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Desorption of Cadmium from Porous Chitosan Beads

Tzu-Yang Hsien and Yu-Ling Liu

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1. Introduction

Cadmium pollution of the environment has become a serious problem due to the increasing consumption of cadmium by industry in the past 20 years. Cadmium is introduced into the environment from the effluence of electroplating industry, and in solid and aqueous discharges from mining operations. Increased environmental awareness has resulted in the promulgation of more stringent legislation in several countries for water quality. For example, in Italy and the United States, the maximum permitted concentrations of heavy metals such as cadmium, lead, chromium, and nickel ions are 5, 50, 50, and 50 $\mu\text{g/l}$ respectively [1,2]. In order to increase the concentration of exposed active sites within chitosan so that the adsorption capacity and transport rate of metal ions into the particle can be enhanced, porous chitosan beads need to be developed. Rorrer, Way, and Hsien [3] described the synthesis of 1 mm and 3 mm porous, magnetic, chitosan beads for cadmium ion separation from aqueous solutions. Complete adsorption isotherms over a large range of cadmium ion concentrations (2-1700 ppm) onto the chitosan beads were obtained. Chitosan is a cationic polymer which can displace adsorbed metal ions by hydrogen ions in a low pH environment. Muzzarelli et al. [4] pointed that a packed column of mercury-adsorbed chitosan could be regenerated by flushing the bed with a 10 mM potassium iodide solution or other eluting agents. Randall et al. [5] regenerated chitosan powder in a packed column by flushing the bed with a 0.2 N NH_4Cl solution. Nickel removal efficiencies were as high as 97 %. The pH effect on the desorption process for regeneration of cadmium-adsorbed chitosan powder was first considered by Jha et al. [6]. An economic comparison of two different processes to recycle chitosan after the adsorption process was provided by Coughlin et al. [7]. Thus, it is valuable to define the optimum regeneration parameters for chitosan beads. The recycle efficiency of the cadmium-adsorbed chitosan beads will also be considered by this study.

The hydrogen ion consumption and optimum pH range for the regeneration of chitosan beads after cadmium adsorption will be studied. Specifically, the desorption process after cadmium

adsorption will be carried out in a spinning-basket reactor with online pH measurement to determine the effect of pH and H^+ consumption on cadmium desorption and bead regeneration efficiency. The objective of this study is to determine the feasible pH range and H^+ consumption for regeneration of cadmium adsorbed chitosan beads. The pH affects cadmium adsorption and desorption on the chitosan beads. In this present study, the adsorption and desorption kinetics for single stage adsorption desorption experiments are determined in a spinning basket reactor. The hydrogen ion capacity of the chitosan beads and the pH of the cadmium solution in the vessel are also measured as a function of time. Finally, an equilibrium model for desorption process is presented in order to describe the competitive relationships associated with displacing adsorbed cadmium ions with hydrogen ions.

2. Materials and Methods

2.1. Chitosan Beads Synthesis

The synthesis of chitosan beads, including chitosan solution preparation, gel beads casting, crosslinking and freeze drying was described in previous studies [3,8]. Specifically, a 5 wt % chitosan solution was casted in the precipitation bath to form chitosan gel beads and then crosslinked with a 2.5 wt % aqueous glutaric dialdehyde. The wet crosslinked chitosan beads were freeze-dried to remove the remaining humidity. The chitosan beads crosslinked with a 2.5 wt % initial glutaric dialdehyde solution were used in this study.

2.2. Single Stage Desorption

Two types of desorption experiments, single stage and multiple stage, were performed. In the single stage experiment, the adsorbed cadmium ions on chitosan beads were released back to the bulk solution by the single addition of a large amount of H^+ . Batch adsorption/desorption experiments were conducted at 25 °C in a spinning-basket reactor (Figure 1), inspired by a basket reactor from Carberry [9]. Prior to desorption, the adsorption process was carried out. Specifically, 0.5 g of chitosan beads were packed into the hollow impeller basket assembly and contacted with 200 mL of 200 mg /L cadmium ion solution at 150 rpm and 25°C for at least 48 hours to ensure that adsorption equilibrium was achieved. After adsorption, 65 mL of 0.1 N HNO_3 solution was added to the vessel to load the bulk solution with the H^+ ions needed to affect the complete desorption and to reach a final pH value of 2.0. The adsorption/desorption parameters for spinning basket reactor experiments are summarized in Table 1.

The high concentration of hydrogen ions loaded to the vessel displaced the adsorbed cadmium ions. The kinetics of cadmium release and H^+ adsorption were followed by measuring the cadmium ion concentration and pH of the bulk solution phase with time. The pH was monitored continuously, whereas 0.5 mL samples were periodically removed from the reactor and analyzed for Cd^{+2} concentration by ion chromatography (IC).

