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Research Article

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Biosorption of copper (II) Ions from aqueous solution by *Nothopanax scutellarium* leaves powder on batch method

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ABSTRACT

The research about biosorption of Cu(II) by Nothopanax scutellarium leaves has been investigated through batch experiment. Based on the experiment optimum condition for adsorption Cu (II) ion was pH 7, biosorbent dosage at 0,1 g, initial concentration of metal ion solution 1200 mg/L and contact time 15 minutes. The biosorption data were fitted to Freundlich isotherm with R^2 0.9848. Characterization of Nothopanax scutellarium was evaluated using Fourier Transform Infra Red (FT-IR) spectroscopy and active functional group estimated were O-H group, C-H group, N-H group and C-N group. The measurement of metal ion concentration conducted by Atomic Absorption Spectroscopy (AAS) and surface analysis before and after adsorption conducted using Scanning Electron Microscopy (SEM). This study showed that Nothopanax scutellarium leaves powder could be used as an efficient adsorbent to remove Cu (II) metal ions.

Keywords: Biosorption, *Nothopanax scutellarium*, Freundlich isotherm, Biosorption capacity.

INTRODUCTION

Copper toxicity may occur from eating food and drinking water, or breathing air enriched with an excess copper. Acute toxicity of copper may cause anemia, intravascular hemolytic, acute liver failure, and acute renal failure with tubular damage, shock, coma and death and mild conditions may result in vomiting, nausea and diarrhea [1]. Presence of high copper compound in the body also effect on aging, schizophrenia, mental illness, Indian childhood cirrhosis, Wilson's and Alzheimer's diseases [2]. Various processes of heavy metals elimination are used, such as precipitation, electroprecipitation, electro coagulation, cementing and separation by membrane, the solvent extraction and the exchange of ions on resins [3]. Recently, biosorption has emerged as a treatment method as an alternative technology to the conventional used ones for the waste water treatment. Biosorption is phenomenon in which the non-living agricultural biomass binds and concentrates metal ions from even very dilute aqueous solutions [4]. Biosorption has emerged as an alternative to these methods with the major advantage such as low cost, high efficiency, minimization of chemical and biological sludge, regeneration of biosorbent and possibility of metal recovery [5]. The present study is focused to explore the ability of environmentally friendly agricultural by product such as *Nothopanax scutellarium* leaves for the removal of Cu (II) from aqueous solution under batch method. Experimental parameters affecting the biosorption process such as pH, contact time, concentration of Cu (II), biosorbent dosage, FTIR and SEM analysis has been investigated.

EXPERIMENTAL SECTION

Chemical and Apparatus

All reagents used are analytical grade obtained from E. Marck (Darmstad, Germany). The apparatus used are analytical balance (Kern & Sohn GmbH), siever450µm, Fourier Transform Infra-Red (Unican Mattson Mod 700) Rotary shaker (Edmund Buhler 7400 Tubingen), Atomic Absorption Spectrophotometer (AAS Variant Spectra AA 240 Spectrometer), pH meter (Lovibond Senso Direct), grinder (Christy Hunt), Scanning Electron Microscope (SEM SU 3500) and the glasswares.

Preparation of Adsorbent

N. scutellarium leaves was collected from traditional market in Padang, washed with deionized water and air dried for one week. The *N. scutellarium* then smoothed using cruiser to form powder. The leaves powder then sieved to 450µm. About 20 gram of samples was activated by soaking in excess of 80mL HNO_3 0,01M, followed by washing thoroughly with deionized water the air dried.

Batch Adsorption Experiments

The adsorption experiments were studied by using batch method experiments. All the experiments were conducted at 25^{o}C and 100 rpm on a mechanical shaker with 0.25 gram adsorbent in 100 mL conical flask containing 10 mL of Cu(II) solution. The effect of pH solution, contact time, biosorben dosage, initial concentration of Cu(II) were studied. The concentration of Cu(II) in solution after equilibrium was reached as determined by Atomic Absorption Spectrophotometer (AAS). To determine the amount of Cu (II) ion adsorbed by *N. scutellarium* leaves powder (qe), the formula used is:

$$qe = \frac{Co - Ce}{m} xv \quad (1)$$

where Co is the initial concentration of metal ions (mg/L), Ce is final concentration at equilibrium state (mg/L), m is biosorbent mass (g) and v is volume solution (L). Biosorption assays were conducted on various pH, initial concentration of Cu(II) ions, biosorbent dosage and contact time. Surface analysis of biosorbent before and after biosorption process was investigated by SEM. The functional groups that involved in biosorption were estimated by FTIR.

RESULTS AND DISCUSSION

Effect of pH on Biosorption of Cu(II) Ions

pH seems to be the most important parameter in the biosorptive process. The solution pH affects metal ion solubility as well as biosorbent total charge. The removal of metal ions is almost negligible at highly acidic pH values and increases by increasing the solution pH up to a certain limit [6]. The effect of pH on biosorption of Cu (II) ions using *N. scutellarium* leaves powder was shown in Fig. 1the optimum condition was found at pH 7 with sorption capacity 0,9516 mg/g. The same result was also reported by Pandey et al (2014) [7]. Pandey et al (2014) reported the ability of *Syzgiumcumini* L to remove copper from aqueous solution and the study was carried out in a pH range 2-11, since copper starts to precipitate above pH 7. The other same result was also reported by Al Homaidan et al (2014) [1] that used biomass of *Spirulina platensis* to remove Cu (II). Biosorption was found to be maximum (90,6%) in a solution containing 100 mg/L Cu (II), at pH 7.

Effect of Initial Concentration on Biosorption of Cu (II) Ions

Effect of initial concentration of Cu(II) ions was carried out at various concentration, ranging from 100 mg/L until 1200 mg/L. The effect of initial concentration of Cu (II) ions was shown in Fig.2shows the effect of initial concentration of Cu (II) ion on sorption capacity (Q) at the constant pH from 100 mg/L until 1200 mg/L. It can be observed that the adsorption of Cu(II) increase linearly as the increase of Cu (II) concentration. The Fig.2 shows that the optimum condition of biosorption process was found at concentration Cu (II) 1200 mg/L with sorption capacity 13.95 mg/g.The initial concentration provides an important driving force to overcome all mass transfer resistance of metal between the aqueous and the solid phase. Increasing amount of metal adsorbed by the biomass will be increased with initial concentration of metals [8]. Higher concentration result in a greater driving force at the liquid solid interface, which in turn enhances the mass transfer [9].

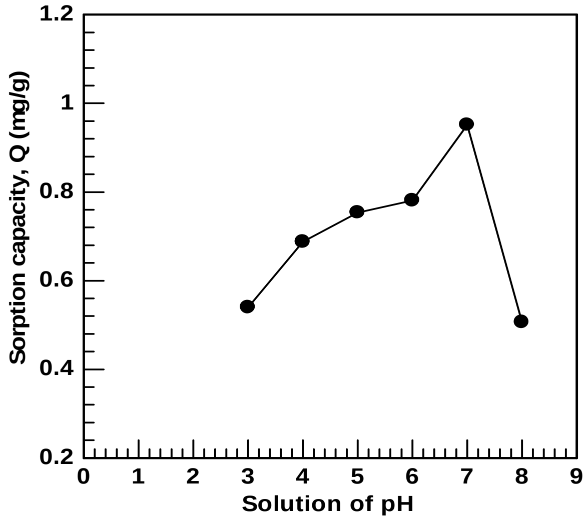

Figure 1. Effect of pH on Cu(II) adsorption, with initial concentration 30mg/L; stirrer speed 100rpm; contact time 15 min; biosorbent dose *N. scutellarium*0.25g

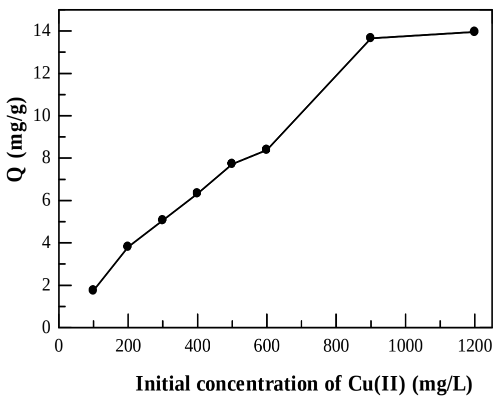

Figure 2. Effect of initial concentration of Cu(II) on sorption capacity (Q) of *N.scutellarium*

Effect of biosorbent dosage on biosorption of Cu (II) ions

Optimum dosages of biosorbent were investigated on condition pH 7, and initial concentration of Cu (II) 1200 mg/L. The dosages of biosorbent ranging between 0,25 – 1 g. The result shown in Fig.3from the result shows that 0,1 g of *N. scutellarium* leaves powder shown an optimum condition for adsorption. The removal efficiency of metal ions is highly dependent on the quantity of biosorbent. Several researches reported that the increase of removal percentage with increase in the sorbent dosage is due to the greater availability of the exchangeable sites or surface area at a higher concentration of the biosorbent [10].However, the result shows that the adsorption capacity decreased sharply with the increasing of adsorbent dosage. These results may due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles [11]. Moreover, the high adsorbent dosage could impose a screening effect of the dense outer layer of the cells, thereby shielding the binding sites from metal ions [12].

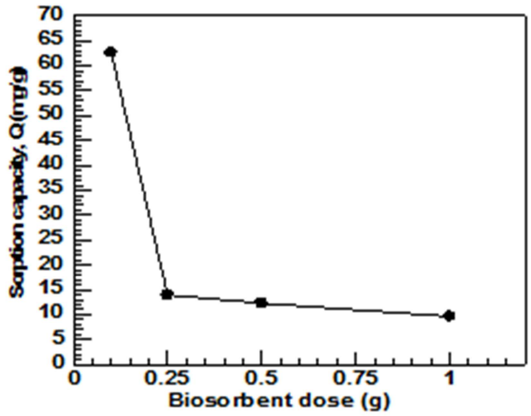

Figure 3. The effect of biosorbent dose on sorption capacity of *N. scutellarium*

Effect of Contact Time on Biosorptionof Cu (II) Ions
To achieve the highest removal of metal ions, the determination of the optimum contact is one of the key factors that should be assessed. Equilibrium time is one of the important parameters for selecting a wastewater treatment system [13]. The result for the effect of contact time on Cu (II) removal by *N. scutellarium* leaves powder are presented in Fig.4 the initial high rate of adsorption of metal ions is due to free active binding sites on the surface of the adsorbent. As the number of available sites decrease, the rate of adsorption of metal ions also decreases [14].

Adsorption Isotherm Studies
The Langmuir isotherm model is expressed as [15]:

$$\frac{c}{(q)} = \frac{1}{qm.b} + \frac{1}{qm} C$$

Where q = mass of solutes adsorbed per mass of adsorbent, c = concentration of adsorbate in solution in equilibrium with the adsorbate, qm and b are constant which are related to sorption capacity and energy of sorbent, obtained by plotting c/q against c. The slope 1/qm while the intercept is 1/qm.b. The Freundlich linear form is given by the following equation [16]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e$$

Where Kf is Freundlich constant and 1/n is an empirical parameter related to the adsorption intensity. Fig.5 shows the values of 1/n and Kf from the slope and the intercept of plot of log q_e vs log Ce.

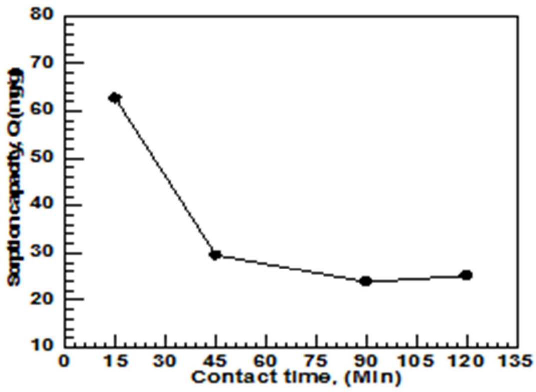

Figure 4. Effect of contact time on biosorption capacity of *N.scutellarium*

Fourier Transform Infrared Spectroscopy
Fig.6 shows the Langmuir isotherm plots for the adsorption of Cu (II) using *N. scutellarium.* It was observed that the experimental data fitted the Freundlich isotherm best. The Langmuir isotherm was far from unity while the Freundlich isotherm model was closer to unity.Table 1 shows the comparison of the Langmuir and Freundlich Regression Coefficient.

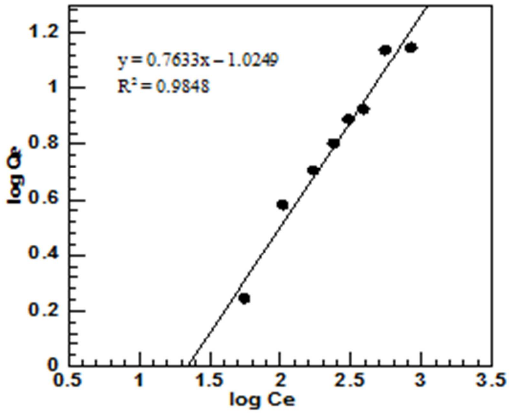

Figure 5a. Langmuir isotherm *N.scutellarium*

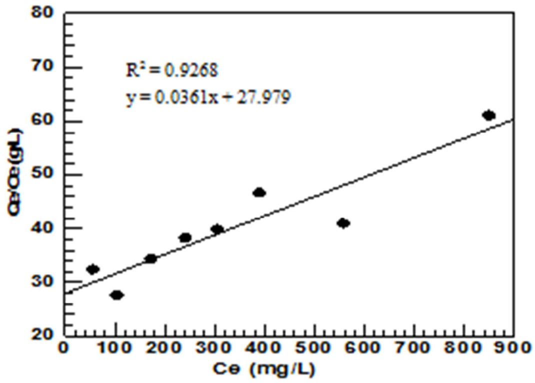

Figure 5b. Freundlich isotherm *N.scutellarium*

Table 1. Comparison of the Langmuir and Freundlich Regression Coefiicient

Langmuir isotherm			Freundlich isotherm		
q_m (mg/g)	b (L/mg)	R^2	K_F	1/n	R^2
27.7008	0.9901	0.9268	0.0944	0.7633	0.9848

