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Nanofiltration coupled with electrolytic oxidation in treating simulated dye wastewater

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ABSTRACT

To investigate the effects of electrolytic oxidation on nanofiltration in treating dye waste water, we put a mesh catalytic electrode on the intercept side of the membrane and apply a voltage to realize the coupling of electrolytic oxidation and nanofiltration. The effects of the electroosmosis, electrophoresis and electrochemical oxidation on the flux were investigated. Experiments show that electroosmosis makes the flux increase linearly with the electric intensity. When there is only an electric filed in the coupling experiments, we get that, with the increase of the electric intensity the flux is accelerating until the electric intensity reach the critical value, after that the flux increase linearly with the electric intensity. With the current density increasing, the degraded organics and the bubbles generated increase, and so the thickness of the concentration polarization and gel layer is reduced in a certain degree. The flux increases with the decrease of the feed concentration in the coupling experiments. The trend that the flux increases with the pressure slows down. The flux increases to a certain value and then keeps constant with the increase of the cross flow velocity. The trend that the flux decreases with time slows down with the increase of the voltage, because of the electroosmosis, electrophoresis and electrochemical oxidation. And when the voltage increases to a certain degree, the flux keeps at a high level and changes less with time because the thickness of concentration polarization and gel layer is reduced to the minimum.

1. Introduction

It is well known that dye wastewater is of high colority, high COD (Chemical Oxygen Demand) and poor biochemical purification ability, especially the effluent of the dye production and the dyeing stages [1,2]. The dye wastewater always contains a variety of organic matter with biological toxicity or "three-induced" properties (carcinogenicity, teratogenicity, mutagenicity) [3–6]. The incomplete degradation products, for example the benzidine and some carcinogenic aromatic compounds, have great toxicity. Such as phenols inhibit the growth of the aquatic plants and various organisms, benzene has significant toxic effects on human nervous and vascular systems [7–9]. Based on the various hazards, the improvement of the wastewater treatment technology plays an extremely important role in maintaining ecological balance, protecting the environment and human health.

The mechanism, characteristic and MWCO (Molecular Weight Cut Off) of nanofiltration membrane make it widely recognized in the world in spite of the existence of concentration polarization and membrane fouling which reduce the permeate flux and shorten the life of the NF membrane [10–13]. So seeking for suitable measures to reduce the concentration polarization and membrane fouling becomes the focus of the research. In addition, the research of Vlyssides et al. shows that the electrolytic oxidation technology used in treating organic wastewater has a lot of advantages (e.g. efficient, easy to operate and so on) [14–19]. The organics are degraded on the anode and the wastewater is decolorized at the same time. However, the only problem of the electrolytic oxidation technology is the high energy consumption [20].

We put the mesh catalytic anode on the intercept side of the membrane, and the cathode is put on the other side of the membrane. By the way above, we combine electrolytic oxidation and nanofiltration together. In addition to the improvement of permeate flux caused by electroosmosis, the electrophoresis and electrochemical oxidation reduce the organics concentration near the membrane, thereby the thickness of the concentration polarization and gel layer is reduced. And the bubbles generated in the electrochemical oxidation enhance the turbulence of the fluid on

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the membrane surface. All these effects contribute to the reduction of the concentration polarization and membrane fouling, and so improving the permeate flux. That means we can get high permeate flux under very low cross flow velocity. So it is helpful to reduce the power consumption of the membrane process and extend the membrane life.

In order to study the effects of the electrolytic oxidation on the concentration polarization and membrane fouling, we prepared the simulated dye wastewater, consisting of 500 mg L^{-1} Reactive Red 118 (purity ≥99%) and 2 g L^{-1} NaCl. The pH of the simulated wastewater was 3.80. This dye wastewater was used in all of the coupling experiments unless stated otherwise. Through the coupling experiments of the electrolytic oxidation and nanofiltration, we researched the effects of electroosmosis, electrophoresis and electrochemical oxidation on nanofiltration, and we also studied the effects of the nanofiltration operating conditions on the permeate flux.

2. Experimental

2.1. Materials

The dye was produced by Tianjin Yadong Group and the reagents used in the experiments were purchased from Jiangtian Chemical Technology Co., Ltd., Tianjin, China. The chamber type electric resistance furnace was the product of Zhonghuan laboratory furnaces Co., Ltd., Tianjin, China. All chemicals were used without further purification and all solutions were prepared using deionized water which was supplied by Chemical Engineering Research Center of Tianjin University.

