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Adsorption of methylene blue on bituminous schists from Tarfaya-Boujdour

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ABSTRACT

In this work, the reactivity of the surface of bituminous schists has been studied using a cation adsorbent, so-called Methylene Blue (MB). This bituminous schist is a calcareous clay rock that contains some amounts of organic matter. The samples were collected from an outcrop of Lamsied (Laâyoune), zone around Tarfaya-Boujdour. Once the granulometry of samples was well determined, the rocks were characterized by X-ray diffraction and they were analysed by X-ray fluorescence. Some parameters were considered relevant on the adsorption of MB by surface rock and they have been studied. One of these parameters is the adsorbed molecules-adsorbent contact time. This is the contact between a starting concentration of MB and a certain mass of gross rock. The analysis of results has shown that adsorption of MB can be well modelled by the Langmuir isotherm and also that a rapid kinetic (<100 min for L-type) can be fitted by a second-order equation model. The gross rock takes 84 % of the amount of MB in aqueous phase at a time less than 1min, using a rock mass of 0.1 g.

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Capsule Summary: In the context of natural material investigation for the radioactive waste containment, this paper describes the preliminary study on the adsorbent capacity of bituminous shales from the Lamsied outcrop (Laayoun-Morocco).

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INTRODUCTION

This work must be considered a partial research of a general investigation on natural material in order to study the

immobilization of stable and radioactive metals and his application to industry waste treatment. One of these applications can be the determination of a geological place to the confinement and storage of radioactive wastes (Jakobsen et al., 2012).

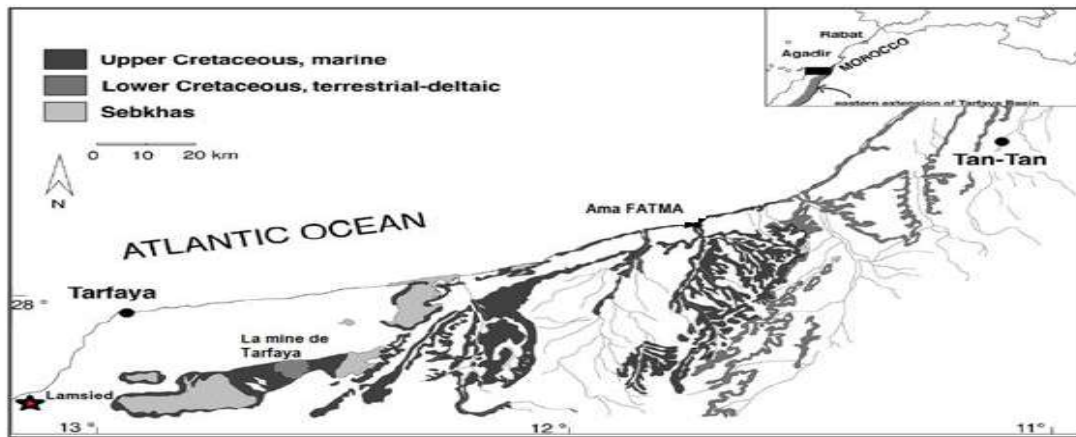


Fig. 1: Simplified geological map of the study area (Gebhardt and Zorn, 2008).

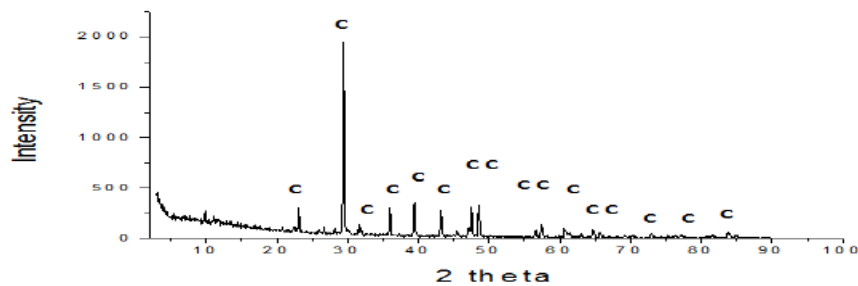
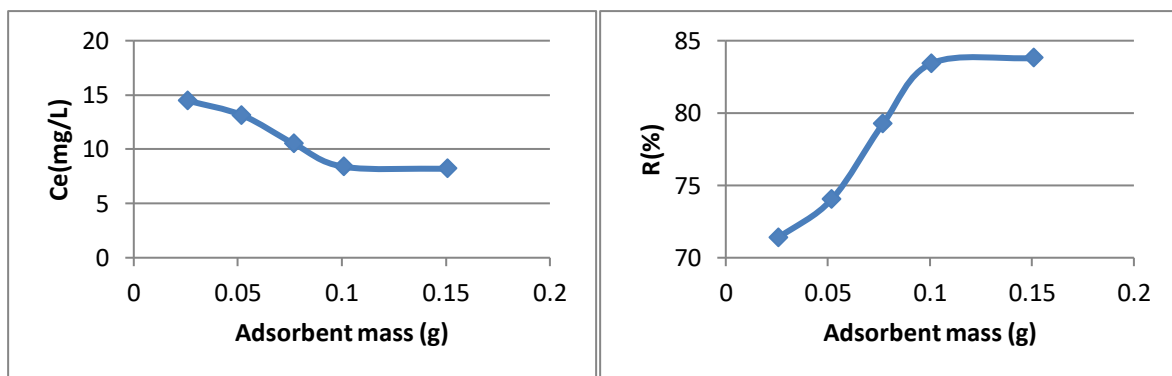


Fig. 2: Spectrum of XRD of sample S6 (1) where the presence of calcite is well observed.



(a) (b)

Fig. 3: (a) variation of final concentration, C_e , of MB. (b) Adsorption ratio R (%) of MB versus adsorbent mass, using an initial concentration, C_0 , equal to 50.8 mg/l and a contact time of 240 min.

