



Arsenic removal from a high-arsenic wastewater using *in situ* formed Fe–Mn binary oxide combined with coagulation by poly-aluminum chloride

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ABSTRACT

In this study, *in situ* formed Fe–Mn binary oxide (FMBO) was applied to treat a practical high-arsenic wastewater (5.81 mg/L). FMBO exhibited a remarkable removal capacity towards both As(III) and As(V), achieving a removal efficiency over 99.5%. However, the FMBO–As particles could not be sufficiently separated by gravitational sedimentation due to their low sizes and negative charges, as being indicated from laser particle size and zeta-potential analysis. Thus, poly-aluminum chloride (PACl) was introduced as a coagulant to facilitate the solid–liquid separation, and it remarkably improved As removal efficiencies. Results of scanning electron microscope (SEM) revealed that PACl contributed to the formation of precipitates with larger sizes and compact surfaces, which was favorable to sedimentation. Moreover, residual soluble As was removed by PACl hydroxides. The optimum dosages of FMBO and PACl were determined to be 60 mg/L and 80 mg/L, respectively. Additionally, the secondary pollution was minimized in FMBO–PACl process. Based on these bench-scale results, a full-scale treatment process was proposed to successfully treat 40,000 m³ of high-arsenic wastewater in a municipal wastewater treatment plant (MWWTP). The average As concentration in the effluent was about 0.015 mg/L. FMBO–PACl process showed the advantages of high effectiveness, low cost, safety, and ease for operation.

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1. Introduction

Arsenic (As) is classified as one of the most toxic and carcinogenic chemical elements [1]. In recent years, the anthropogenic activities, such as mining and smelting, increased the extent of high-arsenic wastewater pollution in China, which greatly threaten the safety of drinking water and water bodies. To minimize adverse impacts on environments, it is of crucial importance to develop feasible and economical technologies to treat high-arsenic wastewater.

The high As concentrations and complex constituents inhibit the application of some technologies available in drinking water treatment for As removal from high-arsenic wastewater. Generally, the enhanced coagulation by ferric (Fe) or aluminum (Al) coagulants has been identified as the least-cost option to treat high-arsenic wastewater [2], and the removal of As is ascribed to As adsorbing onto Fe or Al hydroxides and to the solid–liquid separation of precipitates with adsorbed As by subsequent sedimentation and filtration.

Recently, some researchers reported that the modified adsorption and separation methods could achieve residual As

concentrations of lower than 0.05 mg/L in treatment of high-arsenic wastewater [3–8]. Ferrate [Fe(VI)] may be employed as both an oxidant and a coagulant for As removal, and Fe(VI) at 2.0 mg/L with membrane filtration could lower As concentration from 0.517 to below 0.05 mg/L [3]. The coagulation by FeCl₃, with aiding coagulant of coarse calcite, achieves residual As concentration as low as 0.013 mg/L after membrane filtration [4]. Fe(II)–KMnO₄ process has also been proposed for arsenite (As(III)) removal [5,6]. Additionally, the electro-coagulation also exhibits good capability to treat synthetic acid high-arsenic wastewater, with residual As concentrations being near to 0.01 mg/L [8]. The coagulation by FeCl₃, using bio-oxidation with activated sludge as pretreatment, achieves residual As concentrations of lower than 0.005 mg/L in the effluent [7].

However, there are still some defects inhibiting the application of these methods in practice. First, the efficient removal of As(III) could not be realized without bio-oxidation or adding oxidants such as KMnO₄ and Fe(VI) [5–7]. Second, the membrane filtration as complementary separation was required due to the difficulty in the sedimentation of As-containing particles and Fe hydroxides precipitates [4–6,8]. Therefore, it is desired to optimize the adsorption–separation process for the treatment of high-arsenic wastewater.

Our previous study demonstrated considerable capability of Fe–Mn binary oxide (FMBO) for both As(III) oxidation and arsenate

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Table 1
Chemical compositions of the high-arsenic wastewater sample.

