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Effect of Hydroxyapatite (HAp) Adsorbent Dosage towards Lead Removal

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ABSTRACT

Lead (Pb) is a type of heavy metal that requires removal treatment in the waterworks industry due to its deleterious effects on human health and the ecosystem. In the present work, hydroxyapatite (HAp) nanopowder was successfully developed from *Tilapia sp.* fish scales via chemical heat treatment method. The removal of Pb in solution was investigated by 1, 2, and 4% HAp adsorbent dosage. FESEM analysis shows the formation of the nanoporous structure of the adsorbent, while FTIR analysis exhibit the presence of phosphate and hydroxyl groups that contribute to the chemisorption process. EDX analysis confirms the Ca/P ratio of 1.96, which was slightly greater than the stoichiometric ratio of pure HAp at 1.67. XRD analysis reveals sharp diffraction lines that indicate the crystallinity of HAp adsorbent. Batch adsorption experiment recorded maximum Pb removal at 4 % HAp dosage with 100% removal in 10 min.

Key words: Adsorbent, Adsorption, Fish scale, Hydroxyapatite, Lead.

1. INTRODUCTION

The rapid growth of the metallurgy industrial has led to serious environmental problems especially on the contamination of heavy metals. The presence of heavy metals in the ecosystem is mainly caused by various industry activities including mining, paint, pigment, electroplating, textiles, battery manufacturing, pesticides and petroleum refining [1]. Investigation on heavy metals concentration in the agricultural ecosystem near a lead-acid battery factory showed the potential risk to human health as the concentration detected has exceeded the tolerable limit of 0.2 mg/kg that may cause a potential threat to the environment and human health [2]. Thus, a low concentration of lead contamination has become a major concern to humans as it is listed as one of the chemicals that can emit high negative effects on the public [3].

Several conventional methods have been applied for the removal of heavy metals like lead such as reverse osmosis, ion exchange, chemical precipitation, and adsorption. Among these, adsorption shows promising results in removing heavy metals from water owing to its effective removal, low cost, flexible, easy to produce and more simple operation [4] [1]. Therefore, many researchers have been studied for the development of adsorbents from waste which may potentially be good for the adsorption process. These include eggshells [5], bovine bones [6], spent coffee grounds [7] and fish scales [8]. This study aims to remove lead in tap water source using *Tilapia sp*. fish scales as low cost and environmentally friendly adsorbent.

2. MATERIALS AND METHOD

2.1 Preparation of Hap Adsorbent

Collected *Tilapia sp*. fish scales from the fish processing industries were synthesized using a chemical heat treatment method to produce hydroxyapatite (HAp) adsorbent [9]. The collected fish scales were firstly washed thoroughly with distilled water to remove any dirt and salts before it was air-dried. Then, the scales were soaked overnight in 0.1 M of hydrochloric acid (HCl) before washed several times with distilled water. The remaining proteins were further treated using 5 % (w/v) of natrium hydroxide (NaOH) solution followed by constant heating and stirring at 70 °C for 5 h until fine white particles of HAp was obtained. The product is then re-washed with distilled water and dried at 60 °C. Adsorbent preparation continues by treating the acquired nanopowder with 50 % (w/v) NaOH and reheated at 100 °C with constant stirring for another 1 h. Finally, the HAp was washed thoroughly with distilled water until the washing solution reaches neutral pH prior to drying at 60 °C in the oven to remove any unwanted moisture.

2.2 Adsorbent Characterization

The HAp nanopowder was characterized by several analyses to investigate its physical and chemical properties. This includes Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray Spectroscopy (EDX), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray diffraction (XRD) analysis.

2.2.1. Field Emission Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray Spectroscopy (EDX) Analysis

The morphology and elemental composition of the HAp nanopowder before the adsorption process was characterized through FESEM and EDX analysis. The sample was coated with a thin layer of gold that acts as a conductive coat before the microscopic examination was conducted with a MEGA VIEW-II DOC U digital camera that operates at 20.0 kV.

2.2.2. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The surface functionalization of HAp was characterized at 4 cm^{-1} resolution and frequency ranging between 4000 to 400 cm^{-1} by FTIR analysis using the Attenuated Total Reflection (ATR) technique. The potassium bromide (KBr) pellet method was used in the sample preparation.

