

Adsorption of cationic dye onto Moroccan natural rock

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Abstract: This paper evaluates the ability of a natural rock found in Morocco to remove the pollutant properties of methylene blue (MB) dye. In this regard, the experiments were conceived to test the hypothesis that the rock native of the country's region of Khenifra can be used as a new abundant adsorbent to remove cationic dyes from water through the adsorption technique in order to avoid extra cost and contribute to the valorization of this material. For this, several factors such as pH of the solution, granulometry, mass of adsorbent, initial dye concentration and stirring rate were tested. The adsorption kinetics process was tested through three models, namely, the pseudo-first-order model, pseudo-second-order model and the intraparticle diffusion model, to predict which type of adsorption is best suited in the removal of dye pollution.

The batch study proves that only the granulometry ($G \leq 63\mu\text{m} = 91\%$, $G \leq 80\mu\text{m} = 88.4\%$ and $G \leq 100\mu\text{m} = 70.7\%$) and the adsorbent mass (the more the mass of the adsorbent increases the more the elimination is achieved) can influence the elimination rate of our rock. Meanwhile, the data of the adsorption kinetics test show that the experimental adsorption could be described by the mechanism of the pseudo-second-order model (correlation coefficients near the unit ' $R^2 = 0.99$ '), confirming chemical sorption as a rate-limiting step of the intraparticle diffusion mechanism.

According to the results of this study, the rock collected from the area of Khenifra can be used as a new and efficient adsorbent in the field of wastewater treatment.

Keywords: Rock; methylene blue; adsorption; kinetics; chemisorption.

1. Introduction

Industries in Morocco consume vast quantities of water in their manufacturing processes, which generates tons of polluted water ¹. Once released, the polluted water causes alterations in the aquatic environment because of its stabilities, toxicities and low biodegradability ¹⁻⁵. These pollutants pose a severe threat to the environment, which requires prior treatment to reduce the polluting load before spilling it into the environment ⁶⁻⁷.

A wide variety of physical, chemical and biological techniques have been developed and tested in the treatment of dye-loaded effluents ⁸⁻¹⁰. The adsorption technology is one of the most effective methods for dye removal because of its low cost, high efficiency, simplicity, and insensitivity to toxic substances ¹¹⁻¹⁵.

The adsorbent that is widely used in the removal of dyes from aqueous solutions is activated carbon ¹⁶⁻²⁰. However, it manifests several disadvantages such as high cost, flammability and difficulty to regenerate,

which urges us to look for another efficient and less expensive adsorbent ²¹⁻²³.

Since Morocco is abundant with different varieties of rocks, especially in the Atlas Mountains, we sought to find an adsorption support (adsorbent) alternative to the activated carbon in rocks. In this context, the use of natural resources found in rocks as an adsorbent is particularly advantageous because of its abundance and accessibility in the environment ²⁴.

This work aims to evaluate the retention capacity of Methylene Blue by a Moroccan natural rock native of Khenifra region in northern central Morocco, in order to contribute in the understanding of adsorption processes and valorize rocks in the field of wastewater treatment.

For this purpose, we carried out two studies: a parametric study of the adsorption phenomenon by examining the effect of several factors on the bleaching power of the rock, and another study of the adsorption kinetics using several models.

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DOI:

Received June 3, 2019
Accepted July 17, 2019
Published August 13, 2019

2. Experimental

2.1. Batch adsorption

2.1.1. Adsorption support

The adsorbent used in this work is a “natural rock” collected from the mountain range of the Middle Atlas, in Khenifra region (Morocco). The chosen rock was crushed and sieved to obtain three types of particle sizes in the range of 63 and 100 μ m. The samples were stored in closed bottles to be used in the

adsorption studies without any chemical or physical modification in order to avoid extra costs.

2.1.2. Adsorbate

The dye chosen as a representative of the significant textile pollutants in this study is “Methylene Blue” (MB), belonging to the family of the cationic dyes; in particular, the powerful dye with many chemical properties^{25, 26}. Its main features are represented in Table 1, and its structural formula is shown in Fig. 1.

Table 1. Main features of the MB.

Synonym	Empirical Formula	Molar mass (g/mol)	Wavelength λ_{\max} (nm)
Methylene Bleu	C ₁₆ H ₁₈ ClN ₃ S	319,852	664

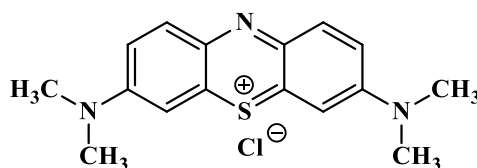


Figure 1. Chemical structure of the MB.

