Design of Experiments for the Modeling of the Phenol Adsorption Process

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The adsorption process of phenol onto activated carbon particles in suspension is modeled with a 2^3 full factorial design. In an earlier study, the optimal operating conditions of temperature, agitation, and pH of the phenol solution were determined. In this present study, the values of these parameters remain constant and equal to their optimum values ($T = (30 \pm 1)$ °C, $\omega = 400$ rpm, and pH = 3). The aim of this article is to find a simple and reliable relation between the three independent variables (the particle diameter, the amount of activated carbon, and the initial concentration of phenol) and the response which is the percent removal of phenol that has been described by a polynomial model. Exploration of the model shows that for adsorption from solutions containing a low initial concentration of phenol the use of a low concentration suspension of powder activated carbon or high concentration suspension of granular activated carbon is advised. Whereas for the adsorption from solutions containing a high initial concentration of phenol, the use of a high quantity of carbon of any particle size is suggested. The results obtained show that there are critical values for those parameters which divide the studied intervals into two zones where the evolution of the adsorptive quantity is different.

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1. Introduction

The adsorption of phenol from aqueous solutions onto activated carbons is one of the most studied of all liquid-phase applications of carbon adsorbents. Several methods have been proposed for modeling adsorption, like using the Langmuir or Freundlich equations to analyze the adsorption isotherms or the extended Langmuir model (ELM), which is based on the mechanism of direct competition for adsorption sites and is the simplest and most widely used model.[1] The Dubinin theory can be applied to the adsorption of a number of solutes from aqueous solution.[2] Monte Carlo techniques are applied for microporous solids; this theory is supported by mechanical statistics that allow the linking up of some microscopic parameters with measurable macroscopic phenomena.[3] The Tóth model is used to reduce the error between experimental data and predicted values of equilibrium adsorption.[4]

Today, it is known that the adsorption process on carbon materials basically depends on several variables such as the pH of the solution, the initial concentration of the solution, the surface area, and the particle size of the adsorbent, etc. The best strategy is then to design an experiment so that valid reliable and sound conclusions can be drawn effectively, efficiently, and economically. This method has a lot of advantages such as a significant reduction in the number of costly experiments, knowledge of effluent parameters, the possibility to value the effect interaction between the parameters, better exactness of results, and mathematical modeling of experiments.[5,6] Although the statistical design of experiments is largely employed in the optimization of industrial process, it is rarely applied to the adsorption process.[7]

In this study, a 2^3 factorial design is used to define the percentage removal of phenol onto activated carbon according to the phenol adsorbent dose, the suspension concentration of activated carbon, and its particle size.

Table 1. Characteristics of Activated Carbon Used in the Experiments

parameters	activated carbon PAC	activated carbon GAC
diameter (mm)	0.045	1.000
moisture %	0.98	0.71
specific surface area ($m^2 \cdot g^{-1}$)	978	632

2. Material and Methods

The crystalline form of phenol used was an analytical grade chemical at 99.5 % of purity. All the solutions are prepared with distilled water. Adjustment of pH was realized with a dilute solution of sulfuric acid (H_2SO_4). The activated carbon used was commercial carbon UP07, which was provided by C.O.G.B of Bejaia. The powder activated carbon (PAC) was obtained from the granular activated carbon (GAC) by grinding it down to 0.045 mm. The experimental procedures were carried out at optimal conditions already determined in an anterior study (pH = 3, $T = (30 \pm 1)$ °C, contact time = 3 h, rotation speed of 400 rpm). All the experiments were carried out for 1 L of phenol solution. The concentration of phenol was measured with a Shimadzu ultraviolet UV−visible spectrophotometer. The absorbance measurements of the samples were carried at the wavelength λ_{max}, corresponding to a maximum absorbance of phenol of 270 nm. The physical characteristics of activated carbon used in the experiments are summarized in Table 1; the experimental apparatus used for the adsorption of phenol is represented in Figure 1.

