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Adsorption of a cationic dye, Methylene Blue, ontoMoroccan Illitic Clay

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Abstract

In this study, Moroccan Illitic Clay (MIC) of Khemisset regionthat was characterised by X-ray diffraction has been used as a low cost adsorbent in the removal of a cationic dye, Methylene Blue(MB), from aqueous solution by a batch adsorption technique. The effects of various experimental parameters such as solution PH, initial dye concentration, contact time, temperature, adsorbent masses and stirring speed were investigated. The results showed that basic PH and high stirring speed were favourable for the adsorption of dye, and the adequate equilibrium time for the adsorption of Methylene Blue onto Moroccan Illitic Clay was 60min.The experimental data were analysed by the linear form of Langmuir, Frendlich, Temkin and Dubinine-Radushkevich isotherm models and showed a good fit with the Langmuir isotherm model. Adsorption kinetic and its mechanism were studied using pseudo first order kinetic equation, second order kinetic equation and intra-particle diffusion model. The adsorption kinetic followed the pseudo second order equation that involved two steps for the dye investigated in this work. Thermodynamic parameters were also evaluated and revealed that the adsorption of Methylene Blue onto Moroccan Illitic Clay was spontaneous, and exothermic in nature.

Keywords: Moroccan Illitic Clay; Methylene Blue; Linear form; Isotherm; Adsorption kinetic.

1. Introduction

Syntheticdyesarearomaticsubstancesthat arewidely used inmany industriessuchas plastic, paper, textile, etc... The effluents from theseindustries arecontaminated withdyes, which can cause the problemstothe environment and to the living beings;hence, it is necessary to treat theseeffluents. Several treatmentmethodscan be used such ascoagulation [1],ozonation [2], membrane separation [3], electrochemical technique [4]and ultrasonictechnique [5]. Adsorption technique is one of the most effective processes of advanced wastewater treatment. It has been found to be superior to other techniques in terms of flexibility and simplicity of design, initial cost, insensitivity to toxic pollutants and ease of operation[6].Many adsorbents are widely used such as activated carbon[7], chitosan [8] and clay [9-11]. The use of clay materials over commercially available adsorbents is becoming popular due their low-cost, their abundant availability, their variety of structural and surface properties, their high chemical stability, their high specific surface area and their high adsorption capacity. A number of clay minerals have been investigated for removal of dyes, such as: kaolinite [12], montmorillonite [13], and bentonite [14].

Methylene Blue is a basic dye which has been shown to have harmful effects on living organisms on short periods of exposure[15]. In the present work, the adsorption of Methylene Blue dye (MB) onto Moroccan Illitic Clay (MIC) was investigated and the obtained experimental data were analyzed using adsorption isotherm models. The effect of contact time, adsorbent dose, initial dye concentration, PH, temperature of dye solution andstirring speed were studied to optimize the conditions leading to maximum removal efficiency.

2. Materials and methods

2.1. Adsorbent

The raw clay used in this study was extracted from a quarry that is located in the Khemisset region (Morocco). It was crushed, sieved through a standard ASTM sieve to obtain lower fractions (<*56µm*), and then dried in an oven at 110°C during 2 hours for the next manipulation. The mineralogical phases constituting the clay have been determined using XPERT-PRO diffractometer. The significant peaks observed on the XRD patterns of the sample indicated that this clay is composed of Illitic and quartz minerals (**Fig.1**). The chemical composition of MIC obtained by using FRX analysis, given in **Table 1**,indicates the presence of silica and alumina as major constituents, along with traces of sodium, potassium, calcium, magnesium, iron, and titanium oxides in the form of impurities.

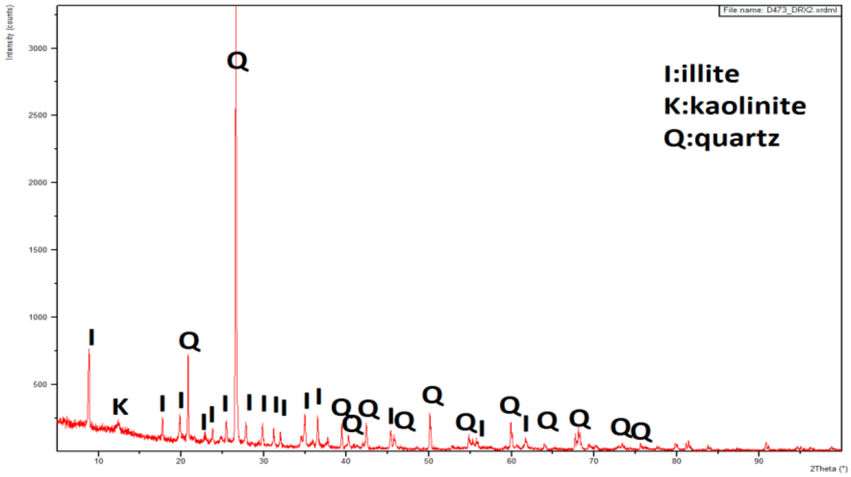

Figure 1: The XRD pattern of MIC

Table 1:The Chemical compositions of MIC.

Chemical Composition of MIC	**(%)**
SiO_2	61.7
Al_2O_3	24.2
Fe_2O_3	2.62
K_2O	3.28
MgO	1.55
Na_2O	0.513
K_2O	3.28
CaO	0.558
TiO_2	0.575
Loss of Ignition	4

2.2. Adsorbate

The dye usedin thisstudy is the Methylene Blue (MB). This is a cationic dye of formula $C_{16}H_{18}ClN_3S$, with *319.852 ± 0.022 g/mol* as a molecular weight. Its structure is shown in **Fig.2**.

The dye stock solution was prepared by dissolving *0.35g* of MB in one liter of distilled water, and the required concentration of the working dye solution was prepared by diluting the stock solution with distilled water.

2.3. Process

The adsorption experiments were carried out using the batch technique. In each experiment, *20 mg* of MIC was added to *20ml* dye solution of desired concentration at various PH, temperature and agitation speed. After filtration, the residual concentration was determined using UV-Visible spectrophotometer *SP 2000 UV* at maximum absorbance wavelength of 665nm, and the dye concentration was calculated from a calibration curve of absorbance versus dye concentration. The amount of adsorbed MB at equilibrium, *Qe (mg/g)* was calculated by the following expression:

$$Q_e = \frac{(C_0 - C_e)}{W} V$$

Where C_0 and C_e *(mg/L)* are the initial and equilibrium concentration of MB solution, *V (L)* is the volume of dye solution, and *W (g)* is the weight of Moroccan Illitic clay (MIC).

