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Removal of Cu(II) with hydroxyapatite (animal bone) as an inorganic ion exchanger

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ABSTRACT

A bone from a vertebrate has a hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) structure which is well known as an excellent inorganic ion exchanger for various heavy metal ions in solution. In order to evaluate the reusability of cow, pig and fish bones as removal material for heavy metals in wastewater, the ionic substitution properties and the removal capacities of these bones for the Cu ion were investigated. The results of X-ray diffraction and FT-IR spectra analyses showed that the surface of the three different bones was irregularly modified as increasing temperature and Cu ions were exchanged in the Ca part of bones. The removal capacity of the three different bones decreased with increasing temperature when the solution pHs were not controlled. Cu ion was removed almost 100% at over pH 7 while 20–60% was removed at pH 4. It is worth noting that bones calcined at 700°C have an ability of pH control of the solution where the reaction was from acidic to alkaline, although its mechanism is not yet clearly understood and thus further study is necessary. The extraction experiment for three different bones which fully reacted with Cu ion shows no significantly re-extracted Cu ion even at pH 3.

Keywords: Adsorption; Hydroxyapatite; Ionic exchanger; Animal bone; Copper removal

1. Introduction

Treatment of heavy metal contamination such as copper in water is an important subject that is of concern regarding environmental regulations and human health. Considerable progress has been made in methods such as electrochemical treatment, coagulative precipitation, adsorption, ion exchange, and reverse osmosis, and filtration. Among the various water treatment techniques such as described, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness.

Many researchers have assessed alternative sorption materials for the removal of heavy metals because sorption is a convenient and inexpensive treatment method: kaolinite [1], grape stalks [2], zeolite [3], crop milling waste [4], olive stone [5], activated carbon [6], sawdust [7], marine green alga [8], etc.

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Hydroxyapatite (HAP) is an efficient adsorbent because of its high capacity of heavy metal ion exchange or absorption. Hydroxyapatite from different origins such as mineral, synthetic, and derived from animal and fish bones have been studied for the treatment of various heavy metals [9–11].

The general formula of apatitic compounds is $Me_{10}(XO_4)_6Y_2$, where Me is a divalent metal such as calcium, sodium, lead, etc.; X is phosphorus, possibly replaced by other elements such as arsenic and vanadium; and Y can be hydroxide, fluoride, or chloride [12]. Bones from vertebrates have a hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) structure, which is well known as an excellent inorganic ion exchanger or absorption and high biological compatibility for various heavy metal ions in solution [13–15]. However, in general, the synthesized materials are very expensive.

In this research, we described the effect of heat treatment of waste bones as a removal material for heavy metals in wastewater, the ionic substitution properties on removal property of Cu(II). The objective of the present work was to investigate the adsorption capacity of three different bone waste-originated hydroxyapatites and estimate the leachability of exchanged HAP.

2. Materials and methods

2.1. Sample preparation

Three different animal bones (pig, cow and fish) were obtained from several restaurants in Gangnung, Korea. The bones were cleaned with distilled water, dried and ground, and then calcined in a furnace (C-MF, Electric Muffle Furnace) at various temperatures (100, 400, 500, 600 and 700°C) for 24 hs. The resultant powder was crushed and ground, then filtered with the mesh between 125 and 75 μm.

2.2. Characterization of sample

The morphology and crystal phase of samples was examined by scanning electron microscope (SEM, ERA-8900FE) and X-ray diffraction apparatus (XRD, Bruker D8 Adrace)

2.3. Sorption experiments

In order to determine the sorption capacity of HAP for Cu^{2+}, equilibrium metal binding experiments were performed by placing a given mass of calcined bone in a 200 ml polypropylene flask and introducing 100 ml of Cu(II) solution. The concentrations of Cu(II) were prepared between 1×10^{-4} M and 1×10^{-1} M using $CuSO_4$. The mixture of powder and solutions was shaken for 24 h. After agitation, the solid was removed by filtration through a 0.45 μm Nucleopore polycarbonate membrane filter. The final concentration of Cu(II) in the filtrates was analyzed using atomic absorption spectrophotometry (Varian Spectr-300). Initial pH values of the solutions were adjusted to the desired value using 0.1 M NaOH and 0.1 M HNO_3. No efforts were made to maintain the pH solution while metal ions were being sorbed.

