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Removal of Cr (VI) from aqueous solutions using chitosan/MWCNT/Fe_3O_4 composite nanofibers-batch and column studies

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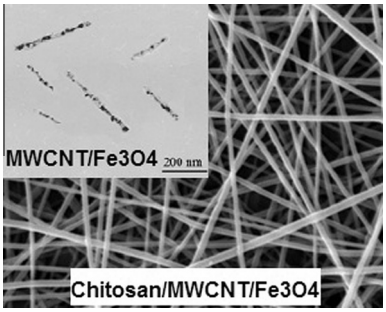
HIGHLIGHTS

- The chitosan/MWCNTs/Fe_3O_4 nanofibers were fabricated via electrospinning.
- Cr (VI) sorption in single and fixed-bed column systems were investigated.
- The sorption process achieved the equilibrium after 30 min.
- The nanofibrous adsorbent were regenerated for five sorption–desorption cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

In the present study, the chitosan/MWCNT/Fe_3O_4 composite nanofibrous adsorbent was fabricated by electrospinning process and its application for the removal efficiency of Cr (VI) ions from aqueous solutions was investigated. The prepared nanofibers were characterized using XRD, FTIR, SEM and TEM analysis. The effects of sorption parameters such as contact time, initial concentration and temperature were evaluated in a batch system. The kinetic and equilibrium data were well described by pseudo-second-order kinetic and Langmuir isotherm models. The spontaneous and endothermic nature of Cr (VI) sorption by the chitosan/MWCNT/Fe_3O_4 nanofibrous adsorbent was achieved. In fixed bed column studies, the Cr (VI) sorption capacity was increased by increasing the flow rate up to 4 mL min^{-1}. Thomas model was well predicted the adsorption capacity of Cr (VI) by the chitosan/MWCNTs/Fe_3O_4 nanofibers in a fixed bed column. The removal efficiency of Cr (VI) ions by the regenerated nanofibers, did not significantly change in both batch and fixed-bed column studies. The results showed the high potential of chitosan/MWCNTs/Fe_3O_4 nanofibers for the removal of Cr (VI) ions from water and wastewater.

1. Introduction

Hexavalent chromium (Cr (VI)) is one of the extremely toxic heavy metals [1,2]. Cr (VI) poisoning in human beings is harmful to the nervous system, bleed, live and bone [3]. Cr (VI) is observed in different industrial wastes including leather tanning, electroplating and metal polishing [4]. Therefore, the removal of Cr (VI) from natural waters and wastewater is one of the great importance. Several methods including chemical precipitation, ion exchange adsorption, membrane filtration and solvent extraction have been used for the removal of Cr (VI) from aqueous systems [5–9]. Among techniques, adsorption process due to its easy operation, high efficiency and low cost is commonly preferred [10].

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Development of new adsorbents with simple synthesis, high specific surface area, easy separation, and good chemical stability should be considered.

The electrospun nanofibers due to a high specific surface area and high porosity with fine pores have been confirmed to exhibit excellent ability for heavy metal ions removing [11–15]. In the previous study, the chitosan nanofibers prepared by electrospinning process, due to the its hydroxyl and amine groups as well as higher specific area, have been used for the removal of Cr (VI) ions from aqueous systems [15].

Nano-sized materials with unique properties including large surface area and many available sorption sites offer high sorption efficiency [16]. Multi-walled carbon nanotubes (MWCNTs) due to the their large surface areas and π–π electrostatic interaction as well as excellent mechanical and chemical properties, exhibited higher adsorption capacity for heavy metal ions removal [17–19]. However, the main drawback of MWCNTs is the poor dispersion into the polymer solution. In the previous studies, researches proved that the dispersion of MWCNTs improved by oxidization of MWCNTs by HNO_3, H_2SO_4 acid, and/or the mixture of these two oxides [20]. Moreover, the separation of MWCNTs can be improved by incorporation of magnetic nanoparticles into the MWCNTs.

In the present studies, the modified electrospun nanofibrous adsorbents have been identified to remove heavy metal ions. In the previous study, we investigated the application of electrospun chitosan/GO nanofibers for the removal of Cu (II), Pb (II) and Cr (II) ions from aqueous solutions [15]. Xu et al. reported the performance of TPEE/iron oxide composite nanofibers for the removal of Cr (VI) [21]. The adsorption of Cr (VI) using polypyrrole/Fe_3O_4 nanocomposite adsorbent was investigated in a continuous flow fixed-bed column by Bhaumik et al [22]. However, there is no study about the potential of chitosan/MWCNT/Fe_3O_4 composite nanofibers for the removal of Cr (VI) from aqueous system.

The cost of adsorbents is also an important parameter. Chitosan as a low cost adsorbent is easily obtained from the shells of shellfish and the wastes of the seafood processing industry [13]. Also, the chemical vapor deposition (CVD) is an economical method for synthesis of MWCNTs [17]. Moreover, Fe_3O_4 is introduced as a low cost adsorbent. Therefore, it can be concluded that the chitosan/MWCNT/Fe_3O_4 nanofibrous adsorbent prepared by electrospinning process can be used as a low-cost adsorbent for the removal of heavy metal ions.

