Optimization of high performance composite flocculant PFZSSB

K Zhang, SQ Li, Z Yan

School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

Abstract: Flocculant PFZSSB (MD-F02) was used to treat coking wastewater. In order to solve the problems such as excessive dosage and low flocculation effect in practical application, the dosing sequence and dosing time in the preparation of MD-F02 were studied to improve the flocculation effect. Based on a lot experiments, the optimal parameters were determined i.e. the dosing sequence of Zn> Fe> B, the dosing time of Zn, Fe, B of 5, 20, 10 min, respectively. The removal rate of SS was up to 90% and the removal rate of chemical oxygen demand (COD) was close to 50% under the dosage of modified MD-F02 of 125 mg/L.

1. Introduction

Coking wastewater is one of the most important pollution sources of water pollution. Its composition is complex and varied. It contains phenols, polycyclic aromatic compounds and heterocyclic compounds such as nitrogen, oxygen and sulfur. It is a typical industrial wastewater containing refractory organic compounds [1]. After the treatment of coking wastewater, the content of phenolic pollutants in effluent can be up to standard, but COD, NH_3-N and other indicators cannot reach the discharge standard [2]-[4]. Therefore, it is of great significance to reduce the pollution of coking wastewater and improve the utilization rate of wastewater.

Flocculation is one of the most widely used and most economical methods in wastewater treatment. Flocculant is core of flocculation technology. Advanced treatment of coking wastewater needs a cheap, high efficiency and simple process flocculant.

Zhou Jing et al. prepared composite flocculant polymeric aluminum silicate boron (PFASSB-MD-F01) by adding Fe, Al and B elements in the polymerization of silicic acid. Coking wastewater was treated by PFASSB, aluminium polychlorid (PAC) and polymeric aluminum sulfate (PAS). The results showed that PFASSB had a higher removal rate of SS and COD.

Yan Zhe et al. [5] made use of sodium silicate, ferric sulfate, zinc sulfate and sodium borate to prepare PFZSSB-MD-F02, and it was applied to the deep treatment of coking wastewater. When the dosage of flocculant was 175mg/L, SS removal rate of coking wastewater was more than 90%, the removal rate of COD was close to 50%, and the floc was larger than that of the same kind of flocculant. The effluent reached the national discharge level B standard.

In the process of coking wastewater treatment, MD-F02 has a lot of problems, such as high dosage and residue. In order to solve these problems, this paper optimized the adding sequence of Zn, Fe and B in the process of flocculant MD-F02 configuration, so as to achieve better treatment effect on coking wastewater and reduce the dosage of flocculant. Through the exploration of its mechanism, it provides some practical guidance and theoretical basis for the advanced treatment of coking wastewater, the development of flocculant and the development of the whole water treatment industry.

2. Experimental materials and methods

2.1. Experimental materials

The wastewater was collected from a Steel Corp after biochemical coking wastewater, contents of COD_{Cr} were 146 mg/L, contents of SS were 252 mg/L, pH=7.3.

The simulated wastewater was prepared with kaolin and sodium humic acid, and the content of SS was 100 mg/L, pH=7.3

Reagent: sulfuric acid, sodium silicate, ferric sulfate, zinc sulfate and sodium borate are all pure chemical reagents of Chinese medicine group.

2.2. Experimental methods

2.2. 1. Preparation of flocculant MD-F02.

The sodium silicate solution with SiO_2 mass fraction of 3% content was prepared. The sodium silicate solution was adjusted to a certain pH value by adding concentrated sulfuric acid. And then sodium silicate solution would be activated with a certain speed of about 60 min. A certain proportion of ferric sulfate, zinc sulfate and sodium borate were added to the activated silicic acid solution, and the stirring reaction was about 60 min. Static curing about 24 h, that is flocculant MD-F02.

2.2. 2. Change of pH value of solution.

