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To cite this article: Dandan Xu et al 2019 IOP Conf. Ser.: Earth Environ. Sci. 227 052049

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Optimization of coagulation-flocculation treatment of wastewater containing Zn(II) and Cr(VI)

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Abstract. In this study, polymeric ferric sulfate (PFS) was employed as a coagulant to treat the wastewater containing Zn(II) and Cr(VI). Based on the mechanism of redox reaction, Cr(VI) was firstly transferred to Cr(III) with the help of $(\text{NH}_4)_2\text{Fe}((\text{SO}_4)_2)$ (FAS) as the reductant. Afterwards, the influence of variable factors including FAS dosage, PFS dosage, pH value and settling time on the coagulation-flocculation treatment of the two heavy metals was estimated. The results show that the optimum removal efficiency of Zn(II) was obtained at a PFS dosage of 100 mg/L, pH 7-8 and settling time of 30 minutes. Meanwhile, the removal efficiency of Cr(VI) reached the highest value when the FAS dosage was 1.2 times of theoretical requirement, with the PFS dosage of 20 mg/L, pH 7-8 and settling time of about 30 minutes.

1. Introduction

With the increasing demand for industrial production of Zinc and Chromium compounds, plenty of heavy metal wastewater containing Zn(II) and Cr(VI) was discharged into the environment [1, 2]. These heavy metals are hard to remove [3] and may cause serious and even irreparable consequence once they were accumulated in the human body [4]. Although Zn is considered to be an essential element of the human beings [5], it is harmful to health if it exceeds the limit [6]. Cr(VI) with strong oxidation ability and water solubility may cause skin irritation and mucous membranes damage, resulting in allergic and even carcinogenic once inhaled [7].

In recent years, vast treatment technologies were applied to remove Zn(II) and Cr(VI), such as adsorption [8], electric process, chemical precipitation, biological techniques and so on. However, electric process and chemical precipitation were of low efficiency, especially when the concentration of the heavy metals were 1 to 100 mg/L, and the two methods often produce a lot of sludge which was hard to treat [9]. Adsorption and biological techniques required high cost when the amount of treated wastewater was large particularly, and they tended to cause secondary pollution [10]. Compared to these approaches, coagulation-flocculation was a physicochemical method which showed high heavy metal removal efficiency and feasibility in adjustment and operation, and it’s appreciable for the treatment of wastewater with large amount and complex composition [11]. In general, the commonly used coagulants include aluminum sulfate, ferric sulfate, poly aluminum chloride (PAC), polymeric ferric sulfate (PFS) and polyacrylamide (PAM), and so on. Among these coagulants, PFS shows better sedimentation property of flocs, higher removal efficiency and lower residual iron than other coagulants [12]. Therefore, PFS was selected to be the coagulants in the process.
In this research, PFS and FAS were employed as coagulant and reductant to treat the wastewater containing Zn(II) and Cr(VI). The effects of variable factors including FAS or PFS dosage, pH value and settling time on the coagulation process were investigated.

2. Materials and methods

2.1. Materials
In this study, the water samples were simulated using zinc nitrate hexahydrate (Zn(NO₃)₂•6H₂O) or potassium dichromate (K₂Cr₂O₇), respectively. NaOH (0.1 mol/L) and HNO₃ (0.1 mol/L) were employed to be pH regulators. Besides, PFS with a mass fraction of 19% (in iron terms) was chosen to be the flocculant. Ammonium ferrous sulfate ((NH₄)₂Fe(SO₄)₂) (FAS) was used to reduce Cr(VI) to Cr(III). Also, anionic polymer polyacrylamide (PAM) (0.1 mg/L) was selected as the aid coagulant. All the above reagents were of analytical grade and purchased from Macklin Biochemical Technology Co., Ltd., Shanghai, China.

2.2. Jar test procedure
A MY3000-6N six mixer (Wuhan Meiyu, China) was used to perform the coagulation tests. The coagulation test was conducted in a plexiglass reactor containing 1L of water. Firstly, the pH regulators were added into the simulated water samples to adjust the pH to a certain value, followed by the addition of PFS with different concentration. Then, samples were stirred at a speed of 250 r/min for 1.5 minutes simultaneously. A fixed intensity (100 rpm for 3.0 min) agitation was then carried out, when an aided coagulant PAM was cast in at the same time. Afterwards, the solutions were stirred at a low speed of 40 r/min for 3.5 minutes. After static precipitation for 30 minutes, the supernatant was extracted 2cm below the liquid level and the remaining metals were then analyzed.

2.3. Chemical analysis
The residual heavy metals were analyzed by an Agilent 5100 Inductively Coupled Plasma Emission Spectrometer (ICP-OES) (Agilent, USA). The pH value was estimated by a PHSJ-3F pH meter (Rex Electric Chemical, China).

2.4. Data analysis
The removal efficiency M of the two heavy metals was calculated using the following equation.

\[
M = \frac{(M_0 - M_i)}{M_0} \times 100
\]  

Where M is the heavy metal removal efficiency (%), and M₀ and Mᵢ are the initial and residual concentrations of each metal in the supernatant (mg/L).

2.5. Effect of FAS dosage
In this study, enhanced coagulation treatment of wastewater containing Cr(VI) included two reaction stages including Cr(VI) reduction and Cr(III) flocculation. First, added proper amount of FAS to reduce Cr(VI) to Cr(III), and then added PFS to precipitate Cr(III). Thus, it is very important to find the best FAS dosage for reducing Cr(VI). As shown in Figure 1, the initial concentration of Cr(VI) was 25mg/L, 50 times of the integrated wastewater discharge standard (GB 8978-1996), and the settling time was set as 30 min when the initial pH was 7. A certain amount of reductant, which was 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 times of the theoretical requirement, was added to the beaker, respectively.

