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STUDY OF THE DESORPTION OF PHENOL AND PHENOLIC COMPOUNDS FROM ACTIVATED CARBON BY LIQUID-PHASE TEMPERATURE-PROGRAMMED DESORPTION

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Abstract—The thermal desorption in water of phenol, 2-dichlorophenol, 2,6-dichlorophenol, 4-nitrophenol and 2,6-dichloro-4-nitrophenol adsorbed onto an activated carbon is studied by temperature-programmed desorption (TPD) in liquid phase and by temperature-programmed adsorption–desorption (TPAD).

The TPAD thermograms indicate that the desorption in water of the five compounds is complete before a temperature of 300°C is reached. The five phenolic compounds are stable below 260°C.

Application of the interruption test shows that diffusion controls the desorption of these compounds in water. High-temperature adsorption isotherms and TPAD thermograms indicate that readsorption occurs during thermal desorption. Study of TPAD permits the calculation of the activation energies of adsorption and desorption. The values of these energies afford values for the adsorption bonding energy that lie within the range of the hydrogen bond. Copyright © 1996 Elsevier Science Ltd

Key Words—A. activated carbon, C. adsorption, thermal analysis, D. diffusion.

1. INTRODUCTION

Phenolic derivatives are compounds that are widely used as intermediates in the synthesis of pesticides, dyes, insecticides, explosives, etc. The degradation of these substances in the environment, with the consequent appearance of phenol and its derivatives, means that phenolic compounds can be included in a group of common environmental contaminants. A strong capacity to bind to solids leads these to being present in many substrates, and owing to their good solubility in water, they are often found as contaminants of drinking water. Different procedures designed to remove them have been proposed, although adsorption onto activated carbon is the most frequently used [1]. In this sense, the literature contains numerous references to the retention of phenolic compounds by activated carbon. Most of these have addressed thermodynamic and kinetic aspects.

Studies on desorption are, however, less numerous. The thermal desorption of these compounds in an inert atmosphere has been investigated in recent years by some authors [2–5]. Interest in thermal desorption rests on the fact that this is the basis of the thermal regeneration of spent carbon. According to those authors, during desorption physically adsorbed phenol is desorbed at temperatures below 500 K. As from this temperature, however, part of the physically adsorbed phenol reacts with oxygenated groups of the carbon, and is converted into chemically adsorbed phenol. Between 600 and 900 K, the chemically adsorbed phenol decomposes and is released in the form of light gases. Above 900 K, the chemically adsorbed phenol is degraded into condensation products and graphite [6]. These carbon residues remain on the surface of the carbon and cannot be eliminated.

In the present work, we have investigated for the first time thermal desorption in the liquid phase of five phenolic compounds adsorbed onto an activated carbon. Desorption takes place in water, that is, in the same medium in which adsorption occurs. The study was performed using temperature-programmed desorption (TPD) in liquid phase [7] and a variant of TPD; namely temperature-programmed adsorption desorption (TPAD) [8].

2. TPD STUDY

2.1 Experimental methods

Darco-activated carbon of plant origin was used. This was supplied by Aldrich and had a particle size between 20 and 40 mesh. Prior to use, the activated carbon was repeatedly washed with boiling distilled water and dried in an oven at 150°C. Characterization of the activated carbon by the physical adsorption of N_2 at 77 K indicated that it was a microporous carbon with a BET surface area of 621 $m^2 g^{-1}$.

Phenol (Ph) and the phenolic compounds 2-chlorophenol (ClPh), 4-nitrophenol (NPh), 2,6-dichlorophenol (DClPh) and 2,6-dichloro-4-nitrophenol (DClNPh) were supplied by Merck and Fluka and were purified according to the procedures described by Perrin and Armarego [9]. Bidistilled water degassed with helium was used in all the solutions and as the carrier liquid.

Prior to the TPD experiments, 1.5 g of dried activated carbon was placed in contact with 500 cm^3 of an aqueous solution of the compound in question. The concentrations of these solutions ranged between 3.0×10^{-3} and 4.0×10^{-3} M for Ph, 2.0×10^{-3} and 5.0×10^{-3} M for ClPh, 2.0×10^{-3} and 4.0×10^{-3} M

for DClPh, 1.0×10^{-3} and 2.0×10^{-3} M for NPh, and 0.5×10^{-3} and 1.0×10^{-3} M for DClNPh. Periodic analyses of these solutions furnished information about the amount of substance adsorbed. When the amount adsorbed was close to the desired amount, the carbon was removed from the solution and washed several times with distilled water. The aim of the washing processes was to remove the phenol bathing the surface, which was not truly adsorbed. The exact initial amount of adsorbate was determined by spectrophotometric analysis of the solution and of the washing water.

Following this, the carbon was dried in an oven at 60°C for 2 hours and stored in a desiccator until use. The size of the samples thus prepared was sufficient to carry out all the experiments that required the same amount of initial adsorbate.

