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# Immersion enthalpy and the constants of Langmuir model in the 3-chloro phenol adsorption on activated carbon

**Liliana Giraldo · Juan Carlos Moreno**

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**Abstract** The adsorption process of 3-chloro phenol from aqueous solution on a activated carbon prepared from African palm stone and which presents a specific surface area of 685 $m^2 g^{-1}$, a greater quantity of total acid groups and a $pH_{PZC}$ of 6.8 is studied. The adsorption isotherms are determined at pH values of 3, 5, 7, 9 and 11. The adsorption isotherms are fitted to the Langmuir model and the values of the maximum quantity adsorbed that are between 96.2 and 46.4 mg $g^{-1}$ are obtained along with the constant $K_L$ with values between 0.422 and 0.965 L $mg^{-1}$. The maximum quantity adsorbed diminishes with the pH and the maximum value for this is a pH of 5. The immersion enthalpies of the activated carbon in a 3-chloro phenol solution of constant concentration, of 100 mg $L^{-1}$, are determined for the different pH levels, with results between 37.6 and 21.2 J $g^{-1}$. Immersion enthalpies of the activated carbon in function of 3-chloro phenol solution concentration are determined to pH 5, of maximum adsorption, with values between 28.3 and 38.4 J $g^{-1}$, and by means of linearization, the maximum immersion enthalpy is calculated, with a value of 41.67 J $g^{-1}$. With the results of the immersion enthalpy, maximum quantity adsorbed and the constant $K_L$, establish relations that describe the adsorption process of 3-chloro phenol from aqueous solution on activated carbon.

**Keywords** 3-chloro phenol · Activated carbon · Adsorption capacity · Immersion enthalpy · pH

## Introduction

Adsorption technology is used extensively for the removal of organic and inorganic micropollutants from aqueous solutions; the activated carbon is the adsorbent most widely used for the removal of a variety of organics from waters [1]; and for this particular application, one of the aspects that has a major influence on the adsorption is the surface chemistry [2]. The surface chemistry depends on the heteroatoms content, mainly groups with oxygen that determine the superficial charge, the hydrophobicity and the electronic density of the graphite layers in the activated carbons. The superficial charge depends on the solution pH and on the activated carbon surface characteristics, and a negative surface charge results from the dissociation the superficial groups with character acid.

Studies on the adsorption process of the activated carbons of phenol and the derivative compounds present in aqueous solutions have been carried out for some time and in fact still continue [2–5] showing that the process presents some complexities and is dependent on the solution characteristics, such as pH, force ionic, the grade of dilution and others. In turn, these characteristics influence the adsorption mechanism of the phenolic compounds [6]. The phenolic derivates are widely used as intermediates in the plastic synthesis, dyes, pesticides and insecticides, and their frequent presence in drinking waters and municipal and industrial waste sites represents a serious danger for the environment as well as—most alarmingly—for human health [7–9].

The intensity of the interaction between the solution and the activated carbon can be determined by the immersion

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L. Giraldo
Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, Bogotá, Colombia

J. C. Moreno (✉)
Grupo de Investigación en Sólidos Porosos y Calorimetría, Departamento de Química, Facultad de Ciencias, Universidad de Los Andes, Bogotá, Colombia
e-mail: jumoreno@uniandes.edu.co

enthalpy in solutions that contain active substances with the surface and that allow to relate the physical and chemical properties of the activated carbon with the adsorption capacity of the compounds that are in solution [10–14]. Adsorption is a spontaneous process, $\Delta G < 0$; during the process molecules that had freedom of mobility in the solution become attached to the surface, leading an increase in the order of the system, then the entropy is negative and in order to conform to a negative value of $\Delta G$, the process must be exothermic, $\Delta H < 0$ [15].

The adsorption processes in liquid phase are efficiently used to purify industrial wastewaters that contain dyes, perfumes and organic or inorganic pollutants in general [16]. The activated carbon is an adsorbent that presents a high and varied grade porosity and a considerable internal surface, characteristics that give them their adsorbent properties, used in applications in both the gaseous and liquid phases. In addition, they represent a certain percentage of superficial chemical groups.

In this work, the adsorption of 3-chloro phenol is studied in aqueous solutions on a activated carbon prepared from African palm stone, in adsorption isotherm and immersion enthalpies at pH values between 3 and 11. Immersion enthalpies of the activated carbon are determined in 3-chloro phenol solutions in function of the concentration at pH of maximum adsorption, establishing a relationship between the quantities adsorbed and the enthalpic values of the solid-liquid interaction.

