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Evaluation of the Effectiveness of Low Cost Adsorbents from Oil Palm Wastes for Wastewater Treatment

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In the present research, oil palm wastes such as palm kernel shell (PKS), empty fruit bunch (EFB) and palm oil sludge (POS) were converted into biochars through pyrolysis. The charred products of PKS (CPKS), EFB (CEFB) and POS (CPOS) were tested for batch adsorption of copper (Cu^{2+}), lead (Pb^{2+}) and cadmium (Cd^{2+}). Their adsorption performances were compared with the respective un-charred form, i.e. the biosorbents. The adsorption equilibrium was evaluated by varying initial metal concentration. Experimental data were analysed by Langmuir, Freundlich, Temkin and Dubinin-Radushkevich models. It was found that for Cu^{2+} removal by POS and Pb^{2+} removal by CPOS, the equilibria were best represented by Langmuir model exhibiting the smallest sum of normalised error (SNE). For Cd^{2+} adsorption onto POS, the equilibrium was best fitted by Freundlich model with the lowest value of SNE.

1. Introduction

Rapid industrialisation in Malaysia has caused greater heavy metal contamination of the aquatic environment. Heavy metals have always been one of the most significant pollutant groups in wastewater due to their non-biodegradability and high toxicity characteristics. The main sources of heavy metal pollution in the water environment are anthropogenic activities such as electroplating, electronics and semiconductor sectors, agricultural activities, shipping activities and mining industry (Shazili et al., 2006). Heavy metals such as Cu^{2+}, Pb^{2+}, Cd^{2+}, zinc (Zn^{2+}) and nickel (Ni^{2+}), are often discharged at level exceeding the allowable discharge standard (Alkarkhi et al., 2008). These harmful metal ions are highly soluble which make them easily absorbed by living organisms. Contact with these heavy metals can bring about various adverse health effects such as liver damage, kidney damage, dermatitis and cancer (Chowdhury et al., 2016).
To date, numerous techniques are available for treatment of wastewater contaminated by heavy metals which include chemical precipitation, coagulation, membrane filtration and ion-exchange. These treatment methods are associated with drawbacks such as high capital and operational costs, low efficiencies and generation of secondary sludge (Lam et al., 2016). Adsorption technique provides a better alternative for heavy metals removal as it is easier to operate, cost-effective and the spent adsorbent can be regenerated for re-use (Fu et al., 2011). Due to its technological flexibility, numerous adsorbing materials have been tested for their heavy metals removal efficiencies, such as Pequi fruit skin (Seolatto et al., 2012), *Salvinia Natans* (Lima et al., 2014), and spent coffee grounds (Lavecchia et al., 2016).
In Malaysia, the oil palm species found in the plantation are mainly *Elaeis guineensis*, which are also known for their high yield of palm oil. Despite being one of the most lucrative industries in Malaysia, palm oil industry generates large amount of solid and liquid wastes which are difficult to dispose of. For every 1 kg of crude palm oil produced, approximately 4 kg of waste materials are generated (Sulaiman et al., 2011). Of the oil palm residues, palm kernel shell (PKS), empty fruit bunch (EFB) and palm oil sludge (POS) are among the most cumbersome wastes to be handled. These materials are wastes in industrial scale which contain lignocellulosic materials, making them excellent precursors for biosorbent and biochar synthesis. While oil palm wastes may be used as biosorbent, their conversion to biochars can be beneficial in terms of increased total surface area and extended storage lifespan. Data on comparison of adsorption performance of oil palm

waste biosorbents with that of their charred forms are scarce in the literature. This research work explores the potential of converting oil palm wastes into value added products, such as biosorbents and biochars, for application in wastewater treatment. The adsorption equilibrium of the oil palm waste-based biosorbent was compared with that of the biochar. The main focus of this study was to establish the biosorption model for removal of heavy metal in industrial wastewater.

