

Study of a Moroccan Clay Siltstone: Physicochemical Characterization and Approach of Their Sorption Properties Using Methylene Blue

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Abstract Natural argillaceous siltstone was sampled from Ourika High Atlas of Marrakech, Morocco, and its application for methylene blue (MB) adsorption from aqueous solution was investigated. Physico-chemical characterization of the natural argillaceous siltstone was determined by X-ray Diffraction, fluorescence X, Scanning Electron Microscopy (SEM), laser diffraction to define particle size distribution and total organic matter content (OM) by Walkley and Black titration method. Batch adsorption studies revealed that MB adsorption on natural argillaceous siltstone decreased with increasing adsorbent amount and also increased with increase in initial solution pH with BM concentration. The adsorption process depends on initial MB concentration and attains equilibrium within 180 min. It was found that the Langmuir equation fit better than the Freundlich and Temkin equation. The adsorption kinetics of methylene blue is described by the pseudo second order reaction model. The obtained results are: (a) high levels of color removal (91%) were achieved with low contact times adsorbent/dye (less than 180 min contact); and (b) natural argillaceous siltstone can be successfully used as adsorbent of methylene blue in aqueous solutions. Natural argillaceous siltstone can be an alternative for more costly adsorbents used for dye removal in waste water treatment processes.

Keywords Adsorption, Natural argillaceous siltstone, Methylene bleu, Environment

1. Introduction

Within the global framework of environment protection and the reduction of pollutant migration, through their containment and storage as waste [1, 2], several previous works focused on the ability of natural geological materials and the role of their physico-chemical properties in trapping polluting elements and limiting their transport in the biosphere and geosphere [3-7]. Among many materials characterized and tested, it is appropriate to quote clays [8, 9], phosphates [10] and coal [11, 5, 12, 13].

The aim of the present work is to investigate for local and low coast materials that can be used as a containment matrix for national waste. After testing the black shales [4], we are

interested in argillaceous siltstones from Triassic age sandstone series located in Ourika, High Atlas of Marrakech area, Morocco.

Before initiating the study of the gross rock physicochemical retention properties, we proceeded in the first place to define its chemical compound, mineralogical characterization, morphological structure and its particle size distribution.

Subsequently, the sorption physicochemical properties of the material have been tested by methylene blue (MB), an adsorbate commonly used for this kind of study [12, 14]. Gross rock characterization was accomplished by X-rays diffraction, particle size distribution by laser diffraction and the morphological structure was by scanning electron microscope. Major elements content was measured by X-Ray fluorescence.

The study of sorption mechanisms of MB onto an argillaceous siltstone (GI2) has been undertaken by quantifying the amount of adsorbed MB as a function of

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initial pH, adsorbent mass, initial MB concentration and adsorbent/adsorbate contact time.

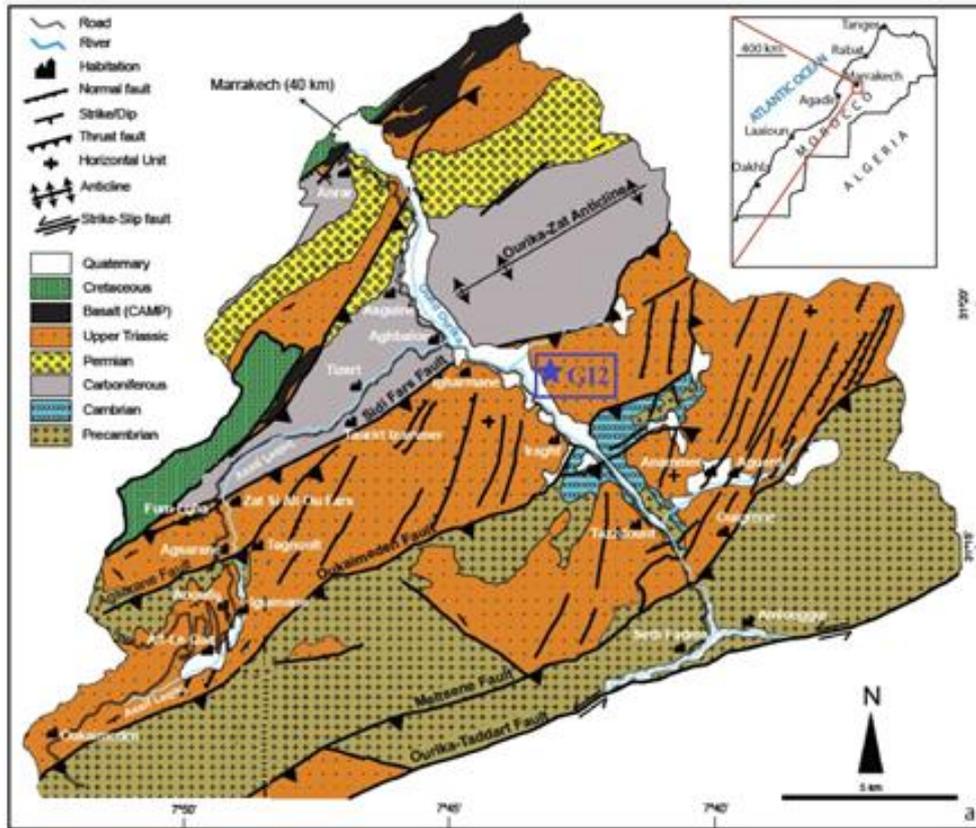


Figure 1. Studied area location in the geological map of the central High Atlas basin [20], modified); GI: Ighermane