The equipment used for the TPD experiments in liquid phase was a patented model that was constructed at the University of Salamanca [7]. A scheme and a description of its manipulation have been published elsewhere [10]. The apparatus works with flow rates of 0–10 cm³ min⁻¹ of carrier liquid under conditions of high pressure (0–300 atm), with which TPD is made to take place in the liquid phase. The temperature range at which the apparatus functions is 0–350°C. It has a temperature programmer with a PID microprocessor, with which heating rates from 0 to 10°C min⁻¹ are achieved.

The desorption chamber used was a quartz-lined stainless steel cylinder measuring 2.5 mm i.d. and 35 mm length. A Shimadzu UV–visible spectrophotometer with a 1.0 cm optical path flow microcuvette was used as a detector. The detector signal is proportional to the desorption rate because a flow system is used.

In order to prevent possible oxidation or other reactions, both of the carbon and of the phenolic compounds, the distilled water used as carrier liquid had previously been distilled twice and degassed with helium. The thermal stability of the phenolic solutions was studied in different ways. One way involved passing solutions of the compounds under study through the oven at different temperatures, then checking the stability of the detector signal at the working wavelength. The complete UV–visible spectra of samples desorbed during a TPD experiment controlling the emission of gases were also recorded. These studies confirmed that decomposition reactions can only take place above 260°C. In no case was the emission of gases detected at the temperatures assayed.

2.2 Results

Figure 1 shows the desorption thermograms of the phenolic compounds assayed under similar experimental conditions (flow rate F = 3.5 cm³ min⁻¹; mass of adsorbent w = 0.0350 g; heating rate β = 2.20°C min⁻¹). In all cases a single maximum is seen; this is broad and poorly defined for the case of DClPh. As
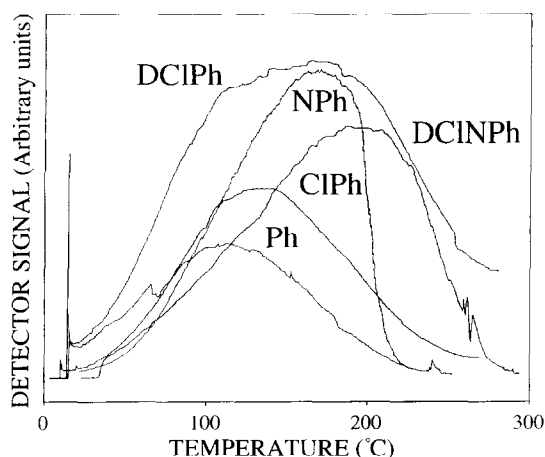

Fig. 1. Desorption thermograms of phenolic compounds from activated carbon.

the number of substituents of the benzene ring increases, this maximum is shifted to higher temperatures, indicating an increase in the stability of adsorbate–surface bonding. In all cases, TPD is only completed above a temperature of 300°C.

These TPD thermograms are very different from those obtained by Ferro-García [5] in the gas phase. In this case, the desorption thermograms had more than one peak, these being attributable to physical and chemical sorption processes. Thermodesorption continued to temperatures above 700°C and was not complete. Additionally, at temperatures above 227°C, alterations in the phenol adsorbed began to be detected.

One of the main applications of TPD is the determination of the activation energy of desorption, which is directly related to the energy that keeps the adsorbate bound to the surface.

The most commonly used procedure for determining this energy is based on the change in the position of the maximum of the desorption thermogram when the heating rate is varied. The plot of $\ln(\beta/T_M^2)$ against $1/T_M$, where β is the heating rate and T_M is the temperature at which the maximum appears, should be a straight line. The activation energy of desorption can be obtained from the slope. The model on which this procedure is based considers simple desorption [11,12]. As reported by the authors of the method, it may be difficult to apply to peaks with a low amount of adsorbate. However, for a large number of desorptions, the method of heating-rate variation may provide an excellent technique for measuring activation energies. It is also valid for desorptions of different kinetic orders and for cases in which the activation energy changes with the amount of adsorbate [12,13].

In this work, the method was applied by performing experiments at a constant initial amount of adsorbate and systematically varying the heating rate.

The flow rate of the carrier liquid was always 3.5

cm^3 min^{-1} and the amount of sample 0.0350 g. The heating rate was varied from 0.76 to 3.9°C min^{-1}. In all cases, an increase in the heating rate was accompanied by an increase in the height of the thermogram and a shift in the position of the maximum to higher temperatures.

Figure 2 shows the plot of $\ln(\beta/T_M^2)$ against $1/T_M$ for some phenolic compounds. Table 1 shows the results of this study for the four phenolic compounds assayed at different initial amounts of adsorbate, N_0. In the case of Ph, ClPh and DClNPh, the calculated activation energy was seen to decrease when the initial amount of adsorbate increased. This dependence was especially pronounced in the case of DClNPh. In contrast, the activation energy of NPh increased with the initial surface coverage. It should be stressed that the activation energies obtained for NPh and for low initial amounts of DClNPh seem to be high if one admits the most commonly accepted hypothesis that the adsorption of Ph and its derivatives occurs through a hydrogen bond [14].

