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ADSORPTION EQUILIBRIUM OF 2,4 DICHLOROPHENOL FROM WASTE WATERS ONTO ACTIVATED CARBON

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ABSTRACT

The batch adsorption of 2,4-dichlorophenol from aqueous solution onto mesoporous activated carbon was investigated for a range of initial concentrations of 50 to 1000 mg/ L, at constant temperature of 293 K. The experimental adsorption isotherms were analyzed with two and three parameters models (i.e., Freundlich, Langmuir, Langmuir-Freundlich, and Brouers-Sotolongo models). The non-linear fitting method was employed for estimating the isotherm parameters. The standard statistical tools were used to check the accuracy of the fit measure, namely: the coefficient of determination R^2, the adjusted coefficient of determination *Adj-* R^2, the residual sum of squares *RSS (*or chi-square function χ^2), and reduced chi-square *Red-* χ^2. The analysis of all the isotherms found that the Brouers-Sotolongo model shows higher correlation coefficients of R^2 and *Adj-*R^2 values and lower values of *RSS* and *Red-*χ^2. Also, the Brouers-Sotolongo model shows a maximum adsorption capacity q_m of 50.46 mg/g, which is very close to the experimental data (48.123 mg/g) value. The adsorption process was mainly physical adsorption on heterogeneous surfaces. The heterogeneous surface of activated carbon was confirmed by FT-IR analysis, the Boehm method, and pH_{PZC}, as presented in our previous studies. The interactions between 2,4 DCP and GAC are mostly a type of dispersion effect between the π electrons in the aromatic ring of the phenolic compound and the π electrons in the structure of the GAC adsorbent. Also, electrostatic attractions may occur between the π electrons in the aromatic rings of 2,4 DCP and the positive surface of the GAC.

Keywords: adsorption, 2,4 dichorophenol, isotherms, non-linear regression

INTRODUCTION

Phenol derivatives, such as chlorophenols and nitrophenols, are emitted into the environment from many industries, such as petroleum and petrochemical industries, industrial resins and adhesives, paper and pulp industries, medical and health products, paint industries, and other manufacturers [1]. Specifically, 2,4-dichlorophenol is an intermediate for manufacturing pesticides, biocides, fungicides, herbicides, dyes, and pharmaceuticals [2]. These compounds are considered environmental contaminants. Their presence in drinking water leads to unpleasant odours and tastes, even at low concentrations. The harmful effects of phenolic compounds on humans, marine organisms and the environment are considered by the US Environmental Protection Agency (EPA) [3] and the National Institute of Public Health and the Environment of the Netherlands [4] which classify them as pollutants priorities. For these reasons, their

removal from wastewater is a major challenge facing the world today. Several biological, chemical, and physical processes can be used to remove phenolic compounds from wastewater [5, 6]. Adsorption is one of the most effective and proven technologies for removing phenolic compounds from wastewater. As a widely used adsorbent, activated carbon always exhibits high performance for phenolic compounds removal. It is also well-known that it has a high surface area and high adsorption capacity, sufficient mechanical strength, and low cost of regeneration [7].

The aim of this study is to investigate the adsorption mechanism of 2,4-dichlorophenol onto granular activated carbon (GAC). The adsorption equilibria were evaluated from two adsorption isotherm models with two parameters (i.e., Langmuir and Freundlich models) and two adsorption isotherm models with three-parameters (i.e., Sips model and Brouers-Sotolongo model). The experimental adsorption equilibrium data for 2,4-dichlorophenol adsorption onto GAC were analyzed by non-linear curve fitting analysis using Origin software. Lastly, some possible adsorption mechanisms were proposed according to the heterogeneous surface of GAC.

MATERIALS AND METHODS

Adsorbate and adsorbent

The main materials used in this work were the granular activated carbon (GAC) and 2,4-dichlorophenol (2,4 DCP).

The 2,4 DCP, as an analytical reagent grade, was supplied by Sigma-Aldrich and used as the adsorbate in this study without further purification. Deionized water was used to prepare all the solutions.

