Removal of Phenol from Aqueous Solutions on Activated Carbon Obtained from Coffee Grounds

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The phenol uptake onto ground coffee converted into activated carbon by chemical activation with ZnCl₂ and H₃PO₄ was studied in the present work. The physical surface properties and the point of zero charge of AC-GC classified the adsorbent as micro-, mesoporous material, with a neutral surface. The equilibrium data of phenol adsorbed on AC-GC were fitted using Langmuir, Freundlich and Dubinin-Radushkevich adsorption isotherms. Our data are in agreement with Langmuir and Dubinin-Radushkevich models, revealing the maximum capacity of adsorption of 28.711 mg·g⁻¹ and 29.516 mg·g⁻¹ respectively. The adsorption free energy calculated by using Dubinin-Radushkevich model (E = 7.437 kJ·mol⁻¹) is specific to physical adsorption. The adsorption kinetic was also investigated in this paper by using three models: pseudo-first order, pseudo-second order and intraparticle diffusion. The pseudo-second order model fit well to our experimental data and the intraparticle diffusion is just one of the steps that kinetically controls the process.

Keywords: phenol; ground coffee; activated carbon; adsorption isotherms

Nowadays, water pollution represents a major global problem, where most of the pollutants coming from industrial and domestic activities are discharged into water. Phenol species are considered as potentially toxic and carcinogenic pollutants. Many sources are taken into account such as: oil and petrochemical industry, coal processing, dyes, pesticides etc. [12]. Above its certain concentration in wastewater, phenols produce an alteration of the water surface. For this reason, an appropriate treatment of the contaminated waters is essential.

The used methods for the phenols removal from the wastewaters, covers a wide range, from the physical to chemical or biological types such as: adsorption, filter membranes, ionic exchange, reverse osmosis, extraction with solvents, electrochemical oxidation, photocatalytic degradation, biological degradation [3-12].

The removal of the phenols from the wastewaters by adsorption is considered as an effective and promising method. Most used adsorbents are the activated carbon type (AC), natural zeolites, synthetic resins, etc. [13,14]. Among these adsorbents, a wide variety of the commercial activated carbon products have been intensively studied, although its high cost represents a disadvantage. Another efficient alternative is the use of the activated carbon which has a good retention capacity for phenols, usually obtained from various agricultural or food wastes [2,4-18]. Activated carbon produced from coffee grounds [15,19,20] shows also promising adsorption results which depends on BET surface area.

The scope of this paper is to investigate the performances of the AC-GC adsorbent produced from coffee grounds. The surface properties as well as the fitting of the adsorption experimental data with Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were studied in this work. The kinetic studies by using three models (pseudo-first order, pseudo-second order and the intraparticle diffusion) was also performed.

Experimental part

Preparation of the activated carbon

The starting material used for obtaining activated carbon is coffee grounds, originated from several types of coffee. An amount of 300 g coffee grounds was mixed with 400 mL containing zinc chloride and phosphoric acid (Merck) [15,18], having 0.5 mol/L each. The resulting mixture is stirred for 24 h at room temperature. After activation, the obtained solid material was filtered and dried for one hour at 105°C. Afterwards, the material was carbonized in furnace (DENKAL) at 450°C in air for one hour. The sample was cooled and washed with 200 mL HCl (20% by weight) to remove the inorganic or organic residues. The washing procedure was continued until the conductivity of the obtained suspension reaches the value close to that of distilled water. The carbonaceous material was subsequently dried at 105°C for 24 h [15], and the final product (namely in this study, AC-GC - Activated Carbon Ground Coffee) was obtained.

Activated carbon characterization

The surface physical properties of AC-GC were performed on a Micrometrics Gemini V instrument. The BET surface area (S_BET) was measured at liquid nitrogen temperature (77 K). The total pore volume (V_t) of activated carbon which has a good retention capacity for phenols, usually obtained from various agricultural or food wastes [2,4-18]. Activated carbon produced from coffee grounds [15,19,20] shows also promising adsorption results which depends on BET surface area.