The model employed to calculate the activation energy does not consider the presence of other phenomena during desorption, such as diffusion and readsorption. As detailed in the sections below, these phenomena are observed in TPD experiments.
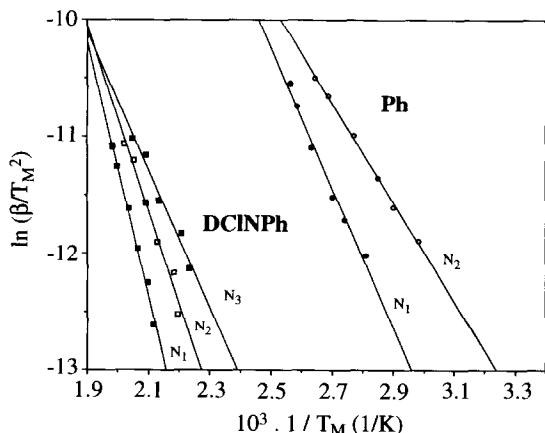

Fig. 2. Determination of activation energy of desorption following the method of varying the position of the maximum as a function of the heating rate.

Table 1. Determination of activation energy of desorption of phenolic compounds on activated carbon using the method of change in the position of the maximum of thermogram by varying heating rate

Compound	$10^5 \times N_0$ (mol)	E_d (kJ mol^{-1})
Ph	1.74	49.7
	2.60	35.0
ClPh	1.50	39.7
	2.89	37.9
NPh	0.29	90.7
	0.63	111.1
	0.15	89.5
DClNPh	0.67	65.4
	1.59	48.7

Accordingly, the energies shown in Table 1 do not correspond to an activation energy of desorption but rather to the energy of the overall process. This would account for the high values obtained for some of the compounds.

3. DIFFUSIONAL PHENOMENA

Another aspect that may seriously affect TPD experiments is intraparticular diffusion of the adsorbate when it leaves the internal surface of the adsorbent. This kind of effect was first analyzed by Cvetanovic and Amenomiya [15], and is also reflected in changes in the position of the maximum and in the shape of the curve. From an experimental point of view, these effects can be partly controlled by using low heating rates that decrease the desorption rate, preventing diffusion from being the limiting step.

With the advances made in research into TPD over the years, different assays have been proposed for detecting the presence of diffusional limitations. Such methods are generally based on the effect caused by the variation in the particle size of the adsorbent on the thermogram [16]. On other occasions, when the kinetics of adsorption on porous adsorbents are being studied, the "interruption test" has been used [17]. This consists of removing the adsorbent from the bulk solution. After some time, the adsorbent is submerged again, adsorption thus continuing. If the adsorption rate is controlled by diffusion, the time of interruption will permit a restructuring of the concentration gradients inside the pores. Thus, the adsorption rate observed as adsorption progresses is greater than that seen at the moment of interruption.

In the present work, we adapted this test to TPD experiments. To do so, it sufficed to stop the increase in temperature in one experiment for desorption to take place under isothermal conditions, and to stop the flow of carrier liquid at a present time. In all cases, 0.0350 g of activated carbon saturated with each phenolic compound was placed in the desorption chamber and a stream of carrier liquid was passed through at a flow rate of 3.5 cm^3 min^{-1}.

Figure 3 shows the results of applying this test to Ph, ClPh, and DClPh. Initially, temperature increased linearly up to 70°C, thereafter remaining constant. An increase was observed in the desorption rate when the flow of carrier liquid was resumed, after interruption times of about 20 minutes.

Figure 4 shows the result obtained on applying the same test to NPh and DClNPh. At 70°C, no alterations occurred in the development of their rate when the flow of carrier liquid was resumed. However, when the test was applied at 125°C, at which temperature the desorption rate was appreciable, diffusional effects began to be detected.

The results of applying the interruption test clearly show that the desorption of these compounds during TPD experiments is diffusion-controlled.
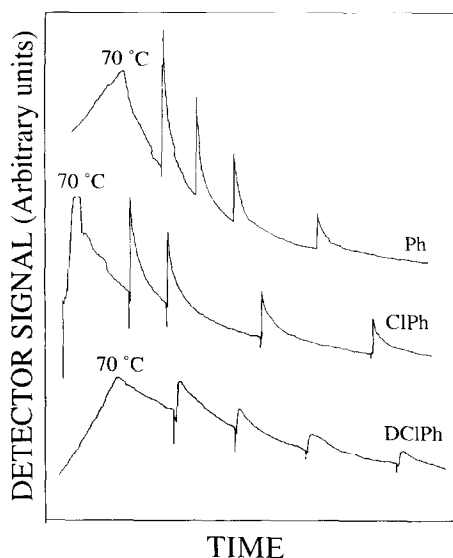
Fig. 3. Interruption tests in the isothermic desorption of phenol, 2-chlorophenol and 2,6-dichlorophenol from activated carbon. Interruption steps of 20 minutes.
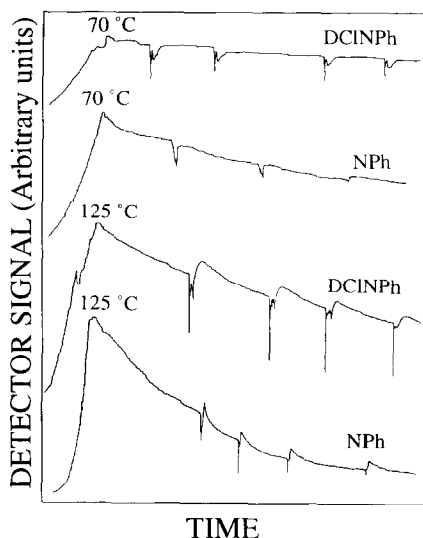