2.1. Elaboration of the Model Equation. 2.1.1. Experimental Methodology. To evaluate the influence and interactions of the initial concentration of phenol [ph], adsorbent dose [Ac], and particle size of adsorbent [dp] on the adsorption of phenol,

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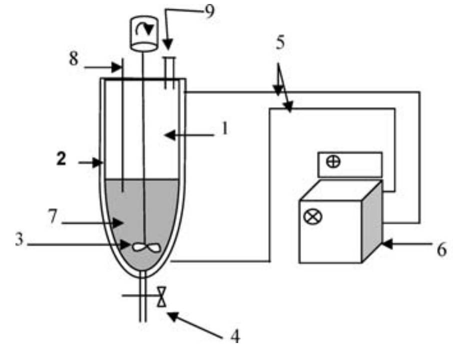


1. Glass column
2. Double jacket for circulating water
3. Steel agitator
4. Extract sluice
5. Heating water pipe
6. Thermostate bath
7. Solution of phenol with suspension of activated carbon
8. Temperature probe
9. Orifice to introduce solution of phenol and activated carbon

Figure 1. Experimental apparatus for the adsorption of phenol.

Table 2. Values of Operating Factors at Two Levels

operating factors	levels −1	levels +1
Z_1: particle size: [dp] (mm)	0.045	1
Z_2: adsorbent dose: [Ac] ($g \cdot L^{-1}$)	1	2
Z_3: initial concentration of phenol: [ph] ($mg \cdot L^{-1}$)	10	100

a 2^3 factorial design was used. The original values of each factor and their corresponding levels are presented in Table 2.

The correlation of independent variables and the response were estimated by a first-order polynomial eq 1 as shown below[8−13]

$$y = b_0 + b_1x_1 + b_2x_2 + b_3x_3 + b_{12}x_1x_2 + b_{13}x_1x_3 + b_{23}x_2x_3 + b_{123}x_1x_2x_3 + \varepsilon \quad (1)$$

where y is the percent removal of phenol and was calculated as follows

$$y\,\% = \frac{C_0 - C_e}{C_0} \cdot 100 \quad (2)$$

where C_0 and C_e are initial and equilibrium liquid-phase concentrations ($mg \cdot L^{-1}$), respectively, b_0, b_1, b_2, b_3, b_{12}, b_{13}, b_{23}, and b_{123} are regression coefficients, called, respectively, constant term (b_0 is the average response in a factorial experiment), linear terms, and linear interaction terms.

$$y = \hat{y} + \varepsilon \quad (3)$$

The term "ε" is the random error component which is approximately normally and independently distributed with mean zero and constant variance. $\hat{y}$ and y are estimated values (estimated by the model) and experimental values, respectively.

In eq 1, x_j are dimensionless variables that correspond to Z_j and are related by the following standardized forms[8]

$$x_j = \frac{Z_j + Z_j^0}{\Delta Z_j} \qquad j = 1, 2, ...\, k \quad (4)$$

$$Z_j^0 = \frac{Z_{j\max} + Z_{j\min}}{2} \quad (5)$$

$$\Delta Z_j = \frac{Z_{j\max} - Z_{j\min}}{2} \quad (6)$$

Here, $Z_{j\max}$ and $Z_{j\min}$ represent the maximum and the minimum level of factor j in the natural unit, respectively.

Table 3 regroups the results for the design matrix for $k = 3$, $N = 8$, and $m = 5$.

2.1.2. Validation of the Model. The coefficients of the fitted equation can be obtained from eq 1 as follows[8−14]

$$b_0 = \frac{1}{N}\sum_{i=1}^{N} y_i \quad (7)$$

$$b_j = \frac{1}{N}\sum_{i=1}^{N} x_{ji}y_i \qquad j = 1, ..., 3 \quad (8)$$

$$b_{jk} = \frac{1}{N}\sum_{i=1}^{N} x_{ji}x_{ki}y_i \qquad \text{for } k = 1,2,3;\ j = 1,2,3; \text{ and } j \neq k \quad (9)$$

$$b_{123} = \frac{1}{N}\sum_{i=1}^{N} x_{1i}x_{2i}x_{3i}y_i \quad (10)$$

From a statistical point of view, three tests are required to evaluate the adequacy of the model, which are[15−17]

1. Cochran test to verify the homogeneity of variances.
2. Student test "t" to determine the significance of coefficients of the regression.
3. The Fisher test for reliability of predicting the regression equation.

