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

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ABSTRACT

Mixed matrix scaffolds were composed through uniform distributed of ion exchange resins (H^+ form Amberjet, ID 780 μm) into the stereo-structural chitosan matrix prepared by dissolving chitosan powder with a middle molecular weight into acetic solutions. Along the synthesis processes of mixed matrix scaffolds, 4 wt% of chitosan solutions containing of resin particles were homogeneous crosslinked with aqueous polyvinyl alcohol (PVA) solutions to produce PVA crosslink mixed matrix scaffolds. Specifically, ion exchange resin particles suspending in a viscous PVA crosslink chitosan solution were poured into cylindrical aluminum containers to prepare PVA crosslink chitosan mixed matrix scaffolds through the freeze-gelation process. PVA crosslink mixed matrix scaffolds were then utilized for removal of copper ions from waste water. The uniform distribution of ion exchange resins embedded in the stereo structure of chitosan matrices can clearly be observed on the images of the scanning electron micrograph (SEM). The adsorption processes were operated by adsorbing copper ions of waste water onto the amine functional groups ($-NH_2$) exposed on the external and porous stereo-structural surfaces of chitosan matrices as well as the sulfonate functional groups at the outer surface of ion exchange resins respectively. Adsorption experiment were carried out at 25°C and pH 6.0 over the concentration ranging from 200 to 3000 mg Cu^{2+}/l. The maximum adsorption capacity for PVA crosslink mixed matrix scaffolds were 93.5 mg Cu^{2+}/g-adsorbents at the initial copper ion concentration of 2500 mg Cu^{2+}/l. The adsorption isotherm curve could be simulated by Langmuir adsorption model. The desorption ratio of copper ions of PVA crosslink chitosan mixed matrix scaffolds was 97.9% at a low initial copper ion concentration of 200 mg Cu^{2+}/l. As the initial copper ion concentrations increased, desorption ratio decreased.

Keywords: Chitosan; Mixed matrix scaffold; Adsorbent

1. Introduction

Treatment of heavy metals in the environment becomes a great concern because of 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]. Adsorption is the most promising and attractive method for heavy metal ion separations from aqueous process waste water. Of particular interest is chitosan, a linear polysaccharide of β-1,4-O-glycosyl-linked glucosamine residues. The adsorption of heavy metal ions from waste water onto chitosan has been documented [2–4]. Rorrer and Hsien [5,6] attempted to summarize previous studies on adsorption isotherm and adsorption kinetic measurements for chitosan and crosslink chitosan beads.

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Mixed matrix membranes (MMMs) preparation by blending various ion exchanger particles together within an ethylene vinyl alcohol (EVAL) copolymer porous polymeric matrix were initially proposed by Avramescu et al. and Borneman et al. [7,8]. Mixed matrix membranes are known as potential adsorbents for pervaporation, gas separation, enzyme capture, and protein recovery [7–10]. However, adsorption of heavy metal ions onto porous mixed matrix membranes or scaffolds has not well characterized on previous works.

Schellekens and Bastiaansen investigated the soild-state drawing behavior and properties of solution-spun polyvinylalcohol fibers [11]. Wan Ngah et al. [12] showed the performance of chitosan and crosslink (GLA,ECH, and EGDE) chitosan beads for the removal of copper ions from aqueous solution. Li and Renbi [13] proposed mechanisms for the adsorption of lead ions onto chitosan/PVA hydrogel beads. Chemical crosslinking of the linear chitisan chains on mixed matrix scaffolds could render chitosan insoluble in acid solutions and also improve the mechanical strength of the scaffolds so that the PVA crosslink chitosan mixed matrix scaffolds is suitable for use in the following desorption process after adsorption of saturated copper ions. However, there are only few literature studies on the adsorption of copper ions onto PVA crosslink chitosan mixed matrix scaffolds with respect to large range of initial copper ion concentrations.

