

The 3rd International Conference on Green Chemical Engineering Technology
(3rd GCET_2017): Materials Science

Kinetics, Isotherms, And Thermodynamic Studies on the Adsorption of Mercury (II) Ion from Aqueous Solution Using Modified Palm Oil Fuel Ash

M.S. Imla Syafiqah^a, H.W. Yussof^{a,*}

^aFaculty of Chemical Engineering & Natural Resources, Universiti Malaysia Pahang, 26300 Gambang, Pahang, Malaysia

Abstract

Palm oil fuel ash (POFA) is a waste material generated from the boiler due to the burning of palm oil biomass e.g. kernel shell and fiber as fuel to generate electricity. The present research focused on the study of adsorption isotherms, kinetics and thermodynamic properties on the removal of mercury (II) ion onto POFA. The prepared POFA was characterized by FTIR, TGA and BET analysis. The equilibrium data at various concentrations were analyzed by Langmuir and Freundlich isotherms models. From this present study, the maximum adsorption capacity obtained from the Freundlich isotherm was 0.99 mg/g. A kinetic study was carried out with pseudo first order and pseudo second order reaction equations. It was found that the mercury (II) ion uptake process followed the pseudo second order rate expression. Thermodynamic parameters of the Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) were also determined. The negative Gibbs free energy change (-788.90 kJ/mol) and the positive enthalpy change (73,680.33 kJ/mol) indicated that adsorption was spontaneous process and endothermic nature. Overall, POFA looks to be a promising adsorbent for removal of mercury (II) ion from aqueous solutions due to its high performance and availability at low cost.

© 2018 Elsevier Ltd. All rights reserved.

Selection and/or Peer-review under responsibility of The 3rd International Conference on Green Chemical Engineering and Technology (3rd GCET): Materials Science, 07-08 November 2017.

Keywords: palm oil fuel ash; mercury; isotherms; kinetics; thermodynamics.

1. Introduction

Malaysia was one of the largest producers and exporters of palm oil in the world in 2003, and it contributed to 49% of world production amounted 13.4 million tons with 58% or 12.2 million tons of total export [1]. However,

2214-7853 © 2018 Elsevier Ltd. All rights reserved.

Selection and/or Peer-review under responsibility of The 3rd International Conference on Green Chemical Engineering and Technology (3rd GCET): Materials Science, 07-08 November 2017.

this one of the important economic activity generates a huge amount of waste which could pollute the environment if not properly treated. One of the waste generated from the palm oil mills boiler is palm oil fuel ash (POFA). POFA is the solid ultrafine ash obtained from combustion of palm kernels and bunches in palm oil mills boiler for steam production at temperatures of 800–1000 °C [2]. The conventional method to discard these wastes. However, this method raises some environmental concerns due to the production of large amounts of POFA [3]. Previous studies have shown the possibility of using POFA as an adsorbent for dye removal [4], generation of electricity [5] and as a cement replacement material [6].

The World Health Organization considers mercury as one of the top ten chemicals or groups of chemicals of major public health concern [7]. Mercury is one of the most harmful environmental contaminants, which cause harmfulness even at low concentrations [8]. Mercury is considered health hazards, and there are numerous reports of mercury poisoning from agricultural, laboratory exposure and industrial wastewater [9]. Therefore, this mercury should be effectively treated before been discarded into drainage.

Due to the growing concerns about the adverse impact of mercury on human health and ecological environments, efforts have been made to find an efficient method for its remediation. There are many common techniques in practices to remove mercury from wastewaters, such as adsorption [10], ion exchange [11], flocculation [12] and ultrafiltration [13]. Among several chemical and physical methods, adsorption process is one of the effective techniques that have been successfully employed for mercury removal from industrial wastewater [7]. Adsorption is widely accepted as one of the simplest, most adaptable, and well established technique for removal of heavy metals including mercury. In most cases, adsorption is an affordable process and does not need advanced technologies. However, for industrial application, the selection of adsorbent material is mostly done by availability of waste material and applicability of the adsorption method taking into account on space, cost, and the amount of wastewater [14].

