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Modeling of adsorption isotherms of methylene blue by olive stones

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ABSTRACT / RESUME

Abstract : *The present study focuses on the recovery of the waste food « the olive stones » in the field of industrial liquid effluent treatment. The material is used in its native form. In order to test the performances of the adsorbent we were interested in cationic dye the methylene blue considered as pollutant. The effects of several parameters such as contact times, initial concentration of dye, solution and pH were studied in batch system.*
Modeling of experimental results was performed using models of Langmuir and Freundlich isotherms, which show that adsorption follows the Langmuir model with high correlation coefficients.

I. Introduction

Today, with technological development, and progress that have various vital sectors. The several industrial activities are constantly increasing, and produce liquid effluents, which are often contaminated with toxic and harmful and toxic substances. Among the industries that generate an important pollution, the textile industry which discharges are mostly loaded dye **[1,2]**, which gives sensation to a rather serious pollution. This industry represents only two-thirds of the total production of dyes, about 10 to 15% of dyes used, are rejected through the effluents **[1].**

The latter, loaded with dye, can have harmful effects, and severe impacts in the receiving environment, as they can affect the activity of photosynthesis in aquatic life, due to the reduction of light penetration. And can also be toxic to some aquatic species, due to the presence of aromatic hydrocarbon, metals, and chloride in their constitutions, which are toxic **[3,4]**. Thus the removal of dyes from these effluents has become a major environmental concern today **[5].**

Current methods used for disposal, include physicochemical methods such as flocculation, oxidation, ozonation, and reverse osmosis, and biological techniques **[6]**. All these methods are different in terms of color removal, operation and financial costs **[7,8].** In recent years researchers are directed to methods of treatment using natural materials such as clays, soft commodities, due to their low cost [**9, 10]**.

The olive stones are product of agricultural waste, available in our country rejected to important quantities annually in the environment.

In the present work, we opted for recovery of these by-products of agriculture olive stones, and their use as adsorbents for the treatment of effluents containing dye, and as we have chosen pollutant methylene blue.

II. Materials and methods

II.1. Preparation of the adsorbent

The olive stones (OS) used in this study was taken from the area of Lakhdaria, during the olive-growing period 2008-2009. The taken sample

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consists of pulps and fragments of cores. It was conditioned in plastic bags. Olive stone formed by beads crushed during the process of production olive oil production is initially washed several times with running water to remove dust and adherent impurities, and then rinsed with distilled water. Fragments of olive stone are then exhausted with hexane to remove residual oils; they are washed with distilled water several times and dried.

These samples will undergo a grinding means by an electric grinder and then sieved through a stack of sieves of different mesh openings. The choice of the desired particle size is between (80 μ to 630 μ). The final step is to dry the adsorbents prepared at 105° C to constant weight. Then keep in desiccators until used.

II.2. Adsorbents

The dye used in this study is a cationic dye is methylene blue (MB), it is chosen because of their strong adsorption on solids. The chemical structure of methylene blue is shown in the following Figure

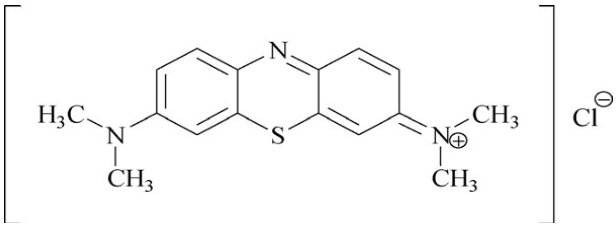

Figure 1. *structure of the Methylene blue (MB)*

The colored solutions are prepared by dissolving a dye mass in distilled water at a concentration of 1000mg / l. The experimental solutions are obtained by diluting the concentration to have the desired concentrations.

III.3. Batch adsorption experiments

III.3.1. pH effect

It was studied by mixing 200 mg of adsorbent with 100 ml of colored solution at a initial concentration of 100 mg / l, and a temperature of 20 ° C. The interval of selected pH is chosen between [2-12]. The initial pH of the solution was adjusted with NaOH solutions with 0.1N and HCL with 0.1N. The agitation was made for 120 minutes with a stirring speed of 150 rpm.

III.3.2. Adsorption kinetics

The experiments were carried by adding 200mg of adsorbent, volume solutions of 100 ml and concentration (20mg / L, 50mg / L, 100mg / L) Stirred at speed of 150 rpm. The samples were taken at predetermined time intervals. The tests were stopped when equilibrium is reached. The samples are filtered through a filter paper and the concentration is measured by a UV-visible spectrophotometer.

