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# Optimization of biosorption process copper using cuttlefish shell (*Sepia recurvirostra*) in water solution

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## ABSTRACT

*The ability of cuttlefish shell (Sepia recurvirostra) to adsorb heavy metals copper in water solutionhave been investigated. The study was conducted in laboratory scale using batch method and using synthetic waste of Cu. Optimum biosorption conditions determined of pH, adsorbent dosage, the initial concentration of metal ions, contact time and temperature. The results showed the highest Cu ion biosorption capacity in synthetic waste of Cu(II) amounted to 29.535 mg/g at pH 4; biosorbent dose of 0.2 g; initial concentration of Cu(II) 140 mg/L and the contact time of 1 hour. Biosorption equilibrium described with Freundlich Isotherm equation and biosorption kinetics known to follow the pseudo second order with a value of $R^2$each 0.9483 and 0.9999. Biosorption thermodynamic parameters are determined by the free energy change ($\Delta G^0$), enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) during biosorption at a temperature of 29-40$^0$C.*

**Keywords**: cuttlefish shell (*sepia recurvirostra),* biosorption, isotherm, kinetic, thermodynamic

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## INTRODUCTION

Heavy metal is one pollutant waters. The presence of these metals is very dangerous, even in small amounts. Human activities such as metal mining, coating and mixing metals, oil and pigment industry, the manufacture of pesticides and tanning industry is potentially generate waste containing heavy metals[1]. As water pollutants, heavy metals are very dangerous for living things. Heavy metals can damage microbial populations at certain concentrations. Some metals classified as heavy metal is silver, mercury, cadmium, copper, lead, chromium and zinc. Heavy metals will damage the habitat and aquatic ecosystems. Besides heavy metals aretoxic substances and generally are carcinogenic. Therefore, the processing of waste containing heavy metals is needed.

One of the heavy metal ions arecopper. Copper is a metal that is widely used in industry. The use of copper can affect human health. Copper can damage liver that causes digestive problems, Wilson's disease, and insomnia. In addition, excess copper content in seawater can damage marine life by damage the gills, liver, kidneys, nervous system and change the sex lives of fish[2]. Therefore, the copper concentration should be reduced to an acceptable level with effluent treatment of industrial waste water before it enters water bodies.

One of the alternatives waste treatment containing heavy metals is the use of biological materials as adsorbent (biosorbent). This process is known as biosorption. Biosorption can show the ability of biomass to adsorb heavy metals from the solution through the metabolic or chemical-physics steps[3]. Some types of microorganisms such as algae, bacteria, fungi and yeasts have known can absorb the heavy metal. Novel waste treatments were used agricultural waste as biosorbent. These materials generally are not used anymore so it can get easily and low prices, such as rice straw, potato skins, fruit skins and leaves and twigs of certain plants.

Cuttlefish is a cephalopod species commonly found in the coastal waters of Europe, Africa, Asia, and the South Pacific. Characteristic of the cuttlefish is a shell that is found in the body. The shell contained calcium carbonate.[4]. In previous studies, it has been tested phytochemical of cuttlefish shells. Where cuttlefish shell extract have chemical compositions of alkaloid, steroid, carbohydrate and amino acid[5].

The purpose of this study was to determine the mechanism of Cu biosorption of heavy metals by animal waste in the form of cuttlefish shells. Cu(II) analyse using AAS and cuttlefish shells are characterization using FTIR, SEM-EDX.

## MATERIALS AND METHODS

**Biosorbent preparation**

Cuttlefish shells crushed and then sieved to obtain an average particle size of <0.125 mm. The powder washed with double destilled water, then with alcohol. The slurry was then dried at $80^0$C for 24 hours. The dry slurry was washed with HCl 1M and then with aquabidest until pH of 7. The result powder already use as biosorbent.

**Biosorption process**

Biosorption was carried out on batch scale at atmospheric pressure. Copper nitrate as biosorbat and cuttlefish shell as biosorbent were mixed with shaker at a certain time, then stopped. The mixture allowed to equilibrate, then filtered at normal condition. Biosorption was performed with variation of biosorbate pH range at 2 to 7, biosorbent dose from 0,2 to 1 g, initial concentration Cu(II) solution from 50 to 160 mg/L, contact time from 5 to 150 minute and temperature range at 24 to $40^0$C.

