

Peat Water Purification by Hydroxyapatite (HAp) Synthesized from Waste Pensi (*Corbicula moltkiana*) Shells

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Abstract. Hydroxyapatite (HAP) were synthesized from Pensi (*Corbicula moltkiana*) shells by hydrothermal method and used as adsorbent for peat water purification. Batch adsorption experiments were performed to investigate the effects of various factors such as contact time, adsorbent dosage, and pH. The obtained materials were characterized by powder X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy and scanning electron microscope (SEM). Results showed that HAP calcined at 900°C (HAP900) and 1000°C (HAP1000) have a poorly crystalline shape. HAP900 also contain Tetracalcium Phosphate (TTCP) with a Ca/P molar ratio 2.18, while HAP 1000 contain HAp with a Ca/P molar ratio 1.67. Optimum condition for peat water purification with HAP900 and HAP1000 were both achieved at 1 hours, 1 grams adsorbent mass at pH 2. SEM micrographs show that after purification, the surface of HAP were covered by organic compounds from peat water.

1. Introduction

In Indonesia, tropical peatlands cover almost 10% of the land surface mostly at low altitudes in coastal and sub-coastal areas on the islands of Sumatra, Borneo, and New Guinea (West Papua, Papua). The extent of peat land, resulting difficult for people to obtain clean water. Peat water is surface water or ground water is widely available in tidal areas, marshy and lowlands, maroon, sour (high acidity level), and has a high organic content. Peat water which contains organic substances (humic acid, fulvic acid and humin) are not qualified to supply as drinking water and needs of households. The existence of humic acid and fulvic acid in water can cause environmental and health serious problems.

Hydroxyapatite (HAP) have been widely used as implant materials due to its its high biocompatibility, good bioaffinity and their similar properties with natural bones, and gained great importance in the field of orthopedics and in the development of dental materials [1-2]. The calcium to phosphorous molar ratio (stoichiometric Ca/P ratio), must be controlled at about 1.67. HAP with the stoichiometric formula $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ and a Ca/P molar ratio=1.67 is the most similar to the inorganic part of bones and teeth. Deviation of the calcium/phosphorus ratio from 1.67 can arise during preparation, leading to the formation of other compounds such as α -tricalcium phosphate and β -tricalcium phosphate [3-5]. Extraction of HAP from natural resources is promising as an alternative choice for the production of HAP.



Corbicula moltkiana or Pensi in local name, is a freshwater clams found in West Sumatera, Indonesia. It is a popular mollusk-based dishes in the local region, resulting in abundant amounts of waste shells every year. *Corbicula* shells (CS) are a rich source for calcium carbonate (CaCO_3), a material with great value to be converted to HAP.

2. Experimental

2.1. Materials preparation

CS biowaste was collected from local market around lake Singkarak, West Sumatera, Indonesia. CS were properly cleaned with detergent solution, washed thoroughly with tap water followed by soaking it with 0.1 M HNO_3 (Merck) to ensure the removal of remove attached materials such as soft tissue. After washing several times with distilled water, the CS was dried at 105°C for 5 h in oven, then crushed into powder with a grinder and finally sieved with a 50-mesh sieve.

2.2. Synthesis of CaHAP

The CS was calcined in an electrical muffle furnace and maintained at various temperatures (900 and 1000°C) for 5 h, the CS transformed into calcium oxide by releasing carbon dioxide. For synthesis, a stoichiometric value of ammonium di-hydrogenphosphate ($\text{NH}_4\text{H}_2\text{PO}_4$, 99.9%; Aldrich) was dissolved in distilled water and added to 10g pyrolysed CS. After heating, the samples were cooled naturally inside the furnace. The reaction was carried out in a 500 mL beaker glass (under atmospheric pressure), and continuously mixed at a speed of 300 rpm using a mechanical stirrer. The temperature was maintained at approximately 90°C for 6 h. The slurry is dried in an oven at 120°C for 5 h and calcined at 600°C for 2 h.

