Utilization of Hydroxyapatite from Tuna Fish Bone Waste as Adsorbent for Cadmium from Aqueous Solutions

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Abstract. This study aims to determine the performance of hydroxyapatite adsorbents from tuna bone waste against cadmium metal ion removal. Hydroxyapatite adsorbents have been activated physically (calcined at 500°C and 700°C) and chemically (using H3PO4). The adsorbent was then characterized using Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR). A batch experiment was conducted to study the effect of initial concentration and contact time on cadmium adsorption. The results of SEM and FTIR analysis showed that the best adsorbent was obtained from calcination results at 700°C. The observation shows that the contact time and initial concentration affect the efficiency of adsorption. The highest removal efficiency of cadmium was 86.28% with an adsorption capacity of 44.62 mg/g obtained at the contact time of 150 minutes and an initial concentration of cadmium 100 mg/L. The results of the isotherm study show that the adsorption equilibrium in the cadmium solution follows the Freundlich isotherm model with values $R^2 = 0.923$, $N = 9.4339$, and $K_F = 7.92$. The adsorption kinetics of cadmium adsorption followed the pseudo-second-order equation with values of $K_2$ and $q_e$ at 0.021534 g.mg$^{-1}$.min$^{-1}$ and 47.61 mg/g, respectively. The results obtained indicate that hydroxyapatite from tuna bone waste is a promising alternative for cadmium adsorption.

1. Introduction

Environmental damages and decrease of quality of public health are negative impacts of heavy metal liquid waste pollution [1]. This pollution can contaminate the soil, groundwater, rivers, ponds, lakes and oceans. Sources of heavy metal waste mostly come from industry, domestic waste, agriculture, and laboratories. The biggest source of heavy metal waste is found in industrial activity discharges [2]. Environmental damages and decrease of quality of public health are negative impacts of heavy metal liquid waste pollution [1].

One of the heavy metal contents in industrial waste is cadmium (Cd$^{2+}$) [2]. Many industries contribute to producing Cd$^{2+}$ pollution, such as textiles, phosphate fertilizer, plastics, battery, cement, and petrochemicals [3]. Cd$^{2+}$ is a toxic waste and difficult to decompose naturally, so it is dangerous for human health and the environment [4].

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According to the World Health Organization (WHO), Cd\(^{2+}\) very easily contaminates the environment. The maximum acceptable limit of Cd\(^{2+}\) content in water is 0.005 mg/L [5]. The handling of heavy metal pollution in liquid waste must be specifically managed by reducing or eliminating the hazardous properties [6]. There are several methods for removing Cd\(^{2+}\), such as flotation [7], liquid-liquid extraction [8], co-precipitation [9], membrane process [10], adsorption [11], electro-coagulation [12], and solid phase extraction [13].

In this paper, we use the adsorption method for removing heavy metal ions because it is highly effective in Cd\(^{2+}\) adsorption, cheap, and easily applied [14]. The common adsorbents used in heavy metal removals include bentonite, biomass cells, activated carbon, clay, zeolite, and rock [15].

Hydroxyapatite (Ca\(_5\)(PO\(_4\))\(_3\)COH) is a promising candidate as an agent of heavy metal adsorption which can be easily extracted from fish bones [16]. The hydroxyl group contained in hydroxyapatite can adsorb heavy metal ions [17]. Content of inorganic substances in fish bones reaches 60% to 70% of its bulk, with high portions of hydroxyapatite and calcium phosphate [18].

The purpose of this study was to investigate characteristics, adsorbent performances, adsorption isotherms, and adsorption kinetics of hydroxyapatite produced from tuna skeletons. In this study, hydroxyapatite was produced by physical and chemical activation, namely calcination in tuna bones and addition of H\(_3\)PO\(_4\), respectively [19]. These activations aimed to form a micropore structure with a large effective surface so that it could be used to adsorb Cd\(^{2+}\) in liquid waste [20].

2. Materials and Methods

2.1 Fabricating adsorbent. The raw material for producing hydroxyapatite is tuna fish bone. Tuna bone is firstly washed, boiled, and dried at 105°C for 5 hours. Calcination was carried out in furnace (F6000 - Thermolyne) at 500°C and 700°C for 30 minutes. The bone mass during calcination is 500 grams. After calcination, the bone was cooled and then mashed using mortar and sieved by a mesh size of 100. The nano-size was made using a ball mill (pulverisette 6 - Fritsch) for 10 hours. The activation process is carried out after carbonization and the mashing process, and the product then inserted into a 6 M H\(_3\)PO\(_4\) solution for chemical activation with a ratio of 1:10 and heated at 90°C for 1 hour. Then, 1 M NaOH is added to raise pH to 10 and allowed to stand for 24 hours. At the final step, activated hydroxyapatite is washed with distilled water to neutralize pH and dried in an oven at 105°C until dry.

