ISSN: 2319-8753

International Journal of Innovative Research in Science, Engineering and Technology

(An ISO 3297: 2007 Certified Organization)

Vol. 3, Issue 8, August 2014

Removal of a Cationic Dye –Méthylène Bleu– From Aqueous Solution by Adsorption onto Oil Shale Ash of Timahdit (Morocco)

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ABSTRACT: This article presents two aspects environnementals: valorization of oil shale ash (OSA) of oil industry on the one hand, and on the other hand to study the effectiveness of cation adsorption of dye such as the Methylene blue (BM) on material (OSA).In this context, we carried out a parametric study of adsorption, in particular, the time of contact, the pH, the amount of the adsorbent, the temperature and the stirring velocity. A study of the kinetics of adsorption was carried out by two models: pseudo-first order and pseudo-second order, and a modeling by the isotherms of adsorption while basing itself on the models of Langmuir and Frendlich. The maximum capacity of adsorption of BM on OSA is of 2,464 mg/g, for a concentration of BM of 5 mg/L, an amount of adsorbent of 2 g/L. Material OSA was characterized by several methods such as diffraction of x-ray (DRX), electronic scan microscopy (MEB), electronic microscopy in transmission (MET), x-ray fluorescence (FX), and the infra-red Spectroscopy with transforms of Fourier (FTIR). In addition, the economic aspect of the use of OSA makes important the re-use of these materials considering their capacity to regenerate itself.

KEYWORDS: adsorption, oil shale ash, isothermal, modeling.

I. INTRODUCTION

The extensive use of dyes in dye-manufacturing industries creates significant problems due to the discharged of colored waste water. The presence of very small amounts of dyes in water is visible and affects the quality of water [1].

Most of these dyes pose acute problems for the ecological system, as they are toxic and have carcinogenic properties, which make the water contaminated with dyes inhibitory to aquatic life [2-4]. With industrialization, the discharge of industrial wastewater has increased. At the same time, there are concerns, and there is the need to find cheap and efficient methods for the industrial waste water prior to disposal into natural waters [5-6].

Various techniques, such as precipitation, membrane filtration, coagulation/flocculation, electrochemical and chemical oxidations, ion exchange, adsorption [7]. The advantages and disadvantages of every removal technique have been extensively reviewed [8-9]. The removal of dyes in an economic way remains an important issue for researchers and environmentalists. The adsorption is an excellent alternative selection especially using inexpensive and high adsorption capacity adsorbent without requiring any additional pre-treatment step before application. Adsorption is superior to other wastewater treatment techniques in terms of its initial cost, flexibility and simplicity of design, ease of operation and insensitivity to toxic pollutants [10-15].

In this work, we were interested in the study of the adsorption of the methylene blue dye on the oil shales calcined taken of a layer of Timahdit, located in the mountains of the Average Atlas (Morocco), is spread out over a surface of 1.000 km^2. The thickness of the layer of the schists in this layer varies from 100 to 150 m. [16].

DOI: 10.15680/IJIRSET.2014.0308071

Oil shale will be one of the most interesting energy and chemical sources in the world after the exhaustion of oil deposits. Morocco is one of the world leading countries in term of oil shale resources. They are very promising. They are estimated in Tarfaya deposit, located in the south western part of Morocco at 86 billion tons within a 2000 km^2 area and in Timahdit deposit, located about 250 km southeast of the capital Rabat, at 18 billion tons within a 196 km^2 area [17].

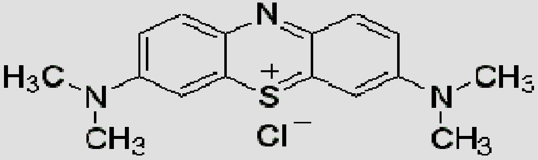
Mining and processing of the oil-shale will significantly disturb the environment, as a result of pollution by dust particles and ash derived from the oil shale [18, 19]. Valorisation of these valuable by product will reduce the environmental impact and will make oil shale development economically feasible for energy production in the future [20].

In this work, we were interested in the study of adsorption of the methylene blue dye on ashes of the oil shales. Various experimental parameters were analyzed: pH, mass of adsorbent, initial concentration while coloring, stirring velocity, and temperature. The capacities of adsorption as of rough clays were given by using the isotherms of Langmuir and Freundlich. The kinetics of adsorption of the methylene blue was studied by using the equations of the pseudo-first order and the pseudo-second-order.

II. MATERIALS AND METHODS

II-1 Adsorbate

The adsorbent used is the Methylene blue, provided by the company Ciba Specialty Chemicals Inc, All the chemicals use come from Merck. Table 1 represents a descriptive card of the methylene blue BM.

Table 1	structure and characteristics of Methylene blue
Name	Methylthioninium chloride (CI 52015)
Chemical structure	
Molecular formula	$C_{16}H_{18}N_3SCl$
Other name	3,7-bis(Dimethylamino)- phenothiazin-5-ium chloride
Molecular weight (g/mol)	319.85

II-2 Preparation of adsorbent

The oil shale, originating in the area of Timahdit, used in this work, was crushed and filtered to obtain fractions < 80 µm then calcined with 800 °C, washed several times with ultrapure water (MILLIPORE, direct-Q, UV3 With Pump) dried with 105 °C during 24 h to obtain oil shale ash.

II-3 Determination of pH zero charge point

The zero point charge pH (pH_{ZPC}) of the OSA adsorbent was measured using the pH drift method [21]. In this fact, the pH_{ZPC} of the adsorbent was determined by adding 20 mL of 5.10^{-2} mol/L NaCl to several 50 mL bêchers of polystyrene. A range of initial pH (pH_i) values of the NaCl solutions were adjusted from 2 to 12 by adding 0, 1 mol/L of HCl and NaOH. The total volume of the solution in each flask was brought to exactly 30 mL by further addition of 5.10^{-2} mol/L NaCl solution. The pH_i values of the solutions were then accurately noted and 50 mg of each adsorbent were added to each flask, which was securely capped immediately. The suspensions were shaken in a shaker at 298 K and allowed to equilibrate for 24 h. The suspensions were then centrifuged at 4000 rpm for 15 min and the final pH (pH_f) values of the supernatant liquid were recorded. The value of pH_{ZPC} is the point where the curve of ΔpH (pH_f–pH_i) versus pH_i crosses the line equal to zero. Measured pH was down by pH-Metre (Hach sension 2 pH ISE meter).

II-4 Experimental procedure

Adsorbent OSA was characterized by various methods of analysis: XDR, of the Panalytical company, by using a Cu radiation K_α (λ = 1, 54060 nm), functioning to 40 kV and 30 mA. The data were collected with 2θ = 10°-80°. XRF, uses a sequential spectrometer AXIOS PANALYTICAL with a channel of measurement bases on only one goniometry covering the complete range of measurement of B to U. FTIR, company BRUKER (Vertex70) by using a range sweeping wavelength 400-7500 cm^{-1}. MEB-EDX,(Quanta 200 FEI equipped with probe EDAX for microanalysis of surfaces) and the MET, (FEI TECNAI G2), with an enlarging from 150 to 500.000 times.