In the process of preparing flocculant, the pH value of the solution was recorded after adding $ZnSO_4 \cdot 7H_2O$, $Fe_2(SO_4)_3$ and $Na_2B_4O_7 \cdot 10H_2O$, respectively. The pH value of the solution was continuously measured by PHSJ-3F type pH meter. The initial pH value of activated silicic acid was 2.5 and the reaction temperature was T=30 ℃.

2.2. 3. Detection methods of SS and COD.

A certain amount of flocculant was added into the wastewater. First, the solution was rapidly stirred for 60 seconds at 300 rpm. The solution was then slowly stirred at 30 rpm for 15 minutes. The solution was allowed to stand for 15 minutes and the contents of SS and COD in the supernatant were measured. SS in sewage using national standard method of measurement-Gravimetric method. The rapid digestion spectrophotometry was used for the determination of COD.

3. Results and discussion

3.1. The pH value of the reaction system was changed by adding Zn, Fe and B

3.1.1. The change of pH value in the activation of poly silicic acid.

Figure 1(a) shows the pH value of solution increased with the increase of Si dissolution time. Sodium silicate produces H_4SiO_4 during activation. In acidic solution, the silicic acid molecules combine with H^+ to form positive ion H_5SiO^{4+}, and the content increases with the decrease of pH value. Then, the silicic acid molecule reacts with the silicic acid monovalent cation to produce the polymerized silicic acid, thereby forming a plurality of monomer. In faintly acid and alkaline solutions, the polymerization of silicic acid with monovalent anions occurs. The OH^- generated in this reaction causes an increase in pH value. Part of the resulting dimer is further polymerized with OH^-.

The generated double silicate anion and silicic acid molecules can continue to participate in the polymerization reaction in accordance with the above reaction. This reaction will produce higher polymerization state of silicate anions and acid molecules. The highly polymerized silicic acid molecule is an important component of the active ingredient of the flocculant. From the whole process, H^+ is consumed continuously along with the activation of silicic acid, which leads to the increase of pH value.
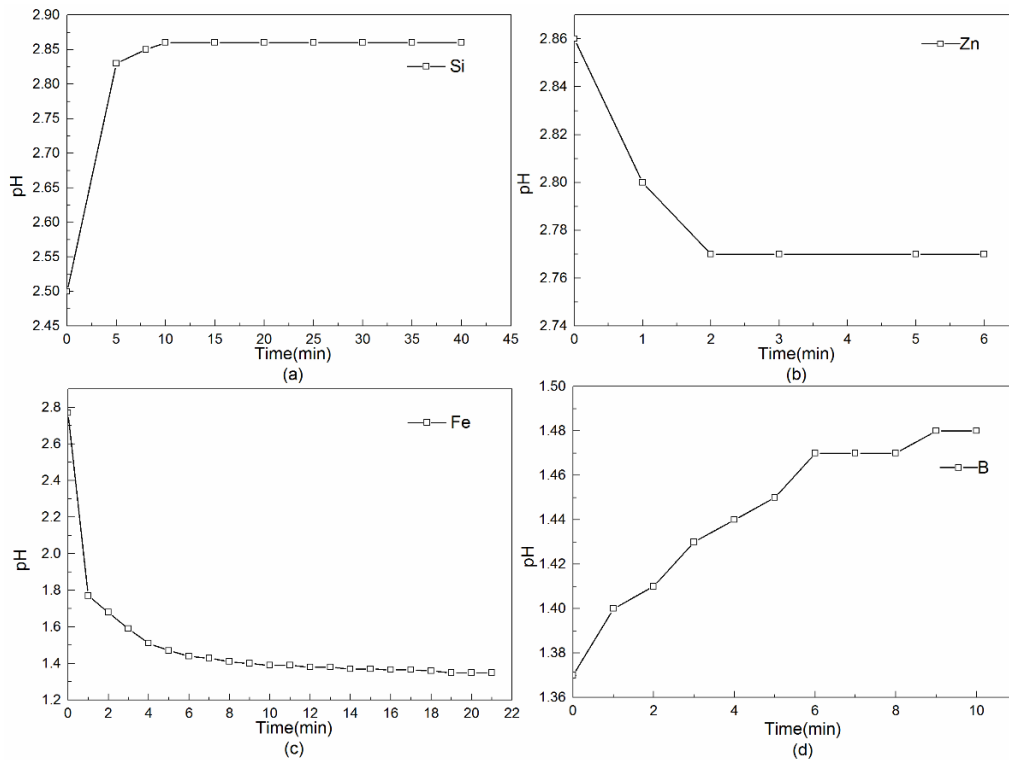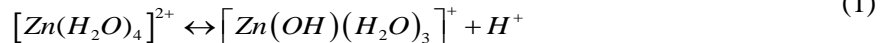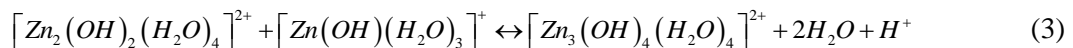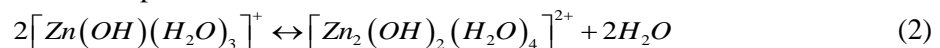
Figure 1 Change of pH value of solution.

