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PREPARATION OF POLYMERIC ALUMINIUM FERRIC CHLORIDE FROM BAUXITE TAILINGS

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Abstract

Bauxite tailings are the main solid wastes in the ore dressing process. The Al_2O_3 and Fe_2O_3 contents in bauxite tailings can reach 50% and 13% respectively. The present study proposed a feasible method to use bauxite tailings to prepare polymeric aluminium ferric chloride (PAFC), a new composite inorganic polymer for water purification. Bauxite tailings roasted reacted with hydrochloric acid under air, pickle liquor which mainly contains Fe^{3+}, Al^{3+} was generated, then calcium aluminate was used to adjust pH value and the basicity of the pickle liquor, the PAFC was subsequently prepared after the polymerization process. The optimal synthesizing parameters for the preparation of PAFC obtained were as follows: the concentration of hydrochloric acid of 24 wt%, ratio of hydrochloric acid to bauxite tailings of 6:1, temperature of 90°C, leaching time of 2.5 hours, ratio of pickle liquor to calcium aluminate of 12:1, polymerization temperature of 90°C and polymerization time of about 3 hours. The basicity of PAFC was higher than 68%, the sum concentration of Al_2O_3 and Fe_2O_3 was beyond 12.5%. The results of flocculation tests indicate that the PAFC has a better performance of removing the turbidity of wastewater compared to PAC, and PAFC prepared by bauxite tailings is a kind of high quality flocculants.

Keywords: *Bauxite tailings; PAFC; Hydrochloric acid leaching; Calcium aluminate.*

1. Introduction

Bauxite tailings are one of the main solid wastes generated in the flotation-Bayer process which uses low grade bauxite ore to produce alumina in China [1]. About 30wt% bauxite tailings are produced in every one ton Al_2O_3 producing. At present, most of them are deposited on land surface without any utilization, which pollutes environment seriously. In recent years, much attention has been paid to utilize bauxite tailings to produce refractory, construction material, absorbent material and alloy material [2-5]. The main chemical components of bauxite tailings include Al_2O_3, SiO_2, Fe_2O_3, TiO_2 and K_2O [6]. The content of alumina and ferric oxide in bauxite tailings are as high as 50% and 13%, respectively, while Fe^{3+} salts and Al^{3+} salts are most commonly used as coagulation in water treatment. Hence, according to the chemical composition of bauxite tailing, it is suitable for the production of polymeric aluminium ferric chloride.

Polymeric aluminum ferric chloride (PAFC in abbreviation) is a new inorganic compound coagulant which is widely used in water purification. The main chemical components in PAFC are Fe^{3+}, Al^{3+}, Cl^-, and OH^-. It has been developed from pre-hydrolyzing $AlCl_3$ and $FeCl_3$ by alkali [7]. It has a higher capacity on flocculating and condensation, and could produce large floc aggregates which can be removed from the waste water in subsequent filtration processes [8]. Raw Material for synthesis of PAFC are various, Genli Wang prepared PAFC by bauxite, but waste acid containing Fe was needed to increase the iron content of PAFC [9]. Shihua Pang prepared PAFC by red mud, but it is low content of Al [10]. Other material like mineral (such as gibbsite, bauxite, hematite), pure reagent (such as aluminium chloride, pure ferric chloride, aluminium hydroxide) and industrial wastes (such as blast furnace dust, gangue, hydrochloric pickle liquor) [11-13] for preparing PAFC are either high-cost or low content of Al and Fe. Bauxite tailings are a kind of solid wastes which contain large amounts of Al and Fe (up to 49% and 13% respectively), so that it is reasonable to suggest that if the high cost of raw materials are replaced by bauxite tailings, it may not only reduce the cost for preparing PAFC, but also be an effective way to utilize bauxite tailings. However, relative works have seldom been reported.

In this paper, a feasibility of the preparation route from bauxite tailings to polymeric aluminum ferric chloride (PAFC) was investigated. The composition of PAFC was characterized, and the flocculation performance of PAFC was investigated as well.

