



# Phosphorus removal performance of acid mine drainage from wastewater

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## ABSTRACT

Acid mine drainage (AMD) in Yunfu iron sulfide mine contain  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$  up to 8000, 1700 and 1200 mg/L, respectively. Phosphorus removal from synthetic wastewater with 10 mg/L of total phosphorus (TP) concentration and second municipal effluent with 3.5–4.0 mg/L of TP concentration were conducted with the AMD by jar tests. Dosage of the AMD and initial pH of water are the two most important parameters affecting the performance of phosphorus removal of the AMD. The optimal phosphorus removal efficiency and residual iron ions (TFe) concentration are 97.0% and 3.0 mg/L, respectively, at 1.61 Fe/P molar ratio and pH 8.03 for synthetic wastewater, and 92.1% and 0.32 mg/L, respectively, for second municipal effluent at 1.41 Fe/P molar ratio and pH 7.3. Resultant heavy metal concentration in effluents and precipitate was very low, and the risk of resultant heavy metal contamination was very small. The phosphorus removal performance of the AMD was much similar to that of ferric sulfate (FS) and polyferric sulfate (PFS), and better than that of  $\text{FeSO}_4$ . And residual TFe concentration in treated water arising from utilization of the AMD was similar to that of  $\text{FeSO}_4$ , and higher than that of FS and PFS. The AMD could be used as coagulant for phosphorus removal from wastewater directly due to the presence of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Al}^{3+}$  largely.

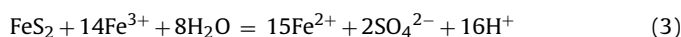
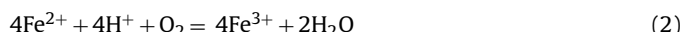
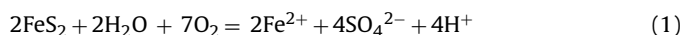
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## 1. Introduction

Acid mine drainage (AMD) is formed when sulfide minerals such as pyrite are exposed to oxygen and water. Naturally occurring bacteria such as *Acidithiobacillus ferrooxidans* can accelerate AMD production greatly [1]. With high acidity and concentrations of heavy metal ions such as As, Cd, Cu, Hg and Pb, etc. [2], AMD is toxic to aquatic organisms, damages ecosystem of receiving rivers and lakes, and corrodes infrastructure [3]. Pyrite is one of the most common sulfide minerals in the earth, and exists not only in the form of ore resource but also as gangue in most metal sulfides and coal deposits. Therefore AMD is very common and one of the worst environmental problems across the globe [4,5].

In order to avoid environmental problems associated with AMD, typical AMD treatment involves addition of neutralizing agents such as lime to raise the pH of the AMD and precipitate heavy metals as AMD sludge which contains a mixture of various metal hydroxides and/or oxides [6,7]. The AMD sludge typically contains a low concentration of solids, and is difficult to be handled and disposed ultimately [8], and then becomes another environmental problem. Thus properly treating or utilizing AMD has been an important problem.

Usually the generation of AMD is described by pyrite oxidation which is illustrated by the following equations [9]:



According to the above equations, the main components of AMD are  $\text{FeSO}_4$ ,  $\text{Fe}_2(\text{SO}_4)_3$  that are common coagulants in water and wastewater treatment and usually used to reduce pollutants such as turbidity and phosphorus (P) concentration in wastewater. As AMD is a hazardous material of environment, utilization of AMD for coagulant is highly desirable. By application of AMD in wastewater treatment for coagulant, AMD and the wastewater could be treated together, and the cost of treating AMD and wastewater would be reduced considerably.

However, AMD in different mines has different characteristics. When AMD is used as coagulants, it will have different coagulation performance and resultant heavy metal concentration in effluent. For example, AMD was used as coagulant in sewage treatment in Derbyshire [10] and in flocculation process of potable water treatment for treatment of surface water from Langsett reservoir [11], and pumped into sewage-impacted river to support amenity value of watercourse [9]. AMD was developed for P removal from municipal wastewater directly, and most of the heavy metal concentrations of the treated water and the sludge were below the standards [12]. However, in another case of using AMD as coagu-

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lant for municipal wastewater [13], AMD was as effective as the commercial coagulant  $\text{FeCl}_3$ , but the resultant heavy metal contamination of the discharge precluded its general use without pretreatment. Therefore, whether AMD could be used as coagulant directly should be tested specially.

Phosphorus (P) is usually considered to be the limiting nutrient of eutrophication, which is another global environmental problem [14,15]. P from secondary municipal effluent into the environment is one of major causes of eutrophication in receiving water bodies [16]. To minimize eutrophication, treatment facilities must reduce phosphorus levels to less than 1 mg/L [17]. Tertiary treatment of secondary municipal effluents to remove P has become increasingly necessary to meet the tough standards of environmental regulations worldwide. Chemical precipitation with coagulants such as  $\text{FeSO}_4$ , ferric sulfate (FS,  $\text{Fe}_2(\text{SO}_4)_3$ ) or polyferric sulfate (PFS) is simple and effective method to remove P from secondary municipal effluent, but the cost of coagulant restricts application of chemical precipitation in P removal broadly.

Yunfu sulfide mine, situated on the outskirts of Yunfu city, Guangdong province, China, is the largest sulfide mine in Asia. Over 2000 m<sup>3</sup> of AMD flow out from the mine, and over 3 tons of lime are used to neutralize the AMD everyday. In the AMD, the concentration of Fe is about 5–10 g/L. Therefore, everyday tons of  $\text{FeSO}_4$  and  $\text{Fe}_2(\text{SO}_4)_3$ , that are common coagulants in wastewater treatment, are wasted after neutralization of the AMD and produced tons of hazardous AMD sludge. In Yunfu city, there is much secondary municipal effluent that need be treated for P removal. If the AMD from the Yunfu sulfide could be used as coagulant for P removal from secondary municipal effluent, economic and environmental value would be achieved simultaneously.