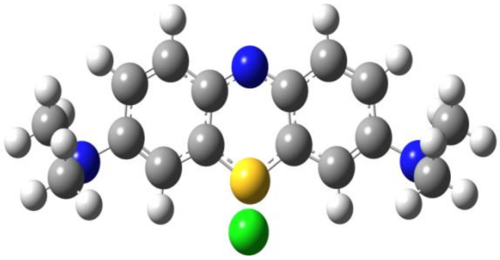

Figure 2: TheChemical structure of Methylene Blue (MB).

For kinetic study,*20mg* of MIC was added into *20ml* of MB solution with two initial dye concentrations *(15-30mg/l)*. The dye adsorption amounts were determined from the residual concentration in the solution at appropriate time, and calculated by the following expression:

$$Q_t = \frac{(C_0 - C_t)}{W} V$$

WhereC_0 and C_t*(mg/L)*are the initial and that aftertime *t* of MB solutionrespectively.

3. Results and discussion

3.1. Effect of adsorbent amount

The removal of MB by MIC was examined at different adsorbent amounts*(5-10-20-40 mg/20ml)* with a fixed dye concentration*(20mg/l)*, a stirring speed of *600 rpm* andwith a contact time of*60min*. As shown in **Fig.3**, the percentagevalues of dye removed increases with increasing in amount of adsorbent. This can be explained by the fact that the number of adsorption sites increases when the amount of adsorbent increases and more adsorbent surface and pores volume will be available for the adsorption. Similar results were reported for the adsorption of Methylene Blue and Crystal Violet from aqueous solution by Palm Kernel Fibre [15], and for the adsorption of cationic, Basic Yellow 2, onto Natural Untreated Clay [16].

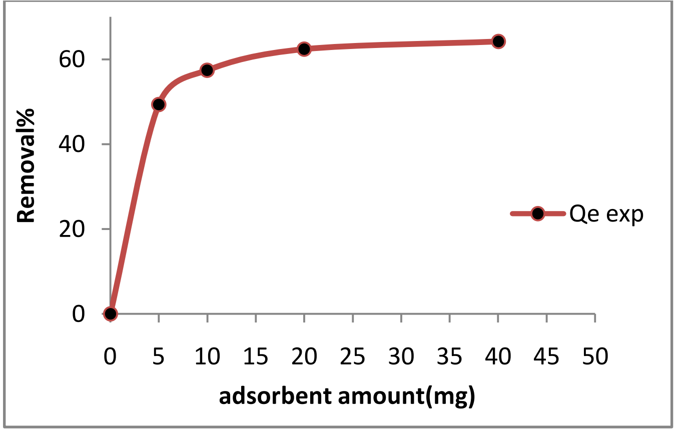

Figure 3: TheEffect of the adsorbent amount on the Methylene Blue uptake onto MIC

3.2. Effect of contact time on dye adsorption

The effect of contact time between MB and MIC was studied for solutions where the concentration of dye was *15mg/L* and *30mg/L* and **Fig. 4** shows this effect. The uptake of MB, as a function of time, was noted to occur in

two phases. In the first phase, the uptake rate of dye was very high for the first five minutes andthis is due to the availability of the negatively charged surface of adsorbent which led to fast electrostatic adsorption of the cationic dye molecules from the solution.This first phase was followed by a slow phase, which indicates that the amount of active sites gradually decreases, and there was no significant increase in the dye removal [17].
As it is seen in **Fig. 4**, when the initial MB concentration increases from *15* to *30mg/L*, the adsorption capacity increases from *13,82mg/g* to *23,37mg/g*. This is due probably to increase in the driving force of the concentration gradient, as an increase in the initial MB concentration.

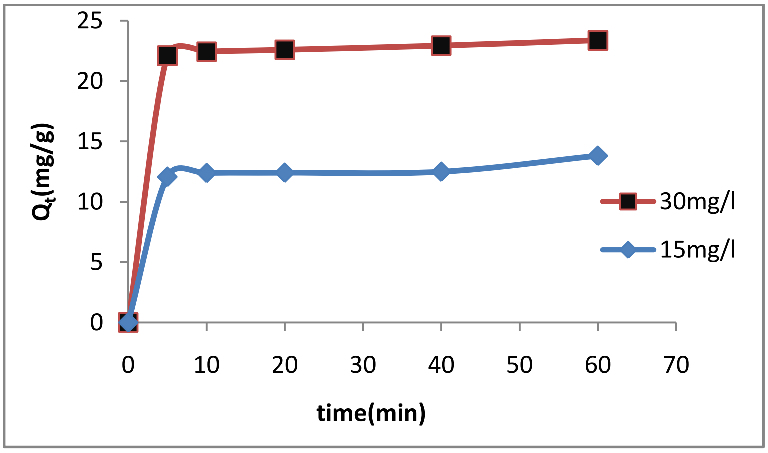

Figure 4: TheEffect of the contact time on the Methylene Blue adsorption onto MIC

3.3. Effect of initial PH

The PH is one of the determined parameters of controlling the adsorption behaviour of cationic molecule onto suspended clay particles [18]. In this study, the effect of this parameter was studiedfor adsorption of MB on MIC at ambient temperature, with *20mg/L* as initial dye concentration. The range of solution *PH* was adjusted between *2* and *12*, with *NaOH* or *HCl* solution *(0,1M)*. As shown in **Fig.5,** the adsorption capacity increases from *11,31mg/g* to *15,11mg/g*when the solution *PH* values increase from 2 to 12.The variation in the removal of MB with respect to *PH* can be explained by considering the surface charge of clay. For this, the zeta potential measurement of MIC was determined by placing *0.03 g* of adsorbent in glass bottle containing *30 ml* of *0.01 MNaCl* solutions. The initial *pH* of these solutions has been adjusted by adding *0.1 M NaOH* or *0.1M HCl*. The suspensions have been shacked for*16 h* and the final pH of supernatant has been measured. The *ΔpH = pH (final)- pH (initial)* have been plotted against the initial *pH* and shown in **Fig.6**.

