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Synthesis of novel mixed matrix scaffolds and adsorption of copper ions of waste water

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ABSTRACT

Mixed matrix scaffolds were synthesized by uniformly distribution of ion exchange resins (H^+ form Amberjet, ID 780 μm) into the stereo-structural chitosan matrix and then used for the removal of copper ions from waste water. Specifically, Amberjet particles suspended in a 1 wt% of viscous chitosan solution were filled with cylindrical aluminum containers to prepare chitosan mixed matrix scaffolds through the freeze-gelation process. The internal surface area of mixed matrix scaffolds is 78 m^2/g. The adsorption processes were performed by chelate copper ions of waste water onto the amine functional groups ($-NH_2$) exposure on the external and porous stereo-structural surfaces of chitosan matrix as well as the sulfonate functional groups on the outer surface of ion exchange resins, respectively. Results of a low initial copper ion concentration of 5 mg Cu^{2+}/L were used to study the adsorption capacities as well as adsorption kinetics experimentally. The kinetic experimental data correlated well with the second order adsorption model, suggesting that the rate limiting step of mixed matrix scaffolds may be the chemical adsorption.

Keywords: Adsorption; Chitosan; Mixed matrix scaffolds; Adsorbent

1. Introduction

Trace amount of copper ions are essential to human beings. However, as the concentration of copper ions above 1.3 mg/L, humans may present symptoms of temporary stomach and intestinal disorders to kidney or liver damage with respect to various exposure time [1]. The removal of copper ions from waste water to meet the increasing stringent environmental standards becomes a significant issue. This will require the development of new separation technologies utilizing novel mixed matrix scaffolds that are capable of removing copper ions from waste water.

Chitosan, glucosamine biopolymer derived from the shells of marine organisms, has widely been studied for the adsorption of heavy metal ions from waste water. However, the low internal surface area of nonporous flaked or powdered forms of chitosan may limit access to interior adsorption functional groups and significantly reduce the metal ions adsorption capacities. The reprocessing of powdered chitosan with embedded ion exchanger resins into highly porous mixed matrix scaffolds can overcome many process limitations. The concept of mixed matrix membranes (MMMs), various ion exchanger particles tightly held together within an ethylene vinyl alcohol (EVAL) copolymer porous polymeric matrix, were presented by Avramescu et al. and Borneman et al. [2,3].

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Figoli et al. [4] prepared nano-structured MMMs by embedded sub-micrometer sized capsules into a polymeric matrix through film formation technique. Anson et al. [5] showed the performance for separation of CO_2 from CH_4 by using mixed matrix composite membranes, blending acrylonitrile butadiene styrene copolymer with micro-mesoporous activated carbons. Pal et al. [6] proposed a new permeation model for MMMs and compared with experimental data. MMMs are known as promising adsorbents for pervaporation, gas separation, enzyme capture, and protein recovery [2,3,7,8]. However, previous work has not well characterized the removal of heavy metal ions by using porous MMSs or scaffolds.

The purpose of this work was to prepare highly porous novel mixed matrix scaffolds, and then evaluate how these scaffolds adsorb various concentrations of copper ions from aqueous solution at pH 4–6. Specifically, ion exchanger resin particles (H^+ form Amberjet, Rohm & Haas) were added into a 2 wt% chitosan solution and then molded into porous mixed matrix scaffolds by a freeze-gelation technique. The adsorption of copper ions (Cu^{2+}) onto the mixed matrix scaffolds was followed in a semi-continuous column contactor. Adsorption isotherms and kinetics data for mixed matrix scaffolds were obtained over a broad range of copper ions concentrations ranging from 5 to 1500 mg Cu^{2+}/L at pH 4–6. Results of kinetic experiment of copper ions onto chitosan mixed matrix scaffolds had been correlated with different kinetic models in order to investigate the rate limiting step. This study was limited to investigating of copper ion adsorption onto porous mixed matrix scaffolds. Desorption processed by adding a dilute acid regenerate solution is reserved for future study.