2.2 Characterization. An iodine adsorption test was carried out to determine the absorption capacity of hydroxyapatite. This test using FTIR (Prestige 21 - Shimadzu) was carried out to find the dominant functional groups of the adsorbent.

2.3 Adsorption test. Adsorption testing is conducted by batch method using a 250 mL beaker glass to contact the adsorbent with an artificial solution of Cd(NO\(_3\))\(_2\). Concentration of artificial solutions are 25, 50, 75, 100, 125, and 150 mg/L. Contact time is varied for 30, 60, 90, 120, and 150 minutes. Stirring speed is 100 rpm. The adsorption solution was tested using atomic adsorption spectrophotometer (AAS - 6300) to determine adsorption efficiency, adsorption capacity, adsorption isotherm, and adsorption kinetics. The equations used to calculate adsorption efficiency, adsorption capacity, adsorption isotherms, and adsorption kinetics are as follows.
2.3.1 Adsorption efficiency. In order to determine adsorption efficiency, the initial concentration of adsorbate \( C_0 \) before adsorption and the final concentration of adsorbate \( C_e \) after adsorption are calculated. Calculation of adsorption efficiency uses the following equation [15]:

\[
\%E = \left( \frac{C_0 - C_e}{C_0} \right) \times 100\%
\]

(1)

2.3.2 Adsorption capacity. Calculation of adsorption capacity uses the equation below:

\[
q_e = \frac{(C_0 - C_e)v}{m}
\]

(2)

where \( q_e \) is amount of the adsorbate, \( v \) is volume of the adsorbate, \( C_0 \) is concentration before adsorption, \( C_e \) is concentration after adsorption, and \( m \) is mass of the adsorbent [21].

2.3.3 Langmuir’s isotherm. For Langmuir’s adsorption isotherm, adsorption-adsorbate equilibrium occurs on the surface of the adsorbent monolayer. Langmuir’s isotherm model follows the equation:

\[
\frac{1}{q_e} = \frac{1}{Q} + \frac{1}{K_L C_e}
\]

(3)

where \( C_e \) is equilibrium concentration of the adsorbate (mg/L), \( q_e \) is the adsorbate equilibrium concentration (mg/g), \( Q \) is maximum capacity of the monolayer (mg/g), and \( K \) is Langmuir’s isotherm constant. The magnitude of \( q_{\text{max}} \) and \( K_L \) are determined from the slope and intercept of the Langmuir curve versus \( \frac{1}{C_e} \) [1].

2.3.4 Freundlich’s isotherm. This is a characteristic of adsorption equilibrium on heterogeneous surfaces. The Freundlich isotherm model follows the equation:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

(4)

where \( K_F \) is Freundlich’s isotherm constant (mg/g), \( n \) is adsorption intensity, \( C_e \) is adsorbate equilibrium concentration (mg/L), and \( q_e \) is the amount of adsorbed adsorbate (mg/g) [3].

2.3.5 Temkin’s isotherm. Temkin’s isotherm describes the types or factors that influence interactions between adsorbent and adsorbate. Temkin’s isotherm model follows the equation:

\[
q = D \ln A_T + D \ln C_e
\]

(5)

where \( D = (RT/b) \) is the constant associated with the heat of adsorption (J/mol), \( A_T \) is the equilibrium constant of Temkin’s isotherm bond (1.075 L/g), \( b \) is Temkin’s isotherm constant, \( R \) is the gas constant (8.314 J/mol.K), and \( T \) is temperature [3].

2.3.6 First-order kinetics model. This kinetics model means that the reaction rate is directly proportional to the first order of the reactant concentration expressed by the following equation:

\[
\log (q_e - q_t) - \log (q_e - \frac{k_1}{2.303} t)
\]

(6)

where \( q_e \) is concentration of adsorbate at equilibrium (mg/g), \( q_t \) is concentration of adsorbate at time \( t \) (mg/g), \( t \) is contact time (minute), and \( k_1 \) is the corresponding pseudo constant (min\(^{-1}\)) [1].

2.3.7 Second-order kinetics model. This kinetics model has a reaction rate that is directly proportional to the second order of the reactant concentration, which can be expressed as:

\[
\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}
\]

(7)
where $q_e$ is concentration of adsorbate after equilibrium (mg/g), $q_t$ is concentration of adsorbate at time $t$ (mg/g), and $k_2$ is the corresponding pseudo constant (g.mg$^{-1}$.min$^{-1}$) [1].