Constituent	As(tot)	As(III)	Fe	Mn	Ca	Cl ⁻	SO ₄ ²⁻	PO ₄ ³⁻	TOC	COD	SS
Concentrations (mg/L)	5.81	3.05	0.01	0.006	8.15	111.5	80.75	1.17	9.46	15.6	214.2

(As(V)) adsorption [9]. As(III) can be oxidized by the manganese oxide within FMBO, and more new sites were formed on surfaces of FMBO, which were available for As(V) adsorption [10]. The impregnated-FMBO diatomite, which could be regenerated easily and economically, was developed for the removal of As from drinking water [11]. In addition, *in situ* formed FMBO was used as an adsorbent for As removal in the integrated process of adsorption, sand filtration, and ultra-filtration [12].

This study investigated the feasibility and capability of *in situ* formed FMBO combined with coagulation by PACI to treat a practical high-arsenic wastewater. The different roles of FMBO and PACI involved in this process were studied, and the optimized parameters were proposed through bench scale studies. Furthermore, the treatment of a practical high-arsenic wastewater by this process was investigated in a full-scale municipal wastewater treatment plant (MWWTP).

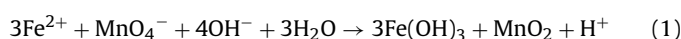
2. Materials and methods

2.1. Characteristics of high-arsenic wastewater

The high-arsenic wastewater (pH=8.67, Eh = -127.3 mV) was taken from the sedimentation tank of an As-polluted MWWTP, and used directly for jar tests. Table 1 shows the main chemical compositions of this high-arsenic wastewater.

2.2. Preparation of *in situ* formed FMBO and properties of PACI

The preparing procedures of *in situ* formed FMBO were detailed as follows: First, the mixed solution of KMnO₄ (0.125 mol/L) and NaOH (0.5 mol/L) was prepared by dissolving 1.975 g KMnO₄ and 2 g NaOH together in 100 ml deionized water. And FeSO₄ solution (0.375 mol/L) was prepared by dissolving 10.425 g FeSO₄·7H₂O in 100 ml deionized water. Then, the two solutions were mixed sufficiently with equal volumes. The solution volumes were in accordance with the needed amount of FMBO, which has a Fe/Mn molar ratio of 3:1. The reaction was as follows in Eq. (1):



The species Fe(III) hydroxide in this system is dependent on solution pH, and the FMBO dosages were therefore expressed as mg/L of Fe and Mn rather than the iron and manganese oxides. Furthermore, FMBO was respectively prepared for each jar of test wastewater to ensure the accurate quantifications.

For the PACI used in this study, the OH⁻/Al ratio (γ) was 1.4, and the species distribution of this coagulant was classified as: 40% of monomeric species (Al_a), 10% of medium polymer species (Al_b), and 50% of species of sol or gel (Al_c). In addition, the ratio of active species in the stock solution was above 10% as Al₂O₃. PACI solutions were diluted with deionized water to get 10% dilution for use.

All the above mentioned reagents were industrial-grade and produced by a local company (Beijing Wanshui Water Purification Agent Co., China).

2.3. Bench-scale experiments

Standard jar tests were conducted on a program-controlled jar test apparatus (MY3000-6k, Meiyu Jar Test Instruments, China) at a room temperature of (25 ± 0.5 °C). To study the As removal efficien-

cies in individual FMBO or FMBO–PACI process, 300 mL wastewater was transferred into a 500 mL beaker, and the mixing procedures included rapid mixing for 6 min (200 rpm), and slow mixing for 20 min (50 rpm). *in situ* formed FMBO (dosages ranging from 10 to 60 mg/L) was dosed 5 seconds after the start of the rapid mixing, and PACI (dosages ranging from 20 to 100 mg/L) was dosed after 5 min of the rapid mixing (in individual FMBO process, the addition of PACI was cancelled). After the slow mixing, there was a 30 min settling. Finally, samples were collected from 2 cm below the surfaces. Prior to analysis, the aqueous samples were acidified with HNO₃ in an amount of 1%, and stored in acid-washed glassware vessels. Each jar tests were preceded in duplicate, and the average values were reported in this paper.