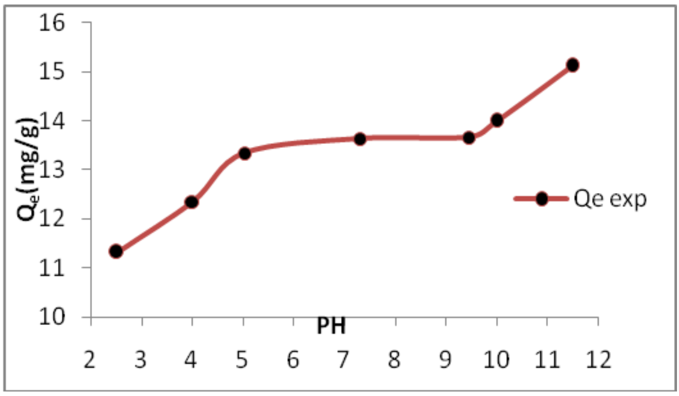

Figure 5: TheEffect of solution PH on the MB adsorption onto MIC

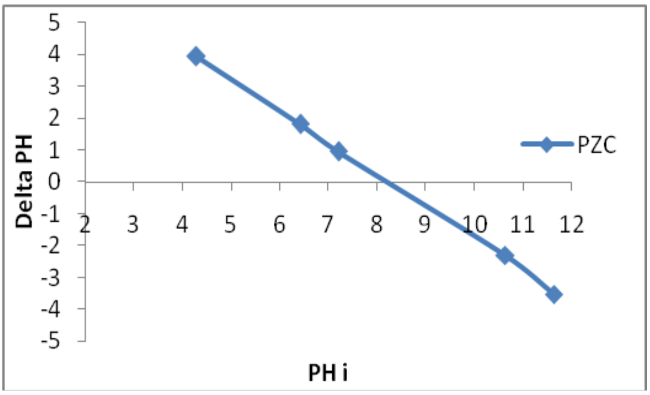

Figure 6: The zeta potential measurement of MIC

The *pH* for which *ΔpH*is equal to zero was taken as a PH_{pzc}. Then, we can say that MIC surface exhibited positive zeta potential at a lower *PH* values from *PH =8,2*, and negative zeta potential at a higher *PH* values from *PH =8,2*. At a lower *PH* than $PH_{pzc}(PH_{pzc} = 8,2)$, the presence of the excess of H^+ ions in solution can develops the positive charge on the surface of adsorbent. Consequently, the electrostatic repulsion increase between positively charge of cationic dye and positively charge of surface adsorbent, causing in decrease in the adsorption capacity of dye adsorbed. With the increase in *PH* value, the adsorbent surface became negatively charged due to deprotonation of the adsorbent surface [19]. The electrostatic attraction between the negatively charged surface and positively charge of cationic dye results in an increase in the sorption of the dye. Similar observation has been reported by *Saeed and al* in adsorption of Crystal violet on grapefruit peel [20].

3.4. Effect of stirring speed

The effect of stirring speed was evaluated by varying the speed of agitation *(i.e., 100, 500 and 700 rpm)* atan initial dye concentration of*20mg/L* and contact time of *60min*. As shown in **Fig.7**, the sorption of MB on MIC increases with increase of stirring speeds. This may be explained by the fact that when the stirring speed increases, all particles are kept in suspension, the contact surface solid/liquid increase, and the transfer of dye molecules to the surface of adsorbent will be favourable [21].

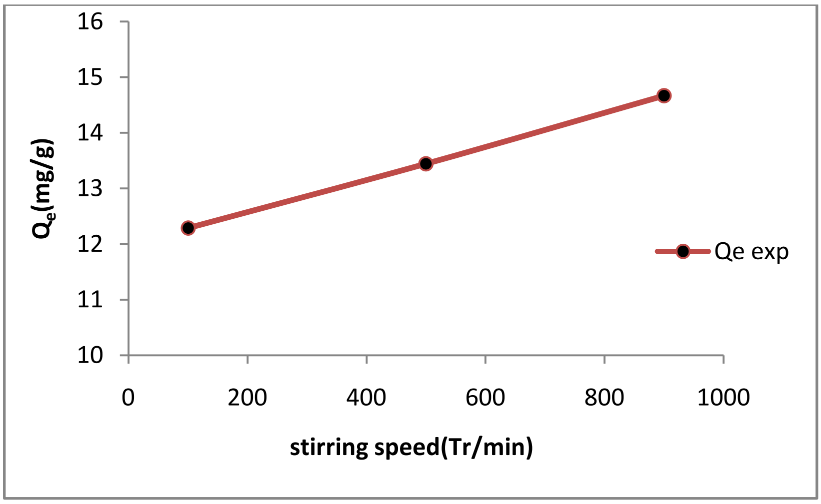

Figure 7: TheEffect of the stirring speed on the Methylene Blue adsorption onto MIC

3.5. Adsorption isotherms

In general, the adsorption isotherm indicates how the quantities of molecules are distributed between the liquid and solid phases when the adsorption processes reach balance [22]. It is employed to establish the maximum capacity of adsorption of adsorbate on adsorbent, which is expressed in terms of quantity of dye adsorbed per unit of mass of adsorbent used. The equilibrium adsorption of MB onto MIC was studied as a function of MB concentration*(5-30 mg/L)* and the amount of dye adsorbed Q_e, plotted against the equilibrium concentration C_e for MB, is given in **Fig.8**.Four isotherm models were tested to describe the equilibrium adsorption: the Langmuir model, the Frendlich model, the Dubinine-Radushkevich model and the Temkin model. The Langmuir isotherm theory assumes the monolayer coverage of adsorbate over a homogeneous adsorbent surface where all sorption sites are found to be identical and energetically equivalent [23]; whereas the Frendlich isotherm model is valid for the multilayer adsorption on a heterogeneous adsorbent surface and predicts that the dye concentration on the adsorbent will increase with the increasing of the adsorbate concentration in the solution [24].Apart from these, the D-R model is applied to distinguish between the physical and chemical adsorptions [25] and lastly, the Temkin isotherm model assumes that the decrease in the heat of adsorption is linear and the adsorption is characterized by a uniform distribution of binding energies [26].

The Langmuir, Frendlich, D-R and Temkin equations are presented in **Table 2**.

