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Novel polyaluminum ferric chloride composite coagulant from Bayer red mud for wastewater treatment

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ABSTRACT

A novel composite inorganic polyaluminum ferric chloride (PAFC) coagulant was prepared from Bayer red mud and was usable for wastewater treatment. The reaction parameters affecting the PAFC coagulant performance such as the type of alkali used as the polymerization adjuster, pH, reaction temperature, and reaction time were examined in this study. The structure and morphology of the product were characterized by infrared spectra (FTIR), X-ray diffraction, and scanning electron microscopy. The optimized conditions for preparation were decided as using $Ca(AlO_2)_2$ and NaOH together as the polymerization adjuster to reach a pH value of 2.47 with the mixture being kept at 80˚C for 6 h. Furthermore, the coagulation performance of the PAFC coagulant was tested in real wastewater samples of pretreated oily sewage and printing and dyeing wastewater. The prepared PAFC coagulant outperformed commercially available PAC coagulant.

Keywords: Bayer red mud; Composite coagulant; Polyaluminum ferric chloride; Wastewater treatment

1. Introduction

Polyaluminum ferric chloride (PAFC) is among the most efficient inorganic coagulant. It possesses the advantage of the presence of both Al and Fe polymers, and thus overcome the problems associated with the individual coagulants such as generating small flocs under slow mixing speed, high residual Al concentration, and the increase in residual color in treated water, etc. [1]. The raw materials for the preparation of the PAFC basically are pyrite mine dregs, coal gangue, high iron bauxite, and calcium aluminates, etc. [2]. It has been proved that the distribution and transformation of Fe–Al species differ in coagulants and thus its wastewater treatment performance often vary with the synthesis conditions. It is essential that the preparative conditions of PAFC coagulant are optimized for a specific method [3–5].

Bayer red mud is a solid waste residue from the aluminum industry formed during the alkaline extraction of alumina from bauxite by the Bayer process. It mainly contains fine particles including hematite (Fe_2O_3), goethite (α-FeOOH), boehmite (γ-AlOOH), titania (TiO_2), quartz (SiO_2), sodalite ($Na_4Al_3Si_3O_{12}Cl$), gypsum ($CaSO_4{\cdot}2H_2O$), and a minor presence of calcite ($CaCO_3$), whewellite ($CaC_2O_4{\cdot}H_2O$), and gibbsite ($Al(OH)_3$) [6]. In addition, it also contains burning

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alkali ingredient and trace other nonferrous metals. Red mud is highly alkaline with a pH usually ranging from 10 to 13 [7–9]. For every ton of alumina produced, approximately one to two tons (dry weight) of bauxite residues are generated [6]. The corrosive nature of the red mud and its enormous quantities (90 million tons yearly worldwide [10]) caused significant ecological problems and considerable negative environmental effects [11]. Thus, disposing or utilization of red mud is of environmental and economic significance [12–14]. However, comprehensive utilization of red mud is still a worldwide problem. Traditional utilizations of red mud include its use as building materials, soil amendments, and in landscaping. Recently, much attention has been paid to exploring red mud as coagulant for wastewater treatment [11]. Though red mud as a porous material is able to adsorb various contaminants from water, its transformation to high-performance high value-added coagulant with a comprehensive waste removal capability is still challenging.

Here, we report a novel strategy for the preparation of high-performance PAFC coagulant for wastewater treatment from red mud by employing the high amount of Al and Fe elements contained in red mud. The preparative conditions were optimized for the maximal performance of PAFC. Furthermore, the performance of PAFC was evaluated in real wastewater samples including pretreated oily sewage and printing and dyeing wastewater.

2. Experimental details

2.1. Materials and instruments

All the chemical reagents used in the experiments were analytic grade except calcium aluminate ($Ca(AlO_2)_2$), which was of technical grade. All the solutions were prepared with deionized water. Bayer red mud used in this study was provided from Shandong Weiqiao aluminum & electricity Co. Ltd., Shandong, China.

The water samples used in this study was simulated water which was employed in the process of optimizing the performance of the PAFC coagulant, and real wastewater samples including oily wastewater, and printing and dyeing wastewater. The simulated water was made by diatomite, the turbidity was 350 NTU. The oily water was obtained from Liaohe Petroleum Exploration Bureau of China, and the COD of which is 534 mg/L and the turbidity is 124 NTU. The printing and dyeing wastewater was obtained from Lanyan Group Co. Ltd.; the COD of which was 1,366 mg/L and the turbidity was 3.8 NTU.

SGZ-2 turbidmeter, Shanghai Yuefeng Instruments & Meters Co., Ltd. Export Department, was employed to measure turbidity; UV765 UV–visible spectrometer, produced by Shanghai Precision & Scientific Instrument CO., Ltd., was used to measure absorbance to determine the amount of $(Fe\text{-}Al)_a$, $(Fe\text{-}Al)_b$, and $(Fe\text{-}Al)_c$. COD was measured by 5B-6 COD reactor and CODCr (potassium dichromate as oxidant), Lian-Hua Tech. Co., China; pH values were determined by pH500 meter, CLEAN, USA.

2.2. Preparation of polyaluminum ferric chloride from red mud

PAFC was prepared from the Bayer red mud following two steps.

