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# Removal of Cu(II) from Industrial Effluents by Citric Acid Modified Rice Straw

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History	Abstract
Received: 29 January 2014 Received in revised form: 27 February2014 Accepted: 19 March 2014 Available online: 15 April 2014	The aim of the present study was to convert rice straw, a by-product of rice production to a metal adsorbent and investigate the potential of using the adsorbent for the removal of Cu (II) ions. The rice straw was modified with citric acid (CA) to enhance its nature's adsorbition canacity. Batch adsorbition studies of Cu
<b>Keywords</b> Adsorption, citric acid, rice straw, copper ions, wastewater	(II) adsorption were carried out under various operating conditions, and found to be pH, initial adsorbate concentration, contact time, and temperature dependent. Experimental data were analyzed using the Langmuir and Freudlinch isotherm models, and can be well described by the Langmuir isotherm model that supports the assumption that adsorption takes place by single layer on homogeneous surfaces. Kinetic studies indicated that pseudo-second-order kinetic equation provides better data correlation than pseudo-first-order kinetic model. Thermodynamic studies show that the standard Gibbs free energy of the process at all temperatures was negative and changed with temperature increase, indicating spontaneous processthat increases with temperature. CA modified rice straw (CARS) shows a considerable potential as a low-cost and highly efficient biomaterial to be a new single-use adsorbent for Cu (II) ions removal from wastewater.

## INTRODUCTION

Heavy metal removal from wastewater is important for the protection of the environment and health. The presence of elevated concentrations of heavy metals such as copper, cadmium, lead, zinc, nickel, and chromium in rivers, lakes, seawater and other natural waters poses toxic hazards to plants and animals and potentially to human health [1, 2]. Heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. Copper is essential to human life and health, but like all heavy metals, is potentially toxic as well [3]. Drinking water that contains higher than normal levels of copper may cause vomiting, diarrhea, stomach cramp and nausea, whereas the chronic effects of high levels of copper are liver and kidney damage [4].

Copper has widespread industrial applications; thereby large quantities of copper-bearing wastewater are generated. It is therefore, essential to provide a systematic discharge method to preserve the environment from copper contamination. Treatment processes for metal-contaminated waste streams include chemical precipitation, membrane filtration, ion exchange, and carbon adsorption [5]. Currently, the major methods for industrial wastewater treatment involve physical and also chemical proces [6]. However, the high cost has limited its use in the real treatment, thus innovative methods for heavy metals removal should be investigated in an ongoing effort to develop a better and economic treatment for wastewaters containing these toxic substances.

The search for low-cost and abundantly available adsorbents has led to the investigation of materials of agricultural and biological origin, as well as industrial by-products. Agricultural by-products are high in volume, low value and underutilized lignocelluloses biomaterials, containing high levels of cellulose, hemicelluloses and lignin [7]. Rice (Oryza sativa) straw is one of the abundant lignocelluloses waste materials in the world. The estimation of annual production of rice by Food and Agriculture Organization (FAO) points to about 600 million tons per year in 2004. On the other hand, every kilogram of grain harvested is accompanied by production of 1 to 1.5 kg of rice straw [8]. This rice straw can cause a lot of environmental problems since it exists with enormous quantities and is not easy to handle or transport. Therefore, direct open burning in the fields is a common option for disposal that causes serious air pollution. Hence, new economical methods for rice straw disposal and utilization must be developed. This is where this research comes into picture, where the utilization of rice straw, a by-product of rice production which is available in abundance in Malaysia, as adsorbents in the adsorption of copper will be an alternative economical treatment method. On the other hand, citric acid (CA) treatment which is often used as the adsorbent activating agent for adsorption of copper from aqueous solution is a low cost chemicals extensively used in the food industry. Derivative corn

by-products with CA indicated considerable improvement in Cu(II) binding [9].

#### MATERIALS AND METHODOLOGY

#### Chemicals

All primary chemicals use was of analytical grade obtained from Merck and Sigma-Aldrich. Copper sulphate, citric acid, sulphuric acid and sodium hydroxide were used without further purification. The aqueous solution was prepared with distilled water.

### **Adsorbent Preparation**

The adsorbent used in this research was derived from rice straw, obtained from local rice plantation in Perlis and treated with CA as in Zhu et al. (2008) for the treatment of raw soybean straw to adsorb Cu(II) ions from aqueous solutions [10]. Rice straw was cut into segment and washed thoroughly with water, and then dried in an oven at 50 °C until constant weight was achieved. The dried straw segment was then milled and sieved to retain the 150 to 300 µm fractions for further pretreatments. For treatment, the rice straw was mixed with 0.6 M CA, and after being stirred, the acidic straw slurries were placed in a stainless steel tray and dried at 50 °C in a forced air oven. After 24 hours, the thermo-chemical reaction between acid and straw was preceded by raising the oven temperature to 120 °C for 90 min. After cooling, the reacted products were washed with distilled water to remove excess CA. Lastly it was dried and cooled down in a desiccator until constant weight was achieved.