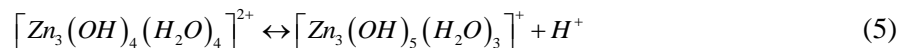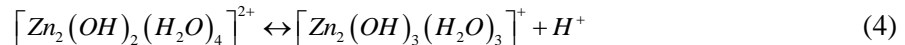### 3.1.2. Effect of Zn dissolution on pH value of silicic acid system.

Figure 1(b) shows the pH value of solution decreased with the increase of Zn dissolution time. Zinc sulfate is easily soluble in water, and the hydrolysis of zinc causes the solution pH to decrease:

$$\left[Zn(H_2O)_4\right]^{2+} \leftrightarrow \left[Zn(OH)(H_2O)_3\right]^+ + H^+ \tag{1}$$

Hydroxyl bridging interactions between hydroxyl complexes polymerize mononuclear complexes to form binuclear or multinuclear complexes:

$$2\left[Zn(OH)(H_2O)_3\right]^+ \leftrightarrow \left[Zn_2(OH)_2(H_2O)_4\right]^{2+} + 2H_2O \tag{2}$$

$$\left[Zn_2(OH)_2(H_2O)_4\right]^{2+} + \left[Zn(OH)(H_2O)_3\right]^+ \leftrightarrow \left[Zn_3(OH)_4(H_2O)_4\right]^{2+} + 2H_2O + H^+ \tag{3}$$

At the same time, the complex will be hydrolyzed:

$$\left[Zn_2(OH)_2(H_2O)_4\right]^{2+} \leftrightarrow \left[Zn_2(OH)_3(H_2O)_3\right]^+ + H^+ \tag{4}$$

$$\left[Zn_3(OH)_4(H_2O)_4\right]^{2+} \leftrightarrow \left[Zn_3(OH)_5(H_2O)_3\right]^+ + H^+ \tag{5}$$

According to the hydrolysis process of zinc, with the continuous hydrolysis of zinc, H^+ was produced at the same time of the formation of polynuclear hydroxyl complex, which led to the decrease of pH value. At the same time, the polynuclear hydroxyl complex produced by the hydrolysis of zinc ions and the silicic acid skeleton were polymerized, which enriched the silicate framework. The pH value of the solution was stable after 5 minutes of zinc addition. Zinc hydrolysis is completed, so the best time for zinc dissolution of 5 minutes.

3.1.3. Effect of Fe dissolution on pH value of silicic acid system.

Figure 1(c) shows the pH value of solution decreased with the increase of Fe dissolution time. Iron (III) salt is ionized in aqueous solution to form Fe^{3+} ion, and Fe^{3+} exists in the form of hydrated ion $Fe(H_2O)_6^{3+}$. The reaction as follows:

$$Fe(H_2O)_6^{3+} + H_2O \xrightleftharpoons{} Fe(H_2O)_5OH^{2+} + H_3O^+ \tag{6}$$
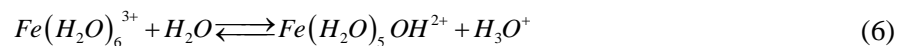
The hydrolysis behavior of iron salt in aqueous solution is similar to that of zinc salt, and the final result is the decrease of pH value. The pH value of the solution was stable after 20 minutes. The hydrolysis of iron is complete, so the optimal time for iron dissolution is 20 minutes.

