Preparation of activated carbon from coconut husk: Optimization study on removal of 2,4,6-trichlorophenol using response surface methodology

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Abstract

Activated carbon was prepared from coconut husk using physicochemical activation method which consisted of potassium hydroxide (KOH) treatment and carbon dioxide (CO_2) gasification. The effects of three preparation variables (CO_2 activation temperature, CO_2 activation time and KOH:char impregnation ratio) on the 2,4,6-trichlorophenol (2,4,6-TCP) uptake and activated carbon yield were investigated. Based on the central composite design, two quadratic models were developed to correlate the preparation variables to the two responses. From the analysis of variance (ANOVA), the most influential factor on each experimental design response was identified. The activated carbon preparation conditions were optimized by maximizing both the 2,4,6-TCP uptake and activated carbon yield. The predicted 2,4,6-TCP uptake and carbon yield from the models agreed satisfactorily with the experimental values. The optimum conditions for preparing activated carbon from coconut husk for adsorption of 2,4,6-TCP were found as follow: CO_2 activation temperature of 750 °C, CO_2 activation time of 2.29 h and KOH:char impregnation ratio of 2.91, which resulted in 191.73 mg/g of 2,4,6-TCP uptake and 20.16 % of activated carbon yield.
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1. Introduction

Chlorophenols are a group of chemicals in which chlorines have been added to phenol. Chlorophenols have been prescribed as priority pollutants by the US Environmental Protection Agency (EPA) due to their toxicity and adverse effects upon human [1]. They are the most common organic pollutants used widely in agriculture, industry and public health. The most important chlorophenol sources are wastewaters from pesticide, paint, solvent, pharmaceutics, paper and pulp industries as well as water disinfecting process [2]. Chlorophenols are weak acids and permeate human skin by in vitro and are readily absorbed by gastro-intestinal tract. The acute toxicity of chlorophenols includes increased respiratory rate, vomiting and nausea [3]. Chlorophenols also create complicated problems to water bodies such as bad odour and taste in drinking water, death of aquatic life, inhibition of normal activities of microbial population in wastewater treatment plant, etc. Therefore, the efficiency of tra-

ditional biological treatment method is not satisfying due to chlorophenol's structural stabilization and toxicity [2]. Besides, they also display a pronounced undesirable effect in potable water at concentration as low as 0.1 mg/l [3]. As one type of the most hazardous materials, they are carcinogenic, mutagenic and resistant to biodegradation, and thus have to be decomposed before discharging into receiving waters, in order to avoid the biomagnified toxicity to aquatic flora and fauna through various food chains [4].

Adsorption on activated carbon has been found to be superior compared to other chemical and physical methods for wastewater treatment in terms of its capability for efficiently adsorbing a broad range of pollutants, fast adsorption kinetics and its simplicity of design. However, commercially available activated carbons are still expensive due to the use of non-renewable and relatively high-cost starting material such as coal, which is unjustified in pollution control applications [5,6]. Therefore, in recent years, many researchers have tried to produce activated carbons for removal of various pollutants using renewable and cheaper precursors which were mainly industrial and agricultural by-products, such as coconut shell [3], waste apricot [7], sugar beet bagasse [8], molasses [9], rubberwood sawdust [10], rice straw

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[11], bamboo [12], rattan sawdust [13], oil palm fibre [14] and coconut husk [15].

Coconut husk is the mesocarp of coconut and a coconut is consists of 33–35% of husk. In Malaysia, about 151,000 ha of land was being used for coconut plantation in year 2001. It was estimated that 5,280 kg of dry husks were become available per hectare per year. At present, coconut husks are used as fuel for coconut processing, as a domestic fuel and as a source of fibre for rope and mats. To make better use of this cheap and abundant agricultural waste, it is proposed to convert coconut husk into activated carbon. Conversion of coconut husk into activated carbon will serve a double purpose. First, unwanted agricultural waste is converted to useful, value-added adsorbents and second, the use of agricultural by-products represents a potential source of adsorbents which will contribute to solving part of the wastewater treatment problem in Malaysia [15]. However, not many studies have been carried out on coconut husk-based activated carbon. Some of them are adsorption of arsenic on copper impregnated coconut husk carbon [16], preparation of activated carbon from digested sewage sludge with the additive coconut husk using $ZnCl_2$ as activating agent [17], production of activated carbons from coconut fibres for removal of phenol, Acid Red 27 dye and Cu^{2+} ions [18] and our recent work on preparation of activated carbon from coconut husk for adsorption of basic dye [15].