## Methodology

The activated carbon that is used in this work is obtained by physically activating the African palm stone. Initially, the material in particles is carbonized to 723 K in $N_2$ atmosphere and the activation is then done with $CO_2$ at 1,073 K during 2 h.

Table 1 presents some of the properties of the 3-chloro phenol that is the adsorbate organic that is studied from the aqueous solution [17].

### The adsorption isotherm of $N_2$

The textural characteristics are established by determining the adsorption isotherm of $N_2$ to 77 K using conventional volumetric equipment, Autosorb 3B, Quantachrome.

**Table 1** Properties of the 3-chlorine phenol

| Molecular weight (mol $g^{-1}$) | Maximum absorption wavelength | pKa to 298 K | Solubility (g/100 g $H_2O$) |
|---|---|---|---|
| 129 | 273 | 8.8 | 2.6 |

### Acid and basic groups

The total acidity and basicity of the activated carbon are determined using the Boehm method [18, 19]. Approximately 1.000 g of the solid is weighed for each determination; a quantity of activated carbon is placed in a glass flask with an emery boarded lid, with 50.0 ml of sodium hydroxide solution, NaOH, 0.1 N and another quantity in a recipient with 50.0 ml hydrochloric acid solution, HCl, 0.1 N. The solutions are agitated mechanically and kept at a constant temperature of 298 K during 5 days. A sample of 10.0 ml of each of the solutions is taken and titrated with a standard solution of sodium hydroxide or hydrochloric acid depending on the case; during the titration, the solution pH is measured with a pHmeter CG 840B Schott.

### Point of charge zero, $pH_{PCZ}$

Quantities of the activated carbons are weighed in a range from 0.010 to 0.600 g. These are then placed in glass flasks of 50.0 ml and 10.0 ml sodium chloride solution is added, NaCl, 0.1 M. The flasks are covered and constantly agitated at temperature of 298 K during 48 h, so that the charge in the activated carbons is in equilibrium. Finally, after 48 h, the pH of each of the solutions is measured with a pHmeter CG 840B Schott.

### 3-Chloro phenol quantity adsorbed

To determine the quantity of 3-chloro phenol adsorbed for the activated carbon, 0.5 g of the phenol is placed in glass flasks with 250 ml of the respective 3-chloro phenol aqueous solution in concentrations range between 20 and 120 mg $L^{-1}$. The samples are agitated mechanically and kept at a temperature of 298 K for a period of 72 h in order to ensure equilibrium. During this time, the pH solution remains at a value fixed in a range between 3 and 11, by adding diluted solutions of HCl or NaOH. The equilibrium concentration the phenolic compound in the solutions is determined after the adsorption, prior to the calibration of each pH value to the maximum absorption wavelength, using a spectrometer UV–VIS Milton Roy Co. Spectronic Genesys SN.

### Immersion enthalpy

The immersion enthalpies of the activated carbon are determined in 3-chloro phenol solutions of different concentrations ranging between 20 and 120 mg $L^{-1}$ for the maximum adsorption pH. The immersion enthalpies are also determined for solutions of 100 mg $L^{-1}$ up to the selected pH values. To conduct this determination, a heat conduction microcalorimeter is used with a calorimetric cell in stainless steel [20, 21]. The temperature of 30 ml of the solution to be used is risen to 298 K; this is then placed in the cell. A sample of activated carbon of approximately 0.500 g is weighed and placed inside the calorimetric cell in a glass ampoule. The microcalorimeter is then assembled. When the equipment reaches a temperature of around 298 K, the potential readings begin after a period of approximately 15 min, with readings done every 20 s in order to break the glass ampoule and register the thermal effect generated. The potential readings continue for approximately 15 minutes more and at the end of the experience, the equipment is calibrated electrically.

## Results and discussion

On Table 2, the textural and chemical characteristics of the activated carbon obtained from African palm stone, which is used in the 3-chloro phenol adsorption, are presented. The activated carbon presents a specific surface area of 685 $m^2$ $g^{-1}$, a finding which concurs with that obtained in other works [22], in studies done under similar conditions. The results obtained for the total volume of pores and the micropores volume show a microporosity content of around 78 percent. The total content of the acid groups is bigger than the content of the basic groups, making the pH the point of charge zero, $pH_{PZC}$. Light acid with a value of 6.8 should be to take into account for the 3-chloro phenol adsorption to the different pH values, since this modifies the superficial charge of the activated carbon.

