



Original Article

Mineralization of Natural Hydroxyapatite for High Efficiency of Pb^{2+} ion Removal in Aqueous Solution

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Abstract: The mineralized hydroxyapatite (m-HA) was prepared by soaking natural hydroxyapatite (n-HA) extracted from pig bone in the simulated body fluid (SBF) for 3 days. The m-HA was much better in comparison with the n-HA for removing Pb^{2+} ions from aqueous solution. After 4 hours of adsorption experiments, m-HA material eliminated almost 100% of lead ions while n-HA removes only 65.4%. The adsorption isotherm study was effectuated for the m-HA. The experimental data was fitted for both Langmuir and Freundlich models in which the Langmuir model was more suitable due to the higher value of R^2 coefficient. The maximum adsorption capacity (Q_m) of Pb^{2+} ions on the m-HA was calculated from the Langmuir isotherm equation, which was the high value of 574.1 (mg/L). The mechanism of lead ion removal for m-HA was determined by XRD analysis. The obtained result highlighted the ion exchange between the m-HA and the Pb^{2+} ions.

Keywords: Natural hydroxyapatite (n-HA), mineralized hydroxyapatite (m-HA), Pb^{2+} , SBF, removal.

1. Introduction

In recent years, water pollution by heavy metal elements due to fast industrialization is a serious problem and harm to public health [1-2]. In particular, Pb^{2+} ions are typical pollutants because of their high toxicity even at low concentrations in water environment. Lead poisoning can cause irreversible damage and

harm to normal development of fetus, growth of teenagers such as their psychology, behavior and cognition [3]. Therefore, the removal of toxic heavy metals such as lead ions is an important issue.

A number of methods have been developed for removing Pb^{2+} ions from waste water including chemical reduction, precipitation, adsorption, electrochemical deposition, membrane technology, ion-exchange and ultra-filtration [4-5].

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Hydroxyapatite (HA - $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) is the main inorganic component in natural bone. It has been proved as an adsorptive material for treatment of lead ion contamination [6-8]. Several studies have performed to separate natural HA (n-HA) from animal bones for the purpose of adsorbing lead ions in water environment. T. Kaludjerovic et al [9] have studied the Pb^{2+} sorption and its kinetic by using natural HA extracted from Lisina ore. J. Cha et al [10] have investigated the adsorption of Pb^{2+} onto HA powder synthesized from waste cow bone. Three-dimensional natural HA has been developed by R. Zhu et al [11], the microspheres of obtained HA can remove some heavy metal ions including of Pb^{2+} ions.

Keep up with the trend of lead treatment according to the above studies, a special type of HA material was developed in this study, which is the mineralized HA (m-HA). The mineralization process was performed by soaking n-HA in Simulated Body Fluid (SBF) with the aim of modifying the surface structure of adsorptive material, thereby increasing the efficiency of lead ion removal in aqueous solution.

2. Materials and methods

2.1. Preparation of natural HA (n-HA)

Natural hydroxyapatite was extracted from pig bone by using a typical thermal treatment without using any chemicals. The separated process of n-HA is briefly described as follows: Firstly, pig bone was boiled for 6 hours to remove fats and impurities. Next, the cleaned bone was heated at 300 °C for 2 hours to burn off some organic compounds. The bone of this step is black color due to some char appeared. Finally, the black sample was heated at 750 °C for 6 hours to remove the remaining char and convert into ceramic material. The obtained sample was crushed to achieve the fine white powder.

2.2. Preparation of mineralized HA (m-HA)

The simulated body fluid (SBF) solution, used for mineralization process, was synthesized

according to Kokubo's method [12]. The SBF solution has an ionic composition similar to that of human blood plasma. The mineralization of n-HA was performed by soaking 500 mg of natural HA powder in 1000 mL of SBF solution for 3 days at room temperature. During this time, the mixture was continuously stirred by using a magnetic mixer. After the end of immersing time, the powder was collected and rinsed with distilled water, then dried at 100 °C for 24 hours. The resulting powder is called m-HA.

