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Removal of pH and Concentration in Biosorpsi of Cu^{2+} Metal Ions withLongan Shell (*Euphoria longan* Lour) that has been Immobilized

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Abstract:

Biosorption as an alternative source for removing heavy metal contaminated. Biosorption by biosorbent of longan shell immobilized using sodium silica in the form of dry powder. Longan shell immobilization can improve biosorbent perfomance in biosorption, increase absorpstion, and can be regenerated without damaging the biosorbent structure used. In this study, using batch method, which examined the variation in pH, concentration and analyzed the functional group of biosorbent longan shell, namely before immobilization, immobilization that had been contacted with Cu^{2+}. The result obtained from each variation werw pH 4, concentration 550 mg/L, having an absorption of 16.05 mg/g. The interaction between the adsorbent and the adsorbate was determined by the equation Langmuir isothrem, in this study the equilibrium of langmuir and qmax = 19.607 mg/g and was characterized using FTIR (Fourier Transform InfraRed).

Keywords **—Immobilization, biosorption,natrium silica, longan shell, ion Cu^{2+}**

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I. INTRODUCTION

Water pollution in heavy metals has a toxic effect on living organisms. Activities from industrial developments are dense, causing water to be contaminated by heavy metals [1]. The problem of heavy metals in industrial wastewater can cause damage to aquatic life, and kill microorganisms so that the proces of water purification becomes disruoted [2].

Heavy metals often found in industrial wastes include Pb (II), Cu (II), Fe (II), and Cr (II). Heavy metal effects can have an effect at very low concentration. If industrial waste contains heavy metal waste that exceeds a predetermined threshold value, it will pose a danger to human health, animals and aquatic plants [3].Copper is a dangerous metal if it is put into water produced from mining, smelting,electroplating, electrolysis and the agricultural sector including fertilizers,

pesticides and others. If it is excessive, there will be potential carcinogenic toxins [4].

Various techniques that have been used for processing industrial waste containing heavy metals by prepitation, adsorption, ion exchange, membrane technology and electrochemistry [2]. The traditional biosorption method is used as an alternative to remove heavy metals from ontaminated water. Some biosorbents effect heavy metals because they have functional groups such as hydroxyl, carboxyl, carbonyl and amines to make metal complexes [4]. However, recent research show that several types of dry biomass such as longan shell, banana peel, orange pell and lemon peel [5] can be used as inexpensive biosorbents. The reason is that dry skin contains functional groups such as $–CO_2H$, -OH, NH, C-H, C=O, C=C, which can from ligands when metal ions survive on the surface. Jaitrong's research [6] states that longan shell has various chemical compounds such as galic acid, flavone glycosides, and hydroxynamic with the main content of flavones in the form of quercetin and kaemferol.

Based on the research that has been done [4], longan shell can be used to remove copper (Cu) metals ions in solution using a column method. From the result obtained, it can be seen that bioactive compounds from longan shell can bind the metal. Optimum conditions were obtained at pH 3, concentration of 400 mg/L and particle size of 250 µm with absorption capacities of 0.3681 mg/g, 3.9895 mg/g and 5.6765 mg/g, respectively. Based on the data above, the authors are interested in conducting a study using biosorbent longan shell immobilized Cu^{2+} metals ion using a batch method which can later be applied to waste. Several studies have shown that immobilization can strengthen bonds and can increase the absorption of metal ions. Research are interested in utilizing longan shell whichis immobilized first as biomass for absorption of Cu metals. This aims to determine for absorption capacity of Cu metal ions by longan shell immobilized with sodium silicate.

II. METHODS

In present works all analytical grade chemical reagents including $CuSO_4.5H_2O$, HNO_3, NaOH,Na_2SiO_3technical, H_2SO_4, and $BaCl_2$.

A. Preparation of Biosorbent

Longanwere obtained from the marketin Padang city. Longanwere cleanedand dried with the sun for 7 days and crushed with particle size to 150 µm[7].

B. Immobilization of Longan Shell

A moxed 75 mL 0f 5% H_2SO_4 with Na_2SiO_3solutions jus enough to up pH 2. Next, the biomass as much 5 g added to the silica solution and stir to 15 minutes. $Na_2SiO_3$was added to reach pH 7. The polymer gel was cleaned with water and when added $BaCl_2$ as much two drops there wasn't white precipitate Barium Clorida was used to indicate whether the sulfates has been removed. The polymer gel was dried overnight at 60ºC and crushed with particle size 150 µm [8].

C. Metal Biosorption Experiments

The biosorption of copper ions on silica immobilized longan shell was applied in flask containing 25 mL of copper solution and biosorbent were stirred at 150 rpm, periods at 60 minute, dosage 0.2 g and particle size 150 µm. We were studied effect of pH 2, 3, 4, 5, 6 and initial metalion concentration 150 mg/L, 250 mg/L, 350 mg/L, 450 mg/L, 550 mg/L, 650 mg/L. The filtrate were measured by Atomic Absorption Spectroscopy.

