Removal of Cu^{2+} from Aqueous Solution by Biosorption on Rice Straw - an Agricultural Waste Biomass

Achanai Buasri, Nattawut Chaiyut, Kessarin Tapang, Supparoek Jaroensin, and Sutheera Panphrom

***Abstract*—The potential of rice straw, agricultural waste, to remove copper (II) from aqueous solution was evaluated in a batch process. Experiments were carried out as function of contact time, initial concentration, pH and temperature. Adsorption isotherms were modeled with the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The data fitted well with the Freundlich isotherm. The equilibrium biosorption isotherms showed that biosorbent possess high affinity and sorption capacity for Cu(II) ions, with sorption capacities of 74.70 mg Cu^{2+} per 1 g biomass. Thermodynamic parameters such as free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) have been calculated on the basis of Langmuir constants. The results indicated that the rice straw could be an alternative for more costly adsorbents used for heavy metal removal.**

***Index Terms*—Biosorption, rice straw, biosorbent, wastewater treatment, heavy metal**

I. Introduction

Industrial wastewater is often characterized by considerable heavy metal content and, therefore, treatment is required prior to disposal in order to avoid water pollution. Heavy metal contamination exists in aqueous waste streams from diverse industries such as metal plating, mining, painting, wire drawing, batteries and printed circuit board manufacturing, as well as agricultural sources where fertilizers and fungicidal sprays are intensively used. Heavy metals, such as Cu, Zn, Pb and Cd, are prior toxic pollutants existent in industrial wastewater, while they also constitute common groundwater contaminants [1]-[2]. Copper ions (Cu^{2+}) are water-soluble, where they function at low concentration as bacteriostatic substances, fungicides, and wood preservatives. In sufficient amounts, they are poisonous to higher organisms, at lower concentrations it is an essential trace nutrient to all higher plant and animal life. The main areas where copper is found in animals are tissues, liver, muscle and bone. A variety of suitable methods can be used for the removal of metal pollutants from such liquid wastes, including filtration, chemical precipitation, coagulation, solvent extraction, electrolysis, ion exchange, membrane process and adsorption. Ion exchange and adsorption are the most common and effective processes for the removal of heavy metal ions [3]-[4]. From last few decades, biosorption process has emerged as a cost effective and efficient alternative for water and wastewater treatment utilizing naturally occurring and agricultural waste materials as biosorbents as these are cheaper, renewable and abundantly available [5]-[8].

Agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin, which includes alcohols, aldehydes, ketones, carboxylic, phenolic and ether groups. These groups have the ability to some extent to bind heavy metals by donation of an electron pair from these groups to form complexes with the metal ions in solution [9]-[10]. The removal of heavy metal ions using low-cost abundantly available adsorbents: agricultural wastes such as sawdusts, palm kernel husk, coconut husk, corncobs, apple wastes, tea leaves and different agricultural by-products were used and investigated [11]-[23]. Rice straw is one of the abundant lignocellulosic waste materials in the world. In terms of total production, rice is the third most important grain crop in the world behind wheat and corn. In terms of chemical composition, the straw predominantly contains cellulose (32-47%), hemicellulose (19-27%) and lignin (5-24%) [24]. The lignin is promptly available to interact with cations, by firstly exchanging with protons and subsequently by chelating with the metallic ion [25]. Rice straw has several characteristics to predict the functional groups on the surface of the biomass that make it a potential adsorbent with binding sites capable to tack up metals from aqueous solutions [26].

In this work, we attempt to use rice straw, which are discarded as waste material available on a farm, as an alternative low-cost biosorbent in the removal of copper (II) from aqueous solutions. Also the influence of various parameters such as contact time, initial concentration, pH and temperature on biosorption potential of agricultural waste material was studied in detail.

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II. Experimental Methods

A. Preparation of Biosorbent

Rice straw used as the biosorbent in this study was collected from a cultivated area near Nakhon Pathom city, Thailand. In a 500 mL, three-necked flask equipped with a nitrogen inlet, a condenser, a thermometer, and a stirrer, 224 g urea was added, heated at 140 ^{o}C and flushed with nitrogen. 30 g rice straw and 168 mL phosphorous acid were added alternatively portionwise to the molten urea in order to reduce the foaming. The reaction was allowed to proceed at 150 ^oC for 2 h. The fiber was washed with distilled water and acetone. A sample of fiber was treated with 0.5 M hydrochloric acid for 24 h under slow stirring. The modified cellulose was washed several times with deionized water to remove excess acid from biosorbent. It was dried for 24 h at 60 ^oC in an oven before starting the experiments.

B. Stock Solution Preparation

All chemicals used were analytical grade reagents (Merck, >99 %purity). Stock solutions of metals were prepared in a concentration of 2,000 ppm using nitrate salts dissolved in deionized water with a resistivity value of 17 MΩ. The chemicals used in the batch experiments was nitrate solutions of $Cu(NO_3)_2$.

C. Batch Adsorption Experiment

The influence of rice straw modification on Cu^{2+} uptake was investigated under the following experimental conditions; a volume of 100 mL of metal solution with biosorbent was placed in a beaker to start the experiments. Batch mode adsorption isotherm was carried out at 30-70 ^oC. Amount of 2.0 g modified cellulose were introduced into conical flasks with heavy metal solution. The flasks were placed in a thermostatic shaker and agitated for 30-180 min at a fixed agitation speed of 700 rpm. The influence of pH on the copper(II) adsorption was studied, varying the pH of solution from 1.0-11.0. The pH of metal solutions was appropriate adjusted by using HNO_3 or NaOH. Samples were taken periodically for measurement of aqueous phase of heavy metal concentrations. Adsorption isotherms were performed for initial heavy metal concentrations of 250-1,250 ppm. The Cu^{2+} concentration of the samples were determined by using a Varian Liberty 220 inductive coupled plasma emission spectrometer (ICP-ES).

The influence of a specific process parameter was determined by calculating Cu^{2+} uptake by rice straw and changing that parameter and keeping other parameters constant. The percent of metal ion removal was evaluated from the equation:

$$\%Removal = [(C_i - C_e)/C_i \times 100] \quad (1)$$

where C_i and C_e are the initial and final (equilibrium) concentrations of the metal ions in the solution (ppm)

The amount of adsorbed Cu^{2+} ions (mg metal ions/g biomass) were calculated from the decrease in the concentration of metal ions in the medium by considering the adsorption volume and used amount of the biosorbent:

$$q_e = \frac{(C_i - C_e)\,V}{m} \quad (2)$$

where q_e is the amount of metal ions adsorbed into unit mass of the biosorbent (mg/g) at equilibrium, V is the volume of metal solution (L) and m is the amount of biosorbent used (g).

D. Adsorption Isotherm Models

Adsorption isotherms for copper ions removal by rice straw in terms of Langmuir, Freundlich, Temkin and Dubinin- Radushkevich models were expressed mathematically. The obtained experimental data here are expectedly well fitted with the linearized form of four two-parameter isotherm models.

The Langmuir model assumes a monolayer adsorption of solutes onto a surface comprised of a finite number of identical sites with homogeneous adsorption energy. This model [27]-[28] is expressed as follows:

$$q_e = \frac{K_L a_L C_e}{1 + a_L C_e} \quad (3)$$

where K_L and a_L are the Langmuir constants related to the adsorption capacity (mg/g) and energy of adsorption (L/mg), respectively. The theoretical maximum monolayer adsorption capacity, q_m (mg/g), is given by K_L/a_L.

The Freundlich isotherm is an empirical expression that takes into account the heterogeneity of the surface and multilayer adsorption to the binding sites located on the surface of the sorbent. The Freundlich model [29] is expressed as follows:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F and n are indicative isotherm parameters of adsorption capacity (mg/g) and intensity, respectively.

Temkin isotherm assumes that decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies. Temkin isotherm [30] is expressed by the following equation:

$$q_e = \frac{RT}{b} \ln\,(K_{Te} C_e) \quad (5)$$

where K_{Te} is equilibrium binding constant (L/g), b is related to heat of adsorption (J/mol), R is the gas constant (8.314 x 10^{-3} kJ/K mol) and T is the absolute temperature (K).

Dubinin-Radushkevich isotherm is applied to find out the adsorption mechanism based on the potential theory assuming heterogeneous surface. Dubinin-Radushkevich isotherm [31]-[34] is expressed as follows:

$$q_e = q_m \exp\left(-K\varepsilon^2\right) \quad (6)$$

where q_m is the maximum adsorption capacity (mg/g), K is a constant related to the mean free energy of adsorption and ε is the Polanyi potential.

E. Adsorption Thermodynamics

Kinetic equations for the first order reversible and first and second order irreversible reactions are the equations most often used to describe the removal of heavy metal ions from polluted water by use of natural material [35]-[36]. To calculate values of the thermodynamic parameters describing the Cu^{2+} uptake by rice straw the following equations were used:

$$\Delta G^o = -RT \ln K \quad (7)$$

$$\Delta H^o = [RT_1T_2/(T_2 - T_1)] \ln (K_2/K_1) \quad (8)$$

$$\Delta S^o = (\Delta H^o - \Delta G^o)/T \quad (9)$$

where R is the gas constant, K, K_1 and K_2 are the equilibrium constants at the temperature T, T_1 and T_2, respectively.

The equilibrium constant was calculated from:

$$K = C_{e,s}/C_{e,l} \quad (10)$$

where $C_{e,s}$ and $C_{e,l}$ were the equilibrium concentrations of Cu^{2+} on the sorbent and in solution correspondingly.

