Study on The Preparation Technology of Poly-Silicate-Aluminum-Ferric (PSiAF) Coagulant Using Coal Gangue as Raw Material

Yuping Yang1,2, Qingcai Zhao1, Furong Zeng1, Yuanfei Zhang1

1School of Chemistry and Chemical Engineering, Anshun University, Guizhou, China
2Huzhou University Qiuzhen College, Zhejiang, China

Corresponding author: Yuping Yang (e-mail: yyp.cc@163.com)

Abstract. Si, Al, Fe were leached from coal gangue to prepare Poly-silicate-aluminum-ferric (PSiAF) coagulant. The optimal technology of preparation of PSiAF was explored through single factor experiment and orthogonal experiment. The effect factor of preparation, such as the content of silica, the molar ratio of Al to Fe (nAl:nFe), the molar ratio of metal (Al+Fe) to Si (nAl+Fe:nSi), the pH of the solution of sodium silicate, were investigated. Results show that The optimal preparation technology were the content of silica of 4%, Al/Fe molar ratio of 1:2, (Al+Fe)/Si molar ratio is 1:1 and pH of 5 of the solution of sodium silicate.

1. Introduction
The coal gangue is a charcoal grey hard solid waste which is produced with the process of coal mining and coal cleaning[1-2]. Its ingredients include aluminium oxide, silicon dioxide, ferric oxide, magnesium oxide, calcium oxide, potassium oxide, sodium oxide, sulfur trioxide, and so on. Coal gangue is usually stored outdoor, it not only takes up a lot of space, but also under the action of weathering, sun and rain, harmful material in coal gangue can cause serious pollution to the surroundings[3-4].

Si, Al, Fe were leached from coal gangue to prepare polymer inorganic coagulant (PSiAF) used in sewage treatment, it is one of the effective ways of coal gangue used, can solve for the occupation of land and environmental pollution caused by coal gangue piled up, at the same time, recycling waste can bring certain economic benefits. Therefore, the study of preparation of flocculant using coal gangue as raw material is very significant.

2. Materials and methods
2.1. Experimental apparatus and reagents
2.1.1. Experimental apparatus. 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.).

2.1.2. Experimental reagents. Coal gangue obtained from a Coal plants in Anshun city.
H₂SO₄ (AR), HCl (AR), NaOH (AR), AgNO₃ (AR), KF (AR), Na₂SiO₃·9H₂O (CP), Fe₂(SO₄)₃·XH₂O (AR), AlCl₃·6H₂O (AR), H₄H₂·H₂SO₄ (AR), C₆H₁₂N₄ (AR)

2.2. Experimental methods

2.2.1. The preparation of poly aluminum-iron solution. At first, the coal gangue power was calcinated in Muffle furnace, and then, leached for 2 hours at temperature of 100°C using mixed solution of sulfuric acid and hydrochloric acid. Filtering, the filtrate were evaporated to remove 50% of the water, the content of aluminum and iron in the filtrate were determined, following, adjust the molar ratio of Al to Fe, then, the pH of the solution was regulated. That is poly aluminum-iron solution.

2.2.2. The preparation of poly silicic acid solution. The filtered residue of 2.2.1 were calcinate again at the temperature 950°C. After that, the ash were leached with 40% sodium hydroxide solution to obtain sodium silicate solution. Adjust the concentration of silica to the amount of demand, the pH of the solution was regulated to help sodium silicate poly to generate poly silicic acid.

2.2.3. The preparation of poly-silicate-aluminum-ferric solution. According to the set proportion, mixing poly aluminum-iron solution with poly silicic acid, stirring at a quick speed, adjust the pH of the solution. Then, the solution is placed for 24 hours to activate and obtain Poly-silicate-aluminum-ferric.

2.2.4. Flocculation experiment and the calculation of the turbidity removal rate. 40 NTU simulated waste water was prepared with hydrazine sulfate and hexamethylenetetramine. 40 NTU simulated waste water was treated by poly-silicate-aluminum-ferric prepared in the experiment of 2.2.3 to investigate its flocculation property. The residual turbidity (Rt NTU) of water samples treated were determined by Uv-vis Spectrometer. Use the following formula to calculate the turbidity removal rate (Trr%).

\[
Trr(\%) = \left( \frac{40 - Rt}{40} \right) \times 100\%
\]

3. Results and discussion

3.1. The influence of the molar ratio of metal(Al+Fe) to Si on flocculation performance
In order to investigate the influence of nₐl⁺Fe⁺ₙₛᵢ on flocculation performance, through changing nₐl⁺Fe⁺ₙₛᵢ we implemented a series of experiments under the invariant condition of the solution pH=5 of the sodium silicate, nₐl⁺Fe⁺:nₛᵢ=1:2, the content of silica of 4%. The experimental results are shown in figure 1.

