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Microwave Irradiated Palm Shell-Polyetheretherketone Porous Carbons as CO_2 Sorbents: Optimization Using Response Surface Methodology (RSM)

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Palm shell being one of the abundant biomass in Malaysia, was used together with polyetheretherketone (PEEK) as precursors for the preparation of porous carbons via microwave induced potassium carbonate chemical activation. Design expert software version 7.1.6 using central composite design coupled with surface response methodology was used in predicting and optimization of the CO_2 adsorption of the porous carbons. Effect of three independent variables (i.e. microwave power, irradiation time and amount of PEEK) on the sorbent performance for CO_2 adsorption was investigated. A quadratic model was developed to calculate the optimum preparation conditions of activated carbon, which relate the factors to the response (CO_2 adsorption). The influence of process parameters on the properties of porous carbon was investigated using analysis of variance (ANOVA) to identify the significant parameters. Microwave power was found to be the most significant factor influencing the porous carbon for CO_2 adsorption. The porous carbons (PCs) preparation conditions were optimized by maximizing the CO_2 adsorption capacity. The predicted CO_2 adsorption capacities from the models agreed satisfactorily with the experimental values. The optimum carbon was obtained at microwave power of 500 W; irradiation time 6.55 min; and amount of PEEK 26.03 %. Therefore, the Microwave-irradiated palm-PEEK was found to be a suitable adsorbent for uptake of CO_2.

1. Introduction

Carbon dioxide is a major greenhouse gas that is highly attributed to climate change (Nasri et al., 2014). Combustion of fossil fuels (coal, oil, and natural gas) is the major source of CO_2 emission, Power plants using carbon-base fuel contributes 1/3 of the anthropogenic CO_2 emission (Shafeeyan et al., 2012). Due the environmental issues related to CO_2 emission substantial effort is exerted on curbing CO_2 emissions. This prompted growing research in this area in order to reduce the cost, while achieving high CO_2 uptake (Garcia et al., 2011). Currently, absorption using amine solutions is the technology that is more studied and it's commercially used for CO_2 capture in power plants. The process involves absorption of CO_2 from flue gas stream in a column containing amine-base solvents. The CO_2 -enriched solution is then heated to remove the CO_2 and regenerate the amine solution. Nonetheless, various shortcomings, such as the corrosion of process equipment, high cost and the high energy input required to regenerate the solvent, leave room for further research (Plaza et al., 2010).Adsorption is considered to be a promising alternative to the amine based process. Unlike liquid absorbents, solid sorbents have low cost, and high stability over

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wide range of pressure and temperature (Rashidi et al., 2014). However, the success of this technology depends on preparation of stable sorbent with high CO_2 adsorption capacity, low cost, easy to regenerate, high selectivity (Samanta et al., 2011). Activated carbon (AC) also has good attributes for CO_2 uptake, such as its good adsorption capacities, hydrophobic character, low cost, and low energy requirement for regeneration, production from variety of sources (Shafeeyan et al., 2010). The characteristics of the AC are dependent on modification conditions, such as treatment temperature, method of heating, duration, type and nature of activation. There are two basic methods of heating in the production of AC: Conventional thermal heating and microwave heating. In conventional thermal methods, external heating are used for the carbonisation and activation of raw material (Hesas et al., 2013). In microwave heating, energy is readily transformed into heat inside the particles by dipole rotation and ionic conduction (Yangmur et al., 2008). Microwave treatment offers advantage of precise temperature control, lower consumption of inert, shorter period of synthesis and producing basic groups on the sorbent material (Hamza et al., 2012).

