UTILIZATION OF CACAO FRUIT PEEL (*Theobroma cacao*)
AS A BIOSORBENT OF Ni(II) IONS METAL

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**Abstract.** Nickel is one of the heavy metals which is very dangerous because it is carcinogenic and can cause a variety of acute and chronic diseases. Biosorption is one alternative method for the removal of heavy metals from the environment using a biomaterial called biosorbent. Biosorption of Ni(II) ion using cacao fruit peel (*Theobroma cacao*) with variation of contact time, pH and concentration has been investigated. The concentration of Ni(II) ion before and after adsorption was determined by Atomic Absorption Spectrophotometer (AAS). The result showed that cacao fruit peel (*Theobroma cacao*) was able to adsorb Ni(II) ion and the optimum biosorption occured at a contact time of 10 minutes and at a pH of 5. Langmuir and Freundlich isotherm models were used to study the adsorption isotherm. Biosorption of Ni(II) ion by cacao fruit peel (*Theobroma cacao*) fulfilled the Langmuir isotherm with a biosorption capacity of 0.21 mmol/g. The functional groups involved in the biosorption of Ni(II) ion by cacao fruit peel (*Theobroma cacao*) are –OH and N-H.

Key Words: biosorption; adsorption isothermal; Ni(II); cacao fruit peel; AAS.

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INTRODUCTION
This encourages the development of mature technology of rapid development in the sector, industry, transport, households, and even health. Advances in technology could have a negative impact in the form of environmental damage caused by heavy metal waste disposal without first processing (Kusuma, 2014). Heavy metals can not be decomposed by microorganisms and can accumulate in the human body and cause damage to organs (Sembodo, 2006).

One of the heavy metals which are environmental pollutants coming from industrial activities are Nickel (Ni) (Aslam et al., 2010). If the concentration of Ni (II) is above the quality standards which when positioned above 0.05 ppm, a variety of acute and chronic diseases can arise in humans such as lung damage and disorders of the kidneys (Borba, et al., 2006). Nickel is carcinogenic and can cause asthma and skin allergies (Aslam et al., 2010).

Several technologies have been developed to remove heavy metals in waters such as precipitation, filtration membranes, ion exchange, and coprecipitation. However, these methods have several shortcomings such as metal removal imperfect, expensive equipment, as well as losses caused by the production of a toxic chemical sludge and sewage treatment becomes unsustainable (Isnaini et al., 2013). Biosorption an alternative method to remove heavy metals from the water because it uses materials easily available biomaterial and the cost is relatively low (Alluri et al., 2007).

Some of biomaterial that is potentially as absorbent of heavy metals is generally derived from agricultural waste. According Sulistyawati 2008, corn cobs contain cellulose which can be used as adsorbents of heavy metals Pb (II). Pectin from citrus fruit peels can be used as adsorbent copper metal ion (Ina et al., 2013). Jengkol skin can be used as absorbent metal ions Cd (II) and Zn (II) (Isnaini et al., 2013). Mangrove bark is used as an absorber ion Cu (II) and Ni (II) (Rozaini et al., 2010). Activated charcoal leather brown fruit (Theobroma cacao l.) Serves as an adsorbent of heavy metals Cd (II) in the solvent water (Masitoh and Sianita, 2013). The results of these studies indicate that agricultural wastes containing functional groups can be further processed as an adsorbent that can be used to absorb heavy metals from waters. Cacao (Theobroma cacao) is one crop that produces waste in the form of skin with large amounts. So far fruit peel in large plantations used as fertilizer or giving nutrients to the plant and as fodder. Cacao fruit peel weighing up to 75% of the entire weight of the fruit, so it can be said that the main waste processing cacao fruit peel. Cacao fruit peel (Theobroma cacao) containing cellulose, pectin, and lignin potentially bind heavy metals such as nickel metal from solution.

Based on the previous description of this study is to study the cacao fruit peel (Theobroma cacao) in a bind Ni (II) and determination of functional groups involved in the biosorption process using transform Fourier infrared (FTIR).

MATERIALS AND METHODS
Materials
The materials used in these experiments are cacao fruit peel (Theobroma cacao), Ni (NO₃)₂.6H₂O EMSURE (Merck), NaOH, HNO₃,
distilled water, Whatman 42 filter paper, and paper labels.