The most important characteristic of an activated carbon is its adsorption capacity or uptake which is highly influenced by the activated carbon preparation conditions. This is because activated carbon preparation variables such as activation temperature, activation time and chemical impregnation ratio will influence the pore development and surface characteristics of the activated carbon produced. Therefore, the challenge in activated carbon production is to produce very specific carbons which are suitable for certain applications. In assessing the effect of treatments on quality attributes, the use of an adequate experimental design is particularly important. Response surface methodology (RSM) has been found to be a useful tool to study the interactions of two or more variables [19]. Optimization of experimental conditions using RSM was widely applied in various processes. Some of the previous studies found in applying RSM in preparation of activated carbons used precursors such as olive-waste cakes [20], Luscar char [21], Turkish lignite [19] and hazelnut shell [22]. In our previous work, the preparation conditions for coconut husk-based activated carbon have been successfully optimized for basic dye adsorption [15].

The focus of this research was to explore the feasibility of coconut husk-based activated carbon being utilized in removal of 2,4,6-trichlorophenol (2,4,6-TCP) from aqueous solutions and also to optimize the activated carbon preparation conditions which would result in high activated carbon yield and high 2,4,6-TCP uptake. A central composite design (CCD) was selected to study simultaneously the effects of three activated carbon preparation variables (CO_2 activation temperature, CO_2 activation time and KOH:char impregnation ratio) on the two responses. Empirical models correlating the 2,4,6-TCP uptake and the carbon yield to the three variables were then developed.

2. Materials and methods

2.1. Activated carbon preparation

Coconut husk used for preparation of activated carbon was obtained locally. The procedure used to prepare the activated carbon was referred to our previous work [15]. The precursor was first washed to remove dirt from its surface and was then dried overnight in an oven at 105 °C. The dried husk was cut and sieved to desired mesh size (1–2 mm) and loaded in a stainless steel vertical tubular reactor placed in a tube furnace. Carbonization of the precursor was carried out by ramping the temperature from room temperature to 700 °C with heating rate of 10 °C/min and hold for 2 h. Throughout the carbonization process, purified nitrogen (99.995%) was flown through at flow rate of 150 cm³/min. The char produced was mixed with KOH pallets with different impregnation ratio (IR), as calculated using Eq. (1):

$$IR = \frac{w_{KOH}}{w_{char}} \tag{1}$$

where w_{KOH} is the dry weight (g) of KOH pallets and w_{char} is the dry weight (g) of char. Deionized water was then added to dissolve all the KOH pallets.

The mixture was then dehydrated in an oven overnight at 105 °C to remove moisture and was then activated under the same condition as carbonization, but to a different final temperature. Once the final temperature was reached, the nitrogen gas flow was switched to CO_2 and activation was held for different period of time. The activated product was then cooled to room temperature under nitrogen flow and then washed with hot deionized water and 0.1 molar hydrochloric acid until the pH of the washing solution reached 6–7 [15].

2.2. Design of experiments

Response surface methodology (RSM) is a collection of mathematical and statistical techniques that are useful for modeling and analysis of problems in which a response of interest is influenced by several variables [23]. A standard RSM design called a central composite design (CCD) was applied in this work to study the variables for preparing the activated carbons. This method is suitable for fitting a quadratic surface and it helps to optimize the effective parameters with a minimum number of experiments, as well as to analyze the interaction between the parameters [21]. Generally, the CCD consists of a 2^n factorial runs with $2n$ axial runs and n_c center runs (six replicates).

In the present study, the activated carbons were prepared using physiochemical activation method by varying the preparation variables using the CCD. The variables studied were (i) x_1, CO_2 activation temperature; (ii) x_2, CO_2 activation time and (iii) x_3, KOH:char impregnation ratio. For each categorical variable, a 2^3 full factorial CCD for the three variables, consisting of 8 factorial points, 6 axial points and 6 replicates at the center points were employed, indicating that altogether 20 experiments

were required, as calculated from Eq. (2) [21]:

$$N = 2^n + 2n + n_c = 2^3 + 2 * 3 + 6 = 20 \qquad (2)$$

where N is the total number of experiments required and n is the number of factors.