The purpose of this work was to synthesize novel PVA crosslink chitosan mixed matrix scaffolds, and then investigate how these scaffolds adsorb various initial copper ions concentrations from aqueous solution at pH 4–6. This study will present the advantages of the feasible geometric formation of chitosan mixed matrix scaffolds as well as the high adsorption loadings of copper ions onto PVA crosslink chitosan mixed matrix scaffolds. Specifically, ion exchanger resin particles (H^+ form Amberjet, Rohm & Haas) were intermixed with a PVA crosslink chitosan solution and then formed porous mixed matrix scaffolds by a freeze-gelation technique. The adsorption of copper ions (Cu^{2+}) onto the mixed matrix scaffolds was evaluated by well-mixed batch adsorption experiment. Adsorption isotherms and kinetics data for PVA crosslink chitosan mixed matrix scaffolds were generated over a broad range of copper ions initial concentrations ranging from 200–3000 mg Cu^{2+}/l at pH 4–6. Results of adsorption experiment of copper ions onto chitosan as well as PVA crosslink chitosan mixed matrix scaffolds were corresponding with formation of orderly stereo-geometric structure along the PVA crosslink process. Desorption was processed by adding a 10^{-2} M EDTA regenerate solution to saturated adsorbed mixed matrix scaffolds over various initial copper ions concentration solutions ranging from 200–3000 mg Cu^{2+}/l at pH 4.6.

2. Materials

2.1. Chemicals

Chitosan flake with 80% deacetylation (Sigma) were grinded into powdered form and sieved to a size less than 300 μm. The average molecular weight of the chitosan was 170000. All reagents for mixed matrix scaffolds synthesis and displacing the remaining water including acetic acid and ethyl alcohol were 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 PVA crosslink mixed matrix scaffolds

A 50 ml of chitosan solution was prepared to 4 wt% concentration by dissolving chitosan powder and same amount of Amberjet particles (ion exchanger resin particles, ~0.3 g, ID: 780 μm) into 0.68 M acetic acid solution. PVA in an amount of 3.0 g was dissolved in 50 mL of deionized water in a beaker and mixed on an orbital shaker at 500 rpm for 12 hours at 25°C. The two solutions were homogeneously blended together and agitated at 200 rpm for 4 h at 25°C.

Fabrication of PVA crosslink chitosan mixed matrix scaffolds including three steps: PVA crosslink chitosan solution preparation, freezing of scaffolds, and gelation of scaffolds followed the similar processes in our previous study for the preparation of chitosan mixed matrix scaffolds [14]. After formation, PVA crosslink chitosan mixed matrix scaffolds were stored in deionized water solutions at room temperature for following adsorption and desorption processes.

2.3. Characterization of crosslink mixed matrix scaffolds

After supercritical drying, the internal surface area of PVA crosslink chitosan mixed matrix scaffolds was determined by the BET method by using N_2 as the adsorbate. The wet PVA crosslink chitosan scaffolds were pretreated by the supercritical fluid (CO_2) drying method (0–33°C, 800–1300 psi) for 1.5 h in order to completely removal of residual water/ethanol solutions in the samples. The diameter of ion exchanger particles incorporated in PVA crosslink scaffolds were measured by a Light Scatter caliper (Coulter, LS230). Microstructures of PVA crosslink scaffolds were characterized using scanning electron microscopy (SEM).

2.4. Batch adsorption measurements

The copper solutions were prepared by dissolving copper nitrate ($Cu(NO_3)_2 \cdot 2.5H_2O$) in deionized distilled water. The initial copper ion (Cu^{2+}) concentration ranged from 200–3000 mg Cu^{2+}/l. Measurements of copper adsorption isotherms were conducted in a well–mixed batch process which was allowed to reach equilibrium.

The parameters for the adsorption isotherm measurement are listed in Table 1. Specifically, 1.5 g of wet PVA crosslink mixed matrix scaffolds were placed in 100 ml of copper nitrate solution within a 250 ml Erlenmeyer flak at 25°C and 100 rpm for 10–80 h. An adsorption experiment was continued until the Cu^{2+} concentration was reaching equilibrium. A 0.5 ml of copper ion solutions were periodically withdrew along the adsorption process. Measurement of Cu^{2+} was performed by using atom absorption spectrophotometer (AAS).