2. Materials

2.1. Chemicals

Flaked chitosan with 80% deacetylation (Sigma) were grounded to powdered form with a size less than 300 μm and then prepared chitosan solutions without further purification. The average molecular weight of the chitosan was 1,70,000. The acetic acid and ethyl alcohol used for dissolving the chitosan powder and displacing the remaining water in mixed matrix scaffolds were of ACS reagent grade. Deionized distilled water was used to prepare chitosan solutions and copper ion solutions for measurement of adsorption isotherms.

2.2. Synthesis of mixed matrix scaffolds

Fabrication of porous mixed matrix scaffolds included three steps: chitosan solution preparation, freezing of scaffolds, and gelation of scaffolds. A 2 wt% chitosan solution containing Amberjet particles (ion exchanger resin particles, ~0.3 g, ID : 780 μm) was poured into a cylindrical aluminum container and then frozen at −20°C for 2 h. The cylindrical frozen chitosan models were placed at 1 M ethanol/sodium hydroxide solution (50/50 v/v, −20°C) for fully gelation in order to prepare porous chitosan mixed matrix scaffolds. After formation, chitosan mixed matrix scaffolds were stored in deionized water solutions at room temperature for following utilization.

2.3. Characterization of mixed matrix scaffolds

After supercritical drying, the chitosan mixed matrix scaffolds were extensively characterized to determine porosity and pore size distribution. The internal surface area of mixed matrix scaffolds was determined by the BET method by using N_2 as the adsorbate. Prior to BET analyses the scaffolds were pretreated by the supercritical fluid (CO_2) drying method (0–33°C, 800–1,300 psi) for 1.5 h to completely removal of residual water/ethanol solutions in the samples. The pore size distribution and mean pore size were estimated from desorption isotherm data by the BJH method of analysis [9]. The diameter of ion exchanger particles were measured by a Light Scatter caliper (Coulter, LS230). Microstructures of chitosan mixed matrix scaffolds were characterized using scanning electron microscopy (SEM).

2.4. Copper ions adsorption measurements

The copper ion solutions were prepared by dissolving copper nitrate ($Cu(NO_3)_2 \cdot 2.5H_2O$) in distilled water. Measurements of copper adsorption were conducted in a well-mixed continuous column process and allowed to reach equilibrium. Specifically, fixed amounts of wet mixed matrix scaffolds were packed in a sealed column and continuously contacted with the copper nitrate solution with a feed flow-rate of 150 mL/min for 72 h at 25°C. The apparatus of column adsorption processes contactor for chitosan beads, matrix and MMMs is shown in Fig. 1. A 2 mL of copper ion solutions were withdrew at specific period of time along the adsorption experiment. Measurement of Cu^{2+} was performed by using atom absorption spectrophotometer (AAS). An adsorption experiment was continued until the Cu^{2+} concentration was reaching constant. The duration of the adsorption experiment was typically 80 h.

The models of first order, second order and intraparticle diffusion equations were applied on

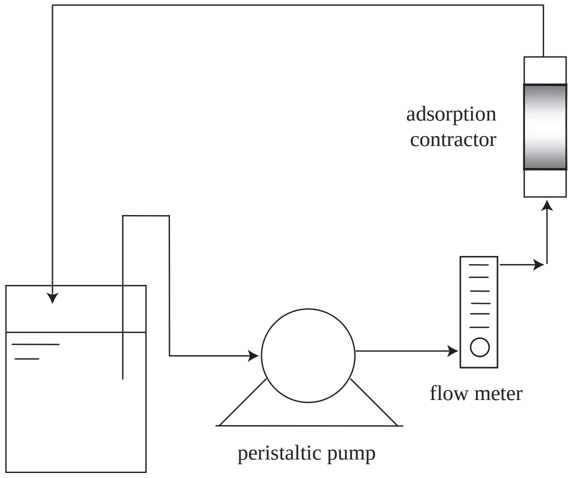

Fig. 1. SEM images of the hollow fiber membranes. Apparatus of column adsorption processes.

