Adsorption of Copper Using Pomelo Peel and Depectinated Pomelo Peel

Penpun Tasaso

Abstract—**The removal of Copper (Cu^{2+}) from aqueous solution by adsorption on pomelo peel (PP) and depectinated pomelo peel (DPP) were studied. Factors affected to adsorption; initial pH, initial concentration, contact time and temperature were investigated. It was found that the highest Cu^{2+} adsorption capacity for PP and DPP were 19.7 mg/g and 21.1 mg/g at the following conditions; pH = 4 , 125 mg/l of initial concentration , temperature of 25 ^{0}C and equilibrium time about 60 min. Adsorption isotherm of both PP and DPP were well described by the Langmuir model. The kinetic studies showed that a pseudo-second-order rate model was adopted to described the Cu^{2+} adsorption. The thermodynamics parameter of the Cu^{2+} adsorption were evaluated at temperature of 25, 35 and 45 ^{0}C. The negative of standard free energy change and enthalpy change revealed that the adsorption process is spontaneous and exothermic.**

Index Terms—**Adsorption, copper, kinetics, pomelo peel.**

I. INTRODUCTION

One of the heavy metals often found from industrial effluent is copper, which from cleaning and plating baths, paper board mills, wood pulp production and the fertilizer industry. This heavy metal is most toxic to living organism. The adsorption process has been widely studied in order to solve the problem of many industries regarding the disposal of their effluent. Systems such as ion exchange resins, electrochemical process, chemical precipitation and activated carbon have been widely used in the process of waste water treatment. Agricultural waste is one of the rich sources of low cost adsorbents besides industrial by-product and natural material. Due to its abundant availability agricultural waste such as rice husk, coconut shell, wheat bran and maize wrapper offer little economic value and moreover create disposal problem [1]. These agricultural by-products usually are composed of lignin and cellulose as major constituents and may also include other polar functional groups of alcohols, carboxylic, aldehydes, phenolic and ether groups. These groups have the ability to some extent to bind heavy metals by donation of an electron pair to form complexes with the metal ions in solution [2]. Pomelo peel is very interesting biosorbent because of their high pectin content [3]. The main structural of pectin in plant cell wall based on α-(1-4) linked D-galacturonic acid , which negative charges of free carboxyl groups in pectin molecules form the covalent bonds with two valence metal ions [4],[5]. Therefore the goal of this study is to investigate the adsorption behavior of copper on pomelo peel and the remaining depectinated peel.

II. RESEARCH METHODOLOGY

A. Adsorbents preparation

Pomelo Peel (PP) : the white albedo was separated from pomelo peels with a knife into a small piece and coarsely chopped with a food blender. It was washed several times with distilled water then washed three times with 95% ethanol to remove the impurities. The washed albedo was dried at 70 ^{0}C for 2-3 h then ground and sieved , size only smaller than 0.42 mm (< 35 mesh) was used.

Depectinated Pomelo Peel (DPP): the DPP was the pomelo peel residues left after the extraction of pectin from the peels. The conditions for pectin extraction are hot acidified water at pH = 1.5 and temperature 115-120 °C for 60 min. The filtrate was precipitated by 95% ethanol to get pectin, the residues solid, DPP was separated by filtration. It was washed several times with distilled water then dried at 70 ^{0}C for 2- 3 h, ground and sieved , size only smaller than 0.42 mm (< 35 mesh) was used.

B. Cu^{2+} Adsorption

1) Effect of pH

The effect of solution pH on the adsorption capacity of Cu^{2+} was invested at pH 3, 4, 5 and 6. The experiments were performed by adding 0.5 g of PP or DPP to 100 ml of 25 mg/l standard copper solution and the pH of the solution was adjusted using 0.1 mol/l HCl or NaOH .The flask were shaken at 150 rpm and 25 ^{0}C for 180 min, the solution mixture were filtered to remove adsorbents and the filtrates were analyzed the Cu^{2+} concentration by atomic absorption spectrophotometer. The amount of copper adsorbed were determined as follows

$$q = \frac{V\left(C_0 - C_f\right)}{m} \tag{1}$$

where q is adsorption capacity in (mg/g) , C_0 and C_f are the initial and final copper concentration (mg/l) respectively, V is the suspension volume (l) and m is the mass of the adsorbent materials (g).

