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EFFECTIVENESS HYDROXYAPATITE FROM CHICKEN EGGSHELLS FOR ADSORPTION OF CHROMIUM (VI) METAL ION ELECTROPLATING WASTE

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Abstract

The largest source of waste comes from household activities. One of the wastes that comes from household activities is chicken eggshell waste. Chicken eggshells contain 94% $CaCO_3$ and can be used as a source of calcium to synthesize hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) by the precipitation method. Hydroxyapatite can be used as an adsorbent material because it has pores, is inert, and is wear-resistant so it can adsorb dissolved metal ions, Cr (VI), contained in liquid waste from the electroplating process. This research aims to synthesize hydroxyapatite from chicken eggshells and determine the optimum pH, contact time, adsorbent mass, and initial concentration of waste that influence the adsorption efficiency using continuous system column adsorption method with fixed flow rate of 25 mL/min. In this study, the metal ions Cr (VI) was chosen as an adsorbate because Cr (VI) is the main component in the electroplating process. This research started with the preparation of chicken eggshells waste, then synthesized into hydroxyapatite and characterized using XRD, FTIR, and SEM to know the structure formed is hydroxyapatite. The initial Cr (VI) concentration was measured using AAS with a wavelength of 357.9 nm. As a result of study, the optimum pH was 5.0, contact time of 60 minutes, 3.5 g of adsorbent mass, and the initial concentration of waste is 10 ppm. The result showed adsorption efficiency is 99,48%, with a final concentration of Cr (VI) is 0,07 ppm. The adsorption process followed the Freundlich isotherm model with a maximum adsorption capacity of 3,93 mg/g hydroxyapatite.

Keywords: chicken eggshells, hydroxyapatite, adsorption column, chromium.

1. INTRODUCTION

The largest source of waste comes from household activities, which account for >35% of the national waste composition based on waste sources [1]. One of the wastes that comes from household activities is chicken eggshells. Chicken eggshells are organic waste that can cause environmental pollution if it accumulates in the environment. Organic waste, when wasted in the soil, can contribute 50-55% methane gas and 40-45% CO_2 gas. It can increase the accumulation of greenhouse gases in the atmosphere and cause global warming. Based on data from the Directorate General of Animal Husbandry and Animal Health of the Republic of Indonesia, Indonesia produces 5,155,998.00 tons of eggs (2021). From the previous year, production of eggs has increased; there are 4,753,382.23 tons (2019); 5,141,570.00 tons (2020). 8-11% of the total egg weight is part of the eggshell [2]. So, in 2021, there will be at least 412,479.8 tons of chicken eggshell waste. Therefore, Indonesia has quite a lot of eggshell waste potential.

Eggshells can be used as adsorbents to decrease the concentration of Cr^{6+} in electroplating liquid waste. The eggshells are cleaned and mashed, and then sieved with mesh sizes of 40, 60, and 80. Samples were analyzed for concentration of Cr^{6+} at time intervals of 0; 10; 20; 30; 40; 50; and 60 minutes. The result was that the concentration of Cr^{6+} decreased by 53,001% in 40 minutes using a mesh size of 80 [3]. Shells and bones are known to be dominated by Ca and other elements, such as Na, Mg, O_2, and H [4]. For the content of this material, eggshells are used as starting

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materials in the synthesis of hydroxyapatite. Hydroxyapatite is synthesized by precipitation method by mixing calcium precursors from calcination CaO with phosphate precursors ($(NH_4)_2HPO_4$) using Ca:P molar ratios of 0.67; 1.67; and 2.67. The result was hydroxyapatite with the highest intensity obtained at Ca:P molar ratio of 1.67 [5].

Hydroxyapatite is used in medical and health. Hydroxyapatite is a component of the main inorganic compounds of bone that can be used as adsorbents through ion exchange reactions [6]. Hydroxyapatite can be used as an adsorbent because it has pores, inert, and wear resistant. Hydroxyapatite from chicken bone waste can be used as an adsorbent and decrease concentration of Pb (II) by 95.09%, the concentration of Cd (II) by 98.96%, and the concentration of Hg (II) by 90.41% in pharmaceutical laboratory liquid waste [7]. Hydroxyapatite contains hydroxyl ions, which have a high ability to exchange ions and heavy metals absorbers [8].

