THE ELIMINATION STUDY OF THE METHYLENE BLUE, BY ADSORPTION ON THE ROUGH OLIVE POMACE IN THE REGION BENI MELLAL (MOROCCO)

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ABSTRACT

The aim and objective of this research project is to valorize a food-processing waste for the olive pomace within the field of the liquid effluent treatment stemming from dyes of textiles.The adsorbent properties of this material are tested on the coloring agent methylene blue (M.B) in aqueous solution. The primary results of tries created, in static regime in an agitated reactor, allowed us to notice that this material has a very important adsorbing power versus molecules of methylene blue.The kinetics of fixation of the methylene blue is extremely quick from the first five minutes, it decreases till the saturation level of the adsorbent. The study of the parameters of adsorption: granulometry, mass of adsorbing and initial concentration in (M.B) allow to give the optimum conditions to affect the modelling of the phenomena of adsorption. The optimum adsorption of the (M.B) follows the models of Langmuir, Freundlich and Temkin. The kinetic study shows that the favorable model is pseudo-second order .

Keywords - Olive pomace, methylene blue, static regime, modelling, kinetic, isotherm.

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INTRODUCTION

The rejectionsof the textile industry constitute enormous nuisances to the human health. thusthe water discharge are powerfully concentratedin coloring agents whose the low biodegradability makes biological treatments hardly applicable, which constitutes a source of degradation of the environment. The Coloring agents have the reputation to be toxic and persistent matter within environment [1], they require physico-chemical techniques to degrade them.

The methylene blue is the cationic coloring agent most usually used in the dye of the cotton, the wood also the silk. It can causeburns responsible for permanent wounds in the eyes of human being also for animals. Its inhalation will create breathing difficulties and its ingestion produces a burning sensation, causes nausea, vomiting, perspiration and plentiful cold sweat [2].The treatment of industrial rejects containing this sort of coloring agent turns out of an enormous interest.

More treatment processes of the liquid rejectionshappen, howeverthe adsorption remains a promising technique owing to the convenience of utilization and to the moderate cost compared with other applications in the processing procedure of coloring agents cationic, especially if the adsorbent is a bit expensive and easily available [3].

Knowing that the olive pomace (noted O.P) obtained in the region of BeniMellal, as byproduct of the olive industry, who is rejected in necessary quantities in the nature. It represents an important source of environmental pollution. The valuation of this waste seems the best solution to decrease its impact on the environment. One of the valuations possible of this material is that the use for the decontamination of waters loaded to coloring agents.

The objective of this research project is to study experimentally this phenomenon by optimization of the parameters involved: the granulometry, the mass of the olive pomace and also the initial concentration of the methylene blue. Then to model this phenomenon for isotherms (Langmuir, Freundlich, and Temkin) in various temperatures.The kinetics of adsorption of the methylene blue has been studied by using the equations of the pseudo-first-order and also the pseudo-second-order.

I. MATERIALS AND METHODS

1.1 Preparation of the sample

All over this research, we have created tries on samples of (O.P) prepared in the following way: the material has been dried in free air then in a temperature of 110°C during 24 hours in a sweating-room, then the material is crushed and sieved by a series of AFNOR sieves, the powder used for the experiments having a granulation between 80µm and 2mm.

1.2 Description of the tries of adsorption

All the experiences have been realized in discontinuous reactors (static system), by setting in contact a mass (m) of (O.P) ofgranulometrygiven with an aqueous solution of concentration C0 (mg/l) of (M.B), then the mixture is shaken in temperature defined well during all the manipulation to assure a good homogenization of the solution, and a better contact between the adsorbate (M.B) and all actives sites of adsorbing (O.P).

After a time of agitation, the samples collected are settled throughout a sufficient time, and also the residual concentration in the equilibrium (Ce), It's determined by an UV-visible spectrophotometer (type UV-3100PC) with the maximal wavelength (λ=664nm).

The yield of elimination of the coloring agent (M.B) was calculated by using the following formula:

$$R(\%) = \frac{C_0 - C_e}{C_0} * 100 (1)$$

The solution of (M.B) was prepared by mixing a crystallized product and distilled water, while pH controlling constantly during the manipulation.

