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Kinetic and Equilibrium Studies on Adsorption of Methylene Blue and Methyl orange in Aqueous Solution onto Activated Carbon by H_3PO_4 Activation from the Hulls of *Vitexdoniana*

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ABSTRACT: A carbonaceous adsorbent prepared from hulls of *Vitexdoniana* by H_3PO_4 treatment was investigated for its efficiency in methylene blue (MB) and of methyl orange (MO) adsorption in aqueous solution. The characterizations of materials are carried out by Fourier Transform Infrared Spectroscopy (FTIR), pH (6.2) and the iodine index measurement which showed that our powder activated carbon is primarily made up of meso and macro pores. The influence of major parameters governing the efficiency of the process such as, solution pH, sorbent dose, initial concentration, ionic strength and contact time on the removal process was explored. The Times of balance of adsorption are obtained to 40 and 50 minutes respectively for the MB and MO. The outputs of elimination of the molecules of the MB and MO to this balance are respectively to 85.92% and 46.60%. The variation of pH showed that the maximum of adsorption of the MB is with pH=10 and for MO, the maximum of adsorption is with pH=3. Four theoretical adsorption isotherms namely Langmuir, Freundlich, Temkin and Dubinin -Radushkevic were used to describe the experimental results. The models of Temkin and Dubinin-Radushkevic describe better the adsorption of the methylene blue. The model of Langmuir is that which corroborates, better than others, with the experimental results in the case of methyl orange. The reaction of adsorption of the two dyes is endothermic and the mechanism of adsorption is chemical. The pseudo-first order kinetic models, pseudo second order, Elovich and intra particulate have been applied to the experimental data and that which is appropriate is the kinetic model of pseudo second order.

KEY WORDS: adsorption, kinetic, Vitexdoniana, dye, methylene blue, methyl orange, activated carbon.

1 INTRODUCTION

Water is a vital element whose importance at the planetary level is unceasingly pointed out. Actually, the industrial and agricultural activities generate significant rejections following the example residues of pesticides, dyes, gases, heavy metals, etc, which very often are poured without any control in the environment.

The synthetic dyes currently occupy a significant place in the industrial sector. They are largely used in the industry of paper, cosmetic, agro alimentary and in particular in textile industry [1]. The intensive use of the dyes in the life generated problems in the food as well in the environment [2]. The methylene blue and methyl orange are two dyes contained mainly in the industrial effluents, they are non-biodegradable and very poisons for the plants, the aquatic animals and the human.

The methylene blue (hereafter MB) to 1ppm is acceptable in water; so it affects the watery ecosystem negatively, because it reduces the diffusion of the sunlight, thus inhibiting the photosynthesis of the aquatic plants [3]. At the human, the methylene blue can cause the following nuisances: the irritation of the respiratory and intestinal tracts, nauseas, vomiting, a diarrhoea, headaches, giddinesses and blindness (irreversible lesion of the optic nerve) [4]. The methyl orange (hereafter MO) is azodye used in several industries. The estimation of the risks of cancer forces to fix a limiting concentration of 3.1µg/L while azodye in drinking water [5]. To exceed this concentration, methyl orange has carcinogenic and genotoxic effects, and can cause nauseas and vomiting. It is thus significant to treat the effluents of industries containing the MB or MO before their rejection in the environment. To mitigate this situation, several methods of decontamination were developed. Namely: adsorption [6], exchange of ions [7], coagulation - flocculation [8], photocatalytic oxidation… etc. The bio-adsorption does not allow a satisfactory elimination of the textile dyes because of the presence of the aromatic nuclei in their molecules [9]. The removal of the dyes by adsorption on solid supports is a cheaper and simple process to implement, effective to weak concentrations, and makes it possible to regenerate the adsorbent. To this purpose several types of adsorbents were already tested in the elimination of the dyes in water among: clays, zeolites, gel of silicate, iron oxides, activated carbon, silicon and titanium oxides. Of all these adsorbents, activated carbon is more used because of its great capacity of adsorption and its great stability [10]. Several low cost materials were used for the manufacture of the activated carbon; in this research, a local waste, the hulls of Vitexdoniana, was used to produce activated carbon. This is due to the availability and low cost of the material with high-carbon and low inorganic content. Moreover, no work has been reported on the production of activated carbon using the hulls of Vitexdoniana.

