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Preparation and characterization of poly-silicic-cation coagulants by synchronous-polymerization and co-polymerization

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HIGHLIGHTS

- Poly-silicic-cation coagulants were prepared by synchronous- and co-polymerization.
- Characteristics of PSiC were analyzed by XRD, FT-IR, UVA and microscopic imaging.
- Coagulation performance of PSiC were evaluated by papermaking wastewater treatment.
- The structure, morphology and performance of PSiCs are better than PSiCc.

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ABSTRACT

Poly-silicic-cation coagulants (PSiCs) were prepared from industrial wastes such as fly ash, pyrite slag and wasted sulfuric acid by synchronous-polymerization and co-polymerization, and were denoted as PSiCs and PSiCc respectively. Their structures and morphologies were characterized and compared by X-ray diffraction (XRD), infrared spectra (IR), ultraviolet/visible absorption (UVA) scanning and microscopic imaging, and their coagulation performances were evaluated by papermaking wastewater treatment. The results show that new complexed compounds are formed in both PSiCs and PSiCc, but the polymerizations and conformations of Fe, Al and Si are different between the two coagulants. Compared with PSiCs, the contents of high polymers and ionic polymerized bonds are decreased obviously, and the cross-copolymerization between Fe(III) and Al(III) hydroxyl polymers disappeared in PSiCc. Morphologic analysis shows that PSiCc has fewer branch-like units than PSiCs, and coagulation experiments indicate that PSiCs exhibits higher coagulation efficiency in removing COD.

1. Introduction

Coagulation is one important process in wastewater treatment as it can effectively remove suspended solids and organic matters from raw water [1–4]. Polysilicate complex coagulants are a type of inorganic polymer coagulants developed in 1990s on the basis of poly-silicic acid (PS) and metal salts [5]. The PS with metal ions can not only improve charge neutralization capacity, but also combine the effects of adsorption and capture. In recent years, preparation and characterization of polysilicate complex coagulants are studied extensively [6–8]. These coagulants are often prepared from industrial-grade materials so some literatures focus on utilization of cheap industrial wastes. However, their preparation methods are complex as most materials need to be calcined, then leached at high temperature for long time and polymerized under heating [9–11].

Composite-polymerization and co-polymerization are two conventional methods to prepare polysilicate complex coagulants. The former is polymerization of PS and hydroxylated metal salts, and the latter is hydroxylation of mixture of metal salts and PS [12]. These coagulants are essentially hydroxylation of Si and metal ions, and their structures and coagulation performances could be influenced by preparation methods. For instance, the poly-ferric-aluminium-silica-sulfate coagulant prepared by composite-polymerization showed better performances in removal of turbidity, COD and chroma than polyaluminum chloride [13]. The study on the reaction mode between Si and Fe in poly-silicic-ferric (PSF) coagulant, which was prepared by co-polymerization, showed that PSF contained some complex compounds and its characteristics were largely affected by reaction time and Si/Fe ratio [14]. The poly-ferric-silicate-chloride synthesized by co-polymeri-

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zation showed three- and two-dimensional growth of Fe species for low and high Si/Fe ratios respectively [15]. The polyferric silicate sulphate coagulants prepared by co-polymerization had a higher coagulation efficiency than those prepared by composite-polymerization [12]. Therefore, preparation of polysilicate complex coagulants by co-polymerization is more popular [3,9,10]. Nevertheless, there is little research on the synchronous-polymerization method, which synchronizes the polymerization of silicate and the hydroxylation of metal salts [8], and even less research on comparison of this method with conventional methods.

In this paper, a synchronous-polymerization method was developed to prepare poly-silicic-cation coagulants (PSiCs) from industrial wastes. In this method, the polymerization of PS and the hydroxylation of metal ions were synchronized, and the resulting coagulant was denoted as PSiCs. PSiC was also prepared by co-polymerization with the same materials and molar ratios as PSiCs, and was denoted as PSiCc. The structures and morphologies of the two coagulants were characterized by X-ray diffraction (XRD), infrared spectra (IR), ultraviolet/visible absorption (UVA) scanning and microscopic imaging. Coagulation performance was evaluated by jar test in papermaking wastewater treatment, so as to compare the polymerisation profiles and product attributes of the two methods.

2. Materials and methods

2.1. Materials

The studied industrial wastes include fly ash, pyrite slag and wasted sulfuric acid, which were obtained from 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.

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	–
K_2O	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. Preparation of PSiCs

The preparation method of PSiC includes the following steps.

(a) Pretreatment

About 50 g of fly ash and 165 ml of 6 mol/L sodium hydroxide (industrial grade) were added into a beaker, heated under stirring to 80–90 °C, and kept for 2 h. After that, the mixture was filtered. The liquid part is a water glass solution which contains 0.4 mol/L SiO_2. The insoluble ash particles and 100 ml of water were added into 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 into the beaker, heated under stirring to 80–90 °C, and kept for 2 h. Then the mixture was filtered. The supernatant part is a metal salt solution, which contains mainly aluminum and iron and few other metals. The concentrations of Fe^{3+} and Al^{3+} are 1.2 and 0.12 mol/L respectively.

(b) Polymerization

About 50 ml of the water glass solution was added into 19 ml of metal salt solution at 1.5 ml/min under stirring, and then waste sulfuric acid was titrated at 1 mL/min to the desired pH 1.5. The solutions were aged at normal temperature for 2 days and PSiCs was prepared. PSiCs is a yellow solution with basicity of 22.3% and density of 1.19 g/cm^3. Basicity was measured by sodium hydroxide titration method using potassium fluoride as a masking agent (GB14591-2006, China).

2.3. Preparation of PSiCc

(a) Pretreatment

The water glass solution was introduced slowly into 5 mol/L wasted sulfuric acid under magnetic stirring until pH 2.0 ± 0.2. And then the Polysilicic acid (PS) solution was aged for 1 h.

The metal salt solution was prepared the same way as 2.2 (a).

(b) Polymerization

Then 19 ml of metal salt solution was added into 50 ml of PS at 1.5 ml/min under stirring, and then 1 mol/L sodium hydroxide was titrated at 1 mL/min to the desired pH 1.5. The solutions were aged at normal temperature for 2 days and PSiCc was prepared. PSiCc is a red–brown solution with basicity of 21.9% and density of 1.16 g/cm^3.

2.4. Characteristics of coagulants

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

2.5. Coagulation performance

Papermaking wastewater with COD of 150 mg/L, turbidity of 66 NTU, chroma of 16 and pH value of 7.5 was used to verify the two coagulants' coagulation performances.

Coagulation performance was evaluated by jar test using a ZR4-6 six-unit stirred system (Zhongrun, China). Pollutant removal efficiencies of PSiCs and PSiCc are measured under optimal dosage (80 mg/L for Fe + Al) and pH (7–8.5) for coagulation, which are determined by pre-experiments. The coagulant was added into the wastewater sample, which was stirred rapidly at 150 r/min for 2 min, followed by slow stir at 30 r/min for 10 min and precipitation for 30 min. Finally, the supernatant was taken from 3 cm below the surface of test wastewater. Turbidity, COD and chroma