Based on the research above, this study aims to obtain hydroxyapatite from chicken eggshells waste and use it as an adsorbent to decrease the concentration of Cr (VI) metal in electroplating waste. Adsorbent is characterized using XRD, FTIR, and SEM to determine the structure of the adsorbent formed which is hydroxyapatite. In the adsorption process, determine the optimum conditions at pH, contact time, adsorbent mass, and waste concentration using the continuous system column adsorption method with a fixed flow rate of 25 mL/min. The concentration of Cr (VI) was measured using AAS.

2. METHODS

The materials used in this study included: chicken eggshells obtained from household waste and martabak merchants in Karawang and Bogor and liquid waste from the electroplating process from Printing Company Karawang, with a concentration of 32.50 ppm. Chemicals solution used are HNO_3, NH_4OH, $(NH_4)_2HPO_4$, pH 10 buffer, distilled water, Whatman filter no. 42, and chromium standard.

The instruments used are an X-Ray Diffractometer (XRD), Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR), Atomic Absorption Spectrophotometer (AAS), an adsorption column with ½" and 30 cm high, analytical balance, blender, oven, furnace, magnetic stirrer, stopwatch, funnel, porcelain cup, and laboratory glassware.

2.1. Hydroxyapatite Synthesis from Chicken Eggshells

Chicken eggshells are soaked for 15 minutes, washed with water, and dried in an oven at temperature 110°C-115°C for ± 15 minutes. Then mashed and calcined to produce CaO for 5 hours at a temperature of 1000 °C using furnace.

Based on stoichiometric calculations, CaO that has been obtained from the preparation of raw materials is weighed then dissolved with HNO_3. Dilute with 100 mL distilled water, then add NH_4OH and buffer to set pH solution at pH 10.

Based on stoichiometric calculations, crystal $(NH_4)_2HPO_4$ is weighed. Dilute with 100 ml distilled water, then add NH_4OH and buffer to set the pH solution at 10.

The Ca solution was dropped into the PO_4 solution using Ca:P ratio of 1.67. Synthesis used a constant temperature of 40°C with stirring speed of 300 rpm. After the Ca solution has been fully reacted, it remains to be stirred for 30 minutes without heating. After being settled for 24 hours, precipitate is filtered using Whatman filter paper no. 42 and washed with distilled water to remove ammonium nitrate [5]. After that, hydroxyapatite that has been formed is characterized by XRD, FTIR, and SEM to determine the structure of the adsorbent.

2.2. Analysis of Chromium (IV) in Electroplating Liquid Waste

Samples were filtered and accurately taking 10 mL into a 100 ml measuring flask. Added 1 ml HNO_3, after that diluted with distilled water and homogenized. Sample and standard were measured at λ 357,9 nm using Atomic Absorption Spectrometry (AAS).

2.3. Adsorption Process Optimization Observation

2.3.1. Waste pH

A total of 1.0 g of hydroxyapatite was weighed and then put into the adsorption column. The waste is conditioned at pH 3, 4, 5, 6, and 7. The waste is flowed into the adsorption column installation with a flow rate

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of 25 ml/min. Effluent sample was collected when it reached 100 ml. After that, the sample was taken accurately. A 10 ml sample is put into 100 ml measuring flask. Added 1 mL HNO_3 65%, diluted with distilled water and homogenized. Using AAS, absorbance was measured at λ 357,9 nm.

2.3.2. Contact Time

A total of 1.0 g of hydroxyapatite was weighed and then put into the adsorption column. The waste that has been conditioned at optimum pH is then flowed into the adsorption column installation at a flow rate of 25 mL/min. Effluent sample was collected when it reached 100 ml after a time interval of 30, 45, 60, 75 and 90 minutes. After that, the sample is taken accurately 10 ml and put into 100 ml measuring flask. Added 1 ml HNO_3 65 %, after that diluted with distilled water and homogenized. Using AAS, absorbance was measured at λ 357,9 nm.

2.3.3. Adsorbent Weight

A total of 2.0; 2.5; 3.0; 3.5; and 4.0 g of hydroxyapatite was weighed and then put into the adsorption column. The waste that has been conditioned at optimum pH is then flowed into the adsorption column installation with a flow rate of 25 mL/min. Effluent samples were collected when it reached 100 ml at an optimum contact time interval. After that, the sample is taken accurately 10 ml and put into 100 ml measuring flask. Added 1 mL HNO_3 65%, after that diluted with distilled water and homogenized. Using AAS, absorbance was measured at λ 357,9 nm.

