BIOSORPTION OF Cu (II) METAL IONS BY DRAGON FRUIT SKIN (*Hylocereus polyrhizus*)

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Abstrak. Biosorpsi merupakan metode yang efektif untuk menghilangkan ion logam berat dari suatu larutan. Biosorpsi ion logam Cu(II) dengan menggunakan biosorben kulit buah naga pada variasi waktu kontak, pH dan konsentrasi telah diteliti. Konsentrasi ion Cu(II) sebelum dan setelah adsorpsi ditentukan dengan menggunakan Spektrofotometer Serapan Atom (SSA). Pengaruh pH dalam proses biosorpsi dipelajari pada pH 2-7. Hasil penelitian menunjukkan bahwa waktu optimum biosorpsi ion Cu(II) biomassa kulit buah naga adalah 10 menit dan pH optimum biosorpsi adalah 4. Model Langmuir dan Freundlich digunakan untuk mempelajari isotermal adsorpsi. Dari hasil penelitian ini, diperoleh informasi bahwa biosorpsi ion logam Cu(II) dengan menggunakan kulit buah naga lebih sesuai dengan model isotermal Langmuir dibandingkan isotermal Freundlich dengan kapasitas adsorpsi (Qo) 20,401 mg/g biosorben. Hasil analisis FT-IR menunjukkan bahwa gugus hidroksil yang berperan dalam pengikatan ion Cu(II).

Kata Kunci : Biosorpsi, SSA, Isotermal Langmuir, ion Cu(II), Kulit Buah Naga.

Abstract. Biosorption is an effective method for removal of heavy metals from their solutions. Biosorption of Cu (II) by contact time, pH, and concentration has been investigated. Concentration of Cu (II) ion before and after adsorption was determined using Atomic Absorption Spectrophotometer (AAS). The effect of the pH process was studied at pH of 2-7. The result showed that the optimum time for biosorption of Cu (II) ion by biomass dragon fruit was 10 minutes and pH 4 was the optimum pH of biosorption. Langmuir and Freundlich models were used for the adsorption of isotherm. Result showed that biosorption of Cu (II) by dragon fruit peel fit better the Langmuir model than Freundich model with the adsorption capacity ($Q_{o)}$ of 20.401 mg/g biosorbent. The result of FT-IR analysis showed that hydroxyl groups were responsible for the binding of Cu (II) ions.

Keywords: Biosorption, AAS, Langmuir Isotherm, Ion Cu (II), Dragon Fruit Peel.

INTRODUCTION

Environmental pollution is an increasingly important problem to solve because it involves the safety, health, and life of living things. Among the many problems of environmental pollution at this time that get serious attention is the problem of environmental pollution caused by heavy metals. This pollution can cause large losses, because generally the waste/waste in the environment contains toxic substances, one of which is Cu (Darmono, 2001).

Cu metals in the aquatic environment can be separated in various ways, such as the way of coating, filtering, settling, and flooding of suspended particles. However, this method is considered to be less effective because it requires relatively high costs, high production of toxic waste sludge and can complicate the handling process and disposal. For that absorption method is used by using materials that are relatively inexpensive, can be obtained easily and have high absorption (Zein et al., 2003 in Lelifajri, 2010).

One alternative in processing wastes containing heavy metals is the use of biological materials as adsorbents. This process is then referred to as biosorption. Biosorption shows the ability of biomass to bind heavy metals from the solution through metabolic or chemical and physical steps. The advantages of using the biosorption process include relatively low costs, minimal sludge formation, and easy regeneration processes (Ashraf et al., 2010).

The biosorption process is influenced by contact time, pH and concentration (Kuraisy, 2008). In addition, the finalprocess was biosorptioncarried out by determining the amount of biosorption capacity adsorbed by metal ions using an isothermal adsorption approach. Common isothermal adsorption is used, namely Freundlich isothermal and Langmuir isothermal (Hawari et al., 2006).

Biological materials that can be used as raw materials for biosorbents are waste from agricultural products. Waste of agricultural products is organic waste which is certainly very easy to find in large quantities. The use and use of agricultural waste as raw materials for biosorbents in addition to helping reduce the volume of waste can also empower waste to become a product that has a selling value. Therefore, the potential of agricultural waste is large enough to be used as raw material for biosorbent of heavy metals (Kurniasari, 2010).