Where Q_e *(mg/g)* and C_e *(mg/L)* are the solid phase concentration and the liquid phase concentration of adsorbate at equilibrium, respectively, K_L *(L/mg)* is the Langmuir isotherm constant ,Q_m *(mg/g)* is the maximum amount of adsorbed dye per an unit weight of adsorbent, K_f *(L/mg)* is the Frendlich isotherm constant , *1/n* is the heterogeneity factor which is limited between 0 and 1,$b = RT/B$ is related to the heat of adsorption *(J/mol)*, e is the Polanyi potential and equal to $RTLn(1+\frac{1}{C_e})$, R is the gas constant *(8,314* $J.\ mol^{-1}.K^{-1}$*)*, T is the absolute temperature *(K)* and K_T is the Temkin equilibrium constant *(L/g)* corresponding to the maximum binding energy.

Table 2: TheNonlinear and linear form of adsorption isotherm models used in this study.

Isotherm	Nonlinear form	Linear form	Plot
Langmuir	$Q_e = \frac{Q_{max}K_LC_e}{1+K_LC_e}$	$\frac{C_e}{Q_e}=\frac{C_e}{Q_{max}}+\frac{1}{Q_{max}K_L}$	$\frac{C_e}{Q_e}=f(C_e)$
Frendlich	$Q_e = K_f C_e^{1/n}$	$LnQ_e = LnK_f + \frac{1}{n}LnC_e$	$LnQe = f(C$
D-R	$Q_e = Q_{max}exp\left(-B_D\left[RT\ ln\left(1+1/Ce\right)\right]^2\right)$	$LnQ_e = LnQ_{max} - B_D\left[RTLn(1+1/C_e)\right]^2$	$LnQe = f(e^2)$
Temkin	$Q_e=\frac{RT}{b}Ln(K_TC_e)$	$Q_e=\frac{RT}{b}LnK_T+\frac{RT}{b}LnC_e$	$Qe = f(\mathrm{Ln}C_e$

The value of B_D is related to the sorption energy E by means of the following relationship: $E=1/(2B_D)^{0.5}$. The mean adsorption energy is the free energy change when *1mol* of ions is transferred to the solid surface from infinity in the solution. The E value obtained gives informations about the adsorption mechanism, for example,if the magnitude of E is between *8* and *16 KJ/mol*, the adsorption process that has taken place is of chemical type and when $E< 8KJ/mol$, the adsorption process proceeds physically [27].

The shape of the isotherm is the experimental tool used to examine the nature of adsorption phenomenon. *Gils* proposes four adsorption phenomenon types according to his shape:*L*,*S*,*H*and *C*[28]. According to the cited classification, the **Fig. 8** shows that the isotherm adsorption of MB onto MIC displayed an *L* curve pattern, and this indicatesthe existence of a high affinity between the clay sample and the dye molecule.

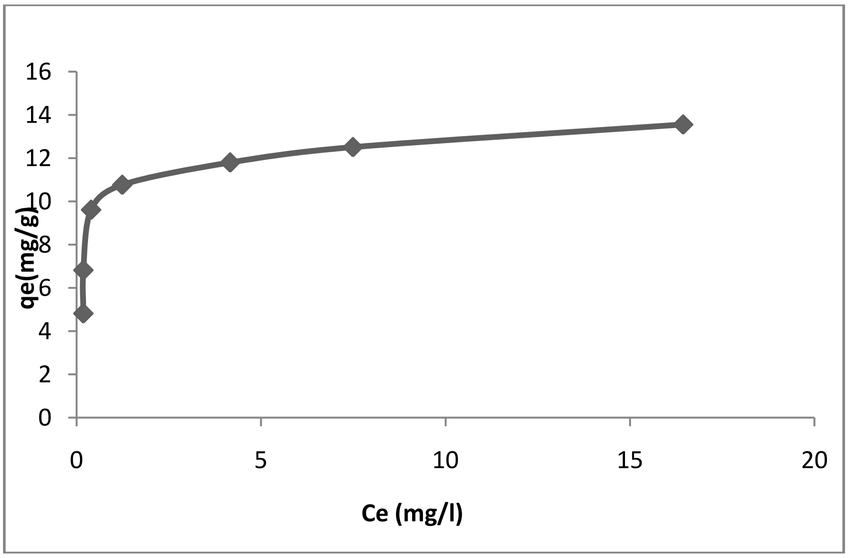

Figure8:The isotherm adsorption of Methylene Blue onto MIC

The experimental equilibrium data of MB onto MIC shown in **Fig.9** were compared with the theoretical equilibrium data obtained from the Langmuir, Frendlich, D-R and Temkin isotherm models**.**Isotherm parameters were obtained by linear regression method.In order to quantitatively compare the applicability of each model in fitting to data, a coefficient of determination $R^2$was calculated[29]:

$$R^2 = \frac{\sum (Q_{cal} - Q_{\mathrm{a,exp}})^2}{\sum (Q_{cal} - Q_{\mathrm{a,exp}})^2 + (Q_{cal} - Q_{\mathrm{exp}})^2}$$

Where Q_{exp} *(mg/g)* is the equilibrium value obtained from experiment, Q_{cal} is the calculated by isotherm model, $Q_{a,exp}$ is the average of Q_{exp}.

Table3: The Isotherm parameters for Methylene Blue adsorption onto MIC.

Freundlich		**Langmuir**		**D-R**		**Temkin**	
K_f(L/mg)	8,885	**Q_{max}(mg/g)**	13,698	**Q_{max}(mg/g)**	12,30	**B**	1,5568
1/n	0,1745	**K_L(L/mg)**	2,393	**B_D(mol/KJ)^2**	0,0352	**K_T(L/g)**	416,25
R^2	**0,7653**	**R^2**	**0,9966**	**R^2**	**0,8795**	**R^2**	**0,8567**