2.4. Effect of pH

The effect of pH was studied in the pH range of 4–12. The initial metal concentration was 300 mg/dm^3, while the initial pH values were adjusted by adding NaOH or HNO_3 solutions. After 24 h of contact, the suspensions were filtered and analyzed for final pH and metal concentrations.

2.5. Desorption experiments

In order to estimate the reversibility of Cu^{2+} sorption, desorption experiments using solutions with different pH were performed. Firstly, HAP was loaded with Cu^{2+}, equilibrating the sorbent with the 10^{-3} M Cu solution. Solid residue was thoroughly washed several times with distilled water and dried at 105°C. Secondly, 1.0 g of the obtained solid phase was treated with the 100 ml of distilled deionized water on a horizontal shaker for 24 h at pH 3.

3. Results and discussion

3.1. Characterization of waste bone

The surface of bones was coated with gold to be observed and photographed. Different pore sizes were observed on the surface of calcined bones as shown in Figs. 1–3. The surface area of calcined bones at 700°C was significantly increased. A greater heterogeneity of surface and micrometer-sized pore diameters was clearly observed in calcined bone at 700°C. Figs. 4 and 5 show the XRD patterns of the hydroxyapatite prepared with two animal bones after heat treatment at 100°C and 700°C.

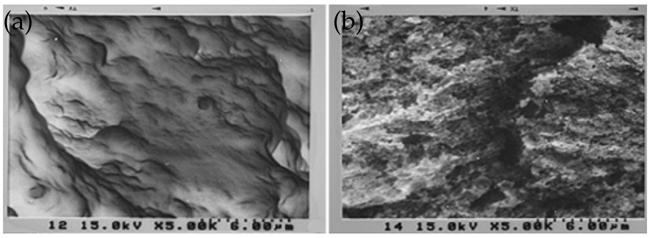

Fig. 1. SEM image of cow bone calcined at (a) 100°C and (b) 700°C.

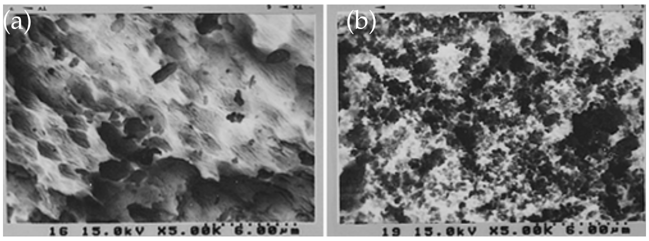

Fig. 2. SEM image of pig bone calcined at (a) 100°C and (b) 700°C.

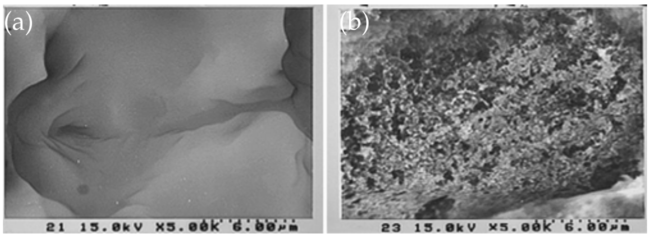

Fig. 3. SEM image of fish bone calcined at (a) 100°C and (b) 700°C.

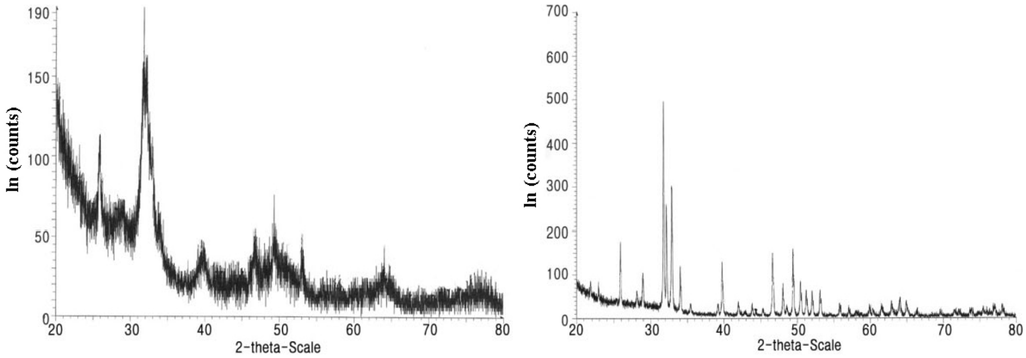

Fig. 4. XRD patterns of cow bone at (a) 100°C and (b) 700°C.

