Removal of Cu(II) from Water by Adsorption on Papaya Seed

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***Abstract* — The use of papaya seeds as the low-cost adsorbents was investigated as a replacement for current costly methods of removing copper ions from aqueous solutions. Batch adsorption studies were conducted to examine the effects of pH, stirring rate, Cu(II) concentration and contact time on the adsorption of Cu(II) by papaya seed. Equilibrium data were analyzed using the Langmuir and Freundlich isotherms whereas the adsorption kinetics data were evaluated by the pseudo-first-order and second-order kinetic models. The optimum pH and stirring rate were found to be at pH 6 and 350 rpm, respectively. Adsorption isotherm analysis data fitted well to the Langmuir model with a maximum adsorption capacity of 212 mg/g. The kinetic experimental data correlated well with the pseudo-second-order kinetic model, which indicated that chemisorption processes could be the rate-limiting step in the adsorption process. The results demonstrated that papaya seed has potential to be employed as the adsorbent for the removal of Cu(II) from aqueous solutions.**

***Index Terms* — Copper, papaya seed, adsorption isotherm, kinetic model**

I. INTRODUCTION

COPPER is widely used in various industrial activities including metal plating, mining, tanneries and car radiator manufacturing. These applications have introduced copper into aquatic ecosystems, which causes serious environmental pollution problems and brings harmful effect to living organisms [1]. Long term exposure of copper can cause irritation of the nose, mouth and eyes as well as headache, stomach aches, dizziness, vomiting and diarrhea. Therefore, it is important to apply an efficient method for copper reduction to very low concentrations before discharge.

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]–[4]. Some of these technologies will also produce chemical or biological sludge and cannot be recovered or regenerated [5]. Adsorption, on the other hand, has emerged as a potential alternative to conventional physicochemical technologies in waste-treatment facilities. Adsorption is an effective separation process that has advantages in terms of cost, flexibility and simplicity of design, and ease of operation compared to other techniques. Adsorption also does not result in the formation of harmful substances [6].

Activated carbon is usually being used as adsorbent by chemical industry for wastewater treatment. However, it has shown disadvantage from the economic consideration due to the expensive activated carbon that causes an increase in the operating costs. Thus, some researchers are looking for the other alternative adsorbents which have characteristics similar to activated carbon in removing metal from aqueous solution. Agricultural wastes that are available in large quantities may have a potential to be used as low cost adsorbents, because they represent unused resources that are widely available and environmental friendly [5]. Agricultural wastes such as sugar beet pulp, dried sunflower leaves, sour orange residue and papaya wood are known to be effective in batch adsorption process on the removal of copper [7]–[10].

In the present study, papaya seed has been used as a new low-cost adsorbent to adsorb copper from water. The major characteristic of papaya seed that is useful in metal removal is due to its chemical composition. As described by [11], papaya seed is composed of lignin and cellulose as major constituents and may also contain other polar functional groups of lignin, which include alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups. These groups have ability to some extent to bind heavy metal ions by donation of an electron pair from these groups to form complexes with the metal ions in solution. Moreover, Malaysia is able to produce 72,000 tonnes of papaya annually [12]. Due to the high production and consumption of papaya fruits, massive amounts of seeds are readily available to be used as biosorbents instead of being disposed and causing environmental problems.

The present study aimed to investigate the efficiency of papaya seeds as adsorbents for the adsorption of Cu(II) from water. Experiments were conducted to investigate the effects of pH, stirring rate, Cu(II) concentration and contact time on the adsorption efficiency of Cu(II) by papaya seed. Adsorption equilibrium and kinetics had been studied under the optimum adsorption conditions. The Langmuir and Freundlich isotherms were applied to evaluate the adsorption properties in the batch experiments. In addition, the pseudo-first-order and pseudo-

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second-order kinetic models were also applied to examine the kinetics of the adsorption process.

II. MATERIALS AND METHODS

A. Materials

Copper sulfate ($CuSO_4$) was used for the preparation of stock standard solutions of Cu(II) in distilled water. For pH adjustment throughout the experiment, 0.1 M hydrochloric acid (HCl) and/or 0.1 M sodium hydroxide (NaOH) were used as necessary. All chemical used in the present study were of analytical grade from Merck, Germany. Atomic adsorption spectrometer (AAS Model HGA 850, USA) was used to measure the Cu(II) concentration.

