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Advanced treatment of textile dyeing secondary effluent using magnetic anion exchange resin and its effect on organic fouling in subsequent RO membrane

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HIGHLIGHTS

- NDMP resin can remove DOC and color of textile secondary effluent effectively.
- Protein and SMP-like were confirmed to be major foulants of RO membrane.
- NDMP resin improved RO flux and mitigated irreversible fouling effectively than UF.

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ABSTRACT

Strict regulations are forcing dyeing factory to upgrade existing waste treatment system. In this study, advanced treatment of dyeing secondary effluent by magnetic anion exchange resin (NDMP) was investigated and compared with ultrafiltration (UF); NDMP as a pre-treatment of reverse osmosis (RO) was also studied. NDMP resin (20 mL/L) gave higher removal of dissolved organic carbon (DOC) (83.9%) and colority (94.9%) than UF with a cut-off of 10 kDa (only 48.6% and 44.1%, respectively), showing that NDMP treatment was effective to meet the stringent discharge limit of DOC and colority. Besides, NDMP resin (20 mL/L) as a pretreatment of RO increased the permeate flux by 12.5% and reduced irreversible membrane fouling by 6.6%, but UF pretreatment did not mitigate RO membrane fouling. The results of excitation-emission matrix fluorescence spectra and resin fractions showed that NDMP had more efficient removal than UF for transphilic acid and hydrophilic fraction, such as protein-like organic matters and soluble microbial products, which contributed to a significant proportion of RO membrane fouling. In sum, NDMP resin treatment not only gave effective removal of DOC and colority of dyeing secondary effluent, but exhibited some improvement for RO membrane flux and irreversible fouling.

1. Introduction

The textile dyeing industry is characterized by high water consumption and high discharge of colored wastewater with high COD and inorganic loads, making it one of the main sources of severe pollution problems worldwide. Usual treatment methods for dyeing wastewater are the combination of biological and physico-chemical processes [1]. Although above 90% of COD removal for dyeing industry wastewater can be achieved using usual wastewater processes, the color removal is not so effective and has become a big challenge over the last decades [2,3]. Moreover, discharge limits imposed on dyeing mills are becoming ever more stringent. For example, in China, discharge limits of COD and colority for dyeing industry will be lowered from 100 mg/L and 70 (dilution ratio) to 80 mg/L and 50 (dilution ratio) in 2015, respectively. Strict regulations are forcing plant managers to upgrade existing wastewater treatment system.

What is more, dyeing companies may face a shortage of available water sources due to water scarcity and limitations of ground water use. In the near future, many dyeing companies will have to reuse dyeing secondary effluent to achieve environmental and economic benefits. Due to low water conductivity requirement for reuse purpose, reverse osmosis (RO) technology can be an optimal process for reuse of dyeing secondary effluents [4,5]. Although RO has become a viable technology for wastewater reclamation, high concentrations of dissolved organic matter (DOM) in the dyeing secondary effluent may cause severe fouling of RO membrane and lead to a great loss of membrane permeate flux and deterioration of

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treated water quality [6–8]. Therefore, RO membrane fouling is still a major challenge in the reuse of dyeing secondary effluents, and proper pretreatment should be preceded as the first line of defense in controlling membrane fouling.

Hence, advanced treatment of dyeing secondary effluent is necessary to not only meet the stringent discharge limit but also reduce RO membrane fouling in reuse. Advanced treatment methods, such as activated carbon adsorption [9], advanced oxidation [10], and ultrafiltration/microfiltration (UF/MF) [11], have been studied widely to remove refractory compounds. Activated carbon adsorption can remove low molecular weight organic compounds; however, it is really hard to be regenerated, which hinders its extensive use. The advanced oxidation processes (AOPs) generally give good results, but are expensive. UF/MF is widely used as the tertiary treatment stage of dyeing wastewater and also considered as a very effective pretreatment technology to RO membrane [12,13]. However, EfOMs rejection is often limited to high molecular weight and highly hydrophobic organic compounds such as humic substances [14]. The fouling agents that pass through MF/UF are still a challenge for RO treatment of secondary effluent [15]. What is worse, MF/UF membrane is also fouled in the process of removing RO foulants [16].

