

Waste to valuable by-product: Palm oil mill decanter cake and its ability to remove Cd, Cu and Pb ions

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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 into adsorbent for the removal of metal ions from waste water. The decanter cake was first dried at 105 °C and then carbonized at various temperatures. 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 °C 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. The concentration of metal ions in the solutions used is in the range of 100 – 1000 mg/L. The results of adsorption studies indicated that the removal of metal ions was highest in the case of Pb when the carbonization temperature was 500 °C and 600 °C in the case of Cd and Cu. Maximum removal of the Cd, Cu and Pb were also observed to take place when the pH of the solution is in the range of 4 – 5. 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 ability of the carbonized decanter cake to remove the metal ions was found to be comparable to that of other adsorbents derived from agricultural waste.

Key words: Adsorption, Metal ions, Decanter cake, Palm oil mill

1. 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 Tinggi, Selangor, Malaysia, found the processing leads to 23.52 wt % of oil and 5.20 wt % of kernel while 71.28 wt % were loss as by-product or waste from the fresh fruit bunch that were milled⁽¹⁾. 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⁽²⁾.

Recent studies have indicated the utilization of agricultural waste as effective adsorbent. The employment of pulp and paper mill sludge as adsorbent has been investigated^(3,4,5), as well as that of sewage sludge^(6,7,8). Agricultural waste or by-products and in some cases appropriately modified have been shown to have high capacity for heavy metal adsorption⁽⁹⁾. Some of agricultural by-products that has been investigated as adsorbent included brown rot fungus *Lentinus edodes*⁽¹⁰⁾, olive pomace⁽¹¹⁾, palm shell⁽¹²⁾, sugar cane bagasse⁽¹³⁾, sugar beet pulp⁽¹⁴⁾, kenaf bark⁽¹⁵⁾, peanut shell⁽¹⁶⁾, and hazelnut husk⁽¹⁷⁾. 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.

Concerning the health hazard, 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 process of adsorption 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⁽⁹⁾.

This study aimed at exploring the use of the decanter cake to remove cadmium (II), copper (II) and lead (II) ions in aqueous solution. The factors that affect adsorption capacity, such as carbonization temperature, pH, and initial concentration of metal ion were examined. Langmuir and Freundlich isotherm adsorption models were used to characterize the adsorption process.

Nomenclature

q_e	= adsorption capacity at equilibrium, mg/g
C_o	= initial concentration of metal ion, mg/L
C_e	= concentration of metal ion at equilibrium, mg/L
V	= volume of metal ion solution, mL
W	= weight of adsorbent in metal ion solution, g
q_m	= Langmuir constant related to the capacity of adsorption, mg/g
K_L	= Langmuir constant related to the binding energy of adsorption, L/mg
K_F	= Freundlich constant related to the capacity of adsorption, mg/g
n	= Freundlich constant related to the energy of adsorption, dimensionless

2. 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 °C for 12 h to remove its moisture content. Dried decanter cake was ground and sieved to obtain 600 µm particle diameters. Decanter cake was placed in closed crucible and heated in muffle furnace at a heating ramp of 10 °C min⁻¹, and held at 300 °C for 1 hour. The procedure was repeated for 400, 500, 600, 700 and 800 °C. After natural cooling to room temperature the decanter cake was ground and sieved to obtain the particle size between 45 and 125 µm. Treated decanter cake was put in powder container and placed in desiccator. Decanter cake which was carbonized at 300, 400, 500, 600, 700, and 800 °C were labelled PDC300, PDC400, PDC500, PDC600, PDC700, and PDC800, respectively.

Metal ion stock solutions were prepared from analytical grade Cd(NO₃)₂·4H₂O, Pb(NO₃)₂, and Cu(NO₃)₂·3H₂O. 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 °C at a heating ramp of 5 °C min⁻¹. The gas was switched into oxygen at 950 °C.

Equilibrium time experiments were performed by batch technique in ambient temperature (22 – 24 °C). Series of 100 ml solution in 250 ml glass flask were used. Each flask were filled with Cd²⁺, Cu²⁺, and Pb²⁺ solutions at 100, 200 and 400 mg/l concentration. A dosage of 10 g/L adsorbent was loaded into the solutions. The conical flask were then agitated in orbital shaker at 200 rpm and liquid samples were taken out at a given time interval for Cd²⁺, Cu²⁺ or Pb²⁺ analyses.

