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Experimental study on coupling photocatalytic oxidation process and membrane separation for the reuse of dye wastewater

Wenshi Ou, Guoqing Zhang*, Xiaojiao Yuan, Pan Su

School of Materials Energy, Guangdong University of Technology, Guangzhou, Guangdong 510006, China

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ABSTRACT

The coupling of photocatalytic oxidation process and membrane separation has been studied for the reuse of dye wastewater. The operating conditions of the reactor such as irradiation time, solution pH, and work pressure were investigated. Water quality and extent of fouling were measured, respectively, in terms of removal rate of water quality index and membrane flux decline. The results showed that the highest activity for congo red degradation was reached under pH 4 in about 90 min of irradiation time. In membrane separation, when pH 10, the decline of the UF membrane flux was slower. However, the decline of the RO membrane flux was slower when pH 4. Taking into accounts of the power savings and efficiency, 0.5 MPa was used as the work pressure of RO. Photocatalysis as a pre-treatment can reduce the membrane flux decline of UF and RO membrane by about 12% and 8%, respectively. After being treated by photocatalysis, UF and RO, the experimental results of chemical oxygen demand (COD), conductivity, hardness and concentration of congo red in the effluent are about 25 mg/L, 88 μs/cm, 28 mg/L and 0.32 mg/L, respectively. All the results exceed the quality standard of reuse water for textile industry.

1. Introduction

Population growth and urbanization have led to a sharp increase in water consumption, especially in engineering and high-tech industries [1]. Nowadays, China faces a severe shortage of water resources and more than 50% of the cities are short of water. Hence, it is extremely important to find other sources of water supply, which includes the reuse of wastewater.

The wastewater produced by the textile industry is the most polluting among the industrial sector [2,3]. The pollution caused by dyestuff losses during the dyeing and finishing processes has been a major environmental problem for many years. Among discharged process water, wastewater from textile and dye industries contains high levels of alkalinity, hardness, turbidity, conductivity, color and non-biodegradable COD. Methods that deal with textile wastewater include absorption method, chemical treatment (coagulation and absorption), biological treatment (standard activated sludge method), oxidation method (ozonation and photocatalytic oxidation and electrochemical oxidation), etc. Recently, membrane filtration technologies which included microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) were applied as advanced treatments to wastewater from textile industry [3–6]. NF and RO are good alternatives for treating the textile wastewater treatment because of their high reductions of conductivity, hardness, COD and color. NF has been shown to be effective in recycling the dye wastewater, because of their high flux, high retention of organic molecules above 300 Da and low maintenance costs, however, most of monovalent ions can flow through the NF membrane [7]. On the other hand, RO widely used in desalination, can separate molecules with particle size greater than 0.1 nm. Earlier experiment studies [8,9] show that the permeate of RO from the most demanding production steps, such as dyeing with light coloration, is water of high quality which can be reused. Nevertheless, due to high solids concentrations, wastewater after conventional treatment cannot be directly used as influent to NF or RO membranes [9]. As a pre-treatment, MF and UF can separate partial impurities, such as suspended solid, colloid, hydrophilic macromolecule dye granule [10]. The MF membrane has limited applications in the textile industry as its pore size is larger than the diameter of the most impurities in dye wastewater. UF can separate molecule with particle size greater than 1 nm, such as suspended solid, colloid, hydrophilic macromolecule dye granule, bacteria and viruses [9]. Therefore, the objective of this paper is to use UF and RO membrane process for dye wastewater reuse.

The main disadvantage of the membrane process is the flux decline caused by membrane fouling [7,11]. Fouling is the

* Corresponding author. Tel.: +86 13632315436.
E-mail address: 715547081@qq.com (G. Zhang).

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accumulation of unwanted deposits on the surface of the membrane or inside the pores of the membrane, which could pose a very detrimental effect to the desalination and purification process [12]. Moreover, after filtration, a concentrated mixture of dyes and auxiliary substances remain, which need further treatment before it can be discharged or reused [9,13]. In order to obtain water of high quality and prevent fouling of the membrane, an innovative pre-treatment is required [9].

Recently, in the field of wastewater treatment, titanium dioxide (TiO_2)-mediated photocatalytic reactions have attracted much attention because of their mild reaction conditions, low cost and low energy consumption, and harmless by-products [14,15]. Several publications have reported the combined use of photocatalysis and membrane separation technology to treat the dye wastewater [16,17]. The majority of photoreactors described in the literature are slurry photoreactor, in which TiO_2 is suspended in the reaction mixture [18]. The slurry type photoreactor has several disadvantages, such as easy to reunite in aqueous solution, narrow range of application, hard to reclaim [15]. On the other hand, the photocatalyst immobilized on a support usually shows a wider range of application. Novel materials with three dimensional network structure of metal foam has now been developed, which is able to overcome disadvantages of the slurry type photoreactor. Hitherto, application of the three dimensional foam nickel photocatalytic net combined with membrane separation treatment of dye wastewater is rarely reported.