Various biosorbents using agricultural or biological materials have been carried out by previous researchers such as biosorption using pineapple leaves (Budiyanto et al., 2010), Bali orange peel (Tasaso, 2014), and sawdust powder (Lelifajri, 2010)

Components which plays a role in the heavy metal adsorption process with adsorbents of biological materials is the active group present in the material. The groups that will attract and bind metals in biomass, groups-groups that include hydroxyl and carboxyl (Ahalya et al., 2003).

One waste that contains many active groups is the dragon fruit skin. From the analysis results show that dragon fruit skin contains nitrogen, carbon, hydrogen, and sulfur (Mallampati, 2013). The compounds contained in dragon fruit peel containgroups -OH and -COOH. The active groups when viewed from HSAB (*Hard Soft Acid Base*) are classified as hard bases while Cu (II) metals are categorized as intermediate acids, so Cu (II) can interact well with the active groups found in dragon fruit skin (Lin et al ., 2002). Namal et al. (2013) have succeeded in conducting research using dragon fruit skin to adsorb Mn (II) ions. This shows that dragon fruit skin has the potential to be used as biosorbent of heavy metal ions (Mallampati, 2013).

Based on the description, the study utilizing dragon fruit skin as biosorbent was carried out for removal of heavy metals Cu^{2+} .

MATERIALS AND METHODS

Materials

The materials used in this study is the dragon fruit leather, crystal $Cu(NO_3)_2.3H_2O$, HNO_3, NaOH, distilled water, akuabides,filter *Whatman* 42paper,label paper, and *tissue roll*.

Equipments

Equipment used in this study were commonly used glassware, sieves (passed 100sieves *mesh* and did not pass 230sieves *mesh*), SPNISOSFD model ovens,stirrers, *magnetic*digital balance *Ohaus* models NO AP210, *crushers*, pH meters , spray bottles, a set ofdevices *centrifuge*, a set of SSA tools, a set of FT-IR spectrophotometer devices SHIMADZU 8201 models of PCs and desiccators.

PROCEDURE

1. Dragon Fruit Biosorbent Preparation (*Hylocereus polyrhizus)*

Dragon fruit skin is cut into small pieces, then washed with running water to remove dirt. Then the dragon fruit skin is rinsed with distilled water, and drained. Dragon fruit skin is dried in the sun for 1 week. Furthermore, dragon fruit skin is dried in the oven at 80 ° C for 24 hours. Then the dragon fruit skin is stored in the desiccator. After that, the dragon fruit skin was crushed / crushed using a *crusher*, and sieved with a size of 100filter *mesh* but did not pass the 230filter *mesh*.

2. Determination of Optimum Biosorption Time of Cu (II) By Dragon Fruit Skin (*Hylocereus polyrhizus*)

Dragon fruit skin powder is weighed as much as 0.2 grams and put in 100 mL erlenmeyer. Then 50 mL of Cu (II) solution with a concentration of 100 ppm was added. The mixture is shaken with a *magnetic stirrer* for 5 minutes and filtered. Filtrate absorbance was measured by Atomic Absorption Spectrophotometer at a wavelength of 324.8 nm. The experiment is then repeated with a time variation of 10; 15; 20; 30; 40; 50; 60; 70; 80; and 90 minutes. Each experiment was repeated two times. The blank experiment was carried out as above but without shaking with a *magnetic stirrer*.

3. Determination of pH Effect of Cu (II) Ion Biosorption by Dragon Fruit Skin (*Hylocereus polyrhizus*)

As much as 0.2 grams of dragon fruit skin powder is put into a 100 mL erlenmeyer glass containing 50 mL of Cu (II) 100 ppm solution. Then shaken with a *magnetic stirrer* with variations in pH 2, 3, 4, 5, 6 and 7 during optimum contact time. Filtered withfilter paper. *WhatmanFiltrate* 42absorbance was measured by Atomic Absorption Spectrophotometer.

4. Determination of Cu (II) Ion Biosorption Capacity by Dragon Fruit Skin (*Hylocereus polyrhizus*)

Dragon fruit skin powder is weighed as much as 0.2 grams and put in 100 mL erlenmeyer containing 50 mL of Cu (II) solution with a concentration variation of 50; 100; 150; 250 and 400 ppm. The mixture is shaken with a *magnetic stirrer* during optimum time and pH and then filtered. The residue was analyzed by FT-IR and the filtrate was analyzed by SSA.

