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Treatment of semi-aerobic landfill leachate using durian peel-based activated carbon adsorption- Optimization of preparation conditions

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Abstract

The treatability of semi-aerobic landfill leachate parameters using durian peel-based activated carbon (DPAC) was investigated. An ideal experimental design was conducted based on central composite design (CCD) using response surface methodology to evaluate individual and interactive effects of operational variables namely activation temperature, activation time and carbon dioxide (CO_2) flow rate on treatment performance in terms of chemical oxygen demand (COD) and colour removal efficiencies. The DPAC was prepared using physical activation method which consists of CO_2 gasification. The adsorptions of COD and colour were described by Langmuir and Freundlich isotherm models. Based on the CCD, quadratic model was developed to correlate preparation variables to the two responses. The optimum DPAC preparation conditions were obtained using 800 °C activation temperature, 2.1 h activation time and 68.68 ml/s of CO_2 flow rate. From the experimental work, the maximum removal of COD and colour obtained were 41.98 and 39.86%, respectively.

Keywords: Activated carbon; CCD; COD; Colour; Leachate.

1. Introduction

Landfilling has emerged as the prominent option for disposing unwanted or non-economic materials. In Malaysia, approximately 95% of the collected municipal solid wastes (17,000 tons daily) are disposed in more than 230 landfills [1]. Due to excessive growth in population, lifestyle and rapid economy expansions, solid waste generation have become difficult to manage and dispose. Besides, vigorous combination of domestic, industrial and schedule wastes recognized as the potential hazard source throughout solid waste disposal on landfills. One distinctive problem associated with landfilling is the generation of dark liquid that flows through solid waste refuse that eventually reacts with rain water in the solid wastes matrix that is called leachate. Leachate is defined as a liquid formed by the percolation of precipitation through an open landfill or through the cap of a finished site [2]. In general, leachate contains significantly huge amounts of pollutants such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), ammonia, and high concentrations of heavy metals [1-3]. Leachate is known to be one of the major problems on landfill operations because of its adverse effects to the surrounding environment. If not properly treated and manage, leachate flows into water bodies or surface drain could trigger imbalance and devastate the ecological system of aquatic life and human being. In general, high strength leachate is defined by its parameter concentrations. Some of the common parameters that can be found in leachate are heavy metals and degradable organics at the beginning of landfill operation, while persistent organic pollutants usually appear later as a result of biotic and abiotic processes in the system [4]. According to Bashir et al. [5], young leachates are characterized by high BOD_5 (4000–40,000mg/L), high COD (6000–60,000mg/L), NH_3–N (<400), BOD5:COD ratio typically $\leq$1.0, and pH range from 4.5 to 7.5. Besides, the high concentrations of colour are mainly contributed by dissolved organic contents in leachate that has stabilized. Humic substances are natural organic compounds made up of complex structure of polymerised organic acids, carboxylic acids and carbohydrates [5]. These organic compounds may be present in the form of recalcitrant material of humic acids.

In operations, leachate treatment is a difficult and expensive process. Nevertheless, various treatment options have been reported. Some of the methods are physical, chemical, and biological. Air stripping [6], adsorption [7], and membrane filtration [8] are major physical leachate treatment methods. Coagulation flocculation [6], chemical precipitation, and chemical and electrochemical oxidation [9] methods are the common chemical methods employed. However, all the methods offered have certain limitation which is, it depends mostly on the leachate characteristics. According to Halim et al. [7], the common features of stabilized leachate are high strengths of ammoniacal nitrogen (3000–5000 mg/L) and moderately high strengths of COD (5000–20,000 mg/L), as well as a low ratio of BOD/COD (less than 0.1). A study done by Aghamohammadi et al. [10] found that 49% of COD could be removed under 2.22 day retention time and 43% by using powdered activated carbon augmented activated sludge in landfill leachate. Halim et al. [7] studied a comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment. They found that up to 80% of COD could be removed by activated carbon compared to zeolite and composite material. Recently, Cotman and Gotvajn [4] in their work reported that the most effective removal of organic substances were achieved at the addition of 50.0 g L^{-1} of activated carbon; remove up to 86% of COD and 63% of NH^{4+}-N. Kurniawan and Lo [11] reported that granular activated carbon adsorption alone could remove about 60% of COD from leachate.

Studies of leachate by activated carbon adsorption have been reported by various authors [10, 12-15]. Activated carbon is considered as one of the most effective adsorbents, especially for substances containing refractory organic compounds that resist biodegradation and persist in the environment. It has been chose as a renowned choice in leachate treatment due to its adsorption properties, a large porous volume, and a vast surface area ranging from 1000 to 1300/m^2 [11]. Its superior performance in terms of removal efficiency and high adsorption capacity is capable to reduce pollutants level in landfill leachate treatment. According to Abbas et al. [16], the main aims of activated carbon adsorption in leachate treatment are to ensure final polishing level by removing toxic heavy metals or organics and support microorganisms during leachate inhabitant. Commercially activated carbon does not have enough adsorption capacity because it usually possesses a non-polar surface due to manufacturing conditions at high temperatures, which is a disadvantage for some applications because of poor interaction with some polar adsorbates. The major drawback of the usage of commercial activated carbon is due to the expensive starting material. Nevertheless, numerous works have reported on the modification of the activated carbon surfaces or to produce composite adsorbent that have the ability to interact with either polar or non-polar adsorbates [7]. Therefore, there is a need to produce activated carbon from alternative material that is cheaper, renewable and readily available. In recent years, focus has been given on the preparation of low cost activated carbon from agricultural wastes such as bamboo waste [17], mangosteen peel [18], rambutan peel [19], tamarind wood [20] and coconut husk [21].

