WASTE TO VALUABLE BY-PRODUCT: KINETIC AND THERMODYNAMIC STUDIES OF CD, CU AND PB ION REMOVAL BY DECANTER CAKE

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ABSTRACT

Palm oil mills generate about 4 - 5 tons of decanter cake for every 100 tons of palm fresh fruit bunch processed. Due to the high organic content, the decanter cake could be converted to adsorbent for the removal of metal ions from waste water. The decanter cake was first dried at 105 oC and then carbonized at 500 oC. Earlier data showed that 500 oC had highest performance in ions removal. The resulting carbonized decanter cake were tested for removing cadmium (II), copper (II), and lead (II) ions. Proximate analysis using thermogravimetry of decanter cake carbonized at 500 oC indicated that the adsorbent contained 4% moisture, 21% volatile, 23% fixed carbon, and 52% ash. Adsorption test was carried out by mixing 1.0 g of the decanter cake in 100 mL aqueous solution of the various ions. Langmuir and Freundlich isotherm models were used to fit the isotherm experimental data. The maximum uptakes of Cd, Cu and Pb onto the carbonized decanter cake in this study were estimated to be 24, 23, and 97 mg/g respectively. The adsorption kinetics was found to follow the pseudo-second-order kinetic model. Thermodynamic parameters such as standard enthalpy ($\square H^{\circ}$), standard entropy ($\square S^{\circ}$) and standard free energy ($\square G^{\circ}$) were determined.

KEYWORDS: *Adsorption, metal ions, decanter cake, kinetic, thermodynamic.*

1.0 INTRODUCTION

Palm oil industries contribute enormous waste and effluent to the environment. More than 70% of fresh fruit bunches processed are released as effluent and waste during the milling process. Previous analysis at FELDA palm oil mill in Sungai Tengi, Selangor, Malaysia, found the processing leads to 23.52 wt % of oil and 5.20 wt % of kernel being produced, while 71.28 wt % were loss as by-product or waste from the fresh fruit bunch that were milled (Mahlia *et.al*., 2001). Decanter cake is a solid waste produced from the three phase separation step of crude palm oil process. The production rate of decanter cake amount to about 4 - 5% weight of fresh fruit bunch processed. Fresh decanter cake contains over 70% moisture, while the dry matter contains oils, fiber and inorganic components. The most common utilization of decanter cake is as fertilizer and animal nutrition sources due to the presence of C, N, P, K and Mg (Chavalparit *et.al*., 2006).

Recent studies have supported the utilization of agricultural waste as effective adsorbent. The employment of pulp and paper mill sludge as adsorbent has been investigated (Battaglia *et.al*., 2003), (Calace *et.al*., 2003) and (Khalili *et.al*., 2002) as well as that of sewage sludge (Rozada *et.al*., 2008), (Seredych *et.al*., 2006) and (Thawornchaisit *et.al*., 2001).

Agricultural waste or by-products and in some cases appropriately modified samples have been shown to have high capacity for heavy metal adsorption (Demirbas, 2008). Some of agricultural by-products that has been investigated as adsorbent included brown rot fungus Lentinus edodes (Chen *et.al*., 2008), olive pomace (Martin *et.al*., 2008), palm shell (Issabayena *et.al*., 2008), sugar cane bagasse (Gurgel *et.al*., 2008), sugar beet pulp (Pehlivan *et.al*., 2008), kenaf bark (Othman *et.al*., 2008), peanut shell (Tao *et.al*., 2008) and hazelnut husk (Imamoglu *et.al*., 2008). Due to the similarity of decanter cake characteristics with other agricultural waste we propose employing decanter cake as an adsorbent for metal ion removal from water.

Heavy metals are among the most detrimental pollutants in source and treated water, and are becoming a severe health problem. Since the damaging effects of heavy metals in environment are known, many methods of treatment for industrial wastewater have been reported in literature. Amongst these methods are neutralization, precipitation, ion exchange and adsorption. For low concentration of metal ions in wastewater, the adsorption process is recommended for their removal. The adsorption process implies the presence of an adsorbent solid that binds molecules by physical attractive forces, ion exchange and chemical binding. It is advisable that the adsorbent is available in large quantities, easily regenerable, and cheap (Thawornchaisit *et.al*., 2001).