There are some published works on the adsorption of metals, organic and inorganic substances by natural material (Bendjama, 1982; Benguella and Benaissa, 2002; Khouya et al., 2006; Sbaa et al., 2001; Seghairi, 1998; Steger, 1973). Following these works, our research has been addressed to determine the physicochemical properties of bituminous schists, which contain some amounts of organic matter.

These schists are calcareous clay rocks located in the outcrop of Lamsied (Laâyoune), near Tarfaya-Boujdour. In our case, we have considered the elimination of Methylene Blue (MB). Stable and radioactive metals will be considered in a next step of our investigation.

The main objective of this work is to observe the retention of methylene blue by a representative sample of

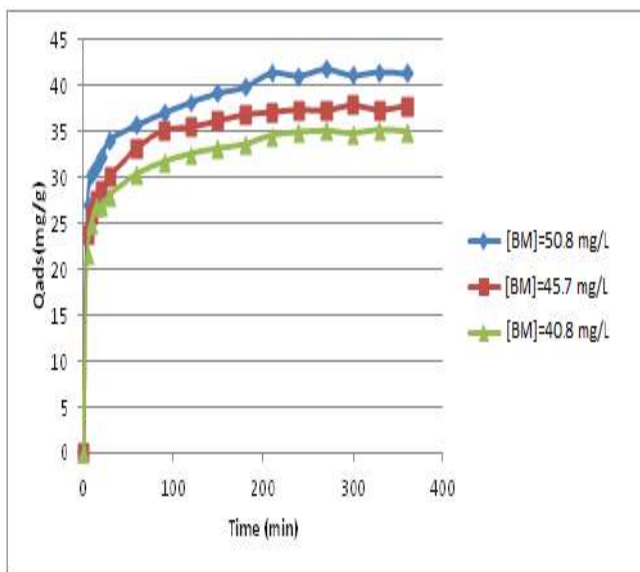


Fig. 4: Variation of the adsorbed amount of MB versus the contact time

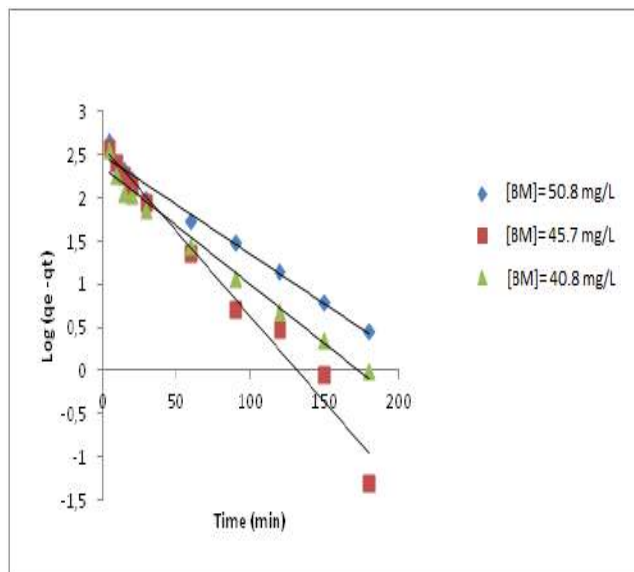


Fig. 5: Fitted lines using a kinetic model of pseudo first order

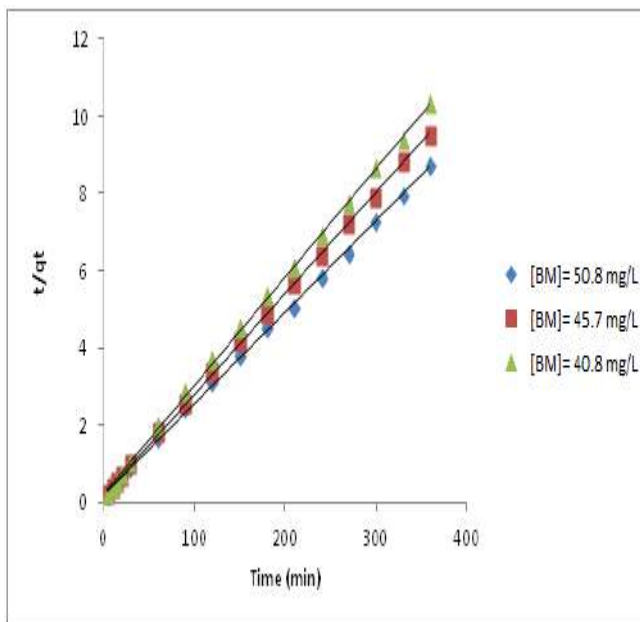


Fig. 6: Fitted lines using a kinetic model of pseudo second order

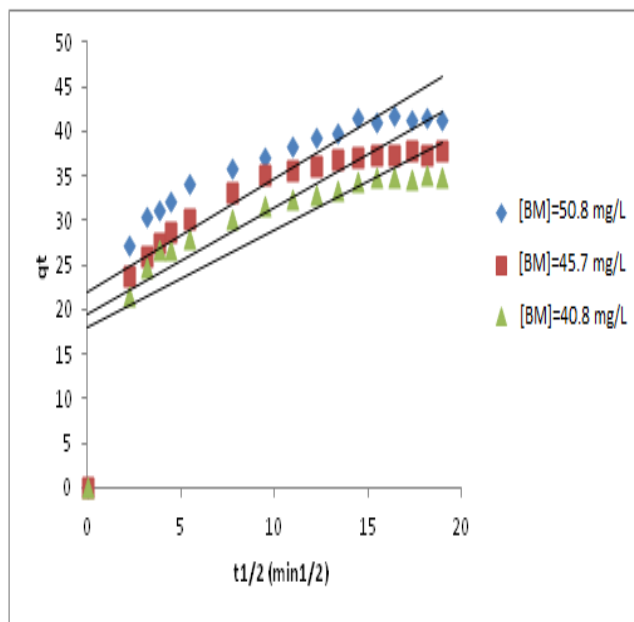


Fig. 7: Fitted lines using a kinetic model of intra-particle diffusion

gross rock S6 (1). An experimental procedure has been developed following two steps: Firstly the gross rock, which will be used as adsorbent, has been characterized. Thus, granulometry of samples has been determined by X-ray diffraction (XRD) using a Malvern Mastersizer 2000 equipment. The mineralogical structure was obtained by XRD and the chemical composition was determined by X-ray fluorescence (XRF).