Process Condition	Variable and Units
Temperature	25 °C
Bead loading (m_b)	0.5 g
Initial solution volume (V)	200 mL
Initial Cd^{+2} concentration (C_o)	200 mg Cd/L
Acid (HNO_3) concentration (C_a)	0.0001 - 0.1 N
Agitation	150 rpm

Table 1. Table 1. The adsorption/desorption parameters for spinning basket reactor experiments

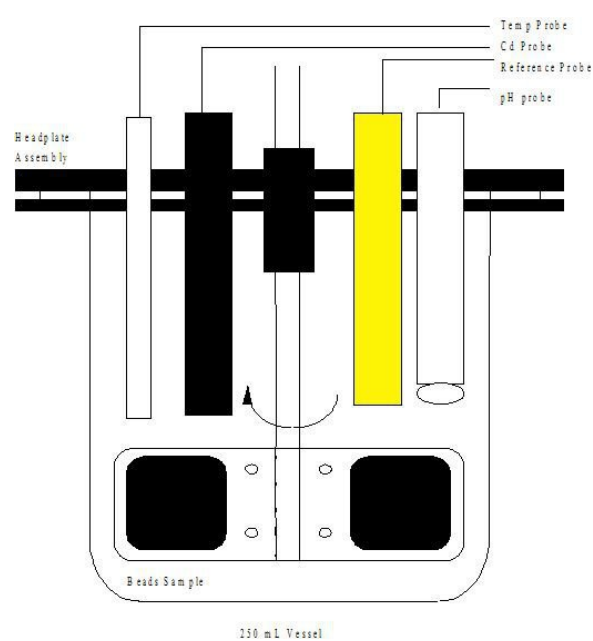


Figure 1. Spinning basket reactor

Two control experiments were performed. In the first control experiment, the pH curve for the chitosan beads was measured to determine the extent of H^+ consumed by adsorption for the case where no cadmium ions were present in the system. Specifically, 0.5 g of chitosan beads were packed in the hollow propeller cells of the spinning-basket reactor and immersed in 200 mL of deionized distilled water for 48 hours. The pH at the start of the experiment was about 7.0. The mixing speed was 150 rpm. Then, 65 mL of 0.1 N HNO_3 solution was added to the vessel and the pH was measured continuously until an equilibrium pH value was reached. During this time, the pH of the bulk solution increased as hydrogen ions adsorbed onto weakly basic $-NH_2$ sites on chitosan.

In the second control experiment, the stability of chelated cadmium ions adsorbed on chitosan beads was tested. Specifically, the cadmium adsorbed chitosan beads were immersed in 200 mL distilled water within the reactor at 25 °C and mixed at 150 rpm. Samples were re-

moved from bulk solution at 123 and 171 hours and analyzed for cadmium ion concentration by ion chromatography (IC).

Shake flask experiments were carried out to determine the equilibrium hydrogen and cadmium loading on the chitosan beads at different pH levels. Specifically, 0.1 g of chitosan beads were mixed with 40 mL of 200 mg /L cadmium ion solution in a 125 mL Erlenmeyer flask and agitated at 120 rpm and 25 °C for 51 hours to ensure that adsorption equilibrium was reached. After adsorption, different doses (1 to 4 mL) of HNO₃ solution (10⁻⁴ to 1 N) was added to the flask to process the desorption for another 140 hours. The adsorption/desorption parameters for shake flask experiments are summarized in Table 2.

Process Condition	Variable and Units
Temperature	25 °C
Bead loading (m _b)	0.1 g
Initial solution volume (V)	40 mL
Initial Cd ⁺² concentration (C _o)	200 mg Cd/L
Acid (HNO ₃) concentration (C _a)	0.0001 - 0.1 N
Agitation	120 rpm

Table 2. Table 2. The adsorption/desorption parameters for shake flask experiments

2.3. Multiple Stage Desorption

In the multiple stage experiment, adsorbed cadmium was gradually displaced by the series addition of small doses of H⁺. A discrete volume of 0.1 N HNO₃ was added to the vessel. If the equilibrium pH was above 2.0, then additional 0.1 N HNO₃ was added. The experiment was completed when an equilibrium pH of 2.0 was achieved.

A modified titration procedure suggested by previous works for studying ion exchange or adsorption characteristics was modified in the present study to determine hydrogen ion adsorption on chitosan beads. Specifically, a 0.5 g of chitosan beads were packed into the hollow propeller cells of the spinning-basket reactor and immersed in 200 mL of deionized distilled water at 150 rpm for 48 hours. After the chitosan beads were saturated with water, a discrete volume of 0.1 N HNO₃ was added to the vessel to initiate hydrogen ion adsorption on chitosan beads. Until an equilibrium pH value was reached, a different amount of 0.1 N HNO₃ solution was sequentially added to the vessel.

2.4. pH and Cadmium Ion Concentration Measurements

The pH measurements were performed with an Orion model 91-02 combination pH electrode and Orion model 720A ion selective electrode (ISE) meter. The pH readings were recorded by a computer every ten minutes during the experiment. The pH saturation curve was expressed as the amount of hydrogen ion sorbed per gram of chitosan beads versus the

equilibrium pH of the bulk solution. The cadmium ion concentration was measured by IC analysis as described earlier.

The cadmium adsorption capacity is calculated by

$$Q = \frac{(C_0 - C(t)) V}{m_b} \quad (1)$$

where $C(t)$ is the cadmium ion concentration in the vessel at different adsorption or desorption times (mg Cd/L), C_0 is the initial cadmium concentration in the vessel before adsorption (mg Cd/L), m_b is the mass (g) of chitosan beads in the spinning basket reactor impeller assembly, Q is the cadmium adsorption capacity on the chitosan beads (mg Cd/g-chitosan), and V is the current cadmium solution volume loaded in the spinning basket reactor vessel (L).