5. Analysis of FTIR

Analysis of FTIR spectrum (*Fourier Transform Infra Red*) was carried out on dragon fruit skin biomass before and after adsorption. The spectra were recorded at the 4000-400 cmwave number area^{-1} with a resolution of 4 cm^{-1} at room temperature using the DTGS detector (*Deuterated Triglycine Sulphate*). Spectra is processed using *Easy Plot Software*.

RESULTS AND DISCUSSION

Optimum Biosorption of Cu (II) Ion with Dragon Fruit Skin (*Hylocereus polyrhizus*)

The amount of Cu (II) ions adsorbed at 5 minutes is 5.001 mg / g. This amount increases at stirring time of 10 minutes until it reaches the optimum limit with an adsorbed ion amount of 5.27 mg / g. After exceeding the optimum time in 10 minutes, the amount of adsorbed Cu (II) ions tends to decrease from 30 minutes to 90 minutes. This data shows that the active side of the surface of the dragon fruit skin is saturated. The amount of Cu (II) ions adsorbed as a function of time is shown in Figure 4.

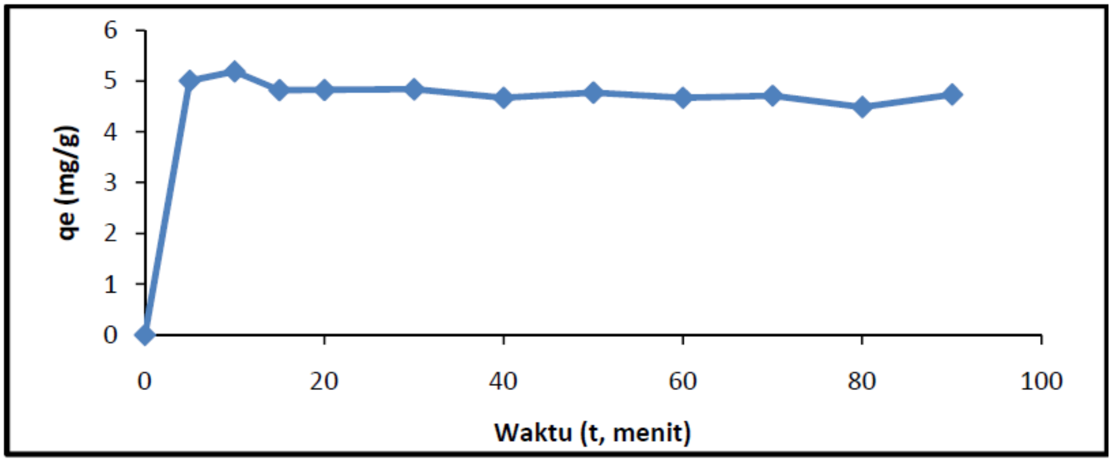


Figure 4. Amount of Cu (II) ions adsorbed vs. contact time with biosorbent of dragon fruit skin (Co= 100 ppm, pH = 5.1).

This is in accordance with the theory which states that the longer the time used more and more dissolved substances are adsorbed. However, the amount of dissolved solute will reach the maximum limit, because the biosorbent surface has been covered by adsorbed Cu (II) ions (Kuraisy,2008).

For further research, time used by Cu (II) ions by fruit peels The dragon is at the 10 minute time is the optimum time.

Effect of pH on the biosorption Ion Cu (II) By Skin dragon fruit*(Hylocereus* polyrhizus)

Effect of pH on ion biosorption Cu (II) by dragon fruit skin is carried out between pH 2 to pH 7 with time stirring during optimum time 10 minutes. Determination of the influence of pH from biosorption of Cu (II) ions by skin biosorbents dragon fruit is determined by counting the number of ions adsorbed (Qe) at various pH. Results of ion biosorption studies Cu (II) is shown in Figure 5.

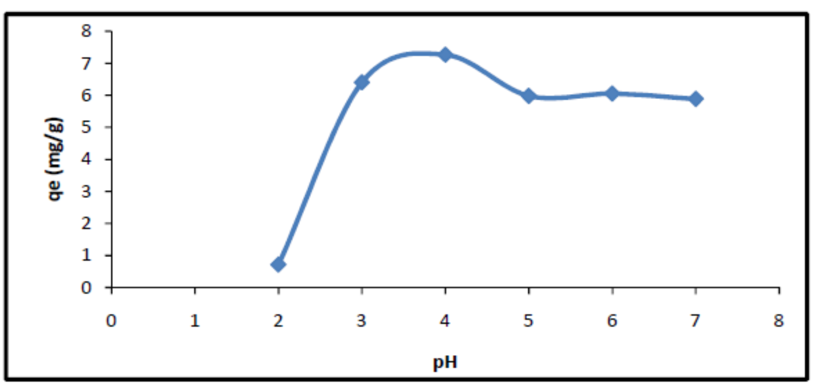


Figure 5. Amount of Cu (II) Ions adsorbed by Dragon Fruit Skin vs. pH (t = 10 minutes, Co = 100 ppm).

