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Sorption Equilibrium and Kinetics of Oil from Aqueous Solution Using Banana Pseudostem Fibers

Nurul Izza Husin [1+] , Nor Aimi Abdul Wahab [1], Norain Isa [1] and Rozan Boudville [2]

[1] Department of Applied Sciences, UiTM Pulau Pinang, Malaysia

[2] Faculty of Electrical Engineering, UiTM Pulau Pinang, Malaysia

Abstract. This study describes the ability of banana pseudostem fibers as an alternative adsorbent for the removal of oil from synthetic oily wastewater. A detailed batch study with respect to its adsorption equilibrium, isotherm and kinetics were carried out at ambient temperature, various initial concentration of oil and agitation time. The batch study clearly shows that banana pseudostem fibers exhibit almost 100% adsorption at lower concentration of oil. Langmuir and Freundlich adsorption model were applied to describe the experimental isotherm and isotherm constants. Equilibrium data fitted well with Freundlich model. The kinetic data were best fitted to pseudo-second-order kinetic model. The result showed that this low-cost adsorbent had a high adsorption capacity, making it suitable for the oily wastewater treatment.

Keywords: Adsorption equilibrium, Kinetic, Oil removal, Banana Pseudostem, Adsorbent

1. Introduction

Over the recent years there has been an increasing concern for environmental risk of industrial activities associated with extraction, hydrocarbons, food processing, transportations and refining. These industries have increased the threat of oil pollution to the environment and subsequently concomitant discharged into the natural environment creates major ecological problem throughout the world. The wastewater is detrimental and need to have a treatment before discharge into the environment, in line with Malaysian Environmental Quality Act 1974. Unlike the free or 'floating' oil spilled in the sea, lakes or rivers, most industrial wastewaters contain oil emulsion, which posess a real problem to treatment due to its high stability and can only be separated with the help of chemical clarification (Ahmad et al., 2005). The treatment of this waste has been address by several techniques such as coagulation, biosorption, adsorption, filtration, screening and many more. Among the various technique adsorption process is one of the effective methods for removing organic and inorganic pollutants in waterway system (Kumar et al., 2000). Traditionally, activated carbon (AC) was used as adsorbent for adsorption process. Due to low efficiency and high cost of activated carbon for oily wastewater treatment (Moazed and Viraraghavan, 2005), the possibility of using inexpensive materials as alternatives was explored by many researchers in the past years. Low cost adsorbent could be generated from agriculture waste because of their low-cost and widespread availability. Some examples of agro waste that have been used for the removal of oil are barley straw (Sharif Ibrahim et al., 2009), walnut shell (Srinivasan and Viraraghavan, 2008), wool fibers (Rajakovic et al., 2007), olive waste (El-Hamouz et al., 2007).

In the present study, the ability of banana pseudostem fibers as a biosorbent for the removal of oil from synthetic oily wastewater was investigated. Therefore, the purpose of this study was to assess the feasibility of banana pseudostem fibers (BP) as sorbent for the removal of oil from oily wastewater. Adsorption isotherms and kinetics of the sorption process were also discussed.

2. Materials and Methods

[+] Corresponding author. Tel.: + 6043823357; fax: +6043822853.
E-mail address: nurulizza.husin@ppinang.uitm.edu.my

2.1. Sorbent

Banana pseudostems fibers from the family of Musa acuminate x balbisiana Colla (ABB Group) cv 'Pisang Awak' were obtained locally. The collected materials were then washed repeatedly with distilled water to remove all the dirt particles. The washed materials were cut into small pieces (1–2 cm) then boiled for an hour. It were then placed in an oven at 45 °C for drying until constant weight, ground and sieved to obtain a particle size range of 300-355 µm. the newly prepared Banana pseudostems fibers powder (hereafter called BP) was used as adsorbent without any pre-treatment.

2.2. Adsorbate

A stock solution of synthetic oily wastewater was prepared by mixing 11.5g of the palm oil with 1000 mL of water. The mixture was then stabilized in a blender at high speed for 15–20 minutes. The resultant solution was milky white, which exhibited the character of chemically stabilized solution. It was later diluted to a desired oil concentration for adsorption test.