The filtrate is done analyzing content of Cu biosorption capacity calculated using the equation,

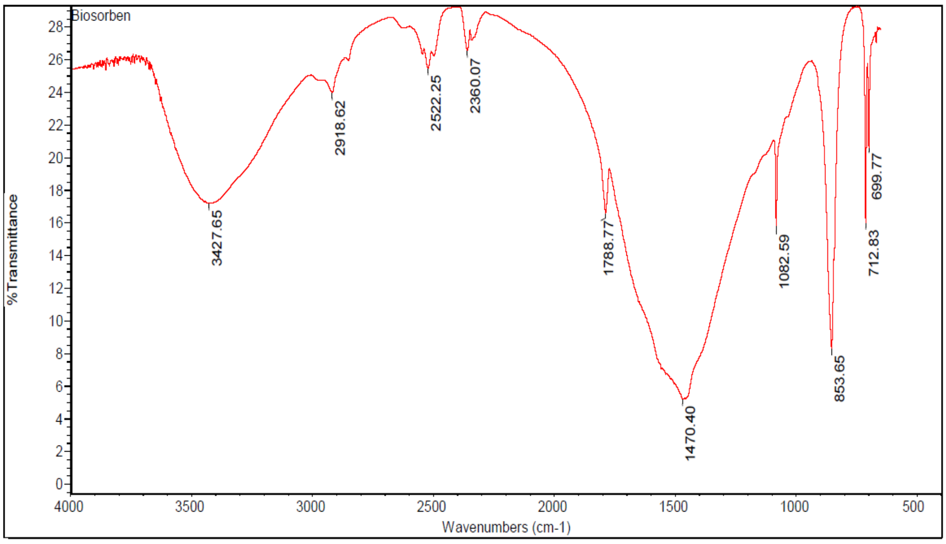
$$q_e = \frac{(\rho_0 - \rho_e)V}{m}$$

where, $\rho_0$and$\rho_e$is initial and equilibrium concentration of Cu(II) ion (mg/L); V is volume of Cu(II) solution (L); and m is biosorbent doses(g).