II. RESULTS AND DISCUSSION

2.1 Effect of the granulometryof the olive pomace

Three types of granulometry of the material (O.P) were used: $G \leq 80\mu m$; $80\mu m \leq G \leq 2mm$; $G \geq 2mm$. The initial concentration used by the (M.B) is: C_0=20mg/l and the mass of the material is m=1g/l. The figure 1 shows the following results:

The analysis of curves shows that the granulometry plays a very important role in the kinetics of adsorption. The products the size of particles of which is lower in 80µm develop important external surfaces so by favoring a high speed of adsorption.

Therefore when the solid particle is small, the adsorption is better and more effective; so the phenomenon depends on the external surface of the adsorbing support which increases with the sharpness of its particles.

2.2 Effect of the mass of the olive pomace

Three masses different of the olive pomace were chosen: 1g/l, 0.75g/l and 0.5g/l.The results obtained are indicated on the figure 2 :

The most results mattering that we can fire by analyzing these curves, it's that the phenomenon of adsorption is made in two stages: the first is faster, during which more than 91 % of (M.B) to adsorb is already fixed in the sites of 1g/l of (O.P). The second is relatively longer, which can be reasoned by made that the active sites occupied lastly are probablydifficult to reach and the rate of adsorption increases with the mass, until its maximum obtained with the value of 1g/l.

2.3 Influence of the initial concentration of the (M.B)

The last parameter which remains in us to study, to optimize the process of adsorption, is the concentration of(M.B). in order to do it, three solutions of different concentrations were chosen in the conditions mentioned in the figure 3 :

The figure 3 showsthe adsorption yield increase according to time until to reach an approximately constant value at the end of seven minutes about is the initial concentration.

moreover, we can conclude that the adsorption yield is better for a concentration of 20mg/l of (M.B).

The optimal conditions which give a better yield (96.5 %) are :

pH=6.2, C_0=20mg/l, m=1g/l, G ≤ 80µm and T=25°C.

2.4 Modelling of adsorption

2.4.1 Types of isotherm of adsorption

The phenomenon of adsorption is described by isotherms, representing the adsorption capacity Qe according to the equilibrium concentration of the adsorbate.

$$Qe=(V/m)\ (C_0\text{-}Ce) \quad (2)$$

Qe : Quantity of adsorbateretained by the adsorbent in mg/g, V : volume of the solution l; and m : mass of the olive pomace;

The shape of these isotherms can suggest the type of interaction between the adsorbate and adsorbent. According to Gilles [4], there are four types: type-C, type-L, type-H and type-S. The figure 4 illustrated the result obtained :

The shape of this curve shows that the isotherm is of type L. Besides, the typical isotherm L can be explained by the models of Langmuir, Freundlich and Temkin, that we have applied to our experiences of adsorption in the following way :

2.4.2 Model of Langmuir

Langmuir [5] proposes the following model :

$$Qe = \frac{K_L\ Qmax\ Ce}{1 + K_L\ Ce}\ (3)\ \text{linearisable in}\ \frac{1}{Q_e} = \frac{1}{Qmax} + \frac{1}{Qmax\ K_L} . \frac{1}{C_e}\ (4)$$

Qmax : maximal capacity of adsorption mg / g and KL : Equilibrium constant of the Langmuir adsorption l/mg ;

By plotting 1/Qe according to 1/Ce we obtain a straight line with a slope of 1/(Qmax.KL) and originally ordered of 1/Qmax.The representation of this equation with various temperatures is shown on the figure 5 :

According to these curves the coefficients of correlation are close to the unit and consequently the molecules of the (M.B) are adsorbed in monolayer whatever the temperature. We also notice that the value of the maximal capacity of adsorption is the order of 333.33mg/g corresponding to the ambient temperature.

2.4.3 Model of Freundlich

The model of Freundlich[6] is expressed by the following equation :

$$Qe = K_F\ .\ C_e^{\ 1/n}\ (5)$$

K_F and 1/n : constants of Freundlich representing respectively the capacity and the intensity of adsorption ;

The isotherm of Freundlich is generally represented its linearized form:

$$\text{Log}Q_e = \text{Log}\ K + \frac{1}{n}\ \text{Log}C_e (6)$$

By plotting ln Qe according to ln Ce, we obtain a right line with slope of 1/n and originally ordered of ln K_F.

