

Adsorption equilibrium of phenol onto chemically modified activated carbon F400

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Abstract

In this work the adsorption of phenol solutions onto activated carbon Calgon F400 has been studied. The carbon was modified by acid treatment, using soxhlet extraction with hydrochloric acid 2N for 120 cycles. The treatment did not affect significantly the surface area of the activated carbon but affected significantly the different functional groups, and thus its adsorption properties. Tóth model reproduced satisfactorily the experimental isotherm data and an adsorption enthalpy of $-17.9 \text{ kJ mol}^{-1}$ was found, which indicates that the process is exothermic. The pH affected significantly to the adsorption process and an empirical polynomial equation was able to reproduce maximum capacity as a function of pH. The isotherms obtained at pH 3 and 7 are very similar and showed a higher adsorption capacity compared with that obtained at pH 13. The use of phosphate buffer solutions decreased the maximum phenol adsorption capacity, due to the competitive adsorption between the phenol and phosphates. Finally, it was demonstrated that the acid treatment introduced chloride ions into the carbon, giving it properties of ion exchanger.

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Keywords: Acid treatment; Heterogeneity; Phenolate; Ion exchange; Langmuir; Tóth

1. Introduction

Phenolic compounds are present in wastewaters arising from a variety of industries (including olive mills, oil refineries, plastics, leather, paint, pharmaceutical, and steel industries). As it is known, these compounds are toxic, even at low concentrations and a previous treatment is required to discharge the effluents to the environment. In appropriate circumstances, the phenolic compounds contained in these wastes can be economically recovered, but usually the best method to treat these wastes is their destruction by chemical oxidation techniques [1–3] or by adsorption followed by regeneration of the adsorbent [4–9]. Other techniques that have been studied for this treatment include electrochemical oxidation [10], chemical coagulation [11,12], solvent extraction [13], membrane techniques [14], and combined methods [15,16].

In this context, granular activated carbon (GAC) adsorption is frequently used for the removal of hazardous organic pollutants

from wastewater. This technology achieves a rapid removal of the organic pollutants from the wastewater and retains them onto the GAC surface. The major disadvantage associated with this technique is saturation of the GAC, which makes it necessary to regenerate the activated carbon, usually by thermal or chemical processes [17]. This regeneration process leads to the loss of GAC and represents the main component of the operating cost for this technology. It has been reported that activated carbon exhibits a high adsorption capacity for phenolic compounds and is cost-effective in their treatment [18].

The adsorption capacity of activated carbons and its applications depends on the base materials involved. Nevertheless, its properties can be affected by altering the original carbon by means of chemical treatments [18,19]. Other factors that influence the adsorption capacity are the temperature, the solution pH [20], the competition of other sorbates and/or organic compounds [21], and even the presence of dissolved oxygen in the bulk solution [22].

The goal of the work described here was to increase our understanding of adsorption mechanism of the phenol onto GAC. To do this, the influence of pH and temperature in the adsorption equilibrium of phenol onto a modified granular activated carbon F400 was studied.

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Nomenclature

| | |
|-----------------|------------------------------------------------------------------------------------------------------------------|
| a_1, a_2, a_3 | parameters of n^∞ and q_m expressions as a function of pH |
| C | liquid phase equilibrium concentration of phenol (mol m^{-3}) |
| C_T | total initial solution concentration of anion species for ion exchange (mol m^{-3}) |
| C^* | liquid phase equilibrium concentration for ion exchange (mol m^{-3}) |
| ΔH | heat of adsorption (kJ mol^{-1}) |
| K | Langmuir equilibrium constant ($\text{m}^3 \text{mol}^{-1}$) |
| K_1 | adsorption equilibrium constant of Tóth model ($\text{m}^{3m} \text{mol}^m$) |
| K_{AB} | separation factor for ion exchange |
| m | dissociation parameter of Tóth model |
| n^∞ | total adsorption capacity obtained by Langmuir equation and it is pH dependent (mol kg^{-1} dry solid) |
| n_{II}^∞ | total ion exchange capacity of the carbon (mol kg^{-1} dry solid) |
| pH | pH of the solution |
| q | solid phase equilibrium concentration of phenol (mol kg^{-1}) |
| q_m | total adsorption capacity obtained by Tóth model and it is pH dependent (mol kg^{-1} dry solid) |
| q^* | solid phase equilibrium concentration for ion exchange (mol kg^{-1}) |
| R | perfect gas constant |
| ΔS | entropy change ($\text{J mol}^{-1} \text{K}^{-1}$) |
| T | temperature (K) |

2. Experimental

2.1. Chemicals

Phenol was the only sorbate used in this study. It was of analytical grade and purchased from Sigma Chemicals Co. Sodium hydroxide, hydrochloric acid and sodium chloride were of analytical grade and were supplied by Panreac. All the solutions were prepared with demineralized water (conductivity under $5 \mu\text{S cm}^{-1}$).

