Journal of Hazardous Materials 339 (2017) 182–190

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Removal of Cu(II) ions from contaminated waters using a conducting microfiltration membrane

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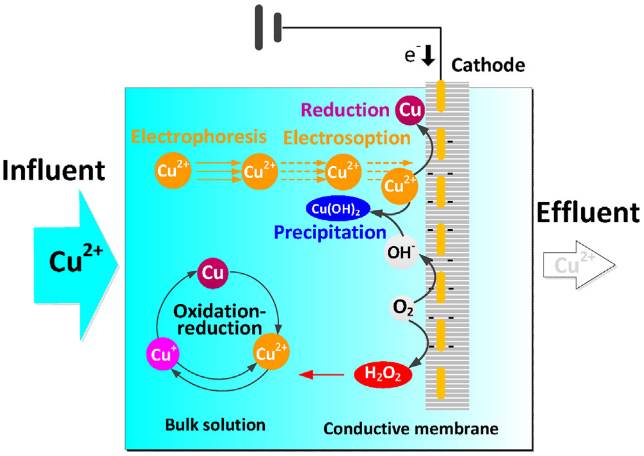
HIGHLIGHTS

- A conducting microfiltration membrane was developed for efficient Cu(II) removal.
- This conducting membrane showed satisfactory electrochemical properties.
- The optimal voltages were 1.0 V and 2.0 V for influent Cu(II) of 5 mg/L and 30 mg/L.
- Cu(II) removal was mainly due to the deposition of Cu(0) and chemical precipitation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 February 2017
Received in revised form 16 June 2017
Accepted 17 June 2017
Available online 19 June 2017

Keywords:
Conducting membrane
Cu(II)
Electrochemical process
Membrane separation
Wastewater treatment

ABSTRACT

Efficient removal of toxic metals using low-pressure membrane processes from contaminated waters is an important but challenging task. In the present work, a conducting microfiltration membrane prepared by embedding a stainless steel mesh in the active layer of a polyvinylidene fluoride membrane is developed to remove Cu(II) ions from contaminated waters. Results showed that the conducting membrane had favorable electrochemical properties and stability as cathode. Batch tests showed that Cu(II) removal efficiency increased with the increase of voltages and leveled off with the further enhancement of electric field. The optimal voltages were determined to be 1.0 V and 2.0 V for the influent Cu(II) concentrations of 5 mg/L and 30 mg/L, respectively. X-ray photoelectron spectroscopy and X-ray diffraction results demonstrated the presence of Cu(0) and $Cu(OH)_2$ on the membrane surface. The removal mechanisms involved the intrinsic adsorption of membrane, electrosorption of membrane, adsorption of deposited layer, chemical precipitation of $Cu(OH)_2$ and deposition of Cu(0) which were aided by electrophoresis and electrochemical oxidation-reduction. Long-term tests showed that the major contributors for Cu(II) removal were the deposition of Cu(0) by electrochemical reduction-oxidation (47.3% ± 8.5%) and chemical precipitation (41.1% ± 0.2%), followed by electrosorption, adsorption by the fouling layer and membrane intrinsic sorption.

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http://dx.doi.org/10.1016/j.jhazmat.2017.06.038
0304-3894/

1. Introduction

Increasingly stringent regulations on the discharge of heavy metals are implemented with the improved awareness of their adverse effects and toxicity on human beings and environment [1,2]. Currently, a number of technologies have been developed to remove heavy metals from contaminated waters, including chemical precipitation [3,4], ion exchange [5,6], adsorption [7,8], membrane separation [9,10], and electrochemical treatment [11,12]. Among the technologies, membrane separation is one of the most promising protocols attributed to its high efficiency, easy operation, decreased footprint, and potential recovery/reuse of metals [13].

Membrane processes for advanced removal of metals are generally nanofiltration [14,15], reverse osmosis [16,17] and emerging forward osmosis [18]. For low-pressure membrane separation processes (e.g., microfiltration and ultrafiltration), the removal of heavy metals is limited by their large pore size allowing heavy metal ions to pass through. Therefore, use of low-pressure membrane processes for removing heavy metals from contaminated waters is a challenging task. If effective low-pressure membrane process can be developed for metal ions removal, the cost-effectiveness of membrane processes can be significantly improved since the low-pressure membrane has much higher flux and lower investment cost compared to the high-pressure membranes and forward osmosis membranes.

To overcome the drawbacks of low-pressure membranes, one of the effective protocols is to develop hybrid ultrafiltration/microfiltration processes to enhance the rejection of heavy metals. Conducting membrane separation, combining membrane separation and electrochemical process, has attracted much attention in recent years [19–24]. To date, conducting membranes have been used for membrane fouling control [25], enhanced energy recovery (anaerobic electrochemical membrane bioreactor) [26], and microbial fuel cell-membrane bioreactor [27]. However, to the best of our knowledge, there are no related studies on using conducting membrane for heavy metal removal.