2.5. Batch adsorption/desorption measurements

In the adsorption/desorption experiment, the adsorbed copper ions onto PVA crosslink scaffolds were released back to the deionized distilled water by the addition of a 10^{-2} M EDTA solution at pH 4.66. Batch adsorption/desorption experiments were conducted at 25°C in a well-mixed flask. Prior to desorption, the adsorption process was carried out. Specifically, 1.5 g of wet PVA crosslink mixed matrix scaffolds were placed in a 100 ml of copper nitrate solution within a 250 ml Erlenmeyer flak at 25°C and 100 rpm for 40–80 h to ensure that adsorption equilibrium was achieved. After adsorption process, a 10^{-2} M EDTA solution was added to the vessel to load the bulk solution to process complete desorption. The desorption ratio was determined by

$$D = Q_d / Q_a \tag{1}$$

where D is the desorption ratio of Cu^{+2} (%), Q_d is the amount of Cu^{+2} after adsorption process (mg Cu^{+2}); Q_a is the amount of Cu^{+2} after desorption process (mg Cu^{+2}).

3. Result and discussions

3.1. Preparation and properties of PVA crosslink mixed matrix scaffolds

The PVA crosslink chitosan mixed matrix scaffolds were prepared by a freeze-gelation technique following the procedures shown in Fig. 1. The purpose of chemical modifications by blending PVA solutions into chitosan solutions was to improve the mechanical strength of mixed matrix scaffolds through the reforming the stereo structure between the hydroxyl functional groups of chitosan as well as the functional groups of PVA, and then evaluate how these chemical modifications affect the adsorption and desorption capacities along the adsorption and desorption processes. Similar procedures of chemical modifications were presented by Wan Ngah et al. [15] and confirmed by the examination of FTIR spectrometer.

Table 1
Parameters for adsorption isotherm measurement

Process condition	Variable and units
Contact time	10–80 h
Temperature	25°C
pH	4–6
Wet scaffolds loading	1.5 g/l
Solution volume	100 ml in 250 ml flask
Agitation	100 rpm in orbital shaker
Initial concentration	200 to 3000 mg Cu^{2+}/l

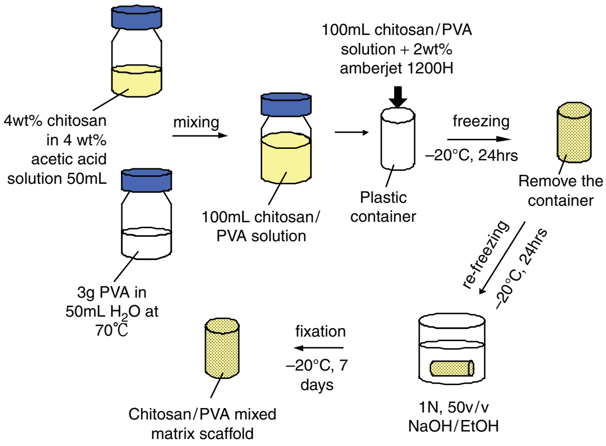
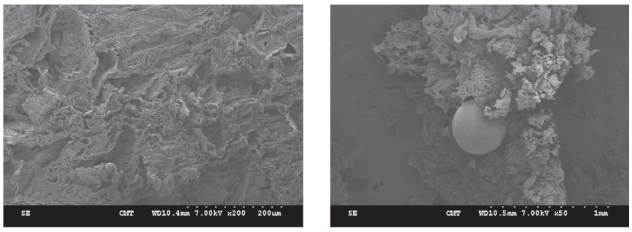


Fig. 1. Flowchart for synthesis of PVA crosslink chitosan mixed matrix scaffolds.

After supercritical fluid drying, the crosslink scaffolds were extensively characterized to determine BET surface area and porous structure by SEM images. Supercritical fluid (CO_2) drying preserved the porous structure of PVA crosslink chitosan mixed matrix scaffolds because the water in the scaffolds was quickly switched by high pressurized supercritical fluid of CO_2 without impairing porous stereo structure of scaffolds.

