMnO_4 , 99%), calcium hypochlorite ($\text{Ca}(\text{ClO})_2$, 70%), lime (CaO , 90%), hydrated ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 95%), and PACI of commercial grade were utilized in the experiments. FMBO was freshly synthesized on-site by combination of the solution of KMnO_4 and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ stoichiometrically.

The arsenic wastewater was obtained from a sulfuric acid factory in central China. The total arsenic concentration was 450–480 mg/L and As (III) in wastewater was about 120–150 mg/L. The pH of the wastewater was as low as 2.31–2.62. The disposal limit of arsenic was 0.05 mg/L and pH was in the range of 6–9.

2.2. Batch experiments

To investigate the behaviors of pre-oxidation, co-precipitation, adsorption and coagulation, experiments were performed in a six-paddle stirrer with 1 L of beakers using conventional Jar-test apparatus (MY 3000-6, Qianjiang MeiYu Instruments Ltd., China).

Appropriate amount of KMnO_4 or $\text{Ca}(\text{ClO})_2$ was added into the 500 mL of arsenic wastewater. The mixture was continuously blended for 2 h at 150 rpm at room temperature ($25 \pm 0.5^\circ\text{C}$). At the end of the pre-oxidation, lime was added and the slurries were kept mixing for 1 h. After settlement for another hour, different dosages of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added into the supernatant and kept reacting with fast mixing (200 rpm) for 10 s, slow mixing for 2 min and settlement for 30 min. Then FMBO was added to finish the adsorption process with blending speed of 150 rpm for 30 min and the suspension was settled for hours. Finally, different amounts of PACI were introduced into the system to perform coagulation. The coagulation procedure consisted of a 2 min rapid mix (200 rpm), 15 min slow mix (50 rpm), and settlement for 30–120 min.

The total arsenic and As(III) concentration were determined by atomic fluorescence spectrometry (AF 610B, Ruili Instrument Ltd., Beijing, China) [11]. Mn(II) concentration was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 2000, PerkinElmer Co., USA). Particle size of FMBO was measured at different settling time (Malvern MasterSizer Series 2000, Malvern Instruments, UK). An Orion pH meter (Model 720 A, Thermo Orion, USA) was used to measure pH.

2.3. Pilot scale system description

The pilot scale treatment procedure for high arsenic wastewater was as follows. Stock solution of 5% KMnO_4 was first added to the wastewater with dosage of 350 mg/L. Four hours later, lime slurry (CaO , 10%) was directly added into the wastewater. After reacted and settled for 15 h, the supernatant was pumped to another tank and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (10%) solution was added and settled for another 15 h. Then FMBO (200 mg/L) was introduced into the system followed by gravitational settlement for 15 h. Finally PACI (200 mg/L) was sprayed and settled till the arsenic concentration was consisted with the discharge limit. The supernatant was discharged and the method for safe treatment of solid waste, such as solidification, was investigated also (results was not shown in this paper).

3. Results and discussion

3.1. Pre-oxidation by permanganate

In the preliminary experiments, KMnO_4 and $\text{Ca}(\text{ClO})_2$ were used as pre-oxidants to oxidize As (III) into As(V). Results showed that KMnO_4 had higher efficiency for As(III) oxidation than that of

Fig. 1. Variation of total As, As(III) and Mn(II) in pre-oxidation of wastewater.

$\text{Ca}(\text{ClO})_2$. So KMnO_4 was chosen as the pre-oxidant. The effect of KMnO_4 concentration on As(III) oxidation was investigated and the variation of total As, As(III) and Mn(II) were shown in Fig. 1. With the addition of KMnO_4 , the concentration of As(III) was decreased dramatically till As(III) was turned into As(V) completely at KMnO_4 dosage of 350 mg/L, and the total arsenic concentration was decreased about 9%.

The KMnO_4 was reduced to Mn(II) during the oxidation of As(III). Fig. 1 showed that the Mn(II) concentration first increased with the increasing KMnO_4 dosage and reached the maximum at the dosage of 200 mg/L and then decreased with further introducing of KMnO_4 . The possible reactions of KMnO_4 and As(III) were shown as Eqs (1)–(3).

Eqs. (1) and (2) showed that KMnO_4 could be reduced to Mn(II) or MnO_2 in acidic solution [10]. And the reaction between KMnO_4 and Mn(II), shown in Eq. (3), could also lead to the formation of MnO_2 . The newly formed MnO_2 could adsorb arsenic, so the total As concentration decreased slightly.