The isotherms are determined at 298 K for the pH values 3–11, and the change is verified by assessing the quantities 3-chloro phenol adsorbed in function of the pH.

The isotherms are Langmuir-type and Fig. 1 shows the isotherms obtained for each one of the pH values. Can to observe that the pH 5 is the pH of maximum adsorption and the pH 11 is in which the smallest adsorption is occured.

Figure 2 presents the fitting lines of the isotherms to Langmuir model; in this figure, the experimental data clearly corresponds to the proposed model once it is charted linearly, with correlation coefficients ranging between 0.9947 and 0.9984. The lines for the data that correspond to the 3-chloro phenol adsorption to a pH of 3, 5 and 7 are similar and the mark values of similar slopes that also reflect the quantities adsorbed are also similar, indicating that adsorption is favored to these solution pH values when the superficial charge of the activated carbon is positive, since the activated carbon presents a $pH_{PZC}$ of 6.8; the lines for the isotherms that are determined to pH values of 9 and 11 show a different behavior and slopes values are higher. Therefore, the 3-chloro phenol quantities adsorbed are minor in approximately 50% of the quantity of the maximum adsorption that is obtained in a solution pH of 5.

Figure 3 presents the relation between the maximum adsorption capacity, Xm, and the pH. The results show that as the pH increases, the 3-chloro phenol adsorption capacity on the activated carbon diminishes, with a minimal value of 46.4 mg $g^{-1}$ for the adsorption capacity at pH 11. Above the $pH_{PZC}$, 6.8, the activated carbon is negatively charged, the electrostatic repulsion between the surface and the 3-chloro phenolate anions results in depletion of the quantity adsorbed [23].

Figure 4 shows the relation between the constant of Langmuir model, $K_L$, in function of the pH. At pH 11 find

**Table 2** Physical and chemical characteristics of the activated carbon

| Lignocellulosic material | Stone of African palm |
|---|---|
| Superficial area BET ($m^2$ $g^{-1}$) | 685 |
| Pore volume ($cm^3$ $g^{-1}$) | 0.42 |
| Micropore volume ($cm^3$ $g^{-1}$) | 0.33 |
| Total acid groups (mmol $g^{-1}$) | 0.96 |
| Total basic groups (mmol $g^{-1}$) | 0.38 |
| pH point of charge zero ($pH_{PZC}$) | 6.8 |

