EFFECT OF PARTICLE SIZE OF HYDROXYAPATITE BASED CORAL AS ABSORBANT OF NICKEL CONTAMINANT

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ABSTRACT

Synthesis of coral-based hydroxyapatite has been carried out by the precipitation method. From diffraction x-ray spectrum data, using of precipitation method on coral can produce calcium phosphate compounds of hydroxyapatite type of 95.1%, and its residue is tricalcium phosphate (TCP). The formation of variations in hydroxyapatite particle size is milling using high energy milling (HEM-3D) at different times. In this study, the duration of milling was carried out for 5, 10, 15, 20 and 25 hours respectively which resulted in particle sizes of 2411 nm, 774.3 nm, 541.5 nm, 252 nm, and 143.4 nm. Hydroxyapatite particle size distribution with 28 hours milling time formed 2 peaks at 11.7 nm with an intensity of 55.8% and 458.7 nm with an intensity of 44.2%. Hydroxyapatite samples with different particle sizes are used to absorb nickel in a simulated solution of nickel waste. The ICP test results showed that the smaller particle size produces the greater percent removal of nickel by hydroxyapatite adsorbents, making it more effective as an adsorbent for nickel heavy metals. The biggest percentage of nickel removal is 99.913% which occurs at a particle size of 11.7 nm.

KEY WORDS : Hydroxyapatite, Coral, Adsorb, Nickel

INTRODUCTION

Increasing industrial development can increase the amount of liquid waste produced. The type of pollutant that is much considered in environmental management is heavy metals. Heavy metal contamination in waste usually includes Cu (II), Cd (II), Cr (VI), Pb (II), and Ni (II). One of the contaminants often found in liquid waste is a nickel. These contaminants can be originated from industries that use nickel as their raw material, such as electricity coating, battery production and so on (Arsyad, 2001).

Nickel waste can affect the quality of environment and human health (Candra *et al.*, 2019). Nickel waste on the human body can cause damage to the skin, lungs, nervous system and mucous membranes (Argun, 2008). Besides, liquid waste contaminated with nickel will also have a bad effect on the environment around the waste disposal area. The nickel content contained in liquid waste is a maximum of 5 mg/L while for drinking water the maximum is 0.1 mg/L (Kandah and Meunier, 2007). Therefore, an effort is needed to eliminate nickel contaminants in liquid waste.

Heavy metals in water can be removed by various methods of purification. Some methods for purifying liquid waste include a membrane, reduction, ion, solvent extraction and adsorption (Kousalya *et al.*, 2010). The purification of liquid waste requires material and operating costs very large. Among these methods, the method that most chosen is the adsorption method because it has the most economical method and an efficient process compared to other methods (Bailey *et al.*, 1999).

The adsorbents choice that is economic with high adsorption ability is very important in the adsorption process. Adsorbents that can be used

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include activated carbon, clay, active alumina, chitosan, silica, zeolite, and hydroxyapatite. In this study, hydroxyapatite was chosen as an adsorbent because it has high-efficiency potential and its raw material availability is high (Bailey, 1999). Some of these raw materials include limestone, eggshells, coral, and cuttlefish bones (Aminatun *et al.*, 2019).

Coral is a potential undersea which is quite abundant in Indonesia. In previous studies showed that the content possessed by sea coral is a compound CaCO3 (Aragonite) of 92% and the other compounds as an impurity (Indarwati, 2007). Hydroxyapatite can be synthesized from coral material through various methods. HA formation methods include sol-gel, hydrothermal. Among these methods, the precipitation method is a quite easy method of hydroxyapatite synthesis. The precipitation method is carried out by mixing compounds containing Ca^{2+} and PO_4^{3-} ions. The source of Ca^{2+} ions is obtained from the coral while the source of PO_4^{3-} ion uses phosphoric acid (H_3PO_4). The interaction of these ions is expected to be more effective if the particle size is getting smaller. The smaller the size of a particle, the greater the ratio of surface area to volume, so that the absorbance process will be more effective.

