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Flocculation kinetics and floc characteristics of dye wastewater by polyferric chloride–poly-epichlorohydrin–dimethylamine composite flocculant

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ABSTRACT

The polyferric chloride–poly-epichlorohydrin–dimethylamine (PFC–ECH–DAM) composite flocculants with different OH/Fe ratios, Fe to organic ECH–DAM mass ratios and cross-linker types were comparatively investigated in terms of formed floc aggregation process and floc characteristics for the treatment of synthetic dyeing wastewater. The effect of OH/Fe molar ratio (*B* value), Fe to ECH–DAM mass ratio (MR value), cross-linker type and ECH–DAM addition on floc characteristics was investigated as function of flocculant dosage and dye wastewater pH. The results demonstrate that the synergic effect of PFC with ECH–DAM promoted the formation of larger flocs with higher growth rate and wider distribution of floc sizes. During the coagulation of reactive red (K-2BP) dyeing wastewater, strengthened floc properties can be obtained at higher flocculant dosage ranges (>80 mg/L) and solution pH of about 7.5. The floc TWV values appear to show that the predominant flocculation mechanism of PFC–ECH–DAM are bridging adsorption and sweep flocculation. In addition, relatively lower OH/Fe molar ratio, higher Fe to ECH–DAM mass ratio and utilizing polyethylene polyamine as cross-linker were favorable for the formation of flocs with larger size, higher growth rate and larger size variation.

1. Introduction

Textile dyeing process is one of the most environmentally unfriendly industrial technologies, due to the fact that this process produces colored wastewaters that are heavily polluted with dyes, textile auxiliaries and chemicals [1]. The discharge of highly colored wastewater creates not only aesthetical problem, but also impedes light penetration, thus upsetting biological processes within a stream [2]. Further, many kinds of dyes are toxic to some organisms and may destruct aquatic communities [1,2]. For this reason, decolorization treatment for textile effluents has attracted great attention in both research and industrial application. Physical and chemical treatment technologies, including coagulation, adsorption, reverse osmosis, chemical oxidation, electrolysis, and biological treatment, have been extensively utilized for dye wastewater treatment [3]. Among these treatment methods, coagulation and flocculation process are widely used as pretreatment steps for the decolorization of dye wastewater [1,4].

Organic and inorganic flocculants are widely used during the decolorization process of the textile dye wastewater. Although chemical coagulation by alum or Al-based chemicals can be used for treating dye wastewater before the biological treatment unit, it has some drawbacks. For example, their effectiveness is strongly pH dependent and purified water may have high residual Al concentrations [5]. Compared to Al-based coagulants, the ferric salts, which are non-toxic, are characterized by formation of larger and denser flocs and less solution pH dependent [6]. Accordingly, the Fe-based coagulants have attracted more attention for the color removal of textile wastewater. However, as an inorganic coagulant, the significant amounts of sludge are produced during coagulation which complicates the handling and disposal procedures and then restricts the application of inorganic Fe-based coagulants. Moreover, it would lead to high operating cost during water/wastewater treatment using organic flocculants. Therefore, it seems reasonable to develop composite products prepared by Ferric salts (especially polymeric speciation) and organic polymers.

During the flocculation process, the decolorization efficiency of textile wastewater depends on both the structure of the flocculants used and the treated dye types [7]. Regarding the dye type during dyeing wastewater treatment, insoluble disperse or hydrophobic dye molecules are prone to be decolorized from the wastewater by chemicals addition. In contrary, for soluble or hydrophilic dyes used in textile printing and dyeing industry, the decolorization becomes difficult [8]. In addition, the flocculation dynamics and the characteristics of flocs during coagulation and decolorization process possess important significance for further investigation of flocculating mechanism, expansion of application range and

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the development of more effective coagulants. Added to this, when utilizing the pre-combination method to prepare dual composite flocculant during the coagulating decolorization process of dye wastewater, the corresponding decolorization efficiency, flocculation dynamics and the floc characteristics can be dramatically influenced by various operating factors, such as coagulant characteristic, dosage, dye wastewater property and synthesis technology of composite coagulants.

Based on the current research tendency, a novel composite flocculant polyferric chloride–poly-epichlorohtdrin–dimethylamine (PFC–ECH–DAM) was prepared by the pre-combination method of polyferric chloride (PFC) and the positively charges copolymer of epichlorohtdrin–dimethylamine (ECH–DAM) with different types of cross-linkers. The reactive red dye (K-2BP) was selected as the model dye compound to determine the flocculation characteristics of PFC–ECH–DAM in color removal. On the basis of preliminary experimental results about coagulation performance, the effect of organic ECH–DAM addition, PFC property, cross-linker type, proportion of organic ECH–DAM, dye wastewater characteristics on the flocculation dynamics, floc size, floc growth rate, degree of floc distinguish were extensively investigated with the Photometric Dispersion Analyser (PDA2000).

