



CHEMICAL AND PHYSICAL ACTIVATION OF OLIVE-MILL WASTE WATER TO PRODUCE ACTIVATED CARBONS

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Olive-mill waste water is produced in large quantities during the manufacture process of the olive oil in mills. This by-product has been used as raw material to produce activated carbons by both chemical and physical activation methods. In the first case, ZnCl_2 and H_3PO_4 were used as activating agent and in the second case, CO_2 at 600 °C for different periods of time. Obtained results indicate that the chemical activation with ZnCl_2 and H_3PO_4 at 600 °C, in an inert atmosphere, yielded activated carbons with the highest area and more developed microporosity, mesoporosity and macroporosity. Adsorption of rate of phenol onto activated olive-mill was studied as a function of several physical-chemical parameters such as temperature, initial concentration in solution and hydrodynamic conditions. Equilibrium parameters of adsorption have been determined using Langmuir constant K.

Keywords: adsorbent, valorisation, olive-mill, activated carbon, waste



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Introduction

The origin of our research has as valorisation of olive-mill in the field of effluent treatment. This waste is produced each day in huge quantities in several countries and rejected in the nature. But, currently, there is no specific utilisation for it. This type of waste has, however, all the characteristics needed to be processed by means of chemical and heat treatments, in order to produce an adsorbing material valuable in different fields because of its physical structure, its adsorbent carbon compounds and the polar and non-polar properties of its constituting molecules [1]. We have then noticed that the activated material presents an important adsorbing power toward organic compound. We decided therefore to apply this type of valorisation in the domain of liquid effluents purification. Furthermore, this type of treatment could be used with several other waste products of vegetal origin.

We must emphasise also that activated carbon is a substance of great interest, its adsorbing properties are used in to separate mineral and organic compounds or to purify liquid solutions by extraction of pollutants [2, 3]. There are numerous industrial applications for this product such as water treatment, sugar refining and precious metal recovery [4]. Activated carbon can also be used for the adsorption of numerous trace organic compounds present in treatable drinking water such as chlorinated phenol after pre-chlorinating [5, 6, 7]. Nowadays, industrial water rejects containing large quantities of phenol are of great concern. During normal activity, a refinery can reject 0,5 mg/l of phenol whereas catalytic cracking of hydrocarbons can reject up to 1 mg/l [8] knowing that the allowed phenol concentration in drinking water is up to 0,001 mg/l [9]. Among the interesting references dealing with adsorption of phenol on activated carbon, are those of the analysis of adsorption isotherms at different temperature putting into evidence a physical process [10, 11].

The making of activated carbon can be done from different materials: woods, coconut, pets, mineral carbon, bone and blood [12, 13]. Commercial activated carbons are activated under atmospheres of CO_2 , O_2 , vapour of water or other gases at temperatures between $800\text{ }^\circ\text{C}$ and $1100\text{ }^\circ\text{C}$ [14, 15] or by chemical activation using oxidising agents such as: H_2SO_4 , H_3PO_4 , HCL , NaOH [16, 17] burned after exposure to temperatures between $300\text{ }^\circ\text{C}$ and $700\text{ }^\circ\text{C}$. The activation of activated carbons causes the elimination of volatile substances and a partial internal consumption giving therefore important physical and chemical properties. Activated carbons present at their surface some functional groupings dependent on their preparation mode [18] which can be considered as adsorption sites of ions.

The objective of this work is to valorise olive-mill in the field of water treatment. We have been particularly interested in adsorption of phenol. We will present the results obtained successively for this purpose during the study of conditions of the phenol adsorption realised under static system. We would like to point out that preliminary to this study a work has been done to adapt an experimental protocol of activation. Conclusions hence established have allowed us to do our experimentation on adsorption of phenol using activated olive-mill with a maximum of information.

Experimental part

Products

Activated carbon (A) used comes from a MERCK granulated carbon (diameter between $0,4$ and $1,7\text{ mm}$) that has been grounded, and sifted to get a particle size below or equal to $50\text{ }\mu\text{m}$. The dimension of the specific area given by the manufacturer is $1100\text{ m}^2/\text{g}$, determined by B.E.T. The dimension of the specific area determined by a micro-calorimeter [19] is 1075 and the meso-porous volume between 2 to 50 nm would be 37% [20].