The scope of this paper is to investigate the performances of the AC-GC adsorbent produced from coffee grounds. The surface properties as well as the fitting of the adsorption experimental data with Langmuir, Freundlich and Dubinin-Radushkevich isotherm models were studied in this work. The kinetic studies by using three models (pseudo-first order, pseudo-second order and the intraparticle diffusion) was also performed.
at 25°C for 24 h and filtered. The final pH of the solutions (pHf) was then measured. The point of zero charge was calculated based on (pHi - pHf) versus pHi.

**Adsorption studies**

The experimental tests for the phenol adsorption on the AC-GC were carried out at pH = 5. A volume of 100 mL of phenol solution with various concentrations (from 25 to 100 mg/L) was mixed with 0.2 g AC-GC or 0.1 g AC-GC (used for kinetic studies) under stirring. The resulting mixtures were stirred at 35°C for 24 h and then filtered. The residual phenol content was determined by using photocolorimeter CECIL CE 1011 instrument. The method refers to the formation of the red colored complex using 4-aminoantipyrine for which phenols species give a maximum of absorption at λ = 500 nm.

The equilibrium adsorption capacity of the activated carbon (AC-GC) was calculated based on the determination of the concentrations in residual phenol with the following formula:

\[
q_e = \frac{C_0 - C_e}{m} \cdot V
\]  

where \(q_e\) is the amount of the phenol adsorbed by AC-GC at equilibrium (mg/g), \(C_0\) and \(C_e\) are the initial and equilibrium concentration of the phenol (mg/L), \(V\) is the volume of the solution (L) and \(m\) is the AC-GC mass (g).

**Results and discussions**

The physical surface properties of AC-GC

The nitrogen adsorption isotherm measured at 77 K is presented in figure 1. The isotherm presents a hysteresis loop specific for the type I and H4 according to IUPAC classification [21]. The isotherm shape indicates that the material consists of micropores and mesopores.

Micro pores represent roughly 64% of the total pore volume and the average pore diameter (4V/A) is 5.08 nm. Table 1 shows the physical surface properties of AC-GC.

<table>
<thead>
<tr>
<th>(S_{\text{BET}}, \text{ m}^2/\text{g})</th>
<th>(S_{\text{SS}}, \text{ m}^2/\text{g})</th>
<th>(S_{\text{micro}}, \text{ m}^2/\text{g})</th>
<th>(V_{\text{T}}, \text{ cm}^3/\text{g})</th>
<th>(V_{\text{micro}}, \text{ cm}^3/\text{g})</th>
<th>(d_p, \text{ nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>396.1</td>
<td>151.4</td>
<td>244.7</td>
<td>149.5</td>
<td>0.189</td>
<td>0.122</td>
</tr>
</tbody>
</table>

**Adsorption isotherms**

The results of the phenol adsorption on the AC-GC were fitted using Langmuir, Freundlich and Dubinin-Radushkevich models.

**Langmuir isotherm**

Langmuir theory considers that the adsorption takes place in monolayer, on a homogeneous surface in terms of energy of adsorption sites, as a result of the interactions between adsorbed and adsorbent species [23]. Thus, an adsorption site, once occupied by an adsorbed species, cannot promote another adsorption. The equation which describes Langmuir isotherm has the following form [24]:

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

where \(q_e\) (mg/g) is the amount of phenol adsorbed by AC-GC at equilibrium, \(C_e\) (mg/L) is the concentration of phenol at equilibrium, \(q_m\) (mg/g) is the maximum adsorption capacity, representing the amount of phenol needed to form a monolayer, \(K_L\) (L/mg) is the Langmuir coefficient which is a measure of the strength of the adsorption process in terms of the rate with which it takes place.