2.2.3. X-ray Diffraction (XRD) Analysis

X-ray diffraction analysis was used to analyse the purity of the produced HAp adsorbent. The data was measured by Cu Kα monochromatic radiation (λ = 1.5406 Å). The HAp nanopowder is compressed in the cassette sample holder and the data is collected from 2θ = 20 ° with a scan step of 0.02 °.

2.3 Batch Adsorption Experiment

The performance of the synthesized HAp nanopowder towards lead removal in solution was conducted via batch adsorption study. Initially, 1000 mg/L lead (Pb) stock solution was prepared by dissolving 1000 mg Pb powder (Bendosen) in nitric acid (HNO_3) and ultrapure water at 350 °C in 1 L volumetric flask. Then, the synthetic Pb solution was diluted to 10 mg/L by spiked the solution in a 500 mL conical flask containing ultrapure water and HAp nanopowder at different dosages. HAp adsorbent dosage was varied from 1, 2 and 4 wt %, with a constant pH of 7 of the tap water. Next, the sample solutions were shaken by orbital shaker at a constant stirring speed of 130 rpm for 60 min at room temperature. 10 mL sample solutions were drawn from each flask at a certain time interval prior to the analysis of Pb concentration using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) (PerkinElmer Optima 8000).

The following equation (1) [10] was applied to calculate the removal of Pb concentration after the adsorption process:

$$\text{Removal (\%)} = \frac{(C_0 - C_f)}{C_0} \times 100\ \% \qquad (1)$$

Where C_0 refers to initial Pb concentration and C_f is the final Pb concentration in the solution. The units are in mg/L or ppm.

3. RESULTS AND DISCUSSION

3.1 Adsorbent Characterization

The nanoporous structure and elemental composition of HAp adsorbent were analysed by FESEM and EDX as shown in Figures 1 and 2, respectively. The white region on the HAp surface represents the inorganic substance in the sample such as P and Ca, meanwhile dark surface refers to an organic composition that contains high protein due to the presence of C and O in the HAp [8]. The purity of HAp can be determined by the Ca/P ratio which is considered as pure at a ratio of 1.67. However, the obtained Ca/P ratio in this study is slightly higher which is 1.96. According to Ramesh et al. [11], a higher Ca/P ratio will result in the high stability of material towards greater temperature.

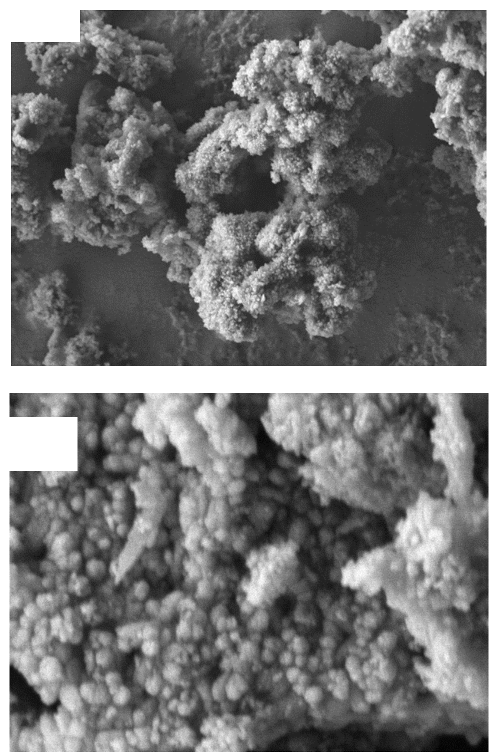


Figure 1: FESEM micrographs of Hap adsorbent at a magnification of (a) 10000 and (b) 50000

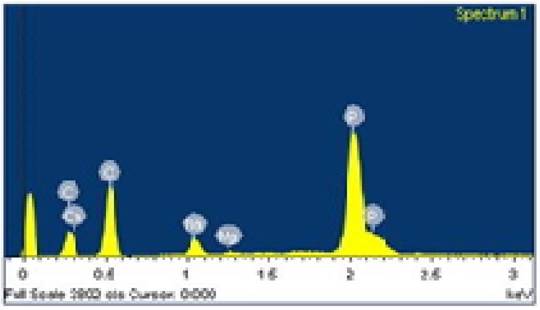


Figure 2: EDX spectrum of HAp nanopowder

The HAp surface functionalization was shown in Figure 3. The stretching at 3246cm^{-1} indicates the presence of OH^- group and peaks at 1417cm^{-1} showed C=C bond. PO_4^{3-} group was represented from the asymmetric stretching mode of vibration at 1018cm^{-1}. The existence of these anion groups on the adsorbent surface contributes to an efficient adsorption mechanism for lead removal by increasing the number of active sites [12].