2.4. Analytical methods

In order to characterize the suspended As and soluble As species, two operational defined fractions were used, namely total As and filterable As based on physical separation through a 0.45 μm membrane. Filterable As included not only soluble As but also colloidal particles of amorphous hydroxides capable of passing through a 0.45 μm membrane. But for total As, besides filterable As, the suspended As adsorbed by FMBO mini-particles was also included, which could be removed by a 0.45 μm membrane. One set of samples were acidified to dissolve suspended precipitates for total As analyzing after they were taken from beakers, and the other set of samples were immediately filtered through a 0.45 μm membrane for filterable As analyzing. Fe, Mn, Al concentrations were determined using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) without membrane filtration (SCIEX Perkin Elmer Elan mode 5000).

2.5. Characterization of FMBO particles and precipitates

A laser particle size analyzer 2000 (Malvern, UK) was used to evaluate the size distributions of *in situ* formed FMBO particles. As the jar tests were being conducted, the suspension was monitored by drawing water through sample cell of the particle size analyzer and back to the jar by a peristaltic pump (LEAD-2, Longer Precision Pump, China) with a 5 mm internal diameter tube at a flow rate of 25 mL/min. Samples were withdrawn from the same position in the jar, where was located between the impeller and the surface of the solution.

The zeta-potential of samples were directly determined with a Zetasizer 3000HSA (Malvern Instruments Ltd., UK) without pre-treatment. The morphology and surface elemental composition of the precipitates were analyzed by a scanning electron microscope (SEM) with an EDAX KEVEX level 4 (Hitachi S-3500N). The samples were collected, washed with deionized water and then freeze-dried before analysis.

3. Results and discussion

3.1. As removal by *in situ* formed FMBO

At the beginning, *in situ* formed FMBO at 3 different dosages were used with membrane filtration for As removal under different pH conditions. Fig. 1 showed the beneficial effect of increased FMBO dosage on the removal of both As(III) and As(tot). At FMBO

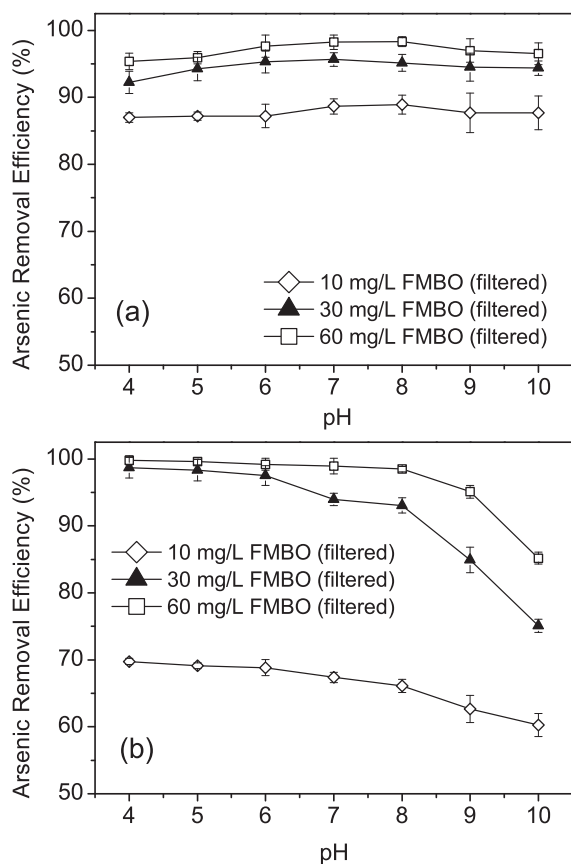


Fig. 1. The removal efficiencies of (a) As(III), and (b) As(tot) using different dosages of FMBO at various pH conditions with membrane filtration.