The internal surface area of 80 m^2/g for mixed matrix scaffolds has been presented in our previous work [14]. After crosslinking, the BET surface area of PVA crosslink chitosan mixed matrix scaffolds determined by BET method was dropped to be 7.85 m^2/g. The dense structure of the surface for PVA crosslink chitosan mixed matrix scaffolds can clearly be seen in the images of the scanning electron micrographs (Fig. 2a). Porous crosssectional matrix possessed open and interconnected porous structure from the morphologies of SEM images at 50X and 1000X (Fig. 2b). Differences in the BET surface area between the chitosan mixed matrix scaffolds and PVA crosslink scaffolds may tentatively attributed by rearranging the geometry of PVA and linear polysaccharide of β-1,4-O-glycosyl-linked glucosamine residues of chitosan after chemical modification of chitosan.

(a) Surface (X100) (a) Surface (X150)



(b) Cross-section (X50) (b) Cross-section (X1K)

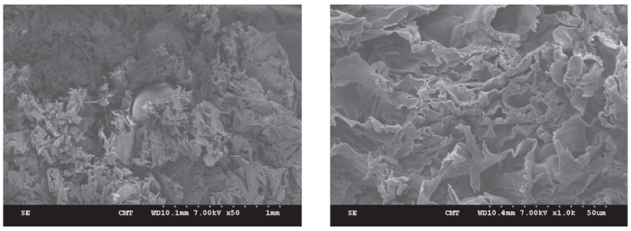


Fig. 2. SEM photomicrographs of the PVA crosslink chitosan mixed matrix scaffolds.

3.2. *Adsorption of copper ions on PVA crosslink mixed matrix scaffolds*

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

$$Q = \left(C_o - C_f \right) V / m_a \tag{2}$$

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 PVA crosslink 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 in the flask was 100 ml and the mass of dried mixed matrix scaffolds was 300 mg. The ratio of scaffolds in the contactor was fixed at 3 g of PVA crosslink scaffolds/l of solution. The initial concentration of Cu^{2+} (in copper nitrate solution) was varied from 200 mg Cu^{2+}/l to 3000 mg Cu^{2+}/l.

3.3. *Adsorption kinetic*

The Cu^{2+} concentration versus time profiles for the PVA crosslink chitosan mixed matrix scaffolds are compared with different initial copper ions concentrations ranging from 200 to 3000 mg/l, as shown in Fig. 3. PVA crosslink chitosan mixed matrix scaffolds at an initial concentration of 3000 mg of Cu^{2+}/l had both a faster initial adsorption rate and a larger equilibrium adsorption capacity than did at lower initial concentrations. During the well–mixed batch adsorption experiment, the pH value of the cooper solution contacting the PVA crosslink chitosan mixed matrix scaffolds rose initially and then leveled off to 6.0–61. The same pH tendencies were observed as the increase of the initial Cu^{2+} concentrations. Along the adsorption processes, hydronium ions competed with copper ions for available amine adsorption sites of chitosan and sulfonic adsorption sites of ion exchanger resins in the PVA crosslink chitosan mixed matrix scaffolds.