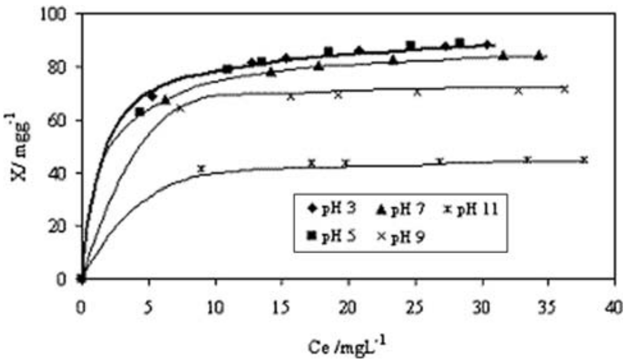

**Fig. 1** 3-chloro phenol adsorption isotherms from aqueous solution on activated carbon to pH 5 and 11. T 298 K

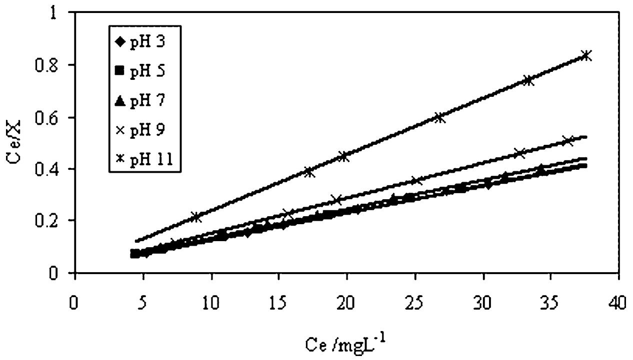

**Fig. 2** Lines of Langmuir model in function of the pH

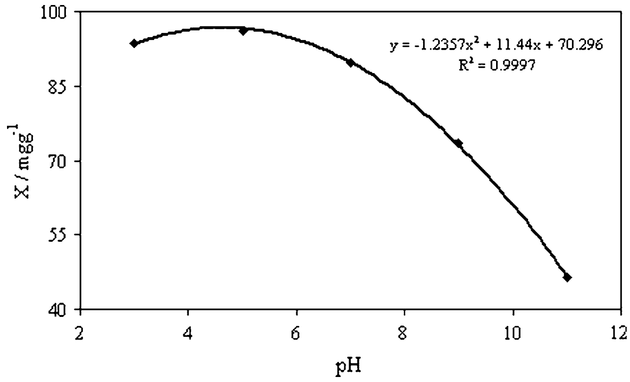

**Fig. 3** Maximum adsorption capacity of the 3-chloro phenol on activated carbon in function of the pH

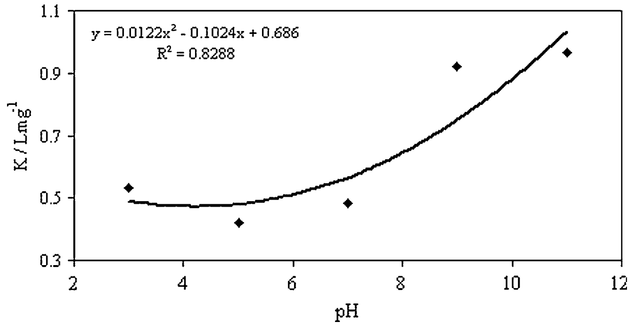

**Fig. 4** Constant of Langmuir model in the 3-chloro phenol adsorption on activated carbon in function of the pH

the highest value for the constant $K_L$ in the series and similar results are obtained for an activated carbon prepared from a rice straw [4]. The adsorption constant values depend on the pH of the solution due that substituent groups contribute to the electron-acceptor characteristics of the aromatic ring of solute; the group –Cl acts as a strong electron-withdrawing in reducing the overall electron density in the $\pi$-system of the ring and the attraction with the activated carbon surface is enhanced [9]. In Figs. 3 and 4, two curves are fitted to functions of a second order: in the case of the adsorption capacity, a decrease is noted when the pH rises, while the constant $K_L$ that is related with the energy process increases when the pH rises.

The immersion enthalpy of the activated carbon in 3-chloro phenol aqueous solutions indicates the energy that is involved in the interaction between the solid and the solution [24, 25]. Therefore, this property allows the influences of the pH in the adsorption process to be determined and it is constituted in a characteristic of the system; in Fig. 5, the relation between the immersion enthalpy of the activated carbon in 3-chloro phenol solution of 100 mg $L^{-1}$ is presented in function of the pH; as can be seen, the curve is similar to that which depicts the relation between the maximum adsorbed quantity and the pH. In other words, the maximum value is obtained for the immersion enthalpy in the pH interval between 3 and 5, with immersion enthalpies of 37.0 and 37.6 J $g^{-1}$ respectively. Given the precision of the calorimetric measure with a standard deviation of ±1.56 J $g^{-1}$, these can be considered equivalent values, indicating that the interactions between the activated carbon and the 3-chloro phenol solutions to pH of 3 and 5 are similar and that the quantities of energy favor the adsorption process under the study conditions. These values are similar with others obtained in previous work for the immersion of activated carbons cloths in HCl and NaOH solutions [26].

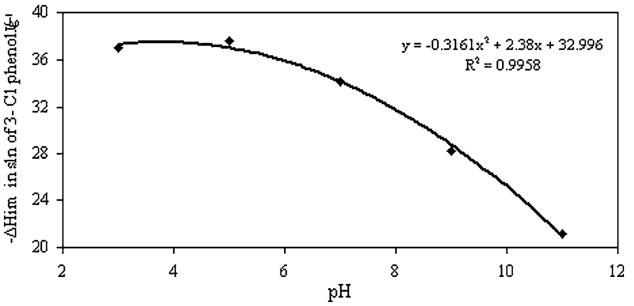

**Fig. 5** Immersion enthalpies of the activated carbon in 3-chloro phenol solution of 100 mg $L^{-1}$ in function of the pH. T 298 K