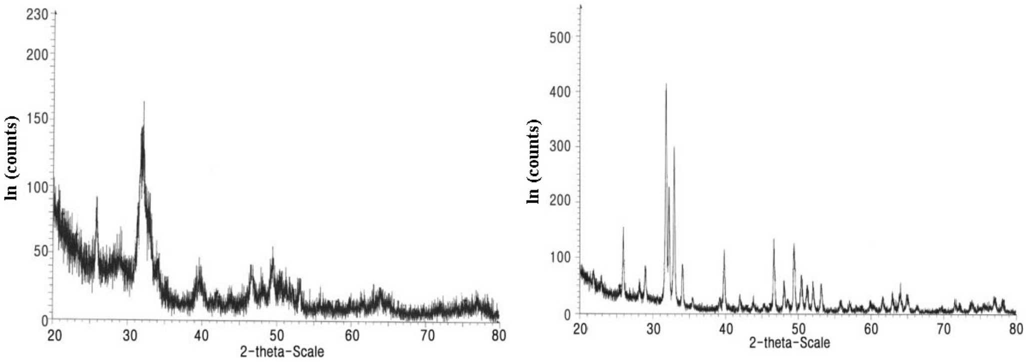

Fig. 5. XRD patterns of pig bone at (a) 100°C and (b) 700°C.

Diffraction peak of bones was observed at 25.5° (201), 31.68° (211), and 33.68° (202) of 2θ value (main peak of hydroxyapatite). The strongest peaks in the XRD pattern were characteristic of pure HAP and closely matched with the JCPDS file No. 09-432 of calcium hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). The XRD patterns of the hydroxyapatites prepared with different animal bones were quite similar without depending on the kind of animal bones and calcination temperatures. The main structural changes of hydroxyapatite were not detected but diffraction peaks of the samples calcined at 700°C showed very sharp compared to that of samples at 100ºC, suggesting a well development of crystallinity at high temperatures.

3.2. Sorption capacity of hydroxyapatite

Sorption of copper by hydroxyapatite was studied using the initial pH range 4–12. After 24 h of contact time, equilibrium pH values as well as the residual metal concentrations were measured. The results at pH 4 and pH 7 are presented in Figs. 6 and 7, respectively. The initial Cu(II) concentrations were 10^{-1} M and 10^{-3} M and the amount of hydroxyapatite was 1.0 g. Under acidic conditions, removal efficiency of copper was about 30% to 55% at pH 4 while copper was completely removed above pH 6. It is considered that copper was removed by precipitation at higher pH ranges. In the absence of any complexing species, the speciation of dissolved copper

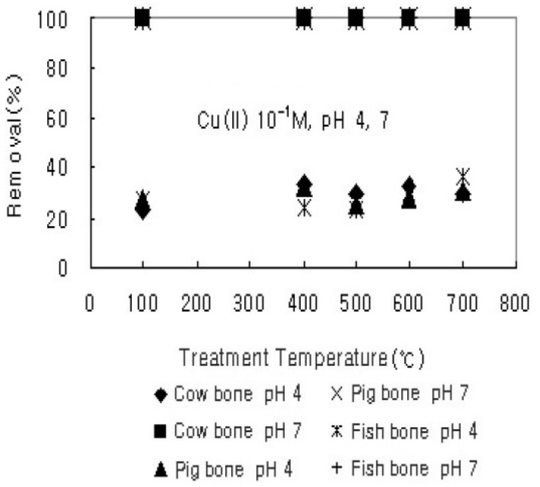

Fig. 6. Removal of Cu(II) with the hydroxyapatite (Cu 10^{-1} M).

