

# Copper Metal Removal using Sludge Activated Carbon Derived from Wastewater Treatment Sludge

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**Abstract.** In Malaysia, according to perspective sludge production factor (SPF), wastewater treatment plants produces about 5.3 million m<sup>3</sup> of sewage sludge annually, most of this sludge are being wasted (unused) in the landfills. This study employed the use of dry activated sludge as low-cost adsorbent for the removal of copper Cu (II) from wastewater. Adsorption of Cu (II) by sludge activated carbon (SAC) was conducted using batch tests. The effect of contact time and adsorbent dosage on the removal of Cu (II) from wastewater were investigated. Initial metal concentration was maintained at 100 mg/L. The removal efficiency was found to have relations with the initial Cu (II) concentration, contact time as well as the SAC dosage. The adsorption kinetics of the Cu (II) by SAC was found to follow pseudo-second-order kinetic model, indicating chemisorption process. The adsorption isotherms studies indicated that the adsorption of Cu (II) by SAC adsorbent was well described by Langmuir isotherm model having correlation of determination ( $R^2$ ) value of 0.9985 at 12hrs equilibrium period. Optimum conditions for Cu (II) removal was achieved at SAC dosages of 10 g/L, contact time 12 hours and at initial Cu (II) concentration of 100 mg/L, respectively. The study indicated that sludge activated carbon can be used as an adsorbent for the removal of Cu (II) from aqueous solution.

## 1 Introduction

In recent years, there has been a tremendous interest in the bio-adsorption approaches, from dry activated sludge which involving the process of converting sludge into dry activated carbon which are efficient in removing heavy metals from aqueous solutions. The level of water contamination is one of the key topics that have attracted much attention globally.

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Activated carbon is a carbonaceous adsorbent with a highly developed porous structure. Its effectiveness in removing pollutants through adsorption concept process has been found superior to many other techniques because of the high quality of the effluent achieved, simplicity of design, ease of operation and insensitivity to toxic substances. The mechanisms of surface adsorption are based upon physical and chemical interactions between metal and activated carbon surface and they are much more dynamic than assumed in the equilibrium models (Flouty and Estephane, 2012). With growth development in the country, the volume of wastewater generated increase annually and the volume of sludge produced from wastewater treatment process are proportionately increased. This initiate so much worries to communities in Malaysia, based on perspective sludge production factor (SPF), about 5.3 million m<sup>3</sup> of excess sludge is produced annum, this comprises of sludge produced from domestic and sewage companies such as households, universities hostels, Indah Water Konsortium (IWK), respectively. Most of this sludge is being wasted in the landfill. Activated sludge is an effective biomaterial for biosorption or bioleaching of the metal ions such as Cu (II) from wastewater.

The removal of heavy metals from wastewater using activated sludge is highly efficient and has low installation, operation and maintenance costs (Buyukgungor and Gurel, 2009; Gavrilescu, 2004; Hussein et al., 2005). The aim of the present research was to investigate biosorption of Cu (II) ions by sludge activated carbon (SAC). Effects of contact time and SAC dosage on biosorption of Cu (II) ions were studied.

## **2 Materials and method**

### **2.1 Preparation of the Adsorbent**

Sludge was obtained from sludge drying bed of sewage treatment plant (STP) of Universiti Teknologi PETRONAS, Malaysia. The sludge was manually grinded to an average size of 5 cm. The sludge was dried in an oven at 105°C for 24 hours until all moisture evaporated and a constant weight was achieved. About 10 g of the dried sludge was weighed and incinerated in a tube furnace at a temperature of 500 °C for a period of 3 hours. Heating rate of 10 °C/min and nitrogen flow rate of about 100 mL/min was maintained during the production process. The resulting sludge activated carbon (SAC) was crushed and sieved into powder size of about 150 µm. The SAC powder was stored in a desiccator before use.

### **2.2 Preparation of the Adsorbate**

A stock solution was prepared by dissolving calculated weigh of copper (II) chloride salt in 1L of distilled water to give a concentration of 1000 mg/L. To obtain further required concentrations, the stock solution was diluted appropriately. The chemical employed are of analytical grade, obtained from Merck (Germany).

