Study on the flocculation condition of Poly-Silicate-Aluminum-Ferric (PSiAF) coagulant prepared with coal gangue as raw material

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Abstract. Si, Al, Fe were leached from coal gangue to prepare Poly-silicate-aluminum-ferric (PSiAF) coagulant. The optimal dosage and the most adaptive pH value was explored when PSiAF was used to treat simulated wastewater, simulated dyeing wastewater and domestic sewage respectively. The flocculation conditions of PSiAF were investigated with the removal efficiency of turbidity, CODCr or chrominance as the inspecting parameters. The experiment results show that, when PSiAF was used to treat the three kinds of water samples, the optimal dosage is 1.2ml/L, and the most adaptive pH is 8 for simulation wastewater, under this condition, the turbidity removal ratio was 76.04%, the CODCr removal ratio was 58.33%. There is no decolorization effect for simulation dyeing wastewater, and PSiAF is not suitable for simulation dyeing wastewater. The optimal dosage is 8.0ml/L, and the most adaptive pH is 6 for domestic sewage, under this condition, the turbidity removal ratio was 67.25.04%, the CODCr removal ratio was 46.15%.

1. Introduction
Useful ingredients were leached from solid wastes such as coal gangue, coal ash, red mud to prepare coagulant, as is one of the effective ways to fully use useful ingredients of these solid wastes[1-2]. It can not only alleviate the increasingly serious resource crisis, but also achieve the purpose of curbing environmental pollution by environmental wastes, and change these environmental wastes into useful substance[3-4].

There are a large number of coal gangue mountains in our country after a long period of accumulation, and these coal gangue mountains take up a lot of ground, further more, which cause serious pollution to groundwater, air and soil by pulltant released from coal gangue. After roasting, coal gangue was infiltrated by acids to extract Al and Fe, then, was infiltrated by alkali to extract Si, following, to prepare polymer inorganic coagulant of poly-silicate-aluminum-ferric (PSiAF) used in sewage treatment, It is one of the effective ways of coal gangue used[5].

In this paper, with the removal efficiency of turbidity, CODCr or chrominance as the inspecting parameters, we mainly studied flocculation conditions of PSiAF prepared with coal gangue as raw material by the means of experiments. The optimal dosage and the most adaptive pH value was explored when PSiAF was used to treat simulated wastewater, simulated dyeing wastewater and domestic sewage respectively.
2. Materials and methods

2.1. Experimental apparatus and reagents

SX-G07103 Muffle furnace (Tianjin Zhonghuan Experiment Electric Furnace CO. LTD.), UV-8000S Uv-vis Spectrometer (Shanghai Metash Instruments CO. LTD.), MY3000-6F Coagulating test mixer (Wuhan Meiyu Instruments CO. LTD.), pHs-3C Acidity meter(Shanghai Boqu Instruments CO. LTD.), DR3900+DRB 200 Laboratory COD analyzer (Shanghai Zhimao Environmental Protection Technology CO. LTD.), and so on.

Coal gangue were obtained from a Coal plants in Anshun city. Domestic sewage was acquired from a pond in the campus of Anshun University. Other reagents are as follows: H₂SO₄ (AR), HCl (AR), NaOH (AR), AgNO₃ (AR), KF (AR), Na₄SiO₄.9H₂O (CP), Fe₂(SO₄)₃.XH₂O (AR), AlCl₃.6H₂O (AR), H₄H₂.H₂SO₄ (AR), C₆H₁₂N₄ (AR), Methylene blue (AR).

2.2. Si, Al, Fe leached from coal gangue

Coal gangue was roasted with a certain amount of Na₂CO₃ at the temperature of 750℃ for 1.5 hours. After that, Al and Fe were extracted by acids under the conditions that the concentration of mixed acid is 20%, the leaching time and temperature are 2 hours and 100℃ respectively, volume ratio of hydrochloric acid and sulphuric acid is 3:1, the solid-liquid ratio is 1:10 (1 g sample to 10 ml mixed acid). leaching ratio of aluminum reached 14.35% and leaching ratio of iron reached 15.76%. After leaching with acids, we infiltrated the residue with 4 mol/l sodium hydroxide to extract Si. The leaching ratio reached 54.57%.

