



poly(ε-caprolactone) electrospun nanofibers-copper hexacyanoferrate composite as an ion exchanger for effective cesium ion removal

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Abstract

In this study, poly(ε-caprolactone) electrospun nanofibers-copper hexacyanoferrate composite ion exchanger (PCL nanofibers–CuHCF) was prepared and used for the cesium ion removal from aqueous solution. The results showed that the obtained composite exhibited excellent performance for the removal of cesium ions. The influences of several variables such as temperature, pH, and contact time were evaluated in batch experiments. The thermodynamic study indicated a spontaneous and endothermic ion exchange process. The adsorption isotherm and kinetics of the PCL–CuHCF composite were evaluated, indicating monolayer chemisorption of the Langmuir type. The maximum sorption capacities by applying the Langmuir equation was 178.7 mg/g.

Keywords: Copper hexacyanoferrate, Poly(ε-caprolactone), Electrospun nanofibers, Composite ion exchanger, Cesium ions removal.

Introduction

As a major fission product of uranium, radioactive cesium widely exists in nuclear waste and its removal is vital yet challenging [1]. Among many methods and materials for the removal of cesium ions, intensive studies have been conducted toward the cesium ion exchange removal process. Among ion-exchangers hexacyanoferrates such as copper (II) hexacyanoferrate (CuHCF) have retained great attention due to their low cost, selectivity, and high capacity [2]. Nevertheless, the fine particle size of this type of ion exchangers prevents easy separation, so immobilization of the particles of ion-exchangers on supporter or matrix has been extensively studied. Nanofibres with their inherent features such as large surface area, high porosity with excellent pore interconnectivity, structural stability, and tunable thickness of the electrospun scaffold have held great potential in remediation of heavy metal ions [3].

In the current study, we report a facile synthesis route for PCL nanofibers–CuHCF composite ion exchanger to remove the cesium ions effectively. The adsorption isotherm and kinetics of the nanofibrous ion exchanger, as well as the influence of pH of solution and temperature, were investigated by batch technique.

Experimental

Preparation of PCL–CuHCF nanofibers

CuHCF was prepared by mixing 0.25 mol/l potassium hexacyanoferrate (II) solution with 0.75 mol/l Cu(NO₃)₂ solution (1:1 (v/v)) at 50 °C for 2 days. The obtained precipitates were filtered and washed with water and dried (60 °C, 12 h). The product was then powdered by a mill and sieved to the size of 224–400 μm.

Fibers of PCL–CuHCF were obtained by electrospinning. Electrospinning solution was prepared

by adding the CuHCF (10 wt% relative to PCL weight) to a N,N-dimethylformamide (DMF)/ chloroform mixture (1: 2 v/v) at 25 °C under magnetic stirring for 30 min. PCL was then added to the CuHCF solution and the stirring was continued overnight at room temperature. Electrospinning was carried out at 12 kV, at a flow rate of 2 ml/h and the distance between the tip of the needle and the ground collector was set at 15 cm.

Cesium ion-exchange experiments

The batch experiments were carried out in series of flask containing 20 ml aqueous solution of CsCl at different initial concentrations with the sorbent dosage of 50 mg. The flask was equilibrated in the shaker bath, operating at 100 rpm and 25 °C except for the temperature dependence studies. The supernatant solution was removed at definite time intervals to analyze the residual Cs⁺ ion concentration. The amount of adsorbed cesium per unit mass of composite nanofibers (q_e (mg/g)) and the cesium ion removal efficiency (R) were calculated according to Eq. (1) and (2), respectively:

$$q_e = (C_0 - C_e) \frac{V}{M} \quad (1)$$

$$R\% = \frac{(C_0 - C_t)100}{C_0} \quad (2)$$

Results and discussion

Fig. 1 shows the SEM images of the composite nanofibers. It can be seen that the diameter of the nanofibers ranged from 350 to 500 nm. It is observed that the fibers are cross-sectionally round and their surfaces are smooth. As can be seen, the PCL–CuHCF exhibited very few bead defects. Magnified SEM image

of the composite nanofibers indicated several spherical particles, which could be CuHCF particles.