2.1.3. Experimental protocol

Batch adsorption experiments were conducted in 250 ml beakers with different masses of the natural rock (0.1-1.0 g) and 100 mL of dye solution indifferent initial concentrations (10–25 mg/L of MB).

The different concentrations used in this study were prepared from a dilution of the methylene blue stock solution; this latter was prepared by dissolving 100 mg of the methylene blue powder in one liter of distilled water.

The dye concentration was determined calorimetrically by measuring at maximum absorbance of the dye (λ_{\max} = 664 nm) using a Shimadzu UV/Visible mini-1240 UV spectrophotometer.

A calibration curve was plotted between absorbance and concentration of the dye to obtain the absorbance-concentration profile of the dye-based on Beer-Lambert's law.

For high concentration, dye samples were diluted before absorbance measurements.

The adsorbed amount of Methylene Blue was calculated using the following formula²⁷:

$$Q_{\text{ads}} = \frac{(C_i - C_t) \times V}{M}$$

Where:

Q_{ads} : quantity adsorbed at time t (mg/g).

V : volume of the solution (ml).

C_i and C_t : are respectively the initial concentration and the concentration at time t of the dye (mg/l).

M : mass of the adsorbent (g).

The rate of decrease $R\%$ of the MB was calculated using the following equation:

$$\%R = \frac{C_i - C_e}{C_i} \times 100$$

Knowing that:

C_i and C_e are the initial and equilibrium dye concentrations in solution (mg/L), respectively.

2.2. Desorption studies

The main objective of this test is an attempt to answer one of the questions asked by the kinetic studies: is the mechanism of the adsorption chemical or physical sorption?

The desorption potential of the natural rock was evaluated using 1 g of adsorbent in contact with 100 mL, 10 mg/L dye solution. The quantity of adsorbed dye was noted, and the adsorbent was filtered and dried in the oven for 12 hours at 105 °C. Afterwards, the adsorbent was soaked into 100 mL of distilled water, agitated for 2 hours, and left in rest for 3 months.

In this research, we will initially study the effect of the main parameters influencing the adsorption capacity such as the pH of the solution, the granulometry, the mass of the adsorbent, the initial concentration of the adsorbate, and the stirring rate. Second, we will determine which kinetic model represents the mechanism of MB adsorption on natural rock. Finally, and as a complementary component, we will answer the kinetic questions related to the mechanism of adsorption.

3. Results and Discussion

3.1. The study of the parameters influencing the adsorption

3.1.1. Effect of the pH

The initial pH of the solution is an important parameter that must be taken into consideration during adsorption studies. It can influence the structure of the adsorbent, the adsorbate and also the adsorption mechanism²⁸.

The effect of this factor on the adsorption capacity was analyzed over a range of pH 2-12, including the normal pH of the colored solution.

The experiments were carried out by adding 0.5g of the raw rock to 100 ml of the dye solution ($C_i = 10$ mg/L) at room temperature $T=25\pm 1^\circ$.

The pH adjustments to the desired values were made by adding HCL (0.1N) or NaOH (0.1N).

The results shown in Figure 2 indicate that the removal rate of MB dye is generally very little influenced by pH variations, which makes the effect of this parameter negligible. These results can be explained by the resistance of the adsorbent's surface charge to pH changes²⁹. This is due to the basic nature of the rock, which can balance the pH and make it partially neutral.

The results obtained in this experiment allowed us to work with the normal pH of the solution in the following tests.

