

Removal of lead (II) ions from aqueous solution by Hydroxyapatite biosorbent extracted from Ostrich bone

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ABSTRACT

Hydroxyapatite (HAp) is a broadly studied bioceramic for biomedical implant and bone tissue regeneration. Despite this, it is a good adsorbent of heavy metal ions. Its chemical formula is $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. It was extracted by the calcination process from Ostrich bone. The obtained HAp was characterized by X-ray diffraction (XRD) and Fourier transforms infrared (FTIR) spectroscopy and was used for removal of lead (II) ion from aqueous solutions. A series of experiments were conducted in order to determine the effects of pH, contact time and sorbent dosage in a optimize condition for maximum adsorption. The results showed that the removal efficiency of Pb (II) ions reached 99.04% with an initial concentration of 50 mgL^{-1} , pH range; 3 to 7 and 1 hour contact time. The adsorption rate of Pb (II) ions onto the HAp was found incredibly fast and equilibrium was reached within 5 minute. Within this time 72.32% of lead (II) ions were removed. The equilibrium removal process of Pb (II) ions at pH range 4.5-5.5 were well described by the Langmuir isotherm model, with a maximum adsorption capacity of 430.7 mg/g.

Key words: Ostrich bone, hydroxyapatite, calcinations, adsorption, Pb (II) ion, pH.

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INTRODUCTION

Heavy metals are the elements having a specific gravity at least five times than water as well as toxic even intake in a low amount¹. These metal ions found in water especially from transition metal series are of foremost concern due to their toxicity to several life forms. Its effect is cumulative and can cause serious health problems including damage of visceral organs and the nervous system. On prolonged exposure, it can cause cancer in these organs which may go ahead to death².

The toxicity of these metal ions is enhanced due to the accumulation in living tissues through food chain³. Among the different heavy metal ions, the lead (II) ion is important on the viewpoint of environmental toxicology⁴. Lead metal and its ionic compounds are widely applied in different industries such as paint and pigments, ceramics and pottery, storage batteries, alloys, and solder as well as in petrol refining⁵. Owing to these uses, this ion often found in industrial effluent and there is a high risk of intermixing with drinking

water resources. Therefore, the removal of this ion from industrial effluent as well as drinking water resources is necessary for public health concern.

Although the different removal techniques have been proposed by different researchers, chemical precipitation, membrane filtration, ion exchange, and biosorption are the most commonly applied techniques⁶. Among these, the biosorption is more reliable and convenient technique because of its low processing cost, high efficiency of adsorption, minimization of chemical and biological sludge, high possibility of regeneration of adsorbent and metal recovery⁷⁻⁹. Because of these beneficial aspects, in this study, the biosorbent technique was applied for the removal from an aqueous medium. HAp biosorbent can be prepared either from chemical precursors or from biogenic resources. In compare to chemical precursors bio-based resources are economical and HAp extracted from this resources are highly preferable for removal of heavy metal ions due to its low water solubility and greater stability under redox conditions. The

elemental components of HAp are hydrogen, oxygen, phosphorous and calcium along with carbon which is expected to have no toxicity¹⁰. Moreover, HAp isolated from biogenic resources have received considerable attention in the field of dental and bone tissue engineering because of its chemical, structural and morphological resemblance with human hard tissue minerals¹¹⁻¹³.

MATERIALS AND METHOD

Bone sample collection

Minimum 2 kg of cortical bone was collected from Ostrich farmhouse located at Gangolya-1, Rupendehi district, the western region of Nepal. The samples were cleaned to remove visible adhered substances and then cut into small pieces using a hacksaw.

Chemicals and Reagents

All necessary analytical grade chemicals and reagents such as $\text{Pb}(\text{NO}_3)_2$, KNO_3 , NaOH , HCl , HNO_3 , NaCl and Acetone were purchased from Merck Chemicals (India) and used without further purification.

Preparation of Biosorbent

Bone pieces were boiled for about 4 hours in a closed container for deproteination after that wash several times by tap water and dried overnight at 120°C in a hot air oven. The dried bone pieces were crushed in an iron mortar and powdered in a high-speed disc pulverized machine. Furthermore, alkaline hydrothermal hydrolysis process was applied for removal of residual collagens and fatty tissues. Finally, the bone powder was calcinated at 650°C in a muffle furnace using a heating rate of $5^\circ\text{C}/\text{min}$ for 6 hours holding time and slow furnace cooling to obtain grayish-white bone ash and recalcinated at 950°C for another 6 hours in the same condition to obtained final product. The flow sheet diagram of preparation process is shown in figure 1.