This study aimed at investigating the kinetic and thermodynamic properties of cadmium (II), copper (II) and lead (II) ions removal in aqueous solution by decanter cake. Equilibrium time and adsorption capacity were first examined. Langmuir and Freundlich isotherm adsorption models were used to characterize the adsorption process.

2.0 EXPERIMENTS

2.1 Preparation of adsorbent and reagents

Decanter cake, a waste material of crude palm oil milling plant, was collected from LKPP Corporation Sdn. Bhd., Lepar, Pahang, Malaysia. Decanter cake was dried in oven at 105^{o}C for 12 h to remove its moisture content. Dried decanter cake was ground and sieved to obtain 400-600 □m particle diameters. Decanter cake was placed in closed crucible and heated in muffle furnace at a heating ramp of 10 oC min-1, and held at 500^{o}C for 1 hour. After natural cooling to room temperature the decanter cake was ground and sieved to obtain the particle size between 45 and 125 □m. Treated decanter cakes were placed in powder container and placed in desiccator.

Metal ion stock solutions were prepared from analytical grade $Cd(NO_3)_2.4H_2O$, $Pb(NO_3)_2$, and $Cu(NO_3)_2.3H_2O$. Metal salts were dissolved in distilled water to obtain concentration of 1000 mg/l. Lead nitrate was obtained from HmbG Chemicals. Cadmium nitrate tetrahydrate was obtained from Fluka. Copper nitrate trihydrate was obtained from R&M Chemicals. Standard solutions of Cd, Cu, and Pb for AAS analysis were purchased from Merck.

2.2 Methodology

Adsorbent was characterized by TA Instruments-Waters' TGA Q 500 Instrument to determine thermal properties and proximate analysis. The samples were heated in nitrogen atmosphere from ambient temperature to 1000^{o}C at a heating ramp of 5^{o}C min^{-1}. The gas was switched into oxygen at 950^{o}C. BET surface area analysis was performed using Quantachrome Instruments.

Equilibrium time experiments were performed by batch technique in ambient temperature (22 – 24^{o}C). Series of 100 ml solution in 250 ml glass flask were used. Each flask were filled with Cd^{2+}, Cu^{2+}, and Pb^{2+} solutions at 100, 200 and 400 mg/l concentration. 1 gram of adsorbent was loaded into the solutions to give a dosage of 10 g/L. The conical flask were then agitated in orbital shaker at 200 rpm and liquid samples were taken out at a given time interval for Cd^{2+}, Cu^{2+} or Pb^{2+} analyses.

The isotherm adsorption studies were conducted by series of batch adsorption for each metal ion at various initial concentrations. Various initial metal concentrations were prepared by serial dilution of 1000 mg/L of stock solution of metals. The isotherm adsorption studies were performed in pH range of 4 – 5. Langmuir and Freundlich isotherm adsorption models were employed to fit the adsorption characteristic of adsorbent. The concentrations of metal ion in aqueous solution for all experiments were analyzed by AAS.

At equilibrium, the amount of target metal adsorbed onto the corresponding adsorbent, qe (mg/g) was found by a mass balance relationship:

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

where C_o (mg/L) and C_e (mg/L) are the initial and the equilibrium liquid-phase concentration of metal, respectively, V (L) the volume of the solution and W (g) the weight of the adsorbent. Fitting of the results to Langmuir (Eq. (2)) and Freundlich (Eq. (3)) isotherm models were found:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{2}$$

where q_m (mg/g) and K_L (L/mg) are the Langmuir parameters, related with the maximum capacity of adsorption and the binding energy of adsorption, respectively. The values of q_m and K_L can be calculated from the intercept and slope of the linear plot of Ce/q_e against C_e (Ren *et.al.*, 2008).

$$q_e = K_F C_e^{1/n} \tag{3}$$

The Freundlich constant K_F and n are related to adsorption capacity and energy of adsorption, respectively (Febrianto *et.al.*, 2009). The Freundlich isotherm can also be linearized by the following:

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

The kinetic studies were conducted by series of batch adsorption for each metal ion at initial concentration of 400 mg/L for Cd and Cu, while 1000 mg/L for Pb; consider the previous result about adsorbent capacity. The procedure of kinetic adsorption tests was identical to that of batch equilibrium tests; however the aqueous samples were taken at preset time intervals.