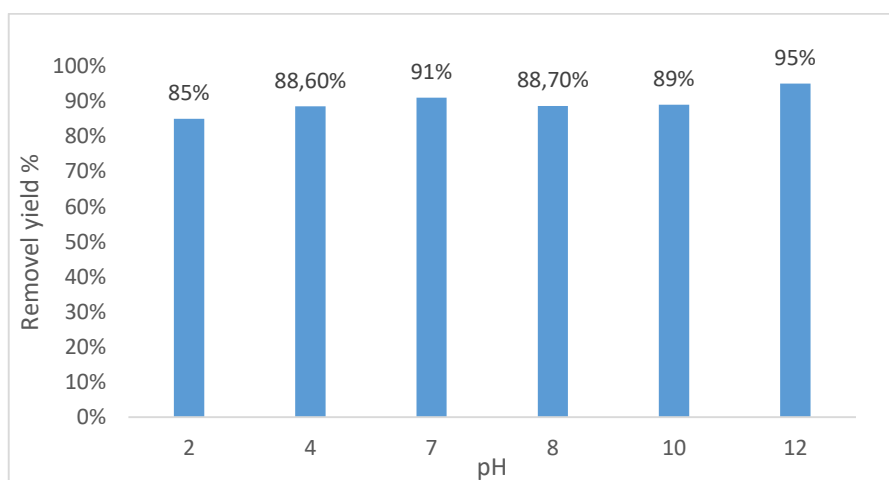


Figure 2. pH effect on dye adsorption

3.1.2. Effect of particle size

In order to study the effect of granulometry on dye adsorption, we used three types of granulates ($G \leq 63\mu\text{m}$, $G \leq 80\mu\text{m}$, and $G \leq 100\mu\text{m}$), while the

mass of the adsorbent was fixed at 0.5g and the initial concentration of the MB at 10 mg/L.

Figure 3 shows the influence of the particle size of the adsorbent on the adsorption of methylene blue.

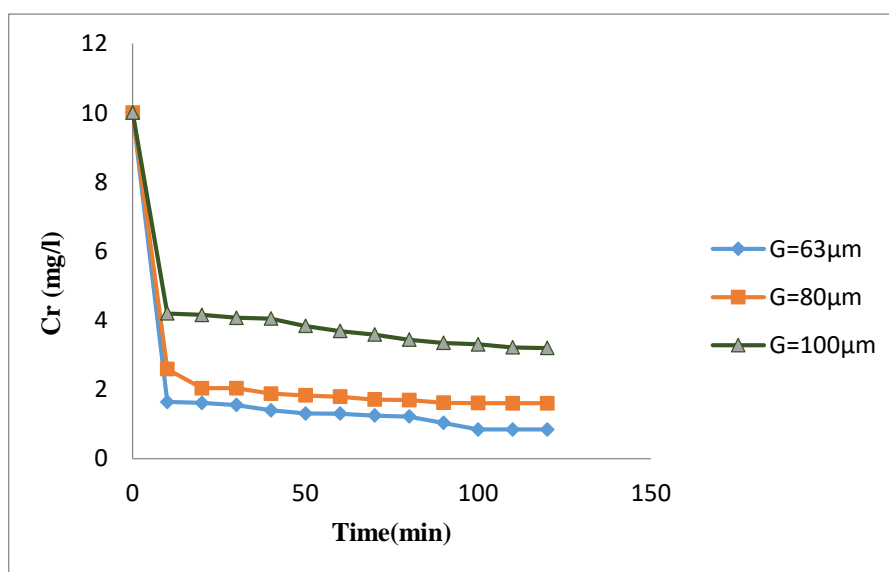


Figure 3. Effect of particle size on dye adsorption

The results illustrated in this figure show that the adsorption equilibrium of methylene blue is quickly achieved in the three types of granulates, but the finest granulometry ($\leq 63\mu\text{m}$) has the higher yield (91.6%) compared to other granulates ($\leq 80\mu\text{m}=88.4\%$ and $\leq 100\mu\text{m}=70.7\%$). Consequently, the external surface of the rock determines the retention rate of the dye's molecule. In other words, the tests carried out show that particle size plays a vital role in adsorption kinetics, which allows us to conclude that the more exceptional particle size of the rock, the higher the adsorption capacity becomes. Therefore, we will carry on our research using the finest size of granulometry.

3.1.3. Effect of the mass of adsorbent

To estimate the optimal quantity of rock added to the colored solution, we will investigate the effect of mass on the adsorption of MB. The experiments were carried out by adding masses between 0.1 and 1g to a volume of 100 ml of MB at initial concentration $C_i = 10 \text{ mg/L}$. The supernatant produced was analyzed so we can calculate the residual concentration of the dye over time, and Figure 4 illustrates the results obtained.