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is an important analytical technique to confirm the functional groups which present in the biosorbents. FTIR provide the information on binding mechanism and possible functional groups involved in the interaction with metal ions [3]. The FTIR spectra of *N. scutellarium* leaves powder, before and after adsorption are shown in Fig.6as shown in Fig.6 the broad and sharp peak at 3200-3500 cm^{-1} indicate the presence of O-H stretch, the peak at 2850-3000 cm^{-1} correspond to C-H stretches, the N-H bend can be seen at 1580-1650 cm^{-1}. The peak at 1020-1250cm^{-1} indicates the C-N stretch.

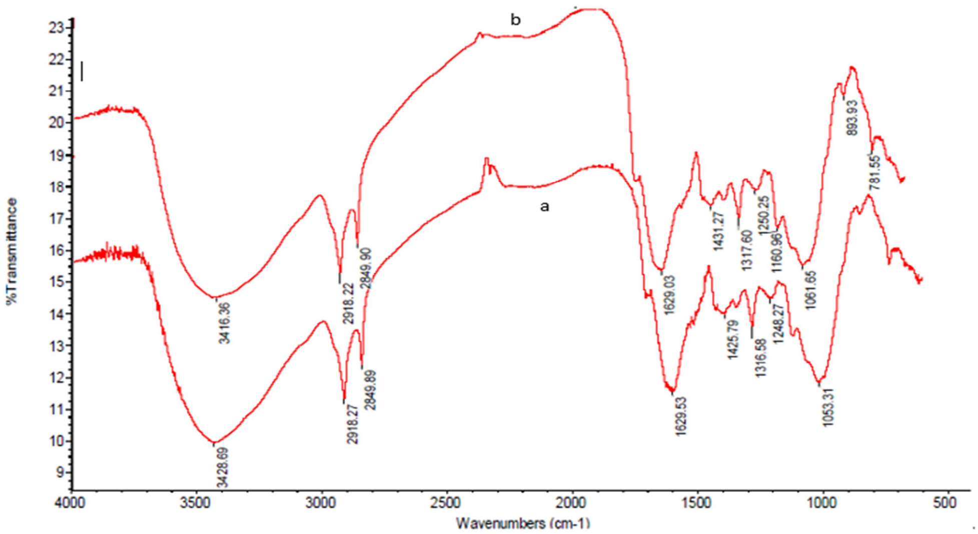

Figure 6. FTIR spectra of *N. scutellarium* leaves (a) before biosorption, (b) after biosorption

Scanning Electron Microscope (SEM)

The scanning electron microscope analysis as conducted to analyze the surface morphology of the biosorbents before and after biosorption process. The image is given in Fig.7. From Fig.7, it can be seen that the surface of *N. scutellarium*leaves is smooth with uniform microporous structure. The biosorbent have porous on their surface that can be filled by metal ions. The structure then becomes rough and tangled after biosorption indicating the modification of the biosorbent.

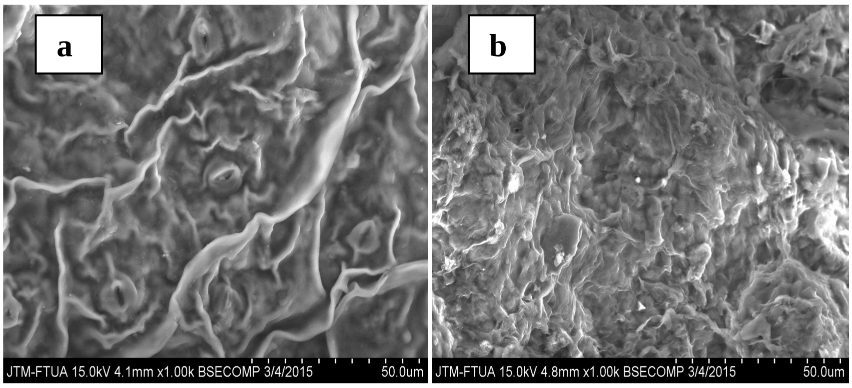

Figure 7. The images seen of *N. scutellarium*leaves powder; (a) before metal uptake; (b) after metal uptake with 1000x magnification

CONCLUSION

The adsorption of Cu (II) ions from aqueous solution using *N. scutellarium* leaves as the low-cost adsorbent was investigated in batch process. The optimum condition was found at pH 7, biosorbent dosage 0.1 g, initial concentration of metal ions 1200 mg/L and contact time 15 min. Many people who live in industrial area and drinking water from corroded copper pipes cannot bottled water from daily consumption. From the study *N. scutellarium* could considered as low cost biosorbent that would be useful for the economic treatment of waster containing copper.

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