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Study of Methylene Blue Dye Adsorption on to Activated Carbons from Olive Stones

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Abstract**—**Activated carbons were produced from olive stones by a chemical process. The activated carbon (AC) were modified by nitric acid and used as adsorbents for the removal of methylene blue dye from aqueous solution. The activated carbons were characterized by nitrogen adsorption and enthalpy of immersion. Batch adsorption experiments were carried out to study the effect of initial different concentrations solution on dye adsorption properties. Isotherms were fitted to Langmuir model, and corresponding parameters were determined. The results showed that the increase of ration of $ZnCl_2$ leads to increase in apparent surface areas and produces activated carbons with pore structure more developed. However, the maximum MB uptakes for all carbons were determined and correlated with activated carbons characteristics.

Keywords**—**Adsorption, activated carbon, chemical activation, enthalpy of immersion.

I. Introduction

SYNTHETIC dyes are one of the main pollutant groups of water and wastewater. Dye contamination in wastewater causes problems in several ways: the presence of dyes in water, even in very low quantities, is highly visible and undesirable; color interferes with penetration of sunlight into waters. These materials are the complicated organic compounds and they resist against light, washing and microbial invasions. Thus, they cannot be decomposed easily. Direct discharge of dyes containing effluents into municipal environment may cause the formation of toxic carcinogenic breakdown products [1], [2]. The highest rates of toxicity were found amongst basic and diazo direct dyes. Therefore, it is highly necessary to reduce dye concentration in the wastewater. The conventional methods for treating dye containing wastewaters are electrochemical treatment, coagulation and flocculation, chemical oxidation, liquid–liquid extraction and adsorption. Adsorption has been shown to be an effective way for removing organic matter from aqueous solutions in terms of initial cost, simplicity of design, ease.

The adsorbents with amorphous porous surfaces and high surface area, such as activated carbon, can be used in industry to decrease the dosage of adsorbent, particularly where selective adsorption of one fluid component from a mixture is important. They have exceptional mechanical properties, unique electrical property, highly chemical stability and large specific surface area, So ACs have attracted researchers interest as a type of adsorbent and offer an attractive option for the removal of organic and inorganic contaminates from water.

In the present work, activated carbons, supplied by our laboratory, were selected as an adsorbent to remove methylene blue from aqueous solution. The main objective of this research was to evaluate the adsorption aptitude of activated carbon for the removal of methylene blue as a model compound for basic dyes. The effects of initial dye concentration and porosity of activated carbons on adsorption capacity were investigated. Moreover, equilibrium models were used to fit experimental data parameters was determined.

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II. Experimental

A. Preparation of Activated Carbons

For the chemical activation, the homogeneous mixture of the olive stones and the zinc chloride is carbonized under a nitrogen flow of at a rate of 5°C.min^{-1} at 600°C and maintained during one hour at this temperature. The obtained carbon is then treated by a hydrochloric acid diluted solution by refluxing during three hours then washed with boiling distilled water until the total elimination of chlorides. After cooling under nitrogen stream, the resulting carbon is washed during three hours then washed with boiling distilled water until the absence of chloride ions and finally oven-dried at 120°C during three hours and kept in hermetic bottles to protect it from air and humidity. We shall note AC1, AC2 and AC3; activated carbons obtained from the precursor, treated successively by 0.5, 1 and 2 g of $ZnCl_2$ per gram olive stones, respectively.

B. Textural Characterization

The textural characterization of the prepared activated carbons was performed by nitrogen adsorption and immersion calorimetry techniques. The nitrogen adsorption-desorption isotherms were measured using an automatic adsorption volumetric apparatus (ASAP 2010, Micromeritics). The surface area (S_{BET}) was calculated by the Brunauer–Emmett–Teller equation [3], the total pore volume (V_T) was determined at P/P_0 = 0.97 and the average pore width (4 V_T/S_{BET}). The micropore volume, W_0, was determined from Dubinine–Radushkevich method [4] through N_2 adsorption up to $P/P_0 \leq 0.1$ and the mesopore volume, V_{meso}, was calculated as the difference between total volume and W_0.

The porosity was also studied by immersion calorimetry in a Calvet calorimeter [5], [6], in two liquids (cyclohexane and tri-2,4-xilyl phosphate).

C. Adsorption of Methylene Blue

The blue methylene adsorption isotherms on various activated carbons are made at different methylene blue concentrations. 0.25g of activated carbon was mixed with 50mL phenol solution and sealed in Erlenmeyer with a regular agitation during 48 hours at 25°C until the equilibrium was attained. The measurement of the concentrations of methylene blue was determined by Spectrophotometer UV-Visible (JASCO V-530). The amount of adsorbed phenol at equilibrium (q_e) was calculated according to the equation:

$$q_e = \frac{(C_i - C_e)}{m}V \quad (1)$$

where C_i and C_e represent initial concentration and equilibrium phenol concentration, respectively.

The adsorption data sample was fitted by Langmuir [7] equation:

$$q_e = \frac{Q_0 K_L C_e}{1 + K_L C_e} \quad (2)$$

The linear transformed form of Langmuir equation is given as:

$$\frac{C_e}{q_e} = \frac{1}{K_L.Q_0} + \frac{C_e}{Q_0} \quad (3)$$

The maximum adsorption capacity Q_0 (mg/g) corresponding to complete monolayer coverage and the Langmuir isotherm constant K_L (L/mg) are determined by plotting $\frac{C_e}{q_e}$ versus C_e.

