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ORGANIC POLLUTANTS ADSORPTION ONTO GRANULAR ACTIVATED CARBON

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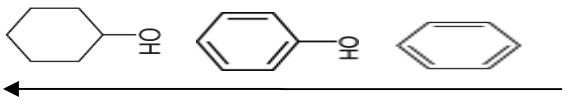
The industry uses benzene as a solvent and raw material for organic synthesis and therefore occurs in releases, phenol is also likely to exist in water of industrial origin, it oxidizes with difficulty, adsorbs little and filter weakly. Cyclohexanol is amphoteric (donor and proton acceptor), it was chosen to make comparisons. In the present work, the granular activated carbon chosen was characterized by different methods. The kinetic adsorption study, in the liquid phase, was conducted using adsorbed quantity - square root of the contact time to elucidate the diffusion of these molecules through the liquid film to the superficial sites of the surface of the solid, which allowed us to understand the influence of some physicochemical properties and the structure of choices molecules on the phenomenon of elimination of pollutants. The results obtained illustrate the competitiveness and adsorption specificity of the molecules as a function of the structure, the grouping, the affinity towards the solid and the porosity of the surface of the latter. The results showed that the molecules chosen are preferentially physisorbed, although some chemisorption can be detected. We have been able to measure the surface tensions by the method of tearing off the ring in order to reach the surface occupied by each of the molecules at the level of the surface of the coal. In this study we assume that the external resistance to mass transfer from the liquid to the surface can be neglected as a control step.



INTRODUCTION

The importance of water in the economy continues to grow. The supply of fresh water becomes increasingly difficult as a result of rising demographics, standard of living and modern industrial techniques. Water was the first environment to be affected by industrial and household discharges. It was undoubtedly the most affected by the pollution problem.[1] The phenol likely to be encountered in water is generally of industrial origin, it is difficult to oxidize, adsorbs little and filters very easily, a greater solubility in water is an increased ability to dissolve polar organic molecules. Benzene is the simplest aromatic hydrocarbon, isolated from tar. It is widely used as a solvent and a raw material for organic synthesis. Cyclohexanol is a secondary alcohol, able to play an acid role (proton donor) or basic (proton acceptor). The crucial problem that currently arises is the purification of water by efficient and economical methods.[2,3]

The adsorption of pollutants or toxic chemicals on an adequate solid seems to be one of the most used processes in the field of waste water treatment, desulphurisation, regeneration of solvents. Granular activated carbon, the most important commercial adsorbent, is a carbonaceous material having an important specific surface area and a high porosity. It is widely used in purification processes, water treatment and catalysis. Granular activated carbon is used as a column feed for gaseous or liquid applications and is regenerated after use. This makes granular coal a versatile adsorbent.[4,5]

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There are solids which have adsorbent properties in relation to a very large number of bodies, others on the contrary have quite marked specificities. The question that arises and to which we will try to answer and justify this specificity, to explain why a given solid is likely to adsorb certain bodies more than others. So, this work aims to, on the one hand: (*i*) the elimination of these products by adsorption on activated carbon; (*ii*) to establish a parallelism between the adsorption capacity or rate of each substance and its physicochemical properties; (*iii*) to study the mechanism of diffusion of molecules towards the surface and superficials sites actives of the solid according to the structure of the molecules of the solutes.

On the other hand, to explain the mechanism of adsorption of phenol which has been shown to be one of the most important pollutants and to see the behavior of the adsorbed layer by checking the application of the Gibbs equation which allows to evaluate the superficial excess or adsorption rate of the dissolved body, to find the molecular area and the disposition of the molecules at the interface.

We chose benzene having an aromatic ring but without functional OH group and cyclohexanol which does not have aromatic nucleus but has an OH group. These molecules are simpler, smaller and easy to analyze, which makes it possible to elucidate the arrangement of molecules on the surface of the solid as a function of their structure.[6-8]

EXPERIMENTAL

In the present work, we used molecules whose properties were grouped together in Table 1. The solvent used is water, its adsorption is the smallest (white test) at λ = 191 nm. During experiments the solubility of the molecules used was respected. The initial concentration for each of the molecules is 0.53 mmol.L^{-1}.