Studies on the effect of carbonization temperature were performed using the same technique as in equilibrium time studies. Different type of adsorbent (PDC300, PDC400, PDC500, PDC600, PDC700, PDC800) were loaded into the solutions, and agitated in orbital shaker until equilibrium was reached. Final concentration of metal ion solutions was analyzed to determine amount of metal ion that was adsorbed by adsorbent.

Experiments with each metal ion were performed to determine the effect of pH on metal ion adsorption. 1 g adsorbent were placed in a 250-mL Erlenmeyer with 100.0 mL of metal ion solution at a fixed concentration (400 mg/L, 400 mg/L, and 1000 mg/L for cells Cd²⁺, Cu²⁺, and Pb²⁺, respectively). The pH range studied was from 1 to 6. The pH was adjusted with HCl or NaOH solutions at 0.01–1.0 mol/L. The reaction times used were obtained from the equilibrium time study.

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 the best pH and the best carbonization temperature obtained from previous experiments. 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, q_e (mg/g) was found by a mass balance relationship:

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

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:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

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 calculate from the intercept and slope of the linear plot of C_e/q_e against C_e ⁽¹⁸⁾.

$$q_e = K_F C_e^{1/n} \quad (3)$$

The Freundlich constant K_F and n are related to adsorption capacity and energy of adsorption, respectively⁽²¹⁾. The Freundlich isotherm can also be linearized by the following:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

3. Result and discussion

Plot of thermogravimetry analysis is shown in Fig. 1. The removal of water from the external surface and moisture from the voids of the structure was completed up to 200 °C with a maximum 6.93% weight loss for PDC400. 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. Thermogravimetry analysis indicated that volatile matter of adsorbent was decrease at higher carbonization temperature. Maximum fixed carbon was obtained in carbonization temperature at 600 °C, while maximum total carbon was at 500 °C. Table 1 shows the proximate analysis of adsorbent at various carbonization temperatures.

Table 1. Proximate analysis of adsorbent from decanter cake at various carbonization temperatures

Adsorbent	Moisture, %	Volatile, %	Fixed carbon, %	Ash, %
DDC110	5.47	64.23	8.84	21.46
PDC300	2.88	40.47	12.7	43.95
PDC400	6.93	20.63	18.06	54.38
PDC500	4.08	21.27	22.96	51.69
PDC600	4.43	12.74	26.43	56.40
PDC700	3.55	9.68	20.93	65.84
PDC800	5.29	8.86	17.06	68.79

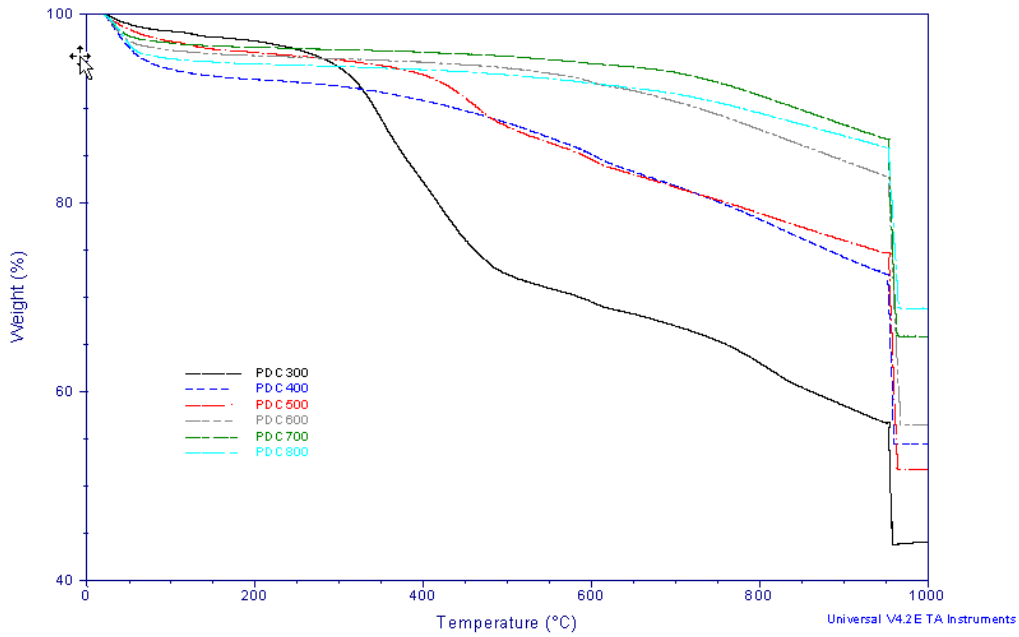


Fig. 1. Thermogravimetry analysis plot for adsorbent at various carbonization temperatures

The scanning electron microscopes of PDC300, PDC500 and PDC700 are shown in Fig. 2. The EDX spectrometry indicates ash of decanter cake contains Al (20.7%), Si (16.6%), Ca (7.8%), K (6.4%), Fe (4.7%) and trace of Cl, P, and S as shown in Table 2.

