Adsorption of Cu(II) using *Sauropus androgynus* (L.) Merr. from aqueous solution

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**ABSTRACT**

The ability of *Sauropus androgynus* L. Merr. as low costs biosorbent to remove Cu(II) ions from aqueous solution has been investigated. Batch method was used to determine adsorption capacity of *Sauropus androgynus* L. Merr. at various parameters. Adsorption capacity achieved maximum value at pH 4, initial concentration 1500 mg/L, biosorbent mass 0.1 g and contact time 15 minutes. Langmuir and Freundlich models have value of $R^2$ 0.9879 and 0.9263, respectively. This result showed that Langmuir model was better to describe adsorption process of Cu(II) ions in aqueous solution. FTIR analysis showed a shift at band of hydroxyl (OH) and carbonyl (C-O) groups that participated in adsorption process. SEM micrograph indicated the surface of *Sauropus androgynus* L. Merr. has pores, wavy and rough.

**Keywords:** *Sauropus androgynus* L. Merr., Copper, Isotherm adsorption, FTIR

**INTRODUCTION**

Wastewater of many industries consists of heavy metals which flow into rivers, lakes and seas. Poor treatment process of this wastewater caused contamination in water bodies. These metal ions are stable and are known to be persistent environmental contaminants since they cannot be degraded or destroyed. They are harmful to aquatic life and water contaminated by them remains a serious public health problem to human health [1].

The conventional methods that are employed to remove heavy metals such as ion exchange, chemical precipitation, reverse osmosis and membrane separation are found to be inefficient and expensive, especially when treating wastewater with low concentration of heavy metals [2]. Adsorption, on the other hand, has emerged as a potential alternative to conventional physiochemical technologies in waste-treatment. Adsorptions an effective separation process that has advantages in terms of cost, flexibility and simplicity of design, and easy of operation compared to other techniques. Adsorption also does not result in the formation of harmful substances [3].

Copper is one of heavy metals contain on wastewater. Copper contamination in streams occurs mainly because of metal cleaning and plating baths, paper, pulp, wood preservative-employing mills, fertilizer industry and soon [4]. Copper can cause liver damage, wilson disease and insomnia. Lead cause damages the fetal brain, diseases of the kidneys, circulatory system and nervous system. While chromium can cause headache, diarrhea, nausea, vomiting and carcinogenic [5].
To remove copper from wastewater there are a few low cost materials which have been used as biosorbent such as Annona muricata L seeds [6], biomass [5,7,8,9,10, 13,15], rice husk ash [11], Punica geranatum [12], Zalacca edulis peel modify [14], Sophora japonica pods [16], Vigna Subterranea (L.) Verdc Hull. [17] and others.

Sauropus androgynus L. Merr., known as katuk, star gooseberry, or sweet leaf, is a shrub grown in some tropical regions as a leaf vegetable [18]. This plant is used as traditional medicine to reduce fever, stimulate lactation, hoarse voice, diabetics, cancer, inflammation, microbial infection, cholesterol and allergy due to its antioxidant effect [18,19]. In the present study, Sauropus androgynus (L.) Merr.leaves was used to remove Cu(II) ions from aqueous solution using batch method and observing some parameters affecting the adsorption process.

EXPERIMENTAL SECTION

Chemical and apparatus

This research was performed using analytical balance (Kern &Sohn GmbH), crusher (Fritsch, Germany), pH meter (Metrohm), shaker (Edmun Buhler 7400 Tubingen), FTIR (Unican Mattson Mod 7000 FTIR), SEM (Hitachi S-3400) and others glassware. All reagents were obtained from E.Merck (Darmstadt, Germany), which are analytical grade.

Leaves Preparation and Biosorption Studies

Sauropus androgynus L. Merr., leaves are collected from home garden at Padang city, West Sumatra, Indonesia. The leaves were washed with distilled water and dried at room temperature. Then Sauropus androgynus L. Merr., leaves were milled by crusher and the powder was soaked into HNO₃ 0.1 mol/L for 2 hours. Furthermore, the leaves powder was rinsed by distilled water and dried. Biosorbent is ready to used. Biosorption assays were conducted on various pH, concentration, biosorbent dosage and contact time. Characterization was carried out by using FTIR and SEM.