2.3. Lead ion adsorption experiments

To compare the efficiency of Pb^{2+} ion removal from aqueous solution of n-HA and m-HA materials, the adsorption experiments were performed according to the reference of the previous study [13]. The Pb^{2+} ion solutions with concentration of 100 ppm and pH of 4.7 were obtained by dissolving $\text{Pb}(\text{NO}_3)_2$ salt in deionized water. The experiments of lead ion removal were carried out by immersion of 50 mg of each powder samples in 100 mL of Pb^{2+} ion solution. The mixtures were stirred with speed of 100 rpm at room temperature for different contact times. At the end of experimental periods, the mixtures were filtered to separate into two parts (liquid and powder). The liquid parts were taken immediately to measure remaining lead contents. The powder samples were rinsed three times with deionized water, dried at 100 °C and further served for characterization. The percentages of lead ions removed by n-HA and m-HA materials were calculated by following equation:

$$\text{Removal (\%)} = \frac{C_0 - C_f}{C_0} \cdot 100 \quad (\text{eq1})$$

Where, C_0 and C_f are initial and final concentrations (mg/L - ppm) of lead ions in solution, respectively.

2.4. Physic-chemical characterizations

X-ray diffraction (XRD) with Bruker D8 Advance diffractometer was used to identify phase composition of n-HA, m-HA and m-HA

after lead ion adsorption. The XRD data were measured with a scanning speed of $1^\circ/\text{min}$. Field emission scanning electron microscopy (FE-SEM) – an innovation technique, was served to observe surface morphology of synthetic HA and mineralized HA. Lead ion concentrations in water environment were investigated by using inductively coupled plasma – mass spectrometry (ICP-MS) following to EPA method 200.8, revision 5.4.

3. Results and discussion

3.1. Characterization of natural HA (n-HA)

The XRD diagram of n-HA was compared with JCPDS PDF no. 09-432 standard HA card [14]. All characteristic peaks of HA were identified and no strange peaks were presented

as seen in Fig. 1. The clear and sharp peaks confirmed the purity and high crystallinity of n-HA material extracted from pig bone by using a typical thermal process in this study.

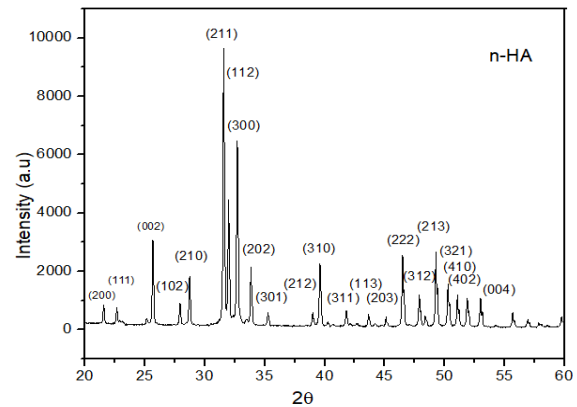


Fig. 1. XRD diagram of n-HA extracted from pig bone.

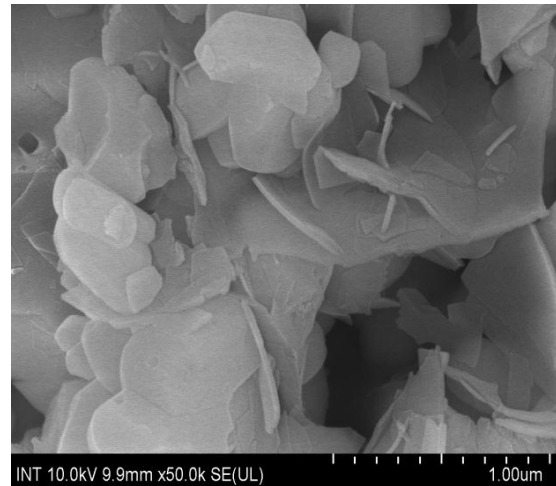
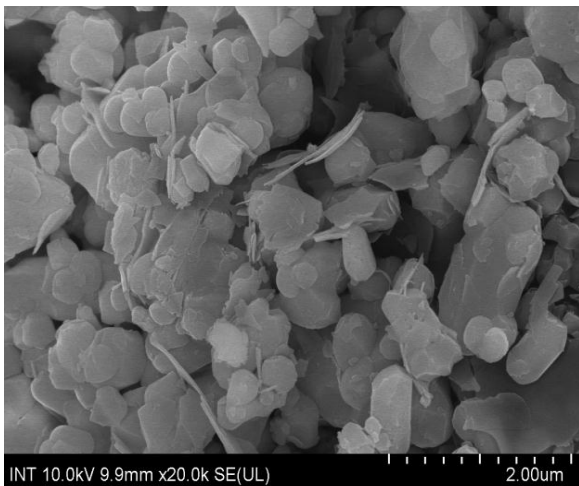