Fig. 4. Interruption tests in the isothermic desorption of 4-nitrophenol and 2,6-dichloro-4-nitrophenol from activated carbon. Interruption steps of 20 minutes.

4. TPAD STUDY

The high values of the energies derived from the TPD study, together with the existence of diffusion phenomena, indicate that desorption occurs through a complex process. Accordingly, we propose the use of the TPAD technique for calculating the activation energies of adsorption and desorption. This technique is a variation of the TPD procedure developed by our team [8,18], and consists of passing a stream of adsorptive at constant concentration through fresh adsorbent, then recording, under thermoprogrammed conditions, the rate of both adsorption and desorption. Experimentally, this is carried out by changing

the carrier liquid for a solution of adsorptive and then proceeding as for a TPD experiment.

At the beginning of the experiment, when the adsorbent is free and temperature is low, the surface begins to become occupied, capturing adsorbate from the circulating solution and producing a net adsorption process. However, if the experiment is continued, a point arrives when the saturation of the adsorbent is considerable and the temperature is high enough for the opposite process to occur; the adsorbent desorbs part of the adsorbate, yielding it back to the solution.

The spectrum of TPAD (Fig. 5) clearly shows these two stages of the process, the first with a net balance in favour of adsorption and the second with a net balance favourable to desorption.

4.1 Determination of the activation energy of adsorption

One of the advantages of the TPAD technique is that it also yields information about the adsorption process, thus permitting one to calculate the activation energy of adsorption. The model considers that adsorption and desorption coexist throughout the experiment.

The rate equation for a temperature-programmed adsorption–desorption process in a flow system is:

$$v(t) = \frac{dN}{dt} = F(C_0 - C) = k_a(N_0 - N)C - k_d N \quad (1)$$

where N is the amount of substance adsorbed at time t, C_0 is the concentration (constant) of the solution before it is passed through the adsorbent, C is the concentration of the solution at time t after passing through the adsorbent, F is the flow rate of the
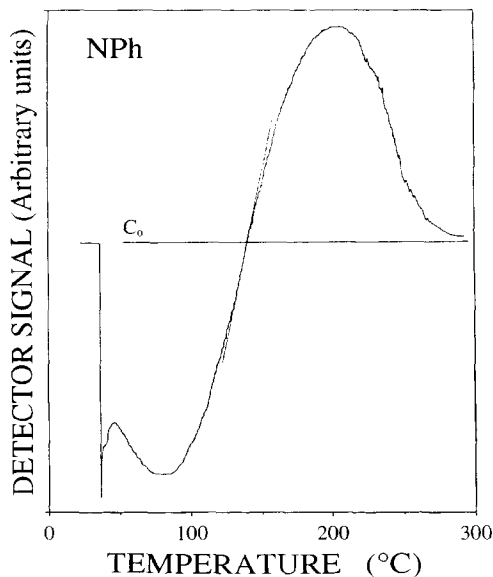

Fig. 5. TPAD thermogram of 4-nitrophenol on activated carbon. $C_0 = 1.12 \times 10^{-4}$ mol dm^{-3}, $F = 4.82 \times 10^{-5}$ dm^3 s^{-1}, mass of adsorbent $= 0.0350$ g, $\beta = 3.952°$C min^{-1}.

circulating solution, N_0 is the amount of substance that the sample of adsorbent would be able to adsorb when it is placed in contact with a solution of very high concentration, and k_a and k_d are the rate constants of adsorption and desorption, respectively. Operating, one obtains:

$$\frac{C_0 - C}{C} = \frac{k_a}{F} N_0 - N\left(\frac{k_a}{F} + \frac{k_d}{FC}\right) \qquad (2)$$

This equation relates the experimental variables N, C and temperature T. k_a and k_d are related to T by the Arrhenius equation $k = A \exp(-E/RT)$. The intercept of the plot of $(C_0 - C)/C$ against N is the value of $k_a N_0/F$.