dosages of 10 mg/L, 30 mg/L, and 60 mg/L, the average removal efficiency of As(III) was 87.7%, 94.5%, and 97.0%, and the average removal efficiency of As(tot) was 67.4%, 93.9%, and 98.9%. Additionally, the As(III) removal efficiency was not obviously dependent on pH values. Driehaus et al. also reported minor influence of pH on the oxidative activity of MnO_2 towards As(III) in pH ranges from 5 to 10 [13]. Contrastively, the removal of filterable As(tot) was more severely affected by pH than that of As(III). With pH increasing from 4 to 10, the removal efficiency of filterable As(tot) decreased from 98.7% to 75.1% at 30 mg/L of FMBO and from 99.8% to 85.2% at 60 mg/L of FMBO. However, at 60 mg/L of FMBO, the removal efficiency of As(tot) was still as high as 95.1% at pH 9. In the treatment of this high-arsenic wastewater with a pH of 8.67, it was indicated that the pH adjustment could be avoided to minimize costs and simplify operation.

The *in situ* formed FMBO exhibited an excellent activity to remove both As(III) and As(V) in this high-arsenic wastewater. As for its engineering application, the key point to be resolved should be the solid–liquid separation of the FMBO–As particles in the wastewater. So it was evaluated that whether gravitational sedimentation could be used as the separation method.

Fig. 2 showed the size distributions of FMBO–As particles in this high-arsenic wastewater at pH 6 and 9. The sizes of the FMBO–As particles were observed to range from 0 to 250 μm . Those with diameters of below 10 μm contributed respectively to about 5.0% and 7.6% at pH 6 and pH 9, implying that at least the process of microfiltration was required to achieve promising removal of these particles [14]. It is obvious that the separation of the tiny FMBO–As particles could not be realized by gravitational sedimentation alone.

But what led to the difficulty in the aggregation and settling by gravity for FMBO–As particles? Results of zeta potential analy-

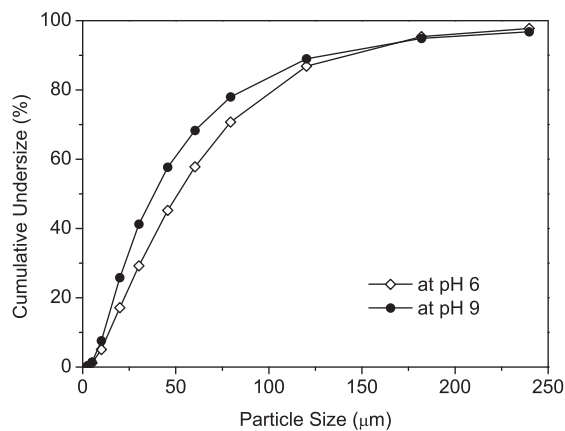


Fig. 2. Size distributions of FMBO–As particles in the high-arsenic wastewater at pH 6 and pH 9.

sis under different pH conditions indicated that FMBO–As particles were consistently negatively charged in the pH range of 4–10, and that zeta potential decreased with elevated pH (Fig. 3). The zero point charge (pH_{ZPC}) of FMBO–As particles in high-arsenic wastewater was less than pH 4.0, which was much lower than that of pure FMBO particles (6.0) in deionized water [9]. So it is clear that the surface charge characteristics of FMBO particles changed remarkably due to the reactions with As and other co-existent anions in this high-arsenic wastewater.

The electrostatic repulsive forces between negatively charged FMBO–As particles inhibited their aggregation and sedimentation. It is essential to find out an optimal separation method for the removal of tiny FMBO–As particles. Coagulants such as polyaluminum chloride (PACl) exhibit effects of charge neutralization, and might be employed to improve the separation of tiny FMBO–As particles and colloids.

3.2. Effectiveness of PACl to facilitate the removal of As by FMBO

Fig. 4a indicated the changes of As removal efficiencies as a function of various PACl dosages in FMBO–PACl process (without membrane filtration). FMBO alone at the dosages of 30 and 60 mg/L showed no distinctive difference in the capability for As removal, with the removal efficiencies of 70.2% and 71.8%, respectively. With the dosages of PACl increasing from 0 to 100 mg/L, the removal efficiency of As increased from 70.2% to 97.1% at FMBO = 30 mg/L, and from 71.3% to 98.7% at FMBO = 60 mg/L. PACl exhibited positive effect more obviously on As removal at FMBO = 30 mg/L than that