examining the adsorption kinetic experiment data in order to investigate the controlling mechanisms of adsorption processes. The first order kinetic model by Chiou et al. [10] and Annadurai et al. [11] was expressed as

$$\log(q_e - q_t) = \log q_e - (k_1/2.303)t, \tag{1}$$

where q_e and q_t are the amount of copper ions adsorbed onto adsorbents (mg g^{-1}) at equilibrium and fixed period of time, respectively, and k_1 is the rate constant of first order of adsorption (h^{-1}). The second order equation [12] was determined by

$$t/q_t = 1/(k_2 q_e^2) + t/q_e, \tag{2}$$

where k_2 is the rate constant of second order of adsorption (g mg^{-1} h^{-1}). The intra-particle diffusion rate [10] can be shown as

$$q_t = k_i t^{0.5}, \tag{3}$$

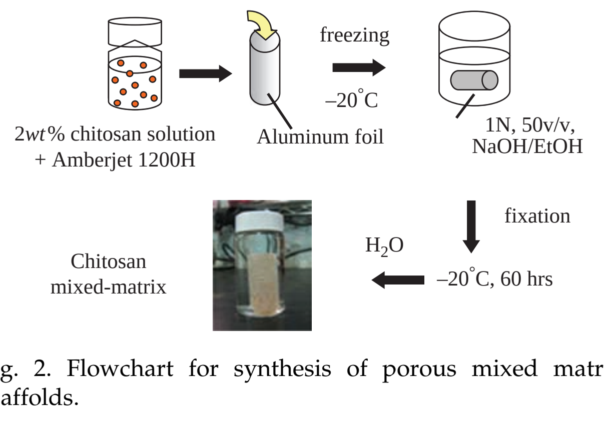

Fig. 2. Flowchart for synthesis of porous mixed matrix scaffolds.

where k_i is the intra-particle diffusion rate (mg g^{-1} $h^{-0.5}$).

3. Result and discussions

3.1. Preparation and properties of mixed matrix scaffolds

The mixed matrix scaffolds were prepared by a freeze-gelation technique using the apparatus shown in Fig. 2. Supercritical fluid (CO_2) drying preserved the porosity of mixed matrix scaffolds because the water in the scaffolds was quickly replaced by high pressurized supercritical fluid of CO_2 without damaging porous stereo structure of scaffolds.

The BET surface area of chitosan matrix without embedded ion exchanger resin particles determined by BET method was upto 150 m^2/g. The porous structure of the surface for chitosan matrix without addition ion exchanger resin particles can clearly be seen in the images of the scanning electron micrographs (Fig. 3a). Porous chitosan matrix possessed open and interconnected porous structure from the morphologies of SEM images at 35× (Fig. 3b). However, the internal surface area of mixed matrix scaffolds was 80 m^2/g, which was comparable to industrial catalysts. Differences in the BET surface area of the mixed matrix scaffolds and chitosan matrix can be tentatively attributed by addition of nonporous ion exchanger resin particles into the stereo structure of porous chitosan matrix in preparation conditions as described previous.

The SEM images for the distribution of Amberjet particles in the porous mixed matrix scaffolds were shown in Fig. 4. The nonporous Amberjet particulates were symmetrically incorporated into the stereo-structure of porous chitosan matrix. Morphology of the mixed matrix scaffolds revealed that more rigid structure observed on the outer surface as well as internal matrix.

3.2. Adsorption of copper ions on mixed matrix scaffolds

The equilibrium adsorption capacity of Cu^{2+} on the chitosan mixed matrix scaffolds (Q), expressed as mg Cu^{2+}/g of scaffolds, was determined by

$$Q = (C_o - C_f)V/m_a, \tag{4}$$

where C_o is the initial concentration of Cu^{2+} (mg Cu^{2+}/L), C_f is the final concentration of Cu^{2+} at equilibrium (mg Cu^{2+}/L), m_a is the dried mass of chitosan mixed matrix scaffolds; Q is the adsorption capacity of Cu^{2+} on the adsorbents (mg Cu^{2+}/g adsorbent), and V is the volume of solution (L) in the contactor. In the experiment, volume of solution was 500 mL and the mass