2.3.4. Initial Concentration of Waste

Hydroxyapatite is weighed with the optimum adsorbent weight and then put into the adsorption column. The waste that has been conditioned at optimum pH and made a variation in the initial waste concentration of 10; 20; 30; 40 and 50 ppm is then flowed into the adsorption column installation with a flow rate of 25 ml/min. Effluent sample was collected when it reached 100 ml after an optimum time interval. After that the sample is taken accurately 10 mL and put into 100 mL measuring flask. Added 1 mL HNO_3 65%, after that diluted with distilled water and homogenized. Using AAS, absorbance was measured at λ 357,9 nm.

3. RESULTS AND DISCUSSION

3.1. Characterization of Hydroxyapatite Adsorbent with XRD

The characterization of hydroxyapatite synthesis from chicken eggshells was analyzed using an X-Ray Diffractometer instrument to provide details about the type of sample and the degree of crystallinity of the structure of its constituent parts. The area where the peak (2θ) appears serves as a clue to the type of mineral or crystalline components that make up the sample. The low intensity of the peak may indicate the degree of crystallinity of the structure of the constituent parts of the sample. The spectra of the analysis were then matched with the 2θ value with JCPDS (Joint Committee on Powder Diffraction Standards) data so that the type of mineral or crystal in the sample could be known. The results are shown in Figure 1 and Figure 2 below.

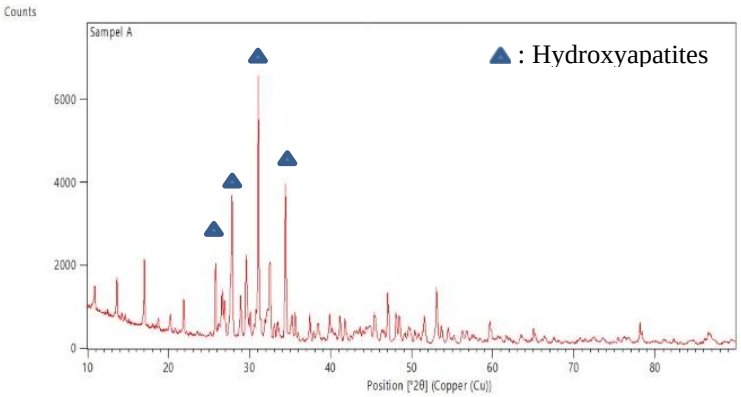

Figure 1. XRD Adsorbent Results

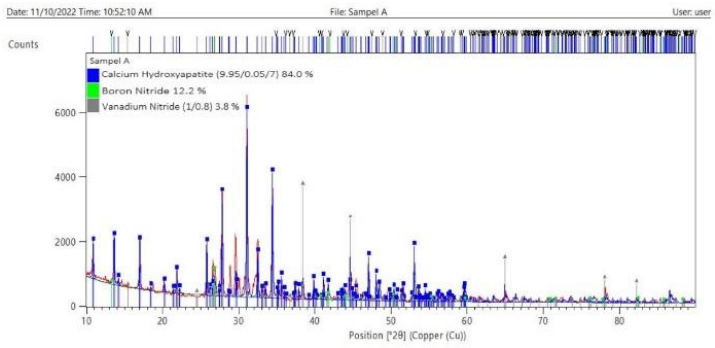

Figure 2. Percentage of Hydroxyapatite in Sample

According to Figure 1, the peaks show the highest intensity of hydroxyapatite at 25.77°; 27.80°; 31.03°; 34.38°. It matches the standard JCPDS No. 09-432. This result can be concluded that hydroxyapatite

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successfully synthesized from chicken eggshells with crystallinity 84.0% according to Figure 2. Meanwhile, the sample contains 12.2% boron nitride and 3.8% vanadium nitride, which may come from impurities in tools and materials in the synthesis process.

3.2. Analysis using FTIR

The adsorbent sample was also analyzed using an FTIR Spectrophotometer to identify the vibrations from their functional groups. The functional groups of hydroxyapatites are shown in Figure 3.