III. Results and Discussion

A. Effect of Contact Time

Experiments conducted with different contact times show that the amounts of Cu^{2+} ions adsorbed per unit mass of rice straw increase with the contact time of metal ions (Fig. 1). It was observed that the biosorption of Cu(II) by rice straw was highly influenced by contact time. The kinetics of metal removal by biosorbent was relatively fast within 30 min and during the first hour was remarkably changed with time. At the equilibrium time the metal ion uptake of 82% for Cu(II) was achieved. The equilibrium time was taken as 120 min for further experimental measurements. Equilibrium time is a crucial parameter for an optimal removal of metal ions in the waste water. The increased uptake of metal ions with contact time can be due to the decreased mass transfer coefficient of the diffusion controlled reaction between the adsorbent and the metal ion [26],[37].

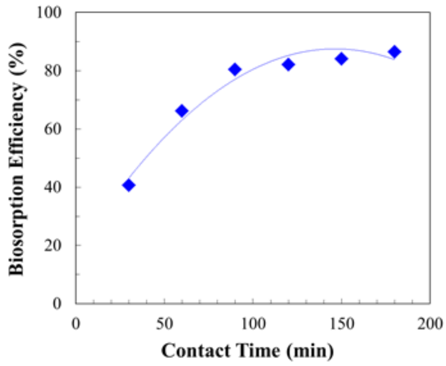

Fig. 1. Effect of contact time on the removal of Cu^{2+} ions onto rice straw (initial concentration = 500 ppm, pH = 5.38 and temperature = 30 °C).

B. Effect of Initial Concentration

Fig. 2 illustrates the biosorption of Cu^{2+} ions by rice straw as a function of initial metal ion concentration. This increase continues up to 500 ppm and beyond this value, there is not a significant change at the amount of adsorbed metal ions. This plateau represents saturation of the active sites available on the biosorbent samples for interaction with metal ions. It can be concluded that the amount of metal ions adsorbed into unit mass of the biosorbent at equilibrium (the adsorption capacity) rapidly increases at the low initial metal ions concentration and then it begins to a slight increase with increasing metal concentration in aqueous solutions in the length between 500 and 1,250 ppm. These results indicate that energetically less favorable sites become involved with increasing metal concentrations in the aqueous solution. The metal uptake can be attributed to different mechanisms of ion exchange and adsorption processes as it was concerned in much previous work [38]-[39].

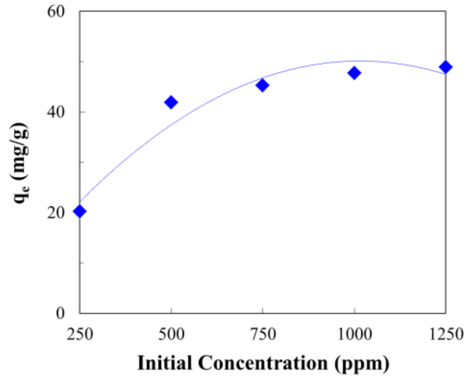

Fig. 2. Effect of initial concentration on the removal of Cu^{2+} ions onto rice straw (contact time = 120 min, pH = 5.38 and temperature = 30 °C).

C. Effect of pH

The pH dependence of Cu^{2+} biosorption onto rice straw is shown in Fig. 3. As it is seen in figure, q_e is low at low pH values. The value of q_e is increased by increasing the pH value and reaches a plateau at a pH value of 7.0 for copper(II). It is apparent that using solutions at pH values between 9.0 and 11.0 gives the highest q_e values due to the precipitation occurs during ion exchange experiments by NaOH. So, this metal ion adsorption process cloud not carried out only at a certain pH value, but also in a wide range of pH values. These results are in agreement with several previous investigations on metal removal by a variety of materials [40]-[41]. It revealed that the adsorption capacity is low at pH values below 5.0 because of the competition between the protons (H^+) and metal ions (Cu^{2+}) for the exchange sites on the biosorbent. So, increased external H^+ concentration (due to lowered pH) may have effected metal ion removal via ion exchange by direct competition effects between the protons and metal ions for the exchange sites on the rice straw.

D. Effect of Temperature

The effect of the solution temperature on the adsorption capacity was investigated for Cu(II) ions solutions at initial concentration 500 ppm and amount of biosorbent 2.0 g. Five different temperatures of 30, 40, 50, 60 and 70 ℃ were considered. From Fig. 4, the amounts of adsorbed copper onto the rice straw increase with an increase in the temperature of heavy metal solution. Raising the temperature from 30 to 70 °C reduces the amounts of metal ions in solution 78.84%. The maximum adsorption capacity was calculated as 74.70 mg Cu^{2+}/g biomass. These results indicate that adsorbent was suitable for heavy metals removal from aqueous media and the adsorption of Cu(II) ions is endothermic in nature [37]-[38].