Fig. 2. FE-SEM images of n-HA at different magnifications.

The FE-SEM micrographs at 20,000 and 50,000 magnifications clearly show the particles, rods, scales and porous holes in the structure of n-HA (Fig. 2). The porous characteristic is an important factor of adsorption material, especially for physical adsorption property. The result obtained by FE-SEM is quite similar to the one reported in the reference [15], in which the authors have extracted the HA material from bovine bone.

3.2. Characterization of mineralized HA (m-HA)

Fig. 3 shows the XRD diagram of m-HA. It is noted that there is a slight expansion of diffraction peaks of m-HA compared to the initial n-HA. This phenomenon can attribute the interaction between n-HA and SBF solution which lead to the expansion of diffraction peaks but all characteristic peaks of HA were remained at the same positions and no strange peaks were

observed. The FE-SEM images of m-HA clearly indicated the newly mineral layer consisting of homogeneous crystalline scales covered on the surface and interwoven into the pores of n-HA after 3 days of immersing in SBF as seen in Fig. 4. The combination of two results XRD and FE-SEM confirmed the formation of newly HA crystal layer after mineralization process.

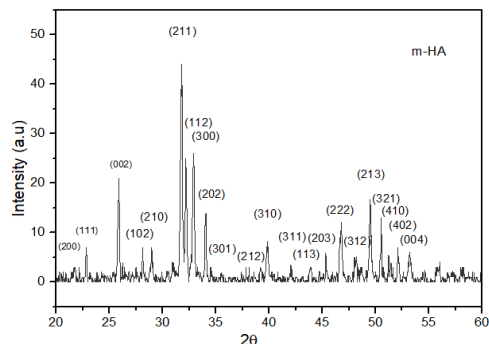


Fig. 3. XRD diagram of mineralized HA in SBF solution.

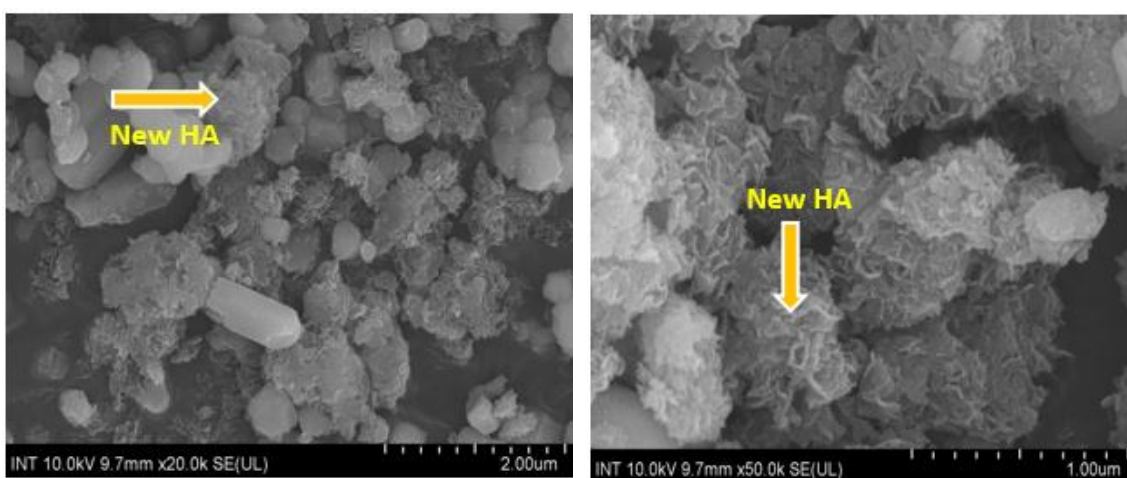


Fig. 4. FE-SEM images of m-HA at different magnifications.