Adsorption efficiency is characterized by more components being separated from the fluid transferred to the surface of the adsorbent. This separation occurs because of the attraction between molecules on the surface of the adsorbent with the fluid. If the attraction between nickel and the adsorbent is greater than the attraction between nickel and the solvent, nickel will be absorbed on the surface of the adsorbent. Hydroxyapatite with small particle size has a larger contact surface area. This allows more nickel to be absorbed by the surface of the adsorbent. The results of the adsorption process for each hydroxyapatite sample will be tested by ICP (Inductively Coupled Atlas) to determine the concentration of nickel in the waste solution after the adsorption process. From this research, it is expected that the relationship between hydroxyapatite particle size and the efficiency of the adsorption of heavy metal nickel in wastewater is known.

MATERIALS AND METHODS

Synthesis of Hydroxyapatite

The hydroxyapatite base material in this study is coral, which is taken from the south coast of Java, it is Banyuwangi beach. The process of changing the size of coral into powder is done through collisions, mortal destruction and High Energy Milling (HEM) for 20 hours. The hydroxyapatite preparation method is done by precipitation method. The reason for using this method is relatively simple compared to other methods, such as the hydrothermal method, the sol-gel method and the solid reaction method (referense, 2018). The method of hydroxyapatite precipitation (HA) starts from calcination at 900°C for 3 hours on coral powder to remove natural elements or compounds that are not needed in the formation of CaO compounds. This compound is susceptible to binding H_2O in the air and forming $Ca(OH)_2$ compounds, hydroxyapatite-forming compounds. To ensure the formation of these compounds was carried out using x-ray diffraction (XRD) observation. The formation of HA is carried out through a reaction between phosphoric acid (H_3PO_4) and calcium hydroxide ($Ca(OH)_2$), such as the following stoichiometric equation.

$$5Ca(OH)_2 + 3H_3PO_4 \alpha\ Ca_5OH(PO_4)_3 + 9H_2O$$
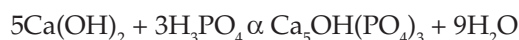
To remove H_2O dehydration was carried out at 110°C for 3 hours and then re-sintering at 900 °C for 5 hours to obtain HA powder. The observation of HA formation was carried out using XRD.

To form a varied HA particle size, milling is done using HEM. The duration for milling will form different particle sizes. In this study, the variations of milling duration were carried out during; 5 hours, 10 hours, 15 hours, 20 hours, 25 hours, and 28 hours. Particle size results from milling can be observed using Beckman Coulter, LS 13 320 Particle Size Analyzer (PSA).

Effectiveness of Nickel Absorbance Test

This test is carried out in two stages, namely, the process of forming a waste solution and the nickel absorption test using the ICP test (Inductively Coupled Plasma). The formation of a solution simulation of nickel-metal waste using Nickel (III) Sulfate hexahydrate ($NiSO_4.6H_2O$) from Sigma-Aldrich with 99% purity. The waste solution is made by dissolving 400 mg $NiSO_4.6H_2O$ into 1 liter of distilled water. For a homogeneous waste solution to be stirred using a magnetic stirrer for 4 hours at room temperature.

The nickel heavy metal adsorption test was carried out on a glass beaker with 100 mL of simulation waste solution. Hydroxyapatite with different particle 9sizes will be used as nickel

adsorbent with an adsorbent concentration of 5 grams/liter. Referring to Santoso (2012) study, the stirring time to achieve adsorption equilibrium is 45 minutes. After the adsorption process is complete, the adsorbent in the beaker glass is filtered and separated from the waste simulation solution.

Then, the waste simulation solution will be tested for metal content using ICP (Inductively Coupled Plasma) test. The ICP test was conducted at the Energy Laboratory of the Sepuluh Nopember Institute of Technology (ITS). From the ICP data can be calculated the amount of metal adsorbed in mg/gram with the following equation,

$$q = \frac{(C_o - C)V}{m} \qquad .. (1)$$

Where Co and C is the concentration of metal ions in mg/liter of data initially and after adsorption, while V is the volume of metal solutions in liters and m is the weight of the adsorbent in grams. To find out the percentage removal value of nickel in solution by each sample can be calculated by the following equation,

$$\% \; removal = \frac{(C_o - C)}{C_o} x100\% \qquad .. (2)$$

Where Co and C are concentrations of metal ions in units of ppm data initially and after adsorption.

RESULTS AND DISCUSSION

The coral XRD spectrum is used as hydroxyapatite material is stated in Figure 1. For the decomposition of $CaCO_3$ into CaO and $Ca(OH)_2$ and CO_2 are calcined at 900 °C with the XRD spectrum stated in Figure 2. Using the Match!® program by searching match, in both spectra, the content of compounds found in coral before and after calcination was obtained as stated in Table 1.