We chose the 2 mm size pellets which are generally used for liquids applications because the adsorption kinetics are more important than the pressure drop. The granular activated carbon prepared from Eucalyptus, a major waste from the growing Algerian wood industry, was activated, before use, as follows: bring the activated charcoal to boiling for one hour, put it in an oven at a temperature of 373 K up to that its mass does not vary anymore and end up putting it in a desiccator.[5,6] The granular char obtained is dried for 2 hours at 378 K before use.

The adsorption of the molecules, in liquid phase, was carried out at 298 K, under constant stirring, the tubes of a volume of 150 mL are placed in a thermostatically controlled tank, the volume of the solution of the different molecules is 100 mL, the activated carbon mass is 100 mg. For equilibrium studies, the duration of the experiment is 48 hours. We used the spectrophotometer UV Beckman type, model 35 with dual beams (200 - 500 nm). The solution in question is brought into contact with a constant mass of activated carbon (m = 100 g). The whole is placed in a stirred thermostatic tank (N_f = 6 turns per seconds) connected to a speed regulator allowing a good fluidization of the activated carbon particles in the center as on the walls (homogenization). At t = 0 seconds, put the amount of activated charcoal in the tank. The samples taken are 5 mL in order to have a non-variable volume resulting in a constant Reynolds.[9,10]

Table 1

Properties of the molecules

Molecule	M_m ($g.mol^{-1}$)	E_b (°C)	λ_{max} (nm)	ρ_{20} ($g.cm^{-3}$)	$Ø_{molecule}$ (nm)	Solubility ($g.L^{-1}$)
phenol	94.11	182	272	1.073	0.577	76
benzene	78.11	80.1	256	0.878	0.526	1.79
cyclohexanol	100.16	161	285	0.960	0.587	40

Table 2

Properties of the coal used

	BET ($m^2.g^{-1}$)	Micropore Volume ($mL.g^{-1}$)	Mesopore Volume ($mL.g^{-1}$)	γ_s ($mJ.m^{-2}$)
Granular activated carbon	459	0.23	0.08	51

Table 3

Elementary analysis of the coal used

	C(%)	N(%)	O(%)	H(%)	S (%)	ashes (%)
Granular activated carbon	52.50	01.00	26.60	02.40	00.00	18.50

RESULTS AND DISCUSSION

We first discussed the determination of the acid functions on the surface of the solid (Fig. 1).

As expected, a jump in pH is established but which is not very clear, the parts of the curve are divided into stages, it seems that there are, on the surface of the particles, several acidic functions. Taking into account the appearance of the curve, it is inappropriate to determine acid concentrations for each jump. The last jump, more visible compared to the others, allows to say that there is, at least, 1.85. 10^{-2} moles per gram of powder.

The adsorbent has a hydrophobic character according to the value of the surface energy measured by goniometer. From the value of the surface energy of granular activated carbon, it can be said that the surface of the coal in question is relatively "less rough", which is far from being the case. The explanation is due to the fact that there is a strong presence of air between the particles, so the measurement performed corresponds to the surface energy of the air / coal powder system. The specific surface (BET method) was determined by adsorption-desorption of nitrogen N_2. The difference between the adsorbed volume and the volume of the micropores gives the volume of the mesopres at atmospheric pressure.[5] Granular activated carbon has a large surface area and an acceptable carbon percentage (Tables 2, 3).

For the zetametry measurements, we prepared, from the granular activated carbon, a powder for the realization of a suspension which did not seem to be an easy thing. For such an analysis, the mixture formed should be slightly cloudy and stable for at least five minutes.

