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Preparation and characterization of poly-silicic-cation coagulant from industrial wastes

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HIGHLIGHTS

- A low-cost poly-silicic-cation coagulant (PSiC) was prepared from industrial wastes.
- Characteristics of PSiC were analyzed by XRD, FT-IR, UVA and microscopic imaging.
- Coagulation performance of PSiC was evaluated by papermaking wastewater treatment.
- The best Si/(Al+Fe) molar ratio for the structure and morphology of PSiC is 0.8.

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ABSTRACT

A simple and low-cost method was developed to prepare poly-silicic-cation coagulant (PSiC) from industrial wastes. The structure and morphology of the coagulants with different Si/(Al + Fe) molar ratios were characterized by X-ray diffraction (XRD), infrared spectra (IR), ultraviolet/visible absorption (UVA) scanning and microscopic imaging, and the coagulation performances were evaluated by papermaking wastewater treatment. The results show that instead of a simple mixture of the raw materials, new complex compounds are formed in all the PSiCs, and distinctive compounds are found in each PSiC. Furthermore, with the increasing dose of silicon in PSiC, the contents of the ionic polymerized bonds and the high polymers are decreased obviously, and the cross-copolymerization of Fe (III) and Al (III) hydroxyl polymers is weakened. Morphological analysis implies that branch-like PSiC units become smaller with the increase of Si/(Al + Fe) molar ratio, and coagulation experiments indicate that the PSiC with lower Si/(Al + Fe) molar ratio exhibits better coagulation performance in removing turbidity, COD and chroma.

1. Introduction

With economic development, environmental protection such as treatment of wastewater and solid wastes is increasingly urgent. Coagulation is one important wastewater treatment process where inorganic coagulants play a key role [1–4]. Polysilicate composite coagulants, such as poly-zinc-silicate-sulfate, poly-aluminum-silicate-chloride and poly-aluminum-silicate-sulfate, are a new-type inorganic polymer coagulant developed in the 1990s on the basis of poly-silicic acid (PS), aluminum and iron coagulants [5–7]. The PS and metal ions in the aqueous solution carry negative and positive charges respectively, and could polymerize to oligomerics and high polymers with different sizes or structures [8,9]. Therefore, polysilicate composite coagulants are superior in neutralization, adsorption and capture. However, their preparation often utilizes expensive industrial-grade materials.

Currently, pollution caused by industrial wastes is very serious. About 6×10^8 t of fly ash is produced by coal-fired thermal power plants around the world per year. The major fly-ash producers include China, Russia and the United States [10]. Worldwide emission of sulfuric acid is about 1.65×10^8 t [11]. Large quantities of pyrite slag as solid wastes are produced as a by-product of industrial sulfuric acid manufacturing. Theoretically, around 67% of pyrite in the feed can be converted to hematite as pyrite slag during roasting in sulfuric acid production. Even though a portion of pyrite slag is used as additive in iron or cement production, the majority is wasted and piled up [12]. Sulfuric acid is widely applied in fertilizers, titanium dioxide and other industries. The wasted sulfuric acid is corrosive and contains a large amount of organic or inorganic impurities. These industrial wastes were mainly discharged or deposited in landfills, which can not only pollute the environment, but also waste resources.

Fly ash and pyrite slag both consist of silicon, aluminum, iron, calcium and a few other compounds, such as magnesium, sodium, potassium and titanium [13–15], which could be used to produce inorganic polymeric

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coagulants [16–18]. The preparation of inorganic polymeric coagulants from industrial wastes was already studied [14–19]. However, in order to ensure good coagulation performance and stability, complex methods were adopted, which put forward higher requirements for raw materials and equipment. Composite-polymerization and co-polymerization are two conventional methods to prepare polysilicate composite coagulants. The former means polymerization of PS and hydroxylated metal salts, and the latter means hydroxylation of mixture of metal salts and PS [17,18]. However, little research studied the methods that can simultaneously carry out the polymerization of silicate and the aggregation of metal salt by hydroxyl.

In this study, a simple and low-cost method which meets the industrial demands was developed to prepare PSiC from industrial wastes. PSiC with different Si/(Al + Fe) molar ratios was characterized by X-ray diffraction (XRD), infrared spectra (IR), ultraviolet/visible absorption (UVA) scanning and microscopic imaging. On the other hand, coagulation performance was evaluated by jar test in papermaking wastewater treatment.

2. Materials and methods

2.1. Materials

The studied industrial wastes include fly ash, pyrite slag and wasted sulfuric acid, which were obtained from the Meixian Sulfuric Acid Plant, Baqiao Thermal Power Plant and Xi'an Modern Chemistry Research Institute (China) respectively. The compositions of the industrial wastes are shown in Table 1. Fly ash and pyrite slag compositions are determined by WFX-130A Atomic absorption spectrophotometer (Beifen-Ruili, China) and wasted sulfuric acid compositions are measured by sodium hydroxide titration (GB/T 176-2008, China) and 2,4-xylenol spectrophotometry (GB 11198.11-89, China).

2.2. Preparation of PSiC

PSiC was prepared in the following steps (Fig. 1).