The objectives of this study were to know the performance of the AMD from the Yunfu sulfide for phosphorus removal from wastewater, and the resultant residual heavy metal contamination in treated water. Furthermore feasibility of AMD from Yunfu sulfide as coagulant directly could be estimated.

## 2. Materials and methods

### 2.1. Coagulants

The used AMD was taken from mining pit of the Yunfu sulfide mine. TFe concentration of the AMD was 9700 mg/L, and  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  concentrations were 1700 and 8000 mg/L, respectively. The concentrations of main contents in the AMD are shown in Table 1.

Conventional iron salt coagulants,  $\text{FeSO}_4$ , FS and PFS, were used for comparison in this research.  $\text{FeSO}_4$  and FS were analytically pure chemicals. PFS was commercial product for water treatment obtained from Nanjing General Company of Chemical Industry, China, and its TFe concentration was 21.5%.  $\text{FeSO}_4$ , FS and PFS solutions were prepared with de-ionized water, and the TFe concentrations of them were 9700 mg/L, the same as that of the AMD.

### 2.2. Test water

There were two kinds of test water. One was synthetic wastewater with total phosphorus (TP) concentration of 10.0 mg/L prepared by dissolving analytically pure  $\text{KH}_2\text{PO}_4$  into the de-ionized water. Another was second municipal effluent from Suojingcun wastewater treatment plant, Nanjing, China, and TP concentration in the effluent was 3.5–4.0 mg/L. The initial pH of tested water was about 7.5–8.0 if not indicated specially.

### 2.3. Jar tests

P removal experiments were carried out with a six paddle stirrer (JJ-4A, Guohua Electric Company, Jiangsu, China) at  $20 \pm 1$  °C. Test

water of 400 ml was transferred into a 600 ml beaker, and mixed 30 s at rapid stirring of 120 rpm, and then one kind of coagulant was added into the test water and then mixed 3 min at rapid stirring speed of 120 rpm and then flocculated 10 min at slow stirring speed of 50 rpm. And at last the test water was settled 30 min. The initial pH of water samples were adjusted by addition of NaOH or  $\text{H}_2\text{SO}_4$ . The tested parameters of the jar test included coagulant dosage, stirring time and stirring speed of mixing and flocculation, sedimentation time, initial pH. At last, supernatant 2 cm below the surface was sampled, and then filtered through 0.45  $\mu\text{m}$  membrane for determining TP, TFe,  $\text{Fe}^{3+}$  concentration and the residual heavy metal ions such as Mn, Zn, Hg, etc. were analyzed when needed.

### 2.4. Analytical methods

TFe,  $\text{Fe}^{3+}$ , TP concentration were determined by spectrophotometric measurement (an UV-vis spectrophotometer, A6, PGENERAL, Beijing) following standard methods (Water and Wastewater Monitoring and Analysis Method, the Fourth Edition, China, 2002) [18]. The pH was measured with portable acidity meter (PHB-4, Leici, Shanghai). The residual heavy metal ion concentrations were determined with ICP (OPTIMA 5300DV, PERKIN ELMER, USA). The components of precipitate were measured with X-ray fluorescence spectrum (ARL-9800).

## 3. Results and discussion

### 3.1. Phosphorus removal from synthetic wastewater

The main parameters of coagulation, dosage, initial pH, mixing rate and time, flocculation rate and time, and sedimentation time, were tested. Synthetic wastewater was treated with the AMD and the conventional iron salt coagulants,  $\text{FeSO}_4$ , FS and PFS. TP and residual TFe concentrations of the supernatant were measured, and compared among the tested coagulants to know the performance of P removal of the AMD.

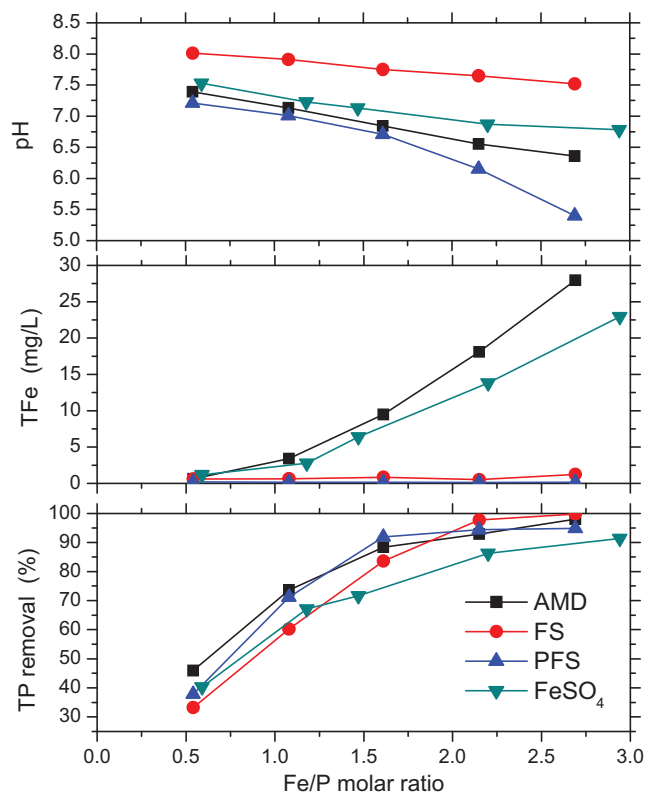
TP removal, residual TFe concentration and effluent pH as a function of dosage of AMD, FS, PFS and  $\text{FeSO}_4$  are comparatively shown in Fig. 1. AMD gave a sharp increase in TP removal at a dosage of less than 1.61 Fe/P molar ratio and then presented a slight rise as the dosage further increased. And the residual TFe concentration increased more and more with increasing AMD dosage. At the dosage of 1.61 Fe/P molar ratio the TP removal, TP and residual TFe concentration were 88.4%, 1.16 and 9.48 mg/L, respectively.