2. Methodology

2.1 Biosorbents and biochars preparation

Oil palm wastes of PKS, EFB and POS were collected from Seri Ulu Langat Palm Oil Mill Sdn. Bhd., Dengkil, Selangor, Malaysia. All collected materials were washed with distilled water and dried in an oven (Memmert) for 72 h at 80 °C. They were then cut into smaller pieces using a sieve grinder (Retsch) and sieved to obtain particles with sizes ranging from 0.5 – 2 mm. The dried PKS, EFB and POS particles were pyrolysed for 1 h under nitrogen atmosphere. The three charred products were thereafter denoted as charred PKS (CPKS), charred EFB (CEFB) and charred POS (CPOS). Proximate analysis was performed using thermogravimetric analyser (TGA, Mettler Toledo). To evaluate the adsorption potential, the prepared adsorbents were tested on removal of Cu^{2+}, Pb^{2+} and Cd^{2+} in aqueous solution. A series of Erlenmeyer flasks containing 50 mL of heavy metal solutions of different concentrations (10 - 300 mg/L) were contacted with 0.5 g of adsorbent. The solutions were shaken in a waterbath shaker (Protech) for 4 h at 100 rpm and 30 °C. Thereafter, the solution was filtered and the final concentration was determined by atomic absorption spectrophotometer (Perkin-Elmer AA400). The percentage removal (R, %) and adsorption capacity (q_e, mg/g) were determined by Eq(1) and Eq(2),

$$\mathrm{R}\,(\%) = \frac{\mathrm{C_0} - \mathrm{C_e}}{\mathrm{C_o}} \times 100\,\% \quad (1)$$

$$\mathrm{q_e} = \frac{(\mathrm{C_0} - \mathrm{C_e})\mathrm{V}}{\mathrm{W}} \quad (2)$$

where C_0 and C_e (mg/L) are the initial and final concentrations, V (L) is the solution volume and W (g) is the adsorbent mass. Experimental adsorption data were fitted to adsorption isotherm models such as Langmuir, Freundlich, Temkin and Dubinin-Radushkevich (D-R) models (Table 1). Langmuir model assumes monolayer sorption occurring on homogenous sites (Langmuir, 1918). The favourability of adsorption can be assessed by Hall separation factor, R_L (dimensionless) (Hall et al., 1966) whereby the process is irreversible if $R_L = 0$, favourable if $0 < R_L < 1$, linear if $R_L = 1$ and unfavourable if $R_L > 1$. Freundlich model considers the adsorption energy reduces exponentially with increase in surface coverage of the adsorbent (Freundlich, 1906). Temkin model assumes that the adsorption energy reduces linearly with an increase in degree of completion of sites (Temkin and Pyzhev, 1940). D-R model assumes adsorption occurs on heterogeneous solid surface (Dubinin et al., 1947). The model parameters were determined by non-linear regression using Microsoft Excel Solver based on the error functions listed in Table 1. The criteria for selecting the optimum model parameters was based on smallest SNE value (Lee et al., 2015).

3. Results and discussion

The thermal stability of PKS, EFB and POS was evaluated by TGA, in which the samples were heated at 5 °C/min. Figure 1 shows the TGA plots for PKS, EFB and POS. The stages of mass loss were in the following order: moisture removal (25 – 110 °C) and devolatilisation (110 – 800 °C) under a nitrogen purge (50 mL/min), as well as combustion (800 – 900 °C) under oxidative condition. The final remaining mass was the ash content. PKS, EFB and POS had moisture contents of 4.53, 3.47 and 5.67 %, respectively. Among the three samples, EFB contained the highest volatile compounds (72.88 %) compared to PKS and POS. PKS was found to be the more promising precursor for biochar as its fixed carbon content (24.91 %) was the highest, followed by EFB and POS.

