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ORIGINAL RESEARCH ARTICLE

Characterization of an abundant illitic clay from the Safi region in Morocco and its exploitation in the treatment of industrial effluents loaded with synthetic dyes

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ABSTRACT

The objective of this work is to valorize abundant illitic clay from Morocco in the treatment of industrial effluents likely to be loaded with synthetic dyes such as the textile, stationery, cosmetic, food, and also pharmaceutical industries. The penitential adsorbing of two dyes: methylene blue (BM) and malachite green (GM) was studied on this clay. Firstly, this clay was characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) analysis and X-ray fluorescence analysis. And on the other hand, Effect of different parameters on adsorption kinetics has been studied, such as contact time, initial dye concentration, pH, salinity and temperature. Adsorption tests results showed that equilibrium was established after 30 min and the adsorption of the two dyes depends on the initial dye concentration and the pH. The results showed was the adsorption of the two dyes can be described by pseudo-second-order kinetics. The results indicate also that the process is a spontaneous endothermic physisorption characterized by disorder of the environment. This study shows that this raw, abundant and low-cost natural illitic clay can be valorized and exploited to treat effluents loaded with synthetic dyes.

Keywords: adsorption; dyes; kinetic; illitic clay; industrial effluent; textile industry

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1. Introduction

Dyes are widely used in various industries such as textiles, printing, cosmetics, and food[1]. However, some dyes may contain harmful chemicals that can be absorbed through the skin, ingested, or inhaled. These chemicals can have toxic effects, including skin irritation, allergies, respiratory issues, and even potential carcinogenicity[2]. Methylene blue and vert malachite are the most commonly used dyes in these industries[3]. However, the discharge of this dyes in the environment is worrying for both toxicological and environment reasons[4]. Therefore, treating effluents containing harmful dyes is important to prevent their negative impacts on receiving waters[5,6]. Among several treating methods physico-chemical of wastewater, the adsorption onto activated carbon, has been found superior compared to other techniques[7,8]. But, commercially available activated carbons are still considered

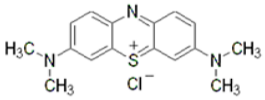
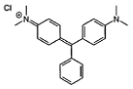
expensive. This is due to the use of non-renewable and relatively expensive starting material such as coal, which is unjustified in pollution control applications[9]. Therefore, in recent years, this has sparked increasing interest from researchers in other natural, available, unprocessed materials with absorbent properties particularly for applications related to wastewater treatment. Clay minerals offer several advantageous properties, making them valuable in various applications[10]. Such as clay minerals have unique properties important for adsorption processes. Among these advantages, clay minerals have a high specific surface area, which provides ample sites for adsorption. The fine particles and layered structure of clays contribute to a significant surface area-to-volume ratio, enhancing their adsorption capacity, its possess a porous structure with interlayer spaces and micro/mesopores, these pores allow for the adsorption of various pollutants, including organic compounds, heavy metals, and dyes. Clay minerals have cation exchange capacity due to their negatively charged surfaces. This property enables the exchange of cations, facilitating the adsorption of positively charged contaminants. Clay minerals can efficiently adsorb a diverse range of adsorbates, making them suitable for the removal of different pollutants from wastewater. Clay minerals are abundant, widely available and relatively low-cost compared to other adsorbents, such as activated carbon. This makes them economically viable for wastewater treatment applications[10]. In terms of simplicity of design, the use of clay minerals for adsorption can be straightforward. The clay minerals can be mixed with the wastewater or incorporated into a filtration system, allowing for the adsorption of contaminants[10]. The simplicity of the design and operation can make clay-based adsorption a viable option, particularly for small-scale or decentralized wastewater treatment systems[10]. These factors contribute to their growing popularity in various environmental and industrial applications[10]. Several types of Clay have been used as adsorbents for dye (bentonite, kaolinite; montmorillonite; soil nanoclays; ghassoul; open burnt clay; moroccan clay; red mud; raw clay; activated clay and TiO_2 interlayer-pillared clays)[10]. In the present work, we were interested in the study of the adsorption of two synthetic dyes (methylene blue and malachite green) on raw clay illitic from the Safi region, Morocco. A characterization of this clay was carried out by different instruments and the effect of different parameters on the absorption of dyes by clay was studied (pH, adsorbent mass, initial dye concentration, temperature, concentration of NaCl in the solution), The Kinetics, thermodynamics and adsorption isotherms has been also studied in order to better understand the mode of dyes fixation.

2. Material and method

2.1. Adsorbate

The dyes used in this study are methylene blue (BM) and malachite green (GM), used without any prior purification, they have a very high degree of purity (99%). **Table 1** presents most of their characteristics. The choice of these molecules initially results from their frequency in waste water from certain textile industries, and secondly to compare the capacity and kinetics of clay retention with respect to these two dyes. The stock solutions were prepared by dissolving 1 g of each reactive dye in 1l distilled water, and to prepare the desired concentrations, dilutions were done.

