Indian Journal of Science and Technology, Vol 10(11), DOI: 10.17485/ijst/2017/v10i11/111447, March 2017
ISSN (Print) : 0974-6846
ISSN (Online) : 0974-5645

Adsorption Kinetics of Pb(II) Ions from Aqueous Solution using Modified Magnetic Nano-Composite of OPEFB

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Abstract

Background/Objectives: A batch adsorption process of Pb (II) ions from aqueous solution using modified magnetic nano-composite from Oil Palm Empty Fruit Bunch (OPEFB). **Methods:** OPEFB waste was ground using grinder and hammer mill prior to magnetize using Fe_2O_3 to produce a nano-composite with a final size range of 0.005-0.02 mm. The adsorbent was characterized using FESEM. Batch adsorption study was performed at different temperatures (298-338K) and initial Pb concentrations (100–1000 ppm). **Findings:** The adsorbent morphology reveals the dense structure with pores that would increase the surface area of adsorbent. The dynamic equilibrium between fluid and solid phase is achieved approximately 60-65 min and 45 min for OPEFB and MN-EFB respectively. MN-EFB exhibits better adsorption efficiency (the best: 93.7%) as compared to raw OPEFB (the best: 78%). The pseudo-second-order kinetic fitted well with the experimental data. The activation energy of sorption obtained was 22.76 kJ mol^{-1} indicates that physical sorption also contributes to the adsorption process. **Application/Improvements:** Bio-sorbent with magnetic properties provides better removal efficiency, high reusability and suitable to be used in the industry to remove heavy metals from wastewater.

Keywords: Batch Adsorption, Heavy Metals Removal and Physisorption, Magnetic Nano Composite

1. Introduction

Nowadays, groundwater contamination is one of the vital environmental matters due to humans, animals, and other biological activities. Even though there are many methods available to remove heavy metals in aqueous solution, the flexibility, simplicity, and efficiency of adsorption method give cause to the rise of its attention. In aqueous refining technology, diverse types of adsorbents such as natural, synthetic, inorganic, organic, modified or activated materials have been used[1-4]. However, cost effective and more efficient alternatives are still needed to be introduced[5]. Natural biosorbents from agricultural wastes have been proved to be able to substitute mineral-based or synthetic adsorbent due to their ability to have the efficient aptitude to adsorb heavy metals such as. papaya wood, Ponkan mandarin peel, banana peel, wheat shell, gooseberry fruit, almond husk, peanut hull, sunflower leaves, sawdust, Ceiba[6-9] and activated carbon made by agricultural waste[10]. Value-added products can be developed from Oil Palm Empty Fruit Bunch (OPEFB), the largest agricultural wastes in Malaysia. While the application of magnetic nano-particle technology has received more attention in the case of resolving the environmental issues as the nano-particle provides large surface area and small diffusion resistance which enhance

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the adsorption process[11]. However, to the best of found knowledge, no studies have been done on the removal of heavy metals using magnetic OPEFB-based adsorbents. In this study, OPEFB magnetic nano-composite was used to remove Pb (II) ions from aqueous solution.

2. Materials and Methods

2.1 Materials

In this study, the Raw OPEFB fibre was obtained from the Oil Palm Mill, FELCRA Nasaruddin, Bota, and Perak, Malaysia and stored at 277.15K. Fe_2O_3 nano-particle (5-50 nm - Merck) was purchased. An appropriate amount of $Pb(NO_3)_2$ (Merck) were dissolved in distilled water to prepare the stock solution of Pb (II).

2.1 Methods

2.2.1 Preparations and Characterization of Samples

Fine sized OPEFB samples of 0.02-0.005 mm were obtained by tow cycle grinding the shredded OPEFB using a grinder and a hammer mill (Janke & Kunkel) subsequently, OPEFB were then subjected a ball mill unit (FRITSCH GmbH). The preparation of the bioadsorbent was followed closely Daneshfozouna et al.[12]

2.2.2 Batch Adsorption Study

Different temperatures (298-338K) were used in this study. 10mL of Pb (II) solution was added to 0.1 g of the adsorbent at different concentration levels (100–1000 mg/L). The subsequent procedures were adapted from our research group[13]. The adsorption capacity of adsorbents was calculated using following equation: $q_e = \frac{(C_o - C_e)\times V}{W}$ (1) and this equation: $\mu = \frac{(C_i - C_e)}{C_i}\times 100$ (2) was used to calculate removal efficiency (μ), where Co and Ce are the initial and equilibrium metal ion concentration of Pb (II) (mg/L), respectively; V is the volume of metal ion solution (L), and W is the weight of biosorbent (g).

3. Results and Discussion

3.1 Characterization

Figure 1 shows the surface morphology of Raw OPEFB and fine sized OPEFB was analyzed using FESEM micrograph. Although both samples show high compact arrangement, the fine sized fibre demonstrates the surface texture with holes and small openings thereby increasing the surface area[13]. The high surface area allows more metal ions to bind to the adsorbent during the adsorption process.