Table 1. Lithostratigraphic column and the characteristic of the samples collected from the studied area

Lithostratigraphic column	samples	nature	Grain size	matrix phase	
	GI7	Fine Sandstone	Very Coarse	Carbonaceous	
	GI6	Fine Sandstone	Very Coarse	Carbonaceous	
	GI5	Fine Sandstone	Very Coarse	Siliceous	
	GI4	Fine Sandstone	Very Coarse	Ferruginous	
	GI3	Clay siltstone	Fine	Carbonaceous	
	GI2	Clay siltstone	Fine	Carbonaceous	
	GI1	Claystone	Very fine	Argillaceous	

2. Experimental and Analytical Methods

2.1. Nature of the Adsorbent: Natural Argillaceous Siltstone

Argillaceous siltstones are continental detrital rocks [15, 16]. Very abundant in Morocco, this kind of rock is primarily composed of quartz, feldspar, clay, mica and iron oxides [17]. Previous works on similar rocks have shown that they present an important sorption capacity of pollutant elements [18, 19]. The studied argillaceous siltstone rocks was chosen from a set of samples collected from Triassic age sandstone series located in Ourika, High Atlas of Marrakech area Morocco (Fig. 1). The analyzed powders are obtained after crushing and grinding the gross rock. In table (1) we gathered the different samples collected from the studied area and their macroscopic features determined using a polarization microscopy available in our laboratory.

2.2. Characterization Technics

2.2.1. Particle Size Distribution

Particle size distribution of the homogenized sample was studied using an equipment of laser diffraction based on wet dispersion process (Malvern Mastersizer 2000), using a dispersion unit of Hydro 2000G. Particles distribution ranges between 0.02 and 2000 μm . A small amount of sample (≈ 1 g) was introduced into dispersion unit containing demineralized water, used as a dispersant, then measured after 10s.

2.2.2. X-ray Diffraction

Mineralogical composition was identified by a diffractometer with XPERT-PRO System and a back monochromator in graphite, operating under 45 kV voltages and 40 mA intensity, with $\text{CuK}\alpha$ radiation as a source.

2.2.3. Organic Matter Content

Organic matter content was determined by the Walkley and Black titration method [21] in the Geology Department laboratory of the Faculty of Sciences Ben M'Sik.

2.2.4. Scanning Electron Microscope (SEM)

SEM analysis was carried out at the materials Platform of UATRS, CNRST of Rabat, Morocco. It was used to study and view the morphological surface of the samples grain.

2.2.5. X-ray Fluorescence

Major elements compound was determined using an Axios X-ray fluorescence spectrometer with 1 kW wave-length dispersion, at the center UATRS of CNRST Rabat, Morocco.

2.3. MB Adsorption on Natural Argillaceous Siltstone

2.3.1. Theoretical Aspects

Methylene blue adsorption on natural rocks was studied by several authors [22, 10, 8]. The kinetic adsorption

modeling was carried out according to the pseudo first order, pseudo-second order and the intra-particles diffusion Kinetics, described successively by Lagergren [23] equation (1), Ho and McKay [24] equation (2) and Weber and Morris [25] equation (3).

$$\text{Log}(q_e - q_t) = \text{Log}(q_e) - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{t}{q_e} \quad (2)$$

$$q_t = K_d t^{1/2} + C_d \quad (3)$$

Where: q_e is the amount of the adsorbate adsorbed at equilibrium ($\text{mg}\cdot\text{g}^{-1}$), t is the contact time (min), K_1 is the adsorption rate constant of the pseudo first order kinetic model (min^{-1}), K_2 is the adsorption rate constant of pseudo-second order kinetic model ($\text{g}\cdot\text{mol}^{-1}\cdot\text{min}^{-1}$) and K_d is the speed constant of the intra-particles diffusion Kinetic model.

Equilibrium adsorption isotherm data were analyzed according to the Langmuir, Freundlich and Temkin models, represented successively by equations (4), (5) and (6).

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \quad (4)$$

$$\text{Log}(q_e) = \text{Log}(K_F) + \frac{1}{n} \times \text{Log}(C_e) \quad (5)$$

$$q_e = B \text{Log}(K_T) + B \text{Log}(C_e) \quad (6)$$

Where K_L is Langmuir binding constant; C_e is the residual concentration at equilibrium in mg/L ; q_e is the adsorbate amount adsorbed at equilibrium in mg/g ; q_m is the maximum adsorbed amount in mg/g ; K_F and n are the empirical Freundlich constants; K_T and B are Temkin constants.