- Acid leaching

Bayer red mud was leached with 30% hydrochloric acid to obtain a solution containing ferric and aluminum cations. 100 g of Bayer red mud and 300 mL of 30% hydrochloric acid were added into a three-neck round-bottom flask. The mixture was stirred at 100°C for 2 h, cooled down to room temperature, and filtrated. The solid residue was washed with 150 mL water. The mother liquor and washing liquor were collected and mixed. The obtained solution contained aluminum of 0.546 mol/L, ferric of 0.725 mol/L, and other metal ions with much lower concentrations.

- Polymerization

The ferric and aluminum cations in the solution were polymerized with alkali to obtain the coagulant. 100 mL of the mixed solution obtained in acid leaching step was first added to a three-neck flask and placed in an electrically heated constant- temperature oil-bath at atmospheric pressures. Secondly, varied amounts of alkali were added into the three-neck flask, and the pH values were regulated in the range 2.20–2.66. Reaction temperatures were elevated up to 100°C with stirring for 2–12 h and cooled down to room temperature. A liquid PAFC coagulant with reddish-brown color was obtained. The optimized parameter for the preparation of PAFC were determined as using NaOH and $Ca(AlO_2)_2$ together (1.5 g $Ca(AlO_2)_2$ and 1.2 g NaOH) as the polymerization adjuster (alkali), and the mixture was kept at a pH value of 2.47 at 80°C for 6 h. When the influence of a single parameter of the reaction conditions was studied by varying it in a range, the other parameters were adopted as the above-mentioned optimized values.

The analysis of the physical–chemical parameter of the new coagulant following the Chinese standard method (GB 14591-2006 & GB 15892-2003) showed that the pH (1% water solution), density, and the concentration of total iron and aluminum (mass fraction) were 2.20–2.66, 1.20–1.34 g/cm^3, and 10–13%, respectively.

2.3. Ferron analysis

In order to classify the aqueous Fe–Al species, a ferron-complexation timed spectrophotometric method was used based on the standard adsorption curves of the reaction between polyaluminum ferric chloride and the ferron reagent (8-hydroxy-7-iodo-quinoline-5-sulphonic acid). The Fe–Al species were artificially classified as $(Fe–Al)_a$, $(Fe–Al)_b$, and $(Fe–Al)_c$, which represented their different extent of hydrolysis and polymerization. $(Fe–Al)_a$ species were defined as free ion and mononuclear hydride–hydroxyl complex. $(Fe–Al)_b$ species were composed of polynuclear complexes, and were the most effective components as coagulants. We take the amount of $(Fe–Al)_b$ as an indicator of the effectiveness of the coagulant. $(Fe–Al)_c$ species were composed of polymer of higher molecular weight. The measurements were performed on an UV–visible spectrometer and the absorbance of the reaction solutions at 362 nm was measured at predetermined time intervals. The absorbance observed within the first minute of the experiment corresponded to the $(Fe–Al)_a$ species. When the absorbance finally ended in a plateau, the absorbance was considered as an indicator of the amount of the $(Fe–Al)_b$ species. $(Fe–Al)_c$ values were calculated by subtracting $(Fe–Al)_a$ and $(Fe–Al)_b$ from the known total Fe–Al content. A more detailed description of this method was provided in the previous study [15].

2.4. Performance of the produced coagulant in testing water samples

Coagulation tests were performed by using simulated water and real wastewater samples. All coagulation tests were conducted in 100 mL beakers using a magnetic stirring apparatus. 100 mL of the test water was placed in a beaker and stirred rapidly at 200 rpm for 2 min after adding the coagulant at room temperature, followed by slow stirring at 40 rpm for 2 min and sedimentation for 10 min. Then, a supernatant sample was taken at 1.0 cm below the surface of the test water for turbidity and COD measurement.

2.5. Characterization of the coagulant

PAFC solution was dehydrated at −50℃ using LGJ-10D vacuum freeze drier to make powder sample for structure and morphology analysis. X-ray diffraction (XRD) were measured for the determination of crystalline phases in solid coagulants using D/max-rA X-ray diffractometer with Cu K radiation in the 2θ range of 3–80° at a scan rate of 8°/min. The solid coagulants were analyzed by FT-IR with the Perkin Elmer spectrum 100 FT-IR spectrophotometer and potassium bromide pellet method. The spectra were scanned in the range of 4,000–500 cm^{-1}. The morphologies of the coagulants were analyzed by Hitachi S-4800 high-resolution ice-emission scanning electron microscopy.

3. Results and discussion

3.1. Preparation of the PAFC coagulant

The red mud as obtained was composed mainly of Fe, Al, Si, and Na oxides, as indicated by the results of chemical analysis of raw Bayer red mud which are given in Table 1.

During the acid leaching step, ferric chloride and aluminum chloride were obtained as the main targeting products, and calcium chloride and sodium chloride were obtained as by-products. The chemical reactions during the process of acid leaching step are illustrated in formula 1–4. In this leaching process, titanium dioxide and silica dioxide remained insoluble as solid. Then, in the polymerizing step, the acidity of the solution was neutralized, and with the increase of the pH value, hydrolyzation of Fe(III) and Al(III) took place, as illustrated in formula 5–6. As a step further, with the polymerization of hydroxyl, copolymerized polyaluminum ferric chloride species took form, as illustrated in formula 7.

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O \quad (1)$$

$$Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \quad (2)$$

Table 1
Average composition of bayer red mud used (% by wt.)