The center points are used to determine the experimental error and the reproducibility of the data. The independent variables are coded to the $(-1, 1)$ interval where the low and high levels are coded as -1 and $+1$, respectively. The axial points are located at $(\pm \alpha, 0, 0)$, $(0, \pm \alpha, 0)$ and $(0, 0, \pm \alpha)$ where α is the distance of the axial point from center and makes the design rotatable. In this study, the α value was fixed at 1.682 (rotatable). The complete design matrix of the experiments carried out, together with the results obtained, are shown in Table 1. The experimental sequence was randomized in order to minimize the effects of the uncontrolled factors. The two responses were 2,4,6-TCP uptake (Y_1) and activated carbon yield (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 given by Eq. (3) [24]:

$$Y = b_o + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i \right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \qquad (3)$$

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.

2.3. Model fitting and statistical analysis

Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was used for regression analysis of the experimental data to fit the equations developed and also for the evaluation of the statistical significance of the equations.

2.4. Batch equilibrium studies

2,4,6-TCP supplied by Sigma–Aldrich (M) Sdn Bhd, Malaysia was used as the adsorbate in this study, and was not purified prior to use. Deionized water was used to prepare all the solutions and reagents. 2,4,6-TCP has a chemical formula of $C_6H_3Cl_3O$, with molecular weight of 197.46 g/mol. Chemical structure of 2,4,6-TCP is shown in Appendix A. Batch adsorption was performed in 20 sets of 250 ml Erlenmeyer flasks where 100 ml of 2,4,6-TCP solution with initial concentration of 200 mg/l was placed in each flask. The pH of the solution was natural without any pH adjustment. 0.1 g of each of the prepared activated carbon, with particle size of 200 μm, was added to each flask and kept in an isothermal shaker of 120 rpm at 30 °C until equilibrium was reached. Aqueous samples were taken from the solutions and the concentrations were analyzed. All samples were filtered prior to analysis in order to minimize interference of the carbon fines with the analysis. The concentrations of 2,4,6-TCP in the supernatant solutions before and after adsorption were determined using a double beam UV–vis spectrophotometer (UV-1601 Shimadzu, Japan) at its maximum wavelength of 296 nm. The 2,4,6-TCP uptake at equilibrium, q_e (mg/g), was calculated by Eq. (4):

$$q_e = \frac{(C_o - C_e)V}{W} \qquad (4)$$

where C_o and C_e (mg/l) are the liquid-phase concentrations of 2,4,6-TCP at initial and at equilibrium, respectively. V is the volume of the solution (l) and W is the mass of dry adsorbent used (g).

2.5. Activated carbon yield

The activated carbon yield was calculated based on Eq. (5).

$$\text{Yield}(\%) = \frac{w_c}{w_o} \times 100 \qquad (5)$$

where w_c is the dry weight (g) of final activated carbon and w_o is the dry weight (g) of precursor.

2.6. Characterization of the prepared activated carbon

Scanning electron microscopy (SEM) analysis was carried out on the activated carbon prepared under optimum conditions, to study its surface texture and the development of porosity. Fourier transform infrared (FTIR) analysis was applied on the same activated carbon to determine the surface functional groups, by using FTIR spectroscope (FTIR-2000, Perkin Elmer), where the spectra were recorded from 4000 to 400 cm^{-1}.

3. Results and discussion

3.1. Development of regression model equation

The complete design matrix together with the values of both the responses obtained from the experimental works are given in Table 1. CCD was used to develop correlation between the activated carbon preparation variables to the 2,4,6-TCP uptake and carbon yield. The 2,4,6-TCP uptake was found to range from 44.14 to 192.07 mg/g, whereas the carbon yield obtained ranged from 3.23 to 23.42%. Runs 15–20 at the center point were used to determine the experimental error. 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. For both responses of 2,4,6-TCP uptake and carbon yield, the quadratic model was selected, as suggested by the software. The final empirical models in terms of coded factors after excluding the insignificant terms for 2,4,6-TCP uptake (Y_1) and carbon yield (Y_2) are shown in Eqs. (6) and (7), respectively.

$$Y_1 = 188.86 + 7.45x_1 + 7.85x_2 + 29.35x_3 - 3.83x_1^2$$
$$- 1.16 x_2^2 - 25.62x_3^2 - 2.37x_1x_2 - 17.32x_1x_3 - 6.83x_2x_3 \qquad (6)$$

$$Y_2 = 17.93 - 5.11x_1 - 2.04x_2 - 1.94x_3 - 2.31x_1^2 - 0.60x_2^2$$
$$+ 0.72x_3^2 - 1.61x_1x_2 + 0.37x_1x_3 + 1.24x_2x_3 \qquad (7)$$

