A NOVEL FIXED-BED REACTOR DESIGN INCORPORATING AN ELECTROSPUN PVA/CHITOSAN NANOFIBER MEMBRANE

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Abstract

Environmental protection is a major concern in communities throughout the world. Environmental health is threatened by increasing rates of heavy metal pollution, and therefore, the removal of heavy metals from the environment is an important problem. In this research, a novel fixed-bed reactor was designed with a nanofiber membrane composed of a polyvinyl alcohol (PVA)/chitosan nanofiber blend prepared using an electrospinning technique. The applied voltage, tip-collector distance, and solution flow rate of the electrospinning process were 18 kV,14.5 cm, and 0.5 mL/h, respectively. Brunauer–Emmett–Teller (BET) theory, scanning electron micro-scope (SEM), and Fourier transform infrared spectroscopy (FT-IR) were employed to characterize and analyze the nanofiber membranes. Homogeneous electrospun nanofibers with an average diameter of 99.47 nm and surface area of 214.12 m^2/g were obtained. The membrane was installed in a new fixed-bed reactor. The test results showed heavy metals absorbed by the PVA/Cs nanofiber membrane. Adsorption experiments were carried out in a batch system to investigate the effect of different adsorption parameters such as pH, adsorbent dose, biomass dose, contact time, and temperature. The kinetic data, obtained at the optimal pH of 6, were analyzed by pseudo first-order and pseudo second-order kinetic models. Three isotherm models and thermodynamic parameters ($\Delta G°$, $\Delta H°$, and $\Delta S°$) were applied to describe the equilibrium data of the metal ions adsorbed onto the PVA/chitosan nanofiber membrane.

Keywords: PVA/chitosan, Fixed-bed reactor, Nanofiber, Heavy metal, Adsorptiona

1. INTRODUCTION

In recent years, researchers have investigated the use of nanofiber membranes created from biomaterials for the removal of heavy-metal ions. Chitin and chitosan are natural polymers with huge potential applications in numerous biomedical and biological fields [1]. In addition, they are well-known adsorbents for transition metals because the amine groups on chitosan can serve as coordination sites for metals [2]. Nanofiber membranes prepared by the electrospinning method have a high specific surface area and high porosity. The electrospinning of chitosan is extremely difficult due to its low solubility, stability, and mechanical properties. To address this, polymers such as PVA have been blended with chitosan to improve the mechanical properties of the nanofibers [2]. In this study, PVA/chitosan nanofiber membranes were produced using a standard electro-spinning process incorporating a metal collector, a capillary tube with a needle, and a high-voltage power supply. Their effectiveness in a novel fixed-bed reactor for the removal of nickel and cobalt ions from real factory effluent was investigated. The effects of various experimental conditions were investigated to obtain the optimal conditions for maximum adsorption capacity.

2. EXPERIMENTAL

2.1 Materials

Chitosan (average Mw 200,000) and poly(vinyl alcohol) (aver-age Mw 72,000) were obtained from Sigma–Aldrich. Nonwoven polyester fabric was purchased from Baftineh, Iran. Acetic acid was purchased from Merck. Deionized water was used for all tasks.

2.2 Preparation of PVA/chitosan solution

Chitosan (5 wt.%) and PVA (9 wt.%) solutions were initially pre-pared separately by dissolving chitosan in acetic acid (2%, v/v) and PVA in deionized water at 45 °C and 65 °C respectively for 15 h in a magnetic heater stirrer. Following this, a PVA/chitosan solution was obtained by blending the chitosan and PVA solutions at a ratio of 7:3 and stirring them for 24 h at 55 °C.

2.3 Electrospinning process

The collector was coated by a nonwoven polyester web and PVA/chitosan nanofibers were produced on this web basis. Following this, a high DC voltage was applied between the needles and the coated collector (**Fig. 1a**). This process was performed at a voltage of 18 kV, with a tip-collector distance of 14.5 cm and flow rate of 0.5 mL/h. The product was then heated in the oven at 100 °C for 15 h and was used for cross-linking of the PVA/chitosan nanofiber membrane to improve its hydrophilic properties (**Fig. 1b**).

