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Comparison of Lead Removal by Various Types of Swine Bone Adsorbents

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Abstract

The removal capacities of lead by bone adsorbents, prepared in various appropriate types, have been studied in a single component system using agitated batch sorption. The adsorbent characteristics before and after sorption were examined by electron microscopy, surface area analysis (BET), crystalline structure by x-ray diffractometer (XRD), chemical compositions by x-ray fluorescence (XRF) and by Fourier transform infrared (FT-IR). The results showed that the main component of swine bone adsorbents is calcium hydroxyl-apatite with Ca/P ratio is 1.70; the calcium ion and the range of mesopores of the appropriate pore sizes are the important factors for the ion-exchange process and the sorption process. The effects of carbonization, activation, initial metal ion solution concentration, contact time and quantities of bone adsorbent mass were studied. The capacity removal of lead onto bone powder, bone char and activated bone char were 417, 1828 and 690 mg/g, respectively, for 10 mg/L and pH 5±0.1 of the initial lead ion solution concentration, with an agitation speed 175 rpm. The sorption isotherm was also studied and indicated that the Langmuir isotherm model closely fits the sorbtion of lead onto bone char.

Keywords: lead; swine bone adsorbent; sorption; isotherm

1. Introduction

Heavy metals are very toxic substances which contaminate the environment, and eventually enter the food chain causing diseases. Bone sorbents are now widely used for the removal of various heavy metal from industrial wastes, agriculture and mining (Ma *et al*., 1993; Choy and McKay, 2005).

In the past, cattle bones have been used for preparing bone char but recently a new biological sorbent prepared from animal bones heated at 80°C for 24 h has been utilized for the recovery of copper and nickel (Sameer *et al*., 1999).

In this study, three types of biological sorbents from bone were prepared: bone powder, bone char and activated bone char. The Pb^{2+} sorption capacity was investigated in a range of metal ion concentrations and sorbent masses. Moreover, their physical properties and chemical components before and after sorption were also studied.

2. Experimental Material and Methods

2.1. Adsorbents: bone powder, bone char and activated bone char

Cooked swine bones were cleaned, soaked in brine, rinsed with tap water and left to dry. After baking at 150°C, 3 h, they were crushed and milled into different particle sizes (0.84-2.36 mm). They were then kept in a desiccator, crushed and milled again to fine powder (mean particle size 45 micron). For the preparation of bone char, bone granule was sieved to discrete size ranges, (0.84-2.36 mm) and then carbonized at 300, 350, 400°C (named bone char BC300-1, BC350-1 and BC400-1, respectively) for an hour. The particles were then milled to <45 micron and collected in a desiccator.

Activated bone char (ABC), was prepared from carbonized bone char (heated at 400°C, 1 h), soaked with saturated NaCl for 6 h, filtered, and then heated at 400°C 1 h. All NaCl was removed by rinsing in distilled water. The char was dried at 105°C for 24 h, milled and sieved to particle sizes <45 micron and collected in a desiccator.

The chemical components and physical properties of bone powder, bone char and activated bone char were tested (P, Ca, Pb, Cd, Fe content were detected by X-Ray Fluorescence Spectrometer (XRF: oxford model ED2000); carbon content; CHNS/O Analyzer (Perkin Elmer PE2400 Series II); Total surface area, Pore size and Pore volume: Surface area analyzer (BET), "Quantachrom" Autosorb-1; Scanning electron microscope: "JEOL" JSM - 6400) using ASTM methods (ASTM.,2006: C1274-00, D2854-96, D2867-04); functional groups by Fourier transform infrared (FT-IR) and the sorbents' structures by X-Ray Diffractometer (XRD: Bruker AXS D8 Discover).

2.2. Adsorbates: metal ion solutions

Synthetic waste solutions were prepared, using analytical grade $Pb(NO_3)_2$ 10-30 mg/L in de-ionized water; pH was adjusted to pH 5.0±0.1 using nitric acid and sodium hydroxide. Previous studies indicate that that the appropriate pH for lead ion sorption onto bone adsorbents is in the range 5-6 (Azab *et al*., 1989; Ma *et al*., 1993).