As second step, the mechanisms physicochemical of MB-rock system have been studied. This study has been addressed to observe the parameters of interest when the adsorption of MB by rock is considered. These parameters

are: (i) the contact time of MB-rock, (ii) the starting concentration of MB in the solution, and (iii) the initial mass of adsorbent.

The experiments have been developed controlling pH (6.8 at start). Under these conditions, the kinetic and adsorption isotherms have been determined.

MATERIAL AND METHODS

Sampling

According to the objectives of this work, some samples of rocks (bituminous schists with organic matter) were

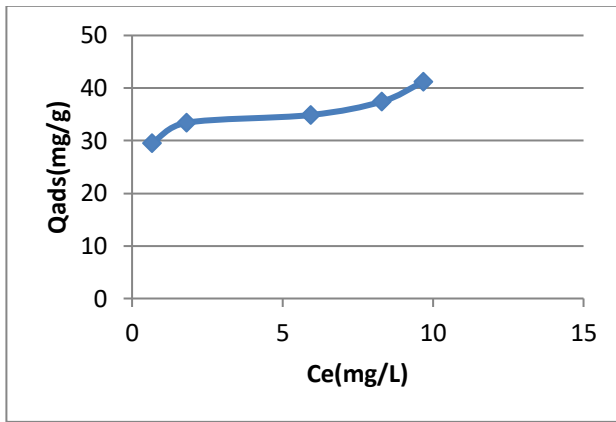


Fig. 8: Adsorption isotherm of MB using schist rock absorbent

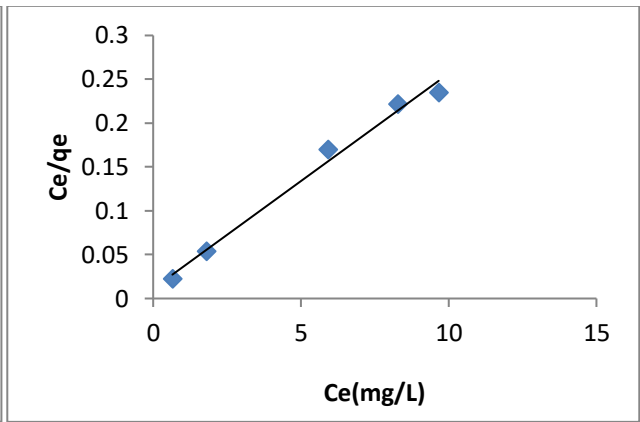


Fig. 9: Fitted line of experimental data using a model of as Langmuir

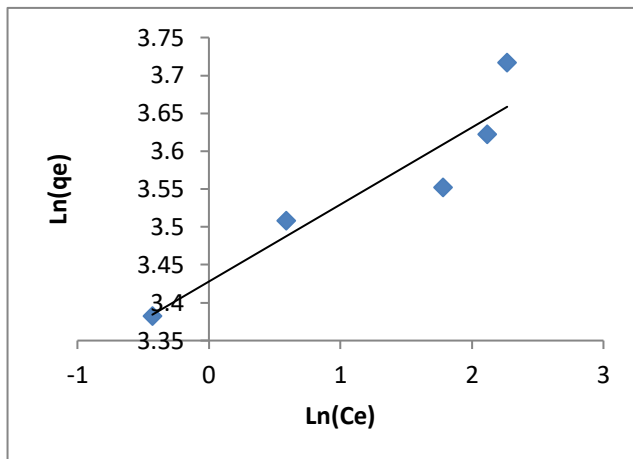


Fig. 10: Fitted line of experimental data using a model Freundlich

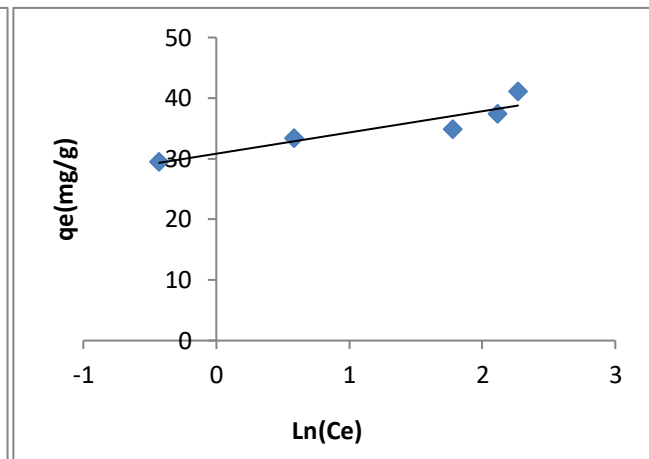


Fig. 11: Fitted line of experimental data using a model of Temkin

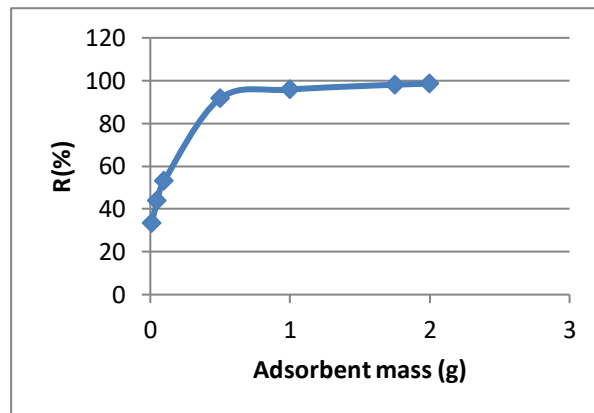


Fig. 12: Adsorption ratio R (%) for ^{134}Cs using bituminous schists collected at Tarfaya sample S1 (14)

collected from the outcrops located in Lamsied (Laâyoune). These samples will play the role of adsorbents of organic and inorganic substances in our study. The sampling area is presented in Figure 1. The sampling area is located on a consolidated plateau, at the side of the stripe of Tarfaya-

Boujdour, which is at the seaside. That covers some Cretaceous formations (especially from Aptian, Cenomanian or Campanian periods).