Figure 6 shows the plot of eqn (2) for five simulated experiments (continuous line) in which the heating rate β was varied while N_0, F and C_0, together with the activation parameters A_a, A_d, E_a and E_d, were assumed to be constant. In these curves, points of the same temperature were chosen.

Figure 6 also shows the fitting of these isothermal points (broken line) to a second-order polynomial and their extrapolation to $N = 0$. The ordinates at the origin of these polynomials of isothermal points will coincide with the values of $k_a N_0/F$ at these temperatures.

On applying the Arrhenius equation to all these intercepts:

$$\ln(\text{intercept}) = \ln\frac{A N_0}{F} - \frac{E_a}{R}\frac{1}{T} \qquad (3)$$

it is possible to obtain the activation energy of desorption from the slope of the plot of ln(intercept) against $1/T$. This procedure for the determination of E_a proved to be wholly satisfactory for the simulation data.

This method was used to calculate the activation energies of adsorption of the phenolic compounds studied. Four TPAD thermograms, with the same amount of adsorbent (0.0300 g) and the same experi-
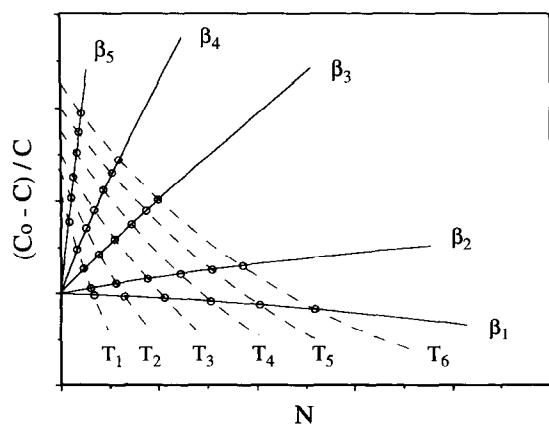
mental conditions ($F = 3.5$ cm^3 min^{-1}, $C_0 = 6.4 \times 10^{-4}$ mol of Ph dm^{-3}, 5.05×10^{-4} mol ClPh dm^{-3}; 1.06×10^{-4} mol NPh dm^{-3}, 4.36×10^{-4} mol DClPh dm^{-3} and 7.47×10^{-5} mol DClNPh dm^{-3}), were obtained for each compound, varying only the heating rate ($\beta = 0.44$, 1.10, 2.19 and 3.95°C min^{-1}).

Figure 7 shows the plot of $(C_0 - C/C)$ against N for the case of NPh and Ph. This figure also shows the fitting of isothermal points to a second-order polynomial. In the case of Ph, only the extrapolation of the isothermal points has been drawn since they lie on almost the same curve. The temperatures chosen for the isothermal points were distributed homogeneously in a temperature range between 15 and 45°C. The values of the variables C and N necessary to construct the above plot were taken from the thermogram. For each of the temperatures chosen, C is read directly and the value of N is obtained by graphic integration of the thermogram.

The plots of ln(intercept) for the five phenolic compounds studied against the reciprocals of temperature, in agreement with eqn (3), are shown in Fig. 8. The values of the activation energies of adsorption obtained are shown in Table 2.

The activation energy of adsorption values of these compounds are low. A clear dependence of these values on the structure of the compounds adsorbed can be seen, together with an increase in energy as the degree of substitution increases. The behaviour of Ph is striking in the sense that at any temperature the ordinate at the origin of the plot of $(C_0 - C/C)$ against surface coverage (Fig. 7) is always the same; that is, the adsorption rate constant does not change with temperature. The Arrhenius plot for this case is a horizontal line, such that the activation energy of adsorption is almost zero (Fig. 8).

The fact that the adsorption energies are so low indicates that the adsorption process is strongly favoured, above all in the case of Ph. Accordingly, it is likely that readsorption phenomena will always be present in TPD processes.