Langmuir adsorption isotherm parameters \(q_m\) and \(K_L\) are calculated from the linear form of the equation (2):

\[
\frac{1}{q_e} = \frac{1}{K_L \cdot q_m} + \frac{C}{q_m}
\]
From the slope and intercept of the line by plotting $C_e/q_e$ as a function of $C_e$ based on the equation (3), $q_m$ and $K_L$ are obtained.

**Freundlich isotherm**

According to this model, the adsorption takes place on heterogeneous surfaces in terms of energy of the adsorption sites. The adsorbed species occupy the strongest binding sites first and then the weakest sites. Moreover, several species can be adsorbed on one adsorption site and a multilayer is formed. In this case, both interactions between the adsorbent and the adsorbed species and between the adsorbed species [23] are involved. The Freundlich adsorption isotherm is mathematically expressed as

$$q_e = K_F C_e^{1/n}$$  \[(4)\]

where $q_e$ (mg/g) is the amount of phenol adsorbed by AC-GC at equilibrium, $C_e$ (mg/L) is the phenol concentration at equilibrium, $K_F$ ([mg/g](1/mg))$^{1/n}$ is the Freundlich equilibrium constant and can be related to the adsorption capacity and $1/n$ is a dimensionless factor which is a measure of the intensity of the adsorption process and of the surface heterogeneity.

In order to determine ($K_F$ and $1/n$), the equation is also written as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  \[(5)\]

$K_F$ and $1/n$ can be calculated from the intercept and slope of the line by plotting $\log q_e$ versus $\log C_e$.

**Dubinin-Radushkevich isotherm**

The Dubinin-Radushkevich model (DR) can be used to determine the nature of the adsorption (physical or ion-exchange) [2]. Since the model is mainly used to describe the adsorption on microporous materials, it considers that adsorption occurs in monolayer [25]:

$$q_e = q_m \exp\left(-\beta \varepsilon^2\right)$$  \[(6)\]

where $q_e$ (mmol/g) is the amount of phenol adsorbed by AC-GC at equilibrium, $q_m$ (mmol/g) is the maximum adsorption capacity, representing the amount of phenol needed to form a monolayer, $\beta$ (mol$^2$/kJ$^2$) is a constant related to the adsorption energy, $\varepsilon$ is the Polanyi potential. The potential can be calculated by the equation expressed below:

$$\varepsilon = R T \ln(1 + 1/C_e)$$  \[(7)\]

where $R$ (kJ/mol·K) is the universal gas constant, $T$ (K) is the absolute temperature, and $C_e$ (mmol/L) is the equilibrium concentration of phenol. Depending on the value of $\beta$, the free energy of adsorption can be calculated, $E$ (kJ/mol), which represents the free energy exchanged to the transfer of one mole of phenol in solution from infinite distance, to the surface of the adsorbent [25]:

$$E = (2\beta)^{1/2}$$  \[(8)\]

By linearization of the equation (6), ($q_m$ and $\beta$) DR parameters are determined from the intercept, respectively the slope:

$$\ln q_e = \ln q_m - \beta \varepsilon^2$$  \[(9)\]

The values of the adsorption isotherms parameters are shown in Table 2.

It is shown that the experimental results are in agreement with the calculated data at 35°C, based on the models described above. Considering the correlation factor $R^2$, the very good data were obtained by using Langmuir model, while the poor results were obtained by Freundlich model (fig. 3).

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$q_m$, mg/g</td>
<td>28.711</td>
</tr>
<tr>
<td></td>
<td>$K_L$, L/mg</td>
<td>0.339</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.998</td>
</tr>
<tr>
<td><strong>Freundlich</strong></td>
<td>$K_F$, (mg/g)(L/mg)$^{1/n}$</td>
<td>10.370</td>
</tr>
<tr>
<td></td>
<td>n</td>
<td>3.665</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.928</td>
</tr>
<tr>
<td><strong>Dubinin–Radushkevich</strong></td>
<td>$q_m$, mol/kg</td>
<td>29.516</td>
</tr>
<tr>
<td></td>
<td>$E_{0\text{a}}$, kJ/mol</td>
<td>7.437</td>
</tr>
<tr>
<td></td>
<td>$R^2$</td>
<td>0.988</td>
</tr>
</tbody>
</table>

