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Elimination of Malachite Green on granular activated carbon prepared from olive stones in discontinuous and continuous modes

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ABSTRACT/RESUME

Abstract: *The objective of this study is the removal of a cationic dye, Malachite Green (MG), by granular activated carbon (GAC) based on olive stones in discontinuous and continuous processes.*
The parametric study of batch adsorption of Malachite Green on granular activated carbon at room temperature has enabled us to highlight the dependence of the efficiency of this adsorbent on the various operating parameters (pH, initial concentration and mass of adsorbent). The Langmuir model was found to describe the adsorption isotherm of Malachite green on the studied GAC. The improvement of the performance of the fixed bed adsorption column requires that the breakthrough curves can be predicted according to the various system parameters (height, flow velocity and concentration of the pollutant). Experimental data were correlated with different mathematical models such as Bohart - Adams, Thomson, and Yoon - Nelson. All models used for the GAC studied were used successfully to describe the breakthrough curves of the dye.

I. Introduction

Using water is practically accepting to pollute it. Indeed, all industrial and domestic activity generate pollutants ejected into the environment which hold all by-products and lost raw materials that have not able to be recovered or recycled. Water thus becomes a vector of pollution [1]. So, the importance that we attach today to the protection of the natural environment and to the improvement of water quality keeps growing significantly in view of the warning of international regulators at the occasion of each disaster as they propose more and more stringent regulations.
The polluting elements that are introduced in important manner in the environment are of an organic nature such as detergents and concentrated dyes in significant amount into residual waters from the textiles industries or of metallic nature present at trace amounts are essential for living organisms.
The textiles industries use large quantities of dyes which are found in their effluents. At the usual concentrations rejected, the dyes are little toxic but the colouring of a water causes a decrease in the penetration of light in the water and a visual pollution.
The dyes are difficult to biodegrade and the colouring is visible at very low concentrations, sometimes below 1 $mg.L^{-1}$ [2]. The coloration may therefore persist in the effluent after a biological treatment, which requires the use of tertiary treatment to eliminate it.
To remedy this situation, biological techniques (elimination on plants) have been used for the elimination of these dyes from effluents. However, the latter techniques were not very successful [3, 4]. On the other hand, adsorption techniques have given good removal yields of organic molecules.

Activated carbon has been extensively used because of its high capacity for adsorption of organic species [5, 6].
At present, the increasing demand for adsorbent materials for processes of environmental protection is arousing additional research in the manufacture of the activated carbons from materials that aren't classic, concretely from vegetable waste. However, to elaborate activated carbons from the vegetable waste is very interesting from of an economic point of view as we benefit from simple transformations of a direct application of these starting materials.

II. Materials and methods

The study is carried out on the adsorption of Malachite Green, a cationic dye of general formula $C_{52}H_{56}N_4O_{12}$ and molecular weight 929 g.mol^{-1} (Sigma-Aldrich product) by GAC based on the olive stones. Malachite green (or aniline green, or diamond green B) is a mainly known toxic chemical product for its qualities as a blue-green dye.
The activated carbon used in this study was prepared depending on the experimental protocol developed in the laboratory of Structure, Elaboration and Application of Molecular Materials [7, 8]. The olive stones were dried in the sun for two days, then in the drying oven for 24 hours at 110°C. The preparation of olive stones consists of chemical activation by a dehydrating agent (50% phosphoric acid). After drying in the oven at 110 °C for 24 hours, the granular activated carbon was crushed in a Crosschop Viersen grinder and sieved on a Retsch 5657 HAAN 1 apparatus, type Vibro, to obtain particles with a diameter in the [0.5-1.0] mm range. So finally, the activated carbon was kept in hermetic containers placed in a desiccator.
The physico-chemical characterizations of activated carbon based on olive stones are grouped in Table 1.

