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# ADSORPTION KINETICS OF AN CATIONIC DYE FFROM AQUEOUSE SOLUTION BY ALGERIAN MINERAL MATERIALS

***K . KHALDI[1]* , M . HADJEL[1], R.CHERRAK[1],Z. SOUIDI[2], A. BENYOUCEF[3]***

*[1] Laboratoire des Sciences, Technologie et Génie des procédés LSTGP, Faculté de Chimie, Université des Sciences et de la Technologie d'Oran Mohamed Boudiaf USTO MB, BP 1505 El M'naouer Bir El Djir, 31000*

*[2]Université de Mascara, Faculté SNV, Laboratoire LRSBG*

*[3]laboratoire de génie des procédés et chimie des solutions ,université Mustapha Stambouli Mascara Bp763 Mascara 29000 (Algeria)*

** Corresponding author:*
*khaldikha@yahoo.fr*

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## Abstract

The objective of this study is to determine the power of two algerian mineral materials (kaolinite and diatomite ) ,in order to remove an cationic dye(methylene blue )from aqueous solution ,materials had been caracterised by diferents techniques .experiences had been studied en bath mode ,the influence of some parameters had been studied , such as , contact time ,the pH of solution and initial concentration .kinetics show that adsorption of methylene blue on to diatomite is faster than processus of adsorption on to kaolni ,and can be demonstrated by the pseudo-second –order model. Diatomite and kaolin used in this study improve their efficiency on elimination of methylene blue and could be low-cost alternative materials.

***Keywords:*** adsorption –methylene blue-kinetics-kaolin-diatomite.

## 1. Introduction

the industrial activities are an important source of pollution and contribute certainly on deterioration of environment , the effluents of textile industry constitute an enormous harm for human health , in particular the different dyes which are used in excess , as a result the ;;;;are heavily concentrated by dyes whose the effect on health human is very harmful ,so , it is necessary to reduce the concentration of dye s in wast water before their biologic treatment [1] Different conventional methods have been used to eliminate the pollutants from water , the most popular methods are made by chemical ,physicochemical and biological route ,such as coagulation ,flocculation ,precipitation and membrane filtration [2]¸ and adsorption , which is the most effectif treatment [3 ] to eliminate dyes .there are several adsorbents , the most known is the carbon activate [4] however ,activated carbon is considered as very expensive material, but can be replaced by low cost materials which have the capacity to absorb organic and inorganic pollutants kaolinite [5],bentonite [6] diatomite [7] chitosan[8] pyrophyllite [9] zéolite[10] . Alegria Is a country that is ful of important materials that can serve environment in treatment of waste water. Among these materials we have chosen for the present study two mineral materials a kaolin from estern of Algeria (Tamazert) and an diatomite of western Algeria (Sig) . We tested their adsorbent power, we choose methylene blue as pollutant nomed in the present paper as(**BM**). Although not very hazardous but may have various adverse effects ,when inhale it may give rise to short periods of rapid or difficult breathing while ingestion through the mouth causes nausea ,vomiting and diarrhea [11] adsorption of BM on mineral materials is likely to be dominated by ion exchange process ,in the present work ,the influence of pH of the solution ,initial concentration of the pollutant , contact time , temperature ,is studied .

## 2.Experimental

### 2.1. *Adsorbent and adsorbate*

The kaolin of Tamazert used as adsorbent ,was graciously offered by the FARGE cement factory . it was washed by the bidistiled water ,dried , crushed and then seaved to 0.009mm.As wel as the sig diatomite offered by ENOF was washed ,crushed and then tamised at 0.009mm. BM is an cationic dye with indice , CI 52015, its formula is C16H18N3 Cl and its molar mass is de 319,85 mol•g-1[12].the BM causes several effects to humans .

