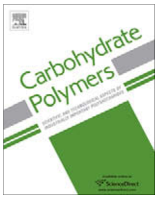
Carbohydrate Polymers 80 (2010) 891–899

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Adsorption of copper (II) and lead (II) ions from aqueous solution on chitosan-coated sand

Meng-Wei Wan [a,*], Chi-Chuan Kan [a], Buenda D. Rogel [b], Maria Lourdes P. Dalida [b]

[a] *Department of Environmental Engineering and Science, Chia-Nan University of Pharmacy and Science, Tainan 71710, Taiwan*
[b] *Department of Chemical Engineering, University of Philippines-Diliman, Diliman, Quezon City, Philippines*

ARTICLE INFO

Article history:
Received 6 September 2009
Received in revised form 20 November 2009
Accepted 23 December 2009
Available online 7 January 2010

Keywords:
Chitosan
Adsorption
Copper
Lead
Sand
Permeable reactive barrier

ABSTRACT

Biodegradable material, known as chitosan-coated sand (CCS), was utilized for removal of copper (II) and lead (II) ions in water. Batch experiments were conducted to investigate the adsorption effect under different initial concentration (C_o = 100, 500, 1000 and 2000 mg/L), solution pH (2, 3, 4, 5 and 6), and contact time (0.5, 1, 2, 4, 6, 12 and 24 h). Desorption studies were performed using diluted HCl solution (pH 1 and 3) and tap water (pH 7) on adsorbed metal ions. Langmuir and Freundlich adsorption models were used to describe static isotherms and constants. The data fitted well with Langmuir model at $Q_{\max}$ value of 8.18 and 12.32 mg/g CCS for Cu(II) and Pb(II) ions at 4 h contact time, respectively. Kinetic studies followed the pseudo second-order reaction, which indicated that the chemical sorption is the rate-limiting step. Results of desorption process signified potential for recovering metal ions from CCS.

1. Introduction

Heavy metal removal from groundwater and industrial wastewater is currently an important environmental concerns. The removal of heavy metal ions from drinking water is a real challenge due to their trace quantities, formation of complexes with natural organic matter, and toxic effect even at very low concentrations (Chu, 2002; Gyliene & Visniakova, 2008; Vieira & Beppu, 2006). The presence of these metals (viz.: Cu, Pb, Cd, Ni, As and Cr) in improperly treated waste is of serious concerns to the public health and ecological systems. Potential sources of these are mining industries, metal-plating and fabrication, fertilizer, illegal landfills, and abandoned waste disposal sites. Other reasons for the metal content of water include natural weathering processes, waste emissions, atmospheric depositions, and anthropogenic activities (Bhattacharyya & Gupta, 2006; Boddu, Abburi, Talbott, & Smith, 2003; Chen, Liu, Chen, & Chen, 2008; Chen, Yang, Chen, Chen, & Chen, 2009).

Copper (Cu) and lead (Pb), in particular, are natural elements predominantly used in production industry applications. Cu is a very common substance that occurs intrinsically in the environment and spreads through natural phenomena, which is extensively utilized by electrical industries, in fungicides, and in anti-fouling paints. It is toxic to humans, causing cancer and promoting oxidation when it is ingested at high concentrations (Schmuhl, Krieg, & Keizer, 2001). Among the ionic species of copper, Cu(II) ions can have alarming effects in aqueous solution, attaching easily to organic and inorganic matter based on solution pH (Hasan, Ghosh, Viswanath, & Boddu, 2008). Moreover, Pb is widely used in industrial applications, such us battery, printing, pigments, fuels, photographic materials, and explosives manufacturing (Paulino et al., 2007; Saifuddin & Raziah, 2007). According to the US Environmental Pollution Agency, it is a highly toxic cumulative element, causing a variety of negative effects on humans, even at low dosages. Pb can contaminate the environment from anthropogenic sources as well as by natural geochemical processes.

Currently, the most widely employed technologies for water purification are based on physicochemical processes, including filtration, chemical precipitation, ion exchange, adsorption, electrodeposition, and membrane systems (Baroni, Vieira, Meneghetti, da Silva, & Beppu, 2008; Boddu et al., 2003; Wan Ngah, Ab Ghani, & Kamari, 2005; Wan, Petrisor, Lai, Kim, & Yen, 2004). These methods have distinct limitations and disadvantages while heavy metals are removed from groundwater. In the past years, adsorption processes have been shown to be effective and economical treatment process, thus many low-cost adsorbents have been investigated (Chiou & Li, 2002; Ng, Cheung, & McKay, 2002).

Biopolymers are potential adsorbents due to their biodegradability, non-toxicity, efficiency. These are inexpensive and thus are competitive with ion-exchange resins and activated carbon. They contains chemically active functional groups that serve as efficient sites to bind metal ions. Notably, chitosan has the highest

---

[*] Corresponding author. Tel.: +886 6 2660615.
E-mail address: peterwan@mail.chna.edu.tw (M.-W. Wan).

0144-8617/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.carbpol.2009.12.048

Nomenclature

b	Langmuir constant, related to the energy or the net enthalpy of adsorption process
C_e	equilibrium concentration, mg/L
C_o	initial concentration, mg/L
K_f	Freundlich constant, an indicator of adsorption capacity
K_L	Langmuir constant incorporating the enthalpy of adsorption
k_1	rate constant of pseudo first-order, min^{-1}
k_2	rate constant of pseudo second-order, g/mg min
m	amount of chitosan-coated sand, g
m_a	amount of metal ion adsorbed, mg/L
m_d	amount of metal ion desorbed, mg/L
n	Freundlich constant
q_e & q_t	amount of metal adsorbed at equilibrium and at any time, mg/g
$Q_{\max}$	maximum capacity or "Langmuir" monolayer sorption capacity, mg/g
Q_o	amount of metal ion adsorbed, mg/g
t	time, min
v	volume of the solution, L

adsorption capacity among the biopolymers. It is a deacetylated derivative of chitin, the second most abundant organic compound in nature next to cellulose, and is extracted from the shells of crustaceans. It has several desirable characteristics such as biocompatibility, biodegradability, renewability, bioactivity, and non-toxicity (Juang, Tseng, Wu, & Lee, 1997; Sakaguchi, Horikoshi, & Nakajima, 1981; Varma, Deshpande, & Kennedy, 2004; Zhou, Yang, & Nie, 2007). For over a decade, chitosan has received considerable attention as an adsorbent for transition metal ions and organic species (Annadurai, Ling, & Lee, 2008). It chelates larger amounts of metal than chitin due to its excellent binding capacity, mostly attributed to the free amino groups exposed after chitin deacetylation. Moreover, chitosan is soft and has a tendency to agglomerate or form gel. It is partially soluble in dilute mineral acids such as nitric acid (HNO_3), hydrochloric acid (HCl), and phosphoric acid (H_2PO_4) (Gyliene & Visniakova, 2008; Nomanbhay & Palanisamy, 2005), and is also soluble in dilute organic acids such as acetic acid (HAc), formic acid, etc. (Chen et al., 2008).

