Modeling of adsorption isotherms of phenol and chlorophenols onto granular activated carbon
Part I. Two-parameter models and equations allowing determination of thermodynamic parameters

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Abstract
The adsorption equilibrium isotherms of five phenolic compounds from aqueous solutions onto granular activated carbon (GAC) were studied and modeled. Phenol (Ph), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP) were chosen for the adsorption tests. To predict the adsorption isotherms and to determine the characteristic parameters for process design, seven isotherm models: Langmuir (five linear forms), Freundlich, Elovich, Temkin, Fowler–Guggenheim, Kiselev, and Hill–de Boer models were applied to experimental data. The results reveal that the adsorption isotherm models fitted the data in the order: Fowler–Guggenheim > Hill–de Boer > Temkin > Freundlich > Kiselev > Langmuir isotherms. Adsorption isotherms modeling shows that the interaction of phenolic compounds with activated carbon surface is localized monolayer adsorption, that is adsorbed molecules are adsorbed at definite, localized sites. Each site can accommodate only one molecule. The interaction among adsorbed molecules is repulsive and there is no association between them, adsorption is carried out on energetically different sites and is an exothermic process. Uptake of phenols increases in the order Ph < 2-CP < 4-CP < DCP < TCP, which correlates well with respective increase in molecular weight, cross-sectional area, and hydrophobicity and decrease in solubility and pK_a. Additionally, for the four tested chlorophenols, it seems that the magnitude of adsorption is directly proportional to their degree of chlorination.

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1. Introduction
Phenolic compounds including substituted phenols which are generated by petroleum and petrochemical, coal conversion, phenol producing industries, and other chemical processes, are common contaminants in wastewater. Phenols are widely used for the commercial production of a wide variety of resins including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins and adhesives, and polyamide for various applications. Phenols as a class of organics are similar in structure to the more common herbicides and insecticides in that they are resistant to biodegradation. Their presence in water supplies is noticed as bad taste and odor. In the presence of chlorine in drinking water, phenols form chlorophenols, which have a medicinal taste, which is quite pronounced and objectionable.

Phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential to harm human health. Because of their toxicity, the US Environmental Protection Agency (EPA) and the European Union have designated phenols as priority pollutants [1,2].

Increasing concern for public health and environmental quality has led to the establishment of rigid limits on the acceptable environmental levels of specific pollutants. Thus, the removal or destruction of phenols from process or waste streams becomes a major environmental problem.
Adsorption is well-established technique for the removal of low concentrations of organic pollutants from large volumes of potable water, process effluents, wastewater, and aqueous solutions. Adsorption onto activated carbon is often considered the most economical and efficient process for the removal of potable water, process effluents, wastewater, and aqueous solutions. Adsorption onto activated carbon is often considered for decades.[3–12]. The adsorption of phenol and substituted phenols from aqueous solutions onto granular activated carbon (GAC). The representation of the adsorption isotherms onto activated carbon can be based on models with two, three, even with more parameters [13–17]. The goal of this first part is to apprehend the interactions phenols–GAC through the validity of isotherm models. In the case of the models with two-parameter, the Langmuir and Freundlich equations are largely used. Additionally, other models such as the Temkin, Fowler–Guggenheim, Kiselev, and Hill–de Boer equations exist and allow the determination of the energy of adsorption, interaction energy between adsorbed molecules, and complex formation between adsorbate.

2. Materials and methods

2.1. Adsorbent

The GAC used in this study was purchased from Pro-labo. Prior to use, the carbon was pretreated by boiling in ultra-high quality (UHQ) water for 1 h and washed repeatedly with UHQ water until the electric conductivity and the UV absorbance were equal to zero, and the pH remains constant. Finally, the washed activated carbon was dried in an oven at 110 °C to constant weight and stored in a desiccator until use. The BET (Brunauer–Emmett–Teller) surface area of the carbon (929 m² g⁻¹) was obtained from N₂ adsorption isotherms at 77 K. The GAC has an average granulometry of 3 mm, a bulk density of 0.45 g cm⁻³, a micropore volume of 0.38 cm³ g⁻¹, an average pore diameter of 16 Å, an ash content of 5.6%, and a pH of zero point charge (pHₚzC) of 4.1. The majority of functional groups on GAC surface were found to be acidic (see the second part).

2.2. Adsorbates

Five organic molecules were selected for the study of adsorption onto granular activated carbon: phenol (Ph), 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP). The adsorbates, purchased from Sigma with purity greater than 99.5%, and UHQ water (Milli-Q 18.2 MΩ) were used to prepare the aqueous solutions for the adsorption tests. The principal characteristics of the studied adsorbates are regrouped in Table 1. The phenolic compounds are weak acids, whose acidity increases with the number of chlorine atoms. The octanol/water partition coefficient (log Kow) of chlorophenols, which can be used as a measure of solvent hydrophobicity, increases with the degree of chlorination.