B. Preparation of Adsorbent

Papaya seeds used in this study were removed manually from a fresh papaya fruit obtained from local fruit stall. The seeds were washed with distilled water and boiled with water for 20 minute to break the structure of papaya seed cell wall [13]. The boiled seeds were then filtered out and dried in an oven at 40°C for 48 hour. The dried materials were crushed by blender. The prepared papaya seed sample was stored in airtight container for future use.

C. Effect of pH on Cu(II) Adsorption

The effect of solution pH on adsorption of Cu(II) was studied by mixing 0.5 g of adsorbent with 200 ml of copper solution of 50 mg/L concentration at different pH value (4 to 8) under 30°C. The pH was adjusted with 0.1 M NaOH or 0.1 M HCl solutions and measured by pH meter. Agitation was made at a constant stirring speed of 150 rpm for 3 hours. The remaining concentration of Cu(II) after adsorption was measured using atomic adsorption spectrometer (AAS).

D. Effect of Stirring Rate on Cu(II) Adsorption

The effect of stirring rate on Cu(II) adsorption was investigated by adding 0.5 g of adsorbent into 200 ml of copper solution of 50 mg/L concentration at optimum pH determined previously. The solution was agitated using water bath shaker at different stirring rates (150 – 350 rpm) under constant temperature of 30°C. The remaining concentration of Cu(II) after adsorption was measured using AAS.

E. Equilibrium Studies of Cu(II) Adsorption

A series of solutions containing different initial concentrations of Cu(II) ions (in the range of 50 – 350 mg/L) was prepared and employed for the batch adsorption studies at 30°C to check the applicability of the Langmuir and Freundlich adsorption isotherms under optimum conditions obtained previously. The remaining concentration of Cu(II) after adsorption was measured using AAS and the amount of adsorption at equilibrium, q_e (mg/g) was calculated by:

$$q_e = \frac{(C_0 - C_e)V}{W} \tag{1}$$

where C_0 and C_e (mg/L) are the liquid-phase concentration of copper at initial and equilibrium, respectively, V (L) is the volume of the solution and W (g) is the mass of dry adsorbent used. The adsorption efficiency of Cu(II) can be calculated as:

$$\text{Adsorption percentage} = \frac{(C_0 - C_e)}{C_0} \times 100 \tag{2}$$

F. Kinetics Studies of Cu(II) Adsorption

The kinetics studies of Cu(II) adsorption were carried out by batch adsorption at optimum conditions evaluated previously. The samples were taken at preset time intervals up to 180 min under temperature of 30°C. The remaining concentration of Cu(II) after adsorption was measured using AAS and the amount of adsorption at time t, q_t (mg/g) was calculated by:

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{3}$$

where C_t (mg/L) is the liquid-phase concentrations of Cu(II) solutions at any time, t.

III. RESULTS AND DISCUSSION

A. Effect of pH on Cu(II) Adsorption

The pH value of aqueous solution is an important parameter in adsorption process because it affects the surface charge of the adsorbent, the degree of ionization and specification of the adsorbate [2]. The batch equilibrium studied at 50 mg/L of Cu(II) concentration with different pH values ranging from 4 to 8 were carried out under 30°C. Fig. 1 shows that maximum percentage of Cu(II) adsorption on papaya seed were observed at pH 6. An increase in the adsorption occurred in the pH range of 4 to 6 and slightly decreased at higher pH values.

As pointed out by [10], little adsorption at lower pH for papaya seed could be ascribed to the hydrogen ions competing with copper ions for adsorption site. At higher H^+ concentration, the adsorbent surfaces become more positively charged, thus reducing the attraction between adsorbent and metal ions. Therefore, adsorption of Cu(II) at lower pH range was not investigated in the present study. At higher pH, the adsorbent surface takes more negative charges, thus attracting more copper ions. However, it was also observed that the adsorption capacity of copper ions decreased with further increases in pH due to the formation of anionic hydroxide which reduced the concentration of free copper ions.