3.1.4. Effect of B dissolution on pH value of silicic acid system.

Figure 1(d) shows the pH value of solution increased with the increase of B dissolution time. B and Si have the similar chemical properties that the electronic acceptance is very strong. When an electron pair donor is present in the reaction environment, B can form a stable coordination compound. Boric acid is produced under strong acid conditions:

$$5H_2O + 2H^+ + B_4O_7^{2-} \rightarrow 4H_3BO_3 \tag{7}$$

Boric acid is a weak acid and its sodium salt is a strong base weak acid salt. Its aqueous solution is strongly alkaline. This explains why the pH value increases in the process of boron dissolution. The pH value of the solution was stable after 10 minutes of boron addition. The hydrolysis of boron is complete, so the best dissolving time is 10 minutes.

3.2. Effects of Zn, Fe and B dosing sequence on flocculation efficiency

According to the law of hydrolysis of Zn^{2+} and Fe^{3+}, the equilibrium of dissolution and precipitation of Zn^{2+} and Fe^{3+} exists in the solution. For the insoluble electrolytes such as $Zn(OH)_2$ and $Fe(OH)_3$, the change of the pH value of the solution will inevitably lead to the change of precipitation-dissolution equilibrium, eventually leading to the occurrence of dissolution or precipitation. From the point of view of the dissolution equilibrium, the hydrolysis polymerization process of Zn^{2+} and Fe^{3+} starts from the minimum value of pH that sol precipitation was found. $Zn(OH)_2$ and $Fe(OH)_3$ have the following dissolution precipitation equilibrium.

$$Fe(OH)_3 \Leftrightarrow Fe^{3+} + 3OH^- \tag{8}$$

$$K_{sp}\left(Fe(OH)_3\right) = \left[Fe^{3+}\right] \times \left[OH^-\right]^3 = 4.0 \times 10^{-38} \tag{9}$$

$$Zn(OH)_2 \Leftrightarrow Zn^{2+} + 2OH^- \tag{10}$$

$$K_{sp}\left(Zn(OH)_2\right) = \left[Zn^{2+}\right] \times \left[OH^-\right]^2 = 1.2 \times 10^{-17} \tag{11}$$

$$H^+ + OH^- \Leftrightarrow H_2O \tag{12}$$

$$K_w = 1 \times 10^{-14} \tag{13}$$

Assuming that the content of zinc ion and iron ion in the solution is 1mol/L, it is obtained from (9), (11):

$$\left[OH\right]^-_{Fe(OH)_3} = 3.42 \times 10^{-13} \tag{14}$$

$$\left[OH\right]^-_{Zn(OH)_2} = 3.46 \times 10^{-9} \tag{15}$$

$$pH_{Fe(OH)_3} = 1.54 \tag{16}$$

$$pH_{Zn(OH)_2} = 5.54 \tag{17}$$

The difference between these two values indicates that the affinity of Fe^{3+} to OH^-ion is much stronger than that of Zn^{2+} on OH^- ion, which means that Fe^{3+} is more prone to hydrolysis polymerization than Zn^{2+}. When Fe^{3+} and Zn^{2+} exist in the solution, the first hydrolysis polymerization is Fe^{3+}, and then with the increase of the pH value of the solution, the hydrolysis polymerization of Zn^{2+} occurs. In order to achieve more effective Zn, Fe complex with silicic acid skeleton, the effect of adding order of Zn and Fe on flocculation effect of MD-F02 should be taken into account.

The addition of sodium borate can cause the rapid rise of pH in silicate solution, leading to the occurrence of gel. Therefore, it is necessary to join the B element with Zn, Fe at the same time or after the Zn, Fe to join, in order to avoid the introduction of B element caused drastic changes in the solution pH value.