2.3. Equilibrium isotherms

For the determination of adsorption isotherms, accurately weighted amount of GAC (0.05–1 g L⁻¹) were continuously

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**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>b</td>
<td>Langmuir constant related to the free energy of adsorption (L mg⁻¹)</td>
</tr>
<tr>
<td>Cₑ</td>
<td>the equilibrium concentration of the solute in the bulk solution (m g L⁻¹)</td>
</tr>
<tr>
<td>C₀</td>
<td>the initial concentration of the solute in the bulk solution (mg L⁻¹)</td>
</tr>
<tr>
<td>GAC</td>
<td>granular activated carbon</td>
</tr>
<tr>
<td>kₙ</td>
<td>the equilibrium constant of the formation of complex between adsorbed molecules</td>
</tr>
<tr>
<td>k₁</td>
<td>Kiselev equilibrium constant (L mg⁻¹)</td>
</tr>
<tr>
<td>Kₑ</td>
<td>Elovich equilibrium constant (L mg⁻¹)</td>
</tr>
<tr>
<td>Kₐ</td>
<td>Freundlich constant indicative of the relative adsorption capacity of the adsorbent (mg⁻¹(1/n) L¹/n g⁻¹)</td>
</tr>
<tr>
<td>Kₐₑ</td>
<td>Fowler–Guggenheim equilibrium constant (L mg⁻¹)</td>
</tr>
<tr>
<td>K₀</td>
<td>Temkin equilibrium constant (L mg⁻¹)</td>
</tr>
<tr>
<td>K₁</td>
<td>Hill–de Boer equilibrium constant (L mg⁻¹)</td>
</tr>
<tr>
<td>K₂</td>
<td>the energetic constant of the interaction between adsorbed molecules (kJ mol⁻¹)</td>
</tr>
<tr>
<td>log K₀w</td>
<td>octanol/water partition coefficient</td>
</tr>
<tr>
<td>n</td>
<td>Freundlich constant indicative of the intensity of the adsorption</td>
</tr>
<tr>
<td>N</td>
<td>the number of experimental points</td>
</tr>
<tr>
<td>qₑ</td>
<td>the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg g⁻¹)</td>
</tr>
<tr>
<td>qₘ</td>
<td>the maximum adsorption capacity (mg g⁻¹)</td>
</tr>
<tr>
<td>ΔQ</td>
<td>variation of adsorption energy (kJ mol⁻¹)</td>
</tr>
<tr>
<td>r</td>
<td>coefficient of correlation</td>
</tr>
<tr>
<td>R</td>
<td>universal gas constant (kJ mol⁻¹ K⁻¹)</td>
</tr>
<tr>
<td>T</td>
<td>temperature (K)</td>
</tr>
<tr>
<td>W</td>
<td>the interaction energy between adsorbed molecules (kJ mol⁻¹)</td>
</tr>
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</table>

**Greek letter**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>θ</td>
<td>surface coverage (qₑ/qₘ)</td>
</tr>
</tbody>
</table>
stirred at 400 rpm with 90 mL of 100 mg L\(^{-1}\) pollutant aqueous solution in thermostated bath. The temperature was controlled at 21 °C. The solution pH for the five phenolic compounds was 5.5. At this pH all the tested phenolic compounds are in their protonated forms. Agitation was provided for 4 days, which is more than sufficient time to reach equilibrium. At the end of the equilibrium period, the contents of the flasks were analyzed for residual concentration of adsorbate using Hewlett Packard 8453 diode array spectrophotometer.

All experiments were conducted in triplicate, and sometimes repeated again and the mean values have been reported.

2.4. Analysis

A well-known procedure for determining phenolic compounds concentrations, based on Beer’s law calibration plots, was applied using a diode array spectrophotometer (Hewlett Packard 8453). The wavelength resolution and the bandwidth were, respectively, 1 and 0.5 nm. The maximum absorption wavelength was determined as equal to 270 nm for Ph, 274 nm for 2-CP, 280 nm for 4-CP, 285 nm for DCP, and 290 nm for TCP. Then, the calibration plot was constructed. The calibration was repeated five times during the period of measurements. The linearization of this plot usually provided determination coefficient close to 99.98%.

3. Theoretical background

3.1. Langmuir model

The Langmuir [18] model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The Langmuir equation may be written as

\[
q_e = \frac{q_m b C_e}{1 + b C_e}
\]

where \(q_e\) is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg g\(^{-1}\)), \(C_e\) the equilibrium concentration of the solute in the bulk solution (mg L\(^{-1}\)), \(q_m\) the maximum adsorption capacity (mg g\(^{-1}\)), and \(b\) is the constant related to the free energy of adsorption (L mg\(^{-1}\)).

Eq. (1) can be linearized to five different linear forms as shown in Table 2.

3.2. Freundlich model

The Freundlich [19] equation can be written as

\[
q_e = K_F C_e^{1/n}
\]

where \(K_F\) is a constant indicative of the relative adsorption capacity of the adsorbent (mg\(^{1-(1/n)}\) L\(^{1/n}\) g\(^{-1}\)) and \(n\) is a constant indicative of the intensity of the adsorption. The Freundlich expression is an exponential equation and therefore, assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases. The linear form of the Freundlich isotherm is shown in Table 2.