2.3. Analytical techniques

The research methodology and all tested parameters followed the reference of American Society for Testing and Materials (ASTM, 2006: C1274-00, D2854-96, D2867-04, D3559-03, D3860-98, D511-03). The concentrations of metal ion solutions were measured by atomic absorption spectrophotometer, AAS (Shimadzu AA-6800F, Japan). Each experiment and each sample was carried out in triplicate and the samples were automatically measured three times in one aspiration, then the average results were recorded.

2.4. Batch sorption experiment

The experiments of the three sorbents were carried on batch approach, using synthetic lead ion solutions and experimental parameters and conditions as mentioned in 2.2, after agitating 175 rpm for 10 min to 72 h and samples were taken at several intervals. Then solutions were filtered (Whatman filter paper no. 42) and the concentrations of metal ion were measured by AAS. Each experiment was carried out in triplicate and the average results were recorded.

2.4.1. Bone char sorption experiment

The appropriate temperatures for maximum adsorptive capacity were studied with BC300-1, BC350-1 and BC400-1 at concentrations 0.006-0.600 g/L. Fifty ml. of 10 mg/L of the synthetic lead ion solution in water was pipetted into 120-ml plastic bottles which were agitated at 175 rpm for up to 72 h at room temperature (25±1°C); bottles were removed after various time intervals up to 72 h. The contents was filtered (paper no. 42) and the metal ion concentrations of effluents, Pb^{2+} and Ca^{2+}, were measured by AAS. The capacity for lead removal and the x/m ratio were calculated and plotted against contact time. The Ca^{2+} concentrations in effluents and Pb^{2+} bound were calculated and plotted.

2.4.2. Bone powder bone char (BC400-1) and activated bone char sorption and contact time experiment

Various amounts of the three sorbents, in the ranges 1-50 mg, 0.3-5.0 mg and 0.3-5.0 mg for bone powder, bone char and activated bone char, respectively, were weighed and the experiments were conducted by as in 2.4.1. The sorbents after sorption were examined and tested by SEM, FT-IR and XRD to compare the results before and after sorption (Figs. 1-3). The lead removal capacity (x/m ratio) was calculated (Table 2).

2.4.3. Effects of bone char sorbent dose and initial lead concentration

Since bone char 400-1 provided the highest adsorptive capacity for lead removal (10 mg/L), further studies were conducted at the same conditions as for bone char sorption by varying the bone char dose from 0.006 g/L to 0.100 g/L and the x/m ratio of initial lead concentrations 10, 20 and 30 mg/L.

2.5. Adsorption equilibrium isotherm for bone char

Following the methods of ASTM(2006, D3860-98A) bone char masses in the ranges 0.2- 0.9 g/L and 30 mg/L of the lead ion solution were agitated for 24 h to allow the sorbent to absorb the metal ions until equilibrium. The initial and final concentrations of the ion solutions in filtrates were estimated by AAS. These data were used to calculate the Freundlich and Langmuir isotherm constants and R^2 (Table 3).

3. Results and Discussion

3.1. Properties of the three types of bone sorbents before and after sorption of lead

The surface of bone powder seemed quite smooth lacking pores [Fig. 1(a)] but after carbonization the bone surface became rough with pores [Fig. 1(b)] which became larger in activated bone char [Fig. 1(c)]. After sorption of lead ion the surface of the three sorbents seemed more dense, with less pores presumably because of replacement of lead ions [Figs. 1(a-c), after]. These results correspond to the physical properties (Table 1).

Table1. Physical and chemical properties of bone powder bone char and activated bone char

