



Pb(II) biosorption using chitosan and chitosan derivatives beads: Equilibrium, ion exchange and mechanism studies

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Abstract

The study examined the adsorption of Pb(II) ions from aqueous solution onto chitosan, chitosan-GLA and chitosan-alginate beads. Several important parameters influencing the adsorption of Pb(II) ions such as initial pH, adsorbent dosage and different initial concentration of Pb(II) ions were evaluated. The mechanism involved during the adsorption process was explored based on ion exchange study and using spectroscopic techniques. The adsorption capacities obtained based on non-linear Langmuir isotherm for chitosan, chitosan-GLA and chitosan-alginate beads in single metal system were 34.98, 14.24 and 60.27 mg/g, respectively. However, the adsorption capacity of Pb(II) ions were reduced in the binary metal system due to the competitive adsorption between Pb(II) and Cu(II) ions. Based on the ion exchange study, the release of Ca^{2+} , Mg^{2+} , K^+ and Na^+ ions played an important role in the adsorption of Pb(II) ions by all three adsorbents but only at lower concentrations of Pb(II) ions. Infrared spectra showed that the binding between Pb(II) ions and the adsorbents involved mostly the nitrogen and oxygen atoms. All three adsorbents showed satisfactory adsorption capacities and can be considered as an efficient adsorbent for the removal of Pb(II) ions from aqueous solutions.

Key words: chitosan and chitosan derivatives beads; ion exchange; mechanism

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Introduction

Lead is one of the most useful metals due to its wide distribution and its easiness to be extracted and to work with. Lead has many functions, ranging from sheets for roofing, to pipes and blocks for screening from radioactive emissions (Lenihan and Fletcher, 1977). However, lead has the most damaging effects on human health, whereby it can enter the human body through uptake of food (65%), water (20%) and air (15%) (Nurchi and Villaescusa, 2008). Acute lead poisoning in humans causes severe dysfunction in the kidneys, liver, brain and the central nervous system (Manahan, 2000; Li and Bai, 2006). It is necessary to develop an effective and efficient method to remove Pb(II) ions from wastewaters. The presence of lead in industrial effluents and waste from development projects that are located within catchments area in Malaysia should not exceed 0.10 mg/L as has been stated in the Environmental Quality (Sewage and Industrial Effluents) regulations established in 1979.

Adsorption using low-cost natural adsorbents such as agricultural wastes, clay materials and seafood processing wastes is one of the few promising alternatives which can be applied to wastewaters with low concentrations of heavy metal ions (Juang and Shao, 2002a, 2002b). Chitosan is well established as an excellent natural adsorbent because

its amine ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) groups may serve as coordination sites to form complexes with various heavy metal ions. However, due to its poor acidic resistance and mechanical strength, further treatments are necessary to improve its chemical resistance. Glutaraldehyde (GLA) is the most frequently used cross-linking agent as it is capable in preventing the dissolution of chitosan in acidic solution. Although the stability of the cross-linked chitosan was improved, this cross-linking process decreases the number of amino groups, resulting in a decrease in the adsorption capacity (Vieira and Beppu, 2006). Currently, other alternatively modifications have been performed to improve the chemical stability without losing the adsorption capacity of chitosan.

Chitosan being a linear polyelectrolyte at acidic pH is capable in forming electrostatic complexes with synthetic or natural polyelectrolyte especially alginate. Alginate is derived from brown algae and it comprises of two repeating carboxylate monosaccharide units. Chitosan and alginate can be blended to form polyelectrolyte complex through ionic interaction between the protonated amines on chitosan and carboxylate moieties found on alginate. This interaction forms a three dimensional matrix, and the beads are known as physically cross-linked (Lawrie et al., 2007). This polyelectrolyte complex has a wide range of usage in the medical and biological field.

In the present study, chitosan, chitosan-GLA and

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chitosan-alginate beads were used to remove Pb(II) ions from aqueous solution in batch adsorption system. The effects of initial pH, adsorbent dosage and initial concentrations of Pb(II) ions were studied. To predict the nature of the adsorption process, the non-linear Langmuir and Freundlich isotherms were used to fit the equilibrium adsorption data. Adsorption study was also conducted in the presence of Cu(II) ions to help to identify the selectivity nature of the adsorbent studied. An ion exchange study was carried out to determine whether the adsorption of Pb(II) ions onto chitosan, chitosan-GLA and chitosan-alginate beads involved ion-exchange process. The ratios of Pb(II) ions adsorbed to Ca^{2+} , Mg^{2+} , K^{+} and Na^{+} ions released were determined.

1 Materials and methods

1.1 Materials

Samples of chitosan flakes with degree of deacetylation of 67.29% (determined using infrared spectroscopy method), were kindly supplied by Chito-Chem (M) Sdn. Bhd., Malaysia. Glutaraldehyde (GLA) and alginic acid sodium salt from brown algae were purchased from Fluka (Germany). All the reagents used throughout this study were analytical-reagent grade. Distilled water was used to prepare solutions.

1.2 Preparation of chitosan beads

Chitosan beads were prepared according to the procedure described previously (Wan Ngah and Fatinathan, 2006, 2008). Chitosan solution was prepared by dissolving 2.00 g of chitosan flakes in 60 mL of 5% (V/V) acetic acid solution. The viscous solution was left overnight before adding it drop wise into 500 mL of 0.50 mol/L NaOH solution and stirred continuously. The beads were left in the solution for about half an hour to ensure that the acetic acid in the chitosan beads was neutralized. The chitosan beads were then filtered, rinsed with distilled water and finally air-dried. The chitosan beads were ground and sieved to a constant particle size ($< 200 \mu\text{m}$).

