A Novel Method for the Fabrication of Granular Hydroxyapatite-bentonite Composite Adsorbents for the Removal of Pb^{2+} from an Aqueous Solution

ThiMinh Hieu Do, Pham ThanhThao Tran, AnhKhoaTon and Minh Vien Le

Department of Inorganic Chemical Engineering, Ho Chi Minh City University of Technology, Ho Chi Minh City 70000, Vietnam

Abstracts: Granular HApB composite adsorbents, with dimensions of 4 mm $\times$ 4 mm, were prepared for the removal of lead from an aqueous solution. The effectiveness of the composites for Pb^{2+} removal from an aqueous solution with different initial concentrations, adsorbent doses and reaction times were examined. The Langmuir isotherms, Freundlich isotherm models and pseudo-second order kinetic model were used in this analysis. It was found that the Langmuir model fitted the experimental data better than the Freundlich model, with a maximum adsorption capacity of 93.37 $\text{mg}\cdot\text{g}^{-1}$. The pseudo-second order kinetic model also fit the experiment data well with an adsorption capacity of 70.73 $\text{mg}\cdot\text{g}^{-1}$ after being reused for 3 times. Furthermore, the composites may possibly be used in processes for industrial water treatment.

Key words: Environment, afforestation, poplar plantations, timber, marketing.

1. Introduction

In recent years, although rapid industrialization has led to significant economic improvement, it has simultaneously damaged the environment through the introduction of a number of different heavy metals such as Co^{2+} , Zn^{2+} , Ni^{2+} , Pb^{2+} , As^{5+} , etc. into natural water sources. This has caused serious environmental pollution and has also become a public health concern. It is known that once substances, such as lead, enter the human body, they are distributed to organs such as the brain, kidneys, liver and bones. At high levels of exposure, lead attacks the brain and central nervous system. In extreme cases it can lead to coma, convulsions and even death. Technologies have been developed to remove toxic heavy metals from waste water, including reduction, adsorption, ion exchange, membrane technologies, and so on [1]. Generally, adsorption is the most common process, and is considered to be relatively simple, efficient and

convenient enough even for application in rural areas.

Recently, hydroxyapatite (HAp) $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ has been shown to play a crucial role in the immobilization of heavy metals as well as for the remediation of ground water pollution in contaminated soil. HAp also has the advantages of biocompatibility, non-toxicity, and chemical inertness as well as a high ion exchange capacity leading to a variety of potential applications in bioceramics, protein purification, catalyst, and methane oxidation [2]. Several studies in the literature have reported on the adsorption properties of HAp. This material is able to adsorb a wide variety of heavy metal ions, including Cd^{2+} [3-5] Co^{2+} [4], Zn^{2+} [3, 4] and Pb^{2+} [4] cations. Mobasherpour, I. et al. [1, 6] successfully synthesized nano HAp from analytical grade reagents with high Pb^{2+} , Cd^{2+} and Ni^{2+} adsorption capacities of 1,000, 143 and 40 $\text{mg}\cdot\text{g}^{-1}$ respectively [7]. Yubo, Y. et al. [8] investigated hydroxyapatite, which was converted from alkaline residue, and determined the optimal conditions for Pb^{2+} removal. Their results confirmed both the pseudo-second order kinetic model and Langmuir isotherm model of Pb^{2+} adsorption. They obtained a

Corresponding author: Minh Vien Le, assistant professor, main research fields: photocatalytic materials and environmental technology.

maximum adsorption capacity of 1,429 mg·g⁻¹.

Previous studies have confirmed that HAp possesses remarkable adsorption properties. In most cases, it has been used in the form of a fine powder dispersed in an aqueous solution. There has been limited investigation of HAp in solid form because of the strength limitation problem with pure HAp powders. The poor mechanical properties of HAp [9] limits its utilization [10]. Recently, the adsorption ability of composite materials, such as magnetic HAp/Fe₃O₄ composites [11, 12], nano hydroxyapatite-alginate composites [10] and hydroxyapatite/chitosan composites [13], has been investigated. The use of composite materials has led to an improvement in their mechanical and chemical properties, and good biocompatibility and reusability. However, fabrication of composite materials increases the cost of the adsorption material. Pellets for granular adsorption are considered the optimal choice to employ in adsorption column applications. Bentonite is a cost efficient aluminum phyllosilicate clay absorbent, possessing the outstanding physicochemical properties of high specific surface area, excellent cation exchange capacity [13], and high Pb²⁺ adsorption capacity after being activated [14, 15]. Therefore, a combination of bentonite and HAp can be expected to produce granular adsorbents with enhanced mechanical and adsorption properties. However, up till now there have been no studies regarding granular hydroxyapatite/bentonite composites.