	Limits		
Items	Bone powder	Bone char (BC400-1)	Activated bone char
Chemical properties			
Phosphorus	9.96 wt%	12.84 wt%	13.61 wt%
Calcium	16.95 wt%	22.14 wt%	23.21 wt%
Ca/P	1.70	1.72	1.71
Carbon Conte	31.173 wt%	22.87 wt%	22.31 wt%
Lead	<0.1 wt%	<0.1 wt%	<0.1 wt%
Cadmium	<0.1 wt%	<0.1 wt%	<0.1 wt%
Iron-as Fe_2O_3	<0.1 wt%	<0.1 wt%	<0.1 wt%
Physical properties			
Bulk density (dry)	834.85 kg/m^3	708.90 $kg./m^3$	667.20 $kg./m^3$
Total surface area	2.78 m^2/g^1	117.51 m^2/g^1	92.79 m^2/g^1
Average pore size	36.44 Å	86.39 Å	110.0 Å
Pore volume, Vp	0.0025 cm^3/g^1	0.2538 cm^3/g^1	0.2553 cm^3/g^1
Moisture	5 wt% max.	5 wt% max.	5 wt% max

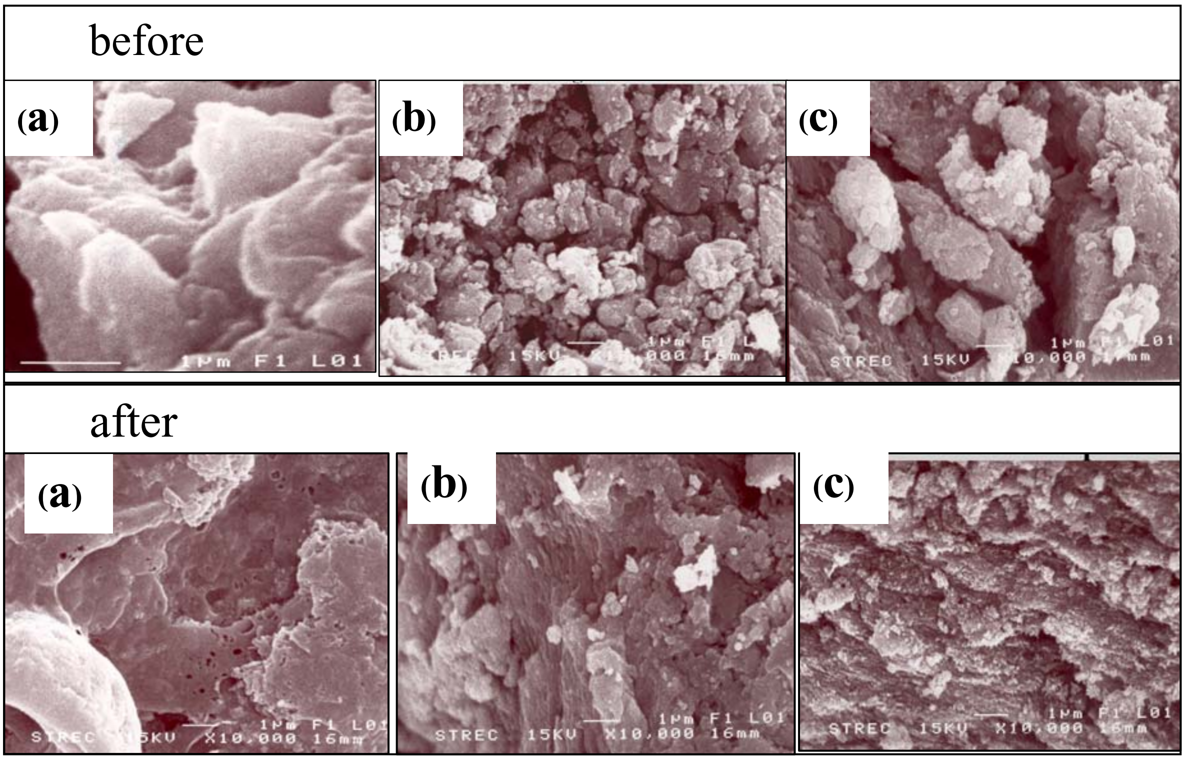

Figure 1. Electron micrographs of the three sorbents: bone (a), bone char (b) and activated bone char (c) from $SMEs_s$ ×10,000 (before and after sorption)