The percentage of cadmium desorbed from the beads is calculated by

$$D(\%) = \left(1 - \frac{C(t) - C_{\min}}{C_0 - C_{\min}}\right) \cdot 100 = \left(1 - \frac{Q(t)}{Q_f}\right) \cdot 100\% \quad (2)$$

or

$$D(\%) = \left(1 - \frac{C(t) - C_{\min,i}}{C_{0,i} - C_{\min,i}}\right) \cdot 100 = \left(1 - \frac{Q_i(t)}{Q_{i,f}}\right) \cdot 100\% \quad (3)$$

where $D(\%)$ is the percentage of cadmium desorbed at a given desorption time, C_{\min} is the lowest cadmium concentration along the adsorption or desorption process (mg Cd/L), $C_{0,i}$ is the initial cadmium concentration in the spinning basket reactor at specific desorption stage " i " (mg Cd/L), and $C_{\min,i}$ is the lowest cadmium concentration along the adsorption or desorption process at a specific desorption stage (mg Cd/L), Q_f is the final cadmium adsorption capacity on the chitosan beads (mg Cd²⁺/g chitosan).

The hydrogen ion adsorption capacity ($\Delta Q_i(H^+)$) on the chitosan beads was based on pH measurements of the bulk solution in the vessel. The hydrogen ion adsorption capacity at i th desorption stage $\Delta Q_i(H^+)$ is given by

$$\Delta Q_i(H^+) = \frac{C_a V_a - (10^{-pH_t} \cdot V_t)}{m_b} \quad (4)$$

where C_a is the concentration of HNO_3 (mole H^+ /L) added into the spinning basket reactor before desorption, pH_t is the pH value at different adsorption or desorption times, $\Delta Q_i(H^+)$ is the hydrogen ion adsorption capacity for chitosan beads at the i th desorption stage (mg H/g-chitosan), V_a is the acid volume (L) added into the spinning basket reactor, V_t is the volume (L) of solution in the spinning basket reactor at a given time.

The accumulated hydrogen ion adsorption capacity $Q(H^+)$ is given by

$$Q(H^+) = \sum_{i=1}^n \Delta Q_i \quad (5)$$

where n is the number of the desorption stage, $Q(H^+)$ is the accumulated hydrogen ion adsorption capacity in the present stage (mg Cd/g-chitosan).

3. Results and Discussion

3.1. Kinetics of Adsorption and Desorption

The cadmium ion concentration versus time profile in the spinning basket reactor is presented in Figure 2 (a) for a single stage adsorption/desorption experiment. The cadmium ion concentration decreased significantly from 200 to 183 mg Cd²⁺/L during the first four hours of adsorption and then slightly decreased to reach a final cadmium concentration of 179 mg Cd²⁺/L at 51 hours. The total solution volume was 196 mL. After adsorption, 65 mL of 0.1 N nitric acid was added to the vessel to initiate the desorption process. The cadmium concentration increased sharply during the first 12 hours of desorption following the addition of nitric acid, and then leveled off after 75 hours of desorption. The hydrogen ion capacity for the chitosan beads and the pH change in the cadmium solution are provided in Figure 2 (b) for both the adsorption and desorption processes. Similarly, the hydrogen ion capacity gradually increased and reached a final value between 8.6 and 9.5 mmole H⁺/g chitosan. The pH of the cadmium solution also decreased with the addition of nitric acid and then rose to a final value of 2.17.

Time (h)	Q (mg Cd/g)	pH	Cd ²⁺ concentration (mg Cd ²⁺ /L)
51	9.86	6.73	0.00
87	9.55	6.31	0.78
144	9.18	6.20	1.71

Table 3. Table 3. Stability of the adsorbed cadmium ion in distilled water at pH 6.0

The stability of the adsorbed cadmium ions in the chitosan beads was determined. Specifically, the cadmium-adsorbed chitosan beads were immersed in 200 mL of distilled water within the spinning basket reactor at 25 °C and mixed at 150 rpm for 93 hours. Only a trace amount of cadmium ions were released back into the water during the desorption (Table 3). From this control experiment, we conclude that the exchange

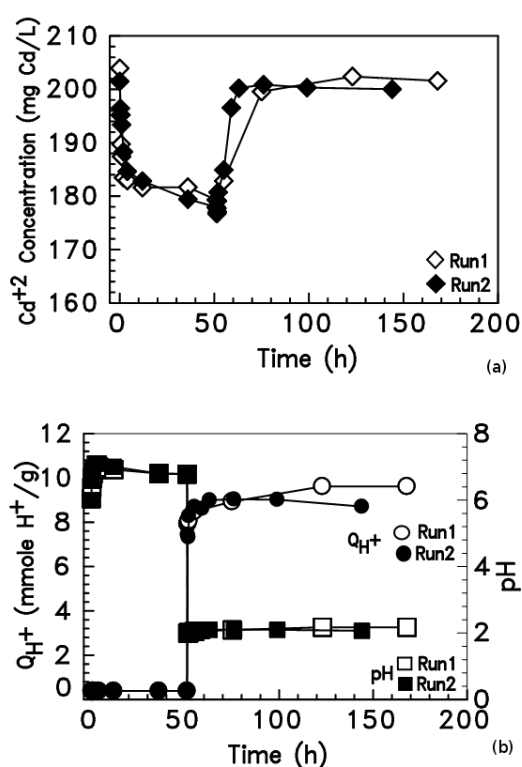


Figure 2. a) cadmium ion concentration versus time (b) hydrogen ion capacity and the pH change in the cadmium solution in the spinning basket reactor for a single stage adsorption/desorption experiment

between the adsorbed cadmium ions with the hydrogen ions on active sites ($-\text{NH}_2$ groups) of the chitosan beads during the desorption process requires hydrogen ions from the addition of the nitric acid.