TP removal curves of AMD, FS, PFS and  $\text{FeSO}_4$  showed the same trend: a sharp increase followed a slight rise with increasing dosage within the tested range. TP removal curve of AMD was very close to that of PFS, a little higher than that of FS, and much higher than that of  $\text{FeSO}_4$  as the Fe/P molar ratio was below 2.0. It suggested that ability of P removal was in the order of  $\text{AMD} \approx \text{PFS} > \text{FS} > \text{FeSO}_4$ . Residual TFe concentration curve of AMD was very similar to that of  $\text{FeSO}_4$ , and quite different from that of FS and PFS that they nearly conducted no residual TFe concentration within the tested dosage range. It demonstrates that AMD, like  $\text{FeSO}_4$ , could bring on excessive residual TFe concentration when used as coagulant for P removal if the dosage could not be controlled well. AMD decreased pH of water too and the decreased extent was similar to FS, PFS and  $\text{FeSO}_4$ . Considering TP removal and residual TFe concentration of the treated water comprehensively, the optimal dosages for AMD, FS, PFS and  $\text{FeSO}_4$  could be 1.61, 2.15, 1.61 and 1.47 of Fe/P molar ratio, respectively.

Fig. 2 shows the effects of initial pH of water on TP removal and residual TFe concentration for AMD, FS, PFS and  $\text{FeSO}_4$ . With increasing initial pH of water from 5 to 9, AMD and  $\text{FeSO}_4$  gave a sharp rise in TP removal and a sharp decrease in residual TFe con-

**Table 1**  
Concentrations of main components of AMD from Yunfu sulfide mine (mg/L).

SS	pH	TFe	Fe <sup>3+</sup>	Fe <sup>2+</sup>	Al	Ca	Mg	Mn	Zn	Si	Na	Sr	Ni	Ba	Cd	Pb	Co	As	Be
86	2.6	9700	1700	8000	1200	543	597	447.9	378	75.8	17.9	1.9	0.85	0.70	0.005	0.34	0.20	0.25	0.14

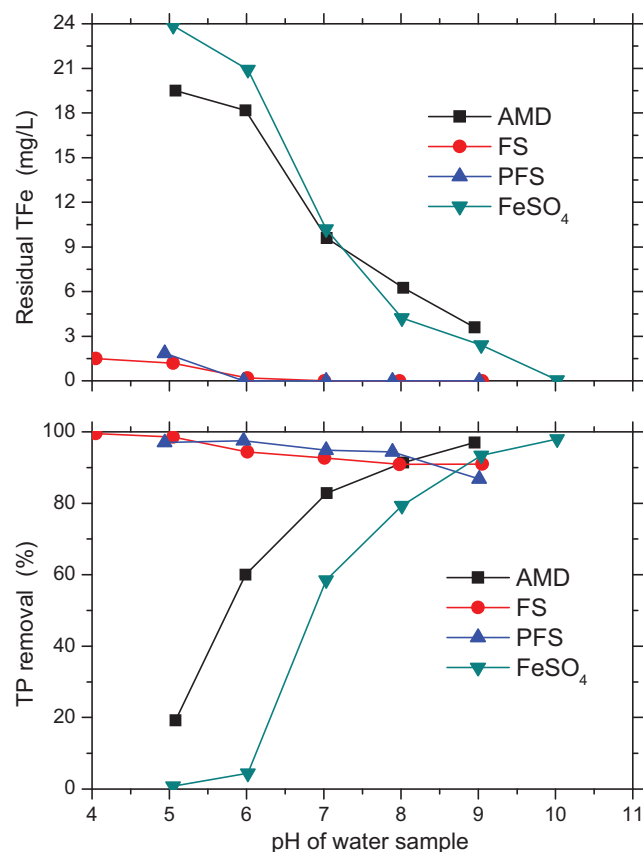


**Fig. 1.** Comparison of dosage effects on TP removal, residual TFe and pH of the effluent between AMD and traditional iron salts.

centration, but FS and PFS gave a slight decrease in TP removal and residual TFe concentration. The effects of initial pH of water on TP removal and residual TFe concentration were very big for AMD and FeSO<sub>4</sub>, but small for FS and PFS. TP removal of AMD was better than that of FeSO<sub>4</sub> within pH range of 5–9. TP removal increased from 20% to 95% and residual TFe concentration decreased from 19 to 3 mg/L for AMD, and for FS and PFS the TP removal decreased from over 98% to about 90%, and residual TFe concentration decreased from 1.5 mg/L to 0 mg/L in the tested pH range. The effective pH range of water for AMD was a little wider than that for FeSO<sub>4</sub>, but much narrower than that for FS and PFS. When the initial pH was 8.03 for AMD, the TP removal and residual TFe concentration were 91.4% and 6.26 mg/L, respectively. The optimal initial pH of water was 8.03, 5.05, 5.96 and 9.04 for AMD, FS, PFS and FeSO<sub>4</sub>, respectively.

At the conditions of the optimal dosage and initial pH, the effects of mixing and flocculation on TP removal and residual TFe concentration are showed in Figs. 3 and 4, respectively. Like the tested conventional iron salt coagulants, the influence of intensity and time of mixing and flocculation on TP removal and residual TFe concentration was very small for AMD. It suggests that the AMD had the same characteristics as FS, PFS and FeSO<sub>4</sub> in the aspects of influences of mixing and flocculation on TP removal and residual TFe concentration.

Settling time is one of important parameters of coagulation. Fig. 5 shows that the effects of settling time on TP removal and residual TFe concentration for AMD and the conventional iron salt coagulants. The effects of settling time on TP removal were



**Fig. 2.** Effects of pH of water on TP removal and residual TFe treated with AMD and the coagulants of FS, PFS and FeSO<sub>4</sub>.

very weak for AMD and the conventional iron salt coagulants. With increasing settling time, the residual TFe concentration was decreased for AMD and FeSO<sub>4</sub> due to increasing of oxidation of Fe<sup>2+</sup>, but changed little for FS and PFS.

Table 2 shows the optimized operation conditions and results of TP removal for AMD and the conventional iron salt coagulants. Under the optimized conditions for AMD, FS, PFS and FeSO<sub>4</sub>, the TP removal were 97.0, 98.5, 97.0 and 94.4%, and residual TFe concentration 3.0, 0.57, 0, and 1.96 mg/L, respectively. It demonstrates that the AMD possess similar performance of TP removal to FS, PFS and FeSO<sub>4</sub> as used to remove TP from synthetic wastewater.