Preparation of Lead (II) ion Stock Solution

Analytical grade lead nitrate, $\text{Pb}(\text{NO}_3)_2$ was used for the preparation of stock solution (1000 mg/L). The experimental solutions were then prepared by diluting the stock solution. The concentration of these solutions was determined by using Flame Atomic Absorption Spectrometer (FAAS).

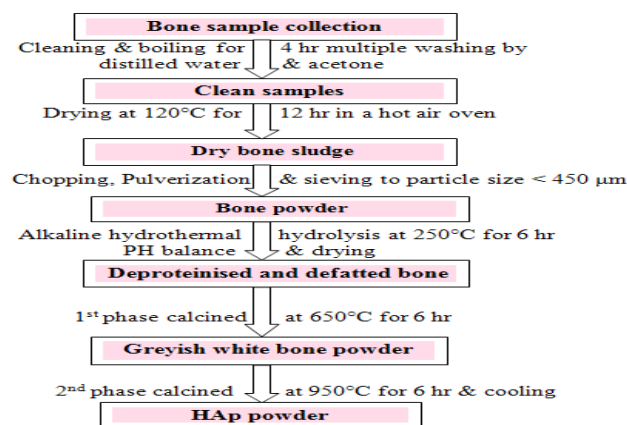


Figure 1. Flow sheet diagram of extraction of HAp biosorbent from Ostrich bone.

Characterization of Biosorbent

To study the crystallinity of the prepared biosorbent, powder X-ray diffraction (Bruker-D2) patterns were recorded using $\text{Cu K}\alpha$ radiation target with a second monochromator at 40 kV and 40 mA. Fourier transform infrared (FTIR) spectroscopic (Shimadzu-8300 IRTF) analysis was performed to identify the presence of major functional groups, and the point of zero charge (pH_{PZC}) was measured by a batch equilibrium technique, with 0.1M of KNO_3 as an inert electrolyte¹⁴.

Determination of Acido-basic Properties

The acido-basic properties of biosorbent were determined by using the point of zero charge (pH_{pzc}) method¹⁴. In this method, 500 mL of 0.01M NaCl solution was degassed by using N_2 in order to remove dissolved CO_2 . 10 mL of 0.01M NaCl solution was taken in 10 different conical flasks and 1-10 pH of each solution in flasks were maintained by adding either HCl or by NaOH standard solution. 10 mg of HAp was added in the solution of each flask and kept in a mechanical shaker for 3 hours with 150 rpm. The final pH of each solution was measured after 24 hours.

Batch Sorption Experiments

Biosorption equilibrium assays were carried out by using the batch adsorption process. Each of the batch adsorption studies was carried out by adding HAp powder within experimental lead (II) ions solution at lab temperature ($25^\circ\text{C}\pm 0.1$). A series of experiments were conducted in order to determine the effects of pH, contact time, and sorbent dosage on the adsorption. Each experiment was conduct

ed in a mechanical shaker at 150 rpm. After the required time to reach equilibrium, all the samples were filtrate and the final concentration of lead(II) ions in solution were determined by using the flame atomic absorption spectrophotometer (Shimadzu AA 6500, air/acetylene gas mixture).

Calculations

All experiments were carried out in triplicate and the mean of the quantitative results was used for further calculations. The amount of lead (II) ions adsorbed onto the biosorbent surface *qt* (mg/g) was calculated by using a mass balance relationship as;

$$qt = \frac{(C_0 - C_t)V}{m} \dots\dots(I)$$

Where *qt* (mg/g) is the adsorption capacity of biosorbent; *C₀* and *C_t* are the initial and equilibrium concentration (mg/L) of lead (II) ions in solution; *V* (L) is the total volume of solution; and *m* (g) is the weight of the adsorbent taken. Similarly, the percentage of lead (II) ions removal by adsorbent was also determined by using the expression;

$$\text{Removal \%} = \frac{(C_0 - C_t) \times 100}{C_0} \dots\dots (II)$$

RESULTS AND DISCUSSION

X-ray Diffraction (XRD) Phases Analysis

The XRD patterns and exhibiting peaks corresponding to extracted HAp were found to be similar with standard HAp data of Joint Committee on Powder Diffraction Standards (JCPDS) card No 01-074-0565, which indicate that there is no secondary phase and the synthesized HAp was pure¹⁵ as shown in figure 2.