Constituent	% (w/w)
Al_2O_3	24.37
Fe_2O_3	25.75
SiO_2	24.03
Na_2O	10.02
CaO	2.27
TiO_2	1.20

$$CaO + 2HCl \rightarrow CaCl_2 + H_2O \quad (3)$$

$$Na_2O + 2HCl \rightarrow 2NaCl + H_2O \quad (4)$$

$$2AlCl_3 + nH_2O \rightarrow Al_2(OH)_nCl^-_{6-n} + nCl^- + nH^+ \quad (5)$$

$$2FeCl_3 + mH_2O \rightarrow Fe_2(OH)_mCl^-_{6-m} + mCl^- + mH^+ \quad (6)$$

$$xAl_2(OH)_nCl^-_{6-n} + yFe_2(OH)_mCl^-_{6-m} \rightarrow Al_{2x}Fe_{2y}(OH)_{xn+ym}Cl^-_{6x-9m+6y-ym} \quad (7)$$

In the process of polymerization, the choice of alkali, the pH value, the reaction temperature, and the reaction time significantly influenced the performance of the coagulant. Thus, influences of these factors were carefully studied in order to provide detailed information in the producing process of the coagulant. The residue turbidity of simulated water sample and the percentage of $(Fe–Al)_b$ were measured as indicators of effectiveness of the coagulant to optimize the preparative conditions. The residue turbidity and COD were followed as indicators of effectiveness of the coagulant in real wastewater samples.

3.1.1. The choice of alkali

Alkali was added in the mixture obtained by acid leaching, in order to neutralize the solution and induce hydrolysis and polymerization of ferric and aluminum ions. NaOH and $Ca(AlO_2)_2$ were chosen as the candidate alkalis. NaOH was highly reactive but it was also of higher price. $Ca(AlO_2)_2$ also displayed alkali character. The dosage of $Ca(AlO_2)_2$ would not only adjust the basicity of the solution, but also would provide extra source of aluminum and thus contribute to the effect. But the reaction rate of $Ca(AlO_2)_2$with the acidic mixture was slow [16]. So, we decided to use $Ca(AlO_2)_2$ and NaOH together (1.5 g $Ca(AlO_2)_2$ and 1.2 g NaOH were added to the 100 mL mixed solution) as the polymerization adjuster to prepare PAFC and achieved higher coagulant performance compared with using either one of the component by itself as the polymerization adjuster, as indicated in Fig. 1.

Fig. 1 shows the effect of different alkalis on residual turbidity. It indicates that using $Ca(AlO_2)_2$ and NaOH together as the polymerization adjuster was better than using NaOH or $Ca(AlO_2)_2$ on turbidity removal; and using $Ca(AlO_2)_2$ was better than using NaOH. Till the dosage of the coagulant was increased to 40 mg/L, the residue turbidity decreased accordingly with the increase of coagulant dosage. When the dosages of the coagulant were higher than 60 mg/L, the residue turbidity increased with increased amount of coagulant. But for every dosage applied, the effect of using $Ca(AlO_2)_2$ and NaOH together as the polymerization adjuster was better than using either alkali alone. The main reason for this could be attributed to the fact that adding of $Ca(AlO_2)_2$ improved the content of aluminum and the adding of NaOH improved product quality.

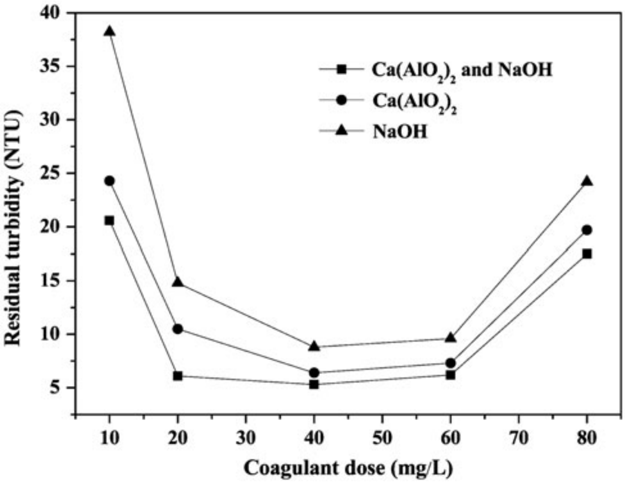

Fig. 1. The effect of different alkalis on residual turbidity.

3.1.2. The effect of pH

In order to study in detail the effect of pH, the pH values of the reaction mixture were systematically adjusted in the range 2.20–2.70, while keeping other parameters as provided in the experimental section. The coagulation performance and Fe–Al species distributions of PAFC coagulants prepared at different pH are shown in Fig. 2. As seen from Fig. 2(a), pH had important influence on turbidity removal efficiency of the PAFC coagulant [17]. The residue turbidity decreased as the pH values increased from 2.20 to 2.47, followed by an increase till pH value reached 2.70. The best performance for the coagulant occurred at pH value 2.47.

As can be seen from Fig. 2(b), pH also had important influence on Fe–Al species distribution of PAFS. In pH ranges lower than 2.47, the amount of $(Fe–Al)_b$ species increased with the increase of pH and maximized at pH value 2.47. In pH ranges higher than 2.47, the amount of $(Fe–Al)_b$ species decreased with the increase of pH and the amount of $(Fe–Al)_c$ species increased. At the optimum condition at pH 2.47, the optimum species distribution was $(Fe–Al)_a$ of 30.1%, $(Fe–Al)_b$ of 45.5%, and $(Fe–Al)_c$ of 24.4%. The fact that