Table 3. Design matrix for $k = 3$, $N = 8$, and $m = 5$

run N	1	2	3	4	5	6	7	8
[dp]	0.045	1	0.045	1	0.045	1	0.045	1
[Ac]	1	1	2	2	1	1	2	2
[Ph]	100	100	100	100	10	10	10	10
x_1	−1	1	−1	1	−1	1	−1	1
x_2	−1	−1	1	1	−1	−1	1	1
x_3	1	1	1	1	−1	−1	−1	−1
y_1, %	85.9118	72.2745	97.3514	94.1393	93.2377	77.3319	88.1659	91.5471
y_2, %	86.7571	73.9651	98.3094	93.7449	94.9283	81.4036	87.0389	93.2377
y_3, %	86. 2500	75.8811	98.1967	93.7449	87.6024	85.9118	88.7295	94.3647
y_4, %	87.4334	77.2899	97.5768	92.6178	89.9890	83.9072	85.3483	93.2377
y_5, %	87.6024	74.6413	96.0553	92.8996	89.293	78.4589	86.4754	92.6742
$\bar{y}$, %	86.7909	74.8104	97.4979	93.4293	91.0101	81.4027	87.1516	93.0123

Table 4. Fisher Test for the Adequacy of the Regression Equation

residual variance (S^2_{res})	reproduction variance (S^2_{rep})	estimated F value
3.7717	1.1914	3.1657

Table 5. Values of Relatives Errors

number of test	x_1	x_2	x_3	$\bar{y}$, %	$\hat{y}$, %	relative error, %
1	−1	−1	1	86.7909	86.7969	0.0069
2	1	−1	1	74.8104	74.8164	0.0080
3	−1	1	1	97.4979	97.5038	0.0060
4	1	1	1	93.4293	93.4352	0.0063
5	−1	−1	−1	91.0101	91.0040	0.0067
6	1	−1	−1	81.4027	81.3966	0.0075
7	−1	1	−1	87.1516	87.1456	0.0069
8	1	1	−1	93.0123	93.0062	0.0065

2.1.2.1. Cochran Test. Cochran's test is relatively simple, and its arithmetic is brought down to calculating

$$C = \frac{S^2_{\text{max}}}{\sum_{i=1}^{N} S_i^2} \qquad (11)$$

where S^2_{max} is the largest variance in a sequence of tested variances and $\sum_{i=1}^{N} S_i^2$ is the sum of all variances in the experiment.

For each experiment, the variance is estimated by

$$S_i^2 = \frac{\sum_{u=1}^{m} (y_{iu} - \bar{y}_i)^2}{m - 1} \qquad i = 1, 2, ..., N \qquad (12)$$

where the average response is

$$\bar{y}_i = \frac{\sum_{u=1}^{m} y_{ui}}{m} \qquad (13)$$

$\sum_{u=1}^{m} y_{ui}$ is the sum of all experimental values for the i^{th} observation.

From the literature table of Cochran, we can find $C_\alpha(N, m - 1) = C_{0.05}(8, 4) = 0.4377$, and if $C = 0.4295 < C_{0.05}(8, 4)$, then the variances are homogeneous.

2.1.2.2. Student Test. The Student's test is given for each effect as follows

$$t_j = \frac{|b_j|}{S_b} \qquad (14)$$

where

$$S_b = \sqrt{\frac{S^2_{\text{rep}}}{mN}} \qquad (15)$$

$$S^2_{\text{rep}} = \frac{\sum_{i=1}^{N} S_i^2}{N} \qquad (16)$$

S^2_{rep} is the reproduction variance, and S_b is the root-mean-square deviation.

The tabulated ≪t≫ value, $t_\alpha(N(m - 1)) = t_{0.05}(32)$, is found to be between 1.684 and 1.697. seeing that only t_3 is less than the tabulated value, then the corresponding coefficient b_3 is not significant; therefore, it is excluded from the regression equation.

2.1.2.3. Fisher Test. The F-test is given by

$$F = \frac{S^2_{\text{res}}}{S^2_{\text{rep}}} \qquad (17)$$

where S^2_{res} is the residual variance.

$$S^2_{\text{res}} = \frac{m \sum_{\text{i}=1}^{N} (\bar{y}_i - \hat{y}_i)^2}{N - l} \qquad (18)$$

$\hat{y}_i$ is the calculated value of the response for the ith observation. l is the number of significant coefficient in the regression equation (here it is equal to 7).