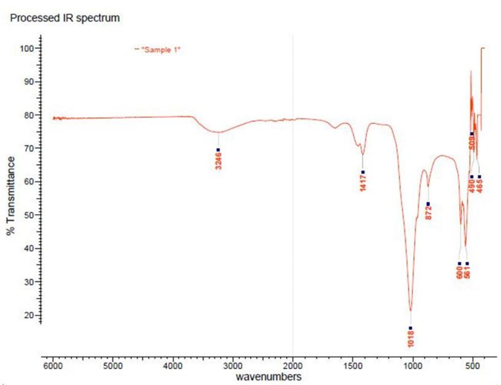


Figure 3: FTIR spectra of HAp

Figure 4 shows the result of the XRD analysis of HAp nanopowder. The obtained peaks showed a relative pattern when compared to the XRD standard of HAp (JDS 00-009-0432). The adsorbent has sharp diffraction lines that indicate the crystallinity of the fish scales [13].

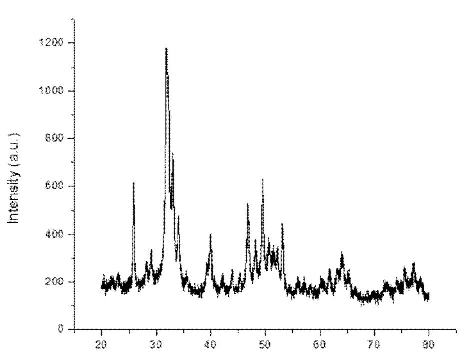


Figure 4: XRD pattern of HAp

3.2 Batch Adsorption Experiment

The batch adsorption study by various adsorbent dosages of 1, 2 and 4% were conducted at an initial Pb concentration of 10 mg/L. Figure 5(a) and (b) show the performance of 1% HAp adsorbent for removal of Pb from the solution. The concentration of Pb was efficiently removed from 99.4% (0.74 mg/L) at initial to the maximum removal of 100% (0.00 mg/L) after 60 min of adsorption process.

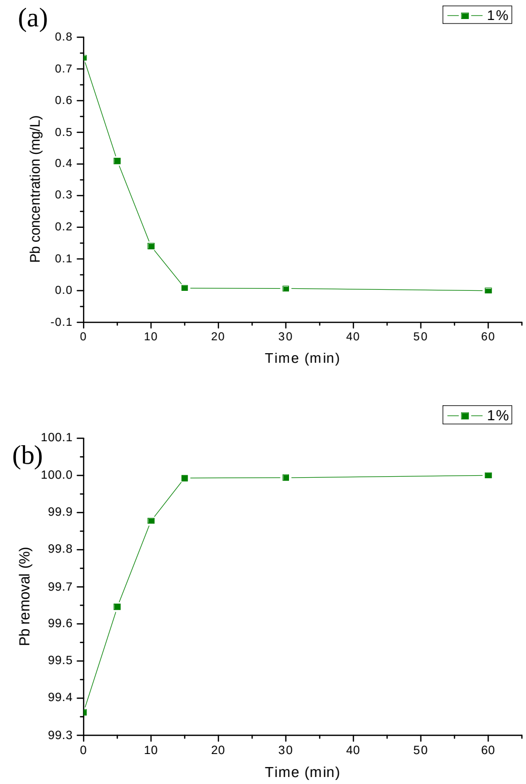
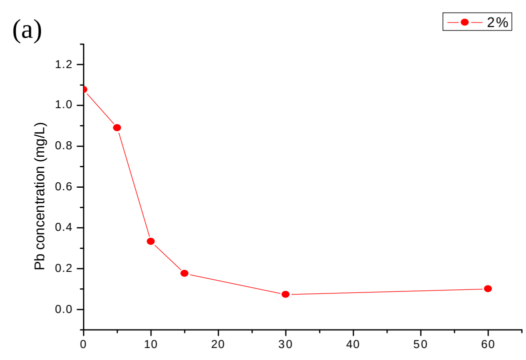


Figure 5: (a) Pb concentration in free solution against time and (b) Pb removal rate at 1% HAp

For the adsorbent dosage of 2%, the Pb concentration shows the highest reduction of 0.07 mg/L after 30 min adsorption process in which the Pb removal reach 100% as shown in Figure 6(a) and (b).