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2. Experiment
2.1 Material and methods

The bauxite tailings (Zhengzhou, Henan Province, China), hydrochloric acid (analytical grade, 37wt%) and calcium aluminate (Gongyi, Henan Province, China), were chosen as raw materials for the preparation of PAFC. Kaolin (Lingshou, Hebei Province, China), Polymeric aluminium chloride (PAC in abbreviation, from Gongyi, Henan Province, China), NaOH and HCl (analytical grade) were chosen as materials for the flocculation performance test of PAFC. All aqueous solutions in this study were prepared with de-ionized water.

The chemical composition of bauxite tailings and calcium aluminate were shown in Table 1. The X-ray diffraction pattern of bauxite tailings were shown in Figure 1. It was observed that Al_2O_3, SiO_2, Fe_2O_3, TiO_2, K_2O had constituted the major main chemical compositions of bauxite tailings, while its main mineral compositions were diaspore, kaolinite, with a small amount of hematite, anatase, etc.

The PAC was provided by Huaming Chemical material Co., in Gongyi, Henan Province, China. It is a kind of buff liquid produce, the content of Al_2O_3 in PAC is higher than 8%, and basicity of PAC is higher than 70%.

2.2 Preparation and characterization of PAFC

The preparation of PAFC consists of 2 main steps, hydrochloric acid leaching and polymerization process.

The objective of hydrochloric acid leaching process is to dissolve Al_2O_3 and Fe_2O_3 in bauxite tailings as much as possible. In this process, bauxite tailings were firstly shattered, grinded and roasted. The preheated bauxite tailings were directly reacted with hydrochloric acid in the air. Aluminum oxide and ferric oxide were dissolved in hydrochloric acid gradually. At the end of this process, the liquor mainly contained $AlCl_3$, $FeCl_3$ and residual acid, while the solid mainly contained SiO_2. After the solid-liquid separation, pickle liquor which mainly contained Al^{3+}, Fe^{3+} and residual acid was gernerated.

The concentration of hydrochloric acid, the ratio of hydrochloric acid to bauxite tailings, the leaching temperature and the leaching time affected the dissolution ratio of Al_2O_3 and Fe_2O_3 in bauxite tailings. Therefore, these 4 parameters were detailed investigated and their synthesis composition were shown in Table 2.

The next process was followed by polymerization process. Al^{3+} and Fe^{3+} in pickle

Table 1. *Chemical compositions of bauxite tailings and calcium aluminate (wt%).*

	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	K_2O	CaO	Na_2O	MgO	Ig
Bauxite tailings	49.87	22.45	13.1	2.61	2.25	0.41	0.23	-	11.5
Calcium aluminate	58.51	-	3.96	0.42	-	26.72	0.11	-	-