To determine the maximum adsorption capacity, it is necessary to operate with constant initial concentration \(C_0\) and variable weights of adsorbent; thus ln \(q_m\) is the extrapolated value of ln \(q\) for \(C = C_0\).

According to Halsey [20]:

\[
K_F = \frac{q_m}{C_0^{1/n}}
\]

where \(C_0\) is the initial concentration of the solute in the bulk solution (mg L\(^{-1}\)) and \(q_m\) is the Freundlich maximum adsorption capacity (mg g\(^{-1}\)).

3.3. Elovich model

The equation defining the Elovich [21] model is based on a kinetic principle assuming that the adsorption sites increase exponentially with adsorption, which implies a multilayer adsorption. It is expressed by the relation:

\[
\frac{q_e}{q_m} = K_F C_e \exp\left(-\frac{q_e}{q_m}\right)
\]

where \(K_F\) is the Elovich equilibrium constant (L mg\(^{-1}\)) and \(q_m\) is the Elovich maximum adsorption capacity (mg g\(^{-1}\)).

If the adsorption obeys Elovich equation, Elovich maximum adsorption capacity and Elovich constant can be calculated from the slopes and the intercepts of the plot ln \((q_e/C_e)\) versus \(q_e\) (Table 2).

3.4. Temkin model

The Temkin [22] isotherm equation assumes that the heat of adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent–adsorbate interactions, and that
the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. Temkin model is given by

$$\theta = \frac{RT}{\Delta Q} \ln K_0 C_e$$

where $\theta$ is the fractional coverage, $R$ the universal gas constant (kJ mol$^{-1}$ K$^{-1}$), $T$ the temperature (K), $\Delta Q = (-\Delta H)$ the variation of adsorption energy (kJ mol$^{-1}$), and $K_0$ is the Temkin equilibrium constant (L mg$^{-1}$).

If the adsorption obeys Temkin equation, the variation of adsorption energy and the Temkin equilibrium constant can be calculated from the slope and the intercept of the plot $\theta$ versus $\ln C_e$ (Table 2).

### 3.5. Fowler–Guggenheim model

Fowler–Guggenheim [23] derived an isotherm equation which takes the lateral interaction of the adsorbed molecules into account. It has the following explicit form:

$$K_{FG} C_e = \frac{\theta}{1-\theta} \exp \left( \frac{2W}{RT} \right)$$

where $K_{FG}$ is the Fowler–Guggenheim equilibrium constant (L mg$^{-1}$), $\theta$ the fractional coverage, $R$ the universal gas constant (kJ mol$^{-1}$ K$^{-1}$), $T$ the temperature (K), and $W$ is the interaction energy between adsorbed molecules (kJ mol$^{-1}$).

Fowler–Guggenheim equation is one of the simplest equations allowing for the lateral interaction. The heat of adsorption varies linearly with loading. If the interaction between the adsorbed molecules is attractive (that is $W$ is positive), the heat of adsorption will increase with loading and this is due to the increased interaction between adsorbed molecules as the loading increases. This means that if the measured heat of adsorption shows an increase with respect to loading, it indicates the positive lateral interaction between adsorbed molecules. However, if the interaction among adsorbed molecules is repulsive (that is $W$ is negative), the heat of adsorption shows a decrease with loading. When there is no interaction between adsorbed molecules (that is $W=0$), this Fowler–Guggenheim equation will reduce to the Langmuir equation.

The linear form of the Fowler–Guggenheim isotherm is shown in Table 2.

### 3.6. Kiselev model

The equation of Kiselev [24] known as the adsorption isotherm in localized monomolecular layer is expressed by

$$k_1 C_e = \frac{\theta}{(1-\theta)(1+k_n\theta)}$$

where $k_1$ is the Kiselev equilibrium constant (L mg$^{-1}$), $\theta$ the fractional coverage, and $k_n$ is the constant of complex formation between adsorbed molecules.

The linear form of the Kiselev isotherm is shown in Table 2.

### 3.7. Hill–de Boer model

Eq. (8) is known as the Hill–de Boer [25,26] equation, which describes the case where we have mobile adsorption and lateral...
interaction among adsorbed molecules:

\[ K_1C_e = \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta} - \frac{K_2\theta}{RT}\right) \]  

(8)

where \( K_1 \) is the Hill–de Boer constant (L mg\(^{-1}\)), \( \theta \) the fractional coverage, \( R \) the universal gas constant (kJ mol\(^{-1}\) K\(^{-1}\)), \( T \) the temperature (K), and \( K_2 \) is the energetic constant of the interaction between adsorbed molecules (kJ mol\(^{-1}\)).

A positive \( K_2 \) means attraction between adsorbed species and a negative value means repulsion, that is, the apparent affinity is increased with loading when there is attraction between adsorbed species, and it is decreased with loading when there is repulsion among the adsorbed species. When there is no interaction between adsorbed molecules (that is \( K_2 = 0 \)), this Hill–de Boer equation will reduce to the Volmer equation.