Table 1. *Physico-chemical characterization of GAC from olive stones [7]*

Parameter	GAC from olive stones
Iodine number (mg.g^{-1})	907.4
BET surface areas (m^2.g^{-1})	1031.5
surface area accessible to Methylene Blue (m^2.g^{-1})	240.7
pH_{ZPC}	3.5
density (g.mL^{-1})	0.462

Iodine number is defined as the milligrams of iodine adsorbed by one gram of material when the iodine residual concentration of the filtrate is 0.02 N (0.01 mol L^{-1}) according to ASTM D4607 standard [9], which is based on a three-point isotherm. A standard iodine solution (0.1 N) is treated with three different weights of sorbent. The sample is treated with 10 mL of 5% (v/v) HCl. The mixture is boiled for 30 s and then cooled at room temperature. 100 mL of 0.1N iodine solution is immediately added to the mixture and stirred for 30 s. The solution is then filtered and 50 mL of the filtrate is titrated with 0.1 N (0.05 mol L^{-1}) sodium thiosulphate solution using thyodene as an indicator.
Methylene Blue (MB) is a reference dye used to estimate the specific surface area of the absorbent accessible to adsorbate corresponding to the surface area of wide micropores and small mesopores. The available specific surface area S_{MB} (m^2 g^{-1}), for MB molecule is calculated by the following equation:

$$S_{MB} = \frac{N.b.S}{M} \qquad (1)$$

where S_{MB} is the surface area (m^2 g^{-1}), b the maximum adsorption capacity (mg g^{-1}) based on a monolayer coverage. It can be determined from the Langmuir model, *N* is Avogadro's number (6.023 10^{23} mol^{-1}), S is surface occupied by a molecule of Methylene Blue (taken as 119 Å^2), and M is the molecular weight of Methylene Blue (319.86 g mol^{-1}) [10].

II.1. Batch process

The objective of this section, consists in determining the effect of certain physico-chemical parameters on the interactions adsorbent adsorbate : equilibrium time, pH and adsorbent dose. This study the first step consists in estimating the contact time necessary for reach adsorption equilibrium.

II.1.1. Effect of contact time

The study of the adsorption of Malachite Green on CAG from olive stones as a function of time makes it possible to determine adsorbent - adsorbate contact time required to obtain an adsorption equilibrium. The tests are made in batch at room temperature (25°C) in beakers, by stirring (using a magnetic stirrer) a fixed mass of 0.1 g GAC in a volume of 25 mL of the Malachite green solution with two concentrations 100 and 200 mg.L^{-1} at 400 rpm until equilibrium is reached. Samples were collected at predetermined time intervals, and are separated from the solid by centrifuge. The analysis of the concentration of this residual dye is carried out by UV/Vis spectrophotometry type JENWAY Model 7305 at the maximum wavelength of 615

nm. The quantity (q_e) was calculated according to the following mass–balance relationship [8]:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

with :

q_e is quantity of dye per gram of adsorbent (mg g^{-1}) ; C_0 is initial concentration of the dye (mg L^{-1}) ; C_e is residual concentration at equilibrium (mg L^{-1}) ; V is volume of the solution (L); m is mass of the adsorbent (g).

II.1.2. Effect of adsorbent dose

To study the influence of the dose of the adsorbent on the adsorption capacity, we have followed the steps of: in a series of beakers containing 25 mL of the malachite green solution, different masses of 0.05 to 0.35 g of the activated carbons studied were introduced successively for a time that was previously determined. After filtration, the solution was analyzed in order to determine its concentration, that will allow determining the percentage of removal of the substance to set.

II.1.3. Effect of pH

In the study, we followed the effect of pH on adsorption of the dye for an initial concentration of 200 mg.L^{-1} and a ratio of 10 g.L^{-1} GAC by adjusting the initial pH of the dye solutions by using the NaOH (0.1 N) and HCl (0.1 N) solutions, for the different pH values studied.

II.1.4. Isothermal adsorption of Malachite Green

Several mathematical models permit a satisfactory description of the adsorption phenomenon [11]. The most applicable models are of Langmuir [12] and Freundlich [13], and they are different by their conditions of validity. The Langmuir model is written:

$$q_e = \frac{K_L \times b \times C_e}{1 + (K_L \times C_e)} \quad (3)$$

The linear representation by (C_e/q_e) as a function of C_e allows the model to be verified. The equation is as following:

$$\left(\frac{C_e}{q_e}\right) = \frac{1}{b} C_e + \frac{1}{b \times K_L} \quad (4)$$

With :

q_e is adsorption capacity in mg adsorbed solute per g of adsorbent; C_e is equilibrium concentration of liquid phase solute (mg.L^{-1}); K_L is Langmuir constant; b is maximum adsorption capacity in mg adsorbed solute per gram of adsorbent (maximum monolayer). From the slope and intercept of the line the value is deduced of parameters b and K_L.