Figure 2 depicts the effect of initial metal concentration on adsorption capacities of Cu^{2+}, Pb^{2+} and Cd^{2+} onto the different biosorbents and biochars. As the initial concentration was increased, the adsorption capacities for heavy metals were increased. This was because at higher heavy metal concentration, a stronger concentration gradient would be formed which could overcome the mass transfer resistance between the solid and liquid phases during adsorption. Adsorbents such as PKS, EFB, CPKS and CEFB reached a plateau at the lower range of initial concentrations and further increment of initial concentration showed no improvement on their adsorption capacities. This trend indicated that the adsorbents might have limited sorption sites.

Table 1: Equilibrium isotherm and error functions.

Model/ Error Function	Equation	Reference
Langmuir	$q_e = \frac{q_m K_L C_e}{1+K_L C_e}$	(Langmuir, 1918)
Hall separation factor	$R_L = \frac{1}{1+K_L C_0}$	(Hall et al., 1966)
Freundlich	$q_e = K_F C_e^{\frac{1}{n}}$	(Freundlich, 1906)
Temkin	$q_e = \frac{RT}{B}\log AC_e$	(Temkin et al., 1940)
Dubinin-Radushkevich	$q_e = q_{DR}\exp(-\beta\varepsilon^2)$	(Dubinin et al., 1947)
Marquardt's percent standard deviation (MPSD)	$100\sqrt{\frac{1}{n_s-p}\sum_{i=1}^{N}\left(\frac{q_{e,\exp}-q_{e,cal}}{q_{e,\exp}}\right)^2}$	(Marquardt,1963)
Chi-square (χ^2)	$\sum_{i=1}^{N}\frac{(q_{e,\exp}-q_{e,cal})^2}{q_{e,cal}}$	(Ho, 2004)
Average relative error (ARE)	$\frac{100}{n_S}\sum_{i=1}^{N}\left\lvert\frac{q_{e,\exp}-q_{e,cal}}{q_{e,\exp}}\right\rvert$	(Ng et al., 2003)
Sum of absolute errors (EABS)	$\sum_{i=1}^{N}\left\lvert q_{e,\exp}-q_{e,cal}\right\rvert_i$	(Ho et al., 2002)
Sum of the squares of the errors (ERRSQ)	$\sum_{i=1}^{N}\left(q_{e,\exp}-q_{e,cal}\right)_i^2$	(Ho et al., 2002)
Residual root mean square error (RSME)	$\sqrt{\frac{1}{n_s-2}\sum_{i=1}^{N}\left(q_{e,\exp}-q_{e,cal}\right)^2}$	(Hadi et al., 2010)

Nomenclature: q_m (mg/g) – Langmuir maximum adsorption capacity, K_L (L/mg) – Langmuir binding energy, K_F ((mg/g)(L/mg)$^{1/n}$) – Freundlich constant, n (dimensionless) – Freundlich exponent, A (L/mg) – maximum binding energy, B (J/mol) – Temkin constant related to the variation of adsorption heat, R (8.314 J/mol K) – universal gas constant, T (K) – absolute temperature, q_{DR} (mg/g) – D-R maximum adsorption capacity, β (g^2/J^2) – activity coefficient related to adsorption energy, ε (= RT/M log (1+1/C_e), J/g) – Polanyi potential, M (g/mol) – adsorbate molar weight, $q_{e,exp}$ (mg/g) – experimental equilibrium adsorption capacities, $q_{e,cal}$ (mg/g) – calculated equilibrium adsorption capacities based on isotherm models, n_s – number of data and p – number of isotherm parameters.