### 2.2 *Characterization of adsorbents*

#### 2.2.1 *BET method*

In order to better understand the relation between the phisico-chemical properties of the two materials ,and their adsorption performances , we measured their specific surface area ,determine by BET analyse (physisorption of azote at 77K) ,with a correlation coefficient of the order of 0.999 it gives information on the texture of the different samples prepared ,this method consist in determining the amount of nitrogen necessary for the formation of monomolecular film adsorbed on the surface of the solid . the texture of the two supports diatomite and kaolin was determined by physical adsorption ($N_2$ à77 K et de $CO_2$ à 273K ) using an automatic system of (autosorb-6,quantrachrome corporation ) after the samples are degassed to 383K empty for 4 hours [13] . the specific surface area of the diatomite is calculated at 26.90 $m^2/g$ and that of the Tamazert kaolin at 21.95$m^2/g$.

**2.2.2 *Chemical composition***

The quantitate analyses of adsorbents kaolin and diatomite was carried out by fluorescence X which make it possible to determine the tensides of the oxides which constitute the materials ,the results obtained are shown in table 1

**2.2. 3 *X –Ray diffraction analyses***

X-Ray diffraction was performed on both samples kaolin and diatomite, by comparing these different diffractogrames ,inforamtions can be optained on the composition of the crystalline phase of our supports diatomite and kaolin .

**2.2.*4 Scanning Electron Microscopy SEM***

Scanning electron microscopic observation allows the observation and determination of the forme of pores diatomite and the kaolin feuillets .

**2.2.5 *Transmission Electron Microscopy TEM***

This new method of analyses is non-destructive and does not require any special preparation of the sample. The joint acquisition under the transmission electron microscope and the diffraction for the same portion of materials particles ,is therefore possible and allows a fine characterization of the chemistry of the sample .the high resolution of this method makes it possible to highlight and characterize heterogeneities within a population of particles.

## 3. Results and discussion

***BET method***

The microporous and mesoporous volumes deduced from the adsorption desorption isotherms of N2 and CO2 respectively as it shown in table 1.

**Tableau 1 :** Caractéristiques physico-chimiques des adsorbants testées

| Samples | SBET (m2/g) | VDR(N2) (cm3/g) | VDR(CO2) (cm3/g) | Vmes(cm3/g) |
|---|---|---|---|---|
| Kaolin | 26.471 | 0 .007 | 0.004 | 0.18 |
| Diatomite | 39.906 | 0.014 | 0.009 | 0 .103 |

**3.1 *chemical composition***

Kaolin is a hydrothermal rock [14]. The chemical composition of this material is reported in( table 2), where we found a dominance of $Al_2O_3$ et $SiO_2$ of the order of 82,02 %. a mass loss of pure kaolin is evaluated at 13,95 %[15]. Diatomite is a marine rock from a massenian environment [16] composed mainly by the accumulation over time of fossilized remains of the diatoms skeleton exhibit high adsorption properties [17] , with a variable density between 1 to 1.2 for the fresh rock and 0.5 for the dry rock . Diatomite has a high silica content ( de 80 % à 90% ). Its chemical composition is thus reported in (table 2).

**Tableau 2 :** chemical composition on % of kaolin and diatomite

| Oxydes | % diatomite | % kaolin |
|---|---|---|
| $SiO_2$ | 91,604 | 59,67 |
| $Al_2O_3$ | 4.936 | 37,98 |
| $Fe_2O_3$ | 1,952 | 0,98 |
| TiO | 0,35 | 0,43 |
| MgO | 0,885 | 0,33 |
| $K_2O$ | 1,040 | 0,882 |
| $ZrO_2$ | 0,007 | — |
| CaO | 0,022 | 0,52 |

**3.2** ***X-Ray diffraction***

Diatomite is mainly composed of amorphous ,very little quartz,calcite and cristobalite .on the X-Ray spectrum of the diatomite , the pics are characteristic of an amorphous materiaal characterize by a thik base line ,domes and peaks characterizing the presence of cristalized material as shown in (figure 1)

theta :20,82°,23,04° ,26,62°, 30,68°,35,91°,39,41°,43,12°,,84,48° et le 29,39° , 47,44° ,for calcium carbonate ,similar studies have been found in the characterization of moroccan diatomite [18] . For kaolin the pick 001 at 7.35Å (2θ) 12.05, la raie 02,11 à 4.42Å (2θ 20.14) et la raie 002 à 3.57 Å (2 θ 24.50), are those of naturel métahalloysite (Ha-Nat) according to Brindley [19].