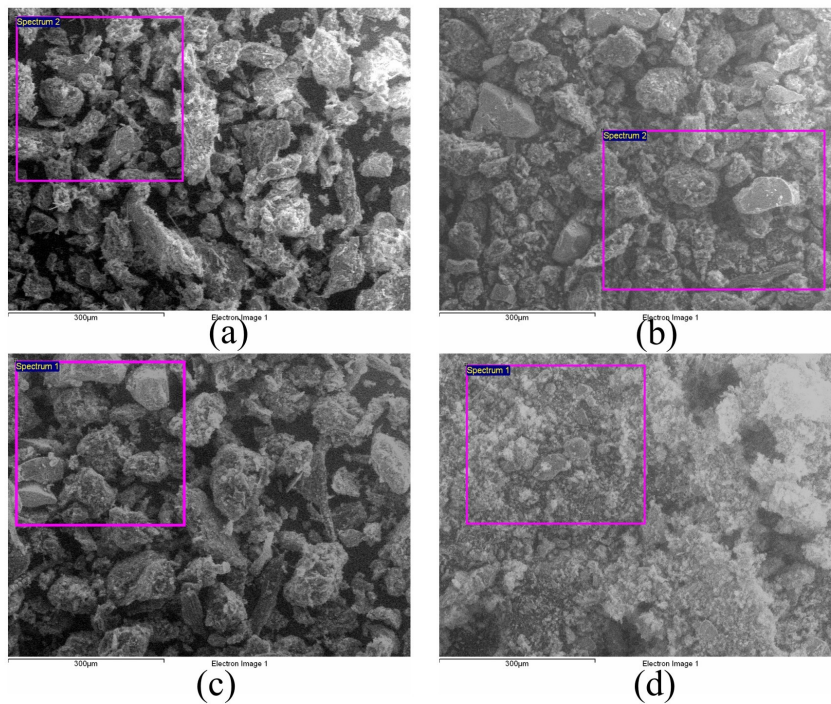


Fig. 2. SEM micrograph of (a) PDC300, (b) PDC500, (c) PDC700, (d) ash.

Table 2. Quantitative result of EDX spectrometry on carbonized decanter cake

Component (%)	DDC	PDC300	PDC500	PDC700	Ash
C	62.1	61.8	58.4	55.5	-
O	35.2	29.4	26.3	22.5	39.2
Si	1.5	4.3	5.5	6.3	16.6
Al	1.2	1.3	4.4	12.2	20.7
Ca	-	1.7	2.9	1.5	7.8
K	-	1.5	2.5	1.5	6.4
Cl	-	-	-	0.6	1.8
Fe	-	-	-	-	4.7
S	-	-	-	-	1.1
P	-	-	-	-	1.6

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_0 as shown in Fig. 3 indicated that the adsorption reached equilibrium at 6 hours for Cd^{2+} and Cu^{2+} , and 60 minutes for Pb^{2+} .