Several studies of metal ion adsorption by chitosan have been carried out in recent years, such as the removal of copper (Săg & Aktay, 2002), chromium (Boddu et al., 2003), cadmium (Evans, Davids, MacRae, & Amirbahman, 2002), iron (Wan Ngah et al., 2005), nickel, and lead ions from aqueous solution (Paulino et al., 2007; Pradhan, Shukla, & Dorris, 2005). The use of permeable reactive barriers for the recovery of metals is a practical technology for the treatment of water. Filters along a contaminated stream of groundwater. The use of chitosan alone would be costly, because construction of filters along the stream requires large quantities of adsorbents. Immobilizing chitosan on a low-cost material would result in lower amounts of chitosan being used but the overall metal adsorption capacity may not be affected (Wan et al., 2004). Unfortunately, there are limited references to adsorption studies that provide readily available support for chitosan in spite of its inherent practical advantages.

In this research, the application of an appropriate immobilization material is essential for the utilization of chitosan in industrial applications. Providing a support material (sand) for the immobilization of chitosan is considered to be both an economical and practical method, which can further enhance its metal binding capacity. The aim of this study is to investigate the removal of heavy metals using chitosan-coated sand (CCS) from subsurface water sources. The adsorption–desorption experimental data were used to determine the effectiveness of CCS to uptake metal ions individually from solutions.

2. Experimental

2.1. Chemicals and reagents

Chitosan (low molecular weight, CAS No. 9012-76-4) was purchased from Sigma–Aldrich; anhydrous $CuSO_4$; $Pb(NO_3)_2$; HCl, fuming 37%; NaOH; ICP Standard Solution, 1000 mg/L Cu(II) and Pb(II) were supplied from Merck Company and Sand (EM Science, Gibbstown, NJ). De-ionized (DI) water of milli-Q purity was used for all reagent solutions.

2.2. Preparation of CCS

Immobilization of the chitosan was similar to the methods found in the literature (Wan et al., 2004) with only slight modifications. About 5 g of chitosan and 100 g of sand were stirred in 300 mL of 5% (v/v) HCl for 5 h. 1 N NaOH was added drop by drop until neutralization occurred. The adsorbent was allowed to settle, washed with DI water and was oven-dried for 24 h at 65 °C. After drying and grinding, the materials were sieved, passed through Mesh No. 25 (0.700 mm) and collected on Mesh No. 35 (0.500 mm). The homogenous particle size of 0.500 mm which illustrated the best adsorption efficiency based on previous optimization study of adsorbent's particle size for Cu adsorption was used in the entire experiments. The new adsorbent adsorbent is called chitosan-coated sand (CCS).

2.3. Characteristic analysis

SEM photographs were taken with HITACHI S-3000N Scanning Microscope to examine the morphology and surface structure of the adsorbents at the required magnification at room temperature. Thermal gravimetric analyses (TGA) were performed on freeze-dried sand, chitosan and chitosan-coated sand (CCS) samples using Rigaku Thermo Plus TG 8120 in the temperature range of 30–800 °C at a heating rate of 10 °C per minute. Surface area of the adsorbents was measured by single point BET (Brunauer, Emmett and Teller) method using Accelerated Surface Area and Porosimetry System (Micromeritics, ASAP 2010).

2.4. Elemental analysis by ICP-OES

A Perkin Elmer 2000DV Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) was used for quantitative determination of metal ion concentration. Standard solutions for the instrument's calibration curve were prepared as indicated: 10 mL of 1000 mg/L of ICP standard diluted to 100 mL with DI water which served as stock solution. Subsequently, different volumes of the stock solution (0.05, 0.1, 0.5, 1.0, 2.0, 4.0, 6.0 and 10.0 mL) were pipetted into 100 mL volumetric flasks and diluted to mark.

2.5. Batch adsorption studies

The adsorption of Cu(II) and Pb(II) ions were analyzed in a batch system at room temperature with varied concentrations ranging from 100–2000 mg/L.

2.5.1. Single metal ions experiment

The experiments were performed using single solutions of the adsorbates maintained at pH 4.5. The solutions were prepared in DI water using the anhydrous $CuSO_4$ and $Pb(NO_3)_2$. 30 mL of single metal ion solution was placed in 100-mL Erlenmeyer flasks and was then combined with 2.5 g of CCS. The equilibration (shaking) time was 24 h at a static speed of 50 rpm. After equilibrium, the solution was filtered using Whatman #40 filter paper. Whatman #40 filter was selected as a clean-up filter in preparation for ICP-OES analysis. The filtrate was analyzed with ICP-OES. The amount of Cu(II) and Pb(II) ions adsorbed per unit mass of CCS was calculated using the equation:

$$Q_o = \frac{(C_o - C_e)v}{m} \tag{1}$$

where C_o and C_e are the initial and equilibrium concentration of metal ion solution (mg/L), respectively; v is the volume of the solution in liter (L); and m is the amount of CCS in grams (g).

The percentage adsorption was determined using the equation:

$$\%\text{Adsorption} = \frac{C_o - C_e}{C_o} \times 100 \tag{2}$$

where C_o and C_e are the initial and equilibrium concentration of metal ion solution (mg/L).

2.5.2. Effect of C_o and contact time

In this study, the effects of initial concentration and contact time are two main parameters in the adsorption of Cu(II) and Pb(II) ions in aqueous solution. This study determines the capacity of CCS to remove specific metal ions in the solution at the equilibrium time. The C_o concentration were 100, 500, 1000 and 2000 mg/L prepared by diluting the stock solution of Cu(II) and Pb(II) ions. The contact times were varied from 0.5, 1, 2, 4, 6, 12 and 24 h.

2.5.3. Effect of solution pH

The metal ion adsorption was studied in pH range 2–6 to eliminate the consequences of precipitation of the metals as hydroxides at higher pH (Chen et al., 2008). The C_o of 100 mg/L was adjusted to the required pH value using 1 N HCl and 1 N NaOH. 2.5 g of CCS were equilibrated at the desired pH of the specified volume of the adsorbates (30 mL) for 24 h at a static speed of 50 rpm. The final pH of the filtrate was determined and its metal ion content was analyzed using ICP-OES.

2.6. Kinetics of adsorption

In order to investigate the controlling mechanism of the adsorption processes, pseudo first-order and pseudo second-order kinetics were applied in the data. This includes the mass transfer and chemical reactions due to the large number and variation of different chemical groups on chitosan chains (Annadurai et al., 2008).

2.6.1. Pseudo first-order kinetics

The pseudo first-order kinetics can be expressed as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{3}$$

where k_1 is the rate constant of pseudo first-order adsorption (min^{-1}); q_e and q_t are the amount of metal ion adsorbed per gram of chitosan-coated sand (mg/g CCS) at equilibrium and at any time t, respectively. A straight line for the plot of $\log(q_e - q_t)$ versus t would give the first-order rate constant k_1 and equilibrium adsorption capacity q_e, from the slope and intercept of the line.