2.2. Preparation of electrode

We chose the Sn–Sb coated titanium electrode ($Ti/SnO_2 + Sb_2O_3$) as the catalytic anode in the experiments because of the high oxygen evolution over potential of it [21]. The thermal decomposition technique was used to prepare the electrode. Before the coating process, pretreatments of titanium mesh, containing grinding, caustic and acid etching, need to be done [22]. First we mixed the glycol and citric acid at 60 °C and the ratio is 4:1. After completely esterification, we got the glycol solution of glycol citric acid ester. Then the solution was heated to 90 °C and added $SnCl_4{\cdot}5H_2O$ and $SbCl_3$, the molar ratio of 100:11. Completely dissolved and kept at 90 °C for 30 min, we got the coating solution [23]. The specific coating process as follows:

(1) *Coating*: Uniformly coat the solution on the titanium mesh, about 0.02 mL cm^{-2}.
(2) *Drying*: Place the well coated titanium mesh in the drying oven for 10 min at 130 °C.
(3) *Thermal oxidation*: It was annealed for 10 min at 500 °C.

It was taken out and cooled to the ambient temperature. After the ashes blowing away, the electrode was coated and roasted again. The procedure was repeated 10 times. At the last time, the anode was annealed for an hour and cooled to ambient temperature in the furnace. After taken out and rinsed with deionized water, we got the Sn–Sb coated titanium electrode ($Ti/SnO_2 + Sb_2O_3$).

After the preparation of the electrode, we carried out the accelerated life test at 2000 mA cm^{-2} in 1.0 mol L^{-1} H_2SO_4. The time of the cell voltage rise to 5 V was the accelerated life, and after calculating through the empirical equation, we can estimate the life of the electrode [24]. The result showed that the electrode life was about 1980 h at general industrial current density (usually 100 mA cm^{-2}).

Table 1
Characteristics and operation parameters of NF membranes.

Model	Charge	MWCO	pH range	Operating pressure
DL	Negative	More than 150	2–11	483–2758 kPa
DK	Negative	More than 150	2–11	483–2758 kPa

2.3. The equipment and processes of the electrolytic oxidation and nanofiltration coupling experiments

We chose the D series commercial nanofiltration membrane of GE water & Process Technologies as the experimental membrane. The membranes of this series are composed of the three-layer composite structure. The surface layer of the membrane is polyamide, the support layer is polysulfone, and between the two layers is the transition zone made of special materials. The D series nanofiltration membranes have high retention rate and good heat, acid and alkali resistance. The main characteristics and operating parameters of the membrane are listed in Table 1. The DL membranes were used in the coupling experiments on account of the higher permeate flux. The pure water flux of the membrane is tested before and after the coupling experiments and the difference is less than 5%, meaning that the membrane has not been damaged in the experiment. Aim to study the effect of the electrophoresis, we covered the electrode with insulated paint to restraint the current. The negative pole of the direct-current power supply (for short DC power supply) is connected to the membrane supporting net, thus the stainless steel net is used as the cathode in the coupling experiments. The electrodes distance is controlled to 1 mm in the coupling experiments, and the structure of the membrane pool can be seen in Fig. 1(b).

The devices and processes of the electrolytic oxidation and nanofiltration coupling experiments are shown in Fig. 1. The feed liquid from tank 15 is pressurized by the screw pump 14 and pumped into the membrane pool 4, the control valve 7 combined with the bypass valve 12 are used to control the operating pressure and the circulation flow rate. Until the system is stable, the penetrating fluid weight and the corresponding time were recorded by the electronic balance and computer program. After calculating we can get the corresponding permeate flux. In the coupling experiments, the pressure, voltage and other operating parameters were separately regulated to research the effects on the permeate flux.

2.4. Main test parameter of the electrolytic oxidation and nanofiltration coupling experiment

Permeate flux J_v: permeate flux refers to the quantity of permeate liquid through unit membrane area in unit time, the formula follows:

$$J_v = \frac{\Delta W}{S\Delta t} \tag{2-1}$$

J_v is the mass flow rate of the membrane, kg m^{-2} h^{-1}; ΔW is the weight of permeate liquid in a certain time Δt, kg; S is the effective area of the nanofiltration membrane, m^2, in this paper $S = 0.0061$ m^2; Δt is the operating time, h.

COD removal R:

$$R = \frac{COD_b - COD_p}{COD_b} \times 100\% \tag{2-2}$$

R is the COD removal; COD_b is the COD of the feed liquid, mg L^{-1}; COD_p is the COD of the penetrating fluid, mg L^{-1}.

The COD removal of the permeate liquid in both the nanofiltration and the coupling experiments are more than 90% and change very little. The decoloration efficiency reaches almost 100%.