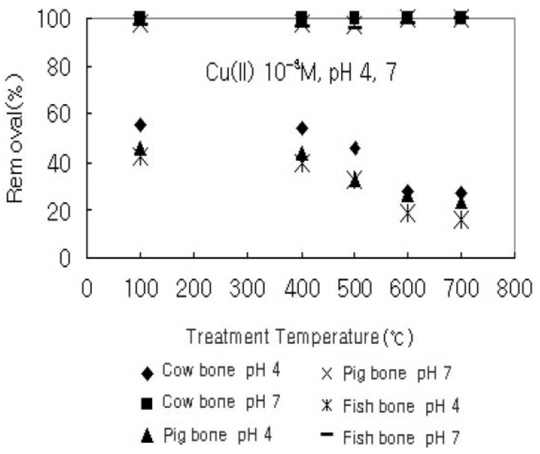

Fig. 7. Removal of Cu(II) with the hydroxyapatite (Cu 10^{-3} M).

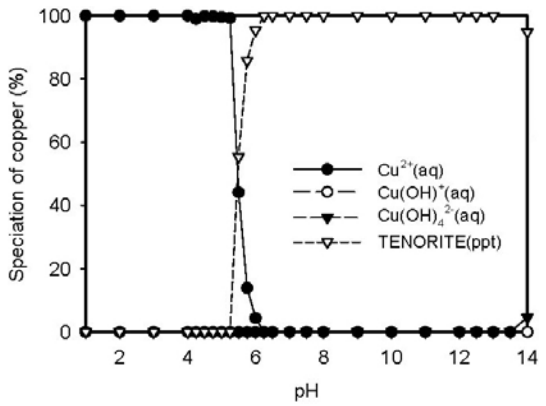

Fig. 8. Speciation of copper ion (10^{-3} M) in aqueous solution predicted by the MINEQL software.

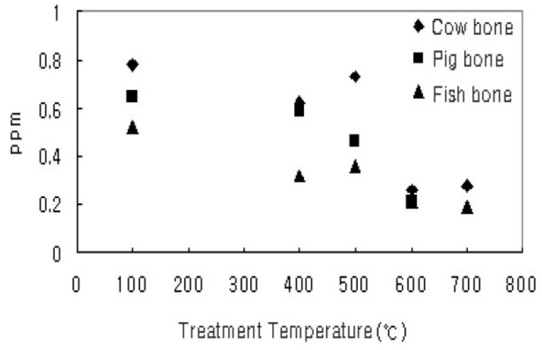

Fig. 9. Cu(II) release after exposing hydroxyapatite to acidic water.

depends only on the solution pH, causing a different distribution of the metal-hydroxyl complex. This was confirmed by the distribution of hydrolyzed copper species (10^{-3} M), as calculated by MINEQL software as shown in Fig. 8. In this simulation result, free Cu^{2+} ion was the major species up to pH 5.25. And precipitation of copper as tenorite was predicted above pH 5.25. There is not much of difference for the removal efficiency of Cu(II) in three different waste bones. Removal efficiency varied with temperature of the heat-treated sample using 10^{-3}M of copper solution as shown in Fig. 7. This result is similar with that of Ozawa and Kanahara [16]. They used fish-bone waste hydroxyapatite for the removal of aqueous lead. They reported that fish-bone heated at 600°C showed higher capability of immobilization for lead than fish-bone heated at 900°C. Lee et al. [17] suggested that removal of cationic heavy metals by hydroxyapatite followed an ion-exchange mechanism from the greatly increased dissolution of Ca^{2+} compared with control test. Therefore, it is assumed from the results that plausible mechanisms in the removal of copper ion by hydroxyapatite are through ion exchange and precipitation.

3.3. Desorption experiments

In order to evaluate the reversibility of copper sorption onto hydroxyapatite, copper desorption from hydroxyapatite was determined. Fig. 8 shows the desorption result with various hydroxyapatites at pH 3. Copper was not detected over pH 3 in desorption tests. The desorbed amount of copper was decreased with increasing treatment temperature of samples. The result from desorption tests suggest that most of copper ion was fixed in hydroxyapatite through ion exchange. The highest desorption percentage was obtained for Cu (11.2%) from fish bone but most were less than 5%.