After calculating the concentration to determine the amount of absorption that occurs by biosorbent can be calculated using the equation Langmuir isothrem is

$$\frac{Ce}{qe} = \frac{1}{qmKl} + \left(\frac{1}{qm}\right) Ce$$

Where,
Ce= the concentration of the adsorbate when balanced (mg/L)
qe= milligrams of adsorbate per gram of adsorbent (mg/g)
qm= miligrams of adsorbate are absorbed under saturated conditions or maximum adsorption capacity (mg/g) adsorbent
K_L= equality constant [9].

Langmuir adsorption isothrem assumes that in the biosorption process only occurs in the monolayer, all surface sites are homogeneous based on kinetic viewpoints. The Langmuir biosorption isothrem equation can be derived theoretically, namely the occurrence of equilibrium between molecules not adsorbed and molecules adsorbed on the biosorbent surface [10].

Freundlich isothrem is one of several initial equations proposed to relate the amount of adsorbed material to the concentration of the material in solution, which is formulated in the equation below:

$$\text{Log qe} = \text{Log K} + 1/n \text{ Log Ce}$$
$$\text{qe} = \text{K}Ce^{1/n}$$

qe = mass of subtance adsorbed per unit mass of adsorbent
Ce = consentration of solution, k and n is constant.

III. RESULTS AND DISCUSSION

A. FTIR Analysis

FTIR (Fourier Transform InfraRed) is an analytical technique that is used to detect the vibration characterstics of functional groups on the surface of the adsorbent. Data from FTIR can find out information about the bonding mechanism and functional groups involved in interactions with metal ions. IR spectra of pure longan shell, after immobilization and after adsorption by Cu^{2+} metal ions at wave numbers 600 – 4000 cm^{-1} , can be show in figure 1.

Based on the result of the FTIR spectrum on the wave image on the longan shell functional group, namely –OH at wave number 3500 – 3200 cm^{-1}, at 2924,92 cm^{-1} was the streaching of C-H group, C=C (streaching) at wave numbers 1648 – 1638 cm^{-1} peak was carboxyl strech in ester, C=C (bending) 850 – 550 cm^{-1}. At 1063,91 cm^{-1} which is the Si-O-Si group.

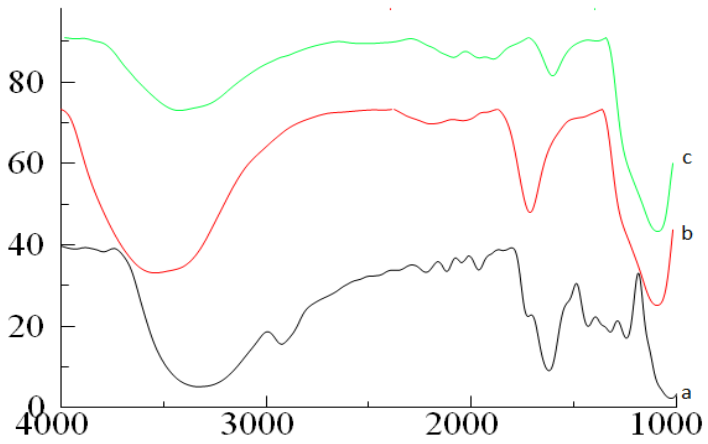

Fig. 1 FTIR spectrum of longan shell, (a) before immobilized, (b) immobilized, (c) after contact copper solution.

B. Influence of pH

One of the factors that influence the ability of adsorbents in bonding ions is the pH of the solution.The pH of the solution effect the adsorbent in the chemical bonding of metal ions on the surface. The measurement of the initial pH variation of the solution starts from 2, 3, 4, 5, and 6.

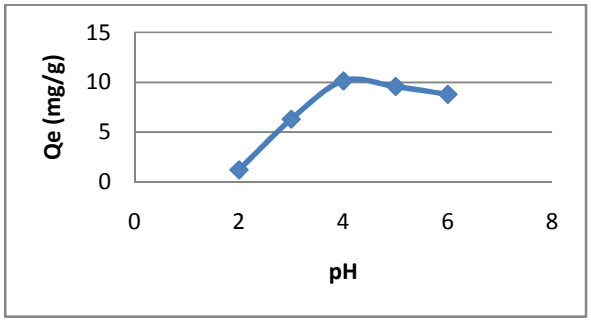

Fig. 2Influence of pH solution on adsorption ofcopper ions by immobilized longan shells, (initial concentration 250 mg/L), particle size 150 µm, dosage biosorbent 0.2 g, contact time 60 min, stirring speed is 150 rpm.

The result shown in figure 2 show that the maximum absorption of ion Cu^{2+}occurs at pH 4 with an absorption capacity of 10.134 mg/g. At low pH there are many H^{+}ions in the solution, so that H^{+} ions will compete with Cu^{2+} metal ions to bind the negative charge to the active group on the surface of the biosorbent, this absorption at that pH is low [11]. A decrease in absorption capacity from pH 5 and 6 can be attributed to the formation of anionic hydroxide complexes in the solution, so that the absorption of the biosorbent surface with ions decreases.