The adsorption isotherms, both experimentally and theoretically derived, are plotted in Figure 3. From the plots, the adsorption capacity of the adsorbents was evaluated. It was found that most biochars exhibited lower adsorption capacities when compared to their un-charred form. This suggests that pyrolysing the raw biomasses has not improved the adsorption performances for the heavy metals assayed. The reduction in adsorption performance of the biochars might be due to elimination of some chemical functional groups present in the raw biomasses. It is known that chemical functional groups play an important role in binding heavy metals. POS showed the highest adsorption capacities for Cu^{2+} (14 mg/g) and Cd^{2+} (25 mg/g). Among the three biochars, CPOS showed the highest adsorption capacity for Pb^{2+} (19 mg/g). With regard to the isotherm curves, most of the heavy metal adsorptions onto the biosorbents and biochars exhibited a convex trend, indicating that their adsorption processes were favourable. The adsorption of Pb^{2+} onto POS was unfavourable as indicated by its concave upward isotherm (McCabe et al., 2005). The adsorption of Pb^{2+} onto CPOS exhibited a convex curve and hence pyrolysis has improved the adsorption favourability of Pb^{2+} on CPOS. These sludge-based adsorbents showed promising results in heavy metals removal. To further assess the maximum adsorption capacity, the experimental data of Cu^{2+} adsorption onto POS, Pb^{2+} onto CPOS and Cd^{2+} onto POS were fitted with equilibrium isotherms such as Langmuir, Freundlich, Temkin and D-R models. As can be seen in Table 2, the adsorption of Cu^{2+} onto POS and Pb^{2+} onto CPOS were well-represented by Langmuir model because of their SNE smallest values. This indicates that uptake of the heavy metals is likely to be governed by monolayer adsorption onto POS and CPOS. Their q_m values were in close proximity with the experimental values along with the R_L values which were within the region of adsorption favourability. The adsorption of Cd^{2+} by POS was however best correlated with Freundlich model with the smallest SNE, K_F of 2.826 (mg/g)(L/mg)$^{1/n}$ and n of 2.226 which was greater than unity. This implied that Cd^{2+} was favourably adsorbed onto the surface of POS.

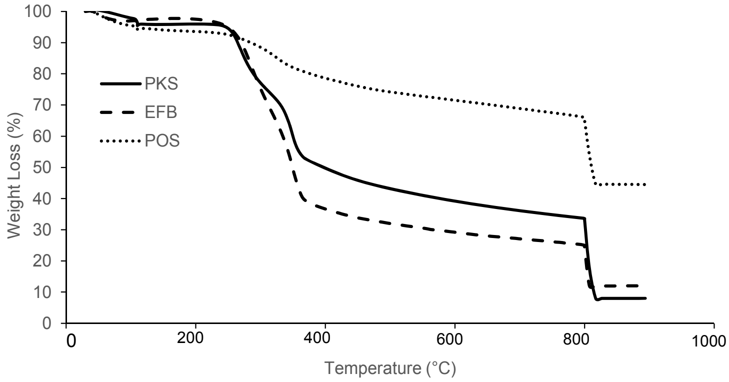

Figure 1: Thermogravimetric plot of PKS (solid line), EFB (dash line) and POS (round dot line).