### **2.3 Batch Experiments**

Batch adsorption experiments were carried out using SAC as adsorbent. A 100 mL synthetic copper (II) solution with predetermined metal ion concentrations was placed in a series of 250 mL Erlenmeyer flasks. The flasks were agitated using an orbital shaker (Protech Model 722) at 150 rpm at room temperature (25 ± 1°C). At the end of scheduled agitation times, the mixtures were separated using Whatman's glass microfiber filters paper (GF/C). Filtered solutions were analysed for residual copper (II) concentration using a spectrophotometer (DR 2800 Hach).

## 2.4 Analytical Methods

Adsorption experiments were conducted to study the effect of initial copper concentration and contact time. The experiment was conducted by placing 0.5, 1.0, 2.5, 5.0, 7.5 and 10.0 g/l of SAC into series of 250 ml Erlenmeyer flasks. A 100 ml of synthetic copper solutions was measured and added into the flasks. The flasks were clamped in an orbital shaker and agitated for 3, 6, 8, 12 and 24 hours, respectively. The agitation speed was maintained at 150 rpm throughout the study. The tests were run in triplicates at metal concentrations of 100 mg/l. At the end of the predetermined interval of time, samples were removed from the shaker and analyzed for residual copper concentration until equilibrium was attained. Equations (1) and (2) were used to compute the metal adsorption efficiency and adsorption capacity of SAC.

$$R = \frac{(C_i - C_e)}{C_i} \times 100\% \tag{1}$$

where, R is the copper removal efficiency (%),  $C_i$  is the initial copper concentration and  $C_e$  is the residual copper (mg/L) concentrations at equilibrium.

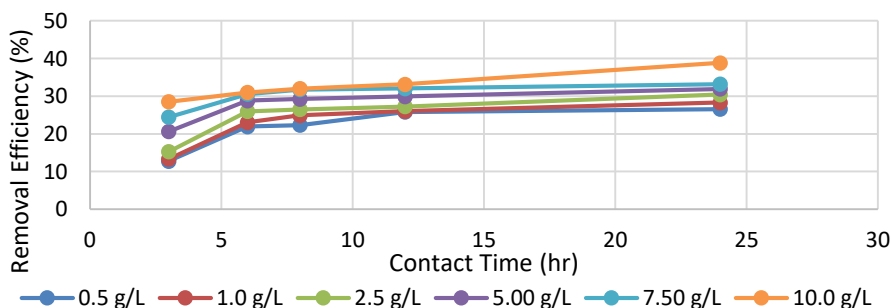
$$Q_c = \frac{(C_i - C_e)}{W} V \tag{2}$$

where,  $Q_c$  is the adsorbent adsorption capacity (mg/g),  $C_i$  is the initial copper concentration and  $C_e$  the residual concentration copper (mg/L) at equilibrium, V is volume of aqueous Copper solution (L) and W mass of SAC (g).

## 3 Results and Discussions

### 3.1 Effect of Contact Time

The equilibrium contact time is an important parameter for adsorption process. In order to determine the effect of contact time, biosorption was performed for 3, 6, 8, 12 and 24 h. Fig. 1 demonstrates contact time effects on biosorption of Cu (II) onto SAC. Removal efficiency rapidly increased during the initial adsorption stage and reached to 32% when contact time was 8 h. The removal efficiency gradually increased with contact time and equilibrium was reached after 12 h for the rest of the dosage. At initial stage, adsorption of Cu (II) onto monolayer surface of SAC may explain the rapid increase in removal efficiency. After that the monolayer surface was saturated, the Cu (II) ions were gradually adsorbed into the inner part of SAC with diffusion; therefore lower biosorption rate was obtained.



**Fig. 1.** Removal Efficiency vs Contact Time

### 3.2 Effect of SAC dosage

Effect of SAC dosage on the removal of Cu (II) at 100 mg/L concentration was also investigated. Fig. 2 shows the removal of Cu (II) at different SAC dosage. Residual copper concentration decreases with an increase in SAC dosage until equilibrium removal was attained. With the increased in adsorbent dosage, more surface areas are available for the adsorption of metal ions.