Table 1. Compound content in pure coral and coral after calcination.

Coral	Compound quantity (%)			
	$CaCO_3$	CaO	$Ca(OH)_2$	$Ca_2)O_5Si$
Before Calcinate	94.4	-	-	5.6
After calcinate	-	4.2	95.8	-

$$CaCO_3(s) \; \rightarrow \; CaO \, (s) + CO_2(g)$$
$$CaO(s) + H_2O \, (l) \; \rightarrow \; Ca(OH)_2(s)$$
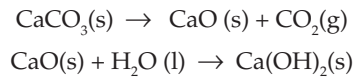
Calcium carbonate when heated will cause the breakdown of atomic bonds so that it becomes soft and forms calcium oxide (CaO). In this phase, each molecule of calcium will combine with 1 oxygen atom and the other molecule binds to oxygen to produce CO_2 gas released into the air. This reaction will continue if the water is added. The reaction will run fast and effectively if in the form of powder and calcium carbonate will release heat. The molecule of CaO will immediately bind water molecules (H_2O) and form calcium hydroxide $Ca(OH)_2$ and be soft.

Hydroxyapatite (HA) is formed by the reaction between $Ca(OH)_2$ and H_3PO_4 using precipitation methods such as press reaction. The result of this reaction precipitate was dried at 110°C for 3 hours, then sintered at 900 °C for 5 hours.
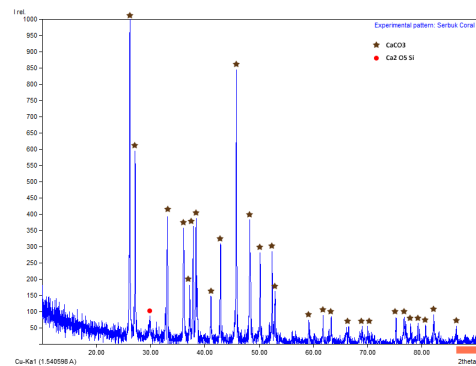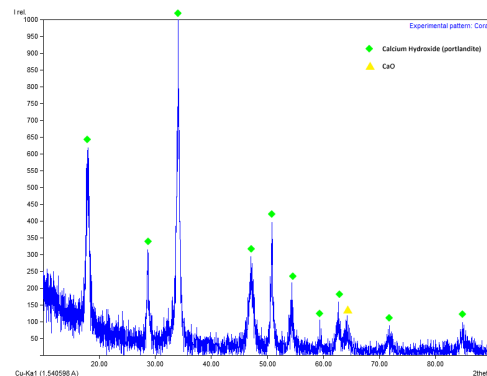

Fig. 1. The XRD spectrum of pure coral

Fig. 2. The XRD spectrum of coral after 900 °C calcination

The final result of this process is HA and can be demonstrated through XRD observations such as Figure 3. And using the Match! ® program that is using a search match, from Figure 3 we can identify the presence of HA, β-TCP, and brushite compounds 95.5 %, 3.1%, and 1.4%. HA and β-TCP compounds are calcium phosphate compounds

with different Ca/P comparisons.

$$10\ Ca(OH)_2(s) + 6\ H_3PO_4(l) \rightarrow Ca_{10}(PO_4)_6(OH)_2(s) + 18\ H_2O(l)$$
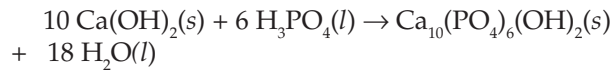
The nickel heavy metal adsorption test using a coral-based hydroxyapatite adsorbent begins with the mixing process of hydroxyapatite powder with a waste simulation solution. The simulation solution of the waste used is 100 mL with the amount of adsorbent as much as 0.5 g and stirring for 45 minutes. Beginning the ICP test the waste simulation solution was used as a control, which showed that the waste simulation solution contained 165.6633 ppm nickel. Furthermore, the ICP test results of various particle sizes of hydroxyapatite as nickel adsorbents can be seen in Table 3. The calculation of the values listed in this equation uses equation (1) and equation (2).

The formation of various particle sizes is carried out by milling HA using HEM at different time intervals, it is 5, 10, 15, 20, 25 and 28 hours. The particle size formed is measured using the Particle Size Analyzer (PSA) as stated in Table 2.