Thus, in this work, the authors take advantage of the extraordinary adsorption ability of HAp and the adhesive properties and the adsorption ability of bentonite to fabricate and analyze a granular apatite/bentonite composite material. The structures of the material and adsorption properties for Pb²⁺ cations in an aqueous solution are also investigated.

2. Materials and Methods

2.1 Nano Crystalline HAp Synthesis

Nano HAp was prepared by the precipitation method

as described in a previous publication [16] from oyster shell powder and phosphoric acid (85%, Merck). After 3 hours of reaction time, the reaction system was cooled down to ambient temperature. The pH of the mixture was adjusted to 11 by using an ammonia solution (Merck, 28-30%). The solution was stirred for 2 hours, and then aged overnight and filtered. The precipitated HAp was dried at 110 °C for 6 hours.

2.2 Bentonite Activation

An acid treatment was applied for bentonite activation. About 50 g of commercial bentonite was added to 250 mL of the 10% HCl solution and left to react at 70 °C for 4 hours. The suspension was filtered and washed with distilled water until no chloride ions were present. Activated bentonite (AB) was obtained by drying the solid at 110 °C and milling to get a finer powder.

2.3 Fabrication of the Granular Hydroxyapatite-bentonite Composite

HAp, AB and AlPO₄ powders in weight ratios of 54.5: 36.4: 9 were mixed with distilled water before being subjected to ball milling for 30 minutes and then dried in an electric oven. An appropriate amount of water was added to the dried powder after which it was mixed using a mortar and pestle to obtain a homogeneous HAp-Bentonite (HApB) paste. The HApB paste was granulated by passing through a mold with holes of 5.0 mm × 5.0 mm. The HApB granules were left to dry at room temperature overnight, and then sintered at 500 °C for 1 h.

2.4 Adsorption Study

Aqueous Pb²⁺ cation solutions of various concentrations were prepared from lead nitrate (> 99.0%) and distilled water. The initial Pb²⁺ concentrations were confirmed by the ICP-OES method. The pH of the starting Pb²⁺ solution was adjusted by introducing a solution of 0.1M NaOH or 0.1M HCl.

All adsorption experiments were performed using granular adsorbents for batch absorption at the ambient

temperature and using a magnetic stirrer. In each experiment, around 0.5 g of the granular HApB composite was added to the Pb²⁺ solution. Small amounts of Pb²⁺ solution had to be introduced or withdrawn in order to adjust the adsorbent-solution ratio to 0.5 g/100 mL, due to a small difference in the weight of the granular adsorbent. After the desired contact time, aliquots of 5 mL were collected for analysis and evaluation of the remaining lead concentration. The adsorption capacity of the Pb²⁺ cations, q (mg·g⁻¹), was calculated according to the Eq. (1):

$$q = \frac{C_0 - C_t}{m} V \quad (1)$$

where C_0 and C_t are the lead concentrations, in ppm, in the solution at the initial time and after the contact time t (min), respectively. The mass and volume of the adsorbent in the solution are represented by m (g) and V (L), respectively.

2.5 Reusability Study

The same conditions were used for the reusability study as in the adsorption study, namely a 500 ppm lead solution with an adsorbent-solution ratio of 0.5 g/100 mL. The pH of the initial solution was adjusted to 5.5 and isotherm adsorption took place under magnetic stirring at the ambient temperature. After 24 h of adsorption time, the adsorbent was separated and immersed in 100 mL of 0.01 M EDTA for over 24 hours [17]. Then, the adsorbent was ultrasonically washed in distilled water for 1 minute, dried at 70 °C for 4 h and fired at 350 °C for 30 minutes. In the second and third adsorption steps, the process was repeated using the same conditions as for the first step. In each step, the process was repeated three times after which the remaining lead concentration in the residue was analyzed.