1.3 Preparation of chitosan-GLA beads

The chitosan-GLA beads were prepared according to the previous method (Wan Ngah and Fatinathan, 2006, 2008). Chitosan beads prepared as in previous section were suspended in 0.025 mol/L glutaraldehyde solution to obtain a ratio of 1:1 (CHO:NH₂, mol:mol) chitosan-GLA beads. CHO groups are found in GLA while -NH₂ groups are found in chitosan. The chitosan beads were left in the solution for 24 hr at room temperature under continuous stirring. After 24 hours, the beads were filtered and rinsed with hot followed by cold distilled water. The chitosan-GLA beads were then air-dried, ground and sieved to a constant particle size ($< 200 \mu\text{m}$).

1.4 Preparation of chitosan-alginate beads

The preparation of chitosan-alginate beads was carried out based on the previous method (Wan Ngah and

Fatinathan, 2008). A 2.00-g of chitosan flakes were dissolved into 60 mL of 5% (V/V) acetic acid solution. A solution of 5% (W/V) of alginic acid was prepared by adding distilled water to the alginic acid sodium salt powder. Both the solutions were left standing overnight. The chitosan gel was then stirred on a hot plate stirrer at 60°C for 30 min. Then, the alginic acid solution was added into the chitosan gel solution and was stirred at 60°C for another 20 min. The blended gel solution was dropped into 500 mL of 0.50 mol/L NaOH solution under continuous stirring. The beads were filtered and rinsed with distilled water to remove excess NaOH. Then the beads were air-dried, ground and sieved to a constant particle size of $< 200 \mu\text{m}$.

1.5 Characterization of chitosan, chitosan-GLA and chitosan-alginate beads

In order to understand the adsorption mechanism, several characterizations were carried out on all three adsorbents. Spectroscopic analysis was carried out using a Fourier transform infrared spectrophotometer (FT-IR System 2000 Model, PerkinElmer, USA) to identify the types of functional groups found in chitosan, chitosan-GLA and chitosan-alginate beads. The contents of carbon, hydrogen and nitrogen were determined by CHNS/O analyzer (Series II CHNS/O Analyzer 2400, PerkinElmer, USA). The surface areas were analyzed for all three beads using a Micromeritics ASAP 2010 gas adsorption surface analyzer (Delta Analytical Instruments Inc., USA).

The pH_{ZPC} values of the adsorbents were determined by modifying the methods described by Onyango et al. (2004) and Santos et al. (2007). The initial pH of 50 mL of 0.01 mol/L NaCl solution was adjusted to a value between of 2 and 12 by adding either 0.1 mol/L HCl or 0.1 mol/L NaOH solution. Then, 0.15 g of the adsorbent was added, stirred and the final pH of the solution was measured after 48 hours. The pH_{ZPC} value of the adsorbent was found based on the plateau obtained by plotting the final pH against the initial pH (Santos et al., 2007).

1.6 Adsorption equilibrium studies

A stock solution of 1000 mg/L of Pb(II) ions was prepared using analytical-reagent grade lead(II) nitrate salt. The stock solution was diluted to appropriate concentrations accordingly. Each experiment was carried out in duplicates and the average values were presented. All filtrate was analyzed using atomic absorption spectrometer (AAAnalyst 200 AA, PerkinElmer, USA) at a wavelength of 283.31 nm for Pb(II) ions while 324.75 nm for Cu(II) ions.

The effect of initial pH on the adsorption of Pb(II) ions was conducted using 0.050 g of adsorbent with 50 mL of 10 mg/L Pb(II) ions solution. The pH range studied was 1–6. The adsorbent was stirred in the Pb(II) ions solution at 400 r/min for 60 min. Once the optimum pH has been determined, the effect of adsorbent dosage was studied by varying the amount of adsorbent from 0.025 to 1.00 g under the optimum pH and agitation period of 100 min.

The isotherm study for chitosan, chitosan-GLA and chitosan-alginate beads in single metal system was

conducted with a constant adsorbent weight and varying the initial concentration of Pb(II) ions in the range of 20–300 mg/L. About 0.20 g of chitosan and chitosan–alginate beads with a contact time of 100 min at pH 4.5 was used for the equilibrium study. Meanwhile, for chitosan–GLA beads, a contact time of 100 min at pH 4.5 with 0.50 g of beads was applied. All solutions were stirred at 400 r/min. The following Eq. (1) was used to calculate the adsorption capacity (q_e) of Pb(II) ions:

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

where, C_0 (mg/L) is the initial concentration of Pb(II) ions, C_e (mg/L) is the final concentration of Pb(II) ions, V (L) is the volume of Pb(II) ions solution and W (g) is the weight of the adsorbent used. The isotherm study was also conducted in binary metal system at room temperature. The initial concentrations of Pb(II) and Cu(II) ions used were in the range of 20–300 mg/L.

An ion exchange study was conducted in the range of 5–30 mg/L of Pb(II) ions solutions for all three adsorbents under the optimum conditions determined earlier. The initial pH of the lead solution was adjusted to 4.5. After adsorption, the amounts of Ca^{2+} , Mg^{2+} , K^+ and Na^+ ions were determined. The final pH of the solution was also measured. A blank experiment was also conducted to determine the possibility of leaching of these four cations from the adsorbents into distilled water. The net release of cations was calculated by subtracting the amount of cations released in the blank from the amount of cations measured in the effluent after Pb(II) ions adsorption.