The activated olive-mill is finely pulverised and sifted in PROLABO equipment with AFNOR standardised sieves. The particle size is then less or equal to $50\text{ }\mu\text{m}$. Since low concentrations of activated carbon and small size particles have been used, there has not been any noticeable change in particle size of olive-mill at the end of the experiment. The phenol used comes from a PROLABO pure product (99%).

Titration

The olive-mill is mixed at $1/4$ (W/W) with a blend of chemical agents of activation ($\text{H}_3\text{PO}_4 + \text{ZnCl}_2$), and burned at $600\text{ }^\circ\text{C}$ in muffle furnace for 30 min . Assays in series of adsorption (of power activated carbon) are done on 1 l distilled water volumes ($\text{pH} = 8,5$) containing phenol at different concentrations. The mixture is stirred in an air free container and after a given period of time,

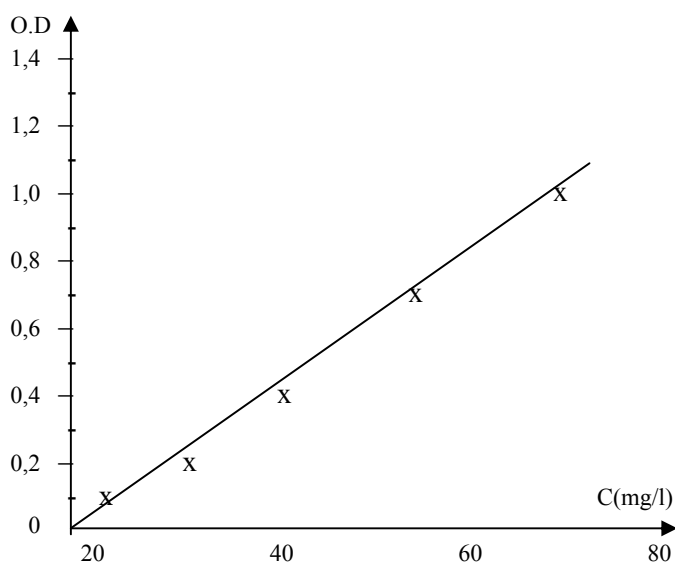
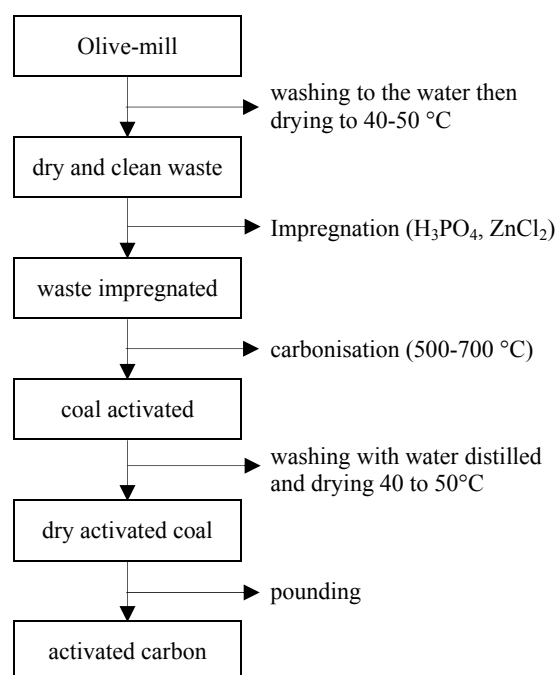


Fig. 1. Evolution of the optical density (O.D) against phenol concentration (mg / l) (C varying 0 to 60 mg / l and O.D of 0 to 1,2 to $\text{pH} = 8,5$)

filtered in a mill-porous filter. The residual concentration of phenol C_R is determined by spectrophotometer. A standard curve (Fig. 1) is then drawn by optical density (OD) at 269.7 nm of aqueous solutions of phenol at different concentrations (0 to 60 mg / l).

Preparation process of activated carbon

The raw material used is a waste of olive-mill. This product must undergo several treatments that will affect drastically its physical-chemical properties which become more efficient to the de-pollution of waters.



Schema. Preparation process of activated carbon from coffee grounds

Adsorption capacity of the activated olive-mill

The adsorption capacity depends on several parameters. Hence, in order to understand the mechanisms of optimal usage of the adsorbent, it was necessary to study the effects of these parameters. Some assays on activation of olive-mill have taken place and given the following results.