In this research, an attempt was made in preparing activated carbon from durian peel (DP) precursor by physical activation process. Native to South-Eastern Asia, durian (*Durio zibethinus*) is the fruit of trees from the genus *Durio* belonging to the Bombacaceae [22]. Landfill leachate parameters, namely COD and colour were tested to evaluate the percentage removal efficiency of DPAC by batch adsorption test. The analysis of the isotherm data namely Langmuir and Freundlich were carried out to predict the suitable model for the operation conditions. The knowledge contribution in this research is deemed important to the determination of optimum conditions of DPAC preparation variables in landfill leachate treatment.

2. Materials and methods

2.1 Semi-aerobic landfill leachate

Leachate samples were collected from Pulau Burung Semi-aerobic Landfill Site (PBLS), which is located within Byram Forest Reserve in Penang, Malaysia. All samples were collected from the influent of the detention pond in 20 L plastic containers, transported to the laboratory and stored at 4°C [23].

2.2 Preparation of DPAC

Durian peel (DP) used as precursor was obtained from a local orchard in Nibong Tebal, Penang, Malaysia. DP was firstly washed and subsequently dried at 105°C for 24 h to remove moisture content. The dried DP were ground and sieved to the size of 1–2 mm and loaded in a stainless steel vertical tubular reactor placed in a tube furnace. Carbonization step of the dried DP was carried out at 700°C for 2 h under purified nitrogen (99.99%). The char produced was further gasified under carbon dioxide (CO_2) influence as the activation process. The activation step was done using similar reactor as in carbonization where the activation temperature, activation time and CO_2 flow rate were based on the results suggested by the Design Expert 6.0.7 software (Stat-Ease Inc., Minneapolis, USA). The activated product was then cooled in room temperature under nitrogen flow. The sample was washed with hot deionised water and either hydrochloric acid (HCL) or potassium hydroxide (KOH) solution until the pH of the washed solution reached 6.5 to 7.

2.3 Batch adsorption test

The concentration of COD was measured by Method 5220 D (closed reflux, colourimetric method) and colour measurement was reported as true colour assayed at 455 nm and reported as platinum-cobalt (Pt-Co), the unit of colour being produced by 1 mg platinum/L in the form of chloroplatinate ion [5]. The two parameters were tested by using DR 2500 Hach spectrophotometer. The batch adsorption test was carried out by pouring 20 g of DPAC into 200 mL of leachate sample in 250 mL Erlenmeyer flasks. The initial concentration of COD and colour were 3100 and 3286 mg/L, respectively. The prepared mixture was agitated at 320 rpm until it reached equilibrium condition using orbital shaker (Bioblock Scientific Agitator 74578). The equilibrium condition was attained when the final concentration of COD and colour produced similar values from spectrophotometer. The supernatant was filtered by GC-50 filter prior to the conduct of tests for COD and colour. The percentage removal at equilibrium was calculated using spectrophotometer as follows:

$$REMOVAL(\%) = \frac{C_i - C_f}{C_i} \times 100 \qquad (1)$$

where C_i and C_f are the initial and final concentration of COD and colour (mg/L), respectively.

2.4 Experimental design

In this work, RSM design called central composite design (CCD) was utilized to investigate the effects of the DP activated carbon preparation variables; activation temperature (x_1), activation time (x_2) and CO_2 flow rate (x_3) towards their responses; COD (Y_1) and colour (Y_2) removal. The response surface methodology (RSM) is a collection of statistical and mathematical techniques that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions [20]. CCD is an effective design that is ideal for sequential experimentation, as it allows reasonable amount of information to test lack of fit when a sufficient number of experimental values exist [24]. These three variables together with their respective ranges were chosen based on preliminary studies as given in Table 1.

Table 1. Independent variables and their coded levels for the CCD

Variable (factors)	Code	Units	Coded variable levels				
			-α	-1	0	+1	+α
Activation temperature	x_1	°C	600	531.82	700.00	800	868.18
Activation time	x_2	h	0.32	1.00	2.00	3.00	3.68
CO_2 flow rate	x_3	ml/s	15.91	50	100.00	150	184.09

2.5 Equilibrium studies

Adsorption isotherms were used to describe the DPAC performance, and the relationship between adsorbent (DP activated carbon) and dissolved adsorbate (COD and colour). For this purpose, 200 ml of leachate sample were mixed with desired dosage of DP activated carbon i.e.; 5, 10, 15, 20, 25, 30 g. An agitating speed of 320 rpm and equilibrium periods of 180 minutes were used to ensure equilibrium conditions. The amount of adsorbate adsorbed at equilibrium, q_e (mg/g) was calculated to determine the percent removal of adsorbate as given by [24]:

$$q_e = \frac{(C_o - C_e)V}{W} \tag{2}$$

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

The CCD consists of 2^n factorial runs, 2n axial runs and six centre runs, where n is the number of factors. For three variables, the full design matrix consists of 8 factorial points, 6 axial points and 6 replicates at the centre points, indicating that altogether 20 experiments [21] as follows:

$$N = 2^n + 2n + n_c = 2^3 + 2(3) + 6 = 20 \tag{3}$$

where N is the total number of experiments required.

The low, centre and high levels of each variable are designated according to face centred CCD as −1, 0, and +1, respectively. The axial points are located at (±α, 0, 0), (α, ±, 0) and (α, 0, ±) where α (1.682) is the distance of the axial point from centre to allow the design rotatable. The responses were COD (Y_1) and colour removal (Y_2). Each response was used to develop an empirical model which correlated the response to the three activated carbon preparation variables using a second-degree polynomial equation as follows [25]:

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i \right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \tag{4}$$

where Y is the predicted response, b_o the constant coefficient, b_i the linear coefficients, b_{ij} the interaction coefficients, b_{ii} the quadratic coefficients and x_i, x_j are the coded values of the activated carbon preparation variables.

