

# Adsorption of *p*-Cresol by Mesoporous Activated Carbon

## I. Kinetics studies and data modeling

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*The kinetic adsorption of p-cresol from aqueous solution onto mesoporous activated carbon was investigated for 100, 500 and 1000 mg L<sup>-1</sup> initial concentrations, at constant 295 K temperature. The kinetic of the adsorption process was discussed using three kinetic models, i.e., pseudo-first order kinetic model, pseudo-second order kinetic model, and Avrami fractionary order kinetic model. In order to provide a mathematically rigorous method for evaluating the kinetic parameters using the original form of the kinetic models, the nonlinear regression was selected as most viable algorithm. The common statistical tools was employed to check the accuracy of fit measure, namely, sum of the squares of the errors SSE, reduced sum of the squares of the errors Red-SSE, coefficient of determination R<sup>2</sup>, adjusted coefficient of determination Adj R<sup>2</sup> and standard deviation SD.*

**Keywords:** adsorption; kinetic; activated carbon; *p*-cresol; modeling; statistical analysis

Cresols are used in their high concentrations in coal tar for asphalt production, wood impregnation, disinfectants, explosives and insecticides [1]. It is also a metabolic product that is formed by microbiologically decomposition of waste material under anaerobic conditions [2,3]. There are several research works on adsorption of *p*-cresol: Singh et al. [3] on parthenium-based activated carbon, Hadjar et al. [4] on a novel diatomite/carbon composite or Huang [5] on carbonylated hypercrosslinked polymeric adsorbent. In adsorption process, the mechanisms is important for the process control because provide information on the factors affecting the reaction rate, and the interactions that occur between the adsorbent and adsorbate [6]. Over the past few decades, linear regression has been frequently used to determine the best-fitting kinetic model. In recent years, nonlinear method has proven as the better way to fit the kinetic parameters, avoiding the errors of linear method [7-10]. Along with the common coefficient of determination ( $R^2$ ), a large number of error functions (sum of absolute error, average relative error, sum of square error, chi-squares, etc) are employed to check the accuracy of fit [11, 12]. Moreover, most of error functions do not consider the degree of freedom in the models and are not reliable to compare and select the most appropriate kinetic model. The objective of this study is to assess the applicability of the statistical analysis, in the non-linear regression of the experimental kinetic data, generated from *p*-cresol adsorption by mesoporous activated carbon. The overall kinetic of the adsorption process it was analyzed by pseudo-first order, pseudo-second order, and Avrami fractionary order kinetic models. The statistical analysis consider five error functions to check the accuracy of fit measure.

### Experimental part

#### Materials and methods

The *p*-cresol was purchased from Merck Romania SRL and used without further purification. The stock solutions of 100, 500 and 1000 mg L<sup>-1</sup> were prepared by dissolving an appropriate amount of *p*-cresol in ultra-pure water. A

mesoporous granular activated carbon (GAC) was supplied by Ecopur System SRL, Romania.

#### Batch kinetic experiments

Amounts of 2 g activated carbon were contacted with 100 mL solutions of various concentrations (100, 500 and 1000 mg L<sup>-1</sup>). The flasks were sealed airtight with double plastic foil and were stirred at 295 K temperature by magnetic stirring with a constant speed of 200 rpm. The pH was measured with a semi-automatic pH-Burette from Crison Instruments SA. All adsorption data were performed without adding any buffer to control the pH. Samples by 5 mL aliquots were collected at different time intervals and the concentrations of *p*-cresol were measured using Jenway V550 UV/Visible spectrophotometer at maximum wavelength of 278 nm. Each experiment was done in triplicate. The amount of *p*-cresol adsorbed,  $q_t$  (mg·g<sup>-1</sup>), by activated carbon, at time  $t$ , was calculated by following equation:

$$q_t = \frac{(C_0 - C_t) \cdot V}{W} \quad (1)$$

where  $C_0$  is the initial concentration,  $C_t$  is the concentration of *p*-cresol at time  $t$  (mg·L<sup>-1</sup>),  $V$  is the volume of aqueous solution (L), and  $W$  is the mass of adsorbent (g).

#### Kinetic modeling

The experimental data of adsorption kinetics is commonly modeled with the pseudo-first and pseudo-second order kinetic equations. In this work, the overall adsorption rate was also represented with Avrami model. The nonlinear forms of these kinetic models are presented in table 1.

Pseudo-first order model assumes that the adsorption occurs due to a concentration difference between adsorbate surface and solution, and this occurs only when external mass transfer controls the process. The pseudo-second order model is based on the assumption that the rate limiting step may be chemisorption which involves chemicals bonds between the adsorbent and the adsorbate

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**Table 1**  
NONLINEAR KINETIC MODELS

Kinetic models	Equation	Equation no.	Parameters	Ref.
Pseudo-first order	$q_t = q_e [1 - \exp(-k_1 t)]$	(2)	$k_1$ - the pseudo first order rate constant ( $\text{min}^{-1}$ ).	[13-15]
Pseudo-second order	$q_t = \frac{k_2 q_e^2 t}{1 + q_e k_2 t}$	(3)	$k_2$ - the rate constant of pseudo-second-order model ( $\text{mg}^{-1} \text{min}^{-1}$ ).	16-18]
Avrami	$q_t = q_e [1 - \exp(-k_{AV} t)]^n$	(4)	$k_{AV}$ - the Avrami kinetic constant ( $\text{min}^{-1}$ ), $n$ - fractionary order which can be related to the possible changes of the adsorption mechanism	[19-22]

[16-18]. An alternative kinetic equation was proposed by Avrami, based on the thermal decomposition. Few researchers [6, 23] suggests that, in the adsorption process, if the fractionary order  $n$  of Avrami model is higher than one, the rate limiting step is surface reaction and this indicate that the adsorption is more approximated to the pseudo-second kinetic order. Conversely, if  $n$  is less than one, external mass transfer can control the process and then the adsorption is more approximated to the pseudo-first kinetic order.

#### Statistical analysis of the kinetic parameters

In order to provide a mathematically rigorous method for evaluating the kinetic parameters using the original form of the kinetic models, the nonlinear regression has selected as most viable algorithm. Most commonly, algorithms based on the Levenberg-Marquardt methods are used [21, 24, 25]. In present study, the kinetic data for *p*-cresol adsorption onto GAC were analyzed by nonlinear fitting methods. Five different error functions (*SSE*, *Red-SSE*,  $R^2$ , *Adj- R*<sup>2</sup>, and *SD*) were examined to evaluate the

applicability of each model kinetic equation to the experimental data (table 2) using the software Microcal Origin 8.0.

In table 2, the significance of terms it is:  $N$  - the number of experimental data;  $Y_{calc}$  - the regression-predicted value of the dependent variable;  $Y_{exp}$  - the experimental value of dependent variable;  $w_i$  - the weighting coefficient or a measurement of errors;  $DF$  - the degree of freedom of regression model, where  $DF = N - P$ ;  $SS_T$  - the total sum of squares;  $\bar{Y}$  - the mean of the experimental data;  $DF_T$  - the total degree of freedom of regression model, where  $DF_T = N - 1$ .

#### Results and discussions

The *pH* of *p*-cresol solution was found in range of 6.94 to 7.99. The adsorption kinetics of *p*-cresol onto GAC were measured through the curves of adsorption capacity as a function of time. Figures 1a, 1b and 1c shows the *p*-cresol experimental adsorption capacity compared with nonlinear fitted curves by pseudo-first order, pseudo-second

**Table 2**  
ERROR FUNCTIONS USED TO EVALUATE THE APPLICABILITY OF KINETIC MODELS

Error functions	Equation form	Eq. no.
Sum of squares errors ( <i>SSE</i> )	$SSE = \sum_{i=1}^N w_i (Y_{exp} - Y_{calc})^2$	(5)
Reduced sum of the squares of the errors ( <i>Red-SSE</i> )	$Red-SSE = \frac{SSE}{DF}$	(6)
Coefficient of determination ( $R^2$ )	$R^2 = \frac{SS_{reg}}{SS_T} = 1 - \frac{SSE}{SS_T}$	(7)
	$SS_T = SS_{reg} + SSE = \sum_{i=1}^N (Y_{calc} - \bar{Y})^2 + \sum_{i=1}^N (Y_{exp} - Y_{calc})^2$	(8)
Adjusted $R^2$ ( <i>Adj- R</i> <sup>2</sup> )	$Adj R^2 = 1 - \frac{SSE / DF}{SS_T / DF_T}$	(9)
Standard deviation ( <i>SD</i> )	$SD = \sqrt{\frac{1}{DF} \sum_{i=1}^N (Y_{exp} - Y_{calc})^2}$	(10)

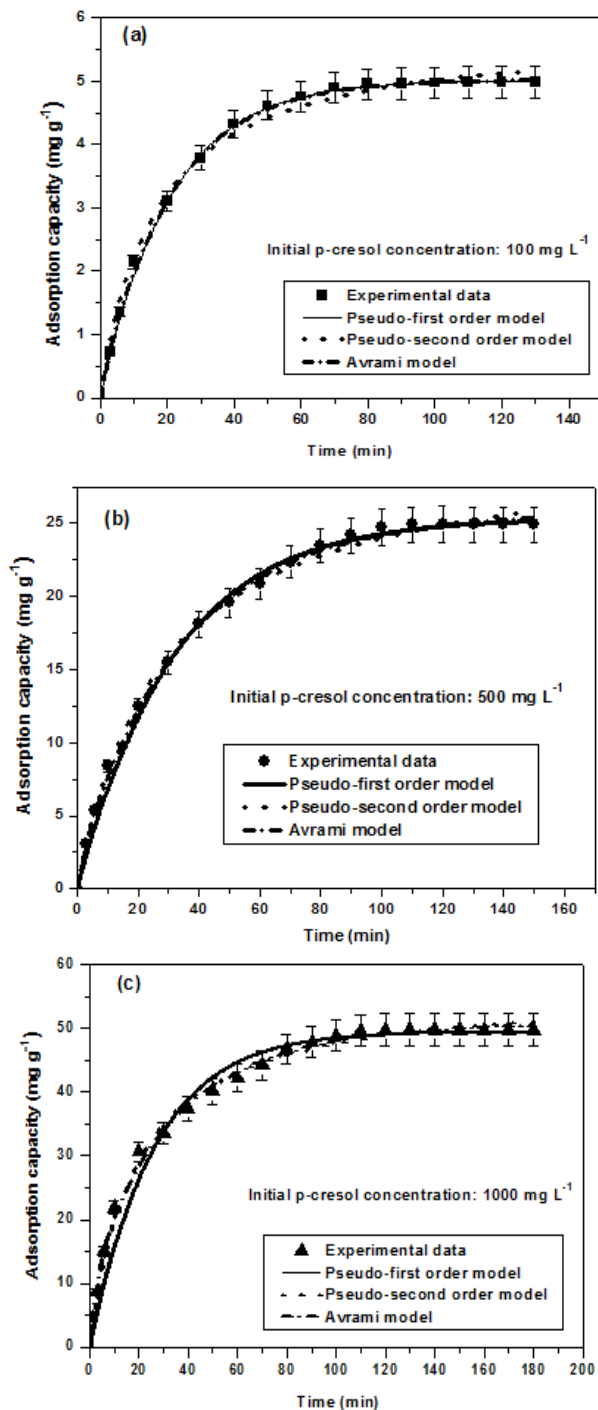


Fig. 1. Effect of contact time on *p*-cresol adsorption on GAC. Experimental conditions: GAC 2 g; stirring speed: 200 rpm; temperature: 295K

order and Avrami kinetics models at 100, 500 and 1000 mg L<sup>-1</sup> *p*-cresol initial concentrations. It has been found that *p*-cresol adsorption capacity  $q_t$  (mg g<sup>-1</sup>) increases with initial concentration and the adsorption rate decreases and then reaches the equilibrium.