Granular activated carbon F400 manufactured by Calgon Carbon Corporation (Pittsburgh, EEUU) and supplied by Chemviron Carbon (Belgium), was used as adsorbent in this study. The activated carbon F400 is made from bituminous coal and activated by steam. The original carbon was conditioned upon received by boiling in deionized water for 4 h, and dried in an oven at 110°C during 24 h. It will be referred to as F400 DW. The objective of this pretreatment was to eliminate impurities and fines particles. To study the influence of the pH, the F400 DW carbon was subjected to acid treatment, using Soxhlet extraction with hydrochloric acid 2 N at 84°C for 120 cycles (each cycle was completed after about 20 min). After this, the carbon was washed with deionized water until pH 5 and finally

dried in an oven at 110°C during 24 h. The carbon obtained by this procedure will be referred to as F400 AW. The goal of this procedure was to reduce heterogeneity of the activated carbon by eliminating some of the functional groups.

2.2. Carbon characterization

Surface area was determined using nitrogen as the sorbate at 77 K in a static volumetric apparatus (Micromeritics ASAP 2010 sorptometer). Specific total surface areas were calculated using BET equation. The carbons compositions were also analysed with a fluorescence detector attached to the Phillips XL30-CPDX41 scanning electron microscope (SEM). FT-IR analyses were carried out using a Perking-Elmer FT-IR 16 PC apparatus.

2.3. Adsorption isotherms measurements

The experimental setup consisted of fifteen 0.1 dm^{-3} Pyrex containers, hermetically sealed and submerged in a temperature-controlled thermostatic bath. The temperature was kept constant within $\pm 0.1 \text{ K}$. The initial phenol solution at fixed pH with an ionic buffer solution was subjected to a N_2 stream to eliminate the oxygen dissolved and the flasks were completely filled to ensure anoxic conditions. The suspension formed by the carbon and solution was vigorously agitated by means of a multipoint magnetic stirrer. Different known masses of carbon, had previously been added to each flask. The accuracy of weighing was $\pm 0.0001 \text{ g}$. Solution and carbon were maintained at fixed temperature ($\pm 0.1 \text{ K}$) under vigorous stirring, until equilibrium was achieved (48 h). At the end of this period, the mixtures were filtered to remove the solid phase and the filtrate was analysed for the determination of the phenol content. Each point was calculated twice.

Buffer solutions were prepared from acid–base phosphate systems. The phenol was analysed by UV detector using high pressure liquid chromatography technique (column Nucleosil C₁₈, mobile phase 40% water/60% acetonitrile, flowrate 0.5 ml min^{-1}), the amount of OH^- was obtained by measure of pH using a GLP 21 Crison pH meter, and the amount of Cl^- was measured by ion chromatography (column Metrosep Anion Dual 2, mobile phase 1.3 mM Na_2CO_3 and 2.0 mM NaHCO_3 , flowrate 0.8 ml min^{-1}).

3. Results and discussion

3.1. Effect of the acid treatment

The surface area, micropore volume and the oxygen, silicium and aluminium versus carbon ratios for the activated carbons used in this study are shown in Table 1. It can be observed that the acid treatment only changes slightly the surface area of the activated carbon and it almost does not affect to the silicium/carbon ratio. On the contrary, this treatment affects significantly to both, the aluminium/carbon ratio and the oxygen/carbon ratio. This was confirmed by the FT-IR spectra (Fig. 1) in which can be observed important differences within both carbons. According to the figure, the presence of a stretching vibration at a broad

Table 1
Activated carbon characterization

| Carbon | Ratios (%) | | | BET surface area (m ² g ⁻¹) | Micropore volume (cm ³ g ⁻¹) |
|---------|------------|------|------|----------------------------------------------------|-----------------------------------------------------|
| | O/C | Al/C | Si/C | | |
| F400 DW | 3.60 | 0.98 | 1.00 | 1026.5 | 0.423 |
| F400 AW | 5.40 | 0.31 | 0.90 | 1000.9 | 0.417 |

band of 3400 cm⁻¹ in the F400 DW spectrum, indicates that this carbon has hydroxyl functional groups. As can be observed in the F400 AW spectrum, this vibration disappears, indicating that the acid treatment could have transformed these groups into carboxylic, carbonyl, or other groups because of the big vibrations that appeared at broad bands of 1200 and 950 cm⁻¹ [23]. It is also possible that with the acid treatment some chlorine remained chemisorbed on the carbon surface as it is indicated by the micropore volume reduction [24].