Most of the processes that produce CO_2 in product streams occur at elevated temperatures (up to 100 °C). Therefore preparation of highly stable activated carbon that can perform satisfactory at relatively high temperature is desirable (Shafeeyan et al., 2012). Such carbon can be regenerated easily and will minimize the cost of cooling before separation. It was observed that PEEK- based porous carbon have excellent properties desirable for high temperature and gas storage applications. This is due to large surface area and micropore volume of PEEK porous carbons together with its semi-crystalline nature (Cansado et. al., 2009). It's on this note that this research focuses on investigation of properties of hybrid PEEK with sustainable Palm shell porous carbons for CO_2 adsorption application. But adsorption is effective, only when the optimum process parameters are employed (Kannan et al., 2010). This necessitates the study of optimisation of process parameters for CO_2 uptake. Single dimensional methods of optimization, which involves varying only one factor at a time, do not give accurate prediction of optimum conditions (Saeed et al., 2014). Response surface methodology (RSM) is a multivariable technique that simultaneously optimizes the process parameters to get best response within the experimental region under study. In this study, microwave assisted heating was used in preparation hybrid palm-PEEK porous carbons as CO_2 sorbents. The main objective of the work was to use RSM based on CCD to obtain optimum preparation conditions for preparation of high temperature palm-PEEK based porous carbons by microwave irradiation towards CO_2 adsorption and improved thermal property. Three numerical variables (Microwave power, irradiation time and amount of PEEK) are the dependent variables while CO_2 adsorption is the dependent parameter. To the best of authors' knowledge, there is no previous work conducted on CO_2 adsorption on microwave palm shell-PEEK hybrid porous carbons.

2. Experimental

The materials used and the procedure followed in obtaining the experimental results are described below.

2.1 Materials

Palm kernel shell (PKS) obtained from Koperasi Kampung Jawi Johor Bharu Berhad, Malaysia was washed thoroughly with deionized water to remove dirt particles from its surface. It was then dried at 105 °C for 24 h and then subsequently grinded and sieved to particle size of 0.85 - 1.7 mm. It was then stored in desiccator for future use. Potassium carbonate, K_2CO_3 was purchased from Merck, Germany. CO_2 (purity 99.99 %) was supplied by Megamount Sdn Bhd., Malaysia. Deionized water was used in preparation of solution. Granulated PEEK (Polyether etheretherketone) was supplied by Vitrex Tech., Lancashire UK.

2.2 Sorbent synthesis

The ground palm shells were carbonized in a tubular reactor placed in a furnace to form chars which were sieved to 0.5 - 0.85 mm sizes. Granulated Victrex PEEK was also pyrolysed at 800 °C in a furnace to form the PEEK Char (PEKC). The PEEK precursor was heated at the rate of 10 °C/min under flow of 90 cm^3/min of nitrogen for 45 min. The resultant PEEK char were sieved to 0.5 - 0.85 mm sizes. PEEK char was blended with Palm kernel char (PKC) at different percentages by weight of 10, 20, 30 and 40 wt% of PEEK char. The blended chars were mixed with impregnating agent (K_2CO_3) in the ratio of 1:1.The impregnation ratio defined as the dry weight of activation agent per weight of char. The mixture of precursor and chemical solution was stirred at 85 °C and 6 rpm for 2 h. It was then placed in an oven for 24 h. The dried mixture was then activated in a modified microwave (Samsung ME0113M model). The activation was performed by loading 10 g of impregnated material in a high temperature quartz glass reactor which was then fixed in the microwave chamber. Different power levels were chosen from the power controller at different set of exposure times. Nitrogen gas was used to purge air and to preheat the

system at a flow rate of nitrogen 200 cm^3/min, power, 100 W for 5 min (Yang et al., 2010). The flow was then switched over to CO_2 at flow rate of 200 cm^3/min. The resultant activated carbon was washed thoroughly with 0.1 M hydrochloric acid and deionized water.

