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Characterization and coagulation behavior of polymeric aluminum ferric silicate for high-concentration oily wastewater treatment

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ABSTRACT

Polymeric aluminum ferric silicate (PAFSi), which is a composite coagulant, was prepared for high-oil-containing wastewater treatment. X-ray diffraction, scanning electron microscopy, and infrared spectra were used to characterize the structure of the PAFSi coagulants. The characterization results showed that PAFSi was a non-stoichiometric compound of basic iron sulfate salt with three-dimensional cluster structure. COD and oil removal rate were employed as indices for evaluating the coagulation ability of PAFSi in high-oil-containing wastewater treatment. Si/Fe molar ratio of 1:4, Al/Fe molar ratio of 1:1, basicity of 0.5, and preparation temperature of 70 °C were favorable to the preparation process. Coagulation tests showed that the optimal conditions for removing high oil concentration were 60–120 mg/L, pH 4–9, and G value of 300–600 s^{-1} with 98.2% COD removal and 98.4% oil removal. Zeta potential analysis indicated that charge neutralization was the main mechanism in reducing the surface charge of colloid particles in oily wastewater treatment. In addition, PAFSi presented superior coagulation–flocculation performance in high-oil-containing wastewater treatment. This coagulant can be used as an alternative method for pretreating high-oil-containing wastewater in industrial wastewater treatment.

1. Introduction

The rapid development of China's oil industry has resulted in the generation of large amounts of oil-containing wastewater from various industries, such as food, textile, leather, steel, transportation, petrochemical, and ship building industries, during oil processing and utilization process (Kumar et al., 2016). Oily wastewater is composed of extremely complex substances, usually high concentrations of dispersed oil, grease, and suspended particles (Yang et al., 2015). Illegal disposal of improperly processed oil-containing wastewater, which does not meet the emission standard, would seriously threaten the environment. The emission standard was "Effluent standard for water pollutants from ship" (GB 3552) of PRC National Standard, and the limit value of oil content was 15 mg L^{-1}. Such threats include air pollution caused by the evaporation of oil and rivers and lake pollution as a result of oil contamination (Zhang et al., 2016). Air pollution and contaminations of the groundwater, surface water, and soil caused by oil contamination eventually affect the human health (Wang et al., 2016).

Different water treatment technologies, such as adsorption (Tee et al., 2016), air flotation (Ngamlerdpokin et al., 2011a; Li et al., 2015), membrane filtration (Liu, 2016), biological treatment (Habashi et al., 2016), flocculation–coagulation (Yang et al., 2010), and electrochemi-

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cal treatment (Li et al., 2016), have been extensively applied to remove oil from oil-containing wastewater. However, utilizing these treatments individually cannot meet the treatment requirements because of the increasing awareness for environmental protection and complex wastewater ingredients, especially for high-concentration oily wastewater treatment (Jaruwat et al., 2010). Jamaly et al. (2015) indicated that the above traditional treatment method could effectively treat the oily wastewater with oil concentration of less than 5000 mg/L. Removal rate of more than 90% is difficult to achieve in the removal of oil/grease concentration of more than 6000 mg/L without high-cost pretreatment (Ngamlerdpokin et al., 2011b).

Meanwhile, the coagulation–flocculation technology, which is widely used in water treatment, showed unique advantages in oily wastewater treatment because of its no phase transition, easy operation, low cost, and good treatment efficiency (Fard et al., 2016). However, the properties of the coagulants seriously hinder the improvement of the coagulation–flocculation performance. Therefore, the preparation of coagulants with effective and efficient coagulation–flocculation performance has been attracting increasing attention for high-concentration oily wastewater treatment (Tong et al., 2014).

Aluminum and iron salts, such as $AlCl_3$, $Al_2(SO4)_3$, $FeCl_3$, polymeric aluminium, and polyferric sulfate, are the most often derived coagulants during coagulation (Teh et al., 2016). Traditional coagulants can be effectively used in treating wastewater with low oil concentration. However, satisfactory results cannot be obtained if these coagulants are used to treat high-concentration oily wastewater (Nogueira et al., 2016). Moreover, all aforementioned technologies are limited by the generation of precipitation and gelation caused by instability (Fu et al., 2009). However, adding other additive functional compounds during preparation is the main technique to improve the performance of the coagulants (Huang et al., 2016). An acid is an essential medium for acidification and co-polymerization during preparation. Activated silicic acid is essential to control and stabilize pH value, and this acid could significantly improve the performance of copolymerized coagulants (Moussas and Zouboulis, 2008a). A novel composite coagulant, commonly known as polysilicate-metal composite coagulant, was developed to overcome the limitations of traditional coagulants. However, very few studies have used activated silicic acid as acid medium to prepare coagulants and investigate the coagulation behavior.