3.3. Lead ion adsorption in aqueous solution of n-HA and m-HA

Fig. 5 and Fig. 6 present the behaviors of lead ion adsorption of n-HA and m-HA respectively as a function of times. For n-HA, lead removal rapidly reached 46.3% after 1 hour of adsorption. This was followed by a slight increase until 4 hours before achieving a saturated period of adsorption from 4 to 8 hours. In the study of Y. Zhou [13], n-HA was separated from pig bone by a different thermal processing which showed only 28.7% of lead ion adsorption within 1 hour in the same conditions of initial concentration of lead ion solution and amount of adsorbent. Therefore, n-HA extracted in this work showed higher levels of lead removal than previous study.

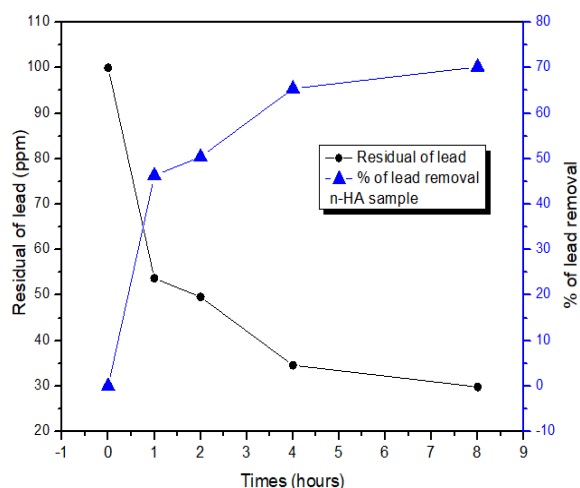


Fig. 5. Lead ion removal efficiency of n-HA as a function of times.

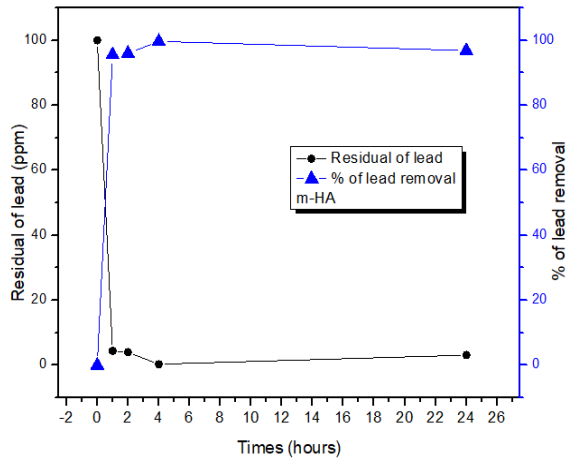


Fig. 6. Lead ion removal efficiency of m-HA as a function of times.

For m-HA, a very effective removal of lead ions was recorded in comparison with n-HA. The percentage of lead ion removal was reached 95.56% after 1 hour of adsorption. This value was almost constant when the contact time increased to 2 hours. Therefore, it is possible to consider that the equilibrium adsorption time is 1 hour. The maximum value of lead ion removal was recorded as 99.67% after 4 hours of adsorption. Then, the efficiency of lead removal represented a slight decrease. At 24 hours of contact time, the percentage of lead removal was 96.86%. Thus, the m-HA expressed the highly efficiency in removing lead ions in aqueous solution. The surface modification of m-HA after mineralized process of n-HA can be an important factor to capture Pb^{2+} ions. The m-HA consists of a newly layer of HA crystals which provides more sites for physical adsorption.