The suspension is introduced into a quartz cell. Inside the latter is applied an electric field that causes more or less rapid movement of particles (principle of electrophoresis). These movements are recorded using a camera and the data is processed by software (Table 4).

The average zeta potential is ξ = -19.71 mV, expressing a hydrophobic character.

After establishing the calibration curves, at λ = 272 nm, for the three molecules whose equations are: Absorbance = 1.44 * C_{Ph}, $R^{\wedge 2}$ = 0.976 for phenol, Absorbance = 0.19 * C_{Be}, $R^{\wedge 2}$ = 0.977 for benzene and Absorbance = 0.3 * C_{Cy}, $R^{\wedge 2}$ = 0.978 for cyclohexanol, we were able to trace the adsorption isotherms Qe = f (Ce) which are of type II or S, this type is encountered in the case of the multilayer phenomenon, that is to say that there is formation of a monomolecular layer and a second branch that may be due to the formation of a polymolecular layer (Fig. 2). This form explains that activated carbon is poorly porous or microporous and that the pore diameter d_p <20 nm correlates with structural analysis.

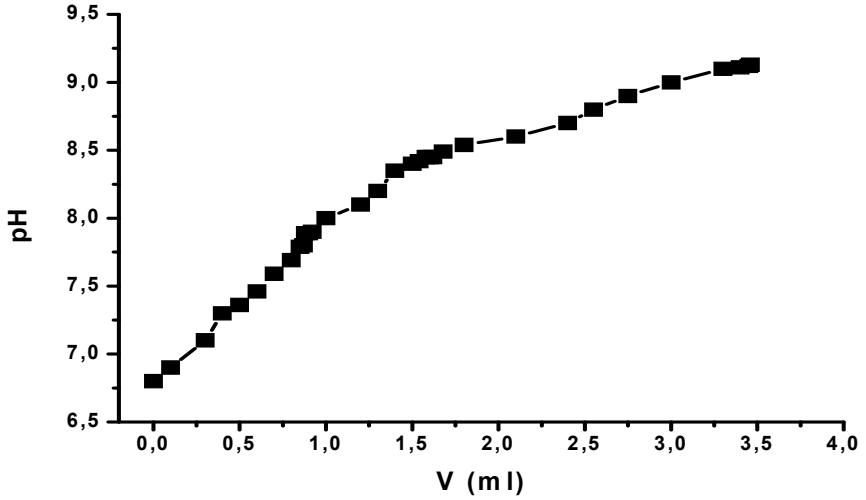


Fig. 1 – Determination of the acid functions of the coal used with a solution of ethylamine (1,5.10^{-2}M).

Table 4

Zeta Potential of Coal

Tests	**1**	**2**	**3**	**4**	**5**
Zeta potential ζ (mV)	-19.67	-19.69	-19.74	-19.71	-19.73