**Table 2**  
The optimized operation conditions and results of phosphorus removal from synthetic wastewater for AMD, FS, PFS and FeSO<sub>4</sub>.

Coagulant	AMD	PFS	FeS	FeSO <sub>4</sub>
Fe/P molar ratio	1.61	1.61	2.15	1.47
Initial pH	8.03	7.03	5.05	9.04
Mixing intensity (rpm)	240	160	200	160
Mixing time (min)	7	3	3	1
Flocculation intensity (rpm)	70	30	70	50
Flocculation time (min)	15	5	15	10
Settling time (min)	70	30	30	30
Residual TP (mg/L)	0.30	0.30	0.15	0.56
TP removal (%)	97.0	97.0	98.5	94.4
Residual TFe (mg/L)	3.0	0.0	0.57	1.96

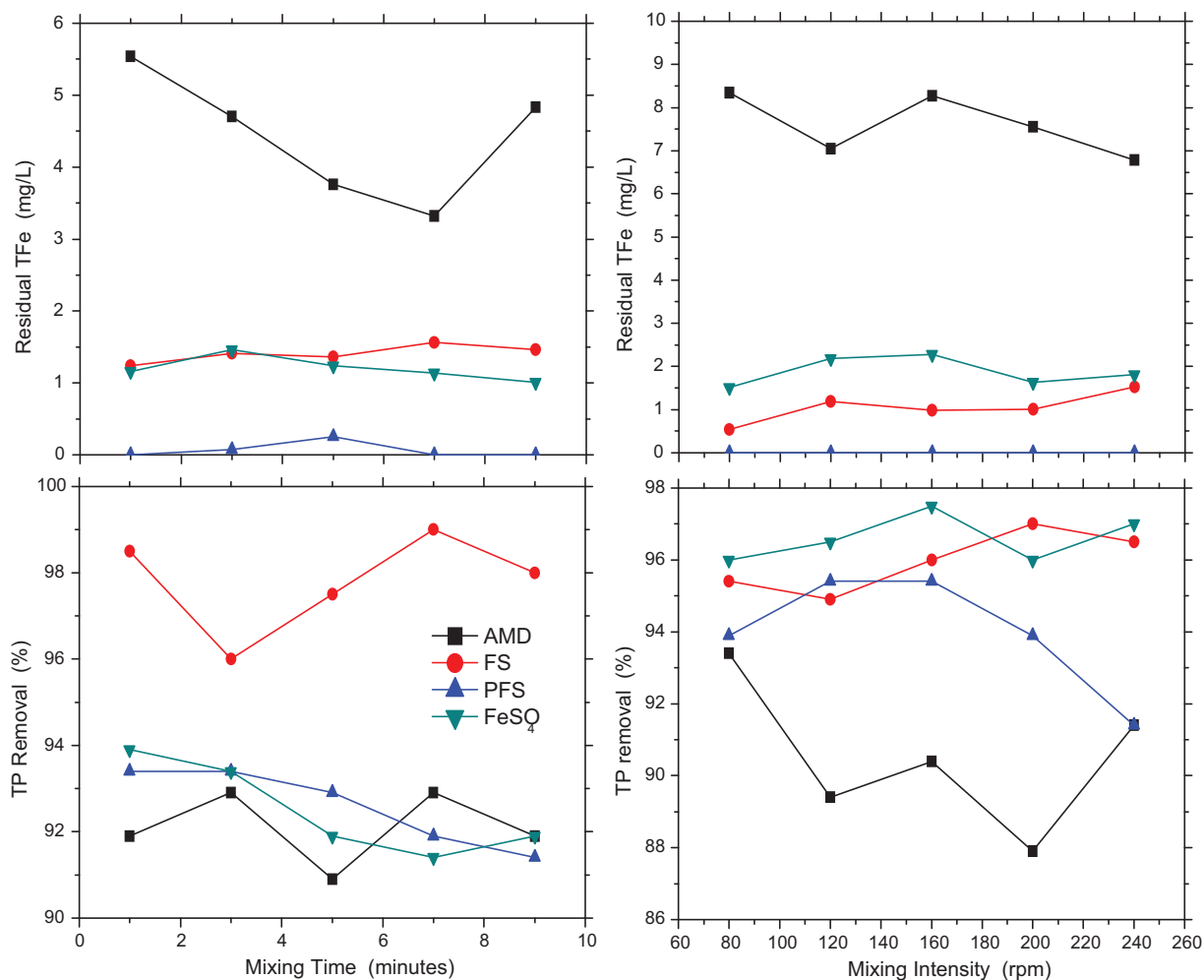


Fig. 3. Effects of intensity and time of mixing on TP removal and residual TFe.

### 3.2. Phosphorus removal from secondary municipal effluent

The secondary municipal effluent is a complex system with much organic matter and many anions which would affect the TP removal, and the P which exists in dissolved and particulate forms could be organic and inorganic matter. The complex components in the secondary municipal effluent would highly affect performance of P removal of AMD. Thus it is much practical to know the performance of P removal of AMD from the secondary municipal effluent.

Fig. 6 shows the dosage of AMD on TP removal from the secondary municipal effluent. With AMD addition the TP removal increased greatly and was 91.52% when the dosage of AMD was 1.41 Fe/P molar ratio, and then further AMD addition made TP removal increase very slowly. The residual TFe concentration was about 0.2 mg/L and changed small as the dosage was below 1.41 Fe/P molar ratio and then increased quickly with further AMD addition. As the dosage of AMD was over 1.41 Fe/P molar ratio, the TP concentration was below 0.32 mg/L, which is lower than 0.5 mg/L, the highest standards of municipal sewage treatment for TP in China. Even the AMD dosage was up to 3.40 Fe/P molar ratio and the TP removal was up to 100%, the residual TFe concentration was only 1.17 mg/L. It indicates that there would not have secondary pollution of iron ion when the AMD was used for P removal from the secondary municipal effluent.