Experiments preliminaries on adsorption, of BM on OSA, showed that balance was established to 10 min with room temperature by using the technique of batch processing. Measurements of adsorption were carried out by mixing various quantities of OSA for the elimination of the potential of the methylene blue dye in series of the beakers out of glass containing 200 ml of the solution coloured with different pH and concentrations by using a heating with numerical control, and a magnetic stirrer (Stuart). Solutions of dye were prepared by using ultrapure water (MILLIPORE, direct-Q, UV3 With Pump) to prevent and minimize the possible interferences, the taking away were carried out, centrifuged (universal 32 hettich) during 15 min with 4000 rpm, thus the supernatant is filtered using a syringe filter of diameter 0,45µm (Minisart, sartorium stedim biotech). The effect of several variables of the OSA amount (1-3 g/L), of pH (2-12), the stirring velocity (300 to 900 tpm), the time of contact (0-120 min), the initial concentration while coloring (1 to 10 mg/L) and of the temperature of the solution (20-60 °C) was studied.
The pH of the solution is adjusted by addition of an minor amount of HCl or NaOH (0, 1 M). At the end of the experiments of adsorption, the concentration of dye was given by measuring the absorptance of the solution with λ = 664 nm using a UV-visible spectrophotometer (Jasco V530). All the experiments were carried out in double and the median values are presented.

The amount of equilibrium adsorption Qe (mg/g) was calculated using the formula:

$$Q_e = \frac{C_0 - C_e}{W} V \qquad (1)$$

Where C_0 and C_e (mg/L) are the liquid concen itially and at equilibrium, V is the volume of the solution (L) and W is the mass of dye adsorbent (g).

The dye removal percentage can be calculated as follows:

$$\%\ \text{of dye removal} = \frac{C_0 - C_e}{C_0} \times 100 \qquad (2)$$

Where C_0 and C_e (mg/L) are the initial a solution.

III.RESULTS AND DISCUSSION

III. 1 Characterization of the adsorbent

A- Quantitative chemical analysis

Chemical analyzes of oil shale ash were performed using X-ray fluorescence spectrometer. Augite is a mineral species of the group of silicates under group of the inosilicates of the family of pyroxenes. It is about a clinopyroxene ferromagnésien and calcic of formula $(Si, Al)_2\ O_6$ (Ca, Mg, Fe, Na) (Mg, Fe, Al, Ti, Cr) [22]. The results are summarized in Table 2, where we noted predominance in SiO_2, Al_2O_3, Fe_2O_3, and CaO. The remaining oxides are partégés in two categories, those which have a little small mass percentage (MgO, Na_2O, TiO_2, P_2O_4, and K_2O) and those which are with the state of trace. A loss on the ignition a little can weak what remains close to pure.

Composé	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na2O	TiO_2	P_2O_5	K_2O	SrO	Cl	P.a.F	Total
% [OSA]	44,1	16,7	11,6	9,28	5,23	4,06	2,69	1,25	1,17	0,295	0,29	2,49	99,155

Table 2: Mineralogical composition, of oil shales ashes OSA

B- Mineralogical analysis

To identify the prevalent phases of mineral of oil shales ashes, of the diffractometric analyzes of x-ray were carried out using the Diffractometer Siemens 5000. The results are gathered in Figure 1.

The decomposition of the oil shales (900°C), generate augite according to the whole of the following equations [23-27]:

$$CaCO_3 \text{ (calcite)} + SiO_2 \longrightarrow CO_2 + CaSiO_3 \text{ wollastonite} \quad (3)$$

$$\text{Illite } KAl_2\,(Si_3Al)\,O_{10}\,(OH)_2 + 6\,CaCO_3 \text{ (calcite)} \longrightarrow 6CO_2 + 2H_2O + K_2O + 3SiO_2 + 3Ca_2Al_2SiO_7 \text{ gehlenite} \quad (4)$$

$$Ca_2Al_2Si_2O_7 + CO_2 \longrightarrow CaCO_3 + (Ca.Mg.Al.Fe)(Si.Al)O_3)_2 \text{ augite} \quad (5)$$

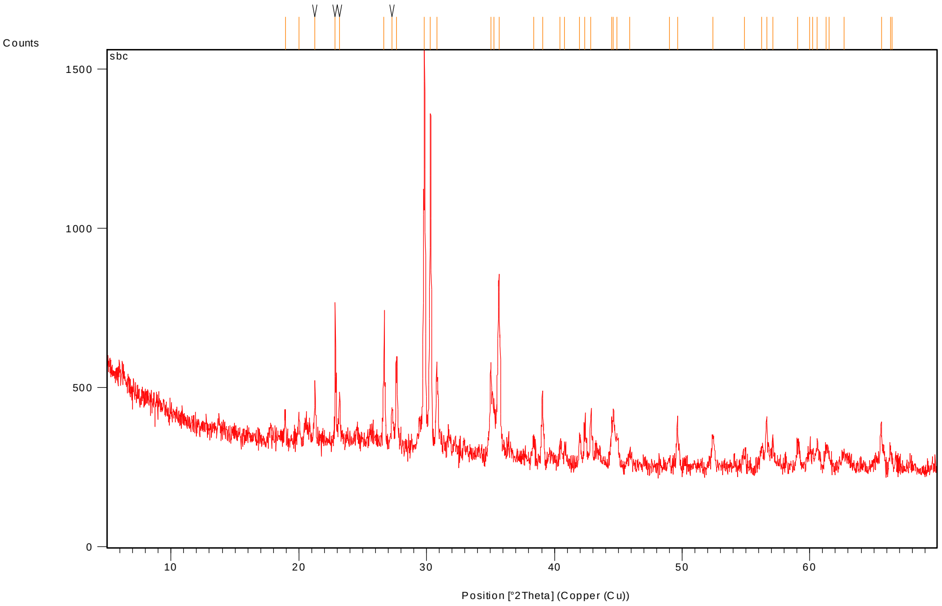


Figure 1: Diffractometric analysis of OSA

The analyzes by diffraction of x-rays gave the same result obtained by the FRX. That wants to say that augite is composed in majority in oil shales ashes.

C- Morphological analysis

Our samples were analyzed by electronic scan microscopy MEB; the use of this technique makes it possible to visualize the morphology of the surface of oil shales ashes. as shown in the Figure 2.