The amount of dye fixed per gram of adsorbent is given by the following relationship:

$$Qt = (Ci - Ct) \times V / M \quad \textbf{(1)}$$

Where:

V is the volume of the solution in (L).

M: mass of adsorbent used (g)

Qt: the amount of dye fixed in mg per gram of adsorbent.

Ci and Ct: are the initial and instantaneous concentrations of the dye, respectively (mg / l)

III.3.3. Adsorption isotherm

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is an important step to find the suitable model that can be used for design purpose [11]. Several models have been published in the literature to describe the experimental data of adsorption isotherms. The Langmuir and Freundlich are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of dye adsorbed and its equilibrium concentration.

III.3.4. Langmuir isotherm

Langmuir's isotherm model suggests that uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir isotherm equation is represented by the following equation [12]

$$C_e/q_e = 1/bQ + C_e/Q \quad \textbf{(2)}$$

where qe is the amount adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of the adsorbate ions (mg/L), Q and b are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and energy of adsorption, respectively.

The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L, defined as [13]:

$$R_L = 1/\,(1+bC_0) \quad \textbf{(3)}$$

where C_0 is the highest initial solute concentration, b is the Langmuir's adsorption constant (L/mg). The R_L value implies the adsorption to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0<R_L < 1$) or irreversible ($R_L = 0$).

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III.3.5. Freundlich isotherm

The Freundlich isotherm describes the non-ideal adsorption of a heterogeneous system and reversible adsorption [14]. The model can be expressed as

$$q_e = K_F\, C_e^{1/n} \quad (4)$$

Eq. (4) can be linearized by taking logarithms:

$$q_e = \ln K_F + 1/n \ln C_e \quad (5)$$

where q_e is the amount of dye adsorbed per unit of adsorbent (mg·g−1), C_e is the concentration of dye solution at adsorption equilibrium (mg·L−1), and K_F (L·g−1) and **(n)** is the Freundlich adsorption isotherm constants.

V. Results and Discussion

V.1.The effect of contact time and initial concentration on adsorption

Adsorption experiments were carried by adding a fixed mass of adsorbent (200 mg) to a volume of 100 ml of dye solution at different initial concentrations (20 mg / l - 50 mg / l - 100 mg / l), pH maintained constant (7) and a temperature of 20° C. The stirring speed was 150 rpm / mn. The selected time interval varies from 5 to 240 min, to ensure that equilibrium has been reached. Fig. 2 represents the evolution of the amount adsorbed versus time. For different values of the initial concentration, equilibrium is reached in a time of contact of 60 min. the fast adsorption of the BM to these various concentrations shows that the adsorption of MB, occurs on the surface of the adsorbent. According to the figures, in the first 10 minutes, the percentage removal of methylene blue was fast. After it stabilizes and reaches equilibrium. The first fast phase may be due to the availability of vacant adsorption site at initial stage. It is noted that the increase of the initial concentration, induced an increase in the adsorption capacity.

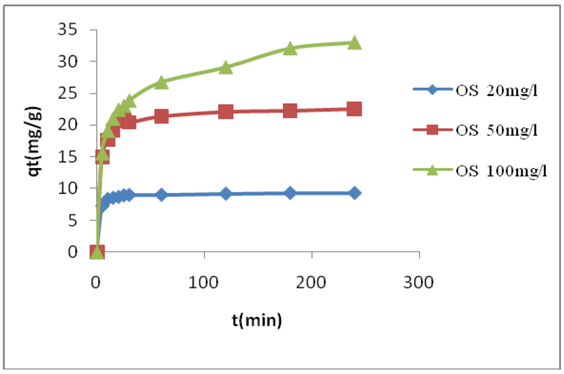

Figure 2*. BM adsorption capacity by OS according to the time of contacts[(Co = 20, 50, 100 mg / l), pH = 5.6, T° = 20 ° C, w = 150 rpm].*

V.2. Effect of the pH of the solution

Fig.3 shows that the adsorption capacity is minimum at pH = 2, and increases with increasing pH to pH = 7 and then remains almost constant between pH values between 7 and 12. At acidic pH, the adsorption capacity is low, this is due to the presence of H^+ ions in excess, which are in competition with dye cations BM^+ for adsorption sites, which causes the decrease adsorption capacity. At high pH, greater than 4, the adsorbent surface may become negatively charged, thereby improving the electrostatic attraction forces between the surface of the adsorbent and the BM^+ cations. Then the acid pH is unfavorable for the adsorption of methylene blue [14,15,16,17]. The maximum adsorbed amount, for our based adsorbent olive pomace was 44.654 mg/g at pH = 12.