Effective pH range is one of important characteristics as the coagulants used for TP removal. Fig. 7 shows the effects of the ini-

tial pH on TP removal from the secondary municipal effluent for AMD. As the initial pH was below 7 the TP removal increased with increasing initial pH, and as the initial pH was over 7 the TP removal decreased with the initial pH increasing. The TP removal and TFe concentration was over 90% and below 0.8 mg/L, respectively, when the initial pH was between 7 and 8, which should be the effective pH range of AMD for TP removal from the secondary municipal effluent.

Figs. 8 and 9 show the effects of mixing and flocculation on P removal and residual TFe concentration, respectively. As the time and strength of mixing and flocculation changed in tested range, the TP removal and residual TFe concentration had slight changes. It is similar to the results of the synthetic wastewater experiments.

The secondary municipal effluent was treated with AMD, FS, PFS and FeSO<sub>4</sub> under the same condition of 1.41 Fe/P molar ratio, pH 7.3, mixing 7 min at 170 rpm, flocculating 5 min at 60 rpm and settling 30 min. The results are shown in Fig. 10. From Fig. 10 the AMD conducted to 92.10% of TP removal and 0.32 mg/L residual TFe concentration. The TP removal of AMD was even higher than all the other tested coagulations.

### 3.3. Resultant heavy metals in treated water and precipitate

According to concentrations of heavy metals in treated water and contents of heavy metals in precipitates, the possible risk of utilization of AMD in wastewater for P removal could be evaluated. Tables 3 and 4 are concentrations of heavy metals in treated

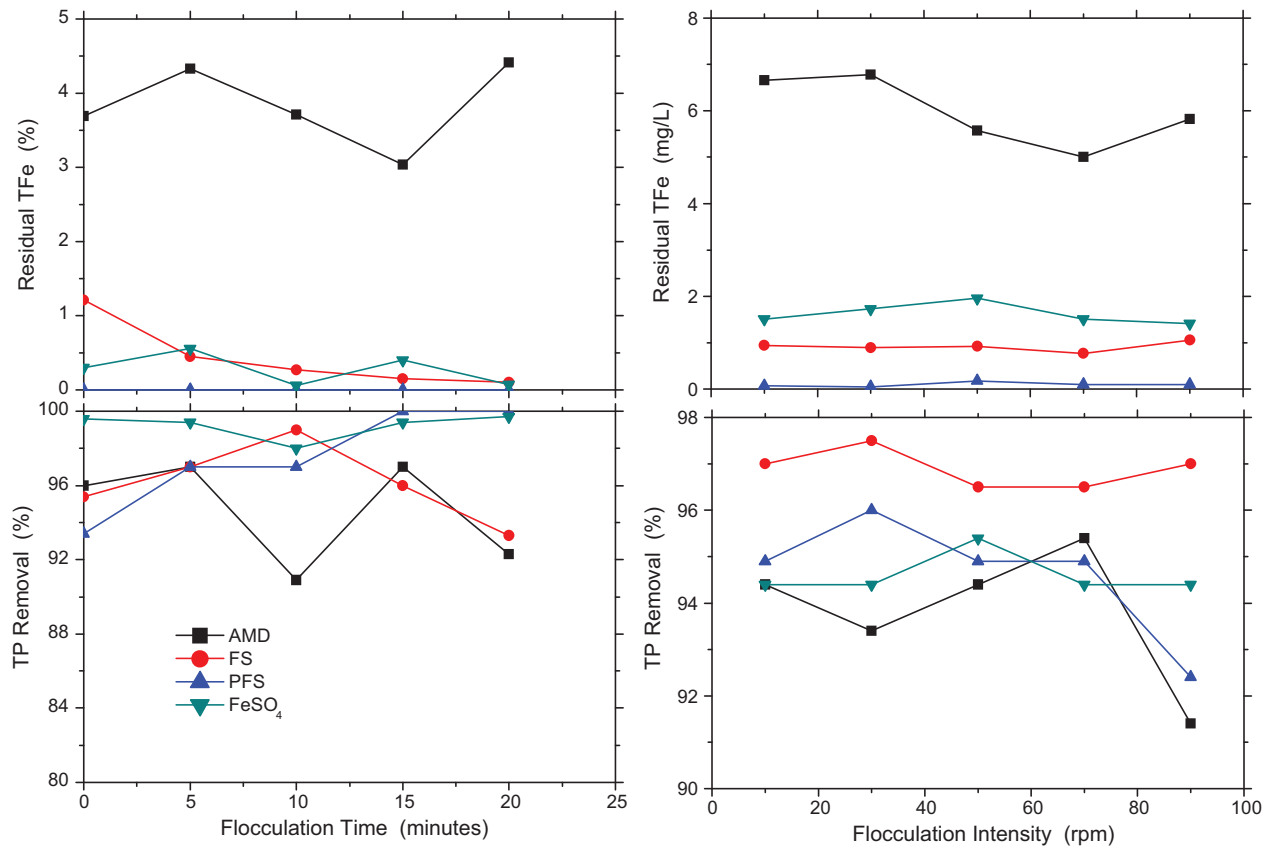


Fig. 4. Effects of flocculation intensity and time on TP removal and residual Fe treated with AMD and the common coagulants of FS, PFS and FeSO<sub>4</sub>.

Table 3

Concentrations of resultant heavy metals in effluent after phosphorus removal with AMD (mg/L).

Irons	Synthetic wastewater	Practical wastewater	Standards <sup>a</sup>
Cd	<0.001	<0.001	0.01
Pb	<0.01	<0.01	0.1
Cu	<0.01	<0.01	0.5
Ni	<0.02	<0.02	0.05
Zn	0.68	0.016	1.0
Mn	1.5	0.284	2.0
As	<0.1	<0.1	0.1

<sup>a</sup> Ref. [19].

water and contents of heavy metals in precipitates from synthetic wastewater, respectively. In treated water Cd, Pb, Co, As, etc. were below the detection limit, and the other ions were below the standards of wastewater treatment [19]. In precipitate from the synthetic wastewater MnO<sub>2</sub>, ZnO, BaO and SrO were 0.5, 0.9, 0.7 and 0.2%, respectively, and the other heavy metals were below the detection limit. These data show that the risks of the second pollution of heavy metal ions from treated water and precipitates were very low as AMD used for coagulant for P removal.