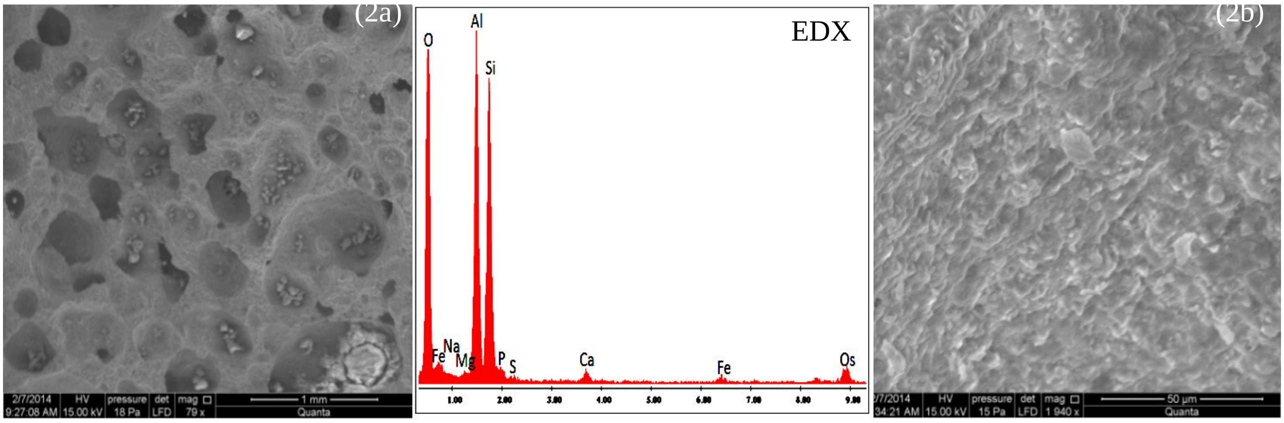


Figure 2: Micrography MEB coupled by EDX of oil shale ash OSA

DOI: 10.15680/IJIRSET.2014.0308071

The image Figure 2a it is an image which is taken in secondary mode of electron with a porous morphology on a some micron scale. What shows us that our material is microporous. The image Figure 2b is an image taken in mode of electron retrodiffused with a contrast of phase:

i : The clear spots correspond to the following light states: C, O, S (See EDX of the Figure 2).
ii : The dark spots correspond to the following heavy states: Al, Si, Fe, Cu (See EDX).

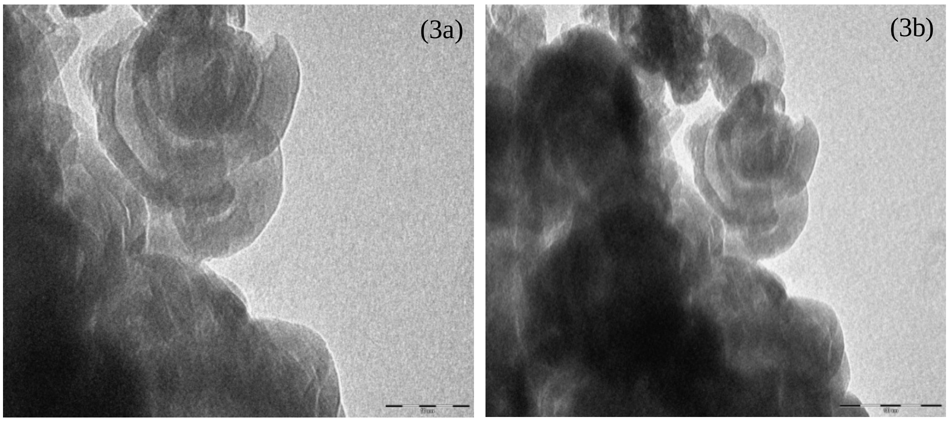
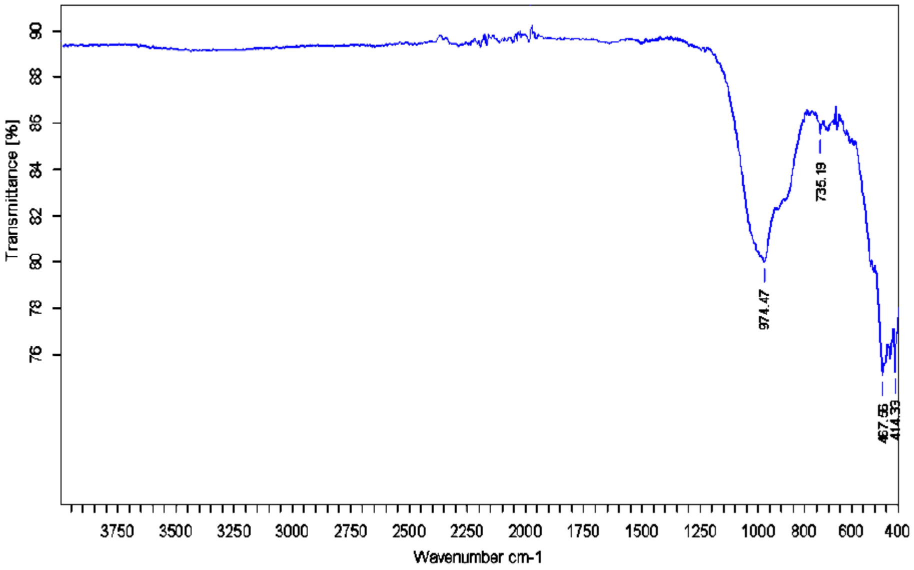


Figure 3 : Micrography MET of oil shales ashes OSA

The figure 3a and 3b shows the analysis by electronic microscopy in transmission MET proving that material OSA presents geometry of stacking in the form of uniformly ordered whorl.

D- Analyzes by infrarouge

The adsorption bands observed, as it is shown in the figure 4, the presence of the connections characterizing oil shale ash OSA. Among these bands one quotes mainly: the band 974, 47 cm^{-1} which can be attributed to stretching Si-O-Si bridge vibration, the tape 735 cm^{-1} corresponds to the vibrations of deformation of O-Si-O, and two bands 467 and 414 cm^{-1} correspond to the vibrations of deformation Si-O-Al.



III.2. Study of effect of various parameters on the adsorption of the methylene blue

A- Influence time of contact on the adsorption of the methylene blue

The study of the kinetics of elimination of the methylene blue BM by oil shales ash OSA in aqueous medium (see Figure 5 which represents the curve of evolution of the quantity of BM adsorbed per gram of OSA according to times of contact with different concentration initial varies from 1 to 7 mg/L while coloring) show that the time of balance very fast and is reached 10 minutes and independent of the initial concentration and that the quantity adsorbed with Qe (mg/g) balance increases with the concentration. The results, presented by table 3 are obtained with constant operating condition T=20°C, [OSA] =2, 0 g/L).