3.2. Lime-ferrous co-precipitation

After pre-oxidation, lime was adopted as a precipitant for its formation of a hardly soluble calcium-arsenic compound [3,12,13]. Results of arsenic removal by lime precipitation were shown in Fig. 2. It can be seen that arsenic concentration decreased with the increasing dosage of lime. With 1200 mg/L of lime, arsenic concentration was reduced to about 50 mg/L and the removal efficiency achieved 90%.

As shown in Fig. 2, the variation of arsenic concentration could be classified into three stages. In the first stage, lime neutralized the acidic substances in wastewater and little arsenic was removed. With the dosage of lime increased from 0 to 390 mg/L, the arsenic removal efficiency was achieved at 12%, but pH increased dramatically from 2.43 to 9.93. In the second stage, the arsenic removal efficiency significantly increased from 12% to 71% with the addition of lime from 390 mg/L to 862 mg/L, while pH increased to 12.58. With further addition of lime, both of pH and the arsenic removal efficiency increased slightly. In the second stage, most of the arsenic was removed by formation of low solubility calcium arsenates, such as $\text{Ca}_3(\text{AsO}_4)_2$. While in the third stage, with the Ca/As ratios increased more complicated precipitations between

Fig. 2. Arsenic removal by lime precipitation.

arsenic and calcium formed [14,15]. Although the lime precipitation was effective, the solubility of $\text{Ca}_3(\text{AsO}_4)_2$ was 130 mg/L, the calculated arsenic concentration was as high as 48 mg/L. In above experiment the arsenic concentration of the effluent was still as high as 50 mg/L. To reduce the arsenic concentration even further, by formation of other insoluble compounds, the addition of iron salts was investigated in this study.

Fig. 3 showed the arsenic removal efficiency by ferrous ion co-precipitation. With the addition of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and increase of settle time, the arsenic concentration of supernatant decreased. With the addition of 180 mg/L of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, the arsenic concentration reached 7.98 mg/L, 3.75 mg/L and 0.21 mg/L when the suspension was settled for 2 h, 5 h and 12 h, respectively. There was no significant increase in arsenic removal efficiency with excessive addition of ferrous ion, so the optimal dose of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was 180 mg/L.

3.3. Adsorption by FMBO combined with coagulation

After pre-oxidation and co-precipitation, the arsenic concentration was reduced to less than 8 mg/L. Then adsorption was more suitable for further treatment. FMBO, the novel adsorbent, was online synthesized and added into the wastewater. The results were shown in Fig. 4.

With the addition of FMBO from 20 mg/L to 300 mg/L, the residual arsenic concentration decreased continually. And the settle time could also affect the results. The arsenic removal efficiency increased quickly till the dose of FMBO reached 150 mg/L and the residual arsenic concentration was reduced to 0.23 mg/L, 0.19 mg/L after settled for 2 h and 12 h, respectively. Then the suspension was

Fig. 3. Variation of arsenic concentration in ferric ion co-precipitation.

Fig. 4. Variation of arsenic concentration with dose of FMBO.

filtered by 0.45 μm Teflon film, the residual arsenic concentration of the filtrate was just as low as 0.08 mg/L. Further increase of FMBO just induced slight decrease of arsenic concentration and the residual arsenic concentration of the filtrate maintained at 0.08 mg/L.

With the addition of 150 mg/L of FMBO, the residual arsenic concentration was detected before and after filtered by 0.45 μm Teflon film according to the settle time. And the results were shown in Fig. 5. It showed that there was no significant variation of the residual arsenic concentration after the suspension settled for over 30 min and filtered, while the total arsenic concentration decreased continually with the settle time. It was revealed that the adsorption process completed quickly but the separation process was very slow due to the colloid character of FMBO. Then the particle size of FMBO, which would influence the arsenic removal efficiency, was investigated further.

The mean diameter of newly formed FMBO was about 112 μm , and after settled for 2 h the mean diameter of FMBO in supernatant was reduced to 19.5 μm . Because of the strong affinity of the colloid FMBO with arsenic, the residual arsenic concentration remained much higher than that of the filtrate. The smaller was the particle size, the slower was the separation process. So in this study, PACI was used as a coagulant for the colloid FMBO particles separation. Results in Fig. 6 showed that with the addition of PACI the residual arsenic concentration decreased dramatically. With 100 mg/L of PACI and 2 h settlement, the arsenic concentration reduced to less than 0.05 mg/L which was in accordance with the disposal limits. And when PACI was increased to 150 mg/L the arsenic concentration could also reduce to less than 0.05 mg/L just after 30 min

Fig. 5. Effects of settling time on arsenic removal by FMBO (dosage: 150 mg/L).