Table 3 shows the calculated constants of kinetic models, the  $q_e$  values and the corresponding error function values of the first level statistical analysis. The regression analysis of experimental data shows that the correlation coefficients  $R^2$  and  $Adj R^2$  for the pseudo-second order kinetic model obtained at all the studied *p*-cresol concentrations were relatively high and the error functions  $SSE$ ,  $Red-SSE$  and  $SD$  are relatively low (table 3). However, although the results of statistical analysis were reasonably acceptable in some cases, the calculated  $q_e$  values obtained from the equation did not give reasonable values, that were too high compared with the experimental  $q_e$

**Table 3**  
KINETIC PARAMETERS FOR *p*-CRESOL ADSORPTION BY USING THE NON-LINEAR REGRESSION

	$C_0$ (mg L <sup>-1</sup> )	100	500	1000
	$q_e$ (exp)	4.981	24.903	49.733
Pseudo-first order model	$q_e$ (mg g <sup>-1</sup> )	5.011	25.361	49.425
	$k_1$ (min <sup>-1</sup> )	0.04977	0.03168	0.03922
	$SSE$	0.00693	3.0219	127.864
	$Red-SSE$	$4.95 \times 10^{-4}$	0.18887	6.72966
	$R^2$	0.99731	0.99219	0.95795
	$Adj R^2$	0.99712	0.9917	0.95574
	$SD$	0.02224	0.43459	2.59416
Pseudo-second order model	$q_e$ (mg g <sup>-1</sup> )	5.780	30.466	55.947
	$k_2$ (mg <sup>-1</sup> min <sup>-1</sup> )	0.01133	0.00122	0.00101
	$SSE$	0.05691	4.49465	43.5818
	$Red-SSE$	0.00407	0.28092	2.29378
	$R^2$	0.97791	0.98838	0.98567
	$Adj R^2$	0.97633	0.98766	0.98491
	$SD$	0.06376	0.53001	1.51452
Avrami model	$q_e$ (mg g <sup>-1</sup> )	5.0265	25.755	50.895
	$k_{AV}$ (min <sup>-1</sup> )	0.04663	0.02631	0.02324
	$n$	0.92192	0.81644	0.57474
	$SSE$	0.00546	1.71832	26.5487
	$Red-SSE$	$4.20 \times 10^{-4}$	0.11455	1.47493
	$R^2$	0.99788	0.99556	0.99127
	$Adj R^2$	0.99755	0.99497	0.99030
$SD$	0.02050	0.33846	1.21447	

values. This finding indicated that the adsorption process did not follow the pseudo-second order kinetic model. In the case of pseudo-first order and Avrami models, it was observed that the  $q_e$  values obtained from those equations were closer to the experimental  $q_e$  values. Values of correlation coefficients  $R^2$  and  $Adj R^2$  of both models are generally higher than 0.99, suggesting that those models gives a good fit. Furthermore, when the values of the  $SSE$ ,  $Red-SSE$  and  $SD$  error functions were analyzed (table 3), it was observed that the values of the error functions were generally lower than those of the pseudo-second order kinetic model.

The statistical analyses exclude the pseudo-second order model as a candidate to describe the adsorption kinetic of *p*-cresol on GAC. In the same time, the statistical analysis do not consider the theoretical assumptions of the kinetics model. So, the final decision can not be based on results obtained. The Avrami model has the ability, by its fractional order to approximate the experimental data to the assumption of the pseudo-first order or the pseudo-second order kinetic models. In the case of *p*-cresol adsorption, for all its initial concentrations, the  $n$  values are

lower than 1. This indicates that *p*-cresol adsorption onto GAC is more approximated to the first pseudo-order kinetic. As mentioned above, the most important assumption of the pseudo-first order is that the adsorption occurs due to a concentration gradient between adsorbate surface and solution, and this occurs only when external mass transfer controls the process. By the findings of Avrami kinetic model, it can be conclude that in *p*-cresol adsorption mechanism, the external mass transfer is often the step that controls the process but it is in competition with another process. The adsorption mechanism will be discussed in the next paper.

### Conclusions

The kinetics of *p*-cresol adsorption onto activated carbon was investigated by pseudo-first order, pseudo-second order and Avrami fractionary order models. The non-linear kinetic models were fit to the experimental data and ranked based on the statistical analysis tools. The common statistical tools to check the goodness of fit measure are: sum of the squares of the errors *SSE*, reduced sum of the squares of the errors *Red-SSE*, coefficient of determination  $R^2$ , adjusted coefficient of determination *Adj R<sup>2</sup>* and standard deviation *SD*. The adsorption kinetic data of *p*-cresol onto activated carbon was found to be well represented by the Avrami model. The *n* values of Avrami model (near 1) indicated that the *p*-cresol adsorption onto GAC is better fitted to the first order kinetic.

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