3. Results and Discussion

3.1 Characterization of Adsorbent

The X-ray diffraction patterns of 500 °C calcined

hydroxyapatite (HAp-500 °C), activated bentonite (AB) and HApB composite after being sintered at 500 °C for 1 h are shown in Fig. 1. The results show that the hydroxyapatite structure has the characteristic peaks at two theta 2θs of 25.9, 31.7, 32.2, 32.9 and 49.5 degrees, corresponding to the JCPDS card No. 09-0432. Additionally, peaks corresponding to quartz in the AB were also observed at 26.5°.

Moreover, the peaks for the AB and HAp structures are all represented in XRD patterns for the HApB composite, confirming its successful fabrication. There was no change in the structure and no reaction between AB and HAp after heat treatment for fabrication of the composite adsorbent.

Fig. 2 shows the FTIR spectrum of the granular HApB composite. The bands at 473, 565, 604 and 630 cm⁻¹ correspond to the PO₄³⁻ groups of the hydroxyapatite [18, 19]. The bands at 3,456 and 1,650 cm⁻¹ are assigned to the OH⁻ group. However, the appearance of peaks at 1,455 cm⁻¹ indicates the presence of CO₃²⁻, HPO₄²⁻ around 879 cm⁻¹ [18, 19] and the peak detected at 1,035 cm⁻¹ confirms the Si-O bond, while the Si-O-Si and Al-O-Si bonds are exhibited at 473 cm⁻¹[20].

The morphologies of the activated bentonite powder, HAp powder and HApB composite granules are

Fig. 1 XRD patterns of the HAp, activated bentonite and granular HApB composite.

Fig. 2 FT-IR pattern of the granular HApB composite.

shown in Fig. 3. The activated bentonite and HAp particles exhibit a uniform structure with estimated particle sizes of 100 nm. The SEM results also show the uniform distribution of the bentonite and HAp particles, with uniform pores and aggregates. In addition, the average stress of the granular HApB composite was measured to be $8.74 \cdot 10^6$ ($N \cdot m^{-2}$).

It is known that the pH of the solution plays an important role in the adsorption kinetics and the adsorption capacity of Pb^{2+} on the surface of HAp due to changes in the surface of the adsorbent [21], the different chemical nature of the Pb^{2+} species present at different pHs and the solubility of HAp in the acidic solution. The solubility of hydroxyapatite in an acidic solution needs to be investigated to prevent the dissolution of HAp into the solution during the

adsorption process. Fig. 4 describes the solubility of the HAp in solutions with a pH ranging from 2-5.5. There is evidence that there is strong dissolution of HAp when the pH value is 2 and the solubility reached 4%. The solubility decreases with increasing pH value and becomes stable at a pH of 4. There is a drop in the solubility of HAp when the pH of the solution is 5.5% to 1.46%. The results indicate that the HAp was stable in an acidic solution with a pH value larger than 4, which is a promising indication for the application of granular adsorbent HAp composites for adsorption in an acidic Pb^{2+} solution.

3.2 Effect of Contact Time

Fig. 5 shows the influence of the contact time on the adsorption of Pb^{2+} by HApB. The initial concentration used in the investigation was 543 mg/L. It is clear that the maximum rate of adsorption occurred within 12 hours of contact time, increased slowly afterwards, reaching equilibrium after 60 min, yielding 80% Pb^{2+} removal. The main reason for the maximum rate of adsorption is the existence of many active sites on the surface during the first stage of the adsorption process. The gradual occupancy of these sites caused the process to slow [22]. The adsorption capacity was measured after 12, 24 and 72 hours to be 52.47, 67.93 and 89.75 ($mg \cdot g^{-1}$), respectively.

Several kinetic models have been proposed to clarify the adsorption mechanism. Among them, the pseudo-second order kinetic model has been shown to be able to more appropriately describe the mechanism

Fig. 3 Scanning electron microscopic images of: (a) nano HAp, (b) activated bentonite and (c) topview of the granular HApB composite.

Fig. 4 The solubility of HAp corresponding to pH solution after 24 h of contact time.

