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Coagulation enhancement of exopolysaccharide secreted by an Antarctic sea-ice bacterium on dye wastewater

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ABSTRACT

The purpose of this paper is to study the enhancement of Bsi20310 exopolysaccharide (Bsi20310 EPS, secreted by an Antarctic sea-ice bacterium *Pseudoalteromonas* sp. Bsi20310), on coagulation of reactive brilliant red X-3B (RX-3B) by ferric chloride. The effect of solution pH, EPS addition timing and NaCl concentration for coagulation of RX-3B was investigated. The results showed that at pH 10, Fe(III) dosage of 55 mg/L, adding 150 mg/L Bsi20310 EPS enhanced the decolorization effectively. NaCl had little effect on the enhancement of Bsi20310 EPS. The EPS had negative surface charge and could combine with positive Fe(III)–dye flocs to form neutralized settleable Fe(III)–dye–EPS flocs. Results of residual Fe(III) concentration and ferric–ferron reaction kinetics indicated that EPS addition led not only more Fe(III) to participate in coagulation but also to form more Fe_b (the most effective ferric hydrolysis species) in coagulation. Bsi20310 EPS enhanced Fe(III) coagulation performance by neutralization, bridging and sweeping to improve the floc aggregation.

1. Introduction

Dye wastewater released from industries of textile dye printing is a considerable source of environmental contamination [1,2]. Dye wastewater generally consists of one or several kinds of materials, such as pigments/dyestuffs, surfactants, salts and alkali, characterized by deep color, high COD and low biodegradability [3]. The discharge of dye wastewater into natural water has caused a series of environmental problems [4]. The presence of color not only affects human's aesthetic merit, but also disturbs photosynthetic activity of hydrophytes by reducing light penetration. In terms of public health, most synthesized dyes and their degradation derivatives (e.g. aromatic amines) are toxic and potentially mutagenic and carcinogenic [5].

Reactive azo dyes characterized by nitrogen to nitrogen bonds (–N=N–) account for a large partial of the dye market worldwide, due to their relatively high reactivity with cellulosic fabrics and simple application techniques. These reactive azo dyes have bright colors, which are highly visible and undesirable even at very low concentrations (less than 1 mg/L) in the effluent [1,6]. RX-3B is a typical reactive azo dye which has been widely used in textile and printing industries. The molecular structure of RX-3B is shown in Fig. 1.

The –OH and two groups of $-SO_3^-$ give it not only high solubility but also high negative charges in aqueous solution, which makes it difficult to be treated effectively [7,8]. Since not all the dyes are exhausted during the dying process and about 10–50% dyes still remained in the effluent, dye wastewater should be decolorized before its release [9].

Many methods have been reported to remove color from dye wastewater, among which coagulation is a widely used process due to its relatively simple operation and low cost [5,7]. The most commonly used coagulants in dye wastewater treatment are Al(III) salts and Fe(III) salts [8,10]. It is suspected that there is a connection between Alzheimer's disease and chronic exposure to aluminum [11]. Thus people's attention has turned to Fe(III) salts, and some better Fe(III) performances than Al(III) have been reported in the color removal of dye wastewater [3]. However, it is found that reactive dye solution is difficult to decolorize by inorganic coagulants which might be effective on decolorizing disperse dye solution. Due to the generally basic characteristic of actual reactive dye wastewater, the coagulation efficiencies are very low. Using Fe(III) coagulants, Kim et al. [8] reported that the decolorization of two reactive dyes coagulated by 0.50 mmol $FeCl_3{\cdot}6H_2O$ was low at about 40%. Moreover, pH values affect the color removal efficiency greatly, especially at pH values higher than 6 [10]. Many efforts

Abbreviations: EPS, exopolysaccharide; RX-3B, reactive brilliant red X-3B; MF, microfiltration; PDA, photometric dispersion analyzer; FI, flocculation index.

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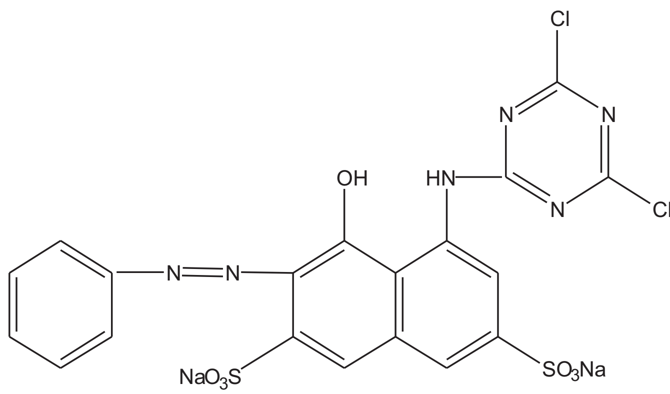

Fig. 1. Molecular structure of RX-3B dye.

had been paid to improve the conditions and coagulation aids have been introduced to enhance the coagulation efficiency on reactive dye wastewater in recent years [7,12]. Many synthetic polymers such as polyacrylamide, polydimethyldiallylammonium chloride, polyepicholorohydrindiamine, have been used as the main coagulant aids and some good results have been reported [7,13,14]. However, the practical application of these synthetic polymers, such as acrylamide, is limited by their potential environmental and health risks. So there is an increasing demand of environmental friendly and effective coagulant aids.