The activated carbon used as adsorbent in our experiments for removing 2,4 DCP from aqueous solutions is a commercial activated carbon, granular, with the physical characteristics shown in our previous study [8] and obtained from Ecopur System SRL, Romania. The surface of the GAC was chemically characterized according to the Boehm titration procedure, by the point of zero charge (pH_{PZC}) of GAC with the help of a pH/Ion/Conductivity/DO meter CyberScan PCD 6500 and by Fourier Transform Infrared (FT-IR) spectra. All detailed procedures and results were reported in our previous studies [9, 10]. Although acidic functional groups predominate, the surface of granular activated carbon also contains basic functional groups. Even if, quantitatively, the acidic groups are three times more than the basic ones, the latter seems to be stronger due to the point of zero charge, which is slightly basic (pH_{PZC} =7.8). It can be assumed that the basic groups can be, particularly, tertiary amines, identified by FT-IR spectroscopy.

Batch adsorption isotherms modeling

The adsorption isotherm models are valuable tools for describing the interaction between the adsorbate and adsorbent. This work used four adsorption isotherm models, i.e., the Langmuir and Freundlich as models with two parameters and the Sips and Brouers-Sotolongo as models with three parameters, to fit the adsorption experimental results.

According to Langmuir isotherm, monolayer adsorption occurs on an adsorbent with a homogeneous structure, and all sites where adsorption occurs are identical and energetically equivalent [13]. Freundlich isotherm describes multilayer adsorption, with

a non-uniform distribution of heats of adsorption and affinity for heterogeneous surfaces [12]. The Sips isotherm is a combination of the Langmuir and Freundlich isotherms, which are applicable for estimating heterogeneous adsorption systems. The Brouers–Sotolongo (B-S) isotherm is in the form of a warped exponential function. The B-S is a novel isotherm model and is based on some assumptions of the Langmuir isotherm. One of this model's useful findings is that the adsorption energy distribution obeys the Levy stable distribution theory [11, 16]. The heterogeneity of the adsorbent surface energy can be measured using the exponent n_S, at the given temperature.

The isotherm equations and their parameters are shown in Table 1.

Table 1. *Adsorption isotherms and their parameters. C_e: equilibrium liquid phase concentration (mg/L); q_e: equilibrium adsorption capacity (mg/g)*

Isotherms	**Expression**	**Parameters**	**Ref.**
Langmuir	$q_e = \frac{q_{mL} b_L C_e}{1 + b_L C_e}$	q_{mL}: the maximum adsorption capacity (mg/g) b_L : constant of Langmuir (L/mg)	[13]
Freundlich	$q_e = K_F C_e^{1/n_F}$	K_F : Freundlich constant related of the relative adsorption capacity of the adsorbent (mg/g)(L/mg)$^{1/n_F}$) n_F = constant of Freundlich	[12]
Sips	$q_e = \frac{K_S q_{mS} C_e^{\frac{1}{n_S}}}{1 + K_S C_e^{\frac{1}{n_S}}}$	q_{mS} : maximum adsorption capacity of the monolayer (mg/g) K_S : Sips isotherm constant (L/g) $1/n_S$: exponent of Sips model	[14, 15]
Brouers–Sotolongo	$q_e = q_{mBS}\left(-K_{BS} C_e^{nBS}\right)$	q_{mBS} : maximum adsorption capacity of the monolayer (mg/g) K_{BS} : constant of B-S model (L/mg); n_{BS} : exponent of B-S model	[16]

Statistical analysis of the isotherms parameters

In our study, the equilibria data for the 2,4 DCP adsorption onto GAC were analyzed by fitting methods using the Microcal Origin 8.0 software. Were employed four different error functions (i.e.: R^2, *Adj-* R^2, *RSS* or χ^2 and *Red-* χ^2) to fit each parameter of the isotherm models. The error functions used to evaluate the accuracy of the isotherm models are shown in next [17]:

- Coefficient of determination (R^2):

$$R^2 = 1 - \frac{\sum_{i=1}^{N}\left(q_{e,meas,i} - q_{e,calc,i}\right)^2}{\sum_{i=1}^{N}\left(q_{e,meas,i} - \bar{q}_{e,calc}\right)^2} \quad (1)$$

where:

$q_{e,meas,i}$ and $q_{e,calc,i}$ are the experimental values, respectively, the model values (calculated);

N indicates the number of the adsorption experimental data;

$\bar{q}_{e,calc}$ are the average values of the calculated adsorption capacities;

The coefficient of determination indicates the quality of the fit over the entire range of the independent variables. R^2 has a value between 0 and 1. This indicator does not consider a model's degree of freedom.

- Adjusted coefficient of determination (*Adj- R^2*) is a correction for the drawback of Eq. (1). Is calculated as follows:

$$Adj - R^2 = 1 - \frac{\sum_{i=1}^{N}\left(q_{e,meas,i} - q_{e,calc,i}\right)^2 /(N-P)}{\sum_{i=1}^{N}\left(q_{e,meas,i} - \bar{q}_{e,calc}\right)^2 / N} \quad (2)$$

where: *N-P* is the degree of freedom.