In another control experiment using the spinning basket reactor, 65 mL of 0.1 N nitric acid were added to 0.5 g chitosan beads to determine the hydrogen ion capacity in cadmium-free water. Profiles for the hydrogen ion consumption and pH are presented in Figure 3. From Figure 3, 8.9 mmole H^+ per gram of chitosan and a final pH value of 2.06 were reached 140 hours after the addition of nitric acid. It is notable that the hydrogen ion consumption of 8.9 mmole H^+ /g chitosan is consistent with the hydrogen ion consumption data presented in Figure 2 (b).

3.2. Optimum pH and Hydrogen Ion Consumption

Hydrogen ions are needed to replace the cadmium ions adsorbed on the amine groups of the chitosan beads. Therefore, different amounts of hydrogen ion were added into the vessel to determine the effect of hydrogen ion consumption on the percentage of cadmium desorbed and the final pH value of the cadmium solution obtained in the single stage desorption process. The percentage of cadmium desorbed is presented in Figure 4 as a function of desorption time for different amounts of hydrogen ion initially charged to the vessel. Specifically, after cadmium adsorption, different amounts of 0.1 N nitric acid (22.2 mL, 50 mL and 65 mL respectively) were dosed into the reactor. At a final pH

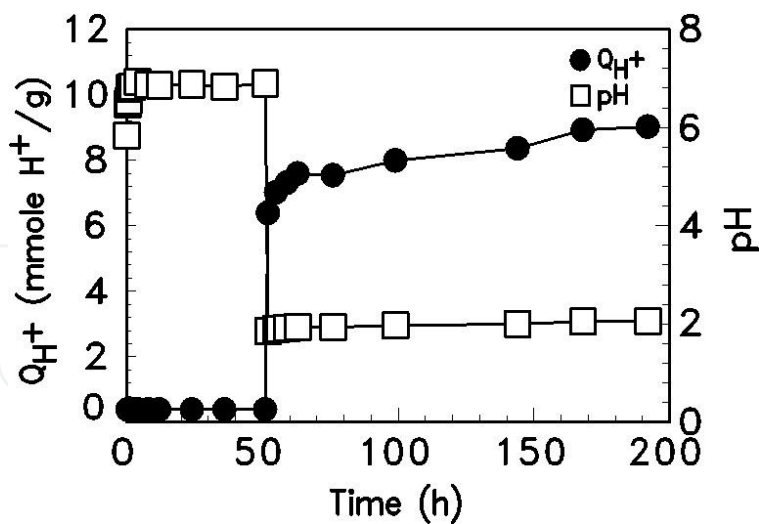


Figure 3. The hydrogen ion consumption and pH versus time for cadmium-free water saturation experiment

value of 2.0, 94 % of cadmium desorption was achieved and 8.3 mmole H^+ per gram of beads were consumed. It is interesting to note that even at a final pH of 4.7, 80 % of cadmium desorption was accomplished.

Stage	Time (h)	pH	D (%)
A-1	48	7.00	
D-1	67	6.80	7.01
D-2	78	6.64	27.42
D-3	90	5.80	39.75
D-4	101	5.48	39.33
D-5	119	4.36	84.66
D-6	141	3.00	95.72

Table 4. Table 4. The effect of pH adjustment on the % of cadmium desorbed (D) for the multiple stage desorption experiment

The multiple stage desorption experiment was carried out by a series addition of nitric acid solution into the spinning basket reactor. The effect of pH on the percentage of cadmium desorbed is given in Table 4. After 6 stages of desorption in series, 95.7 % of the cadmium desorption was achieved at a final pH of 3.0.

Even at an equilibrium pH of 4.36, 84.6 % of cadmium desorption was reached, consistent with the single stage desorption process Figure 4

Previous researchers used shake flask experiments to study the effect of pH on heavy metal ion adsorption capacity. Eric and Roux (1992) used the shake flask experiment to study the influence of pH on the heavy metal ion binding onto a fungus-derived bio-sorbent. Inoue et al. [10]

also used the shake flask experiment to evaluate the effect of the hydrochloric acid concentration on the adsorption of platinum group metal ions onto chemically modified chitosan.

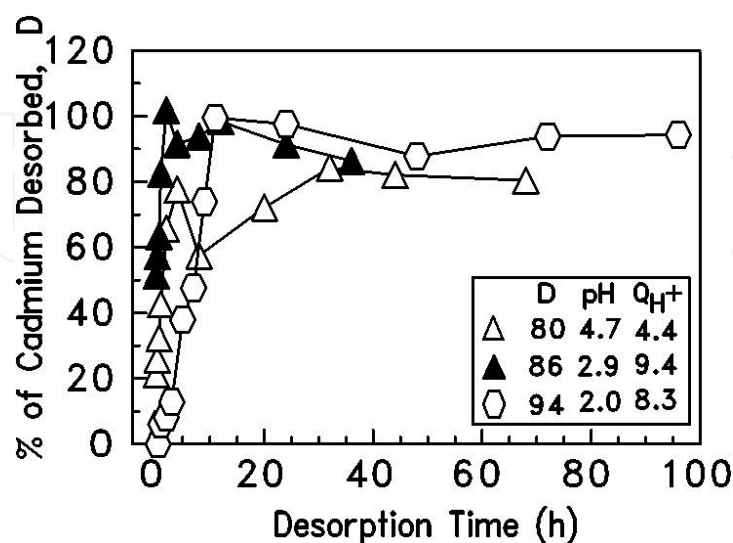


Figure 4. The percentage of cadmium desorbed versus desorption time for different amounts of hydrogen ion initially charged to the vessel