Table 1
Experimental design matrix and results

Run	Levels			Activated carbon preparation variables			2,4,6-TCP uptake, Y_1 (mg/g)	Carbon yield, Y_2 (%)
				Activation temperature, x_1 (°C)	Activation time, x_2 (h)	KOH:char impregnation ratio, x_3		
1	−1	−1	−1	750.00	1.00	1.00	86.840	23.09
2	+1	−1	−1	900.00	1.00	1.00	166.903	17.36
3	−1	+1	−1	750.00	3.00	1.00	128.398	21.74
4	+1	+1	−1	900.00	3.00	1.00	184.548	6.79
5	−1	−1	+1	750.00	1.00	3.90	190.987	16.57
6	+1	−1	+1	900.00	1.00	3.90	187.315	9.54
7	−1	+1	+1	750.00	3.00	3.90	190.775	17.40
8	+1	+1	+1	900.00	3.00	3.90	192.070	6.73
9	−1.682	0	0	698.87	2.00	2.45	176.650	21.90
10	+1.682	0	0	951.13	2.00	2.45	157.556	3.23
11	0	−1.682	0	825.00	0.32	2.45	161.723	21.54
12	0	+1.682	0	825.00	3.68	2.45	187.562	13.25
13	0	0	−1.682	825.00	2.00	0.01	44.140	23.42
14	0	0	+1.682	825.00	2.00	4.89	166.820	18.82
15	0	0	0	825.00	2.00	2.45	188.021	16.66
16	0	0	0	825.00	2.00	2.45	190.293	18.43
17	0	0	0	825.00	2.00	2.45	189.080	18.25
18	0	0	0	825.00	2.00	2.45	190.222	17.87
19	0	0	0	825.00	2.00	2.45	189.080	17.65
20	0	0	0	825.00	2.00	2.45	190.222	18.30

Positive sign in front of the terms indicates synergistic effect, whereas negative sign indicates antagonistic effect. The quality of the model developed was evaluated based on the correlation coefficient, R^2 and also the standard deviation values. The closer the R^2 value to unity and the smaller the standard deviation, the more accurate the response could be predicted by the model. The R^2 value for Eqs. (6) and (7) was found to be 0.881 and 0.957, respectively. This indicated that 88.1% and 95.7% of the total variation in the 2,4,6-TCP uptake and carbon yield, respectively, was attributed to the experimental variables studied. The R^2 of 0.881 for Eq. (6) was considered as moderate to validate the fit, which might lead to large variation in the 2,4,6-TCP uptake predicted from this model. However, for Eq. (7) in the other hand, the R^2 of 0.957 was considered relatively high as the value was close to unity, indicating that there was a good agreement between the experimental and the predicted carbon yield from this model.

The standard deviation for Eqs. (6) and (7) was 18.60 and 1.63, respectively. This shows that the predicted value for carbon yield would be more accurate and closer to its actual value, as compared to the predicted value for 2,4,6-TCP uptake. The possible reason for the lower superiority and higher error of estimation given by Eq. (6) could be there were other parameters affecting the 2,4,6-TCP uptake, other than the three variables (CO_2 activation temperature, CO_2 activation time and KOH:char impregnation ratio) being studied in this work. Further investigations need to be carried out in order to verify this.

The adequacy of the models was further justified through analysis of variance (ANOVA). The ANOVA for the quadratic model for 2,4,6-TCP uptake is listed in Table 2. From the ANOVA for response surface quadratic model for 2,4,6-TCP uptake, the model F-value of 8.25 implied that the model was significant. Values of Prob > F less than 0.05 indicated that the model terms were significant. In this case, x_3, x_3^2 and x_1x_3 were

Table 2
Analysis of variance (ANOVA) for response surface quadratic model for 2,4,6-TCP uptake