2.3 Experimental Design, statistical analysis, model fitting and optimization

RSM has the advantage over one factor at a time method by taking so many factors and their interaction to reach the optimum. In this study design expert software version 7.1.6 (Start-Ease Inc., Minneapolis, USA) was used to generate the experimental designs. The sorbent preparation variables consist of three numerical variables i.e. microwave power x_1 (200 - 600 W), activation/irrradiation time x_2 (0 - 12 min) and amount of PEEK x_3 (0 - 40 %). Central composite design (CCD) coupled with response surface methodology was chosen for the analysis. CO_2 adsorption was taken as the response in the experimental design. The design expert software was used subsequently in statistical analysis, development of regression models and optimization of the sorbent preparations. The CCD consists of 2^n factorial runs with 2n axial runs and n_C centre runs (six replicates) (Eq 1). Therefore in this experiment 2^3 full factorial CCD for the three variables, consisting of 8 factorial points, 6 axial points and 6 replicates at the centre points were employed, for a total of 20 experiments. CO_2 adsorption (Y_a) was taken as the responses in the experimental design. A quadratic polynomial equation was developed to correlates and predicts the dependent variables and the independent as given by Eq(2).

$$N = 2^n + 2n + n_c = 20 \quad (1)$$

$$Y = \beta_0 + \sum_{i=1}^{i=n} \beta_i x_i + \sum_{i=1}^{i=n} \beta_{ii} x_i^2 + \sum_{i=j=1}^{i=j=n} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

Where Y is the predicted response,β_0 is the constant, x_i, and x_j are the coded values of the independent variables, β_0 is the linear term coefficient, β_{ii} is the quadratic term coefficient, β_{ij} is the interaction term coefficient, Ɛ is the random error, and n is the number of factors (Shafeeyan et al., 2012). Every term in the equation was evaluated for its statistical significance (Prob > F value less than 0.05) at a 95 % confidence level. Subsequently, the optimal conditions for sorbent preparation were identified with the aid of the design expert software. An analysis of variance (ANOVA) was used to evaluate the fitness of the model and identify the interactions between the preparation variables and the responses. The implications of the model equations and terms were evaluated by F-test. Using the F-test, the insignificant terms were eliminated, and the final model was obtained. The quality of fit of the polynomial model equation was expressed by the coefficient of determination adjusted (R^2) and and R^2_{adj}. The fitted polynomial equation was expressed as three dimensional surface plots to visualize the individual and interactive effects of the independent variables. Finally, optimum values of the independent variable for maximizing the responses were determined using the software.

3. Results and Discussion

3.1 Development of regression model and statistical analysis

Central composite design was used to correlate the variables and the corresponding responses. The experimental points and the values of the responses are given in Table 1. Software fits linear, two-factor interaction (2FI), quadratic and cubic polynomials to the responses. A fitted equation was obtained by applying multiple regression analysis to the design matrix and the responses. The program recommends quadratic model, which is the equation that can be use subsequently to optimize the preparation conditions for the sorbent. The general response equation in terms of coded factors includes all numerical parameters (i.e., x_1, x_2 and x_3). The final empirical models in terms of coded factors for CO_2 adsorption (Y) is given in Eq(3). 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), which is 0.917. Adequate precision measures the signal-to-noise ratio and compares the range of the predicted values at the design points to the average prediction error. The adequate precision ratio of 13.579 was obtained for the CO_2 adsorption is much greater than 4 and that indicate adequate model discrimination (Shafeeyan et al., 2012).

$$Y = 3.33 + 0.39A + 0.26B + 0.098C - 0.17\,AB - 0.30A^2 - 0.25B^2 - 0.082C^2 \quad (3)$$

An analysis of variance (ANOVA) was applied to evaluate the fitness of the model and identify the interactions between the preparation of variables and the responses. The result of the analysis was given in Table 2. The F-value and p-value were used to determine the regression coefficients, standard error and significance of each coefficient (Hesas et al., 2013).