2.6.2. Pseudo second-order kinetics

The pseudo second-order kinetics can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_2 (g/mg min) is rate constant of pseudo second-order adsorption. The plot of t/q_t versus t would give the pseudo second-order rate constant k_2 and q_e. The pseudo second-order kinetic model is based on the assumption that the rate-limiting factor may be chemisorption involving valence forces through sharing of electrons between the amino group and metal ions (Boddu et al., 2003; Săg & Aktay, 2002).

2.7. Equilibrium isotherms studies

Adsorption isotherm models describe the relationship between adsorbates and adsorbents at equilibrium. The two most well-known isotherm models are the Langmuir and the Freundlich. In this study, equilibrium isotherms were used to determine the adsorption mechanism of CCS for Cu(II) and Pb(II) ions. The adsorbents were combined with fixed volumes (30 mL) of metal ion solutions varying the initial concentrations (100, 500, 1000, and 2000 mg/L) at 4 h contact time. The relation between the amount of adsorbed metal and the remaining concentration of metal ions in solution is described by the isotherm studies.

2.7.1. Langmuir isotherm model

The Langmuir equation, which is valid for monolayer adsorption onto a surface with a finite number of identical sites, can be expressed as:

$$Q_o = \frac{Q_{\max} k_L C_e}{1 + bC_e} \tag{5}$$

where $Q_{\max}$ (mg/g) is the maximum amount of the metal ion per unit weight of CCS to capable of forming complete monolayer coverage on the surface, bound at high equilibrium concentrations C_e; Q_o is the amount of metal ion adsorbed per unit weight of CCS at equilibrium; k_L and b are the Langmuir constants, where b is related to the affinity of binding sites (Boddu et al., 2003). According to the Langmuir equation, the maximum adsorption capacity was derived from the following equation:

$$Q_{\max} = \frac{k_L}{b} \tag{6}$$

where k_L and b can be determined from the linear plot of $1/Q_o$ against $1/C_e$.

2.7.2. Freundlich isotherm model

Another widely used empirical equation, the Freundlich equation, was based on adsorption on a heterogeneous surface. The equation is represented by:

$$Q_o = k_f C_e^n \tag{7}$$

where k_f is roughly an indicator of the adsorption capacity and $1/n$ of the adsorption intensity. A linear form of the Freundlich equation will yield the constant k_f and $1/n$.

$$\ln Q_o = \ln k_f + \frac{1}{n} C_e \tag{8}$$

Therefore, k_f and $1/n$ can be determined from the linear plot of $\ln Q_o$ versus $\ln C_e$. The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption. The obtained values of $n > 1$ signify favorable adsorption conditions (Boddu et al., 2003).

2.8. Desorption studies

Desorption studies were performed using tap water (pH 7) and diluted HCl solutions (pH 1 and 3). These experiments were carried out by immersing the metal ion-loaded CCS in 30 mL of tap water and diluted acid solutions for 4 h at a static speed of 50 rpm. The filtrate was collected and analyzed in ICP-OES. The percentage of desorption was calculated by the following expression:

$$\%\ \text{Desorption} = \frac{m_d}{m_a} \tag{9}$$

where m_d is the amount of metal ion desorbed (mg/L) and m_a is the amount of metal ion adsorbed (mg/L).

3. Results and discussion

3.1. Characteristic analysis

The surface area and pore volume for sand, chitosan and chitosand coated sand (CCS) are shown in Table 1. Among these three bioadsorbents, the CCS illustrates higher surface area and pore volume when compared to the other two adsorbents. Obviously the metal uptake capacity of this adsorbent will be higher due to its free adsorption sites. SEM/EDS analysis was exploited to illustrate the variation of morphology, mineralogical and chemical composition for each adsorbent. The SEM images of the surface on sand, chitosan and CCS are shown in Fig. 1. Fig. 1(a and b) indicates that sand displays a rough structure on surface with a large surface area while chitosan displays a relative smooth structure on surface with less surface area. Fig. 1(c) confirmed the presence of many pores and some cracks on the surface of the CCS adsorbent. The results from EDS are presented in Table 2, the major elements for sand are O (56.35 Weight%), Al (0.30%) and Si (43.35%), while chitoson contents different composition of C (35.76%) and O (64.24%). After the coating process, the CCS bioadsorbent contains C (21.64%), O (56.99%) and Si (21.37%), which also indicates that the aggregation of sand and chitosan was successfully formed.

The results from TGA analysis are presented in Figs. 2–4. Fig. 2 display slow and static increase in weight amounts of sand, which resulted in zero weight loss at 800 °C. As shown in Fig. 3, chitosan which has two main decomposition stages with one starting at 240 °C and another starting at around 320 °C completely burnt out at 600 °C. Based on Fig. 4, the thermogram of CCS which shows similar decomposition stages of chitosan with a relatively less weight loss indicates that about 2% of chitosan is successfully coated on sand.

3.2. Batch adsorption experiment

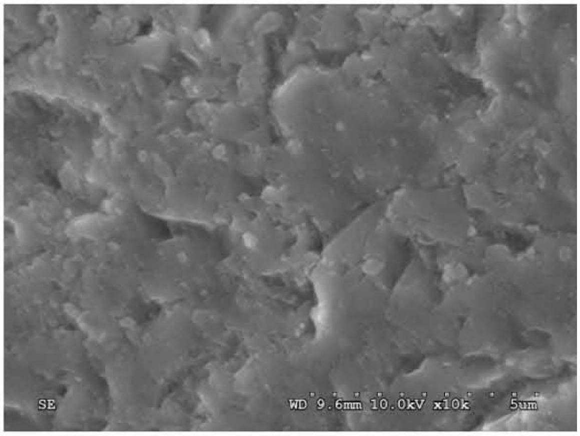
3.2.1. Effect of C_o and contact time

As shown in Fig. 5, it is remarkable that an increase in the initial concentration (C_o) for both Cu(II) and Pb(II) ions led to an increase in the adsorption capacity of chitosan-coated sand (CCS) at various contact times. This can be attributed to the mass transfer effects and the driving force of the concentration gradient being directly proportional to the initial concentrations. Fig. 6 demonstrated that the higher adsorption rates were examined at the beginning. The plateau values indicated that the adsorption equilibrium was gradually attained. Retention of Cu(II) ion was noted to be inversely related to C_o which is supported by results in Table 3. At lowest concentration (100 mg/L), adsorption was almost complete

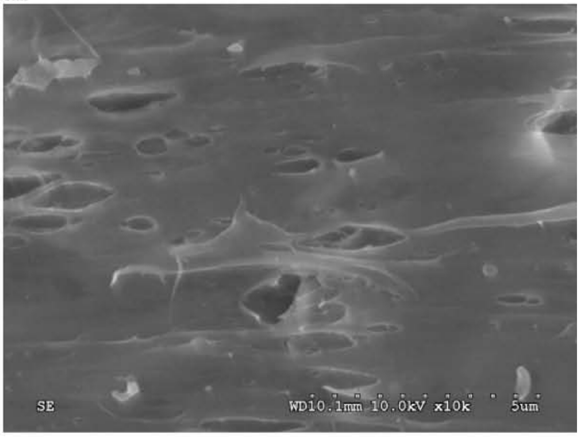
Table 1
The BET analysis results for sand, chitosan and CCS.