| Source	Sum of squares	Degree of freedom (d.f.)	Mean square	F value	Prob > F
Model	25,693.38	9	2,854.82	8.25	0.0014
x_1	757.69	1	757.69	2.19	0.1697
x_2	841.51	1	841.51	2.43	0.1499
x_3	11,761.49	1	11,761.49	34.00	0.0002
x_1^2	211.31	1	211.31	0.61	0.4526
x_2^2	19.51	1	19.51	0.056	0.8171
x_3^2	9,456.53	1	9,456.53	27.34	0.0004
x_1x_2	44.87	1	44.87	0.13	0.7262
x_1x_3	2,400.94	1	2,400.94	6.94	0.0250
x_2x_3	373.45	1	373.45	1.08	0.3233
Residual	3,459.30	10	345.93	–	–
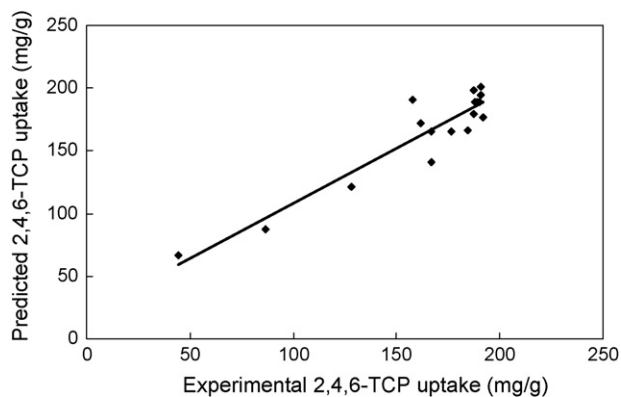
Fig. 1. Predicted vs. experimental 2,4,6-TCP uptake.

significant model terms whereas x_1, x_2, x_1^2, x_2^2, x_1x_2 and x_2x_3 were all insignificant to the response. From the ANOVA for response surface quadratic model for activated carbon yield [15], the model F-value of 24.75 implied that the model was significant as well. In this case, x_1, x_2, x_3, x_1^2 and x_1x_2 were significant model terms.

From the statistical results obtained, it was shown that the above models were adequate to predict the 2,4,6-TCP uptake and the carbon yield within the range of variables studied. Figs. 1 and 2 show the predicted values versus the experimental values for 2,4,6-TCP uptake and carbon yield, respectively. As expected, the errors between the predicted and actual carbon yield were smaller compared to the errors between the predicted and actual 2,4,6-TCP uptake. The predicted carbon yield values were quite close to the experimental values, indicating that the model developed was successful in capturing the correlation between the activated carbon preparation variables to the carbon yield. However, some of the 2,4,6-TCP uptake values predicted by the model were less accurate, especially when 2,4,6-TCP uptake was higher than 150 mg/g. This was due to the low R^2 and high standard deviation values of the model, as explained earlier. The effects of other variables on this response need to be further determined.

3.2. 2,4,6-Trichlorophenol uptake

Based on the F values (Table 2), KOH:char impregnation ratio (x_3) showed the largest F value of 34.00, indicating that it
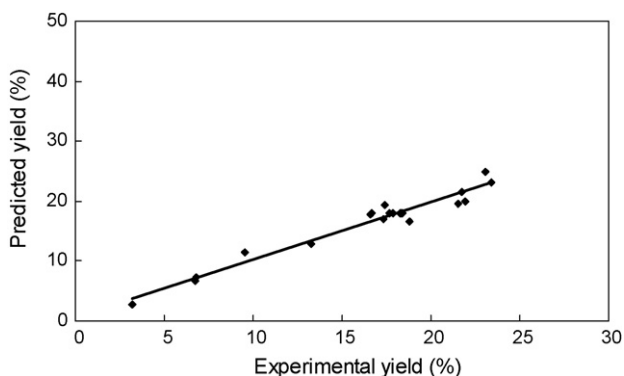

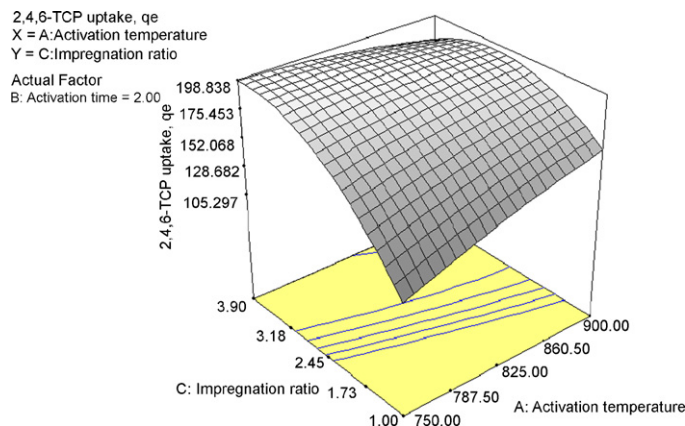Fig. 2. Predicted vs. experimental activated carbon yield.