- Chi-square function (χ^2) or residual sum of squares (*RSS)*:

$$RSS = w_i \sum_{i=1}^{N}(q_{e,meas,i} - q_{e,calc,i})^{\ 2} \quad (3)$$

where: w_i is the weighting factor for each experimental point. In this study, direct weighting is used [17].

- In the nonlinear method, one of the objective functions is the minimization of the Chi-square function χ^2. Smaller values of the function indicate a good quality of the regression. A modified χ^2 expression includes the degree of freedom of the considered model.

$$\mathrm{Re}d\ \chi^2 = \frac{RSS}{N-P} \quad (4)$$

EXPERIMENTAL

Batch adsorption experimental studies

Batch adsorption experiments were carried out at 20 ± 0.1°C. The experiments were performed using 2±0.005 g of activated carbon with 100 mL of aqueous 2,4 DCP solutions in 250 mL glass bottles at various initial concentrations (50–1000 mg/ L). The glass bottles were shaken at a presettled temperature under 200 rpm. Equilibrium studies were carried out for 2.5 hours to ensure equilibrium. All adsorption data were determined without adding any buffer to control the *pH*. All samples were filtered before analysis. The concentrations of the 2,4 DCP samples were determined using a UV–vis spectrophotometer (Jenway V550 UV/Vis) at a maximum wavelength of 280 nm after reaching the equilibrium. The concentrations were determined by comparing absorbance

with a previously obtained calibration curve. All experiments were triplicated, and the mean values were reported.

The 2,4 DCP uptake at equilibrium, q_e (mg/g), was calculated by Eq. (5).

$$q_e = \frac{C_i V_i - C_e V_e}{m} \tag{5}$$

where:

- C_i and C_e (mg/ L) are the initial and equilibrium liquid concentrations of the 2,4 DCP, respectively;
- V_i and V_e (L) is the volume of the initial aqueous solution of the 2,4 DCP and after adsorption;
- m (g) is the mass of GAC adsorbent used.

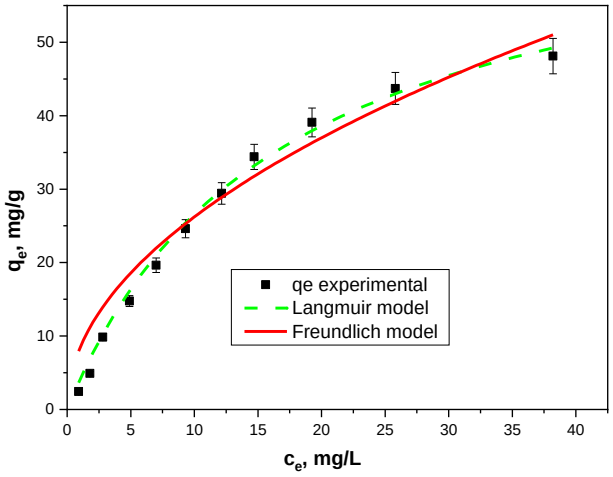
RESULTS AND DISCUSSIONS

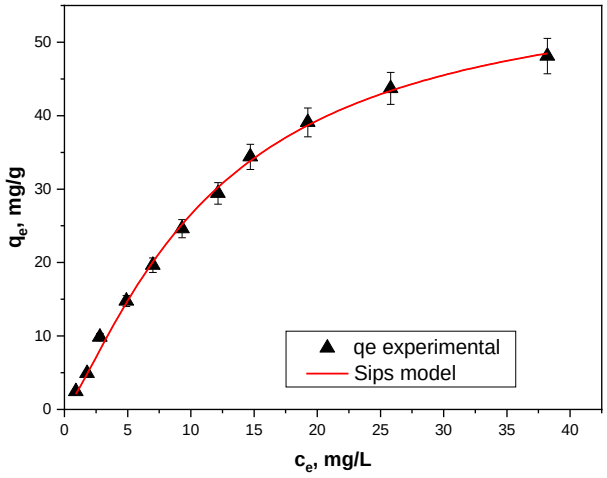
The experimental adsorption isotherm of 2,4 DCP from aqueous solutions onto GAC is presented in Table 2.