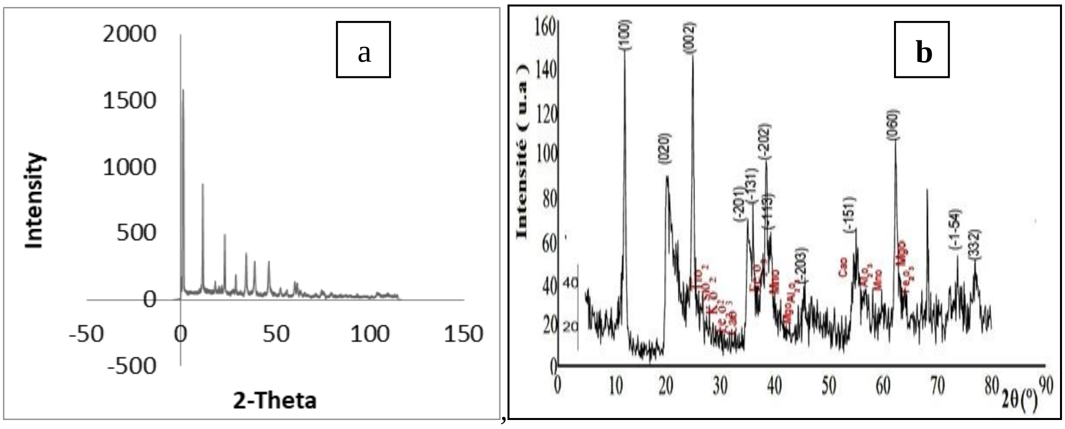


**Figure 1 :** DRX of diatomite **a** and kaolin **b**

**3.3** ***Scanning Electron Microscopy SEM***

Depending on the origin of the substance of the material and the mode of crushing to reduce it to powder,the particles will have different forms .The Tamazert kaolin (figure2) is in the forme of hexagonal plates sometimes remarkably ,well developed, however we deduce a certain disparity in the particle sizes ,the dimension of the crystals are in the order of µm. while the image of diatomite, given by SEM gives a general view of the number and centric form of the open pores ,the particle sizes of the diatoms varies between 0,09 and 0,5 µm .

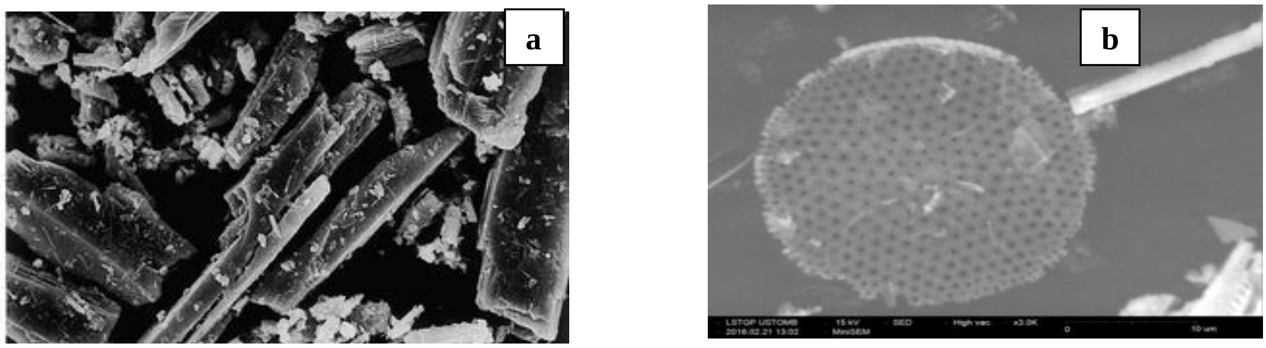


**Figure : 2** SEM image of kaolin **a** and diatomite **b**

**3.4** ***Transmission Electron Microscopy TEM***

The TEM analysis confirmed the texture of and the morphology of pores of the diatomite and plates of kaolinite already seen in SEM.