The empirical relationship of the Freundlich isotherm is of the shape [13, 14]:

$$q_e = K_F \times C_e^{\frac{1}{n}} \quad (5)$$

With :

q_e adsorption capacity in mg adsorbed solute per g of adsorbent; C_e concentration at equilibrium of the solute in liquid phase (mg/L); K_F and (1/n) Freundlich constant. The Freundlich constant (K_F) reflects the adsorbent efficiency of a matrix vis a vis the adsorbate The higher the K_F value, the more significant the adsorption.

We studied isotherms of adsorption of the dye on the activated carbon based on olive stones with the simple models of Langmuir and Freundlich.

In this section, we study the adsorption isotherm of the pollutant examined on the GAC based on olive stones. Into a series of beakers, successively are inserted an optimal mass of GAC which is brought into contact with 25 mL of the solution of known initial concentration, the whole is agitated for a determined contact time and pH.

II.2. Fixed-bed process

The main objective of this study resides in the modeling of the breakthrough curves obtained during the adsorption of basic dye in a packed-bed column depending on various operational parameters such as initial concentration, the supply flow rate and fixed-bed height, by applying the mathematical models, namely : the model of Bohart and Adams, Thomas, and Yoon Nelson. These models, will allow us to express the different parameters controlling the performance of adsorption in dynamic regime. The column used is made of glass of length 50 cm and 1.2 cm internal diameter with sintered glass filter. The column was filled with GAC and at both ends lies the glass wool (for fixing the GAC and achieve uniform distribution) ; the whole forms a fixed bed of known height. A tank at the bottom is filled with the coloured solution of known concentration of the dye, and was coupled by a low flow pump (Peristaltic pump). The pump feeds the packed column GAC then the solution was collected in a tank to then analyzed by spectrophotometry every half an hour.

III. Results and discussion

III.1. Batch mode

III.1.1. Effect of time

Adsorption was studied as a function of time to determine the quantity of dye adsorbed at different time intervals. Equilibrium time is one of the most important parameters in the design of economical wastewater treatment systems [15]. As a first step, it is appropriate to determine the contact time necessary to obtain the adsorption equilibrium of the liquid-solid system studied. Figure 1 shows the results obtained for the adsorption of MG on GAC at two different concentrations. These results

indicate that the equilibrium adsorption was reached within 6 hours by the adsorbent and dye removal percentage increased with increasing contact time [16]. All adsorption experiments will be made for an adsorbent adsorbate contact time of 6 hours, which is assumed to be sufficient for this system.

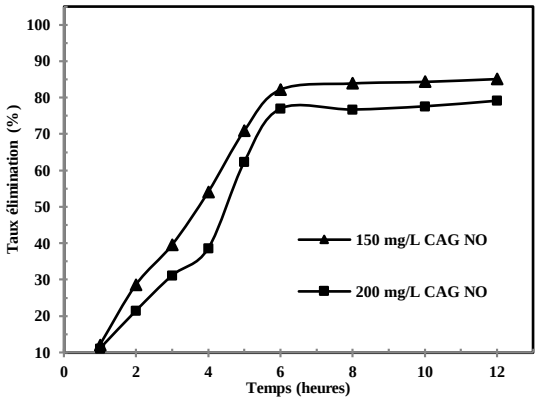

Figure 1. *Removal rate as a function of contact time for the adsorption of Malachite Green by olive stone- based GAC (150 and 200 mg.L^{-1})*

III.1.2. Effect of adsorbent dose on adsorption

The adsorption of Malachite green (MG) on the GAC at doses between 4 and 16 g.L^{-1} was studied under the same conditions (contact time, ambient temperature, and stirring speed).

Figure 2 shows that the quantity of MG adsorbed at equilibrium as a function of the mass of the adsorbent based on olive stones. The percentage of Malachite green elimination increases with increasing adsorbent mass. This is easily understandable, because the increase in % removal was due to the increase of the available sorption and availability of more adsorption sites [17], consequently, the increase in the quantity of the adsorbed dye. We would note that the adsorption of Malachite Green has reached for its maximum for an adsorbent dose of 8 g.L^{-1} on the GAC, this dose has been used for all adsorption processes.

