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Effect of aging period on the characteristics and coagulation behavior of polyferric chloride and polyferric chloride–polyamine composite coagulant for synthetic dying wastewater treatment

Baoyu Gao[a,b,*], Bin Liu[a,b], Ting Chen[a,b], Qinyan Yue[a,b]

[a] School of Environmental Science and Engineering, Shandong University, No. 27 Shanda South Road, Jinan 250100, PR China
[b] Shandong Key Laboratory of Water Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Shandong University, Jinan 250100, China

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ABSTRACT

In this paper, a new composite inorganic–organic coagulant (PFC–EPI–DMA) was prepared by polyferric chloride (PFC) and epichlorohydrin–dimethylamine (EPI–DMA) under a given EPI–DMA/Fe and OH/Fe molar ratio. In comparison with PFC, the Fe (III) species and zeta potential of PFC–EPI–DMA were measured. Then their coagulation performance and coagulation kinetics for treating synthetic reactive dying wastewater were investigated. The results showed that the content of Fe_a and Fe_b in PFC–EPI–DMA and PFC coagulants decreased with increasing aging period. Compared to PFC, PFC–EPI–DMA had higher content of Fe_a but lower content of Fe_b and Fe_c. The zeta potentials of two coagulants decreased with increasing aging period within all tested pH range. For the treatment of reactive red 24, the color removal efficiency treated by PFC–EPI–DMA decreased, while that treated by PFC remained almost constant with increasing aging period. However, the color removal efficiencies of reactive blue 14 treated by two coagulants both decreased with increasing aging period. The results of floc aggregation process confirmed that with increasing aging period, the orders of floc growth rate, ratio and TWV treated by two coagulants were complicated.

1. Introduction

Coagulation/flocculation is a widely used process in water and wastewater treatment and coagulants play an important role for removing suspended particles and coloring materials [1,2]. Traditional inorganic coagulants, based on aluminum and iron salts, are widely used in water and wastewater treatment process [3–5]. The prehydrolyzed polyaluminum salt coagulants are the most widely used coagulants, and extensive research has been focused on them [4]. Since residual aluminum is believed to be harmful to human and living organisms [6–8], iron-based coagulants have attracted more interest and attention [9–11]. It has been recognized that polyferric species was more effective than conventional monomeric ferric salts [12,13]. However, due to the high dosage of inorganic coagulant, large volume of sludge is produced, which requires high cost for sludge disposal, thus restricting the application of inorganic coagulants. Compared to inorganic coagulants, organic polymeric coagulants produce less sludge and are less pH dependent during coagulation process [14]. Though they have been used as coagulant aids in water and wastewater treatment for several decades, they are used alone as primary coagulants in recent years. However, high cost limited their application in water treatment.

For overcoming the limitation mentioned above and increasing the coagulation efficiency, research has been focused on the application of dual-coagulants. In the traditional method of dual-coagulant systems, inorganic coagulant and organic coagulant are usually added into water or wastewater, separately [15,16]. The dual-coagulant systems need two reagent addition systems which will increase the cost of water treatment. Therefore, a new method was developed, in which inorganic coagulant was premixed with organic coagulant before they were added to the water treated. This new dual-coagulant is called composite inorganic–organic coagulant. In recent years, there has been intensive research on composite coagulant [17–19].

In this paper, a novel composite inorganic–organic coagulant (PFC–EPI–DMA) was prepared by polyferric chloride (PFC) and epichlorohydrin–dimethylamine (EPI–DMA). PFC contains a range of pre-formed Fe (III) hydrolysis species of high positive charge [20], which is mostly affected by the basicity, the aging temperature and time [10]. The basicity, defined as the ratio of the moles

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* Corresponding author at: School of Environmental Science and Engineering, Shandong University, No. 27 Shanda South Road, Jinan 250100, PR China.
Tel.: +86 531 88364832; fax: +86 531 88364513.
E-mail addresses: baoyugao_sdu@yahoo.com.cn (B. Gao), liubin19860607@126.com (B. Liu), cangqiong21@163.com (T. Chen), qyyue@sdu.edu.cn (Q. Yue).