2.3 Measurement of peat water

Measurement of peat water absorption spectrum was performed with a UV-Vis spectrophotometer (Thermo Scientific GENESYS 10S Series, USA), at 220-400 nm region. Purification is indicated by the changing pattern of absorption spectra in the UV-Vis due to the reduced organic compounds such as humic acid. Absorbance of each sample was measured both before and after purification.

3. Results and Discussion

3.1 X-ray diffraction analysis

Fig. 1 shows the X-ray diffraction patterns of the synthesized natural HAP at different temperature. As shown in this figure, HAP samples synthesized had similar XRD patterns. The crystalline phases identified mostly correspond to HA (ICSD-157481). All the diffraction peaks were assigned to low-crystalline HAP.

The broad peaks of the XRD patterns indicate that the HAP particles had small sizes and low crystallinity [6]. Poorly crystalline calcium phosphate apatite crystals indicate that they are similar to the crystals of bones and did not dissolve in the physiologic solutions [7]. At 900°C a tetracalcium phosphate (TTCP) peak was observed. TTCP is the only calcium phosphate phase with a Ca/P ratio greater than stoichiometric HAP [8].

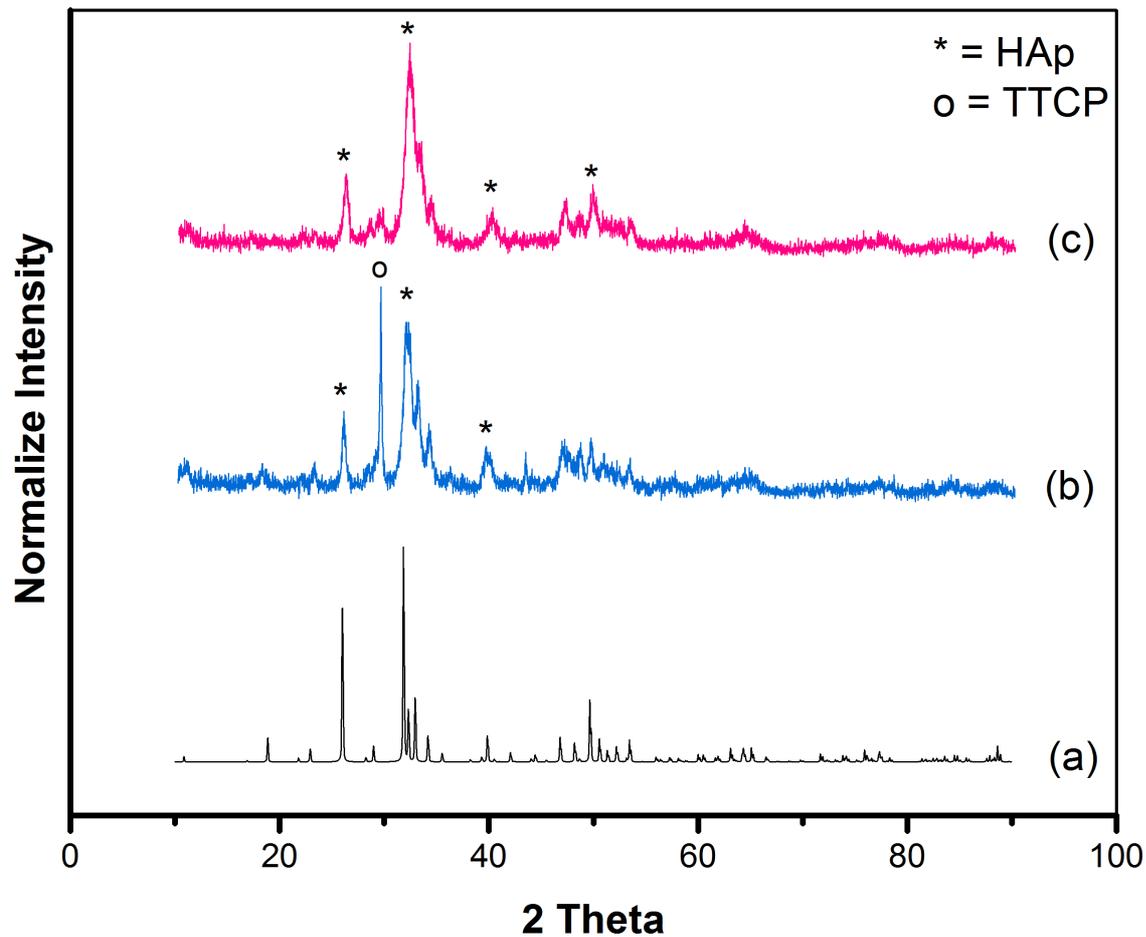


Figure 1. XRD patterns of HAP (a) HA (ICSD-157481), (b) HAP900, (c) HAP1000

3.2 FT-IR analysis

The FT-IR spectra of CS biowaste and HAP are plotted in Fig. 2. Based on Fig. 2. (a) shows the absorption with a strong peak at 1461.89 cm^{-1} indicating the presence of carbonate (CO_3) group and the peak at 1974.47 cm^{-1} indicate the presence of CH bending. C-N group (854.31 cm^{-1}) and C-C (707.49 cm^{-1}) indicates that the CS contains amine and carbonate groups.

The spectra of HAP900 and HAP1000 in Fig. 2 (b) and (c) show phosphate groups at 1024.07 cm^{-1} and 1027 cm^{-1} each with sharp peaks. The carbonate group at 1453.01 cm^{-1} at HAP900 and 1447.29 cm^{-1} appears on the CS HAP1000. The peak at 2196.74 cm^{-1} and 2200.25 cm^{-1} shows the uptake of HOH. The FTIR analysis results show that the synthesized HAP is not pure in the presence of carbonate groups into the crystal lattice HAP. This is also due to CO_2 absorption in the air during sample preparation [9].