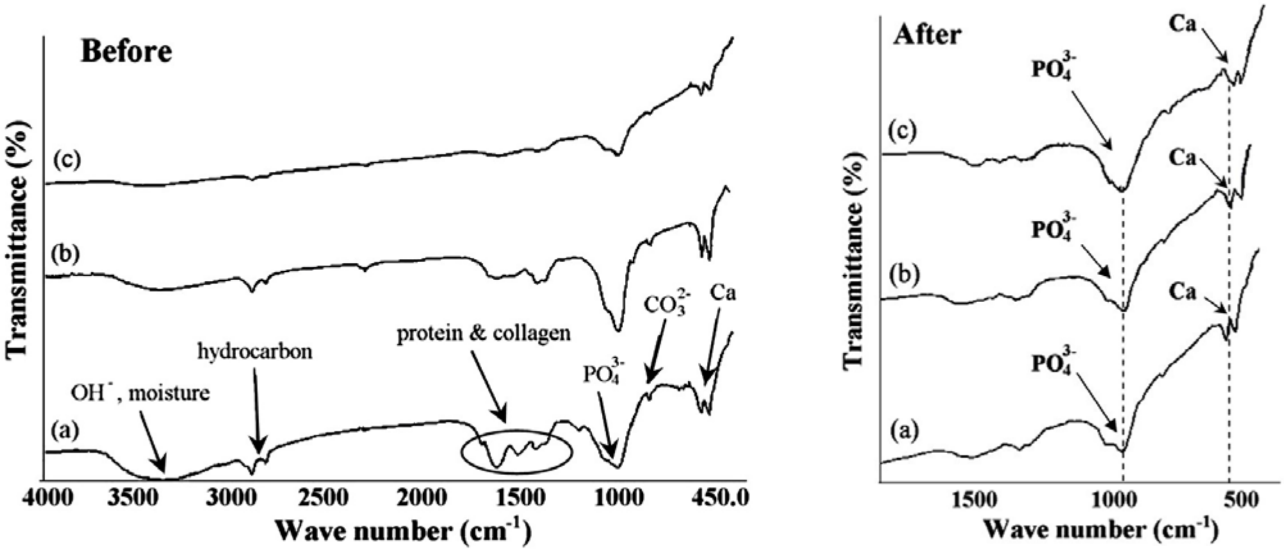

Figure 2. FTIR spectra of bone (a) bone char (b) and activated bone char (c) before and after sorption of lead

Carbonization and activation influenced the physical and chemical properties of the sorbents. The total specific surface areas increased (from 2.78 m^2/g was up to117.5 m^2/g). The total pore volumes increased (from 0.0025 cm^3/g to 0.2553 cm^3/g), and the average pore sizes was enlarged (from 36.44 Å up to 110.0 Å). The proportions by weight of calcium and phosphorus increased (from 9.96% to 13.61% for P and from 16.95% to 23.21% for Ca), but the percentage weight of carbon decreased after carbonization and activation (from 31.17% to 22.31%). However Ca/P ratio remained constant, about 1.71±0.1 (Table 1).

The FTIR spectrum of swine bone powder (Fig. 2, line (a)-before) indicates the presence of moisture and -OH groups (3000-3600 cm^{-1}), hydrocarbon of -CH stretching (2853-2923 cm^{-1}), protein and collagen of -C=O, C=C, C=N (1465-1744 cm^{-1}), a broad and strong band of phosphate, $-PO_4^{3-}$ group (1100-900 cm^{-1}), carbonate of $-CO_3^{2-}$ (720 cm^{-1}), and a broad and strong band of calcium of Ca^{2+} (550-610 cm^{-1}). After carbonization and activation (Fig. 2, line (b) and line (c)-after) protein and collagen peaks disappeared, moisture and -OH group (3000-3600 cm^{-1}) and hydrocarbon of -CH stretching (2853-2923 cm^{-1}), were reduced by heat. However, the main functional groups, phosphate and calcium groups remained. After lead uptake, the peak Ca^{2+} (550-610 cm^{-1}) changed, was not strong and broad (Fig. 2, line (a, b, c)-after) or was substantially lower than that before sorption, suggesting some participation of Ca^{2+} in the binding of lead by the adsorbents and some dissolving in the solution.