2 MATERIAL AND METHODS

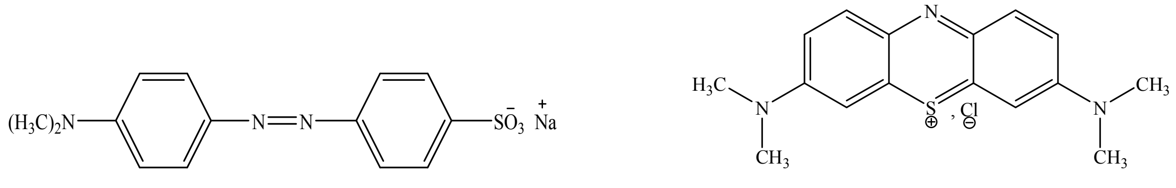
The collected cores of vitexdoniana are abundantly washed with running water to eliminate the impurities, rinsed by distilled water then dried under sun. Once dried, these cores are crushed to separate the hulls from almonds. The hulls are then washed by distilled water then dried with the drying oven at 110°C during 24 hours. The hulls are then crushed in a mortar out of wooden then riddle to retain only particles of size lower than 500 µm. The fractions of the hulls of Vitexdoniana are again dried with the drying oven at 110°C for a period of 24 hours. These fractions of the hulls are impregnated by phosphoric acid (H_3PO_4) respecting a 1:1 ratio. From an initial solution of 95% of phosphoric acid (H_3PO_4); a prepared solution of 10%, by dilution, is then mixed with the raw material. The mixture is homogenized at ambient temperature using a rod of glass until formation of a paste. After impregnation, these samples of the hulls of Vitexdoniana are dried by the drying oven at 110°C during 24 hours and cooled in a desiccator during 3 hours.

The carbonization of our material was done at 400°C during 2 hours, at a heating speed of 10°C/min in a CARBOLITE furnace programming temperature and cooling is done in a progressive way at ambient temperature.

Once cools, the activated carbon is thus washed by the distilled water until obtaining a neutral pH. Then, the samples are dried with the drying oven at 110°C during 24 hours; they are crushed then in a mortar using a porcelain rammer both until obtaining a powder containing only one fraction of particle having a size lower than 80µm: the activated carbon powders are thus ready to be used.

2.1 THE BATCH MODE ADSORPTION STUDY

The studies of adsorption were conducted at ambient temperature (25 °C) in a 250 ml screw-cap conical flask. For each of the experiments, 0.01–0.05 g of adsorbent dose was weighed and placed in the screw-cap flask containing 20 ml of methylene blue or methyl orange solution presenting the desired concentration (varying from 6 to 18 ppm), pH between 2 and 11. The following figure show the chemical structures of the methylene blue and the methyl orange (figure 1).



(a) (b)

Figure 1: The structures of methylene blue (a) and methyl orange (b)

The mixture was stirred by magnetic agitation on the interval of time between 10 –60 minutes. After agitation, the suspension is filtered on whatman paper N°1. The absorbances were measured at the absorption wavelength maximum; 668 nm for the MB and 508nm for MO in acid zone (pH< 3.1) and 465nm in basic zone (pH > 4.4). The quantities adsorbed

(Qe) in milligram per gram of adsorbent and the percentages of retention are calculated by application of the relation (1) and (2) below:

$$Q_e = \frac{C_0 - C_t}{m} V \qquad (1)$$

$$\%R = \frac{C_0 - C_t}{C_0} \times 100 \qquad (2)$$

Where C_0 is the initial concentration; C_t is the concentration at time t (mg.L^{-1}); V is the volume of adsorbate (mL) and m the mass of activated carbon (g).

3 RESULTS AND DISCUSSION

Table 1 presents values of iodine index and pH as characteristics of the activated carbon from the hulls of vitexdoniana.