- Carbonisation temperature 600 °C
- Carbonisation time period 30 min
- The mass ratio $\frac{\text{coffee grounds quantity}}{\text{oxidising agent quantity}} = \frac{1}{4}$

Consequently, this material has become able to adsorb solutes because:

- of its physical structure (as a result of heat and chemical activation): the macro-porous allows diffusion of solutes. Small particle size gives the material an important specific area.
- of its chemical structure for:

- the presence of numerous functional chemical groupings capable of establishing links.
- polarless characteristics of coffee grounds macromolecular allowing hydrophobic interactions with other molecular.

This activated material should have a great affinity with organic solutes such as phenol.

Adsorption protocol

Experiments on adsorption have been done in discontinuous “batch process”. It is by treating constant volume solutions of different concentrations of pollutants prepared with distilled water and pure pollutant (from 1 to 30 mg/l) with a constant quantity of activated carbon (1g) that we obtain different residual quantities in solution (C_R). For this purpose we stir the solution and activated carbon during a period of time corresponding to a pseudo-equilibrium, at a constant temperature, we separate the adsorbing material by filtration.

Results and discussion

Kinetic study

From experimental results of the adsorption, we obtain the adsorption kinetic C_{ad}/m against time (Fig. 2). The examination of both curves puts into evidence the affinity of such compound with both adsorbing materials (activated carbon A and activated olive-mill); the equilibrium is obtained after 30 to 40 min. This can lead to the conclusion that not only retention on hydrophobic sites is easier but also that there is a further interaction of the electron donor-acceptor between aromatic cycles of the graphitic network and those of phenol. The hydrophobic adsorption is obtained by a horizontal orientation of the solute at the surface of the substrate in such a manner that the number of hydrophobic interactions between solute and substrate is maximum.

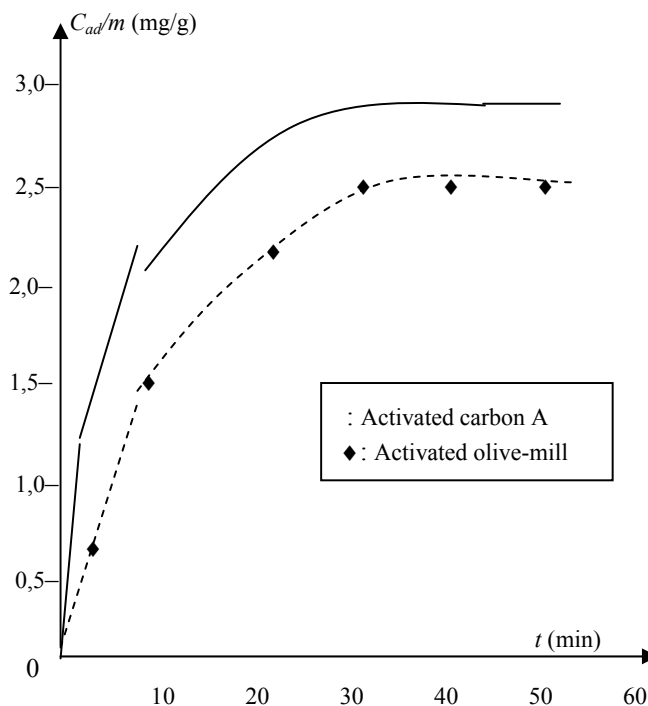


Fig. 2. Adsorption kinetic of phenol: Evolution of the adsorbed quantity C_{ad}/m against time ($C_0 = 30$ mg/l; $m = 1$ g)

The curve therefore presents a horizontal levelling corresponding to the formation of a single layer of solute at the surface of the material.

Effect of temperature

Fig. 3 shows a marked effect of temperature on the rate of adsorption. The influence of this parameter is highly significant. The temperature increase disturbs the existing physical forms. It affects mainly the adsorption equilibrium of the activated coffee grounds. Furthermore, this parameter acts on the structure of the substrate. Its increase causes pores expansion. In such conditions, the solute diffuses more easily in the material and the adsorbing area increases. Hence, the number of adsorbing sites increases. These must therefore be as much important as the molecule of solute is big, to allow its diffusion. Improvement of phenol fixing when the temperature increases can be explained by intervening of endothermic-bonds such as hydrophobic interactions. Note that this influence of temperature appears between 15 and 25 °C as well as between 25 °C and 40 °C even though the increase in temperature is lower.

These results are in accordance with those on adsorption of phenol type compounds [21] that show their great adsorbing power on either granulated or powdered activated carbon. However, the result is reversed when the adsorbing material is more polar (i.e. carbonised wool) hence increasing retention capabilities of polar molecules.

