Journal of Membrane Science 452 (2014) 1–10

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Electro-catalytic oxidation in treating C.I. Acid Red 73 wastewater coupled with nanofiltration and energy consumption analysis

Li Xu [a,b,*], Lichao Zhang [a,b], Lishun Du [c], Shaoxing Zhang [d]

[a] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China
[b] Tianjin Key Laboratory of Membrane Science and Desalination Technology, Tianjin 300072, PR China
[c] Hualu Engineering & Technology Co., Ltd., Xi'an 710065, PR China
[d] Research and Development Department, Tianjin Mainland Hydrogen Equipment Co., Ltd., Tianjin 301609, PR China

ARTICLE INFO

Article history:
Received 14 May 2013
Received in revised form
17 September 2013
Accepted 20 September 2013
Available online 18 October 2013

Keywords:
Electrode
Electro-catalytic oxidation
Nanofiltration
Permeation flux

ABSTRACT

The research was conducted to study the independent impact of electro-catalytic oxidation on the nanofiltration (NF) performance during the separation of C.I. Acid Red 73 (AR 73) wastewater. Ti/SnO_2–Sb_2O_3 electrode modified with rare element yttrium (Y) was successfully prepared by the sol–gel technology, and then it was used as an anode for the degradation of azo dye AR 73 coupling with NF. The electro-catalytic oxidation could be restrained by painting insulating varnish on the surface of anode. Through comparing the permeation flux with the case of not using insulating varnish, we could identify the independent impact of electro-catalytic oxidation in the coupling process. The influence of operating parameters, e.g., applied voltage, initial feed concentration, operating pressure and cross flow velocity on the electro-catalytic oxidation flux and energy consumption was investigated respectively. The results indicated that the accelerated lifetime of the Ti/SnO_2–Sb_2O_3–Y electrode reached 4.1 h, which was 9.1 times longer than that of the Ti/SnO_2–Sb_2O_3 electrode, and the electro-catalytic oxidation flux was enhanced to a great extent by choosing appropriate operating conditions and the coupling process could energy-effectively treat AR 73 wastewater.

1. Introduction

Compared with conventional processing methods of treating industrial dye wastewater, nanofiltration (NF) process is a promising technology and can be attractive alternatively to many conventional separation processes due to its high level of separation, easy to scale-up possibilities, no disposal problem and unique separation capability [1,2]. The major defect of NF is the decline of permeation flux, due to the fouling of the membrane and concentration polarization, which limits the membrane performance, increases the cleaning cost and reduces the functioning life of membrane [3,4]. At high concentration the permeation flux usually declines a factor of 8–10 from its initial value.

There are lots of excellent literatures about the methods to reduce concentration polarization and control membrane fouling, including feed solution pretreatment [5], cleaning [6], hydrodynamic manipulations like insertion of turbulent promoters or using a high flow [7], modification and design of membrane material [8] and application of external body forces [9–15]. Applying the external DC electric field across the membrane in NF, as an effective controlling method, is widely adopted in practice considering the effect of electrophoresis and electroosmosis [9–12]. The electric field imposes the electrophoretic effect on the charged particles dragging them from the surface of membrane. The concentration polarization and membrane fouling are thereby reduced and the permeation flux increases. The solvent flowing across of the membrane can be enhanced by the electroosmosis effect, which also has a large contribution to the total permeation flux. Yang et al. [13] applied an electrically enhanced cross flow microfiltration system for the treatment of oxide-CMP wastewater under different operating conditions. Experimental results indicated that the filtration rate was improved by six-fold when applying electric field. Weng et al. [14] used a laboratory-scale electro-microfiltration module to separate Aldrich HS from water by applying a voltage across the membrane. Results clearly indicated that a combination of electric force with MF could decrease flux decline and increase HS rejection from 30% to 90%. Kim et al. [15] investigated the effect of electric fields application for the reduction of membrane fouling, the inactivation of microorganisms and the enhancement of particle coagulation. They found that coagulant dosage could be saved about 75% compared with non-electric field in terms of the 95% turbidity removal at 10 kV/cm electric field.

Abbreviations: NF, nanofiltration; Y, yttrium; AR 73, Acid Red 73; CMF, crossflow microfiltration; HS, humic substances; MF, microfiltration; DC, direct current; Co., company; GE, General Electric Co.; CA, citric acid; EG, ethyleneglycol; SEM, scanning electron microscopy; ·OH, hydroxyl radicals; MWCO, molecular weight cut off

* Corresponding author at: School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China. Tel.: +86 22 27409839; fax: +86 22 27890515.
E-mail address: xuli620@163.com (L. Xu).

0376-7388/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.memsci.2013.09.064

However, electro-catalytic oxidation when using DC electric field in NF has been given less attention. Some research have shown that the electro-catalytic oxidation technology gains remarkable performance in treating dye wastewater because of its high oxidation efficiency, fast reaction rate and easy operation [16–18]. In the process of indirect electro-catalytic oxidation process, some intermediate products, such as chlorine, hypochlorite, hydrogen peroxide and metal ions, are able to destroy pollutants in the wastewater [19]. Electro-catalytic oxidation of pollutants can also occur directly on anodes by generating physically adsorbed hydroxyl radicals or chemisorbed "active oxygen" [20]. So it has huge potential in purifying dye wastewater effectively and thoroughly [21,22]. Therefore, we attempt to combine NF and electro-catalytic oxidation together to improve the permeation flux. The electro-catalytic electrodes are put on the sides of NF membrane, thus introducing electrophoresis, electroosmosis and electro-catalytic oxidation simultaneously in membrane process. Nevertheless, the effect of electrophoresis and electroosmosis is very poor duo to the small distance (about 1 mm) of the anode and cathode. Hence, the electro-catalytic oxidation plays an important role in NF. Dyestuff in the wastewater can be directly oxidated and degraded on the anode. Moreover, O_2 generating on the anode due to the oxygen evolution reaction and a certain amount of dyestuff is oxidated completely to CO_2. The gas accumulates to bubbles, and then separates from the surface of electrode. The rising of bubbles results in turbulence of the liquid around membrane surface, enhancing the mass transfer coefficient and restraining concentration polarization in some way.