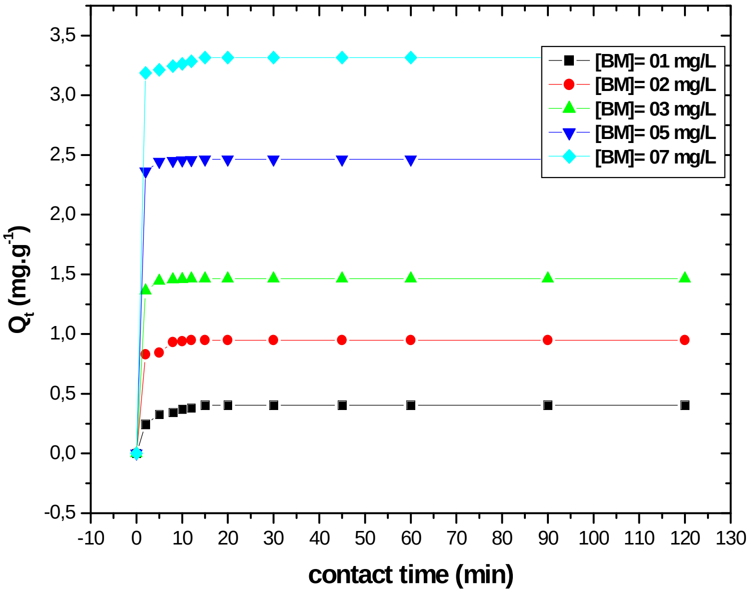


Figure 5: Influence time of contact on the kinetics of adsorption of the methylene blue on (OSA)

[methylene blue] $_0$ mg.L^{-1}		01	02	03	05	07
Q_{ads} (mg.g^{-1})	OSA	0,404	0,948	1,464	2,464	3,316

Table 3: Quantities adsorbed by OSA with various initial concentrations of the BM.

The augmentation of the quantity of adsorption according to the concentration initial of BM, qui' is represented in table 3, explains by the presence of a big number of molecules which will diffuse towards the sites of the surface of the adsorbent and consequently adsorption partial depends on the initial concentration of the dye.

B- Influence amount of adsorbent

With end to optimize the quantity of OSA added to coloured solution BM of the experiments were provided by using 100 ml with the solution with BM (5 mg/L), to the which various quantities of OSA were added (1 - 3 g/L).

The Figure 6 watches which the output increases with the addition of OSA up to 2 g/L, and reached a maximum value of 98% then it is stabilized.

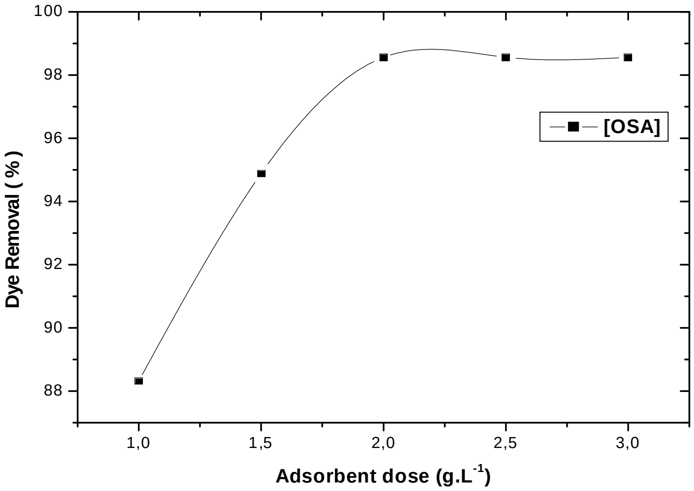


Figure 6 : Effect of adsorbent amounts on dye removal BM

C- Effect of the pH on the holding capacity of the methylene blue dye

One of the main variables affecting the adsorption process is pH, influencing not only the surface charge of adsorbent, the degree of ionization of the material present in the solution and the dissociation of functional groups on the active sites of the adsorbent, but also the solution dye chemistry. In this fact, pH must control the adsorption of dyes onto suspended particles, because both adsorbed molecules and adsorbent particles may have functional groups which are affected by the concentration of H^+ ions in the solution and which are involved in the molecular adsorption process at the active sites of adsorbent [28].

Firstly, the results of blank dye solution studies indicate that the change of the initial pH 2–12 of dye solution has a negligible effect on the λ_{max} of methylene bleu dye. The PZC of ashes of the oil shales is of 8, 05.

Table 4 Effect of pH on the maximum absorbance wavelength λ_{max} (nm) of BM

pH	λ_{max} (nm)
2	662
4	664
6	663
8	664
10	664
12	616

This observation proves that any chemical structural change of dye molecules is not occurred at pH 2–12. The maximum absorbance wavelength λ_{max} (nm) of MB at different pH values is shown in Table 4.The pH of the zero charge of the OS is determined to be 8.05, for pH values higher than 8.05, the surface of the OSA becomes negatively charged and this is opposite for pH < 8.05.

DOI: 10.15680/IJIRSET.2014.0308071

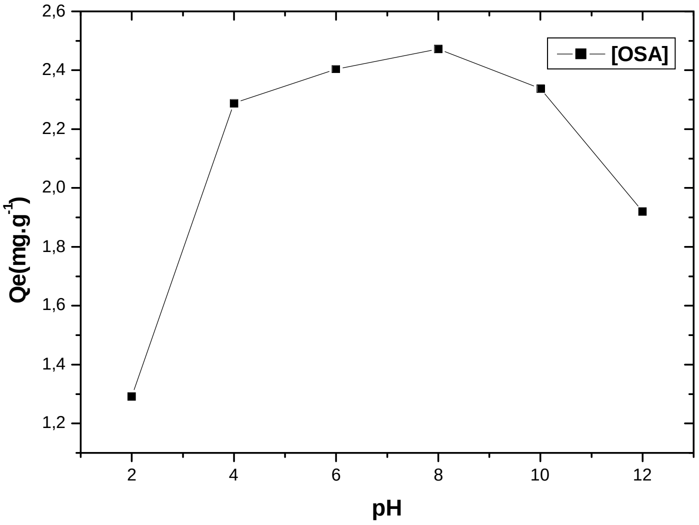


Figure 7 : Influence pH on the capacity of adsorption of the methylene blue

The figure 7 proves that one can as follows explain the increase in the adsorbed quantity of the B.M with the increase in pH (ranging between 2 and 8): The addition of the H^+ cations to lower the pH, involves the neutralization of the negative charge of oil shales ashes on the level of the edges, which disadvantages the adsorption of the cation B.M in very acid medium. In addition when the pH increases there is a reduction in the H^+ cations, therefore the load of the OSA is definitely negative what supports the adsorption of the BM.

After the pH is reached 10 and 12, one records a negative effect on fixing of the dye of BM on ashes of the oil shales, resulting in the reduction in the capacities of adsorption because of the relarguage of blue of methylene.

D- Influence temperature

The temperature of material is a parameter which influences considerably the quantity of adsorption. The temperature used in this study varies in experiments between 20°C and 60°C and [BM] = 05 Mg. L^{-1}, [OSA] =2.0 $g.L^{-1}$.