2.3. Equilibrium Studies

Batch adsorption experiment were carried out by mixing fixed amount of sorbent (1.0 g) with 100 mL synthetic oily wastewater solution at varying concentrations (20–100% v/v) and various contact time (20-120 min). Agitation speed, temperature, and particle size of adsorbent were fixed at 170 rpm, 27 ◦C and 300-355 micron respectively. As for the operating variables; original pH of solution was 6.8 and the volume of emulsified oil solution was set at 100 mL. Throughout the experiment, an Orbital shaker (GFL 3005) was used to agitate the samples and pH of solution was measured using a pH meter (Jenway 3505). Experiments were duplicated under the similar conditions and the mean values were used in calculations. The filtrate was analyzed for oil concentration using the oil and grease method recommended by APHA, AWWA, WPCF (1992) Standard Method of Examination of Water and Wastewater, with n-hexane being used as the oil-extraction solvent. The amount of adsorption at equilibrium, qe (mg/g), was calculated using Eq. 1:

$$\boldsymbol{q_e = \frac{(C_0 - C_e)}{W} V} \tag{1}$$

where C_0 and C_e (mg/L) are the liquid-phase concentrations of oil at initial and equilibrium, respectively. V (L) is the volume of the solution and W (g) is the mass of dry sorbent used.

2.4. Kinetic studies

Kinetic experiments were identical to those of equilibrium tests. The aqueous samples were taken at preset time intervals and the concentrations of oil were similarly measured. The amount of sorption at time *t*, *qt* (mg/g), was calculated by

$$q_t = (C_0 - C_t)V / W \tag{2}$$

where C_t (mg/L) is the liquid-phase concentrations of oil at any time.

3. Results and Discussion

3.1. Effect of initial oil concentration and contact time

The study on effect of initial concentration was performed at room temperature, 27 ^oC while the pH and agitation rate were fixed at pH 6.8 and 170 rpm, respectively. The synthetic oily wastewater was diluted with distilled water to ratio 20%, 40%, 60% and 80%. The original concentration was presented as 100%. The adsorption data was illustrated in Fig. 1. It proves that amount of oil adsorbed increase with the increase in the concentration of oil. The uptake of oil increased from 190.0 to 685.0 mg/g with increase in the initial oil concentration from 20% to 100 %. A higher initial concentration provides an important driving force to overcome all resistances of the oil between the aqueous and solid phases, thus increasing the uptake. In addition, increasing the initial oil concentration increases the number of collisions between oil and the adsorbent, which enhances the adsorption process (Hameed et al., 2008). The effect of contact time on the

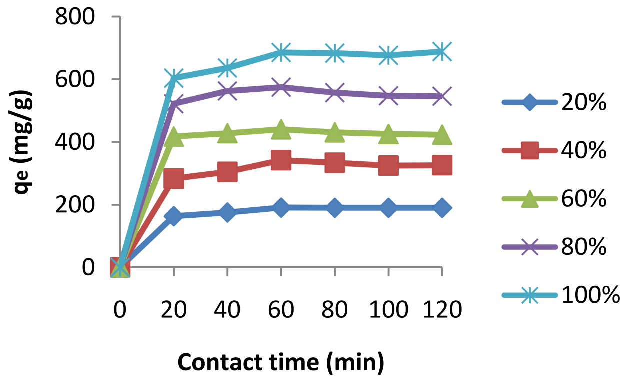

Fig. 1: Effect of contact time on removal of oil by BP at different initial concentration (dosage, 10 g/l; pH 6.8; agitation rate 170 rpm; temperature, 27 ^{o}C)

removal of oil by BP at initial concentration 20%-100% v/v showed the amount of oil adsorbed per unit mass of adsorbent increased at lower times before reaching the plateaus. According to these data, equilibrium is achieved at around 60 min. However, to be sure on the best adsorption conditions at higher concentrations levels, to obtain equilibrium at the solid/liquid interface, all the experiments were carried out with 2 h of contact time. There is no noticeable change in oil removal when the time was prolonged. The initial high rate of oil uptake may be attributed to the existence of the bare surface; however the number of available adsorption sites decreased as the number of oil adsorbed increases (Bhattacharrya and Gupta, 2006).

3.2. Adsorption isotherms

Adsorption isotherm is the relationship between the amount of a substance adsorbed and its concentration in the equilibrium solution at constant temperature. In this study, the adsorption data were analyze using Langmuir and Freundlich adsorption isotherm models to describe the sorption equilibrium. The applicability of the isotherm models to the adsorption study was compared by judging the correlation coefficients, R^2 values.