Fig. 3. Three-dimensional response surface plot of 2,4,6-TCP uptake (effect of activation temperature and chemical impregnation ratio, $t = 2$ h).

had the most significant effect on the 2,4,6-TCP uptake for the prepared activated carbon, compared to CO_2 activation temperature (x_1) and CO_2 activation time (x_2). The effects of activation temperature and activation time on the 2,4,6-TCP uptake were quite similar, with F value of 2.19 and 2.43, respectively, which were considered moderate. Besides, the quadratic effect of KOH impregnation ratio, x_3^2 on the 2,4,6-TCP uptake was relatively significant as well. Fig. 3 shows the three-dimensional response surfaces which was constructed to show the interaction effects of the activated carbon preparation variables (activation temperature and chemical impregnation ratio) on the 2,4,6-TCP uptake (Y_1). For this plot, the activation time was fixed at zero level ($t = 2$ h). As can be seen from Fig. 3, the 2,4,6-TCP uptake generally increases with increase in activation temperature and chemical impregnation ratio.

The results obtained agreed with the works by Sudaryanto et al. [25] which reported that activation time gave no significant effect on the pore structure of activated carbon produced from cassava peel, and the pore characteristics changed significantly with the activation temperature and also the KOH impregnation ratio. Şentorun-Shalaby et al. [26] also found that activation time did not show much effect on the surface area obtained for activated carbons prepared from apricot stones using steam activation. However, in this work, all the three variables studied were found to have synergistic effects on the 2,4,6-TCP uptake of the activated carbons prepared. This was expected as the progressive temperature rise and longer activation time would increase the C–KOH and C–CO_2 reaction rates, resulting in increasing devolatilization which further developed the rudimentary pore structure in the char and also enhanced the existing pores and created new porosities. The increase in activation temperature and time also entailed an opening and enlargement of the pores, which enhanced the adsorption of 2,4,6-TCP [20,27,28]. Besides, the increase in temperature also caused the CO_2 and the surface metal complex to further gasify the carbon, leading to widening of the pores [29]. However, there was a maximum activation temperature above which would probably lead to the melting of the pores formed at previous stage. It was also reported in literature that too long or too short activation time could reduce the surface area and the adsorption capacity of acti-

Table 3
Comparison of carbon yield for various activated carbons

Activated carbon	Activation method	Carbon yield (%)	Reference
Coconut husk-based	KOH treatment and CO_2 gasification	3.23–23.42	Present work
Fir wood-based	KOH etching and CO_2 gasification	4.70–25.20	[29]
Pistachio-nut shell-based	KOH activation	12.35–21.14	[28]
Corncob-based	KOH activation	15.00–22.30	[33]
Pistachio shell-based	KOH activation	19.80–29.70	[34]
Oil-palm shell-based	CO_2 activation	10.20–25.00	[35]

vated carbon prepared, as longer activation time might destroy the pore structure formed previously whereas shorter activation time could not enrich the formation of porosity [30].

KOH:char impregnation ratio played a decisive role in the formation of pores. At high KOH impregnation ratio, the pore development was mostly due to the intercalation of potassium metal in the carbon structure [25]. As the KOH:char IR increased, the catalytic oxidation also caused the widening of pores, therefore increasing the 2,4,6-TCP uptake as well [31]. The increase in KOH could accelerate the reaction rate and therefore the quantity of pores increased correspondingly. However, there was a maximum point for the KOH:char IR beyond which would reduce the 2,4,6-TCP uptake. This was because excessive amount of KOH could cause further reaction between KOH and carbon, which might destroy the pore structure formed at previous stage [30]. The excessive KOH molecules might also decomposed into water which caused the following gasification process under high temperature:

$$2KOH \rightarrow K_2O + H_2O \qquad (8)$$

$$H_2O + C \rightarrow CO + H_2 \qquad (9)$$

Therefore, over gasification might have occurred with the detrimental effect of reducing the surface area, hence the reduction in 2,4,6-TCP uptake [32].

3.3. Activated carbon yield

The data obtained for activated carbon yield (Y_2) were reported in our previous study [15]. Activation temperature was found to have the greatest effect on it, with the highest *F* value of 134.23, while activation time and chemical impregnation ratio showed almost similar effects on the response, which were less significant compared to activation temperature. The quadratic effect of activation temperature on carbon yield was relatively large compared to quadratic effects of activation time and chemical impregnation ratio. However, the interaction effects between the variables were less significant. The effects of activation temperature, activation time and chemical impregnation ratio on yield were studied as all the three variables were found to be significant terms in the model for activated carbon yield. It was concluded that the carbon yield decreased with increasing activation temperature, activation time and chemical impregnation ratio [15].