2. Materials and methods

2.1. Preparation of PFC and ECH–DAM

The inorganic polymeric PFC coagulant was prepared using analytically grade $FeCl_3 \cdot 6H_2O$, Na_2CO_3 and $Na_2HPO_4 \cdot 12H_2O$ by slow base titration. In preparation, Na_2CO_3 solution was gradually added into $FeCl_3$ solution under constant stirring according to the predetermined basicity (B = [OH]/[Fe]). After the disappearance of formed foam, appropriate content of $Na_2HPO_4 \cdot 12H_2O$ ([P]/[Fe] = 0.08) was incorporated into the mixed solution as stabilizer. The target PFC product has the following properties: C(Fe) = 10 g/L; pH = 0.60 ± 0.05; B = 0.5, 1.0 and 1.5.

ECH–DAM copolymer was prepared in this research by polycondensation reaction of epichlorohydrin and dimethylamine with three different cross-linkers [7,9]. The principal product, as cationic polyelectrolyte, has both hydrophobic groups (methyl groups and backbone chain) and hydrophilic groups (positively charged quaternary amines), which can be used to coagulate suspended solids and colloid particles in wastewater by charge neutralization and adsorption-bridging. Ethylenediamine (EDM), diethylenetriamine (DTM), and triethylenetetramine (TTM) were used as cross-linkers. For the polycondensation process, each reaction was conducted in a 250 mL, four-necked, round-bottomed flask equipped with a mechanical stirrer, a thermometer, a dropping funnel and corresponding glass spigots. The reactor containing predetermined amount of epichlorohydrin (A.R.) was cooled to 10 °C from ambient temperature using a thermostated water bath. Then, the chemically-pured dimethylamine was added into the reactor using dropping funnel under constant stirring to form oligomer within 1 h. After that, appropriate amount of cross-linker was introduced into the reaction system with continuous stirring. When peak of the heat emission appeared, temperature of the reaction system was enhanced to 70–75 °C and the mixture was kept at the constant temperature for further 7 h under vigorous stirring. Finally, the viscous and homogeneous polyamine polymers were obtained.

2.2. Synthesis of PFC–ECH–DAM

Appropriate amount of PFC solution and ECH–DAM copolymer were mixed together in distilled water under magnetic stirring for 2 h to prepare the composite PFC–ECH–DAM flocculant. The final PFC–ECH–DAM products were characterized as following: C(Fe) = 5 g/L; B = 0.5, 1.0 and 1.5; pH = 1.23 ± 0.05. The three cross-linkers (EDM, DTM and TTM) were used for the synthesis of the composite coagulant. Added to this, mass ratio (MR) of Fe to ECH–DAM was determined as 2:1, 4:1 and 8:1 in the composite material. During the flocculation process, the flocculant dosage was calculated according to the content of Fe in the reaction systems.

2.3. Simulated test water

A single-species simulated dyeing wastewater with a concentration of 50 mg/L (reactive red, K-2BP) was obtained in this study, in order to prevent the interference of other components in actual wastewater on decolorization performance. Considering the extensive application of reactive dyestuffs in textile industry, the reactive red (K-2BP) obtained from Ji'nan No. 2 Textile Dyeing Mill (China) was selected as model dye compound for investigation. The synthetic dye wastewater was prepared by dissolving certain amount reactive red into tap water under uniform mixing. The reactive red dyeing wastewater had the following characteristics: pH = 8.02–8.16, zeta potential = −30.58 mV to −37.75 mV, maximum absorbance = 0.500–0.515. The raw water pH was adjusted to predetermined value by 0.1 mol/L HCl and 0.1 mol/L NaOH solutions in order to investigate the initial pH influence during reactive red wastewater treatment.

2.4. Procedures for coagulation tests

At room temperature of about 20 ± 1 °C, coagulation experiments were carried out in a conventional jar test apparatus equipped with flat paddle impellers and cylindrical jars containing 500 mL samples of dyeing wastewater. Under rapid agitation of 120 rpm, predetermined amount of composite flocculants was dosed into the simulated dyeing wastewater to coagulate particles for 3 min. The stirring speed was then reduced to 40 rpm for 12 min to allow flocs growth and the suspension was finally allowed to settle for 20 min. The water used for solution dilution and reagent preparation was deionized in all experiments.

2.5. On-line monitoring of floc size during flocculation process

During the flocculation process, flocs can form after the addition of flocculant, and floc size increases significantly due to floc aggregation. After that, a steady state of floc size occurs eventually due to the equilibrium between floc aggregation and floc breakage [9,10]. Through the transformation of optical signals to electrical signals, the Photometric Dispersion Analyzer (PDA 2000) was used to measure the relative floc sizes (flocculation index) as a function of time under the flocculation conditions [11]. Detailed principles of the on-line monitoring of floc size can be found at the investigation of Ching et al. [12]. Experiments were carried out as before on a 1 L cylindrical jar apparatus equipped with the inflow/outflow tubing (5 mm internal diameter). The suspension was monitored by drawing and circulating water by a peristaltic pump at a flow rate of 1.5 L h^{-1} through the optical detector of PDA2000.

In this technique, three typical parameters can be calculated to evaluate the characteristics of formed flocs and to compare the flocculation effectiveness during coagulation/floccualtion process. These parameters can be described as: steady-stage ratio values (Ratio), floc growth rate value of floc aggregation stage (Growth Rate), and a time-weighted average ratio variance of the ratio value during the steady stage (TWV). The calculation equations are denoted as following: