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Statistical optimization of adsorption processes for removal of 2,4-dichlorophenol by activated carbon derived from oil palm empty fruit bunches

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Abstract

The adsorption capacity of activated carbon produced from oil palm empty fruit bunches through removal of 2,4-dichlorophenol from aqueous solution was carried out in the laboratory. The activated carbon was produced by thermal activation of activation time with 30 min at 800°C. The adsorption process conditions were determined with the statistical optimization followed by central composite design. A developed polynomial model for operating conditions of adsorption process indicated that the optimum conditions for maximum adsorption of phenolic compound were: agitation rate of 100 r/min, contact time of 8 h, initial adsorbate concentration of 250 mg/L and pH 4. Adsorption isotherms were conducted to evaluate biosorption process. Langmuir isotherm was more favorable (R^2=0.93) for removal of 2,4-dichlorophenol by the activated carbon rather than Freundlich isotherm (R^2=0.88).

Key words: activated carbon; adsorption; oil palm empty fruit bunches; 2,4-dichlorophenol

Introduction

Phenolic compounds are generally present in refinery and petrochemical wastewaters and are of particular significance as they are potentially toxic to humans and aquatic life; create an oxygen demand in receiving waters, and impact taste and odour to drinking water with even minute concentrations of their chlorinated derivatives (Viraraghavan and Maria-Alfaro, 1998). Water treatment plants normally disinfect water by chlorination, consequently forming the undesirable chlorophenols when phenols are present (Aleksieva *et al*., 2002; Viraraghavan *et al*., 1998). Consequently, phenolics were considered to constitute the 11th of the 126 chemicals which have been designated as priority pollutants by the Environmental Protection Agency in USA (Caturla *et al*., 1988).

Therefore the phenolics need to be removed from the wastewater before it is discharged to the receiving water bodies. One of the alternatives would be the adsorption method by activated carbon. Activated carbon adsorption is a well established, powerful and most widely used method for treating domestic and industrial effluents since it has fast adsorption kinetics and relative ease of regeneration and large adsorption capacity (Chen *et al*., 2002; Jung *et al*., 2001; Tancredi *et al*., 2004). But, the preparation cost of activate carbon is quite high, the higher the quality, the higher the cost (Aksu and Yener, 1998; Calace *et al*., 2002).

The oil palm industry in Malaysia generates approximately 9.9×10^6 t of solid wastes consisting of oil-palm empty fruit bunches, fiber and fruit shell every year (MPOB, 2003). And the biomasses are either left in the plantation as organic nutrients to trees or burned illegally (Suhaimi and Ong, 2001). Therefore, empty fruit bunches (EFB) may provide a potential alternative source of revenue for oil palm industries besides achieving zero waste targets at the plantations through the production of activated carbon for the removal of organic substances from industrial effluents.

Experimental design technique is a very useful tool for this purpose, as it provides statistical models which help in understanding the interactions among the parameters that have been optimized. Another important advantage of the use of statistical models in optimization processes is the requirement of very less number of experiments and therefore minimizes time required to carry out the experiments, also minimizes the amount of chemicals, glassware, and manpower needed. Very limited research have been done on statistical optimization of process conditions for removal of organic content using activated carbons (Ravikumar *et al*., 2005, 2007; Bacaoui *et al*., 2001). Therefore a statistical optimization was carried out to determine the optimum bioprocess conditions for removal of 2,4-dicholophenol from aqueous solution by activated carbon produced from oil palm EFB.

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1 Materials and methods

1.1 Sample collection and preparation of activated carbon

The oil palm EFB sample was collected from a palm oil industry (Seri Ulu Langat Palm Oil Mill Sdn. Bhd.) in Dengkil, Selangor, Malaysia. EFB was collected in plastic bags and stored in the cold room at 4°C for further use. The sample was dried at 105°C for 24 h in the oven to remove the moisture content until it reached the constant weight. The dried sample was heated at 800°C for 30 min in high temperature chamber furnace (Carbolite, UK) in presence of air. The activate carbon was crushed and sieved to size fractions less than 150 μm for adsorption test (Alam *et al*., 2007).