The objectives of the present work were to propose a conducting microfiltration separation technology for efficiently removing heavy metals from polluted waters. A conducting microfiltration membrane was prepared by embedding a stainless steel mesh in the active layer of a polyvinylidene fluoride membrane without varying physicochemical properties of its surface. The removal efficiencies of this conducting membrane separation process were investigated in batch tests and lab-scale continuous flow experiments. Its associated removal mechanisms were also discussed. In this work, copper ions were chosen as a representative pollutant of heavy metals since they are widely detected in industrial effluents and surface/ground waters [28,29]. Excessive uptake of or exposure to Cu(II) ions can induce severe health issues e.g., damage to kidney, liver, heart, pancreas and brain [30,31].

2. Materials and methods

2.1. Reagents

Chemicals of analytical grade (purity over 99%) were used in this study unless stated otherwise. Copper sulfate, sodium sulfate, silicon dioxide and luminol were purchased from Aladdin (China). Deionized (DI) water was used to prepare all solutions. Polyvinylidene fluoride (PVDF) materials of commercial grade were received from Shanghai 3F New Material (China). Dimethyl sulphoxide (DMSO) and polyethyleneglycole (PEG 600) were purchased from Sinopharm, Shanghai, China.

2.2. Preparation and characterization of conducting membrane

The conducting membrane was prepared using phase-inversion method as documented by literature [32]. Briefly, PVDF and PEG (with predetermined amount) were dissolved in DMSO, followed by agitating at 80 °C for 48 h to obtain a homogeneous solution and ultrasonically degassing for over half an hour. The dope solution was then casted on a stainless steel mesh with a pore size 96 μm and thickness of 43 μm which was assembled on non-woven fabric support (Shanghai Tianlue Advanced Textile Co., Ltd.). The composite membrane was formed after immersing in a DI water bath at room temperature. This conducting microfiltration membrane was denoted as conducting membrane (CM) while a pristine PVDF membrane (PM) was used as a control.

Morphologies of membranes were visualized by using a scanning electron microscope (SEM) (XL-30, Philips, Netherlands). Double-potential step chronoamperometry analysis was performed by an electrochemical workstation (CS350, Corrtest Co., China). During the test, a three-electrode cell involving a working electrode (cathode), an Ag/AgCl reference electrode (0.197 V vs. SHE) and a counter electrode (Pt) in Na_2SO_4 electrolyte solution (0.5 mM), was used. The conducting membrane (cathode) and raw stainless steel mesh (as a control) with surface area of 1.0 cm^2 were scanned for 8 steps at a low potential of 0 V and a series of pre-determined high potentials (0.5, 1.0, 1.5, 2.0 and 3.0 V).

2.3. Experimental set-up

A membrane separation reactor with an effective volume of 630 mL was used in this study, in which a conducting membrane was served as the cathode while two pieces of carbon cloths acted as the anodes. The carbon cloths were installed on each side of the conducting membrane module with a distance of 1 cm distance (see Fig. S1 in the supporting information (SI)). A DC power (CHI1030C, Jiecheng Co., Shanghai, China) was used to supply an external electric field for the reactor. Titanium wire was connected to membrane surface with conducting adhesive to immobilize it, which was sealed with epoxy for avoiding metal corrosion. A perforated aeration tube was used to supply oxygen and to induce a turbulence along the membrane surface.

The influent was synthesized using $CuSO_4$ and deionized (DI) water, in which 5 mM Na_2SO_4 was also added to provide a moderate ionic strength [33]. A peristaltic pump (Lange, China) connected to the membrane modules was employed to extracted permeate. A constant membrane flux (25 L/(m^2 h)) was maintained throughout the experiment with *trans*-membrane pressure (TMP) monitored by a pressure gauge.

2.4. Batch experiments and long-term tests

Batch and long-term tests were performed to investigate the transformation, existing status and removal of Cu(II). For the batch experiments, influents with Cu(II) concentrations of 5 mg/L and 30 mg/L were adopted with a range of external electric fields from 0 and 3 V during 10-h operation. Long-term operation was performed with an influent Cu(II) concentration of 5 mg/L and an applied potential of 1 V. Two cycles were performed for the long-term test. Cu(II) ion concentrations were measured with an inductive coupled plasma emission spectrometer (720ES, Agilent, USA) after the solution was pretreated using a membrane with 0.22-μm pore size. The removal efficiency of Cu(II) ions by the conducting microfiltration membrane was determined by Eq. (1):

$$R_e = \frac{C_0 - C_f}{C_0} \times 100\% \qquad (1)$$