2 Results and discussion

2.1 Characterization of chitosan, chitosan–GLA and chitosan–alginate beads

The C, H, and N compositions of chitosan beads determined by CHNS/O analyzer were 37.51%, 6.12% and 6.53%, respectively. Meanwhile, the percentage of C, H and N obtained for chitosan–GLA beads were 41.31%, 6.23% and 5.30%, respectively. The percentage of N in chitosan–GLA beads was lower than the percentage of N in chitosan beads. This is because during the cross-linking process the N atoms of the amine groups were consumed as the imine bond ($\text{C}=\text{N}$) were formed due to the Schiff base reaction between amine groups in chitosan beads with the aldehyde groups in GLA. This cross-linking process brings changes in the chemical structure of N atoms. The percentages of C, H and N for chitosan–alginate beads were 37.85%, 5.96% and 6.48%, respectively. The percentages of all three elements were almost similar to chitosan beads because the formation of the chitosan–alginate beads is due to the strong electrostatic interaction between the carboxylate moieties ($-\text{COO}^-$) on alginate and the protonated amine groups ($-\text{NH}_3^+$) of chitosan. Moreover, during the formation of this polyelectrolyte complex, no new bond was formed and the chemical structure of the N atoms of amine groups does not change as can be observed in the cross-linked beads.

The ratios of C/N for chitosan, chitosan–GLA and chitosan–alginate beads were 5.74, 7.79 and 5.84, respectively. It was found that chemically cross-linked chitosan has a higher C/N ratio while the polyelectrolyte complex (ionic interaction) has C/N ratio almost similar to the chitosan. It shows that chemical modification tend to effect the carbon and nitrogen content in chitosan. The higher the C/N ratio could also contribute to the lowering of the adsorption capacity of polymer.

The pH_{ZPC} values for chitosan, chitosan–GLA and chitosan–alginate beads were 7.29, 7.43 and 7.99, respectively. Based on these values, the prepared adsorbents were all bases. The pH_{ZPC} of chitosan–GLA beads was almost similar to the pH_{ZPC} of the chitosan beads. However, for chitosan–alginate beads the pH_{ZPC} was higher than the pH_{ZPC} of chitosan beads. This could be due to the alginate, which was used to prepare the polyelectrolyte complex. The alginate used in this study was prepared using alginic acid sodium salt.

For chitosan, chitosan–GLA and chitosan–alginate beads the BET surface area were 0.3269, 0.4091 and 0.2903 m^2/g , respectively; the Langmuir surface area were 0.5016, 0.6172 and 0.4475 m^2/g , respectively; and the average pore diameter respectively were 12.86, 12.70 and 16.32 nm, indicating the presences of mesopores on all three beads. The pore diameter obtained for chitosan–GLA beads were almost similar with chitosan beads, however, the surface area increased for chitosan–GLA beads. This indicates that the anatomic structure of the chemically cross-linked beads was changed little and the changes happened on the surface only. However, for chitosan–alginate beads, a lower surface area and a larger pore diameter were observed, which show that the polyelectrolyte complex leads changes in the anatomic structure and on the surface of the beads as well.

2.2 Effect of pH and adsorbent dosage

The initial pH range was set between 1–6 to avoid any uncertainty arising due to the formation of insoluble hydroxide, $\text{Pb}(\text{OH})_2$, at pH values higher than 7. The adsorption of Pb(II) ions was highly dependent on the pH of the metal solution because pH can affect the solubility of the metal ions and at the same time influence the ionization state of the functional groups existing on the adsorbent (Tunali et al., 2006). As shown in Fig. 1, the adsorption capacities were very low for all three adsorbents at pH

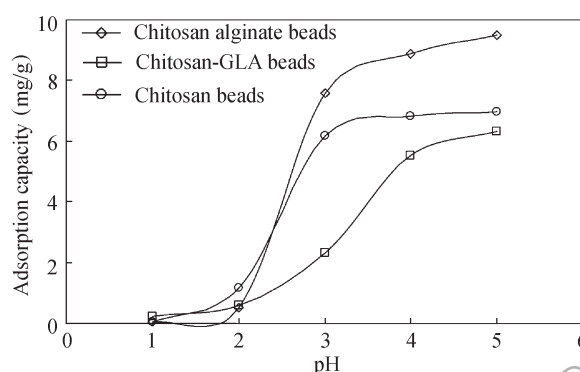


Fig. 1 Effect of initial pH on the adsorption of Pb(II) ions onto chitosan, chitosan–GLA and chitosan–alginate beads.

< 2, due to an increase in the positively charged active sites (NH_3^+) at lower pH for chitosan and chitosan-GLA beads. This causes a repulsion between Pb(II) ions and the protonated NH_3^+ group. Moreover, the H^+ ions in the solution at lower pH will compete with metal ions for the active sites ($-\text{NH}_2$) and therefore reducing the adsorption capacity. In addition to that, the formation of more NH_3^+ sites on the surface will increase the electrostatic repulsion between Pb(II) ions and the surface of the beads, causing a decrease in the adsorption capacity.