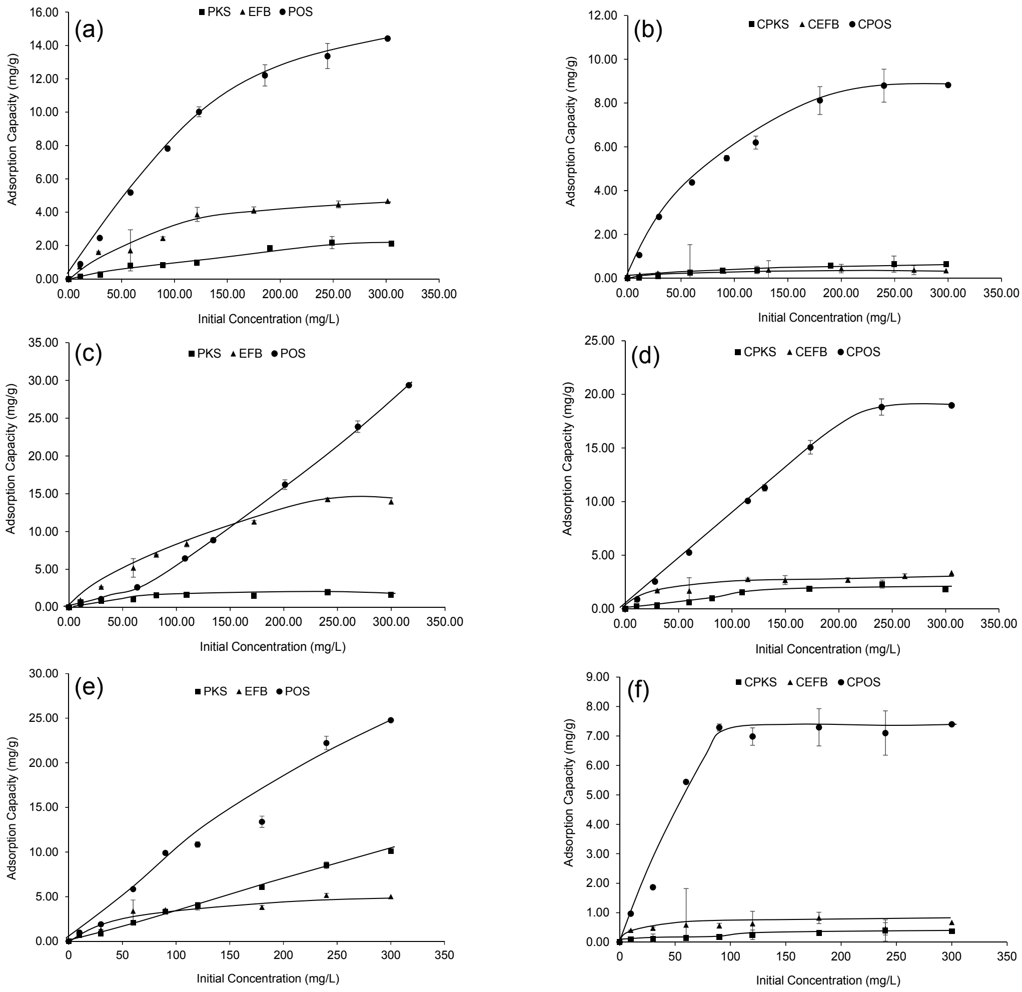

Figure 2: The effect of initial concentration on the adsorption capacities of (a) Cu^{2+}, (b) Pb^{2+} and (c) Cd^{2+} onto different biosorbents, and of (d) Cu^{2+}, (e) Pb^{2+} and (f) Cd^{2+} onto different biochars.