**Table 2**

PARAMETERS OF LANGMUIR, FREUNDLICH AND DUBININ-RADUSHKEVICH ADSORPTION ISOOTHERMS AT 35°C

Table 3 presents the calculated values of the separation factor, $R_L$, at various initial concentrations of phenol. In all cases, $R_L$ values are below 0.11, which suggests that the adsorption of phenol on AC-GC is favorable at this temperature.

**Table 3**

PARAMETERS OF DUBININ-RADUSHKEVICH ADSORPTION ISOTHERMS AT 35°C

In Langmuir model, a dimensionless constant denominated separation factor $R_L$ [26] is calculated based on the parameter $K_F$, which gives information on the performances of the adsorption process:

$$R_L = \frac{1}{1 + K_F C_0}$$  \[(10)\]

As function of the value of $R_L$ factor, the following cases may be considered:

- $R_L > 1$, the adsorption process is unfavorable;
- $R_L = 1$, the adsorption process is linear;
- $0 < R_L < 1$, the adsorption process is favorable;
- $R_L = 0$, the adsorption process is irreversible.

In Fig. 3, the correlation between the experimental and calculated data using Langmuir, Freundlich, Dubinin-Radushkevich adsorption isotherms at 35°C is shown.

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temperature. The higher the phenol concentration is, the more favorable adsorption seems to be.

The maximum adsorption capacity, \( q_{m} \), is 28.711 mg/g, which is higher compared to the Namane’s study (3.22 mg/g at 25°C) [15], on a similar material (AC-GC produced by carbonization at 600°C, instead of 450°C in this study). The maximum adsorption capacity is in good agreement with Yousef’s study [26] on zeolitic tuff (24.9 mg/g at 35°C).

The \( n \) parameter value from Freundlich isotherm is in the range 1 to 10, showing the phenol adsorption on the AC-GC is favorable for the given conditions. Considering that the \( R^2 \) correlation factor has low value, it can be assumed that Freundlich isotherm model is not suitable for characterizing the adsorption of phenol on AC-GC.

The parameters of the Dubinin-Radushkevich isotherm give information about the affinity of AC-GC for phenol, as to the mechanism by which the process of adsorption takes place. Relatively high value of \( R^2 \) (0.988) can be attributed to the fact that this model characterizes the adsorption on microporous surfaces as AC-GC is. Thus, the maximum adsorption capacity values calculated from this isotherm is in good agreement with the calculated values from the Langmuir isotherm. This confirms that the adsorption of phenol on the AC-GC takes place in the monolayer. The adsorption free energy value gives information on how the phenol is retained on the AC-GC surface. Thus, on the AC-GC, the adsorption is mainly physical, the adsorption free energy value being smaller than 8 kJ/mol (\( E = 7.437 \) kJ/mol) [27].

Considering that at \( pH=5 \) (value used for the experiments), the phenol is in the molecular form (\( pK_a = 9.89 \)), the interactions between phenol and AC-GC are mostly of dispersion effects type between the \( p \) electrons in the aromatic rings of phenol and the electrons of the graphitic structure [11,28]. On the other hand, the \( pH \) used for the experiments is under the value of \( pHPZC \) and the adsorbent surface is positively charged. Therefore, is possible to appear electrostatic attractions between the \( p \) electrons in the aromatic rings of phenol and the positive surface of the AC-GC [29], hypothesis supported by the value of the adsorption free energy value, which is at the boundary between physical adsorption (\( E < 8 \) kJ/mol) and the electrostatic interactions one (\( E = 8 - 16 \) kJ/mol).

