



中国高校特色科技期刊
湖北省优秀期刊

ISSN 1672-4321
CODEN ZMDXA3

Zhongnan Minzu Daxue Xuebao
Ziran Kexue Ban

中南民族大学学报

JOURNAL OF SOUTH-CENTRAL UNIVERSITY FOR NATIONALITIES

第28卷第4期

Vol. 28 No. 4

自然科学版

Natural Science Edition

2009 4



ISSN 1672-4321



9 771672 432000

中国·武汉
Wuhan

Journal of South-Central University for Nationalities
(Natural Science Edition)

Vol. 28 No. 4(Sum. No. 93)

December 2009

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Kinetic and Thermodynamic Studies of Cd^{2+} , Cu^{2+} and Pb^{2+} Removal by Decanter Cake from Palm Oil Mill

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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 in waste water. The decanter cake was first dried at 105 °C and then carbonized at 500 °C. The resulting carbonized decanter cake was tested for removing Cd^{2+} , Cu^{2+} and Pb^{2+} ions. Proximate analysis using thermogravimetry of decanter cake carbonized at 500 °C indicated that the adsorbent contained 4 % moisture, 21 % volatiles, 23 % fixed carbon, and 52 % ash. Adsorption tests were 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 fitted 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 including standard enthalpy (ΔH°), standard entropy (ΔS°) and standard free energy (ΔG°) were determined.

Keywords adsorption; metal ions; decanter cake; kinetic; thermodynamic.

中图分类号 O647.32 文献标识码 A 文章编号 1672-4321(2009)04-0001-08

棕榈油厂倾析渣去除镉(Ⅱ)、铜(Ⅱ)及铅(Ⅱ)的 吸附动力学及热力学

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摘要 棕榈油厂的倾析渣含较高有机物质, 可将其用作吸附废水中金属离子吸附剂。倾析渣经 105 °C 干燥后于 500 °C 碳化, 以碳化后的倾析渣去除 Cd^{2+} , Cu^{2+} 和 Pb^{2+} 。采用热重分析法分析碳化后的倾析渣表明: 倾析渣湿度为 4 %, 含挥发物 21 %, 固定碳物 23 %, 灰化物 52 %。运用朗格缪尔 (Langmuir) 等温模型和弗罗因德利奇 (Freundlich) 等温模型分析了含倾析渣 1 g/100 mL 离子水溶液, 结果表明: 碳化后的倾析渣对 Cd, Cu, Pb 的最大吸附量分别为 24, 23, 97 mg/g, 且吸附动力学遵循准二级反应动力学模型。测定了热力学参数标准生成焓 (ΔH°), 标准熵 (ΔS°), 标准自由能 (ΔG°)。

关键词 金属离子; 倾析渣; 动力学; 热力学

Palm oil industries contribute large amount of waste and effluent to the environment. More than

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基金项目 UMP grant (RDU080302)

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 resulted in 23.52 wt % of oil and 5.20 wt % of kernel, while 71.28 wt % was lost as by-product or waste from the fresh fruit bunch milled^[1]. Decanter cake is a solid waste produced from the three phase separation step of crude palm oil sedimentation process. The production rate of decanter cake amounts to about 4 %–5 % weight of fresh fruit bunch processed. Fresh decanter cake contains over 70 % moisture, while the dried decanter cake contains oils, fiber and inorganic components. The most common utilization of decanter cake is as fertilizer and animal nutrition sources due to the contents of C, N, P, K and Mg^[2].

Many studies have recently been reported on the utilization of agricultural waste as effective adsorbent. The employment of pulp and paper mill sludge as adsorbent has been investigated^[3-5], as well as that of sewage sludge^[6-8]. Agricultural waste or by-products and in some cases appropriately modified samples 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 wastewater.

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. Amongst these methods are neutralization, precipitation, ion exchange and adsorption. For low concentration of metal ions in wastewater, the

adsorption process is recommended. The adsorption requires the presence of an adsorbent solid that binds the pollutants by physical attractive forces, ion exchange and chemical binding. It is preferable that the adsorbent is available in large quantities, easily regenerated, and cheap^[9].

This study investigates the kinetic and thermodynamics of Cd^{2+} , Cu^{2+} and Pb^{2+} 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 process.