2) Effect of initial concentration and contact time

Sorption equilibrium studies were conduct at optimum pH = 4, the flask were shaken at 150 rpm for 180 min at controlled temperature at 25 ^{0}C. Isotherm studies were conducted with 0.5 g of PP or DPP and varying initial concentration of Cu^{2+} in the range of 25 – 125 mg/l.

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The effect of contact time also studied to determine the adsorption kinetic of Cu^{2+}. For batch kinetic studies, 0.5 g of PP or DPP were equilibrated at optimum condition, pH = 4 the flask were shaken at 150 rpm with initial concentration between 25 - 125 mg/l, temperature was controlled at 25 ^{0}C, 0.5 ml of sample were withdrawn at time interval between 0-180 min.

3) Effect of temperature

Effect of temperature on adsorption of Cu^{2+} was studied by conducting different sets of experiment, 0.5 g of PP or DPP were equilibrated at optimum condition, pH = 4, the flask were shaken at 150 rpm, initial concentration of 25,75 and 125 mg/l and temperature was controlled at various of 25, 35 and 45 ^{0}C with contact time of 180 min.

4) Copper analysis

The Cu^{2+} in the solution was analyzed using atomic absorption spectrophotometer (Perkin Elmer model 3000) which operates in flame mode.

5) FTIR spectra of adsorbent

The adsorbents PP and DPP were analyzed the FTIR spectrum before and after copper ion adsorption using FT-IR (Perkin Elmer 2000)

III. RESULTS AND DISCUSSION

A. Effect of pH

The effect of pH on the Cu^{2+} adsorption capacity of PP and DPP is found to be significant as shown in Fig. 1. The adsorption capacity of PP and DPP is found maximum at pH = 4 and dramatic decreased at pH higher than 4. Generally, as a result of net negative charge on the different functional group in the cell wall of adsorbents, the ionic state of the different functional such as carboxyl and hydroxyl groups favors reaction with Cu^{2+}[5]. Under high acidic condition, the more proton are available in a free form to protonated carboxyl and hydroxyl groups caused to reduce the number of binding sites of PP and DPP as a result of decreasing the adsorption capacity. At higher pH values the insoluble copper complex starts precipitating from the solutions, which makes true adsorption studies impossible. The result suggests that initial pH would play and important factor in the adsorption of copper using PP and DPP.

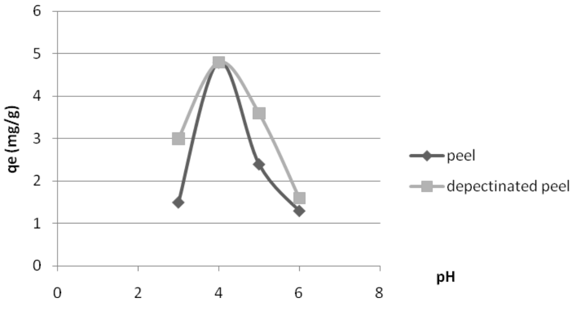

Fig. 1. Effect of initial pH on the adsorption capacity of Cu^{2+} on PPand DPP

B. Effect of Initial Concentration and Contact Time

The effect of Cu^{2+} initial concentration on the adsorption capacity of PP and DPP under optimum conditions of pH and contact time was shown in Fig. 2. The adsorption capacity increased with increasing of Cu^{2+} initial concentration in solution. The plateau value obtained as shown in Fig. 3 showed that as the metal/adsorbents ratio increases, there is a decrease in adsorption efficiency. This can be attributed to the saturation of the binding sites on the adsorbents.

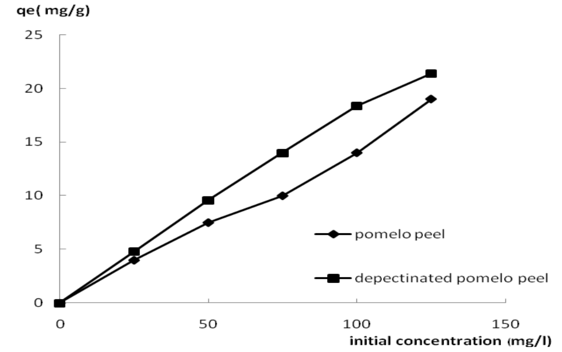

Fig. 2. Effect of initial concentration on the adsorption of Cu^{2+} on PP and DPP