Fig. 5 (a) Effect of contact time and (b) Pseudo-second order kinetic model for adsorption of Pb^{2+} on the HApB composite.

of solute adsorption from an aqueous solution onto an adsorbent, which is usually expressed in linear form as Eq. (2):

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

where q_t and q_e indicate the amount of lead cations adsorbed at time t ($mg \cdot g^{-1}$) and at equilibrium ($mg \cdot g^{-1}$) respectively; and k_2 is the pseudo-second order rate constant ($g \cdot (mg \cdot min)^{-1}$). Fig. 5 shows the plot of $t/(q_t)$ against t , for the experimental data and fitting results. The fitting results demonstrate a high response

to pseudo-second order models with high correlation coefficients, $R^2 = 0.996$. The values of k_2 and q_e are calculated from the intercepts and slopes of the linear plots to be $75.6 \times 10^{-3} (g \cdot mg^{-1} \cdot min^{-1})$ and $96.9 g \cdot mg^{-1}$.

3.3 Effect of Adsorbent Dose and Initial Concentration

Fig. 6 shows that the lead adsorption yield of HApB increased from 16.0 ($85.85 mg \cdot g^{-1}$) to 70.06% ($54.56 mg \cdot g^{-1}$) as the HApB dose increased from $1 g \cdot L^{-1}$ to $7 g \cdot L^{-1}$. A higher adsorption dose would lead to an increase in the surface area, making more adsorption sites available, which gives rise to the greater removal of Pb^{2+} cations.

The adsorption of Pb^{2+} cations was carried out at different initial lead concentrations ranging from 400 to $1,000 mg \cdot L^{-1}$ in an acidic solution of pH 5.5 (Fig. 7). The adsorption capacity and adsorption yield were analyzed after 24 h of contact time for a dosage adsorbent of $5 g \cdot L^{-1}$. It is evident that the Pb^{2+} adsorption capacities of HApB increased with increases of the initial lead concentration, from $52.9 mg \cdot g^{-1}$ (60.61%) to $77.82 mg \cdot g^{-1}$ (34.68%). A higher initial concentration provided the driving force to overcome all mass transfer resistances of the lead cations between the aqueous solution and solid phases, thus increasing the uptake. Moreover, it seems that the equilibrium of adsorption initially reached a lead concentration of around $1,100 mg \cdot L^{-1}$.

Fig. 6 Effect of adsorbent dose on adsorption of Pb^{2+} cations on HApB composites.

Fig. 7 Effect of lead initial concentration on adsorption of Pb²⁺ on HApB composite.

3.4 Adsorption Isotherms

Several isothermic equations have been used to model the equilibrium adsorption system with the Langmuir and Freundlich models being most commonly used to describe the mathematical relationship between the quantity of adsorbent and the equilibrium concentration remaining in the solution at a constant temperature [13].

The Langmuir isotherm assumes a monolayer adsorption of the adsorbent onto identical sites of the adsorbent surface [21]. The Langmuir model is expressed in linear form by Eq. (3):

$$\frac{C_e}{q_e} = \frac{1}{bq_{\max}} + \frac{C_e}{q_{\max}} \quad (3)$$

where q_e (mg·g⁻¹) is the equilibrium adsorption capacity; C_e (mg·L⁻¹) is the equilibrium concentration of lead cations; $q_{\max}$ (mg·g⁻¹) is the maximum adsorption capacity; and b (L·mg⁻¹) is the Langmuir constant [21].

Fig. 7a shows the fit of the Langmuir model in linear form obtained by plotting $C_e \cdot q_e^{-1}$ versus C_e . The maximum sorption capacity $q_{\max}$ (mg·g⁻¹) and the Langmuir constant b (L·mg⁻¹) are calculated from the fitting results to be 93.37 mg/g and 0.0077 L·mg⁻¹ with a regression coefficient value R^2 of 0.972. The Freundlich adsorption isotherm can be expressed in

linear form as Eq. (4) [22]:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (4)$$

where q_e (mg·g⁻¹) is the equilibrium sorption capacity; C_e (mg·L⁻¹) is the equilibrium Pb²⁺ concentration; and k_f and n are the Freundlich isotherm constants which are temperature dependent [13]. The value of the Freundlich parameters, k_f and n , are determined by plotting $\ln q_e$ versus $\ln C_e$, as shown in the inset to Fig. 7. The Freundlich coefficient k_f and adsorption capacity n are calculated to be 12.74 L·mg (mg × g⁻¹)·(mg × L⁻¹)⁻ⁿ, and the regression coefficient value R^2 is set to be 0.921. Table 1 summarizes the values of the Freundlich and Langmuir isotherm constants. It seems that the Langmuir isotherm is the most appropriate model for describing the equilibrium behavior of the granular HApB composite adsorbent for lead cation adsorption.