1 Materials and methods

1.1 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. The decanter cake was dried in an oven at 105 °C for 12 h to remove its moisture content. Dried decanter cake was ground and sieved to obtain 400–600 μm particles and placed in enclosed crucible and heated in a muffle furnace at a heating ramp of 10 °C/min, and held at 500 °C for 1 h. After natural cooling to room temperature, the decanter cake was ground and sieved to obtain particles of sizes between 45 and 125 μm . Treated decanter cakes were placed in containers in desiccator.

Metal ions stock solutions were prepared from analytical grade $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Pb}(\text{NO}_3)_2$, and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$. Metal salts were dissolved in distilled water to obtain concentration of 1 000 mg/L. Lead nitrate was obtained from HmbG Chemicals. Cadmium nitrate tetrahydrate from Fluka. Copper nitrate trihydrate from R&M Chemicals. Standard solutions of Cd^{2+} , Cu^{2+} and Pb^{2+} for AAS analysis were purchased from Merck.

1.2 Methodology

The adsorbents were characterized by TA

Instruments-Waters' TGA Q 500 Instrument to determine thermal properties and for proximate analysis. The samples were heated in a nitrogen atmosphere from ambient temperature to 1 000 °C at a heating ramp of 5°C/min. The gas was switched to oxygen at 950 °C. BET surface area analysis was performed using Quantachrome Instruments.

Equilibration 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 was filled with Cd^{2+} , Cu^{2+} , and Pb^{2+} solutions at 100, 200 and 400 mg/L concentration. 1 g of adsorbent was loaded into the solution to give a dosage of 10 g/L. The conical flasks were then agitated in an orbital shaker at 200 r/min and samples were taken out at given time intervals for Cd^{2+} , Cu^{2+} or Pb^{2+} analyses.

The 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 the 1 000 mg/L stock solutions. The adsorption studies were performed in pH range of 4 – 5. Langmuir and Freundlich isotherm adsorption models were employed to fit the adsorption data. The concentrations of metal ions 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:

$$q_e = (\rho_0 - \rho_e)V/W, \quad (1)$$

where ρ_0 (mg/L) and ρ_e (mg/L) are the initial and the equilibrium liquid-phase concentration of the metal ions, respectively, V (L) the volume of the solution and W (g) the weight of the adsorbent.

Fittings of the data to Langmuir (Eq. (2)) and Freundlich (Eq. (3)) isotherm models were determined from:

$$q_e = (q_m K_L \rho_e) / (1 + K_L \rho_e), \quad (2)$$

where q_m (mg/g) and K_L (L/mg) are the Langmuir parameters, related to the maximum capacity of

adsorption and the binding energy of adsorption, respectively. The values of q_m and K_L can be calculate from the intercept and slope of the linear plot of ρ_e/q_e against ρ_e ^[18].

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

The Freundlich constant K_F and n are related to the adsorption capacity and energy of adsorption, respectively^[19]. The Freundlich isotherm can be linearized to:

$$\ln q_e = \ln K_F + (1/n) \ln \rho_e. \quad (4)$$

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, and 1 000 mg/L for Pb. The procedure of kinetic adsorption tests was identical to that of batch equilibration tests; however the aqueous samples were taken at preset time intervals.

The first order rate expression based on the adsorbent capacity is generally expressed as follows^[20]:

$$dq/dt = k_1(q_e - q). \quad (5)$$

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

$$\ln(q_e - q) = \ln q_e - k_1 t. \quad (6)$$

Pseudo second order model is derived on the basis of the sorption capacity of the adsorbent phase^[18], expressed as

$$dq/dt = k_2(q_e - q)^2, \quad (7)$$

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

$$1/(q_e - q) = 1/q_e + k_2 t. \quad (8)$$

The linear form of Eq. (8) is

$$t/q = t/q_e + 1/k_2 q_e^2. \quad (9)$$

The thermodynamic studies were performed by adsorption 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^{2+} and Cu^{2+} , and 500 mg/L for Pb^{2+} . The distribution coefficient K_d , equals to q_e/ρ_e , were calculated at four different temperatures.

The Gibbs free energy (ΔG°), the enthalpy

(ΔH°) and the entropy (ΔS°) for the adsorption process can be expressed as:

$$\Delta G = -RT \ln K_d, \quad (10)$$

$$\ln K_d = \Delta S/R - \Delta H/RT. \quad (11)$$

The enthalpy change and the entropy change can be calculated from a plot of $\ln K_d$ vs. $1/T$ ^[18].

2 Results 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 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 to oxygen atmosphere at 950 °C. Final weight at 1 000 °C was identified as ash content of materials. Proximate analysis of the adsorbent indicated that it consisted of 4.08 % moisture, 21.27 % volatile, 22.96 % fixed carbon and 51.69 % ash^[21].