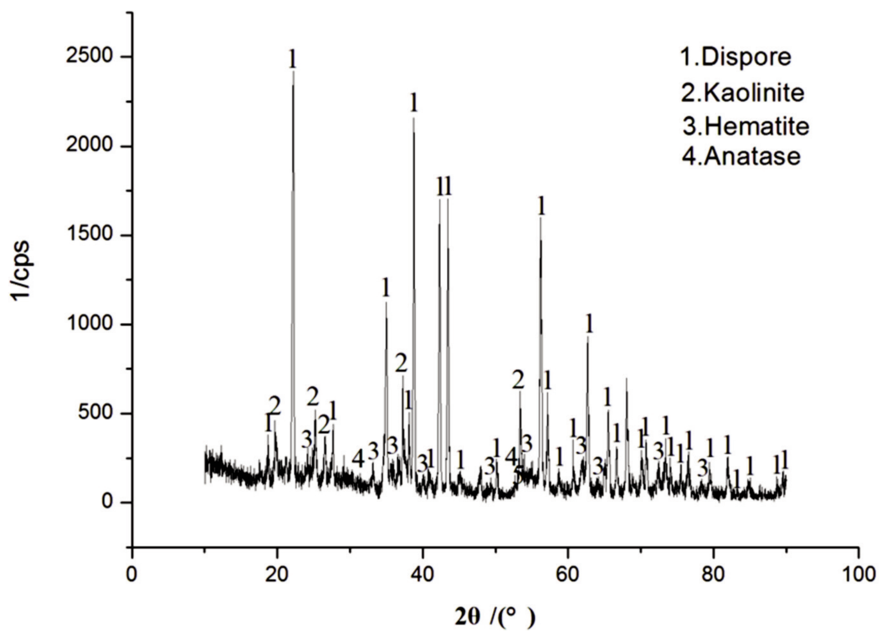


Figure 1. *XRD pattern of bauxite tailings.*

Table 2. *The synthesis parameters in hydrochloric acid leaching process.*

Parameters	Conditions
Hydrochloric acid concentration (C_L)	12%, 16%, 20%, 24%, 28%
Ratio of hydrochloric acid to bauxite tailings (wt/wt)(R_L)	4:1, 5:1, 6:1, 7:1, 8:1
Acid leaching temperature (T_L)	75° C, 80 °C, 85 °C, 90 °C, 95 °C
Acid leaching time (H_L)	1h, 1.5h, 2h, 2.5h, 3h

liquor were expected to be hydrolyzed in this process and then the macromolecule hydroxyl polymer of Al and Fe would generate.

At the beginning of polymerization, Al^{3+} and Fe^{3+} in pickle liquor were exist as $Al(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$, they could not hydrolyze and polymerize in acidic conditions cause of residual acid. Calcium aluminate was added into the pickle liquor to neutralize residual acid and raise the pH value of the pickle liquor. With increased the pH value, $Al(H_2O)_6^{3+}$ and $Fe(H_2O)_6^{3+}$ were gradually hydrolyzed, polymerized and copolymerized. After polymerization and copolymerization reaction reached equilibrium, most Al and Fe existed as polymeric aluminium ferric chloride (PAFC), PAFC was then successfully synthesized.

Basicity (B) is the most characterizations to represent the degree of polymerization of PAFC. It represents the averages quantity of hydroxyl ligands combined with metal atoms. The higher the basicity is, the higher the degree of polymerization is, the better the flocculation performance of PAFC would be.

The basicity of PAFC was deeply depended on the ratio of calcium aluminate to pickle liquor, the polymerization reaction time and the polymerization reaction temperature, respectively. Hence, the relationship between the basicity of PAFC and the polymerization parameters were detailed investigated and their synthesis composition were shown in Table 3.

Table 3. *The Parameters in polymerization process.*

Parameters	Conditions
Ratio of pickle liquor to calcium aluminate (R_P)	60:6, 60:5, 60:4, 60:3
Polymerization temperature (T_P)	70°C, 80°C, 90°C, 100°C
Polymerization time (H_P)	2h, 3h, 4h, 5h

2.3 Flocculation test

Turbidity removal is the most characterizations of the performance of PAFC in flocculation test. Turbidity removal tests were performed in kaolin turbid liquid. The kaolin turbid liquid was prepared by adding 100mg kaolin to 1.0L deionized water. The performance of PAFC were investigated compared with PAC which is widely applied as a traditional flocculant. In the turbidity removal test, varied volumes of PAFC (PAC) were loaded into 1.0L turbid liquid with varied pH value, respectively. Then the mixture was stirred under a rotate speed of 300rmin^{-1} for 3min, and then 30rmin^{-1} for 7min, after it was deposited and kept static for 10min. Finally, the water below surface's 10cm was fetched to perform turbidity removal test by turbid meter.

The Turbidity was measured under varied dose of PAFC and PAC (D_P), pH value of kaolin turbid water (pH_K), respectively. Their synthesis composition was shown in Table 4.

Table 4. *The Parameters in Turbidity removal test.*

Parameters	Conditions
Dose of PAFC and PAC (D_P)	2,4,6….12 ml
pH value of kaolin turbid water (pH_K)	2,4,6….12

2.4 Chemical and phase analysis

The mineral composition of bauxite tailings was measured by X-Ray Diffract meter (XRD) with Cu K radiation in the range 10-100° (2θ) at a scan rate of 5°min^{-1} supplied from Japan. The pH value of pickle liquor was measured by pH meter supplied by PHS-29A from Shanghai, China.