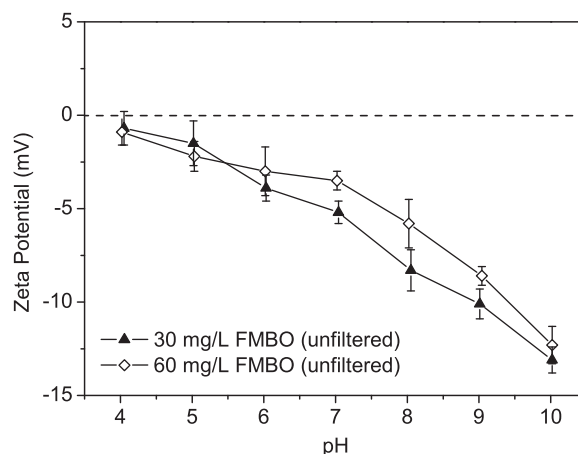


Fig. 3. Zeta potentials of the FMBO–As particles under different pH conditions in the high-arsenic wastewater.

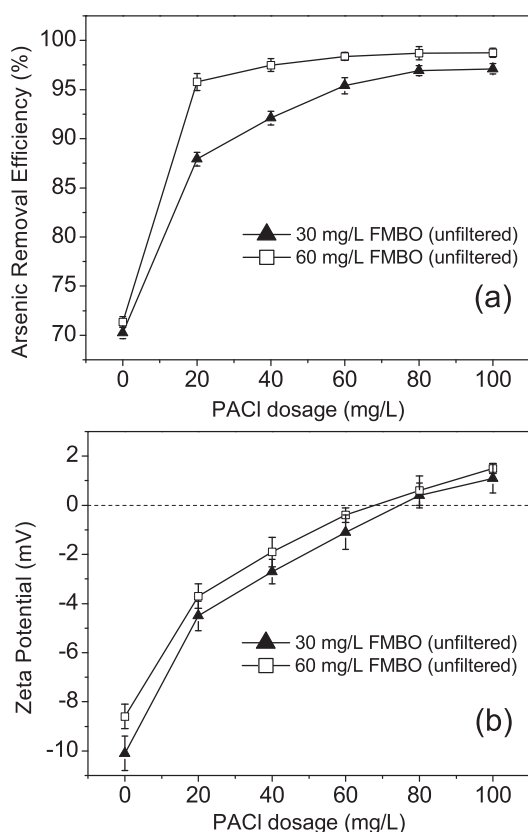


Fig. 4. Total As removal from high-arsenic wastewater and zeta potentials of the FMBO-As particles as a function of various dosages of PACI addition in FMBO-PACI process (experimental conditions: FMBO dosage = 30 mg/L or 60 mg/L, pH = 9).

at FMBO = 60 mg/L, and the gaps of the As removal efficiencies between these two dosages of FMBO decreased with elevated PACI dosages in FMBO-PACI process. It is inferred that PACI contributed not only to the removal of suspended tinny FMBO-As particles, but also to capturing the residual soluble As that had not been removed by FMBO.

Fig. 4b showed that PACI at different dosages obviously increased the zeta potentials at both FMBO dosages of 30 and 60 mg/L due to its charge neutralization effect. The PACI dosage of 80 mg/L was promisingly enough to destabilize these colloids. Though no significant increase of As removal efficiencies (about 0.4%) was observed at PACI dosages of higher than 60 mg/L when the FMBO dosage was 60 mg/L (Fig. 4a), the PACI dosage of 80 mg/L was adopted in treatment process to ensure the residual As (tot) of less than 0.05 mg/L.

Then, to further illustrate the roles that PACI played in FMBO-PACI process, the As removal efficiencies were compared between two conditions in pH range of 4–10: (1) samples taken and filtered through a 0.45 μm membrane with individual FMBO (i.e., FMBO with filtration) and (2) samples taken after settling for 30 min with FMBO + PACI (without filtration).