Adsorbents	BET-surface area (m^2/g)	Average pore size (Å)
Sand	0.3666	4975.98
Chitosan	0.0368	1111.45
CCS	0.3978	4975.38

(a) Sand



(b) Chitosan



(c) Chitosan coated sand

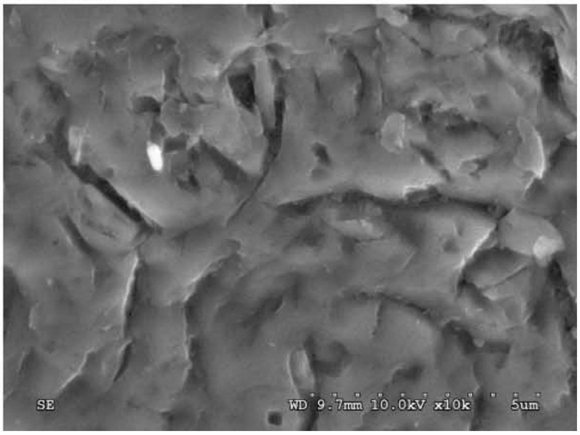


Fig. 1. SEM images of (a) sand, (b) chitosan, (c) chitosan-coated sand.

Table 2
The EDS analysis results for sand, chitosan and CCS.

Adsorbents	Element	Weight%	Atomic%
Sand	O	56.35	69.38
	Al	0.30	0.22
	Si	43.35	30.40
	Total	100.00	100.00
Chitosan	C	35.76	42.58
	O	64.24	57.42
	Total	100.00	100.00
CCS	C	21.64	29.42
	O	56.99	58.16
	Si	21.37	12.42
	Total	100.00	100.00

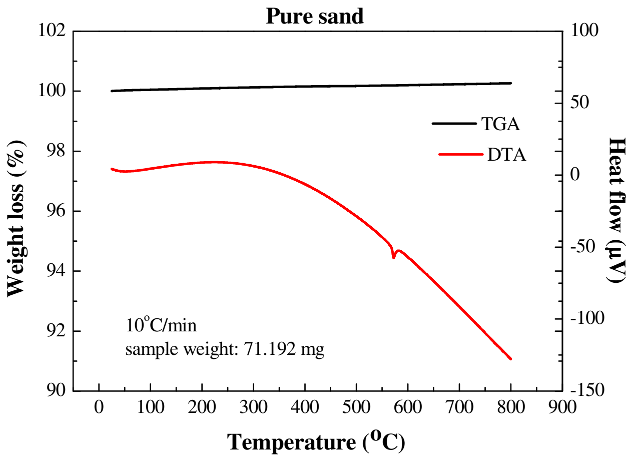


Fig. 2. Thermogravimetric curve of sand only.

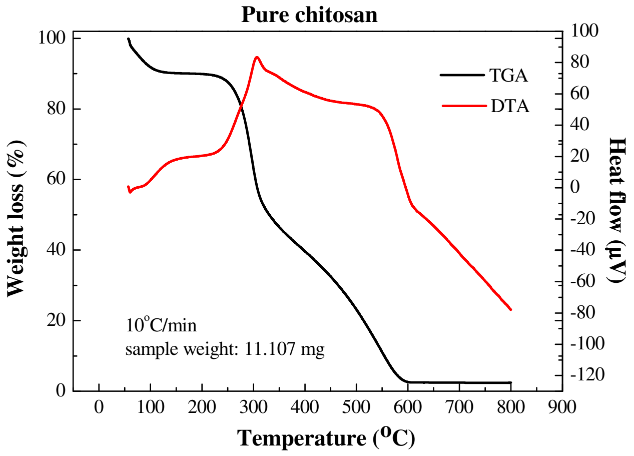


Fig. 3. Thermogravimetric curve of chitosan only.

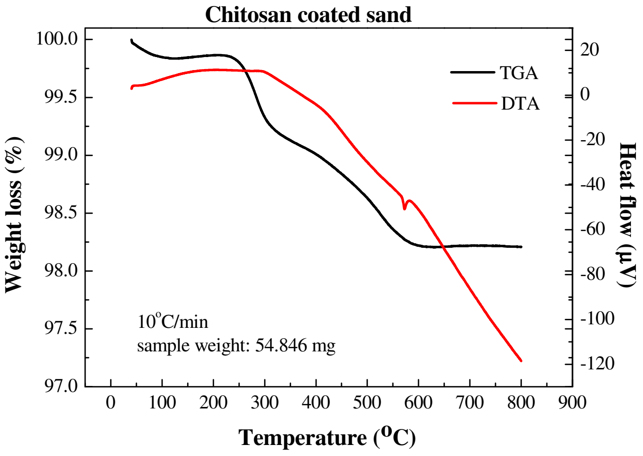


Fig. 4. Thermogravimetric curve of chitosan-coated sand.

(>90%) in the first hour, which facilitated the interaction of the metal ions in the binding sites. Conversely, it took 4–6 h at higher concentrations and more Cu(II) ions were left unabsorbed compared to Pb(II) ions.

As shown in Table 3, the equilibrium adsorption capacity of Cu(II) ions was larger at lower C_o (1.196 and 5.787, Cu mg/g CCS) while Pb(II) ions obtained larger values (11.046 and 22.836 Pb mg/g CCS) at higher C_o. The disparity might be due to the molecular size and hardness of ions. At the lower C_o (100–500 mg/L), the equilibrium adsorption capacities were based on the ionic size. The larger ionic size of Pb(II) deterred the molecular array within the CCS configuration thus eliciting lesser interaction of electrons. At the higher C_o (1000–2000 mg/L), the equilibrium adsorption capacities were attributed to the hardness of the metal ions. Masel (1996) expounded that hardness is inversely related to the ability of the molecule to share electrons. It follows that when the hardness is small, the number of shared electrons will be large and vice versa. A Pb(II) ion is larger but less hardness than a Cu(II) ion. Therefore, more numbers of electrons were shared, which was resulted in stronger covalent interactions with the chitosan at a higher C_o. In this case, the maximum adsorption capacity was achieved after the binding ability of the adsorbent approached saturation at equilibrium time.

As shown in Fig. 6, an exposure time of 24 h was used during batch studies to achieve the equilibrium. It demonstrated that CCS can potentially remove more than 50% of Cu(II) ions at highest concentration and reached the equilibrium at 4–6 h regardless of the initial concentrations (C_o). However, for Pb(II) ions, equilibrium occurred simultaneously for only 2–4 h regardless of the initial concentrations (C_o). At highest C_o, Pb adsorption percentage was almost double (>95%) then that of the Cu(II) ions. It appears that as adsorbate concentration was raised, binding capacity of the adsorbent reached instantaneous saturation resulted in diminishing the overall% adsorption of Cu ions. In addition, Table 4 indicates that extended contact times (Cu(II) > 6 h, Pb(II) > 4 h) have no effect on the adsorption behavior of CCS.