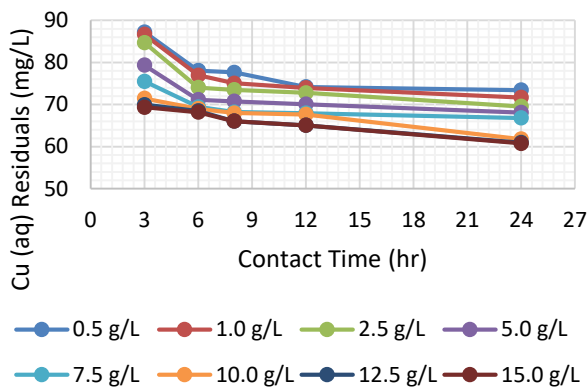


Fig. 2. Removal Copper (aq) Residual vs Contact Time at different dosages of SAC

### 3.3 Adsorption Isotherm

The relationship between adsorbate concentration and its degree of adsorption onto the surface of the adsorbent at a fixed temperature is mainly established by adsorption isotherm studies. In this study, Langmuir and Freundlich isotherm models were used to measure the adsorption capacity of SAC for removal of Cu<sup>2+</sup> from aqueous solution.

Langmuir model is a frequently used model which describes heavy metals sorption onto biosorbent. Langmuir model operates based on three distinct assumptions viz; that all surface sites are the same and can occupy one adsorbed atom, it is limited to monolayer coverage adsorption and capability of a molecule adsorbed at a given site is not dependent on the occupancy of its adjoining sites. Langmuir model is valid for monolayer adsorption containing finite number of identical biosorption sites. In this case interaction between adsorbate particles is negligible. The Langmuir model is given by the following equation (Langmuir, 1918):

$$\frac{C_e}{A_q} = \frac{1}{b_L q_m} + \frac{C_e}{q_m} \quad (3)$$

where  $A_q$  is the quantity of pollutant adsorbed per gram of adsorbent (mg/g),  $b_L$  is the Langmuir constant for equilibrium,  $q_m$  is the adsorbate quantity that is required for a monolayer formation and  $C_e$  is the concentration of residual metal at equilibrium (mg/L). Thus, plot of  $C_e/q_e$  against  $C_e$  will be a straight line with a slope of  $1/q_m$  and intercept of  $1/b_L q_m$  [31]. This important characteristic of the Langmuir isotherm can be expressed in terms of a dimensionless factor,  $R_L$  [44], which is defined as

$$R_L = \frac{1}{1 + b_L q_m} \quad (4)$$

The  $R_L$  values indicate the type of adsorption as either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ), or irreversible ( $R_L = 0$ ).

The equilibrium data were analyzed using the linearized form of Langmuir adsorption isotherm Eq. (3). Langmuir constants and monolayer biosorption capacity  $q_m$  were calculated from the slope and intercept of the plot  $C_e/A_q$  versus  $C_e$  (Fig. 3). The Langmuir isotherm constants are shown in Table 1.

Freundlich isotherm model is a commonly used model for describing adsorption equilibrium based on empirical equation. Freundlich isotherm model have the ability of unfolding adsorption related to both organic and inorganic composites on a wider range of adsorbents inclusive of biosorbent. The Freundlich isotherm model is employed to describe heterogeneous surfaces that represents the binding sites are not equivalent and/or independent. This model considers repulsive interactions between adsorbed solute particles (Freundlich, 1906; Sinha et al., 2012). Freundlich equation is given as follows:

$$\log A_q = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

where  $\log A_q$  is the quantity of the adsorbed pollutant per gram of the adsorbent (mg/g),  $C_e$  is the equilibrium concentration (mg/L),  $K_F$  and  $n$  are Freundlich constants. Plot of  $\log A_q$  against  $\log C_e$  has  $1/n$  as slope and  $\log K_F$  as its intercept.

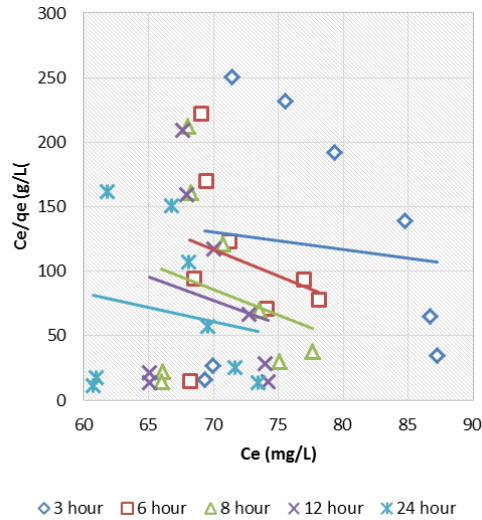
As shown in Fig. 4, the plot of  $\log q_e$  versus  $\log C_e$  was fitted linearly for Freundlich isotherm model. Freundlich isotherm parameters,  $K_F$  and  $1/n$  were calculated from the slope and intercept of linear plots of  $\log q_e$  and  $\log C_e$  (Fig. 4).