The dissolution ratio of Al_2O_3 (Dis_A) and Fe_2O_3 (Dis_F) of bauxite tailings were calculated as shown in equation (1) and (2).

$$Dis_A = {Con_{AB} - Con_{AL}} \Big/ {Con_{AB}} \quad ...(1)$$

$$Dis_F = {Con_{FB} - Con_{FL}} \Big/ {Con_{FB}} \quad ...(2)$$

In the equation (1), Con_{AB} (Con_{FB}) was the content of Al_2O_3 (Fe_2O_3) in bauxite tailings. Con_{AL} (Con_{FL}) was content of Al_2O_3 (Fe_2O_3) in pickle liquor, which was measured by ICP (Inductive Coupled Plasma Emission Spectrometer).

Basicity (B) of PAFC was measured as equation shown in Equal. (3) [14].

$$B = [OH]^- \Big/ 3[Fe_T + Al_T] \times 100\% \quad (3)$$

In the equation (3), $[OH]^-$ were the mole amounts of hydroxyl in pickle liquor after the caluminate aluminate was hydrolyzed. Fe_T and Al_T were the mole amounts Fe^{3+} and Al^{3+} in pickle liquor, it was measured by ICP.

Turbidity of kaolin turbid water was measured by turbid meter WGZ-800 supplied from Shanghai, China.

3. Results and Discussions

3.1 Acid leaching process

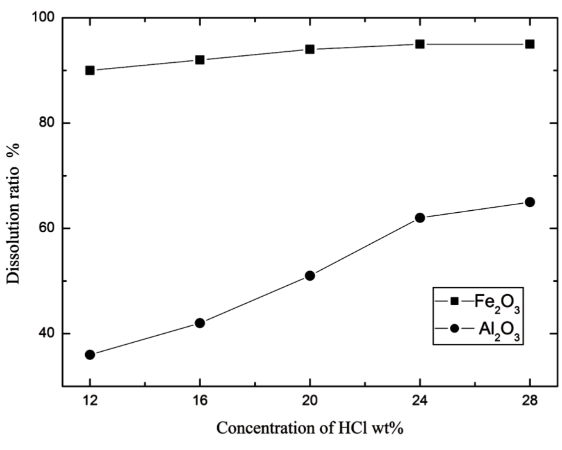
Preparation of PAFC began with the acid leaching process. The preheated bauxite tailings were directly reacted with hydrochloric acid. Al_2O_3 and Fe_2O_3 were dissolved in hydrochloric acid, and pickle liquor which mainly contained Al^{3+} and Fe^{3+} was generated. The main reactions in this process were shown in equation (4) - (5).

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O \tag{4}$$

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \tag{5}$$

Al^{3+} and Fe^{3+} in pickle liquor were the most important components of PAFC. High contents of Al^{3+} and Fe^{3+} will enhance the polymerization in the next process. Hence, higher dissolution ratios of Al_2O_3 and Fe_2O_3 in bauxite tailings were expected. In order to increase the dissolution ratio of Al_2O_3 and Fe_2O_3, the parameters of acid leaching process were detailed investigated, namely, the concentration of hydrochloric acid (C_L), ratio of hydrochloric acid to bauxite tailings (R_L), leaching temperature (T_L) and leaching time (H_L).

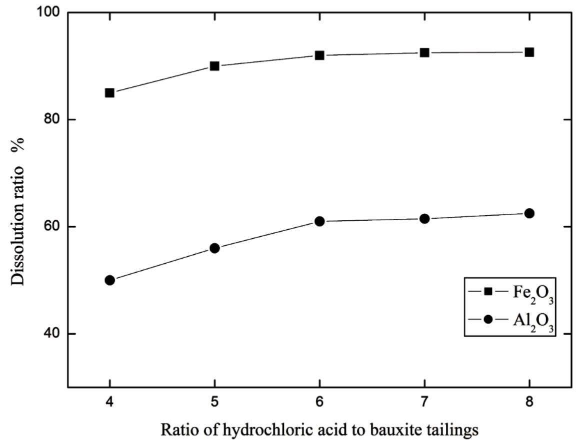
The dissolution ratios of Al_2O_3 and Fe_2O_3 in bauxite tailings depended on each parameter were shown in Figure 2 to Figure 5.