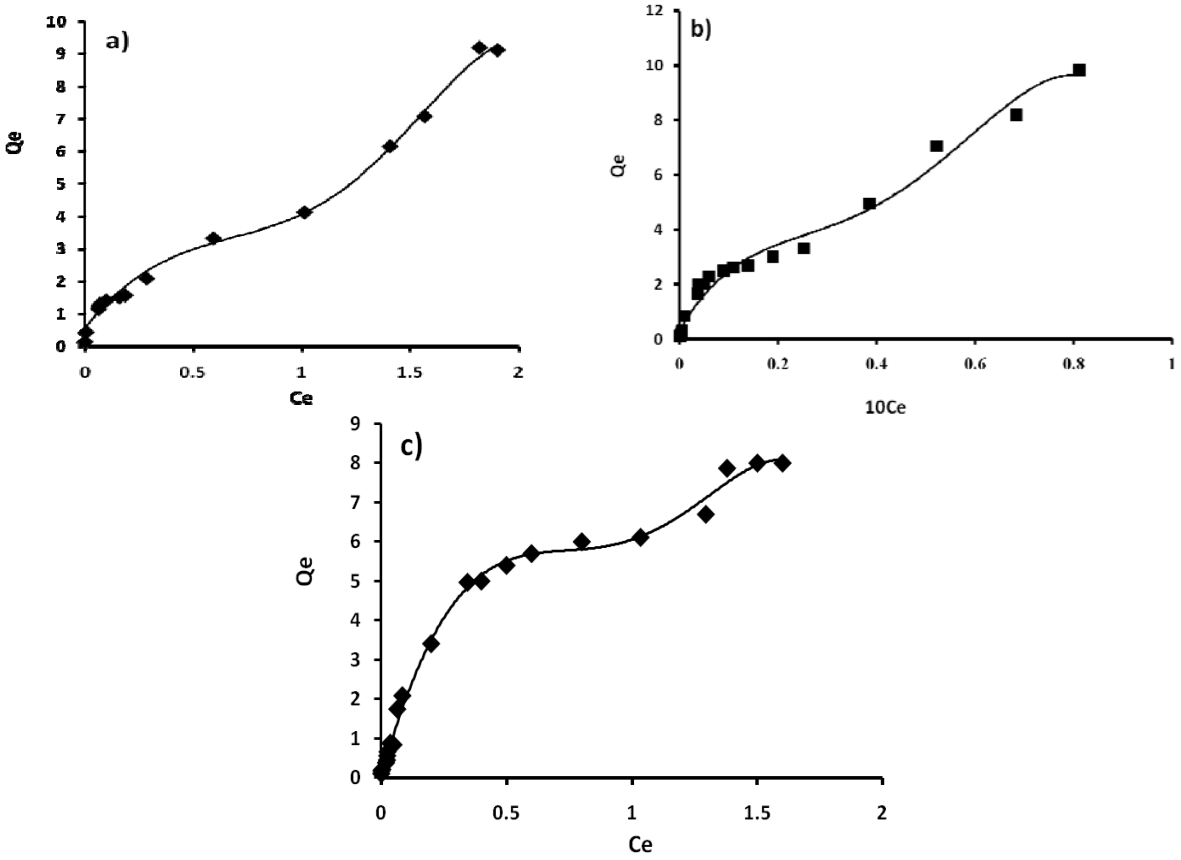


Fig. 2 – Adsorption isotherms at T = 298 K, a) benzene, b) cyclohexanol, c) phenol.

As for the study of the diffusional mechanism (Fig. 3) and in first approximation, we can say that we are in the KNUDSEN domain if the pores are less than 10nm of diameter. The linear variation is explained by the fact that access to superficial sites is through a slow diffusion mechanism.

The second part of the curve shows that we are in the ordinary domain when the pores have more than 10 nm, so our solid contains non-homogeneous pores. The greater or lesser superficial diffusion of the solute influenced the adsorption specificity of the three molecules. The diffusion of phenol is faster compared to benzene which is explained by the presence of the OH radical, but it is less diffusional than cyclohexanol since it has an aromatic nucleus. If we consider that the pore diameter does not influence the adsorption, we confront each other at two points: structure of the molecule, affinity for the adsorbent.[11–13]

The low adsorption of benzene amounts to the few mesopores while the specific adsorption of phenol and cyclohexanol is attributed to the active sites of the solid. Cyclohexanol is more soluble than phenol and benzene and appears to adsorb faster. Adsorption can be promoted by adding an electrolyte and increasing the rate of removal (Fig. 4).

For measurements of the surface tension (stirrup), it is a rectilinear wire stretched horizontally that is made to emerge in the liquid by keeping it always parallel to the surface. In this case we measured the weight of the liquid raised up to the height at which the two meniscuses thus formed are detached. The following procedure is the same for the kinetics except that with the tensiometric method the samples of 5 mL are diluted to 50 mL in order to cover the surface of the stirrup. So, the concentration deduced from the calibration curve will be multiplied by 10.[14]

The study of the behavior of the adsorbed layer by application of the GIBBS equation allowed us to have an idea about the disposition of molecules on the surface of the solid. The molecular areas found, from Γ_{max}, are: a_{Be} = 0.49 nm^2 for benzene, a_{Cy} = 0.51 nm^2 for cyclohexanol and a_{Ph} = 0.44 nm^2 for phenol. This explains the adsorption affinity of phenol compared to other molecules (Fig. 5).