Langmuir model can also be expressed by a constant without dimension (r_L) defined by Weber [26] according to the following expression:

$$r_L = \frac{1}{(1+K_L C_e)} \quad (7)$$

2.3.2. Tests of MB Sorption on Argillaceous Siltstone (GI2)

The used compound in the present work is a pure methylene blue, with $319.86 \text{ g}\cdot\text{mol}^{-1}$ molar weight, supplied by Solvachim. Solutions were prepared by dissolving a required quantity of the dye in distilled water. The predefined pH value of methylene blue solutions was around 5.3. The agitation speed was fixed at 300 rounds per minute and the temperature was maintained ambient in all experiments. The effect of adsorbent mass was determined out by contacting three argillaceous siltstones mass (0.5 g; 1 g and 1.5 g) in a volume of 50 mL with $27.52 \text{ mg}\cdot\text{L}^{-1}$ methylene blue concentration.

The effect of the solution pH was investigated by contacting during 2h, 50 mL of each methylene blue solution at an initial concentration of $26.06 \text{ mg}\cdot\text{L}^{-1}$ with 0.5 g of argillaceous siltstone. Solutions pH were adjusted in a range of 3.07 to 12 using HCl (1%) and NaOH (0.1 mol/L) dilute solutions.

The solution concentration effect was performed by contacting 50 mL of each solution at various initial MB

concentrations (16.09; 27.52; 36.37; 47.31; 59.17 and 82.8 mg.L⁻¹) with 0,5g of natural argillaceous siltstone (GI2), the initial solutions pH was maintained (5.3).

The residual MB concentration in the supernatant solutions was analyzed using an equipment of UV spectrophotometer (UV-1600PC), by monitoring absorption changes at a maximum absorption wavelength (665 nm).

The data obtained was used to calculate methylene blue adsorbed amount at equilibrium, using the following expression [6, 27]:

$$q_t = \frac{V(C_0 - C_e)}{m} \quad (8)$$

Where **V** is the solution volume in liter, **C₀** is the initial concentration in mg.L⁻¹, **C_e** is the methylene blue concentration at equilibrium in mg.L⁻¹ and **m** is the dry mass of the argillaceous siltstone expressed in g.

The adsorption Isotherm for the removal of methylene blue from aqueous solution using argillaceous siltstone sample (GI2) was deduced from initial MB concentration effect.

3. Results and Discussion

3.1. Characterization of the Argillaceous Siltstone (GI2)

3.1.1. Particle Size Distribution

Particle size distribution of the adsorbent (table. 2) shows that the gross rock (GI2) contained 71% silt, 26% clay and 3% sand. This result gives our sample an argillaceous silt character.

Several authors showed that cations adsorption increase with a decrease in the adsorbent particles size [28, 17]. Saglara Mandzhieva [17] indicates that argillaceous siltstone contain secondary minerals (clays, alumina and iron oxides and organic matter), attributing to this rock an important adsorption capacity.

Table 2. Particles size distribution in the studied sample according to the United States Department of Agriculture classification (USDA)

Grain size	Clay	Silt	Sand
	(d < 2 μm)	2 μm < d < 50 μm	50 μm < d < 2 mm
Particle size in %	15,94	75,33	8,73

3.1.2. X-ray Diffraction

X-ray spectrum analysis of the adsorbent illustrated in figure (2), revealed the presence of an intense peak identified as quartz, with other peaks less intense of hematite, dolomite and muscovite, which implies that our adsorbent is heterogeneous. Clay was not detected by the device given its lower content. The organic matter content was 1.86%.

González [29] indicated that the surface of quartz (SiO₂) is in general charged negatively. The muscovite due to its chemical formula K⁺Al₂(Si₃Al)O₁₀(OH)₂, presents negative layers balanced by K⁺ ions [30]. As well, she has inorganic cations at surface which remove by water contact, attributing

to her a strong adsorption capacity of cations [31]. Hematite has a large specific surface area and a very important adsorption capacity [32]. Concerning the dolomite, Steel [33] indicates that it adsorbs effectively at acidic pH.

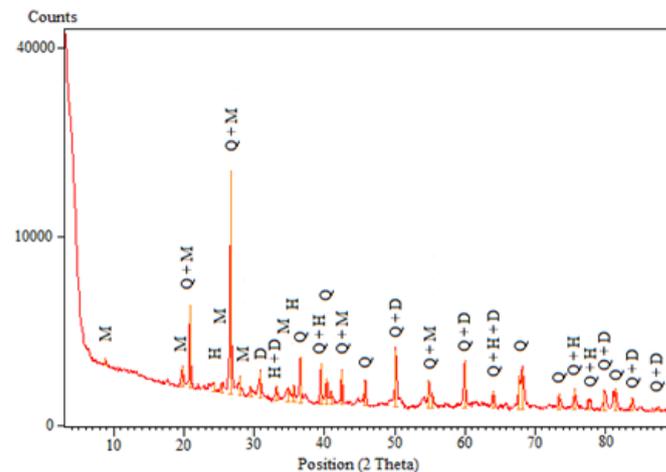


Figure 2. Diffractogramme of studied argillaceous siltstone, Q: Quartz, M: Muscovite, D: Dolomite, H: Hematite

3.1.3. Scanning Electron Microscope

Scanning electron microscope analysis of the studied sample (Figure. 3) shows only the quartz grains with microcavities and micropores on the surface. Clay and dolomite particles are smaller and were not well visualized by the device.