Fig. 5 illustrated that at the same pH conditions, the As removal efficiencies were in the sequences of: individual FMBO with filtration < FMBO + PACI. In the former case, the As removal efficiencies decreased obviously with the pH increasing. Comparatively, in the presence of PACI, the As removal efficiency was stable and nearly 100% in the pH range of 4–9, and declined at pH 10. The decrease of As removal at pH 10 in these two cases may be ascribed to the higher repulsive forces between anionic As species and the FMBO-As particles at elevated pH.

It is suggested that tinny FMBO-As particles could be removed by filtration with a 0.45 μm membrane, but the FMBO-As colloids

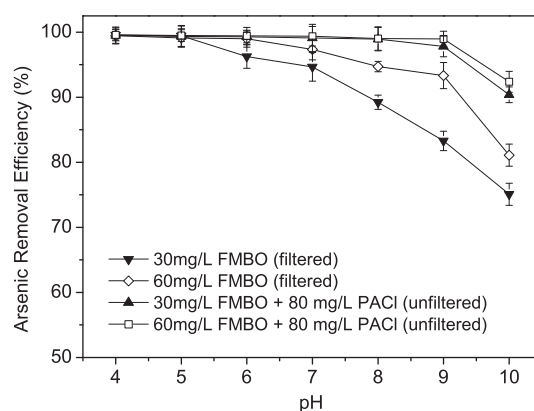


Fig. 5. Comparison of membrane filtration and PACI in the enhancement of As removal by FMBO at different pH conditions (experimental conditions: FMBO dosage = 30 mg/L or 60 mg/L, PACI dosage = 80 mg/L).

and residual soluble As still remained in the filtrates. In contrast, PACI not only accelerated the sedimentation of the FMBO-As colloids and particles, but also captured the residual soluble As (mainly As(V) because of the oxidation by FMBO) in the solution [15]. It is clear that PACI showed better beneficial effect on As removal by FMBO than membrane filtration, especially at neutral and high pH conditions (pH > 6). It may be explained that more residual soluble As was available for PACI to capture under high pH conditions, and membrane filtration could not remove residual soluble As anymore in these cases.

SEM analysis also showed positive effects of PACI on the aggregation of FMBO-As particles (Fig. 6). The FMBO-As particles had rough surfaces with porous structures (Fig. 6a and b), which was consistent with our previous research [9]. The addition of PACI increased particle sizes and contributed to smoother surface of the precipitates (Fig. 6c and d). The flocs with larger particle diameters were more beneficial for the solid-liquid separation than tinny FMBO-As particles.

EDAX analysis revealed that the molar ratio of Fe and Mn ($R_{\text{Fe:Mn}}$) was close to 3:1 on the surface of FMBO-As particles. It was indicated that Fe and Mn were evenly distributed on the surface, as being consistent with our previous research [9]. In the presence of PACI, the value of $R_{\text{Fe:Mn:Al}}$ was close to 4:1:5, and the percentage of Al on the surface was as high as 52%. So the Fe/Mn/Al hydroxides were relatively Al-enriched on the surfaces, suggesting that Al oxides dominate in determining surface characteristics of the mixed metal oxides [16].

The above results showed that the surface characteristics of FMBO-As particles were changed remarkably due to the addition of PACI, and the solid-liquid separation was consequently improved in the treatment of high-arsenic wastewater by FMBO-PACI process. Moreover, PACI contributed to the removal of both soluble As and FMBO-As colloids through combined effects such as adsorption, charge neutralization, and sweep flocculation, showing more positive effects on As removal than membrane filtration.

The concentrations of residual Fe, Mn, and Al were also investigated in FMBO-PACI process at different pH conditions. Fig. 7 showed that residual Fe concentrations in the whole pH range from 4 to 10 were consistently below the level of 5 mg/L, as being required by the wastewater discharge standard. Comparatively, the concentrations of Al and Mn were higher than 10 mg/L at pH 4 and 5, exceeding the discharge standards (Al < 5 mg/L; Mn < 2 mg/L), and then decreased to near 0 mg/L with elevated pH. Considering that the pH of this high-arsenic wastewater was 8.67, the residual concentrations of Fe, Mn, and Al would promisingly comply with the corresponding discharge standards. Additionally, the secondary pollution could be minimized in FMBO-PACI process on