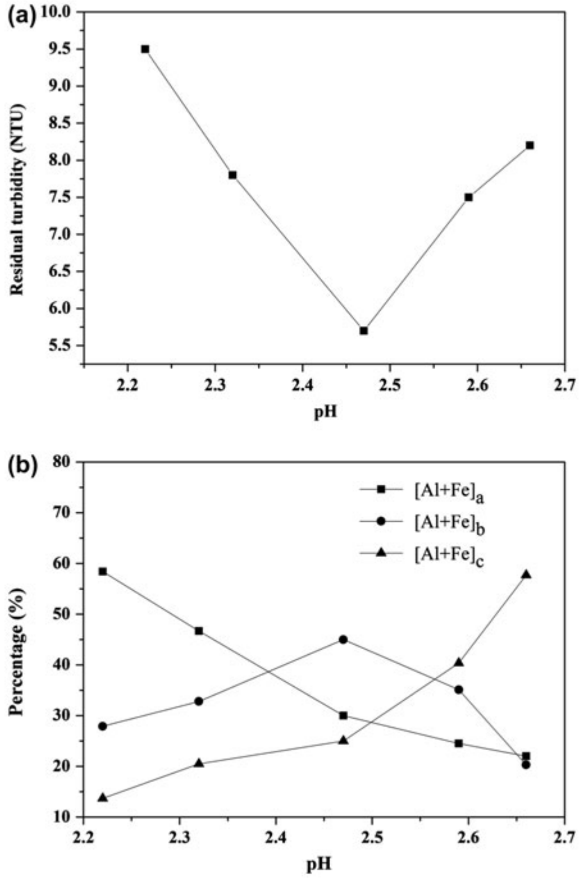

Fig. 2. Effect of pH on (a) turbidity removal and (b) Fe–Al species distribution of PAFC.

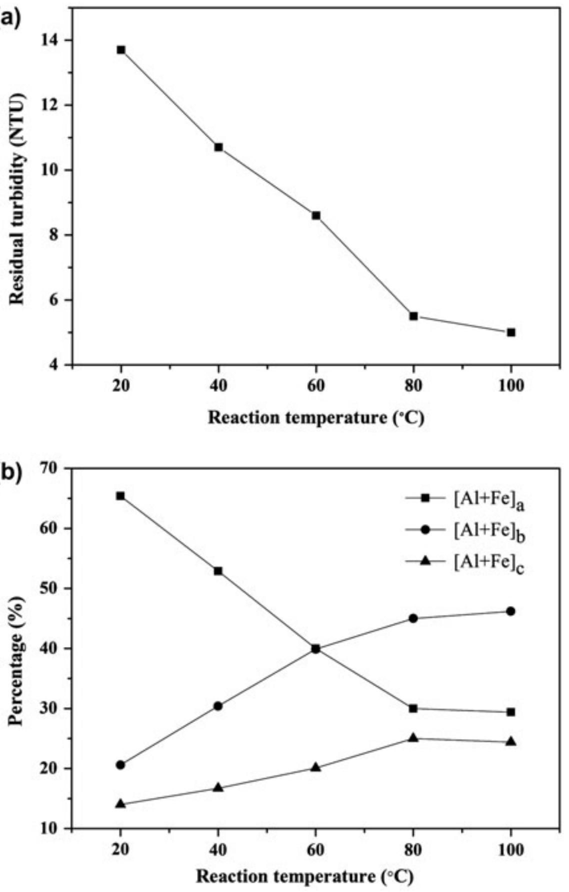

Fig. 3. Effect of reaction temperature on (a) turbidity removal and (b) Fe–Al species distribution of PAFC.

the residue turbidity of the sample hit the bottom at the pH value where (Fe–Al)$_b$ species maximized demonstrated the effectiveness of the (Fe–Al)$_b$ species in removing turbidity. This is consistent with previous literatures.

3.1.3. *The effect of reaction temperature*

In order to study the effect of reaction temperature, other parameters for the preparation of PAFC were kept constant as provided in the experimental section while varying the reaction temperatures from 20 to 100℃. The coagulation performance and Fe–Al species distribution of different PAFC coagulants prepared at different reaction temperatures are shown in Fig. 3. As seen from Fig. 3(a), turbidity removal efficiency increased with the increase of reaction temperature from 20 to 80℃, followed by no obvious change till the reaction temperature reached 100℃. As seen from Fig. 3(b), the content of (Fe–Al)$_b$ species and (Fe–Al)$_c$ species also increased with the increase of reaction temperature from 20 to 80℃, followed by no obvious increase with further elevation of the reaction temperatures. As seen from experimental data, the reaction temperature affected the effect of the coagulant, because it affected reaction rate and extent [1,18,19]. Generally, higher reaction temperature could facilitate the hydrolysis of ferric and aluminum, transforming more (Fe–Al)$_a$ species into (Fe–Al)$_b$ species and (Fe–Al)$_c$ species. But on the other hand, overheating of the reaction mixture (reaction temperature >80℃) had little effect enhancing the reaction extent, leading to a waste of energy. Therefore, optimum reaction temperature for the preparation of the PAFC coagulant was decided as 80℃.