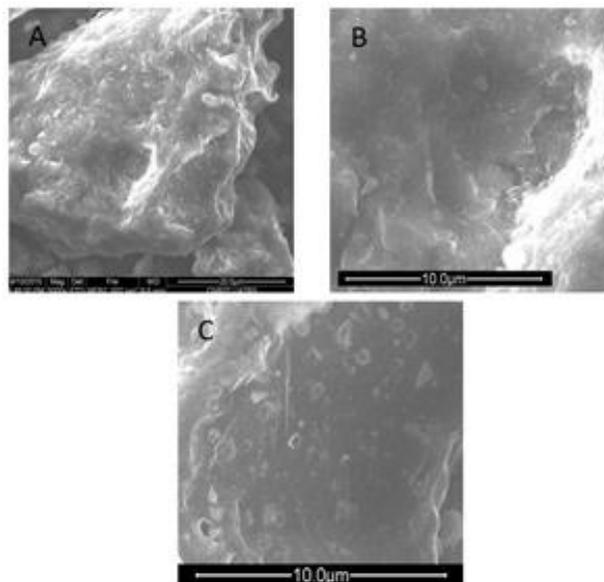


Figure 3. SEM micrographs of argillaceous siltstone. A: angular quartz grain, B: cavity on quartz grain, C: micropores on quartz grains

3.1.4. Major Elements Composition

The major compounds of our sample (table. 3) evolve in descending order, according to the following sequence: SiO₂ > Al₂O₃ > Fe₂O₃ > MgO > CaO > K₂O > Na₂O > MnO₂ > TiO₂ > P₂O₅. Silica high content was assigned to the dilution of the sample by detrital quartz.

Table 3. Major elements compound of argillaceous siltstone (GI2)

Compound	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	K ₂ O
Concentration in %	69,2	13,8	1,75	3,41	1,53
Compound	MgO	TiO ₂	Na ₂ O	MnO ₂	P ₂ O ₅
Concentration in %	2,38	0,574	1,05	0,591	0,0848

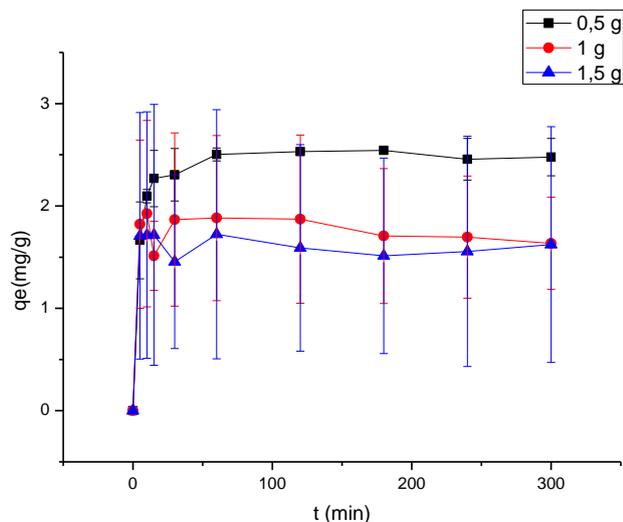
Normalizing major elements content of studied argillaceous siltstone to the upper continental crust values of Haskin et al., (1968) shows a depletion in Na₂O and K₂O, indicating the presence of sodium and potassium plagioclase in low quantity [34]. K₂O/Al₂O₃ ratio (= 0.11) suggests the presence of clay minerals [35]. As well, depletion in CaO content may be due to its high mobility. The enrichment in MnO₂ may be attributed to its fixation by clay and authigenic minerals [36].

3.2. Adsorption Study

3.2.1. Adsorbent Mass Effect

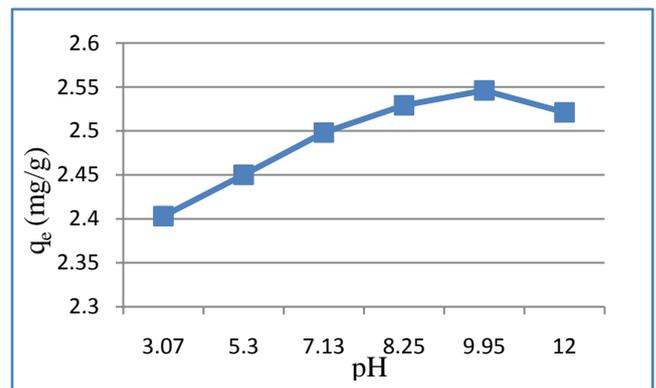
Adsorbent amount is an important parameter which determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The experiments were repeated three times to eliminate uncertainties, and only the mean values were reported in figure (4). As seen in this figure, the adsorbed amounts of MB increase as the adsorbent mass decrease.