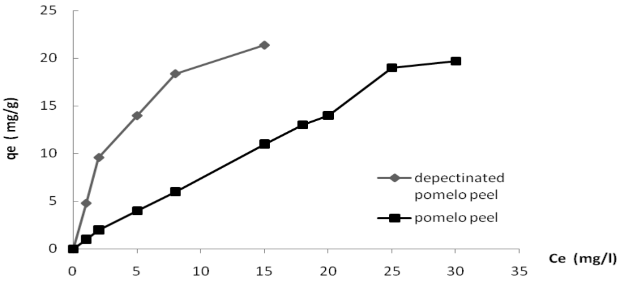

Fig. 3. Adsorption isotherm of PP and DPP at pH=4 and 25^{0}C

The experimental data were also applied to adsorption isotherm both the Langmuir and Freundlich isotherm model.

The Langmuir equation is most often used to described equilibrium sorption isotherm [6], which is valid for monolayer sorption with a finite number of identical sites and is given by

$$q_e = \frac{q_{\max} b C_e}{\left(1 + b C_e\right)} \tag{2}$$

where q_{max} is the maximum sorption at monolayer (mg/g), Ce is a final equilibrium concentration of Cu^{2+} , q_e is the Cu^{2+} bound per unit weight of the PP and DPP at final equilibrium concentration (mg/g) and b is the Langmuir constant related to the affinity of binding sites (ml/mg) . The following linearized plot of the Langmuir equation was used in this study.

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b q_{\max}} \tag{3}$$

The widely used empirical Freundlich equation based on sorption on a heterogeneous surface is given by

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{4}$$

The linearized Langmuir isotherm for Cu^{2+} adsorbed on the PP and DPP adsorbent was shown in Fig. 4 and Fig. **5.** The model parameters are given in Table I.

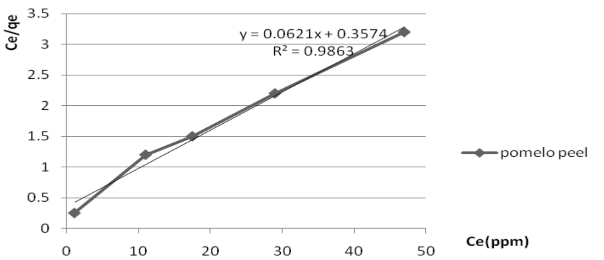

Fig. 4. Linearized Langmuir isotherm model of Cu^{2+} adsorption on pomelo peel

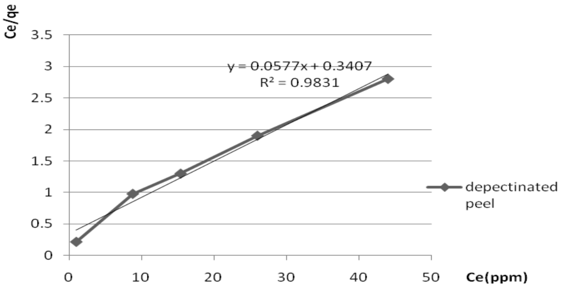

Fig. 5. Linearized Langmuir isotherm model of Cu^{2+} adsorption on depectinated pomelo peel

They showed that adsorption of Cu^{2+} by PP and DPP were better correlate ($R^2 > 0.95$) with the Langmuir equation as compared to Freunlich, indicating that adsorption of Cu^{2+} is more likely monolayer coverage on surface of PP and DPP

TABLE I: ISOTHERM PARAMETER OBTAINED BY USING LINEAR METHOD

Isotherm model	Parameters	Pomelo peel	Depectinated pomelo peel
Langmuir	R^2	0.9863	0.9831
	q_m (mg/g)	19.7	21.1
	b (l/mg)	0.1748	0.1697
Freundlich	R^2	0.9439	0.5089
	K_F (l/g)	4.39	7.04
	n	3.0941	4.8924

The effect of contact time on the adsorption capacity of DPP is as shown in Fig. 6. The increasing of initial metal concentration influenced to the increasing of contact time necessary to reach equilibrium and also increased the adsorption capacity .To analyze the adsorption rate of Cu^{2+} onto PP and DPP, two simple kinetic model were tested.