2.2.1. (a) Pretreatment

About 50 g of fly ash and 165 ml of 6 mol/L sodium hydroxide (industrial grade) were added to a beaker, heated by stirring to 80–90 °C, and kept for 2 h. After that, the leaching liquid was filtered. SiO_2 content was determined by molybdenum blue spectrophotometry (GB/T 176-2008, China) to be 0.4 mol/L. The insoluble ash particles and 100 ml of water were added to the beaker under stirring and dried.

Then 45 g of pyrite slag, 10 g of alkali-leached fly ash and 147 ml of 6 mol/L wasted sulfuric acid were added to the beaker, heated under stirring to 80–90 °C, and kept for 2 h. Finally the mixture was filtered. The supernatant part contains Fe^{3+}, Al^{3+} and little other metals. Fe^{3+} and Al^{3+}contents were determined by EDTA titration (GB/T 176-2008, China) to be 1.2 mol/L and 0.12 mol/L respectively.

Table 1
Composition of industrial wastes.

Composition	Concentration of fly ash (wt.%)	Concentration of pyrite residual (wt.%)	Composition of waste sulfuric acid (wt.%)
Al_2O_3	27.67	4.78	–
Fe_2O_3	9.56	50.43	–
SiO_2	56.78	22.27	–
CaO	1.57	2.58	–
MgO	1.25	0.63	–
K2O	1.12	1.57	–
SO_3	0.55	7.2	–
Na_2O	0.4	0.82	–
ZnO	0.5	1.83	–
Other	0.6	7.89	18.23
Nitric acid	–	–	9.41
Sulfuric acid	–	–	69.26
Nitrogen tetroxide	–	–	3.20

2.2.2. (b) Polymerization

Various amounts of water glass solution were added to the metal salt solution at a flow rate of 1.5 ml/min under stirring, and then waste sulfuric acid was titrated at a flow rate of 1 mL/min to the desired pH 1.5. The solutions were aged at normal temperature for 2 days and PSiC was made.

2.3. Characteristics of PSiC

The PSiC solution diluted by 400 times was scanned from 190–700 nm with a TU-1810 Spectrophotometer (Puxi, China). The liquid samples were dried at 50 °C for 20 h and ground into powder, whose crystalline phases were analyzed with a D/MAX-RB X-ray diffractometer (Rigaku, Japan). Then the solid coagulants were measured by a KBr pressed disk with a Tensor37 IR spectrophotometer (Bruker, Germany). The solution samples were dripped on glass slide, dried at normal temperature, and then were observed and photographed by a microscopic imaging system, which includes XSP(2XC) electron microscopy, complementary metal-oxide-semiconductor and a computer (The Fifth Factory of Optical Instruments, China).

2.4. Coagulation performance

Papermaking wastewater with COD of 150 mg/L, turbidity of 66 NTU, chroma of 16 times and pH of 7.5 was used to verify the coagulation performance of PSiC, which was obtained from Xi'an Wanlong paper mill (China).

Coagulation performance was evaluated by jar test using a ZR4-6 six-unit stirred system (Zhongrun, China) and the doses of PSiC and PAC were 80 mg/L and 360 mg/L respectively. The dose of coagulant was determined by pre-experiment. The coagulant was added to the wastewater sample, which was stirred rapidly at 150 r/min for 2 min, followed by slow stirring at 30 r/min for 10 min and precipitation for 30 min. Finally, the supernatant was taken from 3 cm below the surface of the test wastewater. Turbidity, COD and chroma were measured by HI93703 (HANNA, Italy) turbidimeter, back titration (GB11984-89, China), and colorimetric dilution (GB11903-89, China), respectively.

3. Results and discussion

3.1. XRD analysis

The characteristics of polysilicate composite coagulants could be influenced by many factors, such as ionic concentration, pH and preparation method, especially Si/(Al + Fe) ratio. Fig. 2 illustrates the XRD spectra of PSiCs prepared from five Si/(Al + Fe) molar ratios. Primary compounds in PSiC are shown in Table 2. From Fig. 2 and Table 2, we can see that PSiCs mainly consist of $Na_3H(SO_4)_2$ and $Fe_5Al_4Si_6O_{22}(OH)_2$, but the spectra of diffractive crystals such as $Fe_2(SO_4)_3$, Fe_2O_3, Fe_3O_4, $Al_2(SO_4)_3$, Al_2O_3 and SiO_2 cannot be observed in PSiC. This result implies that Fe, Al and Si were polymerized rather than remaining a simple mixture of the raw materials. In addition, some new compounds were formed (at $2\theta = 19.2$, 24.3 , 25.2 , 29.1 , 33.4 and 48.8), indicating that PSiC contains new complex compounds without standard molecular formula or new matters excluded in the XRD card, which agrees with the suggestions by Tong Sun [17] and P.A. Moussas [18]. However, there are some differences among XRD spectra of PSiCs with five Si/(Al + Fe) molar ratio, which suggest that distinctive compounds are formed in each PSiC. The results imply that Si/(Al + Fe) molar ratio has some effect on PSiC polymerization and conformation. Besides, polymerization of Fe, Al and Si is more complex in PSiC with Si/(Al + Fe) molar ratio of 0.8 than other molar ratios.