Meanwhile, for chitosan-alginate beads the $-\text{COOH}$ groups would retain its protons causing the reduction in the probability of binding between Pb^{2+} and $-\text{COO}^-$ groups. Moreover, the NH_3^+ groups which are not involved in the ionic interaction will be protonated as well, reducing the probability of binding to any positively charged ions (Vijaya et al., 2008). All three adsorbents have high swelling percentages in the acidic solution, as has been reported in the previous work (Wan Ngah and Fatinathan, 2008). Beads with high percentage of swelling are very brittle and are not good adsorbents. At $\text{pH} > 3$, there would be a decrease in the protonation of the active sites, therefore the adsorption capacities for chitosan and chitosan-alginate beads were high ($> 6.95 \text{ mg/g}$), while for chitosan-GLA beads it was gradually increasing as well (Fig. 1). The maximum adsorption of Pb(II) ions onto the three adsorbents occurred at pH 4.5, therefore this pH value was selected as the optimum pH throughout this study.

The dependence of Pb(II) ions adsorption on adsorbent dosage was studied by varying the dosage from 0.025 to 1.00 g while keeping all other parameters at constant. As the dosage was increased, the percentage of removal increased as well (plot was not shown). This was due to the greater availability of exchangeable sites for Pb(II) ions. The percentages of removal for all three adsorbents were more than 60%. However, the adsorption capacity decreased with increasing adsorbent dosage. This was due to the higher number of unsaturated adsorption sites as the adsorbent dosage was increased (Amarasinghe and Williams, 2007). The maximum values of Pb(II) ions removal were 94.35% for chitosan beads (0.2 g), 70.52% for chitosan-GLA beads (0.5 g) and 93.81% for chitosan-alginate beads (0.2 g). Further increment in the dosage did not increase the percentage of removal as a plateau was observed after the particular dosage.

2.3 Equilibrium adsorption isotherm (single metal system)

Adsorption isotherms are very important for the analysis of adsorption process as it indicates how the adsorbate molecules distribute between the liquid phase and the solid phase once the system reached an equilibrium state. The most widely used Langmuir isotherm, is valid for monolayer adsorption onto a surface with a finite number of identical sites and the sites are homogeneous. It can be expressed as Eq. (2) (Septum et al., 2007):

$$q_e = \frac{bQC_e}{1 + bC_e} \quad (2)$$

where, C_e (mg/L) is the equilibrium concentration of remaining metal ions in the solution; Q (mg/g) is the amount of metal ions at complete monolayer and b (mL/mg) is the Langmuir constant related to the affinity of binding sites and is a measure of the energy of adsorption.

The Freundlich isotherm is an empirical equation based on adsorption on a heterogeneous surface. This model is applicable to the adsorption of a single-solute system within a fixed concentration range (Chang and Juang, 2004). The Freundlich isotherm is commonly presented as Eq. (3):

$$q_e = K_F C_e^{1/n} \quad (3)$$

where, K_F and n (dimensionless) are Freundlich constants characterizing the adsorption capacity and intensity, respectively. The metal adsorption data were analyzed based on the non-linear form of the isotherms (plots were not shown). The results obtained are shown in Table 1.

Table 1 Isotherm constants for adsorption of Pb(II) ions onto chitosan, chitosan-GLA and chitosan-alginate beads in single metal system

Isotherm equation	Chitosan beads	Chitosan-GLA beads	Chitosan-alginate beads
Langmuir isotherm			
Q (mg/g)	34.98	14.24	60.27
b (mL/mg)	7.56×10^{-2}	1.81×10^{-2}	0.25
r	0.9575	0.9717	0.9177
Freundlich isotherm			
K_F ((mg/g)(mL/mg))	9.08	1.07	19.94
n	3.74	2.18	3.87
r	0.9772	0.9817	0.8182

Data obtained for chitosan and chitosan-GLA beads fitted well (based on r values) with the Langmuir and Freundlich isotherms, indicating that monolayer biosorption as well as heterogeneous surface conditions may coexist under the applied experimental conditions. Therefore, the adsorption behavior of Pb(II) ions onto chitosan and chitosan-GLA beads was complex, and it involves more than one mechanism, probably ion-exchange, surface complexation and electrostatic attraction (Özcan et al., 2005). The Langmuir constant, b , indicates the affinity of adsorbent to the Pb(II) ions. The greater the value is, the stronger the Pb(II) ions bind to the adsorbent. Based on the Langmuir isotherm, chitosan-alginate beads had the highest adsorption capacity, Q which was in agreement with the highest b value obtained. Chitosan-alginate beads showed a higher agreement with Langmuir isotherm, indicating that monolayer adsorption being more dominant.

The theoretical background of Langmuir isotherm makes the Q quite useful and convincing to be used for comparison in liquid phase adsorption (Chang and Juang, 2004). The adsorption capacities of Pb(II) ions for different adsorbents are compared in Table 2.

