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Removal of Reactive Black W-2N from synthetic wastewater by an integrated membrane coagulation reactor ☆

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ABSTRACT

Herein, a new integrated membrane coagulation reactor (IMCR) was developed to effectively treat synthetic wastewater containing Reactive Black W-2N. The optimal operation conditions were determined as follows: influent pH 5.5, polyferric sulfate (PFS) dose 1.2 mmol/L, and hydraulic retention time 3 h, under which a nearly complete decolorization was achieved and chemical oxygen demand removal reached 92%. Membrane fouling experienced three phases as reflected by different increment rates of the trans-membrane pressure. A high PFS dose aggravated the membrane fouling. The fractal dimension value of flocs increased with the increasing coagulant dose. In comparison to the control experiment, ferrate addition significantly increased the mean size and porosity of the floc particles formed. Because ferrate addition could reduce the trans-membrane pressure increment rate, the steady-state performance of the IMCR process was improved.

1. Introduction

Dyes are being extensively used in textile, dyeing, paper printing, color photography and other industries [1,2]. Over 0.7 million tons and approximately 10,000 different types of dyes and pigments are produced worldwide annually [3]. Among them, a majority of synthetic dyes currently used are highly water-soluble azo reactive dyes. Azo reactive dyes are characterized by the existence of nitrogen–nitrogen double bonds [4]. They differ from all other classes of dyes which bind to the textile fibers (e.g. cotton) to form covalent bonds. They have favorable characteristics such as bright color, water-fastness, easy application and low energy consumption, and thus have been used extensively in textile industries [5].

However, reactive dyes could result in great color problem, which is exacerbated by the dominance of cotton in fashion industry. Human eyes can distinguish reactive dye at a concentration as low as 0.005 mg/L in water. As a result, the presence of dye exceeding this limit will be permitted neither in environmental protection nor in aesthetic viewpoint [6]. In the textile industries, nearly 50% of reactive dyes may be lost to the effluent after dyeing of cellulose fibers [5]. Removal of these dyes from wastewater is an important environmental challenge because reactive dyes cannot be easily removed by conventional wastewater treatment technologies. They are stable to light, heat and oxidizing agents. Besides, they have limited biodegradability in an aerobic environment, and many azo dyes may decompose under anaerobic conditions into potential carcinogenic aromatic amines [7]. Hence, it is urgent to develop dye wastewater treatment processes that are technically and economically feasible.

Due to the water shortage and the continuously deteriorating surface water quality in China, the reuse of production process water has attracted much attention. Membrane processes have been successfully used not only for water purification but also for specific contaminants recycling from industrial effluents [8]. However, constituents in feedwater could foul the membranes [9]. Early studies reported that coagulation tended to be the most successful pretreatment for membrane fouling reduction and flux improvement [10–12]. During the recirculated membrane process, an energy-intensive recirculation pump is required to provide a high feed flow rate. By comparison, immersed low-pressure hollow fiber membrane process can achieve a substantial reduction in energy consumption and has gained an unprecedented popularity not only in wastewater treatment but also in drinking water production [13,14].

Under such circumstances, a novel integrated membrane coagulation reactor (IMCR), which combined coagulation with ultra-filtration (UF), was developed for reactive dye removal from

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simulated wastewater. Ferric ions were used as coagulants. It could achieve easy automation with a low operating pressure and enable excellent liquid/solid separation. The performance of the IMCR removing Reactive Black W-2N was assessed. Besides, the characteristics of membrane fouling with different operating conditions were explored.

2. Materials and methods

2.1. Experimental set-up and procedure

The flow chart of the IMCR used in this study is shown in Fig. 1. The reactor included two units: coagulation unit and membrane separation unit. The volumes of the two units were 8 and 29 L, respectively. The membrane separation unit was equipped with two hollow-fiber ultra-filtration membrane modules (provided by Korean KMS Company) made of polyethylene. The total surface area was 0.97 m^2 and the molecular weight cutoff (MWCO) was 80 kDa. The dye used in this work was Reactive Black W-2N (Beijing Topnew Group, China). Its chromophore group is azo, and its water solubility at 50 °C is 200 g/L. The molecular weight and maximum absorption wavelength (λ_{max}) of the Reactive Black W-2N are 851 and 604 nm, respectively. The synthetic wastewater was prepared by dissolving 5 g Reactive Black W-2N in 50 L tap water under stirring. The dye content was 0.1 g/L, and the pH value of the synthetic wastewater was 7.5. Polyferric sulfate (PFS) was used as coagulant, and NaOH or HCl was used for pH adjustment. In the IMCR, aeration and stirring (200 rpm) was continuously carried out, and filtration was intermittently performed (7 min filtration and 3 min pause) using a suction pump. The bubbles pushed the sludge to flow upward between the membrane modules to minimize membrane fouling. However, membrane fouling occurred inevitably during the IMCR process. To achieve steady flux, the operating pressure had to be enhanced, which aggravated membrane fouling. The membrane fouling of the IMCR could be indexed by an increase of trans-membrane pressure (TMP). When the suspended solids (SS) concentration in the membrane separation unit was low, the TMP varied slightly with an increasing SS; whereas when the SS concentration reached a critical value, the TMP increased sharply. As a result, sludge in the IMCR was discharged and the membrane was cleaned by physical and chemical methods. First, a sludge cake was flushed out by tap water. Second, membrane modules were cleaned chemically by a mixed solution of NaClO and NaOH (effective Cl 3000 mg/L, NaOH 500 mg/L). Finally, the modules were soaked in distilled water for 8 h.