B. Effect of Stirring Rate on Cu(II) Adsorption

The effect of stirring rate on Cu(II) adsorption was investigated by varying the stirring rate from 150 to 350 rpm, as shown in Fig. 2. It is observed that Cu(II) adsorption was enhanced with an increase in the stirring speed to almost 100% at 350 rpm.

This is attributed to the fact that the increase of stirring rate improves the diffusion of the copper ions towards the surface of the adsorbents [14]. Increasing stirring rate reduces the film boundary layer surrounding the adsorbent particles, thus increasing the external film mass transfer coefficient and the rate of metal adsorption [15].

C. Analysis of Adsorption Isotherm

The equilibrium study is important for an adsorption process as it shows the capacity of the adsorbent and describes the adsorption isotherm to express the surface properties and affinity of the adsorbent. In the present study, the equilibrium data for Cu(II) adsorption on papaya seed were evaluated by the Langmuir and Freundlich models.

The Langmuir isotherm is based on assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface, the energy of adsorption is constant, and there is no transmigration of adsorbate in the plane of the surface [16]. In contrast, the Freundlich isotherm can be used for non-ideal adsorption that involves heterogeneous adsorption [17]. The linearized equations for the Langmuir and Freundlich isotherms are expressed as (4) and (5), respectively.

$$\frac{1}{q_e} = \left(\frac{1}{k_a q_m}\right)\frac{1}{C_e} + \frac{1}{q_m} \tag{4}$$

$$\ln q_e = \ln k_F + \frac{1}{n}\ln C_e \tag{5}$$

A linear graph of ($1/q_e$) against ($1/C_e$) for papaya seed adsorbent was plotted based on (4). The Langmuir constants q_m and k_a were determined from the slope and intercept of the plot and tabulated in Table 1. The constant q_m (mg/g) is a measure of maximum adsorption capacity of the adsorbent under the experimental conditions and k_a (L/mg) is a constant related to the energy of adsorption. Table 2 shows the comparative analysis of the maximum adsorption capacity for copper ions using papaya seed in the present study with other adsorbents reported in the literature.

For the analysis of Freundlich isotherm, a linear graph of $\ln(q_e)$ against $\ln(C_e)$ was plotted by referring to (5). The Freundlich constants, n and k_F, were determined from the slope and intercept of the plot, respectively. The constant n indicates the bond energies between metal ion and the adsorbent, whereas k_F (mg/L) is related to bond strength [2].

Results shows that the experimental data was better described by the Langmuir isotherm compared to the Freundlich isotherm. The graph plotted from the Langmuir model yielded a straight line with the regression coefficient (R^2) of 0.98. In contrast, the Freundlich isotherm model was less precise, with lower R^2 value of 0.89. The value of R^2 is regarded as a measure of the goodness-of-fit of experimental data on the isotherm models [2]. Thus, the data of Cu(II) adsorption on papaya seed may be concluded to perfectly fit the Langmuir isotherm model. This indicates that the adsorption of copper on papaya seed takes place as monolayer adsorption on the adsorbent surface, homogenous in adsorption affinity and with constant adsorption energy [7, 12].

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L, which is given by the following equation [12]:

$$R_L = \frac{1}{1 + k_a C_0} \tag{6}$$

where C_0 (mg/L) is the initial liquid-phase concentrations of Cu(II) solutions, and k_a (L/mg) is the Langmuir constant. The value of R_L indicates the shape of the isotherm to be either unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$). The values of R_L are shown in Table 3. R_L values for the present experimental data fall between 0 and 1, which is an indication of the favourable adsorption of the Cu(II) on the papaya seed adsorbents.

D. Analysis of Adsorption Kinetics

The study of adsorption kinetics is important in describing the adsorption process as it explains how fast the process occurs and also provides information on the factors affecting or controlling the adsorption rate. The adsorption of Cu(II) by papaya seed at different contact time is shown in Fig. 3. The adsorption increased with increasing contact time and the adsorption occurred rapidly at the first 15 minutes, followed by a slower adsorption phase after this. The copper adsorption during the rapid phase was amounted to be around 60%, and the adsorption of the remaining copper ions continued in the slower phase until the adsorption achieved almost 100% after 120 minutes.