Table 1 shows the coefficient values obtained from the plots of both Freundlich and Langmuir isotherm models on the adsorption of  $Cu^{2+}$  onto SAC adsorbent.

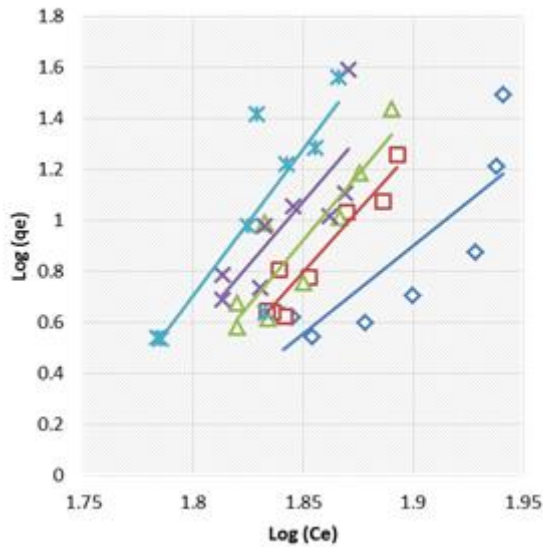
From Table 1, it can be seen that the coefficients of determination  $R^2$  values from the Langmuir isotherm are higher compared with Freundlich isotherms. This suggests that the experimental data obtained from SAC follows Langmuir isotherm model compared to Freundlich isotherm model. This indicates the monolayer coverage of  $Cu^{2+}$  ions on the homogeneous surface of SAC. The Freundlich intensity values are in the range of 0.0874 to 0.1036; this indicates a favorable type of adsorption.

**Table 1.** Freundlich and Langmuir isotherm for  $Cu^{2+}$  adsorption

Freundlich					Langmuir			
Hour	n	$K_F$	$R^2$	Equation	$q_m$	$R^2$	$R_L$	Equation
3	0.1445	$5.728 \times 10^{-3}$	0.7099	$y = 6.9181x - 12.242$	0.755	0.997	0.0107	$y = -1.3245x + 222.73$
6	0.1036	$8.770 \times 10^{-3}$	0.9142	$y = 9.652x - 17.057$	0.2445	0.989	0.0638	$y = -4.0883x + 402.62$
8	0.0977	$9.550 \times 10^{-2}$	0.7954	$y = 10.24x - 18.02$	0.253	0.967	0.0545	$y = -3.953x + 362.78$
12	0.0992	$2.630 \times 10^{-2}$	0.6714	$y = 10.085x - 17.58$	0.2708	0.988	0.0339	$y = -3.6925x + 335.67$
24	0.0874	$1.274 \times 10^{-2}$	0.6969	$y = 11.447x - 19.895$	0.4538	0.998	0.0301	$y = -2.2034x + 214.91$



**Fig. 3.** Langmuir Isotherm graph



**Fig. 4.** Freundlich Isotherm graph

### 3.3 Kinetic Studies

Kinetics of  $\text{Cu}^{2+}$  adsorption using SAC was also studied in the present work. Lagergren first and second order models were employed. The pseudo-first-order kinetic model is expressed generally as Equation (6):

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1}{2.303} t \quad (6)$$

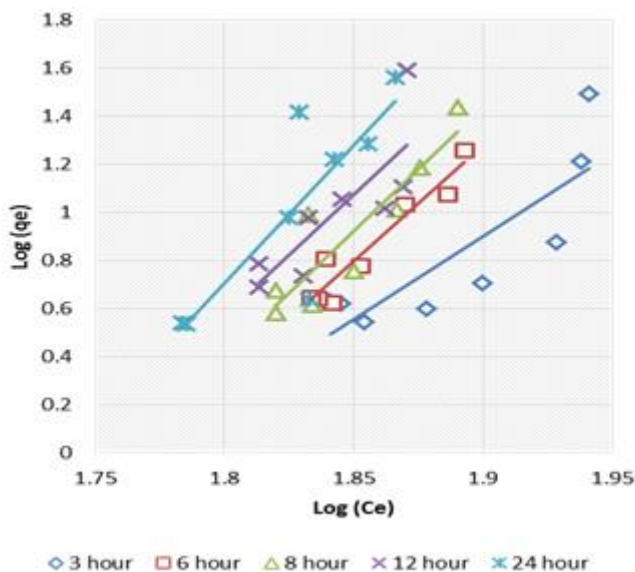
where  $q_{eq}$  is the quantity of adsorbate adsorbed at equilibrium (mg/g),  $q_t$  is the amount adsorbate adsorbed at a given time  $t$  and  $k_1$  is the first order constant rate of adsorption (min<sup>-1</sup>). The plot of  $\log(q_{eq}-q_t)$  against time should be linear with  $k_1/2.303$  and  $\log q_{eq}$  representing the slope and intercept of the line.