3.5 Reusability

One of the most important parameters of adsorption materials is their reusability. In this study, after the first cycle, the adsorbent material was washed in an EDTA solution and subjected to heat treatment. It was then investigated for a second and third cycle. In the first cycle, the measured adsorption capacity was 87.38 mg/g but this dropped to 73.44 mg·g⁻¹ in the second cycle, for a yield of 84.05 %, compared to the first cycle of adsorption. And it was reduced to 68.60 % during the third cycle of adsorption. The results indicate that HApB is a candidate adsorbent for lead removal from wastewater.

Table 1 Langmuir, Freundlich constants for adsorption Pb²⁺ onto the adsorbent surface.

Model	Isotherm parameters		Regression coefficient (R ²)
Langmuir	$q_{\max}$ (mg·g ⁻¹)	k_e (L·mg ⁻¹)	0.972
	93.37	0.0077	
Freundlich	k_f (mg·g ⁻¹)(mg·L ⁻¹) ⁻ⁿ	n	0.921
	12.74	0.28

Fig. 8 Linear fit of experimental data for the adsorption of Pb^{2+} onto granular HApB composites calculated using the Langmuir and Freundlich (inset to Fig. 8) adsorption isotherm models.

Fig. 9 Re-usability of the material after 3 adsorption times by EDTA 0.01M.

4. Conclusions

Granular adsorbent HApB composite sample granules, with dimensions of $4\text{ mm} \times 4\text{ mm}$, were prepared for lead removal from aqueous solutions. Isotherm studies indicated that the Langmuir model fitted the experimental data better than the Freundlich model. The maximum lead adsorption capacity, calculated using the Langmuir model, was $93.37\text{ mg}\cdot\text{g}^{-1}$. The adsorption yield after the third cycle was 68.60%. The results demonstrate that the granular HApB composites may be a promising adsorbent for metal removal from aqueous solutions.

Acknowledgement

This research was funded by the Ho Chi Minh University of Technology-VNU-HCM, under grant number T-KTHH-2016-47.

References

- [1] Mobasherpour, I., Salahi, E., and Pazouki, M. 2010. "Removal of Nickel(II) from Aqueous Solutions by Using Nano-crystalline Calcium Hydroxyapatite." *Journal of Saudi Chemical Society* 15: 105-112.
- [2] Sheha, R. R. 2007. "Sorption Behavior of Zn(II) Ions on Synthesized Hydroxyapatites." *Journal of Colloid and Interface Science* 310: 18-26.
- [3] Alessia, C., Silvano, M., and Vincenzo, F. 2008. "Cadmium Removal from Single- and Multi-metal ($Cd+Pb+Zn+Cu$) by Sorption on Hydroxyapatite." *Interface Journal of Colloid Science* 317: 402-408.
- [4] Javier, G. R., Paula, S., Morando, P. J., and Cierone, D. S. 2006. "Retention of Cd, Zn and Co on Hydroxyapatite Filters." *Technical Note, Chemosphere* 64: 1015-1020.
- [5] Dong, L. J., Zhu, Z. L., Qiu, Y. L., and Zhao, J. F. 2010. "Removal of Lead from Aqueous Solution by Hydroxyapatite/magnetite Composite Adsorbent." *Chemical Engineering Journal* 165: 827-834.
- [6] Mobasherpour, I., Soulati, H., M., Kazemzadeh, A., Zakeri, M. 2007. "Synthesis of Nanocrystalline Hydroxyapatite by Using Precipitation Method." *Journal of Alloys and Compounds* 430: 330-333.
- [7] Mobasherpour, I., Salahi, E., and Pazouki, M. 2012. "Comparative of the Removal of Pb^{2+} , Cd^{2+} and Ni^{2+} by Nano Crystallite Hydroxyapatite from Aqueous Solutions: Adsorption Isotherm Study." *Arabian Journal of Chemistry* 5: 439-446.
- [8] Yan, Y. B., Wang, Y. P., Sun, X. Y., Li, J. S., Shen, J. Y., Han, W. Q., et al. 2014. "Optimizing Production of Hydroxyapatite from Alkaline Residue for Removal of Pb^{2+} from Wastewater." *Applied Surface Science* 317: 946-954.
- [9] Gabriel, L. C. 2009. "Mechanical Properties of Hydroxyapatite Whisker Reinforced Polyether Ketone Composite Scaffolds." *Journal of the Mechanical Behavior of Biomedical Materials* 2: 627-635.
- [10] Fahimeh, G., Ahmad, M., and Rahmatollah, E. 2012. "Lead Sorption Properties of Nano Hydroxyapatite-alginate Composite Adsorbents." *Chemical Engineering Journal* 200-202:471-479.
- [11] Dong, L., Zhu, Z., Qiu, Y., and Zhao, J. 2010. "Removal of Lead from Aqueous Solution by Hydroxyapatite/magnetite Composite Adsorbent." *Chemical Engineering Journal* 165:827-834.