The existence of readsorption phenomena in TPD is also confirmed by other experimental observations. In the TPAD experiments, the balance in favour of adsorption persists until high temperatures are reached (Fig. 5). Additionally, the adsorption isotherms in liquid phase for these compounds at high temperatures indicate the existence of an adsorption–desorption equilibrium (Fig. 9). These adsorption isotherms were obtained using the TPD apparatus. To do so, a sample of fresh adsorbent was placed inside the column. The oven temperature was kept constant and a solution of the chosen phenolic compound was made to recirculate through a closed system until the equilibrium concentration had been reached. The amount of substance adsorbed was determined by the difference between the initial concentration of the solution and the equilibrium concentration.
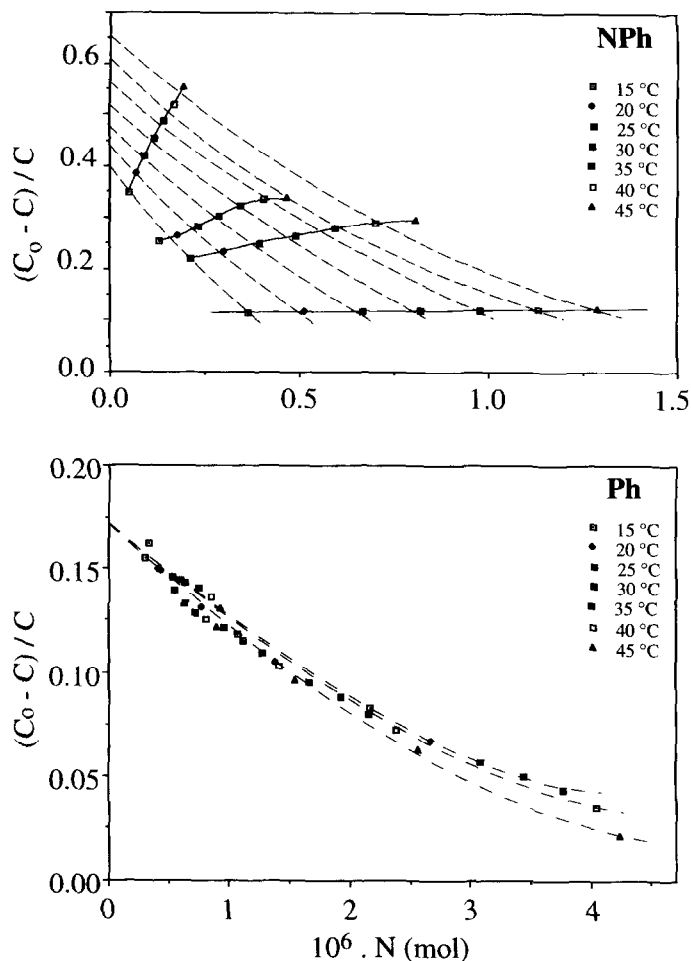

Fig. 6. Plot of $(C_0 - C)/C$ against N from five simulated TPAD experiments at different heating rates and extrapolation of isothermal points $N = 0$.

Fig. 7. Plot of $C_0 - C/C$ against N for the TPAD of phenol and 4-nitrophenol on activated carbon and extrapolation of isothermal points $N = 0$.
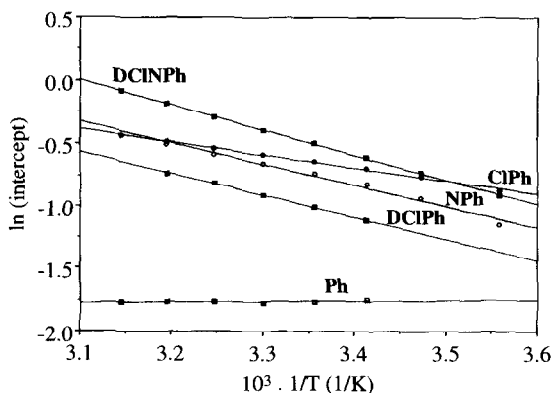

Fig. 8. Determination of activation energy of adsorption according to the Arrhenius plot of some phenolic compounds adsorbed on activated carbon.

Table 2. Values of activation energy of adsorption of phenolic compounds on activated carbon using TPAD

Compound	E_a (kJ mol^{-1})
Ph	0
ClPh	8.5
DClPh	14.5
NPh	14.1
DClNPh	16.4

4.2 Simultaneous determination of the activation energies of adsorption and desorption

Calculation of the kinetic activation parameters involved in the adsorption process is hindered when the process is diffusion-controlled. In these cases, it is necessary to study the system under experimental conditions in which diffusional resistance can be minimized [19]. The usual procedure to achieve this is to work with small heating rates [20]. Despite this, however, it is often impossible to avoid such effects.

In the TPAD thermograms there is a point at which there is no mass transfer between the adsorbent and the solution, such that at that moment in time no diffusion occurs. This point corresponds to a situation of thermodynamic equilibrium in the system. It may be assumed that in the neighbourhood

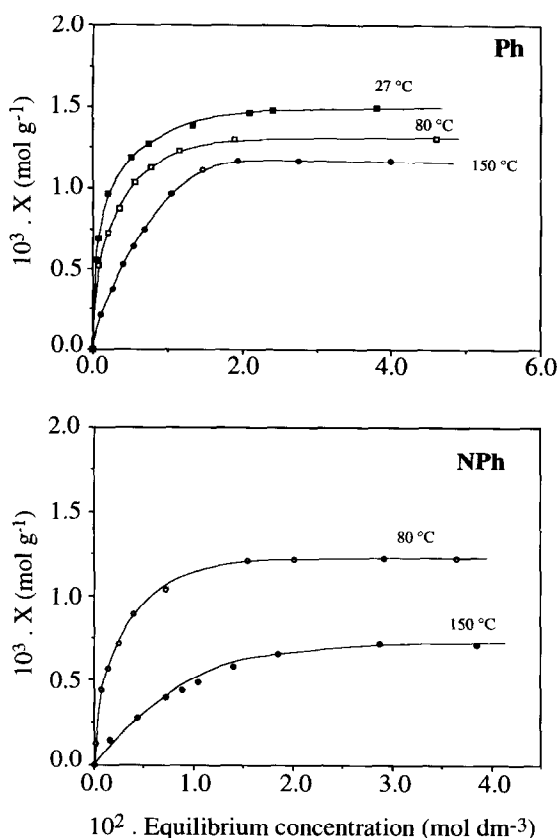10^2 . Equilibrium concentration (mol dm^{-3})

Fig. 9. Adsorption isotherms of phenol and 4-nitrophenol.

of this point, diffusion will continue to be nil or very low.