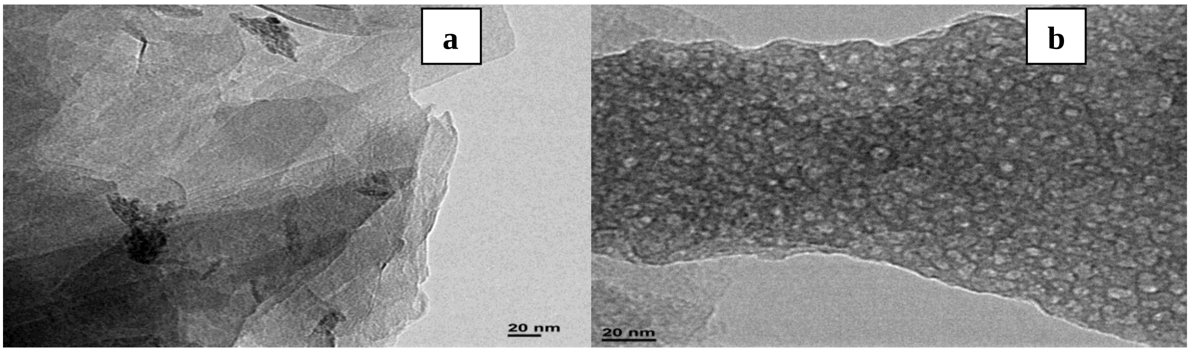


**Figure 3:** TEM Image of kaolin **a** and diatomite **b**

## 4. adsorption study

The adsorption experiments were carried out in bath mode at different initail values of pH;temperature and initial dye concentration , the experiments were realized by by introducing a quantity of 0.5g of adsorbent in a volume of 50ml ,of dye solution at several initial concentrations of the samples were taken every 5mn an then centrifuged at 2500rpm for 10mn .the supernatant was then analyzed using a UV-visible at 664nm .the equilibrium adsorption capacity (qe ) and the removal efficiency (R) of the BM ,adsorbed on the adsorbent (diatomite ,kaolin) is calculated from the equation :

qe= $( c_0 - c_e )$v/m

R=$(c_0 - c_e) \times 100/c$

where qe is the equilibrium adsorption capacity mg/g , R is the removel efficiency ,$C_0$ ,$C_e$ are respectively : initial and equilibrium concentrations of the BM in solution mg /l , V is the volume solution L; m is the mass of the adsorbent. [20]

**4.1.** ***Effect of contact time and initial concentration***

(figurs 4 and 5) show the evolution curves of the adsorption of the methylene blue dye, as a function of time and the concentration , it is noted that the equilibrium time is independent of the concentration and that the adsorbed amount at equilibrium increases with the concentration .It is also noted that the initial rate of adsorption increases with the concentration., this is because of diffusion of the dye molecules from the solution to the surface of the adsorbent and it accelerated by increasing the dye concentration [21]