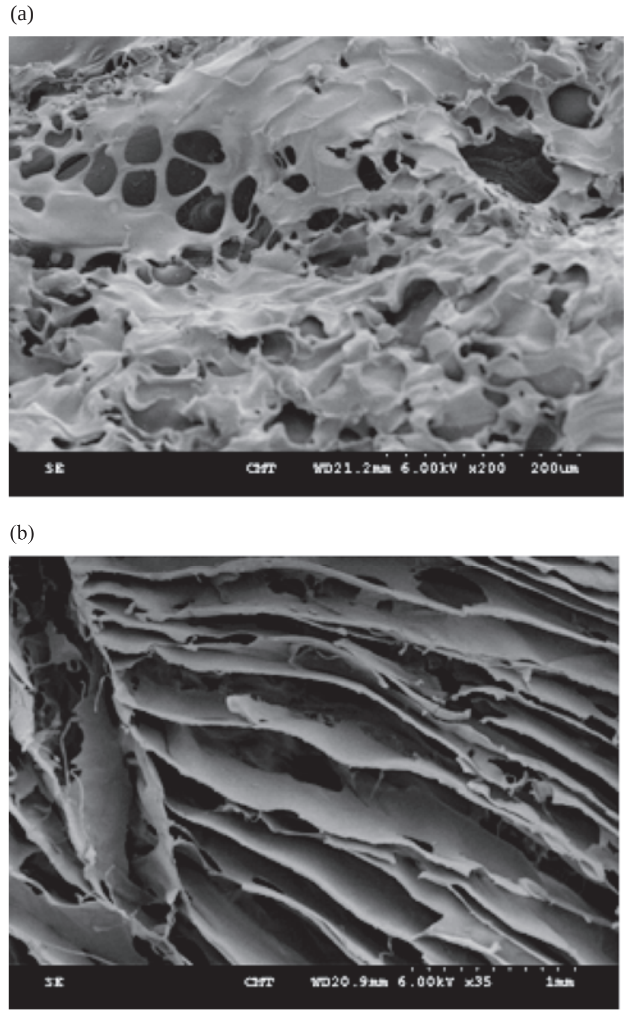

Fig. 3. SEM photomicrographs of chitosan matrix: (a) surface at 200× (b)cross-sectional porous matrix at 35×.

of dried mixed matrix scaffolds was 300 mg. The ratio of scaffolds in the contactor was fixed at 0.6 g of scaffolds/L of solution. The initial concentration of Cu^{2+} (in copper nitrate solution) was varied from 5 to 1,500 mg Cu^{2+}/L.

3.3. Adsorption kinetics

The Cu^{2+} concentration vs time profiles for the mixed matrix scaffolds are compared with various initial Cu^{2+} concentrations, as shown in Fig. 5. Mixed matrix scaffolds at an initial concentration of 1,000 mg Cu^{2+}/L had both a faster initial adsorption rate and a larger equilibrium adsorption capacity than did at initial concentrations of 500 and 5 mg Cu^{2+}/L. During the well-mixed continuous column adsorption experiment, the pH value of the copper solution contacting the mixed matrix scaffolds rose initially and then leveled off to 6.0–602. The pH increasing rate was higher at an initial concentration of 1,000 mg Cu^{2+}/L than those at initial concentrations of 500 and 5 mg Cu^{2+}/L for mixed matrix scaffolds. An increase of pH means a decrease in hydronium ion concentration. Thus, hydronium ions competed with copper ions for available amine adsorption sites of chitosan and sulfonic adsorption sites of ion exchanger resins in the mixed matrix scaffolds.