This study aims to investigate the adsorption isotherms, kinetic and thermodynamic properties of mercury (II) ion removal using POFA. The kinetics of the adsorption process was tested using pseudo-first-order and pseudo second order kinetic models. The Langmuir and Freundlich isotherm models were used to describe equilibrium isotherms. The adsorption mechanisms of mercury (II) onto POFA were also evaluated in terms of thermodynamic properties.

2. Material and methods

2.1. Materials

POFA was obtained from Kilang Sawit Lepar in Kuantan, Pahang. It was washed with distilled water several times to remove dust and impurities and oven dried in 110 °C for 24 hr to control the rate of the moisture content. 50 g of POFA was modified by 0.5 M H₂SO₄ for 24 hr. It was sieved through a 100 µm in order to remove any foreign material and bigger size ash particles and stored in an airtight container.

2.2. Characterization

The BET surface area of the samples was determined by N₂ adsorption on a Micromeritics Accelerated Surface Area Porosimeter 2020 (Micromeritics Instrument Corp., USA). The thermal stability was determined using TGA with a TA Instruments Model Q-500 (USA) on POFA. Measurement was carried out between 50 °C and 1000 °C with heating rate set at 10 °C/min in nitrogenic atmosphere. FTIR of raw POFA and after mercury sorption were recorded on a Spectrum 100 FTIR spectrometer (Perkin Elmer, USA).

2.3. Adsorption experiments

Adsorption experiments were carried out in 250 ml flask containing 50 ml of mercury (II) ions solution at different concentration. The flasks were stirred at 100 rpm in an incubator shaker to the equilibrium. Samples were filtered through vacuum filter and the filtrates were analysed using the direct mercury analyser RA-3310 (Nippon Instrument Corporation, Japan). The pH value was adjusted to 7 by adding 0.1 M HCl or 0.1 M NaOH solution.

The removal efficiency of each adsorbent was calculated using equation 1:

$$\text{Removal Efficiency (\%)} = (C_0 - C_e)/C_e \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration of the adsorbate, respectively, both in mg/L. In order to obtain a more realistic value for sorption capacity, the amount of mercury ions adsorbed per unit mass of each adsorbent was evaluated using equation 2:

$$q_e = (V(C_0 - C_e))/m \quad (2)$$

where q_e is the amount of mercury ions adsorbed per gram of adsorbents in (mg/g), V is the test solution volume (L), and m is the weight of sorbent (g).

2.4. Adsorption kinetics

The kinetic investigations are important for adsorption studies since they can predict the potential rate-controlling step and the mechanism of adsorption reactions. The kinetic studies were carried out using 0.25 g of POFA in 50 ml of different contact time (0, 2, 10, 20, 30, 60, 240 and 360 min) of mercury (II) ion solutions at pH 7.

2.5. Adsorption isotherms

Data from the equilibrium studies carried out at 25 °C with different initial mercury (II) ion concentrations (1, 2, 3,4 and 5 mg/L) of adsorbate was used to check the applicability of Langmuir and Freundlich isotherms under specific conditions, pH of 7, adsorbent dose of 0.25 g, agitation speed of 150 rpm, and contact time of 5 hr.

2.6. Adsorption thermodynamics

The thermodynamic studies were conducted at different temperatures (15, 25,35 and 45 °C) with 5 mg/l of initial mercury (II) ion concentration at pH 7 for investigating the thermodynamic parameters. 0.25 g of POFA were added into conical flasks containing 50 mL of mercury (II) ion solutions. The flasks were shaken for 5 h to ensure equilibrium. After that, the adsorbents were removed by filtration, and the final concentrations of mercury (II) ion in the filtrates were analysed.

3. Results and discussion

3.1. Characterization of POFA

In order to explore the physical properties of modified POFA, including surface area, pore volume and average pore size, samples were characterized by BET. The BET analysis results have been summarized in Table 1. The BET surface area for raw and modified POFA is 20.07 m²/g and 28.48 m²/g, respectively

It can be observed that the modified of the POFA led to a significant increase in the surface area compared to the raw POFA. This increase in surface area is necessary as it enables the modified POFA act as a support material capable of accommodating a larger amount of the impregnating media. Surface area of modified carbon indicated the adsorption property of POFA which bestowed it with the capacity to adsorb mercury (II) ion. Acid activation is reported to have improved the surface area of the ash [15].