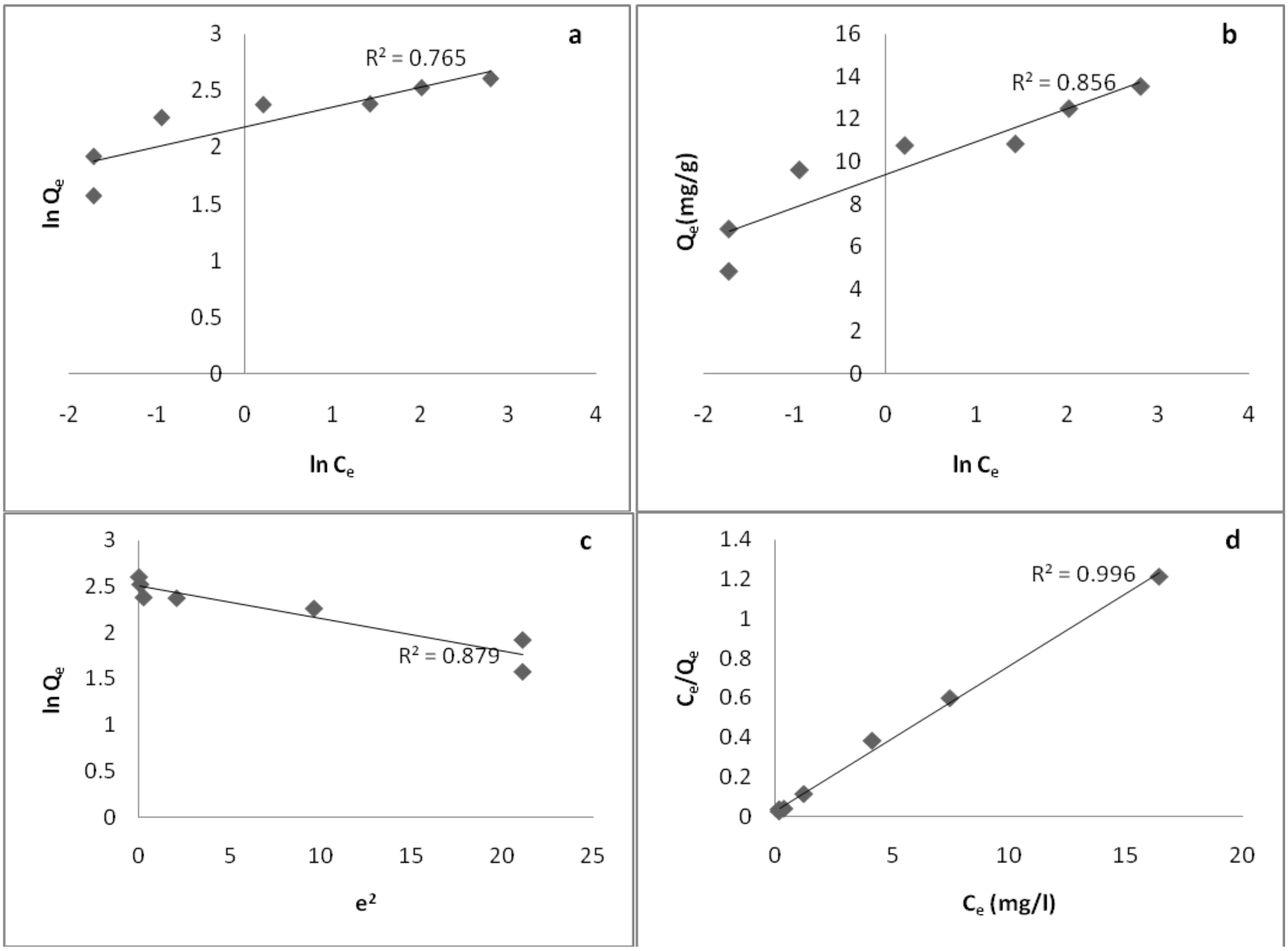

Figure 9: The Comparison of isotherm models with experimental data:
a) Freundlich. **b)** Temkin. **c)**D-R. **d)** Langmuir.

As can be seen from **Table 3**,Langmuir model showed a higher correlation coefficient*(R^2 =0,996)* than D-R, Freundlich and Temkin models. Similar results were reported for the adsorption of MB onto cedar sawdust [30]and tea waste [31] .The Q_{max} of the MIC for MB using Langmuir model were found to be *13,698 mg/g*(Table 1).

The essential feature of the Langmuir isotherm can be expressed by means of a dimensionless constant R_L that is referred to as separation factor or equilibrium parameter. It is defined by the following relationship [32]:

$$R_L = \frac{1}{\left(1+K_L C_0\right)}$$

Where K_L and C_0 *(mg/L)* are the Langmuir constant and the initial dye concentration respectively. As the R_L value lie between 0 and 1, the on-going adsorption process is favorable. From **Table 4**, the $R_L$values for Methylene Blue adsorption onto MIC are between *0,07713074*and *0,01373815*, and therefore,its adsorption was favorable. This can also be concluded from the Freundlich model fitting results. The magnitude of the exponent, *1/n*, gives an indication about the favorability of adsorption such that in favorable adsorption process, the value of *1/n* should be in the range of *0-1* [33]. In this study, the value of *1/n* is equal to *0,1745* which indicates that this adsorption is favorable. The Freundlich constant *n* is a measure of the deviation from linearity of the adsorption. Since the value of *n* is above of the unity ($n = 5,7306$), the adsorption being favorable is of physical nature [34].

Table4: The R_L values for Methylene Blue adsorption onto MIC

MB concentration(mg/L)	R_L
5	0,07713074
7	0,05633485
10	0,04011231
12	0,0336519
15	0,02710394
20	0,02046664
30	0,01373815

The constant *b* related to the variation of adsorption energy concluded from Temkin isotherm, is positive. This indicates that the adsorption reaction was exothermic [35]. The free energy of MBadsorption onto MIC was considered via DubinineRadushkevich (D-R) model. As can be seen from **Table 2**, the energy which is lessthan *8 kJ* mol^{-1}($E= 3,769$ $KJ.mol^{-1}$) confirms that the adsorption process of dye was controlled by physical adsorption process [34].

3.6. Kineticsstudy and adsorption mechanism

The study of adsorption kinetic illustrates how the solute uptake rate and obviously this rate control the residence time of the adsorbate at the solution interface. This rate is most importance when designing the adsorption system and this rate can be calculated from kinetic study [36]. In this work, the adsorption kinetics was studied at *15mg/L* and *30mg/L*, and the adsorption rate was monitored by studying the contact time up to *60 min*. The experimental data obtained for various contact time were analyzed using two kinetic models, namely, pseudo-first-order, pseudo-second order.

The pseudo-first-order equation is expressed as follows [37]:

$$Ln(Q_e - Q_t) = Ln(Q_e) - K_1 t$$

Where Q_t and Q_e*(mg/g)*are the adsorption capacities at time *t(min)* and at equilibrium,respectively, $k_1(min^{-1})$is the rate constant of pseudo-first-order adsorption and*t* is the contact time.The value of $Q_e$and k_1 can be determined from the intercept and the slope of the linear plot of $Ln\ (Q_e - Q_t)$ versus *t*.