This behavior can be explained by the fact that as long as the amount of adsorbent added to the dye solution is low, the dye cations can easily access the adsorbent sites. The addition of adsorbent increase the number available sites, but the dye cations have more difficulty in approaching these sites because of the congestion [37]. Moreover, a large amount of adsorbent creates particles agglomerations, resulting in a reduction of the total adsorption area and consequently a decrease in the amount of adsorbate per unit mass of adsorbent [38].

**Figure 4.** Plot of adsorbent mass variation effect on MB adsorbed amount

3.2.2. Effect of Initial Solution pH

Figure (5) shows the effect of the initial solution pH on MB adsorption by argillaceous siltstone (GI2). From this figure, the adsorbed amount (q_e) is maximum at pH 9.95. As well, the increase of the (q_e) as a function of solution pH is in agreement with interior works [39, 40]. This can be explained by the fact that at low pH values, the adsorbent surface would be surrounded by H⁺ ions, which decrease the interaction of methylene blue ions with the adsorbent active sites, however, in a high pH, H⁺ ions concentration decreases which generates a good interaction between MB ions and the adsorbent surface sites [41]. The pH of the solutions of the other experiments was not adjusted (pH=5,3).

**Figure 5.** Plot of initial solution pH Variation effect on MB adsorbed amount (q_e)

3.2.3. Contact Time and the Initial Concentration Effect

The equilibrium adsorption capacity of the adsorbent for methylene blue increased with increasing initial dye concentration, as it is shown in figure (6). This figure shows that the equilibrium adsorption capacity increases from 2.6 to 5.1 mg.g⁻¹ with an increase in initial MB concentration from 27.52 to 82.8 mg.L⁻¹. These results may be due to the fact that increasing MB concentration induces an elevation of the driving force of concentration gradient, leading to an increase in MB molecules dissemination through the adsorbent surface [42, 43].

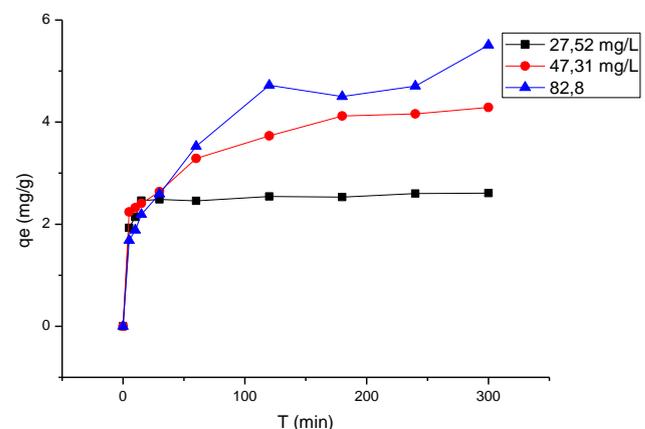
**Figure 6.** Plot of adsorbed MB amount vs. contact time

Table 4. Kinetic parameters of methylene blue adsorption on argillaceous siltstone (GI2)

Models	Parameters	$C_0(\text{BM})= 27,52$ (mg/L)	$C_0(\text{BM})= 47,31$ (mg/L)	$C_0(\text{BM})= 82,8$ (mg/L)
Pseudo 1 st order	R^2	0,124	0,535	0,753
	K_1 (min ⁻¹)	0,0021	0,0033	0,0058
	$q_e.\text{cal}$ (mg/g)	0,548	1,343	3,4739
	$q_e.\text{exp}$ (mg/g)	2,607	4,288	5,510
Pseudo 2 nd order	R^2	0,999	0,996	0,982
	K_2 (g/mg.min)	0,1688	0,0202	0,0091
	$q_e.\text{cal}$ (mg/g)	2,829	4,365	5,420
	$q_e.\text{exp}$ (mg/g)	2,607	4,288	5,510
Intra-particle diffusion	R^2	0,223	0,632	0,771
	k_d (mg/g min ^{1/2})	0,0069	0,0190	0,0281
	C_d	1,846	2,006	1,784