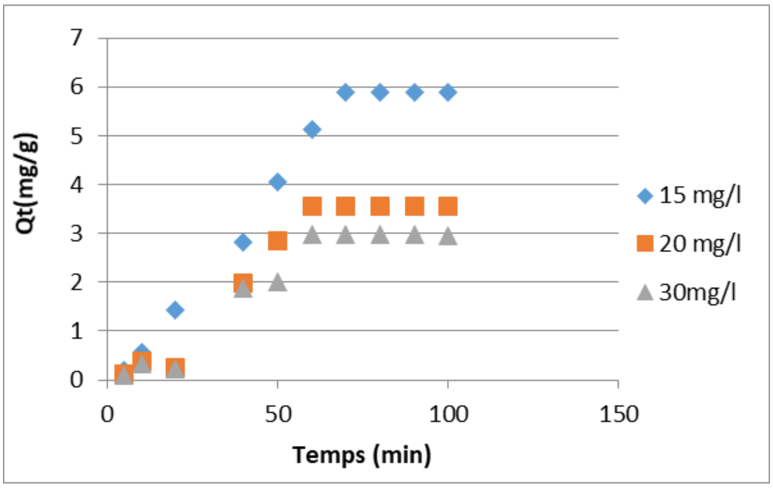


**Figure 4:** Effect of contact time and initial concentration on adsorption of methylene blue by diatomite

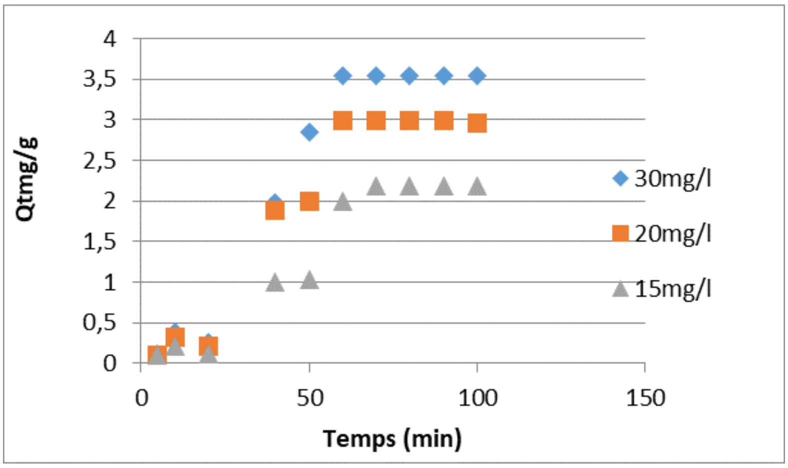


**Figure 5:** Effet du temps de contact et de la concentration initiale sur du bleu de méthylène sur le kaolin

### 4.2 *Effect of agitation vitesse*

Stirring is an very important parameter in adsorption phenomena when it affects the distribution of the solute in the solution and the rate of formation of the outer boundary film [22] The effect of stirring speed in removal rate of MB on kaolin and diatomite was studied in different stirring rate 25°C and pH=6.6 , the data of ( table 3) show achieving percentage of dye removal substantially independent on the agitation rate, used .

**Table3:** effect of steering speed on adsorption of BM

| Stirring speed | 200 | 350 | 500 | 650 | 800 |
|---|---|---|---|---|---|
| Diatomite % | 94.5 | 93.6 | 94 | 94.2 | 93.5 |
| Kaolin% | 90.1 | 92.3 | 93.8 | 90.7 | 91.2 |

### 4.3 *Effect of pH*

If the pH decreases ,the number of sites charged negatively decreases and the number of positively charged sites increases [23] [24]. However this increase in in adsorption capacity (from 52,7 to 59,6 mg/g for diatomite and from 42,8 a 50 mg/g for kaolin) remains low in this pH range 2-12,the retantion rate is appreciable between the pH values ranging from 4-9 with a retention peak towards pH5.