Table 4 gives the values of S^2_{rep}, S^2_{res}, and F estimated for the regression equation. The lower degree of freedom ($f_1 = N - l$) and the upper degree of freedom ($f_2 = N(m - 1)$) are 1 and 32, respectively. The tabulated F value for a 5 % level of significance is between 4.08 and 4.17.

Just as $F <$ FTAB, it was concluded that the response variation can be explained by the regression.

The coefficient of determination R^2 was found to be 0.9998.

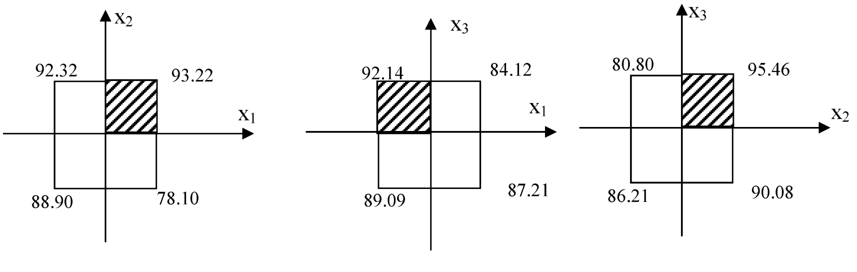
2.1.3. Comparison with Experiments. Finally, the model equation for phenol adsorption on activated carbon is as follows

$$\hat{y} = 88.1381 - 2.4745x_1 + 4.6346x_2 + 2.9225x_1x_2 - 1.5378x_1x_3 + 2.6968x_2x_3 - 0.94451x_1x_2x_3 \qquad (19)$$

Table 5 gives the results of the comparison between average responses given by the experiments and those calculated by the model equation given above, and it shows that the maximum margin between those values for every test is less than 1 %. All those results indicate that the model can adequately represent the data.

3. Results and Discussion

3.1. Interaction Diagrams. Figure 2(a, b, c) gives interaction diagrams for diameter size and the concentration of suspension



a - interaction 1-2 **b -** interaction 1-3 **c-** interaction 2-3

Figure 2. Interaction diagrams.

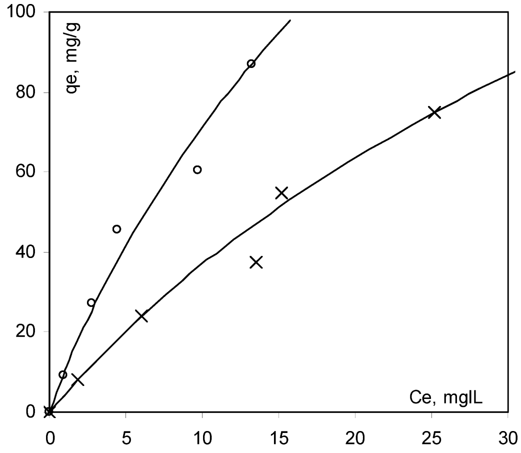


Figure 3. Phenol isotherms on activated carbon (2 g·L^{-1}) for two particle diameter: ○, powder; ×, granular (comparison with the model (full lines)).