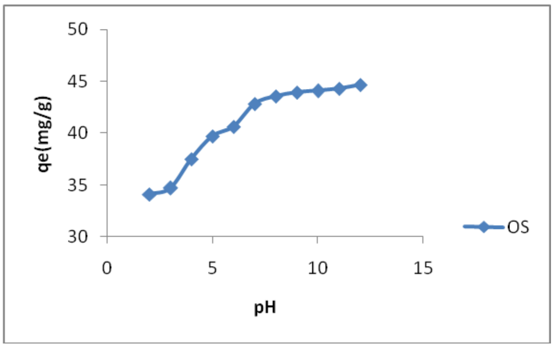

Figure 3. *Effect of pH on the adsorption of methylene blue on the adsorbents in the native state(Ci = 100 mg / l, w = 150 rpm, T° = 20 ° C)*

V.3. Isotherm studies

The result of adsorption isotherms modeling by Langmuir and freundlich model were represented in fig. 3 and fig. 4. All of the parameters are listed in Table I. The correlation coefficient of the Langmuir model was higher than that of the Freundlich model, which indicates that the former gives a better fit than the latter. As seen from Table I, the Langmuir equation represents the adsorption process very well; the R^2 value was higher than 0.99, indicating a very good mathematical fit. The fact that the Langmuir isotherm fits the experimental data very well maybe due to the homogeneous distribution of active sites onto the (OS) surface, since the Langmuir equation assumes that the surface is homogenous . As seen in Table I, the maximum adsorption capacity for methylene blue onto OS at 323 K was found to be 45.45 mg/g.

K_F is a Freundlich constant that shows the adsorption capacity of an adsorbent, and is a constant which shows the strength of the relationship between adsorbate and adsorbent. The value K_F of (OS) for methylene blue at 323 K was 4,4134. It is generally stated that the values of n in the range of 1 to 10 represent good adsorption. In

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the present work, the exponent was 1 < n <10, indicating favorable adsorption.

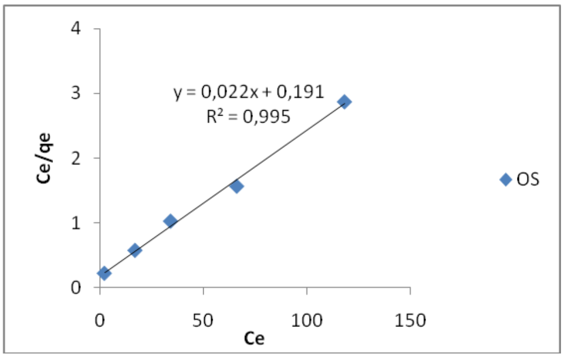

***Figure 4.** Langmuir isotherm fits for adsorption of MB on olive stones with concentration in the range of 20–200 mg/L at 25 °C.*

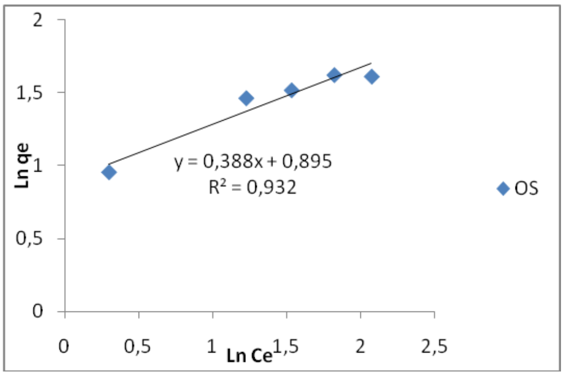

***Figure 5.** Freundlich isotherm fits for adsorption of MB on olive stones with concentration in the range of 20–200 mg/L at 25 °C.*

***Table 1**. Langmuir and Freundlich isotherm constants for methylene blue onto olive stones*

types d'adsorbants	Langmuir isotherm constants				Freundlich isotherm constants		
	q_m (mg/g)	KL	R2	R_L	K_F	1/n	R^2
OS	45,4545	0,1152	0,995	0,1237	4,4134	0,388	0,932

Conclusion

The adsorbent material olive stone that we used in this work showed effectiveness to reduce water pollution from textile waste. The experiments showed that the dye studied (MB), is well adsorbed on the adsorbent prepared olive stone (OS). The study of adsorption in batch system show that the range of the optimum pH for the removal of cationic dye studied (MB), correspond to the basic pH. The dye adsorption isotherm of the adsorbent fit well with Langmuir isotherm.

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