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Treating sulfur black dye wastewater with quaternized poly (phthalazinone ether sulfone ketone) nanofiltration membranes

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ABSTRACT

Two kinds of nanofiltration (NF) membranes were investigated in treating the Sulfur Black B dye wastewater. Negatively charged polypiperazine amide/poly (phthalazinone ether sulfone ketone) (PIP/PPESK) NF membrane was prepared by interfacial polymerization method while positively charged quaternized poly (phthalazinone ether sulfone ketone) (QAPPESK) membrane was prepared by phase inversion method. QAPPESK NF membrane was selected for further study because it performed higher dye rejection and flux compared with the PIP/PPESK NF membrane. The effects of different operation conditions were systematically studied based on the rejection and desalination of the dye. Over 14.5 L/m^2 h flux, 92.3% dye rejection and 10% salts rejection were observed in the long term operation at 60 °C which indicated that the QAPPESK membranes could be successfully applied in the sulfur black dye wastewater treatment and inorganic salts reuse.

1. Introduction

About 15% of the dye is lost during the technological processes like dyeing, textile finishing, dye manufacturing, pulp and paper production [1]. Treatment of wastewater containing dyes is one of the most important ecological problems because the effluents containing the dyes are not only highly colored, but also toxic to aquatic life [2]. Textile effluents are highly variable in a composition. They are generally characterized by high concentrations of color, COD, BOD, TOC and dissolved solids. New tighter restrictions on textile products and wastewater discharges are forcing textile production and dyeing to reuse water and chemicals. This challenge has prompted intensive research in new advanced treatment technologies, some of which currently making their way to full-scale installations [3]. The most widely used treatment systems are conventional activated sludge. These systems poorly remove the widely used reactive dyes and are clearly ineffective in decolorizing textile effluents, even when mixed and treated together with sewage. This leads to highly colored water at the point of discharge and complaints from the public. Powered activated carbon (PAC) is the most commonly used and most successful adsorbent. However, PAC is expensive and the level of color removal depends on the dye type. There are studies into treatment of highly concentrated textile effluent, including ozonation and Fonton's oxidation. However, these methods are expensive to operate and produce undesirable side reactions and products [4]. There is growing interest for use of NF for the minimization and reuse of textile effluents. The interest in membrane processes applied to textile wastewater reuse is increasing thanks to the recent technological innovations that render them reliable and economically feasible in alternative to other systems. Several approaches have been proposed to implement membrane technology to the treatment of textile wastewater from different production streams. Reverse osmosis (RO) and NF were studied as treatment of secondary textile effluents after a suitable pretreatment, such as ultrafiltration (UF) or microfiltration (MF) [5].

Sulfur dyes are widely used to produce economical black, blue, brown and green shades on cellulosic fibers in medium to heavy depths. It is estimated that about one half of the volume of dye used on cellulosic fibers is due to sulfur dyes, in which case about 80% is the sulfur black dye [6]. The products of sulfur dye in China took the third place with 8500 ton in 2007. The sulfur dye was recognized an innocuous dye without damage on health while there was some pollution in synthesizes and application [7]. Its production line will produce a great deal of dyeing wastewater with high COD, high salt concentration and strong color. There are a lot of plants fabricating sulfur dye in China. 300–400 ton of this wastewater is discharged from a factory of Dalian everyday. So we decide to treat this kind of wastewater with membrane technology to economically recycle the dye, inorganic salts and water. Generally, sulfur black dye is synthesized in a reactor with several reagents and then accommodated pH to separate out dye and $Na_2S_2O_3$. These salts and residual impurities must be removed before the dyes are dried for sale as powder because they reduce the purity of the dyes and it is difficult for diluted dye with a lot of salts to reuse. At the same time

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$Na_2S_2O_3$ is not allowed to release because of its high COD. At present in the factory the treatment approach is as follows: the wastewater is accommodated to pH 5.5 and decolored with PAC and neutralized. Then it is pumped to evaporator to condense and reuse the crystalline $Na_2S_2O_3$. Then the solution with NaCl and Na_2SO_4 was discharged. That process will cause very high cost with secondary pollution.