- [12] Cui, L. M., Xu, W. Y., Guo, X. Y., Zhang, Y. K., Wei, Q., and Du, B. 2014. "Synthesis of Strontium Hydroxyapatite Embedding Ferroferric Oxide Nano-composite and Its Application in Pb²⁺ Adsorption." *Journal of Molecular Liquids* 197: 40-47.
- [13] Neha, G., Kushwaha, A. K., and Chattopadhyaya, M. C. 2012. "Adsorptive Removal of Pb²⁺, Co²⁺ and Ni²⁺ by Hydroxyapatite/chitosan Composite from Aqueous Solution." *Journal of the Taiwan Institute of Chemical Engineers* 43: 125-131.
- [14] Naseem, R., and Tahir, S. S. 2001. "Removal of Pb(II) from Aqueous/acidic Solutions by Using Bentonite as An Adsorbent." *Wat. Res.* 35: 3982-3986.
- [15] Hamidpour, M., Kalbasi, M., Afyuni, M., Shariatmadari, H., Holm, P. E., Hansen, H. C. 2010. "Sorption Hysteresis of Cd(II) and Pb(II) on Natural Zeolite and Bentonite." *J. Hazard. Mater* 181: 686-691.
- [16] Xuan, S. N., Thanh, T. P., Minh, V. L., and Truong, B. T. L. 2015. "Synthesis of Hydroxyapatite for Moystershells by Precipitate Method and Evaluation on Adsorptive Removal of Zn²⁺ and Ni²⁺ Cations from Solution." *Journal of Chemistry* 53: 218-222.
- [17] Yadanaparthi, S. K. R., Graybill, D., and Wandruszka, R. V. 2009. "Adsorbents for the Removal of Arsenic, Cadmium, and Lead from Contaminated Waters." *Journal of Hazardous Materials* 171: 1-15.
- [18] Lazarević, S., Tanasković, D., Pavićević, V., Janačković, D., and Petrović, R. 2008. "Sorption of Pb²⁺, Cd²⁺ and Sr²⁺ Ions on Calcium Hydroxyapatite Powder Obtained by the Hydrothermal Method." *Journal of Environmental Engineering* 134: 683-688.
- [19] Pleshko, N., Boskey, A., and Mendelsohn, R. 1991. "Novel Infrared Spectroscopic Method for the Determination of Crystallinity of Hydroxyapatite Minerals." *Biophysical Journal* 60:786-793.
- [20] Eren, E., and Asfın, B. 2008. "An Investigation of Cu(II) Adsorption by Raw and Acid-activated Bentonite: A Combined Potentiometric, Thermodynamic, XRD, IR, DTA Study." *J. Hazard Mater* 151: 682-691.
- [21] Taher, A. S., Ahmad, M. M., Mohamed, A. H., and Bahgat, E. E. 2013. "Development of Nano-hydroxyapatite/chitosan Composite for Cadmium Ions Removal in Wastewater Treatment." *J. Taiwan Inst Chem Eng* (2013), <http://dx.doi.org/10.1016/j.jtice.2013.10.1008>.
- [22] Saeid, Z., and Esmail, I. 2013. "Removal of Nickel from Aqueous Solution by Nano Hydroxyapatite Originated from Persian Gulf Corals." *Canadian Chemical Transactions* 1: 173-190.