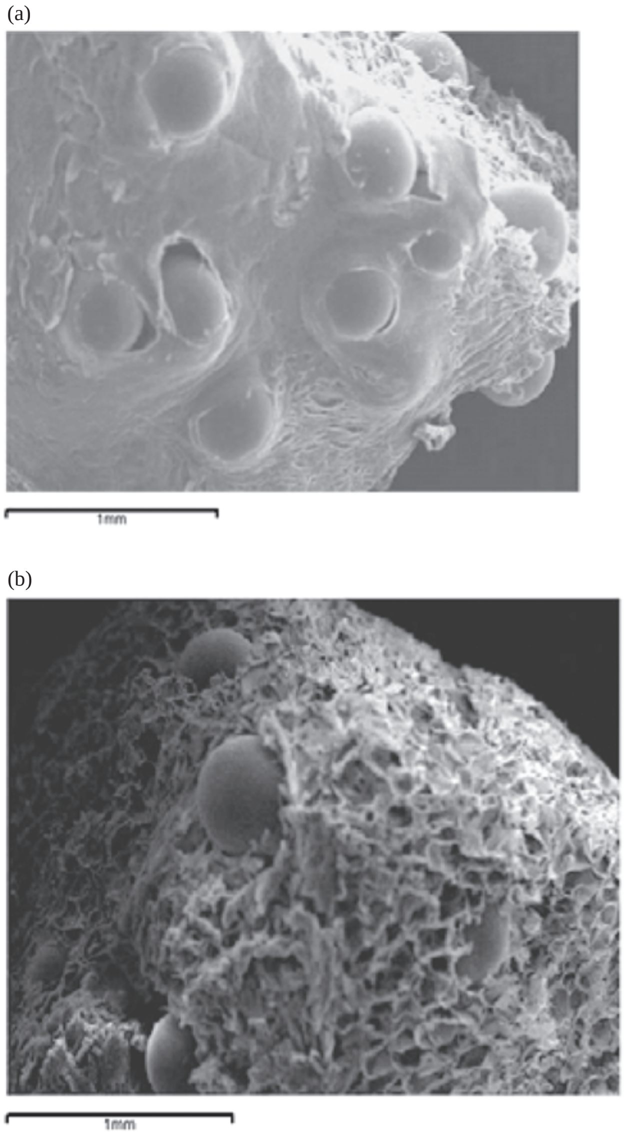

Fig. 4. SEM photomicrographs of the mixed matrix scaffolds (a) surface at 500× (b) cross-sectional structure at 500×.

3.4. Adsorption isotherms and model predictions

Adsorption isotherms and Freundlich or Langmuir adsorption models predictions for the mixed matrix

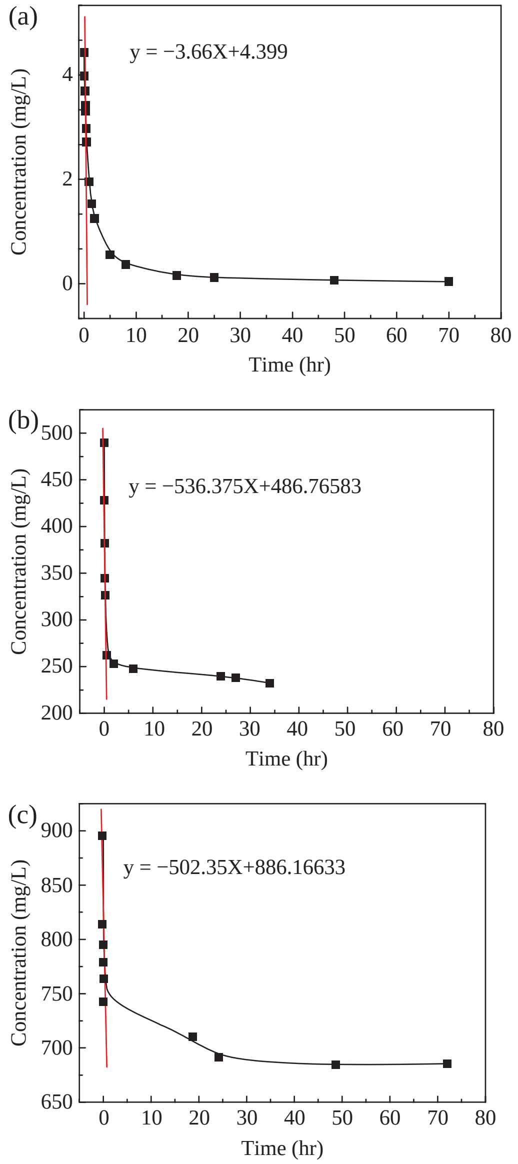

Fig. 5. Adsorption kinetics for the mixed matrix scaffolds at 25? and adsorbent loading of 0.06 g/100 mL. Removal of Cu^{2+} vs time for (a) Co = 5 mg Cu^{2+}/L; (b) Co = 500 mg Cu^{2+}/L; and (c) Co = 1,000 mg Cu^{2+}/L.