3.2.2. Effect of solution pH

To prevent precipitation, experiments were carried out at pH < 6 to ensure the solubility of metal ions (Bhattacharyya & Gupta, 2006; Paulino et al., 2007; Săg & Aktay, 2002). At high pH, precipitation usually occurred with the metallic ions attached to hydroxide ions forming $Cu(OH)_2$ at pH > 6 and $Pb(OH)_2$ at pH > 8.

Table 4 shows the effect of pH and contact time on equilibrium adsorption of both two metals. The CCS adsorption percentage (%) for Pb(II) ions from the aqueous medium was affected by the lower solution pH and slightly perturbed by the contact time. For Pb(II) ions at pH 2, the adsorption percentage was shown to be significantly lower due to the electrostatic repulsion between the metal cation and the protonated amino group. Based on literature reviews (Bhattacharyya & Gupta, 2006; Schmuhl et al., 2001), there is reversal of charge and diminished metal chelating ability of the hard-base chitosan attributed to the low pH that allows high numbers of hydrogen (H^+) ions to favor the protonation of the amino sites. In acidic condition, there is competition between H^+ ions and the heavy metals in terms of binding with the basic NH_2 groups of chitosan (Paulino et al., 2007). Metal adsorption percentage decreased since most of the NH_2 groups of CCS are in the protonated form (NH_3^+).

Taboada, Cabrera, and Cardenas (2003) described a similar phenomena as the following competing reactions, where M^{2+} represents the divalent metal ion and R is the polymer structure of chitosan.

$$M^{2+} + RNH_2 \rightarrow M(RNH_2)^{2+}$$

The amino group of chitosan may react with hydrogen ions (H^+) according to:

$$H^+ + RNH_2 \rightarrow H(RNH_2)^+$$

Conversely, there was improvement in the metal adsorption percentage while the pH value was increased. Enough binding capacity was exhibited by CCS. The adsorption percentage of Pb(II)

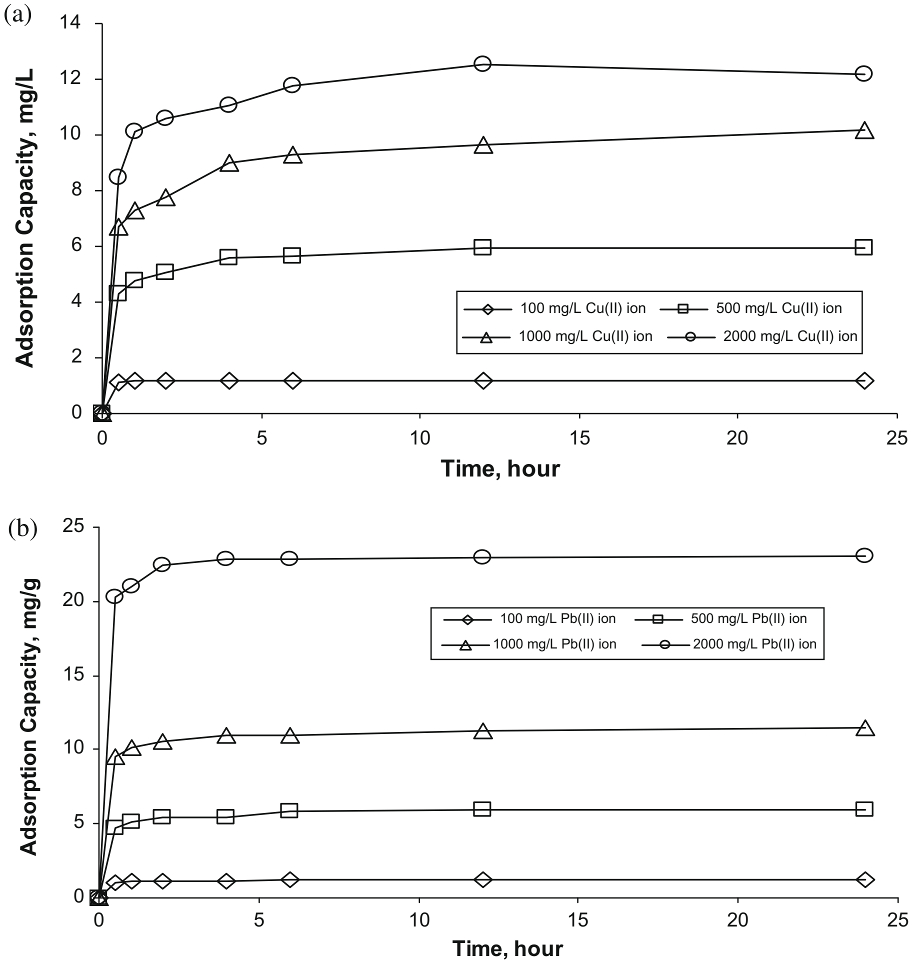


Fig. 5. Effect of initial concentration and contact time on equilibrium adsorption (a) Cu(II) ions and (b) Pb(II) ions onto chitosan-coated sand.

increased from 69.91% to 99.84% over pH range from 2 to 6. However, the influence on retention was minimal for the succeeding values (pH 4–6) regardless of contact time. This effect suggested that the amino group was deprotonated. The chelation mechanism outranked the adsorption mechanism where more metal ions chelate with chitosan.

Adsorption of Cu(II) ions was remarkably different and more successful (>99.84%) than Pb(II) ions at extended contact times with lower pH values (pH 2). Although both Cu(II) and H^+ ions were present at this pH value, Cu(II) ions were able to compete well for the active sites (Hasan et al., 2008). As seen in Table 4, solution pH has an important role in the adsorption of Cu. This behavior might be explained by two possible mechanisms: (1) the bridging ligand effect, and (2) the adsorption of anionic specie. In mechanism (1), there was greater complexion due to the presence of excess chlorine ions (Cl^-) produced by the addition of HCl when the pH was adjusted, which can be explained by the dominant presence of chlorine ions at pH 2 rather than pH 3. It is known that depending on the Cl^- concentration, Cu can form a great variety of complexes using chloride as a bridge (Taboada et al., 2003). Although Pb(II) has similar characteristic, the ionic size of Cu(II) ion is smaller than Pb(II) ion, which produce the reduction of steric hindrance effect. The occurrence of the mentioned complexes can generate retention since more than one metal ion occupies each active sites for adsorption.

Relative to mechanism (2), the adsorption of anionic species emerged at lower pH, since there was also formation of stable sulfates ($SO_4{}^{-2}$) and nitrates ($NO_3{}^-$) from salts of Cu(II) and Pb(II), respectively, which probably led to the interaction between the $NH_3{}^+$ functional group and the anions. The higher charge of $SO_4{}^{-2}$ than $NO_3{}^-$ might be more effective in charge compensation and ionic bonding (Darder, Colilla, & Ruiz-Hitzky, 2003). Furthermore, the chelation of the metal ions was sustained by the stronger binding of sulfates, which resulted in higher adsorption efficacy of Cu(II) ions compared to Pb(II) ions. In this pH range studied, the stability of the metal complexes correlated well with the pH insensitivity of the Cu(II) equilibrium.