The Lagergren first order rate expression based on solid capacity is generally expressed as follows (Argun *et.al*., 2008):

$$\frac{dq}{dt} = k_1(q_e - q) \tag{5}$$

Integration of Eq. (5) with the boundary conditions as follow: t=0, q=0, and at t=t, q=q, gives

$$\ln(q_e - q) = \ln q_e - k_1 t \tag{6}$$

Pseudo second order model is derived on the basis of the sorption capacity of the solid phase (Lester *et.al*., 2007), expressed as

$$\frac{dq}{dt} = k_2(q_e - q)^2 \tag{7}$$

Integration of Eq. (7) with the boundary conditions t=0, q=0, and at t=t, q=q, results in

$$\frac{1}{q_e - q} = \frac{1}{q_e} + k_2 t \tag{8}$$

The linear form of Eq. (8) is

$$\frac{t}{q} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{9}$$

The thermodynamic studies were performed by adsorption experiments at different temperatures. 50 ml of metal ion solution was allowed to equilibrate with 0.5 g of adsorbent. The initial concentration of metal ion was 100 mg/L for Cd and Cu, while 500 mg/L for Pb. The distribution coefficient Kd, equals to qe/Ce, calculated at four different temperatures.

The Gibbs free energy $(\square G^{\circ})$, the enthalpy $(\square H^{\circ})$, and the entropy $(\square S^{\circ})$ for the adsorption process can be expressed as follow:

$$\Delta G = -RT \ln K_d \tag{10}$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{11}$$

The enthalpy change and the entropy change can be calculated from a plot of ln K_d vs. $1/T$ (Ren *et.al.*, 2008).

3.0 RESULT AND DISCUSSION

Plot of thermogravimetry analysis is shown in Figure 1. The removal of water from the external surface and moisture from the voids of the structure was completed at about 200 °C. The volatile matter leaves the adsorbent between 200 °C and 950 °C. Fixed carbon was determined by switching from nitrogen atmosphere into oxygen atmosphere at 950°C. Final weight at 1000 °C was identified as ash content of materials. Proximate analysis of adsorbent indicated it consists of 4.08 % moisture, 21.27 % volatile, 22.96 % fixed carbon and 51.69 % ash (Lester *et.al.*, 2007).

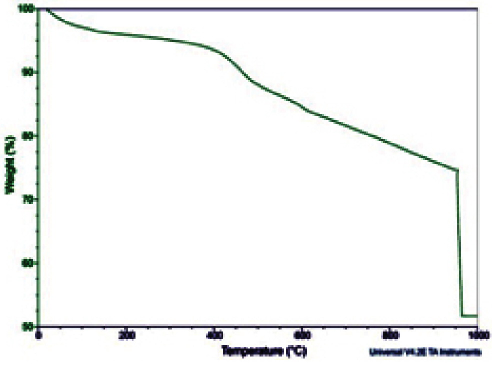


FIGURE 1
Thermogravimetry analysis plot for adsorbent

The scanning electron microscope of adsorbent is shown in Figure 2. The EDX spectrometry indicates adsorbent contains C (58.4%), O (26.3%), Si (5.5%), Al (4.4%), Ca (2.9%) and K (2.5%). BET surface area of adsorbent was 27.27 m^2/g.

Equilibrium time of adsorption was determined by taking 1 g adsorbent with 100 ml of certain initial concentration of metal ions (400 mg/L for Cd^{2+} and Cu^{2+} and 1000 mg/L for Pb^{2+}). The plot of C_e/C_o as shown in Figure 3 indicated that the adsorption reached equilibrium at 6 hours for Cd^{2+} and Cu^{2+}, and 60 minutes for Pb^{2+}.

Adsorption isotherm studies were performed by batch adsorption of metal ions at various initial concentrations. The parameters corresponding to the fitting of these results to the Langmuir and Freundlich isotherm models are shown in Table 1, while the plot of Langmuir and Freundlich adsorption isotherm are shown in Figure 4. The values of R^2 (coefficient of determination) indicate that both isotherm models describe metal adsorption onto the adsorbent appropriately.