Table 1: Experimental design matrix and response results

Run	Code	Actual variable			Response
		Power x_1 (W)	Time x_2 (min)	Amount of PEEK x_3 (%)	CO_2 adsorbed Y_1 (mmol/g)
1	M3P3-3	300.00	3.00	30.00	1.93
2	M4P2-6	400.00	6.00	20.00	3.40
3	M4P2-0	400.00	0.00	20.00	1.67
4	M4P0-6	400.00	6.00	0.00	2.91
5	M5P1-3	500.00	3.00	10.00	3.04
6	M4P2-6	400.00	6.00	20.00	3.35
7	M5P3-9	500.00	9.00	30.00	3.01
8	M5P3-3	500.00	3.00	30.00	3.11
9	M5P1-9	500.00	9.00	10.00	2.96
10	M6P2-6	600.00	6.00	20.00	2.89
11	M4P2-12	400.00	12.00	20.00	3.26
12	M4P2-6	400.00	6.00	20.00	3.41
13	M3P1-9	300.00	9.00	10.00	2.25
14	M3P3-9	300.00	9.00	30.00	2.58
15	M4P4-6	400.00	6.00	40.00	3.36
16	M2P2-6	200.00	6.00	20.00	1.61
17	M4P2-6	400.00	6.00	20.00	3.41
18	M4P2-6	400.00	6.00	20.00	3.31
19	M4P2-6	400.00	6.00	20.00	3.38
20	M3P1-3	300.00	3.00	10.00	1.71

Table 2: Analysis of variance (ANOVA) for response surface quadratic model for CO_2 uptake

Source	Sum of sq.	Degree of freedom	Mean of square	F-value	p-value
Model	7.13	9	0.79	12.80	0.0002
x_1	2.41	1	2.41	38.96	< 0.0001
x_2	1.10	1	1.10	17.74	0.0018
x_3	0.15	1	0.15	2.49	0.1456
x_1x_2	0.23	1	0.23	3.79	0.0801
x_1x_3	0.023	1	0.023	0.37	0.5547
x_2x_3	0.001012	1	0.001012	0.016	0.9007
x_1^2	2.31	1	2.31	37.27	0.0001
x_2^2	1.56	1	1.56	25.22	0.0005
x_3^2	0.17	1	0.17	2.71	0.1310
Residual	0.62	10	0.062		
Pure error	0.007283	5	0.001457		
R-square	0.92				
Model	7.13	9	0.79	12.80	0.0002

From the ANOVA for response surface quadratic model for CO_2 adsorption, the model F-value of 12.8 implied that the model was significant. The fact that the model was significant is reiterated by values of Prob. > F which is less than 0.05. In terms of parameters effect on CO_2 adsorption, probability value lower than 0.05 ($P < 0.05$) indicate that the model term is significant, whereas a value above 0.1 denotes non-significant model terms. In this case, x_1, x_2, x_1^2 and x_2^2 were significant model terms while x_3, x_1x_2, x_1x_3, x_2x_3 and x_3^2 were all insignificant model terms. The fit of the model to the empirical data was tested by calculating the regression coefficients, R^2 and R^2_{adj} values of 0.917 and 0.869 were obtained for the CO_2 adsorption capacity. This shows that 91.7 % and 86.9 % of the total variation could be explained by the quadratic model.

3.2 Effect of sorbent preparation variables

Among the factors studied, based on F value, microwave power (x_1) with the highest F value of 38.96 had much effect on the CO_2 adsorption capacity (Y_1).; followed by irradiation time (X_2) with an F value of 17.74.

Amount of PEEK had less effect with an F value of 2.49. Interaction between the factors (X_1X_2, X_1X_3 and X_2X_3) had less effect on the CO_2 adsorption (Table 2). The quadratic function of microwave power (x_1^2) Three-dimensional (3D) response surface plots of the predictive quadratic model for the CO_2 adsorption capacity on the porous carbons is shown in Figure 1(a and b).