The linear form of the Hill–de Boer isotherm is shown in Table 2.

4. Results and discussion

4.1. Adsorption isotherms

The experimental adsorption isotherms of phenol and chlorophenols from aqueous solutions onto GAC are presented in Fig. 1. The obtained results show that chlorophenols are adsorbed better than phenol. For the four tested chlorophenols, it seems that the adsorbed amounts are directly proportional to their degree of chlorination. For the two monochlorophenols, 4-CP is better adsorbed than 2-CP. The order of adsorption on GAC is: Ph < 2-CP < 4-CP < DCP < TCP.

The shape of the isotherms is the first experimental tool to diagnose the nature of a specific adsorption phenomenon. The isotherms have been classified according to the classification of Giles et al. [27]. Giles have classified adsorption isotherms into four main groups: L, S, H, and C. According to the above classification, the isotherms of phenolic compounds displayed an L curve pattern. The L shape of the adsorption isotherms means that there is no strong competition between solvent and the adsorbate to occupy the adsorbent surface sites. In this case, the longitudinal axes of the adsorbed molecules are parallel to the adsorbent surface (molecules adsorbed flat on the surface).

From Fig. 1, the values of experimental maximum adsorption capacity (\( q_{m,\text{experimental}} \)) for the five phenolic compounds onto GAC are about 218, 267, 310, 364, and 523 mg g\(^{-1}\) for Ph, 2-CP, 4-CP, DCP, and TCP, respectively.

The theoretical maximum adsorption capacities (\( q_{m,\text{theoretical}} \)) calculated using BET surface area of the activated carbon (929 m\(^2\) g\(^{-1}\)) and the molecular cross-sectional area (\( \sigma \)) are regrouped in Table 1. These values are the maximum adsorption capacities, which can be obtained if the molecules are adsorbed flat on the entire adsorbent specific surface.

It is known that phenols undergo oligomerization on the surface of activated carbon in the presence of molecular oxygen [28,29]. This fact has been verified in this work by the desorption of saturated GAC in the presence of ultrasound because these oligomers are difficult to desorb. It has been demonstrated that ultrasound seemed to enable the rupture of strong sorbate–sorbent bonds and improve desorption rate [2,30,31]. The desorption experiments have been conducted using an aqueous mixture of 10% (v/v) tert-butanol, 20% (v/v) ethanol, and 5% (v/v) NaOH (1 M) as regenerant in the presence of ultrasonic irradiation. Analysis of the regenerating solution by HPLC shows that no phenolic dimers, trimers, or polymers have been formed.

4.2. Modeling of adsorption isotherms

Several mathematical models can be used to describe experimental data of adsorption isotherms. The equilibrium data were modeled with the Langmuir (five linearized expressions), Freundlich, Elovich, Temkin, Fowler–Guggenheim, Kiselev, and Hill–de Boer models.

This work aims to find the models that can describe with precision the experimental results of adsorption isotherms, specify the parameters that can be determined, compare the phenolic compounds behavior, and determine the theoretical adsorption isotherms.

The experimental values of \( q_e \) and \( C_s \) are initially treated with the linearized equations in order to determine the models parameters and the isotherms are reconstituted using the determined values. The isotherm curves showed the superposition of experimental results (points) and the theoretical calculated points (lines). Linear correlation coefficients (\( r \)) showed the fit between experimental data and linearized forms of isotherm equations while the average percentage errors (APE) calculated according to Eq. (9) indicated the fit between the experimental and predicted values of adsorption capacity used for plotting isotherm curves:

\[
\text{APE}(\%) = \frac{\sum_{i=1}^{N}|(q_e)_{\text{experimental}}-(q_e)_{\text{predicted}}|/(q_e)_{\text{experimental}}}{N} \times 100
\]

(9)

where \( N \) the number of experimental data.

4.2.1. Langmuir isotherm

The adsorption data for phenol and chlorophenols onto GAC were analyzed by a regression analysis to fit the five linearized
expressions of Langmuir isotherm model. The details of these different forms of linearized Langmuir equations and the method to estimate the Langmuir constants \( q_m \) and \( b \) from these plots were explained in Table 2. Out of the five different types of linearized Langmuir isotherm equations, Langmuir-1 and Langmuir-2 are the most frequently used by several researchers because of the minimized deviations from the fitted equation resulting in the best error distribution. Values of the Langmuir constants are presented in Table 3 for the adsorption of the five phenolic compounds on activated carbon. The values of the coefficient of correlation obtained from Langmuir-2 expression indicate that there is strong positive evidence that the adsorption of phenols on GAC follows the Langmuir isotherm. From Table 3, it was observed that the values of Langmuir parameters obtained from the six linear expressions were different. It is clear that transformations of non-linear model to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least-squares method [32,33]. The lower coefficient of correlation values for the other four Langmuir linear expressions, especially in the cases of 4-CP, DCP, and TCP, suggest that it is not appropriate to use this type of linearization. The values of maximum adsorption capacity determined using Langmuir-2 expression are higher than the experimental adsorbed amounts and correspond to the adsorption isotherms plateaus. In contrast, the monolayer adsorption capacities obtained using the four other linear expressions of Langmuir model are lower than the experimental values for 4-CP, DCP, and TCP, which is unacceptable. It seems that the isotherm obtained from Langmuir-2 expression provided a better fit to the experimental data.