III.1.3. Effect of solution pH on adsorption

The initial pH of the dye solution is an important parameter which controls the adsorption process [18], it has an effect on the quantity adsorbed. pH of solution can change: the charge of the adsorbent surface, the degree of ionization of the adsorbate molecule and extent of dissociation of functional groups on the active sites of the adsorbent [19]. Many studies have shown that pH is an important factor in determining the adsorption potential of cationic and anionic organic compounds [20, 21].

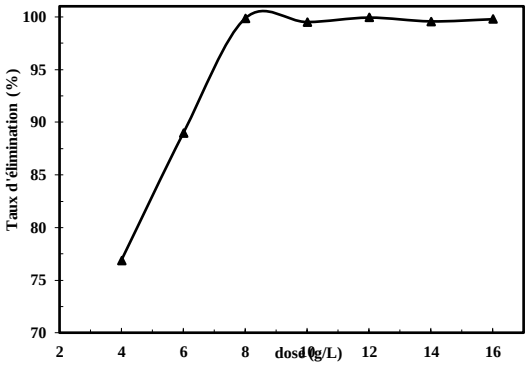

Figure 2. *Effect of the dose on the adsorption of Malachite green by olive stone- based GAC*

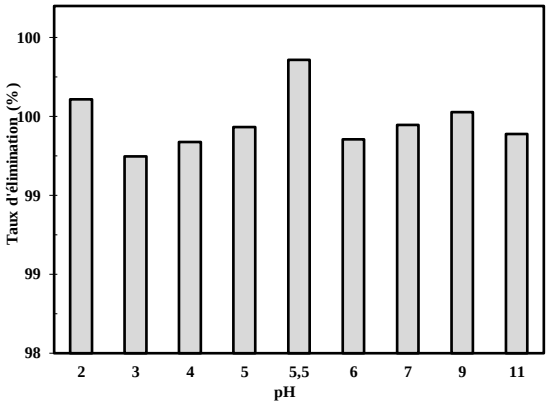

Figure 3. *Effect of pH of the solution on the fixation of Malachite Green by olive stone- based GAC*

From Figure 3, we see that the elimination rate of Malachite Green is highest at a pH of the initial solution of 5.5 by the GAC studied, it is at this pH that will be established the isotherm the Malachite Green adsorption by the GAC based on olive stones. The evolution of the adsorbed quantity in the pH range studied is explained by the fact that when the pH is above the pH_{ZPC}, the activated carbon surface is negatively charged and the molecules of cationic dyes (MG) in solution are positively charged [22]. Adsorption can be obtained by electrostatic interactions between the charge of activated carbon and dye. These interactions increase as the pH increases as the carbon surface becomes more and more negative as the solution is made basic.

III.1.4. Modeling of adsorption isotherm

In this study, the effect of the initial concentration of malachite green on the quantity adsorbed (mg.g^{-1}) by the GAC, was studied in a range of initial concentrations (300 - 1400 mg.L^{-1}). The assembly was agitated during a previously determined contact time, then the filtrate was analyzed at λ= 615 nm and the quantity q_e (mg.g^{-1}) calculated. The adsorption isotherms are evaluated on the plot of

the relationship graph q_e as a function of C_e. The obtained curves are illustrated in Figure 4.

Figure 4 shows that the adsorption capacity of Malachite Green on the CAG increases considerably with the increase in the initial concentration of MG. The isotherm has a plateau-like behavior, indicating the saturation of the sites of the surface and thus the formation of the monolayer. The isotherms of GAC adsorption based on olive stones show a shape (L) according to the Giles classification, indicating a relatively high affinity between the adsorbate and the adsorbent.