The equation that describes the thermogram in this zone can be written assuming only adsorption and desorption:

$$v(t) = \frac{dN}{dt} = \frac{dN}{dT} \beta = k_a(N_0 - N)C - k_d N$$

where β is the heating rate: $\beta = dT/dt$.

The rate of the process as a function of temperature can be written thus:

$$v(T) = \frac{dN}{dT} = \frac{k_a}{\beta}(N_0 - N)C - \frac{k_d}{\beta} N \qquad (5)$$

Deriving eqn (5) with respect to temperature, one obtains:

$$v'(T) = \frac{k_a'}{\beta}(N_0 - N)C - \frac{k_a}{\beta} CN'$$

$$+ \frac{k_a}{\beta}(N_0 - N)C' - \frac{k_d'}{\beta} N \frac{k_d}{\beta} N' \qquad (6)$$

where $v'(T)$, K_a', K_d', C' and N' are the derivatives with respect to the temperature of $v(T)$, k_a, k_d, C and N respectively.

A mass balance of the adsorption–desorption pro-

cess would be:

$$C = C_0 \frac{\beta}{F} \frac{dN}{dT} \qquad (7)$$

where C_0 is the concentration of recirculing solution before it flows through the adsorbent, and F is the flow rate.

Deriving eqn (7) with respect to temperature, one obtains:

$$C' = -\frac{\beta}{F} v'(T); \qquad v'(T) = -\frac{C'F}{\beta} \qquad (8)$$

eqn (6) and eqn (8) lead to:

$$C' = \frac{k_a'}{F}(N_0 - N)C - \frac{k_a}{F} CN'$$

$$+ \frac{k_a}{F}(N_0 - N)C' - \frac{k_d'}{F} N - \frac{k_d}{F} N' \qquad (9)$$

At the point of thermodynamic equilibrium, one has: $C = C_0$, $dN/dT = 0$, $k_{a_e}(N_0 - N_e)C_0 = k_{d_e}N_e$, $k_a' = k_{a_e}(E_a/RT_e^2)$, $k_d' = k_{d_e}(E_d/RT_e^2)$. eqn (9) at that point becomes:

$$C_e' = \frac{E}{RT_e^2}\left(\frac{1}{\dfrac{F}{k_d^e N_e} + \dfrac{1}{C_0}} \right) \qquad (10)$$

where $E = E_a - E_d$, C' is the slope of the straight line tangential to the TPAD curve at that point, m_e, and N_e is the number of moles adsorbed at the equilibrium point. eqn (10) becomes:

$$k_{d_e} = \frac{F}{N_e}\left(\frac{1}{\dfrac{E}{m_e RT_e^2} - \dfrac{1}{C_0}} \right) \qquad (11)$$

This expression relates the desorption rate constant at the point of thermodynamic equilibrium to the adsorption bonding energy, E, and the variables of the process at that point.

The values of the parameters E_a and E_d can be determined with the following procedure. The values of k_{d_e} are calculated from the TPAD thermograms with equilibrium points at different temperatures and assuming a given value for E, according to eqn (11).

The values of k_{d_e} are correlated with temperature by the Arrhenius equation:

$$\ln k_{d_e} = \ln A_d - \frac{E_d}{R} \frac{1}{T_e} \qquad (12)$$

The best fit of this correlation for different values of E assayed determines the value of E_d and E.

According to this method, a set of thermograms was obtained for the five phenolic compounds assayed, in which the amount of adsorbent was kept constant and the concentration of the adsorptive, flow rate or the heating rate were varied. Figure 5 shows one of the thermograms.

Temperature (T_e) can be read directly in the TPAD thermogram at the point at which the curve intersects

with the value of the initial concentration of the adsorptive stream. The number of moles adsorbed up to the point of equilibrium, N_e, was determined by analysis of the solution collected until the point of thermodynamic equilibrium was reached, and the slope value, m_e, was calculated graphically by tracing the tangent to the curve at the point of equilibrium. The values of the adsorption bonding energy, the assumed E, ranged between 5 and 60 kJ mol^{-1}. These values sufficed to find the best fit. In fact, the values obtained lay between 25 and 58 kJ mol^{-1}.