Langmuir isotherm is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. The linear form of Langmuir is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{1}{Q_o} C_e \tag{3}$$

where C_e is the equilibrium oil concentration (mg L^{-1}), q_e the amount of oil adsorbed per unit mass of adsorbent (mg g^{-1}), Q_o and b is Langmuir constants related to adsorption capacity and rate of adsorption, respectively. The values of maximum adsorption capacity can be obtained from the slope of the plot of *Ce*/*qe* versus *Ce* (Fig. 2). The maximum adsorption capacity of oil by BP was 1.69E+02 (see table 1). The correlation coefficient of Langmuir isotherm, R^2 is 0.926. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor R_L that is given in Eq. 4:

$$R_L = \frac{1}{1+bC_o} \tag{4}$$

The value of R_L indicates the type of the isotherm to be either favorable ($0 < R_L < 1$), unfavorable ($R_L > 1$), linear ($R_L = 1$) or irreversible ($R_L = 0$). All the value of R_L lies between 0.014 and 0.065 for the initial oil concentration range from 20% to 100 % v/v. The R_L values show that favorable adsorption of oil on BP takes place. Therefore BP is favorable adsorbent.

Freundlich isotherm model is derived to model the multilayer adsorption and applicable to highly heterogeneous surface, and is given as:

$$q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{5}$$

Table 1: Comparison of Langmuir and Freundlich isotherms constants for BP

Adsorbent	Langmuir			Freundlich		
	B	**q_o**	**R^2**	**K_f**	**N**	**R^2**
BP	7.21E-03	1.69E+02	0.926	38.29	2.880	0.976

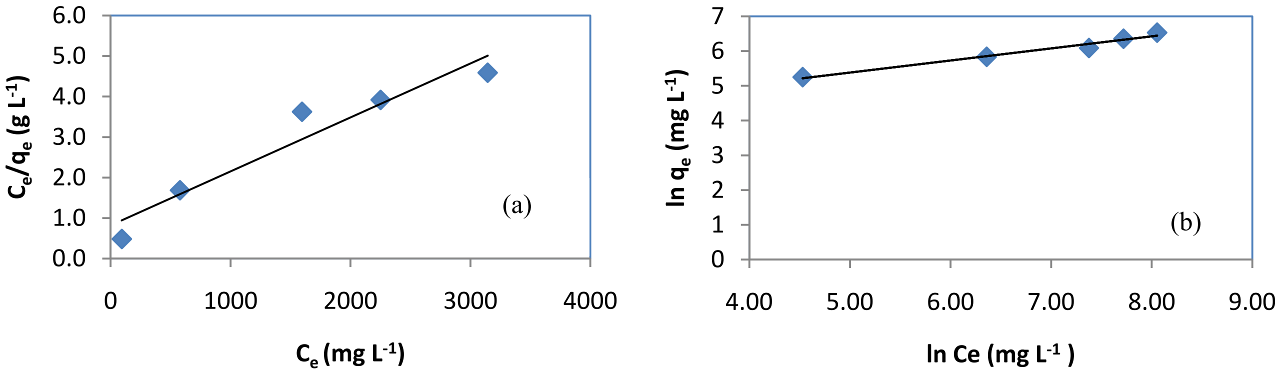

Fig. 2: Plot of (a) Langmuir isotherm, (b) Freundlich isotherm for oil sorption onto BP

where K_F and n related to adsorption capacity of adsorbent and measure of adsorption intensity, respectively. The magnitude of the exponent, $1/n$, gives an indication of the favorability of adsorption. Values of $n > 1$ represent favorable adsorption condition (Ho and Mckay, 1998a). The plot of ln q_e versus ln C_e in Fig. 2 shows a straight line with a correlation coefficient of 0.976. The constant K_F and 1/n value was determined from the plot. The value calculated was listed in table 1. The value of n determined from Freundlich isotherm was 2.88.

As seen from table 1, a high regression correlation coefficient was shown by Freundlich model. This indicates that the Freundlich model was suitable for describing the sorption equilibrium of oil by BP. Similar results were reported for oil adsorption on powder and flakes chitosan (Ahmad et al., 2005). Thus it is reasonable to conclude that the adsorption of oil on the adsorbent that consist of heterogeneous adsorption sites that are similar to each other in respect of adsorption phenomenon.

