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APPLICATION OF ACTIVATED CARBON PREPARED FROM OLIVE STONES IN THE REMOVAL OF TWO BASIC DYES FROM WATER

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ABSTRACT

Olive stones is produced in large quantities during the manufacture process of the olive oil in the Tunisian oleic industry. This by-product. have been converted to granular activated carbon by carbonisation in the nitrogen atmosphere followed by steam activation. Activated carbon so obtained with 1150 m^2/g specific surface area and 0,53 cm^3/g pore volume, essentially microporous, has been used for the adsorption of two basic dyes: Methylene Blue (MB) and Rhodamine B (RB) in aqueous solution. The equilibrium adsorption isotherms of the two dyes at 30°C shows Langmuir shape. The maximum adsorption capacity of MB and RB are found to be 303 mg/g and 217 mg/g respectively. Adsorbent affinity to tested dyes is related to electric and steric effects.

KEY WORDS: Olive stones, activated carbon, Methylene Blue, Rhodamine B, adsorption

INTRODUCTION

Activated carbons are porous materials widely used as adsorbents. The characteristics of the final products depend on the raw material used (Gergova et al. 1993; Rodriguez-Reinoso et al. 1985). The textural and surface chemical properties of activated carbon depend on: the activation process used (chemical or physical), the numbers of steps, the activating agents, the temperature and the time of gasification (Gergova and Eser, 1996; Rodriguez-Reinoso et al., 1984; Rodriguez-Reinoso and Molina-Sabio, 1992). Lignocellulosic materials, such as fruit stones and shells, proved to be excellent precursors for the production of activated carbons (Gergova and Eser 1996). These by-products are abundant in some countries and do not have other direct technical applications (Rodriguez-Reinoso et al. 1992). The availability of an agricultural lignocellulosic waste by-product, olive stones, have encouraged our interest in the preparation of activated carbons. The latter is a by product of considerable amount in the Tunisian oleic industry. The activated carbon production is made in two steps: carbonisation and water vapour activation.

Activated carbon has been successfully employed in the removal of colour from aqueous solution (Sun et al. 1997). Mac Kay (1981) has studied the removal of four major classes of dyestuffs from aqueous solutions using activated carbons and found them as excellent adsorbents. Gupta et al. (1997) have reported the removal of malachite green, a basic dye, by activated carbon is almost 100 % at low concentration.

Methylene blue and Rhodamine B are two basic dyes, used in the paper mill, dyeing process and leather industries (Perrin 1993). In order to study the ability of activated carbon prepared from olive stones (OSAC) for dye removal, MB and RB are selected for the present study. Equilibrium isotherms for each dye-OSAC system will be determined.

MATERIALS AND METHODS

Material

Activated carbon prepared from olive stones

The milled olive stones with particle size in the range of 1,25 – 4 mm have been used as the raw materials. It was first carbonised in a vertical tube furnace heated electrically with a continuous flow of nitrogen flow (9 Nl/h). A sample (25 g) of olive stones was used. The carbonisation time was fixed at 2 hours and the process temperature was 600°C. The char obtained from the first step having a limited developed structure area was activated in the same furnace using steam as oxidising agent. The activation temperature was varied in the range 600-750 °C for a residence time in the range of 2-10 hours.

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Tab. 1: Essential characteristics of activated carbon

bulk density, cm³/g	0,54
particle size, µm	80
specific surface area by N_2, m²/g	1150
micropore surface, m²/g	1075
total pore volume, cm³/g	0,53
micropore volume, cm³/g	0,38
average pore width, Å	28
iodine number, mg/g	1060

Dyestuffs

Methylene blue and Rhodamine B used in this work are Labosi products. The molecular structures, colour index, wave length (λ_{max}) corresponding to maximum absorbency for each dye are listed in Table 2.

Analysis

In accordance with the Lambert-Beer law the absorbency was found to vary linearly with the concentration and dilutions were undertaken when the concentration of dye is high. The concentrations of dyestuffs were measured with a Perkin Elmer spectrophotometer in 1cm light path cell.

Experimental methods

Adsorption isotherms were determined using the batch equilibration technique by mixing 10mg of activated carbon with 200 ml of a dye solution at different concentrations in a 250 ml flask at 30°C. The solutions were mixed for 3 days reaction period find to be largely sufficient for equilibrium attainment for the dye at constant temperature (30°C). After the mixed time, each suspension was filtered using 0,45 µm cellulosic membrane and equilibrium solution concentration is measured by the spectrophotometer apparatus. The amount of dye adsorbed per gram (Q) of activated carbon is calculated as following as:

$$Q = \frac{(C_0 - Ce)}{m_{CA}} V_S$$

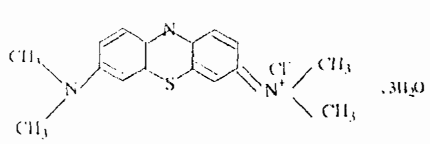
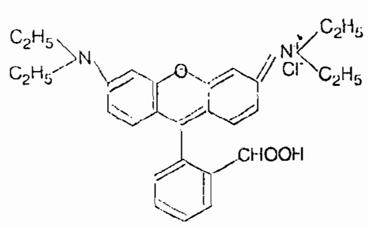
Where: m_{CA} is the amount of activated carbon used (g), C_0 is the initial dye concentration of solution (mg/l), C_e is the equilibrium dye concentration (mg/l) and V_S is volume of the solution (liter).