scaffolds at 25°C are presented in Fig. 6. Isotherms exhibit final plateau shape. Isotherms data over the concentration range of 5–1,500 mg Cu^{2+}/L were fitted to the Freundlich and the Langmuir isotherms, given by the following equations:

$$q_e = kC_e^{1/n} \tag{5}$$

where parameters K and $1/n$, adjustable parameters, indicate measures of the adsorption capacity (mg/g) and adsorption intensity, respectively. The bonding energy decreases with the increase of surface concentration as the value of n is bigger than 1. Values of K and $1/n$ can be derived from the slope $1/n$ and intercept log K by log–log plots of q_e vs C_e.

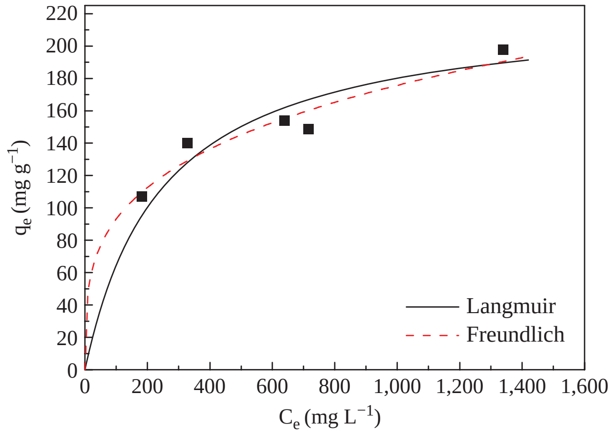

Fig. 6. Adsorption isotherms for Cu^{2+} on the mixed matrix scaffolds at 25? and adsorption models predictions.

$$(C_e/q_e) = (C_e/q_{max}) + (1/q_{mac}b) \tag{6}$$

where q_{max} is the maximum adsorption at monolayer coverage (mg Cu^{2+}/g), b is the adsorption equilibrium constant (L/mg) which is indicating of the energy of adsorption. Values of q_{max} and b can be evaluated from the linearized plot of C_e/q_e vs C_e. Values of K, n, q_{max}, and b are shown in Table 1. Isotherm data fitted the Freundlich isotherm and the Langmuir isotherm models reasonably well with r^2 values of 0.96 or above. Thus, Langmuir or Freundlich models can be applied to these adsorption data.

Considering the controlling mechanisms of copper ions onto chitosan mixed matrix scaffolds, first order, second order and intra-particle diffusion equation models were used to correlate the experimental adsorption kinetic data. The slope of log plot of (q_e–q_t) against t data was evaluated to determine the first

Table 1
Freundlich and Langmuir isotherms constants for Cu^{2+} onto mixed matrix scaffolds

Freundlich	
K (mg/g)	26.10
N	3.62
r^2	0.96
Langmuir	
q_{max}	224.72
B	0.004
r^2	0.98

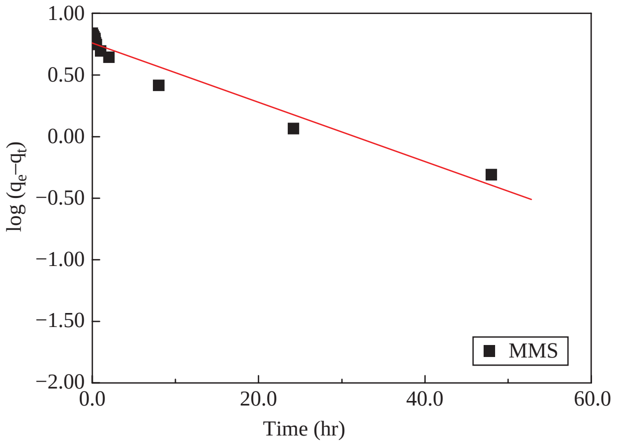

Fig. 7. The plots for first order model for mixed matrix scaffolds.

order rate constant, k_1. Similarly, the plots of t/q_e against t were processed to determine the rate parameter. Finally, the intra-particle diffusion rate was estimated by the slope of the plot of q_t against $t^{0.5}$ (Figs. 7–9).