The results of thermal gravimetric analysis (TGA) test and Fourier Transform Infrared Spectroscopy (FTIR) in Fig. 1(a)(b) were reported in the previous study by [16].

Table 1. BET surface area analysis of the POFA.

Adsorbent	BET Surface area (m ² /g)	Pore diameter (Å)	Pore volume (cm ³ /g)
Raw POFA	20.07	100.94	0.0499
Modified POFA	28.49	132.87	0.0933

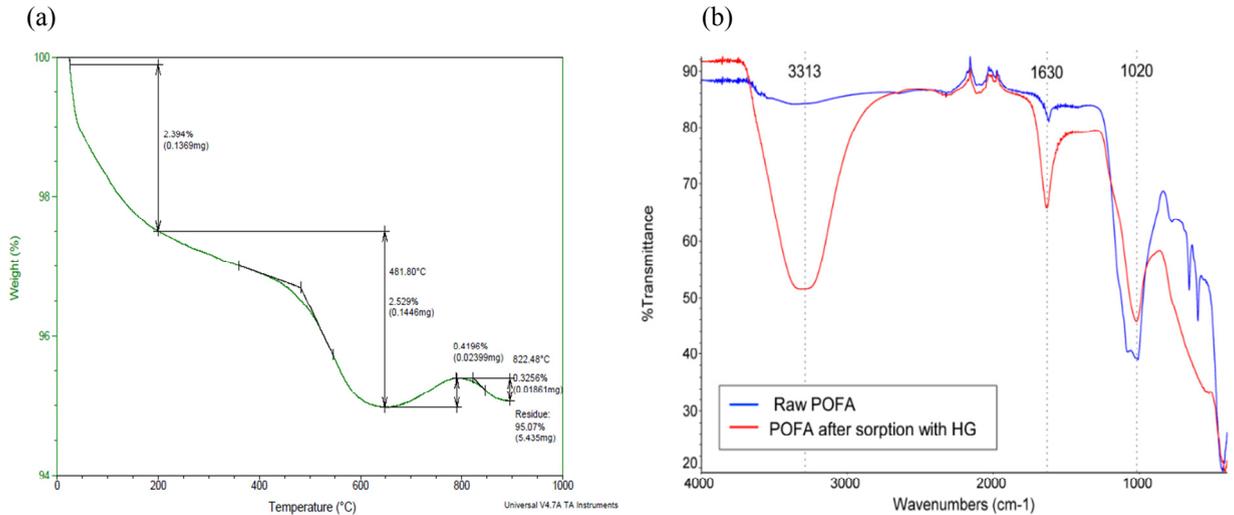


Fig. 1. (a) TGA results on modified POFA, (b) FT-IR spectra of the POFA

3.2. Adsorption kinetics

In order to describe the kinetic process between aqueous and solid phase, the resulting experimental data was plotted and the kinetic model parameters were calculated using the model equations. Furthermore, kinetic models were used to describe the relationship between the adsorption capacity and contact time to explain the adsorption process and the potential rate-limiting step and pseudo second order models were applied to simulate the adsorption data. The equations 3 and 4 are given as:

$$\log (q_e - q_t) = \log q_e - k_1/2.303 t \quad (3)$$

$$t/q_t = 1/(k_2 q_e^2) + t/q_e \quad (4)$$

where q_e and q_t are the amounts of mercury(II) ions adsorbed (mg/g) at equilibrium and at time t (min), respectively, and k_1 (1/min) is the rate constant of first-order adsorption. The values of k_1 are calculated using the plots of $\log (q_e - q_t)$ versus t . The k_2 (g/mg min) is the rate constant of the second order adsorption.

The plots are presented in Fig. 2(a)(b), and the kinetic parameters together with the regression coefficients (R^2) are calculated and shown in Table 1. It can be observed that the R^2 of the pseudo second order model are higher than those of the pseudo first order model. The value of the correlation coefficient R^2 for the pseudo second-order adsorption model is much higher (0.9998) than the value of R^2 for the pseudo first order model (0.9805). The results indicate that the adsorption of mercury(II) ion onto POFA has a more precise fitting towards the pseudo second order equation. Therefore, it was concluded that the pseudo second order adsorption model is more suitable to describe the adsorption kinetics of mercury(II) ion uptake by POFA. Similar kinetic results have also been reported for the adsorption of 4-nitrophenol (4-NP) by NaOH-Modified Palm oil fuel ash [1].