III. Results and Discussion

A. Characterization of the Activated Carbons

The nitrogen adsorption–desorption isotherms corresponding to three activated carbons are represented in Fig. 1.

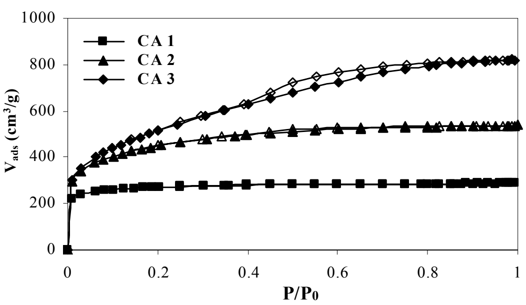

Fig. 1 Adsorption-desorption isotherms of N_2 on activated carbons

Fig. 1 was show that the nitrogen adsorption-desorption isotherms on various coals are in type I, according to the classification of the IUPAC [8]; these materials are then essentially microporous. In the case of AC3, we observe a hysteresis loop of type H_4, characteristic of capillary condensation phenomenon consecutive to the presence of slit-like mesopores.

Texture parameters of the as-prepared and modified samples are summarized in Table I. These all parameters (surface area, the total pore volume, enthalpy of immersion,..) were increased with increasing ratio of $ZnCl_2$. These results suggested that as the activation of olive stones with $ZnCl_2$ is mainly contributed from micropores at lower ratio of $ZnCl_2$ than, while AC3 is predominantly composed of mesopore (ratio of higher than 1). Therefore, it can be seen that AC3 has many pores larger reflected by the high value enthalpy of immersion in tri-2,4-xilyl phosphate (137.48J.g^{-1}).

TABLE I
TEXTURE PARAMETERS OF ACTIVATED CARBONS

	AC1	AC2	AC3
S_{BET} (m^2.g^{-1})	913	1569	1861
V_T (m^3.g^{-1})	0.4431	0.8276	1.2649
W_0 (cm^3/g)	0.4151	0.6359	0.6850
V_{meso}	0.0280	0.1917	0.5799
Φ_m (Å)	19.42	21.09	27.12
$-\Delta H_i$ (C_6H_{12}) (J.g^{-1})	52.71	68.01	85.55
$-\Delta H_i$ ($C_{24}H_{27}O_4P$) (J.g^{-1})	02.10	76.13	137.48

B. Adsorption of Methylene Blue

The methylene blue adsorption isotherms on activated carbons are represented in Fig. 2.

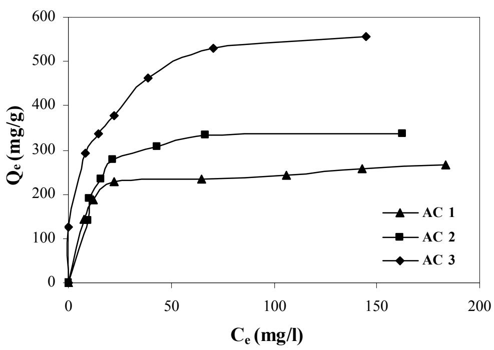

Fig. 2 Adsorption isotherms of methylene blue onto activated carbons

Fig. 2 show the non-linear curve fits of the adsorption isotherms data of MB on different activated carbons. All curves rise steeply at low concentration, and quickly approach a plateau at high concentration for MB. The results from the fitting done for modelling MB adsorption are listed in Table II. The goodness of the fit of the studied Langmuir model, with R^2 was higher than 0.995.

TABLE II
PARAMETERS OF THE LANGMUIR MODEL

	Q_0 (mg.g^{-1})	K_L (L.mg^{-1})	R^2
AC1	270,28	0,17788	0,9996
AC2	400,00	0,08591	0,9952
AC3	625,00	0,07476	0,9980

As shown in Table II, the maximum adsorption value for the BM is for CA3. This result indicates that the adsorption increased.

From these results, one observes that the maximal of methylene blue adsorption capacity, Q_0, is more raised on activated carbon CA3 (625 mg.g^{-1}). On the other hand, we notice that the adsorption capacity of MB increases with increasing the total pore volume and average pore width, this result can be explained by the development of porosity in the higher ratio of $ZnCl_2$ from the accessibility of MB molecules.

IV. CONCLUSION

This work relates to the preparation of activated carbons from an agricultural waste, the olive stones. At first, we proceed to the activation of the olive stones by activation chemical in order to develop the porosity of these materials. The second part of this study was devoted to the textural characterization of the resulting materials using nitrogen adsorption and immersion calorimetry techniques. The obtained results show of one part that the porous texture of activated carbons is more developed; for example, the BET specific surface area of the AC3 reaches a value of 1861 m^2/g. The activated carbons adsorption capacity is determined towards a methylene blue dye. All methylene blue adsorption isotherms on various activated carbons are modeled by Langmuir equation. The larger adsorption capacity of methylene blue was obtained with on activated carbon CA3.

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