The amount of Cu (II) ions adsorbed by dragon fruit skin at pH 2 is 0.72 mg/g. This amount increases and reaches a maximum at pH 4 with adsorbed amount to 7.27 mg/g. After passing pH 4 the amount adsorbed tends to decrease.

According to Pravasant, et al., (2005) the low number of Cu (II) ions adsorbed at low pH is because the solution containsH+ high concentrations ofions so that Cu (II) ions compete with protons in interaction with the active side on the biosorbent surface. At low pH, the biosorbent surface is covered by Hions+ which prevent Cu (II) ions from approaching the biosorbent surface because of the repulsive force.

With increasing pH, the concentration of Hions+ decreases and the surface of the adsorbent becomes more negative so that Cu (II) ions will be more easily adsorbed. At a higher pH which is pH 5 and 6 the amount of Cu (II) ions adsorbed decreases and then tends to be constant up to pH 7. A decrease in the amount of metal ions absorbed in the adsorption process at high pH occurs before reaching the pH where the metal ion settling is caused by the formation of dissolved hydroxyl complexes of metal ions so that metal ions can no longer bind to the active groups the adsorbent (Ahmad et al., 2009). From the data

above the optimum pH to adsorb Cu (II) metal ions by dragon fruit skin is pH 4.

This is similar to that reported by Tasaso (2014) on biosorption of Cu (II) ions by grapefruit skin which is optimum at pH 4, as Gulnaz et al. (2005) reported on biosorption of Cu (II) ions by sludge dry active, Tikupadang (2009) also reported the optimum pH of biosorption of Cu (II) ions by sago pulp at pH 4. Subsequent studies were carried out at pH 4 .

Capacity ion biosorption of Cu (II) with skin dragon fruit (Hylocereuspolyrhizus)

Total Cu (II) adsorbed by the skin of the dragon fruit as a function of the initial concentration of Cu (II) is given in Figure 6. the amount of Cu (II) adsorbed increases with increasing initial concentration. In the concentration range used, the amount of Cu (II) ion adsorbed continues to increase which means the adsorbent has not saturated. Therefore the determination of adsorption capacity was carried out using Langmuir and Freundlich isotherms. Figures 7 and 8 show Langmuir and Freundlich isotherms.

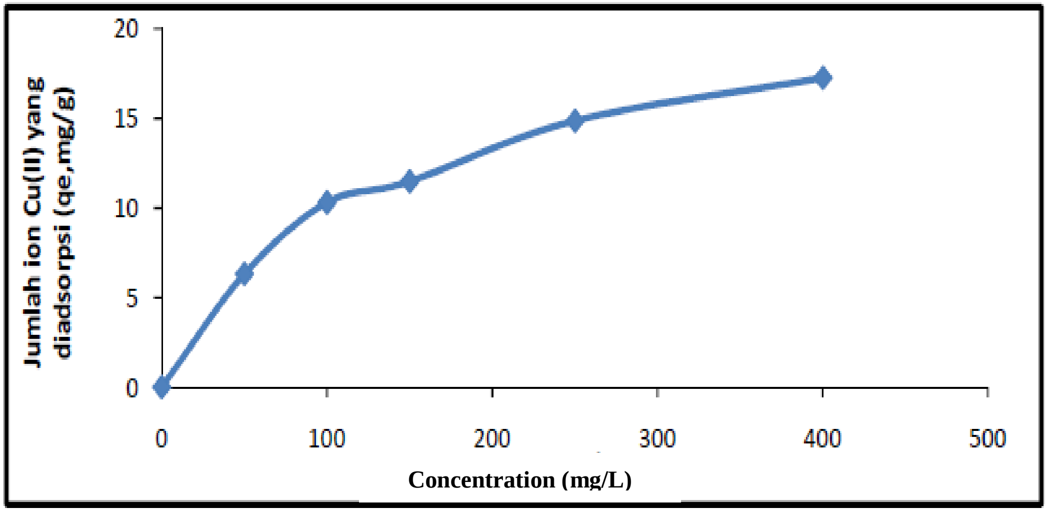


Figure 6. Amount of Cu (II) ions adsorbed by dragon fruit skin vs. Cu (II) ion concentration in solution after adsorption (t = 10 minutes, pH = 4)