2.4 Design process

For this research, we designed a fixed-bed reactor (**Fig. 1**). The reactor was formed from two polyethylene tubes with an internal diameter of 40 mm, and wall thickness of 10 mm, and lengths of 270 mm and 170 mm. These two tubes were connected to each other by a pipeline. For each piece of membrane bed or membrane module (**Fig. 1c**) one layer of membrane was installed and then placed inside a long tube. Air pressure was supplied by a compressor to push the fluid through the tube and across the fixed bed. The 170-mm tube played the role of a gas and liquid phase separator tank. Fluid exited the bottom of the first tube after crossing the fixed bed and then entered the separator. Air was expressed from the separator, and wastewater was pumped to the top of the first tube. This process was repeated at high speed for a certain amount of time. **Fig. 1d** shows a schematic of this process.

2.5 Batch adsorption experiments

Two different samples of effluent containing nickel or cobalt were collected after one stage of biosorption treatment at a Shahrekord, Iran, zinc ingot production plant. The initial concentration of nickel in the first sample was 14.451 mg/L, and the total cobalt content in the second sample was 5.173 mg/L. Batch adsorption experiments on 150 mL of wastewater were carried out in the fixed-bed reactor under different conditions. The effects of pH (2–7, adsorbent dose 0.48 g/L), adsorbent dose (0.08–0.64 g/L, pH 6), and retention time (10–120 min, adsorbent dose 0.48 g/L and 0.4 g/L for nickel and cobalt wastewater respectively at temperatures of 30, 20 and 10 °C, pH 6) were investigated by varying any one of the process parameters and keeping the other parameters constant.

3. RESULTS AND DISCUSSION

3.1 Characterization of PVA/chitosan nanofiber

Each nanofiber membrane layer was 35 mm in diameter with a thickness of about 100 μm. The mass of the layer without the polyester base was 12 mg. The functional groups were characterized by FT-IR spectrometer. In the nanofiber membrane, a broad band at 3200–3550 cm^{-1} was assigned to O–H intermolecular and intramolecular hydrogen bonding. The peaks at 1383 and 1467 cm^{-1} were assigned to the CH_3 symmetrical deformation mode. The C–H group peaks were observed at 1340 and 1370 cm^{-1}. The vibrational band observed between 2850 and 3000 cm^{-1} refers to C–H stretching of the alkyl groups. The broad absorption bands at 985 and 1020 cm^{-1} were assigned to the C–O stretching vibrations of chitosan. C–H group vibration peaks were observed at 1230 and 1323 cm^{-1}. The absorption bands around 3462 cm^{-1} were assigned to the N–H stretching vibrations. Absorption bands in the range of 1545–1560 cm^{-1} were assigned to the primary amino groups. **Fig. 2** shows the different diameter frequencies of the nanofibers determined by image processing of the SEM micrographs. The average diameter of the nanofibers was

found to be 99.47 nm. BET analysis gave an average nanoparticle surface area of 214.12 m^2/g. In an other study, the systems in vestigated were stabilized with cross-linking by heating at 100 °C. Under these conditions a high-PVA fiber structure collapsed, but a low-PVA content PVA/chitosan blend showed promise [3]. Degree of swelling (%) of cross-linked and non-cross-linked PVA/chitosan was compared by immersing the nanofiber membrane parts in 30 °C deionized water for 24 h.

3.2 Batch adsorption studies

3.2.1 Effect of initial solution pH on adsorption

The experimental results were evaluated for the effects of pH on the adsorption process using a 4-layer nanofiber membrane. The contact time was kept constant for all cases (60 min). The adsorption capacity increased with the increasing of pH to a maximum value of 6 and then declined quickly with further increase of pH.

3.2.2 Effect of adsorbent dose

The effect of the adsorbent dose on the removal efficiency(% removal) and the adsorption of nickel were studied, and the results are shown in **Fig. 3a and b**. The adsorption capacity curve in both cases has a peak; the maximum adsorption capacity of nickel and cobalt was observed at adsorbent doses of 0.48 g/L and 0.40 g/L respectively, with 79.28% and 77.12% removal efficiency.