**Apparatus**

The apparatus used in this study are glass apparatus commonly used in the laboratory, Atomic Absorption Spectrophotometer (AAS) buck scientific VGP 205 models, Ohaus balance NO AP210 models, Crusher, oven, magnetic stirrer Velp scientica, sieve size 90-100 mesh, stopwatch, desiccator, angular 6 selecta centrifuges, pH meter WTW 315i and FT-IR spectrophotometer Shimadzu prestige 21.

**Experimental Procedures**

**Preparation of the biosorbent Cacao Fruit Peel (Theobroma cacao)**

Cacao fruit peel (Theobroma cacao) was obtained from one of the gardens in Tana Toraja. Cacao fruit peel (Theobroma cacao) which has taken further cut into small pieces and washed up with distilled water for several times to remove dirt particles. Cacao fruit peel was then dried in the sun to dry. The clean and dried cacao fruit peel (Theobroma cacao) is put at 80 °C for 24 hours in oven and then stored in a desiccator. The dried cacao fruit peel (Theobroma cacao) is then crushed and sieved using a 100 mesh sieve.

**Preparation Stock Ni(II) solution**

The stock Ni(II) Solution (1000 ppm) were prepared by dissolving 4.9564 g of Ni(NO₃)₂.6H₂O in HNO₃ and double distilled water up to a volume of 1 L. Furthermore, the stock solution of Ni (II) 1000 ppm was pipette 100 mL and diluted to a volume of 1 L to create a standard solution of 100 ppm.

**Determination of Optimum Time for the Biosorption of Ni (II) Ions by Cacao Fruit Peel (Theobroma cacao)**

The Powder of the clean and dried cacao fruit peel (Theobroma cacao) each 0.2 g put into 11 pieces 100 ml Erlenmeyer flask and added 50 mL of Ni (II) ions solution with a concentration of 100 ppm and whipped by using a magnetic stirrer for 5,10, 15, 20, 30, 40, 50 and 60 minutes. Then the mixture is filtered using Whatman 42 filter paper and the absorbance of filtrate analyzed using AAS. All experiments were carried out in duplicate.

**Determination of Optimum pH for the biosorption of Ni(II) Ions by Cacao Fruit peel (Theobroma cacao)**

The powder of cacao fruit peel (Theobroma cacao) 0.2 g added to 50 mL of Ni (II) ions solution with a concentration of 100 ppm and at a pH of 2. The mixture was stirred for 10 minutes and filtered using whatman 42 filter paper. Absorbance of filtrate analyzed by AAS. The experiment was repeated with each of the different pH 3, 4, 5, 6, and 7. All experiments were carried out in duplicate. The optimum pH is pH where the concentration of adsorbed the largest.

**Determination of the biosorption capacity of Ni (II) Ions by Cacao Fruit Peel (Theobroma cacao)**

The powder of cacao fruit peel (Theobroma cacao) 0.2 g was put into 6 pieces 100 mL erlenmeyer, then added 50 mL of Ni (II) ions solution with a initial concentration was varied from 50, 100, 150, 250, and 400 ppm. The mixture is stirred for 10 minutes and at a pH of 5, then filtered using Whatman 42 filter paper and the absorbance of filtrate analyzed using AAS All experiments were carried out in duplicate.
Biosorption capacity was calculated using the equation Freunlich or using the Langmuir equation.

FT-IR analysis

Biosorbent of cacao fruit peel (Theobroma cacao) before and after being added with a solution of Ni (II) with a pH and a optimum time and dried at a temperature of 80 °C and then analyzed by FT-IR (Fourier Transform Infra Red) Prestige-21 in the region 4500-340 cm⁻¹ with a resolution of 1 cm⁻¹ at room temperature using DTGS detector (deuterated triglycine sulphate). The sample was crushed with KBr with a mass ratio of 1:10. The mixture was compressed for 10 minutes at a pressure of 72 Torr (8 to 20 tons per unit area) to form a pellet.

Results and Discussion

Determination of Optimum Time for the Biosorption of Ni(II) Ions by Cacao Fruit Peel (Theobroma cacao)

The optimum time biosorption Ni(II) ions by a cacao fruit peel (Theobroma cacao) is determined by calculated the number of Ni(II) ions adsorbed as a function of time. Charts the relationship between the contact time with the number of Ni(II) ions adsorbed by the powder of cacao fruit peel (Theobroma cacao) is shown in Figure 1.

Total of Ni(II) ions adsorbed increases from the 5 min to 10 min and become constant even dropped after that. So while, maximum biosorption occur in 10 min which total adsorbed of Ni (II) ions as much as 7.86 mg/g. The optimum time is used for further experimental.