Figure 1 shows that nₐl⁺Fe⁺ₙₛᵢ can influence tremendously on the flocculation performance. As the diminishing of the molar rate of (Al+Fe)/Si, the change of turbidity removal efficiency as shown in figure 1, the best turbidity removal efficiency appear at nₐl⁺Fe⁺ₙₛᵢ=1:1, because the synergy of both adsorption bridging and charge neutralization is the flocculation mechanism of the composite PSiAF[5-6]. The suspended particles in simulated wastewater are generally negatively charged, so charge neutralization mechanism play a major part for removal of turbidity when the content of positively charged metal (Al+Fe) in composite flocculant is higher than isoelectric. With the increase of silicon content, negatively charged of the polysilicic acid neutralize positive charge of aluminum groups and iron groups, so that, the charge neutralizing abilities of PSiAF is gradual weakening. At the other hand, flocculant molecular chains increase simultaneously with the increase of silicon content increasing, and its adsorption bridging ability increased rapidly, that is why the turbidity removal efficiency increases with increase of silicon content within the scope of the molar rate of (Al+Fe)/Si 3:1~1:1. The best synergy effect of charge neutralization with adsorption synergies was achieved when the molar rate of (Al+Fe)/Si is equal to 1:1, so the flocculation effect is the best. With the further increase
of silicon content, within the range of \( n_{Al+Fe}:n_{Si} < 1:1 \), charged neutralization ability of PSiAF greatly diminished but its adsorption bridging ability no longer increased, this is because the chain is no longer growing due to limits of the principle of aggregation, so that its flocculation performance is gradually weakening, turbidity removal efficiency is relatively poor.

![Figure 1. The influence of the molar ratio of metal(Al+Fe) to Si on flocculation performance.](image)

3.2. The influence of the molar ratio of Al to Fe on flocculation performance

![Figure 2. The influence of the molar ratio of Al to Fe on flocculation performance.](image)

In order to investigate the influence of \( n_{Al}:n_{Fe} \) on flocculation performance, through changing the molar rate of Al/Fe, we conducted a series of under the invariant condition of the solution pH=5 of the sodium silicate, \( n_{Al+Fe}:n_{Si} = 1:1 \), the content of silica of 4%. The experimental results are shown in figure 2.

Figure 2 indicates that In the range from 3:1 to 2:1 of the molar rate of Al/Fe, flocculation effect becomes poor with the aluminum content decreasing. Iron salts dissolved in the water to generate a series of hydroxy complex such as \( Fe_m (OH)_{(3-n \cdot m)^+} \), similarly, aluminium salts can also produce
hydroxy complex such as Alₙ(OH)ₘ⁻(3, n-m)⁺. These two kinds of material can reduce and eliminate zeta potential of suspended particle in water, and accelerate colloidal particles to agglomerate by the mechanisms of charge neutralization and compressed double electric layer\(^7\). But because the volume of Alₙ(OH)ₘ⁻(3, n-m)⁺ is less than the volume of Feₙ(OH)ₘ⁻(3, n-m)⁺, Alₙ(OH)ₘ⁻(3, n-m)⁺ is easier to attract the colloidal particle with negatively charged in water, high aluminum content, is advantageous to the turbidity removal efficiency. Therefore, in determinate proportion of the molar rate of Al³⁺/Fe⁺/Si, within the scope from 3:1 to 2:1 of the molar rate of Al/Fe, the flocculation effect is worse and worse with the decreasing of aluminum content. In the range from 2:1 to 1:2 of the molar rate, flocculation effect gradually increase, this is because the polymer adsorption bridging role gradually dominant advantage, flocculation effect is getting better and better by the synergy with both adsorption bridging and charge neutralization. The best flocculation effect is obtained when \(n_{\text{Al}}:n_{\text{Fe}}\) equals to 1:2, in the case of this, the turbidity removal efficiency is above 95%. As the further increase of iron content, flocculation effect began to reduce, on the one hand it is because adsorption bridging ability no longer increases, on the other hand excess iron content, acid radical ions react with iron to form sediment easily, reduce the charge neutralization effect, thus weaken the flocculation effect.