3.2.3 Effect of contact time and kinetic models

As shown in **Fig. 3c and d**, about 80% of the total adsorption of metal ions occurred within the first 60 min. The process reached the equilibrium state after approximately 120 min of contact time. Therefore, 120 min was selected as the equilibrium time for further experiments. The kinetic data of metal sorption onto the nanofiber membrane fitted well using pseudo first-order kinetic models (**Table 1**).

3.2.4 Modeling of adsorption isotherms

Adsorption isotherms are useful in analyzing the retention or release of a sub-stance from an aquatic environment or porous medium to a solid phase, given constant temperature and pH [5]. The maximum nickel and cobalt adsorption with the Langmuir [4] constants at an optimum pH of 6 and temperature of 10 °C are 46.75 and 20.75 mg g^{-1}, respectively **(Table 2)**. The Freundlich model can be used to describe multilayer adsorption as well as non-ideal sorption on heterogeneous surfaces [6]. As shown in **Table 2**, the maximum K_F values of obtained for nickel and cobalt adsorption were 21.98 and 15.63 (mg/g), respectively. The Dubinin–Radushkevich equation can be used to differentiate physical adsorption of metal ions from chemical adsorption [7]. As can be seen in **Table 2**, the relatively high R^2 values for the Dubinin–Radushkevich model (R^2> 0.98) show that this model was able to give the relationship between the equilibrium concentration of metal ions at liquid phase and the amount of heavy metal uptake in the adsorbent. The free adsorption energy was found for the most part to be lower than 8 kJ mol^{-1}. According to all three adsorption isotherm data analyses shown in **Table 2**, the maximum adsorption capacity (q_{max}) of metal ions reduced with increasing temperature. Nanofiber membrane stability changed with temperature and reaction time in the batch adsorption process. Our results indicated that the process should be initiated at the maximum temperature and then during the process the temperature should be reduced.

3.2.5 Thermodynamic parameters

As shown in **Table 3**, the $\Delta G°$ value was negative. This indicates the feasibility and spontaneity of metal sorption. The positive value of $\Delta H°$ proves the endothermic interaction. The positive value of $\Delta S°$ confirms the increased randomness of the solid/liquid interface during the adsorption process.

3.2.6 Artificial neural network (ANN) model

The ANN architecture incorporated a multilayer perceptron with two hidden layers and feedback architecture; network training was assigned to 70% of the data and testing assigned to 30% of the data. **Fig. 4b and c** shows the correlation between predicted and actual adsorption efficiency with R^2> 0.9674.

4. CONCLUSIONS

In this study, PVA/chitosan nanofiber membranes were pre-pared by an electrospinning process, using heat cross-linking in order to increase their stability. They proved successful for metal ion removal in a novel fixed-bed reactor. The optimal pH level was determined to be 6.0 with adsorbent doses of 0.48 g/L and 0.4 g /L achieving 79.28% and 77.12% removal efficiency for nickel and cobalt adsorption respectively. The kinetic data fitted well with the pseudo first-order model. The adsorption of ions also fit-ted well with the Dubinin–Radushkevich equation. Furthermore, it was found that the process should be initiated at maximum temperature. The calculated thermodynamic parameters showed the feasibility and spontaneity of the metal ion adsorption within the studied conditions, as well as the endothermic interaction. The present study demonstrates a simple method providing an ANN model, and gave results similar to other studies.

Table 1 Summary of sorption data evaluated by different kinetic models

Effluent	q_{max}	First − order model			Second − order model		
		k_1	q_e	R^2	k_1	q_e	R^2
Nickel	27.268	0.0502	58.196	0.938	0.0013	37.878	0.8293
Cobalt	11.162	0.0465	17.681	0.945	0.0045	15.034	0.957

Table 2 Isotherm parameters for metal adsorption onto the PVA/Chitosan nanofiber membrane

Metal	T (K)	Experimental data*			Langmuir isotherm		
		$C_{e,i}\left(\frac{mg}{l}\right)$	$C_{e,f}\left(\frac{mg}{l}\right)$	$q_e\left(\frac{mg}{g}\right)$	$b\left(\frac{L}{mg}\right)$	$q_{max}\left(\frac{mg}{g}\right)$	R^2
nickel	303	12.99	1.54	27.07	0.780	42.753	0.963
nickel	293	12.60	1.94	26.24	1.548	36.914	0.953
nickel	283	12.26	2.28	25.54	0.514	46.751	0.967
cobalt	303	4.45	0.72	11.12	5.275	13.997	0.997
cobalt	293	4.10	1.06	10.26	1.328	17.809	0.920
cobalt	283	3.87	1.29	9.68	0.692	20.755	0.989