RESULTS AND DISCUSSIONS

Olive stones activated carbon and its characteristics

Figure 1 reports massic global yield of activated carbon production versus activation residence time at an activation temperature of 700 °C. We observed a linear decrease in overall yield with the residence time; this indicated an uniform gasification rate. It was accompanied with a linear increase in specific surface area (Figure 2). The latter was uniformly developed with increasing activation time. Similar results were reported by others (Rodriguez-Reinoso et al., 1985; Rodriguez-Reinoso et al., 1984).

Tab. 2: Dye structures with λ_{max}

Dye	Structure	λ_{max} (nm)
Methylene blue (MB) (C.I : 52015)		660
Rhodamine B (RB) (C.I: 45170)		555

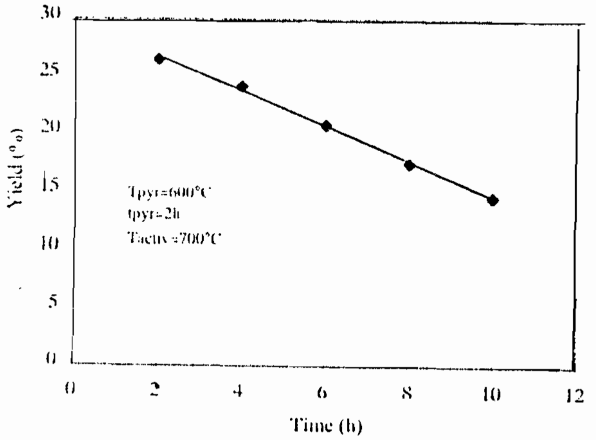


Fig. 1: Effect of residence time in the overall yield of activation step.

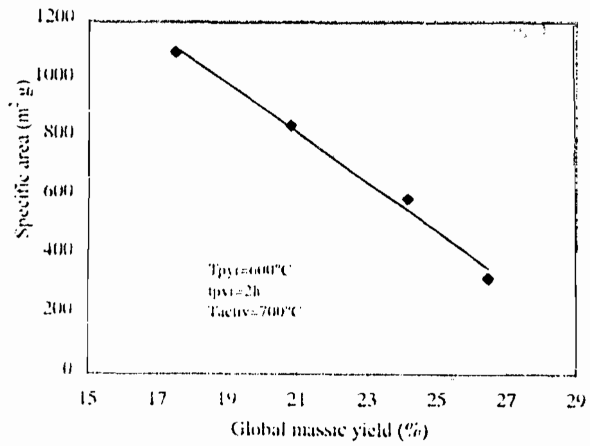


Fig. 2: Nitrogen apparent specific surface area versus overall yield.

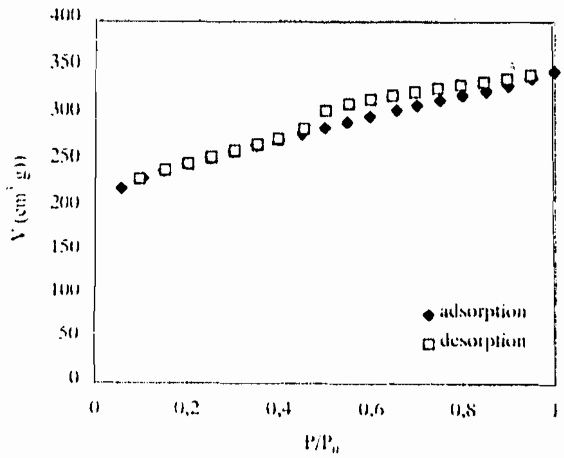


Fig. 3: Adsorption-desorption isotherms of N_2 on OSAC.

Tab. 3: Equilibrium adsorption parameters of Langmuir model for OSAC

Adsorbate	Adsorption capacity (Q_∞), mg/g	Langmuir constant (K_L), l/mg
MB	303	4,12
RB	217	1,84

The porous structure of the char and activated carbon was studied by nitrogen adsorption-desorption using a Quantachrome automated adsorption apparatus. The adsorption isotherms are fitted by the Langmuir model to estimate the internal surface area. This specific area can reach 1000 m^2/g with a global massic yield of 19 %. Those results are comparable to activated carbons produced from others lignocellulosic materials. Figure 3 shows the 77 K nitrogen adsorption-desorption isotherms of the steam-activated carbons prepared at 700 °C activation temperature for activation time of 8h. Isotherm obtained is basically of type I, currently exhibited by microporous solid. The form of the isotherm show that activated carbon produced contains mesopores in addition to the developed microporosity.
The principal characteristics of activated carbon used in this work are listed in Table 1.