The results showed that the adsorption of Ni(II) ions by cacao fruit (Theobroma cacao) increased with the length of time that contact occurs between the adsorbent with adsorbat but at a certain time (optimum time) the total of Ni(II) ions which has adsorbed so that the maximum number of ions Ni(II) are adsorbed not increased. The optimum time biosorption Ni(II) ions in several other studies have shown different results, depending on the type biosorbent used.

The optimum time obtained in the study biosorption Ni (II) and Cd (II) ions using rice straw by El-Sayed et al., (2010) is 90 minutes for ion Ni (II). Amaliah et al., (2012) in the study of coral biomass utilization as biosorbent Ni(II) ion also obtain the optimum time of 90 minutes. While the optimum time in the study of adsorption of Ni (II) using palm shell activated carbon by Onundi et al., (2010) is 75 minutes. The optimum time differences of biosorption process depends on compounds contained in biosorbent surface. According to Setiawan et al (2013), the optimum time is the time to reach equilibrium, when biosorbent have functional groups on the metal ion binding to the fullest and after equilibrium is reached bond between the active groups on the surface of the metal ions biosorbent and weakened so that the desorption process occurs. The interactions between of the functional groups on the surface of the biosorbent of cacao fruit peel and the Ni(II) ions reaches equilibrium at 10 minutes and after equilibrium is reached the adsorbed of Ni(II) ions was dropped because the bond between of the Ni(II) ions and functional groups on the surface biosorbent weakened and eventually escape back into solution. The time required is relatively fast because the ion Ni (II) adsorbed chemically to form a layer on the surface biosorbent and after
coating the surface is covered then no longer able to adsorp of the Ni(II) ions to the maximum.

Figure 1. The relationship between of the contact time and the total adsorbed of Ni(II) ions (qe) by cacao fruit peel (pH = 5.1 and C₀ = 100 ppm)

**Determination of Optimum pH for the biosorption of Ni(II) Ions by Cacao Fruit peel (Theobroma cacao)**

pH is one of the important factors governing biosorption of metal ions without time. Effect of pH change in the biosorption of Ni(II) ion by cacao fruit peel is shown in Figure 2.

Figure 2 shows that the total of Ni(II) ions adsorbed is low at low pH values, and increased with increasing pH of the solution up to obtained the optimum pH at pH of 5 which the total adsorbed of Ni(II) ions is 5.53 mg/g.

The influence of pH can be related with the fact that in an acid environment competition between metals and H⁺ ions that cause the binding of metal ions is reduced. With increasing pH, electrostatic repulsion decreases due to reduction of positive charge density on the sorption sites thus resulting in an enhancement of metal adsorption (Amaliah et al., 2012). Total adsorbed of Ni(II) ion decreased at pH 6-7 because the soluble hydroxyl complexes of Nickel ions is formed (Ahmad et al., 2009). Nickel which are not in the form of ionic is difficult bind to the active groups on the surface of the biosorbent consequently the amount of Ni(II) ions adsorbed is likely to be decreased. The optimum (pH 5) is used to determine of the capacity biosorption.
Figure 2. The relationship between the pH and the total adsorbed of Ni(II) ions (qe) by cacao fruit peel (contact time = 10 min and $C_0 = 100$ ppm)

**Determination of the biosorption capacity of Ni (II) Ions by Cacao Fruit Peel (*Theobroma cacao*)**

Total adsorbed (qe) of Ni(II) ion as a function of concentration is determined to calculate the biosorption capacity. Biosorption capacity is determined by the concentration of the metal ions solution. Effect of the concentration from the Ni(II) ions in the biosorption process is shown in Figure 3. Graph of relations between $q_e$ and $C_e$ in Figure 3 shows that the total adsorbed of Ni(II) ions increases with increasing concentration of the adsorbate.

Figure 3. The relationship between of the total adsorbed of Ni(II) ions (qe) by cacao fruit peel with concentration ($C_e$) at the equilibrium (contact time = 10 minutes and pH = 5)

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Figure 3 shows that the saturation of the adsorbent has not happened so Langmuir equation and Freundlich equation were used to determine of the capacity biosorption of Ni(II) ions by cacao fruit peel (Theobroma cacao). The result is shown in Figures 4 and 5.

Figure 4. Langmuir isotherm using cacao fruit peel (Theobroma cacao)

Figure 5. Freundlich isotherm using cacao fruit peel (Theobroma cacao)

Figures 4 and 5 show that the Langmuir isotherm is better obeyed than (Theobroma cacao), as is evident from the values of R² obtained for Langmuir the Freundlich isotherm by the adsorption isothermal is 0.997 and for the Freundlich isotherm is 0.913.
Biosorption parameters of Ni(II) ions by cacao fruit peel (*Theobroma cacao*) which calculated using the Langmuir isothermal and isothermal Freunlich are shown in Table 1.

