

BIOSORPTION OF Ni (II) IONS BY ARABICAN COFFEE FRUIT (*Coffea arabica*)

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Abstrak. Kulit buah kopi arabika merupakan material yang melimpah dan murah. Material ini telah digunakan sebagai adsorben dalam proses biosorpsi untuk penghilangan ion logam Ni(II) dari limbah cair. Biosorpsi ion logam Ni(II) oleh kulit buah kopi arabika dilakukan pada variasi ukuran partikel, waktu kontak, pH dan konsentrasi. Kapasitas adsorpsi ion Ni(II) oleh kulit buah kopi ditentukan dengan menggunakan isothermal adsorpsi Langmuir dan Freundlich. Konsentrasi ion logam Ni(II) sebelum dan setelah adsorpsi ditentukan dengan menggunakan Spektrofotometer Serapan Atom (SSA). Hasil penelitian menunjukkan bahwa waktu optimum yang diperoleh adalah 50 menit dan pH optimum adalah 6 dengan menggunakan ukuran partikel 120 mesh. Dari hasil penelitian ini diperoleh bahwa biosorpsi ion logam Ni(II) dengan menggunakan kulit buah kopi arabika sesuai dengan model isothermal Langmuir dengan nilai kapasitas biosorpsi (Q_0) yakni sebesar 18,86 mg/g. Gugus fungsi yang terlibat dalam biosorpsi ion logam Ni(II) oleh kulit buah kopi adalah gugus hidroksil (-OH).

Kata Kunci: Biosorpsi, SSA, Isothermal Adsorpsi, Ni(II), Kulit Buah Kopi Arabika

ABSTRACT. Arabica coffee fruit peel is a material that is abundant and cheap. The material has been used as an adsorbent in the biosorption process for the removal of metal ions of Ni(II) from wastewater. Biosorption of Ni(II) ion by dragon fruit peel was done on the variation of particle size, variation of contact time, pH and concentration. Adsorption capacity was studied by both isotherm adsorptions of Langmuir and Freundlich. The concentration of metal ions Ni(II) before and after adsorption was determined using Atomic Absorption Spectrophotometer (AAS). Results showed that the optimum time was 50 minutes and the optimum pH was 6 with 120 mesh of particle size of biosorption. Results showed that the biosorption of Ni(II) ion using Arabica coffee fruit peel fulfilled the isotherm Langmuir model with the biosorption capacity (Q_0) of 18.86 mg/g. The functional group involved in metal ion biosorption of Ni(II) by the peel of coffee fruit is a hydroxyl group (-OH).

Keyword: Biosorption, AAS, Adsorption Isotherm, Ni(II), Arabica Coffee Fruit Peel.

INTRODUCTION

The rapid growth of the world population and the rapid development of the industry has caused more toxic waste materials to be thrown into the environment. These waste materials will later become waste and pollute the environment in an amount that is difficult to control properly. Pollutants

are dominated by heavy metal waste, one of which is Nickel (Tangio, 2013).

Nickel (Ni) is one of heavy metals, which is widely used in kitchen equipment (spoons and cooking utensils), house and building ornaments, and industrial components. Apart from being an essential metal, nickel also has a dangerous effect (Axtell et al., 2003). Nickel is more toxic to plants. The nickel

threshold in drinking water is 0.04 mg / L (Suhendrayatna, 2001). Basically heavy metals in waste water can be separated in various ways, namely physical and chemical methods (Wisjnuaprpto, 1996 in Soeprijanto et al., 2005). Physical processing is generally carried out by adsorption for example with activated carbon and membrane filtering. Other methods are used such as oxidation / reduction, ion exchange, filtration, evaporation, reverse osmosis and extraction. But these techniques or methods have deficiencies such as imperfect metal binding, require a lot of chemicals and energy, and produce toxic sediment and water products as a by-product (Vierra and Volesky, 2000). Whereas biological processing or biosorption is done by utilizing the ability of heavy metal accumulation by microorganisms (Soeprijanto et al., 2005).

Biosorption is an alternative to absorb heavy metals due to the presence of biological material components that have a large binding capacity (Kratochvil et al., 1998 in Nova et al., 2012). Biosorption is the process of absorption of analytes by biomass. Biosorption utilizes the ability of biological materials to accumulate heavy metals from solutions metabolically or physically-chemically (Diantariani et al., 2008).

Some biomaterials have the potential to absorb heavy metals generally from agricultural wastes. Aslam et al. (2010) prove that peepal leaves (*Ficus Religiosa*) which contain carboxylic, hydroxyl, and amino groups can bind Nickel metal. In 2010, Raj et al. Proved

that amino acids from *Moringa* seeds can adsorb Ni (II) ions. Hasar (2002) reported that mangrove stem skin containing polysaccharides, lignin, polyphenols, and hydroxide acid has also been proven to absorb Cu (II) and Ni (II) ions. Watermelon skin which has the content of pectin, cellulose and protein is capable of being adsorbent of Ni²⁺ and Co²⁺ + metals (Lakshmiopathy and sarada, 2013).

The results of these studies indicate that agricultural waste containing functional groups can be further processed as an adsorbent that can be used to absorb heavy metals from the waters. The skin of Arabica coffee (*Coffea arabica*) is an agricultural waste that has a very large presence. In coffee plantations, solid waste of coffee fruit skin has not been used optimally.