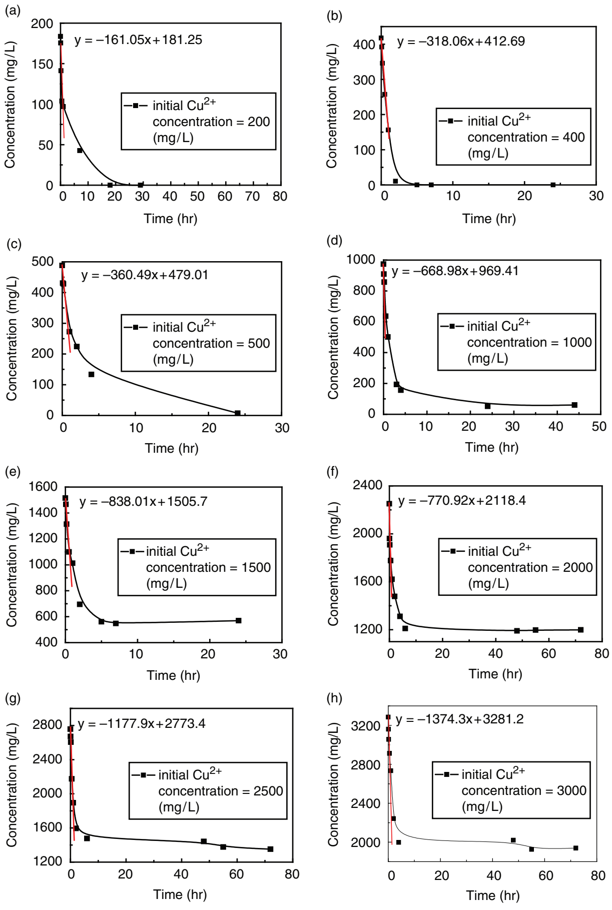


Fig. 3. Adsorption kinetics for PVA crosslink chitosan mixed matrix scaffolds at different initial copper ion concentrations, 25°C, and final pH 6.1. Batch removal of Cu^{2+} vs. time for (a) Co = 200 mg of Cu^{2+}/l; (b) Co= 400 mg of Cu^{2+}/l;. (c) Co = 500 mg of Cu^{2+}/l; (d) Co = 1000 mg of Cu^{2+}/l; (e) Co = 1500 mg of Cu^{2+}/l; (f) Co= 2000 mg of Cu^{2+}/l; (g) Co = 2500 mg of Cu^{2+}/l; (h) Co = 3000 mg of Cu^{2+}/l.

In order to evaluate the effect of PVA crosslinking on the copper ion adsorption capacities of different adsorbents, adsorption experiment were carried out by adding same amount of chitosan mixed matrix scaffolds and PVA crosslink chitosan scaffolds to copper ion solutions with the same initial concentration of 1000 mg Cu^{2+}/l through the adsorption processes at 25°C. Results showed that PVA crosslink chitosan scaffolds performed a faster trend to reach an equilibrium concentration from 1000 to 200 mg Cu^{2+}/l after 4 h of adsorption experiment (Fig. 4) than did of chitosan mixed matrix scaffolds. PVA crosslinking may rearrange the stereo-geometric structure between PVA as well as the hydroxyl functional groups of chitosan in order to enhance higher probability of chelate reactions for cooper ions onto the amine functional groups ($-NH_2$) exposure on the external and porous stereo-structural surfaces of PVA crosslink chitosan matrix as well as the sulfonate functional groups on the outer surface of ion exchange resins, respectively. Thus, PVA crosslink process not only increases the chemical stability of adsorbents but also retains the copper ions adsorption capacity of the PVA crosslink chitosan mixed matrix scaffolds. In previous work, Wan Ngah et al. [15] also obtained a similar result for copper ions adsorption onto chitosan and chtiosan/PVA beads, which provided further support for the recombination of geometric formation between functional groups of PVA and chitosan along crosslinking.

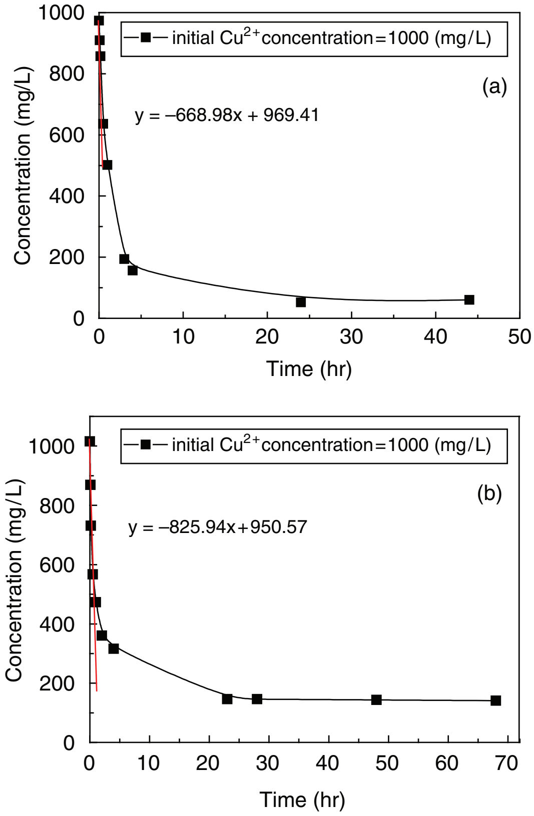


Fig. 4. Adsorption kinetics comparison for different adsorbents, (a) chitosan and (b) PVA crosslink chitosan mixed matrix scaffolds, at 25°C and the same initial copper ion concentration of 1000 mg/l.