The representation of this equation with various temperatures is shown on the figure 6 :

The coefficients of correlations are always superior to 0.98 indicate that the isotherms obtained follow correctly the model of Freundlich, this shows that the molecules of (M.B)

take place on heterogeneous sites , with a maximal capacity of adsorption lower than that planned by Langmuir (271.4mg/g in 25°C).

2.4.4 Model of Temkin

The isotherm of Temkin [7] was transposed into the liquid phase by Zarrouki [8].

$$\frac{Q_e}{Q_{max}} = \theta = \left(\frac{RT}{\Delta Q}\right) \ln (K_T . C_e) \text{ (7)}$$

The linearization of this equation leads in

$$Q_e = \left[Q_{max}\left(\frac{RT}{\Delta Q}\right)\right] . lnC_e + \left[Q_{max}\left(\frac{RT}{\Delta Q}\right)\right] . lnK_T \text{ (8)}$$

Θ : Rate of covering of the surface of adsorbent ; ΔQ : the variation of energy of adsorption (kJ.mol-1) ; Qmax : theoretical maximal capacity of adsorption expressed in (mg/g); K_T : Equilibrium constant and R=8.314 J.mol-1.K^{-1} constant of perfect gas.

By plotting Qe = f(lnCe), we obtain a right line whose the slope and the orderly originally allow to determine the energy of adsorption ΔQ and the equilibrium constant K_T.

The representation of this equation with various temperatures is shown on the figure 7 :

According to the linear track of Temkin we notice that the Equilibrium constant increases with the increase of the temperature, it means that the reaction of adsorption is endothermic. On the other hand, we notice that the energy of adsorption varies of a temperature in other what lets suggest that the connections so involved between adsorbing it and the adsorbate are of different nature. In other words, it is many about the heterogeneous existence of sites such as it planned by the model of Freundlich.

2.5 Kinetics

2.5.1 Reversible model of the first order [9]

The reversible model of the first order supposes that the speed of adsorption at the moment t is proportional in the difference between the capacity adsorbed in the equilibrium Qe, and the quantity Qt adsorbed at this moment. In other words, the adsorption is fast all the more as the system is far from the equilibrium. The law of speed spells:

$$\frac{dQ_e}{dt} = K_1 . (Q_e - Q_t) \text{ (9)}$$

The integration of the equation of the used model is the following one:

$$\ln(Q_t - Q_e) = lnQ_e - K_1 . t \text{ (10)}$$

K_1 : the constant of speed for a kinetics of the first order; Qt : the capacity of adsorption at the moment t. The linear representation of ln(Qe-Qt) according to time, illustrated in the figure8, is used to determine the value of theoretical Qe and that of constant of speed K_1.

2.5.2 Reversible model of the second order [10]

The model of the second order suggests the existence of a chimisorption, an exchange of electron for example between molecules of adsorbate and adsorbing it solid. It is represented by the following formula :

$$\frac{dQ_e}{dt} = K_2.(Q_e - Q_t)^2 \quad (11)$$

K_2 : the constant of speed for kinetics of the second order.

The integration of this equation gives :

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_2.Q_e^2} \quad (12)$$

The linear representation of t/Qt according to t illustrated the figure 9 is used to determine the values of theoretical Qe of the second order and K_2.

The kinetic parameters 1st and 2nd order for the adsorption of (M.B) on (O.P) illustrated on table1 :

According to these values, we see clearly that it is a question of one kinetics pseudo-second order, and it about is the concentration chosen at first. What shows that the adsorption of (B. M) on the (O.P) is a chimisorption.