Table 1: characteristics of the activated carbon from the hulls of vitexdoniana

Parameters	**Values**
Iodine index	411.98 mg/g
pH	6,22

On the FTIR spectrum (figure 2), we observe a band at 3224 cm^{-1}, corresponding to the band of stretching of the hydroxyl grouping - OH of phenol and the hydrogen bonds of alcohols. We observe also a band at 1694 cm^{-1} which indicates the C=O grouping and 1588 cm^{-1} indicates the presence of C=C bond (aromatic). The band located at 1416 cm^{-1} indicates the presence of the stretching of N–H bond; the bands at 1117 cm^{-1} and 1083 cm^{-1} respectively indicate a rocking of –OH and –COOH grouping and a rocking of - C-O-C grouping of ether. The band at 1010 cm^{-1} indicates the stretching of the P - O bond resulting from the activation of material by H_3PO_4. There are a wagging corresponding to CH at 873 cm^{-1} and a band indicating a wagging of CH of benzene at 834 cm^{-1}. The bands at 804 cm^{-1} indicate the stretching of C=C bond of para substituted benzene. The bands at 762 cm^{-1} and 750 cm $^{-1}$ respectively indicate the stretching of C=C bond of meta and ortho substituted benzene. At 737 cm^{-1} the spectrum presents a monosubstituted aromatic vibration of C=C. Thus, the spectrum suggests the presence of the groupings like phenol, carbonyl, amine, ether and carboxylic.

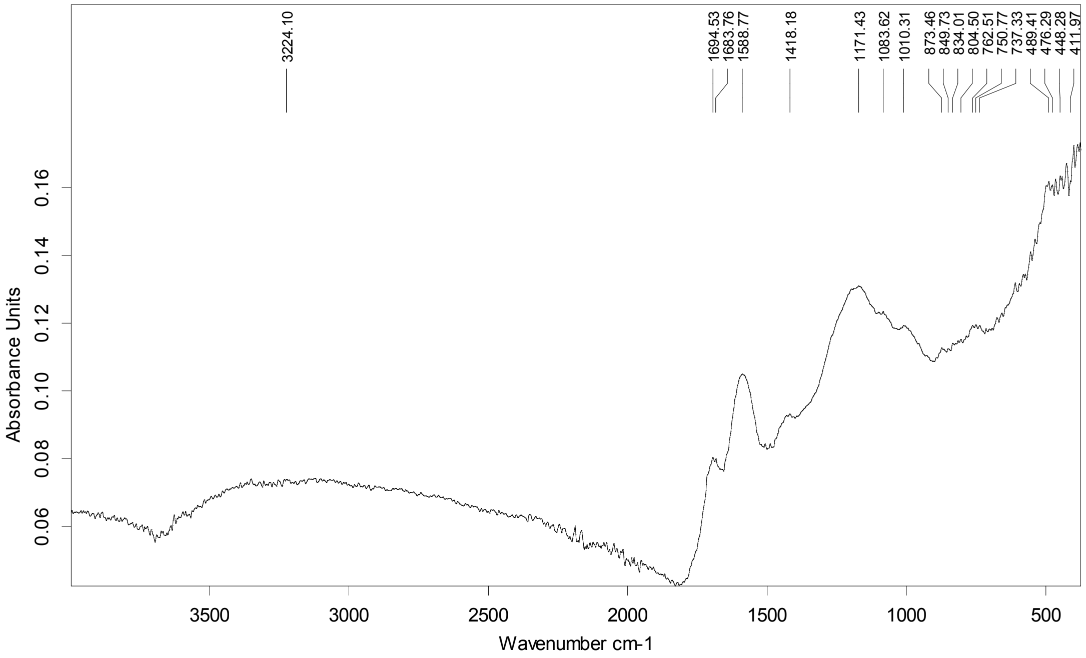


Figure 2: FTIR spectrum of activated carbon

3.1 THE EFFECTS OF CONTACT TIME

The adsorption of the molecules of MB and MO in aqueous solution of initial concentration 18 mg/L with initial pH for the MB and pH=3 for MO is carried out on 0.05g of activated carbon; and for increasing times of agitation give the results represented in Figure 3.

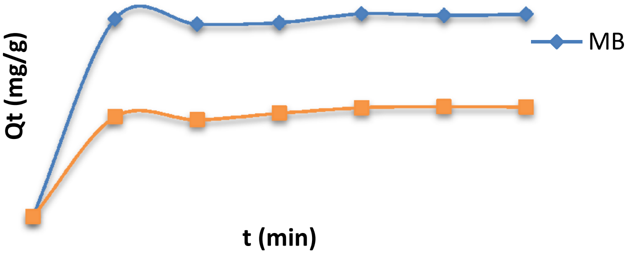


Figure 3: The effects of contact time on sorbent-sorbate interaction time.