2.6 Characterization of DPAC

The surface area, pore volume and average pore diameter of the DP activated carbon were determined by using Autosorb AS 1 (Quantachrome, USA) volumetric adsorption analyzer. The BET surface area was measured from the adsorption isotherms using Brunauer–Emmett–Teller equation method. The total pore volume was estimated to be the liquid volume of nitrogen at a relative pressure of 0.98. The surface morphology of the samples was examined using a scanning electron microscope (Leo Supra 55 VP, Germany). The proximate analysis was carried out using thermogravimetric analyzer (Perkin Elmer TGA7, USA). The elemental analysis was performed using Elemental Analyzer (Perkin Elmer Series II 2400, USA).

3. Results and discussions

3.1 Development of regression model equation

The complete design matrix together with the values of both responses based on the experimental runs is shown in Table 2. Run 15–20 at the centre point were conducted to determine the experimental error and the reproducibility of the data [18]. COD and colour removal were observed in the range from 35.21 to 47.50 % and 10.54 to 59.53 %, respectively. According to the sequential model sum of squares, the models were selected based on the highest order polynomials where the additional terms were significant and the models were not aliased [17]. For COD and colour removal, quadratic models were suggested by the software. The final empirical formula models for COD (Y_1) and colour removal (Y_2) in terms of coded factors are represented by Eqs.(5) and (6), respectively.

$$Y_1 =+35.89 +2.59x_1 +1.13x_2 -0.68\ x_3 +1.71x_1^2+1.63x_2^2 +1.31x_3^2 -1.38\ x_1x_2-2.23\ x_1x_3+0.69x_2x_3 \quad (5)$$

$$Y_2 =+57.58 +7.23x_1 +3.47\ x_2 +7.04x_3 -13.54x_1^{\ 2} -8.71\ x_2^2 -5.85x_3^{\ 2} -0.16\ x_1\ x_2 +4.91x_1x_3+0.025x_2x_3 \quad (6)$$

The coefficient with one factor represent the effect of the particular factor, while the coefficients with two factors and those with second-order terms represent the interaction between two factors and quadratic effect, respectively [18] The quality of the fit polynomial model was expressed by correlation coefficient, R^2 In this experiment, the R^2 values were 0.9159 and 0.8899, for COD and colour removal, respectively. These indicate that 91.59 and 88.99% of the total variation were accurate as explained by the model and attributed to the experimental variable studied. In general, the regression models obtained for COD and colour removal were satisfied since the values of R^2 were relatively high and close to unity. Subsequently, a high R^2 coefficient ensures a satisfactory adjustment of the quadratic model to the experimental data [24]. R^2 values obtained were relatively high and show that the predicted values for COD and colour removal were accurate and closer to its actual value and ensure a satisfactory adjustment of the quadratic model to the experimental data.

Table 2. Experimental design matrix for preparation of DP activated carbon

Run	Level			DPAC preparation variables			COD removal, Y_1 (%)	Color removal Y_2 (%)
				Activation temperature, x_1 (°C)	Activation time, x_2 (h)	CO_2 flow rate (ml/s) x_3		
1	-1	-1	-1	600.00	1.00	50.00	35.25	17.47
2	+1	-1	-1	800.00	1.00	50.00	44.56	19.15
3	-1	+1	-1	600.00	3.00	50.00	37.43	16.65
4	+1	+1	-1	800.00	3.00	50.00	44.60	19.51
5	-1	-1	+1	600.00	1.00	150.00	35.71	20.43
6	+1	-1	+1	800.00	1.00	150.00	39.50	43.56
7	-1	+1	+1	600.00	3.00	150.00	44.01	21.53
8	+1	+1	+1	800.00	3.00	150.00	38.90	42.20
9	- 1.682	0	0	531.82	2.00	100.00	35.52	10.54
10	+1.682	0	0	868.18	2.00	100.00	47.50	40.54
11	0	- 1.682	0	700.00	0.32	100.00	39.65	24.89
12	0	+1.682	0	700.00	3.68	100.00	42.89	53.49
13	0	0	- 1.682	700.00	2.00	15.91	42.05	35.05
14	0	0	+1.682	700.00	2.00	184.09	38.70	59.53
15	0	0	0	700.00	2.00	100.00	35.55	56.45
16	0	0	0	700.00	2.00	100.00	36.43	57.54
17	0	0	0	700.00	2.00	100.00	36.80	57.83
18	0	0	0	700.00	2.00	100.00	35.57	57.55
19	0	0	0	700.00	2.00	100.00	35.51	56.54
20	0	0	0	700.00	2.00	100.00	35.21	57.40

3.2 Statistical analysis

Tables 3 and 4 show the results of the surface quadratic mode for COD and colour using analysis of variance (ANOVA), respectively. ANOVA is requisite to identify the significance and adequacy of the models developed. The mean squares were obtained by dividing the sum of the squares of each of the variation sources, the model and the error variance, by the respective degrees of freedom [19]. If the value of Prob.>F less than 0.05, the model terms are considered as significant while values greater than 0.1000 indicate that the model terms are not significant [21]. From Table 3, the model F-value of 12.09 and low Prob.> F of 0.0003 implied that the model was significant for COD removal and there is only a

0.01% chance that model *F*-value this large could occur due to noise. In this case, x_1, x_2, x_1^2, x_2^2, x_3^2 x_1x_2, and x_1x_3 factors were significant model terms whereas x_3 and x_2x_3 factors were insignificant model terms to the responses.

From Table 4, the model *F*-value of 8.98 and Prob. > *F* of 0.0010 indicated that the model was significant. x_1, x_3, x_1^2, $x_2^2$and x_3^2 factors were significant model terms whereas x_2, and x_1x_2, x_1x_3 and x_2x_3 factors were insignificant model terms to the responses. The lack of fit test values for COD and colour removal were 11.45 and 398.43, respectively. It shows that there are only 0.91 and 0.01% chances for both models that the lack of fit *F*- values this large could occur due to noise. It was also contributed by some systematic variation unaccounted in the hypothesized model resulted to undesirably significant lack of fit.

Based on the results of the statistical analysis, the response surface model constructed for predicting COD and colour removal were adequate and within the range o the variable studied. The finding was also further justified with the plot of predicted values versus experimental values for COD and colour removal as shown in Figures 1and 2. It can be seen that the models developed were successful in capturing the correlation between the DP activated carbon preparations variables to the responses when the predicted values obtained were quite close to the experimental values.

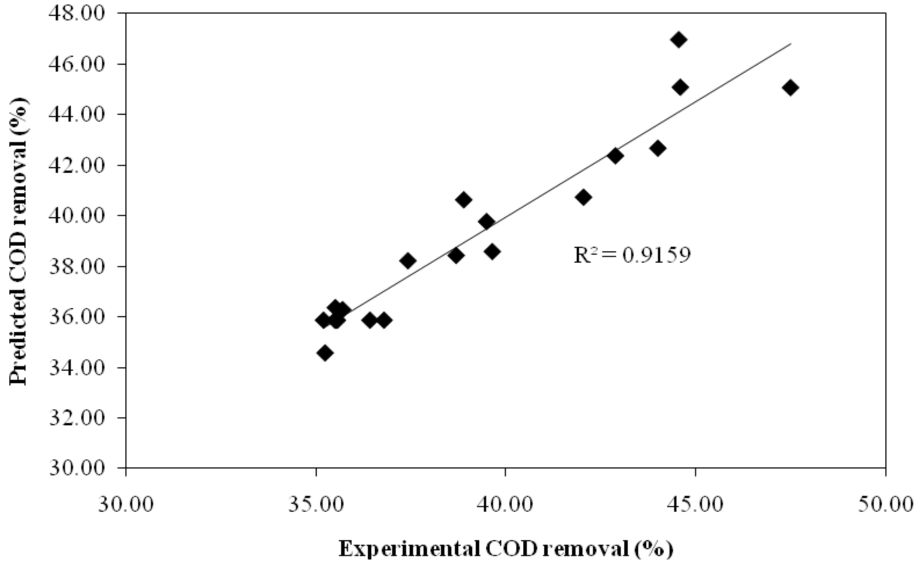


Figure 1. Predicted versus experimental COD removal of DP activated carbon

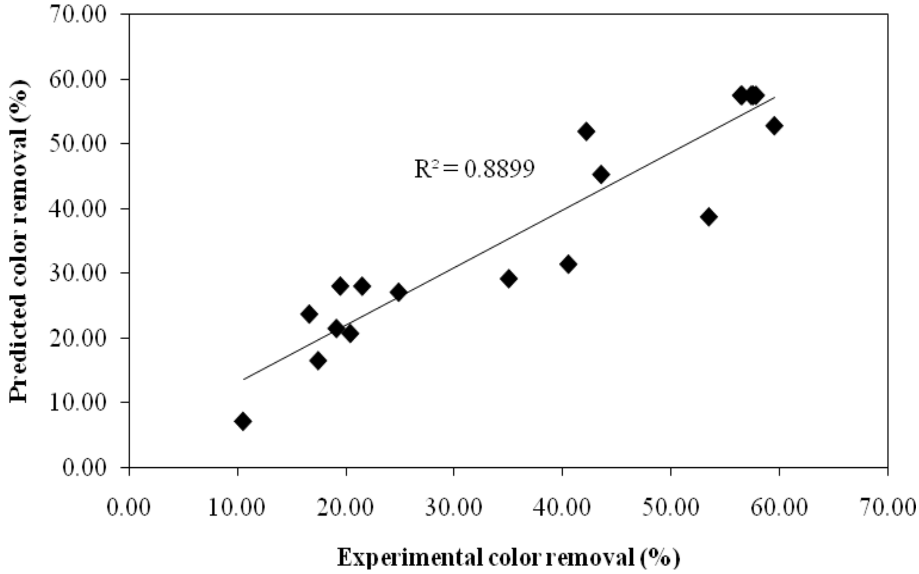


Figure 2. Predicted versus experimental of color removal of DP activated carbon

3.3 COD removal

From Table 3, it was observed that the *F*-value of 37.95 and Prob.>*F* of 0.0001 for activation temperature are the highest among all factors. It shows that COD removal is significantly influenced by the activation temperature of the DP activated carbon compared to the others factors. The effect of activation time was significant as well. However, it was found that the effect of flow rate contributes less effect to the response. Three-dimensional response surface curves were plotted by statistically significant model to investigate the interaction of the medium components. Figure 3 demonstrates the effect of activation time and activation temperature on the COD uptake, with CO_2 flow rate fixed at zero level (Q= 100 ml/s). From the figure, the COD removal increases with the increase in activation time and activation temperature.

Table 3. Analysis of variance (ANOVA) for response surface quadratic model for COD removal of DP activated carbon

Source	Sum of squares	Degree of freedom (DF)	Mean square	*F*-Value	Prob. > *F*	Comment
Model	261.81	9	29.09	12.09	0.0003	significant
x_1	91.28	1	91.28	37.95	0.0001	
x_2	17.30	1	17.30	7.19	0.0230	
x_3	6.41	1	6.41	2.66	0.1337	
x_1^2	42.30	1	42.30	17.59	0.0018	
x_2^2	38.21	1	38.21	15.89	0.0026	
x_3^2	24.81	1	24.81	10.31	0.0093	
x_1x_2	15.24	1	15.24	6.33	0.0306	
x_1x_3	39.60	1	39.60	16.47	0.0023	
x_2x_3	3.75	1	3.75	1.56	0.2400	
Residual	24.05	10	2.41			
Lack of fit	22.12	5	4.42	11.45	0.0091	significant

Generally, as the activation temperature increases, higher reaction rate between carbon and CO_2 occur which caused higher releasing of volatile matter. This could accelerate the reaction between C and CO_2, subsequently; the speed of widening pores was faster than that of developing pores. Thus, increases in pore diameters were expected. Further, it was observed that the activation time played an important role during CO_2 gasification. The time should just be enough to eliminate all the moisture and most of the volatile components in the precursor to cause pores to develop. Therefore, the capability of DP activated carbon was further enhanced to adsorb COD which mainly constitutes from organic contents in leachate sample.