3.4. Adsorption isotherm studies

From the obtained results in the section 3.3, the time of adsorption equilibrium for m-HA is chosen as 1 hour. The Pb^{2+} ion adsorption isotherms for m-HA were investigated with a series of experiments by immersing the powder samples (each 50 mg) in 100 mL of Pb^{2+} solution with pH of 4.7 at different initial concentrations of 50, 100, 150, 200, 250 and 300 mg/L for 1

hour. The obtained data was examined using the two well-known isotherm models as follows:

Langmuir isotherm model:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L \cdot Q_m} \quad (eq2)$$

Freundlich isotherm models:

$$\ln Q_e = \ln K_F + \frac{1}{n} \cdot \ln C_e \quad (eq3)$$

Here, C_e (mg/L) and Q_e (mg/g), respectively, represents the concentration and adsorption capacity at the equilibrium; The Q_m (mg/g) is the maximum adsorption capacity; K_L and K_F are the Langmuir and Freundlich constants, respectively; n is the Freundlich coefficient.

The Q_e values were calculated as following equation:

$$Q_e = \frac{(C_o - C_e) \cdot V}{m} \quad (eq4)$$

The calculated values for Langmuir and Freundlich models are summarized in Tab. 1. Their adsorption isotherm equations were established as presented in Fig. 7 and Fig. 8. Based on these isotherm curves, the experimental constants were identified as shown in Tab. 2. It is clearly that both of adsorption isotherm models can be fitted to describe the adsorption of Pb^{2+} ions by m-HA material. However, the Langmuir model is more suitable for describing the Pb^{2+} ion adsorption because its R^2 coefficient is higher than that of Freundlich model. From Langmuir isotherm equation, the maximum adsorption capacity Q_m of Pb^{2+} ions on m-HA was calculated as 574.1 (mg/g). The Q_m of m-HA is much higher than that of n-HA without mineralization process as reported in the scientific papers [9, 10, 13]. In those studies, the Q_m values are 9.52, 40, 96.1 (mg/g) for n-HA extracted from cow bone, Lisina natural ore and pig bone, respectively. Thus, the m-HA obtained by mineralization in this study has a significant potential application for removing Pb^{2+} ions from aqueous media.

Tab. 1. The calculated values for Langmuir and Freundlich models

C ₀ (mg/L)	C _e (mg/L)	LnC _e	Q _e (mg/g)	LnQ _e	C _e /Q _e (g/L)
50	1.8	0.588	96.4	4.568	0.019
100	4.4	1.480	191.2	5.253	0.023
150	10.2	2.322	279.6	5.633	0.036
200	23.3	3.148	353.4	5.867	0.079
250	34.3	3.535	431.4	6.070	0.080
300	51.2	3.940	497.6	6.210	0.103

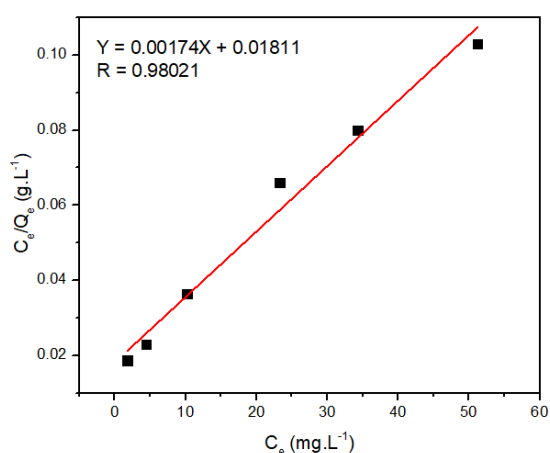


Fig. 7. Langmuir adsorption isotherm for Pb²⁺ adsorption on m-HA.

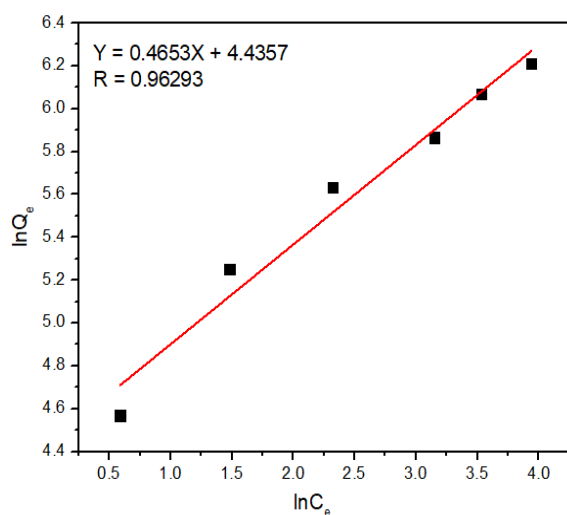


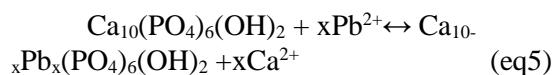
Fig. 8. Freundlich adsorption isotherm for Pb²⁺ adsorption on m-HA.