Metal	T (K)	Freundlich isotherm			D-R isotherm			
		n	$K_F\left(\frac{mg}{g}\right)$	R^2	$q_{DR}\left(\frac{mmol}{g}\right)$	$\beta_{DR}\left(\frac{mol^2}{J^2}\right)$	$E\left(\frac{kJ}{mol}\right)$	R^2
nickel	303	1.649	21.978	0.99	0.736	0.737×10^{-8}	7.728	0.981
nickel	293	1.428	17.660	0.98	0.915	1.153×10^{-8}	6.285	0.992
nickel	283	1.339	14.825	0.97	0.922	1.394×10^{-8}	5.989	0.993
cobalt	303	1.721	15.631	0.96	0.217	0.744×10^{-8}	8.194	0.995
cobalt	293	1.338	11.508	0.89	0.224	1.085×10^{-8}	6.788	0.997
cobalt	283	1.276	8.619	0.95	0.225	1.392×10^{-8}	6.154	0.998

* The best experimental data in optimal conditions

Table 3. Thermodynamic parameters for metal adsorption onto the PVA/Chitosan nanofiber membrane

Metal	kd			$\Delta H^{\circ}(kj/mol)$	$\Delta S^{\circ}(j/mol\ K)$	$\Delta G^{\circ}(kj/mol)$		
	10 °C	20 °C	30 °C			10 °C	20 °C	30 °C
Nickel	5.371	6.472	8.403	16.043	70.487	-3.957	-4.552	-5.365
Cobalt	2.985	3.853	6.153	25.716	99.59	-4.277	-3.287	-2.756