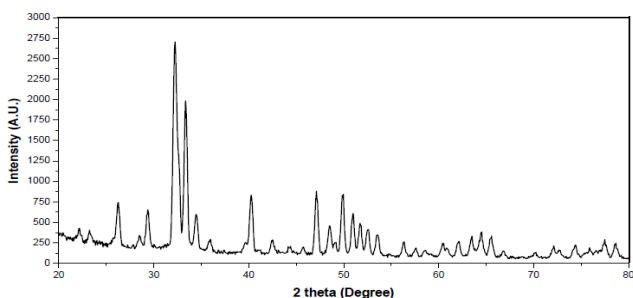


Figure 2. X-ray diffraction (XRD) patterns of HAp biosorbent extracted from Ostrich bone.

FTIR Analysis

The Fourier transform infrared (FTIR) analysis was performed to identify the presence of different functional groups in biosorbent. The FTIR spectrum of the HAP after two phase calcination is shown in figure 3. The spectrum noticeably shows the presence of phosphate bands at 1062.78, 871.83, 607.57 and 570.95 cm⁻¹ and hydroxyl bands at 3570.24 and 3479.59 cm⁻¹ which indicate the presence of major functional groups¹⁶⁻¹⁹ in addition with carbonate bands at 2015.61 and 2362.80 cm⁻¹.

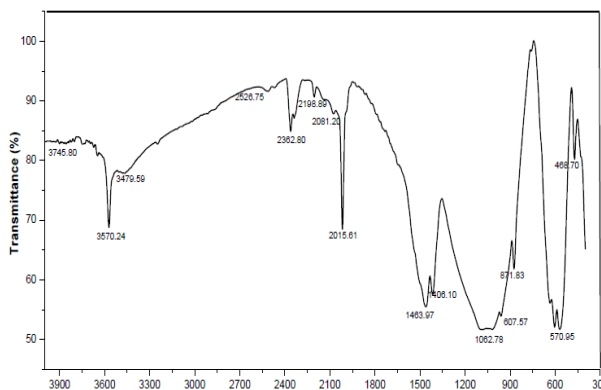


Figure 3. FTIR spectra of HAp biosorbent extracted from Ostrich bone.

Point of Zero Charge (pHpzc)

Point of zero charge method was used to determine the acido-basic properties on HAp surface²⁰. It is defined as the pH at which the total surface charges of biosorbent become zero. The plot of pHpzc is shown in Figure 4. The graph is plotted against the difference data of initial pH (i.e. pH₀) and final pH (i.e. pH_f) values (i.e. ΔpH = pH₀ - pH_f) versus initial data of pH. The point of intersection of the resulting curve at abscissa gave the pH_{PZC} value of HAp. In this study, this value was found exactly 3.0. The value signify that at pH less than 3.0, the positive charge surface of the HAp was predominated, while at pH greater than 3.0, the negative charge surface was predominated. This study shows that pH is the significant domain for determining the charge on HAp surface in aqueous medium which greatly influence the adsorption process²¹.

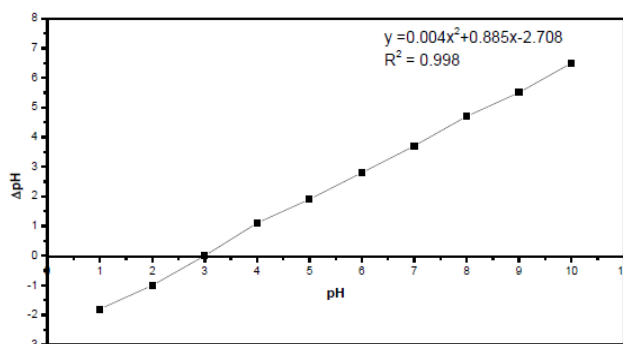


Figure 4. Point of zero charge (pHpzc) of HAp biosorbent extracted from Ostrich bone.

Effect of pH

The effect of solution pH on adsorption of lead (II) ions was investigated by varying the solution pH from 1 to 8. The solution pH was adjusted by using 0.1M HNO₃ and 0.1M NaOH and recorded in a digital pH meter. The initial lead (II) ion concentration was taken 50 mg/L. Figure 5 shows the efficiency of removal was increased significantly as pH increased from 1 to 6 and remains constant beyond 6.