3.2.4. MB Adsorption Kinetic onto Argillaceous Siltstone

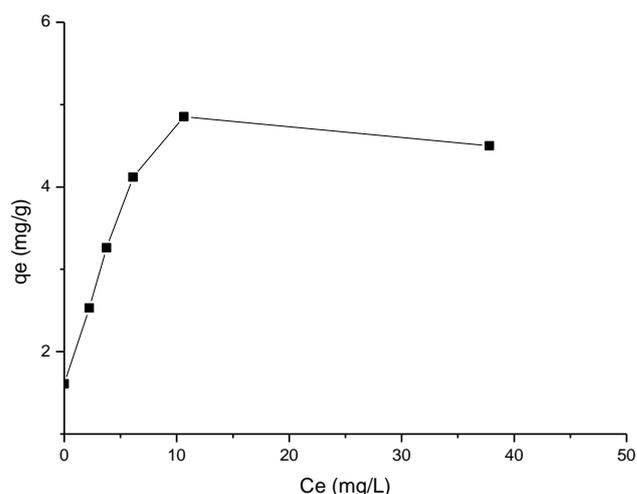
The behavior of the MB adsorption process was analyzed by using the pseudo-first order, pseudo-second-order, and intraparticle diffusion models. The constants values, the adsorbed amount values and the correlation coefficients R^2 values were calculated from the slopes of the respective linear plots of each model and are summarized in table (4). The best-fit model was selected based on the linear regression correlation coefficient, R^2 , values.

Analyzing the obtained results reveals that Pseudo-second order model reflects perfectly the adsorption kinetics of MB by GI2. The correlation coefficients for the second-order kinetics model are greater than 0.99, indicating the applicability of this kinetics equation and the second order nature of the adsorption process of methylene blue onto natural argillaceous siltstone (GI2). As well, the adsorbed amount values calculated for each initial MB concentration were very close to the experimentally obtained values, suggesting that the mechanism that governed sorption phenomenon of MB by argillaceous Siltstone (GI2) is chemisorption [24]. It is obvious that the adsorption of MB on argillaceous siltstone (GI2) follows the Pseudo-second order model, due to the important surface negative charge of the adsorbent minerals [44].

3.2.5. Adsorption Isotherms

According to the work of Giles [45], the graphical representation of the adsorbed amount versus residual concentration at equilibrium, indicates the adsorption isotherm type. However, figure (7) indicates that the adequate isotherm is that of type *L*, suggesting that the adsorption of MB by argillaceous siltstone (GI2) process occurs in a monolayer.

Adsorption isotherms were obtained from the linear representation of equations (4), (5) and (6) by using experimental adsorption results in these equations. The calculated parameters of each model are grouped in table (5).

**Figure 7.** Isotherm of MB adsorption onto argillaceous siltstone after Giles (1960)**Table 5.** Parameter values of adsorption isotherm of MB on argillaceous siltstone (GI2)

Isotherms	Parameters	Values
Langmuir	R^2	0,9959
	K_L (L/mg)	0,7701
	q_m (mg/g)	4,617
	r_L	0,033-1
Freundlich	R^2	0,7768
	K_f ((mg/g) (L/mg) ^{1/n})	1,3536
	n	3,4235
Temkin	R^2	0,8005
	K_T	2,7013
	B	2,0311

As seen in Table (5), the best fit of experimental data was obtained with the Langmuir model with R^2 value higher than 0.99 and its maximum adsorbed amount very close to that determined experimentally. This result showed that MB is homogeneously adsorbed by means of ionic adsorption

assured by the negatively charged surface of the natural argillaceous siltstone (GI2) [46].

The coefficient values r_L expressed by equation (7) range between 0.033 and 1, indicating that GI2 can be used for removal of methylene blue from aqueous solutions.

4. Conclusions

The main aim of this work was to test a Moroccan argillaceous siltstone performance in the retention of organic and inorganic substances. The study of this rock and its application to eliminate methylene blue from aqueous solution allowed us to conclude that:

- ✓ The adsorbent is rich in silt with a non-negligible clay amount and a small amount of sand.
- ✓ The mineralogical compound revealed the presence of a large amount of quartz and a very low amount of hematite, dolomite and muscovite, indicating the heterogeneity of this material.
- ✓ Morphological analysis of the sample shows the presence of micro-cavities and micro-pores on the quartz surface.
- ✓ The low oxide levels such Fe_2O_3 , MgO , CaO , Na_2O , K_2O and MnO_2 is due to the high content in silica, which is assigned to the dilution of our sample by quartz.
- ✓ The adsorption rate increases as much as the adsorbent mass decreases to reach a maximum percentage removal of 94,73% for 0.5g adsorbent mass;
- ✓ The adsorbed MB amount increases with increase of solution pH;
- ✓ The kinetic study shows that equilibrium time depends on initial MB concentration. When the initial MB concentration increases the methylene blue adsorbed amount increases, while the percentage removal decreases.
- ✓ The adsorption kinetic is described by the Pseudo-second order model, suggesting that the MB adsorption on argillaceous siltstone (GI2) is done by chemisorption process;
- ✓ The adsorption isotherm is well described by Langmuir model which indicates that MB adsorption on argillaceous siltstone (GI2) is done in monolayer and the homogeneous distribution of active sites onto the surface of the studied argillaceous siltstone.