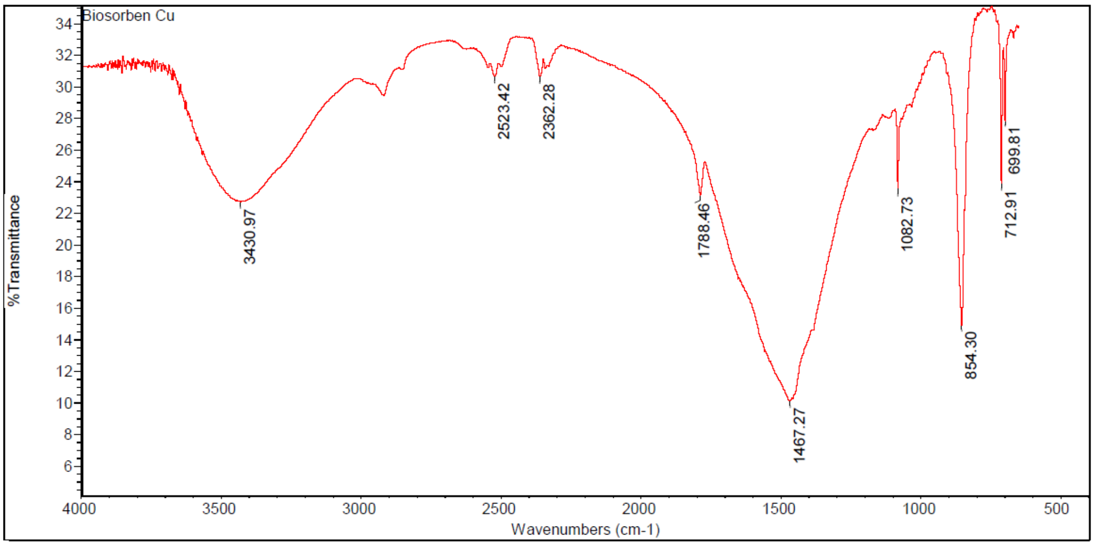
## RESULTS AND DISCUSSION

**Biosorbent characterization**

Peak area and intensity of the absorption peak at 3427$cm^{-1}$ corresponds to OH-stretching vibration of water adsorption. The peak of 2918 $cm^{-1}$ can be linked to the CH-stretching vibrations of the methyl groups, methylene and methoxy. The presence of peaks in 1788 $cm^{-1}$ and 1470 $cm^{-1}$ indicates vibration of C=O bond and an alkyl group (CH) vibrations of methylene groups (Cuttlefish shells FTIR spectra are shown in Figure 1)




(a)




**(b)**
**Figure1. FTIR spectra of biosorbent (a) before and(b) after biosorption process**

After the process of biosorption of Cu(II) by the biosorbent, a shift in the peak, but not too significant, show biosorption process is a process of ion exchange on the surface of biosorbent. After biosorption of Cu(II), OH-stretching vibration shifted to 3430 $cm^{-1}$ and peak alkyl (CH) occurs at 1467 $cm^{-1}$.

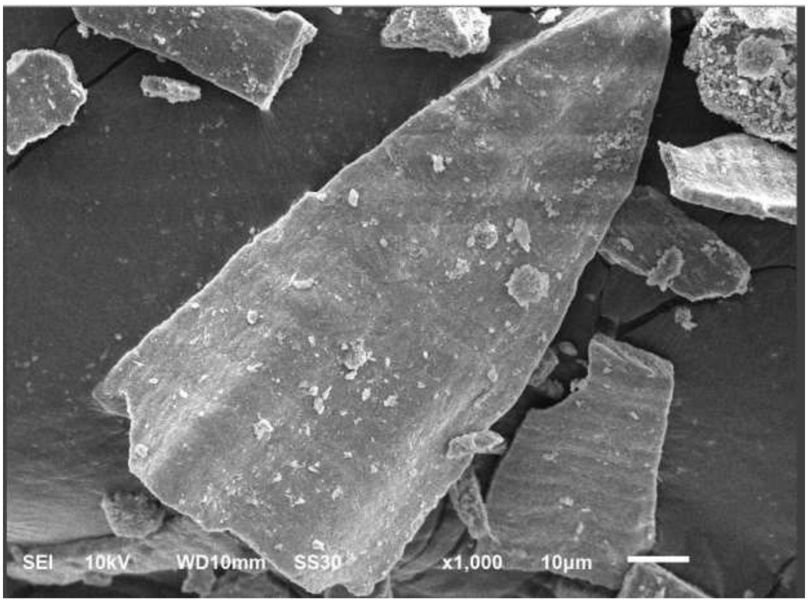



**Figure2. SEM graph of cuttlefish shell**

Characterization of cuttlefish shell was performed using SEM to see the topography and surface morphology biosorbent as metal ion Cu biosorption area. Biosorbent surface was found to form plates big enough. The composition of the elements contained in biosorbent characterized by EDS. The result shown calcium (Ca) content was the highest in biosorbent with a mass of 60.23%-w. Other contents such as C, O, N and Cl was found 10.95%-w, 24.04%-w, 1.81%-w and 2.96%-w respectively.

**Acidity Effect in Biosorption**

The degree of acidity (pH) is one of the most important parameters that control the surface properties of the biosorbent, functional groups, and the degree of ionization biosorbate. pH strongly influence the specifications and the availability of metal ions biosorption. Fig 4.shown the effect of pH on adsorption of Cu(II) were observed at pH 2 to 7. Biosorption capacity decreases with increasing pH reaches optimum Ph at 4 with the biosorption capacity of 4.647 mg/g and the amount of metal adsorbed 99.089 %.