Adsorption isotherms

Adsorption isotherms of OSAC for the MB and RB at a temperature 30°C are presented in Figure 4. The equilibrium adsorption data could be described (Figure 5) satisfactorily by the Langmuir isotherm:

$$\frac{C_e}{Q_e} = \left(\frac{1}{Q_\infty}\right)C_e + \frac{1}{Q_\infty K_L}$$

Where Q_e is the equilibrium adsorption capacity, C_e is the concentration at equilibrium, Q_∞ is the capacity of adsorption of activated carbon , K_L is the Langmuir constant .
The experimental values of the model parameters for the two studied colorants are summarised in Table 3.
The two cationic dyes were highly adsorbed on this activated carbon. The greater affinities of basic dyes for OSAC can be attributed to the negative charge of this material.
The adsorption capacity of MB is much higher than that of the RB. However, MB molecule is smaller than RB molecule and consequently more accessible to the micropores of OSAC.

To have more idea about microporosity of OSAC, one can use the $(S_{N2}-S_{MB})/S_{N2}$. We note that the specific surface areas related to the MB used previously was calculated from the following equation:

$$S_D\ (m^2/g) = \frac{q_m\ \sigma\ N_A}{M_D}$$

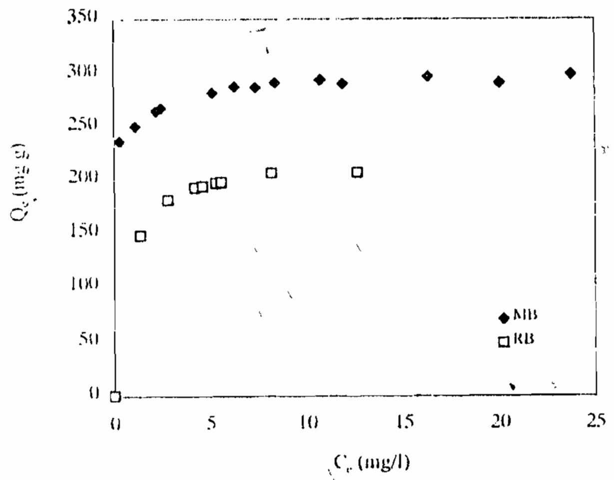


Fig. 4: Adsorption isotherms of MB and RB on OSAC.

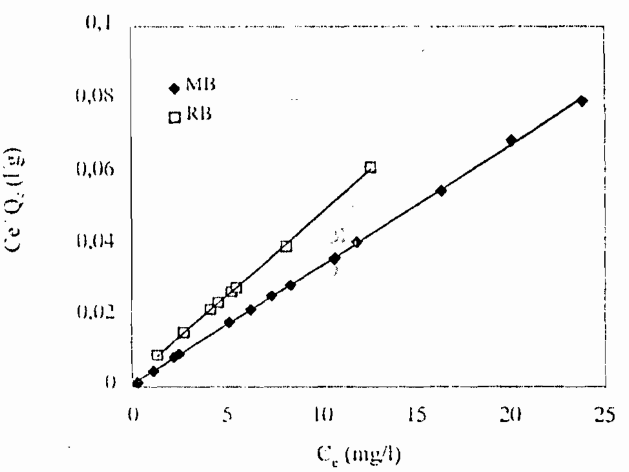


Fig. 5: Langmuir linear adsorption isotherms of MB and RB on OSAC.

where: q_m: adsorption monolayer (g/g), σ: cross section of dyestuff (m^2), N_A: Avogadro number (mol^{-1}) and M_D: molecular weight of dye (g/mole). The value of σ is 130 A^2 for MB (Santamarina et al., 2002). We note that only 36 % (S_{MB} calculated is equal to 740 m^2/g) of N_2 area is not accessible to MB. This portion of surface has a very narrow microporous with a width smaller than 9 Å, the minimum dimension of the MB molecule.

CONCLUSIONS

As discussed above, carbonisation of olive stones in the nitrogen atmosphere followed by steam activation produces an activated carbon with acceptable yield and high surface area. The process developed in this work is a simple way able to give a final product at 19 % massic global yield with 1000 m^2/g specific area.

Activated carbon that was obtained was used to eliminate two cationic colours: metylene blue and rhodamine B from water by adsorption. Results obtained showed that the adsorption of those colours on activated carbon prepared from olive stones was quite effective. Equilibrium adsorption isotherms can be represented by Langmuir model. The adsorption capacities were 303 mg of MB and 217 mg of RB per gram of activated carbon.

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