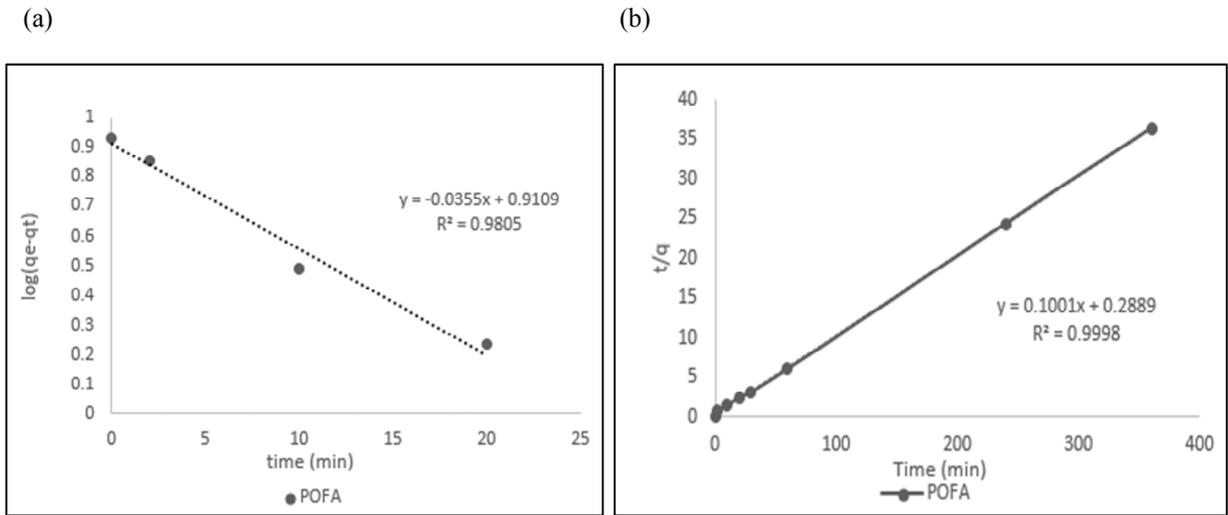


Fig. 2. (a) Pseudo first order, (b) pseudo second order kinetics of mercury (II) ion onto POFA

Table 2. Kinetic parameters for the adsorption of mercury(II) ion by POFA

Adsorbent	Pseudo first order kinetic model			Pseudo second order kinetic model		
	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 (mg/(gmin))	q_e (mg/g)	R^2
POFA	0.0818	8.1452	0.9805	0.0347	9.9900	0.9998

3.3. Adsorption isotherms

Adsorption isotherm describes the relationship between the amount of a solute adsorbed and its concentration in the equilibrium solution at a constant temperature. Adsorption isotherm is important to understand the solute-adsorbent interactions and improve the use of adsorbents. Several models have been investigated to describe experimental data of adsorption isotherm. The equilibrium isotherms like Langmuir and Freundlich isotherms were analysed in this study. The isotherm illustrates the relationship between the equilibrium amount of solute on the adsorbent and the solute concentration in solutions. Langmuir model is based on a monolayer of the adsorbate adsorbed and it is only favorable for the homogeneous surface. Freundlich model suggests neither homogeneous site energies nor limited levels of adsorption. This means that the Freundlich model can describe the experimental data of adsorption isotherm whether adsorption occurs on homogeneous or heterogeneous sites and it is not controlled by the formation of the monolayer [1]. Additionally, Freundlich isotherm is commonly used to describe the both multilayer adsorption and adsorption on heterogeneous surfaces where the interaction of adjacent adsorbed molecules exists. The non-linear and linear forms of Langmuir model and the Freundlich model are expressed by Equations. (5)-(8), respectively.