3.4 Colour removal

From Table 4, it can be seen that the *F*-value of 39.56 and Prob.>*F* less than 0.0001 for activation temperature was the highest among all factors. It was followed by the quadratic factor of activation time with the *F*-value of 16.38. It can be inferred that the quadratic effects for both activation temperature and time played significant role for colour removal from leachate. It was further observed that the effect of flow rate contributes less effect to the response. Three-dimensional response surface curves were plotted by statistically significant model to investigate the interaction of the medium components.

Figure 4 demonstrates the effect of activation time and activation temperature on the COD uptake, with CO_2 flow rate was fixed at zero level (Q= 100 ml/s). From the figure, as the activation temperature and time increase, the colour removal was also increased. Generally as activation temperature increase with time, some surface metal complexes are produced, which are responsible for further carbon gasification and release of gaseous products such as CO_2, CO and H_2. The removal of colour was also dependent by kinetic rate of adsorption which was found to be influenced not just by film diffusion and by the rate of adsorption and the internal surface diffusion on the solid surface of the adsorbent [2].

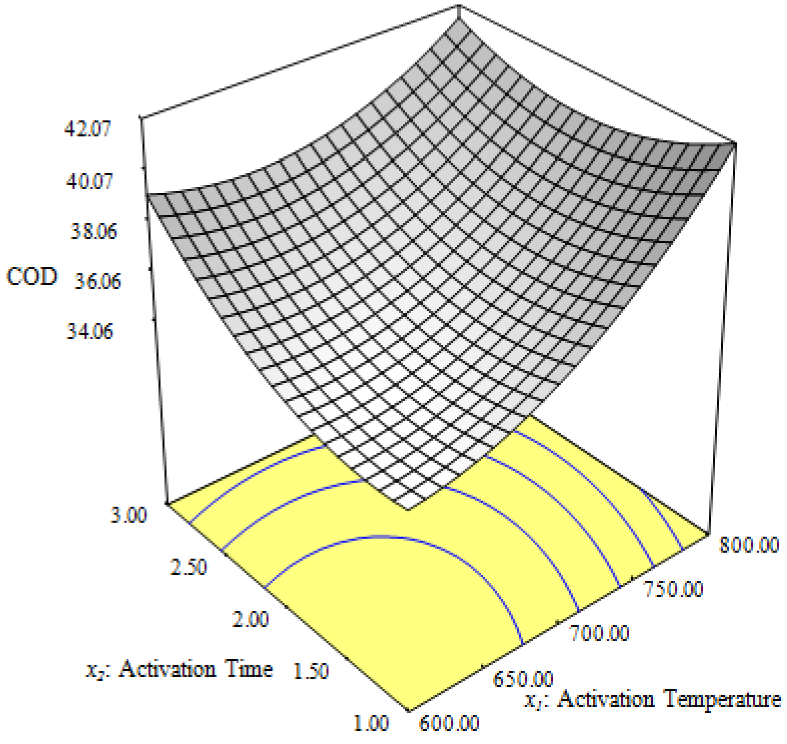


Figure 3. Three-dimensional response surface plot of COD removal of DPAC (effect of temperature and time, flow rate = 100 ml/s)

Table 4. Analysis of variance (ANOVA) for response surface quadratic model for color removal of DP activate carbon

Source	Sum of squares	Degree of freedom (DF)	Mean square	*F*-Value	Prob. > *F*	Comment
Model	5394.77	9	599.42	8.98	0.0010	significant
x_1	714.67	1	714.67	10.71	0.0084	
x_2	164.37	1	164.37	2.46	0.1477	
x_3	676.38	1	676.38	10.13	0.0098	
x_1^2	2640.63	1	2640.63	39.56	< 0.0001	
x_2^2	1093.39	1	1093.39	16.38	0.0023	
x_3^2	492.61	1	492.61	7.38	0.0217	
x_1x_2	0.20	1	0.20	3.068E-003	0.9569	
x_1x_3	192.67	1	192.67	2.89	0.1202	
x_2x_3	5.000E-003	1	5.000E-003	7.491E-005	0.9933	
Residual	667.47	10	66.75			
Lack of fit	665.80	5	133.16	398.43	< 0.0001	significant