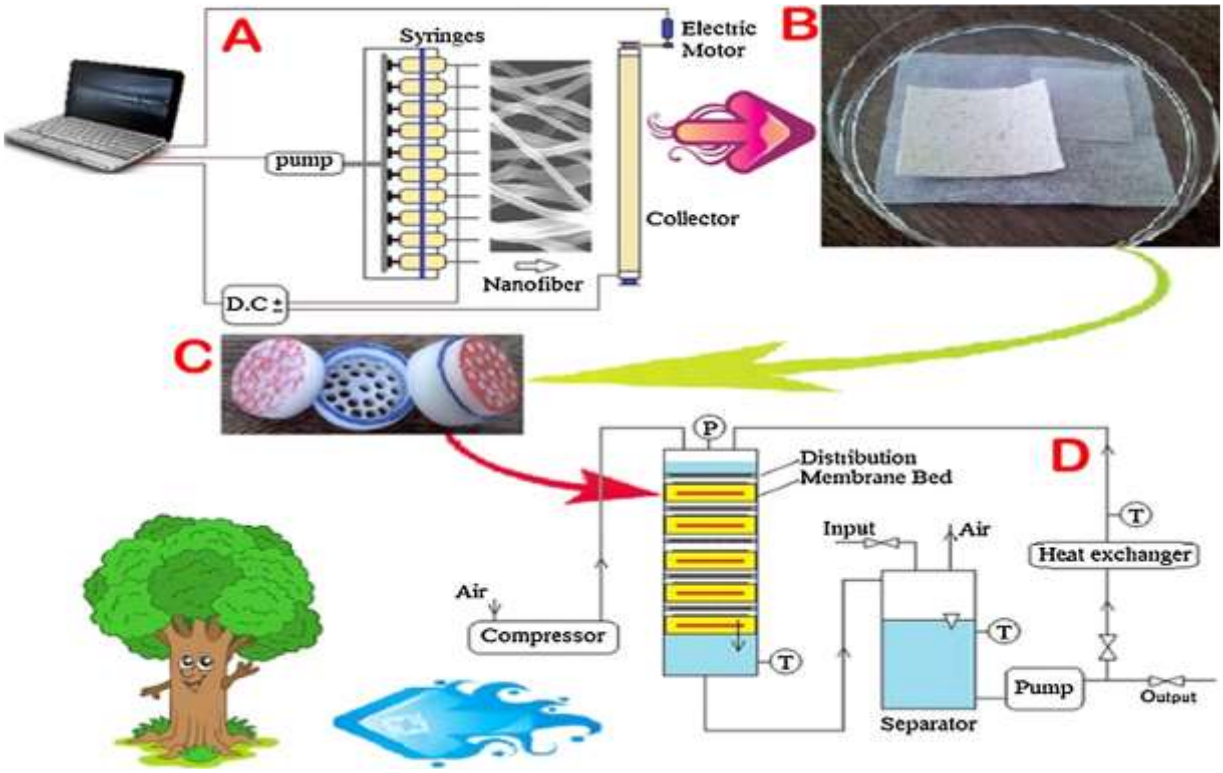

Fig. 1. Schematic of the electrospinning process (a), non-woven polyester web before electrospinning process and, chitosan/PVA nanofiber membrane produced on thenon-woven polyester web after electrospinning process (b), membrane module (c), schematic of adsorption process.

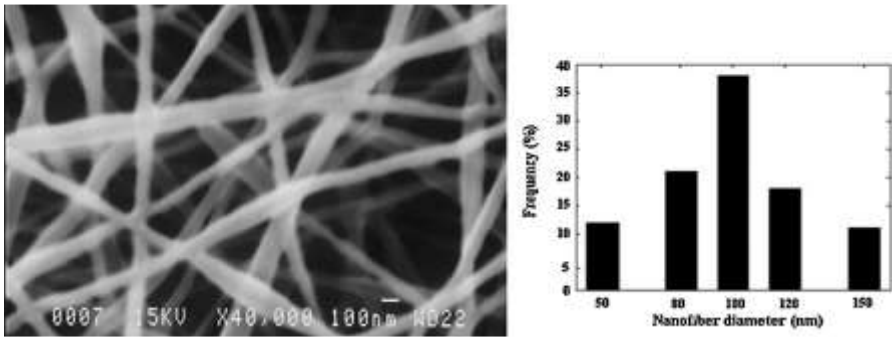

Fig. 2. The SEM image and diameter distribution of chitosan/PVA nanofiber membranes.