From these curves, it comes out that the adsorption of the molecules of MB and MO respecting the activated carbon is fast during the first 10 minutes to reach the balance which is 40 min for the MB and 50 min for MO with adsorbed quantities maximum which are 6.187mg/g and 3.356mg/g respectively. The fast speed of adsorption of the first phase (fast phase) can be explained by the fact why at the beginning of the phenomenon, the sites of adsorption are free on the surface of our adsorbent material. Once that the molecules of MB or MO are fixed, they blocks the pores, thus slowing down the speed of adsorption, there is apparition of a plate of saturation, from where the second phase (slow phase). This trend agrees with the report of other investigators [11].

3.2 THE EFFECT OF ADSORBENT DOSE

The studies are carried out with a mass alternative from 0.010g to 0.050g ; a time of agitation of 40min and 50min respectively for the MB and MO; a volume of 20mL for 18 mg/L of concentration. The figure 4 is noticed, that the quantities of pollutants adsorbed decrease with the increase in the mass of adsorbent and tend to be stabilized for great values of masses. This can be explained by the fact that, the increase of mass involves a growth of the electrostatic interactions between the particles of the adsorbent which leads to the desorption of the molecules of the MB or the MO of the sites of the adsorbent, thus led an agglomeration of the particles of the adsorbent; thus forming aggregates; there is thus reduction in the surface of contact by the fact that active sites of the activated carbon become masked. Consequently there is increase in the way of diffusion of the known as molecules with respect to the active sites. These results are in agreement with those observed by other authors [12].The mass of 0.01g of activated carbon was retained for the continuation of our work for the two adsorbates; because the quantity adsorbed one maximum with this value.

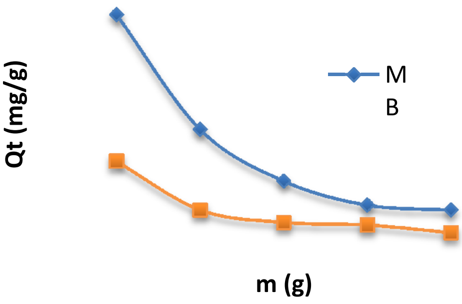


Figure 4: The effect of carbon dose for the uptake of methylene blue and methyl orange

3.3 THE EFFECT OF PH ON MB AND MO ADSORPTION BY ACTIVATED CARBON FROM VITEXDONIANA

This study is carried out starting from the solutions of the MB and MO of initial concentration 18 mg/L; with a mass of 0.01g of the activated carbon; a volume of 20mL and with times of contact. The effect of pH was studied in the range from 2.0 to 11.0 and the results are represented by figure 5: It arises that the adsorbed quantity of the MB increases with the pH, this increase can be due to the fact that the surface of activated carbon would be negatively in charge with values of basic pH, which supports the adsorption of the methylene blue (basic dye). On the other hand, for values of acid pH, the surface of activated carbon would be charged positively, and thus likely to push back the cations of the dye. In addition, lower it arises that the adsorbed quantity of the MB increases with the pH, this increase can be due to the fact that the surface of activated carbon would be negatively in charge with values of basic pH, which supports the adsorption of the methylene blue (basic dye). On the other hand, for values of acid pH, the surface of activated carbon would be charged positively, and thus likely to push back the cations of the dye. In addition, lower adsorption of methylene blue at acidic pH might be due to the presence of excess H^+ ions competing with dye cations for the available adsorption sites. Similar results were observed by other authors [13].

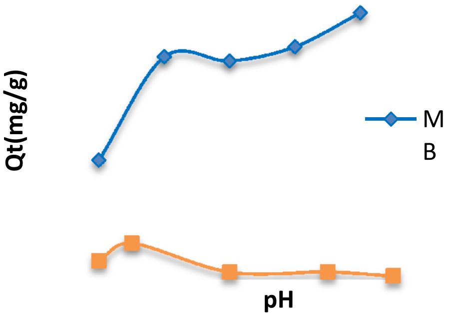


Figure 5: The effect of pH on methylene blue and methyl orange adsorption by activated carbon from Vitexdoniana

Furthermore, it is noted that the adsorbed quantities of MO by the activated carbon generally are overall weak for the basic zone and the more acid zone (pH=2). The adsorbed quantity is maximum with pH equal to 3.0 in this study; and it is worth 4.403mg.g^{-1}. This can be explained by the fact why in basic zone, the load of surface of the activated carbon is negative, if the pH is higher than pKa 3.7 of methyl orange, and one has the ionized shape of this acid (ion sulphonate (SO_3^-) There is thus repulsion between the surface of the activated carbon and the groupings sulphonates (SO_3^-) of methyl orange. This result is in agreement with those observed in the literature [14].