Fig. 6. Further removal of arsenic by flocculation of PACl.

settlement. So the dose of PACl and the settle time could adjust flexibly according to the real situation.

3.4. Pilot scale treatment and economic evaluation of the combined process

Batch test showed that the combined process, consisting of KMnO_4 pre-oxidation, lime and ferrous co-precipitation, FMBO adsorption and PACl coagulation and flocculation, could effectively reduce the arsenic concentration from 462 mg/L to less than 0.05 mg/L. The pilot scale treatment for the high arsenic content wastewater was conducted with the combined process. The main parameters of the system, which based on the laboratory results but had a little change to adapt to the practical application, were as follows: KMnO_4 , 350 mg/L, hydraulic retention time (HRT), 4 h; Lime, 1 g/L, HRT, 15 h; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 200 mg/L, HRT, 15 h; FMBO, 200 mg/L, HRT, 15 h; PACl, 200 mg/L, HRT, 8 h. The pilot scale treatment results of the combined process were shown in Table 1.

Chemical pre-oxidation and co-precipitation process proved to be effective in the removal of arsenic (removal efficiency higher than 98%) and subsequent adsorption and coagulation process as a final treatment efficiently removed the residual arsenic. The average total removal efficiency of arsenic in the pilot-scale combined technology was 99.998% which was giving an average effluent concentration of 0.008 mg/L, consistent with the disposal limit (<0.05 mg/L).

Table 2 showed the evaluation of economic performance of the combined process. Due to the high price of the KMnO_4 , the cost of pre-oxidation took over 60% of the total cost. Although most of the arsenic was removed by lime and ferrous co-precipitation process, the cost of the lime and ferrous ion co-precipitation took only 2.7% of the total cost. It was seemed that FMBO adsorption process was a little expensive. But the FMBO adsorption and PACl coagula-

Table 1
Pilot scale treatment of high arsenic wastewater.

Process	As concentration (mg/L)		Removal efficiency per process (%)
	Range	Average	
Raw water	450–480	465	
Pre-oxidation	426–430	423	9.03
Lime co-precipitation	18–26	24	94.33
Fe^{2+} co-precipitation	6–7.6	6.8	71.67
FMBO+PACl	0.002–0.013	0.008	99.88
Total removal efficiency (%)			99.998

Table 2

Economic evaluation of pilot scale combined process.

Chemical reagent and dosages	Price(¥/kg)	Process Cost(¥/m ³)
KMnO_4 , 0.30 kg/m ³	12.00	3.60
Lime, 1 kg/m ³	0.10	0.10
$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.2 kg/m ³	0.30	0.06
FMBO, 0.2 kg/m ³	10.00	2.00
PACl, 0.2 kg/m ³	1.00	0.20
Total cost		5.96

tion and flocculation process could effectively reduce the arsenic concentration from several mg/L to less than 0.05 mg/L. It was indicated that the combined system was very practical in treating emergency.

4. Conclusions

High arsenic acidic wastewater with average concentration of 465 mg/L was effectively and safe treated and disposed by the combined process of pre-oxidation, lime and ferrous precipitation, FMBO adsorption and PACl flocculation. Pre-oxidation was necessary because of 120–150 mg/L of As(III) in the acidic wastewater. KMnO_4 could completely oxidize As(III) and the byproduct of MnO_2 could also adsorb arsenic. The removal efficiency of pre-oxidation was about 9%. In lime and ferrous co-precipitation process a series of hardly soluble compounds formed and settled. The arsenic concentration was reduced from 423 mg/L to about 6.8 mg/L. FMBO was used to further remove arsenic by adsorption and the residual arsenic could be nearly completely adsorbed by FMBO. But it was hard for FMBO to settle down thoroughly due to its colloid characters and the PACl coagulation was necessary in practical. About 5000 m³ of industrial wastewater, with average arsenic concentration of 465 mg/L, was effectively, economically and safe treated and disposed. The arsenic concentration of the final effluent was less than 0.013 mg/L. The current results and the economic evaluation suggested that the combined process could be advantageous and feasible for the treatment of high concentration of arsenic wastewater.

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