The favorable nature of adsorption can be expressed in terms of dimensionless equilibrium parameter of Hall et al. [34]: \( R_L = \frac{1}{1 + bC_0} \), where \( b \) is the Langmuir constant and \( C_0 \) is the initial concentration of the adsorbate in solution. The values of \( R_L \) indicates the type of isotherm to be irreversible (\( R_L = 0 \)), favorable (0 < \( R_L < 1 \)), linear (\( R_L = 1 \)) or unfavorable (\( R_L > 1 \)). The dimensionless separation factors calculated for Ph, 2-CP, 4-CP, DCP, and TCP are, respectively, 0.123, 0.115, 0.044, 0.037, and 0.017. \( R_L \) values were less than 1 and greater than zero indicating favorable adsorption.
In order to check the validity of the Langmuir model, it is interesting and essential to recalculate the adsorbed amounts using the equilibrium concentration values and Langmuir parameters determined using the five linearized forms of the equation. The calculated average percentage errors are shown in Table 3. The simulated isotherm curves determined using the Langmuir-2 expression are given in Fig. 2. This figure shows the superposition of experimental results (points) and theoretical calculated points (lines). It is clear from the average percentage errors shown in Table 3 that the Langmuir-1, Langmuir-3, Langmuir-4, and Langmuir-5 expressions are unable to describe the equilibrium data for the majority of the studied compounds. In spite of the extremely higher coefficients of correlation obtained using Langmuir-2 expression, this model does not describe perfectly the equilibrium data because of the higher values of average percentage error. Thus, it is not appropriate to use the coefficient of correlation of the linear regression method for comparing the best-fitting isotherms.

4.2.2. Freundlich isotherm

The equilibrium data were further analyzed using the linearized form of Freundlich equation using the same set experimental data, by plotting $\ln q_e$ versus $\ln C_e$. The calculated Freundlich isotherm constants and the corresponding coefficient of correlation values were shown in Table 3. The coefficients of correlation are high ($\geq 0.992$) showing a good linearity. From Table 3, if just the linear form of Langmuir-2 is used for comparison, Langmuir-2 was more suitable for the experimental data than was the Freundlich isotherm because of the higher values of correlation coefficient. In contrast, if using the linear form of the other Langmuir equations, the Freundlich isotherm was more suitable for the experimental data than was the Langmuir isotherm in most cases. The values of maximum adsorption capacity determined using Freundlich equation are higher than those calculated using Langmuir-2 expression for 4-CP, DCP, and TCP.

The magnitude of the exponent $n$ gives an indication on the favorability of adsorption. It is generally stated that values of $n$ in the range 2–10 represent good, 1–2 moderately difficult, and less than 1 poor adsorption characteristics [35]. The activated carbon is good adsorbent for phenol and chlorophenols ($2.793 \leq n \leq 6.821$).

Predicted and experimental isotherms are shown in Fig. 3. It is clear from Fig. 3 and average percentage error values (Table 3) that there is a good agreement between the experimental and predicted values, suggesting that the Freundlich model is valid for the experimental equilibrium data. Freundlich isotherm is more suitable for the experimental results than is the Langmuir-2 expression because of the lower average percentage error values (Table 3). Nevertheless, Freundlich isotherm slightly diverges with the experimental results for higher equilibrium concentrations.

4.2.3. Elovich isotherm

The Elovich isotherm constants, $K_E$ and $q_m$, as well as the coefficient of correlation, $r$, for the phenolic compounds adsorption systems using activated carbon are obtained using the linear form of the equation (Table 3). In all cases, the Elovich isotherm exhibited higher coefficients of correlation, but lower than those obtained for Langmuir-2 expression and Freundlich equation. In spite of the good correlation coefficients, the values of maximum adsorption capacity determined using the linear transformation of the Elovich equation (Table 3) are much lower than the experimental adsorbed amounts at equilibrium corresponding to the plateaus of the adsorption isotherms. This means that the assumption of the exponential covering of adsorption sites that implies multilayer adsorption is not in agreement with the experiment in the studied concentration range. Therefore, the Elovich model is unable to describe the adsorption isotherms of phenol and chlorophenols onto GAC.