Once the maximum adsorption pH is established based on the isotherms results, the immersion enthalpy of the activated carbon is determined in 3-chloro phenol solutions of different concentrations. The values of the immersion enthalpy rose when the solution concentration increases to a maximum, just as happens on the graph of the isotherm, of 38.4 J $g^{-1}$ for a concentration of 120 mg $L^{-1}$. Figure 5 shows the relation between the immersion enthalpy and the 3-chloro phenol solutions concentration; the form of the graph suggests that enthalpic variations are present in minor concentrations which are muffling as the solution concentration rises, yielding a difference of 0.4 J $g^{-1}$ between the values of the immersion enthalpy for the solutions of 120 and 100 mg $L^{-1}$.

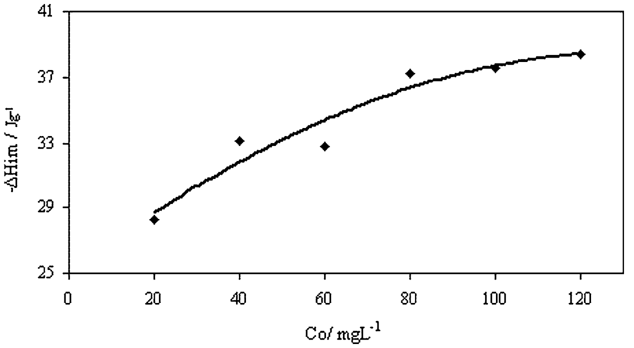

**Fig. 6** Immersion enthalpies in function of 3-chloro phenol aqueous solution concentration to pH 5. T 298 K

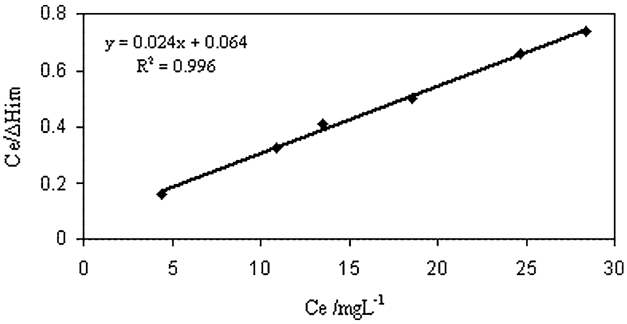

**Fig. 7** Linearization of the immersion enthalpy data in function of equilibrium concentration

When carrying out a Langmuir-type linearization [27] of the immersion enthalpies in function of the equilibrium concentration, as with the data on adsorbed quantities, the slope of the maximum immersion enthalpy is determined. Figure 7 shows the linearization of the immersion enthalpy data and the equilibrium concentration, with a correlation coefficient of 0.996.

The maximum immersion enthalpy calculated for values in Fig. 7 is 41.67 J $g^{-1}$, a finding which concurs with the experimental values obtained from Fig. 6. This additional information obtained in the calorimetric experiment on the adsorption process of 3-chloro phenol from aqueous solution on the obtained activated carbon prepared from African palm stone shows that the process is exothermic, allowing the capacity and the immersion enthalpy maximum to be calculated as characterization parameters.

## Conclusions

The adsorption of 3-chloro phenol from aqueous solution on a activated carbon prepared from African palm stone with a specific surface area of 685 $m^2$ $g^{-1}$ and with a pH at a point of charge zero of 6.8 in function of the solution pH shows that the adsorption capacity diminishes as the pH rises.

The isotherms obtained to for the different pH values (3–11), are fitted using Langmuir model and the maximum quantity adsorbed is between 96.2 and 46.4 mg $g^{-1}$. In addition, the constant $K_L$ shows values ranging between 0.422 and 0.965 L m $g^{-1}$. The pH of 5 is obtained as the maximum adsorption rate.

The immersion enthalpies of the activated carbon in a 3-chloro phenol solution of 100 mg $L^{-1}$ at different pH values range between 37.6 and 21.2 J $g^{-1}$, which indicates that the pH of more enthalpic interaction is 5. This concurs with the values of the adsorption capacity.

In terms of the 3-chloro phenol solution concentration, immersion enthalpies show a tendency similar to the isotherm curve and the data are fitted to a Langmuir-type linearization that allows the maximum immersion enthalpy to be calculated at a value of 41.67 J $g^{-1}$.

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