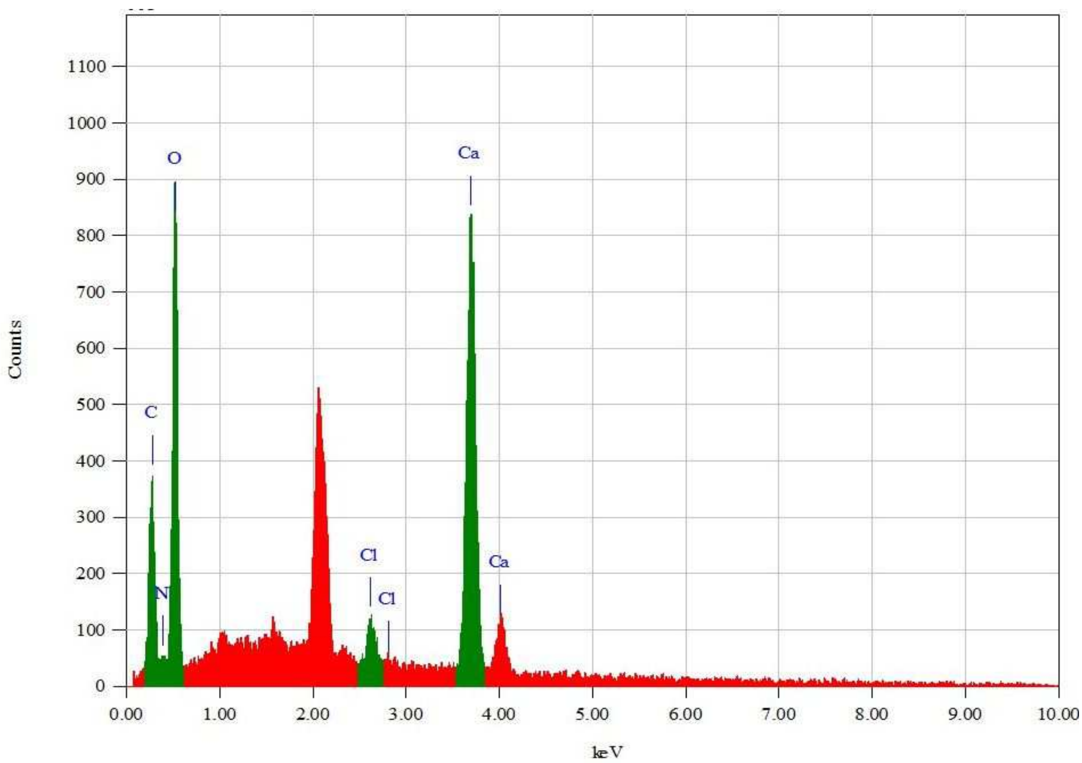



**Figure 3. EDS pattern of cuttlefish shell**

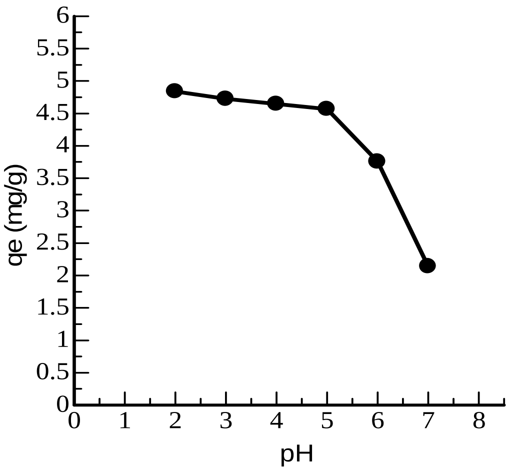



**Figure4.pH effect in biosorption of Cu(II) ionat29$^0$C; 50 mL Cu(II)100 mg/L; biosorbent dose 1 g; contact time 1h**

In this condition, the solution is not too acidic so that competition $H^+$ with metal ion to occupy the active site of biosorbent reduced causing increased metal ion biosorption. While at high pH (alkaline), metal ions tend to bind with OH from solution to form larger molecules, settles and difficult to adsorbed by biosorbent. pH4 was selectedan optimum pH and for the process of biosorption of Cu(II) further. Several previous studies are agreed with this pH for biosorption of Cu(II)[6-8].