#### 4. Discussions

Table 1 indicates that there were many metal ions in the AMD from Yunfu iron sulfide mine, and Fe<sup>2+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> were the

most three ions, and their concentrations were 8000, 1700 and 1200 mg/L, respectively. Concentrations of heavy metals were very low in the AMD. Fe<sup>2+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> are commonly used for P removal from wastewater, so the AMD could be used for P removal from wastewater.

In the conventional jar test for P removal with Fe<sup>2+</sup>, few Fe<sup>2+</sup> would be oxidized to Fe<sup>3+</sup> for the oxygen supply was deficient [20], thus the oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> could be ignored in this study. Therefore, P removal of the coagulants is mainly decided by the concentrations of Fe<sup>2+</sup>, Fe<sup>3+</sup> and Al<sup>3+</sup> and pH of water. As the AMD and the other coagulants were added into the wastewater, the following chemical reactions might be the main reactions related to P removal and residual TFe concentration. Log of equilibrium constants [21,22] of them were shown as below:

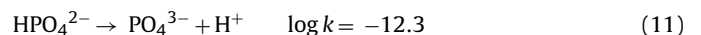
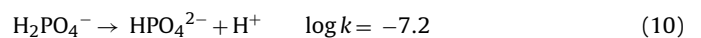
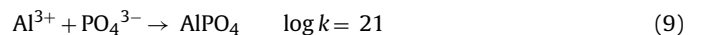
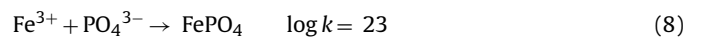
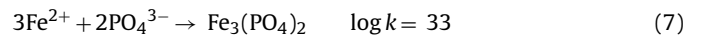
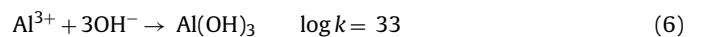
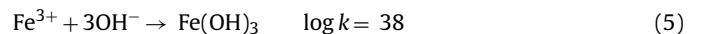
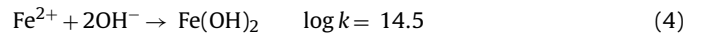


Table 4

Compositions of precipitate as AMD used for phosphorus removal from synthetic wastewater.

Components	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	ZnO	SO <sub>3</sub>	SiO <sub>2</sub>	K <sub>2</sub> O	Cl	MnO	BaO	MgO	SrO
Contents (%)	53.3	30.2	11.6	1.7	0.9	0.8	0.7	0.3	0.2	0.1	0.1	0.1	0.2

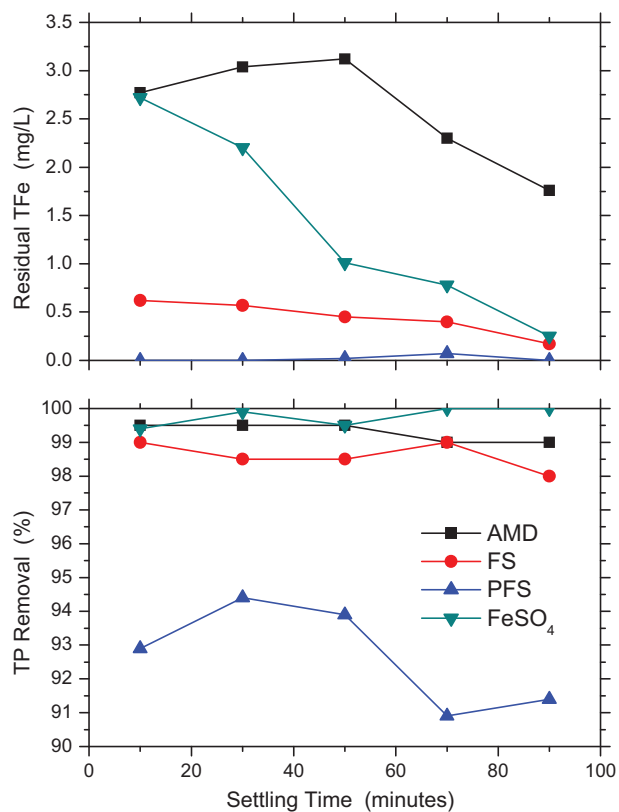


Fig. 5. Effects of settling time on TP removal and residual TFe.

With increasing dosage of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  into the tested wastewater, the equilibriums of Eqs. (4)–(9) move to the right, more  $\text{PO}_4^{3-}$  and  $\text{OH}^-$  were precipitated, thus the pH of the effluent decreased and then P removal increased. When the concentration of  $\text{PO}_4^{3-}$  was very low, further increasing dosage of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  resulted in little increasing P removal and much more  $\text{OH}^-$  precipitated. So the effects of dosage of AMD, FS, PFS and  $\text{FeSO}_4$  on TP removal, residual TFe present as Fig. 1. According to the equilibrium constants of Eqs. (4)–(6) there is more residual  $\text{Fe}^{2+}$  than residual  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  in treated wastewater at the same pH of water. That is the reason that the residual TFe concentration in the effluent with coagulant of AMD was similar to that with coagulant of  $\text{FeSO}_4$ , and much higher than that with coagulants of FS and PFS. On the one

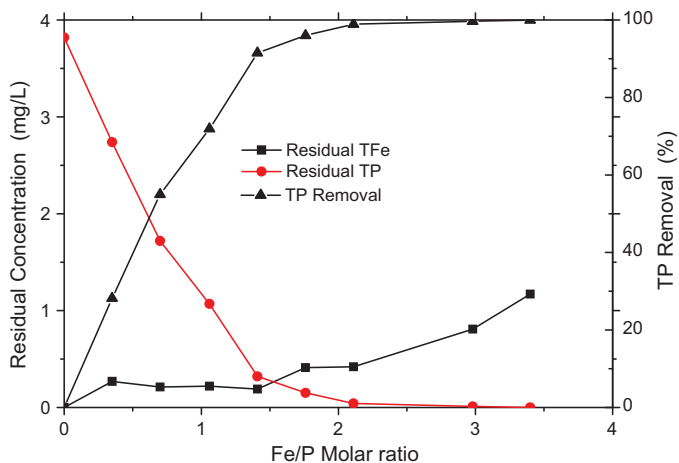


Fig. 6. Effects of dosage of AMD on phosphorus removal from the secondary municipal effluent.