Previous works (Espitalié et al., 1977; 1985; Lüning et al., 2004; Walkley and Armstrong Black, 1934; Walkley,

1947) have shown that the analysed samples had very high concentrations of total organic carbon (TOC) (Davison, 2005; Elkhatib et al., 1995; Gebhardt and Zorn, 2008; Kolonic et al., 2002; Kuhnt et al., 1997; 2001; 2005; 2009; Mort et al., 2008). The characteristics of samples are listed in Table 1. The analysis of the table shows that the samples are divided into three lithologies:

S6 (1), S6 (3), S6 (5) samples are rich in total organic carbon (TOC), the S6 (1), S6 (3) samples contain higher calcite contents to the silicates while the sample S6 (5) contains a silicate content higher than that of calcite.

Clay limestone: samples S6 (2), S6 (4) which contain a similar content and low in TOC compared to other lithologies and consist of a remarkable amount of calcite (CaCO₃) compared to silicates.

Limestone clay: S6 (6), S6 (7) samples, which contain a significant content of silicates compared to calcite, S6 (7) has a high TOC content and is higher than that of S6 (6).

In this work a sample, S6 (1), rich in total organic carbon (TOC), has been used to study the adsorption of MB by natural materials (bituminous schists).

Granulometry

The granulometry, using laser diffraction, has been determined in the sample S6 (1). The distribution of particle sizes determined using an equipment of wet laser diffraction (Malvern Mastersizer 2000). This system has a Hydro dispersion unit 2000G (Mejjad et al., 2016). The equipment and a protocol reach a distribution range from 0.02 to 2000 µm particle size. To determine the granulometry, 1 g of sample was introduced in the dispersion unit, which contained demineralised water, dispersant agent. Every measurement takes 10 s, the period used for dispersion of agglomerates by ultrasonic waves.

X-Ray diffractometry

Mineralogic structures of sample S6 (1), the adsorbent in the experiment, has been determined X-ray diffractometry. The samples have been powdered and has been analysed in a diffractometer 2-cerclesX'Pert Pro MPD PANalytical. This equipment has a theta-theta goniometer, an ultra-rapid detector X'Celerator and a sample stages.

X-Ray fluorescence

The majority elements, in oxidised form in the inner adsorbent, have been determined using a spectrometer of X-ray fluorescence, so-called Axios system. The characteristics of this spectrometer are a weak power (1 kW), a refrigeration system that uses SST tubes. These allow an energy excitation range of 20-60 kV and a current in the range 10-50 mA.

The adsorbed

Prior to developing procedures for the containment of radionuclides by this raw or conditioned natural material, we have firstly studied its physicochemical adsorption

properties by means of methylene blue (MB) removal tests from aqueous solutions (Avena Et al., 2001, Hang and Brindley, 1970, Kahr and Madsen, 1995).

Test of adsorption

The experimental test is to introduce a known mass of adsorbent in an aqueous solution of MB. Once the adsorbent, sample S6 (1), is in the solution the ensemble is stirred until equilibrium at room temperature. A part of adsorbed remains in solution and other fraction is fixed on the solid.

The starting concentration of MB and its final concentration, before and after equilibrium in the test, are determined by absorbance in an Ultraviolet-visible spectrophotometer UV-3100PC using $\lambda = 664$ nm. The equipment calibration is done before measurements using some diluted solutions of a MB solution of 100 mg/l. The starting pH in the test was 6.8. This pH is recommended by some authors (Miyah et al., 2015). Thus, experiences developed at pH=6.8 showed an easy adsorption of MB by clays when starting when pH increases and becomes stable if pH reaches 7. This fact is also observed by Ghosh and Bhattacharyya (Gosh and Bhattacharyya, 2002) in the case of using Kaolinite an adsorbent. This behaviour is explained by the neutralization of negative charges of adsorbents per H⁺ in acid media. For that we have selected pH= 6.8 as starting value in the whole of the tests.

Once the physicochemical equilibrium of adsorption can make sure, the amount of MB adsorbed, noted as Q_{ads} and expressed in mg of MB par g of adsorbent, is calculated using the equation (1) (Dbik et al., 2014).

$$Q_{ads} = \frac{C_0 - C_{res}}{m} \times V \quad (1)$$

Where, Q_{ads} is the amount of MB that is adsorbed per gram of adsorbent (mg/g). C₀ is the starting concentration of MB in the aqueous phase (mg/l). C_{res} is the final concentration of MB in the aqueous phase, once the equilibrium is reached (mg/l). m is the adsorbent mass (g). V is the volume of solution (l).

Kinetic study and isotherm of adsorption

The studies on kinetic and isotherms of adsorption of MB by the gross rock, sample S6 (1) in Table 1, were done using conditions previously mentioned. Before any operation of adsorption, the rock was finely grinded and homogenised.

The kinetic of absorption of MB by the gross rock has been studied. For this, 500 ml of MB, with concentrations of 50.8, 45.7 and 40.8 mg/l were initially added into 0.5 g of adsorbent: sample S6 (1). The pH of liquid-solid system was controlled (pH=6.8) and stirred at room temperature, using 300 rpm. Different extractions from the top of solution were done at different moments from 0 to 360 min. The separation of phases is fulfilled at 2000 rpm for 15 min. Isotherms of adsorption were analysed in the same conditions. The contacting time was 240 min and the initial concentrations of MB were from 30.1 mg/l to 50.8 mg/l.