3.2 The Adsorption Efficiency

The results show that at 60 min the system reaches the dynamic equilibrium between the fluid and a solid phase in all investigated solution concentration and temperatures for OPEFB and MN-EFB respectively (cf. Figure 2a). As

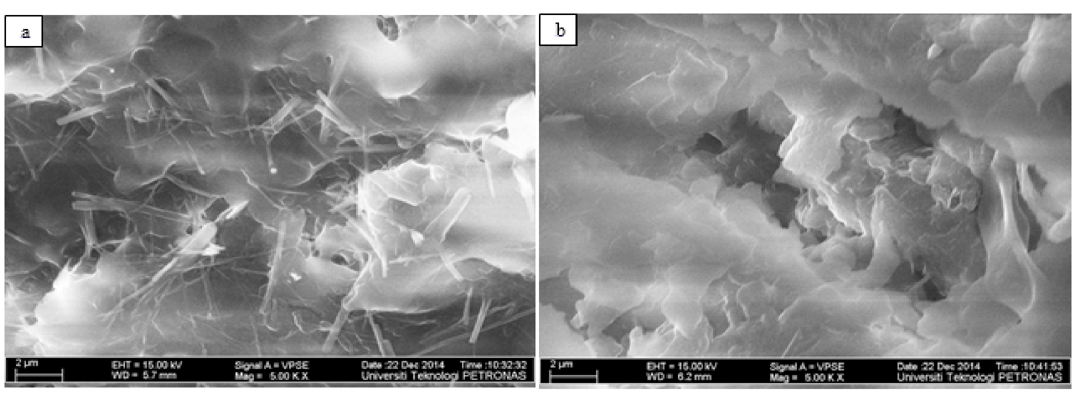

Figure 1. FESEM images of OPEFB fibres (magnification 5Kx). (a) Raw OPEFB fibre (b) fine sized OPEFB fibre.

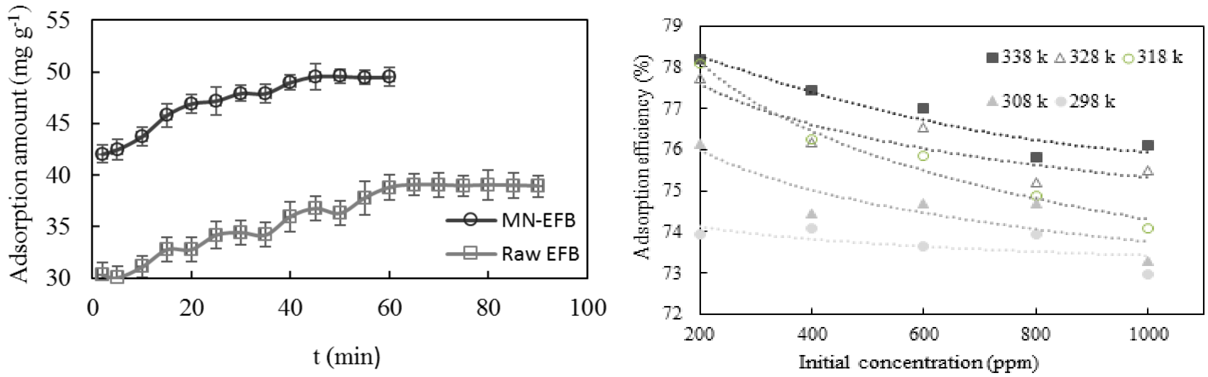

Figure 2. a) Effect of contact time on adsorption amount (concentration: 500 mg l^-1, temperatures 338 K, pH (5-5.5). b) The adsorption efficiency of Pb (II) onto the Raw EFB (equilibrium time 60 min) at various temperatures.

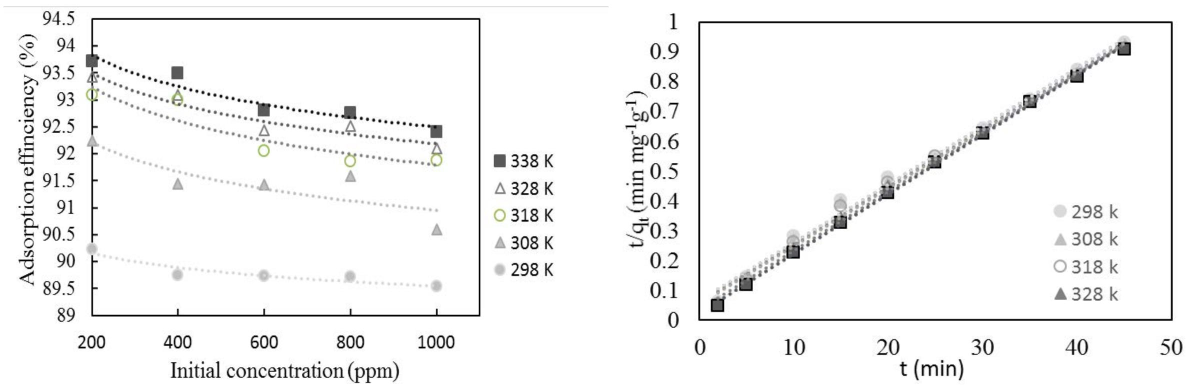

Figure 3. a) The adsorption efficiency of Pb(II) onto the MN-EFB (equilibrium time 45 min) at various temperatures b) Effect of temperature on pseudo-second-order kinetics of Pb (II) onto the MN-EFB (500 mg l^-1 initial solution concentration).

