IMMERSION ENTHALPY OF ACTIVATED CARBON IN AQUEOUS SOLUTION OF 3-CHLOROPHENOL

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Introduction

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 [1] 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 [2]. 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 [3].

In this work, the 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.

Experimental

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 1073 K during 2 hours.

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.

Acid and Basic Groups. The total acidity and basicity of the activated carbon are determined using the Boehm method [4].

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 mgL^{-1}. The samples are agitated mechanically and kept at a temperature of 298 K for a period of 72 hours 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 mgL^{-1} for the maximum adsorption pH. The immersion enthalpies are also determined for solutions of 100 mgL^{-1} up to the selected pH values. To conduct this determination, a heat conduction microcalorimeter is used with a calorimetric cell in stainless steel [5]. 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 minutes, with readings done every 20 seconds 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

Table 1. Physical and chemical characteristics of the activated carbon

Lignocelullsic material	Stone African palm
Superficial area BET (m^2g^{-1})	685
Pore volume (cm^3g^{-1})	0.42
Micropore volume (cm^3g^{-1})	0.33
Total acid groups ($mmolg^{-1}$)	0.96
Total basic groups ($mmolg^{-1}$)	0.38
pH_{PZC}	6.8

In 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.

Figure 1 shows a typical thermogram obtained with a heat conduction calorimeter Calvet type used in this work.

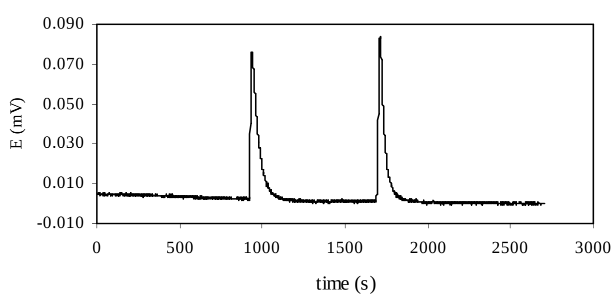

Fig 1. Calorimetric response obtained in the immersion of activated carbon in 3-chloro phenol solution

The first peak corresponds to the heat generated for the contact of the porous solids with the respective immersion liquid and the second one corresponds to the electrical calibration when an electrical work during a measured time is supplied For a relation between the areas under the peaks it is possible to determine the value of the solid immersion enthalpy.

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.

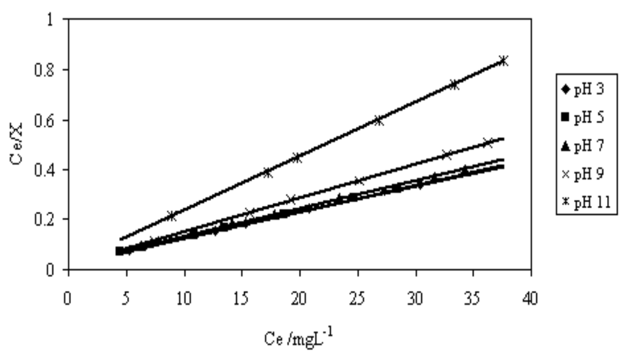

Fig 2. Lines of Langmuir model in function of the pH

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 [6]. 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 Figure 3, the relation between the immersion enthalpy of the activated carbon in 3-chloro phenol solution of 100 mgL^{-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 Jg^{-1} respectively. Given the precision of the calorimetric measure with a standard deviation of ± 1.56 Jg^{-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.

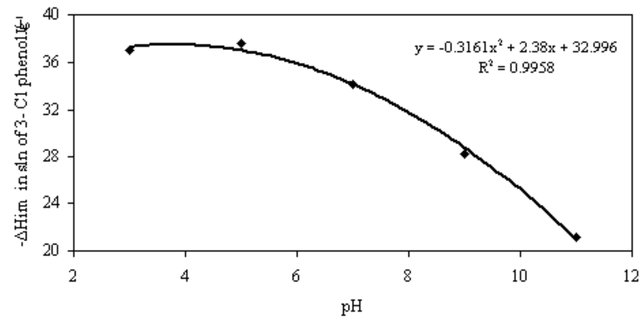

Fig. 3. Immersion enthalpies of the activated carbon in 3-chloro phenol solution of 100 mgL^{-1} in function of the pH. T 298 K

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^2g^{-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 to 11), are fitted using Langmuir model and the maximum quantity adsorbed is between 96.2 and 46.4 mgg^{-1}. In addition, the constant K_L shows values ranging between 0.422 and 0.965 Lmg^{-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 mgL^{-1} at different pH values range between 37.6 and 21.2 Jg^{-1}, which indicates that the pH of more enthalpic interaction is 5. This concurs with the values of the adsorption capacity.

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