In this paper, an advanced treatment system which can treat the dye wastewater to the standard of reuse water is described. The system is formed by coupling photocatalytic oxidation process and membrane separation. Important parameters affecting the treatment, such as the effects of irradiation time, pH and work pressure, are included in the description.

2. Materials and methods

2.1. A foam nickel support coated with TiO_2

The three dimensional foam nickel photocatalytic net (thickness, 3.12 mm; area, 0.033925 m^2; total weight, 16.44 g; model, 35 PPI; voidage, 95%; surface density, $500 \pm 50\,g/m^2$; TiO_2 loading density, 30 g/m^2; and grain diameter, 20 nm) was prepared by composite electrodeposition method. Nanoscale TiO_2 was loaded evenly on the surface of this net. The performance indicators of this foam nickel catalyst net have been authenticated by TUV, SGS, Technical Institute of Physics and Chemistry (CAS), Microbial Testing Center of Guangdong Province, and many other authoritative testing institutions. It should be noted that each experiment used four pieces of this foam nickel photocatalytic net, and their total area and weight were 0.1357 m^2 and 65.76 g, respectively.

Fig. 1 shows the SEM images (a) in 100 magnifications and (b) in 10,000 magnifications of the three dimensional foam nickel support coated with TiO_2. The SEM images showed that TiO_2 was well dispersed in metal surface. The three dimensional foam nickel support coated with TiO_2 not only has high specific surface area, but also has good permeability. Under the irradiation of ultraviolet lamp, the photocatalytic net can produce free electrons and holes. Holes with strong oxidation ability will react with the surrounding water and oxygen, which can produce free radicals with strong oxidation ability (reactive hydroxyl, super oxygen ions and so on) [19]. These free radicals can easily destroy the structure of the dye molecules and convert it into CO_2, H_2O and other small molecules, which can achieve the goal of treating printing and dyeing wastewater [20].

Three dimensional foam nickel support coated with TiO_2 was analyzed via EDS (S-3400N-II, Japan), and the results are shown in Table 1. The surface of foam nickel was mainly composed of five elements, such as Cl, C, Ti, O and Ni. C element may be caused by incomplete combustion in the process of heat treatment. Cl element may be the adsorption of chlorine ion in the surface of foam nickel. Ni element may be caused by foam nickel substrate. The results show that the mass fraction and the atomic fraction of Ti were 5.97% and 4.77%, respectively.

2.2. Membrane filtration

The UF hollow fiber membranes (HAITAO) made of hydrophilic polyacrylonitrile (PAN) have an operation pressure of under 0.3 MPa, 180 L/h of pure water flux (for one module), the filter aperture of 0.01–0.02 μm, escherichia coli removal up to 99%. Low pressure RO membrane (VONTRON) made of polyamide have an operating pressure of 0.3–0.7 MPa, 8 L/h of pure water flux (for one module), 99.5% of desalination rate, which is certified by NSF/ANSI 58.

2.3. Configuration of dye wastewater

A regular analysis was carried out for the secondary effluent in a textile industry located in Guangzhou (China). According to the worst possible water qualities monitored in terms of COD, hardness, conductivity and color, simulated dye wastewater was made as an influent to the coupling treatment system. The simulated dye wastewater compositions are listed in Table 2. Congo red produced by Kermel (TianJin, China) were used as model azo dyes. Selected dye is widely used in the textile, paper and leather. The initial concentration of dye was equal to 40 mg/L. The solution of dye was prepared using ultrapure water. In order to increase COD, hardness and salinity of the simulated dye wastewater, potassium hydrogen phthalate (Kermel; TianJin, China), calcium chloride and sodium sulfate were added to the solution.

2.4. Water quality analysis

The water quality parameters such as color, hardness, COD, and conductivity were measured using the Chinese standard methods for water and wastewater. COD was measured using the dichromate method, and hardness was measured using the ethylene diamine tetraacetic acid (EDTA) titration method. Conductivity was measured using LeiCi DDS-307 model conductivity meter from China, and pH was measured using LeiCi PHC-3C model pH meter from China. The concentration of dye solution was determined from its absorbance at 498 nm using PuXi TU-1901 model ultraviolet and visible spectrophotometer from China. Scanning electron microscopy(SEM, S-3400N-II) from Japan has been used to observe the image of photocatalyst and membrane.

The removal rate of water quality indexes was calculated by the following equation [19,21]:

$$R = \left(\frac{1 - C_p}{C_f}\right) \times 100\% \quad (1)$$

where C_p is the treated water quality indexes and C_f is the feed water quality indexes. Water quality indexes include COD, hardness, concentration of congo red and conductivity.

The membrane flux decline was calculated according to the following equation:

$$r = \frac{J_v}{J_0} \quad (2)$$

where J_v is the membrane flux after filtration, J_0 is the pure water flux of virgin membrane.