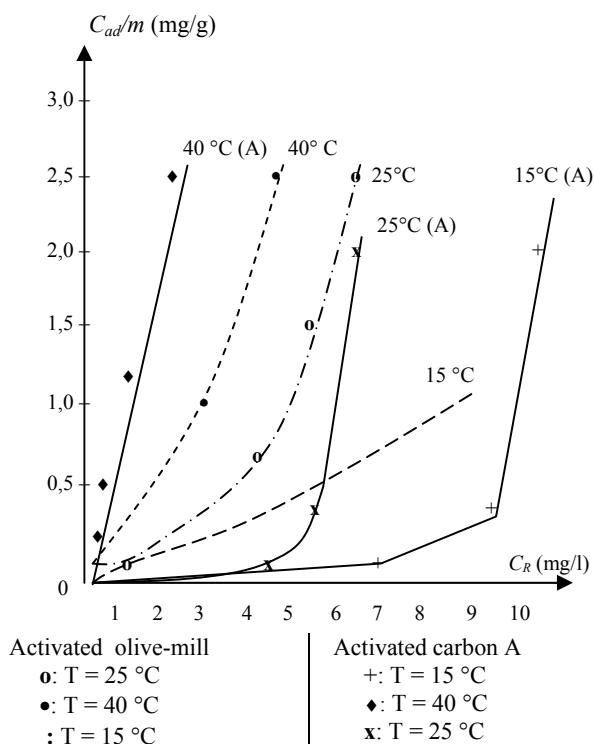


Fig. 3. Saturation curves of the activated olive-mill and activated carbon A by phenol at varying temperatures

Effect of stirring

Examination of experimental results shows that the greater the adsorbed quantity of phenol, the higher the speed of agitation for a given concentration.

This can be explained by the fact that the speed reduces the limit layer of the system and increases therefore, the external diffusion of mass flow.

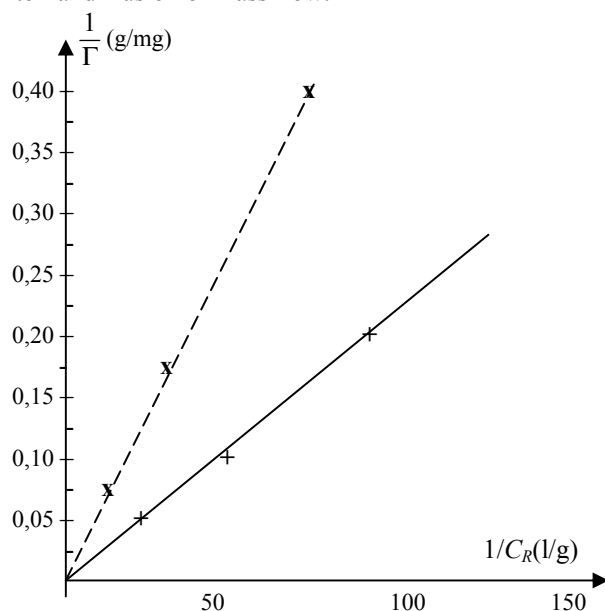


Fig. 5. Langmuir isotherm in reverse co-ordinates invert: evolution of $1/\Gamma$ against $1/C_R$ for phenolics of initial concentration: $C_0 = 10$ mg/l of the temperature (+: 22 °C and x: 40 °C)

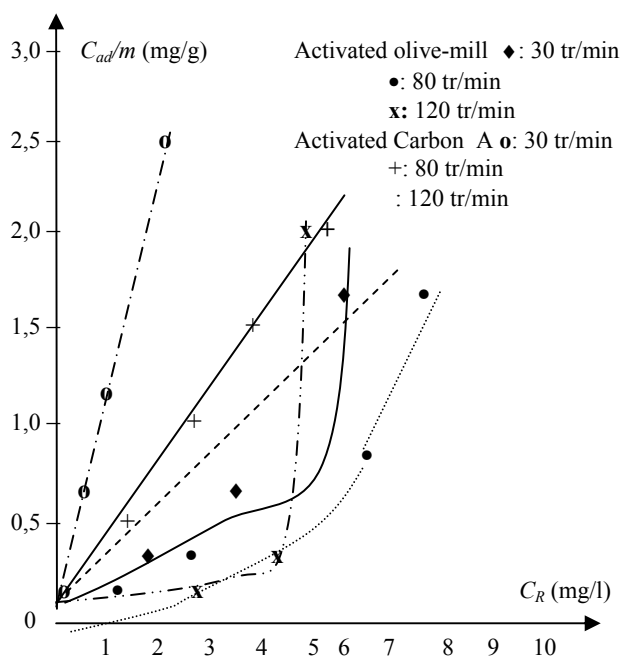


Fig. 4. Saturation curves of the activated olive-mill and activated carbon (A) with variable stirring speed

The different isotherms obtained during adsorption assays of phenol are drawn on Fig. 5 and the Γ^∞ values and K are reported in Table 1.