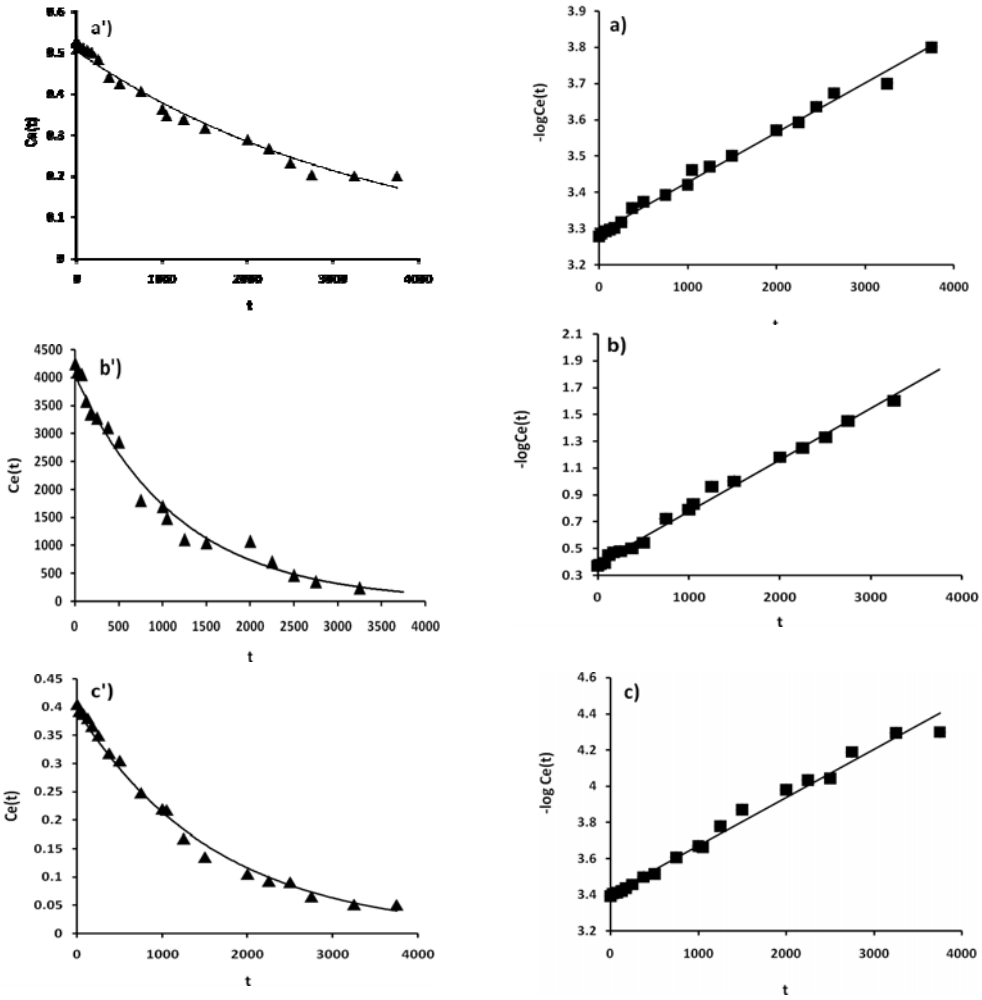


Fig. 3 – Diffusion mechanism: a) benzene, b) cyclohexanol,
c) phenol, and adsorption kinetics: a, a') benzene; b, b') cyclohexanol; c, c') phenol.