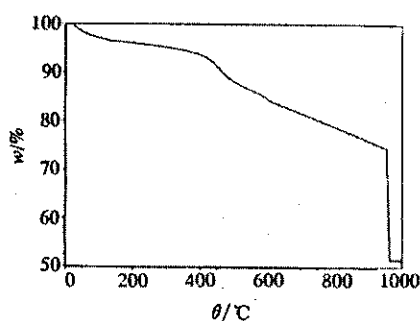


Fig. 1 Thermogravimetry analysis plot for adsorbent

The scanning electron microscope image of the adsorbent is shown in Fig. 2. The EDX spectrometry indicates that the adsorbent contained C(58.4 %), O(26.3 %), Si(5.5 %), Al(4.4 %), Ca(2.9 %) and K(2.5 %). BET

surface area of the adsorbent was 27.27 m²/g.

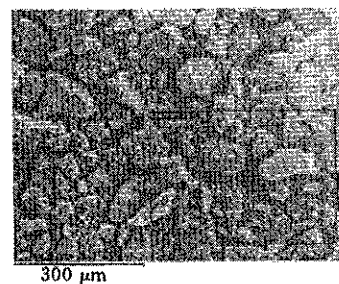


Fig. 2 SEM micrograph of pyrolyzed decanter cake

Equilibrium time of adsorption was determined by taking 1 g adsorbent in 100 mL of certain initial concentration of metal ions (400 mg/L for Cd²⁺ and Cu²⁺ and 1 000 mg/L for Pb²⁺). The plot of ρ_e/ρ_0 as shown in Fig. 3 indicates that the adsorption attained equilibrium at 6 h for Cd²⁺ and Cu²⁺, and 60 min for Pb²⁺.

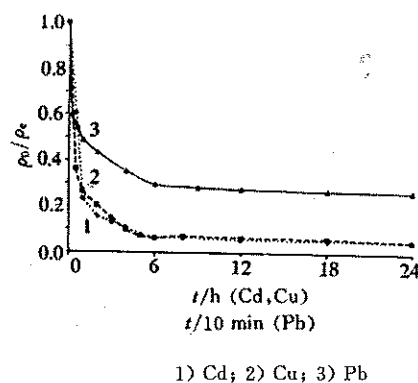


Fig. 3 Equilibrium time for Cd²⁺, Cu²⁺ and Pb²⁺

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 Fig. 4. The values of R^2 (coefficient of determination) indicate that both the isotherm models were obeyed.

Tab. 1 Langmuir and Freundlich parameters for adsorption of metal ions on pyrolyzed decanter cake

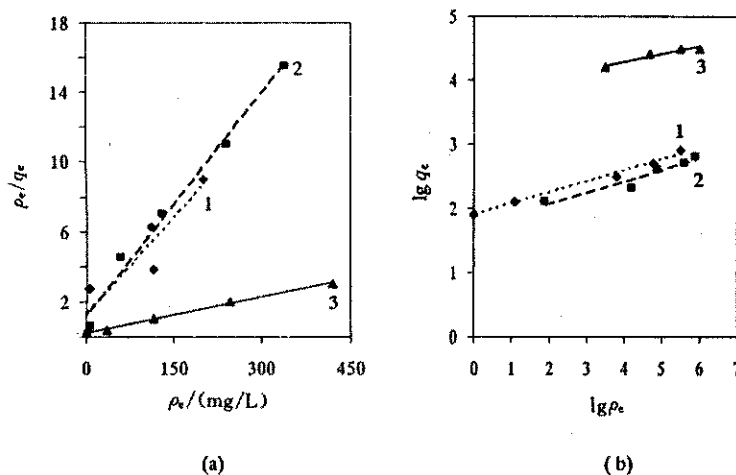
Langmuir isotherm			Freundlich isotherm		
$q_m/(mg/g)$	$K_L/(L/mg)$	R^2	$K_F/(mg/g)$	n	R^2
24.30	0.149 9	0.980 2	8.00	0.199 7	0.979 7
22.88	0.058 3	0.982 4	5.78	0.242 9	0.954 9
96.72	0.229 6	0.990 4	24.20	0.261 0	0.877 8

The prediction of adsorption rate gives important information for designing batch adsorption systems. Information on the kinetics of metal ion uptake is required for selecting optimum operating conditions for full-scale batch process. Pseudo-first-order and pseudo-second-order kinetic models were applied in the experiment data. Plots

of the linear forms of both models are shown in Fig. 5. Table 2 indicates that pseudo-second-order kinetic model provided better correlation for Cd^{2+} , Cu^{2+} and Pb^{2+} adsorption on decanter cake than pseudo-first-order kinetic model. This result is comparable with other studies as shown in Table 3.