3.3. Kinetics of adsorption

To investigate the controlling mechanism of the adsorption processes, pseudo first-order and pseudo second-order kinetic equations were examined. Table 5 shows the adsorption kinetic studies of Cu(II) and Pb(II) ions onto CCS at different C_o where the experimental data was best fitted for the pseudo second-order equation. The pseudo first-order kinetic model did not adequately describe the adsorption results with a low correlation coefficient for the entire data (Cu(II) = 0.2608–0.1894 and Pb(II) = 0.4347–0.1304). R^2 for the Pb(II) ions were lower than those for the Cu(II) ions except for the lowest concentration. However, the pseudo second-order kinetic model provided an impressive and comparable correlation for the adsorption of both ions in contrast to the pseudo first-order model.

The pseudo first-order rate expression has been widely used for sorption of metals (Săg & Aktay, 2002), which was widely used for reversible reactions with an equilibrium being established

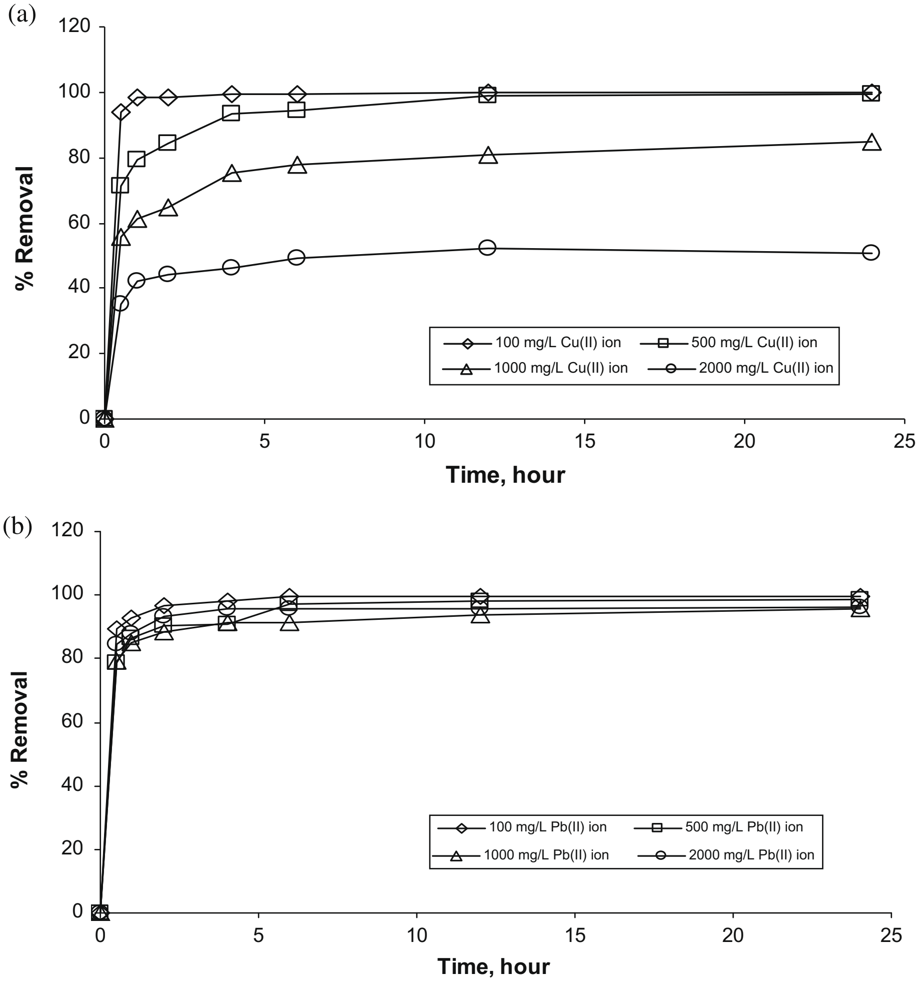


Fig. 6. Adsorption percentage at different concentration and contact time of (a) Cu(II) ion and (b) Pb(II) ion onto chitosan-coated sand.

Table 3
Adsorption kinetic of metal ions onto chitosan-coated sand (CCS).

Initial concentration, mg/L	Copper(II)		Lead(II)	
	Equilibrium adsorption capacity, mg/g	% Adsorption	Equilibrium adsorption capacity, mg/g	% Adsorption
100	1.196	99.77	1.188	99.14
500	5.787	96.57	5.697	95.06
1000	9.530	79.53	11.046	92.17
2000	12.159	50.79	22.836	95.15

Table 4
Effect of pH and contact time on% adsorption: (a) Cu(II) ions and (b) Pb(II) ions onto chitosan-coated sand (CCS).

pH	Time (h)						
	0.5	1	2	4	6	12	24
(a) Cu(II) ions							
2	93.46	97.23	97.43	98.53	98.91	99.85	99.88
3	93.54	98.14	98.31	99.24	99.34	99.79	99.89
4	93.70	98.21	98.33	99.46	99.50	99.90	99.94
5	95.24	98.95	99.48	99.50	99.84	99.90	99.89
6	99.07	99.38	99.58	99.81	99.92	99.88	99.93
(b) Pb(II) ions							
2	43.77	52.26	58.45	63.85	64.04	64.04	69.91
3	86.75	90.96	94.24	94.91	98.13	98.13	99.26
4	93.76	95.77	98.65	99.56	99.61	99.61	99.84
5	93.76	95.77	98.65	99.56	99.61	99.61	99.84
6	90.98	96.94	98.04	99.60	99.63	99.63	99.84

between liquid and solid phases. In many cases, the pseudo first-order do not fit well to the whole range of contact time and is generally applicable over the initial stage of adsorption process (Ho & McKay, 1998).

Ho (2006) illustrated that the pseudo second-order reaction was used to distinguish the kinetic equation based on the concentration of a solution from the adsorption capacity of a solid. In this study, the rate constant k_2 was determined experimentally by plotting the slopes and intercepts of t/q_t against t. The high correlation coefficient shown in Table 5 illustrated an agreement of experimental data with the pseudo second-order kinetic model (Eq. (4)) for different Cu(II) and Pb(II) ion concentrations. The overall adsorption rate for both ions appeared to be controlled by the chemical process. The conclusion is based on the assumption that chemisorption involved sharing or exchange of electrons as covalent forces between the transition metal cations and adsorbent and ion exchange (Ho, 2006).

Based on the equation, the adsorption rate dq/dt is proportional to the second-order of $(q_e - q)$. High adsorption equilibrium capacity, q_e, will result in fast adsorption rates and short equilibrium times. Short equilibrium times coupled with high adsorption capacity indicates a high degree of affinity between Cu(II) and Pb(II) ions and CCS (Chiou and Li, 2002). Moreover, several studies

Table 5
Adsorption kinetic studies of Cu(II) and Pb(II) ions onto chitosan-coated sand (CCS).