$$\text{Langmuir nonlinear equation } q_e = (QbC_e)/(1 + bC_e) \tag{5}$$

$$\text{Langmuir linear equation } C_e/q_e = 1/Qb + C_e/Q \tag{6}$$

$$\text{Freundlich nonlinear equation } q_e = K_f C_e^{1/n} \tag{7}$$

$$\text{Freundlich linear equation } \log q_e = \log K_f + 1/n \log C_e \tag{8}$$

where q (mg/g) is the maximum amount of adsorption with the complete monolayer coverage on the adsorbent surface and b ($L\ mg^{-1}$) is the Langmuir constant, which is related to the energy of adsorption. The terms $K_f [(mg\ g^{-1})(L\ mg^{-1})^{1/n}]$ and $1/n$ is the heterogeneity factor which is related to the capacity and intensity of the adsorption, respectively which related to the Freundlich constants. The values of q and b can be calculated from the slope and the intercept, respectively from the linear plots of C_e/q_e against C_e . The K_f and $1/n$ values can be calculated from the intercept and the slope of the linear plot between $\log C_e$ versus $\log q_e$, respectively. The dimensionless separation factor, R_L which is expresses the essential characteristic of the Langmuir equation is also calculated by the following equation 9:

$$R_L = 1/(1 + K_L C_o) \quad (9)$$

where K_L is the Langmuir constant and C_o is the initial mercury (II) ion concentration. The separation factor “ R_L ” indicates the nature of the adsorption process as given in Table 3.

Table 3. The nature of the process depending on the value of separation factor (R_L).

Value of separation factor (R_L)	Nature of the process
$R_L > 1$	Unfavourable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

The results on both Langmuir and Freundlich models are shown in Fig. 3(a)(b) and the adsorption parameters along with correlation coefficients R^2 are given in Table 4. It was found that the value of $1/n$ is 0.5077 which is in fact between 0 and 1, indicating the heterogeneity of the POFA surface and the affinity of mercury (II) ions [7], which indicates the adsorption of mercury (II) ion onto POFA is favourable. The most precise match was acquired using the Freundlich model based on a higher R^2 values. The correlation coefficient R^2 of the linearized equation of the Freundlich model for the adsorption of mercury (II) ion was 0.9943, which is higher than the R^2 value of the Langmuir model at 0.9828. Freundlich’s isotherm model suggests that multilayer adsorption was involved in the adsorption of mercury (II) ion onto the POFA [17]. Consequently, the assumption of multilayer adsorption is well fitted with the obtained experimental data in the studied initial mercury (II) ion concentration range. According to [18] the Freundlich model suggests that the adsorption on the surface is heterogeneous, that interactions among adsorbed molecules can occur, and that multilayer adsorption is possible. In fact, [19] report that the adsorption of dyes using nanowires adsorbent shows the same general trend when Freundlich equation gives the best fit and the values of $1/n$ was between $0 \leq 1/n \leq 1$ represent good adsorption of dyes onto nanowires adsorbent.

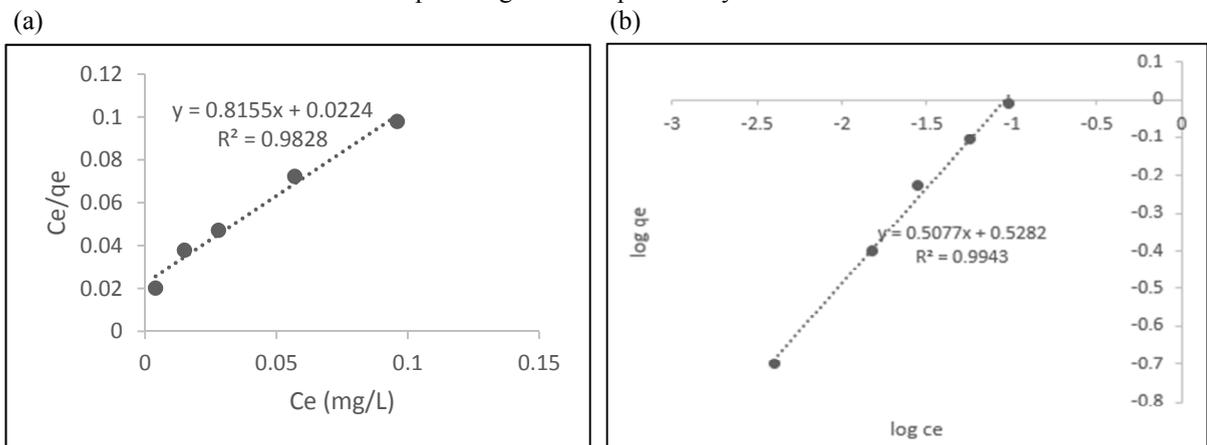


Fig. 3. (a) Langmuir, (b) Freundlich adsorption isotherm of mercury (II) ion onto POFA