Table 1: Characteristics and lithology of samples collected at Lemsied region (El batal, 2014)

Sample	TOC (%) (Rock Eval)	CaCO ₃ (%)	Silicates (%)	Altitude	Lithology	Geologic period
S6 (1)	6	55.93	35.07	0.5 m	Marl with high concentration of organic matter	Late Cretaceous period
S6 (2)	0.59	91.53	7.59	2 m	Clay (calcareous)	
S6 (3)	3.83	47.46	46.80	4 m	Marl with high concentration of organic matter	
S6 (4)	0.58	84.75	14.38	6m	Clay (calcareous)	
S6 (5)	3.19	38.98	56.23	8m	Marl with high concentration of organic matter	
S6 (6)	1.94	16.95	80.14	10m	Clay (calcareous)	
S6 (7)	5.04	27.12	65.32	12m	Clay (calcareous)	

Table 2: Distribution of particle size of adsorbent S₆ (1)

Particle size (μm)	Lower than 2	from 2 to 50	from 50 to 2000
Volume (%)	0.25	58.48	41.27
	Clay	Lime	Sand

Table 3: Content in % of oxides in the sample S6 (1) that is used as adsorbent

Compounds	CaO	Na ₂ O	SiO ₂	SO ₃	Al ₂ O ₃	MgO	P ₂ O ₅	K ₂ O	Fe ₂ O ₃
Concentration (%)	20.70	14.40	9.03	3.69	2.14	0.95	0.55	0.43	0.33

Models of kinetics of adsorption

The studies on kinetics were developed for a better comprehension of mechanisms of reaction, especially the case of adsorption. Three models on kinetic of adsorption of MB by the rock S6 (1) were tested. These models are:

The pseudo-first order model: This model is based on the equation (2) (Srivastava et al., 2006).

$$\text{Log}(q_e - q_t) = \text{Log}(q_e) - \frac{k_1}{2.303} t \quad (2)$$

The pseudo-second order model: This model is based on the equation (3) (Ho and McKay, 1999; Liu et al., 2010).

$$\frac{t}{q_t} = \frac{t}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

Linear model of intra-particle diffusion: This model is based on the equation (4) (Laabd et al., 2015).

$$q_t = K_d t^{1/2} + C_d \quad (4)$$

Where, q_e is the adsorbed amount at equilibrium (mg/g), q_t is the adsorbed amount at time t (mg/g), k_1 is a velocity of adsorption constant for the pseudo-first order (1/min), k_2 is a velocity of adsorption constant for the pseudo-second order (g/mg min), K_d is a velocity of diffusion through pores (mg/g min^{1/2}), C_d is the ordinate at origin (mg/g), t is the time (min).

Models of isotherms of adsorption

The transformed, linear, of models of isotherms of adsorption done by Langmuir, Freundlich and Temkin are presented in equations (5), (6) and (7), respectively (Laabd et al., 2015; Baghriche et al., 2008 ; Laabd et al., 2015).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (5)$$

The separation factor r_L (without magnitude) is evaluated using the following equation:

$$r_L = 1 / (1 + K_L C_e)$$

The factor r_L can be interpreted according to (Giles et al., 1960), If $0 < r_L < 1$: adsorption is favourable, If $r_L > 1$: adsorption is not favourable, If $r_L = 1$: adsorption is linear AND If $r_L = 0$: adsorption is irreversible .

$$\text{Ln } q_e = \text{Ln } K_T + \frac{1}{n} \times \text{Ln } C_e \quad (6)$$

$$q_e = B \text{Ln } K_T + B \text{Ln } C_e \quad (7)$$

Where, K_L : Binder constant of Langmuir, C_e : Final concentration in solution at equilibrium of adsorption in mg/l, q_e : Amount of adsorbed MB at equilibrium in mg/g, q_m : Maximum adsorbed amount in mg/g, K_T , n : Empiric constants of Freundlich and K_T , B : Constants of Temkin model.

Table 4: Parameters of kinetic models and maximal amount adsorbed of MB on the surface of sample S6 (1)

Model	Parameters	C ₀ (BM)= 50.8 (mg/l)	C ₀ (BM)= 45.7 (mg/l)	C ₀ (BM)= 40.8 (mg/l)
Pseudo first order	R ²	0.98	0.97	0.98
	K ₁ (min ⁻¹)	0.011	0.02	0.013
	q _{e.cal} (mg/g)	12.2	13.44	10.53
	q _{e.exp} (mg/g)	41.45	37.15	34.45
Pseudo second order	R ²	0.99	0.99	0.99
	K ₂ (g/mg.min)	0.003	0.003	0.003
	q _{e.cal} (mg/g)	42.37	38.31	35.58
	q _{e.exp} (mg/g)	41.45	37.15	34.45
Intra-particle diffusion	R ²	0.60	0.62	0.61
	k _d (mg/g min ^{1/2})	1.26	1.19	1.09
	C _d	21.95	19.39	18.04

Table 5: Parameters of models of adsorption isotherms of Langmuir and Freundlich and Temkin using MB and sample S₆ (1)

Isotherms	Parameters	Values
Langmuir	R ²	0.99
	K _L	2.16
	q _m (mg/g)	40.82
	r _L	0.045-0.41
Freundlich	R ²	0.88
	K _f	30.81
	n	9.83
Temkin	R ²	0.85
	K _T	6666
	B	3.5

RESULTS AND DISCUSSION

Study on particle size

According to results shown in Table 2, the main material of sample S6 (1) is lime (58.48 %), next sand grains (41.27 %) and finally clay (0.25 %). The analysis by spectrometry of X-ray fluorescence of absorbent S6 (1) shows that (Table 3): The higher concentrations correspond to the following oxides: CaO > Na₂O > SiO₂ > SO₃ > Al₂O₃ > Fe₂O₃. The presence of CaO is explained by the marine origin of the rock. The ratios SiO₂/Al₂O₃ = 4.22 can show the presence of a high amount of free quartz in the sample. The low concentration of Fe₂O₃ is related to the absence of nodules of oxides and hydroxides of iron. The low concentration of MgO is explained due to no dolomitisation phenomenon in the rock. The low concentration of K₂O is related to a poor presence of illite in the rock. Other oxides, such as P₂O₅ and Na₂O, can be

explained by precipitation on this material that is rich in organic matter and kerogen (El Batal, 2014).