Coffee skin is a by-product of harvest which has been a waste and is only used as organic material and animal feed (Budiari, 2014). Nuraini (2012) in Disafitri (2012) revealed that the skin of Arabica coffee fruit contains cellulose, and lignin which has the potential to bind heavy metals such as nickel metal from solution. The compounds contained in the skin of Arabica coffee fruit contain –OH and –COOH groups. The active groups when viewed from Hard Soft Acid Base (HSAB) are classified as hard bases while Ni (II) metals are categorized as borderline acids.

MATERIALS AND METHODS

Research Materials

The materials used in this study were Arabica (*Coffea arabica*) coffee skin, Ni (NO₃) 2.6H₂O, aquades, Whatman 42 filter paper, ordinary filter paper, label paper, and universal pH.

Research Tools

The tools used in this research are glass tools commonly used in laboratories, Atomic Absorption Spectrophotometer (SSA) 205 VGP models, analytic balance, ovens, magnetic stirrers, sieves size 60, 80, 120 and 150 mesh, stopwatch, desiccator and spectrophotometer FT-IR Shimadzu prestige 21.

PROCEDURE

Preparation of Arabica Coffee Skin Biosorbent (*Coffea arabica*)

The skin of Arabica coffee fruit that has been taken is washed with clean water to remove dirt and other particles. Then the skin of Arabica coffee is washed again with distilled water until clean and then drained. Coffee skin is dried at room temperature. The dried Arabica coffee skin is then milled and sieved with variations of filters 60, 80, 120 and 150 mesh. Clean Arabica coffee skin powder stored in an oven 80 oC for 24 hours then stored in a desiccator before weighing.

Making Ni (II) 100 mg / L

Raw Solution For the manufacture of a standard solution of Ni (II) 1000 mg / L carried out by means of Ni (NO₃) 2.6H₂O weighed as much as 4.9564 grams, then dissolved with aquabides to volume 1 L. Furthermore, the standard solution of Ni (II) 1000 mg / L was pipetted 100 mL and diluted to volume 1 L to make a standard solution of 100 mg / L.

Determination of the effect of particle size on biosorption of Ni (II) ions by the skin of Arabica coffee (*Coffea arabica*)

Arabica coffee fruit skin powder with variations in size of 60 mesh, 80 mesh, 120 and 150 mesh inserted as much as 0.2 grams into 4 erlenmeyer pieces of size 100 mL, then inserted 50 mL of Ni (II) with a concentration of 100 mg / L at pH 5.1. The mixture is stirred for 10 minutes then filtered and the filtrate is collected to measure the levels of Ni (II) with AAS. The levels of Ni (II) in Ni (II) solution before adsorption were also measured. Each experiment is conducted in duplicate. The blank experiment is carried out as above.

Determination of Optimum time Biosorption of Ni (II) Ions by Arabica Coffee Fruit Skin (*Coffea arabica*)

Clean and dry Arabica coffee bark powder is 0.2 grams each into 10 100 mL Erlenmeyer flasks and 50 mL of Ni (II) solution with a concentration of 100 mg / L and be shaken using a magnetic stirrer for 10, 15, 20, 30, 40, 50, 60, 70, 80, and 90 minutes. Then the mixture is filtered and the filtrate is collected to measure the nickel content (Ni²⁺) with SSA. Each experiment was repeated two times. The blank experiment is carried out as above but without stirring. The optimum time is where the concentration of adsorption (Cadsorption) is greatest.

Determination of Optimum pH Biosorption of Ni (II) Ion by Arabica Coffee Fruit (*Coffea arabica*)

0.2 grams of Arabica (*Coffea arabica*) coffee powder is added to 50 mL of Ni (II) metal ions with a concentration of 100 mg / L at pH 2. The mixture is shaken during the optimum time and filtered. The filtrate absorbance

was measured by AAS. The experiment was repeated with different pHs of 3, 4, 5, 6 and 7. The blank experiments were carried out as above but without agitation. The optimum pH is pH where the greatest adsorbed concentration (Cadsorption).

Determination of Biosorption Capacity of Ni (II) Ions by Arabica Coffee Fruit Skin (*Coffea arabica*)

Clean and dry Arabica coffee peel powder is 0.2 grams each into 6 Erlenmeyer sizes of 100 mL, then 50 mL of a solution of Ni (II) metal ions with a concentration of 50, 100, 150, respectively. 200, 250 and 300 mg / L. The mixture is shaken during the optimum time and pH, then filtered and the filtrate is collected to measure the nickel content (Ni²⁺) with AAS. The levels of Ni (II) in Ni (II) solution before adsorption were also measured. Done in duplicate. The blank experiment is done as above but without shuffling.