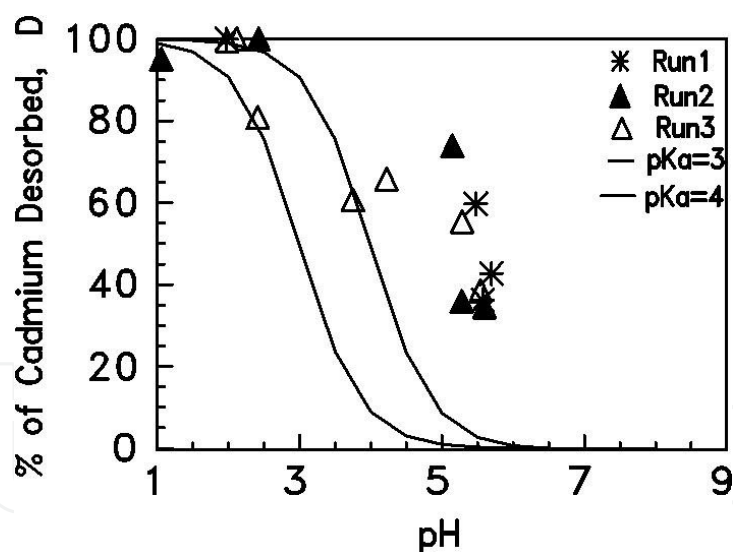


Figure 5. The experimental and predicted percentages of cadmium desorbed versus equilibrium pH for shake flask experiments

Shake flask desorption experiments were also performed in this present study and compared to the results from the spinning basket reactor experiments and to previous works. Data for the percentage of cadmium desorbed is plotted as a function of the equilibrium pH in Figure 5. At an equilibrium pH of 2.1, 100 % cadmium desorption was achieved. Increasing the equilibrium pH decreased the percentage of cadmium desorbed according to an S-

shaped profile. This S-shaped profile was also observed by Schultz et al. [11] and Aldor et al. [12]. Jha et al. [6] also found that 88 % of cadmium desorption was obtained 24 hours after addition of 0.01 N hydrochloric acid to 100 mg of cadmium-loaded chitosan. Also, 80 % cadmium desorption occurred at pH 3.0, a similar result as the present study. Hayes and Leckie [13] presented an S-shaped profile for Cd^{+2} and Pb^{+2} adsorption on goethite, which has a complimentary profile to the present desorption study.

Results of the percentage of cadmium desorbed from the shake flask desorption experiment were consistent with the spinning basket desorption experiment. However, the results for hydrogen ion consumption were quite different. The inconsistent hydrogen ion consumption may be due to the sensitivity of the pH measurement. A small change in pH near 2 resulted in a significant difference in hydrogen ion consumption. Also the modes of mixing between the spinning basket reactor experiment and the shake flask experiment were different. The mixing in the spinning basket reactor was more uniform and resulted in more repeatable and reliable pH measurements. Therefore, the measurements for H^+ adsorption on the chitosan beads for the shake flask experiments at low pH need to be interpreted with caution.

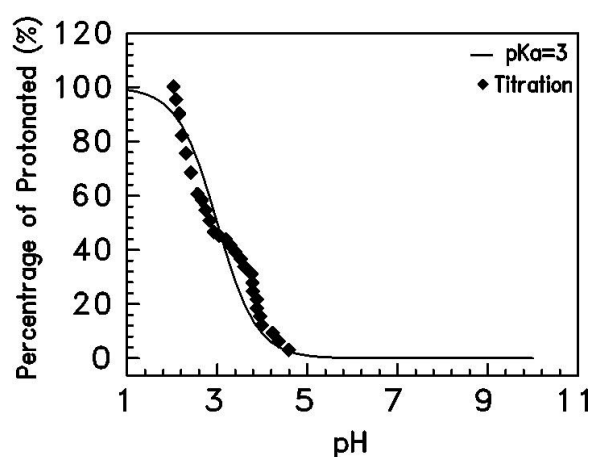


Figure 6. The titration curve for crosslinked chitosan beads

The titration curve describing the equilibrium relationship between the pH and hydrogen ion capacity on the crosslinked chitosan beads is presented in Figure 6. A similar titration curve was observed by Yoshida et al. [14] for adsorption of hydrochloric acid on poly(ethylene imine) chitosan. The titration curve in Figure 6 apparently has two equivalent points. For the first equivalent point of 4.0, hydrogen ions exchange with the imino groups ($=\text{NH}$) on the chitosan beads within the crosslinked outer shell. The second equivalent point at pH of 2.5 shows that hydrogen ions penetrate deeper to the un-crosslinked core of bead to exchange with the free amine groups ($-\text{NH}_2$).

3.3. Exchange Between Cadmium Ions and Hydrogen Ions

The proposed competitive ion exchange scheme for cadmium ions and hydrogen ions with nitrogen atoms on crosslinked chitosan is presented in Figure 7. The addition of hydrogen

ions displaces the adsorbed cadmium ions. A Langmuir-Freundlich equation for multiple components is developed below to model the competition between the hydrogen ions and the adsorbed cadmium ions on the crosslinked chitosan beads.