#### **Adsorbent Characterization**

The physical characteristics of CA modified rice straw (CARS) were determined by the well-known method, i.e. the American Society for Testing and Materials (ASTM) standard test methods for apparent density, moisture and ash content, whereas particle size analysis were done by using a standard sieve. The morphological characteristics of adsorbent, before and after the adsorption were observed using Scanning Electron Microscope (SEM) (model JOEL/JSM 6460LA) with 15 kV acceleration voltage and 10 µm working distance.

#### **Batch Adsorption Method**

Batch adsorption tests were conducted at room temperature to obtain the Cu(II) removal, its adsorption rate and equilibrium data. The 250 mL conical flasks, each filled with 100 mL of copper solutions were utilized in all batch experiments to investigate changes in pH, initial concentration, contact time, and temperature. The pH test was carried out using 5 conical flasks; each was adjusted using sulphuric acid or sodium hydroxide solution to obtain desired initial pH in the range of 2 to 6. To study the effect of initial concentration and contact time, experiments were carried out using 6 sets of 12 conical flasks, each filled with copper sulphate solutions at initial Cu(II) concentration of 1, 2, 5, 10, 15 and 20 mM. The flasks were removed from the shaker for analysis one after another at 10, 20, 40, 60, 90, 120, 150, 180, 210, 240, 270 and 300 minutes. Three different sets of sample were agitated at three different temperatures (i.e. 301, 311 and 321K) to assess the effect of

temperature on adsorption equilibrium. The contact time allowed for each flask; filled with 0.5 g adsorbent and 100 mL of adsorbate was 2 hours. After being agitated, the supernatant was filtered out using filter paper. Following filtration, the filtrate was then analyzed using Atomic Adsorption Spectrometer (AAS) (model Perkin Elmer AAnalyst 700) for final Cu(II) concentrations. The calibration curves were determined several times within the period of analysis.

## **RESULTS AND DISCUSSION**

#### **Adsorbent Characterization**

Table 1 illustrates the values of apparent density, moisture content, total ash content and particle size of CARS. Higher density provides greater volume activity and normally indicates better quality adsorbents. Moisture content affects the ability of the adsorbents to perform against certain gases and vapours, and was reported as a percent by weight. The ash contents are generally not desirable and considered as an impurity as it reduces the overall activity of adsorbent and efficiency of reactivation.

Table 1. Sciected physical properties of CAR	Table	1:	Selected	physical	properties	of	CARS
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Parameters	Values	ASTM test standard
Apparent density (g/cm <sup>3</sup> )	0.2314	D2854-96
Moisture content (%)	15.68	D2867-04
Ash content (%)	7.38	D2866-94
Particle size (µm)	150-300	

Figure 1 shows the SEM images of raw rice straw and CARS at 2,000 times magnification. Both of the samples are clearly porous, with pores of varying sizes. The raw rice straw exhibits rigid and highly ordered fibrils, while the fibres of CARS appear to be separated from the initially connected structure and are fully exposed. This increases the external surface area and the porosity of the materials. Comparison of the micrographs reveals that CA modification significantly changes the morphology of the raw rice straw surface structure. Its heterogeneous characteristics can then facilitate the adsorption of Cu(II) ions onto different sites on the material surfaces.





Figure 1: SEM micrographs of rice straw: (a) raw, (b) CARS

#### **Initial pH Setting**

The experiments were carried out at pH values below the pH where copper hydroxide chemical precipitation occurs, which has been estimated at pH less than 6.3 [11]. The uptake and removal efficiency of Cu(II) from aqueous solution were strongly affected by initial pH of the solution as illustrated by Figure 2. The Cu(II) adsorption capacities were minimized at an initial pH of 2, and gradually increased as the initial pH values were increased from pH 2 to 5.



Figure 2: Effect of pH on Cu(II) adsorption onto CARS

For CARS, its practical functional group is carboxyl group and the  $pK_a$  value of the carboxyl group is about 3. When the pH is less than 3, the non-ionic form of carboxyl group, –COOH predominates, thereby the efficiency of Cu(II) adsorption will be reduced by the absence of electrostatic interaction. Vice versa, when pH is higher than 3, the carboxyl group is ionized into –COO<sup>-</sup>, thus Cu(II) adsorption is profoundly enhanced [12]. This may be due to the fact that pH strongly influences not only the active sites on the surfaces of adsorbents, but also the speciation and the bioabsorption availability of the heavy metals.