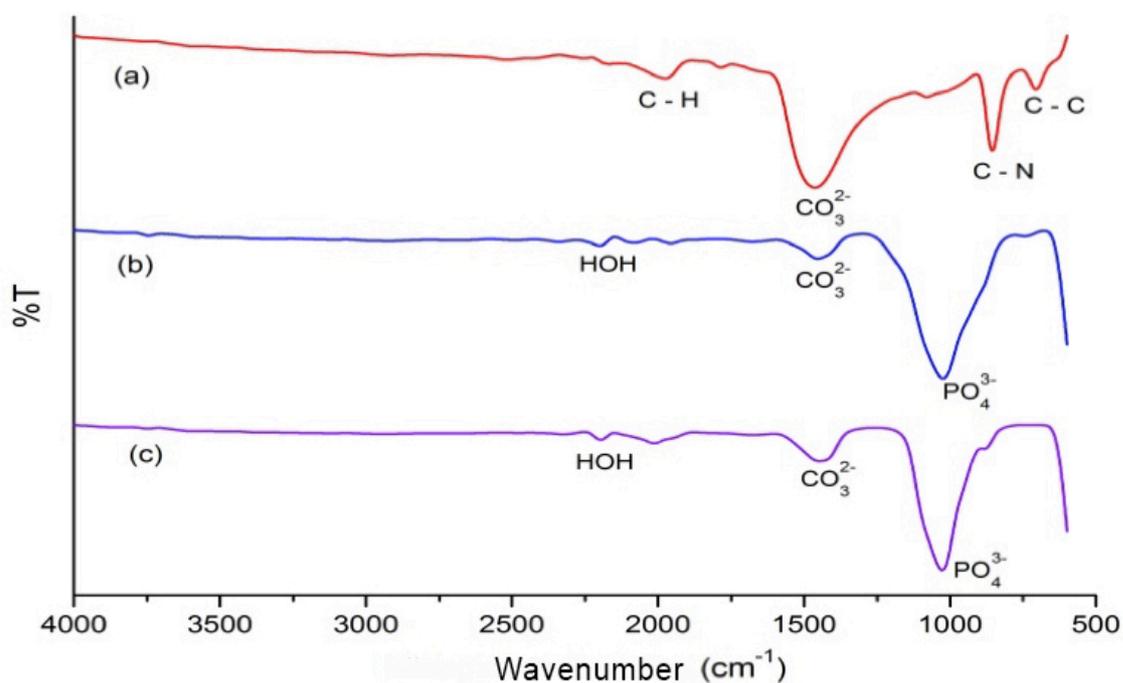


Figure 2. FT-IR spectra of (a) CS biowaste (b) HAP900 and (c) HAP1000.

3.3 UV-Vis analysis

The content of organic compounds in peat water is dominated by humic acid (HA). The properties of humic acid molecules can be described by UV-Vis spectroscopy widely as a simple and informative method [10]. The UV-Vis spectrum of humic acid is wide and monotonically decreases with increasing wavelength. The absorbance of the UV region spectrum can be used to analyze HAP [11].

UV absorption at 280 nm represents the overall aromaticity, since the electron transition π - π^* occurs in this UV region (270-280 nm) such as phenolic, benzoic acid, aniline derivative, poly and polycyclic aromatic hydrocarbons with two or more rings and also absorbents at 280 nm can be used to characterize peat humidity [12]. To find out the reduction of humic acid contained in peat water, this is done by comparing the absorbance at 280 nm before and after clearance. This measurement aims to determine the reduced content of humic acid contained in peat water. The lower the absorbance of peat water the more the humic acid content is reduced.

HAP900 and HAP1000 are added 0.5 grams into the erlenmeyer and then added 10 mL of peat water. Stirring at 250rpm was carried out for a various contact time (0.5, 1, 2, 3, 4 h). The mixture was filtered and the filtrate was analyzed by UV-Vis Spectrophotometer at λ 220-400 nm range. The measurements of the UV spectrum of peat water and after purification can be seen in Fig. 3.