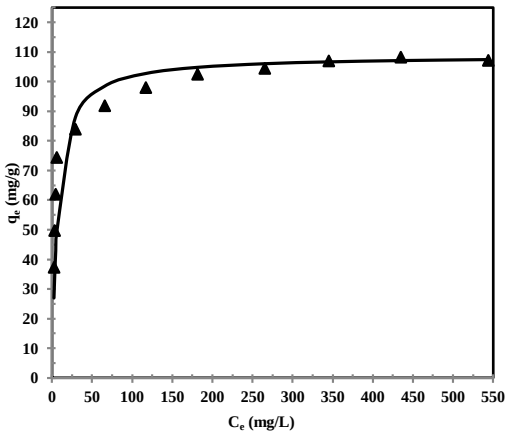

Figure 4. *Isotherms of Malachite green adsorption on the studied GAC*

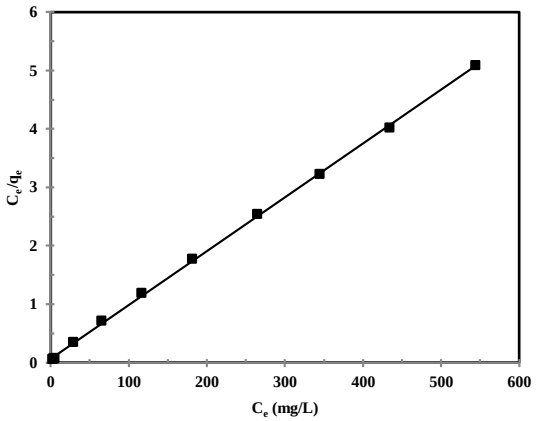

Figure 5. *Linear modeling by the Langmuir model of the Malachite green isotherm on the studied GAC*

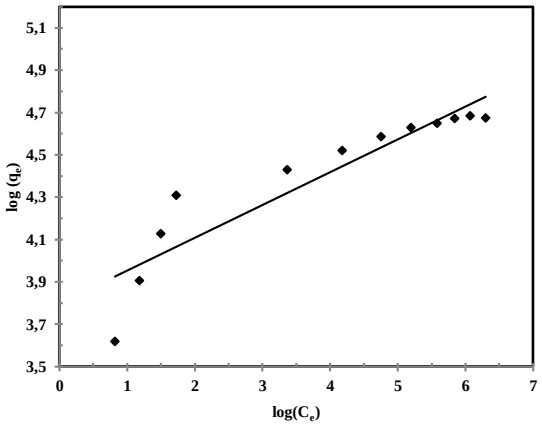

Figure 6. *Linear modeling by the Freundlich model of the Malachite green isotherm on the studied GA*

Table 2. *Parameters of Langmuir and Freundlich for the adsorption of Malachite Green on the studied GAC*

Langmuir Model			Freundlich Model		
b (mg.g^{-1})	***K_L***	***R^2***	***n***	***K_F***	***R^2***
108.69	0.145	0.9996	6.46	44.66	0.8477

Langmuir and Freundlich isotherm models were employed to describe the adsorption process in this study [23]. The dye fixation in the GAC was processed according to the Langmuir and Freundlich linear equations. The purpose of this linearization is to be able to verify the model according to which is done the adsorption and to infer the maximum amount adsorbed as well as the affinity of the adsorbate with respect to the adsorbent. The line is obtained by plotting (C_e/q_e) versus (C_e). We can see that the correlation coefficient R^2 of the Langmuir model is very close to one (R^2 = 0.9996). Langmuir isotherm is based on the assumption that adsorption on a homogenous surface, the surface consist of identical sites, equally available for adsorption and with equal energies of adsorption and that the adsorbent is saturated after one layer of adsorbate molecules forms onto surface [24, 25]. The graphical representation of log(q_e) as a function of log(C_e) is a line of correlation coefficient R^2, the slope of the line (1/n) and the intercept the log(K_F), (Figure. 6).

The numerical values of K_F and n calculated respectively, from the intersection with the ordinate at the origin and the slope of the line, are shown in Table 2. According to the results obtained from the two models, it can be seen that the Langmuir isotherm better describes the phenomenon of adsorption of MG on the GAC with respect to the Freundlich isotherm.

III.2. Breakthrough curve

From the study of the continuous mode of the adsorption phenomena of MG by a fixed bed, the breakthrough curve can be obtained. Improving the performance of an adsorption column on a fixed bed of granular activated carbon demands the ability at predicting the breakthrough curve of the filter according to the various system parameters. This curve presents the concentration profile of the pollutant to be removed at the outlet of the column. These parameters are the effect of height, the effect of supply rate (flow rate) and the effect of initial solute concentration.

III.2.1. Effect of bed height on the breakthrough curve

The effect of bed height on the breakthrough curve is examined by letting a dye of constant initial concentration flow with a low flow rate at different bed heights. The concentration C_t is measured against time at the output of the column and when $C_t = C_0$, the system is closed. The breakthrough curves are obtained by plotting $(C_t/C_0) = f(t)$.