#### Initial Cu (II) Concentration and Contact Time

Figure 3 illustrates the effect of initial concentration and contact time on the uptake and removal efficiency of Cu(II) from aqueous solution. Figure3 shows that the adsorption of Cu(II) at different initial concentrations increases with contact time until equilibrium is reached. It can be seen that the adsorption rate is rapid during the first 20 minutes regardless of the initial Cu(II) concentration.

Within the next 60 to 120 minutes, the adsorbent capacity becomes saturated and the curve is flattened.



Figure 3: Effect of initial concentration and contact time on Cu(II) adsorption onto CARS

Initially, the adsorption sites were unoccupied, and Cu(II) ions could easily interact with the adsorbent sites and hence a higher rate of adsorption was observed. Besides, the driving force for adsorption, the concentration difference between the bulk solution and the solid-liquid interfaces, is higher initially, resulting in a higher adsorption rate [10]. After the initial period, slow adsorption rates can be observed, possibly due to slower diffusion of solute into the interior of the adsorbent [13]. After the adsorbed materials forms a molecule of thick layer, the capacity of the adsorbent becomes exhausted and then the uptake rate was controlled by the rate at which the adsorbent is transported from the exterior sites of the adsorbent particles [14].

#### **Temperature Studies**

Figure 4 shows that the uptake and removal efficiency of Cu(II) from aqueous solution increase with increasing temperature. Temperature may influence adsorption by the formation of some active sites or by an increase of the diffusion rate of metal ions from the bulk solution to the surface of adsorbent [15]. Further, it is clear that the adsorption was endothermic in nature, where increasing temperature enhanced the value of adsorption capacity. The result is typical for adsorption of most metal ions from their solutions as temperature increment commonly increases the mobility of metal ions.



Figure 4: Effect of temperature on Cu(II) adsorption onto CARS

### **Adsorption Isotherms**

The Langmuir and Freundlich isotherms were employed to describe the adsorption equilibrium. Theoretically derived Langmuir model assumes adsorption energies are uniform and independent of surface coverage and complete coverage of the surface by a monolayer of adsorbate indicates maximum adsorption. On the other hand, Freundlich model is an empirical equation that supports the heterogeneity of the adsorbent surface, the exponential distribution sites and their energies [16]. The linear form of Langmuir and Freundlich isotherm is expressed as the following:

$$\frac{1}{q_e} = \frac{1}{Q_0} + \frac{1}{Q_0 b C_e}$$
(1)
$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$
(2)

Where  $q_e$  is the amount of Cu (II) adsorbed per unit weight of adsorbent (mg/g) and  $C_e$  is the equilibrium concentration of Cu (II) in solution (mg/L). The values of Langmuir and Freundlich constants were obtained from the linear correlation plots between the values of  $1/q_e$  versus  $1/C_e$  and  $\ln q_e$  versus  $\ln C_e$ . Table 2 show the respective Langmuir and Freundlich constants for Cu (II) adsorption onto CARS.

Table 2: Adsorption parameters for Cu (II) adsorption onto CARS using Langmuir and Freundlich isotherm models

Langmuir isotherm				
$Q^{o}(\text{mmol/g})$	b	$R^2$		
8.9366	0.1100	0.9797		
Freundlich isotherm				
$K_f$ (mmol/g)	n	$R^2$		
0.8663	1.2024	0.9402		

Based on the high correlation coefficients,  $R^2$  presented in Table 2, it is concluded that the adsorption data of Cu(II) ions onto CARS could be described by both models. The adsorption data shows slightly better fit to Langmuir model with only slightly higher  $R^2$  value. This suggests that the adsorption data of Cu(II) ions onto CARS can be well represented by Langmuir isotherm model and support the assumption that adsorption takes place on homogeneous surfaces [17]. The model considers that the adsorption energy of each molecule is the same, independently of the surface of the material, and the adsorption takes place only on some sites and there are no interactions between the molecules [18]. The  $Q^o$  value, as listed in the same table, is indicative of the relative adsorption capacities of CARS for Cu(II) removal from aqueous solutions.

#### **Adsorption Kinetics**

The pseudo-first-order and pseudo-second-order models can be generally respectively expressed as:

$$\ln(q_{e} - q) = \ln(q_{e}) - k_{1}t$$
(3)
$$\frac{t}{q} = \frac{1}{k_{2}q_{e}^{2}} + \frac{1}{q_{e}}t$$
(4)

Where qe is equal to the amount of solute adsorbed at equilibrium per weight of adsorbent (mg/g), q is the amount of solute adsorbed at time t per unit weight of adsorbent (mg/g) and k'1, k'2are constants. Higher correlation coefficients, R2 values as presented in Table 3 indicate that the pseudo-second-order kinetic provides better data correlation than pseudo-first-order kinetic model for Cu(II) adsorption onto CARS. The fit of experimental data to this kinetic model suggests that the process controlling the rate may be a chemical adsorption involving the valence forces through sharing or exchange of electron between adsorbent and adsorbate [19].