The membrane separation technique is proved to be a preferred technique during the development in the latest 30 years because it is efficient, economical, process simple and friendly to the environment. Owing to the thermal instability of polymers, most polymeric membranes have been limited to application at low operation temperatures (usually below 50 °C). If those membranes were chosen in this work, the effluent must be cooled below 50 °C which might cause more costs. At the same time the membrane fouling occurs more easily because of high viscosity of the effluents at low operation temperature. A series of polymer of poly (phthalazinones) containing phthalazinone moiety were synthesized by Jian et al. [8] and Meng et al. [9,10]. PPESK has excellent comprehensive properties as membrane materials in gas separation, UF, and sublayer of NF and RO. It could be applied for dyes and salts separation at high operation temperature because of its outstanding thermal stability [11–17]. Also, the SPPESK and other sulfonated poly (phthalazinones) were applied for proton exchange membrane materials [18–21]. QAPPESK for positively charged NF membrane was also studied. QAPPESK NF membrane had about 90% rejection for $MgCl_2$ and the rejection to the different salt solutions followed the following sequence: $MgCl_2 > MgSO_4 > NaCl > Na_2SO_4$. Furthermore, the thermal resistance of the QAPPESK NF membrane was high [22–24]. In order to treat the wastewater and reuse the water and chemical, appropriate membranes with good hydrophilicity, excellent thermal resistance should be chosen to separate dye and salts.

2. Experimental

2.1. Materials and instrument

All the membranes used in this experiment were prepared in our laboratory. Salt concentrations were measured by a Conductmeter Model DDS-11A (Shanghai Leici Instruments, China). The membrane feed solution side was stirred magnetically to reduce concentration polarization. A flat-sheet dead-end membrane cell (Ecological Environment Center of Chinese Academy of Science) having an effective separation area of 41 cm^2 and a feed volume of 500 mL was used in all membrane flux characterization and separation experiments. Spectrophotometer 752 PC (Shanghai Spectrum Instrument Co., Ltd., Shanghai, China) was employed for measuring the concentration of Sulfur Black B.

2.2. Membrane performance characterization

The salts (Na_2SO_4, $MgCl_2$ and $Na_2S_2O_3$) solution and wastewater were characterized in the dead-end membrane cell after the membranes were pretreated for 30 min. The pressure used depended on the kinds of membranes. The permeation flux, *F*, was calculated as follows:

$$F = \frac{V}{At} \quad (1)$$

where *V* was the total volume of the solution permeated during the experiment; *A* was the membrane area; and *t* was the operation time. Rejection, *Re*, was calculated using the following equation:

$$Re = \left(1 - \frac{cp}{cf}\right)\% \quad (2)$$

where C_p and C_f were the concentrations of permeate and feed solution, respectively.

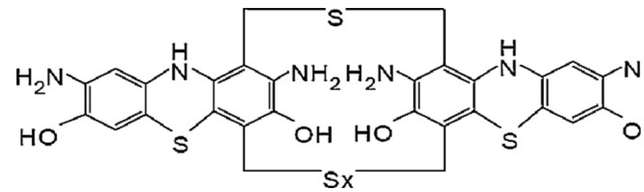

Fig. 1. The chemical structure of the dye ($x = 3.35$ Sulfur Black B, $x = 3.7$ Sulfur Black BR and $x = 3.8$ Sulfur Black DR 588).

2.3. Membrane morphology

The morphologies of the cross-section and external surface of membranes were observed with a scanning electron microscope (SEM; JSM-5600L, JEOL, Japan). The samples were fractured in liquid nitrogen and sputtered with gold after they were immersed with ethanol and hexane to observe the structure of the membranes.

2.4. Procedure

The feed solution was pretreated with sand funnel and PPESK UF membrane ($Re_{PEG10000} = 93\%$, $F = 183$ L/m^2 h at 0.1 MPa and 20 °C) which were used to decrease the fouling potential of suspended solids for the long term process of NF filtration.

2.5. Feed solution

Sulfur black dye production process is almost similar in different products process. So if the Sulfur Black B dye wastewater was studied, the others can be treated with the same method. Sulfur Black B (657 Da) was offered by a dye factory in Dalian and its chemical structure was introduced in Fig. 1. The information of the wastewater is listed in Table 1.

3. Results and discussions

3.1. Selection of the membranes

3.1.1. The decolorization performance of the membranes

630 nm, the maximal absorbance wavelength detected by UV/vis spectra, was chosen to quantify the dye concentration in solution.

According to Table 1, because of massive inorganic salts, high COD and chroma value in the wastewater, membrane technology should be chosen for its economical character. However, the high

Table 1
The information of Sulfur Black B wastewater.

	Aggregate reducing agent (g/L)	$Na_2S_2O_3$ (g/L)	pH	Chroma	Density (g/cm^3)	Temperature (°C)
1	76.66	311.08	11.03	125,000	1.428	50–60
2	77.25	311.72	11.05	62,500	1.286	50–60
3	69.78	284.31	11.56	82,500	1.255	50–60
Average	74.56	302.37	11.21	90,000	1.323	50–60