

Contents lists available at SciVerse ScienceDirect

# **Chemical Engineering Journal**

Chemical Engineering Journal

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

## Static and dynamic adsorption of copper ions on chitosan/polyvinyl alcohol thin adsorptive membranes: Combined effect of polyethylene glycol and aminated multi-walled carbon nanotubes

E. Salehi<sup>a</sup>, S.S. Madaeni<sup>b,\*</sup>, L. Rajabi<sup>c</sup>, A.A. Derakhshan<sup>c</sup>, S. Daraei<sup>d</sup>, V. Vatanpour<sup>e</sup>

<sup>a</sup> Department of Chemical Engineering, Faculty of Engineering, Arak University, Arak, Iran

<sup>b</sup> Membrane Research Center, Chemical Engineering Department, Razi University, Kermanshah, Iran

<sup>c</sup> Polymer Research Center, Chemical Engineering Department, Razi University, Kermanshah, Iran

<sup>d</sup> Xavaran Kontrol Azarbaijan (X.K.A) Company, 29918 Tabriz, Iran

<sup>e</sup> Faculty of Chemistry, Kharazmi (Tarbiat Moallem) University, Tehran, Iran

### HIGHLIGHTS

▶ Introducing MWCNT-NH<sub>2</sub> and PEG enhance sorption capacity of CS/PVA membranes.

► MWCNTs improve reusability, adsorption rate and stability of the membranes.

▶ PEG increases pore capacity compared to MWCNT.

► Adsorption of copper on CS/PVA membranes was endothermic and spontaneous.

► CPMP membrane offers superior adsorption–filtration performance.

#### ARTICLE INFO

Article history: Received 21 September 2012 Received in revised form 14 November 2012 Accepted 16 November 2012 Available online 27 November 2012

Keywords: Membrane adsorption Chitosan Aminated MWCNTs Porogen Kinetic

#### ABSTRACT

Polyethylene glycol (PEG) and amino-modified multi-walled carbon nanotubes (MWCNT-NH<sub>2</sub>) were utilized to modify chitosan/polyvinyl alcohol (CS/PVA) thin adsorptive membranes for copper ion adsorption. SEM, AFM, water affinity and mechanical analysis were performed for membrane characterization. Batch adsorption experiments were conducted to determine the effects of additive, pH, metal concentration and temperature on adsorption. Macroporous membranes were prepared by introducing PEG into the casting dopes; however, the upper limit for PEG loading was 5 wt%. Adsorption capacity of CS/PVA membrane was increased from 11 to 30 mg/g by addition of 5 wt% PEG to the blend. Addition of MWCNT-NH<sub>2</sub>, especially at optimal concentration of 1 wt%, improved membranes adsorption/transport behavior by creation of nanochannels and supplementary interstices in the compact CS/ PVA matrix. Copper ion adsorption on CS/PVA membrane was elevated from 11 to 19 mg/g by introducing 1 wt% MWCNT-NH<sub>2</sub>. Thermodynamic parameters ( $\Delta H^{\circ}$ ,  $\Delta S^{\circ}$  and  $\Delta G^{\circ}$ ) revealed endothermic nature, favorability and spontaneity of the adsorption. Moreover, kinetic studies showed that MWCNT-NH<sub>2</sub> plays primary role in adsorption rate enhancement. Adsorptive membranes containing combined MWCNT-NH<sub>2</sub> and PEG (called 'CPMP'), demonstrated superior sorption capacity ( $\sim$ 35 mg/g) and reusability among tested membranes. Finally, thin adsorptive membranes were tested in dynamic mode using a deadend filtration setup. CPMP showed superior performance as expected. Based on the results, introducing combined MWCNT-NH2-NH2 and PEG can greatly elevate CS/PVA membranes capability for adsorptive removal of copper ions from water.

© 2012 Elsevier B.V. All rights reserved.

#### 1. Introduction

Heavy metals as common contaminants of industrial wastewaters should be typically removed prior to wastewater discharge due to toxicity. Recently, treatment of effluents containing low concentrations of heavy metals is of great concern [1,2]. Techniques such as chemical precipitation, membrane filtration, ion exchange, extraction, carbon adsorption and co-precipitation/ adsorption have been investigated for heavy metal elimination from aqueous solutions [3–5]. Membrane adsorption offers superiority over conventional processes due to favorable hydrodynamic, high removal efficiency, acceptable reusability and small footprint [6–9].

<sup>\*</sup> Corresponding author. Tel.: +98 831 4274530; fax: +98 831 4274542. *E-mail address*: smadaeni@yahoo.com (S.S. Madaeni).

<sup>1385-8947/\$ -</sup> see front matter @ 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.cej.2012.11.071