2.2. Analytical methods

The absorbance at λ_{max} of the simulated wastewater was measured and the full wavelength scanning (from 190 to 1000 nm) was performed on a spectrophotometer (HACH DR-5000). Color removal efficiency was calculated by comparing the absorption values (at λ_{max} = 604 nm) of the treated wastewater to original wastewater. The equation used to calculate the color removal efficiency is as follows:

$$\text{Color removal } (\%) = \frac{\text{Abs}_o - \text{Abs}_t}{\text{Abs}_o} \times 100 \quad (1)$$

where Abs_o and Abs_t are the absorbance (at λ_{max} = 604 nm) of the original and treated wastewater. Distilled water served as a reference. Supernatants were withdrawn from the membrane separation unit and then centrifuged at 8000 rpm for 10 min to remove the suspended solids. The COD concentrations of the samples were analyzed according to standard methods [15]. All samples were analyzed in triplicate and the mean values were reported. The zeta potentials and sizes of floc particles in raw and coagulated water were measured using a zeta meter (Zetasizer, Malvern, UK) and a particle size analyzer (Mastersizer 2000, Malvern, UK), respectively.

For scanning electron microscopy (SEM) observations, the samples were fixed in a 2.5% (v/v) glutaraldehyde solution, dehydrated in water–ethanol solutions (i.e. 30%, 50%, 70%, 80%, 90%, 95% and 100%), dried under vacuum, and then sputter-coated with gold before images were taken with a JEOL JSM-500LV microscope. The surface hydrophilicity of the original and fouled membranes was assessed with the contact angle measurement [16]. Each sample was analyzed in triplicate, and each measurement was completed within a ten-minute timescale.

Floc structure was represented by the fractal dimension (dF). Based on the small-angle static light scattering theory, the fractal dimension was calculated from a logarithmic plot of intensity (I) vs. wave number (Q). To precisely calculate the fractal dimension from the $\log I$–$\log Q$ plot, Gaussian cutoff function was used to cover Guinier regime data. The detailed relevant information had been discussed in a previous work [17].

3. Results and discussion

3.1. Performance of the IMCR under different operation conditions

3.1.1. Decolorization and COD removal with PFS dose

Coagulant dose is an important factor that affects the membrane coagulation process. The decolorization and COD removal

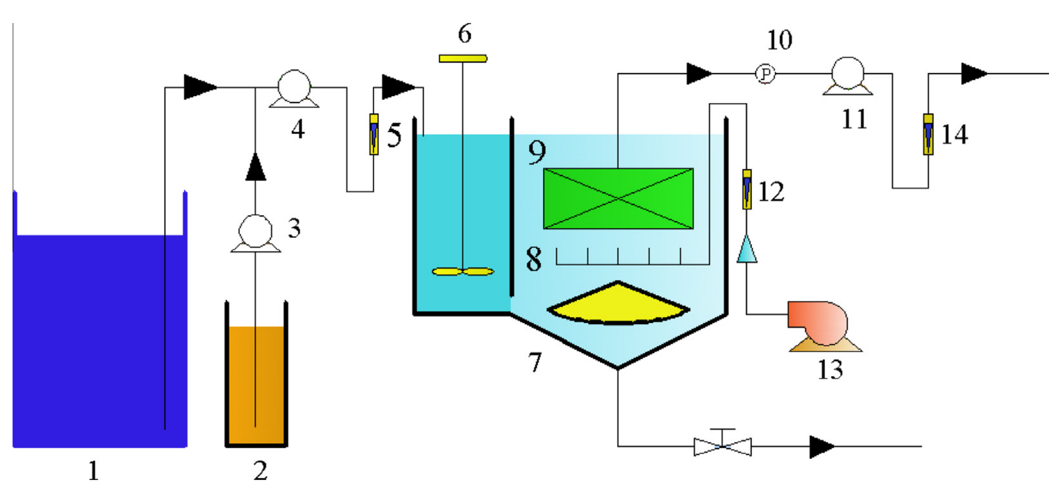

Fig. 1. Schematic diagram of the IMCR treating textile wastewater (1-feed tank; 2-coagulant tank; 3, 4, 11-pumps; 5, 14-liquid flowmeters; 6-stirrer; 7-IMCR; 8-air diffuser; 9-membrane module; 10-manometer; 12-air flowmeter; 13-air compressor).