The kinetic parameters of first order, second order and intra-particle diffusion equation models for copper ions onto mixed matrix scaffolds were listed in Table 2.

Results showed that the adsorption of copper ions onto chitosan mixed matrix scaffolds, correlated well ($R > 0.99$)with the second order kinetic model as compared to the first order kinetic model and the intra-particle diffusion rate model. It may suggest that the rate limiting step was chemical adsorption. Similar results had been observed by Wu et al., Sağ and Aktay, and Wan Ngah et al. [13–15].

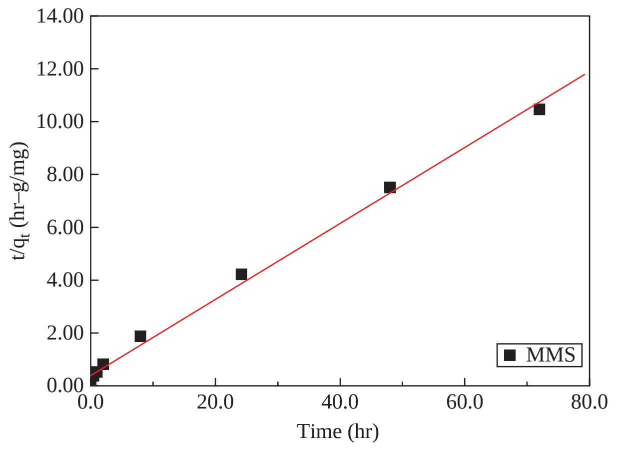

Fig. 8. The plots for second order model for chitosan adsorbents.

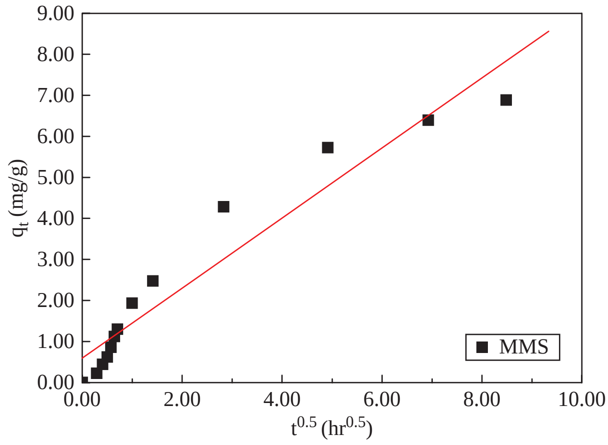

Fig. 9. The plots for intra-particle diffusion model for mixed matrix scaffolds.

4. Conclusions

In this study, novel mixed matrix scaffolds selective for heavy metals using the expensive polysaccharide biopolymer chitosan and ion exchanger resin particles has been easily fabricated. To overcome the limitation of the low internal surface area of flaked or powdered chitosan, a chitosan solution containing uniform distributed ion exchanger ion particles was used to develop porous chitosan mixed matrix scaffolds along freeze-gelation techniques. The mixed matrix scaffolds we have prepared have internal surface area exceeding 80 m^2/g. The kinetic adsorption data showed that hydronium ions competed with copper ions for available amine sites of chitosan as well as sulfonic sites of ion exchanger resin. The behavior of the adsorption isotherms suggest that mixed matrix scaffolds can be utilized over a broad initial copper ion concentration range.

In future work with the metal ion adsorption experiments will address on other toxic metal cations such as Ni^{2+} and Cr^{3+}. Additionally, the rates of metal ion desorption will be evaluated as a function of dilute

Table 2
Kinetic parameters of Cu^{2+} adsorption onto mixed matrix scaffolds

	Mixed matrix scaffolds
First order	
K_i	0.0553
R^2	0.9541
Second order	
K_i	0.0484
R^2	0.9970
Intra-particle	
K_i	0.8538
R^2	0.9278

acid regeneration solution pH and the concentration of metal initially loaded on the mixed matrix scaffolds.

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