2.3. The preparation of poly-silicate-aluminum-ferric solution

The Poly-silicate-aluminum-ferric solution was prepared with the solution including Al, Fe and Si extracted in the experiment 2.2. The preparation conditions are as following: the content of silica of 4%, Al/Fe molar ratio of 1:2, (Al+Fe)/Si molar ratio is 1:1 and the solution pH of 5 of sodium silicate[6].

2.4. Flocculation experiment

40 NTU simulated waste water was prepared with hydrazine sulfate and hexamethylenetetramine. Simulated dyeing wastewater was prepared with methylene blu. Domestic sewage was acquired from a pond in the campus of Anshun University. 400ml water samples were contained in 500ml beakers. pH value of these water samples were adjusted by the solution of 1 mol/L sulfuric acid or 1 mmol/Lsodium hydroxid. After that, Flocculation experiments were implemented by coagulating test mixer. Stirring speed is set as following: at first, quickly stir at 400 r/min speed for 2 min, then slowly stir at 50 r/min speed for 15min. After quickly stirring for 30 seconds, the PSiAF prepared in the experiment 2.3 were added into the beakers with water samples. The water samples were place quietly for 30 min when slow stirring was over, Then, The clear liquid under 2 cm of the liquid level was taken to detect the residual turbidity, CODCr, and chromaticity.

2.5. Calculation method

2.5.1. The turbidity standard curve and the calculation of the turbidity removal rate

Turbidity(T) standard solutions of 0, 4, 10, 20, 40, 80 and 100 NTU were prepared with simulated waste water, the absorbance of these standard solutions were detected at a wavelength of 680nm by Uv-vis Spectrometer, the standard curve was plotted, as was shown in figure 1. Fitting equation is A=0.00157T-0.02233. The absorbance of water samples treated by PSiAF were detected under the same condition as turbidity standard sloutions, then the residual turbidity(RT NTU) of water samples was obtained through the turbidity standard curve. Use the following formula to calculate the turbidity removal rate (Tr%).
2.5.2. The chrominance standard curve and the calculation of the chrominance removal rate

A series of standard solution of methylene blue, which concentration were respectively 0 μg/l, 2 μg/l, 4 μg/l, 6 μg/l, 8 μg/l, 10 μg/l, were prepared, then absorbances of standard solutions were determined successively at the wavelength of 664 nm, the next, the standard curve was prepared as figure 2. the fitting equation is following: \( A = 0.874C - 0.00267 \), \( R = 0.99978 \). \( C \) is concentration of methylene blue, unit is μg. \( A \) is absorbance. Use the following formula to calculate the chrominance removal ratio. Chrominance means the concentration of methylene blue.

\[
\text{the chrominance removal ratio} \% = \frac{\text{raw water chrominance} - \text{residual chrominance}}{\text{raw water chrominance}} \times 100\%
\]

2.5.3. The calculation of COD Cr removal rate

COD Cr (mg/l) of the water samples treated by PSiAF were detected with DR3900+DRB 200 Laboratory COD analyzer. According to the following formulas to calculate the removal ratio of COD Cr:

\[
\text{removal ratio of } \text{COD Cr} \% = \frac{\text{raw water COD Cr} - \text{residual COD Cr}}{\text{residual COD Cr}} \times 100\%
\]

3. Results and discussion

3.1. The optimal dosage

The dosage of the flocculant influence tremendously the flocculation effect when wastewater or sewage was treated with the flocculation method. In general, the flocculation effect is increasing with the increase of dosage. But after a certain dosage the flocculant effect will no longer increase, sometimes the flocculant effect even declines. Therefore, it is necessary to determine the optimal dosage of the flocculant.

3.1.1. The dosage experiment result for simulating wastewater treated with PSiAF

Flocculation experiments were carried through according to the step 2.4 in five beakers filled 400 ml. Simulated wastewater, FSiAF prepared in the step 2.3 was added into the five beakers, the dosages were respectively 0.8 ml/L, 1.0 ml/L, 1.2 ml/L, 1.4 ml/L, 1.6 ml/L. After flocculation experiment, the turbidity removal rates were calculated according to the step 2.5.1. So the optimal dosage of
PSiAF was detected when FSiAF was used to treat simulated wastewater. The experiment results are shown as figure 3.