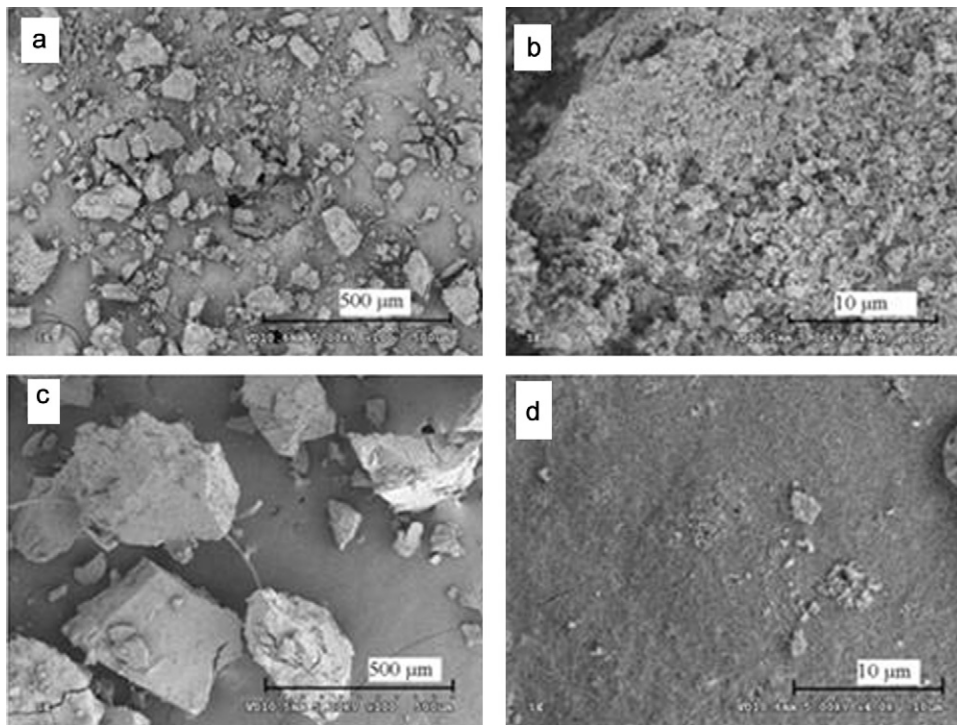


Fig. 6. SEM analysis for the precipitates collected in enhanced coagulation for As removal at pH=9 (a) FMBO dosage=60 mg/L, magnification factor=100, (b) FMBO dosage=60 mg/L, magnification factor=4000, (c) FMBO dosage=60 mg/L, PACI dosage=80 mg/L, magnification factor=100 and (d) FMBO dosage=60 mg/L, PACI dosage=80 mg/L, magnification factor=4000.

the premise that the treated wastewater complied with the pH discharge standard (in the pH range of 6–9).

3.3. Full-scale engineering application in a municipal wastewater plant

The encouraging results from these bench-scale tests led to the approval and establishment of the full-scale treatment process for a practical high-arsenic wastewater in a MWWTP in China, which was polluted by illegal discharge of industrial wastewater. In this MWWTP the oxidation ditch process was used for municipal wastewater treatment, which was comprised of two parallel treatment systems with one oxidation ditch (6000 m³) and one sedimentation tank (4000 m³).

After this illegal discharge, this MWWTP had to cease regular operation because the inflow pipe networks, the horizontal-flow

grit, oxidation ditches, and sedimentation tanks were all filled with this high-arsenic wastewater. The parameters to be employed in full-scale treatment of this high-arsenic wastewater were determined through former bench scale tests. Based on the above studies, the strategy for the full-scale treatment of this high-arsenic wastewater was proposed as follows:

First, the high-arsenic wastewater in all units was discharged to a ditch nearby this MWWTP for temporary storage. The empty ditches and tanks were well cleaned to be used as the treatment facilities after the existing sludge was pumped to the condensed tank for subsequent treatment. Then, the high-arsenic wastewater was pumped to the grit chamber as the influent at the flow rate of 500 m³/h, and this corresponded to the hydraulic retention time (HRT) of 12 h and 8 h in the oxidation ditch and the sedimentation tank, respectively. The solutions of FeSO₄ and KMnO₄ were simultaneously piped into the influent at the dosage of FMBO = 60 kg/m³, and were then well mixed in a static-mixer. The aeration brushes at the external area of the oxidation ditch were also turned on to enhance the interactions between FMBO and As anions.