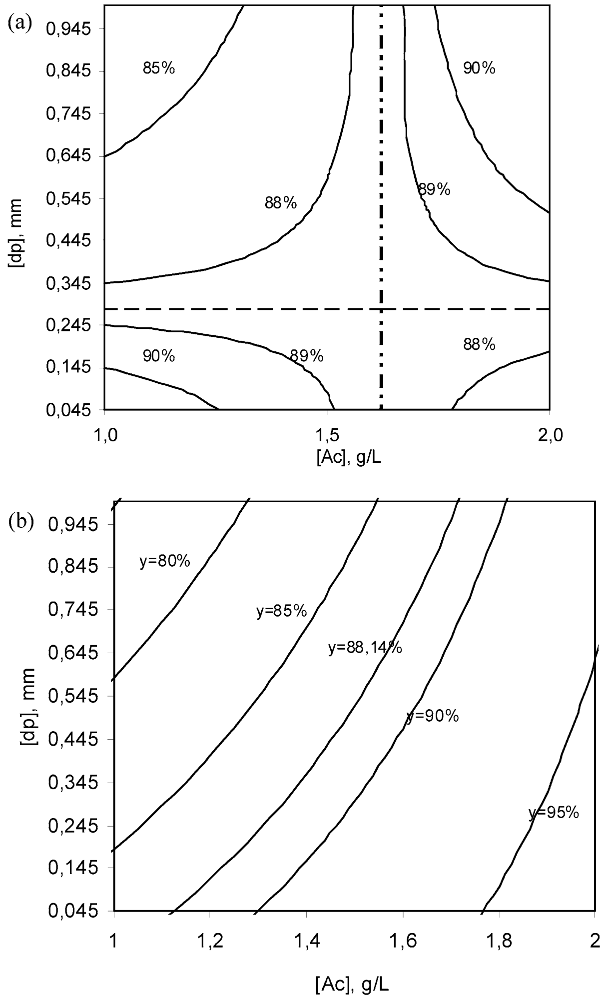


Figure 4. Iso-response plots in the plane particle size versus concentration of suspension. (a) [ph] = 10 mg·L^{-1}; (b) [ph] = 100 mg·L^{-1}.

(1-2), diameter size, and the initial concentration of phenol (1-3), and the concentration of suspension and initial concentration of phenol (2-3), respectively.[18]

It shows that the best results were obtained for:

- High concentration of suspension and big diameter (93.22 %) (Figure 2(a)).
- Small size of particle and high concentration of phenol (92.14 %) (Figure 2(b)).

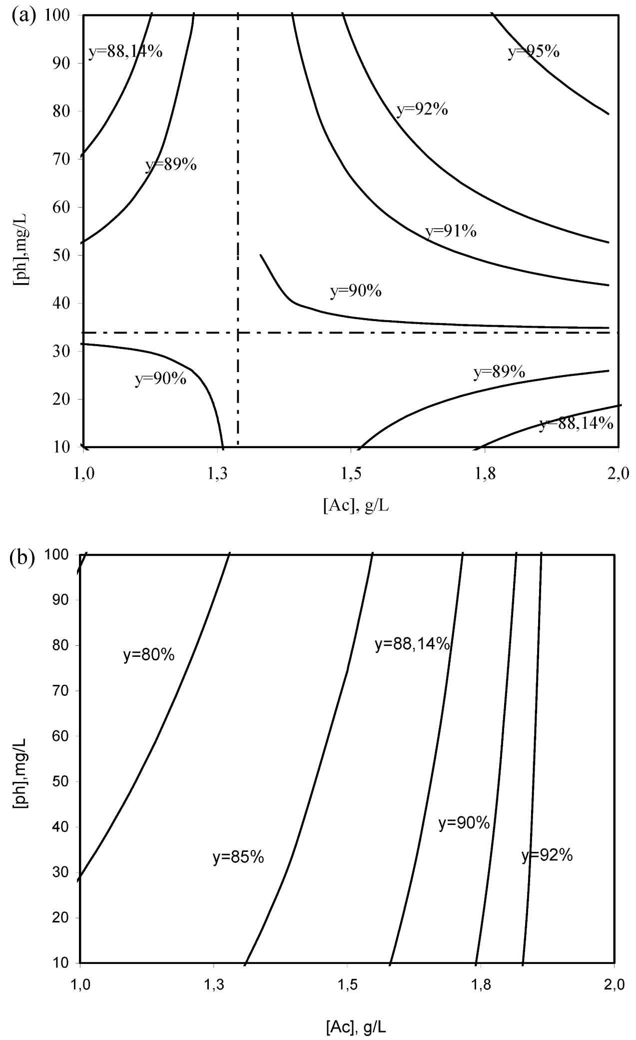


Figure 5. Iso-response plots in the plane initial phenol concentration/ concentration of suspension. (a) [dp] = 1 mm; (b) [dp] = 0.045 mm.

- High concentration of phenol and high concentration of suspension of activated carbon (95.46 %) (Figure 2(c)).

3.2. Adsorption Isotherms. For the adsorption isotherms, Figure 3 shows a similarity between the theoretical results and the experimental data. Consequently, we deduce that the linear model with factor interactions can be used for modeling this equilibrium adsorptive process.

3.3. Response Surface Plots. 3.3.1. Plane of Particle Size/ Concentration of Suspension. In Figure 4(a, b) are shown contour plots of the response for particle size [dp] and concentration of suspension [Ac] for two concentrations of phenol (10 mg·L^{-1} and 100 mg·L^{-1}). Figure 4(a) shows, on the one hand, that the best responses were obtained with large particle sizes and high concentration of suspension or small particle size and low concentration of suspension.