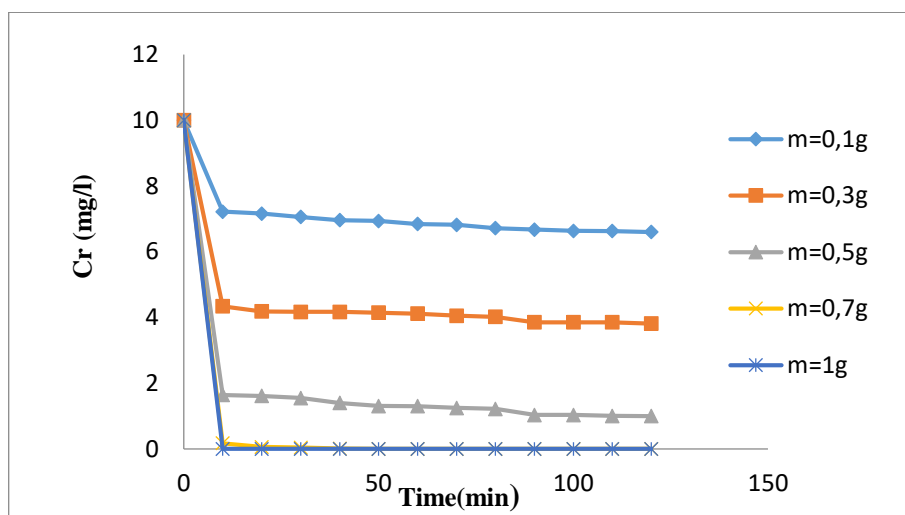


Figure 4. Effect of the mass adsorbent on removal dye

Figure 4 shows that the quantity of the adsorbed dye increases with the addition of the adsorbent. This result was expected because of the available sites of adsorption given by the increased mass from 0.1g to

1.0g, to take up more dye molecules, and makes the phenomenon of discoloration easier. It can be clearly seen that the removal of MB dye increase with increasing the amount of rock.

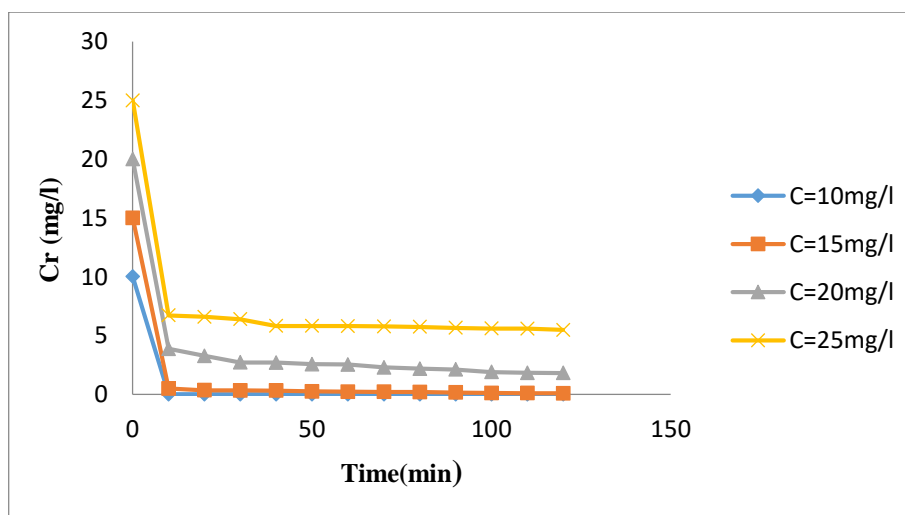


Figure 5. Effect of initial concentration on the adsorption of MB

3.1.4. Effect of the initial dye concentration:

In order to study the initial concentration effect on the rock's retention capacity, 1g of the rock was added to 100 ml of MB solutions with an initial concentration range of 10-25 mg/l while fixing the previous

parameters. In Figure 5, it is clearly shown that the adsorption of MB dye was fast at all concentrations, due to the available sites, and as the concentration increases, the amount of the adsorbed dye increases as well. In fact, by increasing concentrations, the ratio

between the first number of dye molecules and the available surface area becomes high, which explain the total occupancy of the adsorption sites and the persistence of few free dye molecules in the solution. Based on these results, it appears that the equilibrium time is independent of initial concentration and the amount adsorbed at equilibrium increases with increasing concentration.

3.1.15. Effect of stirring speed

Agitation is an essential parameter in the adsorption phenomenon; it influences the distribution of the solute in the solution and the formation rate of the

external boundary film³⁰. The effect of agitation speed on the removal of MB dye by the rock was studied at different agitation speeds (400, 800, 1200 rpm) while fixing the previous parameters (pH = normal pH of the solution, granulometry = $\leq 63\mu\text{m}$, mass of the adsorbent = 1g, initial concentration of the dye = 15 mg/l.)

The data in Figure 6 show a significant removal percentage. However, this removal is independent of the stirring rate used, which means that the stirring rate does not affect the adsorption capacity of the natural rock.