The pseudo-second-order equation is[38]:

$$\frac{t}{Q_t} = \frac{t}{Q_e} + \frac{1}{K_2 Q_e^2}$$

Where $k_2(mg^{-1}.g.min^{-1})$is the rate constant of pseudo-second-order adsorption. The value of $Q_e$and k_2 can be determined from the intercept and the slope of the linear plot of t/Q_t against *t*. The **Fig. 10** shows the plots of the pseudo-first-order model and the pseudo-second order model for adsorption of MB onto MIC.**Table5** lists the results of the kinetic parameters calculated using the pseudo-first-order and pseudo-second-order models. The values of regression coefficient R^2 for the pseudo-second-order model are nearly unity *(>0,99)* than the pseudo-first-order model for two initial dye concentration studied (for *15 mg/L* and for *30 mg/L* as initial dye concentration).The calculated Q_e, values (obtained by pseudo-second-order model) are closedvery well to that of experimentally values Q_e, (**Table5**). These results indicate that the adsorption of MB ontoMIC belongs to the second-order kinetic model. Similar trends were observed for the adsorption of MB and CV onto Palygorskite [39] and for the adsorption of MB and CVby Palm Kernel Fiber [15].

Table5:The Kineticsparameters for the adsorption of Methylene Blue onto MIC.

		Pseudo-first-order kinetic model			**Pseudo-second-order kinetic model**		
	$Q_{e,exp}$(mg/g)	**K_1(min^{-1})**	**$Q_{e,cal}$(mg/g)**	**R^2**	**K_2(g/mg.min)**	**$Q_{e,cal}$(mg/g)**	**R^2**
15mg/L	13,82502	0,0773	6,20651781	**0,7601**	0,04417017	13,7931034	**0,9947**
30mg/L	23,37139	0,0696	4,49380598	**0,737**	0,07856104	23,4741784	**0,9998**

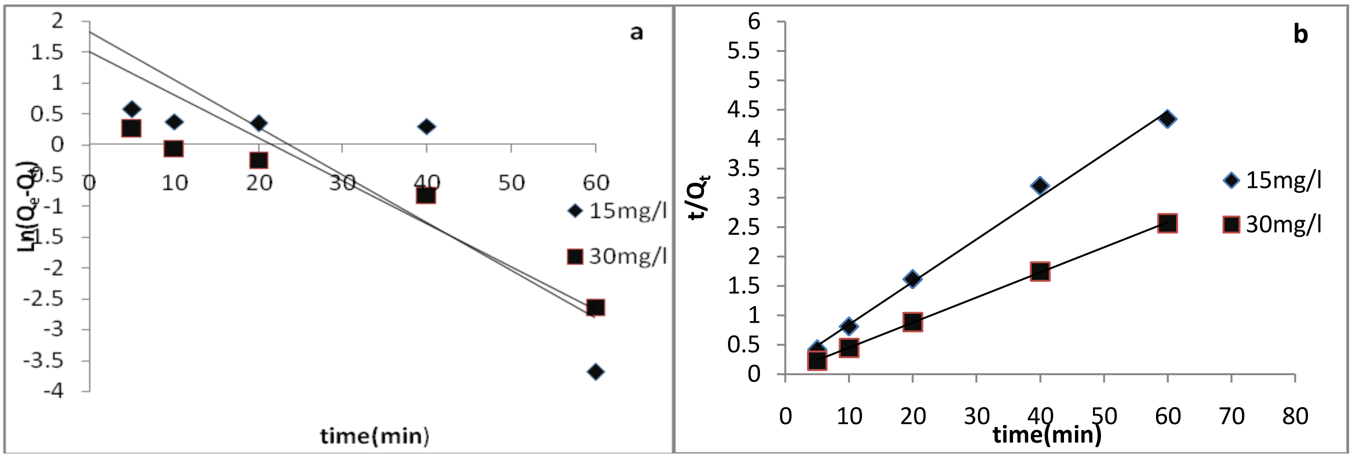

Figure 10: The Kinetic models for adsorption of MB onto MIC a) Pseudo-first order. b) Pseudo-second-order.

Generally, the adsorption mechanism for dyes removal by adsorption using an adsorbent material can be assumed as involving three steps in which bulk diffusion is considered to be instantaneous[40]:

1. Diffusion of dye through the boundary layer to the surface of the adsorbent.
2. Dye transfer from the exterior surface of the adsorbent to the interior pores of particle through intraparticle diffusion mechanism.
3. Adsorption of dye in an active site on the surface of material.

According toWeber and Morris [41] for most adsorption process,it is possible that intraparticle diffusion will be the rate controlling step only. Since, the amount of adsorption varies almost proportional with $t^{1/2}$ rather than with the contact time and can be expressed as:

$$Q_t = K_{id} t^{0.5} + C_i$$

WhereQ_t*(mg/g)*is the adsorption capacities at time *t(min)*, k_{id}*(mg/g.min$^{0.5}$)*is the rate constant of intra-particle diffusion model, and C_i*(mg/g)* is a constant that gives an idea about the thickness of the boundary layer. The larger C_i indicates that the boundary layer effect will be greater.If the regression of Q_t versus $t^{1/2}$is linear and passes through the origin, then adsorption process is controlled by intraparticle diffusion only.

The values of k_{id} and intercept C_i are presented in **Table 6**.**Fig. 11** shows the plots of $Q_t$versus $t^{1/2}$for adsorption of MB onto MIC. The adsorption plots are not linear over the whole time range and can be separated into a few linear regions. This may reveal that there are two adsorption stages taking place. Initial curved portion, followed by a plateau. The initial sharper, indicating a boundary layer effect, was due to the transfer of the dye molecules to the external surface of clay particle through film diffusion (external mass transfer). The boundary layer (values of *C* parameter in **Table 6**) increases with increasing initial concentration, this indicates that the boundary layer effect becomes prominent at higher initial concentration. The second linear part corresponds to the gradual adsorption stage where the dye molecules were entered onto clay particles by intraparticle diffusion through pores. Both lines did not pass through the origin indicating that film diffusion and intra-particle diffusion occurred simultaneously.Similar results have been observed by *B.K Nandi & al*inremoval of cationic dyes, crystal violet and brilliant green from aqueous solution by kaolin[42].