Because of the strict requirements on marine and river water environmental protection, effective measures must be adopted to treat oily wastewater from ships. Therefore, the motivation of this work was to develop highly efficient coagulants for the pretreatment of high-concentration oily wastewater from ship. In the present paper, a novel composite coagulant polymeric aluminum ferric silicate (PAFSi) was synthesized using activated silicic acid as acid medium under different conditions. The structure and morphology of the PAFSi coagulants were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and infrared (IR) spectra. The effect of Si/Fe molar ratio, Al/Fe molar ratio, basicity, and preparation temperature on the coagulation–flocculation performance was investigated to optimize the synthetic conditions. In addition, coagulation performance was optimized by investigating the effect of wastewater initial pH, dosage, and velocity gradient on COD and oil removals. Meanwhile, the flocculation mechanism was systematically discussed using a detailed investigation of the effect of coagulant dosage and pH on the zeta potential.

2. Experimental

2.1. Materials

All reagents used in this study were of analytical grade except for ferrous sulfate ($FeSO_4 \cdot 7H_2O$), which was of technical grade. All reagents were purchased from NanJing Shengjianquan Chemical Glassware Instrument Co., Ltd. (Nanjing, China) and used in the experiments without further purification.

2.2. The characteristic of the wastewater samples

The simulated oil-containing wastewater was prepared with oil and surfactant according to the method in MEPC.107 (49). The raw water was characterized by measuring the oil and COD. Chemical analysis of the wastewater showed that the concentrations of oil, COD, and pH values were 5000 ± 100 mg/L, 20000 ± 400, and 7.0 ± 0.2, respectively. The oil content of the wastewater was measured according to the petroleum and natural gas industry standard SY/T0530-93 of the People's Republic of China.

2.3. Preparation of PAFSi

A series of Al–Fe composite coagulants were prepared in the laboratory. $FeSO_4 \cdot 7H_2O$ (50–70 g) was oxidized using sodium chlorate and slowly stirred in a beaker until a homogeneous liquid mixture was obtained. Then, 10%–40% $Al_2(SO4)_3$ solution was added into the reaction vessel to prepare a new liquid mixture containing Al and Fe. The new liquid mixture was stirred slowly for 30 min in a thermostatic water bath at a temperature 70 °C to obtain active Al–Fe solution. Then, a measured amount of polysilicic acid was slowly added into the metal salt solution under stirring. After adding silicic acid for 10 min, a measured amount of $NaHCO_3$ powder was added into the solution to obtain the desired basicity (basicity =OH/Fe molar ratio). After continued stirring for 60 min in a thermostatic water bath, the reaction mixture was stored at room temperature for 24 h for further polymerization and aging.

2.4. Characterizations of PAFSi

2.4.1. XRD analysis

The samples of liquid coagulants were dried in a vacuum oven at 70 °C for several days and ground into powders. XRD patterns of prepared samples were measured in the range of 5°–90° (2θ) (D/Max-3C, Japan).

2.4.2. Scanning electron microscopy (SEM)

The morphology of the coagulants was examined using scanning electron microscopy (SEM) (TES-CAN Company, Czech Republic). The SEM images were recorded by magnifying 3000 times and 5000.

2.4.3. FTIR

The FTIR spectra of the powder PAFSi were recorded using potassium bromide (KBr) pellets on a 550Series II infrared spectrometer (BRUKER Company, Switzerland). The spectrum of FTIR was measured in the range of 4000–400 cm^{-1}.

2.5. Zeta potential analysis

The zeta potential of wastewater was measured immediately after flocculation using a zetasizer (Malvern zetasizer Nano ZS90, Malvern Instruments Ltd., UK). The zeta potential was exported by the computer through the calculation of zetasizer software. The zeta potential measurements were carried out as a function of PAFSi dosage at pH 7 and as a function of initial wastewater pH value at 60 $mg\,L^{-1}$ PAFSi.