FT-IR Analysis

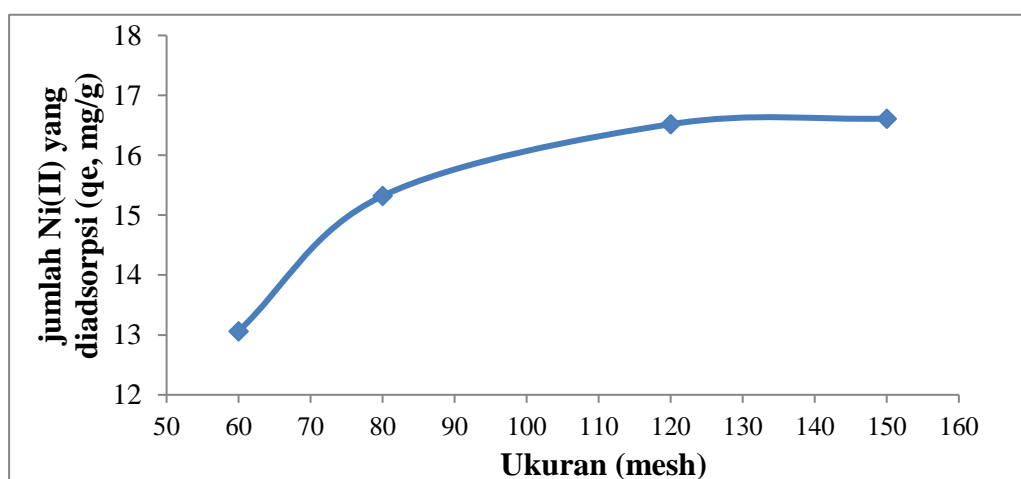


Figure 1. Effect of particle size on the amount of Ni (II) ions adsorbed by the skin of Arabica coffee fruit.

Furthermore, the coffee skin biosorption capacity at 150 mesh absorption was 16.61 mg/g. Testing on small coffee fruit

Biosorbent of Arabica coffee fruit skin before and after adding with Ni (II) solution concentration of 100 mg / L with optimum pH and time and dried at 50 oC then analyzed with FT-IR (Fourier Transform Infra Red). The sample is smoothed with KBr in mortar using a mass ratio of 1:10. The results of the mixture are put into a special spherical place and then mixed to release water. The mixture is pressed for a moment (10 minutes) at a pressure of 72 Torr (8 to 20 tons per unit area) to produce thin circles. Readings of IR data spectra using the Grams Research software.

RESULTS AND DISCUSSION

Effect of Particle Size on the Ni (II) Ion Biosorption by Arabica Coffee Fruit (*Coffea arabica*)

Figure 1 shows that the number of Ni (II) metal ions absorbed by 60 mesh particle size is 13.06 mg / g. This number continues to increase along with the smaller particle size given. At 120 mesh particle size the number of Ni (II) ions adsorbed was 16.51mg / g.

skin particle size causes high absorption of Ni metal. This happens because the smaller the size of the coffee fruit skin

particles, the more dissolved material is filtered, so that the anion and cation content reacts more quickly with the metals contained in the adsorbent (Nurhayati, 2011 in Wibowo, A and Ardian, P., 2013)

The smaller the diameter size of the adsorbent, the greater the reduction in the level of Ni (II). This is because the smaller the diameter size of the adsorbent means the contact surface area between the adsorbent and the Ni (II) metal ion is greater. In addition, the surface area is also directly proportional to the number of pores that are owned per

Based on Figure 2 it can be seen that the amount of Ni (II) ions adsorbed at minute 10 is 14.53 mg / g. This amount continues to increase until it reaches the optimum limit with the amount of ion adsorbed at 16.12 mg / g in the 50th minute. The adsorption ability of Ni (II) metal drops to near the saturation point after passing 50 minutes. This condition is in accordance with the theory that the longer the contact time between the

unit of particle adsorbent (Aji, et al, 2012).

Based on the amount of absorption effectiveness which shows the absorption percentage for size 120 with 150 which the percentage difference is very small. Further research used 120 mesh particle size with a capacity of 16.51 mg / g, in addition to facilitating the screening process to avoid aggregation events.

Effect of Optimum Biosorption Time of Ni (II) Ion by Arabica Coffee Fruit (Coffea arabica)

adsorbent and the solute, the more dissolved substances will be adsorbed. However, the amount of adsorbed solute will reach the optimum limit at a certain time. This shows that the active side of the surface of the coffee fruit skin is saturated. The decrease in adsorption capacity after the optimum time can also be caused by the desorption process which shows reversible adsorption (Ekmekyapar, et al, 2006).