Table 2. *Adsorption data for 2,4 DCP onto GAC at 20°C and 200 rpm*

Initial concentrations of 2,4 DCP (mg/L)	**Volume after adsorption (L)**	**Equilibrium concentrations of 2,4 DCP (mg/L)**	**Mass of GAC (g)**	$q_e = \frac{x}{m}$ **(mg/g)**
1000	96	38.2	2.0018	48.123
900	96	25.8	2.0023	43.711
800	95	19.3	2.0001	39.084
700	95	14.7	1.9950	34.388
600	94	12.1	2.0009	29.416
500	95	9.3	1.9956	24.612
400	94	7.0	2.0028	19.643
300	95	4.9	2.0015	14.756
200	96	2.8	2.0038	9.847
100	94	1.8	2.0034	4.907
50	95	0.9	2.0046	2.452

The experimental adsorption data has been modeled using Langmuir, Freundlich, Sips, and Brouers-Sotolongo isotherms. A comparison between the experimental and calculated q_e values is shown in Fig. 1.





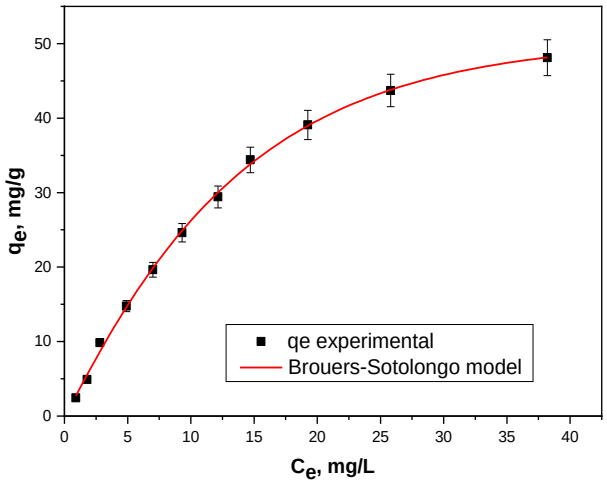


Fig. 1. *Comparison of measured and calculated qe values for two-parameter isotherms (Freundlich and Langmuir models) and for three-parameters isotherms (Sips and Brouers-Sotolongo models).*

The parameters of the selected adsorption isotherm models and the values of error-functions are shown in Table 3.

Table 3. *Fitting parameters of the adsorption isotherms and the statistical comparison values for two-parameter and three-parameter models*

Two-parameters models		***Three-parameters models***	
Langmuir		**Sips**	
q_m (mg /g)	70.55	q_{mS} (mg/g)	59.015
b_L (L/mg)	0.06042	K_S (L/g)	0.08553
-	-	n_S	1.28944
R^2	0.99264	R^2	0.99767
Adj- R^2	0.99183	*Adj-* R^2	0.99709
RSS (χ^2)	14.4767	*RSS* (χ^2)	4.57712
Red- χ^2	1.60852	*Red-* χ^2	0.57214
Freundlich		**Brouers-Sotolongo**	
K_F (mg/g)(L/mg)$^{1/n}$	8.35649	q_m (mg/g)	50.46
n_F	2.01385	K_{BS} (L/mg)	0.06226
-	-	n_{BS}	1.07127
R^2	0.95352	R^2	0.99892
Adj- R^2	0.94835	*Adj-* R^2	0.99865
RSS (χ^2)	91.46761	*RSS* (χ^2)	2.13118
Red- χ^2	10.16307	*Red-* χ^2	0.2664

The results from Table 3 show promising results of the regression of the experimental data with the Langmuir model, which would make us believe that the adsorption is in a monolayer on the heterogeneous surface of the adsorbents. At the same time, if we were to refer to the theoretical assumptions of the Langmuir model, we could believe that in GAC adsorbent, all sites are energetically equivalent. Also, the b_L parameter is a constant related to the affinity of the binding sites and is an indicator of the favourability of adsorption.

Table 3 shows the value of the n_F parameter of the Freundlich model. The parameter n_F, known as the heterogeneity factor, can indicate the adsorption phenomenon's favourability. A higher value of n_F indicates easier adsorption: if the adsorption is linear ($n_F = 1$), if a chemical process takes place ($n_F < 1$), or if a physical process is favorable ($n_F > 1$). The n_F parameter value of GAC is slightly above 2, which indicates that the adsorbent is favorable for 2,4 DCP adsorption and that the adsorption is predominantly physical. Comparing the error function values used in non-linear regression of the two-parameters models, it can be seen that the Langmuir model shows higher correlation

coefficients R^2 and $Adj\text{-}R^2$ values and lower values of *RSS* and Red- χ^2 than those of the Freundlich model, and these findings suggest that Langmuir model fit better the experimental data than Freundlich model. The two-parameter models have brought important information about the adsorption of 2,4 DCF on GAC, but the adsorption mechanism still needs to be fully elucidated.