On the other hand, for a diameter higher than 0.2832 mm and a concentration of suspension lower than 1.6211 g·L^{-1}, the ratio of adsorption obtained is small.

However, the relatively higher adsorption with higher concentration of suspension may be attributed to the fact that a higher concentration of suspension yields a higher number of available activated sites

For the initial concentration of phenol equal to 100 mg·L^{-1}, Figure 4(b) shows that the best rate of adsorption is obtained with a high concentration of powder activated carbon because probably the molecules of the solute have an ability to dissociate

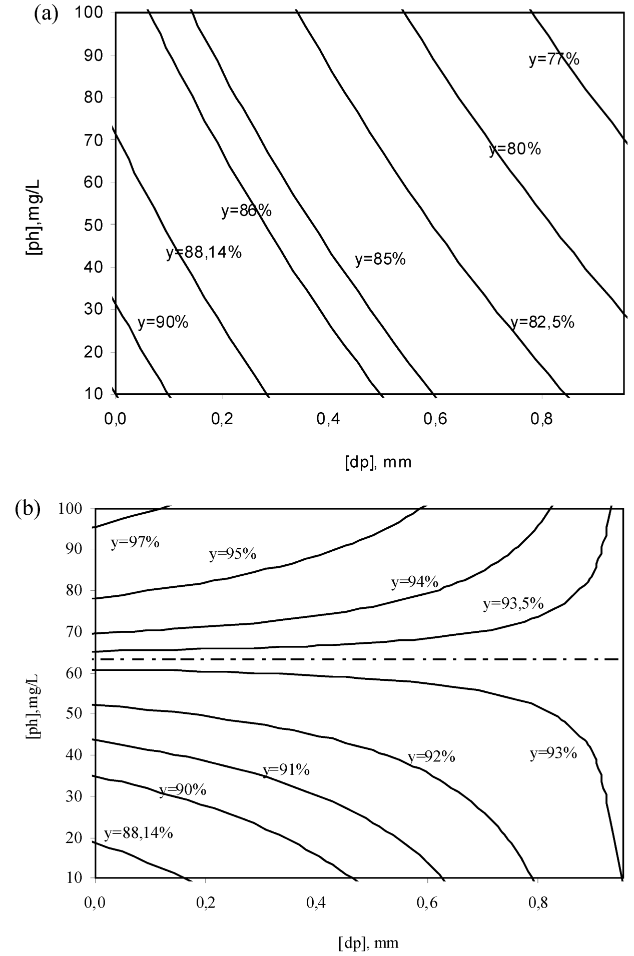


Figure 6. Iso-response plots in the plane initial concentration of phenol/particles size for (a) [Ac] = 1 g·L^{-1}, (b) [Ac] = 2 g·L^{-1}.

aggregates of particles of the powder activated carbon which have been formed in the solution.

3.3.2. Plane of Initial Concentration of Phenol/Concentration of Suspension. Figure 5(a) shows that adsorption is significant when a high quantity of activated carbon and high initial concentration of phenol are used; this result agrees with interaction studies 2-3 (between the suspension concentration and the initial concentration of phenol).

Concerning the powder activated carbon (Figure 5(b)), it is recommended to use a low initial concentration of phenol and a high suspension concentration to have a high amount of adsorption; this is in relation to the specific surface area of activated carbon.

3.3.3. Plane of Initial Concentration of Phenol/Particle Size. The amount of adsorption is better for a powder activated carbon and low initial concentration of phenol (Figure 6(a)). For a suspension concentration equal to 2 g·L^{-1} (Figure 6(b)), the amount of adsorbed phenol is maximized with powder activated carbon and a high initial concentration of phenol. Perhaps, a concentrated solution of phenol stops the formation of aggregates which are produced by a higher concentration of powder activated carbon.

However, for a concentration of phenol lower than a critical value (63.1215 mg·L^{-1}), adsorption is better for a granular activated carbon.