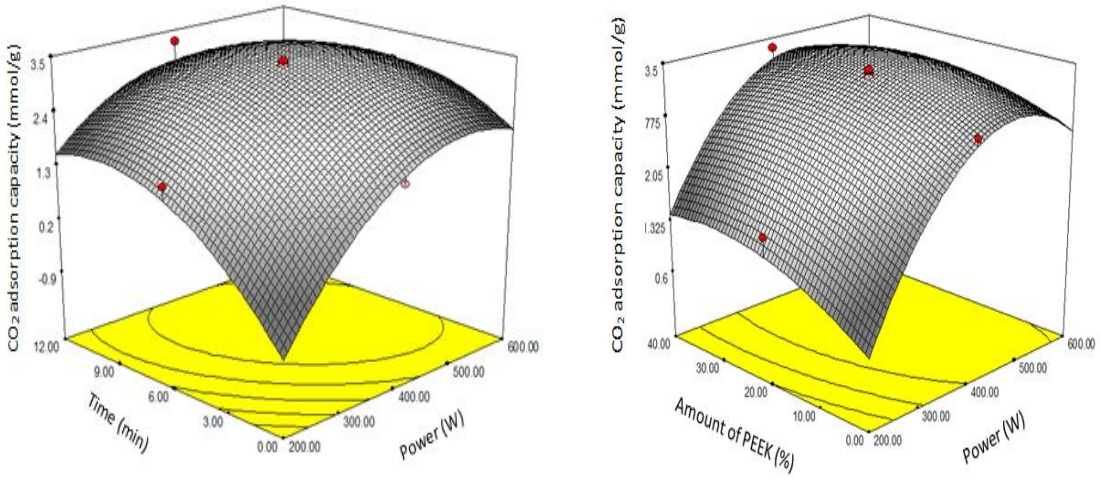

Figure 1: Three-dimensional response surface plot: (a) the effect microwave power and irradiation time, (b) the effect of microwave power and amount of PEEK and on the activated CO_2 adsorption capacity

The plots show the variation in the CO_2 adsorption capacity of the porous carbon with respect to the microwave irradiation power, Irradiation time and amount of PEEK. The response surface was generated based on (Eq 3). The CO_2 adsorption capacity increases with increase in microwave power and time initially (Figure 1a). The maximum CO_2 adsorption capacity was notice around 400 - 500 W microwave power and then gradually decreases with increase in microwave power and time. It was previously reported that the CO_2 adsorption increases with increase in microwave power (Hesas, et al., 2013). Increase in microwave power with time brings about substantial increase in porosities of activated carbon. This is due to continual reaction of the char with the activation agents (Foo and Hameed 2012). From Figure 2(b). It was notice that there is increase in CO_2 Uptake with increase in microwave power and irradiation time. It was explained that, by prolonging activation time, the reaction and the devolatilization rate increases with increase in activation time. Therefore, the adsorption capacity increases due the development of porosity and the rudimentary pore structure. Beyond the optimum point, the adsorption performance then reduces due enlargement of micropores and mesopres (Foo and Hameed, 2012b). Though, the CO_2 adsorption capacity exhibited no much considerable changes with increase in amount of PEEK (Figure 2b). For effective preparation CO_2 sorbent, high CO_2 adsorption capacity is necessary for economically viable process (Shafeeyan et al., 2011). Based on the results obtained from the CCD, the level of significance of the variables were optimized using point predictions in the design expert software. The optimum conditions were 500 W microwave power, 6.89 min irradiation time, and 21.91 % amount of PEEK.

4. Conclusions

Response surface methodology using central composite design was used to optimize the preparation of palm shell-PEEK porous carbon in order to maximize CO_2 adsorption. Effects of three preparation variables were studied: microwave power (x_1), time (x_2) and amount of PEEK (x_3). The optimum preparation conditions of the porous carbon from palm shell-PEEK precursors by impregnation with K_2CO_3 and microwave irradiation are around: microwave power of 500 W, irradiation time of 6.89 min and amount of PEEK 21.91 %. Quadratic response surface model was found to be suitable to predict CO_2 adsorption capacities under the range of variables investigated. Based on the results obtained, microwave power and irradiation time were the most significant factors affecting the CO_2 adsorption with an F-value of 38.96 and 17.74.

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