Initial Conc. (mg/L)	Copper				Lead			
	Pseudo first-order		Pseudo second-order		Pseudo first-order		Pseudo second-order	
	k (min^{-1})	R^2	k (g/mg min)	R^2	k (min^{-1})	R^2	k (g/mg min)	R^2
100	0.00003	0.2608	0.8328	1.0000	0.00005	0.4347	0.8369	1.0000
500	0.0003	0.2201	0.1663	0.9997	0.0003	0.1805	0.1680	0.9998
1000	0.0004	0.2294	0.0979	0.9986	0.0004	0.1509	0.0870	0.9997
2000	0.0004	0.1894	0.0806	0.9991	0.0004	0.1304	0.0433	1.0000

Table 6
Summary of adsorption isotherms studies for Cu(II) and Pb(II) ions onto chitosan-coated sand(CCS).

Time (h)	Langmuir isotherm				Freundlich isotherm			
	Copper		Lead		Copper		Lead	
	R^2	Q_{max}	R^2	Q_{max}	R^2	n	R^2	n
0.5	0.9900	6.62	0.9883	14.77	0.9896	2.54	0.9533	1.23
1	0.9862	7.00	0.9931	16.75	0.9994	3.01	0.9796	1.25
2	0.9893	7.47	0.9874	13.59	0.9942	2.94	0.9316	1.39
4	0.9916	8.18	0.9824	12.32	0.9729	3.38	0.8921	1.49
6	0.9906	8.40	0.9860	11.01	0.9784	3.38	0.9696	1.96
12	0.9902	8.64	0.9901	11.92	0.9625	4.44	0.9437	2.01
24	0.9908	8.76	0.9910	12.38	0.9417	4.51	0.9834	1.86

for adsorption of divalent metals on heterogeneous sorbents reported that the majority of the metal sorption kinetics follows pseudo second-order mechanisms (Ho, 2006).

3.4. Adsorption isotherm

The experimental adsorption data were examined by Langmuir and Freundlich isotherm equations to indicate the possible adsorption mechanism. In this work, the regression coefficients were selected to indicate good linearity, which confirmed that the Cu(II) and Pb(II) ions followed the two theories of adsorption (Table 6). The calculated data of Langmuir isotherm which exhibited the highest regression correlation for both ions (>98%) described a better fitting model than it of Freundlich isotherm. The poorer agreement of Freundlich isotherm with the experimental data was justified by the low R^2 even if the magnitude of the exponent for both ions is greater than 1. However, the values of n (>1) for both ions indicate favorable condition and good adsorption onto CCS.

The Langmuir isotherm model is most suitable for monolayer adsorption based on the assumption described that there are finite numbers of adsorption sites. All sites are equivalent and there is no interaction between adsorbed ions. The result indicates the applicability of monolayer coverage on the surface of CCS in spite of the surface modification.

As illustrated in Table 6, the maximum adsorption capacities of Cu(II) and Pb(II)ions were obtained (8.18 mg Cu/g and 12.32 mg Pb/g CCS) at the equilibrium period (4 h). From the Q_{max} results provided by Langmuir isotherm, the higher adsorption capacity of Pb(II) on CCS over Cu(II) were consistent with the batch adsorption studies. The strong intermolecular attraction of the adsorbate to the surface of CCS has been clearly justified by the isotherm (Annadurai et al., 2008).

3.5. Desorption studies

Desorption illustrates the stability and potential recovery between the adsorbate and adsorbent. Recovery of adsorbed material is important for metal ion recycling processes. In this investigation, tap water and diluted HCl solution with pH 1 and 3 were used. As shown in Tables 7 and 8, HCl solution (pH 1) obtained higher desorption capacity in both conditions. More than 95% of both ions were stripped at the low-pH condition, which exhibited probability for recovering the adsorbed metal ions. Moreover, desorption study using tap water resulted in lesser amount of metal ions leached out from the CCS. Tap water contributed very low% of recovery (Cu(II) $\leqslant$ 5.03% and Pb(II) $\leqslant$ 33.15%) suggested strong and stability bonding between metal ions and CCS under neutral conditions.

Table 8 indicated that increasing the contact time is insignificant in the desorption of Cu(II) and Pb(II) ions in acidic medium. Consistently, there was a higher percentage of desorption of the latter regardless of initial concentration, which was strongly influenced by a considerable amount of Pb in solution. Moreover, variation in Cu concentrations illustrates little effect on desorption from CCS. Finally, the results of these desorption studies convey the enormous potential for recovering Cu(II) and Pb(II) ions from CCS, which has practical implications for building filters along a contaminated stream of groundwater. CCS could be a beneficial

Table 7
Percent desorption using diluted HCl solution at pH 1, pH 3 and tap water for Cu(II) ion from Cu(II)–chitosan-coated sand and Pb(II) ion from Pb(II)–chitosan-coated sand.

Desorption solution	Initial conc. (mg/L)	Cu(II) ions adsorbed (mg/L)	Cu(II) desorbed (mg/L)	% Desorption	Pb(II) ions adsorbed (mg/L)	Pb(II) desorbed (mg/L)	% Desorption
HCl (pH = 1)	100	98.35	92.18	93.73	96.55	85.36	88.41
	500	421.77	417.44	98.97	451.31	441.86	97.91
	1000	646.96	641.94	99.22	883.67	841.45	95.22
	2000	881.40	837.81	95.05	1869.49	1770.08	94.68
HCl (pH = 3)	100	99.518	8.6906	8.73	97.904	54.10	55.26
	500	467.97	52.48	11.21	455.24	241.16	52.97
	1000	750.88	98.07	13.06	913.31	389.49	42.65
	2000	922.00	113.37	12.30	1911.12	567.46	29.69
Tap water (pH = 7)	100	99.97	2.03	5.03	99.56	9.08	9.12
	500	494.71	5.37	1.09	491.61	79.58	16.19
	1000	808.00	8.79	1.09	938.84	249.45	26.57
	2000	1046.80	2.39	0.23	1911.46	633.64	33.15

Table 8
Percent desorption of metal ion from metal-CCS using dilute acid solution of pH 3.

Initial conc. (mg/L)	% Cu(II) desorption		% Pb(II) desorption	
	4-h adsorption studies	6-h adsorption studies	4-h adsorption studies	6-h adsorption studies
100	8.73	8.41	55.26	55.88
500	11.21	10.46	52.97	49.65
1000	13.06	12.40	42.65	43.27
2000	12.30	11.99	29.69	32.11

bioadsorbent in creating a permeable reactive barrier for the recovery of metals.

4. Conclusion

Chitosan-coated sand (CCS) bioadsorbent has demonstrated high efficiency in removing Cu(II) and Pb(II) ions from water. The amount of adsorbed metal ions was higher with increasing pH for Pb(II) ion but were insignificant for Cu(II). The equilibrium studies were described by using both Langmuir and Freundlich isotherm models. The Langmuir isotherm illustrated the best description of the metal adsorption mechanism. The maximum adsorption capacity of Cu(II) and Pb(II) ions were 8.18 and 12.32 mg/g, respectively. Moreover, the equilibrium kinetics agreed very well with pseudo second-order kinetics, which indicated that the adsorption was controlled by chemisorption. Moreover, desorption studies illustrated that adsorbed metal ions could be recovered under acidic conditions. The bonding strength between metal ions and bioadsorbent exhibits higher stability under neutral conditions.