RESULTS AND DISCUSSION

Effect of pH on adsorption of Cu(II) ion

The initial solution pH is one of the most important environmental factors in the adsorptive removal of heavy metals from aqueous solutions, because this parameter affects not only the site dissociation, but also the speciation and solubility of metal ions [5]. The pH level affects the network of negative charge on the surface of the biosorbent walls, as well as physicochemistry and hydrolysis of the metal. Therefore, preliminary experiments have been performed to find out the optimum pH for maximizing the metal removal [4]. Result revealed the maximum adsorption capacity of Sauropus androgynus L. Merr at pH 4, 0.6881 mg/g (fig. 1). Adsorption capacity dramatically decreased after reached optimum condition. With an increase in pH, the negative charge density on the biosorbent rises which results in attraction between these negative charges and the metal ions and therefore in increasing the biosorption [12] and decrease in biosorption at higher pH is also due to the formation of soluble hydroxilated complexes of the metal ions and their competition with the active sites, and as a consequence, the retention would decrease [5]. Similar result also reported by Peyman Salehi [12] although Chia-Chay Tay et al [15] and Mohamed W. Amer et al [16] reached optimum condition at pH 5 and 6, respectively.

Effect of initial concentration on adsorption of Cu(II) ion

Fig. 2 shown concentration affecting to adsorption capacity of Sauropus androgynus L. Merr leaves. Initial concentration was conducted ranging 100-2100 mg/L. Adsorption capacity of Sauropus androgynus L. Merr leaves increased with increasing concentration of metal ion and then gradually decreased. Adsorption capacity of Sauropus androgynus L. Merr leaves got up to maximal value when initial concentration of Cu(II) solution 1500 mg/L with adsorption capacity 23.124 mg/g. Increasing the initial metal ion concentration causes an increase in the biosorption capacity of the biosorbent which stems from the fact that the probability of collusion between metal ions and biosorbent increases in this condition which enhances the biosorption ability [12]. Less competition between the free bonding sites caused faster initial adsorption. When the unoccupied bonding sites decreased, copper adsorption became more difficult and slower until equilibrium was achieved [9].

Effect of biosorbent dose on adsorption of Cu(II) ion

Contact time effect was carried out ranging mass 0.1-1 g at pH 4 and initial concentration 1500 mg/L. As illustrated in fig. 3 adsorption capacity of Sauropus androgynus L. Merr leaves dramatically decreased as biosorbent mass increased. Increase in the adsorption with increasing dose of adsorbent is expected due to the increase in adsorbent surface area and the availability of more adsorption sites [4,5]. The decrease in biosorption efficiency with further increase in biosorbent dose could be explained as a consequence of a partial aggregation of biomass, which results in a decrease in effective surface area for the biosorption process [5]. When the biosorbent ratio is small, the active
sites for binding metal ions on the surfaces less, so the biosorption efficiency is low. As the biosorbent dose increased, more active sites to bind metal ions, thus it results an increase in the biosorption efficiency until saturation [16].

![Fig. 1 Effect of pH on adsorption of Cu(II) ion, biosorbent mass 0.25 g; agitation rate 100 rpm; initial concentration 30 mg/L; contact time 15 minutes.](image1)

![Fig. 2 Effect of initial concentration on adsorption of Cu(II) ion, pH 4; biosorbent mass 0.25 g; agitation rate 100 rpm; contact time 15 minutes.](image2)

![Fig. 3 Effect of biosorbent dose on adsorption of Cu(II) ion, pH 4; initial concentration 1500 mg/L; agitation rate 100 rpm; contact time 15 minutes.](image3)
Effect of contact time on adsorption of Cu(II) ion

The rate of biosorption is important for designing batch biosorption experiments [16]. Effect of contact time on adsorption capacity of *Sauropus androgynus* L. Merr. was conducted ranging time 15-120 minutes at pH 4, initial concentration 1500 mg/L, and adsorbent dose 0.1 g. As shown in fig. 4 adsorption capacity of *Sauropus androgynus* L. Merr. gradually decreased when time increased. This biosorbent reached optimum condition when contact time 15 minutes with capacity of adsorption was 30.18 mg/g. This revealed that microporous surface of biomaterial facilitates the diffusion process and surface active sites are easily occupied by Cu(II) ions [15].

Adsorption Isotherms

The sorption capacity of a biosorbent can be described by equilibrium sorption isotherm, which is characterized by definite constants whose values express the surface properties and affinity of the biosorbent [5]. Langmuir and Freundlich isotherm models were used to describe the adsorption equilibrium.

