Contents lists available at ScienceDirect

Chemical Engineering Research and Design

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

Performance of chitosan based nanocomposite hollow fibers in the removal of selenium(IV) from water

M.S. Seyed Dorraji[a,*], A.R. Amani-Ghadim[b,1], Y. Hanifehpour[c,2], S. Woo Joo[c,**], A. Figoli[d,3], M. Carraro[e,4], F. Tasselli[d,***]

[a] Applied Chemistry Research Laboratory, Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan, Iran
[b] Department of Chemistry, Faculty of Science, Azarbaijan Shahid Madani University, Tabriz, Iran
[c] School of Mechanical Engineering, WCU Nano Research Center, Yeungnam University, Gyeongsan 712-749, South Korea
[d] Institute on Membrane Technology, ITM-CNR, Rende, CS 87030, Italy
[e] Department of Chemical Sciences, University of Padova, Via Marzolo, 1, 35131 Padova, Italy

ARTICLE INFO

Article history:
Received 10 June 2016
Received in revised form 2 September 2016
Accepted 21 October 2016
Available online 31 October 2016

Keywords:
Adsorption
Selenite
Fe_3O_4
Chitosan hollow fibers
Central composite design

ABSTRACT

Fe_3O_4-chitosan nanocomposite hollow fibers were prepared via impregnation of Fe_3O_4 nanoparticles on dry-wet spun chitosan hollow fibers (CS-HFs) and its performance in the removal of selenium(IV) from water was investigated. The prepared nanocomposite was characterized using XRD, SEM and TEM analyses confirming the formation of Fe_3O_4 nanoparticles throughout the heterogeneous surface of CS-HFs. Response surface methodology (RSM) was utilized to optimize Se(IV) adsorption and investigate operational parameters including nanocomposite amount, Se(IV) concentration, pH and contact time. The polynomial second order regression, which is conventionally developed in RSM for describing the process, did not accurately fit the experimental data owing to significant lack of fit. However, in modified polynomial third order regression, all model evaluation criteria had been confirmed the accuracy of the developed model. The adsorption of Se(IV) on prepared Fe_3O_4-CS HFs followed from pseudo-second-order kinetics with participating both intraparticle and boundary layer diffusion in the rate-controlling step.

1. Introduction

Selenium occurs naturally in the environment, but it is also introduced into the environment by anthropogenic activities, such as mining and combustion of fossil fuels. Selenium is commonly found in mining wastewaters in concentrations ranging from 3 to >12,000 $\mu g\,L^{-1}$ (Yamani et al., 2014; Bleiman and Mishael, 2010; Wasewar et al., 2009a). Selenium can exist in different oxidation states in the environment:

* *Corresponding author*. Fax: +98 2433052477.
** *Corresponding author*. Fax: +82 538101456.
*** *Corresponding author*. Fax: +39 984 402103.
E-mail addresses: saeed_dorraji@yahoo.com, dorraji@znu.ac.ir (M.S. Seyed Dorraji), a.r_amani@yahoo.com (A.R. Amani-Ghadim), y_hanifehpour@yu.ac.kr (Y. Hanifehpour), swjoo@yu.ac.kr (S. Woo Joo), a.figoli@itm.cnr.it (A. Figoli), mauro.carraro@unipd.it (M. Carraro), f.tasselli@itm.cnr.it (F. Tasselli).
[1] Fax: +98 4124327541.
[2] Fax: +82 538101456.
[3] Fax: +39 984 402103.
[4] Fax: +39 498 275239.
http://dx.doi.org/10.1016/j.cherd.2016.10.043

elemental selenium (Se°), selenide (S^{2-}), selenite (SeO_3^{2-}), selenate (SeO_4^{2-}) and organic selenium (Sharrad et al., 2012). In water, selenium exists predominately as selenate (Se(VI)) and selenite (Se(IV)) dependent on redox conditions (Gonzalez et al., 2012). Selenite is present in mildly oxidative and neutral pH environments. In addition, the selenite ion is more toxic and mobile in water than the selenate ion, which only exists at high pH and in oxidative conditions (Szlachta and Chubar, 2013). The level of Se in environment is very significant because it possess a dual role as an essential trace nutrient and on the other hand, as a toxic substance at higher levels (Chen and An, 2012). As drinking water is a primary source in which selenium can enter the human body, the U.S. Environmental Protection Agency has set the maximum contaminant level for Se in drinking water at 50 ppb, while the World Health Organization (WHO) has recommended a limit of 10 ppb (Gonzalez et al., 2012).

Multiple technologies have been developed for the remediation of Se in water including coagulation, bacterial reduction, ion exchange, membrane filtration, reverse osmosis and chemical reduction. However, high operating and maintenance costs and use of toxic chemical severely limit the application of these treatment technologies (Yamani et al., 2014; Gonzalez et al., 2012).

Adsorption could be introduced as an alternative technology for remediation of Se. It has been widely investigated over the past decade because of the possibility of sustainable implementation including the regeneration and reuse of the adsorbing media (Martinez et al., 2006; Rovira et al., 2008; Chan et al., 2009; Tuzen and Sari, 2010; Kongsri et al., 2013; Ning et al., 2008).