The Sips equation has a flexible isotherm expression that can simulate both the behaviors of the Langmuir and Freundlich isotherms, more precisely: at low concentrations of the adsorbate, the model reduces to the Freundlich isotherm, while at high concentrations, it predicts a monolayer adsorption capacity, characteristic of the Langmuir isotherm. The parameter n is a measure of the system heterogeneity. Therefore, the Sips model is reduced to the Langmuir model when $n = 1$. The value $n > 1$ reflects a more heterogeneous system. As can be observed from Table 3, for 2,4 DCP adsorption on GAC, the n = 1.28944, which indicates a heterogeneous surface of the GAC.

The Brouers-Sotolongo model shows a maximum adsorption capacity q_m of 50.46 mg/g that is close to that of the Sips isotherm (59.015 mg/g) and very close to the experimental data (48.123 mg/g) value. Also, the affinity parameters of the Brouers-Sotolongo model (i.e., K_{BS}= 0.06226 L/mg) show a similar value to those of the Langmuir model (i.e., b_L = 0.06042 L/mg).

The analysis of all the isotherms found that the Brouers-Sotolongo and Sips models show higher correlation coefficients R^2 and $Adj\text{-}R^2$ values and lower values of *RSS* and $Red\text{-}\chi^2$. Finally, it can be concluded that the three-parameter models best fit the experimental equilibrium data of 2,4 DCP onto GAC. So, the adsorption mechanism is complex. Taking into account the heterogenous surface of GAC, possible physical adsorption mechanisms onto multilayer sites will be explained in the following.

The width, depth, and thickness of 2,4 DCP are equal to 0.6478, 0.5547, and 0.4817 nm, respectively, and these dimensions allow easy access within the porous structure of GAC, which has the average pores diameter at 2.96 nm. Supplementary, the presence of surface functional groups plays an essential role in the removal mechanism. The heterogeneous surface of activated carbon was confirmed by FT-IR analysis, Boehm method, and pH_{PZC}, as presented in our previous studies [8, 9, 10]. As demonstrated by the FT-IR analysis and Boehm method, the main adsorption groups to be considered for the GAC are the basic groups, which could be mainly the tertiary amines, carboxylic acid, phenols, lactonic groups, and the aromatic structure of the graphene layer.

The adsorption processes were carried out at pH =7, which is lower than the value of pKa (i.e., 7.8), and the 2,4 DCP will be found in non-ionized form. The interactions between 2,4 DCP and GAC are primarily a type of dispersion effect between the π electrons in the aromatic ring of the phenolic compound and the π electrons in the structure of the GAC adsorbent. On the other hand, the pH at which the processes occurred is below the pH_{PZC} value of GAC, and the surface of the adsorbent is positively charged. Therefore, electrostatic attractions may occur between the π electrons in the aromatic rings of 2,4 DCP and the positive surface of the GAC.

CONCLUSIONS

Granular activated carbon (GAC) has proved to be an effective adsorbent for removing 2,4 DCP from aqueous solutions. For equilibrium studies, the experimental adsorption data isotherms were evaluated using Langmuir and Freundlich as two-parameter models and Sips and Brouers-Sotolongo as three-parameter models. The model's parameters were fitted by non-linear regression with the help of Microcal Origin 8.0 software. Four different error functions (i.e., R^2, *Adj-* R^2, *RSS* or $\chi 2$, and *Red-* $\chi 2$) were employed to evaluate the accuracy of the regression. Concerning the best values of the errors function, it followed the order Brouers–Sotolongo > Sips > Langmuir > Freundlich. Also, the Brouers-Sotolongo model shows a maximum adsorption capacity qm of 50.46 mg/g, which is very close to the experimental data (48.123 mg/g) value.

Substituent groups on the GAC surface strongly influenced the possible adsorption mechanism of 2,4 DCP onto GAC. In order to confirm the heterogeneous surface of activated carbon was employed FT-IR analysis, Boehm method, and $pH_{PZC,}$ method, as was presented in our previous studies [8, 9, 10]. The electrostatic and dispersion interaction mechanisms show the different interactions that may occur in the 2,4 DCP-GAC adsorption system.

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