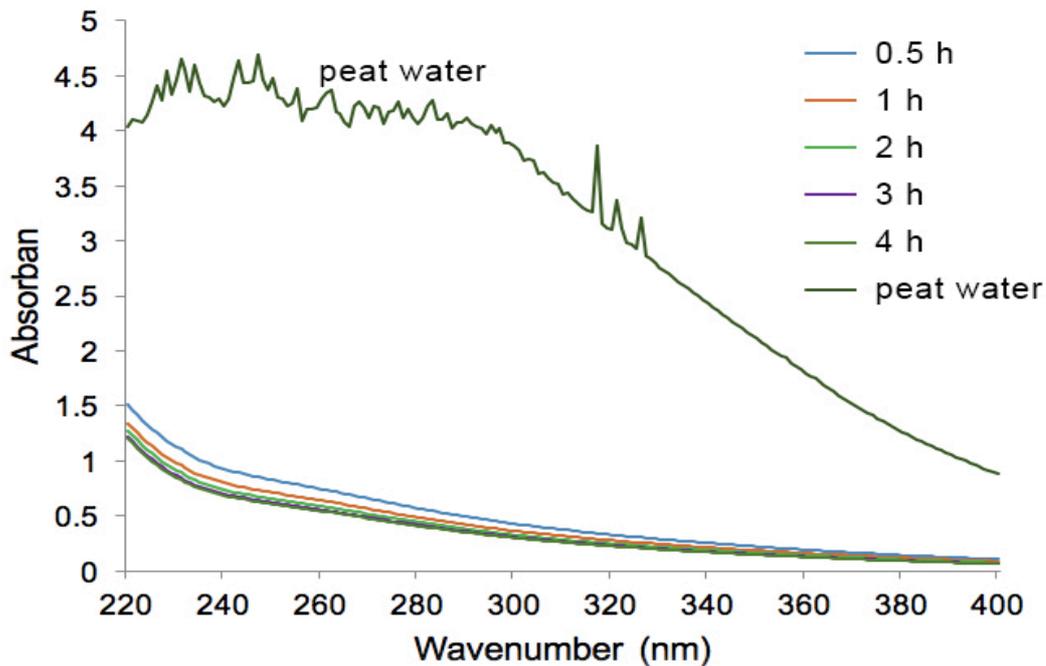
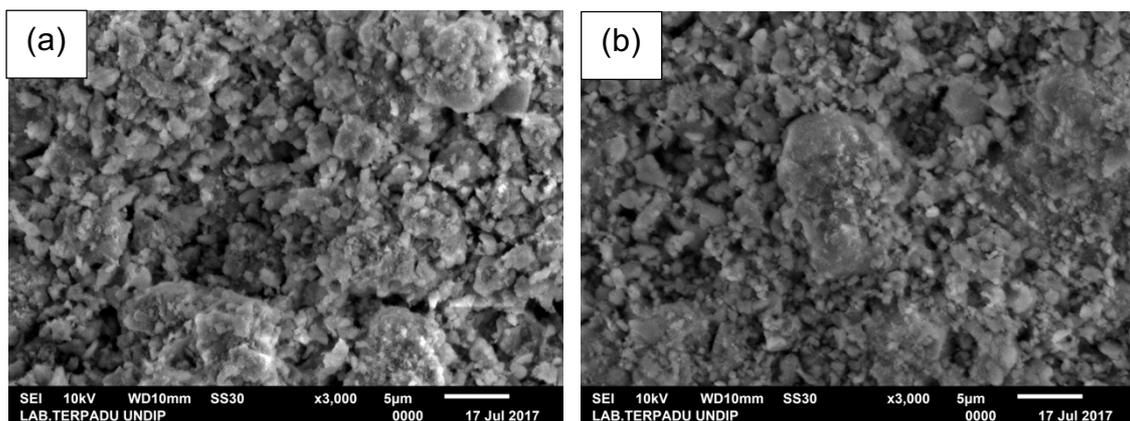


Figure 3. UV spectra of peat water before and after purification by HAP.

3.4. SEM analysis

Surface morphology of the synthesized hydroxyapatite before and after peat water purification were analyzed by SEM and are shown in Fig.4. The morphology of HAP900 and HAP1000 (Fig. 4 (a) and (b)) at 3000 x magnification were seen to have agglomeration with variable size pore distributed evenly. HAP900 and HAP1000 experience changes in the surface morphology after purification as shown in figure 4C and 4D. The surface pores of HAP900 and HAP1000 are covered by organic compounds originated from peat water.