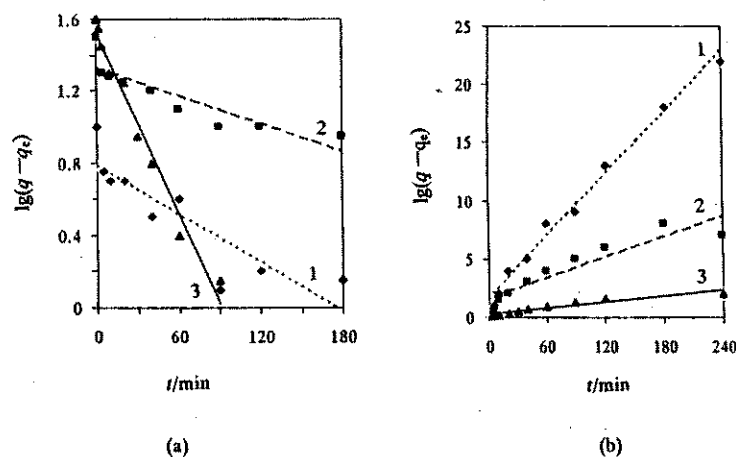
Tab. 2 Pseudo-first-order and pseudo-second-order kinetic model parameters for Cd^{2+} , Cu^{2+} and Pb^{2+} adsorption onto decanter cake

metal ion	pseudo-first-order kinetic model				pseudo-second-order kinetic models			
	k_1/min^{-1}	$q_e/(\text{mg/g})$	R^2	$q_e(\text{exp})/(\text{mg/g})$	$k_2/(\text{g}/(\text{mg} \cdot \text{min}))$	$q_e/(\text{mg/g})$	R^2	$q_e(\text{exp})/(\text{mg/g})$
Cd^{2+}	0.005 43	14. 25	0. 788 8	21. 87	0. 002 31	22. 70	0. 977 5	21. 87
Cu^{2+}	0. 002 23	19. 49	0. 734 8	19. 49	0. 001 32	27. 02	0. 994 6	29. 13
Pb^{2+}	0. 019 00	34. 73	0. 927 8	34. 73	0. 004 75	117. 66	0. 999 1	116. 62



1) Cd; 2) Cu; 3) Pb

Fig. 4 Plot of Langmuir (a) and Freundlich (b) adsorption isotherm for Cd^{2+} , Cu^{2+} and Pb^{2+} onto decanter cake



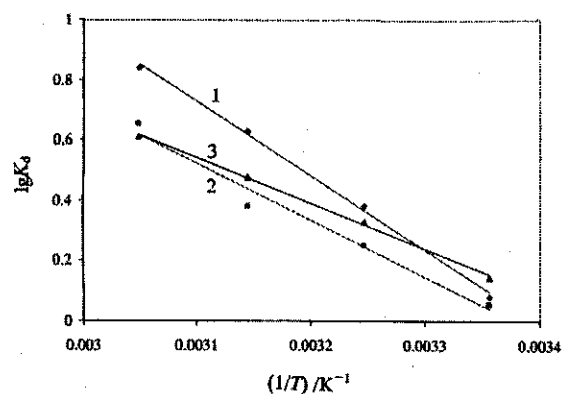
1) Cd; 2) Cu; 3) Pb

Fig. 5 Plot of pseudo-first-order (a) and pseudo-second-order (b) kinetic models for adsorption of Cd^{2+} , Cu^{2+} and Pb^{2+} onto decanter cake

Tab. 3 Comparison of pseudo-second-order kinetic parameters for selected adsorbent

type of adsorbent	$k_2/(\text{g}/(\text{mg} \cdot \text{min}))$			$q_e/(\text{mg}/\text{g})$			Ref.
	Cd^{2+}	Cu^{2+}	Pb^{2+}	Cd^{2+}	Cu^{2+}	Pb^{2+}	
decanter cake	0.002 31	0.001 32	0.004 75	22.70	27.02	117.66	this study
dried activated sludge	0.015 7	—	0.006 2	9.80	—	83.50	[22]
tea waste	—	0.013 3	0.009 1	—	19.00	35.00	[23]
lignin	0.013 1	0.045 1	0.040 9	18.21	17.53	62.99	[24]
cedar sawdust	—	0.005 93	—	—	31.35	—	[25]
tree fern	0.107 0	—	—	12.00	—	—	[26]