The optimum value of E was determined by correlating $\ln k_{d_e}$ with $1/T_e$, in accordance with the Arrhenius equation (eqn (12)). The criterion chosen to discriminate the best fit was the lowest sum of quadratic deviation. The optimum correlations for the five compounds assayed are shown in Fig. 10. From the slopes of these correlations one obtains the activation energies of desorption, E_d, which, together with the value of E, allow one to calculate E_a. These values are shown in Table 3.

The values of E_a are small but increase with the increase in the degree of substitution of the benzene ring. The fact that they are low explains why readsorption can occur during the TPD process.

The values of E_d range between 26.2 (Ph) and 74.0 kJ mol^{-1} (DClNPh). The relationship between E_d and the structure of the compound adsorbed is not as clear as that observed for the values of E_a.
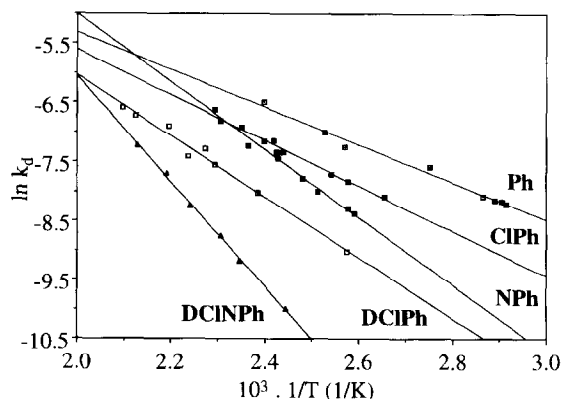
The adsorption bonding energies obtained give

Fig. 10. Determination of activation energy of desorption according to the Arrhenius plot of some phenolic compounds adsorbed on activated carbon.

Table 3. Values of activation energies of adsorption and desorption of phenolic compounds on activated carbon

Compound	E_a (kJ mol^{-1})	E_d (kJ mol^{-1})	$E = E_d - E_a$ (kJ mol^{-1})
Ph	1.2	26.2	25.0
ClPh	6.8	31.8	25.0
DClPh	15.5	42.6	27.1
NPh	12.1	47.5	35.4
DClNPh	17.7	74.0	57.3

values within the range of energies assigned for hydrogen bonds. The hypothesis of adsorption through hydrogen bonds for these compounds is the one most widely accepted [14,21,22]. This hydrogen bond may be formed through the formation of donor–acceptor complexes between the OH group of the adsorbate and groups present on the surface of the carbon. It has also been reported that the donor–acceptor complex could be formed through the π electrons of the aromatic ring. Additionally, it is seen that this energy does not increase with ring substitution, but rather with the increase in the electrophilic nature of the substituents. Analysis of this in the compounds studied reveals that the NO$_2$ group exhibits a negative inductive effect, favouring the displacement of electrons and giving rise to a charge defect precisely in the ortho- and para- positions, such that the hydrogen bond would be strengthened in the case of NPh. The chlorine atom also exerts a negative inductive effect by withdrawing electrons from all the positions of the ring, such that DClPh would be expected to display a stronger hydrogen bond than NPh. However, the adsorption energy obtained is lower. These results can be explained if it is taken into account that the negative inductive effect of the chlorine atom is partially compensated by a positive electromeric effect arising from the existence of non-competing electron couples in the chlorine atom (mesomeric effect).

On comparing these activation energies of adsorption with those shown in Table 2, good agreement is found. However, one would expect a discrepancy between the results of both methods, since in the first case the presence of diffusional effects was not taken into account. Despite this, owing to the characteristics of the method, which uses the adsorption rate at an amount of adsorbate tending towards zero, one can consider that at those moments no control owing to diffusion would exist. Adsorption would therefore occur on the external surface of the adsorbent.

It was also considered useful to perform a comparative study of these activation energies of desorption with those obtained in the TPD study; the results are shown in Table 1. These results clearly differ from those offered in Table 3. Such discrepancies can be explained taking into account that the method used to vary the heating rate is based on a very simplistic model that does not consider readsorption or diffusion. The values obtained there would correspond to an activation energy of the overall process, such that higher values would be expected. In the light of this, we feel that the method used for varying the heating rate should not be applied to the desorption of phenolics in solution from activated carbon.

5. CONCLUSIONS

In the present work, the thermal desorption of phenols in liquid phase from activated carbon has been analyzed.

The TPD thermograms obtained in liquid phase are different from those found in the literature for the gas phase. Thermodesorption in liquid phase is completed at lower temperatures, indicating greater ease of desorption under these conditions.

Study of TPD and the interruption test confirmed the complexity of the desorption mechanism, the existence of diffusion control and readsorption being detected.

Use of the TPAD technique to determine the bonding energy of adsorption is especially useful in these systems with readsorption and diffusion. The results obtained using the technique afford values of adsorption energies that lie within the range of the energies of the hydrogen bond. Additionally, it confirmed that these energies are directly related to the electrophilic character of the substituents (Ph < ClPh < DClPh < NPh < DClNPh), but not with the degree of substitution of the benzene ring.

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