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of base added and/or bounded to the moles of Fe^{3+} ($[OH^-]/[Fe^{3+}]$), and the aging temperature can be controlled during manufacturing. However, the Fe (III) species distribution was affected by aging period, which meant the coagulation performance and kinetics of PFC was influenced by aging period. EPI–DMA is a synthetic organic polymeric coagulant, which has been used in water and wastewater treatment processes. They are effective in wide pH range, easy to handle, and immediately soluble in aqueous solution [21]. Since PFC and EPI–DMA were premixed to produce PFC–EPI–DMA composite coagulant, the Fe (III) species distribution and coagulation performance of PFC–EPI–DMA were also affected by aging period. However, there is very limited research on the effect of aging period on characteristics and coagulation performance of polyferric coagulants, and particularly, there is no available literature concerning the relationship between aging period and the coagulation performance of polyferric–organic composite coagulant. The objective of this work is to investigate the effect of aging period on the characteristics of composite coagulant PFC–EPI–DMA and PFC, including the Fe (III) species and zeta potential variation. Moreover, to evaluate coagulation performance, coagulation experiments were conducted for the treatment of synthetic reactive blue and reactive red dying wastewater. Finally, the floc aggregation process was investigated with the Photometric Dispersion Analyser (PDA 2000).

2. Materials and methods

2.1. Preparation of PFC and PFC–EPI–DMA

PFC was prepared using $FeCl_3 \cdot 6H_2O$ (A.R.) and Na_2CO_3 (A.R.) in our laboratory. Firstly, $FeCl_3$ solution with a concentration of 7% (w/w) was prepared by dissolving $FeCl_3 \cdot 6H_2O$ in distilled water. Then, the solution was mixed with Na_2CO_3 powder (C.P.) by stirring at room temperature to reach the desired $[OH^-]/[Fe]$ ratio (B) value. Finally, $Na_2HPO_4 \cdot 12H_2O$ (A.R.), as a stabilizer, was added to the solution ($[Na_2PHO_4]/[Fe] = 0.08$). PFC with 1 d, 10 d and 30 d aging period was denoted as PFC_1, PFC_{10} and PFC_{30}, respectively. The target PFC had the following characteristics: $w(Fe) = 7\%$; $B = 0.5$; pH = 0.6–0.75.

EPI–DMA was also prepared in our laboratory. The initial reactive temperature was 30 °C. Firstly, dimethylamine (33%, C.P.) was added to a 250 mL glass reactor equipped with a temperature controller and a mechanical stirrer. Then epichlorohydrin (A.R.) at a selected weight was gradually added by dropping into the reactor under constant stirring. After that, 1,2-diaminoethane at a chosen weight percentage in the mixture was added into the reactor under stirring. And then, the reactive temperature was raised slowly to 60–75 °C. After 7 h reaction, the polyamine polymers were obtained. The polyamine had the following characteristics: $\eta = 850$ mPa s (intrinsic viscosity); cationicity = 3.5 mmol/g.

For the preparation of composite coagulant PFC–EPI–DMA, EPI–DMA with a measured amount was added to PFC solution under thorough stirring at room temperature. The aging temperature of PFC–EPI–DMA was 20 ± 1 °C. PFC–EPI–DMA with 1 d, 10 d and 30 d aging period was denoted as PFC–E_1, PFC–E_{10} and PFC–E_{30}, respectively. The target PFC–EPI–DMA solution had the following characteristics: $w(E) = 7.0\%$ (the weight percentage of EPI–EMA); pH = 0.7–0.8; $\rho = 1.22$ g/cm^3; turbidity = 5.9–6.2 NTU (with 30 d aging period).