Chitosan-alginate beads has the highest adsorption capacity in comparison to chitosan and chitosan-GLA beads because the adsorption of Pb(II) ions may involve $-\text{COOH}$ and $-\text{NH}_2$ groups which were not involved during the formation of the polyelectrolyte complex. The COO^- ions formed due to the dissociation of the carboxylate groups

Table 2 Comparison of adsorption capacities of Pb(II) ions in single metal system with other reported adsorbents

Adsorbent	Q (mg/g)	Reference
Carboxymethylated-bacterial cellulose	65.53	Chen et al., 2008b
Tea waste	65.00	Amarasinghe and Williams, 2007
Chitosan-alginate beads	60.27	This study
<i>Enterobacter</i> sp.	50.9	Lu et al., 2006
Tree fern	39.8	Ho et al., 2002
Chitosan beads	34.98	This study
Epichlorohydrin-crosslinked chitosan	34.13	Chen et al., 2008a
Carboxymethylated cellulose	24.59	Chen et al., 2008b
Chitosan-GLA beads	14.24	This study

will attract the positively charged Pb(II) ions while the lone pair electrons on N atom of $-NH_2$ groups will form complex with Pb(II) ions. Chitosan beads will have only one kind of adsorption sites which are the amine groups to form complexation with Pb(II) ions. This would give rise to a lower adsorption capacity than the adsorption capacity obtained for chitosan-alginate beads. The chitosan-GLA beads had the lowest adsorption capacity among all three beads studied because the cross-linking reaction will consume the $-NH_2$ groups and also, might induce the saturation of the amine sites which are unavailable for further adsorption of Pb(II) ions.

Meanwhile, for Freundlich isotherm the magnitude of the exponent n value gives an indication of the favourability of adsorption. Based on Table 1, it can be seen that all three adsorbents had n values greater than 1, which represents a favourable adsorption condition (Septum et al., 2007). However, the significantly greater value of K_F for chitosan-alginate beads than that of chitosan and chitosan-GLA indicates a higher affinity of Pb(II) ions to chitosan-alginate beads. This agrees well with the highest adsorption capacity observed for chitosan-alginate beads based on the Langmuir isotherm.

2.4 Equilibrium adsorption isotherm (binary metal system)

Figure 2 shows the non-linear plot for chitosan, chitosan-GLA and chitosan-alginate beads based on the Langmuir and Freundlich isotherm equations for Pb(II) and Cu(II) ions in binary metal system. The calculated results of the Langmuir and Freundlich isotherms are summarized in Table 3.

The uptake of Pb(II) ions in the binary system were reduced in the presence of Cu(II) ions. All three adsorbents showed adsorption capacities, Q , much lower than the values obtained in the single metal system. This shows that there was a competition between the two metal ions for the binding sites. Apart from that, the adsorption capacities based on Langmuir isotherm for Cu(II) ions were slightly lower than the values reported in the single metal system (Wan Ngah and Fatinathan, 2008). However, the affinity of adsorbent, b , for Cu(II) ions was higher than the b values obtained for Pb(II) ions. This showed that in the presences of both metal ions, there were a strong competition and selective adsorption behaviour of Cu(II) ions over Pb(II)

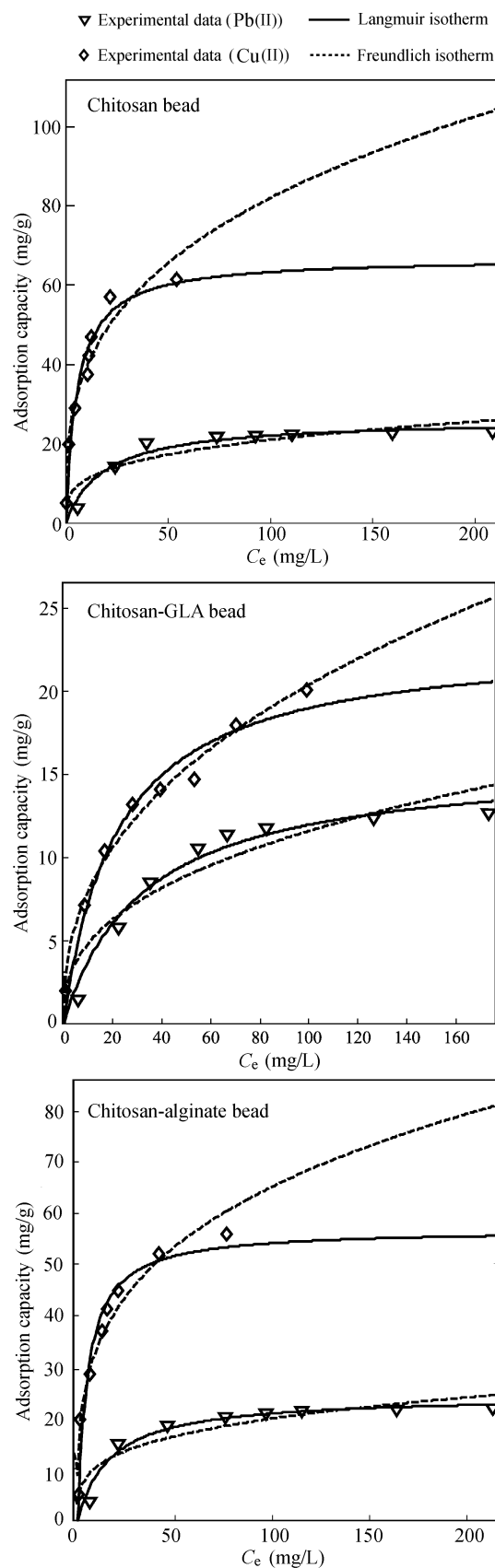


Fig. 2 Non-linear Langmuir and Freundlich isotherms for the adsorption of Pb(II) and Cu(II) ions in binary metal system onto chitosan, chitosan-GLA, and chitosan-alginate beads.

ions onto the three adsorbents.