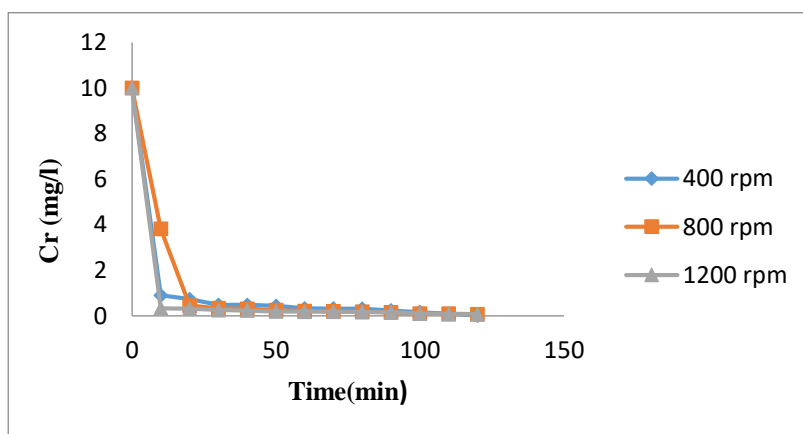


Figure 6. Stirring speed effect on removal yield of MB

2. The study of adsorption kinetics

The kinetics study of the adsorption is a crucial step to define the sorption link between the adsorbent and the adsorbate³¹. Several kinetic models can be used to investigate the retention mechanism and test the experimental results of adsorption.

In this work, the adsorption reaction is carried out between the surface of the adsorbent (the rock) and the ions of the basic dye with a positive charge (methylene blue) in aqueous solution. The kinetics tests were carried out by mixing 100 ml of colored solutions at concentrations between 10 and 25 mg/l, with 0.5g of the natural rock, at room temperature and normal pH of the dye solution.

The solid-liquid homogenization is ensured by a magnetic stirring rod with a constant stirring speed of 800 rpm. Samples were taken at different time intervals, then the adsorbent and adsorbate were separated, and the residual concentration of the dye was determined by spectrophotometry.

In this study, the models chosen to evaluate the adsorption kinetics and define the adsorption mechanism of the natural rock are pseudo-first-order, pseudo-second-order, and intraparticle diffusion.

2.1. Pseudo-First order model

The first-order model is described by the following equation³²:

$$q_t = q_{e,1}(1 - e^{-k_1 \cdot t})$$

Where:

$q_{e,1}$: amount adsorbed at equilibrium (mg/g);

q_t : amount adsorbed at time t (mg/g);

k_1 : the first order kinetic constant (min⁻¹)

t: adsorption time (min).

The linearity expression of the equation with a plot of $\ln(q_e - q_t)$ versus t gives³³:

$$\ln(q_e - q_t) = -k_1 \cdot t + \ln q_{e,1}$$

The first-order model suggests that adsorption is reversible and fast when the system is far from equilibrium time.

2.2. Pseudo-Second order model

The second-order model is represented by the following equation³⁴:

$$q_t = \frac{k_2 \cdot q_{e,2}^2 \cdot t}{1 + k_2 \cdot q_{e,2} \cdot t}$$

Where:

$q_{e,2}$: amount adsorbed at equilibrium (mg/g);

q_t : amount adsorbed at time t (mg/g);

k_2 : the second order kinetic constant (min⁻¹)

The linearity expression of the equation with a plot of t/q_t versus t gives³⁴:

$$\frac{1}{q_t} = \left(\frac{1}{q_{e,2}} \right) t + \frac{1}{q_{e,2} \cdot k_2}$$

The second-order model suggests the existence of chemisorption³⁵, which describes adsorption by an exchange of electrons between adsorbate and adsorbent molecules³⁶.

2.3. Intra-particle diffusion model

The intraparticle diffusion model proposed by Weber and Morris (1963) is used to explain the mechanism of diffusion in the adsorbent pores³⁷.

The model is represented by the following equation³⁷:

$$q_t = k_D \cdot t^{1/2} + C_D$$

With :

- K_D : the rate constant of the intra-particle diffusion model (mg/g.min^{1/2}).
- C_D : constant associated with the thickness of the boundary layer (mg/g).

In case the lines do not pass through the origin, it indicates that the diffusion into the pores is not the only mechanism limiting sorption kinetics³⁷.

The parameters of the pseudo-first-order model, the pseudo-second-order model and intraparticle diffusion are given in the following tables

Table 2. Parameters of the first-order model.