3.1.4. *The effect of reaction time*

In order to study the effect of reaction time, other parameters were kept constant as in the experimental section while the reaction time was varied from 0 to 12 h. The coagulation performance and Fe–Al species distribution of different PAFC coagulants prepared at different reaction time are shown in Fig. 4. As seen from Fig. 4(a), turbidity removal efficiency increased with the increase of reaction time (from 0 to 6 h), followed by decrease after the reaction time was longer than 6 h. The turbidity removal efficiency of the coagulant with a reaction time of 6 h was the highest. Fig. 4(b) shows that the content of (Fe–Al)$_b$ species increased with the increase of reaction time (from 0 to 6 h), followed by decrease after the reaction time was longer than 6 h. In the whole range of reaction time, the content of (Fe–Al)$_c$ species increased with the increase of reaction time and the content of (Fe–Al)$_a$ species decreased with the increase of reaction time. The main reason for such phenomena was that the Fe–Al species underwent polymerization first to form the most effective component (Fe–Al)$_b$ and then would transform to (Fe–Al)$_c$ with an inferior turbidity removal effect with the increase of the reaction time [20,21]. The more the (Fe–Al)$_b$ species, the better the performance. In 6 h, the turbidity removal efficiency was the highest. Therefore, the optimum reaction time for the preparation of the PAFC coagulant was determined as 6 h.

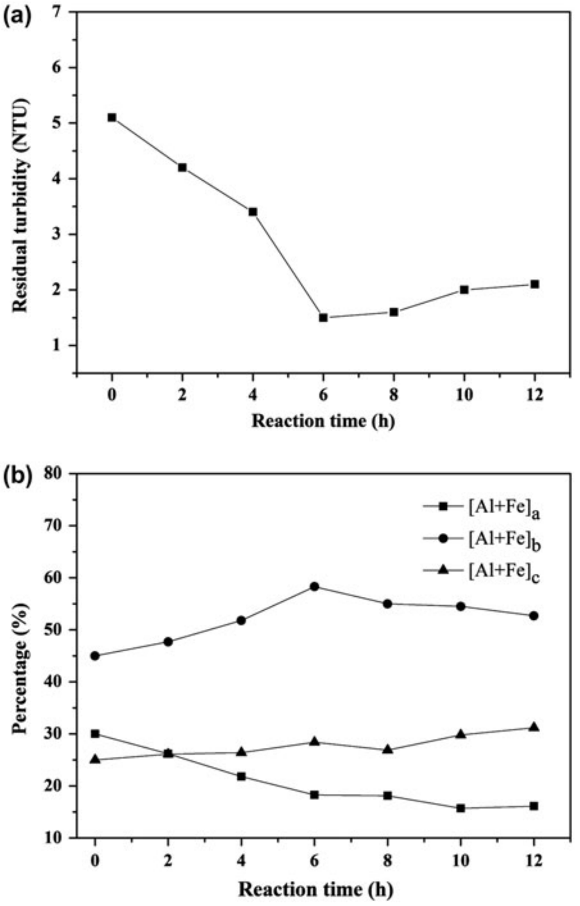

Fig. 4. (a) Effect of aging time on turbidity removal and (b) Fe–Al species distribution of PAFC.

3.2. Structure and morphology analysis of the final coagulant product

The final product following the optimized preparative conditions were analyzed with XRD, IR, and scanning electron microscopy (SEM) to obtain detailed structural and morphological information. Fig. 5 illustrates the XRD patterns of solid PAFC samples and the analysis results showed that the NaCl and $AlCl_3$ were present in the sample. The signals of $FeCl_3$ were absent and, in addition, there were peaks at 2θ values of 18.4°, 29.8°, 66.4°, and 75.5° that could not be assigned to a specific compound. These results indicated that some ions such as Fe^{3+} and Al^{3+} might have been polymerized into a new compound which was excluded in the XRD card or did not give a standard molecular formula. This speculation suggested that PAFC contained new chemical species rather than a simple mixture of the raw materials, and was consistent with the chemical transformation that took place during the preparative process of the coagulant.

The possible chemical bonds in PAFC were investigated by the FTIR spectra and were compared with industrial grade PAC coagulant (Fig. 6). The two samples showed similar FTIR spectra. Both

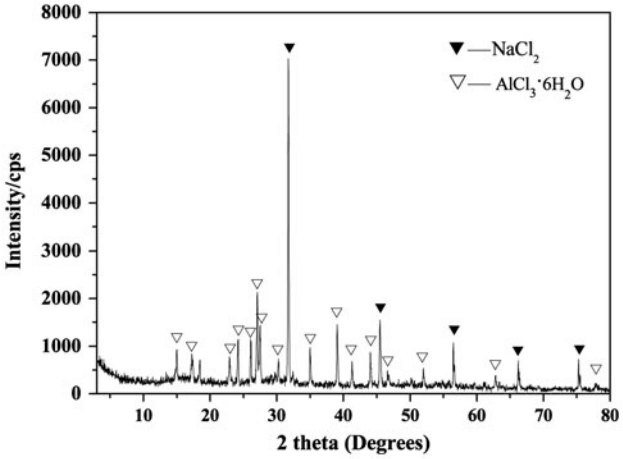

Fig. 5. XRD pattern for the PAFC coagulant.

