Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

Chemical Engineering Journal

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

Preparation and antibacterial property of polyethersulfone ultrafiltration hybrid membrane containing halloysite nanotubes loaded with copper ions

Yifeng Chen^a, Yatao Zhang^{a,*}, Jindun Liu^a, Haoqin Zhang^{a,*}, Kaijuan Wang^b

^a School of Chemical Engineering and Energy, Zhengzhou University, Zhengzhou 450001, PR China
^b College of Public Health, Zhengzhou University, Zhengzhou 450001, PR China

HIGHLIGHTS

- ► Halloysite nanotubes act as a carrier of antibacterial agent for loading copper ions.
- ▶ PES UF membranes containing HNTs loaded with copper ions were prepared.
- ▶ The membranes showed good antibacterial performance against Escherichia coli and S. aureus.

ARTICLE INFO

Article history: Received 29 April 2012 Received in revised form 28 August 2012 Accepted 29 August 2012 Available online 10 September 2012

Keywords: Halloysite nanotubes (HNTs) Copper ions Polyethersulfone ultrafiltration membrane Antibacterial activity

ABSTRACT

Polyethersulfone ultrafiltration membrane containing halloysite nanotubes loaded with copper ions $(Cu^{2+}-HNTs/PES)$ were prepared via phase inversion method using polyethersulfone (PES) as membrane material and $Cu^{2+}-HNTs$ as an antibacterial agent, which were synthesized by chemical modification of HNTs with silane coupling agent, and then mixed with copper dichloride for complexing copper ions. The morphology and performance of the membranes were characterized by SEM, AFM, TEM, contact angle, and mechanical measurements. The hybrid membranes were shown to be more hydrophilic, with a higher pure water flux. Mechanical test revealed that the mechanical strength of hybrid membranes increased as the addition of $Cu^{2+}-HNTs$. It was also found that $Cu^{2+}-HNTs$ were dispersed uniformly in the membrane. The antibacterial test indicated that the hybrid membranes showed good antibacterial performance against Gram-negative bacteria (*Escherichia coli*) and Gram-positive bacteria (*Staphylococcus aureus*).

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Polyethersulfone (PES) membranes have been widely used in water treatment, food processing and biomedical fields because of their excellent chemical resistance, good thermal stability, oxidation resistance and mechanical properties [1–5]. However, PES membrane is liable to be attached by bacteria in water treatment, which leads to membrane biofouling. Membrane biofouling results in the loss of water throughput increased the operational pressure and system downtime for cleaning [6,7]. Furthermore, biofouling cannot be reduced by pretreatment, because of its self-replicating nature [8].

One of the current trends in preventing membrane biofouling is to improve the antibacterial property of membranes by chemical modification and physical blending. Qiu et al. grafted Poly (4-vinylpyridine) (P4VP) onto polysulfone (PSF) membranes by surfaceinitiated atom transfer radical polymerization (SI-ATRP) and then immobilized copper (II) ions on the modified membrane. Copperloaded membranes exhibited excellent antibacterial properties [9]. Yao et al. prepared novel antibacterial polyurethane (PU) fibrous membranes by electro-spinning the polymer followed by plasma pretreatment, UV-induced graft copolymerization and quaternization reaction. The antibacterial activities of the modified PU fibrous membranes were assessed against *S. aureus* and *Escherichia coli* [10]. Taurozzi et al. prepared polysulfone–silver nanocomposite membranes via the wet phase inversion process by physical blending PSF casting solution with silver. The polysulfone–silver nanocomposite membrane was shown to effectively prevent biofouling [11]. Compared with chemical modification, the physical blending with antibacterial agent was a convenient and effective method for practical utilization.

Recently, various heavy metals as antibacterial agent has been widely used or studied in the ultrafiltration (UF) process including silver, copper, zinc, and so on. Among them, copper represents a more promising metal for antibacterial applications due to its excellent antimicrobial properties, low toxicity, and low cost [9,12]. The



^{*} Corresponding authors. Tel.: +86 371 67781724; fax: +86 371 67781734.

E-mail addresses: zhangyatao@zzu.edu.cn (Y. Zhang), zhanghaoqin@zzu.edu.cn (H. Zhang).

^{1385-8947/\$ -} see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.cej.2012.08.100