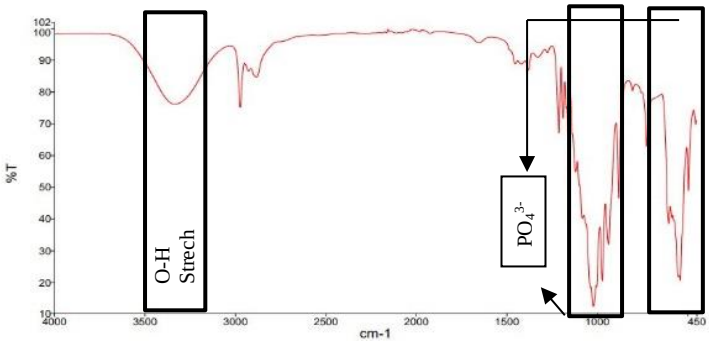

Figure 3. The Functional Groups of Adsorbent

According to Figure 3, PO_4^{3-} groups form intensive IR absorption bonds at 553-600 cm^{-1} and 1000-1100 cm^{-1}. Meanwhile, the presence of OH^- group in the spectrum above was identified at 3300-3500 cm^{-1} as OH-Strech. Whereas, OH- ion proves presence of Hap [5]. The PO_4^{3-} and OH^- groups are known to be constituent active groups of hydroxyapatites derived from the compound calcium hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$]. Adsorption ability of hydroxyapatite against metals is due to the active group [9]. Ca (II) bond by PO_4^{3-} group can be replaced by Cr (VI) metal. Therefore, hydroxyapatite can be used as an adsorbent.

3.3. Morphology Characterization

To observe the morphology of the resulting hydroxyapatite was identified using the Scanning Electron Microscopy (SEM). The observation with a magnification of 20.000 x as seen in Figure 4.

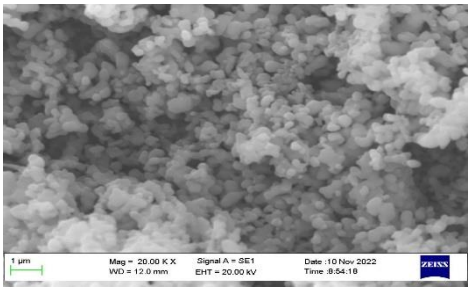

Figure 4. Morphology of Hydroxyapatite

From Figure 4 hydroxyapatite particles formed into granular close to spherical according to hydroxyapatite synthesis from research [5]. The surface morphology of hydroxyapatite particles shows irregular fine grains. It also shows that agglomeration occurs due to nanometer size of the material. High temperature will increase the constituent atoms so that diffusion with adjacent particles occurs binding. Hydroxyapatite has cavities between particles so that can be used as an adsorbent.

3.4. Optimization of Adsorption Process

3.4.1. Study of pH

In this study, waste pH varied at pH= 3, 4, 5, 6, and 7. The effectiveness of adsorption can be seen based on the efficiency of Cr (VI) adsorption using adsorption column is in Figure 5.

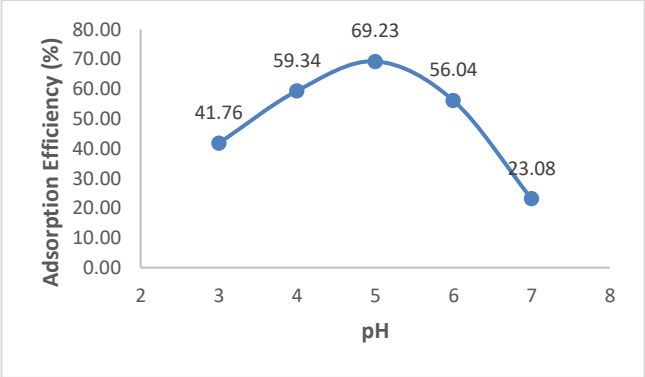

Figure 5. Graph of pH to Adsorption Efficiency of Cr (VI) by Hydroxyapatite

Adsorption efficiency increases at low pH or in acidic conditions, at pH 3 until it reaches a maximum at pH 5. In conditions of low pH or acid, the adsorption efficiency of Cr (VI) is good, this is because hydroxyapatite begins to demineralize at pH below 5.5 which causes the release of Ca (II) [9]. Then the process of adsorption Cr (VI) by adsorbent occurs replacing Ca (II) ion by the phosphate group. However, under acidic pH conditions, part of the adsorbent active group binds to H^+ ions because there is competition between H^+ ions and Cr (VI) metal ions to bond to adsorbent surface and causing fewer Cr (VI) metal ions to be adsorbed and reducing adsorption efficiency.