X-ray diffraction of the three types of adsorbent showed the crystalline structure: hexagonal of calcium hydroxyl-apatite ($Ca_{10}(PO_4)_6(OH)_2$) or calcium phosphate hydroxide (as * label peak in Fig. 3-before), and the sizes are very close to those of mineral fluor-apatite $Ca_5F(PO_4)_3$ and bone material. The three dimensions of hexagonal crystallized of mineral fluor-apatite are a and b=9.410, c=6.880 (Beevers *et al.*, 1945) and bone material- hexagonal with cell dimension of a=b=9.423 Å, c=6.875 Å (Aoki, 1991). The three dimensions of swine bone crystallized structure before adsorption were a and b length 9.4180 Å, c was 6.8840 Å, and the hexagonal angles, alpha and beta was 90.0, gamma was 120.0 (from the comparing to the data base library of the instrument). After the sorption of Pb^{2+} onto bone adsorbent, the size was bigger (from a=b=9.4180 Å was up to 9.826 Å, c= 6.8840 Å was up to 7.357 Å) because of the formation of lead phosphate, $Pb_3(PO_4)_2$ or lead hydroxyl-pyromorphite ($Pb_{10}(PO_4)_6(OH)_2$) as the XRD patterns show the strong peak intensities at 31.91° and 32.15° [Fig. 3(a)]; at 31.87° and 32.15° [Fig. 3(b)] and at 31.86° and 32.92° [Fig. 3(c)] for bone powder, bone char and activated bone char, respectively. This results correspond to Ma (1994) who used hydroxyl-apatite to remove lead.

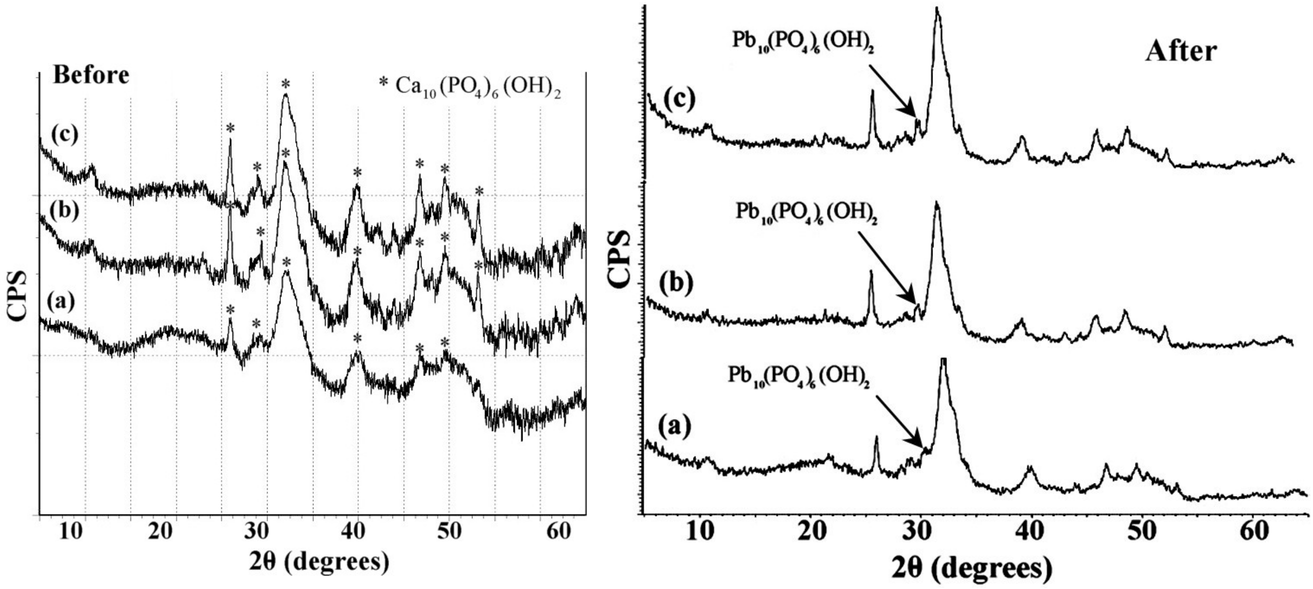

Figure 3. X-ray diffraction patterns of bone (a) bone char (b) and activated bone char (c) before and after sorption of lead