III. FIGURES AND TABLES

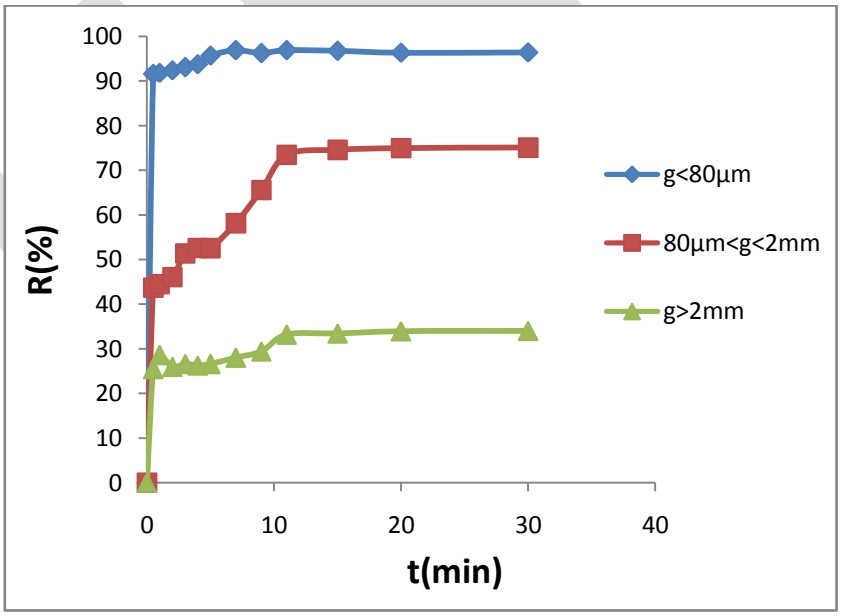


Fig1 : Effect of the granulometry of the (O.P). (pH=6.2, C0=20mg/l, Vagitation=300t/min and m=g/l).

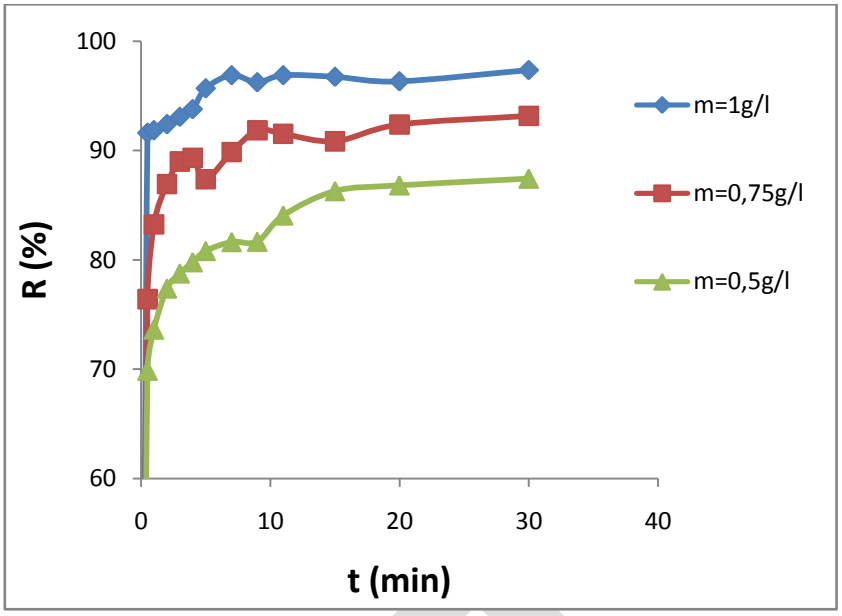


Fig2 : Effect of the mass of the (O.P) on the adsorption of the (M.B). (pH=6.2, C_0=20mg/l, $V_{agitation}$=300t/min and granulometry=80µm).