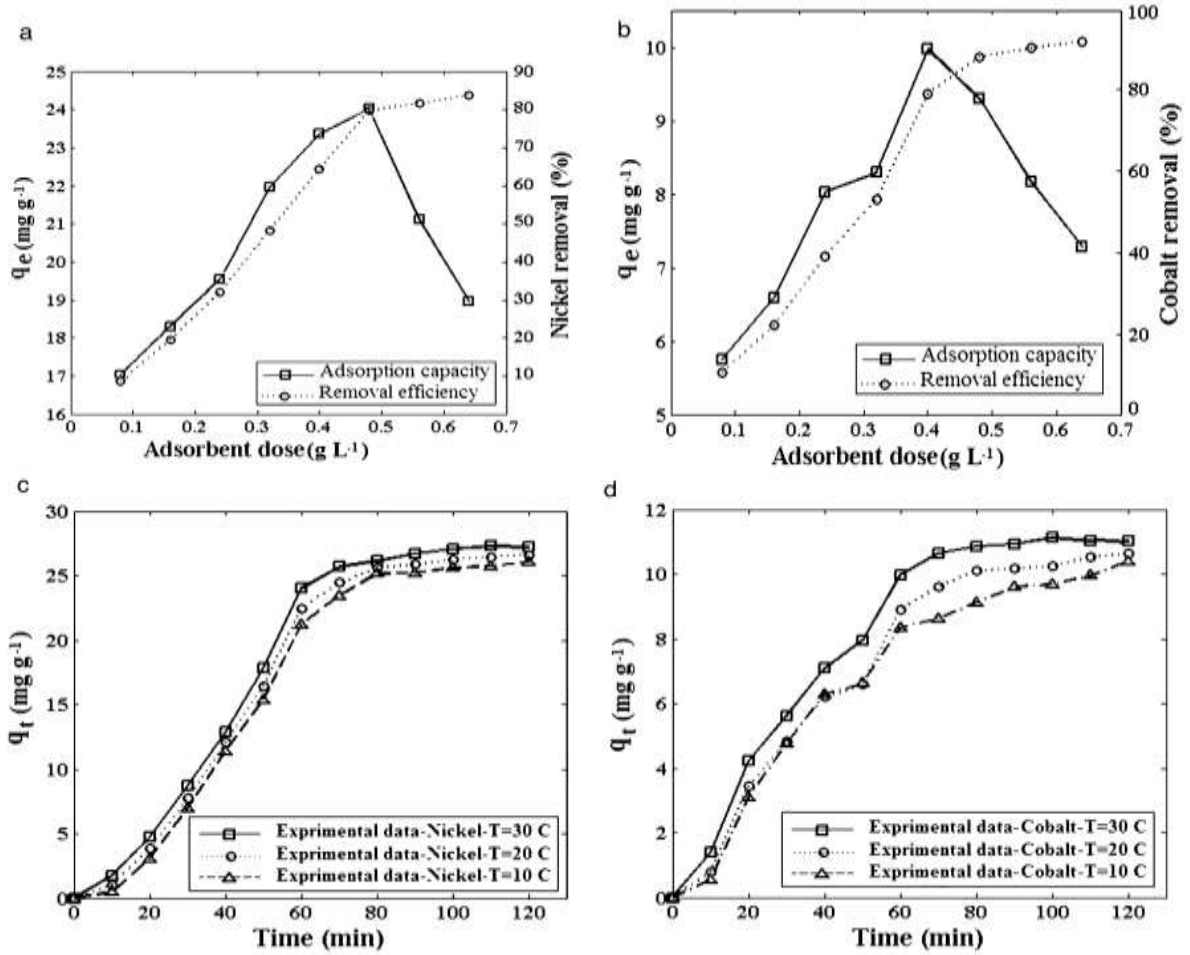

Fig. 3. Effect of adsorbent dose on the removal efficiency (% removal) and the adsorption capacity of chitosan/PVA nanofiber membranes for nickel (a) and cobalt (b). Effectof contact time on adsorption capacity of chitosan/PVA nanofiber membranes for nickel (c) and cobalt (d) at different temperatures: 30°C, 20°C and 10°C.

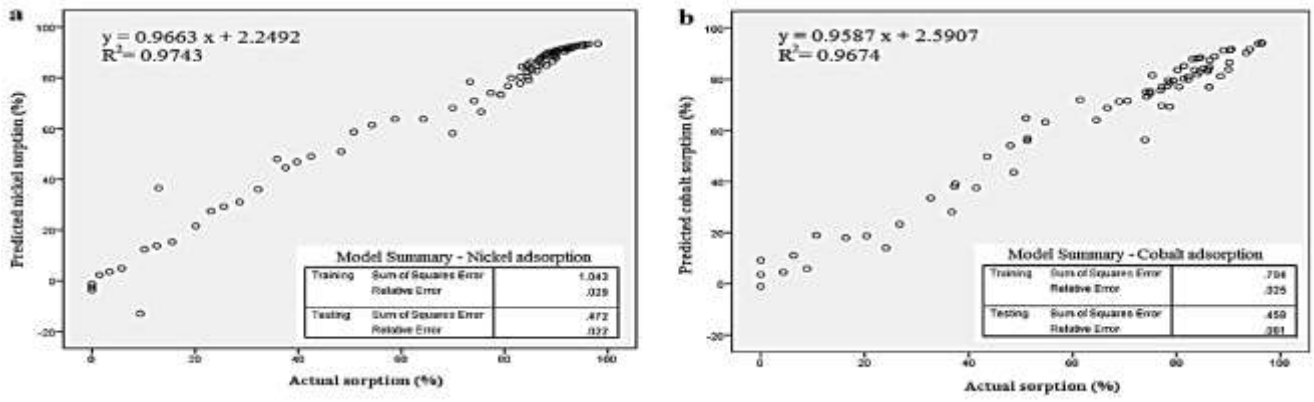

Fig. 4. Comparison of model results and the actual removal efficiency (b and c).

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