The effect of temperature on the adsorption equilibrium of Cd^{2+} , Cu^{2+} and Pb^{2+} on the pyrolyzed decanter cake was investigated. Adsorption of Cd^{2+} , Cu^{2+} and Pb^{2+} increased as the temperature was increased from 298 to 328 K. The values of thermodynamic parameters were calculated from the plots of $\ln K_d$ versus $1/T$ as shown in Fig. 6, while the results are listed in Table 4. These results are comparable with other adsorbents as described in Table 5.

1) Cd^{2+} ; 2) Cu^{2+} ; 3) Pb^{2+} Fig. 6 Plot of $\ln K_d$ vs. $1/T$ for Cd^{2+} , Cu^{2+} and Pb^{2+} decanter cakeTab. 4 Thermodynamic parameters for adsorption of Cd^{2+} , Cu^{2+} and Pb^{2+} onto pyrolyzed decanter cake

metal ion	$\Delta H^\circ/(\text{kJ}/\text{mol})$	$\Delta S^\circ/(\text{J}/(\text{mol} \cdot \text{K}))$	R^2	$\Delta G^\circ/(\text{kJ}/\text{mol})$			
				298 K	308 K	318 K	328 K
Cd^{2+}	20.52	70	0.990 3	-0.24	-0.93	-1.63	-2.32
Cu^{2+}	15.63	53	0.995 1	-0.10	-0.62	-1.15	-1.68
Pb^{2+}	12.58	43	0.996 2	-0.38	-0.81	-1.25	-1.68

Tab. 5 Comparison of thermodynamic parameters for selected adsorbent

type of adsorbent	ion	$\Delta H^\circ/(\text{kJ}/\text{mol})$	$\Delta S^\circ/(\text{J}/(\text{mol} \cdot \text{K}))$	$\Delta G^\circ/(\text{kJ}/\text{mol})$	temperature range/K	Ref.
decanter cake	Cd^{2+}	20.52	70	0.24~2.32	298~328	this study
	Cu^{2+}	15.63	53	0.10~1.68		
	Pb^{2+}	12.58	43	0.38~1.68		
raw bentonite	Pb^{2+}	39.00	200	21.60~28.60	303~338	[27]
<i>S. albus</i> biomass	Pb^{2+}	17.18	68.40	3.22~5.27	288~318	[28]
$\text{Cu}(\text{II})$ -MICA	Cu^{2+}	10.70	40	1.22~2.42	298~328	[18]
chelating resin (CR10)	Cu^{2+}	-10.60	37.16	21.67~22.77	298~328	[29]
<i>P. simplicissimum</i> biomass	Cd^{2+}	20.03	130.90	18.27~20.88	293~313	[30]
phosphate rock	Cd^{2+}	16.93	122	19.19~22.12	283~313	[31]
	Cu^{2+}	10.80	110	16.97~19.47		
	Pb^{2+}	23.00	164	24.59~27.20		

Positive ΔH° value indicate the endothermic nature of the adsorption, which was supported by the increase in the adsorption of Cd^{2+} , Cu^{2+} and Pb^{2+} with temperature. This result suggested that

ion-exchange may have played a significant role in the adsorption. The adsorption free energy (ΔG°) has negative values for all ions under all conditions which reflect the spontaneity of the process. The

positive ΔS° revealed that the degrees of freedom increased at the solid-liquid interface during the adsorption.

3 Conclusion

In conclusion, pyrolyzed decanter cake could be considered a good candidate for the adsorption of metals, in particular cadmium, copper and lead. The experiment results showed that the adsorption capacity for lead was obviously higher than for cadmium and copper. The experimental 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 fits the adsorption process of Cd^{2+} , Cu^{2+} and Pb^{2+} on the pyrolyzed decanter cake. Thermodynamic properties of Cd^{2+} , Cu^{2+} and Pb^{2+} adsorption onto the pyrolyzed decanter cake are comparable with other adsorbents.

Acknowledgement The authors gratefully acknowledge Universiti Malaysia Pahang for supporting the research through RDU080302. One of the authors N. Dewayanto also acknowledges the university for financial support through the Graduate Research Scheme.

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