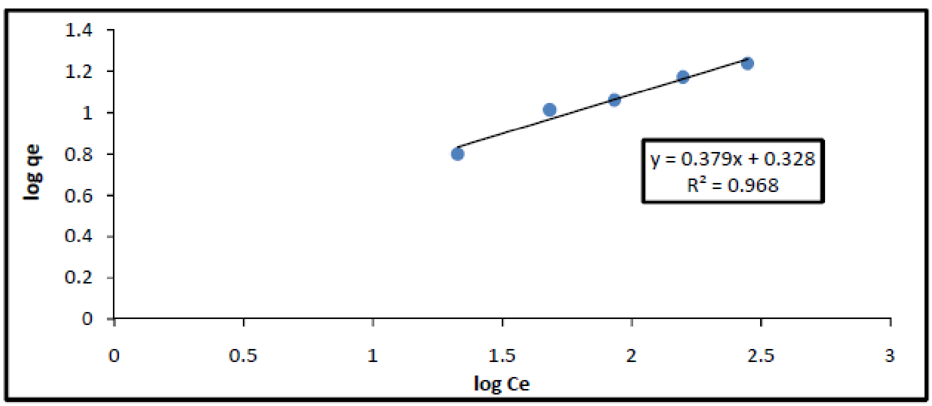


Figure 7. Langmuir isotherm with variations in concentration of 50 mg / L, 100 mg/L, 150 mg/L 250 mg / L, 400 mg / L at pH 4.

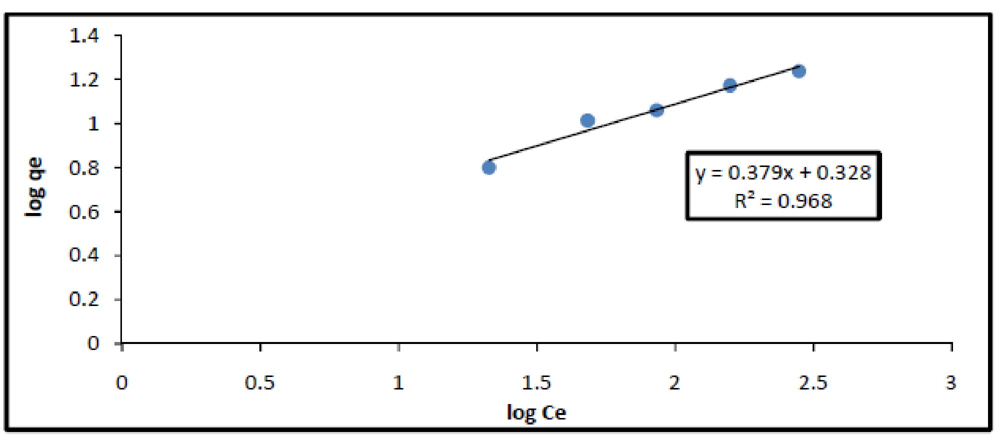


Figure 8. Freundlich isotherm with varying concentrations of 50 mg / L, 100 mg / L , 150 mg /L, 250 mg / L, 400 mg / L at pH 4.