3.4 THE EFFECT OF THE IONIC STRENGTH

The Figure 6 shows that, the adsorption of the molecules of MB decreases then increases gradually with the addition of the small quantities of NaCl, while for MO the adsorbed quantities increase with the addition of small quantities of NaCl salt.

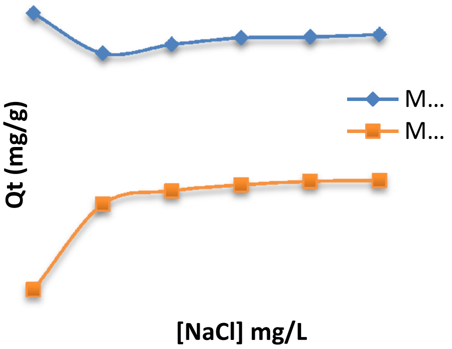
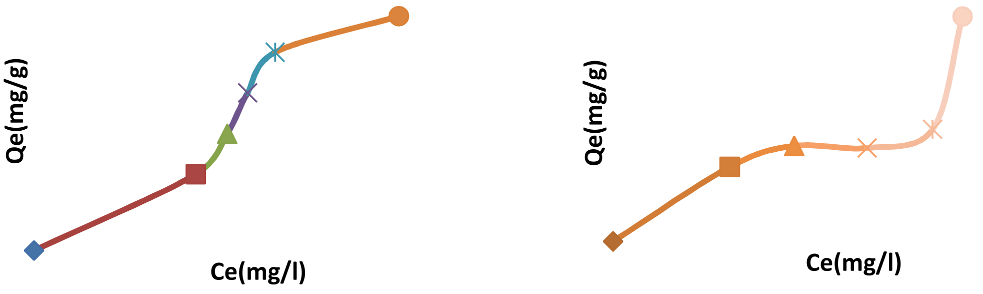


Figure 6: the effect of the ionic strength of NaCl on the adsorption of the MB and MO by the activated carbon.

The NaCl addition led to the increase in the adsorption of the dye the addition of salt supports the process of bringing together association of the particles of the activated carbon, therefore the formation of a new porosity and new sites of surface where the molecules and the aggregates of dyes would be trapped [15]. A number of intermolecular forces were suggested to explain this aggregation, these forces include: the forces van der Waals [16]; forces of dipole-ion and the forces dipole-dipole which occur between the molecules of the dyes in solution. Consequently, the rise in the capacity of the adsorption of the molecules of MB and MO under these conditions can be allotted to the aggregation of these last armatures by the action of the NaCl ions, In other words, the molecules of MB and MO are bound increasing the extent of the adsorption on the surface of activated carbon.

3.5 ISOTHERM OF ADSORPTION AND KINETIC MODEL

The isotherm was obtained by varying the initial concentration at an ambient temperature. The results are represented by the figures 7.



(a) *(b)*

Figure 7: Isotherm of adsorption of the MB (a) and MO (b) by the activated carbon from hulls of Vitexdoniana

The isotherms of adsorption of the molecules of MB and MO by the activated carbon are of type V and type II respectively, according to the classification of the isotherms according to I.U.P.A.C. In the case of adsorption of the MB the isotherm translates a capillary phenomenon of condensation inducing a delay or a precocity of the attack of the plate of saturation; this behavior is representative of stronger interaction between the molecules compared with the interaction between the molecules and the adsorbent; and that of MO shows that adsorption is done initially into full-course then into multi-layer until capillary condensation. The stage indicates that once the full-course attack, and if the concentration of adsorbate increases, there is formation of a new layer covering the first adsorbed layer.

The experimental results thus have been faced four models of isotherm in order to describe this adsorption with balance: models of Langmuir, Freundlich, Dubinin-Radushkevich(D-R) and Temkin; four model kinetics were also used.

Taking into consideration this table 2, the linear coefficients of correlation of adsorption are higher for the models of Temkinand Dubinin-Radushkevich for the adsorption of the MB. In the case of MO, with the sight of the coefficient S of linear correlation, no models has $R^2 > 0.90$. The model of Dubinin-Radushkevich which shows a good affinity with the process brought into play implies that we can have a homogeneous distribution or heterogeneous of the sites. The model of Temkin which has also a good linear coefficient of correlation for the MB shows us here that our adsorption has heterogeneity of surface but also that adsorption was done into multi-layer.