3.2. Effect of temperature

Three adsorption isotherms (corresponding to 288.13, 298.13 and 308.13 K) of phenol onto both activated carbons used in this work were obtained to study the effect of temperature. To avoid the effect of pH, the liquid solution was buffered to pH 7.0 by means of a phosphate buffer solution.

In order to fit the experimental data, two models have been used in this work: the Langmuir and the Tóth models. Both are widely used in literature to describe acceptably different adsorption isotherms.

The Langmuir model describes satisfactorily monolayer adsorption processes [5,25]. It has two parameters: n^∞ which is the total monolayer capacity and K that is the Langmuir equilibrium constant:

$$q = n^\infty KC / (1 + KC)$$

The Tóth model describes adequately heterogeneous systems [5,26] and has three parameters: q_m that represents the total adsorption capacity, m the dissociation parameter, and K_1 the adsorption equilibrium constant:

$$q = q_m C / (1/K_1 + C^m)^{1/m}$$

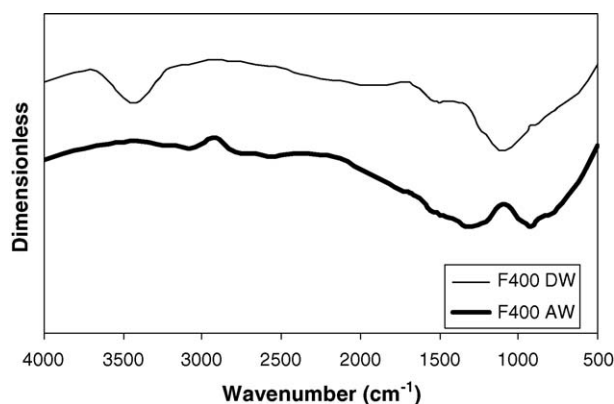


Fig. 1. FT-IR spectra for both carbon types.

To take into account the effect of temperature in both models, it can be assumed that the maximum adsorption capacity (in both models) and the dissociation constant (in the Tóth model) do not depend on the temperature and that the equilibrium constant can be related with temperature through the following equation, in which ΔH is the heat of adsorption and ΔS is the entropy change [26].

$$K_1 \text{ or } K = \exp((\Delta S/R) - (\Delta H/RT))$$

Taking into account this, the three isotherms obtained were simultaneously fitted to one equilibrium equation using Langmuir equation or Tóth model and the thermodynamic expression for the equilibrium constant as a temperature function. A non-linear least-square method was used to estimate the parameters (parameters of the equilibrium model and the thermodynamic values). Parameters obtained after this fitting procedure and the determination coefficient (R^2) for each isotherm model used are summarized in Table 2. Experimental data and modeling results achieved with Tóth model for both carbons are shown in Fig. 2.

As can be seen in Table 2, the Langmuir equation offers a poor fit of the experimental data for both types of carbons with very low regression coefficients. On the contrary, Tóth equation reproduces them satisfactorily. It supports that the surfaces of the carbons are heterogeneous and contain different functional groups. The important improvement in the regression coefficient obtained when Langmuir model is used to fit the experimental data of the carbon F400 AW, confirms the reduction of the heterogeneity with the acid treatment. The higher heterogeneity of the F400 DW is also observed in Fig. 2.

On the other hand, Fig. 2 shows that the adsorption equilibrium decreases as the temperature increases, indicating that the adsorption phenomena is exothermic. The enthalpy values obtained for both models were similar, and lower than 40 kJ mol⁻¹ (this value is considered to be the upper limit of the enthalpy for physical adsorption in a general adsorption process). These small values indicate that the adsorption of phenol by F400 DW and F400 AW is a physical adsorption process [5,26].