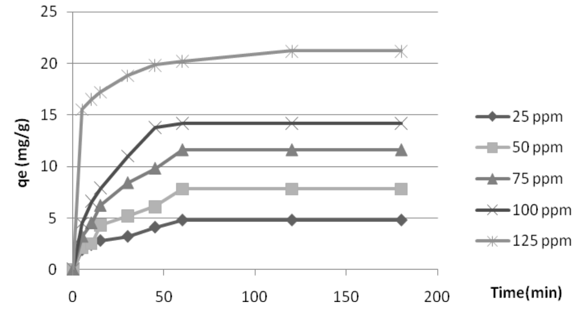

Fig. 6. Adsorption kinetic of depectinated pomelo peel at different initial concentration

Pseudo-first order model is generally described in the linearized version [7] by the following equation

$$\ln(q_e - q_t) = \ln q_e - k_{1ad}t \qquad (5)$$

where q_e is the amount of Cu^{2+} adsorbed at equilibrium per unit weight of adsorbent (mg/g) and q_t is the amount of Cu^{2+} adsorbed at any time (mg/g) , k_{1ad} is the rate constant (min^{-1})

The pseudo-second–order model is based on the assumption that adsorption follows a second order mechanism, whereby the rate of sorption is proportional to the square of the number of unoccupied sites. It is described in the linearized version by the following equation [7].

$$\frac{t}{q_t} = \frac{1}{k_{2ad}}q^2 + \frac{t}{q_e} \qquad (6)$$

where k_{2ad} is the rate constant of second order. The linearized pseudo-second –order model gave a good fit with R^2 were 0.99 either for PP and DPP. This means that the adsorption kinetic can be described by a pseudo-second-order rate equation hence q_e and k_{2ad} were evaluated and presented in Table II.

TABLE II: RATE CONSTANT FOR CU2+ ADSORPTION ON PP AND DPP

	Pseudo-first order			Pseudo-second order			
	k_{1ad}	q_e	R^2	k_{2ad}	q_e	q_e(exp)	R^2
PP	0.070	3.82	0.9931	0.081	19.69	19.7	0.9961
DPP	0.060	2.82	0.8095	0.070	21.02	21.1	0.9974

C. Effect of Temperature

In order to determine the thermodynamics parameters, experiments were carried out at three different temperature. (25, 35 and 45 ^{0}C) The Cu^{2+} adsorption capacity decrease with increasing temperature as shown in Fig. 7. indicating that the reaction is exothermic. Thermodynamics parameters can be determined from the variation of the thermodynamic equilibrium constant K_0 with temperature.

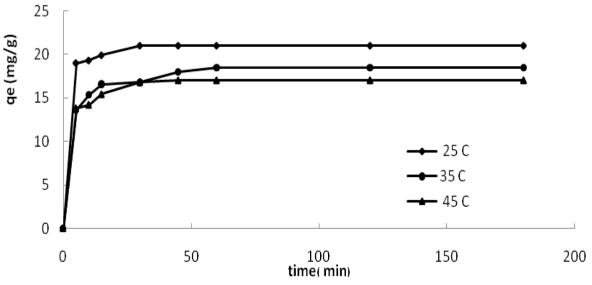

Fig. 7. Effect of temperature on the adsorption capacity of Cu^{2+} on DPP

For adsorption reactions, K_0 is defined as follows :

$$K_0 = \frac{\gamma_s C_s}{\gamma_e C_e} \qquad (7)$$

where Cs is the surface concentration of Cu^{2+}(mmol/g), Ce is the Cd^{2+} concentration in solution at equilibrium (mmol/ml), γ_s and γ_e are activity coefficient of the adsorbed Cu^{2+} and Cu^{2+} in solution respectively. As the Cu^{2+} concentration in solution declined to zero, K_0 can be obtained by plotting ln(Cs/ Ce) versus Cs and extrapolating Cs to zero. The straight line obtained is fitted by lease-square method Its intercepts with the vertical axis yields the value of K_0. The adsorption standard free energy change (ΔG°) can be calculated from

$$\Delta G^0 = -RT\ln K_0 \qquad (8)$$

where R is the universal gas constant (8.314 J/mol K) and T is temperature in Kelvin. The average standard enthalpy change (ΔH°) is determined from the Van't Hoff equation[8].

$$\ln K_0(T_3) - \ln K_0(T_1) = \frac{\Delta H^0}{R}\left(\frac{1}{T_3} - \frac{1}{T_1}\right) \qquad (9)$$

The standard entropy change (ΔS°) is given by

$$\Delta S^0 = \frac{-\left(\Delta G^0 - \Delta H^0\right)}{T} \qquad (10)$$

The value K_0 of Cu^{2+} adsorption on PP and DPP were evaluated and plots was shown in Fig. 8. and all thermodynamic parameters of Cu^{2+} adsorption on PP and DPP were presented in Table III. A negative standard enthalpy change of -32.18 kJ/mol of PP and -24.89 kJ/mol of DPP obtained in this study indicates that the adsorption system is exothermic . Negative value of ΔG° confirmed that the feasibility of the spontaneous nature of adsorption. This is also confirms the possibility of physical adsorption.