Figure 3 showed that the turbidity removal ratio of simulating wastewater was increasing with increasing the dosage of PSiAF within the dosage scope of 0.6~1.2ml/l, the turbidity removal ratio simulating wastewater was declining with increasing the dosage of PSiAF within the dosage scope of 1.2~1.4ml/l. The highest turbidity removal ratio equals to 70.83 when the dosage of PSiAF is 1.2ml/l.

3.1.2. The dosage experiment result for simulating dyeing wastewater treated with PSiAF
The simulating dyeing wastewater was treated referring to the experiment 3.1.1. the dosages were respectively 4.0ml/l, 5ml/l, 6.0ml/l, 7ml/l, 8ml/l. the chrominance of simulating dyeing wastewater are 5μg/l methylene blue. After flocculation experiment, the chrominance removal rates were calculated according to the step 2.5.2. So the optimal dosage of PSiAF was detected when FSiAF was used to treat simulated dyeing wastewater. the experiment results are shown as table 1.

| The dosage of PSiAF (ml/l) | Absorbance(Abs) | Residue chrominance(μg) |
|---------------------------|-----------------|------------------------|
| 4.0                       | 0.455           | 5.12                   |
| 5.0                       | 0.457           | 5.26                   |
| 6.0                       | 0.455           | 5.24                   |
| 7.0                       | 0.469           | 5.40                   |
| 8.0                       | 0.449           | 5.17                   |

From table 1, we can observe residual chrominance of water samples treated by PSiAF are bigger than 5μg of raw water chrominance. The data in the table 1 shows PSiAF is no decolorization effect to simulated dyeing wastewater prepared with methylene blue. Residual chrominance becomes bigger, the possible reason is that methylene blue reacted with certain component in PSiAF to produce new material which has a stronger absorption ability.

3.1.3. The dosage experiment result for domestic sewage treated with PSiAF
The domestic sewage was treated referring to the experiment 3.1.1. the dosages were respectively 5ml/l, 6.0ml/l, 7ml/l, 8ml/l, 9ml/l. After flocculation experiment, the turbidity removal rates were calculated according to the step 2.5.1. So the optimal dosage of PSiAF was detected when FSiAF was used to treat domestic sewage. the experiment results are shown as figure 3. Raw domestic sewage turbidity is 24.17 NTU under the condition of measurement.

Figure 4 showed that the turbidity removal ratio of domestic sewage was increasing with increasing the dosage of PSiAF within the dosage range of 5~8ml/l, the turbidity removal ratio simulating wastewater was declining with increasing the dosage of PSiAF within the dosage range of 8~9ml/l. The highest turbidity removal ratio equals to 62.07% when the dosage of PSiAF is 8ml/l.
3.2. The most adaptive pH of FSiAF used to treat water samples

During the flocculation process, the pH of water sample can affect the existence form of coagulant in water sample, so as to influence the treatment effect. The most adaptive pH must be investigated when PSiAF was used to treat water sample.

3.2.1. the adaptive pH experiment results for simulating wastewater treated with PSiAF

Flocculation experiments were carried through according to the step 2.4 in five beakers filled 400ml Simulating wastewater, FSiAF prepared in the step 2.3 was added into the five beakers, the dosages were 1.2ml/L. pH of raw water solutions were adjusted as 2, 4, 6, 8, 10 respectively. After flocculation experiment, the turbidity removal rates were calculated according to the step 2.5.1. The CODCr removal rates were calculated according to the step 2.5.3. So the adaptive pH of PSiAF was detected when FSiAF was used to treat simulated wastewater. The experiment results are shown as figure 5.

Figure 5 showed that the turbidity and CODCr removal ratio of simulating wastewater were increasing with increasing the pH of water samples within the pH range of 2–8, the turbidity CODCr removal ratio of simulating wastewater were declining with increasing the dosage of PSiAF within the pH range of 8–10. The highest turbidity and CODCr removal ratio equal to 76.04% and 58.33% respectively when the pH of simulating is 8.
3.2.2. the adaptive pH experiment results for simulating dyeing wastewater treated with PSiAF

In order to investigate decoloration effect of PSiAF at different pH, we used PSiAF to treat simulating dyeing wastewater referring to the experiment 3.2.1. The dosages were 9ml/L. pH of raw water solutions were adjusted as 3, 5, 7, 9, 11 respectively. After flocculation experiment, The chrominance removal rates were calculated according to the step 2.5.2. The chrominance of simulating dyeing wastewater are 5μg/l. The experiment results are shown in the table 2.