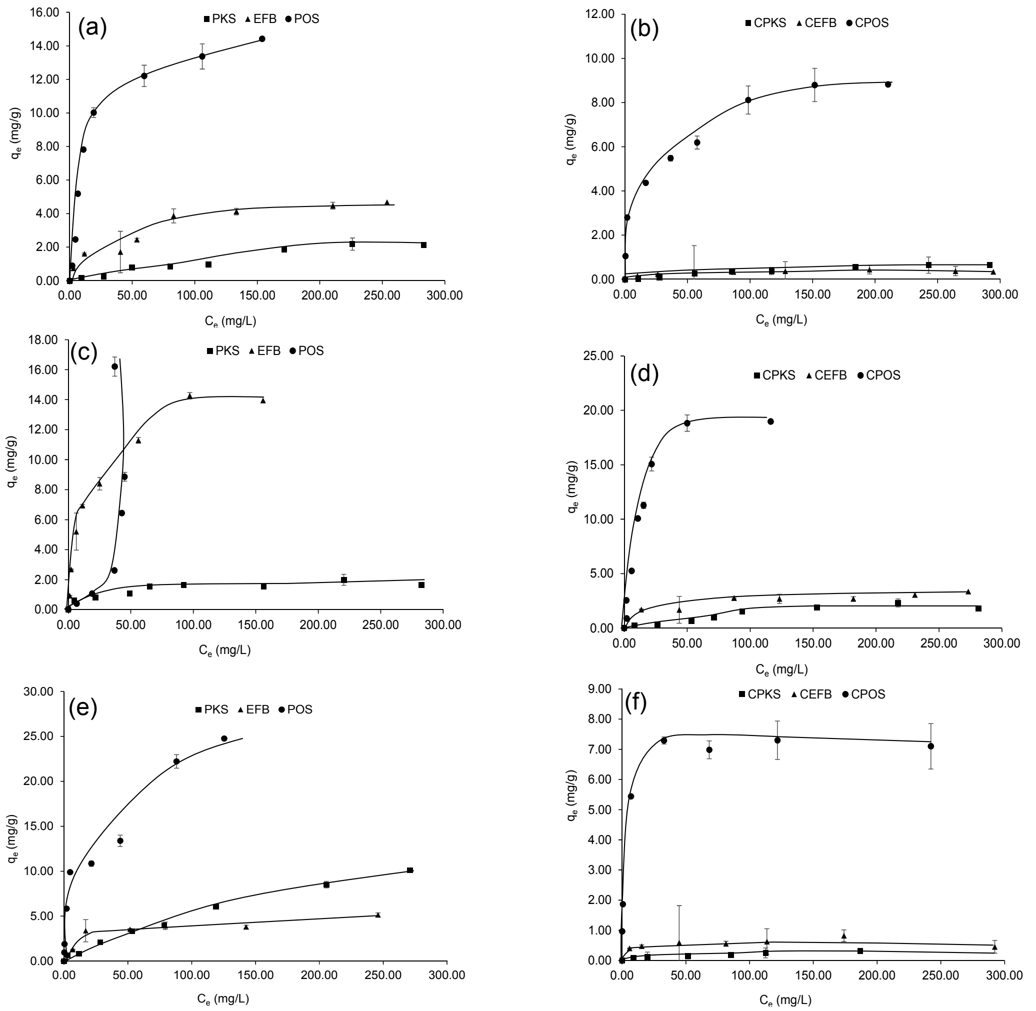

Figure 3: The isotherm plots of (a) Cu^{2+}, (b) Pb^{2+} and (c) Cd^{2+} adsorption onto different biosorbents, and of (d) Cu^{2+}, (e) Pb^{2+} and (f) Cd^{2+} adsorption onto different biochars.

Table 2: SNE analysis for Langmuir, Freundlich, Temkin and D-R models.

Model	Model parameters	Adsorption Matrix		
		Cu^{2+} on POS	Pb^{2+} on CPOS	Cd^{2+} on POS
Langmuir	q_m (mg/g)	16.56	25.64	20.65
	K_L (L/mg)	0.0521	0.0441	0.1274
	R_L	0.0601	0.0703	0.0255
	SNE	1.369	1.383	4.781
Freundlich	K_F ((mg/g)(L/mg)$^{1/n}$)	1.457	1.747	2.826
	N	2.064	1.811	2.226
	SNE	9.308	7.512	2.027
Temkin	B (J/mol)	732.7	477.7	981.2
	A (L/mg)	0.6199	0.5709	11.26
	SNE	2.469	2.550	2.717
D-R	q_{DR} (mg/g)	12.54	18.11	23.32
	B (g^2/J^2)	0.0291	0.5030	0.2487
	SNE	3.277	3.478	8.870

4. Conclusions

Pyrolysis of PKS, EFB and POS was successfully carried out. TGA results showed that PKS had high potential to be developed as biochars. The biosorbents and obtained biochars were tested on the removal of Cu^{2+}, Pb^{2+} and Cd^{2+} in batch mode. The results indicated that Cu^{2+} and Cd^{2+} were best removed by POS while Pb^{2+} was best removed by CPOS. The equilibria of Cu^{2+} adsorption onto POS and Pb^{2+} onto CPOS were well represented by Langmuir model while the equilibrium of Cd^{2+} adsorption onto POS was well correlated to Freundlich model.

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