Bacterial EPSs have received much attention for their utilization in wastewater treatment recently [15]. Sea ice provides one of the coldest habitats on the earth for marine life, with temperatures ranging from 0 to −35 °C [16]. The large quantity of EPSs, secreted by Antarctic sea-ice extremophiles bacteria, which can protect the microbe surviving in low temperature and high salinity conditions, shows some different characteristics from the ordinary bacterial EPSs. For example, molecular weight of EPSs produced by sea-ice isolated bacteria showed about 5–50 times greater than that of the average other marine microbe EPSs [17]. The high molecular weight of EPSs may be helpful to promote floc growth in coagulation process [18]. *Pseudoalteromonas* sp. Bsi20310 is a psychrotolerant bacterium isolated from Antarctic sea-ice, which could grow in a wide range of temperatures and secret a large quantity of EPS. However, the optimum growth of the bacteria does not result in the largest yield of EPS. Its optimum growth temperature is 32 °C, but it can still survive at 0 °C, while the largest yield of EPS is obtained at 15 °C. Many reports showed that, the optimum temperature for growth is usually different from that for EPS production [19]. A decrease in temperature causes a decrease in growth rate and cell wall polymer biosynthesis, making more precursors available for exopolysaccharide synthesis. A low incubation temperature can also cause reduction in growth rate and cell mass, which in turn resulted in long logarithmic phase of growth, higher viscosity and greater production of exopolysaccharide as compared to high temperature [20,21]. Bsi20310 can survive in low temperature and high salinity conditions. This is very important for reactive dye removal as most dye wastewater contains lots of salts which make the treatment very difficult.

Our previous study showed that Bsi20310 EPS was a high molecular weight polysaccharide with carbon backbones consisting of functional groups such as hydroxyl, carboxyl and glycosidic bond, and these groups could combine with ferric ions [22]. The characteristics of Bsi20310 EPS suggested it may be favourable to enhance the coagulation process. However, many concerned characteristics of Bsi20310 EPS in the coagulation process, such as, influence of some dye water traits and operation parameters on the coagulation efficiency, the roles and mechanism of the EPS in coagulation process, etc., are still unknown.

The main purpose of this study is to evaluate the enhancement of Bsi20310 EPS on decolorization of simulated RX-3B dye wastewater coagulated by $FeCl_3{\cdot}6H_2O$ on the parameters of initial solution pH, EPS addition timing and NaCl concentration. Zeta-potential of flocs, floc characterization, residual Fe(III) concentration and Fe(III) hydrolysis kinetics were also analyzed to give better insights into the possible coagulation mechanism of Bsi20310 EPS enhancement.

2. Experimental

2.1. Cultivating of Pseudoalteromonas sp. Bsi20310 and preparation of the EPS

Isolated *Pseudoalteromonas* sp. Bsi20310 strain was cultivated in culture medium (75 ml) on a rotary shaker (150 rpm) at 15 °C for 72 h. Details in medium composition and preparation of crude Bsi20310 EPS were reported in previous study [22]. The crude EPS was dissolved in deionized water (2 g/L) and then stored at 4 °C in a refrigerator.

2.2. Measurement of the specific surface area of Bsi20310 EPS

The method of methylene blue adsorption was applied to measure the specific surface area of Bsi20310 EPS [23]. 50 ml methylene blue solutions over the range of 10–300 mg/L were taken into conical flasks with plugs and added EPS dosage of 40 mg/L, respectively. The flasks were placed in a horizontal shaker and shaken at 200 rpm and 20 °C for 12 h. Then the samples were filtered by 0.45 μm cellulose acetate membrane and measured by spectrophotometer (UV-752, Shanghai) at 665 nm, then the dye concentration was calculated by a regression equation: $Y = 0.00763 + 0.18278X$ ($R^2 = 0.9964$), in which X was the concentration, mg/L and Y was the absorbance. Blank samples were carried out by replacing Bsi20310 EPS solution with equal volume of deionized water. The methylene blue uptake (Q, mg/g) can be determined as Eq. (1):

$$Q = \frac{V(C_i - C_e)}{W} \tag{1}$$

where C_i and C_e are the concentrations of initial and equilibrium methylene blue in the solution (mg/L), respectively; V is the solution volume (L); W is the mass of Bsi20310 EPS added (g).

Langmuir isotherm (Eq. (2)) was employed to obtain the theoretical maximum adsorption capacity (Q_m, mg/g):

$$\frac{1}{Q_e} = \frac{1}{Q_m} + \left(\frac{1}{Q_m K_L}\right)\frac{1}{C_e} \tag{2}$$

where C_e and Q_e are the methylene blue equilibrium concentrations in solution (mg/L) and adsorbent (mg/g), respectively; K_L is the Langmuir equilibrium constant (L/mg). The values of Q_m and K_L for the adsorption can be derived from the linear plot of $1/Q_e$ versus $1/C_e$, respectively.

The specific surface area (S, m^2/g) was calculated by the following equation:

$$S = \frac{Q_m \times A \times N}{1000 \times M} \tag{3}$$

where Q_m is the maximum adsorption capacity (mg/g); A is the occupied surface area of one molecule of methylene blue, $197.2 \times 10^{-20}\ m^2$; N is Avogadro's number, $6.02 \times 10^{23}\ mol^{-1}$; and M is the molecular weight of methylene blue, 373.9 g/mol.

2.3. Preparation of synthetic dye wastewater

RX-3B dye was bought from Yongxing Dye Co. Ltd., Shandong, China. The synthetic dye wastewater was prepared by dissolving