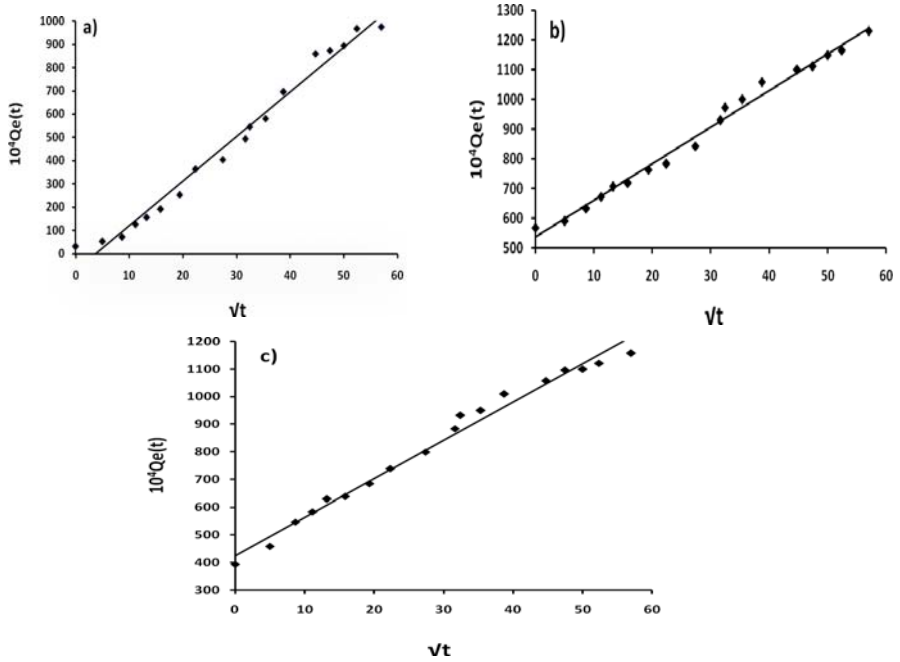


Fig. 4 – Dispersion rates within granular activated carbon grains: a) benzene, b) cyclohexanol, c) phenol.