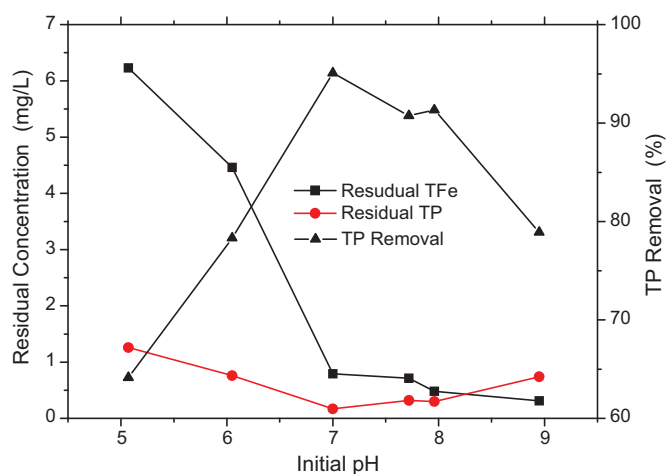


Fig. 7. Effects of initial pH on phosphorus removal from the secondary municipal effluent with AMD.

hand the molar of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  in the AMD were about 52% of the molar of  $\text{Fe}^{2+}$ , and on the other hand when seemingly Fe/P molar ratio of AMD was equal to FS, PFS and  $\text{FeSO}_4$ , virtually molar of ions for P removal in the AMD were more than that in FS, PFS and  $\text{FeSO}_4$ , therefore P removal performance of the AMD was very similar to PFS, and higher than  $\text{FeSO}_4$  as shown in Fig. 1. Because of formation of hydroxides expended lots of  $\text{Fe}^{3+}$  of FS the order of optimal Fe/P molar ratio was  $\text{FS} > \text{AMD} > \text{FeSO}_4$ .

Both dissociation of  $\text{H}_2\text{PO}_4^{3-}$  to release  $\text{PO}_4^{3-}$  and affinity of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  toward  $\text{PO}_4^{3-}$  and  $\text{OH}^-$  were depended on pH. With increasing pH, P removal of AMD and  $\text{FeSO}_4$  increased quickly as shown in Fig. 2. And the optimal initial pH was 8.03 and

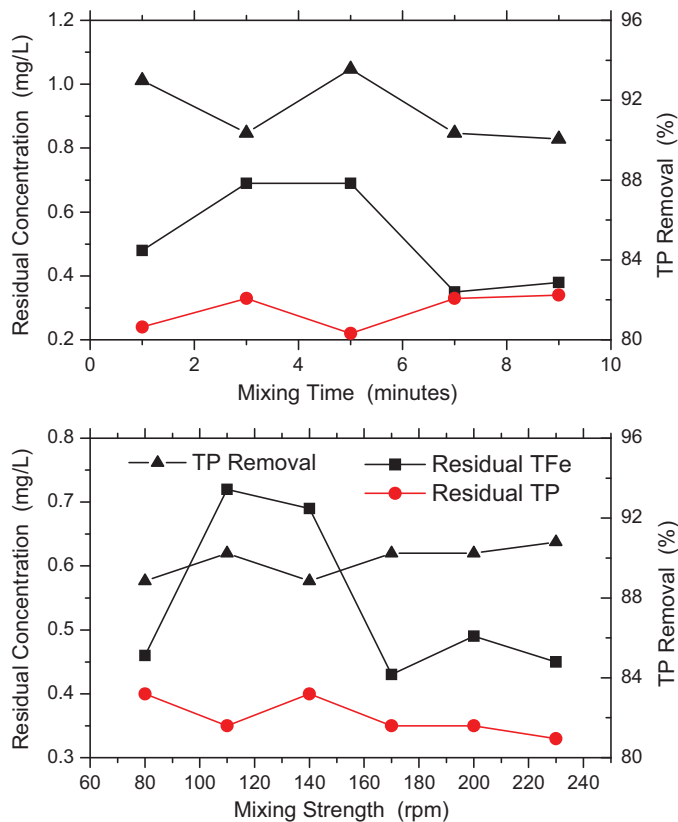


Fig. 8. Effects of mixing on phosphorus removal from the secondary municipal effluent with AMD.

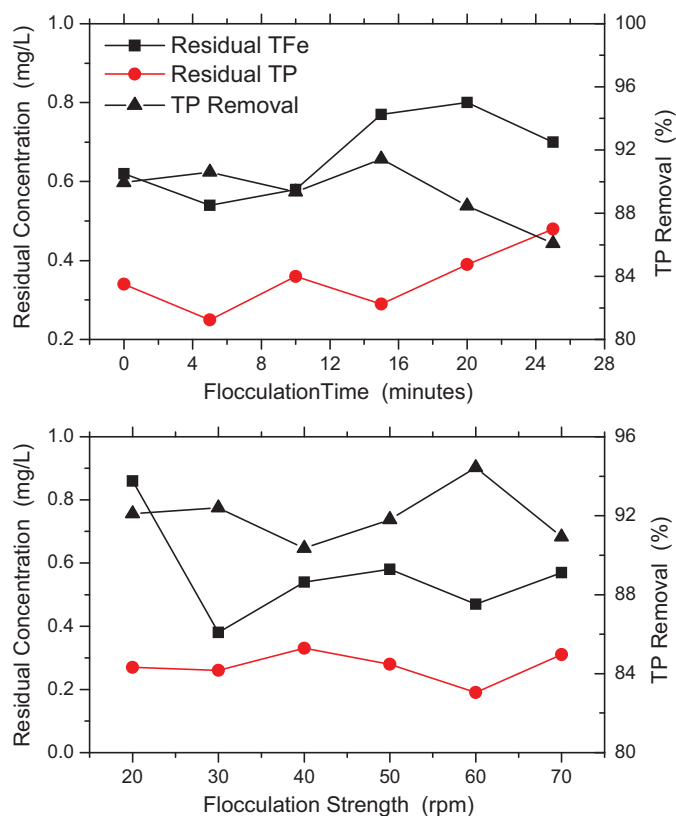


Fig. 9. Effects of Flocculation on phosphorus removal from the secondary effluent with AMD.