Table 2. the adaptive pH experiment result for simulating dyeing wastewater treated with PSiAF

| pH of water samples | Absorbance(Abs) | Residue chrominance(μg) |
|---------------------|-----------------|------------------------|
| 3                   | 0.468           | 5.39                   |
| 5                   | 0.459           | 5.28                   |
| 7                   | 0.448           | 5.16                   |
| 9                   | 0.462           | 5.32                   |
| 11                  | 0.450           | 5.18                   |

From table 2, we can observe residual chrominance of water samples treated by PSiAF are bigger than 5μg of raw water chrominance. The data in the table 2 shows PSiAF is no decolorization effect to simulated dyeing wastewater prepared with methylene blue within the pH range of 3~11. Residual chrominance becomes bigger, the possible reason is that methylene blue reacted with certain component in PSiAF to produce new material which has a stronger absorption ability.

3.2.3. the adaptive pH experiment results for domestic sewage treated with PSiAF

The domestic sewage was treated referring to the experiment 3.2.1. the dosages were 8ml/L. pH of raw water solutions were adjusted as 4, 6, 8, 10, 12 respectively. After flocculation experiment, the turbidity removal rates were calculated according to the step 2.5.1. The CODCr removal rates were calculated according to the step 2.5.3. So the adaptive pH of PSiAF was detected when PSiAF was used to treat domestic sewage. The experiment results are shown as figure 6. Raw domestic sewage turbidity is 24.17 NTU under the condition of measurement. The experiment results are shown as figure 6.

Figure 6. the pH experiment result for domestic sewage treated with PSiAF.

Figure 6 showed that the turbidity and CODCr removal ratio of domestic sewage were increasing with increasing the pH of water samples within the pH range of 4~6, the turbidity CODCr removal ratio of domestic sewage were declining with increasing the dosage of PSiAF within the pH range of 6~12. The highest turbidity and CODCr removal ratio equal to 67.25% and 46.15% respectively when the pH of domestic sewage is 6.
From the experiment results above, we can observe that there are the optimal dosages and the most adaptive pH range of water samples when PSiAF was used to treat simulating wastewater or domestic sewage. The reasons for this situation are that, on the one hand, contaminant particles in water samples are negatively charged, on the other hand, flocculation mechanism includes mainly charge neutralization, adsorption bridging and precipitation trapping. The zeta potential of water samples will change with the different of dosage of PSiAF and pH of water samples. Change neutralization has the best effect at isoelectric point of water samples, at this time the turbidity and CODCr removal ratio reach the highest level. The optimal dosages and the most adaptive pH are just the isoelectric point of water samples[7-8].

4. Conclusion
Leaching silicon, aluminum, iron in coal gangue for preparation poly-silicon-aluminum-iron flocculant is feasible.
Leaching conditions of aluminum and iron are as following: the concentration of mixed acid is 20%, the leaching time and temperature are 2 hours and 100℃ respectively, volume ratio of hydrochloric acid and sulphuric acid is 3:1, the solid-liquid ratio is 1:10.
Leaching conditions of silicon are as following: 4 mol/l sodium hydroxide.
The preparing condition of PSiAF are as following: the content of silica of 4%, Al/Fe molar ratio of 1:2, (Al+Fe)/Si molar ratio is 1:1 and the solution pH of 5 of sodium silicate.
The optimal dosage and the most adaptive pH are different when PSiAF was used to treat different water samples[9]. The flocculation effect was also different. Three kinds of water samples were treated with PSiAF. The flocculation conditions of PSiAF are as following: the optimal dosage is 1.2ml/L, and the most adaptive pH is 8 for simulation wastewater, under this condition, the turbidity removal ratio was 76.04%, the CODCr removal ratio was 58.33%. There is no decolorization effect for simulation dyeing wastewater, and PSiAF is not suitable for simulation dyeing wastewater. The optimal dosage is 8.0ml/L, and the most adaptive pH is 6 for domestic sewage, under this condition, the turbidity removal ratio was 67.25.04%, the CODCr removal ratio was 46.15%.

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