3.3. Kinetic studies

In order to analyze the sorption kinetics of oil on BP, two simplified kinetic model were applied to the experimental data. First, the kinetic adsorption was analyze by the Lagergren pseudo-first-order equation as despicted in Eq. 6:

$$\log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \quad (6)$$

where q_e and q_t are the amount of oil adsorbed on adsorbent at equilibrium and time t, respectively (mg/g), and k_1 is the rate constant of first order adsorption (min^{-1}). Value of k_1 at ambient temperature were calculated from the plots of log ($q_e - q_t$) versus t for different initial concentration of oil (figure not shown). The parameters of pseudo-first-order model were summarized in table 2. The set of R^2 value obtained in all cases were poor and the experimental q_e value did not agree with the calculated value obtained from the linear plot. This suggests that the adsorption of oil onto BP is not a first-order reaction.

Table 2: Comparison of Langmuir and Freundlich isotherms constants for BP

Adsorbent	Initial Concentration	Pseudo-first order kinetic model				Pseudo-second order kinetic model		
		$q_{e\,(exp)}$	k_1	$q_{e\,(cal)}$	R^2	k_2	$q_{e\,(cal)}$	R^2
BP	20%	190.72	0.08	1.08	0.96	0.06	200.00	0.999
	40%	342.20	1.02	4.68	0.69	0.04	344.80	0.995
	60%	440.40	0.86	5.71	0.93	1.32	434.78	0.999
	80%	574.80	0.77	11.07	0.83	0.54	555.55	0.998
	100%	688.50	2.13	1.39	0.98	0.02	714.28	0.999

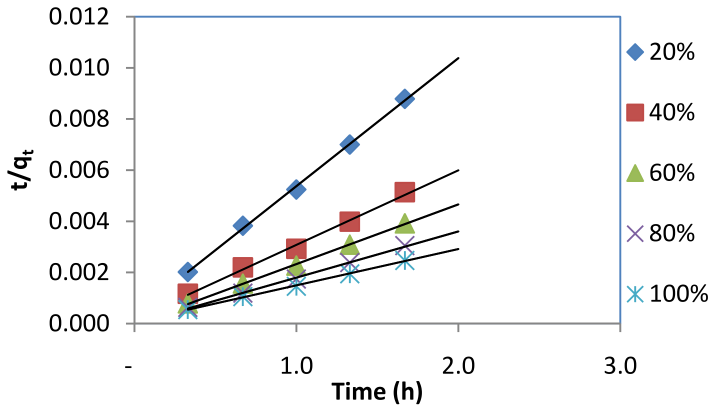

Fig. 3: Pseudo-first-order sorption kinetics of oil onto BP

While for pseudo-second-order equation based on equilibrium adsorption is expressed as Eq. 7:

$$\frac{t}{q_t}=\frac{1}{k_2q_e^2}+\frac{1}{q_e}t \qquad (7)$$

where, k_2 is the pseudo-second-order rate constant of adsorption (g $mg^{-1}min^{-1}$). The straight linear line in plot t/q_t vs. t (Fig. 3) proves a good agreement of experimental data with the kinetic model. The q_e and k_2 values can be calculated from the slopes and intercepts of the plot respectively.

Table 2 also lists the computed results obtained for the second-order kinetic model. The correlation coefficient (R^2) for the second-order kinetic model is almost equal to 1.0. Furthermore the calculated q_e values obtained agree very well with the q_e of the experimental data. Indicated that this model was applicable to describe the adsorption process of oil onto BP, based on assumption that the rate-limiting step maybe chemical sorption or chemisorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate, provide the best correlation of data (Ho and Mckay, 1999). Similar results were reported for the adsorption of oil by powder and flake chitosan (Ahmad et al., 2005).

4. Conclusion

The present study demonstrated that Banana pseudostem fibers (BP), which abundantly available in Malaysia, is an efficient sorbent for the removal of oil in water and it may be an alternative to more costly adsorbents such as activated carbon. The batch studies clearly suggest that BP exhibits almost 100% adsorption at lower concentration of oil. Equilibrium data fitted well with Freundlich model, which suggests a heterogeneous coverage of oil molecules on the surface of BP. The kinetic data were best fitted to pseudo-second-order kinetic model.

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