Pseudo-second-order kinetic model was also used to analyze the data from the experiments and the mechanism that best fits the data was determined. Linearized form of pseudo-second-order kinetic model is shown in Equation (7). The slope and the intercept of the equation were determined by plotting  $t/q_t$  against time.

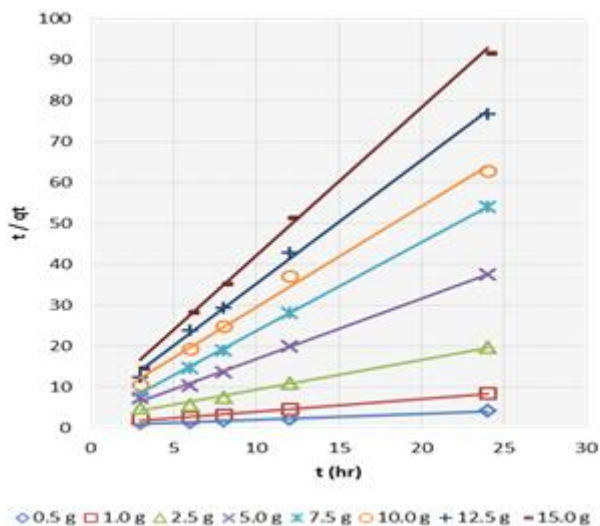
$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{1}{q_{eq}} \tag{7}$$

where  $k_2$  is the second order adsorption rate constant (g/ mg.min) and  $q_{eq}$  is the adsorbed quantity of pollutant at equilibrium (mg/g). The second order plots of  $t/q_t$  against time will yield a straight line.

Fig 5 and 6 shows Pseudo 1<sup>st</sup> and 2<sup>nd</sup> Order graphs. From the plots, the pseudo-second-order kinetic model presented high values of coefficient of determination ( $R^2$ ). All the values were close to unity. There was a deviation between the experimental  $q_{e, exp}$  values and the calculated  $q_{e, cal}$  values for the pseudo-first-order kinetic model. This indicates a poor fit of the pseudo-first-order model to the experimental data. On the other hand, the calculated  $q_{e, cal}$  values obtained from pseudo-second-order model agreed effectively with the experimental  $q_{e, exp}$  values. Therefore, it can be concluded that the adsorption of  $Cu^{2+}$  ions onto SAC is a pseudo-second-order reaction model. This suggests that the rate limiting step is chemisorption or chemical adsorption that involves valence forces through electrons exchange between the adsorbent (SAC) and the adsorbate ( $Cu^{2+}$ ) [16].



**Fig. 5.** Pseudo first order plot



**Fig. 6.** Pseudo second order plot

## 4 CONCLUSION

The present study shows that activated carbon produced from the sugarcane bagasse using tube furnace can be engaged as an environment friendly and low cost adsorbent for the removal of  $\text{Cu}^{2+}$  ions from aqueous solution. The study on the effect of pH revealed that the competitions between  $\text{H}^+$  and metal ions at low pH values are the main leading factors that affects the adsorption characteristics of SAC. Equilibrium time of 12 hours was considered optimum for the adsorption of  $\text{Cu}^{2+}$  by SAC. Number of adsorption sites increased due to an increase in SAC dosage and optimum removal efficiency of 50.8% was achieved at SAC dosage of 10 g/L. The kinetics analysis results obtained from pseudo-first-order and pseudo-second-order showed that the experimental data fitted well with pseudo-second-order kinetic model. The obtained experimental uptake capacities were almost the same as the calculated values from pseudo-second-order kinetic models. Removal isotherm for  $\text{Cu}^{2+}$  using SAC was well described by Langmuir isotherm models with correlation coefficients of 0.988 at 12 hrs equilibrium time. This indicates the monolayer coverage of  $\text{Cu}^{2+}$  ions on the homogeneous surface of SAC.

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