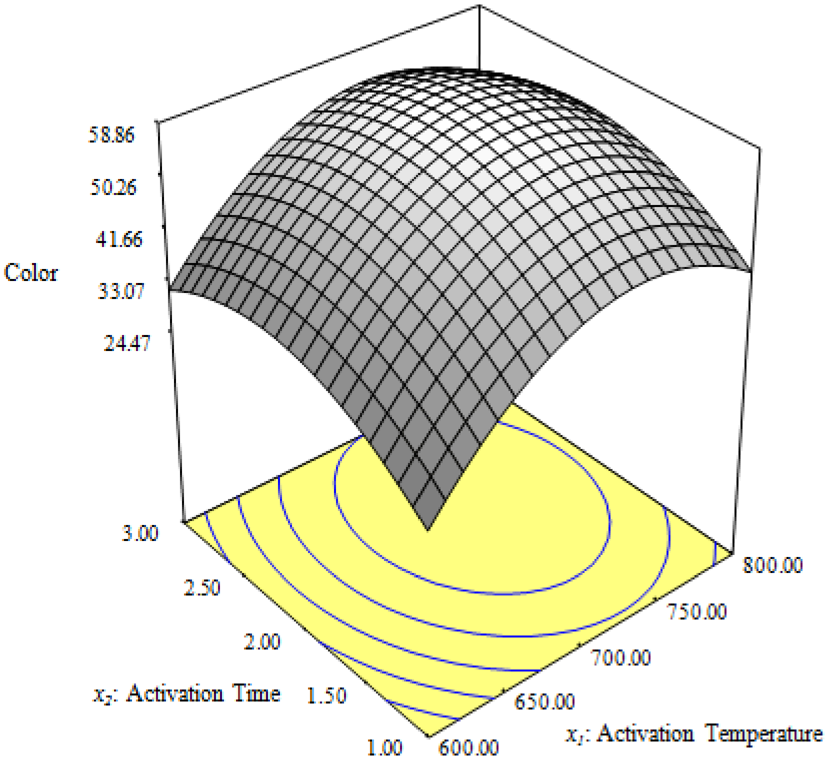


Figure 4. Three-dimensional response surface plot of color removal of DPAC (effect of temperature and time, flow rate = 100 ml/s)

3.5 Process optimization

CCD has been used to optimize the parameters affecting the COD and colour removal responses. Since the desired interest region for both COD and colour removal was equivalent, the function of desirability was applied using Design-Expert software to co-joint the factors. In this case, the desired goal for variables was chosen within the range while the responses set at maximum values. The program combines the individual desirability's into a single number, and then searches to maximize this function [24]. The predicted and experimental results of COD and colour removal obtained were shown in Table 5. The optimum DP activated carbon preparation conditions were obtained by using activation temperature of 800 °C, activation time of 2.1 h and flow rate of 68.68 ml/s. The optimum DP activated carbon showed COD and colour removal of 42.47 and 39.86%, respectively. It was observed that the experimental values obtained were in good agreement with the values predicted from the models, with relatively small errors, which were only 1.16 and 4.72 %, respectively for COD and colour.

Table 5. Model validation

Model desirability	Activation Temperature, x_1 °C	Activation time, x_2 h	CO_2 flow rate, x_3 ml/s	COD removal (%)			Color removal (%)		
				Predicted	Experimental	Error	Predicted	Experimental	Error
0.613	800.00	2.10	68.68	42.47	41.98	1.16	41.74	39.86	4.72

3.6 Equilibrium studies

The equilibrium studies of the experiment were carried out by using Langmuir and Freundlich isotherm models. Langmuir isotherm is based on the assumption that the adsorbed layer will be one molecule thick (homogeneous) while Freundlich isotherm assumes that the adsorbent has a heterogeneous surface composed of different classes of adsorption sites, with adsorption on each class of site following the Langmuir isotherm [26]. The Langmuir isotherm equation is expressed by the following equation:

$$\frac{x}{m} = \frac{QbC}{1+bC} \tag{7}$$

The linear form of Langmuir isotherm equation is given by following equation:

$$\frac{1}{(x/m)} = \frac{1}{QbC} + \frac{1}{Q} \tag{8}$$

where x is the amount of material adsorbed (mg), m is the weight of adsorbent (g); C is the equilibrium concentration of adsorbate in solution after adsorption is complete (mg/L); Q (mg/g) and b is the Langmuir adsorption constant related to the maximum adsorption capacity and the energy adsorption.
The Freundlich isotherm assumes that adsorption occurs on a heterogenous surface through a multilayer adsorption mechanism and that the adsorbed amount increases with the concentration according to the following equation:

$$q_e = K_F C_e^{1/n} \tag{9}$$

where q_e is the amount of adsorbate adsorbed at equilibrium, (mg/g), C_e is the equilibrium concentration of adsorbate, (mg/L), K_f is the Freundlich constant, (mg/g)(L/mg)1/n and n is the Freundlich heterogeneity factor. The equation is conveniently used in the linear form by taking the logarithmic of both sides as:

$$\log_e = \log K_f + \frac{1}{n}\log C_e \tag{10}$$

Table 6 summarizes all the constants and correlation coefficients, R^2 values obtained from the three isotherm models applied for adsorption of COD and colour on the DP activated carbon. On the basis of the R^2, it can be seen that Freundlich model fitted the data better than Langmuir. This is confirmed by the high value of correlation coefficient, R^2 (0.855) for the Freundlich isotherm model compared to Langmuir (0.800) indicating surface heterogeneity of the adsorbent and thus is responsible for multilayer adsorption due to the presence of energetically heterogenous adsorption sites [27]. Langmuir isotherm model of the DP activated carbon prepared showed relatively large COD adsorption with adsorption capacity of 61.72 mg/g it is relatively high compared to some previous works which employed commercial activated carbon for COD adsorption such as [7] (Q = 37.88 mg/g), and [5],(Q = 4.16 mg/g). For the case of colour adsorption, it can be seen that adsorption of colour is well represented by Langmuir isotherm considering high values of correlation coefficient, R^2 of 0.774 compared to Freundlich (R^2= 0.619) indicating that the adsorption of colour on DP activated carbon takes place as monolayer adsorption on a surface that is homogeneous in adsorption affinity [24]. By comparing the adsorption capacity of DP activated carbon, this result is considered relatively high when compared to previous work which utilized commercial activated carbon to remove colour from landfill leachate such as [5] (Q= 12.5 mg/g).