Pseudo First Order					
Materials	C_i	$Q_{e,th}$ (mg/g)	$Q_{e,exp}$ (mg/g)	K_1	R^2
MB-R	15	2.452	0.608	0.0235	0.7856
	20	2.746	4.3089	0.0013	0.948
	25	3.193	0.191	0.0237	0.8306

Table 3. Parameters of the second-order model.

Pseudo Second Order					
Materials	C_i	$Q_{e,th}$ (mg/g)	$Q_{e,exp}$ (mg/g)	K_2	R^2
MB-R	15	2.452	2.531	0.8986	0.999
	20	2.746	2.649	1.1351	0.997
	25	3.193	3.125	0.3503	0.999

Table 4. Parameters of the intraparticle diffusion model.

	Concentration	K_D (mg/g.min ^{1/2})	C_D (mg/g)	R^2
Intra-particle Diffusion	15 mg/l	4,9.10-3	2,2333	0.9296
	20 mg/l	8,2.10-3	2,5609	0.987
	25 mg/l	13,1.10-3	2,9395	0.9342

The data shown in [Table 2](#) represent the parameters of the pseudo-first-order model, which give as an idea about the application of this model on our adsorbent. The plot of the PSO model shows low values of the coefficient correlation (R^2), and the $Q_{e,exp}$ is different of $Q_{e,th}$, which leads as to conclude that the kinetic adsorption does not follow this model.

Based on the results obtained from the kinetic study ([Table 3](#)), we can observe that the experimental equilibrium could follow the pseudo-second-order model. This is due to the high values of correlation coefficients (R^2) close to the unit. Meanwhile, the theoretical values of Q_e are equal to experimental; which confirms that the adsorption kinetics is pseudo-second-order and suggests chemisorption.

The study of the adsorption mechanism carried out by the intraparticle diffusion model indicates that the diffusion rate constant K_D increases in the same

direction as the initial dye concentration, which makes the diffusion stronger when the concentration is high³⁸.

The curves plotted in this model (q vs. $t^{0.5}$) do not pass through the origin, and according to Weber and Morris, this mechanism will not be the only one limiting the adsorption, and there are most undoubtedly multistep mechanisms involved, like chemisorption (valence forces, sharing or exchange ions) confirmed by the best fit shown in the PSO model.

3. Desorption studies

The desorption test was used to confirm the chemisorption hypothesis of the kinetic study. After leaving the mixture in rest for 3 months, we can observe that the water is clear and there is no desorption ($C_{res} = 0$ mg/L), which confirms the mechanism of the pseudo-second-order, chemisorption.

Conclusion

The main objective of this study is to find a new adsorbent to enable us to avoid the extra charge and

evaluate the adsorption of dyes existing in wastewater using a natural rock in Morocco's central region of Khenifra. This is undertaken in an attempt to reduce the pollutants contained in this wastewater, which pose a severe threat to the environment spilt into. Based on the results obtained, the rock used in this work can remove MB dye with a high yield that depends on various determining factors such as granulometry, and rock's mass while the other effect (pH solution and agitation rate) showed a low action on adsorption yield which demonstrates their futility in future experiments.

The execution of the kinetic study on adsorption shows that the process is speedy, which explains the 95% disappearance of the MB during the first ten minutes, then the rate slows down to 20 minutes, which corresponds to the experimental equilibrium time. The mechanism determining the adsorption reaction can describe by the pseudo-second-order model and the intraparticle diffusion model, explained by their high R^2 and the equality between the values of $Q_{e,exp}$ and $Q_{e,th}$.

The results obtained in this study show that our natural rock could be used as an excellent natural adsorbent that allows the removal of methylene blue and other cationic dyes at low cost and high efficiency.

Acknowledgements

I thank Mr Ezzoubeir JABRANE for his help in editing the English version of this work.