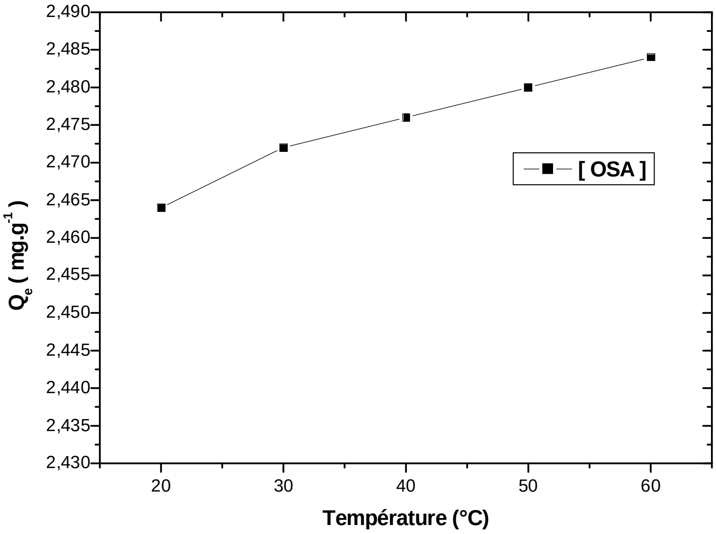


Figure 8 : Evolution of the quantity of the methylene blue adsorbed on the surface of adsorbent OSA according to the temperature,

DOI: 10.15680/IJIRSET.2014.0308071

The results obtained in the figure 8 at the time of these test watch that the quantity of adsorption increases with the temperature in the interval studied. This means that the interaction between adsorbent OSA and adsorbate BM is of nature endothermic.

E- Influence speed of agitation

The speed of agitation plays a big role in the transfer of the molecules of aqueous solution towards the adsorbent; it is thus interesting to study this parameter. The balance with [OSA] = 2.0 g.L^{-1}, [BM] = 05 mg/L, T=20°C.

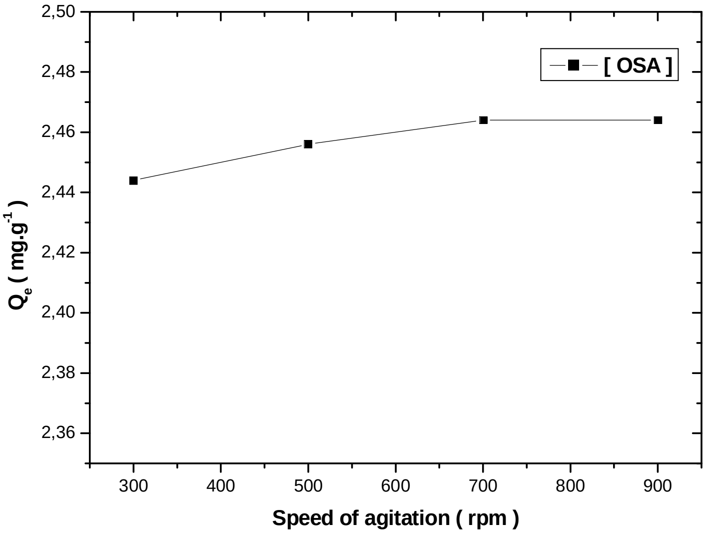


Figure 9 : Influence speed of agitation on the quantity of the methylene blue adsorbed with

The study of the kinetics shows us, in the figure 9, that the adsorption of BM on the OSA in aqueous medium believes slightly with the speed of agitation (of the 300 up to 700 rpm), and it becomes constant beyond 700 rpm.

III.3. Adsorption kinetics

The model of the kinetics of first order is adapted the most for the weakest concentrations of aqueous solution. This model is presented by the relation of Lagergren [29], based on the adsorbed quantity, is the first equation speed established to describe the kinetics of adsorption in a liquid/solid system. This model of pseudo-first-order is represented by the following relation [30]:

$$\ln(q_e - q_t) = ln q_e - K_1 t \tag{6}$$

Where qt: quantity of adsorbate adsorbed with time t (mg.g^{-1}), q_e: quantity adsorbed with balance (mg.g^{-1});
k1: constant speed of adsorption of the pseudo model - first order (min^{-1}), T: time (min).

Evolution of ln (q_e-q_t) according to time, presented in our work. If the Lagergren relation is checked, while carrying ln(q_e-q_t) according to time, we must obtain a line of slope - K_{ads}. This indicates that the kinetics of adsorption of the BM on OSA does not correspond to the kinetics of the pseudo-first order.

The reaction speed of pseudo-second-order depends on the quantity adsorbed on the surface on the adsorbent and the quantity adsorbed with balance. The model of pseudo-second-order can, being represented in the following form [31]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{7}$$

Where k_2: constant speed of adsorption of the model of pseudo-second-order (g.mg-1.min^{-1}).

DOI: 10.15680/IJIRSET.2014.0308071

If this equation is checked, by tracing t/q_t according to t, we must obtain a line of slope $1/q_e$ and ordinate in the beginning equal to $1/(K_2\ q_e^2)$.

The modeling of the kinetics of adsorption of BM on adsorbent OSA by the model of pseudo-second order is presented on Figure 10. These results are obtained with constant operating condition: with 20°C ([BM] = 05 mg. L^{-1}, Vagitation = 500 tpm and [OSA] = 2. 0 $g.L^{-1}$).

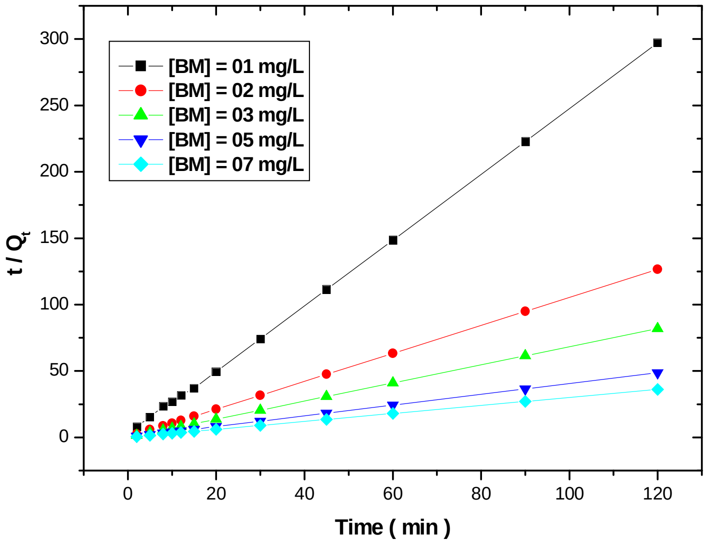


Figure 10 : Model of the pseudo-second-order for the adsorption of the methylene blue on adsorbe OSA

The corresponding parameters were gathered in the Table 5 which also presents the coefficients of correlation. These calculated coefficients are more about the unit for the kinetic model of pseudo second-order. That indicates that this last model described well the experimental results of the adsorption of the BM on the two adsorbents.