Various models can be used to analyze the kinetics of the adsorption process. The pseudo-first-order and second-order kinetic equations of Largergren are the most widely used for the adsorption of solutes from a liquid solution [18]. The linear form of equations for the pseudo-first-order and second-order kinetic models can be represented by (7) and (8), respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \tag{8}$$

A graph of $\log(q_e - q_t)$ versus time, t was plotted based on the pseudo-first-order model. The parameter of k_1 (L/min) is the first-order reaction rate equilibrium constant and q_e (mg/g) is the amount of metal adsorbed at equilibrium. The pseudo-first-order kinetic model considers that the rate of occupation of adsorption site to be proportional to the number of unoccupied sites.

In contrast, for the pseudo-second-order equation, k_2 (g/mg.min) represents the second-order reaction rate constant. By plotting t/q_t against t, the constant k_2 was determined from the slope of the linear curve. A comparison of the reaction rate constants and R^2 values estimated from the pseudo-first-order and second-order equations is presented in Table 4.

From Table 4, R^2 value for the pseudo-second-order model is higher than the pseudo-first-order model. This shows that the adsorption of copper on papaya seed is well-fitted to the pseudo-second-order kinetics model compared to the first-order model. Based on the high regression coefficient value, it can be concluded that the pseudo-second-order kinetics model provides a good correlation for the adsorption of copper ions on papaya seed and it also suggests that the chemisorption process could be the rate-limiting step in the adsorption process.

IV. CONCLUSION

The adsorption of copper from aqueous solution using papaya seed as the low-cost adsorbent was investigated in batch process. The optimum pH value and stirring rate for copper adsorption were found to be 6 and 350 rpm, respectively. The Langmuir adsorption isotherm was best fitted to the experimental data with a maximum adsorption capacity of 212 mg/g. Adsorption kinetics of Cu(II) adsorption on papaya seed followed the pseudo-second-order kinetic model where the chemisorption process may be the rate-limiting step in the adsorption process. This study shows that papaya seed has high potential to be employed as an effective adsorbent in removing copper ions and would be useful for the design of wastewater treatment plants for heavy metal removal.

It is suggested that further research can be conducted to enhance the existing results. Chemical modification of the papaya seed adsorbents using acids or bases can be attempted to further improve the adsorption capacity of adsorbents. This is because the number of active binding sites or functional groups on the adsorbents that responsible for metals uptake might be increased as a result of chemical modification. Since modification might change the surface of adsorbent, it is also recommended that the characterization studies of adsorbent can be carried out to have a better understanding on the properties of adsorbent in heavy metal adsorption.

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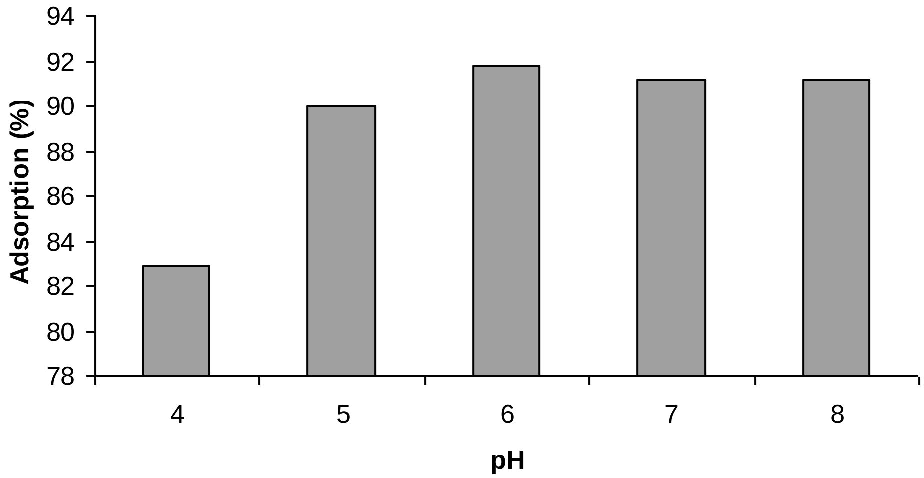