expected, the adsorption efficiency of Pb(II) for both samples increased with increasing temperature as high temperature would enhance the mobility of the solute, as well as the pore size of adsorbent. Figures 2b and 3a depict the highest adsorbent efficient occur at low concentration (200 ppm) due to high affinity between Pb (II) ions and adsorbent[14]. MN-EFB exhibits better adsorption efficiency (the best: 93.7%) compared to raw OPEFB (the best: 78%) for all lead concentrations. The existence of magneticnano-particles around the adsorbent surface provides a higher surface area for adsorption process. Thus, more metal ions bind to MN-EFB as compared to raw OPEFB which produced a higher efficiency of Pb (II) removal.

3.3 Kinetics Study

To identify the metal adsorption mechanism and evaluate the performance of each individual adsorbent for metal removal, kinetic models can be used. Three prominent kinetic models have been evaluated in this study to describe the kinetics of Pb (II) removal with the MN-EFB;

- The pseudo-first order kinetic model of Lagergren[15] $\ln(q_e - q_t) = \ln q_e - k_1 t$,
- The pseudo-second-order kinetic model based on solid phase sorption: $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ and Intra-particle diffusion: $q_t = k_i t^{1/2} + c$ where q_e and q_t are the amounts of metal adsorbed at equilibrium and any time (mg g^{-1}), respectively and K_2 is the rate constant for pseudo-second-order reaction (g mg^{-1} min^{-1}). Where K_i is rate constant of the intra-particle diffusion (mg g^{-1} $min^{-1/2}$) and c is the intercept. In this model, pore diffusion is consumed to be surface

Table 1. Comparison of three different kinetics models for Pb (II) onto the MN-EFB (500 mg l^-1) initial solution concentration)

T(K)	$q_{e,exp}$ (mg g^{-1})	Kinetic Model										
		Pseudo First Order				Pseudo Second Order				Intra-particle Diffusion		
		$q_{e,cal}$ (mg g^-1)	K_1 (min)	R^2	SSE (%)	$q_{e,cal}$ (mg g^{-1})	K_2 (g mg^{-1} min^{-1})	R^2	SSE (%)	K_i (mg g^{-1} $min^{-0.5}$)	C (mg g^{-1})	R^2
298	48.25	27.058	0.090	0.943	0.093	51.28	0.0058	0.992	0.050	3.450	26.23	0.87
308	48.60	25.790	0.092	0.940	0.107	50.01	0.0071	0.999	0.027	3.096	28.90	0.91
318	49.18	19.880	0.071	0.913	0.117	50.28	0.0079	0.994	0.041	2.830	30.57	0.94
328	49.27	15.210	0.075	0.921	0.234	50.51	0.0110	0.998	0.024	2.010	35.98	0.89
338	49.53	9.630	0.061	0.939	0.321	50.76	0.0180	0.993	0.024	0.970	39.62	0.94

sorption. In the case of pseudo- first model study, the plots of ln (q_e-q_t) versus t (Figures are not shown) is used to calculate the values of K_1. Although the obtained R^2 values were good, the disagreement between the experimental values, q_e, and the estimated values from the linear plots (cf. Table 1) implied that the adsorption of Pb (II) does not follow pseudo-first-order kinetics. On the other hand, Figure 3b shows a kinetic model of Pb (II) agree well with the pseudo-second-order sorption kinetics which has values of R^2 (correlation factor) almost unity. It seems the temperature has an insignificant effect on the adsorption efficiency. Based on these 3 models under studied, the pseudo-second-order kinetics was chosen as it agrees well with the experimental data.

4. Conclusion

The modified magnetic nano-composite material derived from OPEFB exhibits higher adsorption efficiency compared to raw OPEFB in all temperatures and concentrations studied. The adsorption efficiency increased from 78% to 93.7%. The equilibrium time achieved is 45 min. The pseudo-second-order kinetic well-described the kinetics of sorption processes. The rates determining steps for sorption process is intra-particle diffusion kinetics and pseudo-second order Kinetics. The models fitted well when Langmuir, Freundlich, and Dubinin-Redushkevich (D-R) isotherm models were used for experimental data control.

5. Acknowledgement

The authors would like to thank University Technology PETRONAS for providing research facilities.

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