9.04 for AMD and  $\text{FeSO}_4$ , respectively. It was consistent with Recht and Ghassemi's results [23] that the efficiency of orthophosphate removal with iron (II) is strongly pH dependent with maximum removal obtained in the vicinity of pH 8. Increasing pH will bring about equilibriums of equations of (4)–(6), (10) and (11) moving to the right directly, thus concentrations of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  will decrease and concentration of  $\text{PO}_4^{3-}$  will increase. The decrease of concentration of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  is a little more than the increase of concentration of  $\text{PO}_4^{3-}$ , but the decrease of concentration of  $\text{Fe}^{2+}$  is much smaller than the increase of concentration of  $\text{PO}_4^{3-}$ . Thus the equilibrium of equation of (7) moves to the right quite a lot and the equilibriums of equations of (8) and (9) move to the left a little. So the equilibrium concentration of  $\text{PO}_4^{3-}$  for equation (7)

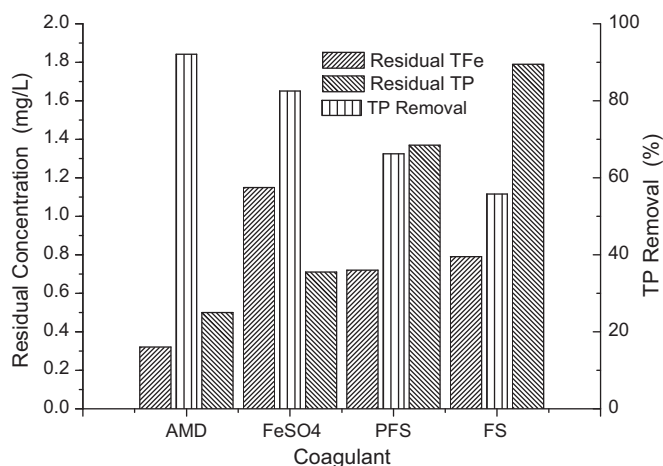


Fig. 10. Performances of phosphorus removal with AMD, FS, PFS and  $\text{FeSO}_4$ .

will decrease a lot and the equilibrium concentrations of equations of (8) and (9) will increase a little. Therefore TP removal increases quickly for AMD and  $\text{FeSO}_4$  and decreases slowly for FS and PFS with increasing pH, and TP removal for the AMD is higher than that for  $\text{FeSO}_4$  for containing lots of  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  in the AMD.

In coagulation with iron salts, mixing and flocculation have big influence on turbidity. However, in P removal of this study, their influences were very small. It agreed with the previous study [22]. The reason was that mixing and flocculation have big influence on floc formation, but small on phosphate precipitate formation. Once phosphate precipitates were formed, P was removed in this study. With increasing settling time, more  $\text{Fe}^{2+}$  would be oxidized to  $\text{Fe}^{3+}$  which was easy to precipitate. Thus residual TFe concentration decreased with increasing settling time.

Because Fe/P molar ratio and initial pH of water were not under the optimal conditions of FS, PFS, and  $\text{FeSO}_4$ , P removal of AMD was much higher than FS, PFS and  $\text{FeSO}_4$  as shown in Fig. 10.

Table 3 shows the contents of precipitate from synthetic wastewater as AMD dosage was 1.61 Fe/P molar ratio. By analyzing Table 3 the Fe/P and (Fe + Al)/P molar ratio were 1.65 and 2.22, respectively. It shows that there were a lot of iron and aluminum hydroxides in the precipitate. Iron and aluminum hydroxides have some abilities of P removal and are good adsorbent of some heavy metal ions, and they are beneficial to P and heavy metal ions removal [24,25]. As pH of water was about 7, many heavy metal ions could precipitate in form of hydroxides. Due to adsorption and precipitation the residual heavy metal ions were very low in the treated wastewater.

As a whole, as AMD is used for P removal in second municipal effluent, characteristics of P removal and residual TFe concentration are similar to that in synthetic wastewater. It demonstrates that mechanisms of P removal from second municipal effluent and synthetic wastewater were the same for AMD. AMD has good performance of P removal from wastewater, and little risk of resultant heavy metals.

## 5. Conclusions

In AMD from Yunfu iron sulfide mine, concentrations of  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  were up to 8000, 1700, and 1200 mg/L, respectively, and heavy metal ions were rather low. It was used to remove phosphorous from synthetic wastewater and second municipal effluent. AMD could obtain P removal up to 97.0% from synthetic wastewater and up to 92.1% from second municipal effluent. In parameters of coagulation of dosage, pH of water, mixing, flocculation and settling time, phosphorus removal was affected vastly by dosage and initial pH of water, but little by mixing, flocculation and settling time. By comparison with FS, PFS and  $\text{FeSO}_4$ , AMD was similar to FS and PFS and better than  $\text{FeSO}_4$  in phosphorous removal, and similar to  $\text{FeSO}_4$  and much higher than FS and PFS in residual TFe concentration. Resultant heavy metals in water and precipitates were very low as AMD was used for phosphorus removal.

AMD from Yunfu iron sulfide mine possess good performance of phosphorus removal from wastewater, and the possible risk of resultant heavy metals was very low. Utilization of AMD as coagulant to wastewater for phosphorous removal is a good way to treat AMD and wastewater simultaneously, and can achieve economical and environmental values.

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