3.3. The influence of the solution pH of sodium silicate on flocculation performance
In order to investigate the influence of the solution pH of sodium silicate on flocculation performance, through changing the solution pH of sodium silicate, we conducted a series of experiments under the invariant condition of \(n_{\text{Al}}:n_{\text{Fe}}=1:2, n_{\text{Al}+\text{Fe}}:n_{\text{Si}}=1:1\), the content of silica of 4%. The experimental results are shown in figure 2.

![Figure 3. The influence of the solution pH of sodium silicate on flocculation performance.](image)

The figure 3 indicated that, in range of pH from 2 to 5, the turbidity removal effect was constantly enhancing with the pH increasing of the sodium silicate solution, and the pH of the sodium silicate solution was 5.0, the flocculation performance was the best and the turbidity removal efficiency was the highest. The flocculation effect became poor again when the pH of the sodium silicate solution further increased, the reason of this change rule is because the activating pH of the sodium silicate solution determines the polymerization speed of silicic acid and the chain length of polysilicic acid molecular, if the pH is too low, the polymerization speed of the sodium silicate solution is slower that
the activation time is longer, the chain length of flocculant is shorter, the turbidity removal efficiency is poorer. If the pH is too high, the polymerization speed is faster, the molecular chain of polysilicic acid rapidly enlarges in very short time, it easily induce the molecular of polysilicic acid from chain molecules into three-dimensional molecular, then appear gelling, at this time, flocculation effect will be worse. The experimental result suggested than 5 is the most appropriate pH.

3.4. The influence of the content of silica on flocculation performance

In order to investigate the influence of the content of silica on flocculation performance, through changing the content of the sodium silicate solution, we conducted a series of experiments under the invariant condition of n_{Al}:n_{Fe}=1:2, n_{Al+Fe}:n_{Si}=1:1, the solution pH=5 of sodium silicate. The experimental results are shown in figure 4.

![Figure 4. The influence of the content of silica on flocculation performance.](image)

It can be seen from the figure 4 that, within the scope of the silica content of 2-4%, the sodium silicate solution polymerized to form linear molecules under acid condition, this is advantageous to the adsorption bridging of flocculant. The longer is the polysilicic acid molecular chain the stronger is adsorption bridge ability, the molecular chain of PSiAF became synchronously longer, therefore the flocculation effect enhanced. After the content of SiO_2 is more than 4%, the polysilicic acid molecular chain gradually became bigger from the linear into bulk, the flocculation effect became poor. The content of SiO_2 is 4%, flocculating effect is the best, the turbidity removal efficiency is the highest.

3.5. Orthogonal test

The results of the single factor experiment suggested that, the molar rate of Al/Fe, the molar rate of Al+Fe/Si, the solution pH of sodium silicate and the content of silica, four factors have important impacts on flocculation effect, in order to investigate the interaction influence of four factors together on flocculation effect, we carried out the orthogonal experiments of four factors three levels (L_{3}^{4}) shown as table 1, the experimental results are shown in table 2.

| Table 1  | Level of factors |
|----------|------------------|
|          | n_{Al}:n_{Fe} (A) | n_{Al+Fe}:n_{Si} (B) | pH (C) | SiO_2% (D) |
| level    | The molar ratio   | The molar ratio of   | the solution pH of | the content of |
|          |                   |                   |             |            |
of Al/Fe  Al+Fe/Si  sodium silicate  silica

|    | of Al/Fe | Al+Fe/Si | sodium silicate | silica |
|----|----------|----------|-----------------|--------|
| 1  | 1:1      | 2:1      | 3               | 3      |
| 2  | 1:2      | 1:1      | 4               | 4      |
| 3  | 1:3      | 1:2      | 5               | 5      |

**Table 2** Plan and result of orthogonal test

| serial number | A   | B   | C   | D   | turbidity removal efficiency % |
|---------------|-----|-----|-----|-----|--------------------------------|
| 1             | 1   | 1   | 1   | 1   | 40.875                         |
| 2             | 1   | 2   | 2   | 2   | 82.291                         |
| 3             | 1   | 3   | 3   | 3   | 90.666                         |
| 4             | 2   | 1   | 2   | 3   | 84.375                         |
| 5             | 2   | 2   | 3   | 1   | 93.625                         |
| 6             | 2   | 3   | 1   | 2   | 85.916                         |
| 7             | 3   | 1   | 3   | 2   | 84.375                         |
| 8             | 3   | 2   | 1   | 3   | 88.333                         |
| 9             | 3   | 3   | 2   | 1   | 58.333                         |
| I             | 213.832 | 209.625 | 215.124 | 192.833 | Impact order: D>B>C>A          |
| II            | 263.916 | 264.249 | 224.999 | 252.582 |
| III           | 231.041 | 234.915 | 268.666 | 263.374 |
| K₁            | 71.277  | 69.875  | 71.708  | 64.278  |
| K₂            | 87.972  | 84.803  | 89.555  | 87.791  |
| K₃            | 77.014  | 78.305  | 89.555  | 87.791  |
| R             | 16.695  | 18.208  | 17.847  | 23.513  |