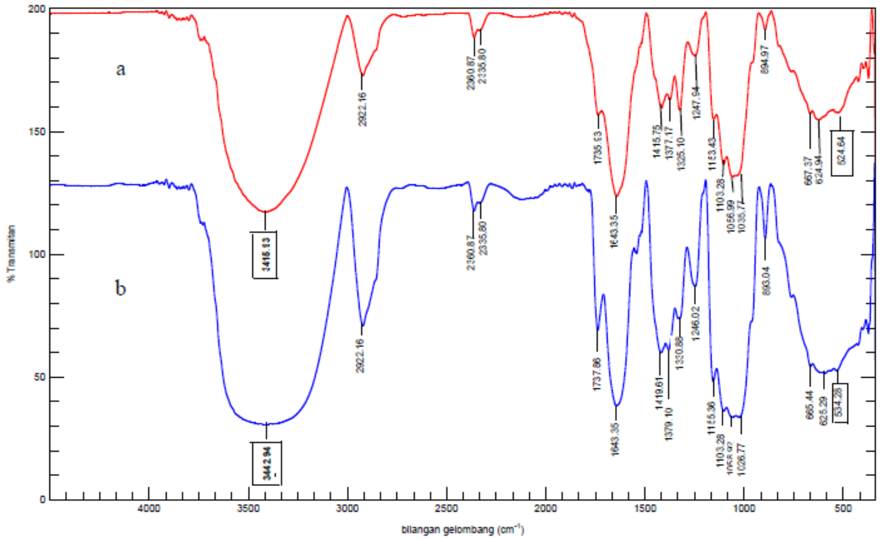
By comparing line values least square, the model will be selected suitable isothermal adsorption. Figure 7 and 8 shows that ion adsorption Cu (II) on dragon fruit skin is more suitable where is Langmuir isothermal adsorption where the point tends to indicate a straight line relationship according to value least square where R2 is obtained (0.995), whereas in isothermal adsorption Freundlich obtained R2 of 0.968. Intercept and isothermal slope from adsorption Langmuir provides capacity value biosorption (Qo) of 20.401 mg/g or 0.321 mmol/g and b (biosorption intensity) amounting to 0.02 L / mg.

Tikupadang (2009) shows that biosorption of Cu (II) ions by sago pulp also according to Langmuir isothermal with a value of Qo = 10.92 mg / g. The thing that the same was reported by Moo (2010) who use tofu dregs as biosorbent Cu (II) ion with a value of Qo = 7.91 mg/g. Septiany (2008) shows that biosorption of Cu (II) ions by rhizome biomass T. hemprichii is in accordance with isothermal Langmuir with a Qo value of 37.03 mg/g. But Lesage et al. (2006) show that biosorption of Cu (II) ions by the plant Myriophyllum spicatum L. according to Freundlich's isotherm with k= 29 mg/g. According to Kojima and Lee (2001) in Pravasant, et al.,(2005), different adsorbents provide different adsorption characteristics. Therefore, compatibility of isothermal adsorption depends on the biosorbent used.

Results of FT-IR Analysis of FT-IR

FT-IR spectrum of dragon fruit skin before and after biosorption can be seen in Figure 9. Some of the peaks detected in the sample prior to biosorption as in the sample 1056.99 cm^{-1} (stretched CO), 1643.35 cm^{-1} (stretched C = O) , 2922.16 cm^{-1} (stretching −CH aliphatic) and 3415.93 cm^{-1} (stretching −OH). The peaks were also observed in the spectrum after biosorption except the peak at 3415.93 $cmstretch^{-1}$ (−OH) experienced a shift to 3442.94 cm^{-1}. This shows the interaction of Cu (II) ions with hydroxyl groups contained in dragon fruit skin. In addition, in the regions, the wave 524.64 cm^{-1} also experienced a shift to 534.26 cm^{-1}. This absorption peak shift is caused by the bond between Cu (II) and oxygen (Cu-O strain) (Gatial et al., 2014).

Based on the results of FT-IR analysis, interactions are expected to occur between hydroxyl (-OH) groups derived from lignin and cellulose with Cu (II) ions due to the presence of hydroxyl (-OH) groups in cellulose and lignin which are not impeded by transient steric effects on pectin, the hydroxyl group is blocked by the presence of steric effects and also the group (-OH) in the pectin that comes from the group (-COOH), oxygen in the group (-OH) and group (-CO) has the same ability to draw electrons because of the conjugate effect so the possibility of shifting is the group (-CO).



3500 3000 25 2.16

Figure 9. Spectrum Analysis Results of FT-IR Dragon Skin Biosorbents (a) Before Contacting with Ions of Cu (II) and (b) After Contact with Metals Cu (II)

Figures 10 and 11 show the difference in bond energy in the group hydroxyl $(-OH)_1$ is the lignin blocked by steric and group (-OH) effects 2 which is not blocked by the steric effect. Difference this bond energy indicates that the group which tends to bind to ions Cu (II) is group $(–OH)_2$ which is not blocked by steric effects. Cluster $(-OH)_2$ the smaller the energy of the bond tends to be more stable and from the structure of the group $(–OH)_2$ is more free than cluster $(OH)_1$ which is blocked by the effect steric. The proposed reaction is given to Figure 12.