The results of the PSA test in Table 2 show that the longer the duration milling of hydroxyapatite, the smaller the particle size. The smaller the size of a particle, the more easily the particles react with compounds in the environment. This is caused by the greater ratio between the surface areas of the particle volume.

The amount of nickel absorbed by HA is the same for particle size (33-774) nm which is 33.10 mg/gram while particle size with the order of thousands of nanometers is slightly lower. This happens because HA with smaller particle size has a larger contact surface area with nickel elements in the waste, so that nickel which is absorbed by the surface of hydroxyapatite particles increases.

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The process that occurs when the hydroxyapatite surface adsorbs the nickel element is the separation of nickel from the waste solution because of the Van der Waals forces between the nickel element and the hydroxyapatite surface. If the nickel pulling force with the surface of the adsorbent is greater than the attractive tensile force of nickel and its solvent, the nickel element which is initially dissolved in the waste, is separated from the solvent and moves to the surface of the hydroxyapatite adsorbent. Besides, chemical bonds between hydroxyapatite and nickel elements are separated from the solvent. As reported by Salahi (2010) through the results of the XRD test from the sediment from the adsorption process, it shows that Ca_{10}-xNix $(PO_4)_6(OH)_2$ is formed, as in the following equation.

$$Ca_{10}(PO_4)_6(OH)_2 + xNi^{2+} \rightarrow Ca_{10-x}Ni_x(PO_4)_6(OH)_2 + xCa^{2+}$$
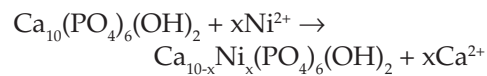
When compared to research conducted by Pujiastuti and Adi Saputro (2008), the most optimum percent removal of nickel is 51.1% with
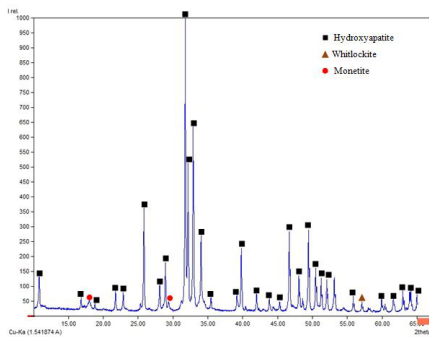

Fig. 3. XRD spectrum as a result of HA formation

Table 3. Effectiveness of Nickel Adsorban Test Results

Particle Size of Adsorbents (nm)	Nickel Concentration after adsorption (ppm)	The amount of Nickel Absorbed by HA (mg/g)	% Removal
2411	0.2200	33.09	99.867
774	0.1700	33.10	99.897
542	0.1641	33.10	99.901
252	0.1512	33.10	99.909
143	0.1494	33.10	99.910
33	0.1443	33.10	99.913

Table 2. Particle Sizes of Hydroxyapatite Sample

Times of Milling (hour)	Particle Sizes (nm)
5	2411
10	774.3
15	542
20	252
25	143
28	33

the type of zeolite adsorbent. Based on these results, it can be seen that the coral-based hydroxyapatite adsorbent is more effective as a nickel adsorbent compared to zeolite adsorbent. Whereas in the research conducted by Salahi *et al.* (2010) producing hydroxyapatite which can adsorb 46.7 mg nickel/gram HA. This value is higher when compared to the optimum value in this study, which is 33.10 mg nickel/gram HA. This is possible because there is a time difference in the adsorption process. Salahi *et al.* (2010) carried out the adsorption process for 120 minutes, while the adsorption process in this study was only 45 minutes. Therefore, further research needs to be done on nickel adsorption by hydroxyapatite with variations in the adsorption time to increase the effectiveness of hydroxyapatite as an adsorbent of nickel heavy metals.

CONCLUSION

Hydroxyapatite used in this study has a purity of 95.5% with β-TCP and brushite as an impurity in 3.1% and 1.4% respectively as nickel heavy metal absorbers. Variations in particle size of absorbance formed using milling are 2411 nm, 774 nm, 542 nm, 252 nm, 143 nm, and 33 nm. The ICP test results show that the smaller the particle size of hydroxyapatite absorbance, the greater the absorbance rate of nickel waste. Besides, the smaller the particle size of hydroxyapatite, the higher the percentage removal value of nickel in waste, and more effective as an adsorbent of nickel heavy metal contaminants.

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