By range value (R) of orthogonal test, the impact order of the four factors followed as decreasing order: the content of silica in sodium silicate solution, the mole ratio of Al+Fe/Si, the solution pH of sodium silicate, the mole ratio of Al/Fe. From the results of the orthogonal test, the most optimal preparation conditions of PSiAF is that \( n_{Al} : n_{Fe} = 1:2 \), \( n_{Al+Fe} : n_{Si} = 1:1 \), the pH of sodium silicate solution = 5, the content of silica = 5.0%. In the single factor experiment, we found that the content of SiO₂ was more than 4%, polymerization speed was very fast, the stable time of the polysilicic acid was very short, the polysilicic acid solution would gel in 2 hour\(^{[10-11]}\), this will lead to unable to carry through the next step of preparation of PSiAF. Further, the data of the orthogonal experiment indicated that the difference value of the turbidity removal efficiency was only 3.597% when the content of silica was 4% and 5% respectively. The effect is very good with 4% of the silica to prepare PSiAF, flocculation effect has a bit of a loss, but the stability of the flocculant is greatly increased, so 4% was choosed as the content of silica. Then, the orthogonal experiment results are consistent with the results of single factor.

### 4. Conclusion

Leaching silicon, aluminum, iron in coal gangue for preparation poly-silicon-aluminum-iron flocculant is feasible.

By single factor experiments and orthogonal experiments, the optimum preparation conditions for poly-silicon-aluminum-iron flocculant was explored. The experiment results suggested that the most optimal preparation conditions of PSiAF is that \( n_{Al} : n_{Fe} = 1:2 \), \( n_{Al+Fe} : n_{Si} = 1:1 \), the pH of sodium silicate solution = 5, the content of silica = 4.0%.
Acknowledgments
This research was supported by grants from three-way joint funds of Science and technology department of Guizhou province, Science and technology administration office of Anshun city and Anshun University ([2016]7270), and the Doctor Fund of Anshun University (asubsjj201502).

References
[1] Sun C B, Zhang J S and Cao Z 2016 Resource Utilization ways of coal gangue and its development Multipurpose. Util. Miner. Resour. 12 1-12.
[2] Lin M 2018 Comprehensive utilization of coal gangue Shanghai. Build. Mater. 4 29-31.
[3] Wang R G and Wang L M 2013 Preparation of polymeric aluminum chloride from coal gangue and its application on wastewater treatment Technol. Water. Treat. 39 48-50.
[4] Lopamudra P, Pradip K B, Surendra K B, Venugopal, R and Mandre N R 2013 Performance evaluation for selectivity of the flocculant on hematite in selective flocculation Int. J. Miner., Metall Mater 12 1123-29
[5] Heiderscheidt E, Saukkoriipi J, Ronkanen A K and Bjorn K 2013 Optimisation of chemical purification conditions for direct application of solid metal salt coagulants: Treatment of peatland-derived diuse run off J. Environ. Sci. 25 659–69
[6] Gao B Y, Chu Y B, Yue Q Y and Wang Y 2009 Purification and characterization of Al13 species in coagulant polyaluminum chloride J. Environ. Sci. 21 18–22
[7] Jiang S J, Liu Z Y and Liang J J 2009 Effects of pH value and coagulant dosage on contact filtration of humic substances J. Cent. South. Univ. Technol. 16(s1) 384–90
[8] Wang Y F, Gao B Y, Yue Q Y and Wang Y 2011 Effect of viscosity, basicity and organic content of composite flocculant on the decolorization performance and mechanism for reactive dyeing wastewater J. Environ. Sci. 23 1626–33
[9] Ma H X, Li Y C and Xiao Z 2012 The preparation and application of chitosan compound flocculant meteor. Environ. Res. 3 22–24, 29
[10] Niu X X, Li X L, Zhao J H, Ren Y G and Yang Y Q 2011 Preparation and coagulation efficiency of polyaluminium ferric silicate chloride composite coagulant from wastewater of high-purity graphite production J. Environ. Sci. 23 1122–28
[11] Ferreira F, Sidney S, Margarida M and Rosemeire A L 2013 Interference of iron as a coagulant on MIB removal by powdered activated carbon adsorption for low turbidity waters J. Environ. Sci. 25 1575–82