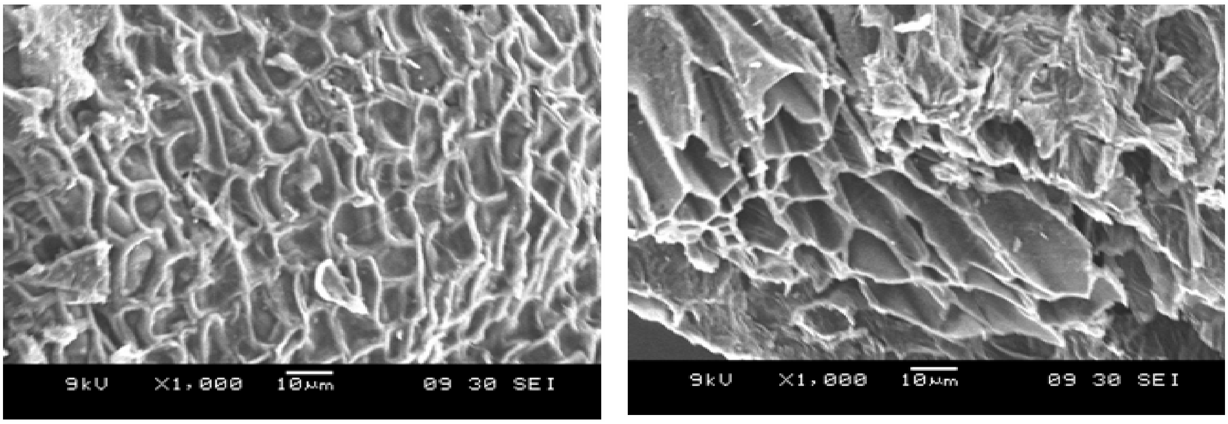
Table 6. Langmuir and Freundlich equations for COD and color removal

Leachate parameters	Isotherm					
	Langmuir			Freundlich		
	Q (mg/g)	b (L/mg)	R^2	K_F (mg/g (L/mg)$^{1/n}$)	1/n	R^2
COD	61.72	$1.53\text{x}10^{-3}$	0.800	$2.87\text{x}10^{-8}$	3.289	0.855
Color	100.00	0.111	0.774	$2.38\text{x}10^{-6}$	2.538	0.619

3.7 Characterization of activated carbon prepared under optimum condition

The BET surface area, total pore volume and average pore diameter of the prepared activated carbon were found to be 763.31 m^2/g, 0.35 cm^3/g and 6.02 nm, respectively. The average pore diameter of 6.02 nm indicates that the DP activated carbon prepared was in the mesopores region according to the IUPAC classification IUPAC [28]. The physical activation process has contributed to the relatively high surface area and total pore volume of the prepared activated carbon. The activated carbon development porosity is associated with gasification reaction.

Figures 5 (a) and (b), respectively shows the SEM images of the precursor and the DP activated carbon. By referring to Figure 5 (a), before activation process took place, the surface texture of raw DP was uneven, rough and undulating with very little pores available on the surface. After activation process, the resulted DP activated carbon produced large and well-developed pores on its surface as shown in Figure 5 (b). It also can be seen that almost homogeneous type pores structure were distributed on the surface of the DP activated carbon. This result revealed that the activation process CO_2 was effective in creating well-developed pores, resulting to large surface area activated carbon with good mesoporous structure. According to Aworn et al. [29], the pore evolution of the activated carbons occurred from continual devolatilization and carbon–CO_2 reaction whereby enhanced pores development on the surface of activated carbon.



(a) (b)

Figure 5. SEM images; (a) Raw DP (b) DP activated carbon (magnification 1000 x)

Table 7 presents the proximate and elemental analysis of precursor, char and DP activated carbon. After undergoing carbonization and activation process, the volatile matter content of the precursors decreased significantly whereas the fixed carbon content increased in activated carbons. It can be seen that the carbon content of DP was increased from 38.78 to 62.85% from the elemental analysis. This might be due to pyrolytic effect at high temperature where most of the organic substances have been degraded and discharged both as gas and liquid tars leaving a material with high carbon purity [19].

Table 7. Proximate and elemental contents

Sample	Proximate analysis (%)				Elemental analysis (%)			
	Moisture	Volatile Matter	Fixed Carbon	Ash	C	H	S	$(N+O)^a$
DP precursor	10.13	69.30	16.76	3.80	38.78	3.87	0.42	56.93
Char	10.88	54.86	26.40	7.86	70.84	2.54	0.20	26.82
DPAC	17.09	13.63	60.78	8.49	62.85	1.44	0.12	35.59

[a] Estimated by difference

4. Conclusion

In this research, response surface methodology was successfully used to investigate the effects of activation temperature, activation time and CO_2 flow rate, on the percentage removal of COD and colour from semi-aerobic landfill leachate. The optimum DP activated carbon preparation conditions were obtained using 800 °C activation temperature, 2.1 h activation time and 68.68 ml/s of CO_2 flow rate. From the experimental work, the maximum removal of COD and colour obtained were 41.98 and 39.86%, respectively. Through analysis of the response surface, activation temperature and activation time were found to give significant effects on both COD and colour removal. The DP activated carbon prepared demonstrated high surface area and well-developed porosity. According to this study, DP activated carbon can be utilized as the replacement of commercial activated carbon for semi-aerobic landfill leachate. The equilibrium data were well represented by the Freundlich isotherm for COD adsorption whereas for colour adsorption, Langmuir isotherm giving maximum monolayer adsorption capacity as high as 100 mg/g.

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References

[1] Bashir, M. J. K., Aziz, H. A., Yusoff, M. S., Aziz, S. Q. & Mohajeri, S. (2010) Stabilized Sanitary Landfill Leachate Treatment Using Anionic Resin: Treatment Optimization By Response Surface Methodology. Journal Of Hazardous Materials, 182, 115-122.

[2] Aziz, S. Q., Aziz, H. A., Yusoff, M. S. & Bashir, M. J. K. (2011) Landfill leachate treatment using powdered activated carbon augmented sequencing batch reactor (SBR) process: Optimization by response surface methodology. Journal of Hazardous Materials, 189, 404-413.

[3] Satyawali, Y. & Balakrishnan, M. (2008) Wastewater treatment in molasses-based alcohol distilleries for COD and color removal: A review. Journal of environmental management, 86, 481-497.

[4] Cotman, M. & Gotvajn, A. Z. (2010) Comparison of different physico-chemical methods for the removal of toxicants from landfill leachate. Journal of Hazardous Materials, 178, 298-305.