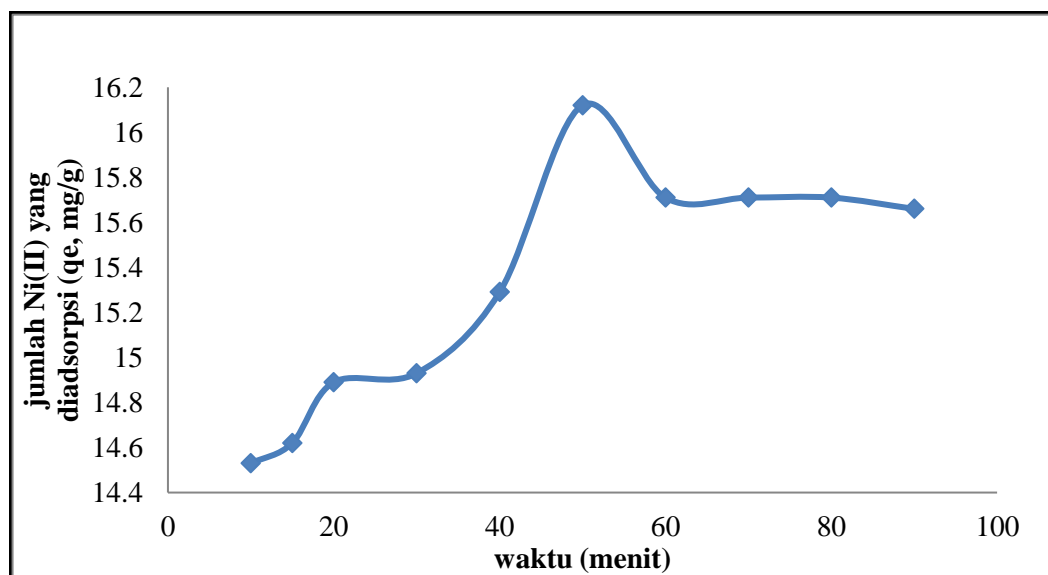


Figure 2. Effect of contact time on the adsorption capacity of Ni²⁺ ions by the adsorbent of Arabica Coffee fruit skin.

The same was reported by Effendi (2015) who used activated rice husk charcoal to adsorb Ni (II) and Pb

(II) metals. Where the optimum contact time at 50 minutes Amaliah et al. (2012) in the study of coral utilization as

biosorbent, Ni (II) metal ions obtained an optimum time of 90 minutes. Krishna and Swamy (2011) in the Ni (II) metal adsorption study using papaya seeds obtained contact time of 90 minutes. Abbasi, et al. (2013) obtained optimum contact time of 30 minutes in the study of absorption of Co^{2+} and Ni^{2+} metals from waters using banana peels. The optimum contact time for Ni (II) biosorption of metals in several studies

showed different results, depending on the type of biosorbent

Effect of pH on the absorption of Ni (II) ions by Arabica coffee fruit skin (*Coffea arabica*)

Determination of optimum pH was carried out to determine the pH of the interaction where biosorbent absorbed Ni (II) to the maximum

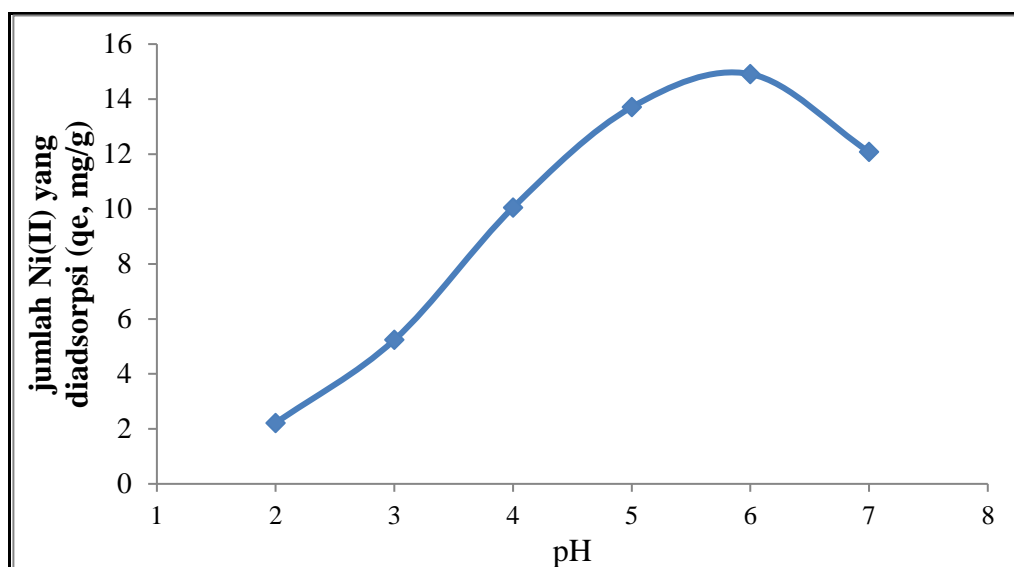


Figure 3. Effect of pH on the adsorption capacity of Ni^{2+} ions by the adsorbent of Arabica Coffee fruit skin.

Figure 3 shows that at a low pH the amount of Ni (II) ions adsorbed by coffee fruit peels is very small at 2.21 mg / g. This is because at low pH H^{+} ions compete with Ni^{2+} metal cations to bind to active groups on the adsorbent (Ahmad et al., 2009). This amount continues to increase until it reaches the optimum limit with the amount of adsorbed ion amounting to 14.91 mg / g at pH 6. The increase in this increase is due to the greater pH, the active groups of adsorbents are deprotonated and have a negative charge ie OH^{-} ion which is very reactive to metals so that the adsorbed metal gets bigger. At pH 7 the concentration of adsorbed Ni decreases. This is probably due to the

fact that there is an equilibrium in the active site of the biomass with metal ions and this condition is probably due to sedimentation. Ni (II) ions form deposits with OH^{-} ions in the form of $\text{Ni}(\text{OH})_2$ bonds. As a result of this precipitation, the Ni (II) ions present in the solution are reduced so that the amount adsorbed also decreases. The same was reported by Amaliah, in a study of coral utilization as biosorbent of metal ion Ni (II) with maximum adsorption capacity at pH 6. The use of activated charcoal from coffee bean skin to adsorb dyes Methylene blue was also optimal at pH 6 and Naphthol yellow optimal at pH 2 (Purnomo, 2010). Mildayati (2009) reported the optimum biosorption of Ni

(II) metal at pH 5 using sago pulp. Malimongan (2015) reported the use of cocoa peel as biosorbent of Ni (II) metal ions with optimum adsorption capacity at pH 5. This is in accordance with that reported by Shofiyani and Gusrizal (2006) that the adsorption of Ni (II) occurs optimally in a wide range of acidic media which is at pH 5-9.