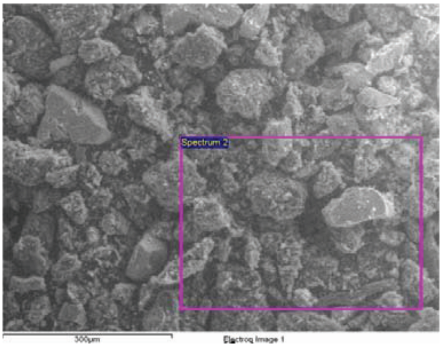
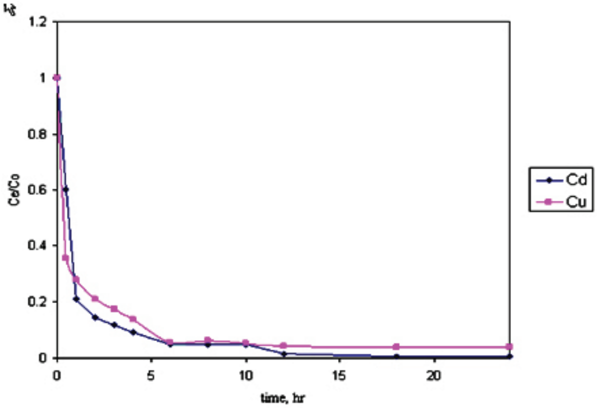


FIGURE 2
SEM micrograph of pyrolized decanter cake.



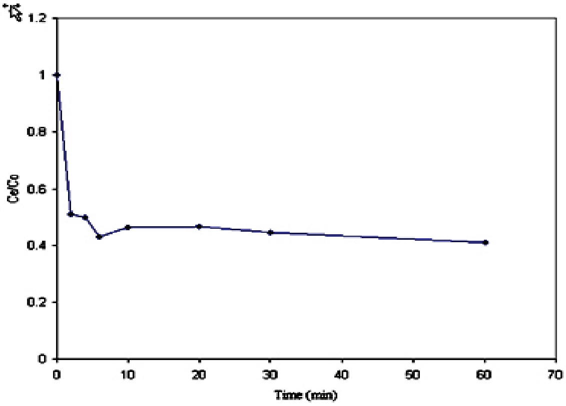
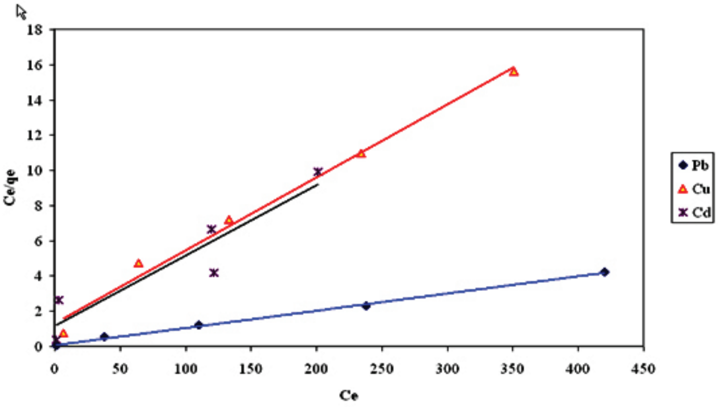
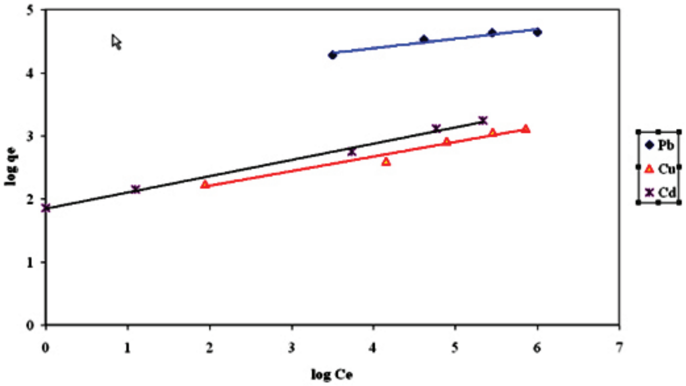


FIGURE 3
Equilibrium time for Cd and Cu (a), and Pb (b

The prediction of adsorption rate gives important information for designing batch adsorption systems. It because of the simplicity of this system compare to continuous system. Information on the kinetics of metal ion uptake is required for selecting optimum operating conditions for full-scale batch process. Lagergren's pseudo-first-order and pseudo-second-order kinetic models were applied in this experiment data.

Plot of linear form of both models are shown in Figure 5. Table 2 indicates that pseudo-second-order kinetic model provided better correlation for Cd(II), Cu(II) and Pb(II) adsorption onto decanter cake than pseudo-first-order kinetic model. This result is comparable with other studies as shown in Table 4.