Table6:The Intraparticule diffusion parameters for the adsorption of Methylene Blue onto MIC

	15mg/L		**30mg/L**	
	Step 1	**Step 2**	**Step 1**	**Step 2**
K_{id}(mg/g.min)	5,39	0,258	9,88	0,2137
C_i(mg/g)	1.10^{-15}	11,39	3.10^{-15}	21,66
R^2	**1**	**0,7168**	**1**	**0,9776**

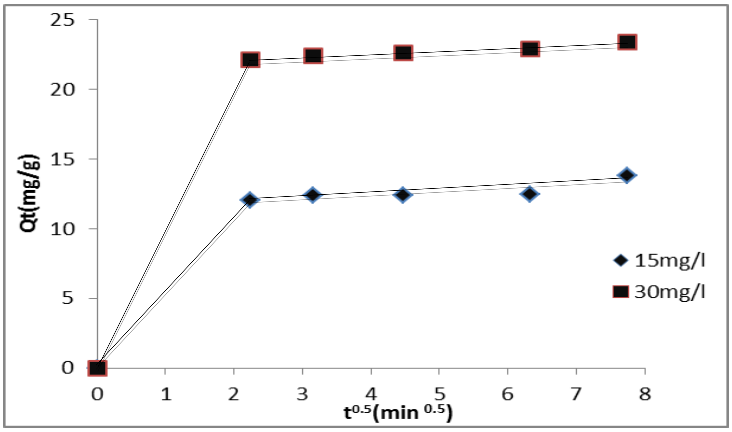

Figure 11: TheIntraparticle diffusion model

3.7. Effect of Temperature

The temperature is usually an important factor which affects many adsorption processes, and it is an indicator of the adsorption nature. If the adsorption capacity increases with increasing temperature, then the adsorption is an endothermic process [43], and the decrease of adsorption capacity with increasing temperature indicates that the adsorption is an exothermic process [44]. The thermodynamic parameters such as enthalpy and entropy of adsorption process can be related to the distribution coefficient of the solute between the solid and liquid phases. By using the following equations, the thermodynamic parameters of the adsorption process may be determined from the experimental data:

$$LnK_c = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$$\Delta G = \Delta H - T.\Delta S$$

Where ΔH*(KJ/mol)*, ΔS *(J/mol.K)*, ΔG *(KJ/mol)* and *T (K)* are the enthalpy, entropy, Gibbs free energy, and absolute temperature, respectively.*R (8.314 J/mol.K)* is the gas constant and *Kc(L/g)*[45] is the equilibrium constant defined by Q_e/C_e.

The variation temperature effect from *293* to *333 K* on the adsorption of MB by MIC with a constant initial concentration of *20mg/L* at *650rpm* after equilibrium *(60 min)*was studied, and the values of ΔH and ΔS were determined from the slope and intercept, respectively, of the Van' Hoff plot (**Fig.12**). **Table 7** lists the derived thermodynamic parameters for the dye adsorption process. The adsorption was found to decrease slightly with increasing temperature solution (decrease in K_c) from *293* to *333K*, thereby suggesting that the adsorption process was thermodynamically stable. The negative value of ΔH *(= -6.80592354 kJ/mol)* indicates that the adsorption wasof physical nature and involves the weak forces of attraction and was also exothermic.The negative value ofΔS *(= -19.9070416 J/mol.K)*reflects the decreasing randomness at the MIC/MB solution interface during the adsorption, and no significant changes was occur in the internal structure of the MIC through the adsorption. Similar results that studiedthe Red Congo adsorption by clay materialswere reported by *Vimonses and al*[44].

The negative value of standard free energy change ΔG for the experimental range of temperatures suggests that the adsorption was spontaneous, and that the system does not gain energy from an external source. When thetemperature increases from 293 to 333K,the magnitude of ΔGchange shifts to low negative value; this suggests that the adsorption was rapid and more spontaneous at low temperature [34]. Generally, when the ΔG value is between 0 and-20 *KJ/mol*, this is consistent with the electrostatic interaction between adsorption sites and the adsorbing ion (physical adsorption); while, when a ΔG value is more negative and is ranging from -80 to -400 *KJ/mol*, this indicates that the adsorption involves charge sharing or transferring from the adsorbent surface to the adsorbing ion to form a coordinate bond (chemisorption) [33]. By evaluating the ΔG values (from *-0.97018649* to *-0.17390649 kJ/mol*), the adsorption of MB onto MIC seems to be a physical adsorption involving weak forces of attraction.

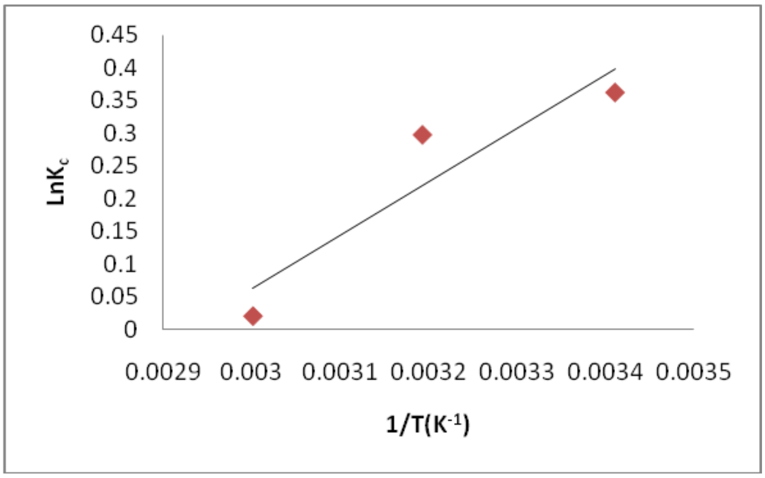

Figure12: The Plot of LnK$_c$vs 1/T

Table 7:The thermodynamic parameters of Methylene Blue adsorption onto MIC.