(R_L=8:1, T_L=95°C, H_L=3h)

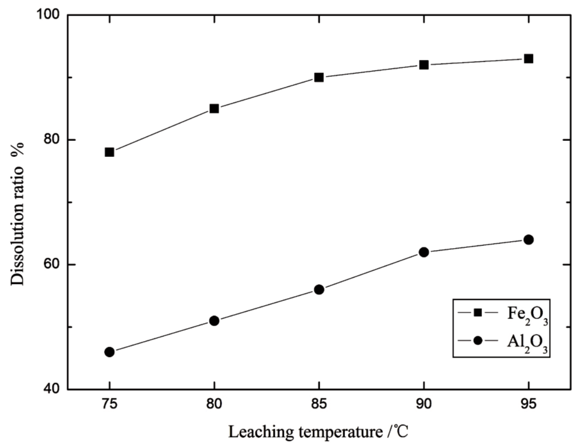
Figure 2. *Dissolution ratio of Al_2O_3 and Fe_2O_3 under varied C_L.*

From Figure 2 to Figure 5, it was shown that the dissolution ratio of Al_2O_3 and Fe_2O_3 in bauxite tailings increased along with the increase of the concentration of hydrochloric acid (C_L), ratio of hydrochloric acid to



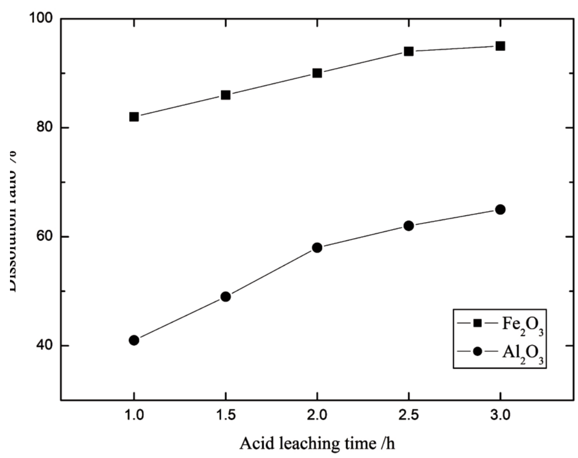
(C_L=24 wt%, T_L=95 °C, H_L=3h)

Figure 3. *Dissolution ratio of Al_2O_3 and Fe_2O_3 under varied R_L.*



(C_L=24wt%, R_L=6:1, H_L=2.5 h)

Figure 4. *Dissolution ratio of Al_2O_3 and Fe_2O_3 under varied T_L.*



(C_L=24wt%, R_L= 6:1, T_L=90 °C)

Figure 5. *Dissolution ratio of Al_2O_3 and Fe_2O_3 under varied H_L.*

bauxite tailings (R_L), leaching temperature (T_L) and leaching time (H_L). Because as the increase of C_L and T_L, kinetic condition of acid leaching process improved, the dissolution rate increased therewith. However, too high C_L and T_L would lead to the volatilization of hydrochloric acid. So, C_L of 24wt% and T_L of 90^{o}C were selected as the best parameters. With the increase of R_L, surplus acid was increased which was beneficial to the dissolution of Al_2O_3 and Fe_2O_3. But exorbitant R_L would generate much residual acid in pickle liquor which would consume large amounts of calcium aluminate to neutralize in the next process. Therefore, R_L of 6:1 was chosen as the optimal parameter. With the increase of H_L, leaching reaction continued, but the reaction reached equilibrium at H_L of 2.5 hours, so it was selected as the best parameter. Finally, according to the analysis above, C_L of 24wt%, R_L of 6:1, T_L of 90 ^{o}C and H_L of 2.5 hours were the optimal parameters of the acid leaching process, the dissolution ratio of Al_2O_3 and Fe_2O_3 reached 62.4% and 93.5% under this circumstances, respectively.