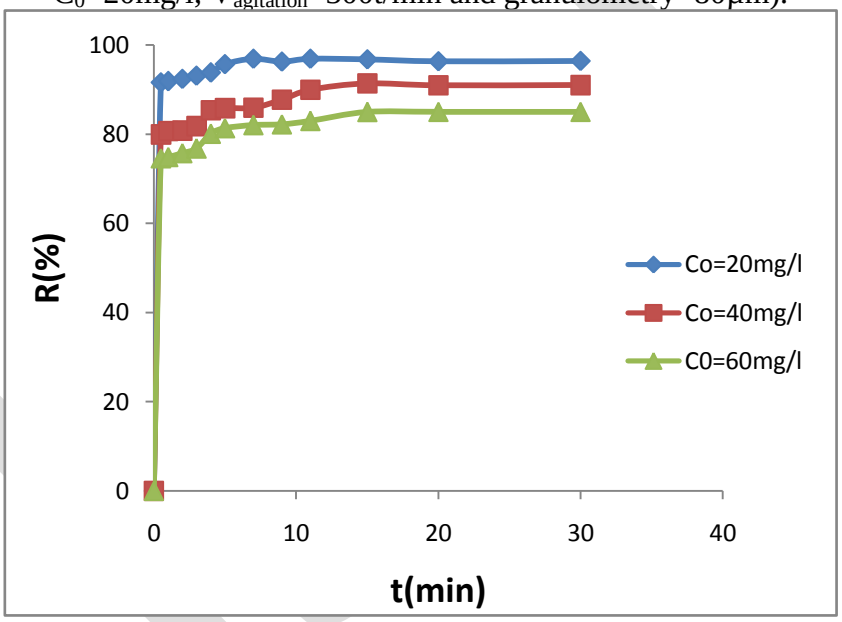
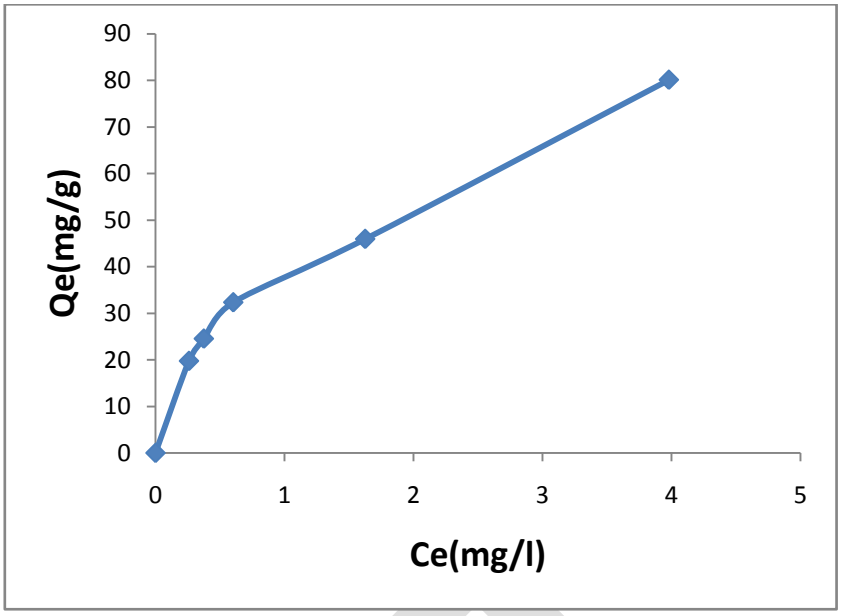
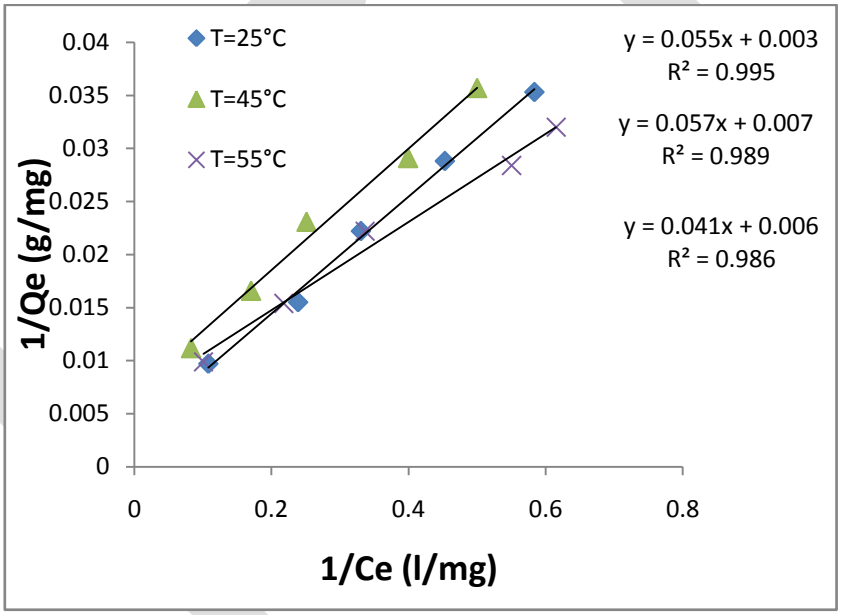