Model Development. Three major assumptions are made for the equilibrium model. First, the adsorption of cadmium ions on the crosslinked chitosan beads may follow the chelation binding mechanism validated by Inoue et al. [15], which shows that divalent cadmium ions adsorb onto amine groups of chitosan to form metal-chelate complexes with composition of 1 mole of cadmium to 2 mole of glucosamine unit. Second, the Cd^{2+} ions chelate only with imino ($-\text{CH}=\text{N}-$) groups in the outer shell of the crosslinked chitosan. In Chapter 3, it was shown that the crosslinked chitosan bead contains a crosslinked outer shell where all amine groups are derivativized to imino

($-\text{CH}=\text{N}-$) crosslinks, and an inner core of uncrosslinked chitosan containing free amine ($-\text{NH}_2$) groups. In the present desorption experiments, the maximum adsorption capacity was around 15 mg Cd^{2+} /g chitosan. Thus, the value for r_M from previous study [8] is 1.32 mm, which is larger than r_c value of 1.29 mm for the crosslinked chitosan beads used in the desorption experiments. Consequently the adsorbed cadmium is only localized in the crosslinked outer shell of the chitosan beads where only imino chelation sites are present. Therefore, the chelation reaction is expressed as

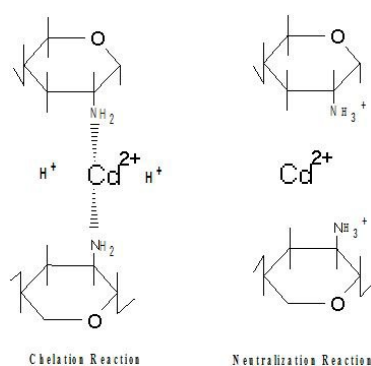


Figure 7. The competitive ion exchange scheme



The third assumption is that the equilibrium constants for the adsorption of hydrogen ions on the chitosan beads may follow the acid/base neutralization reactions of the form





In other words, the equilibrium constant K_a' is assumed to be the same for either imino or amine groups. Consequently, Figure 6 is assumed to have only one apparent $\text{p}K_a$ value at pH 3.0. From equations (6) and (7), K_{cd} and K_a' are defined as

$$K_{\text{Cd}} = \frac{[-\text{C=NH} \bullet \text{Cd}^{+2}]}{[-\text{C=NH}][\text{Cd}^{+2}]^{1/2}} \quad (9)$$

$$K_a' = \frac{[-\text{C=NH}_2^+]}{[-\text{C=NH}][\text{H}^+]} \quad (10)$$

If the overall active number of adsorption sites on the crosslinked chitosan bead is conserved, then the equilibrium constants K_{cd} and K_a' can be expressed as

$$K_{\text{Cd}} = \frac{2 q_{\text{Cd}}}{(Q_M - 2 q_{\text{Cd}} - q_{\text{H}}) C_e^{1/2}} \quad (11)$$

$$K_a' = \frac{q_{\text{H}}}{(Q_M - 2 q_{\text{Cd}} - q_{\text{H}}) C_{\text{ae}}} \quad (12)$$

where C_e is the equilibrium cadmium ion concentration in the vessel (mole/L), C_{ae} is the equilibrium hydrogen ion concentration in the cadmium solution (mole/L), K_a' is the equilibrium constant $(\text{mole/L})^{-1}$ for the neutralization reaction, K_{cd} is the equilibrium constant $(\text{mole/L})^{-1/2}$ for chelation, Q_M is the theoretical maximum capacity of chitosan (6.2 mmole active sites/g chitosan), q_{cd} is the equilibrium cadmium ion capacity of the crosslinked chitosan beads (mmole Cd^{+2} /g chitosan), and q_{H} is the equilibrium hydrogen ion capacity of the crosslinked chitosan beads (mmole H^+ /g chitosan).

By solving for q_{cd} and q_{H} from equations (10) and (11), the following Langmuir-Freundlich equations were derived, based on the binary mixture model presented by Ruthven [16]:

$$q_{\text{Cd}} = \frac{K_{\text{Cd}} C_e^{1/2} Q_M / 2}{1 + K_a' C_{\text{ae}} + K_{\text{Cd}} C_e^{1/2}} \quad (13)$$

$$q_{\text{H}} = \frac{K_a' C_{\text{ae}} Q_M}{1 + K_a' C_{\text{ae}} + K_{\text{Cd}} C_e^{1/2}} \quad (14)$$

The sum of q_{Cd} and q_H is expressed as q , given by

$$q = q_{Cd} + q_H = \frac{K_{Cd} C_e^{1/2} Q_M / 2 + K_a' C_{ae} Q_M}{1 + K_a' C_{ae} + K_{Cd} C_e^{1/2}} \quad (15)$$

In equations (12) and (14), $Q_M/2$ is equal to 3.1 mmole Cd^{+2}/g chitosan.

Recall from equation (3) that the percentage of cadmium desorbed (D) is given by

$$D (\%) = \left(1 - \frac{q_{Cd}}{q_{Cd,f}} \right) \cdot 100 \% \quad (16)$$

where $q_{Cd,f}$ is the final cadmium adsorption capacity before the desorption process is initiated (mmole Cd^{+2}/g chitosan). Therefore, the percentage of the cadmium desorbed into the cadmium solution during the desorption process is expressed as

$$D (\%) = \left(1 - \frac{K_{Cd} C_e^{1/2} Q_M / 2}{1 + K_{Cd} C_e^{1/2} + K_a' C_{ae}} \frac{1}{q_{Cd,f}} \right) \cdot 100 \% \quad (17)$$

Estimation of Equilibrium Constants. The pK_a value of the crosslinked chitosan beads was obtained from the pH value at which 50 % of the active sites were protonated. The pK_a value estimated from Figure 6 was 3.0. In other words, the pK_b value of the conjugated base was 11.0 (Snoeyink and Jenkins, 1982 [17]). In this study K_a' is defined as the inverse of K_a . Based on the relationship between pK_a and K_a ($pK_a = -\log K_a$), the value of K_a' was equal to 10^{pK_a} . Therefore, the K_a' value was 1000 (mole/L)⁻¹. Muzzarelli [18] found that the pK_a value for chitosan was 6.3. Similarly, the pK_b for the base -C-NH₂ was 7.7. The pK_b differences may suggest that the crosslinked imino group (=NH) on chitosan is a weaker base than the uncrosslinked amine group (-NH₂). Both the titration curve for adsorption of hydrochloric acid onto poly(ethylene imine) chitosan beads and the derived pK_a value of 4.0 by Yoshida et al. [14] are similar with the results of this present work.