C_o (BM) ($mg.L^{-1}$)	Q_{exp} ($mg.g^{-1}$)	Kinetics of the 2nd order		
		K_2 ($g.mg^1.min^{-1}$)	Q_{cal} ($mg.g^{-1}$)	R^2
[OSA]=01 mg/L	0,404	3,15	0,400	0,999
[OSA]=02 mg/L	0,948	6,20	0,950	0,999
[OSA]=03 mg/L	1,464	15,43	1,464	0,999
[OSA]=05 mg/L	2,464	12,611	2,464	0,999
[OSA]=07 mg/L	3,316	3,004	3,320	1,000

Table 5 : Parameters characterizing the kinetics of adsorption of BM on adsorbe OSA.

III.4. Isotherms of adsorption

Isotherms of adsorption were obtained by presenting different concentration from the methylene blue (between 1 and 10 mg. L^{-1}) and a concentration while adsorbing of 1.0 $g.L^{-1}$ for OSA. The experiments of adsorption were carried out in an engine to dig containing 200 ml of solution of BM with 20°C. The experiments were carried out during a time of contact of 120 min to make sure of the establishment of balance of adsorption/desorption.

Equilibrium adsorption isotherm data were analyzed according to the Langmuir and Freundlich models. The Langmuir equation is suitable to describe the adsorptive behaviour of homogeneous surfaces. The Langmuir adsorption model is established on the following hypotheses: uniformly energetic adsorption sites, monolayer coverage, and no lateral interaction between adsorbed molecules. A mathematical expression of Langmuir can be written as [32]:

$$q_e = \frac{Q_{max} K_L C_e}{1 + K_L C_e} \tag{8}$$

DOI: 10.15680/IJIRSET.2014.0308071

Where q_e (mg/g) is the adsorbed amount at equilibrium, C_e is the equilibrium concentration of the adsorbate (mg/L), K_L is Langmuir equilibrium constant ($L.mg_{-1}$) and Qmax the maximum adsorption capacity (mg/g). The linear form of Langmuir equation is:

$$\frac{C_e}{Q_e} = \frac{1}{K_L Q_{max}} + \frac{C_e}{Q_{max}} \tag{9}$$

If the equation of Langmuir is checked, we must obtain while placing on the figure 11 our experimental points in $C_e/Q_e = f(C_e)$, a line whose slope and ordinate in the beginning enable us to determine Q_{max} and K_L.
The essential characteristic of Langmuir isotherm can be expressed by the dimensionless constant called equilibrium parameter, R_L, definedby:

$$R_L = \frac{1}{1 + K_L C_0} \tag{10}$$

Where C_0 is the initial dye concentration (mg/L). R_L values indicate the type of isotherm to be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), and unfavorable ($R_L > 1$) [33].
The isotherm of adsorption of Freundlich [34] supposes that adsorption occurs on a heterogeneous surface by a multi-layer mechanism of adsorption, and that the adsorbed quantity increases with the concentration. A mathematical expression of Freundlich isotherm was as follows:

$$q_e = K_F C_e^{1/n} \tag{11}$$

Where K_f (L/mg) is Freundlich constant and n is the heterogeneity factor. The K_f value is related to the adsorption capacity; while the $1/n_f$ value is related to the adsorption intensity. $1/n_f$ values indicate the type of isotherm to be irreversible ($1/n_f = 0$), favorable ($0 < 1/n_f < 1$), unfavorable ($1/n_f > 1$) [34] can be rearranged to linear form:

$$lnQ_e = lnK_f + \frac{1}{n_f} lnC_e \tag{12}$$

The model of Freundlich was applied to the experimental results of the isotherms of adsorption of the BM to OSA.

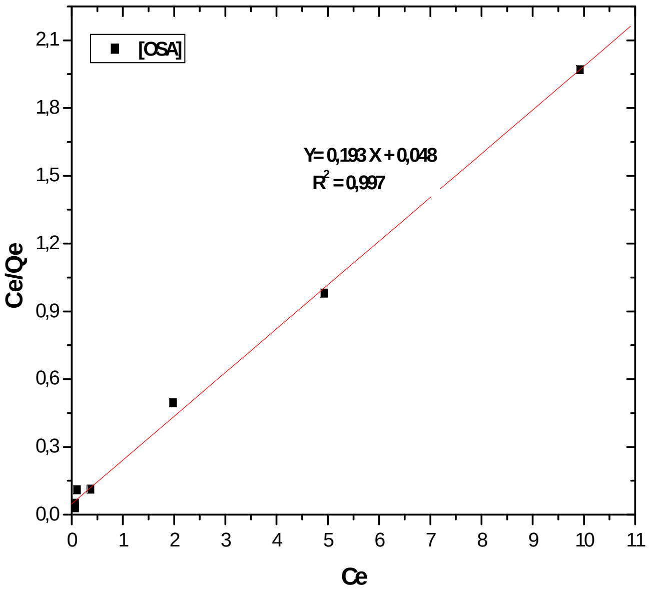


Figure 11: Isotherm of Langmuir (2nd Form)

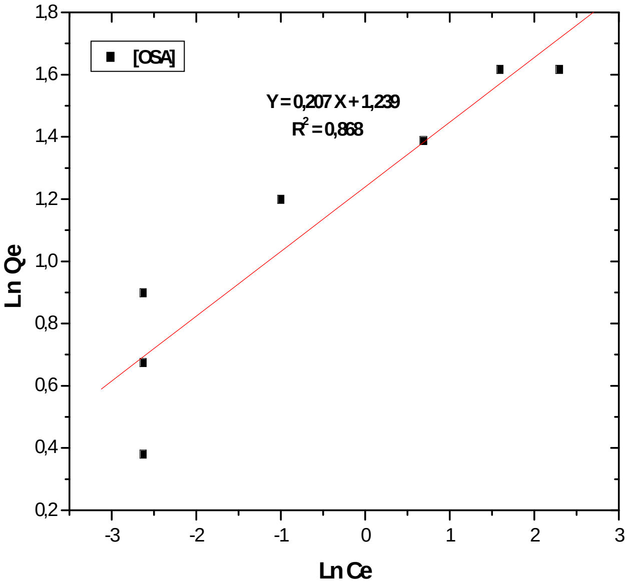


Figure 12: Isotherm of Freundlich

DOI: 10.15680/IJIRSET.2014.0308071

The results obtained are presented on Figure 12 and the parameters of Freundlich are consigned in Table 6.

	Langmuir				Freundlich		
OSA	Q_{max} (mg/g)	K_L (L/mg^{-1})	R_L	R^2	K_f (mg/g)	n_f	R^2
	5,1813	4,020	0,04	0,997	3,452	4,9	0,868

Table 6 : The estimated parameters of the isotherms of adsorption of Langmuir and Freundlich

The estimated parameters of the isotherms of adsorption of Langmuir and Freundlich, for the adsorption of methylene blue dye, by using adsorbents (OSA), are gathered in Table 6.