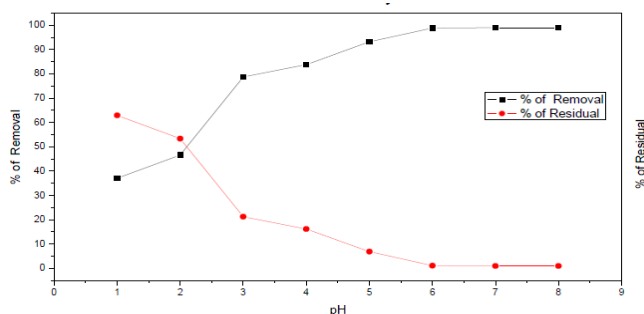


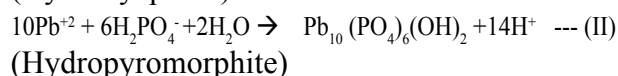
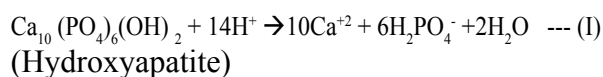
Figure 5. Effect of pH on percentage of removal of pb(II) ion on HAp surface.

A result shows that adsorption process is strongly pH dependent. Previous studies shows 49% of HAp is dissolved at pH 1 and 16 % at pH 2²². In one fold, there is no great effect of dissolution of HAp at pH 3. Therefore, the adsorption of lead (II) ions was suppressed at pH less than 3 due to the damage of crystalline phase of HAp as well as it may also be caused due to the formation of soluble hydroxyl complexes in acidic environments²³⁻²⁵. But in another fold, increasing the pH of solution, the competition between the positive charge bearing lead (II) ions becomes decreases due to the domination of negatively charged surface active

sites of HAp which improve the adsorption of the positively charged lead (II) ions by electrostatic force of attraction^{26,27}. As a result, on conducting the experiments at optimum pH range from 4-6 make sure the presence of the divalent form of lead ions as well as conserve the chemical stability of HAp. Moreover, in one hand, the pHpzc value of HAp was found 3.0 which signify that, HAp surface has +ve charged at solution pH less than 3.0 due to which lead(II) ions were repelled with HAp surface resulting in the reduction of adsorption. In another hand, at pH elevated than pHpzc, the surface of HAp starts to deprotonated (i.e. it bears negative charge) due to which adsorption kinetics increases^{28, 29}. Thus, at optimum pH (4-6) the removal efficiency was reached up to 98.86 %. This result is in good agreement with the results of previous works of Mousa *et al.*

Removal mechanism

Among the different prescribed mechanisms such as; ion exchange, surface complexation, dissolution, precipitation of metal phosphate and substitution of calcium ion of HAp by metal ion during re-crystallization, presented by Meski *et al.* dissolution and precipitation is the most preferable for removal of lead (II) ion from aqueous solution. According, to these mechanism, at optimum pH, HAp ionize to provide free hydrogen phosphate (H₂PO₄⁻) ion and this ion combines with Pb(II) ions in aqueous medium to form insoluble lead complex which is precipitate as a hydroxyromorphite and decrease the concentration of lead (II) ion in solution. The reactions of removal mechanism are shown below;



Effect of contact time

Result shows that the adsorption of lead (II) ions onto the HAp surface was remarkably fast and equilibrium was reached within 5 minutes in which the removal percentage reached up to 72.32% as shown in the figure 6. The adsorption curve was single, smooth and continuous, leading to saturation and indicated the possible monolayer coverage on the surface of the adsorbent by the lead (II) ions.

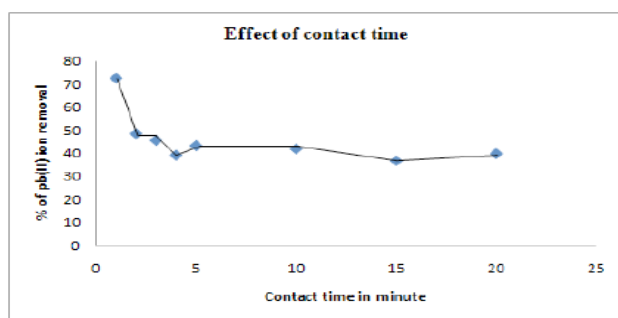


Figure 6. Effect of contact time on percentage of removal of pb(II) ion on HAp surface.