Finally, it is possible to make sure the abundance of calcars with presence of quartz. The low concentration of iron could be related to perytisation phenomena because this material is rich in organic matter and kerogen.

Mineralogical composition

Analyses by XRD can make sure the presence of calcite (CaCO₃) in the sample. It is clearly deduced of spectrum shown in Figure 2. Other minerals cannot be observed in the spectrum due to high intensity of its lines in the spectrum. These results confirm those obtained by XRF.

Effect of mass of absorbent

The influence of the rock amount, sample S6 (1), used as adsorbent, has been determined. The experiments were done

using the conditions already mentioned. The masses were in the range from 0.02 g to 0.15 g. Samples were stirred using an initial concentration of MB, C_0 , equal to 50.6 mg/l and a volume of 100 ml. Figure 3a shows the rapid decrease of final concentration of MB (C_e), with mass and how this concentration is stabilized when masses are higher than 0.1 g. Figure 3b confirm this behaviour. In this Figure is presented the values of adsorption rate, R (%) versus mass of adsorbent. Indeed, the adsorption rate increases (linear) with mass of adsorbent until it reaches a maximum, 84 %, with masses higher than 0.1 g. This fact, which is considered as a limitation of cation adsorption by MB, though the sites of adsorption had increased, may be considered as competitive reactions of adsorption of H^+ , with sizes lower than MB and that becomes more abundant after the adsorption of 84.5 of MB. More theoretical and experimental efforts are necessary to study the fact of exchange at the solid-liquid interface.

Study of kinetics

Figure 4 shows the variation of the adsorbed MB amount, Q_{ads} , versus time. According to this Figure, we can suggest that, the curves of variation of Q_{ads} versus time, obtained using different concentrations of MB are similar to previously reported works (Dbik et al., 2014). Concerning the plateau, the adsorbed concentration of MB increases with the initial concentration of MB in aqueous phase. This fact was already observed in previous works (Abd El-Latif et al., 2010; Ouasif et al., 2013). The kinetic of adsorption occurs in two steps: In the first step is rapid and takes 15 min. At this moment the MB can find active sites on the surface of adsorbent. The second step starts after 15 min with a slow adsorption and takes 100 min. The equilibrium is then reached, with a maximum of 42 mg/g using an initial concentration of MB of 50 mg/l. The existence of this plateau confirms the hypothesis of a competitive reaction of adsorption of H^+ (that become predominant once at the start of plateau).

Models of kinetic of adsorption of MB

The experimental data has been fitted according to the three models of kinetics previously presented. The fitted lines are presented in Figures 5, 6 and 7. The value of parameters of each model, the absorbed amounts and regression coefficients are presented in Table 4.

Figure 7 corresponds to intra-particle diffusion. Regression coefficient, R^2 , is around 0.6. This means a weak result considering the three initial concentrations of MB in aqueous phase. On the other hand, the values of adsorbed amount, q_e , are lower than experimental data. For the pseudo first order model (Figure 5), the regression coefficient, R^2 , are 0.98 (initial concentration of MB 50.8 mg/l), 0.97 (45.7 mg/l) and 0.98 (40.8 mg/l). However, the calculated values of q_e are lower than experimental data. For that, neither intra-particle diffusion model nor pseudo first order model could describe the adsorption of MB in the experimental conditions.

Figure 6 corresponds to pseudo-second order model of the kinetics of adsorption of MB by the gross rock (sample S6 (1)). The calculated q_e and the regression coefficients, R^2 , for the three initial concentrations of MB (Table 4) shows values of R^2 equal to 0.99 and calculated q_e at equilibrium are similar to experimental data. Then the experiment can be fitted using a pseudo second-order model.

Isotherms of adsorption

Figure 8 shows the variation of adsorbed amount, Q_{ads} , at equilibrium versus equilibrium concentration. According to this Figure, the curve is an isotherm L type following Giles classification (Giles et al., 1960). This fact means the adsorption of MB processes could be monolayer.

The application of models of Langmuir, Freundlich and Temkin to adsorption isotherms, through the equations (5), (6) and (7), respectively, is presented in the Figures 9, 10 and 11. The values of parameters of each model are listed in Table 5. The analyses of isotherms can indicate that Langmuir model fits perfectly the processes of adsorption of MB. Indeed, the value of correlation coefficient for this model is close to unity (0.99) and the maximal along evaluated by the model of Langmuir is very close to one determined by experiments.

Test of adsorption of ^{134}Cs

To finish the study on adsorption by natural material, marl with high concentration of organic matter, we have developed an experiment of adsorption of a radionuclide ^{134}Cs , by a rock (sample S1 (14)) similar to the other sample (S6 (1)). The sample S1 (14) was collected in Coupe d'Oued MA FATMA (Tarfaya). The clay proportion was 65 % (35 % of clay in S6 (1)). Figure 12 shows the preliminary results. Thus, the adsorption ratio, R (%), is close to 100 % for 2g of mass of sample. Previous works have explained this experimental result by the role of organic matter integrated in the mineral part of sample (Khouya et al., 2004).