T(K)	K$_c$(L/g)	ΔG(kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
293	1,435778755	-0,97018649	-6,80592354	-19,9070416
313	1,346188141	-0,57204649		
333	1,021705724	-0,17390649		

Conclusion

The adsorption of Methylene Blue (MB), as a basic dye, from aqueous solution ontoMoroccan Illitic Clay(MIC) has been studied. Adsorption experiments were carried out as a function of contact time, adsorbent dose, initial dye concentration, PH, temperature of dye solution and stirring speed. The results showed that the adsorption was found to be favourable with the increasing the PH of solution, and increasing the stirring speed. On the other hand, the results indicated that when the temperature increasing, the ability of adsorption decreasing indicating an exothermic process. The adsorption data was well described by the Langmuir isotherm model. The maximum removal capacity for the MB by the used clay is *13,698 mg/g*.Also, evaluation of the adsorption results obtained on the basis of different kinetic models showed that the adsorption of MB onto MIC was best described by the pseudo-second order model. The present investigation concludes that the Moroccan Illitic Clay (MIC) could be employed as a low cost adsorbent for removal of Methylene Blue (MB) from textile effluents.

References

1. Klimiuk E., Filipkowska U., Libecki B., *Polish J. Environ. Stud.*, 8 (1999) 81.
2. Snider E.H, Porter J.J., *J. Water. Pollut. Contr. Feder.*, 46 (1974) 886.

3. Ahmad A. L., Harris W. A., Seng S. B., *J. Tekn.*, 36 (2002) 31.
4. Sieng H., Peng L. C. F., *War. Res.*, 28 (1994) 277.
5. Zhu H., *Ind. Safety. Envir. Prot.* 12 (2007).
6. Mustafa Y. T., Kanti S.T., Sharmeen A., Ang H.M., *Adv. Coll. Inter. Sc.*, 209 (2014) 172.
7. Wang L., Zhang J., Zhao R., Li C., Li Y., Zhang C., *Desalination*, 254(2010) 68.
8. Annadurai G., Ling L., Lee J., *J. Hazard. Mater.*, 152 (2008) 337.
9. Weng C.H., Pan Y.F., *J. Hazard. Mater.*, 144 (2007) 355.
10. Gürses A., Doğar Ç., Yalçın M., Açıkyıldız M., Bayrak R., Karaca S., *J. Hazar. Mater.*, 131 (2006) 217.
11. Mouzdahir Y. El, Elmchaouri A., Mahboub R., Gil A., Korili S.A., *Desalination*, 250 (2010) 335.
12. KamelM.M, Youssef B.M., *Dyes Pigments*, 15(1991) 175.
13. Wang C.C, JuangL.C., Hsu L.C, Lee C.K., Lee J.F., Huang F.C., *J. Coll. Intef. Sci.*, 273 (2004) 80.
14. TahirS.S., RaufN.,*Chemosphere*, 63 (2006) 1842.
15. El-Sayed G. O., *Desalination*, 272(1) (2011) 225.
16. Öztürk A., Malkoc E., *App. Surf. Sc.*, 299 (2014) 105.
17. ElassK., Laachach A., Alaoui A., Azzi M., *App. Clay Sc.*, 54(1) (2011) 90.
18. Karim A. B., Mounir B., Hachkar M., Bakasse M., Yaacoubi A., *J. Hazard. Mater.*, 168(1) (2009) 304.
19. Karaoğlu M. H., Doğan M., Alkan M.,*Desalination*, 256(1) (2010) 154.
20. Saeed A., Sharif M., Iqbal M.,*J. Hazard. Mater.*, 179(1) (2010) 564-572.
21. Errais E., Duplay J., Darragi F., M'Rabet I., Aubert A., Huber F., Morvan G., *Desalination*, 275 (2011) 74.
22. Brdar M., Šćiban M., Takači A., Došenović T., *Chem. Eng. J.*, 183 (2012) 108.
23. Langmuir I., *J. Am. Chem. Soc.*, 40 (1918) 1361.
24. FreundlichHMF., *J. Phys. Chem.*, 57 (1906) 385.
25. DubininM.M., *Chem. Rev.*, 60 (1960) 235.
26. TemkinM.I., PyzhevV., *Acta Phys. Chem.,USSR* 12 (1940) 327.
27. Helfeererich F., *McGraw-Hill, New York*, 1962.
28. Giles C. H., Smith D., Huitson A., *J. Coll. Inter.Sc.*, 47(3) (1974) 755.
29. Gunay A., *J. Hazard. Mater.*, 148(3) (2007) 708.
30. Hamdaoui O., *J. Hazard. Mater.*,135 (2006) 264.
31. Uddin M.T., Islam M.A., Mahmud S., Rukanuzzaman M., *J. Hazard.Mater.*,164 (2009) 53.
32. Hameed B.H., Ahmad A.A., Aziz N., *Chem. Eng. J.*, 133 (2007) 195.
33. Ozdes D., DuranC., Senturk H. B., AvanH., Bicer B., *Des. Water Treat.*, 52(1-3) (2014) 208.
34. Özcan, A. S., Erdem B., Özcan A., *Coll.Surf., A: Phy. Chem. Eng. Aspects*, 266(1) (2005) 73.
35. Hadi M., Samarghandi M. R., McKay G., *Chem. Eng. J.*, 160(2) (2010) 408.
36. YagubM. T., Sen, T. K., Afroze, S., Ang, H. M., *Adv.Coll.Interf. Sc.*, 209 (2014) 172.
37. Lagergren S.,*Handlingar*, 24 (4) (1898) 1.
38. Ho Y.S, McKay G. *Proc.Saf. Env. Prot.* 76,(1998) 183.
39. Al-Futaisi A., Jamrah A., Al-Hanai R., *Desalination*, 214(1) (2007) 327.
40. Guimarães Gusmão K. A., AlvesGurgel L. V., Sacramento MeloT. M., Gil L. F., *Dyes. Pig.*, 92 (2012) 967.
41. Weber W.J, Morris J.C., *J. San. Eng. Div.*, 89(SA2) (1963) 31.
42. Nandi B. K., Goswami A., Purkait M. K., *App. Clay Sc.*, 42(3) (2009) 583.
43. Al-Degs Y. S., El-Barghouthi M. I., El-Sheikh A. H., Walker G. M., *Dyes.Pig.*, 77(1) (2008) 16.
44. Vimonses V., Lei S., Jin B., Chow C. W., Saint C., *Che. Eng. J.*, 148(2) (2009) 354.
45. Chu B. S., Baharin B. S., Che Man Y. B., Quek S. Y., *J. Food Eng.*, 62(1) (2004) 97.