Tab. 2. The experimental constants in Langmuir and Freundlich models

Langmuir			Freundlich		
Q _m	K _L	R ²	n	K _F	R ²
574.	0.09	0.9802	2.14	84.	0.9629
1	6	1	9	4	3

3.5. Identification of type of lead ion adsorption by XRD analysis

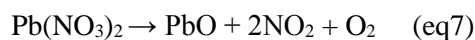
The above results confirmed the efficiency of lead ion adsorption by using m-HA. To identify the types of lead ion adsorption, the XRD diagrams of n-HA, m-HA and m-HA after lead adsorption for 1 hour were coupled as presented in Fig. 9. According to the literatures [16-19], different phases were determined on m-HA diffraction pattern after adsorption processing. All characteristic peaks of HA material were found but they were slightly shifted to the right side. This result is attributed to the exchange of lead ions in aqueous solution with m-HA material according to the following reaction:



The appearance of Pb(NO₃)₂ phase can be assigned to sign of the physical adsorption of m-HA. When m-HA soaked in Pb(NO₃)₂ solution, Pb²⁺ and NO₃⁻ ions adhere to the surface or infiltrate in the pores of absorbent. These ions recombine to make lead nitrate salt when the material sample dried after adsorption processing. In addition, the presence of PbO and PbCO₃ phases can be explained by chemical reactions that occur during the experiment. The phase of PbCO₃ may be due to the combination of Pb²⁺ cations and CO₃²⁻ anions produced by dissolving CO₂ in atmosphere into the aqueous solution.



The phase of PbO can be generated by Pb(NO₃)₂ decomposition when drying absorbent sample after adsorption experiment.



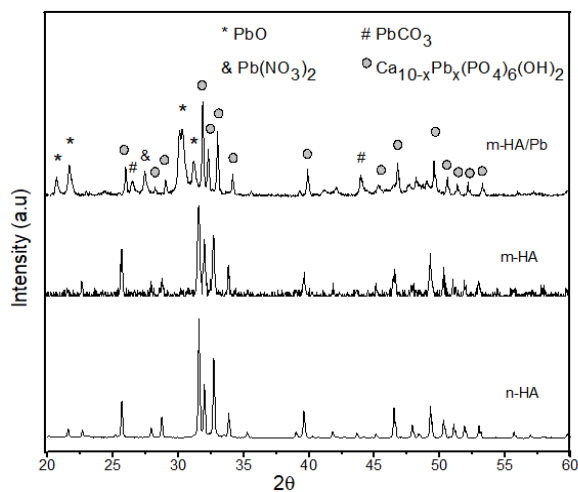


Fig. 9. XRD identification of phases on m-HA after lead ion adsorption.

4. Conclusion

The natural hydroxyapatite (n-HA) was successfully extracted from pig bone by using a thermal processing. The mineralized HA (m-HA) was achieved by soaking n-HA powder in Simulated Body Fluid (SBF) for 3 days. Experiments of lead ion adsorption were effectuated for both n-HA and m-HA. The obtained results showed that the m-HA expressed a high efficiency of lead ion removal in comparison with n-HA. The lead ion removal percentage reached 95.56% for m-HA after only 1 hour of experiment while this value was only 46.3% for n-HA in the same contact time. The maximum efficiency of lead ion adsorption for m-HA was almost 100% after 4 hours. The adsorption process of Pb^{2+} ions on the m-HA follows both Langmuir and Freundlich models. However, the Langmuir model is more suitable due to the higher value of R^2 coefficient. The maximum adsorption capacity (Q_m) of m-HA is much higher than that of n-HA without mineralization process. The mechanism of lead ion removal for m-HA was investigated to clearly define the ion exchange of absorbent material. So, m-HA was proven to be a potential adsorbent for lead ion removal compared to n-HA.

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