1.2 Adsorption test

To evaluate the adsorption capacity of the activated carbon toward the phenolic compound (2,4-dicholophenol, pK_a 7.9), 0.25 g of activated carbon was added to three 100 ml-conical flask containing 25 ml aqueous solution of 2,4-dichlorophenol. The samples were agitated in rotary shaker at room temperature (30±2°C) at 150 r/min. The activated carbon and solutions were separated by filtration and the total phenol content was determined according to Box (1983).

The absorbance was measured at 725 nm against distilled water and reagent blank using UV Spectrophotometer (Anthelie Junior, Secomam, France). The final concentration was measured from the standard calibration curve with known concentrations. The standard calibration curve was constructed with the absorbance versus known concentration of 2,4-dicholophenol (pK_a 7.9).

The adsorption capacity q was calculated from the difference between the initial concentration and equilibrium phenolic compound concentration, which is as follows:

$$q = \frac{(C_0 - C_e) \times V}{M} \tag{1}$$

where, q is the adsorption capacity (mg/g), C_0 and C_e are the initial and equilibrium concentration (mg/L), respectively, M is the adsorbent dosage (g) and V is the solution volume (L).

1.3 Optimization study

The optimal design for the adsorption of 2,4-dichlorophenol by the activated carbon produced from EFB is a very important aspect in the development of adsorption process. Response surface methodology is a statistical method that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions. The dependant variable selected for this study was the residual concentration of 2,4-dichlorophenol, expressed in mg/L, and the independent variables chosen were the agitation rate, contact time, initial concentration of 2,4-dichlorophenol and pH. A statistical optimization was conducted by using central composite design with four factors and five levels. The experimental data were analyzed using a statistical software MINITAB to develop the polynomial regression model for determining the optimum conditions. The range and the levels of these variables are given in Table 1.

Table 1 Range of levels for parameters used in adsorption capacity test

Parameters	Range of levels				
	–2	–1	0	1	2
Agitation speed (r/min)	50	100	150	200	250
Contact time (h)	2	4	6	8	10
Initial conc. (mg/L)	50	100	150	200	250
pH	2	4	6	8	10

2 Results and discussion

2.1 Production rate of activated carbon

The final yield of activated carbon produced from EFB at 800°C were calculated based on the initial weight of EFB before activation. Normally, in the production of commercial activated carbons, relatively high yields of the final products are expected. The final yield obtained was 15.5%. Therefore, the production rate is 0.155 kg-activated carbon/kg-dried EFB.

2.2 Adsorption capacity test

From Table 2, the highest adsorption capacity of 2,4-dichlorophenol was observed in run (26), 22.2 mg/g where the agitation speed was 150 r/min, contact time of 6 h, initial concentration of the phenolic compound at 250 mg/L and pH value of 6. While the lowest adsorption capacity was observed in run (25), 4.5 mg/g, where the agitation speed was 150 r/min, contact time of 6 h, initial concentration of the phenolic compound at 50 mg/L and pH value of 6.

2.3 Optimization study

An experimental design, i.e., central composite design, a polynomial regression equation was developed to analyze factor interactions by identifying the significant factors contributing to the regression model and to determine the optimal values. The polynomial regression equation was developed by using Minitab software. Therefore the model equation is shown in Equation (2):

$$\begin{aligned} Y(\text{adsorption capacity}) = {} & -5.20 + 0.0233a + 0.669b + \\ & 0.102c + 0.246d - 0.00172ab - 0.000060ac + \\ & 0.000011ad + 0.00143bc - 0.0127bd - 0.00115cd - \\ & 0.000031a^2 - 0.0324b^2 - 0.000016c^2 - 0.00385d^2 \end{aligned} \tag{2}$$

where, a is the agitation speed (r/min); b is the time (h); c is the initial concentration of 2,4-dichlorophenol (mg/L); d is pH of the solution.