4. Conclusions

Hydroxyapatite prepared from animal bone waste was investigated for the removal of copper from aqueous solution and the following conclusions can be drawn from the results of the present study:

- Copper ions in aqueous solutions strongly interact with hydroxyapatite from animal bones.
- Removal efficiency of copper was obtained about 30% to 55% at pH 4 while copper was completely removed at over pH 6 ranges.
- The highest desorption percentage was obtained for Cu (11.2%) from fish bone but most of them were less than 5%.
- From the results obtained, the mechanism of metal ion removal by hydroxyapatite includes ion exchange/adsorption and precipitation.
- Animal waste bone would be an effective alternative to synthetic hydroxyapatite for removal of divalent heavy metal ions from aqueous solutions.

Acknowledgement

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References

[1] Ö. Yavuz, Y. Altunkaynak and F. Güzel, Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. Water Res., 37 (2003) 948–952.
[2] I. Villaescesa, N. Fiol, M. Martínez, N. Miralles, J. Poch and J. Serarols, Removal of copper and nickel ions from aqueous solutions by grape stalk wastes. Water Res., 38 (2004) 992–1002.
[3] E. Erdem, N. Karapinar and R. Donat, The removal of heavy metal cations by natural zeolites. J. Coll. Interface Sci., 280 (2004) 309–314.
[4] A. Saeed, M. Iqbal and M.W. Akhtar, Removal and recovery of lead (II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). J. Hazard. Mater. B, 117 (2005) 65–73.
[5] N. Fiol, I. Villaescesa, M. Martínez, N. Miralles, J. Poch and J. Serarols, of Pb (II), Ni (II), Cu (II) and Cd (II) from aqueous solutions by olive stone waste. Sep. Purif. Technol., 50 (2006) 132–140.
[6] E. Demirba, Adsorption of cobalt(II) ions from aqueous solution onto activated carbon prepared from hazelnut shells. Adsorpt. Sci. Technol., 21 (2003) 951–963.
[7] B. Yu, Y. Zhang, A. Shukla and S.S. Shukla, The removal of heavy metals from aqueous solutions by sawdust adsorption—removal of lead and comparison of its adsorption with copper. J. Hazard. Mater. B., 84 (2001) 83–94.
[8] K. Vijayaraghavan, M. Thilakavathi, K. Palanivelu and M. Velan, Continuous sorption of copper and cobalt by crab shell particles in a packed column. Environ. Technol., 26 (2005) 267–276.
[9] S. Al-Asheh, F. Banat and F. Mohai, Sorption of copper and nickel by spent animal bones. Chemosphere, 39 (1999) 2087–2096.
[10] E. Deydier, R. Guilet and P. Sharrock, Beneficial use of meat and bone meal combustion residue: an efficient low cost material to remove lead from aqueous effluent. J. Hazard. Mater. B, 101 (2003) 55–64.
[11] A. Krestou, A. Xenidis and D. Panias, Mechanism of aqueous uranium (VI) uptake by hydroxyapatite. Miner. Eng., 17 (2004) 373–381.
[12] T.S.B. Narasaraju and D.E. Phebe, Some physico-chemical aspects of hydroxylapatite. J. Mater. Sci. 31 (1996) 1–21.
[13] B. Sutter, L.R. Hossner and D.W. Ming, Dissolution kinetics of iron–manganese and copper-containing synthetic hydroxyapatites. Soil Sci. Soc. Am. J., 69(2) (2005) 362–370.
[14] I. Shashkova, A. Rat'ko and N. Kitikova, Removal of heavy metal ions from aqueous solutions by alkaline–earth metal phosphates. Colloids Surf.:A Physicochem. Eng. Asp., 160 (1999) 207–215.
[15] J.A. Gomez, P.J. Morando and D.S. Cicerone, Natural materials for treatment of industrial effluents: comparative study of the rentention of Cd, Zn and Co by calcite and hydroxyapatite. J. Environ. Manage.,71 (2004) 169–177.
[16] M. Ozawa and S. Kanahara, Removal of aqueous lead by fish-bone waste hydroxyapatite powder. J. Mater. Sci., 40 (2005) 1037–1038.
[17] C.K. Lee, H.S. Kim and J.H. Kim, The removal of heavy metals using hydroxylapatite. Environ. Eng. Res., 10 (2005) 205–212.