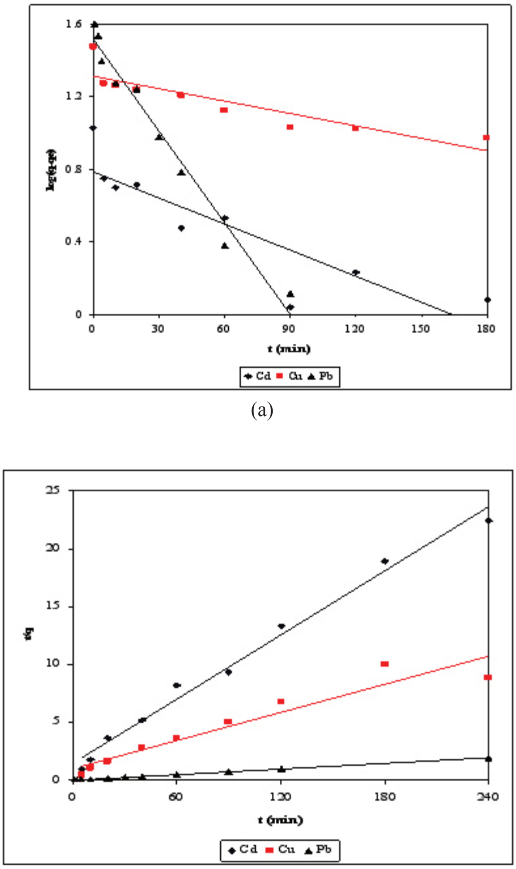
(b)

FIGURE 4
Plot of Langmuir (a) and Freundlich (b) adsorption isotherm for Cd(II), Cu(II), Pb(II) – decanter cake

TABLE1
Langmuir and Freundlich parameters for adsorption of metal ions onto pyrolized decanter cake

Metal ion	Langmuir isotherm		
	q_m (mg/g)	K_L (L/mg)	R^2
Cd^{2+}	24.30	0.1499	0.9802
Cu^{2+}	22.88	0.0583	0.9824
Pb^{2+}	96.72	0.2296	0.9904
Metal ion	Freundlich isotherm		
	K_F (mg/g)	K_F (mg/g)	K_F (mg/g)
Cd^{2+}	6.37	6.37	6.37
Cu^{2+}	5.77	5.77	5.77
Pb^{2+}	42.68	42.68	42.68

The effect of temperature on the adsorption equilibrium of Cd(II), Cu(II) and Pb(II) onto pyrolized decanter cake was investigated. Adsorption of Cd(II), Cu(II) and Pb(II) increased as the temperature increased from 298 to 328 K. The values of thermodynamic parameters were calculated from the plots of ln Kd versus 1/T as shown in Figure 6, while the result is listed in Table 3. This result is comparable with other adsorbent as described in Table 5.



(a)

(b)

FIGURE 5
Plot of pseudo-first-order (a) and pseudo-second-order kinetic models for adsorption of Cd(II), Cu(II) and Pb(II) onto decanter cake

TABLE 2
Pseudo-first-order and pseudo-second-order kinetic model parameters for Cd(II), Cu(II) and Pb(II) adsorption onto decanter cake

Parameter	Cd	Cu	Pb
		pseudo-first-order kinetic model	
k1, min^{-1}	0.00543	0.00223	0.01900
qe, mg/g	14.25	19.49	34.73
R^2	0.7888	0.7348	0.9287
qe(exp), mg/g	21.87	29.13	116.62
		pseudo-second-order kinetic models	
k2, g/(mg.min)	0.00231	0.00132	0.00475
qe, mg/g	22.70	27.02	117.66
R^2	0.9775	0.9946	0.9991
qe(exp), mg/g	21.87	29.13	116.62