Because the amount of Ni (II) ions adsorbed by the skin of Arabica (*Coffea arabica*) coffee fruit is maximum at pH 6, further research to determine the adsorption capacity is carried out at that pH.

Adsorption Capacity of Ni (II) Ions by Arabica Coffee Fruit Skin (*Coffea arabica*).

The picture above shows that the higher the concentration, the greater the number of Ni (II) ions adsorbed by the coffee fruit peels and then tends to remain caused by biosorbents which have experienced saturation. This is as reported by Amini (2008) and Dilek (2001), which states that the number of metal ions adsorbed by biosorbents will increase with increasing concentration of a solution as long as the bond side is not.

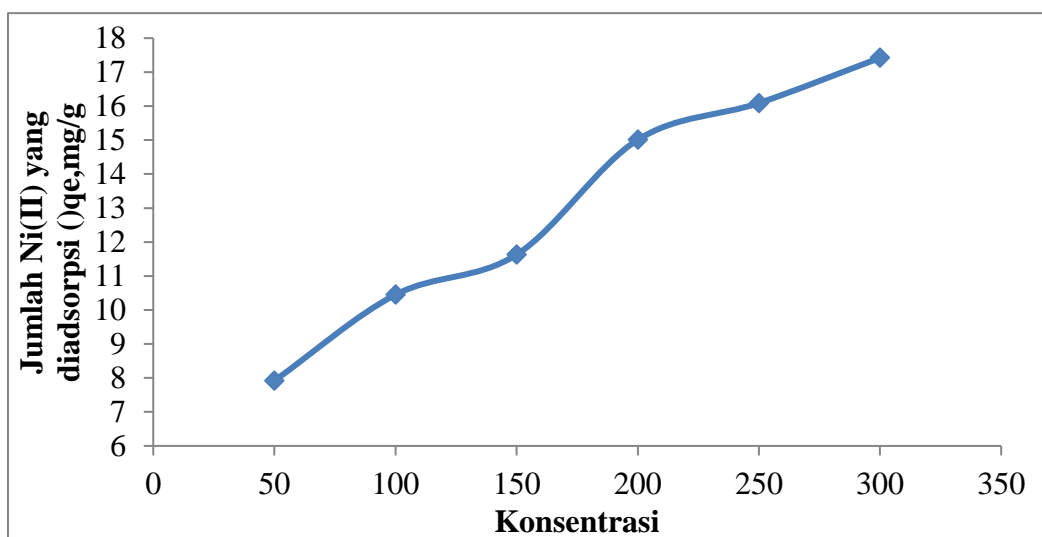


Figure 4. Number of Ni (II) ions adsorbed as a function of concentration at 50 minutes and pH 6.

To determine the biosorption capacity of Ni (II) ions by the skin of Arabica Coffee (*Coffea arabica*) fruit,

the Langmuir equation and the Freundlich equation were used. The

results can be seen in Figure 5 and Figure 6.

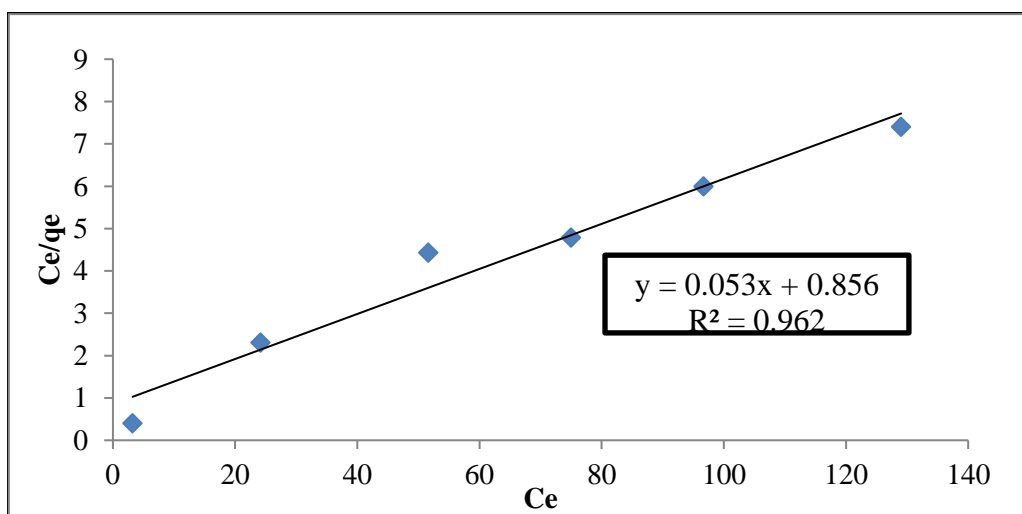


Figure 5. Langmuir isotherm for biosorption of Ni (II) ions by the fruit bark of arabica coffee (*Coffea arabica*).