CONCLUSIONS

This work can be considered as a part of other wider work addressed to the study of natural materials to be used as confinement and stocker of radioactive wastes. This is the case of the study of schist rocks, marls with high concentrations of organic matter. The study of adsorption of Methylene Blue (MB) by a bituminous schist rock has the following conclusions. The analysis of granulometry shows the existence of a high proportion of limes in the adsorbent and a lower proportion of sand grains. On the contrary it is poor in clay fraction. The mineral structure is calcareous with quartz. The low levels of iron oxides may be due to perytisation phenomena occurred in a material riche in organic matter and kerogen. The adsorption ratio increases linear with adsorbent mass until a maximum value of 84 % with masses higher than 0.1 g. The kinetic study shows adsorption in three steps: the first is rapid (takes 15 min), the

second step is more slow than the first and take a time in the range from 15 to 100 min. Finally the system reaches the equilibrium of sorption. In the table, the adsorbed concentration of MB increases with initial concentration of MB in aqueous phase. The kinetics of adsorption is followed by Langmuir model. This means adsorption of MB on the adsorbent S6 (1) is made as monolayer. It is possible to conclude that natural material collected in the outcrop located in the Tarfaya Boujdour zone must be deeply studied as confinement of wastes (organics, inorganics and radioactive wastes). Indeed, the first adsorption test of ^{134}Cs by this raw material shows that the sorption rate of this radioactive element can reach 100% for 0.5g of this new adsorbent.

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REFERENCES

- Abd El-Latif, M.M., Ibrahim, A.M., El-Kady, M.F., 2010. Adsorption Equilibrium, kinetics and thermodynamics of methylene blue from aqueous solutions using biopolymer oak sawdust composite. *Journal of American Science* 6, 267-283.
- Avena, M.J., Valenti, L.E., Pfaffen, V., DE Pauli, C.P., 2001. Methylene blue dimerization does not interfere in surface-area measurements of kaolinite and soils. *Clays and clay minerals* 49, 168-173.
- Baghriche, O., Djebbar, K., Sehili, T., 2008. Etude cinétique de l'adsorption d'un colorant cationique (vert de méthyle) sur du charbon actif en milieu aqueux. *Sciences & Technologie A - N°27 Volume-B*, 57-62.
- Bendjama, Z., 1982. Sorption du mercure par des bentonites algériennes activées. Thèse de Magister en Génie - Chimique, E.N.P.
- Benguella, B., Benaissa, H., 2002. Cadmium removal from aqueous solutions by chitin. *Wat. Res* 36, 2463-2474.
- Davison, I., 2005. Central Atlantic margin basins of North West Africa: Geology and hydrocarbon potential (Morocco to Guinea). *Journal of African Earth Sciences* 43, 254-274.
- Dbik, A., El Messaoudi, N., Lacherai, A., 2014. Valorisation du bois des noyaux des dattes d'une variété de palmier de la région de Tinghir (Maroc): Application à l'élimination de bleu de méthylène (Valorisation of wood dates stones of a variety of palm tree of Tinghirregion (Morocco): Application to eliminate methylene blue). *J. Mater. Environ. Sci* 5, 2510-2514.
- El Batal, Y., 2014. Le potentiel pétrolier du bassin méso-cénozoïque Tarfaya-Boujdour : Caractérisation sédimentologique, lithostratigraphique, géophysique et géochimique de la roche mère d'âge Crétacé supérieur. Thèse de Doctorat en géologie, Faculté des Sciences Ben M'sik, Maroc.
- Elkhatib, J., Ruellan, E., Elfoughali, A., Elmorabet, A., 1995. Evolution of the Southern Morocco Atlantic Margin - Tarfaya-Laayoune Basin. *Comptes Rendus De L Academie Des Sciences Serie II* 320, 117-124.
- Espitalié, J., Deroo, G., Marquis, F., 1985. La pyrolyse Rock-Eval et ses applications. *Revue Institut Français du Pétrole*. Part I 40, 563-578, Part II 40, 755-784.
- Espitalié, J., Laporte, J.L., Madec, M., Marquis, F., Leplat, P., Paulet, J., Boutefeu, F., 1977. Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. *Revue Institut Français du Pétrole* 32, 23-42.
- Gebhardt, H., Zorn, I., 2008. Cenomanianostracods of the Tarfaya upwelling region (Morocco) as palaeoenvironmental indicators. *Revue de micropaleontology* 51, 273-286.
- Ghosh, D., Bhattacharyya, K.G., 2002. Adsorption of methylene blue on kaolinite. *Applied Clay Science* 20, 295 - 300.
- Giles, C.H., MacEwan, T.H., Nakhwa, S.N., Smith, D., 1960. Studies in adsorption. Part XI. A system of classification of solution adsorption isotherms, and its use in diagnosis of adsorption mechanisms and in measurement of specific surface areas of solids. *Journal of Chemical Society, Part XI*, 3973-3993.
- Hang, P.T., Brindley, G.W., 1970. Methylene blue absorption by clay minerals. Determination of surface areas and cation exchange capacities (clay-organic studies xviii). *Clays and clay minerals* 18, 203-212.
- Ho, Y.S., McKay, G., 1999. Pseudo-second order model for sorption processes. *Proc. Biochem.*, 34, 451-465.
- Jakobsen, S., Gianolio, D., Wragg, D.S., Nilsen, M.H., Emerich, H., Bordiga, S., Lamberti, C., Olsbye, U., Tilset, M., Lillerud, K.P., 2012. Structural determination of a highly stable metal-organic framework with possible application to interim radioactive waste scavenging: Hf-UiO-66. *Physical Review B* 86, 125429.
- Kahr, G., Madsen, F.T., 1995. Determination of the cation exchange capacity and the surface area of bentonite, illite, and kaolinite by methylene blue adsorption. *Appl. Clay Sci* 9, 327-336.
- Khouya, E.H., Fakhi, S., Ichcho, S., Legrouri, K., Hannache, H., Nourredine, A., Pailler, R., Naslain, R., 2006. New adsorbents prepared by phosphoric acid activation of