Table 3: Comparison between pseudo-first-order and pseudosecond-order reaction rate constants and correlation coefficients for Cu (II) adsorption onto CARS at different initial concentration

Pseudo-first-order kinetic model				
Initial Cu(II)	$k'_{l}$ (min <sup>-1</sup> )	$R^2$	$\Delta q$ (%)	
concentration (mM)				
2	0.0401	0.6458	0.70	
5	0.0270	0.7951	0.78	
10	0.0332	0.9506	0.70	
15	0.0333	0.6460	0.73	
20	0.0322	0.6150	0.73	
Pseudo-second-order kinetic model				
Initial Cu(II)	$k'_2$ (g mol	$R^2$	$\Delta q$ (%)	
concentration (mM)	$\min^{-1}$ )			
2	6.8655	0.9999	0.28	
5	1.8783	0.9998	0.27	
10	0.2183	0.9997	0.25	
15	0.8553	0.9999	0.28	
20	0.3143	0.9990	0.27	

In order to quantitatively compare the applicability of the two solid-phase kinetic models; i.e. pseudo-first-order and pseudo-second-order, a normalized standard deviation  $\Delta q$  (%) is calculated [20].

$$\Delta q(\%) = 100 \times \sqrt{\frac{\sum [(q_{\exp} - q_{cal})/q_{\exp}]^2}{n-1}}$$
(5)

where *n* is the number of data points. Based on the values of normalized standard deviation,  $\Delta q$  of each model presented in Table 3, it can be clearly seen that the adsorption kinetics follow the pseudo-second-order model. This result agrees with the  $R^2$ values obtained earlier and proves that the adsorption of Cu(II) adsorption onto CARS could be best described by the pseudo-second-order model that predicts the behaviour over the whole range of studies, strongly supporting the validity and agrees with chemisorption as rate-controlling mechanism [21].

### **Adsorption Thermodynamics**

The thermodynamic parameters of the adsorption, i.e. the standard Gibbs free energy ( $\Delta G^0$ , kJ/mol), enthalpy change ( $\Delta H^0$ , kJ/mol), and entropy change ( $\Delta S^0$ , J/mol K) can be calculated according to the following equation:

$$\ln K_{c} = \frac{\Delta S^{0}}{R} - \frac{\Delta H^{0}}{RT}$$
(6)  

$$\Delta G^{0} = -RT \ln K_{c}$$
(7)  

$$\Delta G^{0} = \Delta H^{0} - T\Delta S^{0}$$
(8)  

$$K_{c} = \frac{q_{e}}{C_{e}}$$
(9)

where the universal gas constant, R equals to 8.314 J/mol K, standard thermodynamic equilibrium constant,  $K_c$  defined by  $q_c/C_e$  and T is the temperature in K. The values of enthalpy change and entropy change were determined from the slope and intercept of the linear Vant't Hoff plots of  $\ln q_e/C_e$  ( $\ln K_c$ ) versus 1/T for each different initial concentration. The average values of enthalpy change and entropy change, was applied to calculate the standard Gibbs free energy as presented in Table 4 for adsorption of Cu(II) onto CARS. The average standard Gibbs free energy of the process at all temperature was negative and changed with the rise in temperature. This indicates that the process is spontaneous in the nature of the adsorption increases with temperature.

The positive values of enthalpy change suggest that the adsorption process is endothermic in nature, while the positive value of entropy change shows the trend of system to equilibrium and may suggest some changes on surface structure of CARS. The enhancement of adsorption at higher temperature may be attributed to the enlargement of active sites on the CARS surfaces. When the ions areadsorbed at the surface of adsorbents, water molecules that were previously bounded to the metal ions are released and dispersed in the solution, resulting to an increase in the entropy change [18].

Table 4: Thermodynamic parameters for Cu (II) adsorption onto CARS at different initial concentrations

Temperature (K)	$\Delta G^0$ (kJ/mol)	$\Delta H^0$ (kJ/mol)	$\Delta S^0$ (J/mol K)
301	-0.12		
311	-0.83	21.35	71.32
321	-1.54		

#### CONCLUSION

Rice straw, a by-product of rice production which abundantly available in the country can be utilized as low-cost adsorbents in the removal of Cu(II) ions from aqueous solutions. Simple chemical modification using CA and heat treatment enhances the adsorption capacity, thereby preserving the economical aspects of the treatment. The adsorption equilibrium can be well described by Langmuir isotherm model and support the assumption that adsorption takes place on homogeneous surfaces. Kinetic studies indicates that the pseudo-second-order kinetic equation provides better correlation data than pseudo-first-order kinetic model, and this result agrees with the values of normalized standard deviation,  $\Delta q$  of each model.

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