C. Influence of Solution Concentration

Concentration is one of the important things that can effect metal absorption. The effect of concentration on the absorption of Cu^{2+} metal was used by concentration variations of 150, 250, 350, 450, 550, and 650 mg/L.

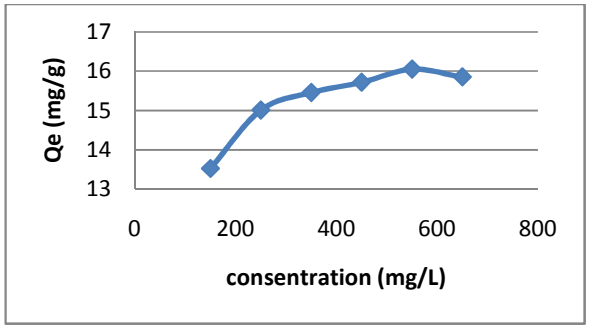

Fig. 3 Influence of solution concentration on adsorption ofcopper ions by immobilized longan shells, optimum at pH 4, particle size 150 µm, dosage biosorbent 0.2 g, contact time 60 min, strring speed is 150 rpm.

The result are shown in figure 3. At concentrations of 150, 250, 350, 450, 550 and 650 mg/L the adsorption of metal ions continues to increase because the number of metal ion adsorbed by the union of the longan shell mass increases with increasing concentration. Seen on the graph of 550 mg/L absorption capacity reaches the maximum value with a value of absorption capacity of Cu^{2+} ions of 16.05 mg/g.

D. Adsorption Isotherm Study

In the variation of concentration used in this study, it can be seen that the data obtained fulfills the equation of the Langmuir isothrem. Can be seen in figure 4. Which is the linear curve of adsorption of Cu metal by immobilized longan shell.

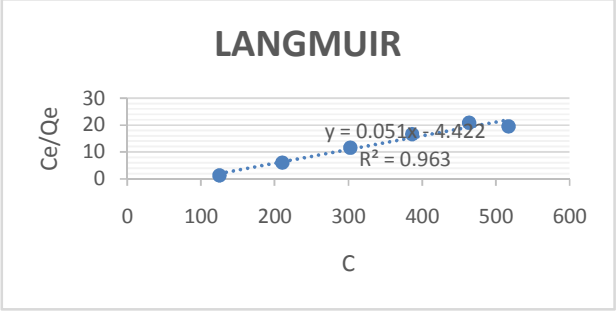

Fig. 4 Langmuir Isotherm

From the above data it can be concluded that the absorption of Cu^{2+} by longan shell immobilized fulfills the Langmuir isothrem adsorption equation, with coefisien correlation (r^2) 0.9631 approaching 1 with y = 0.051x – 4.4221, which means that Cu metal ion adsorption by longan chemically

immobilized. The maximum capacity of absorption of Cu metal ions is 19.607 mg/g.

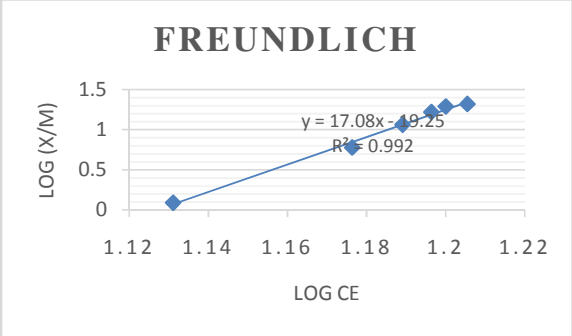

Fig. 5 Freundlich Isothrem

From the graph above, it can be concluded that the absorption of Cu^{2+} by longan shell immobilized fulfills the Freundlich isotherm adsorption equation, with coefisien correlation (r^2) 0.9927 approaching 1 with y = 17.087x – 19.255, which means that adsorption of Cu metal ions by immobilized longan shell in physics. Physical adsorption occurs because there is a van der waals force that goes back and forth [12]. Physical adsorption takes place quickly, so that adsorbed molecules are easily released again by reducing the pressure of subtances, and can form several layers [13].

IV. CONCLUSION

Longan shell (*Euphoria longan* Lour) can be used as biosorbent which can absorbion of Cu^{2+} ions in solution. Immobilized longan shell can improve biosorbent perfomance in biosorption, increase absorption, and can be regenerated without damaging the biosorbent structure used. The optimum conditions for adsorption of Cu^{2+} ions have a pH of 4 and a concentration of 550 mg/L by cantacting dosage 0.2 gram of longan shell immobilization with sodium silica using particle size 150 µm, strring speed 150 rpm, contact time 60 minutes with absorption of 16.05 mg/g. Immobilized longan shell has an absorption capacity of 19.607 mg/g.

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