3.4. Adsorption isotherms

Copper ion adsorption data over the different initial concentrations range of 200–3000 mg/l for PVA crosslink chitosan mixed matrix scaffolds were listed on Table 2. Adsorption isotherms performing a final plateau shape at 25°C are presented in Fig. 5. Freundlich or Langmuir adsorption models were used to predict the behavior of adsorption isotherms for the PVA crosslink chitosan mixed matrix scaffolds Isotherms data over the concentration range of 5–2000 mg Cu^{2+}/l were fitted to the Freundlich and the Langmuir isotherms, given by equations 3 and 4.

$$q_e = kC_e^{1/n} \tag{3}$$

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

Table 2
Copper ions adsorption for the PVA crosslink chitosan mixed matrix scaffolds at different copper ions initial concentrations and 25°C

Initial C_o (mg Cu^{2+}/l)	Equilibrium C_e (mg Cu^{2+}/l)	Loading q_e (mg Cu^{2+}/g)
200	0	11.92
400	0	26.96
500	7.4	29.31
800	0	52.89
1000	60.3	56.84
1500	569.43	64.16
2000	1197.97	70.34
2500	1351.35	93.46
3000	1939.19	89.39
3500	2253.15	79.89

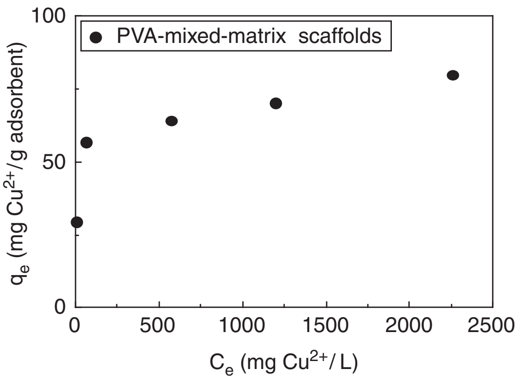


Fig. 5. Adsorption isotherms for PVA crosslink chitosan mixed matrix scaffolds at 25°C.

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 versus C_e.

$$(C_e/q_e) = (C_e/q_{\max}) + (1/q_{\max}b) \tag{4}$$

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 versus C_e. Values of *K*, *n*, $q_{\max}$, and *b* are shown on Table 3. Isotherm data fitted the Langmuir isotherm models reasonably well with r^2 values of 0.99. Thus, Langmuir model can be applied to these adsorption data. Analysis suggests that PVA crosslink process may not decrease the adsorption capacity as well as binding strength while promoting monolayer coverage of the adsorbed copper ions on the exposed surfaces of the PVA crosslink chitosan mixed matrix scaffolds.

3.5. Adsorption/desorption kinetic experiment

The Cu^{2+} concentration versus time profiles for the PVA crosslink chitosan mixed matrix scaffolds are compared with different initial copper ions concentrations ranging from 200–2000 mg/l, as shown in Fig. 6. PVA crosslink chitosan mixed matrix scaffolds at an initial concentration of 2000 mg of Cu^{2+}/l had the sharpest initial desorption rate than did at lower initial concentrations. This result showed that a higher adsorption capacity for PVA crosslink chitosan mixed matrix scaffolds at an initial concentration of 2000 mg Cu^{2+}/l indicated more copper ions were adsorbed onto adsorbents. While desorption process, more adsorbed copper ions generated a higher mass transfer momentum to release adsorbed Cu^{2+} back to deionized distilled water due to the metal ions concentration difference between adsorbents and bulk solutions. However, the