**Table 1.** Parameters of Ni(II) ions by cacao fruit peel (*Theobroma cacao*)

<table>
<thead>
<tr>
<th>Langmuir Model</th>
<th>Freunlich Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q₀ (mmol/g)</td>
<td>b (L/mg)</td>
</tr>
<tr>
<td>0.21</td>
<td>0.03</td>
</tr>
<tr>
<td>R²</td>
<td></td>
</tr>
<tr>
<td>0.997</td>
<td></td>
</tr>
<tr>
<td>K (mmol/g)</td>
<td>n</td>
</tr>
<tr>
<td>0.05</td>
<td>4.03</td>
</tr>
<tr>
<td>R²</td>
<td></td>
</tr>
<tr>
<td>0.913</td>
<td></td>
</tr>
</tbody>
</table>

The higher value of regression coefficient (R²) of Langmuir isothermal is indicates the metal ion biosorption process has scope single layer (monolayer) on the cacao fruit peel (*Theobroma cacao*). In other words, the biosorption of Ni(II) occurs with the functional groups on the surface of the cacao fruit peel (*Theobroma cacao*) which is considered as monolayer adsorption. Different biosorbent can give different adsorption characteristics, so that the suitability of the adsorption isotherm is very dependent on the type of biosorbent used.

**Determination of the Functional Groups Involved in Biosorption of Ni(II) Ion by Cacao Fruit peel (*Theobroma cacao*)**

The powder of cacao fruit peel before adsorption and after adsorption were analyzed using FTIR. Interaction between of the Ni(II) ion with a cacao fruit peel (*Theobroma cacao*) is shown on the spectrum of IR spectroscopy. Figure 6 shows the FTIR spectra of cacao fruit peel (*Theobroma cacao*) before and after adsorption. Several peaks appearing before the adsorption, such as the wave number 3402.43 cm⁻¹ was assigned of -OH group. -OH group supported by CO group from alcohol at the band of 1253.73 cm⁻¹. The band at 1614.42 cm⁻¹ is assigned the NH group from amine, this group is estimated to come from protein of the cacao fruit peel which amplified by the band at 1737.86 cm⁻¹ which is assigned the C = O (peptide bond). After adsorption occurred some shift wave number. This band at 3402.43 cm⁻¹ was shifted to 3419.79 cm⁻¹, which indicated an interaction between the –OH group of the cacao fruit peel biosorbent with the Ni(II) ions. This band at 1614.42 cm⁻¹ shifted to 1625.99 cm⁻¹ which indicate the interaction of the NH group from biosorbent with the Ni(II) ions. This proves that the Ni(II) ion bound to the functional -OH and NH groups. The shift also occurs in the band at 526.57 cm⁻¹ to 514.99 cm⁻¹ assigned to Ni-O bond. And the shifted of the band at 366.48 cm⁻¹ to 376.12 cm⁻¹ assigned to Ni-N bond. It is appropriate of literature that the vibration of metal Ni with O group from the ligand will appear at 600-400 cm⁻¹, and vibration of Ni metal bond with group N from the ligand will appear at 300-390 cm⁻¹ (Triyani et al., 2013).
Figure 6. Infrared spectra of cacao fruit peel (*Theobroma cacao*) before biosorption and after biosorption

Based on the shifted of wave number, it is predicted that the interaction between Ni(II) with a hydroxyl group (OH) of lignin and cellulose and Ni(II) with the NH group of the protein. Forms of possible interactions between Ni(II) with lignin, cellulose, and protein is shown in Figures 7, and 8.

Figure 7. Forms of interaction between Ni(II) with lignin and cellulose
Conclusion

From the results of the present study, it is be concluded that the optimum time biosorption of Ni(II) ion by cacao fruit peel (Theobroma cacao) is 10 minutes. The optimum pH of biosorption Ni(II) ions by cacao fruit peel (Theobroma cacao) is pH 5. Biosorption of Ni(II) ion by cacao fruit peel (Theobroma cacao) fulfilled the Langmuir isotherm with a biosorption capacity of 0.21 mmol/g. The functional groups involved in the biosorption of Ni(II) ion by cacao fruit peel (Theobroma cacao) are –OH and N-H.

References


Figure 8. Forms of interaction between Ni(II) with protein