In a neutral pH, hydroxyapatite is balanced with many Ca^{2+} and PO_4^{3-} ions. Increased pH or alkaline conditions will cause Ca (II) in apatite to be difficult to release so that the interaction of Cr (VI) with hydroxyapatite becomes less effective and its adsorption efficiency will also decrease.

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3.4.2. Contact Time and Kinetic Study of Adsorption Process

Determination of the effect of contact time optimization on the adsorption of Cr (VI) metal by hydroxyapatite at pH 5 as the optimum pH. The variations in contact time used in this study were 15; 30; 45; 75; and 90 minutes.

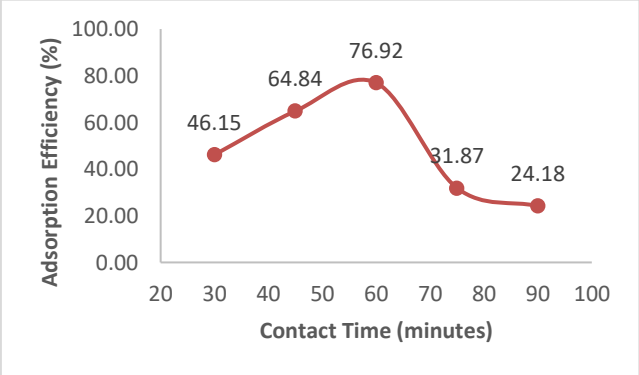

Figure 6. Graph of Contact Time to Adsorption Efficiency of Cr (VI) by Hydroxyapatite

The effect of contact time on the effectiveness of Cr (VI) adsorption by hydroxyapatite is shown in Figure 6. The optimum contact time for the adsorption of Cr (VI) by hydroxyapatite was 60 minutes. The longer the adsorption time, the longer the interaction time of Cr (VI) with the adsorbent, so that the absorption of Cr (VI) by the adsorbent will be greater [9]. At a contact time of 75 minutes there is a decrease in adsorption efficiency, because, at a longer time the adsorption rate becomes reduced so that the Cr (VI) ions in the adsorbent surface will be saturated and there is a process of desorption or re-release of Cr (VI) ions that have been absorbed by the adsorbent. Cr (VI) changes to free Cr in solution and causes its adsorption efficiency to decrease. Meanwhile, at contact times of 30 minutes and 45 minutes, Cr (VI) contained in waste has not been perfectly adsorbed, so the adsorption efficiency is not optimal.

Adsorption data at contact time variation used were analyzed by using first-order kinetic model and second-order kinetic model. Graph of first order and second order reaction models is shown in Figure 7 and Figure 8.