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REFERENCES

- [1] Perronnet, M. Réactivité des matériaux argileux dans un contexte de corrosion métallique. (Institut National Polytechnique de Lorraine, 2004).
- [2] Windt, L. D. Modélisation de la durabilité des géomatériaux et du transfert de polluants en valorisation ou stockage de déchets industriels et radioactifs. (Université Pierre et Marie Curie - Paris VI, 2011).
- [3] Lee, C.-P. *et al.* Sorption of cesium on granite under aerobic and anaerobic conditions. *Radiochim. Acta* 94, 679–682 (2009).
- [4] Khouya, E. H. *et al.* New adsorbents prepared by phosphoric acid activation of Moroccan oil shales: Influence of the experimental conditions on the properties of the adsorbents. *Ann. Chim. Sci. Mater. Paris* 31, 583–596 (2006).
- [5] Kavitha, D. & Namasivayam, C. Experimental and kinetic studies on methylene blue adsorption by coir pith carbon. *Bioresour. Technol.* 98, 14–21 (2007).
- [6] Pehlivan, E., Özkan, A. M., Dinç, S. & Parlayici, Ş. Adsorption of Cu^{2+} and Pb^{2+} ion on dolomite powder. *J. Hazard. Mater.* 167, 1044–1049 (2009).
- [7] Ruprecht, C., Pini, R., Falta, R., Benson, S. & Murdoch, L. Hysteretic trapping and relative permeability of CO_2 in sandstone at reservoir conditions. *Int. J. Greenh. Gas Control* 27, 15–27 (2014).
- [8] Auta, M. & Hameed, B. H. Chitosan–clay composite as highly effective and low-cost adsorbent for batch and fixed-bed adsorption of methylene blue. *Chem. Eng. J.* 237, 352–361 (2014).
- [9] Ghosh, D. & Bhattacharyya, K. G. Adsorption of methylene blue on kaolinite. *Appl. Clay Sci.* 20, 295–300 (2002).
- [10] Barka, N., Assabbane, A., Nounah, A., Laanab, L. & Ichou, Y. A. Removal of textile dyes from aqueous solutions by natural phosphate as a new adsorbent. *Desalination* 235, 264–275 (2009).
- [11] El Qada, E. N., Allen, S. J. & Walker, G. M. Adsorption of Methylene Blue onto activated carbon produced from steam activated bituminous coal: A study of equilibrium adsorption isotherm. *Chem. Eng. J.* 124, 103–110 (2006).
- [12] Kannan, N. & Sundaram, M. M. Kinetics and mechanism of removal of methylene blue by adsorption on various carbons — a comparative study. *Dyes Pigments* 51, 25–40 (2001).
- [13] Khelifi, A., Temdrara, L. & Addoun, A. Ebscohost | 57759688 | Effet De La Texture Poreuse Et De La Structure Chimique Sur L'Adsorption Du Bleu De Methylene Par Des Charbons Actifs Oxydes. (2009). (Accessed: 12th June 2017).
- [14] Bulut, Y. & Aydın, H. A kinetics and thermodynamics study of methylene blue adsorption on wheat shells. *Desalination* 194, 259–267 (2006).