According to the results obtained, although the shapes of the isotherms are significantly different, both carbons present a similar adsorption capacity. This indicates that the acid treatment does not affect the adsorption capacity of the carbon although

Table 2
Adsorption parameters of F400 DW and F400 AW carbons at different temperatures

| Parameters | F400 DW | | F400 AW | |
|----------------------------------------------------|----------|--------|----------|--------|
| | Langmuir | Tóth | Langmuir | Tóth |
| n^∞ (mol kg ⁻¹) | 2.438 | – | 2.474 | – |
| q_m (mol kg ⁻¹) | – | 3.774 | – | 3.823 |
| $-\Delta H$ (kJ mol ⁻¹) | 17.906 | 17.906 | 17.901 | 17.906 |
| $-\Delta S$ (J mol ⁻¹ K ⁻¹) | 46.651 | 46.650 | 50.602 | 47.150 |
| m | – | 0.225 | – | 0.225 |
| R^2 | 0.618 | 0.890 | 0.755 | 0.956 |

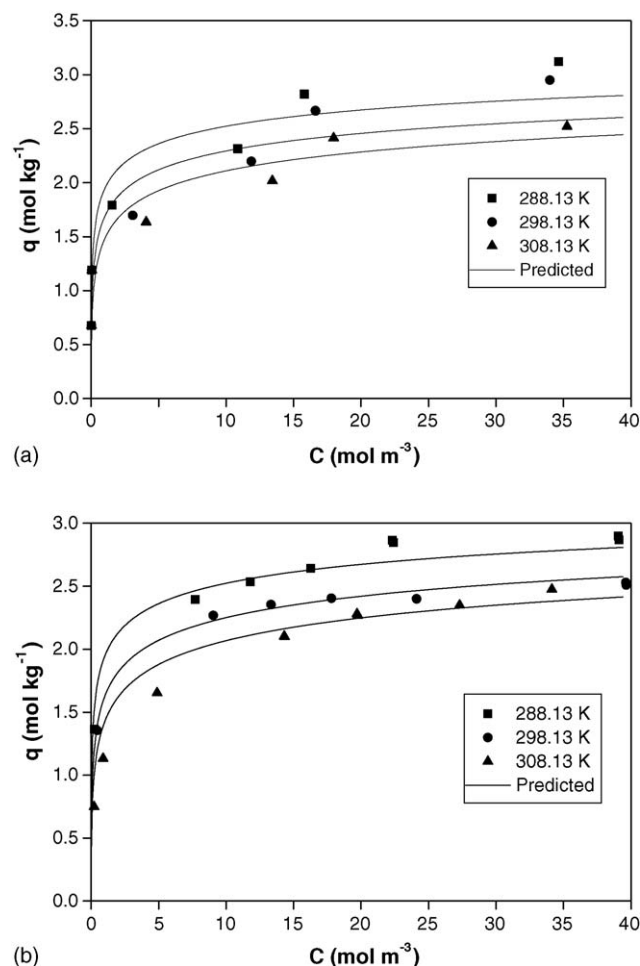


Fig. 2. Isotherms at pH 7 and at different temperatures, using the Tóth model: (a) phenol onto activated carbon F400 DW and (b) phenol onto activated carbon F400 AW.

it destroys or builds some functional groups and decreases the carbon heterogeneity [27].

3.3. Effect of the solution pH

In order to study the effect of the pH on the adsorption of phenol onto activated carbon, several experiments were carried out with carbon F400 AW at natural pH (range of 4–6), and at fixed pH maintained by means of ionic buffer solutions (phosphates buffers). To consider the pH effect in the Langmuir and Tóth models it can be assumed that this variable only affects to the maximum adsorption capacity. To take account of this influence, Chern and Wu [26] proposed the following polynomial equation:

$$q_m \text{ or } n^\infty = a_0 + a_1 \text{pH} + a_2 \text{pH}^2$$

Experimental equilibrium isotherms, together with theoretical ones obtained with the Tóth model are plotted in Fig. 3. Fitting parameters and regression coefficients obtained are shown in Table 3. As it can be observed, good agreement between experimental data and model predictions are obtained.

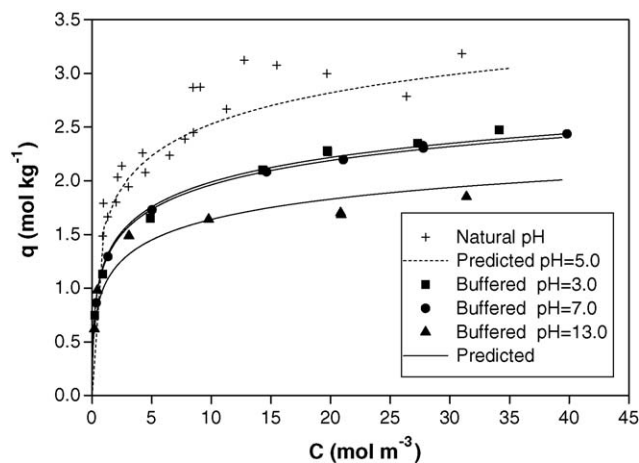


Fig. 3. Isotherms of phenol onto activated carbon F400 AW at $T=308.13$ K for different pHs, with pH control by ionic buffer solution and at natural pH, using the Tóth model.