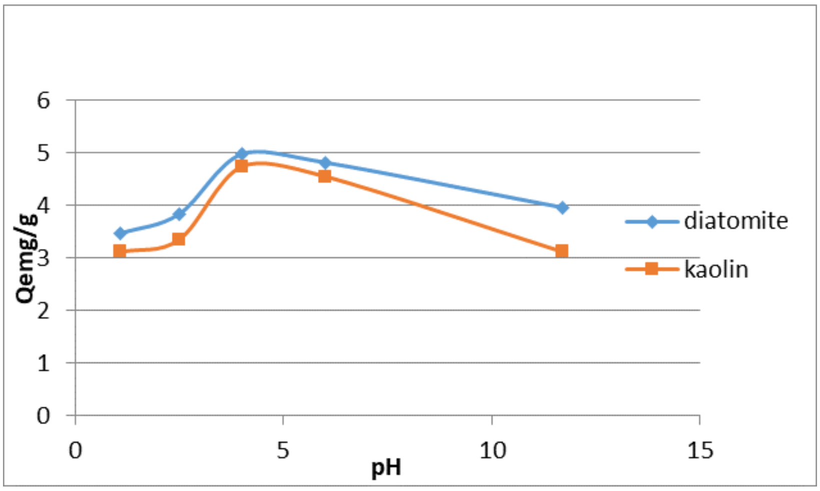


**Figure 6:** influence of pH of solution on adsorption of methylene blue by kaolin and diatomite.

**4.4 *Isothermes d'adsorption***

From the results obtained ,we observe that the adsorption isotherms of methylene blue on the surface of diatomite andd the kaolin are of type I ( classeL) according to the classification of Gilles [25 .] the isotherms show the better adsorption capacity is for diatomite .

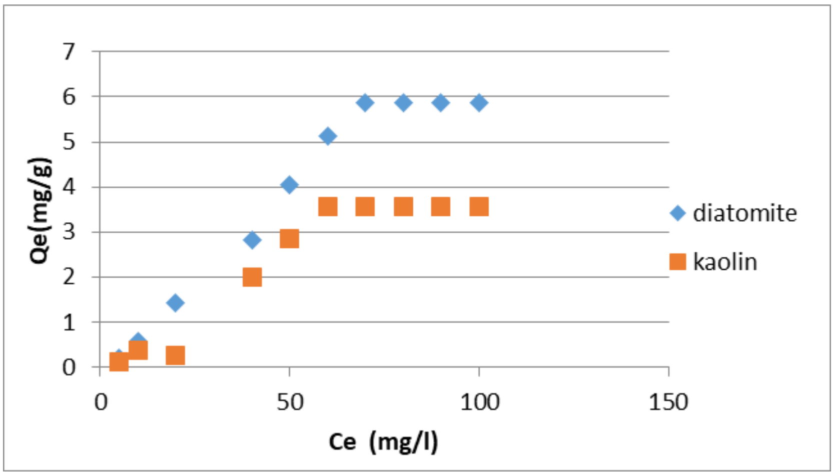


**Figure 7 :** Isotherm adsorption of methylene blue by diatomite and kaolin at pH=5 T=25°C, initiale concentration c= 30ppm

**Table 4 :** paramètres cinétique de l'adsorption du BM sur kaolin et diatomite

| *Adsorbents* | C0 (ppm) | *Pseudo-premier ordre* K | Qe cal./mg g−1 | R² | *Pseudo-second- ordre* K | Qe cal./mg g−1 | R² |
|---|---|---|---|---|---|---|---|
| KAOLIN | *15* | *0.251* | *0.97* | 0,879 | 1,564 | 1.75 | 0,990 |
| | *20* | *0.460* | *2.65* | 0,980 | 1,403 | 2.89 | 0,983 |
| | *30* | *0.223* | *2.88* | 0,938 | 2,129 | 2.98 | 0,996 |
| DIATOMITE | *15* | *0.105* | *0.69* | *0.9668* | 1,468 | 1.45 | 0,990 |
| | *20* | *0.470* | *1.50* | *0.9654* | 1,643 | 1.75 | 0,985 |
| | *30* | *0.877* | *1.90* | *0.949* | 2,739 | 1.98 | 0.998 |