Table 3
Freundlich and Langmuir isotherms constants for Cu^{2+} onto PVA crosslink mixed matrix scaffolds

Langmuir		
$q_{\max}$ (mg/g^{-1})	K (ml/mg^{-1})	R^2
80	0.015	0.99
Freundlich		
K_f (mg/g^{-1})	*n*	R^2
24.187	6.0	0.90

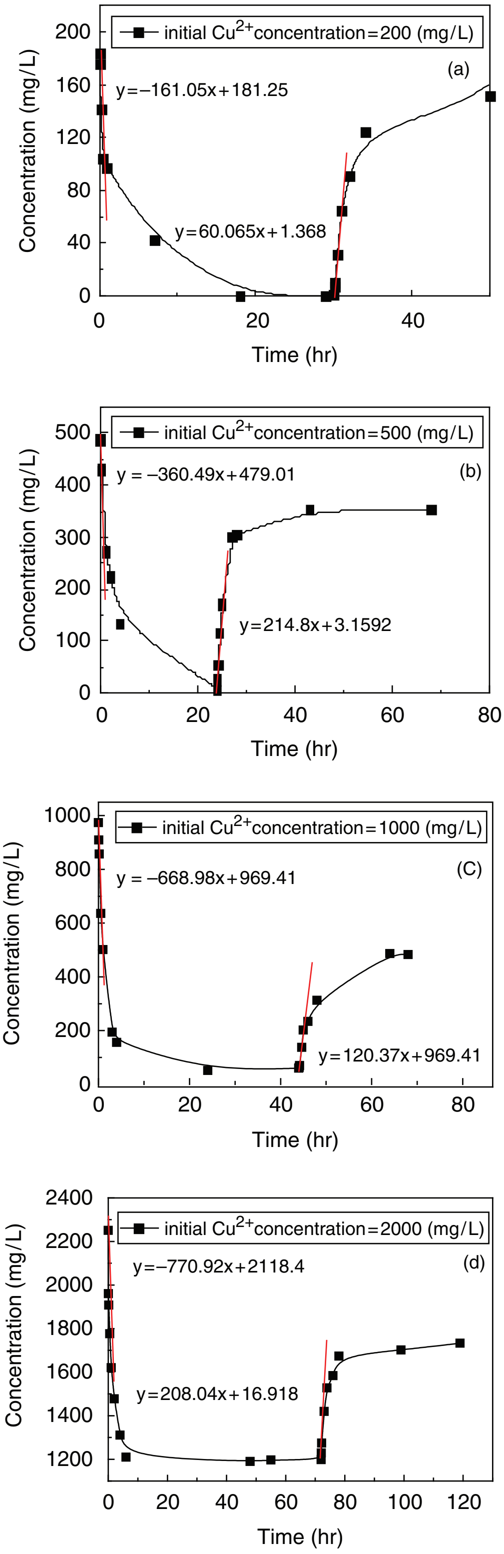


Fig. 6. Adsorption and desorption kinetics for thePVA crosslink chitosan mixed matrix scaffolds at 25°C and different initial copper ion concentrations (a) 200 mg Cu^{2+}/l (b) 500 mg Cu^{2+}/l (c) 1000 mg Cu^{2+}/l (d) 2000 mg Cu^{2+}/l.

desorption ratio of copper ions of PVA crosslink chitosan mixed matrix scaffolds was 97.9% at a lower initial copper ion concentration of 200 mg Cu^{2+}/l. As the initial copper ion concentrations increased, desorption ratio decreased.

4. Conclusions

In this study, novel PVA crosslink chitosan 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 chemical stability of the adsorbents, PVA homogeneous crosslinking was used to increase the mechanical strength of porous chitosan mixed matrix scaffolds. 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 PVA crosslink chitosan mixed matrix scaffolds can be utilized over a broad initial copper ion concentration range. Desorption kinetic study suggested that adsorbents containing adsorbed copper ions could be completely regenerated by addition of EDTA solution. In future work with the metal ion adsorption experiments will address on other toxic metal ions such as Ni^{2+} and Cr^{3+}.

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