The coefficient of determination (R^2) was 0.99 which ensured a satisfactory data and indicated that approximately 99% of the variability in the dependent variable (adsorption capacity) could be explained by the model. The

Table 2 Experimental and expected results from polynomial regression model obtained from statistical analysis

Run no.	Agitator (r/min)		Time (h)		$C_{i\,(Initial)}$(mg/L)		pH		C (residual, mg/L)	q (experimental, mg/g)	q (expected, mg/g)
	C	A	C	A	C	A	C	A			
1	+1	200	+1	8	+1	200	–1	4	22.4	17.8	18.2
2	+1	200	–1	4	+1	200	+1	8	29.7	17.0	17.6
3	–1	100	–1	4	–1	100	+1	8	11.8	8.8	9.0
4	–1	100	+1	8	–1	100	–1	4	7.9	9.2	9.4
5	0	150	0	6	0	150	0	6	14.4	13.6	13.7
6	–1	100	–1	4	+1	200	–1	4	24.7	17.5	17.7
7	–1	100	–1	4	–1	100	–1	4	14.5	8.6	8.7
8	+1	200	–1	4	–1	100	+1	8	13.5	8.6	8.9
9	+1	200	–1	4	+1	200	–1	4	25.2	17.5	17.8
10	–1	100	–1	4	+1	200	+1	8	27.3	17.3	17.6
11	0	150	0	6	0	150	0	6	14.4	13.6	13.7
12	–1	100	+1	8	+1	200	+1	8	13.2	18.7	19.2
13	–1	100	+1	8	+1	200	–1	4	7.8	19.2	19.5
14	+1	200	+1	8	–1	100	+1	8	11.1	8.9	9.4
15	0	150	0	6	0	150	0	6	14.6	13.5	13.7
16	+1	200	–1	4	–1	100	–1	4	14.7	8.5	8.7
17	+1	200	+1	8	+1	200	+1	8	26.4	17.4	18.3
18	+1	200	+1	8	–1	100	–1	4	11.3	8.9	9.1
19	0	150	0	6	0	150	0	6	14.5	13.6	13.7
20	–1	100	+1	8	–1	100	+1	8	9.9	9.0	9.3
21	0	150	0	6	0	150	+2	10	17.6	13.2	13.7
22	+2	250	0	6	0	150	0	6	24.8	12.5	13.4
23	0	150	–2	2	0	150	0	6	26.4	12.4	12.9
24	0	150	0	6	0	150	0	6	14.6	13.5	13.7
25	0	150	0	6	–2	50	0	6	4.8	4.5	4.5
26	0	150	0	6	+2	250	0	6	27.8	22.2	22.8
27	0	150	0	6	0	150	–2	2	13.3	13.7	13.6
28	–2	50	0	6	0	150	0	6	11.3	13.9	14.0
29	0	150	+2	10	0	150	0	6	13.8	13.6	14.5
30	0	150	0	6	0	150	0	6	14.9	13.5	13.7

C: Coded values from statistical software (MINITAB); A: actual values.

adjusted R^2, which is more suited for comparing models with different numbers of independent variables, was 0.98. From the regression equation above, trial and error was done to obtain the maximum adsorption capacity and it can be concluded that the optimum value for adsorption capacity of 2,4-dichlorophenol are as below: agitation rate 100 r/min, contact time 8 h, initial concentration 250 mg/L and pH 4.

From previous studies by Aksu and Yener (1998) in the investigation of phenol and monochlorinated phenols on dried activated sludge, it was found that the equilibrium sorption capacity of biomass for phenol, *o*-chlorophenol, and *p*-chlorophenol increased with the initial pollutant up to 500 mg/L. The increase of loading capacity of biosorbent with the increase of pollutant concentration may be due to collision between pollutants and biosorbent.

2.4 Adsorption isotherms

Two isotherm equations have been tested in the present study: Langmuir and Freundlich models. The applicability of the isotherm equations is compared by judging the correlation coefficients, R^2. These adsorption isotherms were made based on the data obtained from 2,4-dichlorophenol adsorption data.