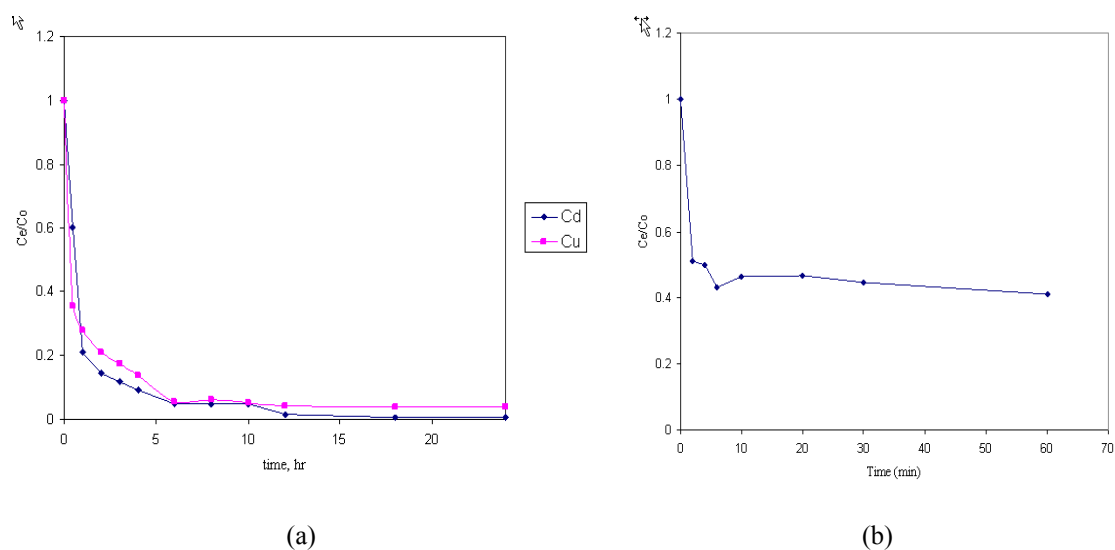


Fig. 3. Equilibrium time for Cd and Cu (a), and Pb (b)

Effect of carbonization temperature in adsorption study was carried out at equilibrium time of each metal ion as determined by previous experiment. Figure 4 shows the effect of carbonization temperature in Cd, Cu and Pb adsorption onto treated decanter cake. Only small amount of metal ions were adsorbed onto PDC 300. This is due to the high oil content as evidence in high % of volatile shown from TGA. Moreover the adsorbent tend to cluster together and cannot be dispersed through the solutions. At higher carbonization temperature, adsorption capacity was increased, and reached maximum capacity at 500 °C of carbonization temperature for Pb and 600 °C of carbonization temperature for Cu and Cd. The adsorption capacity significantly decreased at carbonization temperature above 600 °C.

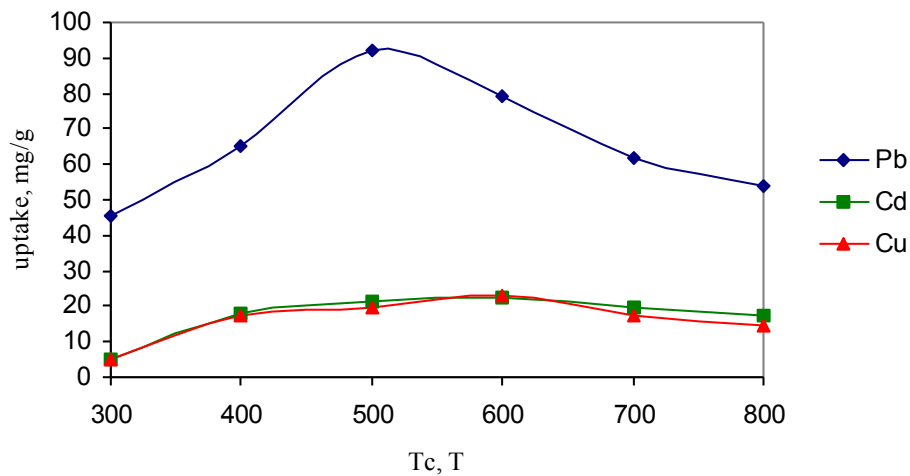


Fig. 4. Effect of carbonization temperature in adsorption of Cd, Cu and Pb onto carbonized decanter cake

The pH of the solution is one of the most important factors in controlling the adsorption of metal ions on the surface of adsorbent. The removal of metal ions was highly dependent on the initial pH condition⁽¹⁹⁾. The maximum uptake of cadmium often happened in acid conditions. To avoid the precipitation in alkaline condition, the adsorption of Cd, Cu and Pb were carried out in acid conditions in this study. Initial concentration of metal ions in aqueous solution for this experiment was 300, 400 and 1000 mg/L for Cd, Cu and Pb respectively. Figure 5 shows the effect of pH on the adsorption capacity of Cd, Cu and Pb by PDC 500. At pH 1, very small amount of metal ions were adsorbed in the experiment. With the increase of pH in the solution, higher uptake of metal ions was occurred. When pH increased from 1 to 4, the adsorption capacities rapidly increased from 0.9 to 14.77, 6.33 to 24.97, and 14.93 to 86.63 mg/g for cadmium, copper and lead respectively. In this range of pH, the functional groups in the adsorbent such as carboxyl or hydroxyl were deprotonated and negatively charged. Consequently, the attraction of positively charged Cd^{2+} , Cu^{2+} and Pb^{2+} ion enhanced. At pH 6, no lead adsorption was observed in the experiment because of precipitation started to occur. The maximum adsorption capacities were reached at pH range 4 – 5. However, above this pH, adsorption decreases.