References

- 1- F. Ouzidan, M. El Kouali, M. Talbi, R. Atmani, Adsorption of Methylene Blue onto Artichoke Waste, *Oriental Journal of Chemistry*, **2015**, 31, 2037-2041.
- 2- F. Falil, F. Allam, B. Gourich, Ch. Vial, F. Audonnet, Adsorption of Astrazon Orange G onto natural Moroccan phosphate rock: A mechanistic study, *Environmental Chemical Engineering*, **2016**, 4, 2556-2564.
- 3- A. Mittal, J. Mittal, A. Malviya, V. K. Gupta, Removal and recovery of Chrysoidine Y from aqueous solutions by waste materials, *Journal of Colloid and Interface Science*, **2010**, 344 (2), 497-507.
- 4- V. K. Gupta, Arunima Nayak, Shilpi Agarwal, Bioadsorbents for remediation of heavy metals: Current status and their future prospects, *Environmental Engineering Research*, **2015**, 20(1), 1-18.
- 5- V. K. Gupta, T. A. Saleh, Sorption of pollutants by porous carbon, carbon nanotubes and fullerene- An overview, *Environmental Science and Pollution Research*, **2013**, 20(5), 2828-2843.
- 6- J. De Zuane, *Handbook of Drinking Water Quality Standards and Controls*, Van Nostrand Reinhold, New York, **1990**, pp. 64-69.
- 7- N. Mohammadi, H. Khani, V. K. Gupta, E. Amereh, S. Agarwal, Adsorption process of methyl orange dye onto mesoporous carbon material-kinetic and thermodynamic studies, *Journal of colloid and interface science*, **2011**, 362(2), 457-462.
- 8- J. Ma, F. Yu, L. Zhou, L. Jin, M. Yang, J. Luan, Y. Tang, H. Fan, Z. Yuan, J. Chen, Enhanced Adsorptive Removal of Methyl Orange and Methylene Blue from Aqueous Solution by Alkali-Activated Multiwalled Carbon Nanotubes, *ACS Applied Materials & Interfaces*, **2012**, 4, 5749-5760.
- 9- V. K. Gupta, I. Ali, T. A. Saleh, M. N. Siddiqui, S. Agarwal, Chromium removal from water by activated carbon developed from waste rubber tires, *Environmental Science and Pollution Research*, **2013**, 20(3), 1261-1268.
- 10- R. Saravanan, M. Mansoob Khan, V.K. Gupta, E. Mosquera, F. Gracia, V. Narayanan, A. Stephen, ZnO/Ag/CdO Nanocomposite for Visible Light-Induced Photocatalytic Degradation of Industrial Textile Effluents, *Journal of Colloid and Interface Science*, **2015**, 452, 126-133.
- 11- V.K. Gupta, A. Mittal, A. Malviya, J. Mittal, Adsorption of carmoisine A from wastewater using waste materials—Bottom ash and deoiled soya, *Colloid and Interface Science*, **2009**, 335, 24-33.
- 12- M. Ahmaruzzaman, V. K. Gupta, Rice Husk and Its Ash as Low-Cost Adsorbents in Water and Wastewater Treatment, *Industrial & Engineering Chemistry Research*, **2011**, 50(24), 13589-13613.
- 13- M. Ghaedi, S. Hajjati, Z. Mahmudi, I. Tyagi, Shilpi Agarwal, A. Maity, V.K. Gupta, Modeling of competitive ultrasonic-assisted removal of the dyes - Methylene blue and Safranin-O using Fe₃O₄ nanoparticles, *Chemical Engineering Journal*, **2015**, 268, 28-37.
- 14- V. K. Gupta, Suhas, I. Tyagi, S. Agarwal, R. Singh, M. Chaudhary, A. Harit, S. Kushwaha, Column operation studies for the removal of dyes and phenols using a low-cost adsorbent, *Global Journal of Environmental Science and Management*, **2016**, 2(1), 1-10.
- 15- S. S. Salih, T. K. Ghosh, Adsorption of Zn(II) ions by chitosan coated diatomaceous earth. *International journal of biological macromolecules*, **2018**, 106, 602-610.
- 16- B. H. Hameed, A.A. Ahmad, Batch adsorption of methylene blue from aqueous solution by garlic peel, agricultural waste biomass, *Hazardous Materials*, **2009**, 164, 870-875.
- 17- S. S. Salih, T. K. Ghosh, Preparation and characterization of bioadsorbent beads for chromium and zinc ions adsorption. *Cogent Environmental Science*, **2017**, 3, n: 1, 1401577.
- 18- V. K. Gupta, A. Nayak, S. Agarwal, I. Tyagi, Potential of activated carbon from Waste Rubber Tire for the adsorption of phenolics: Effect of