Chitosan (CS) is one of the most abundant biopolymers in nature and has been widely used as an alternative adsorbent for the removal of metal ions from waters mainly due to the low cost of obtaining this material (Wan Ngah et al., 2011; Gérente et al., 2007). The surface area increasing of an adsorbent results in its performance improvement. Preparation of adsorbent as fibrous structure could be a procedure for increasing its surface area. In this case, hollow fibers are the preferred membrane configuration in order to increase the surface area (Vincent and Guibal, 2001; Han and Bai, 2010; Seyed Dorraji et al., 2014; Mirmohseni et al., 2012). On the other hand, recent studies demonstrate that selenium species have a strong affinity for iron oxides such as Mg–Fe hydrotalcite-like compounds, hematite, magnetite, iron-coated activated carbon and magnetic Fe–Mn oxide nanomaterials (Szlachta and Chubar, 2013; Das et al., 2002; Duc et al., 2006; Martinez et al., 2006; Zhang et al., 2008; Gonzalez et al., 2010).

Therefore, the preparation of CS nanocomposite by introducing the desired nanoparticles is key issue in order to enhance its metal sorption capacity. This study aims to evaluate the potential application of Fe_3O_4 nanoparticles impregnated on wet-spun chitosan hallow fibers (CS HFs) for removing selenium(IV) from water in batch condition. Response surface methodology (RSM) was employed to optimize and survey the effect of operational parameters including initial selenium concentration, amount of Fe_3O_4 chitosan hallow-fibers nanocomposite (Fe_3O_4-CS HFs) in solution, pH and contact time on selenium removal. RSM is statistical design of experiments which develops an adequate relationship between number of variables and response using mathematical and statistical techniques. Generally, RSM offers orthogonal design matrix of experiments and subsequently develops polynomial model based on the experimental responses to optimize the processes. It is expected that the results of this study will provide some basic information for Se(IV) removal by Fe_3O_4-CS nanocomposite hollow fibers in industrial wastewater treatment.

2. Experimental

2.1. Materials

Chitosan powder in low viscous grade was purchased from Sigma–Aldrich. Glutaraldehyde was obtained and used as crosslinking agent from Amersham Biosciences. Stock solution of selenite was prepared by dissolving sodium selenite (Sigma–Aldrich) in distilled water. The working solutions were freshly prepared by diluting the stock solution as needed. All of the chemicals used in this study were of analytical grade and deionized water was used throughout.

2.2. Preparation and characterization of adsorbent

Fe_3O_4-CS nanocomposite hollow fibers were prepared according to our previously reported dipping-drying method (Seyed Dorraji et al., 2015). The preparation of Fe_3O_4-CS HFs was carried out as follows. First, the as-spun CS hollow fibers were crosslinked by immersing in glutaraldehyde bath (5 g L^{-1}) for 1 h. The reason for choosing high concentration of glutaraldehyde was to prevent dissolving of CS HFs in solutions containing of iron ions. After removal from the glutaraldehyde solution, the crosslinked CS HFs were rinsed with distilled water. Then, the crosslinked CS HFs were soaked in the $FeCl_3{\cdot}9H_2O$ solution (0.1 M) for 30 min. The chitosan HFs were washed with deionized water, and soaked in the $FeSO_4{\cdot}7H_2O$ (0.05 M) solution for 30 min. After that, the CS HFs with iron ions were washed with deionized water. This cycle was repeated three times and Fe (II, III)—CS HFs complex was obtained. Finally, the HFs were soaked in the NaOH (3 M) solution for 12 h at 60 °C to achieve Fe_3O_4-CS nanocomposite hollow fibers. Then the Fe_3O_4-CS HFs were washed with deionized water and dried. Removing water directly from a wet hollow fiber in the air may cause changes of its morphology. Therefore, solvent exchange drying in a two-step procedure was used as an effective method to minimize changes of HFs morphology according to previously published procedures. Although the crosslinking reaction of CS with glutaraldehyde determines a worsening of mechanical properties, nevertheless the prepared CS hollow fibers loaded with Fe_3O_4 nanoparticles have acceptable mechanical properties.

The Fe_3O_4-CS HFs X-ray diffraction (XRD) pattern was recorded on Siemens D5000 with Cu K_α radiation. Scanning electron microscopy (SEM) images were performed at QUANTA 200 FEI ESEM scanning electron microscope. Transmission electron microscopy (TEM; ZEISS EM 10) was used to observe the morphology of prepared nanocomposite hollow fibers. Samples were investigated by XPS with a Φ 5600ci Perkin-Elmer spectrometer, using a standard aluminium (Al K_α) source, with an energy of 1486.6 eV operating at 200 W. The working pressure was $\leq 5 \times 10^{-8}$ Pa–10^{-11} torr.

2.3. Adsorption experiments

Flasks of 100 mL were used to perform the batch adsorption experiments, each of which contained 50 mL of a Se(IV) solution and appropriate amount of Fe_3O_4-CS HFs, and shaken at 150 rpm in a shaker. Solutions of 0.1 M HCl and 0.1 M NaOH were used for pH adjustment.

After the desired adsorption periods, the Fe_3O_4-CS nanocomposite hollow fibers were separated from the aqueous phase, and the residual Se(IV) concentrations in aqueous samples were measured on hydride generation atomic absorption spectroscopy (HG AAS).

The selenium adsorption capacity was calculated according to the mass balance equation:

$$q = \frac{(C_o - C)\,V}{m} \quad (1)$$