## 5 .Kinetic study

The adsorption experiments of the dye methylene blue at various initials concentrations on diatomite or kaolin, were carried out for 120 min . the adsorption of dye on the both samples occurred rapidly during the first ten minutes (figurs 4et 5),then evolves slowly and stabilized after 50 min .Two models have been applied to describe the mechanism of adsorption kinetics: the pseudo-first-order and the pseudo-second-order . The figure 9 shows that **Log (qe-qt)**,as a function of time is nonlinear . It is deduced that the kinetics adsorption of methylene blue On kaolin and diatomite can not be described by the kinetics of the pseudo-first-order. On the other hand the linear representation (figure8) de t/qt as a function of time, the equilibrium adsorption capacities and the correlation coefficient calculated from the pseudo-second order (tableau 3), describe the kinetics behavior of adsorption of the dye on the both supports. Indeed ,it is noted ,that the correlation coefficient $\mathbf{R^2}$ are close to 1 and the values of calculated adsorption capacities (qe cal) ,are very close to the values obtained experimentally (qe exp) (table3) .The pseudo-first order expressed by the equation of Lagergren [26] . the pseudo-first order constants have been determined by extrapolating **log(qe-qt)** ***vs.t*** .(figure8) .The values of the adsorbed quantities (qe),and the pseudo –first order are given in (table4). The pseudo-second order is expressed by equation [27]The constants can be determined by plotting the line **1/qt** ***vs.*** **t**.(figure 9)