4.2.4. Temkin isotherm

If the adsorption data obeys Temkin equation, the variation of adsorption energy, $\Delta Q_e$, and the Temkin equilibrium constant, $K_0$, can be calculated from the slope and the intercept of the plot $\theta(q_e/q_m)$ versus $\ln C_e$. It remains to define the value of $q_m$ that can be used to calculate the surface coverage, $\theta$. It is possible to take the values of $q_m$ determined using Langmuir, Freundlich or Elovich equations, after checking the validity of these values with the experimental results. The second possibility is to
Table 4
Parameters of the Temkin model for the adsorption of phenolic compounds onto GAC

<table>
<thead>
<tr>
<th>Compound</th>
<th>q_m (mg g(^{-1}))</th>
<th>Ph</th>
<th>2-CP</th>
<th>4-CP</th>
<th>DCP</th>
<th>TCP</th>
</tr>
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<td>Theoretical</td>
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<tr>
<td>K_0 (L mg(^{-1}))</td>
<td>0.888</td>
<td>0.911</td>
<td>5.871</td>
<td>11.305</td>
<td>341.240</td>
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<tr>
<td>ΔQ (kJ mol(^{-1}))</td>
<td>23.15</td>
<td>23.37</td>
<td>28.69</td>
<td>31.22</td>
<td>36.54</td>
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<tr>
<td>r</td>
<td>0.999</td>
<td>0.999</td>
<td>0.993</td>
<td>0.997</td>
<td>0.989</td>
<td></td>
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<tr>
<td>APE (%)</td>
<td>1.07</td>
<td>1.67</td>
<td>5.54</td>
<td>3.39</td>
<td>4.60</td>
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<td>Langmuir-2</td>
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<tr>
<td>K_0 (L mg(^{-1}))</td>
<td>0.888</td>
<td>0.912</td>
<td>5.866</td>
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<td>340.911</td>
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<td>ΔQ (kJ mol(^{-1}))</td>
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<td>r</td>
<td>0.999</td>
<td>0.999</td>
<td>0.993</td>
<td>0.997</td>
<td>0.989</td>
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<tr>
<td>APE (%)</td>
<td>1.07</td>
<td>1.68</td>
<td>5.54</td>
<td>3.39</td>
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</tr>
<tr>
<td>K_0 (L mg(^{-1}))</td>
<td>0.888</td>
<td>0.912</td>
<td>5.868</td>
<td>11.315</td>
<td>340.010</td>
<td></td>
</tr>
<tr>
<td>ΔQ (kJ mol(^{-1}))</td>
<td>11.37</td>
<td>11.81</td>
<td>16.76</td>
<td>19.01</td>
<td>26.63</td>
<td></td>
</tr>
<tr>
<td>r</td>
<td>0.999</td>
<td>0.999</td>
<td>0.993</td>
<td>0.997</td>
<td>0.989</td>
<td></td>
</tr>
<tr>
<td>APE (%)</td>
<td>1.07</td>
<td>1.66</td>
<td>5.54</td>
<td>3.39</td>
<td>4.59</td>
<td></td>
</tr>
</tbody>
</table>

use the value of the theoretical maximum adsorption capacity (q_m theoretical) calculated using BET surface area of the activated carbon (929 m\(^2\) g\(^{-1}\)) and the surface area available for one solute molecule, σ (Table 1).

The adsorption data for phenol and chlorophenols onto GAC were analyzed by a regression analysis to fit the Temkin isotherm model. The values of surface coverage, θ, are calculated using the theoretical maximum adsorption capacities (q_m theoretical) as well as those determined from the Langmuir and Freundlich models.

The parameters of Temkin model as well as the correlation coefficients are given in Table 4. The very higher values of the coefficient of correlation show a good linearity whatever the maximum adsorption capacity used for the calculation of surface coverage. The variation of adsorption energy, ΔQ = (−ΔH), is positive for all the studied compounds, which indicates that the adsorption reaction is exothermic. In order to seek a systematic for the observed changes between the variations of adsorption energy of the tested phenolic compounds, it seems that the chloro group has a negative increment (exothermic effect).

The theoretical isotherm curves are compared with the corresponding experimental data in Fig. 4 and the obtained average percentage error values are presented in Table 4. The experimental equilibrium curves are very close to those predicted by the Temkin model. Consequently, the Temkin isotherm can describe adequately the adsorption isotherms of phenol and chlorophenols onto GAC. This model perfectly describes the adsorption isotherms because of the very higher coefficients of correlation and relatively low values of the average percentage error (Table 4). The mean values of the average percentage error for the phenolic compounds are 3.26, 3.25, and 3.25% for the Langmuir, Freundlich, and theoretical maximum adsorption capacities, respectively.

4.2.5. Fowler–Guggenheim isotherm

The adsorption data for the five phenolic compounds onto GAC were analyzed by a regression analysis to fit the Fowler–Guggenheim isotherm. The plot of the Fowler–Guggenheim equation is carried out by calculating the surface coverage using the theoretical values of the maximum adsorption capacity as well as those obtained from Langmuir and Freundlich models. The coefficients of correlation and the parameters of the Fowler–Guggenheim model are summarized in Table 5. It is important to notice that the Fowler–Guggenheim isotherm is only applicable for θ < 0.6 when the Langmuir and Freundlich maximum adsorption capacities are used. The parameters of the Fowler–Guggenheim equation are placed in grey frames (Table 5) when the linearization is bad.