PFS doses varying from 5 to 25 mg/L were added to the samples of wastewater, and then the FAS dosages under different PFS dosage were optimized. As it can be seen in Figure 1, an optimum removal efficiency was obtained when the FAS dosage was 1.0-1.2 times of the theoretical value. Ultimately, a FAS dosage 1.2 times of the theoretical value was determined to be the actual reductant addition.
2.6. Effect of PFS dosage

During coagulation and flocculation, the removal efficiency of the heavy metals was greatly affected by the dosage of PFS [13]. Figure 2 shows a gradual increase of effect of PFS dosage on the removal efficiency of Zn(II) when the initial concentration of Zn(II) was 100mg/L (pH₀=7), and the dosage of PFS ranged from 10 to 120 mg/L. When the PFS dosage was 10-90 mg/L, it exhibited a poor coagulation effect and the removal rate of heavy metals was about 80-96%. At this time, there was still some flocs suspended in the supernatant for a period of time, resulting in a poor settling effect. When the dosage of PFS was increased to 100 mg/L, the residual concentration of Zn(II) in water was below 2 mg/L, and there was an unobvious removal rate with a further addition of PFS. Therefore, at the initial pH condition of 7, when the initial concentration of Zn(II) in water was 100 mg/L, an optimum removal effect was obtained with a PFS dosage of 100 mg/L.

Similarly, the effect of PFS dose on the treatment of Cr(VI) was shown in Figure 3. The removal efficiency presented a dramatic increase as the PFS dosage ascended from 2 to 25mg/L, whereas it reached the maximum value with an addition of 20mg/L PFS and showed insignificant fluctuation afterwards. Hence, a PFS dosage of 20mg/L was chosen to be the optimum condition.

2.7. Effect of pH

The pH value can affect the form of heavy metals and the hydrolysis products of coagulants greatly [14, 15]. As presented in Figure 4, when the initial concentration of the two heavy metals and PFS dosage were constant, pH had a significant effect on the removal of the target wastewater. For Cr(VI), it was beneficial to reduce Cr(VI) to Cr(III) at an acidic condition, which provided sufficient Cr(III) for the subsequent coagulation precipitation reaction. However, when the pH was too low to form Cr(OH)₃ and the iron hydroxide colloidal particles, the coagulation effect was thus poor and the removal efficiency was undesirable accordingly. When the pH of raw water was higher than 8, it tended to generate iron hydroxide colloids, resulting in a negative effect on the reduction reaction of Cr(VI) under alkaline conditions, thus there was insufficient Cr(III) to produce Cr(OH)₃. In conclusion, pH of 7-8 was defined as the desirable coagulation condition.

In addition, for Zn(II) (Figure 4), the residual concentration of Zn(II) in the water decreased continuously as pH increased from 3 to 7, but when the pH value was higher than 8, the removal rate declined. It can be seen that when the pH of the wastewater was at 7-8, the concentration of Zn(II) was lower than 2 mg/L, which met the Integrated Wastewater Discharge Standard (GB 8978-1996). Therefore, the pH value in the range of 7 to 8 was the requirable reaction parameter.
Figure 2. Effect of PFS dosage on the removal of Zn(II). Zn(II): 100mg/L, PFS dosage: 10~120mg/L, pH₀=7.

Figure 3. Effect of PFS dosage on the removal of Cr(VI). Cr(VI): 25mg/L, FAS dosage: 1.2 times of the theoretical value, PFS dosage: 1~25mg/L, pH₀=7.

Figure 4. Effect of pH on the removal of Zn(II) and Cr(VI). Zn(II):100mg/L, Cr(VI): 25mg/L, PFS dosage: 100mg/L, 20 mg/L, respectively.

2.8. Effect of settling time
The settling time of flocs generated in the coagulation reaction influences the solid-liquid separation and thus affects the efficiency of the whole process. Figure 5 illustrated the effect of settling time on the removal rate of the two heavy metals. The removal rates of the heavy metals increased at first and then declined during the settling time ranged from 10 to 90 minutes. Consistently, a maximum removal efficiency was achieved at about 30 min for the two kinds of wastewater. Once the settling time was further prolonged, it showed a negative effects on the treatment process unexpectedly. The settling velocity mainly determined the precipitation time, and it was affected by the particle size and compactness which was related to the kinds and dosage of coagulants. Thus, factors such as coagulant dosage and pH should be considered in practical treatment of heavy metal wastewater.
Figure 5. Effect of settling time on the removal of Zn(II) and Cr(VI). Zn(II):100mg/L, Cr(VI):25mg/L, PFS dosage: 100mg/L, 20mg/L, respectively. pH$_0$=7.

3. Conclusions
In this study, PFS was used in the coagulation treatment of wastewater containing Zn(II) and Cr(VI), and the coagulation parameters were optimized to ensure the high removal efficiency. Firstly, the effect of reductant (FAS) dosage on the treatment of Cr(VI) was investigated based on reduction reaction mechanism, and 1.2 times of theoretical requirement was found to be desirable. Afterwards, the optimization of several factors including PFS dosage, pH and settling time for the treatment of Cr(VI) was conducted. Results show that PFS of 20 mg/L, pH 7-8 and settling time of 30 min were the optimal condition for the coagulation of Cr(VI). Meanwhile, an optimum removal efficiency was obtained when the PFS dosage was 100 mg/L, pH 7-8 and settling time was 30 min for the coagulation of Zn(II). In conclusion, various factors should be comprehensively optimized in the actual coagulation process.

Acknowledgement
This study was financially supported by the National Science and Technology Major Project of “Water Pollution Control and Governance” (No. 2017ZX07107-005-02).

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