As can be seen in Fig. 3, the pH presents a high influence on the maximum adsorption capacity, and the isotherm obtained at natural pH shows a higher adsorption capacity than all the isotherms obtained in buffer solutions.

The isotherms corresponding to pH 3 and 7 are very similar and show a higher adsorption capacity compared with that obtained at pH 13. Thus, the modified carbon does not have many different functional groups and tend to be homogeneous with the acid treatment and the phenol removal is only function of phenol dissociation. The main differences between both cases is that at pH 13 most of the phenol is present as phenolate ($pK_a = 9.83$) while at the acidic pH 3 and 7 the main species is undissociated phenol. As it is expected, the carbon is able to trap a higher amount of neutral species but it is possible that the carbon presents ion exchange properties because of a high amount of phenol was removed from the liquid phase at high pH, condition at which the phenol is in its ionic form, as it was discussed above.

On the other hand, the higher adsorption capacity in non-buffered isotherm can be interpreted in terms of the competitive adsorption of phenol and the phosphates contained in the buffer system. According to that, when buffer solutions are used to know the pH effects, on the adsorption, the carbon adsorption capacity for the sorbate is diminished due to the buffer solution uptake.

Table 3
Adsorption parameters of F400 AW at different pHs

| Parameters | Buffered | | Natural pH | |
|-----------------------------------------------|----------|---------|------------|--------|
| | Langmuir | Tóth | Langmuir | Tóth |
| K ($\text{m}^3 \text{mol}^{-1}$) | 1.534 | – | 1.534 | – |
| K_1 ($\text{m}^{3m} \text{mol}^m$) | – | 2.957 | – | 2.957 |
| a (mol kg^{-1}) | 2.1525 | 4.3094 | 2.700 | 19.771 |
| a_1 ($\text{mol kg}^{-1} \text{pH}^{-1}$) | 0.0475 | 0.0924 | 0.250 | –5.716 |
| a_2 ($\text{mol kg}^{-1} \text{pH}^{-2}$) | –0.0056 | –0.0107 | –0.0482 | 0.580 |
| m | – | 0.225 | – | 0.225 |
| R^2 | 0.909 | 0.982 | 0.942 | 0.972 |

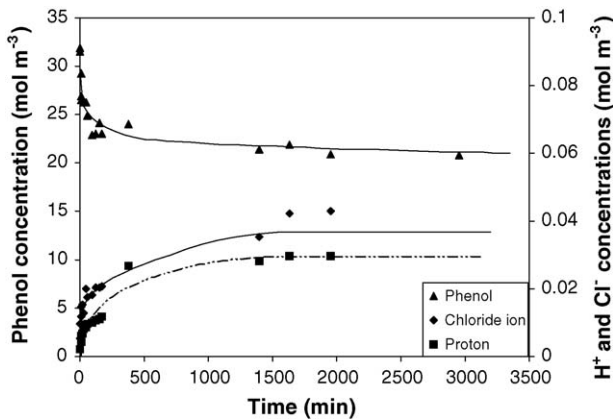
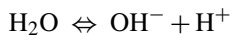


Fig. 4. Dynamic response of phenol adsorption by carbon F400 AW at natural pH, $T=308.13$ K, 700 rpm.

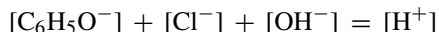
3.4. Role of the ion exchange in the overall adsorption process

Fig. 4 shows the dynamic response of an adsorption experiment at anoxic conditions in which 3.0 g of activated carbon F400 AW are placed into 2.0 dm³ of a solution containing 3000 ppm of phenol at natural pH.