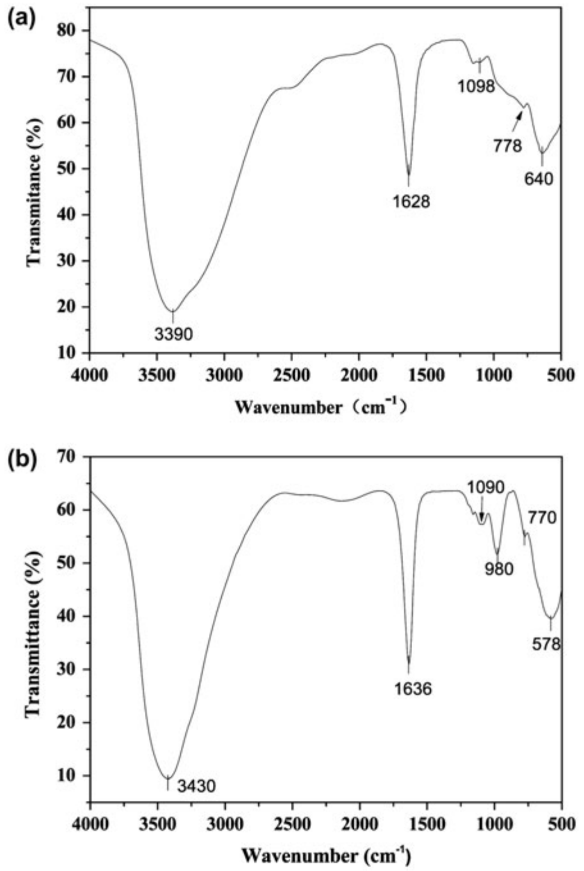

Fig. 6. FTIR spectra for (a) PAFC and (b) industrial grade PAC.

spectra exhibited a broad absorption peaks in the range of 3,200–3,650 cm^{-1} (3,390 cm^{-1} for PAFC and 3,430 cm^{-1} for PAC), which could be assigned to the stretching vibrations of –OH groups. The peaks in the range of 1,600–1,700 cm^{-1} (1,628 cm^{-1} for PAFC and 1,636 cm^{-1} PAC) were attributed to the bending vibrations of water absorbed, polymerized, and crystallized in the coagulant. The industrial grade PAC was not a pure substance, which contains iron ions. The peak at 1,098 cm^{-1} for PAFC and the peak 1,090 cm^{-1} for PAC were attributed to the asymmetric stretching vibration of Fe–OH–Fe or Al–OH–Al [22]; furthermore, there were two peaks at 778 cm^{-1} and 640 cm^{-1} for PAFC and two peaks at 770 cm^{-1} and 578 cm^{-1} for PAC, which were attributed to bending vibrations of Fe–OH and Al–OH, respectively [23].

The morphologies of the prepared PAFC coagulant in the micrometer range were observed with SEM (Fig. 7(a) and (b)). The PAFC coagulant prepared from red mud displayed rough surfaces covered with ridges and wrinkles. Compared with the relatively much smoother surface of commercial PAC coagulant (Fig. 7(c) and (d)), the rough surface morphology of the prepared PAFC coagulant might result from a larger extent of dehydration during the preparation of the SEM sample in vacuum.

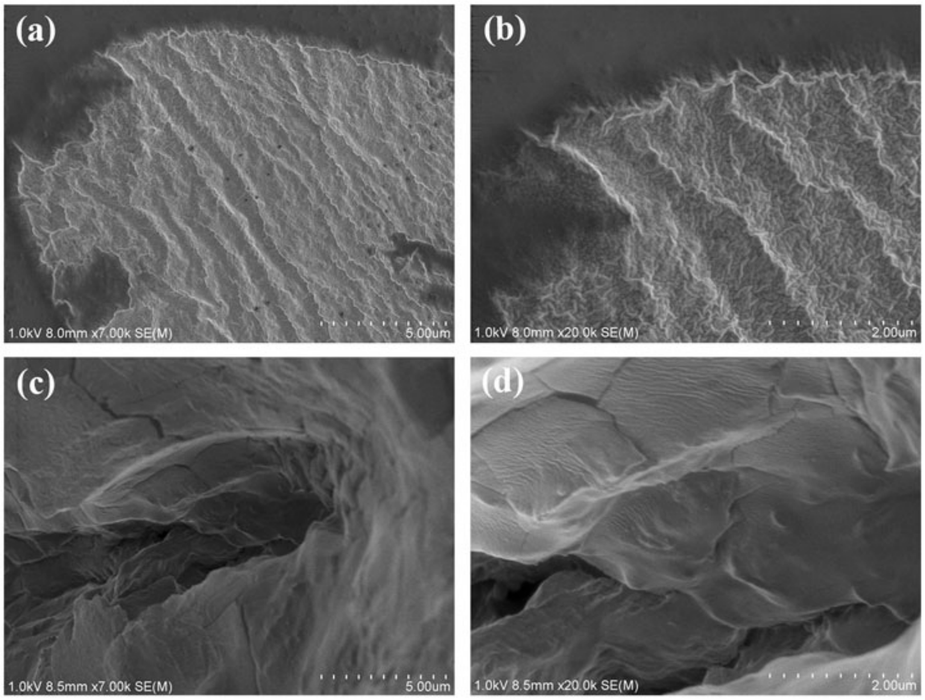

Fig. 7. SEM images of (a,b) the PAFC coagulant and (c,d) the commercially available PAC coagulant.

3.3. Application of the coagulant in pretreated oily sewage and printing and dyeing wastewater

3.3.1. Application of the coagulant in oily sewage

In order to investigate the coagulation performance of the new coagulant, it was applied in the treatment of pretreated oily sewage and compared with conventional PAC coagulant. The result of the comparison of the performance of the PAFC coagulant and conventional PAC coagulant are presented in Fig. 8. As shown in Fig. 8, the residual turbidity and COD value first decreased and then increased with the increase of coagulant doses in the range 0–100 mg/L and had the minimum value when the coagulant dose was 60 mg/L. The turbidity and COD removal effect of PAFC were better than PAC when the coagulant doses were the same in the treatment of pretreated oily sewage. Therefore, at the same turbidity removal and COD removal level, the consumption of the PAFC coagulant was much less than PAC. The treatment results proved that the PAFC coagulant could be effectively used for the treatment of pretreated oily sewage.