Table 4. Langmuir and Freundlich isotherm parameters for adsorption of mercury (II) ion onto POFA

Adsorbent	Langmuir				Freundlich		
	q_e (mg/g)	b (L/mg)	R_L	R^2	$1/n$	K_F [(mg/g)(L/mg) ^{1/n}]	R^2
POFA	1.2262	36.41	0.0055	0.9828	0.5077	3.3744	0.9943

3.4. Adsorption thermodynamics

The feasibility of the adsorption process was estimated by the determination of thermodynamic parameters of free energy change (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) which are calculated from the following equation (10)-(13):

$$K_C = C_{Ae}/C_e \quad (10)$$

$$\Delta G^\circ = -RT \ln K_C \quad (11)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (12)$$

$$\ln K_C = (\Delta S^\circ)/R - (\Delta H^\circ)/RT \quad (13)$$

where K_C is the equilibrium constant, C_e is the equilibrium concentration in solution (mg/L), and C_{Ae} is the amount of mercury(II) ion adsorbed on the adsorbent per liter of solution at equilibrium (mg/L). ΔG° , ΔH° and ΔS° are changes in Gibbs free energy (kJ/mol), enthalpy (kJ/mol), and entropy (J/molK), respectively, R is the gas constant (8.314 J/molK), and T is the temperature (K). The values of ΔH° and ΔS° can be obtained from the slope and intercept of a plot of $\ln K_C$ versus $1/T$ (Fig. 4), respectively. The parameters for the adsorption process are listed in Table 5.

From the result, it was found that the value of negative ΔG° increases with an increase in temperature from 288 to 318 K. The negative value of Gibbs free energy changes indicate that the adsorption process is favorable and spontaneous. The positive values of ΔH° and ΔS° indicate the endothermic nature and randomness during mercury (II) ion adsorption, respectively. This was also supported by the increase in adsorption capacity of mercury (II) ion with increase in temperature [20]. The enthalpy values indicated the possible domination of chemical forces in the mercury (II) ion adsorption system. The increase in the randomness may be associated with the fact that the adsorbed water molecules which are replaced by the adsorbate species gain more translational entropy, which allows the prevalence of randomness in the system [17].

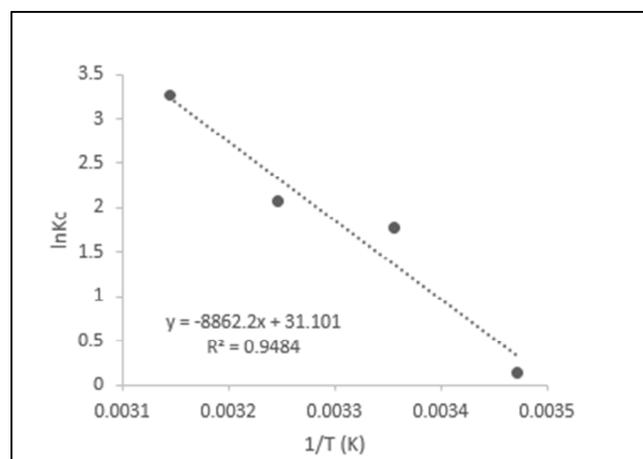


Fig. 4. Thermodynamic study for mercury (II) ion adsorption onto POFA

Table 5. Thermodynamic parameters for the adsorption of mercury (II) ion BY POFA

Temperature (K)	Thermodynamic parameters		
	ΔG° (kJ.mol ⁻¹)	ΔH° (kJ.mol ⁻¹)	ΔS° (J.mol ⁻¹ .K ⁻¹)
288	-788.90		
298	-3,374.64		
308	-5,960.37	73,680.33	258.57
318	-8,546.11		

4. Conclusions

Modified palm oil fuel ash was used as an adsorbent for the removal of mercury (II) ion from an aqueous solution. According to the values of correlation coefficients, R^2 the pseudo second order kinetic model fits very well with the adsorption data. The Freundlich model agrees very well with the equilibrium isotherm. The R_L values showed that modified palm oil fuel ash was favorable for the adsorption of mercury (II) ion. The thermodynamic analysis showed that the adsorption process of mercury (II) ion using POFA was endothermic reaction and a spontaneous process. Overall, the present investigation showed that modified palm oil fuel ash was a promising low cost adsorbent to be used in the removal of mercury (II) ion from aqueous solutions.