3. Results and Discussions

3.1 Functional group analysis

FTIR analysis on hydroxyapatite adsorbents aims to identify functional groups and components contained in the adsorbent. FTIR spectra of the samples with calcination temperature of 700°C and addition of chemical activation is depicted in Figure 1.

![Figure 1. FTIR spectra for analyzing functional groups of nano hydroxyapatite by calcination temperature of 700°C and chemical activation by H$_3$PO$_4$.](image)

The wavelengths of FTIR analysis are in the range of 500 cm$^{-1}$ to 4000 cm$^{-1}$. The results identified the presence of functional groups in the form of hydroxyl (OH), phosphate (PO$_4$) and carbonate (CO$_3$), where their corresponding wavelengths are: 3429.43 cm$^{-1}$ and 570.93 cm$^{-1}$, 601.79 cm$^{-1}$, 1041.56 cm$^{-1}$ and 1413.82 cm$^{-1}$; and 1462.04 cm$^{-1}$ and 1633.71 cm$^{-1}$, respectively. Also present is a C = H bond at a wavelength of 875.68 cm$^{-1}$ [24]. These findings prove that tuna fish bone produces hydroxyapatite which can adsorb heavy metal ions [15].

Previous works also reported the same results, but with slightly different wavelengths for the three functional groups (OH, PO$_4$, and CO$_3$), which occur at 3570 cm$^{-1}$ and 628 cm$^{-1}$ for hydroxyl [23], 1415 cm$^{-1}$, 1090 cm$^{-1}$ and 600 cm$^{-1}$ for phosphate [15], and 1466 cm$^{-1}$ and 1411 cm$^{-1}$ for carbonate [23].

3.2 Iodine adsorption analysis

Adsorption activity of hydroxyapatite to iodine solution had a range of 318.99 to 331.06 mg/g. The concentration of iodine adsorption can be seen in Figure 2. Hydroxyapatite with chemical activation resulted in higher iodine adsorption compared to the others. Higher calcination temperature and addition of H$_3$PO$_4$ activator establish a pore with a larger surface area so that the iodine adsorption is higher [20]. The highest adsorption value is 331.06 mg/g at calcination temperature of 700°C. By considering the values of iodine adsorption in this section, the adsorption isotherm and kinetics can be evaluated.
3.3 Adsorption effectivity

Adsorption efficiency of Cd$_{2}^{2+}$ over contact time is shown in Figure 3. With longer adsorption time, the effectiveness of adsorption will increase as shown by sample with initial concentration of 100 mg/L. For variables with initial concentrations of more than 100 mg/L, adsorption effectiveness will tend to be stable after 90 minutes. The best adsorption efficiency is 86.28%, obtained by the variable with initial concentration of 25 mg/L and contact time of 150 minutes. However, if the initial concentration of 25 mg/L and the contact time is increased, the adsorption efficiency can still increase until it reaches the equilibrium time. High calcination temperature and chemical activation cause a large adsorbent pore surface area so that the adsorption of the adsorbate is higher. The longer adsorption times also provide more adsorbate, which is adsorbed by the adsorbent until stable at equilibrium time [1].

3.4 Adsorption capacity

As depicted in Table 1, the highest adsorption is achieved by the sample with initial concentration of 100 mg/L at contact time of 150 minutes, i.e. 44.62 mg/L. From this observation, when contact time between adsorbent and adsorbate increases, the adsorption capacity will increase up to the equilibrium [24]. When contact time is longer, the more adsorbent pore is filled by the adsorbate until saturation time, when there is no longer free space inside the adsorbent [21]. Based on Table 1, the highest adsorption capacity is obtained at initial concentration of 100 mg/L. For variations of lower than 100 mg/L, the sample still experienced an increase in adsorption capacity up to 150 minutes.
Meanwhile, for samples with initial concentrations of more than 100 mg/L, adsorption capacity tended to be stable at 120 minutes and 150 minutes. At this point, the samples are close to saturation and no longer able to adsorb Cd$^{2+}$ [21].