The shape of the experimental adsorption equilibrium isotherm is L type according to the classification proposed by Gilles et al. [23]. This type of isotherm is the widespread in the case of adsorption of phenolic compounds from water and suggests that the aromatic ring adsorbs parallel to the surface and no strong competition exists between the adsorbate and the solvent to occupy the adsorption sites [11].

According to Rodrigues’s studies [22], the adsorption is favored if the pore diameter of the adsorbent is comparable with the molecule size of the phenol. In this case, the average pore diameter is 5.08 nm, while the cross-sectional area of phenol in flat orientation [15] is 5.22 nm. Moreover, it was demonstrated that the function of mesopores was just to provide for phenol molecules an easy access to micropores [11]. The phenol adsorbed by mesopores is negligible. In the case of AC-GC, the surface contain pores with average diameter closely of phenol molecule diameter and that allow the access of these molecules to the micropores that are predominant (>60%).

### Table 3

<table>
<thead>
<tr>
<th>( C_0, \text{mg/L} )</th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_L )</td>
<td>0.1055</td>
<td>0.0557</td>
<td>0.0378</td>
<td>0.0287</td>
</tr>
</tbody>
</table>

Estimation of deviation from adsorption isotherms

For a better validation of the model by which the adsorption process takes place, the deviation of the experimental data was calculated as function of the estimated values (\( q_{est} \)) from the - Langmuir, Freundlich and Dubinin-Radushkevich models and the experimental values (\( q_{exp} \)) obtained. The deviation (in %) was calculated with the following equation:

\[
\% \text{ deviation} = \left( \frac{q_{exp} - q_{est}}{q_{exp}} \right) \times 100
\]

Figure 4 shows the deviations (in %) for the used models at 35°C.

The superior results were obtained for the Dubinin-Radushkevich model, with a deviation between -3 and +5% and Langmuir model with a deviation between (-7 and +7%), which are in good agreement with the value of the correlation factor for these models, 0.988 and 0.998, respectively. This indicates that the adsorption occurs mainly in monolayer [25].

#### The kinetics of the adsorption

During the adsorption of liquid on the solid surfaces, the transport of solvate species towards solid surfaces is influenced either by the external mass transfer (by diffusion at the boundary layer) or by intra particle diffusion, or by both. The dynamic of the adsorption involves the following phases:

- transport of the solute from bulk solution, through the liquid film, towards the external surface of the adsorbent;
- solute diffusion into the pore of adsorbent except for a small quantity of adsorption on the external surface and parallel to this is the intraparticle transport mechanism of the surface diffusion;
- adsorption of solute on the interior surface of the pores and in the capillary spaces of the adsorbent [30].

In order to study the mechanism of phenol adsorption on AC-GC, the following kinetic models (the pseudo-first order kinetics, the pseudo-second order kinetics, and the intraparticle diffusion) were used.

The kinetics tests were carried out in the glass flasks and 50 ml phenol with concentration of 75 mg/L was mixed with 0.1 g AC-GC, under stirring at 40°C with \( pH = 5 \). The samples were collected for analysis at various time intervals from 0 to 210 min and the amount of phenol adsorbed on AC-GC was calculated using the equation (1).
The pseudo-first order model

The pseudo-first order model is based on the assumption that there are no species adsorbed on the adsorbent surface and the species accumulation occurs on the adsorbent surface during the adsorption [31]. The linear form of the equation which describes this model is written below [32]:

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  

where \( q_e \) (mg/g) represents the adsorbed phenol at equilibrium, \( q_t \) (mg/g) is the adsorbed phenol at time \( t \) (min) and \( k_1 \) (min\(^{-1}\)) is the first-order adsorption rate constant. \( k_1 \) and \( q_e \) are calculated from the slope and intercept of the plot of \( \ln(q_e - q_t) \) versus \( t \).