Adsorption was performed with a constant feed rate and concentration at the inlet of the column, of 3 $mL.min^{-1}$ and 150 $mg.L^{-1}$ respectively. The evolution of the concentration at the exit of the column as a function of time for each height (5 to 7 cm) are shown in Figure 7. All the breakthrough curves are S-shaped [26]. Compared to the breakthrough curves obtained, we observe that the increase in operation time of the fixed bed with the increase in the height of the bed. For each bed height, the saturation time increases with the height of the bed, this translating in the fact for greater quantity of adsorbent in the column. Axial dispersion is more often dominant over actual expected mass transfer of solute during column adsorption when shorter bed heights are used as opposed to longer bed height [27]. The increase of the height the bed, The increase of the height the bed, gives an increase in the breakthrough time and adsorption capacity of the MG. More the quantity of removed per GAC is important, more the breakthrough time is greater and more the capacity retention is increasing. This indicates that increasing the quantity of GAC is improving the number of active sites.

III.2.2. Effect of MG flow rate

The flow rate is a very important parameter which influences the capacity of the adsorbent [28].

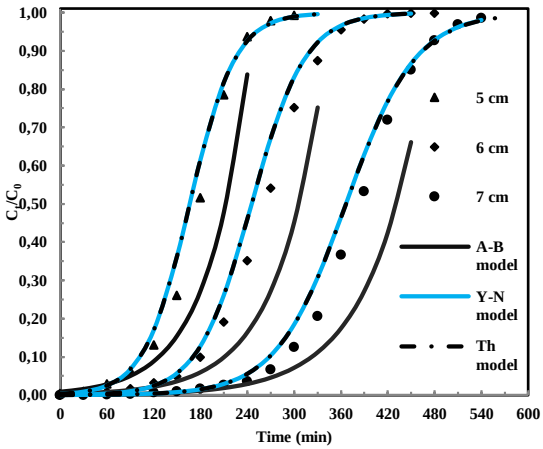

Figure 7. *Breakthrough curves for the olive stone GAC bed with 150 mg. L^{-1} and 3 $mL.min^{-1}$ flow rates*

The breakthrough curves (C/C_0) versus time by the GAC from the olive stones are plotted at the initial concentration of 150 $mg.L^{-1}$ and by varying the flow rate (from 3 to 4 then 5 $mL.min^{-1}$). The results obtained are shown in Figure 8 for the selected flow rates. As regards to the GAC, we notice that the flow rate has an important influence on the breakthrough time. These representative curves show that a low flow rate gives a better breakthrough time. A selected height (7 cm) for carbon from olive stones by maintaining the initial concentration of 150 $mg.L^{-1}$ and varying the flow rate shows that a low flow (3 $mL.min^{-1}$) gives the best breakthrough time (t_b = 265 min).

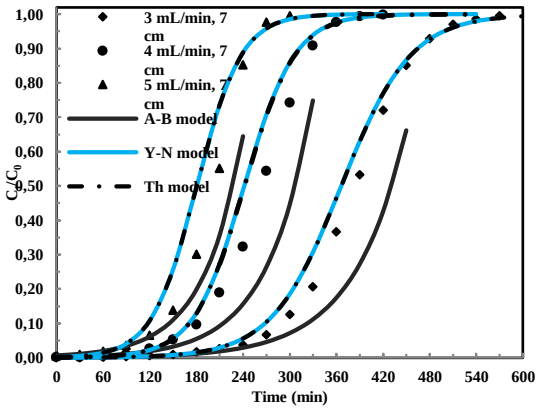

Figure 8. *Effect of MG flow rate on the breakthrough curves for the olive stone GAC (7 cm and 150 $mg.L^{-1}$)*

3.2.3. Effect of initial concentration on the breakthrough curves

The initial dye concentration has a role very important in the continuous adsorption process on adsorbents. The breakthrough curves obtained to concentrations of MG (100, 150, 200 $mg.L^{-1}$) are illustrated in Figure 9 with the bed height (7 cm) and a feed rate of 3 $mL.min^{-1}$. The variation of the initial concentration influences the breakthrough curve since it is in the range of concentration used.

These results demonstrate that the increase in concentration influences the bed saturation and the breakthrough time, the phenomenon may be explained by the fact that the lower the concentration, the larger the adsorption zone. Depending on the results, we can observe that an increase in the concentration of MG leads to a decrease in the breakthrough time on activated carbon.