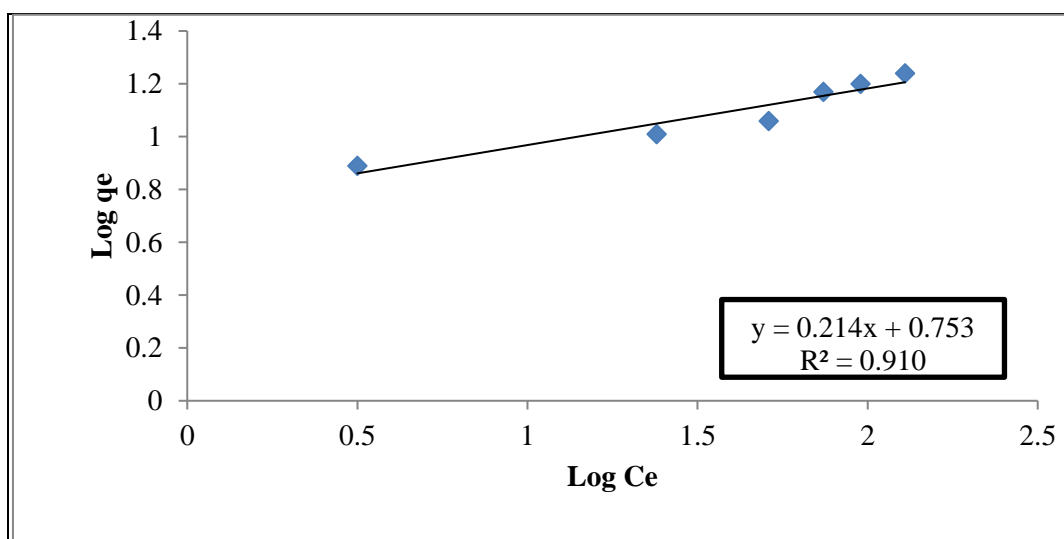


Figure 6. Isothermal Freundlich for ion Ni(II) biosorption by coffe fruit skin arabika (*Coffea arabica*)

The appropriate adsorption isothermal model can be seen by comparing the least squares value. Figures 5 and 6 show that the adsorption of Ni (II) ions by the skin of arabica (*Coffea arabica*) coffee is more in accordance with the isothermal langmuir. This can be seen from the correlation coefficient R² with the largest value (close to 1), which is 0.962

while the isothermal Freundlich adsorption is R² by 0.910. Intercept and isothermal slope from Langmuir adsorption gave a value of biosorption capacity (Q₀) of 18.86 mg / g or 0.31 mmol / g and b (biosorption intensity) of 0.061 L / mg.

Langmuir isotherm assumes that the active sites found on the surface of the adsorbent are homogeneous where

the site is active and the energy that occurs is the same, the interaction between the adsorbent and adsorbate occurs in the first layer or called monolayer on the adsorbent surface so that a strong bond between sites occurs. active with Ni(II)

According to Kojima and Lee (2001) in Pravasant et al (2005), different adsorbents provide different adsorption characteristics. Therefore, the suitability of isothermal adsorption depends on the biosorbent used.

Determination of Function Groups Involved in Biosorption of Ni (II) Metal Ions by Arabica Coffee Fruit Skin (Coffea arabica)

Determination of functional groups that play an active role in the skin of arabica coffee (Coffea arabica) is determined using FTIR. Coffee fruit skin powder before and after adsorption was analyzed using FTIR. The interaction between Ni (II) ions and the skin of Arabica coffee (Coffea arabica) can be seen in the spectrum of IR spectroscopy readings.

According to Pavasant, et al (2005), in comparing between samples before and after adsorption, it can be seen from the shift that is > 10 cm⁻¹. This shift shows the existence of a metal binding process on the surface of the sample used. Figure 7 shows the FTIR spectrum of Arabica coffee fruit peel before and after adsorption