Acknowledgements

This research work was funded by the Universiti Malaysia Pahang under Internal Grant PGRS 170382 and RDU 170350. The authors would like to thank Mr. Mohamad Zaki Bin Sahad for his support and assistance with this research.

References

- [1] H.A. AL-Aoh, M.J. Maah, A.A. Ahmad, M.R. Abas, *Journal of Purity, Utility Reaction and Environment*, 1(2) (2012) 104-120.
- [2] M.I. Khan, K. Azizli, S. Sufian, Z. Man, A.S. Khan, *Rsc Advances*, 5(27) (2015) 20788–20799.
- [3] C. Acquah, L. Sie Yon, Z. Tuah, N. Ling Ngee, M.K. Danquah, *Journal of Cleaner Production*, 139 (2016) 1098–1104.
- [4] W.A. Khanday, F. Marrakchi, M. Asif, B.H. Hameed, *Journal of the Taiwan Institute of Chemical Engineers*, 70 (2017) 32–41.
- [5] B.S. Thomas, S. Kumar, H.S. Arel, *Renewable and Sustainable Energy Reviews*, 80 (2017) 550-561.
- [6] S. Pourakbar, A. Asadi, B.B.K. Huat, M.H. Fasihnikoutalab, *Transportation Geotechnics*, 3 (2015) 24-35.
- [7] M. Attari, S.S. Bukhari, H. Kazemian, S. Rohani, *Journal of Environmental Chemical Engineering*, 5(1) (2017) 391–399.
- [8] T. Esfandiyari, N. Nasirizadeh, M. Dehghani, M.H. Ehrampoosh, *Chinese Journal of Chemical Engineering*, 25(9) (2017) 1170–1175.
- [9] S.S. Khaloo, A.H. Matin, S. Sharifi, M. Fadaeinia, N. Kazempour, S. Mirzadeh, *Water Science and Technology*, 65(8) (2012) 1341–1349.
- [10] P. Hadi, M.H. To, C.W. Hui, C.S.K. Lin, G. McKay, *Water Research*, 73 (2015) 37-55.
- [11] A. Oehmen, D. Vergel, J. Fradinho, M.A.M. Reis, J.G. Crespo, S. Velizarov, *Journal of Hazardous Materials*, 264 (2014) 65–70.
- [12] Y. Huang, D. Wu, X. Wang, W. Huang, D. Lawless, X. Feng, *Separation and Purification Technology*, 158 (2016) 124–136.
- [13] Y. Huang, J.R. Du, Y. Zhang, D. Lawless, X. Feng, *Separation and Purification Technology*, 154 (2015) 1–10.
- [14] D.K. Mondal, B.K. Nandi, M.K. Purkait, *Journal of Environmental Chemical Engineering*, 1(4) (2014) 891–898.
- [15] S.S. Shenvi, A.M. Isloor, A.L. Ahmad, B. Garudachari, B. A.F. Ismail, *Desalination and Water Treatment*, 57(55) (2016) 26414-26426.
- [16] I. Syafiqah, H.W. Yusoff, A.A. M. Azoddein, S. Chandraseagar, F.W. Ishak, *Chemical Engineering Transactions*, 56 (2017) 1501–1506.
- [17] A. Wang, K. Zhou, X. Liu, F. Liu, C. Zhang, Q. Chen, *Journal of Colloid and Interface Science*, 505 (2017) 947–955.
- [18] M. Arshadi, M.J. Amiri, S. Mousavi, *Water Resources and Industry*, 6 (2014) 1–17.2014.
- [19] M. Dastkhooon, M. Ghaedi, A. Asfaram, M.H. Ahmadi Azqhandi, M.K. Purkait, M. K. *Chemical Engineering Research and Design*, 124 (2017) 222–237.
- [20] S. Kondapalli, K. Mohanty, *Journal of Water Resource and Protection*, 3(6) (2011) 429–439.