Table 2: summary table of the constants and the coefficients of correlation of the isotherms models

MODELS	**Langmuir**			**Freundlich**			**D-R**			**TemKin**		
Parameters	K_L	Q_m (mg/g)	R^2	K_F	N	R^2	K' 10^{-6}	Q_m (mg/g)	R^2	B	A	R^2
MB	0.491	3448	0.831	30.235	0.755	0.823	0.3	67.22	0.918	28.03	2.95	0.902
MO	0.086	7.63	0.661	0.676	1.377	0.601	4	4.678	0.455	2.89	0.38	0.485

The adsorbed quantities maximums that are obtained thanks to the Langmuir model which are of 34.48 mg/g and 7.63mg/g respectively for MB and MO bring are closer to the experimental values which are of 33.56mg/g and 6.99mg/g. The values of the dimensional parameter R_L are equal to 0.102 and 0.392 respectively for the MB and the MO which are both ranging between 0 and 1 ($0<RL < 1$), shows that the isotherms of adsorption of the MB and MO are favorable.

The value of constant n of the model of Freundlich for the MB equal to 0.755 lies between 0.5 and 1 indicating as well as adsorption is Moderated, then qu E in the case of MO, adsorption is weak because coefficient n equal to 1.377 is higher than 1. Thus, one can say that there is good affinity with our activated carbon and the molecule of MB, on the other hand for MO, it is weak. The value of the energy E of adsorption given starting from the model of Dubinin- Radushkevic gives an indication of the type of adsorption. The values of energy of adsorption E are equal to 1290.99 $KJ.mol^{-1}$ for the MB and 353.55 $KJ.mol^{-1}$ for MO. These experimental values of energy are all higher than 40 $KJ.mol^{-1}$, which indicates that the adsorption of the MB and MO by the activated carbon is of type chemical. The variations of the energy of adsorption ΔQ equal to 88.39 KJ/mol and 857.29 KJ/mol respectively for the MB and MO rising from the Linearization of the model of Temkin are positives. That means the reaction of adsorption is endothermic [17].

It arises from table 3, that the models of pseudo-first order, Elovich and the intra particulate diffusion cannot be applied to explain the adsorption of the MB and MO because of their low values of the coefficients of correlation R^2 which are all lower than 0.90. However, the coefficient of correlation of the kinetic model of pseudo-second order is more about the unit. This result indicates that the kinetic model pseudo-second order describes well the experimental results of the adsorption of the MB and the MO by the activated carbon. The values of the calculated theoretical adsorbed quantities (6.257 and 3.491 mg/g) of the model of pseudo-second order are very close to adsorbed quantities obtained experimentally (6.186 and 3.355 mg/g). The mechanism of adsorption of the MB and MO is thus done according to the assumption of the kinetic model of pseudo-second order in two stages:

- The first is the diffusion of the MB and MO towards the surface of the adsorbent;
- The second is the interaction between the molecules of adsorbates (MB and MO) and surfaces it the adsorbent (activated carbon).

Table 3: Constants Speed and Coefficients of correlation of the Kinetic Models.

MODELS	**Pseudo-first order**			**Pseudo-second order**			**Elovich**			**Intra-particulate diffusion**		
Parameters	k_1 (min^{-1})	Q_m (mg/g)	R^2	k_2 (g/min.g)	Q_e (mg/g)	R^2	B	A	R^2	C $m^2.S^{-1}$	K_{int} ($mg.L.min^{1/2}$)	R^2
MB	0.053	11.302	0.799	6.561	6.257	0.999	8.278	$2.33.10^{19}$	0.35	5.752	0.052	0.439
MO	0.075	1.107	0.718	1.401	3.491	0.998	4.557	$1.56x10^4$	0.73	2.691	0.088	0.786

4 CONCLUSION

This study confirms that the activated carbon from the hulls of Vitexdoniana allows the elimination of the methylene blue and methyl orange in aqueous solution. The optimal pH of adsorption of the MB is equal to 10.0 and that of MO is equal to 3.0. The amount of the adsorbent and the ionic strength has a significant influence on the process of sorption. The balance of adsorption of the MB is reached with 40min and that of MO is reached with 50min. the kinetic one of adsorption for the two dyes is of the pseudo-second order. The models of isotherm of Dubinin-Radushkevich and Elovich are enough adapted to describe the isotherm of adsorption of the MB. The model which better describes the adsorption of MO is the model of Langmuir. The energies calculated by the model of Dubinin-Radushkevich indicate that the mechanism of adsorption is chemical. On one hand, there is a good affinity between our activated carbon from Vitexdoniana by H_3PO_4 and the molecules of MB (basic dye), on the other hand for MO (acid dye), it is weak.