The pseudo-second order model

This model considers that the adsorption capacity is proportional with the number of occupied active sites [31]. The linearized form of the equation which describes this model is [32]:

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  

where \( q_e \) (mg/g) is the adsorbed phenol adsorbed at equilibrium, \( q_t \) (mg/g) is the adsorbed phenol at time \( t \) (min) and \( k_2 \) (g·mg\(^{-1}\)·min\(^{-1}\)) is the second-order adsorption rate constant. \( k_2 \) is calculated from the intercept of the plot of \( t/q_t \) as function of \( t \).

The intraparticle diffusion model

Based on this model one can determine whether the intraparticle diffusion is considered as the rate limiting step in the adsorption process [32]. Equation (14) describes the intraparticle diffusion model:

\[ q_t = k_p t^{1/2} + L \]  

where \( q_t \) (mg/g) is the adsorbed phenol at time \( t \) (min), \( k_p \) is the rate constant of the intraparticle diffusion (mg·g\(^{-1}\)·min\(^{-1/2}\)) and \( L \) is a measure of the thickness of the boundary layer [32]. \( k_p \) and \( L \) are determined from the slope and intercept of the plot of \( q_t \) as function of \( t^{1/2} \). If the plots described by the equation (14) is a straight line passing through the origin, then the intraparticle diffusion is the determinant rate step of the adsorption process. If the plots has several linear portions, the intraparticle diffusion is only a step of the adsorption process and not the rate limiting step [32].

Table 4 shows the kinetic parameters by using the following models: pseudo-first order, pseudo-second order and the intraparticle diffusion. It was found that the pseudo-first order model shows a large deviation regarding the amount of phenol adsorbed at equilibrium, experimentally measured (9.58 mg/g versus 14.7 mg/g). For the pseudo-second order model, much closer is the calculated value of \( q_e \) (15.37 mg/g) and considering the high value of \( R^2 > 0.999 \), it can be concluded that the pseudo-second order model describes well the adsorption [33]. Moreover, this kinetic model does not properly correlate the data for the entire domain being mostly applicable in the initial stage of the adsorption [34, 35].

The plot of the intraparticle diffusion model presents three stages (fig. 5). The first one correspond to a gradually curved shape rather than to a linear segment, which is attributed to the transport of the solute from bulk solution, through the liquid film to the external surface of the adsorbent or the boundary layer diffusion of phenol molecules. The second one, plotted in solid line, shows the fast adsorption stage where intraparticle diffusion rate is rate controlling. The linear regression was applied to this stage and the corresponding \( k_p \) and \( L \) values are estimated (table 4) [29]. Thereafter, the plot shows a plateau profile to represent the third adsorption stage. In this last stage, the phenol adsorption on AC-GC becomes slow due to its low concentration in solution, and finally the adsorption equilibrium was attained. Considering the fact that the plots of \( q_t \) versus \( t^{1/2} \) doesn’t pass through the origin, it can be said that the adsorption of phenol takes place in several stages and the intraparticle diffusion is just one of the steps that kinetically controls the process [32] and can be admitted that the boundary layer diffusion is involved [29]. Table 4 shows a large value of intercept \( L \) which can be attributed to a significant effect of the boundary layer [36].

Conclusions

The adsorbent AC-GC obtained from ground coffee is a material having microporous and mesoporous structure. It was found that it has low BET surface area compared with other activated carbon materials and a neutral nature of the surface. The Langmuir model fit well to the experimental adsorption data followed by Dubinin-Radushkevich model, showing that the maximum
adsorption capacities are 28.711 mg/g, and 29.516 mg/g, respectively. The adsorption of phenol on AC-GC is favorable, and the separation factor is below 0.11. The adsorption is considered mainly physical, and the value of the adsorption free energy is lower than 8 kJ/mol (E = 7.437 kJ/mol) and it can be attributed to p-p interactions between electrons of the aromatic rings in the phenol structure and the electrons of the graphitic structure, with an electrostatic interaction component, knowing that pH < pH PZC and consequently the adsorbent surface is positively charged. The pseudo-second order model fit well to the kinetics and the intraparticle diffusion is considered just as one of the step that kinetically controls the process.

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References

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