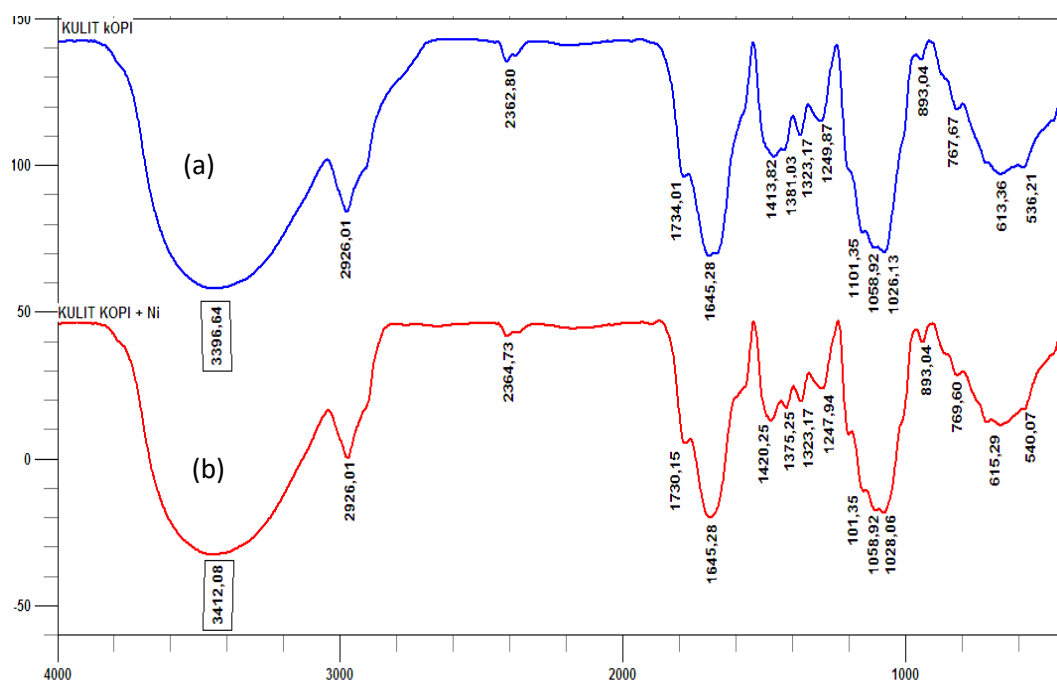


Figure 7. Spectrum of Analysis Results of FT-IR Skin Biosorbents of Arabica (Coffea arabica) Coffee Fruit (a) Before Contact with Ni (II) and (b) Ions After Contact with Ni (II) Metals

Both the FTIR spectrum images above do not show a significant difference. Characterization data of adsorbent of

coffee fruit skin before and after adsorption can be shown in Table 1.

Table 1 Characterization of FT-IR spectra on Arabica Coffee fruit skin adsorbent before and after adsorption (Zahroh, 2010)

IR Peak	Adsorption Peak (cm-1)		Functional Groups
	Before adsorption	After Adsorption	
1	3396,64	3412,08	-OH group bond
2	2926,01	2926,01	-CH Vibration
3	1734,01	1730,15	C=O
4	1413,82	1420,25	CH ₂ bend
5	1381,03	1375,25	C-H
6	1249,87	1247,94	C-O stretch
7	767,67	769,60	O-H bend
8	536,21	540,07	C-C stretch

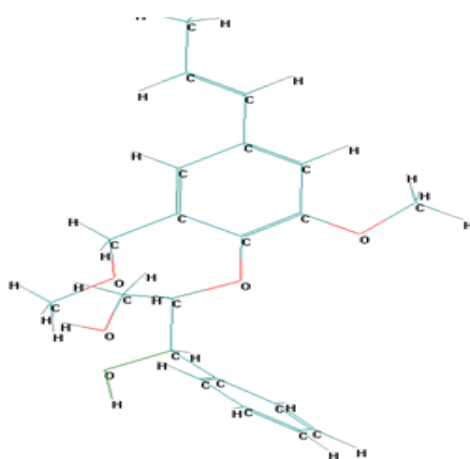
In FTIR spectra of coffee fruit skin biomass after being interacted with Ni (II) as in Figure 7 (b), it can be seen that some absorption experiences a shift in wave numbers. This can be seen in the shift of wave numbers from 3396.64 cm-1 and 1413, 82 cm-1. The absorption experiences a difference in the shift of a larger wave number than the other absorption.

The shift of wave number from 3396.64 cm-1 to 3412.08 cm-1 (stretch-OH). This shows the interaction of Ni (II) ions with the hydroxyl (-OH) functional groups found in the skin of Arabica coffee fruit. The wave number in the area of 2926 cm -1 indicates the presence of -CH vibrations of the alkyl group of cellulose. Wave number 1413

cm-1 shows the formation of CH₂ in the cellulose monomer structure. It was also strengthened by changes in the formation of the CH group at wave number 1381.03 cm-1.

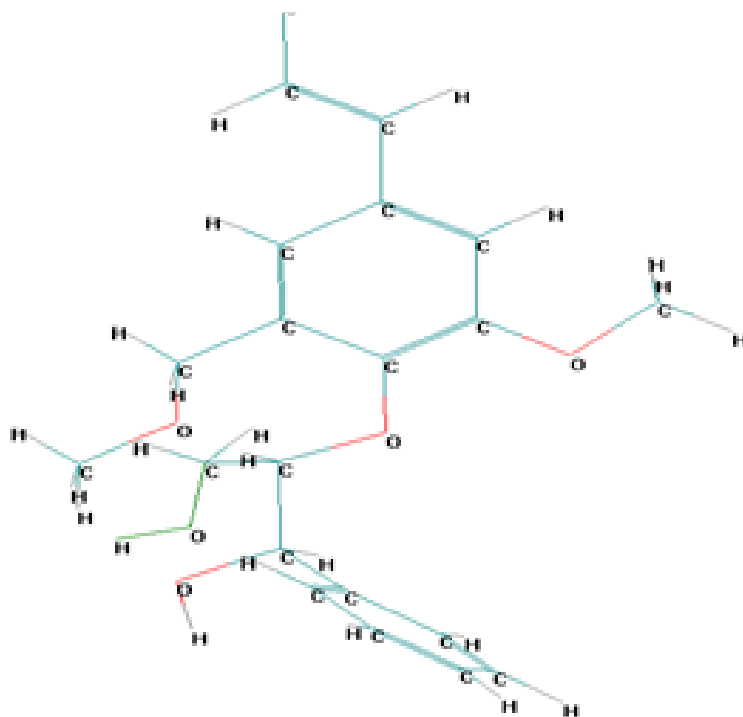
To form a complex, the empty orbitals in 4s² undergo hybridization providing 4 orbitals namely 4s and 4p, then filled with 4 electron pairs derived from the hydroxyl group (-OH) as ligands that occupy a 3d orbital, one in 4s orbitals and two 4p orbitals .