### Table 1. Adsorption capacity the hydroxyapatite to Cd$^{2+}$

| Time (minutes) | $C_0 = 25$ mg/L | $C_0 = 50$ mg/L | $C_0 = 75$ mg/L | $C_0 = 100$ mg/L | $C_0 = 125$ mg/L | $C_0 = 150$ mg/L |
|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 30            | 6.35            | 9.7             | 8.76            | 10.18           | 18.83           | 16.76           |
| 60            | 9.08            | 12.43           | 17.62           | 16.05           | 35.8            | 21.36           |
| 90            | 14.2            | 17.59           | 26.37           | 39.45           | 34.87           | 38.69           |
| 120           | 16.6            | 24.51           | 25.84           | 42.02           | 36.07           | 39.86           |
| 150           | 17.4            | 23.42           | 26.43           | 44.62           | 37.39           | 38.65           |

### 3.5 Isotherm model of the adsorption

Figure 4 depicts three equilibrium models which describe adsorption process of the adsorbent. Freundlich’s isotherm model was found to be more suitable for this adsorption, indicated by the highest $R^2$ value (0.923) in linear regression approximation. It also shows that a complex layer occurs when cadmium ions are adsorbed by the hydroxyapatite.

Figure 4. Isotherm model with chemical activation, calcination temperature $T = 700^\circ$C, and concentration $C_0 = 50$ mg/L. (a) Langmuir, (b) Freundlich, and (c) Temkin.
This indicates that adsorption is more physically dominant and van der Waals force triggers adsorbate (Cd\(^{2+}\)) to stick with surface of the adsorbent. Table 2 provides detailed parameters for Langmuir, Freundlich, and Temkin models from each model which has the highest R\(^2\) value [1].

| Isotherm type | Parameters |
|---------------|------------|
| Langmuir      | Q\(_m\) (mg/g) = - 62.50  
                 | K\(_L\) (mg/g) = - 7.0     
                 | R\(^2\) = 0.906           |
| Freundlich    | N = 9.4339  
                 | K\(_F\) = 7.92            
                 | R\(^2\) = 0.923           |
| Temkin        | B = 3.951   
                 | A\(_r\) = 4.186           
                 | R\(^2\) = 0.914           |

3.6. Adsorption kinetics

Figure 5 shows adsorption kinetics for first- and second-order models of adsorption of Cd\(^{2+}\) metal using hydroxyapatite. The calculation results can be seen in Table 3, where q\(_e\) value of the second order of the pseudo model is closer to the experimental results with higher R\(^2\) than to the first order. This proves that pseudo-second-order model more accurately describes the kinetics of Cd\(^{2+}\) using hydroxyapatite. A high R\(^2\) value can determine diffusion rate of adsorption [25]. This result is in line with [21], which used nano hydroxyapatite for adsorption of metal Pb\(^{2+}\), Cd\(^{2+}\), and Cu\(^{2+}\). The study also stated that experimental value of q\(_e\) obeys pseudo-second-order model.

![Figure 5](image.png)

**Figure 5.** Kinetics of adsorption on metal Cd\(^{2+}\) with chemical activation, calcination temperature T = 700°C, and concentration C\(_o\) = 125 mg/L. (a) pseudo-first-order and (b) pseudo-second-order model.
Table 3. Adsorption kinetics of the hydroxyapatite to Cd\(^{2+}\)

| \(q_e\) (Experiment) (mg/g) | First order of the pseudo model | Second order of the pseudo model |
|-----------------------------|---------------------------------|----------------------------------|
|                             | \(K_1\) (min\(^{-1}\))         | \(q_e\) (Calculation) (mg/g) R\(^2\) | \(K_2\) (mg.mg\(^{-1}\) min\(^{-1}\)) | \(q_e\) (Calculation) (mg/g) R\(^2\) |
| 37.39                       | 0.02303                         | 20.37042 0.631                    | 0.021534 47.61905 0.960                  |

In Table 3, it is known that \(K\) is the adsorption rate that occurs between each Cd\(^{2+}\) ion in the solution to the surface of the adsorbent. The pseudo-second-order model assumes adsorption capacity is proportional to the surface of hydroxyapatite and depends on its ability to adsorb Cd\(^{2+}\) [25]. The obtained value is in agreement with the second order [3].

4. Conclusion

Hydroxyapatite from tuna fish bone with physical (calcination at 700°C) and chemical activation (using H\(_3\)PO\(_4\)) is the best adsorbent for Cd\(^{2+}\) adsorption in this study. Adsorption by batch method shows that the adsorption of Cd\(^{2+}\) using hydroxyapatite is very dependent on the contact time and initial concentration of adsorbate. The optimal adsorption value of Cd\(^{2+}\) by hydroxyapatite adsorbents was 86.28% and the optimal adsorption capacity was 44.62 mg/g. The adsorption isotherm obeys Freundlich’s isotherm, and the reaction kinetics satisfies the second order of the pseudo model. Based on this analysis, tuna skeletons can be used as a raw material for fabricating hydroxyapatite for Cd\(^{2+}\) removal.

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