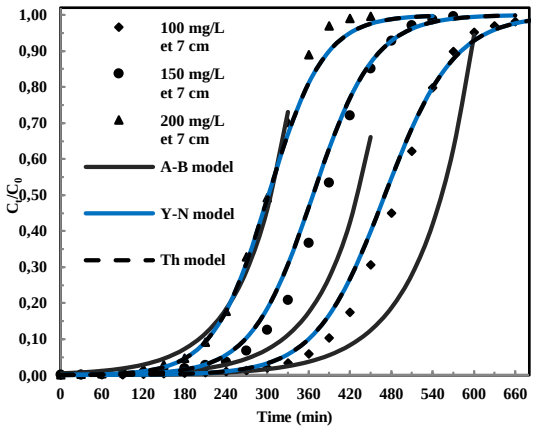

Figure 9. *Effect of MG flow rate on the breakthrough curves for the olive stone GAC (7 cm and 3 mL min^{-1})*

III.3. Modelling of the breakthrough curves

This section provides the numerical models used to access the pollutant concentration profile at the outlet of the adsorption column.

Different simple mathematical models such as the Bohart-Adams, Thomas and Yoon and Nelson models have been developed to predict the dynamic behaviour of the column. In this study, we used three mathematical models recently developed from the equations developed by Adams and Bohart (1920) [29], Thomas (1944) [30] and Yoon-Nelson [31] to describe, predict and estimate experimental data obtained from fixed-bed dynamic studies to predict breakthrough curves.

III.3.1. Model of Adams- Bohart

The following equation gives the breakthrough time versus operating parameters of the adsorber [29]:

$$ln\left(\frac{C_0}{C_b}-1\right)=\frac{k_{AB}\times N_0\times Z}{U}-k_{AB\times}C_0\times t_b \quad (6)$$

With

t_b is breakthrough time (min); C_0 is initial concentration (mg.L^{-1}); U is velocity in the supposedly empty reactor (cm.min^{-1}); N_0 is dynamic adsorption capacity (mg.L^{-1}); Z is packing height (cm); k_{AB} is Adams- Bohart constant.

III.3.2. Model of Thomas

Various mathematical models can be used to describe adsorption through a fixed bed column. The model most cited in the literature is from Thomas [30]. This model can be described by the following form:

$$\left(\frac{C_t}{C_0}\right)=\frac{1}{1+exp\left(\frac{K_{TH}.q.m}{F}-K_{TH}.C_0.t\right)} \quad (7)$$

where, C_0 and C_t are respectively the influent and effluent concentrations (mg.L^{-1}), K_{TH} is the Thomas rate constant (mL.mg^{-1}.min^{-1}), q is maximum capacity of adsorption (mg.g^{-1}), m quantity of adsorbent in the column (g), F is the feed flow (mL.min^{-1}) and t is time (min).

3.3.3. Model of Yoon-Nelson

Yoon and Nelson proposed an alternative model to describe the breakthrough curves for adsorption of vapours or gases on a column packed with carbons. It is presented in the following form [31]:

$$\left(\frac{C}{C_0-C}\right)=exp(K_{YN}.t-\tau.K_{Yn}) \quad (8)$$

where, K_{YN} is the rate constant (mn^{-1}), τ is time required for 50 % adsorbate breakthrough (mn) and t is time (mn).

Yoon-Nelson's model is only a modified Thomas model. It is applied to determine the time values (τ) corresponding to the adsorption of 50% of the pollutant

Table 3 combines the parameters obtained from the Bohart-Adams, Thomas and Yoon-Nelson model for the dye studied on the GAC: (K_{BA}, K_{TH} and K_{YN}) constant rate of adsorption and (N_0 and q_0) maximum adsorption capacity and (τ) time corresponding to the adsorption of 50% of adsorbate.

From the results of the tables, it can be seen that as the height increases, the adsorption capacity of the bed for the MG on the GAC increases and the adsorption rate constant decreases. The best adsorption capacity of MG (N_0) 31.1 mg.mL^{-1} and the best adsorption rate constant (K_{AB}) 7.7×10^{-3} L.min^{-1}.mg^{-1} are obtained for GAC from olive stones. We also find that the adsorption capacity decreases and the adsorption rate constant increases with increasing flow rate for the MG on the CAG. One can see that the initial concentration is the adsorption capacity of the bed increases and the adsorption rate constant decreases, the values of N_0 varies from 22.9 to 31.1 mg.mL^{-1} and the values of K_{AB} range from 1.35×10^{-4} to 0.77×10^{-4} L.min^{-1}.mg^{-1} with a change in MG concentration from 100 to 200 mg.L^{-1} for based on olive stones. We notice that the majority of the regression coefficients R^2 are greater than 0.91, therefore the model of Bohart - Adams described some of the MG breakthrough curves on the GAC studied.