- pre-treatment conditions, *Journal of Colloid and Interface Science*, **2013**, 417, 420-430.
- 19- V. K. Gupta, C.K. Jainb, I. Alib, S. Chandraa , S. Agarwal, Removal of lindane and malathion from wastewater using bagasse fly ash-a sugar industry waste, *Water Research*, **2002**, 36, 2483-2490.
- 20- R. Saravanan, S. Karthikeyan, V.K. Gupta, G. Sekaran, V. Narayanan, A. Stephen, Enhanced photocatalytic activity of ZnO/CuO nanocomposite for the degradation of textile dye on visible light illumination, *Materials Science and Engineering:C*, **2013**, 33, 91-98.
- 21- N. Thinakaran, P. Baskaralingam, M. Pulikesi, P. Panneerselvam, S. Sivanesan, Removal of Acid Violet 17 from aqueous solutions by adsorption onto activated carbon prepared from sunflower seed hull, *Hazardous Materials*, **2008**, 151, 316-322.
- 22- F. Moughaoui, A. Ouaket, A. Laaraibi, S. Hamdouch, Z. Anbaoui, A. Abourriche, M. Berrada, A novel approach for producing low cost and highly efficient activated carbon for removing cationic dyes, *Mediterranean Journal of Chemistry*, **2019**, 8(2), 74-83.
- 23- T. A. Khan, M. Nazir, I. Ali, A. Kumar, Removal of Chromium(VI) from aqueous solution using guar gum-nano zinc oxide biocomposite adsorbent, *Arabian Journal of Chemistry*, **2013**, 10, S2388-S2398.
- 24- T. Ngulub, J.R. Gumbo, V. Masindi, A. Maity, Calcined magnesite as an adsorbent for cationic and anionic dyes: characterization, adsorption parameters, isotherms and kinetics study, *Heliyon*, **2018**, 4, e00838.
- 25- K. Vasanth Kumar, V. Ramamurthi, S.Sivanesan, Modeling the mechanism involved during the sorption of methylene blue onto fly ash, *Colloid and Interface Science*, **2005**, 284, 14-21.
- 26- H. Tahir, M. Sultan, N. Akhtar, U. Hameed, T. Abid, *Saudi Chemical Society*, **2012**, 20, S115-S121.
- 27- B. Volesky, Biosorption and me, *Water Research*, **2007**, 41, 4017-4029.
- 28- P. K. Malik, Use of activated carbons prepared from sawdust and rice-husk for adsorption of acid dyes: a case study of Acid Yellow 36, *Dyes and Pigments*, **2003**, 56, 239-249.
- 29- G. Spagnoli, D. Rubinos, H. Stanjek, T. Fernandez-Steeger, M. Feinendegen, R. Azzam, Undrained shear strength of clays as modified by pH variations, *Bulletin of Engineering Geology and the Environment*, **2012**, 71, 135-148.
- 30- N. Fayoud, S. Alami Younssi, S. Tahir, A. Albizane, Etude cinétique et thermodynamique de l'adsorption de bleu de methylene sur les cendres de bois, *Materials and Environmental Science*, **2015**, 6, 3295-3306.
- 31- H. Es-sahbany, S. Nkhili, M. Berradi, H. Nassali, N. Aziane, M. Befaquir, M.S. Elyoubi, Performance of adsorption of heavy metals contained in model wastewater solutions by two types of Moroccan clay: type of copper, *Applied Journal of Environmental Engineering Science*, **2017**, 3, 1-6.
- 32- Y. S. Ho, G. McKay, Sorption of dye from aqueous solution by peat, *Chemical Enginee*, **1989**, 70, 115-124.
- 33- H. N. Tran, S.J. You, A. Hosseini-Bandegharaei, H. P. Chao, Mistakes and inconsistencies regarding adsorption of contaminants from aqueous solutions: A critical review, *Water Research*, **2017**, 120, 88-116.
- 34- S. J. Allen, G. Mckay, K.Y.H. Khander, Equilibrium adsorption isotherms for basic dyes onto lignite, *Chemical Technology and Biotechnology*, **1989**, 45, 291-302.
- 35- C. C. Tavis, E.L. Etnier, A survey of sorption relationships for reactive solutes, *Journal of Environmental Quality*, **1981**, 10, 8-17.
- 36- T. Chouchane, S. Chouchane, A. Boukari, A. Balaska, M.H. Samar, Elimination du plomb en solution par la sciure de bois, *Revue des Energies Renouvelables*, **2011**, 14, 613-626.
- 37- W. J. Weber, J.C.J. Morris, Kinetics of Adsorption on Carbon from Solution, the Sanitary Engineering Division, **1963**, 89, 31-60.
- 38- S. M. de Oliveira Britoa, H.M.C. Andrade, L.F. Soares, R.P. de Azevedo, Brazil nut shells as a new biosorbent to remove methylene blue and indigo carmine from aqueous solutions, *Hazardous Materials*, **2009**, 174, 84-92.