The results obtained in this study were in agreement with the work done by Sudaryanto et al. [25] where activation tem-

perature was found to play an important role on the yield of activated carbon whereas activation time did not show much effect on the carbon yield. The increase in temperature would release increasing volatiles as a result of intensifying dehydration and elimination reaction and also increased the C–KOH and C–CO_2 reaction rate, thereby resulting in decreasing yield [28,31]. Indeed, the increase in activation temperature quickens the gasification reactions of carbon and therefore, the attack of the amorphous components which obstruct the pores causes a decrease in the carbon yield [20]. Şentorun-Shalaby et al. [26] observed that at higher activation temperature, activation of apricot stones became more extensive and resulted in a lower solid yield with a more widened porous stucture. The yield for activated carbon prepared from fir wood was also found to decrease gradually with increase in duration of CO_2 gasification [29].

The activated carbon yield was also strongly affected by the chemical impregnation ratio where increasing impregnation ratio decreased the yield and increased the carbon burn-off. This was because when higher impregnation ratio was used, the weight losses were due to increasing release of volatile products as a result of intensifying dehydration and elimination reactions [31]. KOH would promote the oxidation process, therefore with high KOH:char IR, the gasification of surface carbon atoms was the predominant reaction, leading to increase in the weight loss of carbon [25].

Table 3 lists the comparison of carbon yield for various activated carbons. The results obtained in the present work were comparable with the works reported in the literature. The variation in the carbon yields might be due to the different precursors as well as the activation methods and/or conditions used to prepare the activated carbons.

3.4. Process optimization

In the production of commercial activated carbons, relatively high product yields are expected for economical feasibility and the most important property of activated carbon is its adsorption capacity. Therefore, the activated carbon produced should have a high carbon yield and also a high adsorption capacity for economical viability. However, to optimize both these responses under the same condition is difficult because the interest region of factors are different. When Y_1 increases, Y_2 will decrease and vice versa. Therefore, in order to compromise between these two responses, the function of desirability was applied using Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA). The experimental conditions with the highest desirability

Table 4
Model validation

Activation temperature, x_1 (°C)	Activation time, x_2 (h)	KOH:char impregnation ratio, x_3	2,4,6-TCP uptake (mg/g)		Carbon yield (%)	
			Predicted	Experimental	Predicted	Experimental
750.00	2.29	2.91	192.07	191.73	20.00	20.16

were selected to be verified. The activated carbon was prepared under the experimental conditions given in Table 4, together with the predicted and experimental values for 2,4,6-TCP uptake and carbon yield. The optimal activated carbon was obtained using preparation condition as: 750 °C activation temperature, 2.29 h activation time and 2.91 KOH:char IR, which resulted in 20.16% of carbon yield and 191.73 mg/g of 2,4,6-TCP uptake. It was observed that the experimental values obtained were in good agreement with the values predicted from the models, with relatively small errors between the predicted and the actual values, which was only 0.18 and 0.8%, respectively for 2,4,6-TCP uptake and carbon yield.

The performance of the prepared activated carbon on 2,4,6-TCP was highly satisfactory, with the removal efficiency as high as 97.52%, for a solution concentration of 200 mg/l. From literature, Radhika and Palanivelu [3] found that the maximum adsorption capacity for 2,4,6-TCP on coconut shell-based activated carbon and a commercial activated carbon was 122.336 and 112.35 mg/g, respectively. Hameed [36] in the other hand reported that the maximum adsorption capacity for 2,4,6-TCP on activated clay was 123.46 mg/g. This shows that the activated carbon prepared in this work was suitable to be used to remove 2,4,6-TCP from aqueous solutions, with 2,4,6-TCP uptake as high as 191.73 mg/g. Through process optimization, coconut husk was proved to be a promising precursor for production of activated carbons with high carbon yield and high adsorption capacity on 2,4,6-TCP. The process was considered economically feasible as the precursor was cheap, yet it gave a high activated carbon yield besides giving high quality activated carbon with high adsorption performance.