3.2. Metal ion removal capacities of bone sorbents and contact time

The experiments showed that the adsorptive capacity of lead on to bone chars, BC300-1, BC350-1 and BC400-1 were 123, 1796, 1828 mg/g, respectively; especially BC350-1 and BC400-1 could remove more than 99% of 10 mg/L of lead ion, whereas BC300-1 can removed 50%. The appropriate contact time for lead removal, providing the maximum adsorptive capacity were 24, 72 and 36 h for the removal of lead onto bone chars, BC300-1, BC350-1 and BC400-1, respectively, and 24, 48 h. for bone powder and activated bone char.

Bone char is the best sorbent, and bone powder the worst for lead removal, the adsorptive capacity were 417, 1828 and 690 mg/g for bone powder, bone char and activated bone char with higher than 99% of the removal for 10 mg/L of the initial concentration of lead (Table 2). These results indicate that increasing surface areas result in higher sorption. Moreover, bone char appears to have the appropriate physical characterization with high total surface areas and average proper pore size in the range of mesopores which provided the maximum adsorptive capacity (Pb^{2+} radius is 1.33 Å, covalent radius is 1.54 Å) (Choy and McKay, 2005). Furthermore they agree with the studies of Pattanatecha (2002) and Sanchai (2005) who used bone char and activated bone char from cow bone for Pb^{2+} and Cd^{2+} removal.

3.3. Effect of bone char sorbent dose and initial lead concentration

The lead removal of initial lead concentration 10 mg/L was about the same 99.28% vs 99.75% as the bone char dose was increased from 0.006 to 0.100 g. However, an increase in sorbent doses was linked to the decrease in adsorptive capacity which decreased from 1,828 to 220 mg/g. Bone char dose 0.006 g/L was adequate for lead removal, an increase in sorbent dose resulted in surplus of the sorption sites. This result agrees with the study of Sameer *et al* (1999) and Choy *et al* (2005).

The adsorptive capacity of bone char at equilibrium decreased from 1828 to 1225 and 49 mg/g as the lead concentration increased from 10 to 20 and 30 mg/L, respectively and can remove lead more than 99%.

Table 2. Comparison of adsorptive capacity of lead onto bone powder, bone char and activated bone char by contact time. Conditions: initial lead concentration 10 mg/L; pH 5±0.1; speed 175 rpm.

	bone powder	bone char	activated bone char
Percentage removal	99.9	99.3	98.9
Removal capacity (mg/g)	417	1828	690
Contact time	24	36	48

Table 3. Adsorption isotherm of lead onto bone char

Freundlich isotherm constants	Langmuir isotherm constants
log q_e = 1.7789 + 0.1092 log Ce	1/ q_e = 0.0003(1/Ce) + 0.0156
n = 9.1575	b = 52
k = 60.1	q_m = 64.1
R^2 = 0.9195	R^2 = 0.9900

3.4. Adsorption equilibrium isotherm

The distribution of metal ions between liquid and solid phases is generally described by using Freundlich (1906) and Langmuir (1916) adsorption isotherm models. The concept of Freundlich isotherm model is derived based on a multilayer adsorption and applicable to highly heterogeneous surfaces, and is given as: log $q_e = \log k + 1/n \log C_e$ where, *k* (mg/g) is the maximum adsorptive capacity and *n* is related to adsorption intensity. The values of *n* determined from Freundlich isotherm were greater than 1 (Table 3), indicating that Pb^{2+} ions are favorably adsorbed by bone char.

The Langmuir model assumes uniform energies of adsorption onto the sorbent surface and no transmigration of adsorbate in the plane of the surface, a monolayer homogeneous surfaces adsorption process and is given as: $Ce/q_e = 1/q_m.b + Ce/q_m$ where, *Ce* (mg/L) is the equilibrium of lead concentration, q_e (mg/g) is the amount of lead adsorbed at equilibrium, q_m (mg/g) is the maximum adsorptive capacity, *b* (L/mg) is a constant related to energy of the adsorption which quantitatively reflects the affinity between the adsorbent and adsorbate. The values of q_m can be obtained from the slope of the plot of Ce/q_e versus Ce based on Langmuir isotherm model. The two isotherm model constants and the linear equations are shown in Table 3. The Langmuir model was found to best represent the isotherm data for lead sorption onto bone char of swine with $R^2 = 0.9900$.