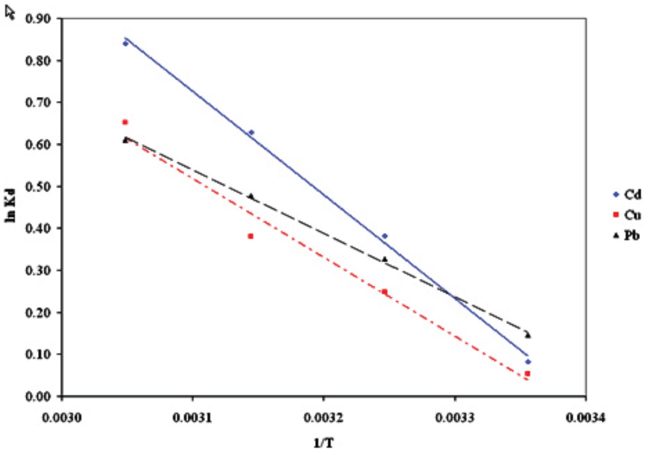


FIGURE 6
Plot of ln Kd vs. 1/T for Cd(II), Cu(II), Pb(II) – decanter cake

Positive *(□H◦),* value indicated the endothermic nature of adsorbent, which fact was supported by the increase in the adsorption of Cd(II), Cu(II) and Pb(II) with temperature. This result suggested ion-exchange may play a significant role in the adsorption process (Ren *et.al*., 2008). The adsorption free energy *(□H◦),* has negative values for all ions under all conditions which reflect the spontaneity of the process. The positive *(□S◦)* revealed that the degrees of freedom increased at the solid-liquid interface during the adsorption.

TABLE 3
Thermodynamic parameters for adsorption of Cd(II), Cu(II) and Pb(II) onto pyrolized decanter cake

Parameter	Cd(II)	Cu(II)	Pb(II)
□H◦ kJ/mol	20.52	15.63	12.58
□S◦ J/molK	70	53	43
R^2	0.9903	0.9951	09962
□G◦ kJ/mol			
298 K	-0.24	-0.10	-0.38
308 K	-0.93	-0.62	-0.81
318 K	-1.63	-1.15	-1.25
328 K	-2.32	-1.68	-1.68

TABLE 4
Comparison of pseudo-second-order kinetic parameters for selected adsorbent

Type of adsorbent	k_2, g/(mg.min)			q_e, mg/g		
	Cd(II)	Cu(II)	Pb(II)	Cd(II)	Cu(II)	Pb(II)
Decanter cake (this study)	0.00231	0.00132	0.00475	22.70	27.02	117.66
Dried activated sludge	0.0157	-	0.0062	9.80	-	83.50
Tea waste	-	0.0133	0.0091	-	19.00	35.00
Lignin	0.0131	0.0451	0.0409	18.21	17.53	62.99
Cedar sawdust	-	0.00593	-	-	31.35	-
Tree fern	0.1070	-	-	12.00	-	-

TABLE 5
Comparison of thermodynamic parameters for selected adsorbent

Type of adsorbent	Ion	ΔH^o kJ/mol	ΔS° J/molK	$-\Delta G^\circ$ kJ/mol	T range K
Decanter cake (this study)	Cd(II)	20.52	70	0.24 – 2.32	298 – 328
	Cu(II)	15.63	53	0.10 – 1.68	
	Pb(II)	12.58	43	0.38 – 1.68	
Raw bentonite	Pb(II)	39.00	200	21.60 – 28.60	303 – 338
S. albus biomass	Pb(II)	17.18	68.40	3.22 – 5.27	288 – 318
Cu(II)-MICA	Cu(II)	10.70	40	1.22 – 2.42	298 – 328
Chelating resin (CR10)	Cu(II)	-10.60	37.16	21.67 – 22.77	298 – 328
P. simplicissimum biomass	Cd(II)	20.03	130.90	18.27 – 20.88	293 – 313
Phospate rock	Cd(II)	16.93	122	19.19 – 22.12	283 - 313
	Cu(II)	10.80	110	16.97 – 19.47	
	Pb(II)	23.00	164	24.59 – 27.20	

4.0 CONCLUSION

In conclusion, pyrolized decanter cake may be considered a good candidate for the adsorption of metals, in particular cadmium, copper and lead. The experiment result showed adsorption capacity for lead was obviously higher than cadmium and copper. Data were found to fit the Langmuir and Freundlich isotherm models. The orders of the adsorption capacities from the Langmuir isotherm equation for three metal ions are as follow: $Pb^{2+}>Cd^{2+}>Cu^{2+}$. Pseudo-second-order kinetic model is suitable for the adsorption process of Cd(II), Cu(II) and Pb(II) onto pyrolized decanter cake. Thermodynamic properties of Cd(II), Cu(II) and Pb(II) adsorption onto pyrolized decanter cake are comparable with other adsorbent, and within the range of them of agricultural waste based adsorbent that was reported in literature.

5.0 ACKNOWLEDGEMENT

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