Based on Figure 7, the peak FTIR (-OH) spectrum is not lost but only shifts, it can be concluded that the bond that occurs is a coordination covalent bond. Then shifting the wave number becomes larger, indicating the stronger the bond that occurs (Tannasal, 2015).



Total Energy = 74,029 kkal/mol

Figure 8. The –OH hydroxyl group which is not blocked by the steric effect



Total Energy= 104.602 kkal/mol

Figure 9. Hydroxyl –OH group which is blocked by the steric effect

Looking at the FT-IR results in Figure 7, it is estimated that there is a bond between the hydroxyl (-OH) functional groups derived from lignin and cellulose with Ni (II) ions due to the presence of hydroxyl (-OH) groups on cellulose and lignin which are not blocked by the effect while the steric on the hydroxyl group pectin is blocked by the presence of steric effects and also the group (-OH) in the pectin derived from

the group (-COOH), oxygen in the group (-OH) and in the group (-CO) has the same ability to attract electrons due to the conjugate effect so the possibility of shifting is the group (-CO) (Tannasal, 2015). The -OH group without steric can be seen in Figure 8 and the steric obstacle in the -OH group can be seen in Figure 9. The estimated form of interaction produced can be seen in Figure 10

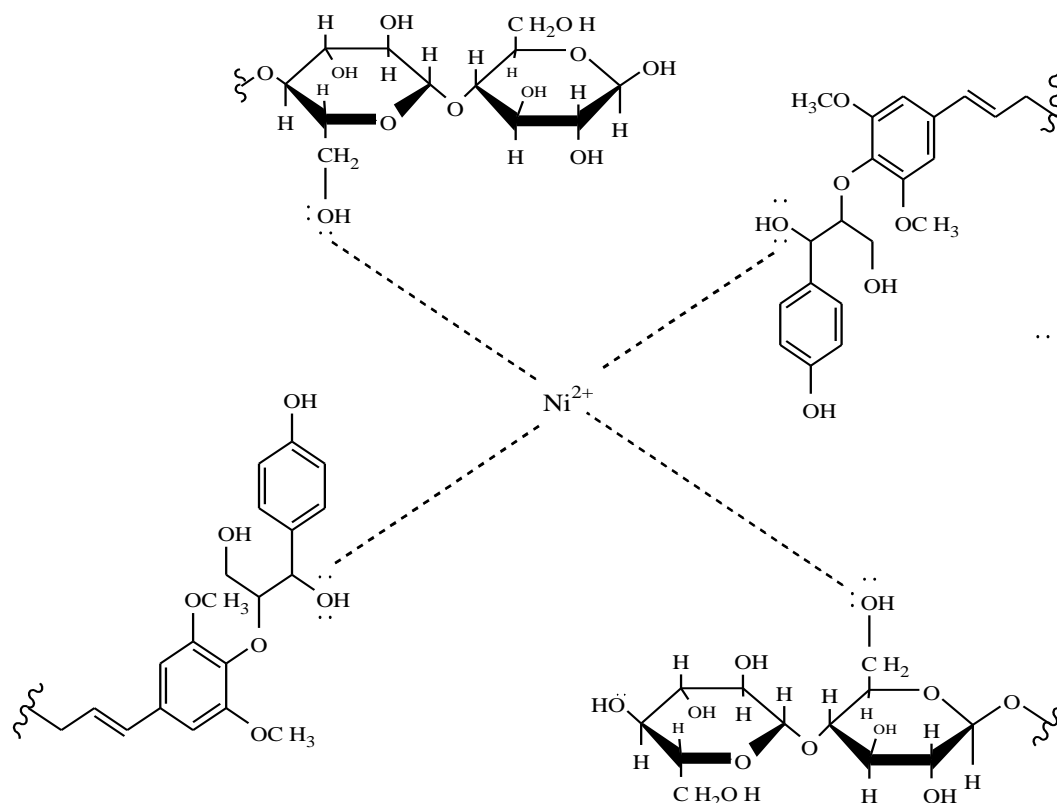


Figure 10. Form of Interaction between Ni (II) ion and Lignin and cellulose (this reaction is adopted from the reaction form between metal Cd (II) and Red Meranti Wood (La Nafie dkk.,2012).

CONCLUSION

Adsorption of Ni (II) ions with optimum Arabica (*Coffea arabica*) coffee peel powder at 120 mesh with optimum time of 50 minutes and optimum pH 6. Biosorption of Ni (II) ions by Arabica coffee fruit shells fulfills Langmuir isotherm with a Q_0 value of 18, 86 mg / g or 0.31 mmol / g. The functional group involved in biosorption of Ni (II) ions by the skin of Arabica coffee fruit, namely the hydroxyl group (-OH).

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