In our earlier works, the research about the electro-catalytic oxidation coupled with NF in treating simulated dye wastewater had demonstrated that the permeation flux was significantly enhanced, which was attributed to the synergy of electro-catalytic oxidation and NF [23]. However, though the Ti/SnO_2–Sb_2O_3 anode had good conductivity, high catalytic activity and high over-potential, the deactivation of the electrode led to a short lifetime of service. In addition, the mechanism of electro-catalytic oxidation of treating AR 73 wastewater in the coupling process was not discussed and the independent effect of electro-catalytic oxidation on permeation flux was not investigated solely.

In the present paper, in order to improve stability of the anode, we used yttrium (*Y*) as a dopant to fabricate a SnO_2–Sb_2O_3 coating on the Ti substrate by the sol–gel method. Then we investigated the independent impact of electro-catalytic oxidation in the coupling process at different operating parameters such as applied voltage, initial feed concentration, operating pressure and cross flow velocity. Besides, the mechanism of electro-catalytic oxidation for controlling the fouling of the membrane and concentration polarization was explained in detail. Introducing electro-catalytic oxidation in NF process was effective in fouling reduction, but the energy consumption involved was not investigated previously, so the present study sought to analyze the energy consumption per unit volume of permeation with electro-catalytic oxidation in NF treating AR 73 wastewater.

2. Experimental

2.1. Apparatus

The schematic of the coupling unit constructed in stainless steel is shown in Fig. 1. All experiments were conducted in the cross flow membrane filtration module with an active membrane surface area of 13.85 cm^2. The circular cross section of the feed chamber was about 0.74 mm, with the diameter of 42 mm. A vane pump with a total flow rate of 2.5 L min^{-1} was used to deliver the feed to the module. The trans-membrane pressure inside the coupling unit was maintained by operating the bypass valve and was measured by a pressure gauge inserted in the retentate line, whereas the concentrate flow rate was measured by a rotameter in the concentrate line.

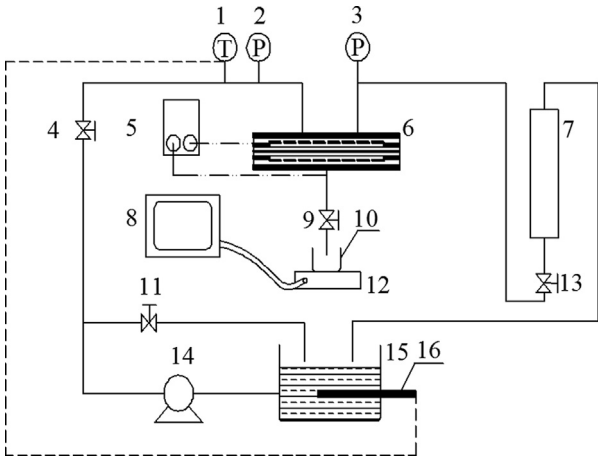

Fig. 1. Flow diagram of the coupling experiments. 1,16-device of controlling temperature; 2,3-pressure gage; 4,9,11,13-ball valve; 5-DC stabilized power supply; 6-membrane module; 7-rotameter; 8-computer; 10-beaker; 12-electronic balance; 14-pump and 15-feed.

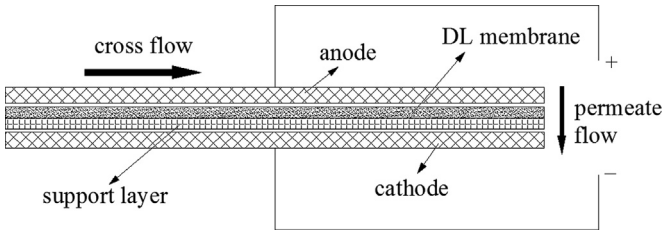

Fig. 2. Relative position of the electrodes and NF membrane in the membrane cell.

In order to enable electro-catalytic oxidation, a netty Ti cathode was fixed behind the membrane on the permeation liquid side which served as a support for the membrane and a netty Ti/SnO_2–Sb_2O_3–Y with electro-catalytic activity was place on the feed side. The detailed assembly is shown in Fig. 2. A DC potentiostat with a voltage range of 0–30 V was used as the power supply for electro-catalytic oxidation coupling with NF, which controlled the magnitude of the voltage or current density.

2.2. Chemicals and materials

The following reagents were used, as purchased, in the preparation of the electrodes and the simulated dying wastewater: tin (II) chloride (98%), antimony(III) chloride (99%), yttrium nitrate (38%), sodium hydroxide (96%), sodium chloride (99.5%), oxalic acid (99.5%), citric acid (99%), and ethyleneglycol were purchased from Tianjin Guangfu Chemical reagents factory, and all of the chemicals were of analytical grade. The titanium net, 0.5 mm thick, was supplied by Baoji Lonsheng Co.

Deionized water from Tianjin Lanjing Ultrapure Co. with a resistivity near to 18.2 MΩ cm was used for the preparation of all solutions. Acid Red GR 73# (supplied by Qingdao Chuanlin Dyestuffs Co.) was selected as the model compound in this research work, which was commercial dyes and used without further purification. Its chemical structure is given in Table 1.

DL membrane of GE Water & Process Technology was applied in the coupling experiments, and the performance parameters are shown in Table 2.