As for the Thomas model , the width of the adsorption front requires a significant time to meet equilibrium in the filling layers, the increase in bed height increases the adsorption capacity and decreases the adsorption constant (K_{TH}). The values of the adsorbed quantity under different conditions show that the increase in feed rate decreases the adsorption capacity of the Malachite Green (MG) and increases the adsorption constant (K_{TH}). Increasing the initial concentration increases the adsorption capacity and decreases the adsorption constantt (K_{TH}), the variation in the concentration of MG from 100 to 200 $mg.L^{-1}$ leads to an increased adsorption capacity from 36.9 to 47.4 $mg.g^{-1}$, and decreases the adsorption constant (K_{TH}) from (1.99×10^{-4} to 1.25×10^{-4} $L.min^{-1}.mg^{-1}$) for the olive stone GAC. The obtained values of the regression coefficients R^2 more than 0.95 shows that the Thomas model describes all MG breakthrough curves on the studied CAG. These results illustrate that Thomas model is representative of our system. By comparison, the adsorption quantity in batch and in column systems, the values in batch systems are usually greater than those in column. The adsorption equilibrium (column saturation) is not met at the moment of the material balance.

The values of the Yoon-Nelson parameters (K_{YN} and τ) were determined from this model with respect to time (t) under a variety of conditions operating (Table 3). The adsorption constant K_{YN} values increased with increasing flow rates, while the τ (time corresponding to the adsorption of 50%) values decreased as the flow rate increased. Increasing the initial concentration decreases the time corresponding to the adsorption of 50% breakthrough (τ) and increases the adsorption constant (K_{YN}), as was observed when the bed height has been increased (Table 3). The regression coefficient (R^2) values indicate good condition in any cases, which shows that the Yoon-Nelson model may be used to describe the fixed-bed adsorption system.

Table 3. *Calculated mathimatic models parameters versus experimental data*

model			**Bohart - Adams**			**Thomas**			**Yoon-Nelson**		
Z cm	***C_0 mg/L***	***F mL/min***	***N_0 mg/mL***	***$K_{AB}\times10^{-4}$ L/min.mg***	***R^2***	***q_0 mg/g***	***$K_{TH}\times10^{-4}$ L/(min.mg)***	***R^2***	***K_{YN} min^{-1}***	***τ min***	***R^2***
5	150	3	19.9	1.25	0.9219	27.4	2.29	0.9921	0.034	166	0.9921
6	150	3	23.0	1.13	0.9119	33.2	1.95	0.9855	0.029	245	0.9855
7	150	3	27.2	0.99	0.9414	43.1	1.49	0.9894	0.022	366	0.9894
7	150	4	26.3	1.16	0.9260	37.9	2.06	0.9785	0.031	242	0.9785
7	150	5	24.9	1.31	0.9687	35.4	2.33	0.9558	0.035	180	0.9558
7	100	3	22.9	1.35	0.9416	36.9	1.99	0.9912	0.020	470	0.9912
7	200	3	31.1	0.77	0.9559	47.4	1.25	0.9722	0.025	302	0.9722

IV. Conclusion

This present study had the objective to apply granulated activated carbon (GAC) based on olive stones prepared in the laboratory to the adsorption of Malachite Green by discontinuous (batch) and continuous processes (fixed bed) for the assessment of the adsorption capacity of this support.

Batch adsorption study shows that the Langmuir model suitably described the adsorption of Malachite Green for the GAC studied better than the Freundlich model. The study of the adsorption of Malachite Green shows that the adsorption capacity reached 108.69 $mg.g^{-1}$ in the GAC from olive stones.

The adsorption of Malachite Green was also studied in dynamic mode. For the same concentration and flow rate, the time of breakthrough and saturation increased with bed height.

The models of Bohart-Adams, Thomas and Yoon-Nelson were applied to the experimental data obtained from the dynamic studies performed in a fixed bed to predict the breakthrough curves. All models are generally well simulated to describe the whole (Thomas and Yoon-Nelson) or part (Bohart-

Adams) of the Malachite Green breakthrough curves on the GAC from olive stones.

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