2.2. Measurement of coagulant characterization

The Fe (III) species distribution in PFC and PFC–EPI–DMA solutions was measured by a timed complexation spectroscopy method involving reactions of Fe with Ferron (8-hydroxy-7-iodoquinoline-5-sulphonic acid) [22]. Visible light absorbance was measured as a function of time at a wavelength of 600 nm (for Fe) to quantify the amount of Fe complex formed. The reactions of Fe (III) monomeric species with Ferron were completed in 1 min (denoted as Fe_a), and the reactions of Fe (III) polymeric species (denoted as Fe_b) with Ferron finished in the next 3 h, and the unreactive Fe (III) species after 3 h was considered to be Fe (III) colloidal and precipitated species (denoted as Fe_c).

The zeta potential of PFC–EPI–DMA at dosage of 100 mg/L (as Fe) was measured by the JS94H Micro-Electrophoretic Mobility Detector, and comparison was made with PFC [23]. During experiments, pH of the coagulant solutions was adjusted by adding HCl (1 mol/L) or NaOH (1 mol/L). After 5 min of gentle stirring, the samples were analyzed and the data were recorded.

2.3. Jar test procedures

Reactive dyes are the most commonly used dyestuffs in textile industry. Hence, reactive blue (K-GL) and reactive red (K-2BP) which were characterized by different types were chosen for investigation. The dyes were obtained from Jinan No. 2 Textile Dyeing Mill, China. Their color index (CI) numbers are reactive blue 14 and reactive red 24, respectively. The synthetic dye wastewater was prepared by dissolving 0.5 g of dye in 10 L tap water. The CI number, type, molecular structure and the wavelength of maximum absorbance of two dyes are shown in Table 1. The synthetic reactive blue wastewater samples had the following characteristics: pH = 8.00 ± 0.01; maximum absorbance = 0.500–0.515; turbidity = 6.80–7.70 NTU. The synthetic reactive red wastewater samples had the following characteristics: pH = 8.06 ± 0.01; maximum absorbance = 0.885–0.900; turbidity = 0.90–1.13 NTU.

Coagulation experiments were carried out by using a conventional Jar-test apparatus (the DC-506 Laboratory Stirrer) at room temperature (19–21 °C). Appropriate amounts of coagulants were injected into the wastewater samples (500 mL). The dosages of coagulants were calculated by the quantity of their effective component, i.e. PFC by Fe, and PFC–EPI–DMA by Fe plus the weight of EPI–DMA. After dosing of coagulants, the wastewater samples were stirred fast at 120 rpm paddle speed for 2.5 min. Then the samples were stirred at the paddle velocity of 40 rpm for 12 min, followed by sedimentation for 20 min. After that, supernatant samples were withdrawn for analyzing color removal efficiency, which was calculated by comparing the absorbance value for the treated wastewater sample to the absorbance value for the original synthetic dye wastewater. Distilled water served as a reference.

2.4. Coagulation kinetics

The formation of floc during coagulation–flocculation process can be monitored by Photometric Dispersion Analyzer (PDA 2000; Rank Brothers Ltd.). During the coagulation periods, the suspension was continuously sampled by peristaltic pump (LEAD-1, Baoding Longer Precision Pump Co. Ltd., China) and monitored by a PDA 2000 to obtain data. The detailed theory of PDA 2000 has been reported in some published literatures [24,25]. The curves as shown in Fig. 1 were plotted using the typical ratio obtained from the experiments and can be divided into three specific regions: lag region, growth region and steady-state region. The ratio values were related to the mean concentration and the size of dispersed particles. In this study, three parameters were calculated to analyze the data collected by PDA 2000 during the coagulation–flocculation process. These parameters included a floc growth rate of the growth region, a time-weighted average steady-state ratio value and a time-weighted ratio variance (TWV) of the steady-state ratio value. The slope of the growth region is an indicator of the rate at which flocs developed. The floc growth rate which is denoted as the linear