From Table 5, the interaction energy, W, is positive, which indicates that there is repulsion between the adsorbed molecules. For the studied compounds, the linearization is good, except for
in order to verify the validity of the Fowler–Guggenheim model, it is interesting and necessary to recalculate the adsorbed amounts using the equilibrium concentration values and the Fowler–Guggenheim parameters. The variables $q_e$ and $C_e$ cannot be separated in the Fowler–Guggenheim equation and a mathematical treatment using a computer code is needed for each equilibrium concentration. The experimental and simulated isotherms using the equation of Fowler–Guggenheim are shown in Fig. 5. It is noticed that the Fowler–Guggenheim model perfectly describes the equilibrium isotherms when the theoretical maximum adsorption capacities were used for the calculation of the values of surface coverage. For all the studied molecules, the values of the average percentage error fluctuate from 2.64 to 19.26% and 2.78 to 12.67% for the maximum adsorption capacities determined using the Langmuir and Freundlich models, respectively.

4.2.6. Kislev isotherm

The equilibrium data were modeled using the linearized form of Kislev model by plotting $1/[C_e(1 - \theta)]$ versus $1/\theta$. The calculated Kislev isotherm parameters and the corresponding coefficient of correlation values were shown in Table 6. For the values of surface coverage ($\theta$) calculated using the maximum adsorption capacities determined from the Freundlich model, the Kislev isotherm is only valid for $\theta > 0.68$.

It is important to notice that the linearization is bad in all cases for 4-CP, and any interpretation should be avoided. For all the tested compounds, the values given in grey frames in Table 6 are the result of a bad linearization.

The equilibrium constant of the formation of complex between adsorbed molecules, $k_n$, is negative, which is surprising because it is an equilibrium constant and it should be positive. The fact of having negative values of $k_n$ indicates that there is no formation of complex between the adsorbed molecules.

In order to test the validity of the Kislev model, it is interesting and indispensable to recalculate the adsorbed amounts using the equilibrium concentration values and the Kislev parameters determined using the linearized form of the equation. The calculated average percentage errors are shown in Table 6. The simulated isotherm curves determined using the Kislev expression are given in Fig. 6. This figure shows the superposition of experimental results (points) and theoretical calculated points (lines). As the variables $q_e$ and $C_e$ cannot be separated in the Kislev model, for each equilibrium concentration, a mathematical treatment using a computer code is necessary. From Fig. 6 and Table 6, the description of equilibrium isotherms by Kislev model deviates from the experimental results because of the higher average percentage error values. The average percentage error values for the tested phenolic compounds are 7.23 and 8.38%, in the case of the theoretical maximum adsorption capacities and the monolayer adsorption capacities determined using the Langmuir equation, respectively. For Ph and 2-CP and if the Freundlich maximum adsorption capacities are used for the calculation of surface coverage values, it is not possible to simulate all the concentration intervals because of the negative and inadmissible values of the equilibrium constant $k_1$ (Table 6).
4.2.7. Hill–de Boer isotherm

The Hill–de Boer isotherm constants, \( K_1 \) and \( K_2 \), as well as the coefficients of correlation, \( r \), for the phenolic compounds adsorption systems using activated carbon are obtained using the linear form of the isotherm (Table 7).

It is important to notice that the Hill–de Boer isotherm is applicable only for the values of surface coverage calculated using the theoretical maximum adsorption capacity. The Hill–de Boer parameters are placed in grey frames (Table 7) when the linearization is of bad quality.

The Hill–de Boer model allows verifying the assumptions made by the Fowler–Guggenheim equation, in spite of the low coefficient of correlation, obtained for TCP, showed in grey frames in Table 7. For all the studied phenolic compounds, the energetic constant of the interaction between adsorbed molecules, \( K_2 \), is negative indicating repulsion between the adsorbed molecules. This result is in agreement with that obtained using the Fowler–Guggenheim equation.

If we try to seek a logic in the observed variations between the values of the energetic constant of the interaction between adsorbed molecules for the tested phenolic compounds, we can estimate that chloro group has a negative increment. Ph and 2-CP deviate from this logic.

In order to examine the agreement of the Hill–de Boer model with the experimental results of the adsorption isotherms, the adsorbed amounts at equilibrium are calculated using the equilibrium bulk concentrations and the Hill–de Boer parameters \( K_1 \) and \( K_2 \). For each concentration and owing to the fact that the variables \( q_e \) and \( C_e \) are not separable, iterations using a computer code are needed. Simulation of equilibrium isotherms for the adsorption of phenolic compounds are presented in Fig. 7. This model describes adequately the adsorption isotherms because of the relatively low values of the average percentage error (Table 7) as well as the acceptable coefficients of correlation (≥0.957), except for TCP. The mean value of the average percentage error for the studied phenolic compounds is 3.08%.