**Biosorbent Dosage Effect in Biosorption**

Biosorbent doses affecting metal ion biosorption capacity. Increasing of biosorbent doses means more active sites so that the metal ions biosorption process will increase. This fact can be seen in Figure 5.

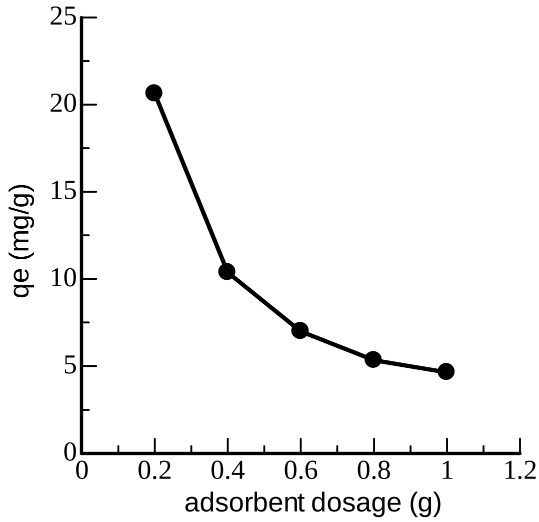



**Figure 5.Effect of biosorben dosage in biosorption Cu(II) ion at 29$^0$C;50 mL Cu(II)100 mg/L; pH 4:contact time 1 h**

Biosorption capacity of Cu(II) by a shell of cuttlefish decreased with increasing biosorbent dose from 0.2 g to 1 g, obtained the highest biosorption capacity of 20.63 mg/g at 0.2 g biosorbent. This point shows the optimum condition adsorption of Cu(II).

If biosorbent dosage improved while the contact time and the concentration of metal ions remain in biosorbent agglomeration will occur leading to reduced active surface area biosorbent to adsorbed heavy metals. Therefore, the lower the biosorption capacity with increasing biosorbent dose[9].

**Initial Concentration of Cu(II) Effect In Biosorption**

The influence of the initial concentration of metal ions Cu(II) to the metal ion biosorption processes studied by varying the initial concentration of metal ions Cu(II).

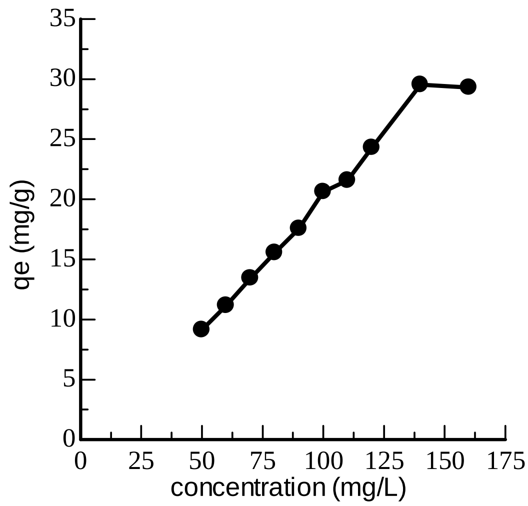



**Figure 6. Effect of initial concentration of ions Cu(II)in biosorption Cu(II) at 29$^0$C; 50 mL Cu(II); pH 4; biosorbent dose 0,2 g; contact time 1 h**

Figure 6.shown biosorption results with variation of the initial concentration of the metal ion. Biosorption capacity increase at an initial concentration of Cu(II) 50 mg/L to 140 mg/L, then reaches optimum at this point. If the initial concentration of Cu(II) to be improved, after the optimum point, the adsorption capacity will decrease which indicates the saturation of the active site binding of metal ions on the biosorbent. Increasing of biosorption capacity indicates the amount of Cu(II) adsorbed on active sites biosorbent greater. High concentrations will increase the amount of Cu(II) in solution so that more likely absorbed. Biosorption optimum capacity is achieved 29.535 mg/g at concentration of Cu(II) 140 mg/L.