This study has evidenced that the possible adsorption behavior of CCS to remove copper and lead ions from water. Desorption study has also evaluated the possible metal recovery from bioadsorbents. In conclusion, these preliminary results indicate the possibility of using CCS to establish inexpensive large-scale filters as a permeable reactive barrier for metal removal in contaminated groundwater plumes.

Acknowledgements

The author would like to acknowledge Sonia Buscano, University of Philippines-Diliman, Diliman, Quezon City, Philippines, and Prof. Teh-Fu Yen, University of Southern California, CA., U.S. for their technical assistance in preparing this manuscript, and Taiwan National Science Council (NSC 96-2221-E-041-003) for their financial support.

References

Annadurai, G., Ling, L. Y., & Lee, J. F. (2008). Adsorption of reactive dye from an aqueous solution by chitosan: Isotherm, kinetic and thermodynamic analysis. *Journal of Hazardous Materials, 152*, 337–346.

Baroni, P., Vieira, R. S., Meneghetti, E., da Silva, M. G. C., & Beppu, M. M. (2008). Evaluation of batch adsorption of chromium ions on natural and crosslinked chitosan membranes. *Journal of Hazardous Materials, 152*, 1155–1163.

Bhattacharyya, K. G., & Gupta, S. S. (2006). Kaolinite, montmorillionite, and their modified derivatives as adsorbents for removal of Cu(II) from aqueous solution. *Separation and Purification Technology, 50*, 388–397.

Boddu, V. M., Abburi, K., Talbott, J. L., & Smith, E. D. (2003). Removal of hexavalent chromium from wastewater using a new composite chitosan biosorbent. *Environmental Science & Technology, 37*, 4449–4456.

Chen, A. H., Liu, S. C., Chen, C. Y., & Chen, C. Y. (2008). Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin. *Journal of Hazardous Materials, 154*, 184–191.

Chen, A. H., Yang, C. Y., Chen, C. Y., Chen, C. Y., & Chen, C. W. (2009). The chemically crosslinked metal-complexed chitosans for comparative adsorptions of Cu(II), Zn (II), Ni(II) and Pb(II) ions in aqueous medium. *Journal of Hazardous Material, 163*(2–3), 1068–1075.

Chiou, M. S., & Li, H. Y. (2002). Equilibrium and kinetic modeling of adsorption of reactive dye on cross-linked chitosan beads. *Journal of Hazardous Materials, B93*, 233–248.

Chu, K. H. (2002). Removal of copper from aqueous solution by chitosan in prawn shell: Adsorption equilibrium and kinetics. *Journal of Hazardous Materials, B90*, 77–95.

Darder, M., Colilla, M., & Ruiz-Hitzky, E. (2003). Biopolymer–clay nanocomposites based on chitosan intercalated in montmorillonite. *Chemistry Material, 15*, 3774–3780.

Evans, J. R., Davids, W. G., MacRae, J. D., & Amirbahman, A. (2002). Kinetics of cadmium uptake by chitosan-based crab shells. *Water Research, 36*, 3219–3226.

Gyliene, O., & Visniakova, S. (2008). Heavy metal removal from solutions using natural and synthetic sorbents. *Environmental Research, Engineering and Management, 43*, 28–34.

Hasan, S., Ghosh, T. K., Viswanath, D. S., & Boddu, V. M. (2008). Dispersion of chitosan on perlite for enhancement of copper (II) adsorption capacity. *Journal of Hazardous Materials, 152*, 826–837.

Ho, Y. (2006). Review of second-order models for adsorption systems. *Journal of Hazardous Materials, B136*, 681–689.

Ho, Y. S., & McKay, C. (1998). Kinetic model for Lead(II) sorption on to peat. *Adsorption Science and Technology, 16*, 243–255.

Juang, R. S., Tseng, R. L., Wu, F. C., & Lee, S. H. (1997). Adsorption behavior of reactive dyes from aqueous solutions on chitosan. *Journal of Chemical Technology & Biotechnology, 70*, 391–399.

Masel, R. I. (1996). *Principles of adsorption and reaction on solid surfaces*. Wiley-IEEE. p. 143.

Ng, J. C. Y., Cheung, W. H., & McKay, G. (2002). Equilibrium studies of the sorption of Cu(II) ions onto chitosan. *Journal of Colloid and Interface Science, 255*, 64–74.

Nomanbhay, S. M., & Palanisamy, K. (2005). Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic Journal of Biotechnology, 8*, 43–53.

Paulino, A. T., Guilherme, M. R., Reis, A. V., Tambourgi, E. B., Nozaki, J., & Muniz, E. C. (2007). Capacity of adsorption of Pb^{2+} and Ni^{2+} from aqueous solutions by chitosan produced from silkworm chrysalides in different degrees of deacetylation. *Journal of Hazardous Materials, 147*, 139–147.

Pradhan, S., Shukla, S. S., & Dorris, K. L. (2005). Removal of nickel from aqueous solutions using crab shells. *Journal of Hazardous Materials, B125*, 201–204.

Săg, Y., & Aktay, Y. (2002). Kinetic studies on sorption of Cr(VI) and Cu(II) ions by chitin, chitosan and *Rhizopus arrhizus*. *Biochemical Engineering Journal, 12*, 143–153.

Saifuddin, N., & Raziah, A. Z. (2007). Removal of heavy metals from industrial effluent using *Saccharomyces cerevisiae* (Baker's Yeast) immobilized in chitosan/lignosulphonate matrix. *Journal of Applied Sciences Research, 3*, 2091–2099.

Sakaguchi, T., Horikoshi, T., & Nakajima, A. (1981). Adsorption of uranium by chitin phosphate and chitosan phospate. *Agricultural and Biological Chemistry, 45*, 2191–2195.

Schmuhl, R., Krieg, H. M., & Keizer, K. (2001). Adsorption of Cu(II) and Cr(IV) ions by chitosan: Kinetics and equilibrium studies. *Water SA, 27*, 1–7.

Taboada, E., Cabrera, G., & Cardenas, G. (2003). Retention capacity of chitosan for copper and mercury ions. *Journal of the Chilean Chemical Society*, *48*, version on-line.

Varma, A. J., Deshpande, S. V., & Kennedy, J. F. (2004). Metal complexation by chitosan and its derivatives: A review. *Carbohydrate Polymers, 55*, 77–93.

Vieira, R. S., & Beppu, M. M. (2006). Dynamic and static adsorption and desorption of Hg (II) ions on chitosan membranes and spheres. *Water Research, 40*, 1726–1734.

Wan Ngah, W. S., Ab Ghani, S., & Kamari, A. (2005). Adsorption behaviour of Fe(II) and Fe(III) ions in aqueous solution on chitosan and cross-linked chitosan beads. *Bioresource Technology, 96*, 443–450.

Wan, M. W., Petrisor, I. G., Lai, H. T., Kim, D., & Yen, T. F. (2004). Copper adsorption through chitosan immobilized on sand to demonstrate the feasibility for in situ decontamination. *Carbohydrate Polymers, 55*, 249–254.

Zhou, Y. S., Yang, D. Z., & Nie, J. (2007). Preparation and characterization of crosslinked chitosan-based nanofibers. *Chinese Chemical Letters, 18*, 118–120.