Once K_a' was obtained, K_{Cd} was estimated. The $q_{Cd,f}$ values at C_e around 200 mg Cd^{+2}/L (1.79 mmole Cd^{+2}/L) and pH at 6.5 to 7 were between 0.13 and 0.17 mmole Cd^{+2}/g chitosan. After substitution of K_a' , C_{ae} , C_e , Q_M and $q_{Cd,f}$ values into equation (15), K_{Cd} was determined when the minimum sum of squares between the data points given in Figure 4.5 for the percentage of cadmium desorbed (D) and the predicted values from equation (15) was achieved. The K_{Cd} value was estimated to be 0.57 (mole/L)^{-1/2}. This chelation reaction constant was also compared to the stability constant data for metal complexes on organic ligands (IUPAC, 1979) which showed that the binding constant of cadmium on pyridine (imine ligand) and serotonin (amine ligand) were $10^{1.36}$ and $10^{3.6}$ (mole/L)^{-1/2} respectively. Therefore, the value for estimated K_{Cd} indicated that the cadmium did not bind very strongly to imino groups on chitosan. This low binding constant facilitated the desorption process as the hydrogen ions

easily displaced the cadmium ions to accomplish the neutralization reaction. However, hydrogen ions were still required for desorption because water alone could not desorb the bound cadmium.

Another approach for the calculation of K_{cd} was considered by using the low cadmium concentration adsorption isotherm data for 2.5 wt % crosslinked chitosan beads in previous study [8]. In the previous study, q_{cd} is equal to 30.66 mg Cd^{+2} /g chitosan (0.27 mmole/g chitosan) at an equilibrium cadmium concentration of 234.4 mg Cd^{+2} /L (2.09 mmole Cd^{+2} /L). According to equation (12), when the pH is greater than or equal to 7.0, the product of the K_a' C_{ae} will be much smaller than the product of $K_{cd}C_e^{1/2}$. The value of K_{cd} was determined by setting C_e , Q_M and q_{cd} equal to 2.09 mmole/L, 6.2 mmole/g, and 0.27 mmole/g respectively in equation (12). The K_{cd} value estimated at pH 7.0 was 2.12 (mole/L) $^{-1/2}$ which is higher than the K_{cd} value of 0.57 (mole/L) $^{-1/2}$ estimated by equation (15). However, the values of K_{cd} estimated by both methods are in general much smaller than the value of K_a' . The value of K_{cd} is not sensitive to the prediction of the percentage of cadmium desorbed by Langmuir-Freundlich equation, since the K_a' value was three orders of magnitude bigger than the value of K_{cd} . Thus, the K_a' value (pK_a value) determines how adsorbed cadmium ions are displaced by hydrogen ions. In other words, the value of the K_a' is the limiting parameter for the predicting desorption profile.

At pH ranging from 1 to 8, the percentage of cadmium desorbed was predicted using equation (15). The experimental and the predicted percentages of cadmium desorbed are plotted in Figure 5 as a function of pH. In Figure 5, the majority of the adsorbed cadmium ions were desorbed at pH ranging from 3.0 to 5.5. As mentioned previously in Figure 6, the titration curve has two equivalent points at pH of 2.5 and 3.9. Since the experimentally occurred percentage of cadmium desorbed was significant even at pH values above 4.0, the first equivalent point at pH 3.9 may determine the actual pK_a required for desorption. Therefore, for comparison, the predicted desorption profile assuming pK_a equal to 3.9 is also provided in Figure 5.

The experimental data for three repeat runs is scattered in the pH range from 4.5 to 6.0, as shown in Figure 5. Equation (15) does not accurately predict the behavior of desorption in this pH range. At pH ≥ 5.0 , the desorption process may be more complex than the model suggests. The ion exchange behavior can not fully predict the chelation reaction.

4. Summary and Conclusions

Chitosan is nature's most abundant biopolymer next to cellulose. It is well known that chitosan is a selective adsorbent for heavy metal ions. However, the chitosan raw material needs to be modified for use in low pH environments. To address this need, chemically modified porous chitosan beads were synthesized.

In order to fabricate porous chitosan beads, chitosan in acetic acid solution was cast into spherical gel beads of 3 mm diameter and precipitated to a gel in 2 M NaOH solution.

Chemical modifications of chitosan were considered. First, the linear chitosan chains within gel beads were heterogeneously crosslinked by glutaric dialdehyde solution. The chitosan gel beads were then freeze dried to form porous beads.