3.5. Characterization of activated carbon prepared under optimum conditions

Fig. 4 shows the SEM image of the activated carbon prepared under optimum conditions (750 °C activation temperature, 2.29 h activation time and 2.91 KOH:char impregnation ratio). Large and well-developed pores were clearly found on the surface of the activated carbon. This might be due to the activation process used, which involved both chemical and physical activating agents of KOH and CO_2. Pore development in the char during pyrolysis was also important as this would enhance the surface area and pore volume of the activated carbon by promoting the diffusion of KOH and CO_2 molecules into the pores and thereby increasing the KOH–carbon and CO_2–carbon reactions, which would then create more pores in the activated carbon. The well-developed pores on the prepared activated carbon could be the main factor that had lead to the high 2,4,6-TCP uptake in this study.
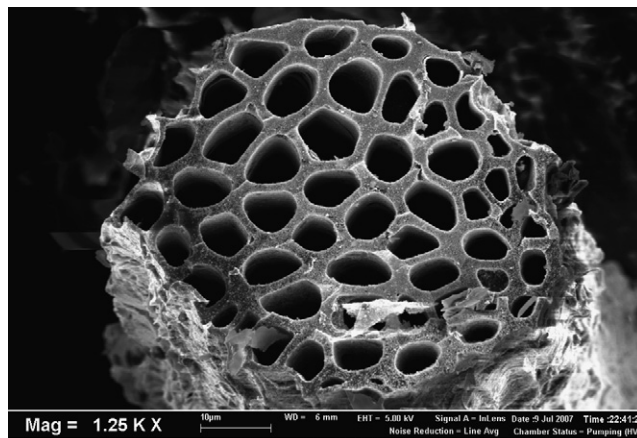

Fig. 4. Scanning electron micrograph (1250×) of activated carbon prepared under optimum conditions (CO_2 activation temperature = 750 °C, CO_2 activation time = 2.29 h and KOH:char impregnation ratio = 2.91).

The FTIR spectrum obtained for the prepared activated carbon displayed the following bands:-

- $3434.99 \, cm^{-1}$: O–H stretching vibrations;
- $2380 \, cm^{-1}$: C≡C stretching vibrations;
- $1567.5 \, cm^{-1}$: C=C stretching vibration;
- $1384.48 \, cm^{-1}$: C–CH_3 deformation;
- $1138.2 \, cm^{-1}$, $1052.98 \, cm^{-1}$, $1017.53 \, cm^{-1}$: C–O–H stretching vibrations;
- $767.32 \, cm^{-1}$: C–H out-of-plane deformation;
- $651.54 \, cm^{-1}$, $607.23 \, cm^{-1}$: C–O–H twist

The FTIR spectra obtained were in agreement with the results reported in the study carried out on commercial granular activated carbons [1] and activated carbon prepared from cherry stones [37]. The band in the region of ≈1600 cm^{-1} has been observed by many previous researchers but has not been interpreted definitely, however, for most carbonaceous materials, C=C stretching absorption frequently occurs at this region [1]. The spectrum in the region of 1200–1000 cm^{-1} represented C–O stretching vibrations of functional groups such as alcohols, ethers, carboxylic acids and esters.

4. Conclusions

A central composite design was conducted to study the effects of three activated carbon preparation variables, which were the activation temperature, activation time and chemical impregnation ratio, on the 2,4,6-TCP uptake and activated carbon yield. Quadratic models were developed to correlate the preparation variables to the two responses. Through analysis of the response

surfaces derived from the models, KOH:char impregnation ratio was found to have the most significant effect on 2,4,6-TCP uptake whereas activation temperature showed the most significant effect on activated carbon yield. Process optimization was carried out and the experimental values obtained for the 2,4,6-TCP uptake and carbon yield were found to agree satisfactorily with the values predicted by the models. The optimal activated carbon was obtained using 750 °C activation temperature, 2.29 h activation time and 2.91 KOH:char impregnation ratio, resulting in 20.16% of carbon yield and 191.73 mg/g of 2,4,6-TCP uptake. From the SEM image obtained, large and well-developed pores were clearly found on the surface of the activated carbon. Various functional groups on the prepared activated carbon were determined from the FTIR results.

Acknowledgment

Appendix A. Chemical structure of 2,4,6-TCP
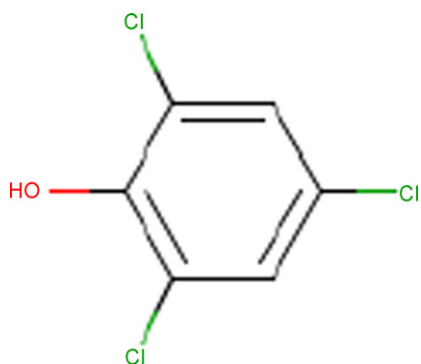
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