3.4. Evolution of the Amount of Adsorption. 3.4.1. Effect of the Initial Concentration of Phenol. For a low concentration of suspension (1 g·L^{-1}), whatever the particle size is, the amount of adsorption decreases with an increase of the initial concentration of phenol (Figure 7(a)) in accordance with the rule of Lundelius.[19]

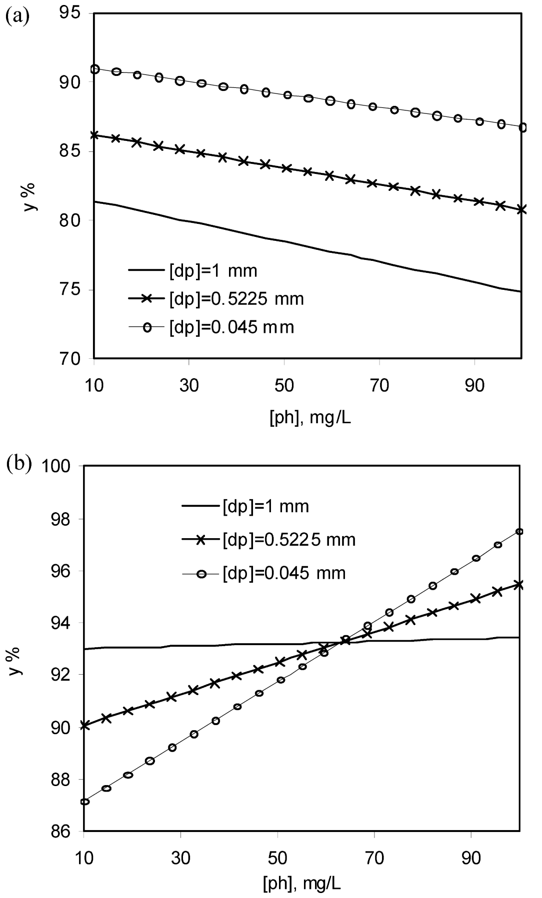


Figure 7. Evolution of the amount of adsorption versus initial concentration of phenol. (a) [Ac] = 1 g·L^{-1}; (b) [Ac] = 2 g·L^{-1}.

However, this evolution is inversed for a high concentration of suspension (2 g·L^{-1}), except for the amount of adsorption related to granular activated carbon which remains constant whatever the initial concentration of phenol is (Figure 7(b)). For a low particle size, the increase of the initial concentration of phenol causes higher mass transfer to the particles which favors the adsorption.

3.4.2. Effect of the Particle Size. When the amount of activated carbon is small ([Ac] = 1 g·L^{-1}), the amount of adsorption decreases when [dp] increases, whatever the initial concentration of phenol is (Figure 8(a)). In this case, the decrease is caused only by the decrease of the total surface area of the adsorbent.

The same result is obtained for [Ac] = 2 g·L^{-1} for the higher initial concentration of phenol (Figure 8(b)). But for a low initial concentration of phenol (10 mg·L^{-1}), the increase of particle size increases the adsorbed quantity: perhaps they remain adsorption sites. For the intermediate initial concentration of phenol, the adsorbed quantity remains constant.

3.4.3. Effect of the Adsorbent Concentration. The effect of the amount of activated carbon used in the removal of the phenol from solution was studied for two initial concentrations of phenol [(100 and 10) mg·L^{-1}] (Figure 9).

Figure 9(a) reveals that the percentage of the phenol removed increases with an increase of adsorbent dosage whatever the [dp] may be. An increase in the adsorption with the adsorbent dosage can be attributed to a greater surface area and the availability of more adsorption sites.[20]