The Langmuir isotherm assumes monolayer adsorption on a uniform surface with a finite number of adsorption sites. Once a site is filled, no further sorption can take place at that site [16]. The Langmuir isotherm model suggests a homogenous surface with uniform bonding sites, monolayer adsorption and no reaction between adsorbed adsorbate [9]. The linear form is given as:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

where $q_m$ (mg/g) is the saturated amount of adsorption, which is uniform for a given adsorbate and adsorbent; $K_L$ (L/mg) is the adsorption constant, related to energy consumption in the adsorption process; $C_e$ (mg/L) is the concentration of copper in solution at equilibrium [5]. Langmuir model of *Sauropus androgynus* L. Merr. was shown in fig. 5.
Freundlich isotherm model is the well-known earliest relationship describing the adsorption process. This model applies to adsorption on heterogeneous surfaces with the interaction between adsorbed molecules and the application of the Freundlich equation also suggests that sorption energy exponentially decreases on completion of the sorption centers of an adsorbent. This isotherm is an empirical equation and can be employed to describe heterogeneous systems and is expressed as follows in linear form [16]:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

where \( K_F \) (mg/g) (L/mg)^1/n and \( n \) (\( n > 1 \)) are constants, dependent on temperature, adsorbate, and adsorbent. \( K_F \) is related to the maximum adsorption capacity while \( n \) is a measurement of adsorption intensity. Freundlich model of *Sauropus androgynus* L. Merr. was illustrated in fig. 6.

![Fig. 6 Freundlich isotherm of Sauropus androgynus (L.) Merr.](image)

**Table 1. Adsorption characteristics of Langmuir and Freundlich models on Cu(II) adsorption by Sauropus androgynus L. Merr.**

<table>
<thead>
<tr>
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<th>Langmuir model</th>
<th>Freundlich model</th>
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<tr>
<td>( q_m ) (mg/g)</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>( K_l ) (L/mg)</td>
<td>0.0049</td>
<td>0.9879</td>
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<tr>
<td>( R^2 )</td>
<td>0.9879</td>
<td>0.9263</td>
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The coefficient determination of Langmuir and Freundlich models are 0.9879 and 0.9263 on adsorption of Cu(II), respectively. The value of \( R^2 \) between Langmuir model and Freundlich model shown that Langmuir model fit to adsorption behaviour of *Sauropus androgynus* L. Merr.

**FTIR Analysis**

FTIR analysis was done to determine functional group present in the sample and was involved in adsorption process. The broad band at 3423.05 cm\(^{-1}\) could describe of O-H stretching group (fig. 7A). This spectrum shifted to 3421.51 cm\(^{-1}\) in metal uptake into biosorbent *Sauropus androgynus* L. Merr. indicating this functional group has participated on adsorption process. The band at 2918.16 cm\(^{-1}\) (fig. 7A) indicated the presence of C-H stretching group. Fig. 7B shown that C-H group band did not change significantly, from 2918.16 cm\(^{-1}\) to 2918.18 cm\(^{-1}\). The band at 1655.00 cm\(^{-1}\) (fig. 7A) shown the presence of carbonyl group which shifted to 1654.27 cm\(^{-1}\) after metal ions loaded. The shifted of the band before metal ions uptake and after metal ions uptake indicated that functional groups have been involved on biosorption process [16].
Figure 7. FTIR analysis of *Sauropus androgynus* L. Merr., (A) Before loaded; (B) After loaded

Figure 8. SEM micrograph of *Sauropus androgynus* L. Merr., (A) Before loaded; (B) After loaded

**SEM Analysis**

SEM is a primary tool for characterizing the surface morphology and fundamental physical proportion of the adsorbent. It is useful for determining the particle shape, porosity, and appropriate size distribution of the adsorbent [14]. As shown in fig. 8 SEM analysis has been observed at 1000x magnification. It indicated that *Sauropus androgynus* L. Merr. has pores, wavy and rough surface before metal ions loaded (fig 8A). But after metal ions loaded in to biosorbent the surface of *Sauropus androgynus* L. Merr. was filled by particle of metal ions which indicated adsorption process has occurred.

**CONCLUSION**

This study showed biosorption process of *Sauropus androgynus* L. Merr. as low cost biosorbent is an effective biosorbent to remove Cu(II) ion from aqueous solution. Optimum conditions was reached at pH 4, initial concentration 1500 mg/L, biosorbent mass 0.1 g and contact time 15 minutes. *Sauropus androgynus* L. Merr. could
remove Cu(II) ion from aqueous solution to the tune of 20.12 %. Coefficient determination ($R^2$) of Langmuir model was better than Freundlich model for describing adsorption equilibrium of *Sauropus androgynus* L. Merr. to remove Cu(II) ion. SEM micrograph showed pores on the surface of *Sauropus androgynus* L. Merr. supporting adsorption process.

REFERENCES