It can be observed a decrease in the concentration of phenol and an increase in the concentration of both H⁺ and Cl⁻ ions. This behaviour is obtained in all the experiments carried out at natural pH. According to the equilibrium in solution for both acid–base phenol and water, a decrease in the concentration of phenol should deal to an increase in the pH, as the concentration of the acid (phenol) decreases in the bulk solution:



Thus, in order to justify the decrease in the pH and the appearance of chloride ions other processes must be considered. Taking into account that the charge balance must be accomplished, the increase in the concentration of H⁺ indicates that the phenolate and/or the OH⁻ ions were exchanged by Cl⁻ from the carbon:



These observations can be justified taking into account that the acid treatment introduces chloride ions to the activated carbon and this type of ions can be released from the solid phase by ion exchange. Then, it is possible that a high pH, the anionic phenolate could be load to the carbon by ion exchange and that this mechanism has an important role in the understanding of the overall adsorption process at any pH. The higher adsorption capacity at acidic pH values indicates that, the carbon prefers neutral specie than ionic phenolate, but even at non alkaline pH the ion exchange process has to be considered to explain the overall process as indicates the observed chloride release, which can not be justified only in terms of hydroxyl ion exchange. It is also well known that at high initial concentration the controlling step to mass transfer is the internal diffusion. Thus, the time required to achieve the equilibrium is high.

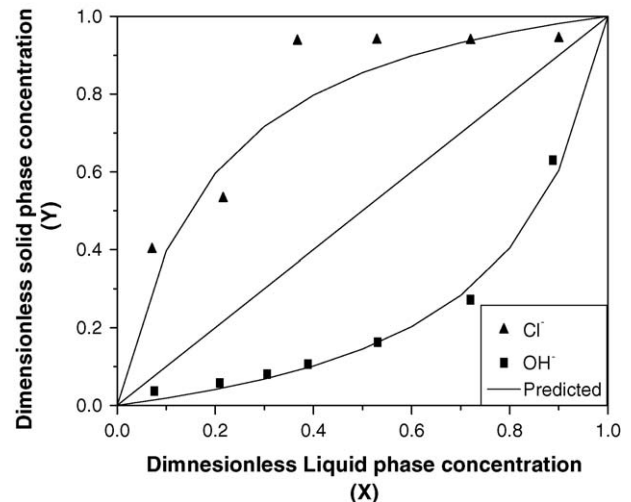


Fig. 5. Isotherm of ion exchange for activated carbon F400 AW at $T=308.13$ K, using the Langmuir type empirical equation.

In order to clarify the role of the activated carbon as ion exchanger, different amounts of activated carbon F400 AW were added to sodium hydroxide solutions (without phenol). In every case it was observed that the pH decreases and the concentration of chloride ions increase, indicating an ion exchange between hydroxyl and chloride ions. The following Langmuir-type empirical equation was used to model the experimental data:

$$Y_B^* = X_B^* / (R_1 + (1 - R_1)X_B^*)$$

where

$$R_1 = 1/K_{AB}, \quad X_B^* = C^*/C_T, \quad Y_B^* = q^*/n_{II}^\infty$$

where K_{AB} is the separation factor. This equation has been successfully applied in literature [28–31].

The experimental data obtained for both ions in dissolution, were fitted to previous equation by nonlinear least-squares regression analysis. The values of n_{II}^∞ and K_{AB} obtained were 0.55 mol kg⁻¹ and 5.91, respectively. The predicted isotherm is plotted together with the experimental data in Fig. 5.

As can be observed, the model fits well with the experimental data. The dimensionless form of the isotherm allows to conclude that ion exchange equilibrium is unfavorable for OH⁻ and favorable for Cl⁻. As it was expected, the maximum capacity obtained by ion exchange (0.55 mol kg⁻¹) is lower than the value obtained by adsorption at lower pH values.

4. Conclusions

From this work the following conclusions must be drawn:

An acid treatment, using soxhlet extraction with hydrochloric acid 2N for 120 cycles, does not affect significantly to the surface area of the activated carbon but it affects significantly to the different functional groups, and thus to the adsorption properties.

The adsorption of phenol by F400 DW and F400 AW is an exothermic physical adsorption process. The enthalpy values obtained for both activate carbons were similar ($-17.9 \text{ kJ mol}^{-1}$). Tóth model reproduces satisfactorily the experimental isotherm data.

The isotherms corresponding to pH 3 and 7 are very similar and show a higher adsorption capacity compared with that obtained at pH 13. The effect of the pH on the adsorption capacity can be satisfactorily modeled using an empirical polynomial equation. A higher adsorption capacity is observed in non-buffered isotherms. This can be interpreted in terms of the competitive adsorption of phenol and the phosphates contained in the buffer system.

The acid treatment introduced chloride ions into the carbon, giving it properties of ion exchanger.

Ion exchange must be considered in the understanding of the overall adsorption process of phenol onto activated carbon. It helps to justify the changes in the pH observed during this process.

Ion exchange isotherm allows to conclude that this carbon prefers the Cl^- than OH^- ions.

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