[5] Foul, A. A., Aziz, H. A., Isa, M. H. & Hung, Y. T. (2009) Primary Treatment Of Anaerobic Landfill Leachate Using Activated Carbon And Limestone: Batch And Column Studies. International Journal Of Environment And Waste Management, 4, 282-298.

[6] Guo, J. S., Abbas, A. A., Chen, Y. P., Liu, Z. P., Fang, F. & Chen, P. (2010) Treatment Of Landfill Leachate Using A Combined Stripping, Fenton, Sbr, And Coagulation Process. Journal Of Hazardous Materials, 178, 699-705.

[7] Halim, A. A., Aziz, H. A., Johari, M. A. M. & Ariffin, K. S. (2010) Comparison study of ammonia and COD adsorption on zeolite, activated carbon and composite materials in landfill leachate treatment. Desalination, 262, 31-35.

[8] Zouboulis, A. I. & Petala, M. D. (2008) Performance Of Vsep Vibratory Membrane Filtration System During The Treatment Of Landfill Leachates. Desalination, 222, 165-175.

[9] Papastavrou, C., Mantzavinos, D. & Diamadopoulos, E. (2009) A comparative treatment of stabilized landfill leachate: Coagulation and activated carbon adsorption vs. electrochemical oxidation. Environmental technology, 30, 1547-1553.

[10] Aghamohammadi, N., Aziz, H. A., Isa, M. H. & Zinatizadeh, A. A. (2007) Powdered activated carbon augmented activated sludge process for treatment of semi-aerobic landfill leachate using response surface methodology. Bioresource Technology, 98, 3570-3578.

[11] Kurniawan, T. A. & Lo, W. (2009) Removal of refractory compounds from stabilized landfill leachate using an integrated H2O2 oxidation and granular activated carbon (GAC) adsorption treatment. Water research, 43, 4079-4091.

[12] Aziz, H. A., Adlan, M. N., Zahari, M. S. M. & Alias, S. (2004) Removal of ammoniacal nitrogen (N-NH3) from municipal solid waste leachate by using activated carbon and limestone. Waste Management & Research, 22, 371.

[13] Çeçen, F., Erdinçler, A. & Kiliç, E. (2003) Effect of powdered activated carbon addition on sludge dewaterability and substrate removal in landfill leachate treatment. Advances in Environmental Research, 7, 707-713.

[14] Rivas, F. J., Beltrán, F. J., Gimeno, O., Frades, J. & Carvalho, F. (2006) Adsorption of landfill leachates onto activated carbon: Equilibrium and kinetics. Journal of Hazardous Materials, 131, 170-178.

[15] Kurniawan, T. A., Lo, W.-H. & Chan, G. Y. S. (2006) Physico-chemical treatments for removal of recalcitrant contaminants from landfill leachate. Journal of Hazardous Materials, 129, 80-100.

[16] Abbas, A. A., Jingsong, G., Ping, L. Z., Ya, P. Y. & Al-Rekabi, W. S. (2009) Review on LandWll Leachate Treatments. Journal of Applied Sciences Research, 5, 534-545.

[17] Ahmad, A.A. & B.H. Hameed, Effect of preparation conditions of activated carbon from bamboo waste for real textile wastewater. Journal of Hazardous Materials, 2010. 173(1-3): p. 487-493.

[18] Ahmad, M. A. & Alrozi, R. (2010) Optimization of preparation conditions for mangosteen peel-based activated carbons for the removal of Remazol Brilliant Blue R using response surface methodology. Chemical Engineering Journal.

[19] Ahmad, M. A. & Alrozi, R. (2011) Optimization of rambutan peel based activated carbon preparation conditions for Remazol Brilliant Blue R removal. Chemical Engineering Journal.

[20] Sahu, J. N., Acharya, J. & Meikap, B. C. (2010) Optimization of production conditions for activated carbons from Tamarind wood by zinc chloride using response surface methodology. Bioresource Technology, 101, 1974-1982.

[21] Tan, I. A. W., Ahmad, A. L. & Hameed, B. H. (2008) Optimization of preparation conditions for activated carbons from coconut husk using response surface methodology. Chemical Engineering Journal, 137, 462-470.

[22] Wai, W. W., Alkarkhi, A. F. M. & Easa, A. M. (2009) Optimization of Pectin Extraction from Durian Rind (Durio zibethinus) Using Response Surface Methodology. Journal of food science, 74, C637-C641.

[23] APHA, A. (1992) Standard Methods for The Examination of Water and Wastewater. Public Health Association, Washington.

[24] Bashir, M. J. K., Aziz, H. A., Yusoff, M. S. & Adlan, M. (2010) Application of response surface methodology (RSM) for optimization of ammoniacal nitrogen removal from semi-aerobic landfill leachate using ion exchange resin. Desalination, 254, 154-161.

[25] Singh, K. P., Gupta, S., Singh, A. K. & Sinha, S. (2010) Experimental design and response surface modeling for optimization of Rhodamine B removal from water by magnetic nanocomposite. Chemical Engineering Journal.

[26] Benefield, L. D., Judkins, J. F. & Weand, B. L. (1982) Process Chemistry for Water and Wastewater Treatment. Prentice-Hall Inc. USA.

[27] Ahmad, A., Rafatullah, M., Sulaiman, O., Ibrahim, M. H. & Hashim, R. (2009) Scavenging behaviour of meranti sawdust in the removal of methylene blue from aqueous solution. Journal of Hazardous Materials, 170, 357-365. 29.

[28] IUPAC (1972), IUPAC manual of symbols and terminology, Pure Appl. Chem. 31

[29] Aworn, A., Thiravetyan, P. & Nakbanpote, W. (2008) Preparation and characteristics of agricultural waste activated carbon by physical activation having micro- and mesopores. Journal of Analytical and Applied Pyrolysis, 82, 279-285.