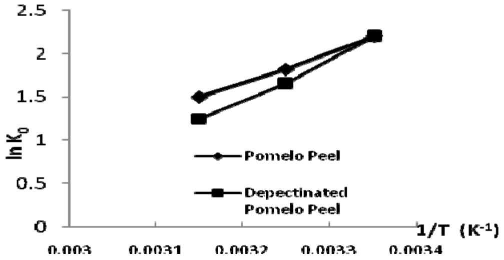

Fig. 8. plots of K_0 at various temperature

TABLE III: Values of Thermodynamics Parameters for Cu^{2+} Adsorption on PP and DPP

Adsorbents	Temp (K)	K_0	ΔG° (kJ/mo)	ΔH°(kJ/mol)	ΔS° (kJ/mol)
PP	298	8.77	-5.38	-32.18	0.09
	308	5.13	-4.19		
	318	3.74	-3.49		
DPP	298	8.86	-5.40	-24.89	0.08
	308	6.32	-4.72		
	318	4.58	-4.02		

D. FT-IR Spectra of PP and DPP

The FT-IR spectra of PP and DPP are presented in Fig. 9 and Fig. 10 respectively. To observe which peak shift during adsorption, the FT-IR before and after adsorption of PP and DPP were compared. All spectra of PP and DPP before adsorption show the 1650 – 1600 cm^{-1} bands represented the free carboxylate groups and typical peaks for – OH group at 3424 – 3250 cm^{-1}. But after adsorption the COO^{-}.peak of both PP and DPP shifted pronouncedly by 30 cm^{-1}, clearly demonstrating the involvement of this group in Cu^{2+} sorption.

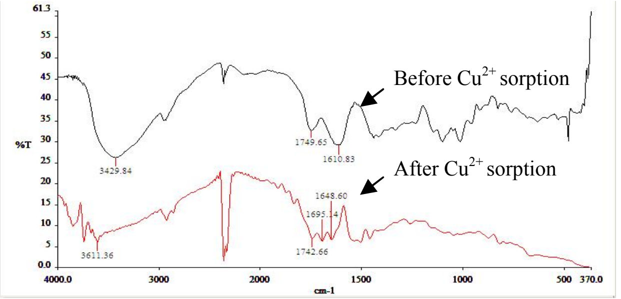

Fig. 9. Comparison the FT-IR spectra of pomelo peel before and after Cu^{2+} adsorption

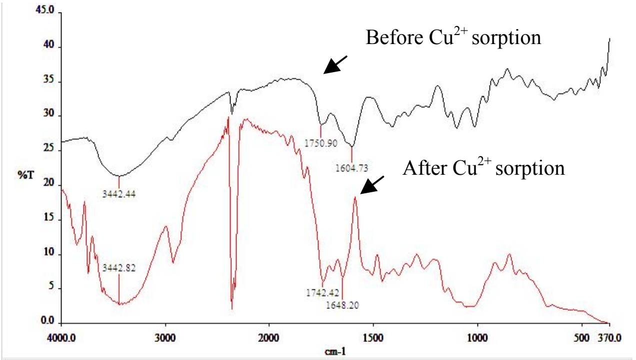

Fig. 10. Comparison the FT-IR spectra of depectinated pomelo peel before and after Cu^{2+} adsorption

IV. CONCLUSION

Adsorption of copper from aqueous solution was possible using pomelo peel and depectinated pomelo peel. Equilibrium study showed that Langmuir isotherm is well fitted. The pseudo-second – order rate model fits very well with this adsorption kinetic. Thermodynamics constant of the Cu^{2+} adsorption were evaluate at temperature of 25, 35 and 45 ^{0}C. The results of ΔH °, ΔS° and ΔG° of all adsorbent were -32.2 to -24.9 kJ/mol, 0.09-0.06 kJ/mol and -4.7 to -4.4 kJ/mol respectively. The negative value of standard enthalpy change and standard free energy change suggested that the adsorption of copper by pomelo peel and depectinated pomelo peel was exothermic and spontaneous.

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