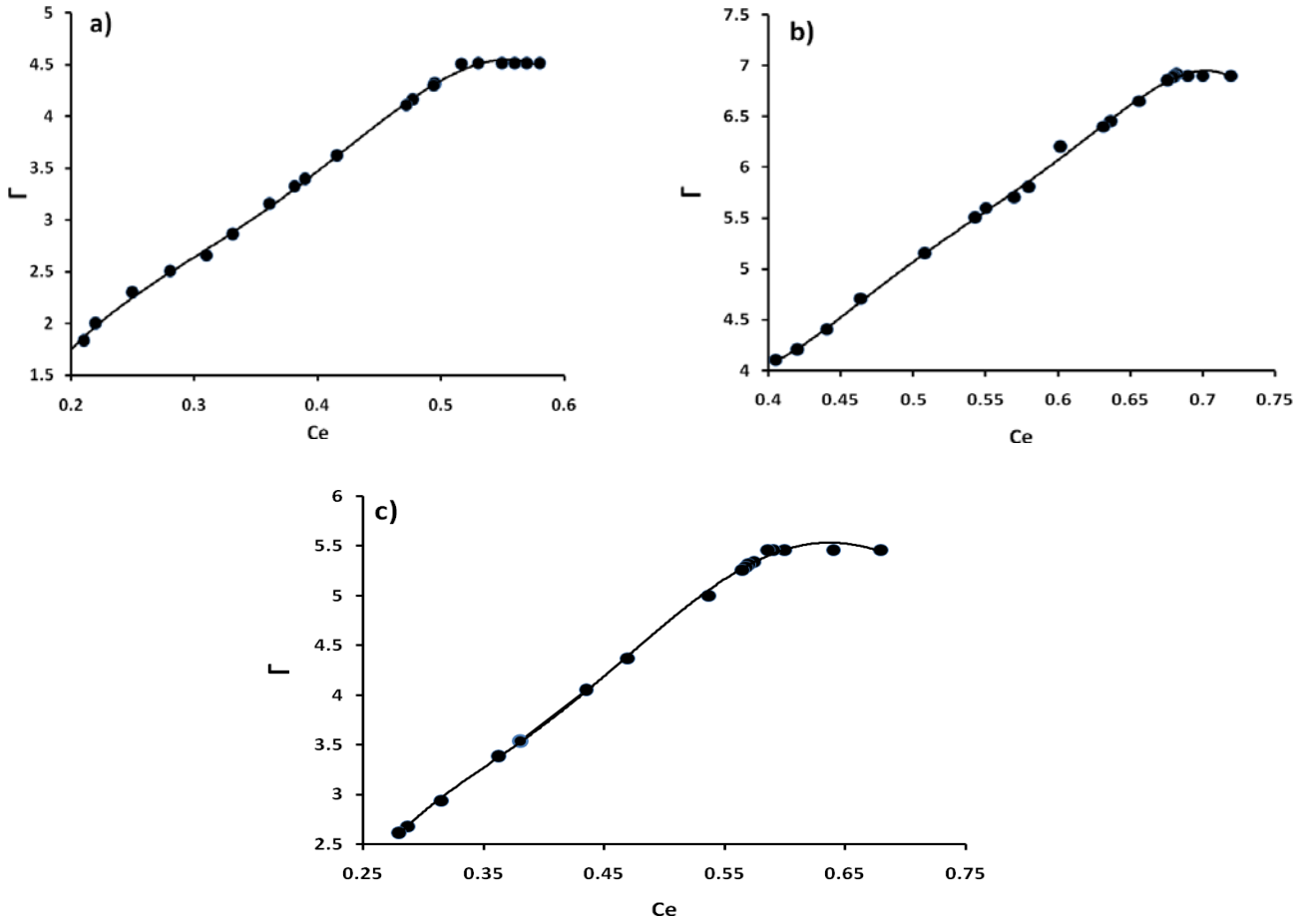


Fig. 5 – Measurement of specific adsorption areas to explain arrangement of molecules on the surface of the solid: a) benzene, b) cyclohexanol, c) phenol.

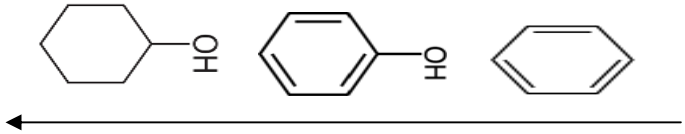
CONCLUSIONS

The adsorption of the solute is complicated by the adsorption of solvent, an immediate relationship between the structure of the solute and the solid is not always possible, which makes it difficult to make correlations.

This study allowed us to characterize our solid by different, simple and available methods, and to explain the adsorption mechanism of some organic molecules used by the industry. According to the results obtained, we can conclude that the access to the superficial sites is made by a mechanism of slow diffusion, that one is in the ordinary domain when the pores have more than 100 Å. So our solid contains non-homogeneous pores. The greater or lesser area diffusion of the solute influenced the adsorption specificity of the three molecules.[13]

The diffusion of cyclohexanol is faster compared to phenol and benzene, which is explained by the presence of the OH radical. If we consider that the pore diameter does not influence the adsorption, we confront each other at two points: structure of the molecule, affinity for the adsorbent.[15]

We can conclude that the phenomenon of diffusion is related to the affinity of the molecule in relation to the surface, the porosity of the solid and the structure of the molecule (functional group, aromatic nucleus, etc.). In view of the results obtained, the proposed order in terms of competitiveness is: cyclohexanol > phenol > benzene and that the disposition of the molecules on the surface of the coal is as follows:



It remains to make comparison with other types of local powder activated carbon.

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