Further increase in contact time has no radical effect on the removal percent. Therefore, 5 minute shaking time was sufficient to reach equilibrium for maximum adsorption. The decrease in the rate of removal with contact time may be due to aggregation of lead (II) ions around HAp surfaces. This aggregation may hamper the migration of lead (II) ions from bulk to HAp surface as the adsorption

sites become saturated, as well as resistance to the diffusion of lead (II) ions in the adsorbents increases³⁰. Moreover, this aggregation of lead (II) ions with increase in contact time makes it almost impossible to diffuse lead (II) ions deeper into the HAp structure at the highest energy sites. These results are in good agreement with the results of earlier studies of Meski *et al.*

Effect of adsorbent dosage

Principally adsorption process is the surface phenomenon, on that basis effectiveness affect by surface area and available active sites of adsorbent which depends on its amount taken³¹. In this study, effect of adsorbent was studied at various experimental dosages: 10mg/L, 20mg/L, 25mg/L, 30mg/L, 40mg/L, 50mg/L and 100mg/L at constant initial concentration of Pb(II) ion (i.e. 50mg/L), constant pH range of 4.5-5.5 and fixed contact time of 90 minutes as shown in table 1.

Table 1. Amount of lead (II) ions removal by HAp biosorbent.

| SN | Initial conc. of Pb (II) ion (C_0) | Final conc. of Pb(II) ion (C_f) | Adsorbent dosage | pH range | qt = $(C_0 - C_f)V/m$ |
|----|--|-------------------------------------|------------------|----------|-----------------------|
| 1 | 50mg/L | 6.93 mg/L | 10 mg/L | 4.5-5.5 | 430.7 mg/g |
| 2 | 50mg/L | 13.31mg/L | 20 mg/L | 4.5-5.5 | 183.45 mg/g |
| 3 | 50mg/L | 5.79 mg/L | 25 mg/L | 4.5-5.5 | 176.84 mg/g |
| 4 | 50mg/L | 2.71 mg/L | 30 mg/L | 4.5-5.5 | 157.63 mg/g |
| 5 | 50mg/L | 1.21mg/L | 40 mg/L | 4.5 -5.5 | 121.23 mg/g |
| 6 | 50mg/L | 0.91 mg/L | 50 mg/L | 4.5-5.5 | 98.18 mg/g |
| 7 | 50mg/L | 0.52 mg/L | 100 mg/L | 4.5-5.5 | 49.48 mg/g |

In adsorbent dose 10 g/L, there is a significant removal of lead (II) ions. A previous study shows that adsorption processes are mainly a surface phenomenon; therefore, adsorption efficiency can be considerably affected by surface area and availability of active sites which is ultimately related to the mass of adsorbent³². As the adsorbent dosage increases there are inverse trends of removal due to the aggregation and overlapping of active sites of adsorbent which show the way to the decrease in the effective surface area required for maximum adsorption^{33, 34}.

CONCLUSION

This study shows that the biosorbent extracted from Ostrich bone has a good result for adsorp-

tion of lead (II) ions from aqueous solution. The adsorption was greatly pH dependent, with a high uptake (430.7mg/g) of lead (II) ion at pH range 4 - 6. Results also show the lead (II) ion adsorption is very sensitive to the initial concentration of lead ion in solution. The mechanism of dissolution of HAp and precipitation of hydrophyromorphite was dominant by a low concentration (50mg/L) and in optimum (4-6) pH range. The adsorption of lead (II) ions is very fast and the equilibrium was attended within 5 minutes. 72.32% lead (II) ions were removed within this time. There is an inverse relationship between contact time and percentage of removal. A similar trend was also found in between adsorbent dosage and amount of removal of lead (II) ions from aqueous solution.

SCOPE OF THE STUDY

The application of HAP as a biosorbent has shown the better potential for removing lead ion (II) from aqueous solution. Results obtained in this study are significant to previous research works which proved that it is a well-known biosorbent and provide good background for further investigation of removal of other heavy metal ions like Cd (II), Cr (III), Hg (II), Sb (III) and Ni (II) from aqueous solution. Furthermore, this biosorbent has the potential on removing different color dyes such as; Methylene blue, Congo red, Reactive yellow, Lemon yellow, Cheery red etc from industrial effluents of dye industries. Further characterization of this biosorbent is highly recommended before and after adsorption study.

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