Table 1. Some characteristics of methylene blue and malachite green.

Dyes	**Methylene blue (BM)**	**Malachite green (GM)**
Molecular structure		
Chemical formula	$C_{16}H_{18}ClN_3S$	$C_{52}H_{54}N_4O_{12}$
Molar mass (g/mol)	319.85	929.02
Maximum wavelength λmax (nm)	670 nm	618 nm

2.2. Preparation and characterization of Adsorbent

The raw clay used in this work is clay taken from a natural basin, the "barrage quarry" in the Safi region (Morocco). It is available and very abundant clay, known literally by its retention capacity and its adsorbent potential, hence the choice of its use. This clay was crushed then ground and sieved to obtain fractions < 63 µm, finally it was dried at 105 °C for 24 h (**Figure 1**), some physicochemical parameters were measured for the raw clay studied before starting this work such as pH, humidity, porosity and loss on ignition.

Figure 1. Outcrop of raw red clays from the Safi dam quarry and macroscopic appearance of the screened clay.

Clay characterization is an essential process to determine the composition and properties of clay materials. The techniques used in this study to identify the major's constituents of clay are flowing, we have used Scanning Electron Microscopy Quanta 200 equipped with an EDAX probe for surface microanalysis (SEM): for to visualize the surface morphology, particle size, and shape of clay minerals. X-ray diffraction (XRD) analysis was performed also using a powder diffractometer, to identify the mineralogical composition of clay by examining the diffraction patterns produced when X-rays interact with the crystal lattice structure of clay minerals, and Fourier Transform Infrared Spectroscopy (FTIR): FTIR is used to analyze the functional groups present in clay minerals. It provides information about the chemical composition and bonding within the clay lattice.

2.3. Specific surface determination

The specific surface area of the sample collected is determined by two methods:

- BET method: Nitrogen porosimetry using a Quantasorb Junior device (ANKERSMITH). This technique makes it possible to determine the amount of adsorbable nitrogen on the surface of a powdery compound. The Brunauer, Emmett and Teller (BET) theory then make it possible, from the results obtained, to determine the specific surface area of the aerosol analyzed.
- Methylene blue method: A mass of about 1 g of finely ground sample was mixed in a 100 mL beaker with 20 mL of distilled water to suspend continuously stirring for a few minutes. Then, the latter is metered with a methylene blue solution with a known mass concentration (drop by drop), until the persistence of the light blue halo which surrounds the central deposit of the spot formed on the filter paper.

The specific surface S_s is given by the following relation:

$$S = (q_m A_{MB} N_A \times 10^{-20})/M_{MB} \quad (1)$$

where, q_m: the maximum adsorption capacity (mg/g), A_{MB}: the area occupied on average by a molecule of BM equals 120 $A^{°2}$, N_A: number of Avogadro, (6.02×10^{23} mol^{-1}), M_{MB}: the molar mass of MB (319.85 g mol^{-1}). $S_s = (0.8056 \times 120 \times 602)/319.85 = 181.95$ m^2/g.

2.4. Adsorption kinetics

Adsorption tests were performed in batches by constant temperature stirring of colored BM and GM synthetic solutions in the presence of clay. Homogenization of the mixture was ensured by continuous stirring with a magnetic stirrer for 60 min. Samples were taken periodically, and after separation of the adsorbates using a syringe filter with a diameter of 0.45 µm (Minisart, Sartorium Stedim Biotech), the

absorbance of the supernatant was measured using a UV-visible spectrophotometer (Shidmzu 1900i). The percentage of elimination of dyes is calculated by the following formula (Equation (2))[11],

$$E\ (\%) = 100(C_0 - C_t)/C_0 \quad (2)$$

and others adsorption tests were carried out under different conditions in order to study the effect of the physicochemical parameters: contact time, initial dye concentration, pH, temperature and salinity.

2.5. Modeling of the adsorption isotherm

The classic Langmuir and Freundlich models characterizing the formation of a monolayer will be used for their ease of implementation[12]. After determining the residual concentrations, we followed, on the one hand the evolution of LnQ_t as a function of LnC_e according to the Freundlich model and on the other hand, the evolution of C_e/Q_t as a function of C_e according to the model of Langmuir.

2.6. Mechanism of adsorption kinetics

In order to examine the adsorption mechanism, the pseudo-first-order and pseudo-second-order kinetic models were used to test the dynamic experimental data[12].

The pseudo first order model is expressed as follows:

$$dQ_t/d_t = k_1(Q_e - Q_t) \quad (3)$$

where Q_e and Q_t are respectively the quantities of the dye (mg g^{-1}) adsorbed on the clay at equilibrium and at time t. k_1 is the speed constant (min^{-1}) by integrating and applying the initial conditions (at $t = 0$, $Q_t = 0$ and at $t = t_e$, $Q_t = Q_e$), Equation (4) takes the form:

$$Ln(Q_e - Q_t) = LnQ_e - (k_1/2.303)t \quad (4)$$

k_1 and Q_e are obtained by representing $Ln(Q_e - Q_t)$ as a function of t.