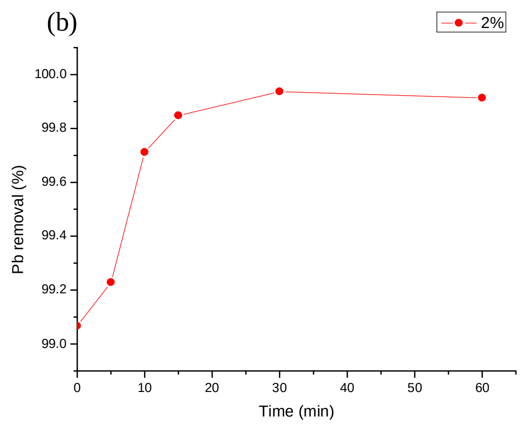


Figure 6: (a) Pb concentration in free solution against time and (b) Pb removal rate at 2% HAp

The Pb removal was 100% after 10 min of the adsorption process using 4% HAp nanopowder as in Figure 7(a) and (b). The concentration of Pb was significantly removed from 0.327 mg/L to 0.1 mg/L.

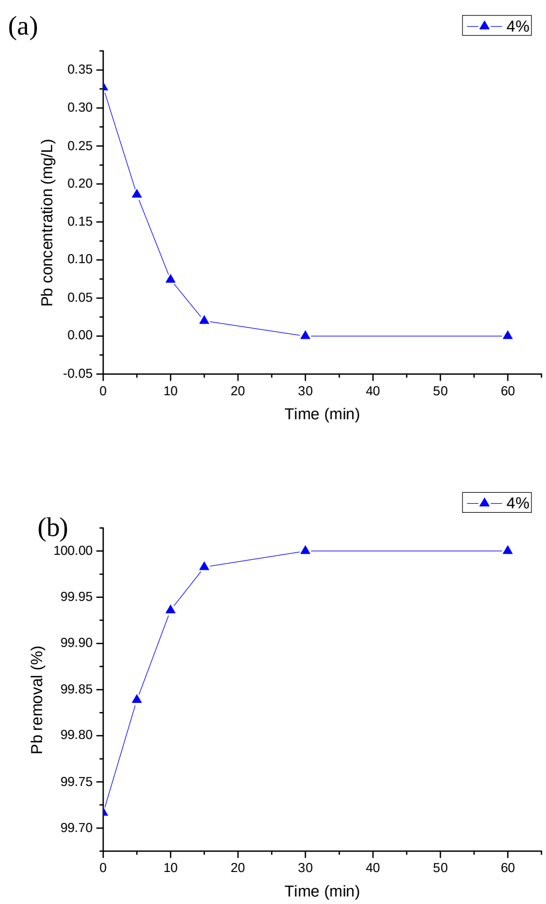


Figure 7: (a) Pb concentration in free solution against time and (b) Pb removal rate at 4% HAp

Based on these findings, there is a correlation between HAp adsorbent dosage towards Pb removal. The adsorption of Pb in solution increases with the increase of adsorbent dosage as reported in previous study [14]. This happens due to the increase in active site availability that causing a greater removal rate. According to Aksu et al. [14], higher initial HAp concentration acts as an important driving force to overcome all mass transfer resistances of the Pb between the solid and aqueous phases, therefore increases the Pb uptake.

4. CONCLUSION

This work revealed that the HAp nanopowder synthesized from *Tilapia sp.* fish scale is a potential adsorbent to be used for the removal of Pb in aqueous solution. The most efficient adsorbent dosage was attained by 4% of HAp adsorbent with 100% Pb removal in 10 min of pH 7. The increase of adsorbent dosage will increase the adsorption process owing to its high active site availability as shown in the HAp nanoporous structure in FESEM analysis. The existence of PO_4 and OH functional groups also contribute to the Pb adsorption mechanism. The peaks detected in XRD and EDX analysis confirm the crystallinity and 1.96 Ca/P ratio of the HAp adsorbent, respectively.

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