The desorption of cadmium from cadmium-adsorbed chitosan beads with dilute nitric acid was tested to evaluate the feasibility of recovering the cadmium and regenerating the adsorbent. Hydrogen ions were needed to displace the cadmium ions adsorbed on the chitosan beads. Two types of desorption experiments, single stage and multiple stage, were performed using a Carberry spinning basket reactor. In the experiments, 0.5 g of chitosan beads were packed into the hollow impeller basket assembly and contacted with 200 mL of 200 mg /L cadmium ion solution at 150 rpm and 25 C until the adsorption equilibrium was achieved. After adsorption, different doses of 0.1 N HNO₃ solution were added to the vessel to initiate the desorption process. The cadmium concentration increased sharply during the first 12 hours of desorption following the addition of nitric acid, and then leveled off. At a final pH value of 2.0, 94 % of cadmium desorption was achieved, and 8.3 mmole H⁺ per gram of beads was adsorbed to displace the bound cadmium. Equilibrium shake flask experiments were carried out to determine the equilibrium hydrogen and cadmium loading on the chitosan beads at different pH levels. Decreasing the equilibrium pH increased the percentage of cadmium desorbed according to an S-shaped profile, consistent with the ion-exchange mechanism. A Langmuir-Freundlich model proposed that the desorption process is accomplished by displacing adsorbed cadmium ions with hydrogen ions. Based on the high efficiency of the desorption treatment, cadmium recovery and adsorbent regeneration is feasible.

In summary, the adsorbent can be regenerated by dilute acid treatment, and 100 % cadmium recovery from the chitosan beads is feasible at pH less than 3.0. Two recommendations for future research are suggested:

1. Many industrial waste water matrices contain several heavy metal ions. Therefore, determine the multi-component heavy metal ion adsorption capacity on the chitosan beads.
2. Modify the bead synthesis process. The freeze drying process does not improve the adsorption capacity. Therefore, consider alternative drying methods that do not reduce the adsorption capacity and are less expensive than freeze drying.

5. Nomenclature

C(t)	cadmium ion concentration in the vessel at different adsorption or desorption times, mg Cd/L
C _a	concentration of HNO ₃ added into the spinning basket reactor before desorption, mole H ⁺ /L
C _{ae}	equilibrium hydrogen ion concentration in the cadmium solution, mole/L
C _e	equilibrium cadmium ion concentration in the vessel, mole /L
C _o	initial concentration of Cd ⁺² , mg Cd ⁺² /L
C _f	final concentration of Cd ⁺² at equilibration, mg Cd ⁺² /L

C_{\min}	lowest cadmium concentration along the adsorption or desorption process, mg Cd/L
$C_{\min,i}$	lowest cadmium concentration along the adsorption or desorption process at a specific desorption stage, mg Cd/L
$C_{0,i}$	initial cadmium concentration in the spinning basket reactor at specific desorption stage " i ", mg Cd/L
D	percentage of cadmium desorbed at a given desorption time, %
D_{Ae}	effective diffusion coefficient of glutaric dialdehyde within the crosslinked zone of the gel bead, cm ² /sec
K	measure of the adsorption capacity or binding strength
Ka'	equilibrium constant for the neutralization reaction, (mole/L) ⁻¹
K_{cd}	equilibrium constant for chelation, (mole/L) ^{-1/2}
$M_{w,Cd+2}$	molecular weight of the cadmium ions, g/mole
m_b	mass of chitosan beads in the spinning basket reactor impeller, g
n	number of desorption stage
$1/n$	measure of adsorption intensity
pH_i pH	value at different adsorption or desorption times
Q	cadmium adsorption capacity on the chitosan beads, mg Cd/g-chitosan
Q_f	final cadmium adsorption capacity on the chitosan beads, mg Cd ⁺² /g chitosan
$Q(H^+)$	accumulated hydrogen ion adsorption capacity in the present stage, mg Cd/g-chitosan
q_{Cd}	equilibrium cadmium ion capacity of the crosslinked chitosan beads, mmole Cd ⁺² /g chitosan
Q_M	theoretical maximum capacity of chitosan, 6.2 mmole active sites/g chitosan
q_H	equilibrium hydrogen ion capacity of the crosslinked chitosan beads, mmole H ⁺ /g chitosan
R	radius of the gel bead, cm
r	radial position within the gel bead, cm
r_C	radial position within the gel bead defining the boundary between the outer crosslinked zone and the inner unreacted core zone, cm
r_M	cadmium un-saturation zone, cm
t	time of crosslinking
V	current cadmium solution volume loaded in the spinning basket reactor vessel, L
V_a	acid volume added into the spinning basket reactor, L
V_t	volume of solution in the spinning basket reactor at a given time, L
$X_{Bgroups}$	weight fraction of chitosan in the gel bead, g chitosan/g of gel bead extent of crosslinking, moles of crosslink/total moles of -NH ₂
X_T	moles of glutaric dialdehyde consumed by the gel bead/total moles of -NH ₂ groups within the gel bead
X_R	moles of glutaric dialdehyde crosslinked per total mole of -NH ₂ groups within the gel bead

Y_B	total moles of amine groups/g of chitosan
β	moles of glutaric dialdehyde consumed to form a crosslink/moles of $-NH_2$ crosslinked
ρ_b	overall density of the gel bead, g/cm ³
u	chelation coordination number for cadmium, 2 moles active sites/mole Cd^{+2}
$\Delta Q_i (H^+)$	hydrogen ion adsorption capacity for chitosan beads at the i th desorption stage mg H/g-chitosan

Author details

Tzu-Yang Hsien^{1*} and Yu-Ling Liu²

*Address all correspondence to: tyhsien@cute.edu.tw

1 General Education Center, China University of Technology, Taipei

2 Teacher Education Center, Ming Chuan University, Taoyuan

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