Based on the conclusion of Liu et al. (2008), it was

Table 3 Isotherm constants for adsorption of Pb(II) and Cu(II) ions onto chitosan, chitosan-GLA and chitosan-alginate beads in binary metal system

Isotherm	Chitosan beads		Chitosan-GLA beads		Chitosan-alginate beads	
	Pb(II)	Cu(II)	Pb(II)	Cu(II)	Pb(II)	Cu(II)
Langmuir						
Q (mg/g)	26.11	66.85	15.85	23.14	24.31	56.86
b (mL/mg)	5.20×10^{-2}	0.17	3.04×10^{-2}	4.53×10^{-2}	5.85×10^{-2}	0.20
r	0.9751	0.9747	0.9861	0.9863	0.9771	0.9741
Freundlich						
K_F ((mg/g)(mL/mg))	5.58	18.47	1.97	3.10	5.56	17.56
n	3.49	3.09	2.61	2.45	3.63	3.51
r	0.8856	0.9668	0.9295	0.9925	0.8901	0.9764

proven that for diethylenetriamine (DETA)-functionalized polymeric adsorbent, the earlier adsorbed Pb(II) ions will be displaced by later adsorbed Cu(II) ions. Similarly, an analysis was conducted to prove whether the same process took place in the chitosan, chitosan-GLA and chitosan-alginate beads system. Chitosan beads loaded with 1.96 mg/g of Pb(II) ions was added into a 10 mg/L of Cu(II) ions solution and was stirred under optimum conditions. The filtrate was then analyzed for both Pb(II) and Cu(II) ions. A blank experiment was also conducted to prove that the displacement of the adsorbed ions only occurred in the presence of another metal ions. It was found that 2.48 mg/g of Cu(II) ions were adsorbed and 0.52 mg/g (26.51%) of Pb(II) ions was leached out. A similar procedure was repeated but the chitosan beads were loaded with 2.49 mg/g of Cu(II) ions firstly and then introduced into 10 mg/L of Pb(II) ions solution under optimum conditions. It was found that 1.46 mg/g of Pb(II) ions were adsorbed but merely 0.61 mg/g (1.54%) of Cu(II) ions were leached out. Chitosan-GLA and chitosan-alginate beads showed a similar trend whereby the Pb(II) ions leached out were more than 27%, but the amount of Cu(II) ions leached out were around 2% only. This proves that Cu(II) ions indeed replaced the adsorbed Pb(II) ions. This further proves that in the binary metal system, the initially adsorbed Pb(II) ions would be displaced causing the amount of Pb(II) ions adsorbed lower than the amount of Pb(II) ions adsorbed in the single metal system.

2.5 Mechanism of adsorption

The displacement of Ca^{2+} , Mg^{2+} , K^+ , Na^+ and H^+ ions by metal adsorption was examined over the concentration range 5–30 mg/L. The study was conducted under optimum conditions. Based on Fig. 3, it can be observed that chitosan, chitosan-GLA and chitosan-alginate beads released all four cations during the uptake of Pb(II) ions.

As the concentration of metal ion solution was increased, there was a proportional increase in the adsorption of Pb(II) ions by all three adsorbents. However, the release of the cations showed different behavior. The amount of ions released during the adsorption of Pb(II) ions was almost similar throughout the concentrations studied. This showed that cations Ca^{2+} , Mg^{2+} and K^+ played a minor role in the ion-exchange process as the amount of cations released was low. However, the amount of Na^+ ions released, increased as the adsorption of Pb(II) ions increased but to a certain extent only. After that point, the release of Na^+ ions was almost plateau even though there was an

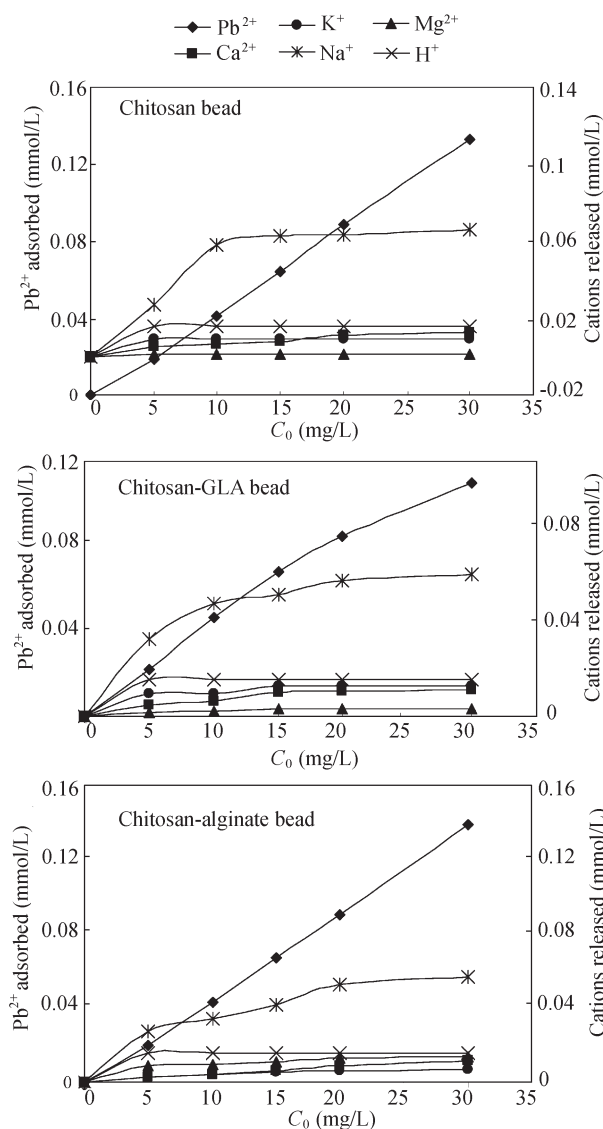


Fig. 3 Adsorption of Pb(II) ions in single metal system and displacement of Ca^{2+} , Mg^{2+} , K^+ , Na^+ , and H^+ by chitosan, chitosan-GLA, and chitosan-alginate beads.

increase in the adsorption of Pb(II) ions.