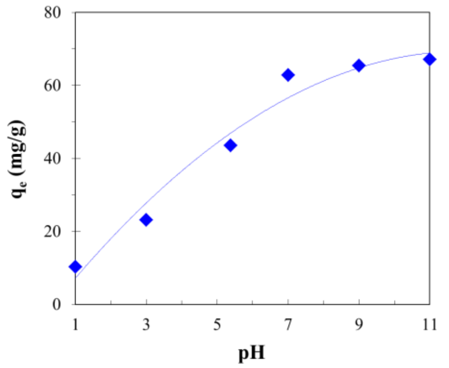

Fig. 3. Effect of pH on the removal of Cu^{2+} ions onto rice straw (initial concentration = 500 ppm, contact time = 120 min and temperature = 30 °C).

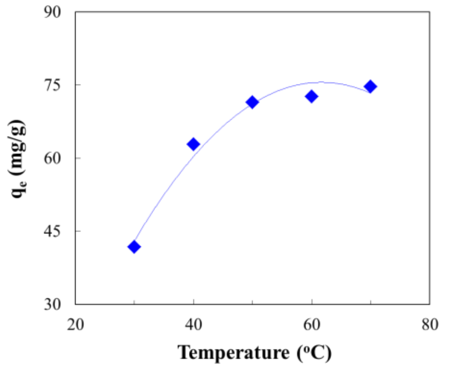

Fig. 4. Effect of temperature on the removal of Cu^{2+} ions onto rice straw (initial concentration = 500 ppm, contact time = 120 min and pH = 5.38).

E. Isotherm of Biosorption

In addition to the experimental data, the linearized forms of Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms using Eqs. (3), (4), (5) and (6), are compared. The isotherm constants and corresponding correlation coefficients for the biosorption of Cu^{2+} is presented in Table I. The correlation coefficients demonstrate that Langmuir, Freundlich and Temkin models adequately fitted the data for Cu(II) adsorption. However, the coefficient of determination (R^2) values is higher in the Freundlich model for copper adsorption when compared to other models [34],[42]. The experimental data for heavy metal ions fit well with the linearized Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. R^2 values ranged from 0.8601 to 0.9961 for adsorption of Cu^{2+}. These results indicated that the equilibrium biosorption data of copper conformed reasonably well to the four two-parameter isotherm models equations.

F. Thermodynamic of Biosorption

Thermodynamic parameters for the process of Cu^{2+} uptake by rice straw are presented in Table II. Values found for ΔG°, ΔH° and ΔS° are indicative of the spontaneous nature of the uptake process. The increase of the equilibrium constant with increasing temperature and positive values obtained for ΔH° show the endothermic nature of Cu^{2+} uptake. Results obtained in our experiments generally agree with the results previously found for the uptake of heavy metal ions by natural materials [38].

TABLE I: ISOTHERM CONSTANTS FOR THE BIOSORPTION OF COPPER(II) IONS ON RICE STRAW.

Isotherm constants	
Langmuir model	
K_L (mg/g)	12.4720
a_L (L/mg)	0.2216
R^2	0.9951
Freundlich model	
K_F (mg/g)	3.5785
n	2.9585
R^2	0.9961
Temkin model	
K_{Te} (L/g)	2.6547
b	1.0379
R^2	0.9942
Dubinin-Radushkevich model	
q_m (mg/g)	9.3877
K	0.6401
R^2	0.8601

TABLE II: THERMODYNAMIC PARAMETERS FOR THE BIOSORPTION OF COPPER(II) IONS ON RICE STRAW.

Temperature (K)	Biosorption Efficiency (%)	K (-)	ΔG° (J/mol)	ΔH° (J/mol)	ΔS° (J/mol.K)
303	42.43	0.62	-13,661	2,708	57.41
313	64.81	1.19	-14,403	2,722	57.55
323	74.90	1.71	-15,331	2,807	57.73
333	88.52	8.98	-16,323	2,953	57.86
343	97.11	95.21	-17,004	-	-

IV. CONCLUSION

Rice straw is an environmentally friendly potential biosorbent for heavy metals. This work examined the efficiency of this sorbent in removal of Cu^{2+} ions from aqueous environment. The results indicated that several factors such as contact time, initial concentration, pH and temperature affect the biosorption process. The physico-chemical characteristics of wastewaters from varying sources can be much more complex compared to the aqueous metal solution used in this study. Because of this, the effects of other components of wastewaters on commercial metal adsorption process should be determined. However, this work can be considered a preliminary study to conclude that rice straw is suitable and efficient material for the adsorption of Cu^{2+} from aqueous solution. The experimental results were a good fit with the adsorption isotherm models.

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