3.2 Polymerization process

After the acid leaching process, pickle liquor mainly contained Al^{3+}, Fe^{3+} and residual hydrochloric acid. Al^{3+} and Fe^{3+} existed as $Al(H_2O)_6^+$ and $Fe(H_2O)_6^+$. They couldn't hydrolyze under a very low pH value. Then, calcium aluminate ($CaO{\cdot}Al_2O_3$, $CaO{\cdot}2Al_2O_3$) was added into the pickle liquor gradually to neutralize the residual acid and raise the pH value of pickle liquor. Calcium aluminate was mainly made up of alkaline oxides as shown in table 1, once it was added into the pickle liquor, reaction immediately occurred as equation (6) and (7) showing.

$$CaO\cdot Al_2O_3 + 8HCl \rightarrow CaCl_2 + 2AlCl_3 + 4H_2O \quad (6)$$

$$CaO\cdot 2Al_2O_3 + 14HCl \rightarrow CaCl_2 + 4AlCl_3 + 7H_2O \quad (7)$$

With the progressing of reaction, residual hydrochloric acid was gradually neutralized, the content of Al^{3+} in pickle liquor slowly increased, and pH value of pickle liquor increased too, $Al(H_2O)^{6+}$ and $Fe(H_2O)^{6+}$ hydrolyzed gradually as shown in equation (8) - (11). Also, polymer of Al and Fe were generated gradually by the polymerization and copolymerization as shown in equation (12) - (14) [14].

$$Al(H_2O)_6^{3+} + H_2O \leftrightarrow Al(OH)(H_2O)_5^{2+} + H_3O^+ \quad (8)$$

$$Al(H_2O)_5^{2+} + H_2O \leftrightarrow Al(OH)_2(H_2O)_4^{2+} + H_3O^+ \quad (9)$$

$$Fe(H_2O)_6^{3+} + H_2O \leftrightarrow Fe(OH)(H_2O)_5^{2+} + H_3O^+ \quad (10)$$

$$Fe(H_2O)_5^{2+} + H_2O \leftrightarrow Fe(OH)_2(H_2O)_4^{+} + H_3O^+ \quad (11)$$

$$2FeCl_3 + nH_2O \rightarrow Fe_2(OH)_nCl_{6-n}^{\ -} + nCl^- + nH^+ \quad (12)$$

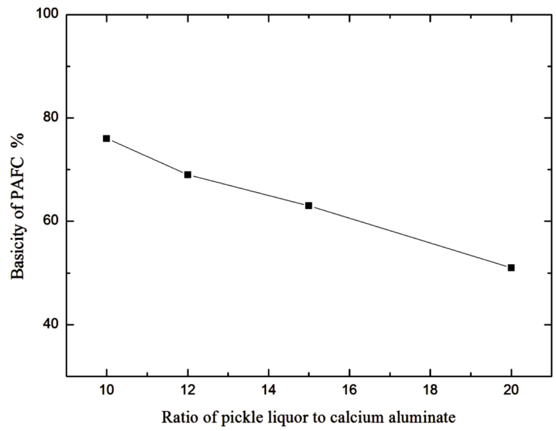
$$2AlCl_3 + mH_2O \rightarrow Al_2(OH)_mCl_{6-m}^{\ -} + mCl^- + mH^+ \quad (13)$$

$$xFe_2(OH)_nCl_{6-n} + yAl_2(OH)_mCl_{6-m} \rightarrow \rightarrow Fe_{2x}Al_{2y}(OH)_{xn+ym}Cl_{6x-xn+6y-ym} \quad (14)$$

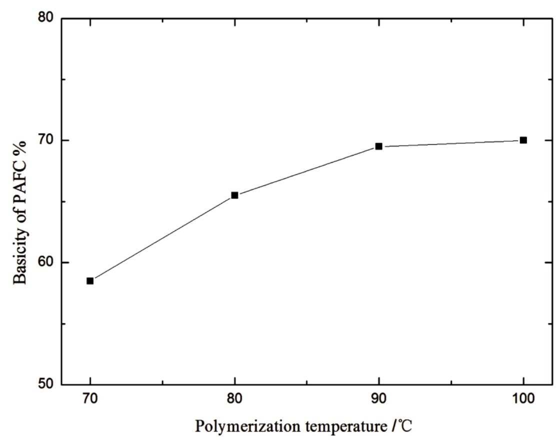
At the end of the polymerization process, most Al and Fe exited as polymeric aluminium ferric chloride, PAFC was successfully synthesized.