REFERENCES

[1] V. K. Garg, R.Gupta, T. Juneja, “Removal of a Basic Dye (Rhodamine-B) From Aqueous Solution by Adsorption Using Timber Industry Waste”, *Chem. Biochem. Eng.*, vol.19, no. 1, pp. 75–80, 2005.

[2] L. Zhenwang, C. Zhenlu, L. Jianyan, “The PT dye molecular structure and its chromophoricluminescences mechanism”, *15th World Conference on Non-Destructive Testing, 15-2 1 October Rome*, 2000.

[3] J.N. Ndi, M. J. Ketcha, “The adsorption efficiency of chemically prepared activated carbon from cola nut shells by $ZnCl_2$ on methylene blue”, *Journal of chemistry*, ID469170, 7P, 2013.

[4] Dipa Ghosh, G. Krishna Bhattacharyya, “Adsorption of methylene blue on kaolinite”, *Applied Clay Science*, vol. 20, pp 295 – 300, 2002.

[5] J.S. Bae and H.S. Freeman, “Aquatic Toxicity Evaluation of Copper Complexed Direct Dye to the Daphnia Magnia”, *J. Dyes and Pigments,* vol. 73, pp. 126-132, 2007.

[6] N. Ababou, D.Meziane, A. Kherbeche, A. Chaqroune, “Etude de l'adsorption de colorants textiles sur une diatomite marocaine”, *Phys. Chem. News,* vol. 6, pp. 130 -134, 2002.

[7] EPA,) “Integrated Risk Information System”, Azobenzene, CASRN 103-33-3, 1998.

[8] J. Panswed, and s. wongchaisuwan, *water SciTechnol*, vol., no. 18, 139, 1986.

[9] H. Nozet, Textiles chimiques. Fibres modernes, *Eyrolles*, Paris, 1976.

[10] F.C. Wu, R.L. Tseng, R.S. Juang, “Preparation of highly micro porous carbons from fir wood by KOH activation for adsorption of dyes and phenol from water”, *Separation and Purification Technology*, vol. 47, pp. 10-19, 2005.

[11] R. Slimani, A. Anouzla, Y. Abrouki, Y. Ramli, S. El Antri, R. Mamouni, Solazar, M. El Haddad, “Removal of cationic dye - methyle blue- from aqueous media by the use of animal bone meal as a new low cost adsorbent”, *J. Mater.Environ.sci.* vol. 2, no.1, pp. 77-87, 2011.

[12] J.N. Ndi., M. J. Ketcham, “The adsorption efficiency of chemically prepared activated carbon from cola nut shells by ZnCl2 on methylene blue”, *Journal of chemistry*, ID469170, 7P., 2013.

[13] B. K. Asmaa, B M. adia, H. Mohsine, B. Mina, Y. Abdelghani, “Élimination du colorant basique bleu de méthylène en solution aqueuse par l’argile de SAFI”, *Journal of water science*, vol. 23, no. 4, pp. 375-388, 2010.

[14] M. Vinoth, H. Y. Lim, R. Xavier, K. Marimuthu, S. Sreeramanan, H. M. H. Masrosemal, S. Kathiresan, “Removal of methyle orange from solution using yam leaf fibers”, *Int. J. Chem Tech Res.*, vol. 2(4), 1892-1900, 2010.

[15] A. P. P. Cione, C.C. Schmitt, M.G. Neumann Gessner, “The effect of added salt on the aggregation of clay particles”, *Journal of colloid and interface science*, vol. 226, pp. 205-209, 2000.

[16] G. Alberghina, R. Bianghini, M. Fichera, S. Fisichella, “Dimerization of cibacron Blue F3GA and other dyes influence of salts and temperature”, *Dye and pigment.* 46(3), pp. 129-137, 2000.

[17] N. Bouanimba, “Modélisation et optimisation de la cinétique de dégradation photo catalytique de polluants organiques en solution aqueuse”, Magister en chimie, Université Mentouri-constantine, faculté des sciences exactes, Algérie, 166 f, 2009.