3.3.2. Application of the coagulant in printing and dyeing wastewater

In order to prove that the advanced performance of the prepared PAFC was universal in treating different kinds of wastewater, we also evaluated its coagulation performance in printing and dyeing wastewater and compared it with conventional PAC coagulant. The performance of the complex coagulant at different dosages for turbidity and COD removal are presented in Fig. 9. Fig. 9 shows that with the increase of the dosage of PAFC till 800 mg/L, residue turbidity and residue COD decreased, indicating enhancement of turbidity and COD removal effect. With a dosage larger than 800 mg/L, both the residue turbidity and residue COD increased with

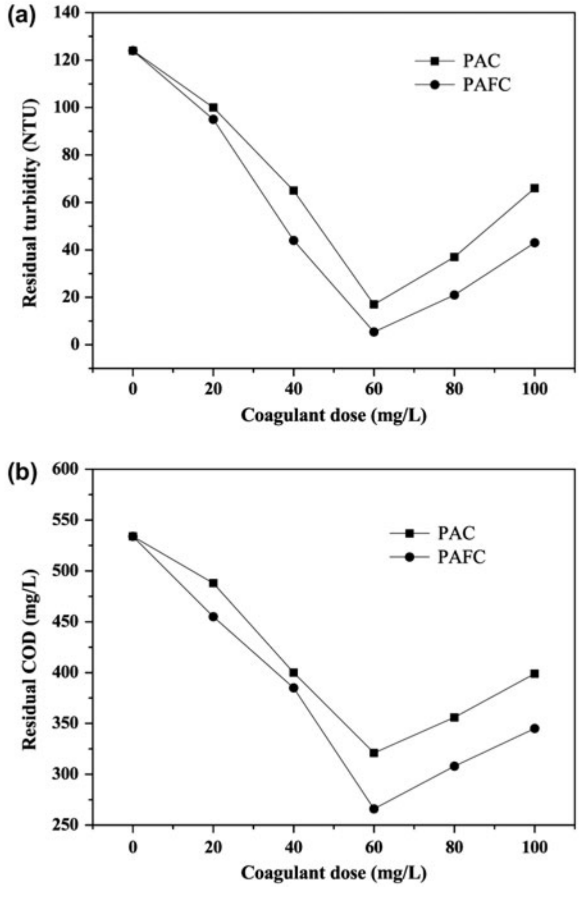

Fig. 8. Effect of coagulant dose on (a) turbidity removal and (b) COD removal for pretreated oily sewage.

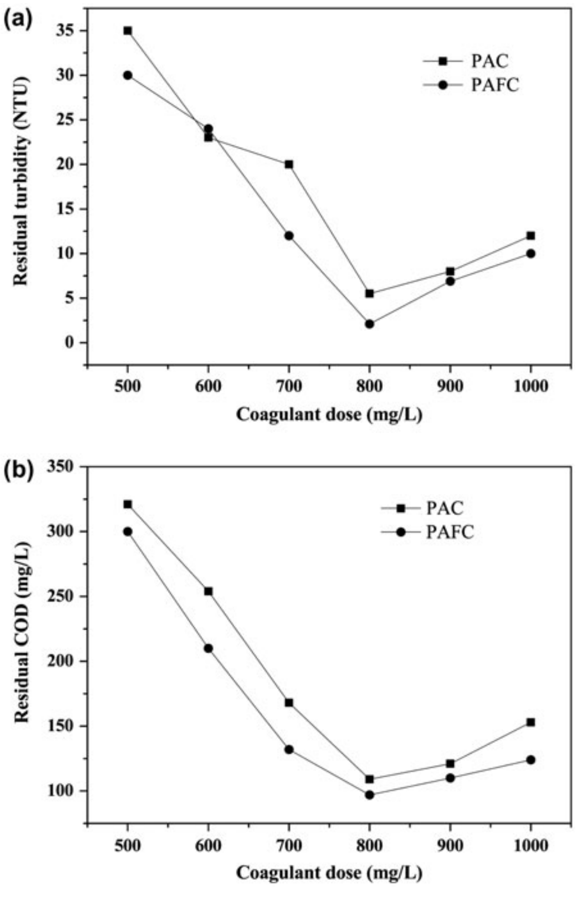

Fig. 9. Effect of coagulant dose on (a) turbidity removal and (b) COD removal for printing and dyeing wastewater.

increased dosages of PAFC coagulant. This curve implied that the optimal dosage of PAFC coagulant was 800 mg/L for the printing and dyeing wastewater. And with this optimal dosage, the residue turbidity lower than 5 NTU and residue COD lower than 100 mg/L could be achieved. Both minimal value of reside turbidity and residue COD achieved by PAFC were obviously smaller than the values achieved with conventional PAC coagulant, indicating the advanced performance of the prepared PAFC coagulant compared with the conventional PAC coagulant.

4. Conclusion

In this research, the preparation of PAFC coagulant from red mud with advanced performance compared with conventional PAC coagulant was achieved. Reaction conditions including the choice of polymerization adjuster (alkali), the pH value, the reaction temperature, and reaction time were thoroughly studied to optimize the performance of the prepared coagulant. The optimized parameters to prepare PAFC coagulant were decided as using $Ca(AlO_2)_2$ and NaOH together as polymerization adjuster, reaction pH value as 2.47, reaction temperature as 80°C, and reaction time as 6 h, respectively. The performance tested with real samples of oily sewage and printing and dyeing wastewater showed that the prepared PAFC outperformed the conventional PAC coagulant at almost every dosage applied.