In order to investigate the effect of changing the dosing sequence on the flocculation effect, the following five dosing sequence schemes were set up:

Figure 2 shows that the order of addition play a key effect on the flocculation of MD-F02. Through the comparison of flocculation effect, the best dosing sequence is Zn>Fe>B. The reason is that iron elements can significantly reduce the pH of the solution system, compared to the effect of zinc and boron on the pH of the solution system. The pH value can affect the degree of polymerization of silicic acid molecules, the decrease of pH value can reduce the degree of polymerization of silicic acid molecules, weaken the bridging ability of MD-F02, and then influence the flocculation effect of flocculant.

3.3. Effect of optimized MD-F02 on coking wastewater treatment
Figure 3 shows the treatment effect of the modified flocculant MD-F022 is much higher than MD-F021. When the dosage of MD-F022 was 50 mg/L, the removal rate of SS was up to more than 90%. When the dosage of was 125 mg/L, the floc was the largest, and the removal rate of COD was up to 47%. The results show that the order of addition of Zn> Fe> B is more favorable for the polymerization of elements and poly silicic acid.
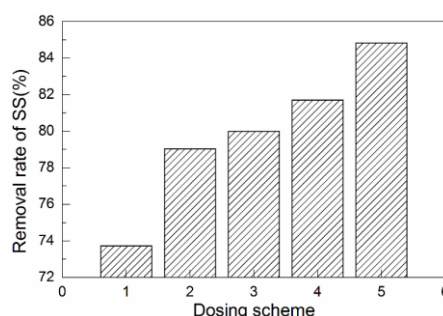

Figure 2. Flocculation effect of different dosing schemes.

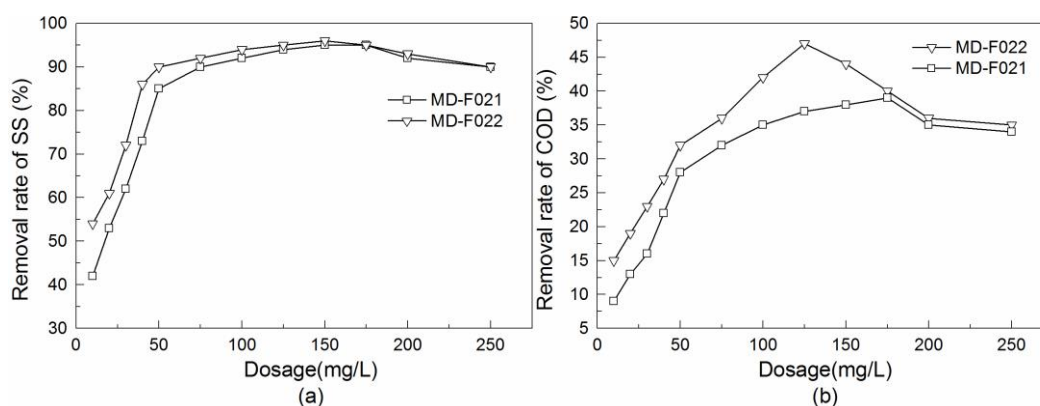(1# Fe=B=Zn; 2# Fe>B>Zn; 3# Fe>Zn>B; 4# Zn>B>Fe; 5# Zn>Fe>B)

Figure 3. Comparison of coking wastewater treatment.

4.   Conclusions
The effects of the addition of iron, zinc and boron on the pH value of the reaction system and the effect of the dosage sequence on the flocculation effect in the synthesis of MD-F02 were studied. The following conclusions were summarized:
(1) The dosage and time of Zn, Fe and B played a key effect on the flocculation efficiency of MD-F02, the best dosing sequence was Zn>Fe>B, and the corresponding optimal dissolution time was 5 min, 20 min, 10 min.

(2) When the dosage of modified flocculant MD-F02 was 125 mg/L, the SS removal rate of coking wastewater was above 90%, and the removal rate of COD was close to 50%, and the effluent reached the first grade B standard.

5.   References

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