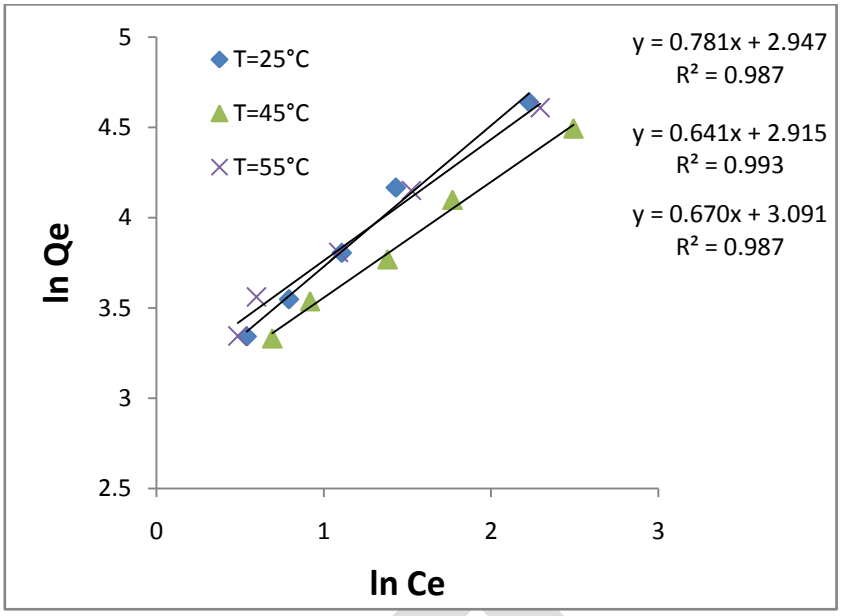
Fig3 : Effect of the initial concentration of the (M.B). (pH=6.2, m=1g/l, $V_{agitation}$=300t/min and granulometry≤80µm).



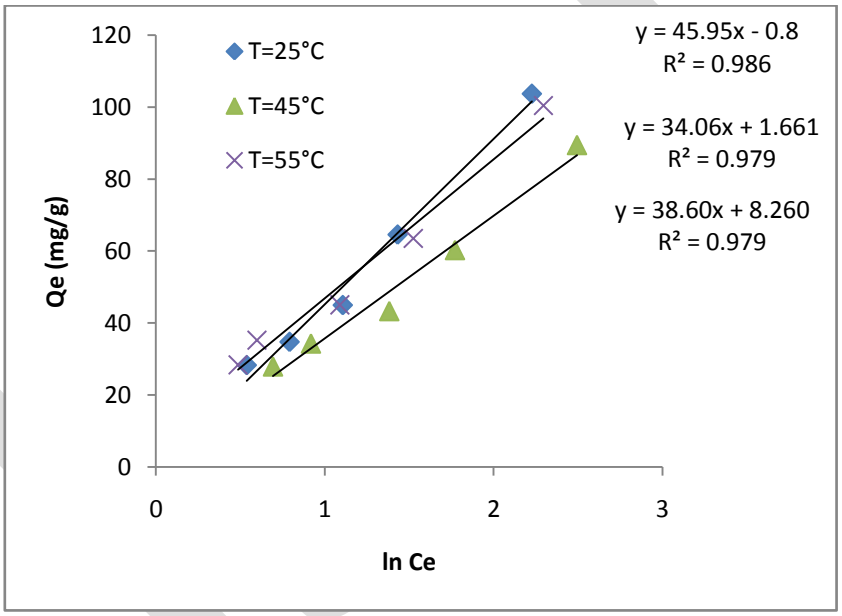
Fiq4 : Isotherm of adsorption of (M.B) on the (O.P). (pH=6.2, C0=20mg/l, $V_{Agitation}$=300t/min, granulometry ≤ 80µm and ambient temperature).



Fiq5 : Modelling of the isotherms of adsorption by the equation of Langmuir.



Fiq6 : Modelling of the isotherms of adsorption by the equation of Freundlich.



Fiq7 : Modelling of the isotherms of adsorption by the equation of Temkin.