**Contact Time Effect in Biosorption**
Biosorption capacity of Cu (II) is determined as time dependent to obtain the optimum contact time for biosorption ion Cu(II). Fig 7. show results biosorption equilibrium ion Cu (II) against time.

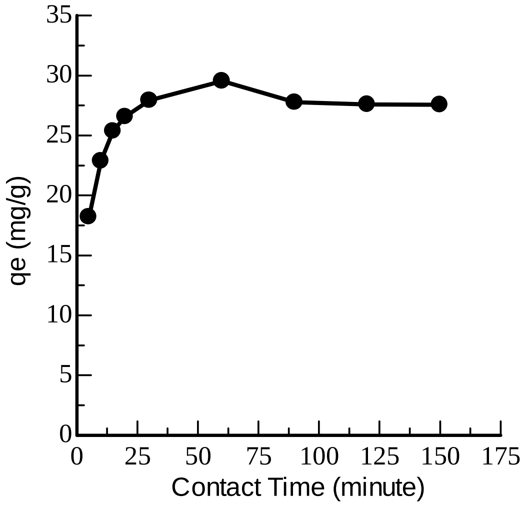



**Figure 7.Effect of contact time in biosorption Cu(II) at 29$^0$C; 50 mL Cu(II) 140 mg/L; pH 4; biosorben dosage 0,2 g**

Figure 7.shownbiosorption process is very fast and reached optimum about 60 minutes. Biosorption capacity increase until it reaches equilibrium, after that the increase is not very significant in proportion to the contact time of 150 minutes. The highest biosorption capacity obtained at 60 minutes contact time of 29.535 mg/g.

Equilibrium and/or optimum point means that if contact time continued, the biosorption capacity will even tend to decline due to the instability binding of Cu(II) by biosorbent so that Cu(II), which was originally bound (adsorbed) by the biosorbent would detaching.

**Temperature Effect in Biosorption**

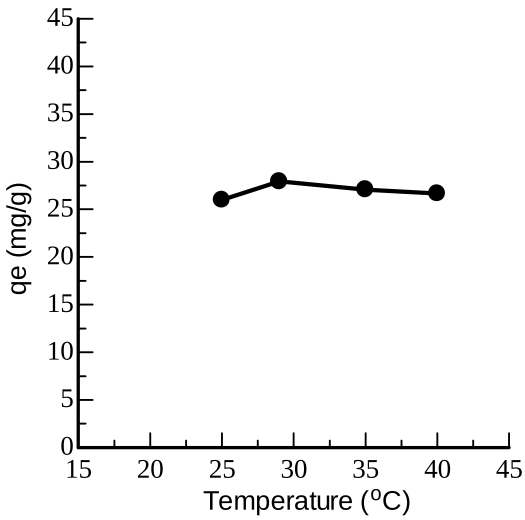



**Figure 8.Effect of temperature in biosorption Cu(II) at several temperature; 50 mL Cu(II) 140 mg/L; pH 4; biosorben dosage 0,2 g; contact time 30 min**

The effect of temperature in biosorption of Cu(II) was studied in the temperature range of 25-40$^0$C. Fig 8.illustrates the effect of temperature in biosorption of Cu(II) by biosorbent. The results show that the temperature does not affect significantly biosorption capacity for copper biosorption. The same condition is also reported several previous studies on the adsorption of Cu (II) with a variety of biomass.[10]

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## CONCLUSION

Biosorption of Cu(II) by shell of cuttlefish (*sepia recurvirostra*) successfully done in laboratory scaleand batch method. The maximum biosorptioncapacity of Cu(II) obtained at $29^0$C and atmospheric pressure with initial concentration of Cu(II) 140 mg/L; pH 4; biosorbent dosage of 0.2 g;contact time about60 minutes was obtained 29.535 mg/g. Cuttlefish shells FTIR characterization results indicate shift functional groups on biosorption process and illustrates that the biosorption process that occurs is a physical adsorption process (ion exchange). EDS characterization shows cuttlefish shell mostly contain of Ca and severalelement as C, O, N, Cl.

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