Meanwhile, the pH of the solution increased after the adsorption of Pb(II) ions for all three adsorbents. These showed that H^+ ions were adsorbed during the adsorption of Pb(II) ions. A control experiment was conducted and it was found that once the adsorbent was added into the Pb(II) ions solution at an initial pH of 4.5, the pH immediately rose to 5.08 and then constantly increasing until it became stable after almost 80 min. An increase in

the pH indicates a decrease in the hydronium ions concentration. This rules out an ion-exchange mechanism for the adsorption of Pb(II) ions onto chitosan, chitosan-GLA and chitosan-alginate beads, because during an ion-exchange process hydronium ions on ion-exchange sites are displaced as the metal ions are adsorb onto the site, leading to a decrease in pH with time (Prasad and Saxena, 2004; Rorrer and Hsien, 1993). According to Rorrer and Hsein (1993), since the beads were originally formed in a sodium hydroxide precipitation bath, these amino sites were in the form of $-\text{NH}_2$. As the beads were introduced into the Pb(II) ions solution, the Pb(II) ions and hydronium ions will compete for the available amino adsorption sites ($-\text{NH}_2$). The adsorption of Pb(II) ions will occur along side with the protonation of $-\text{NH}_2$ sites by the hydronium ions, and this eventually causes an increase in the pH of the solution as the concentration of H^+ decreases. This protonation process continues up to a certain point whereby it becomes stable. At this point it can be concluded that no amino site is available as most of the sites have been occupied either with Pb(II) ions or H^+ ions. The ion-exchange mechanism can also be studied based on the $R_{b/r}$ ratio (Šćiban et al., 2006):

$$R_{b/r} = \frac{C_{\text{Cu}^{2+}}}{C_{\text{Ca}^{2+}} + C_{\text{Mg}^{2+}} + \frac{C_{\text{Na}^+}}{2} + \frac{C_{\text{K}^+}}{2} + \frac{C_{\text{H}^+}}{2}} \quad (4)$$

where, the concentration of cations is expressed in mmol/L. According to Šćiban et al. (2006), the $R_{b/r}$ ratio has to be equal to unity if the adsorption process involves predominantly ion exchange mechanism while higher $R_{b/r}$ ratio means that the sum of cations released is smaller than the amount of Pb(II) ions adsorbed. Based on Table 4, it can be observed that as the initial concentration of Pb(II) ions solution increased, the $R_{b/r}$ ratio also increased. Chitosan, chitosan-GLA and chitosan-alginate beads have $R_{b/r}$ ratio almost close to unity at low concentrations of Pb(II) ions, but the ratio increased as the concentration of metal ions solution was increased. This showed that at low concentrations, ion-exchange mechanism played an important role in the removal of Pb(II) ions but at high concentrations, complexation and other mechanism plays a more crucial role.

Table 4 $R_{b/r}$ ratio at different Pb(II) concentrations in single metal system

Pb(II) conc. (mg/L)	$R_{b/r}$		
	Chitosan bead	Chitosan-GLA bead	Chitosan-alginate bead
5	0.69	0.60	0.78
10	0.70	0.82	1.33
15	0.98	0.99	1.37
20	1.28	1.11	1.41
30	1.84	1.37	1.90

2.6 FT-IR spectra analysis of chitosan, chitosan-GLA and chitosan-alginate beads

Infrared analysis were performed for all three adsorbents before and after being in contact with Pb(II) ions solution.

Infrared spectroscopy helps to identify the possible functional groups involved in the binding of Pb(II) ions. The infrared spectra shown in Fig. 4 were obtained before and after Pb(II) adsorption.

The major peaks observed for chitosan beads (Fig. 4a) were around 3421 cm^{-1} which can be assigned to the stretching vibration of $-\text{OH}$ and $-\text{NH}$ groups. The peak at 2868 cm^{-1} is due to the $-\text{CH}$ stretching vibration in $-\text{CH}$ and $-\text{CH}_2$. Meanwhile, the peak at 1650 cm^{-1} is attributed to the secondary amide $\text{C}=\text{O}$ bond contributed by the remaining acetamido groups and 1594 cm^{-1} peak is attributed to $-\text{NH}$ bending vibration in $-\text{NH}_2$. The $-\text{NH}$ deformation vibrations is represented by the peak at 1421 cm^{-1} . The $-\text{CH}$ symmetric bending vibration in $-\text{CHOH}$ was observed at 1379 cm^{-1} . In addition, the peaks at 1320 cm^{-1} and 1154 cm^{-1} are due to the $-\text{CN}$ stretching vibration while, the peaks at 1081 cm^{-1} and 1029 cm^{-1} are due to the $-\text{CO}$ stretching vibrations in $-\text{COH}$ (Li and Bai, 2005). After the adsorption of Pb(II) ions, the transmittance of the strong broad band observed at 3421 cm^{-1} was reduced. Other changes observed were