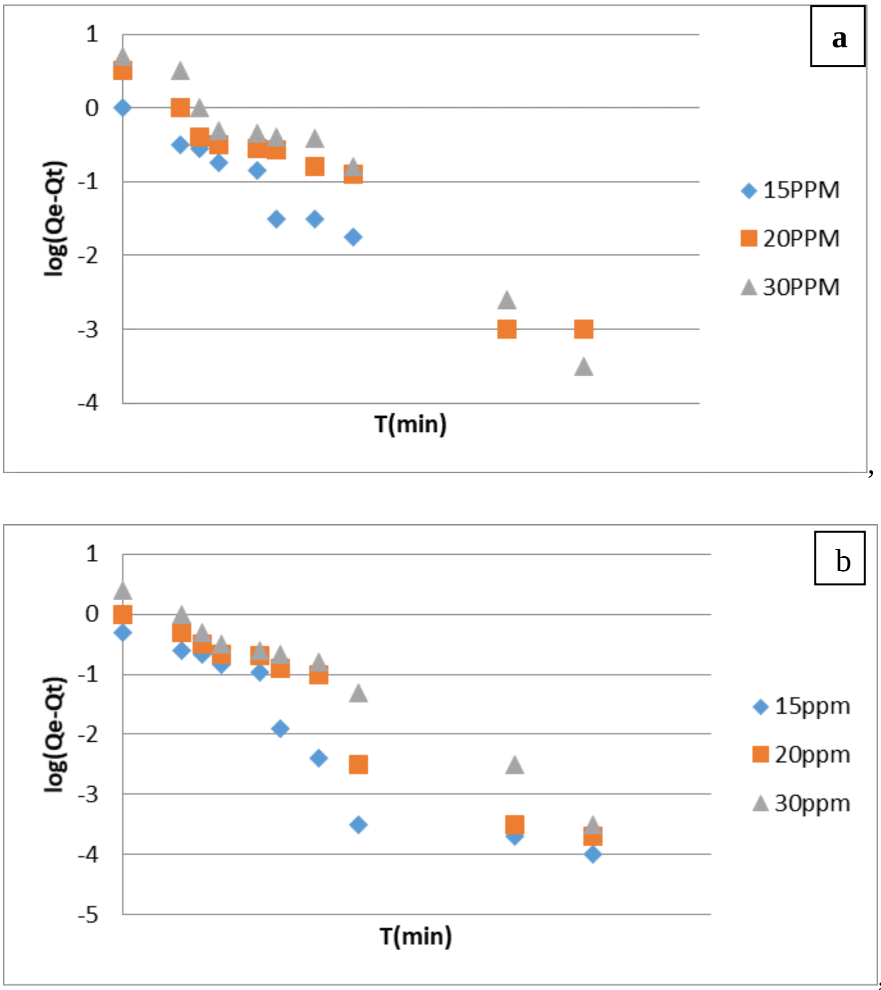


**Figure 8 :** « pseudo-first-order »kinetic applied to the adsorption of BM on diatomite **a** and kaolin **b**

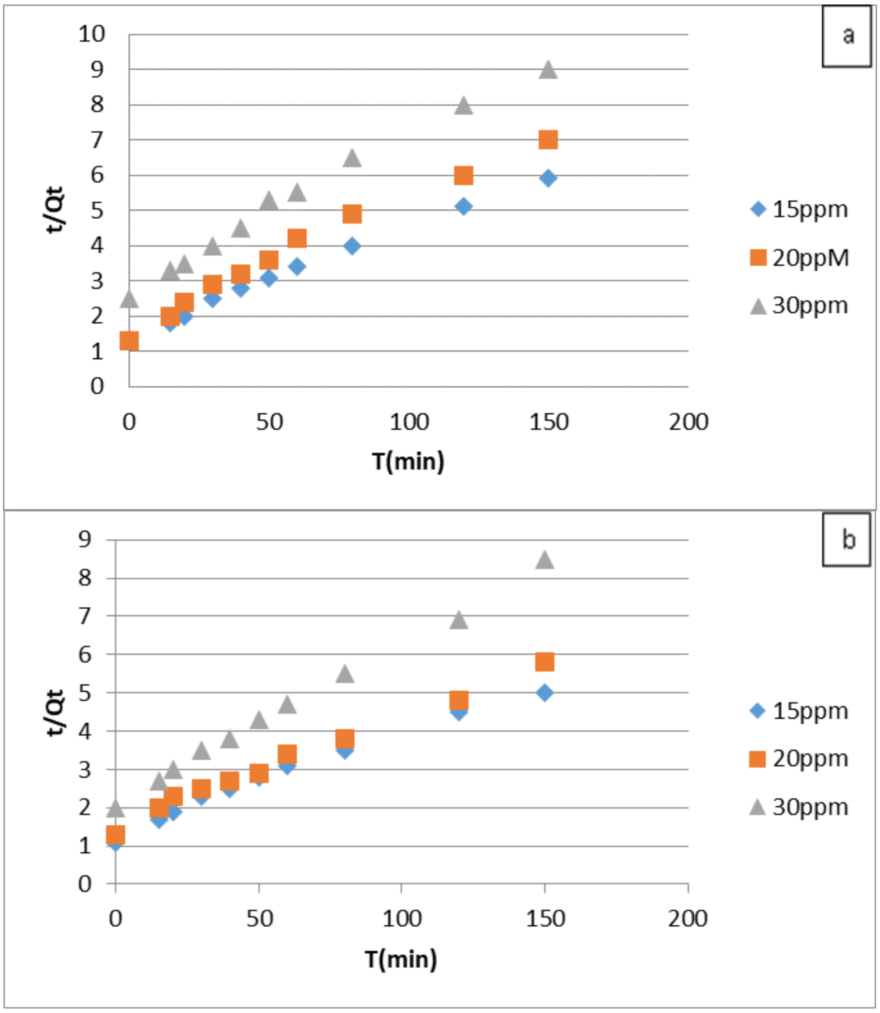


**Figure 9 :**Application of pseudo-second order model for adsorption of BM sur la diatomite a and kaolin b

## Conclusion

This study focuses on the adsorption of cationic dye methylene blue on diatomite and kaolin. The experimental results show that the adsorption process, depends on the pH of solution and the initial dye concentration ,the amount of adsorbed dye per gram of diatomite or kaolin powder , increases with the pH the initial dye concentration .The kinetic study of the dye adsorption on diatomite and kaolin shows that the adsorption process is very fast ; 95 % of adsorbed quantity of dye BM , is reached the first ten minute and the adsorption mechanism, can be described by the pseudo-second .These values show that the diatomite exhibits a better adsorption capacity because it contains a higher percentage of clay fraction .

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