Basicity (B) is the most characterizations representing the degree of polymerization of PAFC. Basicity signifies the average quantity of hydroxyl ligands combined with Al and Fe atoms. Higher basicity will enhance the flocculation performance, but the PAFC will precipitate easily when the basicity is higher than about 80%. Therefore within the approved basicity, higher basicity will achieve a better flocculation performance of PAFC. In the condition that PAFC was stable without precipitation, the highest basicity was reported to be around 70% [15].

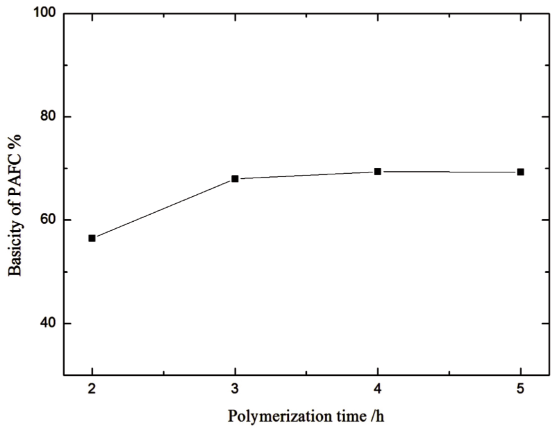
The ratio of pickle liquor to calcium aluminate (R_P), polymerization temperature (T_P) and polymerization time (H_P) affected the basicity of PAFC, therefore, these 3 parameters were investigated as shown in Figure 6 to Figure 8.



(T_P=90^{o}C, H_P= 4h)
Figure 6. *Basicity of PAFC under varied R_P.*



(R_P=12, H_P= 4h)
Figure 7. *Basicity of PAFC under varied T_P.*



(R_P=12, T_P= 90 °C)

Figure 8. *Basicity of PAFC under varied H_P.*

From Figure 6, it was shown that, with the decrease of R_P, the dosage of calcium aluminate added into pickle liquor increased. Therefore the hydroxyl generated by hydrolyzing of calcium aluminate increased, as a result the basicity of pickle liquor increased. While the optimum basicity of PAFC is about 70% according references [15], So R_P of 12:1 was chosen to be the optimal parameter.

From Figure 7, it was shown that the basicity of pickle liquor was increased with the increase of polymerization temperature (T_P). That's because, with the increase of T_P, kinetic condition of polymerization process improved, therefore the dissolution rate of calcium aluminate and polymerization rate of PAFC increased, so the basicity increased. However as the T_P is 90 °C, basicity reached a maximum, exorbitant T_P would lead to the evaporation of liquid which was useless to the polymerization process. So T_p of 90 °C was selected to be the best parameter.

Figure 8, it showed that with the increase of H_P, the basicity of pickle liquor was increased. Because, as H_P increased, the dissolution ratio of calcium aluminate and polymerization ratio of PAFC increased. However, the reaction reached equilibrium as polymerization time was 3 hours. So H_P of 3 hours was chosen to be the optimal parameter.

Finally, according to the analysis above, R_P of 12:1, T_p of 90 °C and H_P of 3 hours were the optimal parameters of polymerization process.

PAFC was successfully synthesized after the polymerization process under the optimal synthesis parameters. The basicity of PAFC was higher than 68%. According to the ICP measurement, the sum concentration of Al_2O_3 and Fe_2O_3 was beyond 12.5% (the concentration of Al_2O_3 and Fe_2O_3 were calculated from the concentration of Al^{3+} and Fe^{3+} in the pickle liquor).