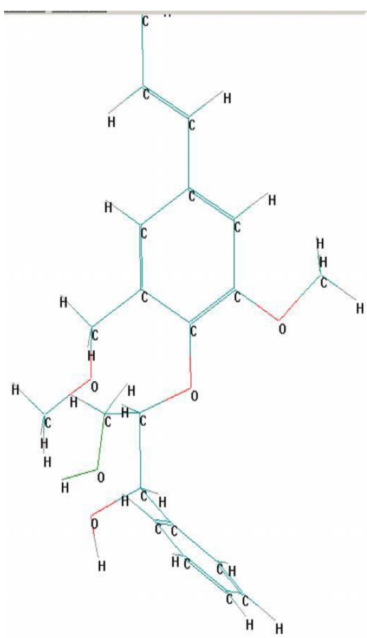


Figure 10. The Hydroxyl Group (-OH) which is blocked by the steric effect of group $(-OH)_1$ is blocked by effects steric. Total Energy =104.602 kcal / mol

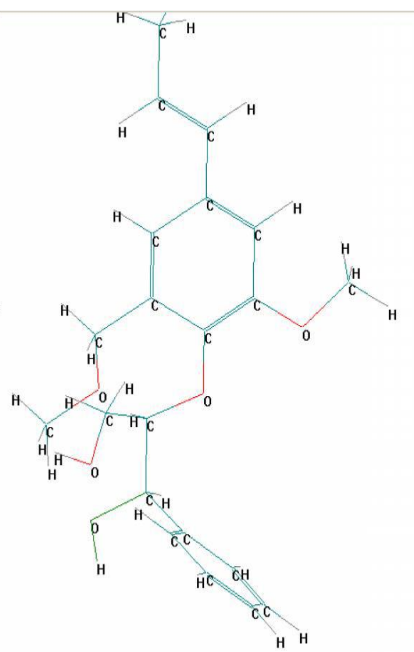


Figure 11. The Hydroxyl (-OH) group which is not blocked by the steric effect Total Energy = 74,029 kcal/mol

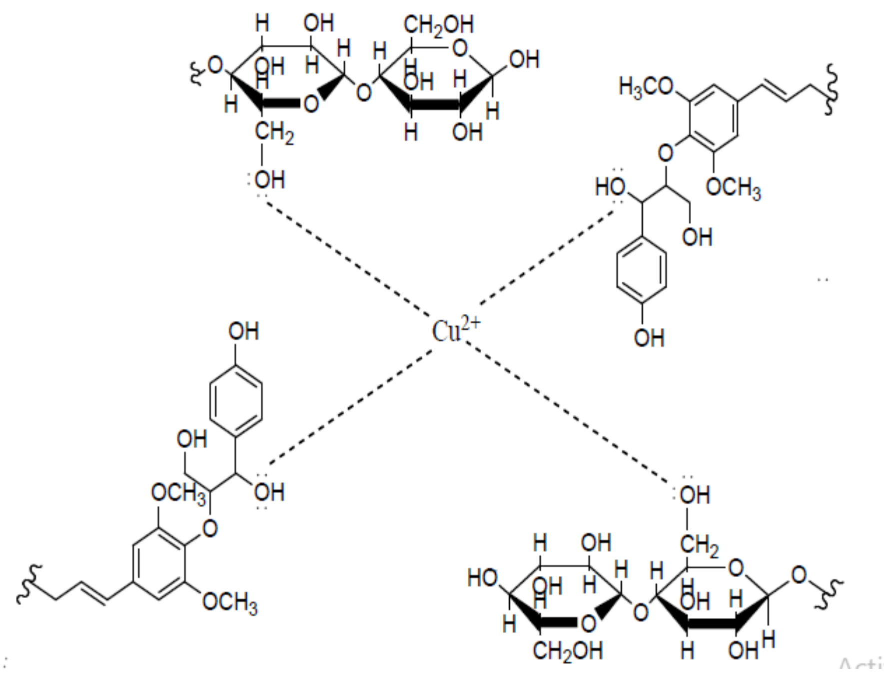


Figure 12. the reaction between Cu (II) with a group of lignin and cellulose

CONCLUSION

The optimum time biosorption Cu (II) by the skin of the dragon fruit is 10 minutes, with the optimum pH is 4. ion biosorption of Cu (II) by the skin of the dragon fruit meet with the Langmuir isothermal Qvalue$_{o\ of}$ 20.401 mg / g or 0.321 mmol / g. The functional group involved in biosorption of Cu (II) ions by dragon fruit peel namely hydroxyl group (-OH).

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