- Moroccan oil shales: Influence of the experimental conditions on the properties of the adsorbents. *Annales de Chimie. Science des Matériaux* 31, 583-596.
- Khouya, E.H., Fakhi, S., Hannache, H., Abbe, J.C., Andres, Y., Naslain, R., Pailler, R., Nourredine, A., 2004. New adsorbents from oil shales: Preparation, characterization and U, Th isotope adsorption tests. *Journal of Radioanalytical and Nuclear Chemistry* 260, 159-166.
- Kolonic, S., Damste, J.S.S., Bottcher, M.E., Kuypers, M.M.M., Kuhnt, W., Beckmann, B., Scheeder, G., Wagner, T., 2002. Geochemical characterization of Cenomanian/Turonian black shales from the Tarfaya Basin (SW Morocco) - Relationships between palaeoenvironmental conditions and early sulphurization of sedimentary organic matter. *Journal of Petroleum Geology* 25, 325-350.
- Kuhnt, W., Chellai, E.H., Holbourn, A., Luderer, F., Thurow, J., Wagner, T., El Albani, A., Beckmann, B., Herbin, J.P., Kawamura, H., Kolonic, S., Nederbragt, S., Street, S., Ravillious, K., 2001. Morocco basins sedimentary record may provide correlations for Cretaceous paleoceanographic events worldwide. *EOS Transactions* 82, 361-364.
- Kuhnt, W., Holbourn, A., Gale, A., Chellai, E., Kennedy, W.J., 2009. Cenomanian sequence stratigraphy and sea-level fluctuations in the Tarfaya Basin (SW Morocco). *Geological Society of America Bulletin* 121, 1695-1710.
- Kuhnt, W., Luderer, F., Nederbragt, S., Thurow, J., Wagner, Th., 2005. Orbital-scalerecord of the Late Cenomanian-Turonian oceanic anoxic event (OAE-2) in the Tarfaya Basin (Morocco). *International Journal of Earth Science* 94, 147-159.
- Kuhnt, W., Nederbragt, A., Leine, L., 1997. Cyclicity of Cenomanian-Turonian organic-carbon-rich sediments in the Tarfaya Atlantic Coastal Basin (Morocco). *Cretaceous Research* 18, 587-601.
- Laabd, M., EL Jaouhari, A., Chafai, H., Aarab, N., Bazzaoui, M., Albourine, A., 2015. Etude cinétique et thermodynamique de l'adsorption des colorants monoazoïques sur la polyaniline (Title). *J. Mater. Environ. Sci* 6, 1049-1059.
- Liu, Y., Zheng, Y., Wang, A., 2010. Enhanced adsorption of Methylene Blue from aqueous solution by chitosan-g-poly (acrylic acid)/vermiculite hydrogel composites. *Journal of Environmental Sciences* 22, 486-493.
- Lüning, S., Kolonic, S., Belhadj, E.M., Belhadj, Z., Cota, L., Baric, G., Wagner, T., 2004. Integrated depositional model for the Cenomanian-Turonian organic-rich strata in North Africa. *Earth-Science Reviews* 64, 51-117.
- Mejjad, N., Laissaoui, A., El-Hammoumi, O., Benmansour, M., Benbrahim, S., Bounouira, H., Benkdad, A., Bouthir, F.Z., Fekri, A., Bounakhla, M., 2016. Sediment geochronology and geochemical behavior of major and rare earth elements in the Oualidia Lagoon in the western Morocco. *J Radioanal Nucl Chem* 309, 1133-1143.
- Miyah, Y., Idrissi, M., Zerrouq, F., 2015. Etude et Modélisation de la Cinétique d'Adsorption du Bleu de Méthylène sur les Adsorbants Argileux (Pyrophyllite, Calcite) [Study and Modeling of the Kinetics Methylene blue Adsorption on the Clay Adsorbents (Pyrophyllite, Calcite)]. *J. Mater. Environ. Sci* 6, 699-712.
- Mort, H.P., Adatte, T., Keller, G., Bartels, D., Follmi, K.B., Steinmann, P., Berner, Z., Chellai, E.H., 2008. Organic carbon deposition and phosphorus accumulation during Oceanic Anoxic Event 2 in Tarfaya, Morocco. *Cretaceous Research* 29, 1008-1023.
- Ouasif, H., Yousfi, S., Bouamrani, M.L., El Kouali, M., Benmokhtar, S., Talbi, M., 2013. Removal of a cationic dye from wastewater by adsorption onto natural adsorbents. *J. Mater. Environ. Sci.* 4 (1) (2013) 1-10.
- Sbaa, M., Chergui, H., Melhaoui, M., Bouali, A., 2001. Tests d'adsorption des métaux lourds (Cd, Cu, Ni, Pb, Zn) sur des substrats organiques et minéraux de la ville d'Oujda. *Revue Marocaine des Sciences Agronomiques et Vétérinaires* 21, No 2.
- Seghairi, N., 1998. Possibilités de rétention des matières organiques par adsorption sur la bentonite. Thèse de Magister en Sciences Hydrauliques, Université de Biskra, Algérie.
- Srivastava, V.C., Swamy, M.M., Malli, D., Prasadet, B., Mishra, I.M., 2006. Adsorptive removal of phenol by bagasse fly ash and activated carbon: Equilibrium, kinetics and thermodynamics. *Colloids Surfaces A: Physicochem. Eng. Asp* 272, 89-104.
- Steger, H.F., On the Mechanism of the adsorption of trace Copper by bentonite. *Clays and Clay Minerals* 21, 429-436.
- Walkley, A., 1947. A critical examination of a rapid method for determination of organic carbon in soils - effect of variations in digestion conditions and of inorganic soil constituents. *Soil Science* 63, 251-257.
- Walkley, A., Black, I.A., 1934. An examination of Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. *Soil Science* 37, 29-37.