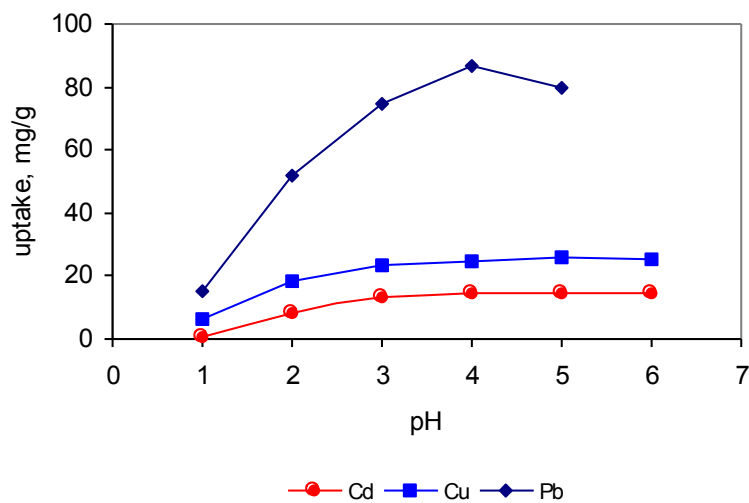


Fig. 5. Effect of pH on adsorption capacity of metal ions in aqueous solution

The experiments of isotherm adsorption were performed using PDC500 for Pb adsorption and PDC600 for Cd and Cu adsorption. pH of adsorption was set at the best pH according to previous experiments. The parameters corresponding to the fitting of these results to the Langmuir and Freundlich isotherm models are shown in Table 3. The values of R^2 indicate that both isotherm models describe metal adsorption onto the adsorbent appropriately. The experimental data showed adsorption ability of decanter cake was comparable to that of other adsorbents as summarized in Table 4.

Table 3. Langmuir and Freundlich parameters for adsorption of metal ions onto pyrolyzed decanter cake

Metal ion	Adsorbent	pH	Langmuir isotherm			Freundlich isotherm		
			q_m (mg/g)	K_L (L/mg)	R^2	K_F (mg/g)	n	R^2
Cd ²⁺	PDC600	4.8	24.30	0.1499	0.9802	6.37	0.2582	0.9954
Cu ²⁺	PDC600	4.8	22.88	0.0583	0.9824	5.77	0.2317	0.9678
Pb ²⁺	PDC500	4.2	96.72	0.2296	0.9904	42.68	0.1489	0.8519

Table 4. Estimated parameters with Langmuir model by different adsorbents

Adsorbents	Cd(II)		Cu(II)		Pb(II)	
	q_m (mg/g)	K_L (L/mg)	q_m (mg/g)	K_L (L/mg)	q_m (mg/g)	K_L (L/mg)
Pyrolyzed decanter cake (this study)	24.30	0.1499	22.88	0.0583	96.72	0.2296
Aspergillus niger ⁽²⁰⁾			33.54	0.0260	34.92	0.0390
Tea waste ⁽²¹⁾			48.00	0.0076	65.00	0.0494
Grape bagasse ⁽²²⁾	53.84	0.0527			42.27	0.0074
<i>Caulerpa lentillifera</i> ⁽²³⁾	4.69	0.0742	5.57	0.0760	28.99	0.0711
Baker's yeast ⁽²⁴⁾	3.90	1.3200			19.01	1.0600
Lignin ⁽²⁵⁾	25.40	0.1421	22.87	0.4309	89.51	0.2081
<i>Mimosa pudica</i> ⁽²⁶⁾	25.30	0.0392	22.70	0.0614	26.10	0.0413
Activated sludge ⁽²⁷⁾	28.10	0.3200	19.06	0.1201	142.96	0.1000

4. Conclusion

In conclusion, pyrolyzed 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. Maximum adsorption uptakes of metal ion were obtained at carbonization temperature of 500 °C for Pb and 600 °C for Cd and Cu. The adsorption of metal ion in aqueous solution with initial pH between 4 and 5 showed to have highest adsorption capacity. 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: Pb²⁺>Cd²⁺>Cu²⁺.

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