Fig. 1. Effect of pH on the adsorption of Cu(II) by papaya seed

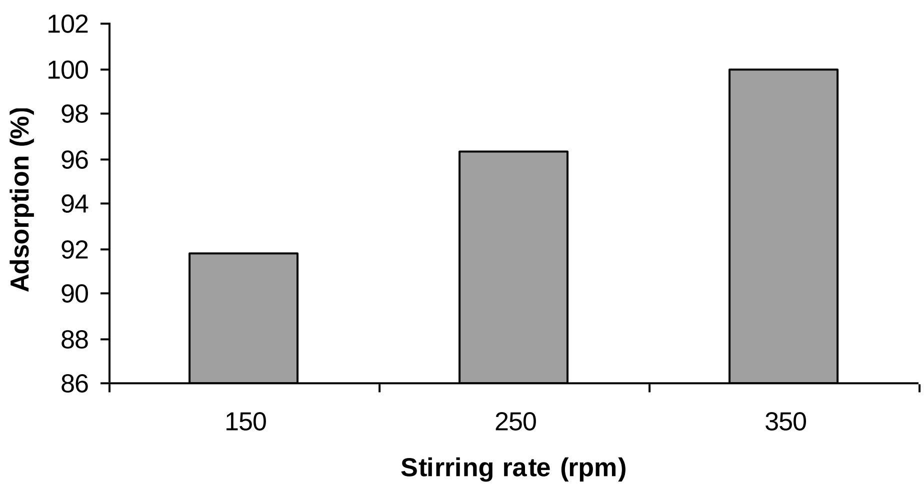

Fig. 2. Effect of stirring rate on the adsorption of Cu(II) by papaya seed

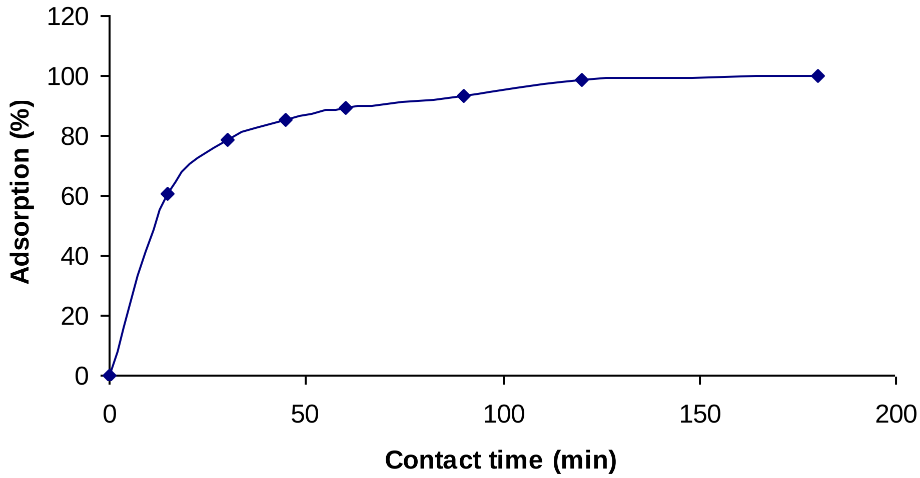

Fig. 3. Effect of contact time on the adsorption of Cu(II) by papaya seed

Table 1. Isotherm parameters for the adsorption of Cu(II) by papaya seed

Langmuir isotherm			Freundlich isotherm		
R^2	q_m (mg/g)	k_a (L/mg)	R^2	n	k_F (mg/L)
0.9804	212.766	0.0182	0.8963	1.0231	1.8865

Table 2. Adsorption capacities for copper ions using different adsorbents

Adsorbent	Adsorption capacity (mg/g)	References
Papaya seed	212.77	Present study
Treated sugar beet pulp	119.43	[7]
Dried sunflower leaves	89.37	[8]
Sour orange residue	21.70	[9]
Papaya wood	19.88	[10]
Tree fern	10.50	[17]
Pomegranate peel	1.32	[2]
Potato peel	0.3877	[16]

Table 3. R_L values at different concentrations of Cu(II)

Initial Cu(II) concentration, C_0 (mg/L)	R_L value
50	0.5236
150	0.2681
250	0.1802
350	0.1357

Table 4. Parameters of kinetic models for the adsorption of Cu(II) by papaya seed

Pseudo-first-order model		Pseudo-second-order model	
k_1 (L/min)	R^2	k_2 (g/mg.min)	R^2
0.0327	0.9581	0.1471	0.9926