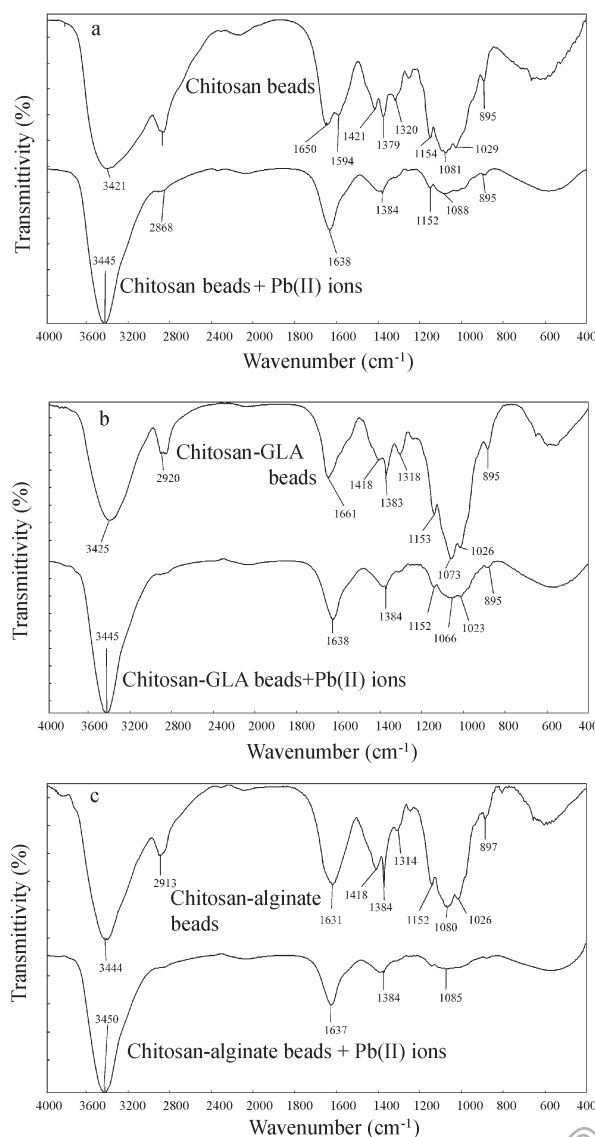


Fig. 4 FT-IR spectra before and after the adsorption of Pb(II) ions onto (a) chitosan, (b) chitosan-GLA, and (c) chitosan-alginate beads.

at 1594 cm^{-1} and 1421 cm^{-1} . These wavenumbers were related to the -NH bending and deformation vibrations. This indicates that the nitrogen atoms could be the main adsorption sites for Pb(II) ions attachment.

The infrared spectrum for chitosan-GLA beads (Fig. 4b), showed a new peak at 1661 cm^{-1} due to the imine bonds, C=N . There was a reduction in the intensities at 1594 cm^{-1} and 1421 cm^{-1} , indicating that the primary amino groups were involved in the cross-linking process. The absence of the peak at 1720 cm^{-1} proved that there was no unreacted pendant aldehyde group (Monteiro Jr and Airoidi, 1999). A comparison of the spectrum for chitosan-GLA beads with that of lead-loaded beads revealed a change in the stretching vibrations of -OH and -NH groups, which shifted from 3425 cm^{-1} before lead adsorption to 3445 cm^{-1} after adsorption. There was also a decrease in the absorbance at the wavenumbers 1418 cm^{-1} and 1318 cm^{-1} . These wavenumbers are due to the -NH deformation and -CN stretching vibrations, respectively. This suggested an interaction between Pb^{2+} ions with nitrogen atoms. The vibration intensity of -NH group was reduced after the attachment with Pb(II) ions because of the molecular weight of Pb(II) ions (Jin and Bai, 2002).

Meanwhile, for chitosan-alginate beads (Fig. 4c), the new peak at 1631 cm^{-1} can be attributed to the symmetric $\text{-NH}_3\text{C}$ deformation. The sharp peak at 1418 cm^{-1} was attributed to the -NH_3^+ groups of chitosan interacting with the -COO^- groups of alginate (Simsek-Ege et al., 2003; Smitha et al., 2005). After the adsorption of Pb(II) ions, -CN stretching vibrations (1320 cm^{-1} and 1152 cm^{-1}) and -CO stretching vibrations in -COH (1080 cm^{-1} and 1026 cm^{-1}) were affected. This proved that the Pb(II) ions was attached to the nitrogen and oxygen groups found in chitosan as these groups still existed in the chitosan-alginate beads. The wavenumber that was also affected after the adsorption Pb(II) ions was at 1418 cm^{-1} corresponding to the interaction between -NH_3^+ and -COO^- of chitosan-alginate beads.

3 Conclusions

Equilibrium adsorption study showed that chitosan, chitosan-GLA and chitosan-alginate beads can be effectively used to adsorb Pb(II) ions. Adsorption study also suggested that adsorption of Pb(II) ions onto chitosan and chitosan-GLA beads followed both Langmuir and Freundlich isotherms, with the corresponding maximum adsorption capacities 34.98 and 14.24 mg/g , respectively. Meanwhile, chitosan-alginate beads have the highest adsorption capacity (60.27 mg/g). In the competitive adsorption study, all three adsorbents showed a higher affinity towards Cu(II) ions. The ion-exchange played an important role in the adsorption process but only at low Pb(II) ion concentrations. At high concentrations, there was a lower amount of ion exchanged.

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