Table 1
The extrapolated ultimate values adsorption capacity Γ^∞ from the Langmuir isotherms for different temperatures and the values of the K constant corresponding to the adsorption equilibrium

Temperature, °C	Langmuir		Freundlich	
	Γ^∞ (mg/g)	K (l/g)	K (l/g)	$1/n$
22	27,77	9,61	121,50	0,65
40	42,86	52,64	104,58	0,527

Thermodynamic study

Determination of the enthalpy or heat of adsorption:

Assumptions:

$1 < H_{ads} < 10$ Kcal (physical-sorption)

$10 < H_{ads} < 25$ Kcal (chemical-sorption)

The heat of adsorption is determined by a relationship linking the constant relative to the adsorption energy K and the temperature T which is given by:

$$K = K_0 e^{\frac{-H_{ads}}{RT}}, \quad \text{Ln}k = \text{Ln}K_0 - \frac{H_{ads}}{RT},$$

where R – Perfect gas constant (cal/mol.°K), T – absolute temperature (°K).

In drawing $\ln K$ against $1/T$, we get a straight line the slope of which can determine ΔH_{ads} and the ordinate at the origin allows us to calculate adsorption entropy ΔS_{ads} (Fig. 6).

The slope of this line is $\Delta H_{ads} = 11.40 \text{ Kcal / weak}$.

According to the value ΔH_{ads} , we can conclude that the adsorption is chemical where reactions in the surface are endothermic, which confirms our previous results (effect of temperature).

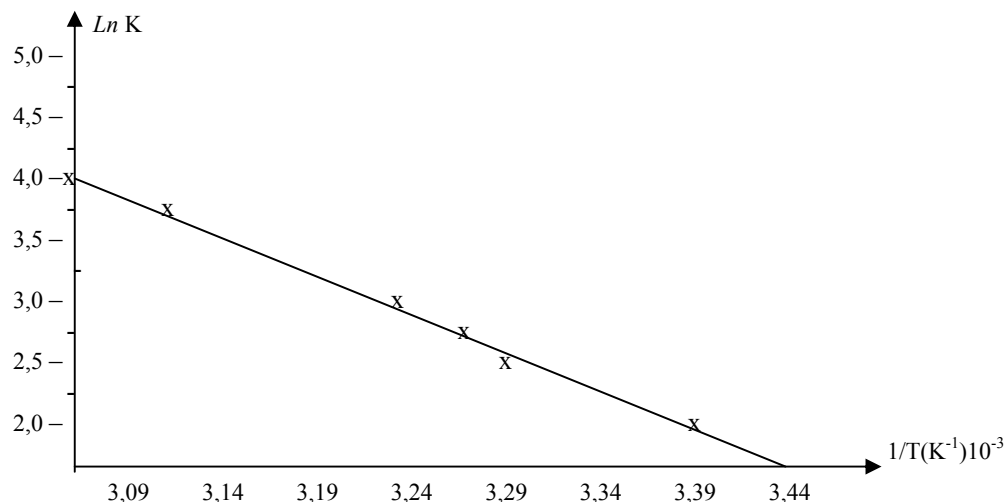


Fig. 6. Determination of the heat of adsorption

Conclusion

The olive-mill, considered up until now as waste, can be valorised by adapting an activation protocol in view of its use in the field of liquid effluent treatment. In this study, we have focused on the adsorption of phenol with concentration levels usually found in waters by using powdered activated olive-mill. The experimental results obtained under static conditions show a great retention power of phenol on activated olive-mill, which leaves us to suppose the existence of specific interactions between aromatic compounds and the graphitic network of substrate. However, the adsorption capacity of this material remains low compared to the commercial activated carbon. The experimental assays we have done have given good results and show that the activated olive-mill has a significant depolluting action and its use could offer real advantages. The extension of these results to other food industry wastes is promising as far as the application of this type of valorisation to all food industry wastes is concerned.

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