3.3 Flocculation test

Turbidity removal test was carried out in kaolin turbid liquid. The pH value and turbidity of the kaolin turbid liquid were 7.2 and 130NTU, respectively. Dose of PAFC and PAC (D_P) affected the performance of flocculation test. Also, pH value of kaolin turbid liquid (pH_K) was an important factor for the turbidity removal test as well. The turbidity removal performance of PAFC and PAC under varied D_P and pH_k were investigated as shown in Figure 9 and Figure 10.

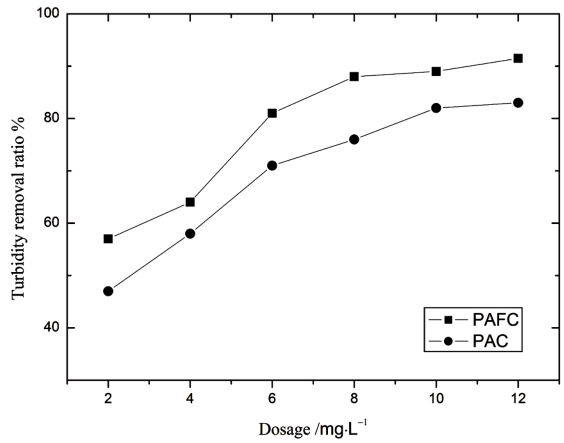
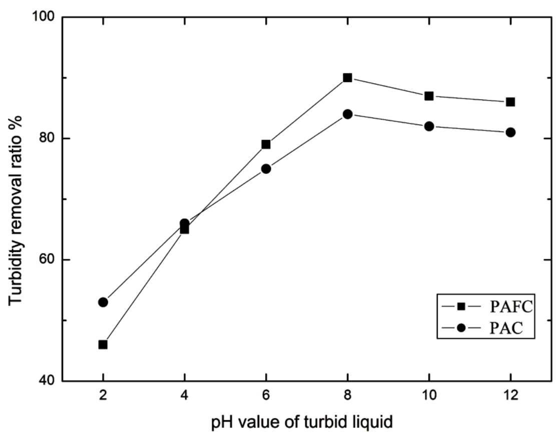


Figure 9. *Effect of coagulant dosage on the turbidity removal ratio. (pH_K=7.2)*



(D_P=10ml·L^{-1})

Figure 10. *Effect of pH value of kaolin turbid water on the turbidity removal ratio*

As shown in Figure 9, in the range of dosage, the turbidity removal ratios of PAFC were evidently higher than that of PAC. Turbidity removal ratios reached about 80% as the dosage of PAFC was around 6ml·L^{-1}, compared with PAC of 8 ml·L^{-1}. It proved PAFC was more effective than PAC on turbidity removal test.

From Figure 10, it was shown that the turbidity removal ratio of PAFC and PAC both increased as pH value of turbid liquid increased from 2 to 8, and both slightly decreased as pH value increased from 8 to 12. Therefore, too high pH value of turbid liquid was not conducive to the coagulant efficiency, the optimal pH value for the PAFC flocculation performance was about 8. In the range of pH value of turbid liquid researched, basically, turbidity removal ratio of PAFC was higher than that of PAC,

According to the flocculation test results, it indicates that PAFC prepared by bauxite tailings had an excellent flocculation performance, and it was more effective than that of PAC.

4. Conclusions

PAFC was successfully synthesized from bauxite tailing in the present study, and the synthesizing parameters were investigated. The optimal synthesizing parameters attained include: the concentration of hydrochloric acid of 24 wt%, ratio of hydrochloric acid to bauxite tailings of 6:1, temperature of 90^oC, leaching time of 2.5 hours, ratio of pickle liquor to calcium aluminate of 12:1, polymerization temperature of 90^oC and polymerization time of about 3 hours respectively. The basicity of PAFC is higher than 68%, the sum concentration of Al_2O_3 and Fe_2O_3 was beyond 12.5%. According to flocculation tests, it indicated that the PAFC has a better performance of removing the turbidity of wastewater compared to the PAC. PAFC prepared by bauxite tailings is a kind of high quality flocculants.

Acknowledgements

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