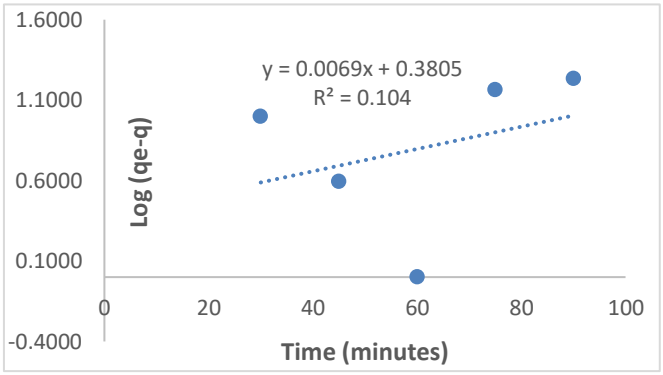

Figure 7. Graph of First Order Reaction

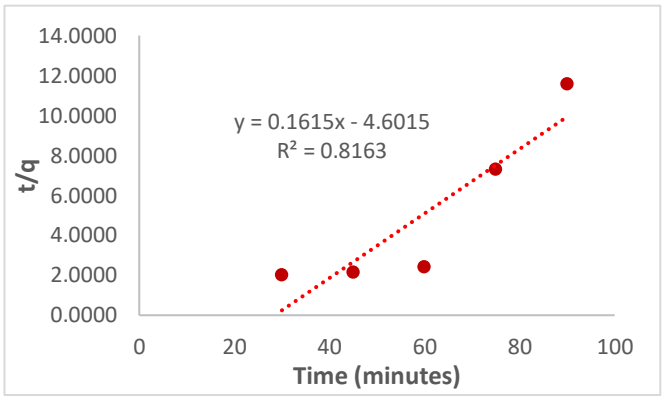

Figure 8. Graph of Second Order Reaction

According to Figure 7 and Figure 8, this study has a high correlation value (R^2) for second order kinetic model of 0,8163. The high R^2 value indicates that the kinetic study of adsorption process followed the second-order reaction. The second-order kinetic model shows that the adsorption process consists of two stages, there are fast initial stage and a slower second stage. The optimization of the contact time shows that the adsorption process occurs quickly as the contact time increases, but after adsorption occurs at the optimum time the adsorption process decreases and takes place more slowly after some subsequent contact time. The second order reaction also assumes that the adsorbent capacity is proportional to the amount of hydroxyapatite surface which also depends on the ability of the adsorbent to adsorb Cr (VI).

3.4.3. Study of Adsorbent Weight

The determination effect of adsorbent weight optimization in adsorbing Cr (VI) metal is conditioned on an optimum pH and contact time of pH 5 and contact time of 60 minutes. The weight variation of adsorbents used in this study was 2.0; 2.5; 3.0; 3.5; and 4.0 g in a

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waste volume of 1500 ml. The effect of adsorbent mass on the effectiveness of Cr (VI) adsorption by hydroxyapatite is shown in Figure 9.

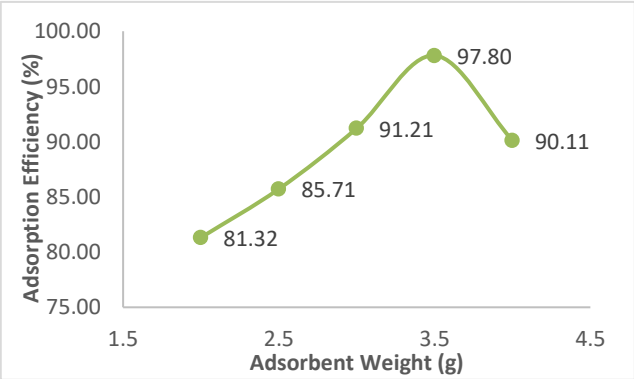

Figure 9. Graph of Adsorbent Weight to Adsorption Efficiency of Cr (VI) by Hydroxyapatite

The highest Cr (VI) adsorption efficiency was obtained at an adsorbent weight of 3,5 g in 1500 mL samples, which was 97.80%. The amount of Ca (II) in hydroxyapatite structure can be exchanged for Cr (VI) in waste sample. The increasing of adsorbent weight will be increasing the amount of Cr (VI) absorbed. This is because of the increasing adsorbents surface area due to the availability of active side. Therefore, adsorption efficiency will be directly proportional to the weight of adsorbent. The adsorption efficiency of Pb, Cd, and Hg metals has increased along with the increase in weight of the adsorbent used. In an adsorbent mass of 4.0 g, adsorption efficiency decreases due to the adsorbent surfaces that overlap and cover each other [7]. Cr (VI) becomes narrow in movement to be bound to adsorbent surface. The adsorption process will take place quickly and reach saturation as much as adsorbent weight. Therefore, the adsorption speed is greater than the desorption speed, then the adsorbate will be easier to detach from adsorbent surface and easier to desorption.

3.4.4. Study of Initial Concentration of Cr (VI)

In this study, the sample is conditioned at pH= 5, using contact time of 60 minutes, and the adsorbent weight used is 3.5 g. The initial concentration of the sample used was 13.86; 24.64; 35.00; 48.64; and 57.64 ppm.

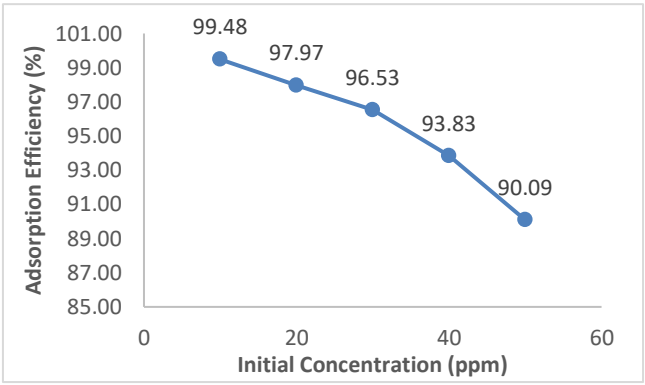

Figure 10. Graph of Sample Concentration to Adsorption Efficiency of Cr (VI) by Hydroxyapatite

Figure 10 shows the efficiency of Cr (VI) adsorption. The increasing concentration will affect the low efficiency because of the ability to adsorb metal has reached its maximum. It is caused by the amount of metal in solution not being balanced with the number of pores available on hydroxyapatite adsorbent. The adsorbent will reach its saturation point, then the process becomes desorption. The greatest adsorption efficiency in this study reached 99.48% at 10 ppm as initial Cr(IV) concentration.