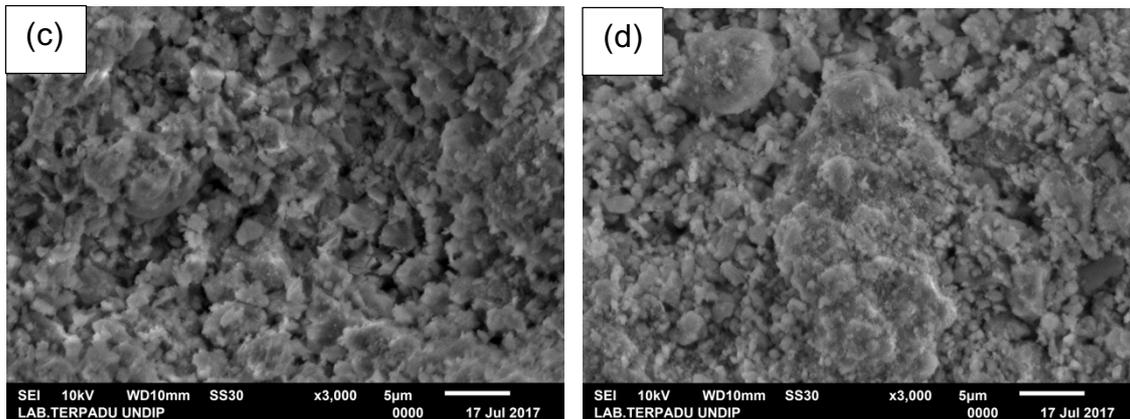


Figure 4. SEM images of (a) HAP900, (b) HAP1000, (c) and (d) HAP900 and HAP 1000 after peat water purification treatment respectively.

4. Conclusion

CS biowaste can be used for hydroxyapatite material by hydrothermal method. Based on XRD analysis HAP900 have TTCP phase with a molar ratio of Ca / P 2.18. HAP1000 was dominated with HAP (molar ratio of Ca / P 1.67). Both HAP900 and HAP1000 shows an amorphous crystal structure. HAP from CS biowaste was able to purify peat water. Optimum condition for peat water purification by HAP900 and HAP1000 were both achieved at 1 hours, 1 grams adsorben mass at pH 2.

References

- [1] Vahabzadeh S, Roy M, Bandyopadhyay A and Bose S 2015 Phase stability and biological property evaluation of plasma sprayed hydroxyapatite coatings for orthopedic and dental applications *Acta Biomater.* **17** 47–55
- [2] Rau J V, Cacciotti I, Bonis A De, Fosca M, Komlev V S, Latini A, Santagata A and Teghil R 2014 Fe-doped hydroxyapatite coatings for orthopedic and dental implant applications *Appl. Surf. Sci.* **307** 301–5
- [3] Li Y, Weng W and Tam K C 2007 Novel highly biodegradable biphasic tricalcium phosphates composed of a-tricalcium phosphate and b-tricalcium phosphate *Acta Biomater.* **3** 251–4
- [4] Boutinguiza M, Pou J, Comesaña R, Lusquinos F, De Carlos A and León B 2012 Biological hydroxyapatite obtained from fish bones *Mater. Sci. Eng. C* **32** 478–86
- [5] Pon-On W, Suntornsaratoon P, Charoenphandhu N, Thongbunchoo J, Krishnamra N and Tang I M 2016 Hydroxyapatite from fish scale for potential use as bone scaffold or regenerative material *Mater. Sci. Eng. C* **62** 183–9
- [6] Kim H, Kim Y, Park S, Rey C, Lee H, Glimcher M J and Ko J S 2000 Thin film of low-crystalline calcium phosphate apatite formed *Biomaterials* **21** 1129–34
- [7] Kim H, Rey C and Glimcher M J 1995 Isolation of Calcium-Phosphate Crystals of Bone by Non-Aqueous Methods at Low Temperature *J. Bone Miner. Res.* **10** 1589–601
- [8] Moseke C and Gbureck U 2010 Tetracalcium phosphate : Synthesis , properties and biomedical applications *Acta Biomater.* **6** 3815–23
- [9] Wei W, Yang L, Zhong W, Cui J and Wei Z 2015 Poorly crystalline hydroxyapatite: A novel adsorbent for enhanced fulvic acid removal from aqueous solution *Appl. Surf. Sci.* **332** 328–39
- [10] Shirshova L T, Ghabbour E A and Davies G 2006 Spectroscopic characterization of humic acid fractions isolated from soil using different extraction procedures *Geoderma* **133** 204–16
- [11] Uyguner C S and Bekbolet M 2005 Evaluation of humic acid photocatalytic degradation by UV – vis and fluorescence spectroscopy *Catal. Today* **101** 267–74

- [12] Chin Y, Alken G and Loughlins E O 1994 Molecular Weight, Polydispersity, and Spectroscopic Properties of Aquatic Humic Substances *Environ. Sci. Technol.* **28** 1853–8

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