In recent years, conventional and magnetic anion exchange resins have received considerable attention for removal of natural organic matter (NOM) from natural water [17–19]. These resins can be regenerated with sodium chloride solution. Depending on specific water characteristics, anion exchange process can remove 30–80% of NOM [20]. Specifically, magnetic ion exchange resin has a polyacrylic matrix, quaternary amine functional group, and a macro-porous structure [21], all of which are considered to be favorable to DOM adsorption [20,22]. Moreover, the adsorption and desorption kinetics of magnetic anion exchange resin is faster because of its smaller size (0.15–0.18 mm) than that of conventional resins (0.3–1.2 mm). Recently, anion exchange resin has been investigated as a means of improving membrane performance by removing a significant fraction of NOM from drinking water sources [16,23]. Despite many literatures available on removal of NOM in the natural surface water, there have been only a handful number of studies on treating dyeing secondary effluent using anion exchange resin and evaluating its feasible as RO pretreatment. Moreover, the organic matters in the secondary effluent were quite different from those in natural water. Besides NOM, dissolved organic compounds (DOM) in the secondary effluent also comprises soluble microbial products (SMPs) derived from biological treatment processes [24], which contribute to a significant proportion of membrane fouling [25,26].

In this study, the treatment of the dyeing secondary effluent using magnetic anion exchange resin was investigated and compared with UF treatment. A second objective was to evaluate magnetic anion exchange resin and UF for improving RO membrane performance in reuse of dyeing secondary effluent. The fractions of dissolved organic compounds (DOM) in the raw and treated feed water and membrane foulants were analyzed using excitation-emission matrix (EEM) fluorescence spectroscopy and resin fractionation method. The results may provide some insight into the application of magnetic anion exchange resin for advanced treatment of the dyeing secondary effluent and development of a potential pretreatment for reducing RO membrane fouling in reuse of the dyeing secondary effluent.

Table 1
Typical characteristics of feed water.

Parameters	Value
pH	8.7
COD (mg/L)	129.6
DOC (mg/L)	28.9
$UV_{254\,nm}$ (cm^{-1})	2.4
SUVA (Lmg/m)	8.3
Colority (dilution ratio)	110
Conductivity (us/cm)	6110.2
Alkalinity (mg/$CaCO_3$/L)	996.8
Sodium (mg/L)	1401.9
Potassium (mg/L)	34.0
Calcium (mg/L)	56.0
Magnesium (mg/L)	10.2
Iron (mg/L)	0.006
Sulfate (mg/L)	1938.2
Chloride (mg/L)	643.9

2. Materials and methods

2.1. Feed water

The secondary effluent was collected from a dyeing industry treatment plant locating in Changzhou (China), in which reactive anionic dyes were used. Primary sediment, anaerobic anoxic-oxic process (AAO), and coagulation–flocculation were used as the treatment methods of wastewater. The secondary effluent was prefiltered by 0.45 μm cellulose nitrate filter to remove particulate matters, after which the filtrate was denoted as feed water. The typical characteristics of the feed water were shown in Table 1.

2.2. Magnetic anion exchange resin

Magnetic anion exchange resin (NDMP) was chosen to remove the dissolved organic matters from the secondary effluent. NDMP resin was prepared in our laboratory and its preparation was reported in the previous study [27]. The NDMP resin has a polyacrylic matrix, quaternary amine functional group, and a macroporous structure. The NDMP resin size is 0.1–0.15 mm and its anion-exchange capacity is 3.8 mmoL/g dry resins. Before NDMP resin was used, it was rinsed repeatedly with distilled water until the effluent was neutral.

2.3. Pretreatment methods

For NDMP resin pretreatment, NDMP resin at 2.5, 10, and 20 mL/L was added to three conical flasks containing feed water, respectively, and the suspensions were stirred at 150 rpm for 30 min at 293 K. After settling, the supernatant was poured out for subsequent RO experiments. For comparison, ultrafiltration (UF) pretreatment was conducted in a cross-flow unit. The UF membrane used in this study was made of polyether sulfone with a molecular weight cut-off (MWCO) of 10 kDa (V-win Company, China). The operating pressure and crossflow velocity were controlled at 0.2 MP and 0.8 m/s by means of by-pass and regulating valves, respectively. The filtration unit was operated in a concentration mode with permeate continuously saved for subsequent RO experiments and the concentrate fully recycled.

2.4. RO membrane fouling experiments

One of the main purposes of this study is to investigate the organic fouling behavior and mechanism of RO membrane by DOM. In order to avoid the interference of inorganic scale, therefore, the feed water before RO filtration was treated by strong cation exchange resin in sodium form to remove Ca^{2+} and Mg^{2+}, etc. In practical application, inorganic scale fouling on RO membrane can be mitigated using the antiscalants.

Fouling experiments were carried out using a laboratory-scale cross-flow RO membrane test unit consisting of feed tank, membrane cell, temperature control system, and computer-interfaced