- [15] AitMalek, O. *et al.* Geochemistry of Triassic Sandstones (High Atlas of Marrakech, Morocco): Implications for Provenance, Weathering, and Tectonic Setting. *International Journal of Advanced Research* 464–475 (2016).
- [16] Cullers, R. L. The geochemistry of shales, siltstones and sandstones of Pennsylvanian–Permian age, Colorado, USA: implications for provenance and metamorphic studies. *Lithos* 51, 181–203 (2000).
- [17] Mandzhieva, S. *et al.* The role of particle-size soil fractions in the adsorption of heavy metals. in 16, 17007 (2014).
- [18] Muherei, M. A., Junin, R. & Bin Merdihah, A. B. Adsorption of sodium dodecyl sulfate, Triton X100 and their mixtures to shale and sandstone: A comparative study. *J. Pet. Sci. Eng.* 67, 149–154 (2009).
- [19] Mell, P., Scarfone, K. & Romanosky, S. Common Vulnerability Scoring System. *IEEE Secur. Priv.* 4, 85–89 (2006).
- [20] Taj-Eddine, K. & Pignone, R. L'Ourika: Haut Atlas-Haouz de Marrakech, Maroc. *Un Patrim. Geol. Biol. Cult. Except. Florence SELCA Scale* 1, 1 (2005).
- [21] Walkley, A. & Black, I. A. An Examination of the Degtjareff Method for Determining Soil...: Soil Science. *LWW* (1934).
- [22] Doğan, M., Alkan, M. & Onganer, Y. Adsorption of Methylene Blue from Aqueous Solution onto Perlite. *Water. Air. Soil Pollut.* 120, 229–248 (2000).
- [23] Lagergren, S. About the Theory of So-called Adsorption of Soluble Substances. 24, 1–39 (1898).
- [24] Ho, Y. S. & McKay, G. Pseudo-second order model for sorption processes. *Process Biochem.* 34, 451–465 (1999).
- [25] Weber, W. & Morris, J. Kinetics of adsorption on carbon from solution. *J. Sanit. Eng. Div.* (1963).
- [26] Weber, T. W. & Chakravorti, R. K. Pore and solid diffusion models for fixed-bed adsorbers. *AIChE J.* 20, 228–238 (1974).
- [27] Mamindy-Pajany, Y., Hurel, C., Marmier, N. & Roméo, M. Arsenic adsorption onto hematite and goethite. *Comptes Rendus Chim.* 12, 876–881 (2009).
- [28] Minkina, T. M., Pinskii, D. L., Mandzhieva, S. S., Antonenko, E. M. & Sushkova, S. N. Effect of the particle-size distribution on the adsorption of copper, lead, and zinc by Chernozemic soils of Rostov oblast. *Eurasian Soil Sci.* 44, 1193 (2011).
- [29] GONZÁLEZ, G. & MIDDEA, A. Asphaltenes Adsorption by Quartz and Feldspar. *J. Dispers. Sci. Technol.* 8, 525–548 (1987).
- [30] Theng, B. K. G. *Formation and Properties of Clay-Polymer Complexes.* (Elsevier, 1979).
- [31] Wang, J., Kalinichev, A. G., Kirkpatrick, R. J. & Cygan, R. T. Structure, Energetics, and Dynamics of Water Adsorbed on the Muscovite (001) Surface: A Molecular Dynamics Simulation. *J. Phys. Chem. B* 109, 15893–15905 (2005).
- [32] Shuibo, X. *et al.* Removal of uranium (VI) from aqueous solution by adsorption of hematite. *J. Environ. Radioact.* 100, 162–166 (2009).
- [33] Steel, E. W. & McGhee, T. J. *Water Supply and Sewerage.* (McGraw-Hill, 1985).
- [34] Armstrong-Altrin, J. S. Provenance of sandstones using geochemistry. *J. Sediment. Res.* 74, (2004).
- [35] Cox, R., Lowe, D. R. & Cullers, R. L. The influence of sediment recycling and basement composition on evolution of mudrock chemistry in the southwestern United States. *Geochim. Cosmochim. Acta* 59, 2919–2940 (1995).
- [36] Wyborn, L. A. I. & Chappell, B. W. Chemistry of the Ordovician and Silurian greywackes of the Snowy Mountains, southeastern Australia: An example of chemical evolution of sediments with time. *Chem. Geol.* 39, 81–92 (1983).
- [37] Sakr, F., A. Sennaoui, A., Elouardi, M., Tamimi, M. & Assabane, A. Étude de l'adsorption du Bleu de Méthylène sur un biomatériau à base de Cactus (Adsorption study of Methylene Blue on biomaterial using cactus). *J. Mater. Environ. Sci* 397–406 (2015).
- [38] Karim, A., Mounir, B., Hachkar, M., Bakasse, M. & Yaacoubi, A. Élimination du colorant basique «Bleu de Méthylène» en solution aqueuse par l'argile de Safi. *Rev. Sci. Eau J. Water Sci.* 23, 375–388 (2010).
- [39] Gupta, V. K., Suhas, Ali, I. & Saini, V. K. Removal of Rhodamine B, Fast Green, and Methylene Blue from Wastewater Using Red Mud, an Aluminum Industry Waste. *Ind. Eng. Chem. Res.* 43, 1740–1747 (2004).
- [40] Janoš, P., Buchtová, H. & Rýznarová, M. Sorption of dyes from aqueous solutions onto fly ash. *Water Res.* 37, 4938–4944 (2003).
- [41] Amela, K., Hassen, M. A. & Kerroum, D. Isotherm and Kinetics Study of Biosorption of Cationic Dye onto Banana Peel. *Energy Procedia* 19, 286–295 (2012).
- [42] Deniz, F. & Saygideger, S. D. Equilibrium, kinetic and thermodynamic studies of Acid Orange 52 dye biosorption by *Paulownia tomentosa* Steud. leaf powder as a low-cost natural biosorbent. *Bioresour. Technol.* 101, 5137–5143 (2010).
- [43] Özer, A., Akkaya, G. & Turabik, M. Biosorption of Acid Red 274 (AR 274) on *Enteromorpha prolifera* in a batch system. *J. Hazard. Mater.* 126, 119–127 (2005).
- [44] Ho, Y. S. & Chiang, C. C. Sorption Studies of Acid Dye by Mixed Sorbents. *Adsorption* 7, 139–147 (2001).
- [45] Giles, C. H., MacEwan, T. H., Nakhwa, S. N. & Smith, D. 786. 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. *J. Chem. Soc. Resumed* 3973–3993 (1960). doi:10.1039/JR9600003973.
- [46] Wang, S., Boyjoo, Y. & Choueib, A. A comparative study of dye removal using fly ash treated by different methods. *Chemosphere* 60, 1401–1407 (2005).