4.3. Relation between adsorption capacity and adsorbate characteristics

Fig. 8 illustrates the variation in the maximum adsorption capacity determined experimentally, theoretically, and from the Freundlich model in relation to five physico-chemical properties of the substrates in question. These are: molecular weight, \( pK_a \), Solubility, octanol/water partition coefficient

### Table 7
Parameters of the Hill–de Boer model for the adsorption of phenolic compounds onto GAC

<table>
<thead>
<tr>
<th>( q_e ) (mg g(^{-1}))</th>
<th>Ph</th>
<th>2-CP</th>
<th>4-CP</th>
<th>DCp</th>
<th>TCP</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Theoretical</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( k_1 ) (L·mg(^{-1}))</td>
<td>0.072</td>
<td>0.070</td>
<td>0.413</td>
<td>0.790</td>
<td>12,847</td>
</tr>
<tr>
<td>( k_2 ) (kJ·mol(^{-1}))</td>
<td>-6.156</td>
<td>-6.012</td>
<td>-10.686</td>
<td>-13.240</td>
<td>-14,659</td>
</tr>
<tr>
<td>( r )</td>
<td>0.988</td>
<td>0.987</td>
<td>0.957</td>
<td>0.985</td>
<td>0.905</td>
</tr>
<tr>
<td>APE %</td>
<td>1.01</td>
<td>1.06</td>
<td>4.70</td>
<td>2.68</td>
<td>5.97</td>
</tr>
</tbody>
</table>
Fig. 5. Comparison of experimental and predicted adsorption isotherms of phenol and chlorophenols onto GAC according to Fowler–Guggenheim model.

The solubility seems play a very significant role in adsorption. A decrease in solubility and $pK_a$ is associated to an increase in adsorption capacity. The adsorption capacity for phenol and chlorophenols are function of molecular weight and cross-sectional area. Additionally, it seems that the adsorption capacity is directly proportional to the adsorbate hydrophobicity.

For the two monochlorophenols, 2-CP shows lower adsorption capacity than 4-CP although its solubility and $pK_a$ are lower. Even the octanol/water partition coefficient is directly proportional to the adsorption capacity; it is interesting and indispensable to try to explain these adsorption tendencies by the determination of the type of interactions between adsorbates and adsorbent. It is reported that the adsorption of phenols on acti-
Activated carbon may imply dispersion forces between \( \pi \)-electrons in phenols and \( \pi \)-electrons in activated carbon [36,37]. This conclusion can be applied to the interpretation for the series of phenolic molecules. The adsorption capacity increases as the degree of chlorination is higher. The chloro group is an electron-withdrawing group and therefore, the electron density in aromatic ring decreases as the number of chloro group increases. As a result, TCP shows the highest affinity to the \( \pi \)-electrons in activated carbon. For the two monochlorophenols, electron density in aromatic ring for 4-CP (para) is lower than that of 2-CP (ortho) and therefore the affinity of 4-CP to \( \pi \)-electrons in activated carbon is higher.

The shape of adsorption isotherms, according to Giles et al. [27] classification, shows that phenolic compounds are adsorbed in flat position on the graphite layers, which confirms the adsorption driving forces due to \( \pi-\pi \) dispersion interactions between the aromatic ring of phenols and the aromatic structure of the activated carbon.

5. Conclusion

Adsorption isotherms of phenolic compounds on activated carbon were studied and modeled using different isotherm models. The Langmuir equation is not appropriate for the experimental results. The mode of linearization of the equation influences the estimation of parameters. The model of Freundlich is more suitable than that of Langmuir, but it slightly diverges with the experimental results for the higher values
of equilibrium concentrations. The Elovich representation does not lead to a correct determination of the maximum adsorption capacity. The equation of Temkin leads to the determination of the variation of adsorption energy. The adsorption reaction of the phenolic compounds onto GAC is exothermic. This model adequately fits the equilibrium adsorption data. The Fowler–Guggenheim model effectively describes the adsorption isotherms of phenol and chlorophenols on activated carbon, and shows that the interaction among adsorbed molecules is repulsive. The Kiselev isotherm presents a notable difference between experimental and theoretical curves and it is important to handle the obtained results with precaution. The model of Hill–de Boer does not apply easily to the experimental results. In practically all cases, there is repulsion between the adsorbed molecules. For these reasons, interactions of phenolic compounds with activated carbon surface is localized monolayer adsorption, that is adsorbed molecules are adsorbed at definite, localized sites. Each site can accommodate only one molecule. The interaction among adsorbed molecules is repulsive and there is no association between them, adsorption is carried out on energetically different sites and is an exothermic process.

The adsorption isotherms displayed the following order of adsorption capacity: Ph < 2-CP < 4-CP < DCP < TCP. On the basis of the order of adsorption, the main characteristics of phenols playing an important role in adsorption mechanisms are hydrophobicity, solubility, molecular weight and cross-sectional area, and acidity. The adsorption driving forces due to dispersion interactions between \( \pi \)-electrons of the aromatic ring of phenols and those of the aromatic structure of the activated carbon perfectly correlates the adsorption capacity.

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**References**