In this work, the chitosan/MWCNT/Fe_3O_4 composite nanofibers were prepared by electrospinning process and their application for the removal of Cr (VI) in a batch and fixed bed column systems. The MWCNTs were oxidized with HNO_3 and following the Fe_3O_4 nanoparticles were embedded into the oxidized MWCNTs. Then, different concentrations of MWCNTs/Fe_3O_4 were incorporated in chitosan solution and finally, the chitosan/MWCNTs/Fe_3O_4 nanofibers were fabricated by electrospinning process. XRD, SEM and FTIR analysis were used to determine the morphology and structure of prepared nanofibers. The kinetics, equilibrium, and thermodynamic tests were conducted in batch system. The experimental data were also fitted to the Thomas model in fixed bed column system. Desorption studies were carried out in both batch and fixed bed column systems.

2. Experimental

2.1. Materials

Chitosan (average Mw = 200 kD) was provided by Sigma–Aldrich (Germany). N, N-dimethyl formamide (DMF), HCl, H_2O_2, HNO_3 and NaOH were purchased from Merck & Co (Germany). Multi-walled carbon nanotubes (MWCNTs) were synthesized using a catalytic chemical vapor deposition (CCVD) system at atmospheric pressure [23]. The obtained MWCNTs have average diameters of 30–70 nm and length of 1–2 μm. $FeCl_3{\cdot}6H_2O$ and $FeCl_2{\cdot}4H_2O$ were obtained from Fluka (Germany).

2.2. Synthesis of MWCNT/Fe_3O_4 composite

The MWCNT/Fe_3O_4 composites were synthesized according to the method described previously [24]. For oxidation of MWCNT, 0.3 g of MWCNT was added to 70 mL of 3 M HNO_3 and the mixture was sonicated for 2 h. Then, the slurry was filtered, washed with distilled water and the process repeated using hydrogen peroxide (30% v/v, H_2O_2). Finally, the obtained slurry dried under vacuum at 50 °C to obtain the oxidative MWCNTs [17]. Then 0.5 g of synthesized MWCNTs were dispersed in 200 mL of distilled water in an ultrasonic bath for 30 min. After that, 3.5 g of $FeCl_3{\cdot}6H_2O$ was added into the mixture under stirring for further 30 min. Then, 0.65 g of $FeCl_2{\cdot}4H_2O$ was added into the mixture and stirring was continued under vacuum for further 30 min. Finally, the MWCNT/Fe_3O_4 composite solution was dried under vacuum at 50 °C for 12 h.

2.3. Electrospinning process

The chitosan solution was prepared by dissolving chitosan (3.5 wt.%) in 0.5 M acetic acid under magnetic stirring condition for 24 h at 30 °C. Then, the various contents of MWCNT/Fe_3O_4 composite (0.5%, 1%, 1.5%, 2%, 3% and 5%, mass of MWCNT/Fe_3O_4 to chitosan) were slowly dispersed to the chitosan solution at room temperature and stirring was continued for extra 6 h.

The prepared solution was loaded into a 5 mL plastic syringe equipped with a syringe needle of 0.9 mm inner diameter. Then, a high voltage was applied between the needle and collector to produce the chitosan/MWCNT/Fe_3O_4 nanofibrous adsorbent. A voltage of 25 kV, with a tip-collector distance of 12 cm, at a feeding rate of 0.5 mL h^{-1} was applied to fabricate the chitosan/MWCNT/Fe_3O_4 nanofibers. The set-up of electrospinning process was provided by the Nanomeghyas Fanavaran Company (Iran).

2.4. Characterization tests

The powder's X-ray diffraction (XRD) patterns were recorded at 25 °C on a Philips instrument (X'pert diffractometer using Cu-Kα radiation) with a scanning speed of 0.03° (2θ) min^{-1}. The functional groups of nanofibers were determined by Fourier transform infrared spectroscopy (Vector22-Bruker Company, Germany) in the range of 400–4000 cm^{-1}. The morphology of the nanofibers was determined using a scanning electron microscopy (SEM, JEOL JSM-6380). The average diameter and diameter distribution of nanofibers were obtained with an image analyzer (Image-Proplus, Media Cybrernetics). From each image, at least 100 different fiber segments were randomly selected and their diameters were measured to generate an average fiber diameter. The final concentration of Cr (VI) ions in the adsorption medium was determined using an inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Thermo Jarrel Ash, Model Trace Scan).

2.5. Adsorption experiments in a batch system

The sorption experiments were carried out in 250 mL flasks containing 50 mg of the adsorbent in 100 mL of Cr (VI) ions solutions on a rotary shaker at 200 rpm for 1 h. The Cr (VI) ions sorption onto the chitosan/MWCNT/Fe_3O_4 nanofibers was carried out as functions of contact time (0–60 min), initial concentration (20–1000 mg L^{-1}) and temperature (25–45 °C) in a batch system. For regeneration of nanofibrous adsorbents, the nanofibers were