After that, PACI at 80 kg/m³ were dosed in the effluent of oxidation ditches at the water supply well, where a mechanic mixer was installed for sufficient mixing. Afterwards the coagulation and sedimentation was completed in the sedimentation tank (clarifier), and the supernatant water flowed out through the overflow weirs. Finally, the treated wastewater was discharged outside to a river nearby through the chlorination tank.

Fig. 8 showed the As concentrations of the effluents from the oxidation ditch and sedimentation tank during the full scale treatment of this wastewater, with average values of 0.118 mg/L and 0.015 mg/L, respectively. The residual As concentrations were consistently below the required value of 0.05 mg/L, and the secondary pollution such as Fe, Mn, and Al were also minimized. Fig. 8 indicated effectiveness of FMBO–PACI process in the treatment of this wastewater. Moreover, in comparing to other processes such as coagulation combined with membrane filtration, the membrane

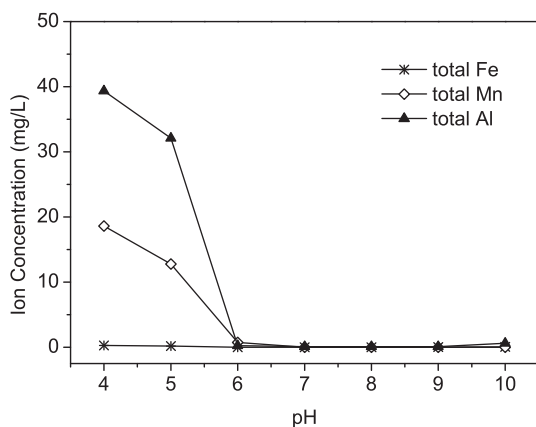


Fig. 7. Residual concentrations of Fe, Mn and Al in the solution after the coagulation with PACI (experimental conditions: FMBO dosage=60 mg/L, PACI dosage=80 mg/L).

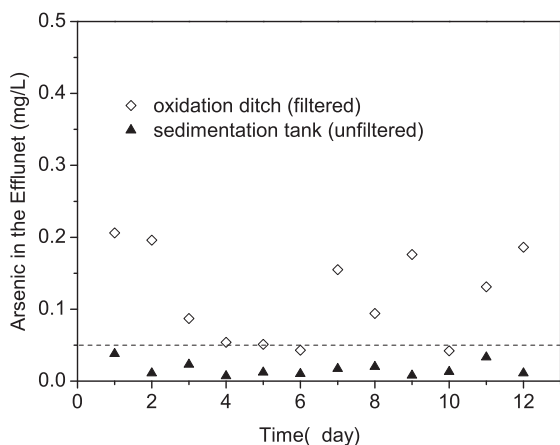


Fig. 8. Residual concentrations of As in the effluent of the oxidation ditch (filtered) and the sedimentation tank (unfiltered).

filtration facility was avoided to save the cost of investment and operation. Therefore, FMBO–PACl process was economical and operative in the treatment of this wastewater.

4. Conclusions

The *in situ* formed FMBO could efficiently remove As(III) and As(V) in this high-arsenic wastewater, and PACl considerably enhanced the removal efficiency of As through several effects such as adsorption, destabilization, and facilitating the formation of particles with larger sizes. The full scale practice demonstrated the feasibility, economical efficiency, and simplicity in operation of FMBO–PACl process for the treatment of high-arsenic wastewater. In addition, the secondary pollution problems, such as Fe, Mn, and Al, were also avoided. FMBO–PACl process may be one of the attractive methods for the treatment of high-arsenic wastewater in practice.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2010.10.003.

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