III.5. Thermodynamics of adsorption

The concept of thermodynamics supposes that in an isolated system where energy cannot be gained or lost. The thermodynamic parameters which must be considered to determine the process are changes of the standard enthalpy (ΔH°), the standard entropy (ΔS°) and free standard energy (ΔG°) due to the transfer of the unit of the body dissolved starting from the solution to the solid-liquid interface. The values of ΔH° and ΔS° were calculated by using the equation of Van't Hoff [35]:

$$\frac{Q_e}{C_e} = e^{\left(\frac{\Delta S}{R} - \frac{\Delta H}{RT}\right)} \quad ==> \quad lnK_d = \frac{\Delta S°}{R} - \frac{\Delta H°}{RT} \quad \text{with} \quad K_d = \frac{Q_e}{C_e} \qquad (13)$$

Where R: constant of perfect gas (R = 8.314 J.mol^{-1}.K^{-1}), and T: absolute temperature of solution (°K)

K_d: partition coefficient, where Q_e: quantity adsorbed on the solid with balance (mg.g^{-1}), and C_e: concentration with balance (mg. L^{-1}).

The values of ΔH° and ΔS° were calculated starting from the slope and of the interception of the layout of lnK_d according to 1/T as the figure.13 shows. ΔG° can be calculated below by using the relation:

$$\Delta G° = -RTlnK_d \qquad \Delta G° = \Delta H° - T\Delta S° \qquad (14)$$

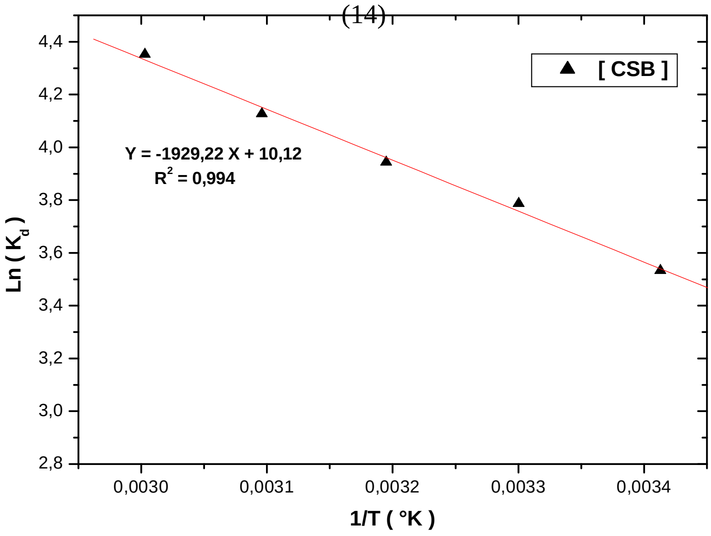


Figure 13 : Layout of lnK_d in function 1/T;

The states of adsorption: initial concentration =05mg. L^{-1}, dosage adsorbing =2.0 g.L^{-1}.

	ΔH° (kJ.mol^{-1})	ΔS° (J.mol^{-1}.K^{-1})	ΔG° (kJ.mol^{-1})				
			20°C	30°C	40°C	50°C	60°C
OSA	16,04	84,13	-8,60	-9,44	-10,28	-11,12	-11,96

Table 7: Thermodynamic parameters of the process of adsorption of the methylene blue on OSA at various temperatures,

Endothermic nature is also indicated by the increase in the quantity adsorbed with the increase in the temperature, wish is obtained by Table 7.

III.6. Regeneration of the support of oil shales ashes

The economic aspect and environmental of the use of adsorbent materials, makes important the re-use of materials, sight their low costs and their capacity to regenerate itself [36].

Regeneration influences the capacity of adsorption OSA by the thermal treatment a temperature of 500 °C during 6:00 after adsorption of 5 mg/L of BM. Indeed for a concentration of 5 ppm, one noted are capacities of adsorption relatively less important than those obtained at the beginning.

The table 8 displays the difference in capacity of first and second cycle is due to the reduction in the specific surface of this material following the heat treatment carried out.

	Capacity of adsorption (mg/g)	Capacity of 1st cycle (mg/g)	Capacity of 2nd cycle (mg/g)
Capacity of adsorption of [SBC]	2,464	2,456	2,444
Output %	98,56	98,24	97,76

Table 8 : capacity of adsorption and percentage of elimination of the BM by OSA for 1st and the 2nd cycle of regeneration

IV.CONCLUSION

In this study, OSA shows promising adsorption capacity for methylene blue removal. The operating parameters for the maximum adsorption were dye solution concentration (5mg/L), adsorbent dosage (2g/L), contact time (10 min) and temperature (323 K). Removal of methylene blue dye is pH dependent and the maximum removal was attained at pH 8. The kinetic studies of dyes on BM indicated that the adsorption kinetics of dyes on OSA followed the pseudo- second order at different dye concentration values.

The equilibrium data have been analyzed. The results were fitted well the Langmuir and Freundlich isotherm models. Thermodynamic studies indicated that the dye adsorption onto OSA was a spontaneous (the negative ΔG°), endothermic and physical reaction (the positive ΔH° and ΔS°). Finally, the economic aspect of the use of oil shales ashes OSA, makes important the re-use of these materials seen being able to them to regenerate itself, to be re-used in the adsorption of the methylene blue dye.

REFERENCES

[1] Banat, I. M., Nigam, P., Singh, D., and Marchant, R., “Microbial decolorization of textile-dye-containing effluents: a review”, Bioresource Technology, Vol.58, pp.217-227, 1996.

[2] Crini, G., “Non-conventional low-cost adsorbents for dye removal”, a review, Bioresource Technology, Vol.97, pp.1061-1085. 2006.