3.4.5. Adsorbent Sorption Characteristics

To determine the adsorbent sorption in the adsorption of Cr (VI) metals by comparing the results of the adsorption isotherm equation obtained. The adsorption isotherms used are Langmuir and Freundlich. The relations coefficient (R^2) close to the value of 1 can be used to determine the data from this study, whether using the Langmuir or Freundlich adsorption isotherm model.

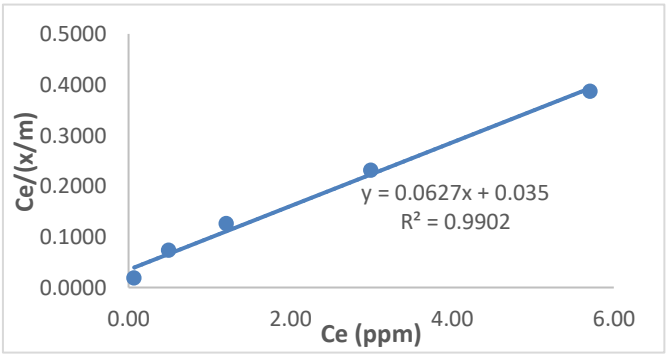

Figure 11. Graph of Langmuir Isotherm

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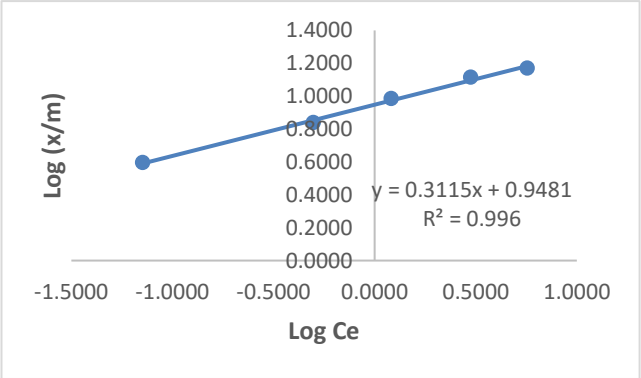

Figure 7. Graph of Freundlich Isotherm

Based on the Langmuir and Freundlich adsorption isotherm that have been described, in general, the adsorption that takes place in this study has a high correlation value (R^2) for the Freundlich adsorption isotherm of 0.9960, as found in Figure 11 and Figure 12. The high R^2 value indicates that the adsorption process of Cr (VI) metal ions with hydroxyapatite adsorbent in this study followed the Freundlich model and resulting Cr (VI) adsorption capacity was 3.93 mg/g hydroxyapatite due to the predominance of multilayer physical bonds in the bonds formed in the adsorption of Cr (VI) ions by hydroxyapatite. Freundlich equation supposes that adsorption that occurs can be on more than one surface, the side is heterogeneous due to the difference in binding energy on each side, forming many layers or multilayers, there is an active side of adsorption that has high affinity, and the other side has low affinity.

4. CONCLUSION

Chicken eggshell was successfully made into hydroxyapatite adsorbent using the precipitation method. This approach resulted in the highest intensity at 2θ from XRD. Characterization with FTIR also showed PO_4^{3-} and OH^- groups with the morphology formed granular and have cavities between their particles which indicates characteristic as adsorbents. The optimum process of Cr (IV) adsorption was observed at pH 5, 60 minutes contact time, with 3.5 g adsorbent weight in 1.5 L of 10 ppm Cr (IV). It shows 99.48% efficiency of adsorption process with the final concentration 0,07 ppm. This study followed the Freundlich model with the equation y = 0,3115x + 0,9481 with a value of R^2 = 0.9960 with maximum adsorption capacity of 3.93 mg/g hydroxyapatite.

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