Acknowledgments

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References

[1] G. Zhu, H. Zheng, W. Chen, W. Fan, P. Zhang, T. Tshukudu, Preparation of a composite coagulant: Polymeric aluminum ferric sulfate (PAFS) for wastewater treatment, Desalination 285 (2012) 315–323.

[2] T.S. Ma, Study on Preparation and Application of Compound Water Purifying Agent, Pollut. Control Technol. 9 (1996) 37–39.

[3] J.T. Kloprogge, D. Seykens, J.B.H. Jansen, J.W. Geus, A Al-27 nuclear-magnetic-resonance study on the optimalization of the development of the Al-13 polymer, J. Non-Cryst. Solids 142 (1992) 94–102.

[4] W. Seichter, H.J. Mogel, P. Brand, D. Salah, Crystal structure and formation of the aluminium hydroxide chloride [Al-13 (OH)24(H2O)24]Cl-15·13H2O, Eur. J. Inorg. Chem. 6 (1998) 795–797.

[5] W.Z. Wang, P.H. Hsu, The nature of polynuclear OH–Al complexes in laboratory-hydrolyzed and commercial hydroxyaluminum solutions, Clays Clay Miner. 42 (1994) 356–368.

[6] S.B. Wang, H.M. Ang, M.O. Tade, Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes, Chemosphere 72 (2008) 1621–1635.

[7] C.X. Lin, G. Maddocks, J. Lin, G. Lancaster, C.X. Chu, Acid neutralising capacity of two different bauxite residues (red mud) and their potential applications for treating acid sulfate water and soils, Aust. J. Soil Res. 42 (2004) 649–657.

[8] N.W. Menzies, I.M. Fulton, W.J. Morrell, Seawater neutralization of alkaline bauxite residue and implications for revegetation, J. Environ. Qual. 33 (2004) 1877–1884.

[9] R.N. Summers, J.D. Pech, Nutrient and metal content of water, sediment and soils amended with bauxite residue in the catchment of the Peel Inlet and Harvey Estuary, Western Australia, Agr. Ecosyst. Environ. 64 (1997) 219–232.

[10] S. Kumar, R. Kumar, A. Bandopadhyay, Innovative methodologies for the utilization of wasters from metallurgical and allied industries, Resour. Conserv. Recycl. 48 (2006) 301–314.

[11] Y.J. Liu, R. Naidu, H. Ming, Red mud as an amendment for pollutants in solid and liquid phases, Geoderma 163 (2011) 1–12.

[12] G. Maddocks, C. Lin, D. McConchie, Effects of bauxsol (TM) and biosolids on soil conditions of acid-generating mine spoil for plant growth, Environ. Pollut. 127 (2004) 157–167.

[13] R.K. Paramguru, P.C. Rath, V.N. Misra, Trends in red mud utilization – A review, Miner. Process. Extr. Metall. Rev. 26 (2005) 1–29.

[14] K.E. Snars, R.J. Gilkes, M.T.F. Wong, The liming effect of bauxite processing residue (red mud) on sandy soils, Aust. J. Soil Res. 42 (2004) 321–328.

[15] Y.Y. Hu, C.Q. Tu, H.H. Wu, Species distribution of polymeric aluminium-ferrum – timed complexation colorimetric analysis method of Al-Fe-Ferron, J. Environ. Sci. 13 (2001) 418–421.

[16] W. Li, T. Hua, Q.X. Zhou, Preparation, morphology and coagulation characteristics of a new polyferric chloride coagulant prepared using pyrite cinders, Environ. Technol. 32 (2011) 911–920.

[17] G.C. Zhu, H.L. Zheng, Z. Zhang, T. Tshukudu, P. Zhang, X. Y. Xiang, Characterization and coagulation-flocculation behavior of polymeric aluminum ferric sulfate (PAFS), Chem. Eng. J. 178 (2011) 50–59.

[18] D. Uzun, M. Gulfen, Dissolution kinetics of iron and aluminium from red mud in sulphuric acid solution, Indian J. Chem. Technol. 14 (2007) 263–268.

[19] W. Lan, H.Q. Qiu, J. Zhang, Y.J. Yu, K.L. Yang, Z.Z. Liu, G.J. Ding, Characteristic of a novel composite inorganic polymer coagulant-PAFC prepared by hydrochloric pickle liquor, J. Hazard. Mater. 162 (2009) 174–179.

[20] C.H. Feng, X.P. Ge, D.S. Wang, H.X. Tang, Effect of aging condition on species transformation in polymeric Al salt coagulants, Colloids Surf. A 379 (2011) 62–69.

[21] Z. Wu, P. Zhang, G.M. Zeng, M. Zhang, J. Jiang, Humic acid removal from water with polyaluminum coagulants: Effect of sulfate on aluminum polymerization, J. Environ. Eng. 138 (2012) 293–298.

[22] Y.M. Fang, X.D. Zhao, X.L. Zhang, Study on the image, structure and coagulation behavior of polysilicate-aluminum ferric, Ind. Saf. Environ. Prot. 33 (2007) 22–24.

[23] T. Sun, C.H. Sun, G.L. Zhu, X.J. Miao, C.C. Wu, S.B. Lv, W.J. Li, Preparation and coagulation performance of poly-ferric-aluminum-silicate-sulfate from fly ash, Desalination 268 (2011) 270–275.