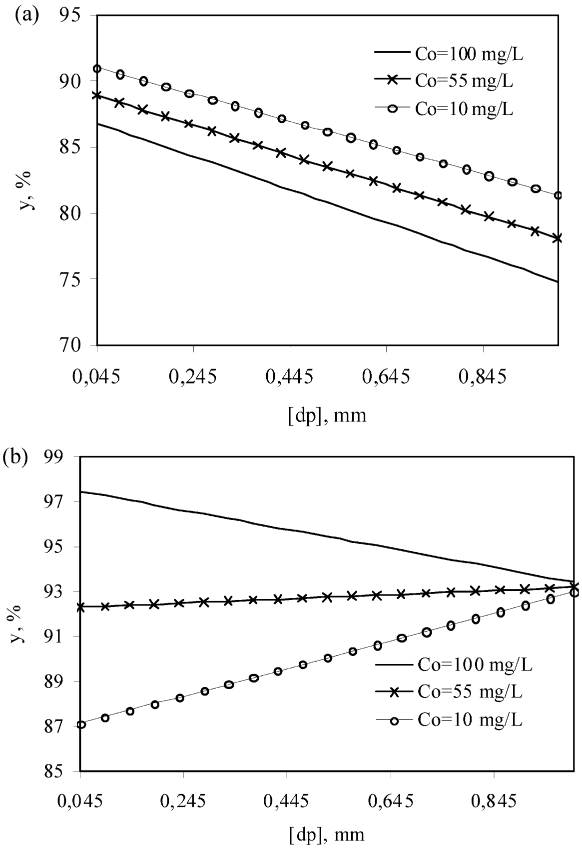


Figure 8. Evolution of the amount of adsorption versus particle diameter. (a) [Ac] = 1 g·L^{-1}; (b) [Ac] = 2 g·L^{-1}.

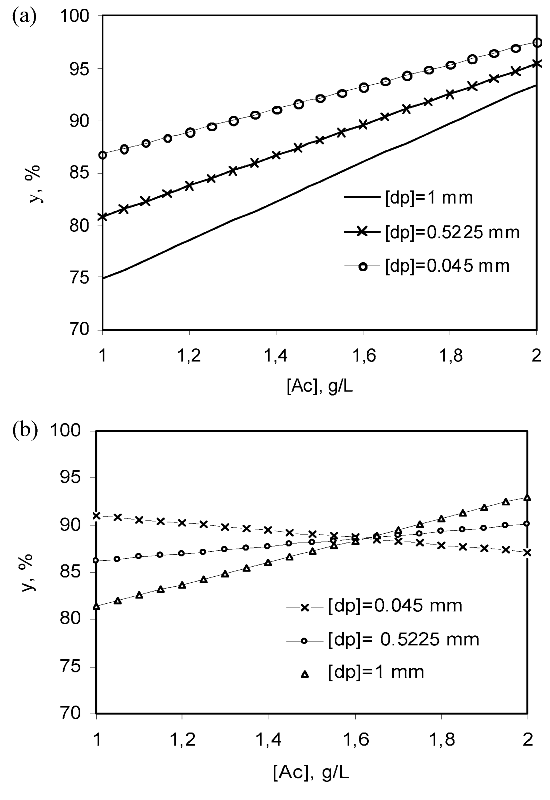


Figure 9. Evolution of the amount of adsorption versus concentration of activated carbon. (a) [ph] = 100 mg·L^{-1}; (b) [ph] = 10 mg·L^{-1}.

However, for a low concentration of phenol (Figure 9(b)), another phenomenon appears for powder activated carbon ([dp] = 0.045 mm): when the concentration of suspension of powder activated carbon is high, particles of carbon have a tendency to agglomerate to reduce the total area of adsorption, and therefore the amount of phenol adsorbed decreases. The results also clearly indicate that the removal efficiency increases up to the optimum dosage beyond which the removal efficiency is negligible.[21] Thus, there are a critical concentration of suspension and a critical concentration of phenol.

4. Conclusion

Through this study, we conclude that the phenol adsorption phenomenon can be modeled with a mathematical model of first order with interaction. The achieved results show that for adsorption from solutions containing a low initial concentration of phenol the use of a low concentration of suspension of powder activated carbon or a high concentration of suspension of granular activated carbon is suggested. As for the adsorption from solutions containing a high initial concentration of phenol, we suggest the use of a high quantity of carbon whatever the particle size. The results obtained clearly show that there are critical values for those parameters which divide the studied intervals into two zones, where evolution of the amount of adsorption is made in different manners. If powder activated carbon ([dp] = 0.045 mm) is used, the critical values are 33.8415 mg·L^{-1} for the initial concentration of phenol and 1.3488 g·L^{-1} for the concentration of suspension. However, if an initial concentration of phenol equal to 10 mg·L^{-1} is used, the critical values are 0.2832 mm for the diameter of the particle of activated carbon and 1.6211 g·L^{-1} for the concentration of suspension. In case we use a concentration of suspension equal to 2 g·L^{-1}, the critical initial concentration of phenol is 63.1215 mg·L^{-1}.

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