The validity of the Langmuir equation assumes that a monolayer sorption of 2,4-dichlorophenol on a surface containing a finite number of sites takes place in the studied systems. The constant parameter q_m and K_L of Langmuir model explained in literature (Alam *et al*., 2006)

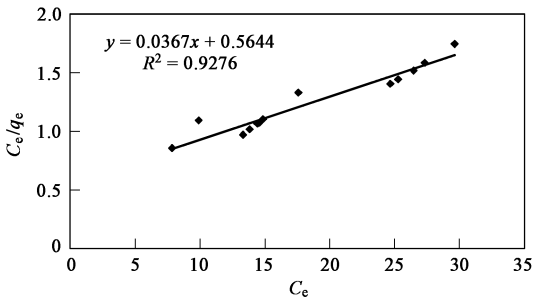

Fig. 1 Langmuir isotherm for removal of 2,4-dicholophenol using activated carbon derived from empty fruit bunches. Adsorbent dosage: 0.5% w/v; temperature: 30°C; pH: 4; agitation: 100 r/min.

can be determined directly from the slope and intercept of a plot C_e/q_e against C_e from Fig.1, respectively, as shown in Table 3.

Table 3 Constant parameters for Langmuir model

Activated carbon	$1/q_m$	$1/(K_L \cdot q_m)$	q_m	K_L	R^2
EFB 800	0.037	0.56	27.25	0.06502	0.93

The Freundlich isotherm is an empirical equation and shown to be satisfactory for low concentration (Tsai *et al*., 2001). A plot of ln q_e vs. ln C_e that enables the empirical constants K_F and $1/n$ to be determined from the intercept and slope of linear regression from Fig.2 is shown in Table 4 (Alam *et al*., 2006). The slope $1/n$ ranging between 0 and 1, is a measure of adsorption intensity or surface

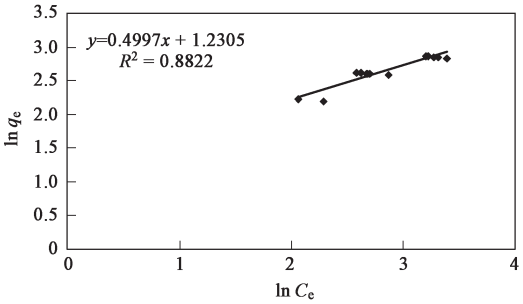

Fig. 2 Freundlich isotherm for removal of 2,4-dicholophenol using activated carbon derived from empty fruit bunches. Adsorbent dosage: 0.5% w/v; temperature: 30°C; pH: 4; agitation: 100 r/min.

heterogeneity, becoming more heterogeneous as its value gets closer to zero (Tsai *et al*., 2001).

Table 4 Constant parameters for Freundlich model

Activated carbon	1/*n*	ln K_F	K_F	R^2
EFB 800	0.50	1.23	3.42	0.88

The correlation coefficient showed that the data were better fitted in the Langmuir isotherm model (R^2=0.93) than the Freundlich isotherm model (R^2=0.88). Even though, the Langmuir and Freundlich constant q_m and K_F have different meanings, they led to the same conclusion about the correlation of the experimental data with the sorption model. The basic difference between K_F and q_m is that Langmuir isotherm assumes adsorption-free energy independent of both the surface coverage and the formation of monolayer whereas the solid surface reaches saturation, while the Freundlich isotherm does not predict saturation of the solid surface by the adsorbate, and thus, the surface covering being mathematically unlimited (Mohan and Singh, 2002). The magnitude of q_m , the Langmuir constant (27.25) indicates that the amount of 2,4-dichlorophenol per unit weight of sorbent to form complete monolayer on the surface was significantly high for the activated carbon. A value of K_L (0.065) related to binding energy also implied the strong bonding of 2,4-dichlorophenol to the activated carbon.

3 Conclusions

The activated carbon produced from empty fruit bunch at 800°C showed a good adsorption capacity of 2,4-dichlorophenol. The equilibrium time observed for the activated carbon was 8 h. The adsorption capacity was observed to be higher at lower pH of 4 and at higher concentration (250 mg/L) of 2,4-dichlorophenol solution with a moderate agitation speed of 100 r/min. The regression coefficient (R^2) showed that Langmuir isotherm (R^2 = 0.93) fits the results better than the Freundlich isotherm (R^2 = 0.88). Removal of phenolic compounds by the activated carbon derived from EFB was found to be favorable and hence, activated carbon could be considered as alternatives to commercial absorbents for the treatment of phenol(s) in industrial wastewater as well as any other effluents that contain heavy metals and organic substances.

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