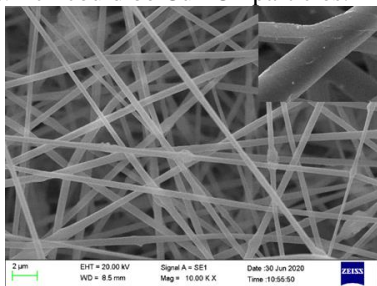


Fig. 1 SEM images of the composite nanofibers.

The XRD analysis of the fibrous sample represented sharp and strong diffraction peaks at $2\theta = 21.05^\circ$, 21.24° , and 23.4° , which can be attributed to (110), (111) and (200) crystal planes of PCL, respectively. PCL-CuHCF have also the characteristic diffraction peaks of CuHCF, located at 2θ values of 17.3, 24.6, 35.2, 39.6, 43.4, and 54.1° , which can be assigned to the (200), (220), (400), (420), (424), and (440) planes of the cubic crystal structure of CuHCF.

The BET results showed that after the addition of CuHCF the surface area increased from 7.3 to 13.5 m^2/g for PCL and PCL-CuHCF nanofibers, respectively, which can be attributed to an increase in the surface roughness because of the presence of the CuHCF.

The TGA result shows one main degradation with an inflection point at 420°C , which could be attributed to the degradation of poly(ϵ -caprolactone). The results revealed that CuHCF particles are very stable and no decomposition takes place in the range of $25\text{--}600^\circ\text{C}$.

Cesium ion exchange studies

Based on a competitive assay, PCL nanofibers were not efficient in Cs^+ ion removal. The results of the experiments evaluating the effect of pH on the sorption of Cs^+ ions on nanofibrous mat showed that the Cs^+ removal efficiency is continuously improved by increasing pH value from acidic to alkali medium and the maximum removal was obtained at pH 9.0.

The sorption of cesium ions increases with increasing the contact time, before reaching the equilibrium state. The uptake of cesium ions is relatively fast and equilibrium state has attained during the 40 min.

In order to evaluate the cesium adsorption kinetics, the experimental data were fitted by the intra-particle diffusion, pseudo-first-order, and pseudo-second-order kinetic models by using the MATLAB software.

The results of kinetic models fitting to the experimental data are shown in Table 1. As it is obvious from the table, the pseudo-second-order kinetic model (R^2 98%) is the most appropriate kinetic model among the three evaluated models, which indicates the applicability of the pseudo-second order kinetic model in determining the rate of Cs^+ ions removal.

Table 1. The parameters for kinetic adsorption models.

Kinetic model	Kinetic constant	Value	R^2
Pseudo-first-order	q_e (mg/g)	12.93	0.89

$q_t = q_e [1 - \exp(-k_1 \times t)]$	k_1 (min^{-1})	0.036	
Pseudo-second-order	q_e (mg/g)	22.34	0.98
$q_t = \frac{k_2 \times t \times q_e^2}{(1 + k_2 \times t \times q_e)}$	k_2 (g /mg min)	0.005	
Intra-particle diffusion	k_p ($\text{min}^{-0.5}$)	1.045	0.66
$q_t = k_p t^{1/2} + I$	I	7.72	

The results showed that the removal efficiency of Cs^+ by PCL-CuHCF composite nanofibers ion exchanger was promoted at high temperatures. This observation can be explained by the faster motion of the metal ions at higher temperatures, which is mainly due to the weaker electrostatic interactions and lower solvation. The results reveal that the ion exchange process was spontaneous and endothermic according to the obtained negative and positive ΔG° and ΔH° values, respectively. Several isotherm models were analyzed to explore the adsorption mechanism and express the sorption process as a function of the equilibrium concentration. Here, the experimental equilibrium data were fitted with Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich models. The results showed that among the different isotherm models, the Langmuir model could predict the experimental data during a wide range of concentrations.

Conclusions

The preparation, characterization, and application of PCL-CuHCF composite nanofibers for Cs^+ ion removal were reported. The composite nanofibers were proven to be effective ion exchanger for the removal of Cs^+ from aqueous solution. The optimum conditions are: pH of 9, contact time 40 min, and $T=75^\circ\text{C}$. The Langmuir isotherm model showed a better correspondence with the equilibrium data than the other studied models. Chemisorption was found to be the possible main rate-determining step based on kinetic studies. The nature of cesium ions removal was endothermic and spontaneous.

References

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