These agree with Ko *et al* (2004), they studied the sorption equilibria of Cd^{2+}, Cu^{2+} and Zn^{2+} onto bone char and concluded that the Langmuir isotherm was the fit model to the data for metal ions adsorption in all cases. In-addition, Choy and McKay (2005) also explained that using the Crank diffusion model.

3.5. Ion exchange study

Bone char BC400-1 is the best adsorbent and therefore the ion-exchange process was investigated by following the release of Ca^{2+} and H^+ to the effluent after the sorption of Pb^{2+} during a period of time (10, 20, 30 min... 72 h). The release of cations from the control, consisting of the sorbent and de-ionised water, was measured as well. The adsorption of Pb^{2+} increased, therefore, the amount of Ca^{2+} increased, quite constant and reached a maximum when the system was close to the equilibrium (Fig. 4). This result corresponds to the results from FTIR and XRD study, indicating that the Ca^{2+} group plays an important role in the ion-exchange process. Moreover, the pH of the Pb^{2+} solution is higher and close to pH 7, or more, when the removal system is close to the equilibrium stage, indicating the release of H^+ to the solution.

These results describe that chemisorption occurred in the liquid-solid phase of Pb^{2+} solution and the surface of the bone char. Pb^{2+} replaced Ca^{2+} in the bone because of the existing of Ca^{2+} in the filtrate (Fig. 4) and a white precipitate of lead hydroxyl-apatite, $Pb_{10}(PO_4)(OH)_2$ appeared in the solution (results from observation and XRD pattern) after shaking in a period of time corresponding to research conducted by Sameer and coworkers (1998) who used animal bone for the sorption of copper and nickel. Furthermore, Lower and Ma previously described bone char for the removal of lead and other metals (Lower *et al.*, 1998; Ma *et al.*, 1993).

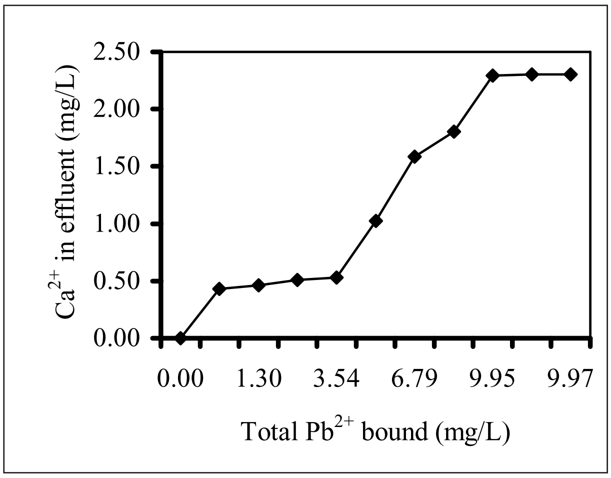

Figure 4. Relation of total lead ion bound and amounts of Ca^{2+} release. Conditions: initial lead ion concentration 10 mg/L; pH 5±0.1; volume 50 ml; bone char weight 0.005 g.

The ion-exchange studies of swine bone agree with most previous observations on biosorption concluding that ion-exchange could be a predominant mechanism for the binding of metals by biosorbents (Sameer *et al*., 1999; Sciban *et al*., 2006; Wan Ngah and Hanafiah, 2008).

4. Conclusions

The efficiency and capacity of lead removal of the three types of bone adsorbents depend on the initial concentration of sorbate, quantities of sorbents, contact time and the conditions of sorbents. Bone char is the best for lead removal among the three types of bone sorbents, bone powder, bone char and activated bone char. The appropriate agitation times depend on the sorbent concentrations. Langmuir adsorption isotherm provides a close fit to the Pb^{2+} removal process. The removal mechanism processes are diffusion, precipitation, chemi-sorption, physi-sorption and ion-exchange. Ca^{2+} group of the bone components plays an important role of the ion-exchange process.

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