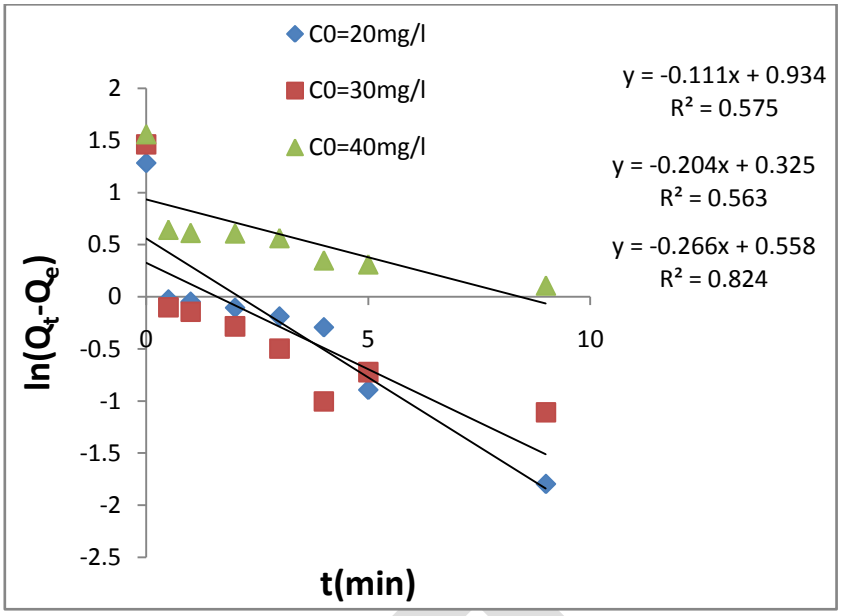


Fig8 : Kinetic Model of the first order (pH=6.2, m=1g/l, $V_{agitation}$=300t/min and granulometry=80µm).

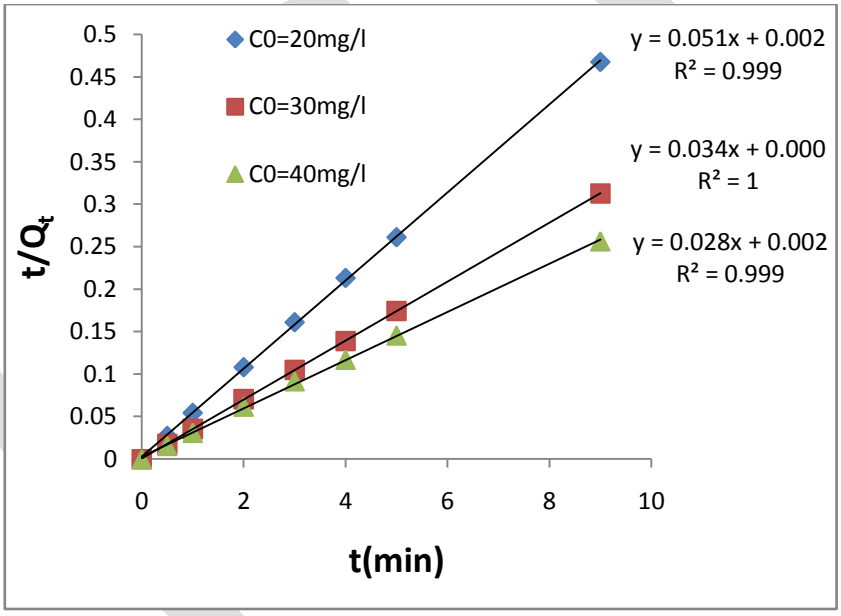


Fig9: kinetic Model of the second order. (pH=6.2, m=1g/l, $V_{agitation}$=300t/min and granulometry≤80µm).

Table 1 : The kinetic parameters 1st and 2nd order for the adsorption of (M.B) on (O.P).

	C_0 (mg/l)	Qe(calc) (mg/g)	Qe(exp)	R^2
Kinetic model 1st ordre	20	8.591	19.268	0.575
	30	2.113	28.257	0.563
	40	3.614	36.376	0.824
Kinetic model 2nd order	20	19.608	19.268	0.999
	30	29.412	28.857	0.999
	40	35.714	36.376	0.999

CONCLUSION

In this experimental study of the adsorption of the (M.B) on (O.P) showed that the maximal capacity of this natural substance is of the order of 333.33mg/g, within the optimal conditions: pH= 6.2, C_0=20mg/l, m=1g/l, G≤80µm and T=25°C.

The application of the models thermodynamics (Langmuir, Freundlich and Temkin) revealed a number of informations:

- The adsorption is a monolayer type (Langmuir) ;
- Sites are heterogeneous (Freundlich) ;
- The transformation is endothermic (Temkin).

According to our kinetics study we found that the adsorption of the (M.B) on (O.P) is a reaction of the pseudo-second order as a result of this the adsorption is a chimisorption.

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