[3] Weng, C. -H., and Pan, Y. -F., “Adsorption of a cationic dye (methylene blue) onto spent activated clay”, J. Hazard. Mater, Vol.144, pp.355-362, 2007.
[4] Bhattacharyya, K. G., and Sharma. A., “Kinetics and thermodynamics of methylene blue adsorption on Neem (Azadirachta indica) leaf powder”, Dyes Pigments, Vol.65, pp.51-59, 2005.
[5] Gürses, A., Dogar, Ç., Yalçin, M., Açikyildiz, M., Bayrak, R., and Karaca, S., “The adsorption kinetics of the cationic dye, methylene blue, onto clay”, J. Hazard. Mater. Vol. B 131, pp.217-228, 2006.
[6] Wang, S., Zhu, Z.H., Coomes, A., and Haghseresht, F. GQ Lu., “The physical and surface chemical characteristics of activated carbons and the adsorption of methylene blue from wastewater”, J. Colloid Interface Sci., Vol.284, pp.440-446, 2005.
[7] Chiou, M. S., and Chuang, G. S., “Competitive adsorption of dye in acid solutions on chemically metanil yellow and RB15 cross-linked chitosan beads”, Chemosphere, Vol.62, n°5, pp.731-740, 2006.
[8] Hameed, B. H., “Spent tea leaves: a new non-conventional and low-cost adsorbent for removal of basic dye from aqueous solutions”, J. Hazard. Mater, Vol.161, pp.753-759, 2009.
[9] Salleh, M. A. M., Mahmoud, D. K., Karim, W. A. W. A., and Idris, A., “Cationic and anionic dye adsorption by agricultural solid wastes: a comprehensive review”, Desalination, Vol. 280, No.1–3, pp.1-13, 2011.
[10] Alexandro, M. M. V., Andre, L. C., Marcos, H. K., Tais, L. S., and Vitor, C. A., “Adsorption of methylene blue on activated carbon produced from flamboyant pods (Delonix regia): Study of adsorption isotherms and kinetic models”, Chemical Engineering Journal, Vol.168, No.2, pp. 722-730, 2011.
[11] Al-Ghouti, M. A., Khraisheh, M. A. M., Ahmad, M. N. M., and Allen, S., “Adsorption behavior of methylene blue onto Jordanian diatomite: a kinetic study”, J. Hazard. Mater, Vol. 165, pp.589-598, 2009.
[12] Akgul, M., and Karabakan, A., “Promoted dye adsorption performance over desilicated natural zeolite”, Micropor. Mesopor. Mater, Vol.145, pp.157-164, 2011.
[13] Sachdeva, S., and Kumar, A., “Preparation of nanoporous composite carbonmembrane for separation of Rhodamine B dye”, Journal of Membrane Science, Vol.329, pp. 2-10, 2009.
[14] Tan, I. A. W., Ahmad, A. L., and Hameed, B. H., “Adsorption of basic dye on high-surface area activated carbon prepared from coconut husk: equilibrium, kinetic and thermodynamic studies”, Journal of Hazardous Materials, Vol.154, pp.337-346, 2008.
[15] Gupta, V. K., Jain, R., Varshney, S., “Electrochemical removal of hazardous dye Reactofix Red 3 BFN from industrial effluents”, Journal of Colloid and Interface Science, Vol.312, pp.292–296, 2007.
[16] Saoiabi, A., Doukkali, A., Hamad, M., Zrineh, A., Ferhat, M., Debyser, Y., “Timahdit (Morocco) oil shales: composition and physicochemical properties”, Comptes Rendus de l’Académie des Sciences-series IIC-chemistry; Paris, Chimie / Chemistry, Vol.4, No.5, pp.351-360, 2001.
[17] National office of hydrocarbons and the mines (ONYHM), Office nationale des hydrocarbures et des mines, “to contact the site of the office”.
[18] Jaber, J. O., and Probert, S. D., “Environmental-impact assessment for the proposed oil-shale integrated tri-generation plant”, App Energy, Vol.62, No.3, pp.169-209. 1999.
[19] Toomik, A., Liblik, V., “Oil shale mining and processing impact on landscapes in north-east Estonia”, Landscape and Urban Planning, Vol.41, No.3-4. pp.285-292, 1998.
[20] Hamadi, A., and Nabih, K., “Alkali Activation of Oil Shale Ash Based Ceramics”. E-Journal of Chemistry, Vol.9, No.3, pp.1373-1388, 2012.
[21] Calvete, T., Lima, E. C., Cardoso, N. F., Dias, S. L. P., Pavan, F. A., “Applications of carbon adsorbents prepared from the Brazilian pine fruit shell for removal of Procion Red MX 3B from aquoeus solution: kinetic, equilibrium and thermodynamic studies”. Chemical Engineering Journal, Vol.155, pp.627-636. 2009.
[22] Rudolf weenk, H., and Bulkh, A., “deliver Minerals”, Vol. 203, pp.472-475, 2004.
[23] Ohashi, Y., and Finger, L.W., “The role of octahedral cations in pyroxenoid crystal chemistry-L Bustamite, wollastonite and the pectoliteschizolite- serandite series”, Amer. Mineral., Vol. 63, pp.274-288, 1978.
[24] Peters T, Iberg R. “Mineral changes during firing of calcium-rich brick clays”. Ceram Bull, Vol.57, No.5, pp. 503-509, 1978.
[25] Korczak P and Raaz F, “Verfeinerung der Kristallstruktur von Gehlenit unter Zugrundelegung des Gallium-Gehlenites”. OEAW Math Naturwissenschaftliche Klasse., Vol.104, pp. 383-387. 1967.
[26] Bowen, N. L., “The evolution of igneous rocks”, NJ: Princeton University press, pp.321-322, 1928.
[27] Okui, Haruo M., S and Fumiyuki, M., “Structure refinement of a nonstoichiometric pyroxene synthesized”, Physics and chemistry of minerals., Vol.25, pp.318-322, 1998.
[28] El Haddad, M., Slimani, R., Mamouni, R., ElAntri, S., Lazar, S., “Removal of two textile dyes from aqueous solutions onto calcined bones”, Journal of the Association of Arab Universities for Basic and Applied Sciences Vol.14, pp.51-59, 2013.
[29] Feng, D., Aldrich, C., “Elution of ion exchange resins by use of ultrasonication”, Hydrometallurgy, Vol.55, pp.201-212, 2000.
[30] Liu, X., Quan, X., Bo, L., Chen, S., Zhao, Y., “Simultaneous pentachlorophenol decomposition and granular activated carbon regeneration assisted by microwave irradiation”, Carbon Vol.42, pp.415-422, 2004.
[31] Ho, Y. S., McKay, G., “Pseudo-second order model for sorption processes”, Chem. Eng. J. Vol.76, pp.183, 1998.
[32] Langmuir, I., “The constitution and fundamental properties of solids and liquids”. Amer. J. Chem. Soc, Vol.38, pp.2221-2295, 1916.
[33] Mahmoodi, N.M., Arami, M., “Modelling and sensitivity analysis of dyes adsorption onto natural adsorbent from colored textile wastewater”, Journal of Applied Polymer Science, Vol. 109, pp. 4043-4048, 2008.
[34] Freundlich, H. M. F., “Uber die adsorption in losungen”. Z. Physik. Chemie (Leipzig), Vol.57A, pp.385-470, 1906.
[35] Ozcan, A., Oncu, E.M., Ozcan, A.S., “Kinetics, isotherm and thermodynamic studies of adsorption of Acid Blue 193 from aqueous solutions onto natural sepiolite”, Colloids and Surfaces, Vol. A277, pp.90-97, 2006.
[36] Ulibarri, M. A., Pavlovic, I., Hermosin, M. C., and Cornejo, J., “Hydrotalcite-Like Compounds as Potential Sorbents of Phenols from Water”, Applied Clay Science, Vol. 10, No.1-2, pp. 113-145, 1995.

DOI: 10.15680/IJIRSET.2014.0308071