The pseudo-second-order model is expressed as follows:

$$dQ_t/d_t = k_2 \times (Q_e - Q_t)^2 \quad (5)$$

k_2 is the pseudo-second-order rate constant (g•mg^{-1}•min^{-1}).

By integrating and applying the conditions (at $t = 0$, $Q_t = 0$ and at $t = t_e$, $Q_t = Q_e$), Equation (6) takes the linear form:

$$t/Q_t = (1/k_2Q_{e2}) + (1/Q_e)t \quad (6)$$

Q_e and K_2 are obtained by representing t/Q_t as a function of t.

2.7. Thermodynamic study

The thermodynamic parameters of the adsorption process of dyes on clay, such as enthalpy $\Delta H°$, entropy $\Delta S°$ and free enthalpy $\Delta G°$ were determined by implementing the adsorption at four different temperatures and using the following equations:

$$Ln(k_d) = \Delta S°/R - \Delta H°/(R \times T)$$
$$\Delta G° = \Delta H° - T\Delta S° \quad (7)$$

With $k_d = Q_e/C_e$ is the distribution coefficient, R is the ideal gas constant and T (K) is the temperature of the solution. Knowing that; Q_e (mg g^{-1}) is the quantity adsorbed at equilibrium and C_e (mg L^{-1}) is the concentration at equilibrium[13]. The values of $\Delta H°$ and $\Delta S°$ are calculated from the slope and the ordinate at the origin of the line $Ln(k_d)$ as a function of $1/T$, using these values we can calculate $\Delta G°$ by Equation (3).

3. Results and discussion

3.1. Characterization

The results obtained for clay are shown in **Table 2**. The chemical composition is given as a mass percentage of the oxides present in combined or free form. They show that alumina, silica and calcium is

very important, which implies that the proportions of SiO_2 (50%–60%), Al_2O_3 (10%–20%), Fe_2O_3 (5%–15%) and CaO (1%–5%) are the main constituents.

Table 2. Mineralogical composition of clay.

Elements	Percentage (%)
SiO_2	53.61
Al_2O_3	17.13
Fe_2O_3	5.47
CaO	4.41
MgO	2.46
K_2O	1.59
TiO_2	0.94
Na_2O	0.23
P_2O_5	0.16
L.O.I (*)	13.21

(*): loss of mass obtained after heat treatment at 1000 °C for 1 h.

The analysis by X-ray powder diffraction shows the presence intense line which implies the crystalline state of this material (**Figure 2**). The X-ray diffractogram indexing was which noted the existence of the majority phases: quartz, kaolinite; muscovite, traces of calcite and potassium feldspar, with low peaks intensity not indexed, similar results were found by Denga et al.[14], they found that SiO_2, Al_2O_3 are the main constituents of the two clays (raw and purified), These authors also found that raw clay from Safi in Morocco, shows the presence of intense lines which respectively characterize illitc, kaolinite, quartz, calcite and dolomite.

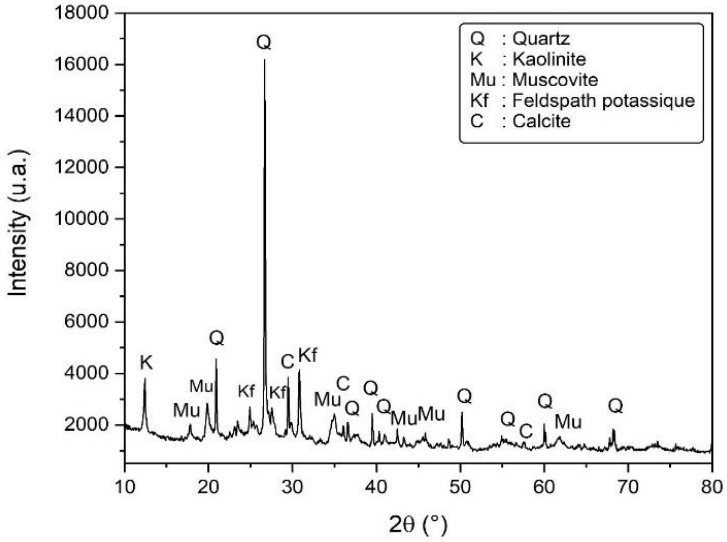


Figure 2. Diffractometric analysis of clay.

The examination of the IR spectra of clay (**Figure 3**) shows the presence of a band characteristic of illitc (muscovite); another band corresponds to H_2O molecules characteristic bands of carbonates (calcite) were observed. The quartz also is observed, this results are consistent with Chaari et al.[11].

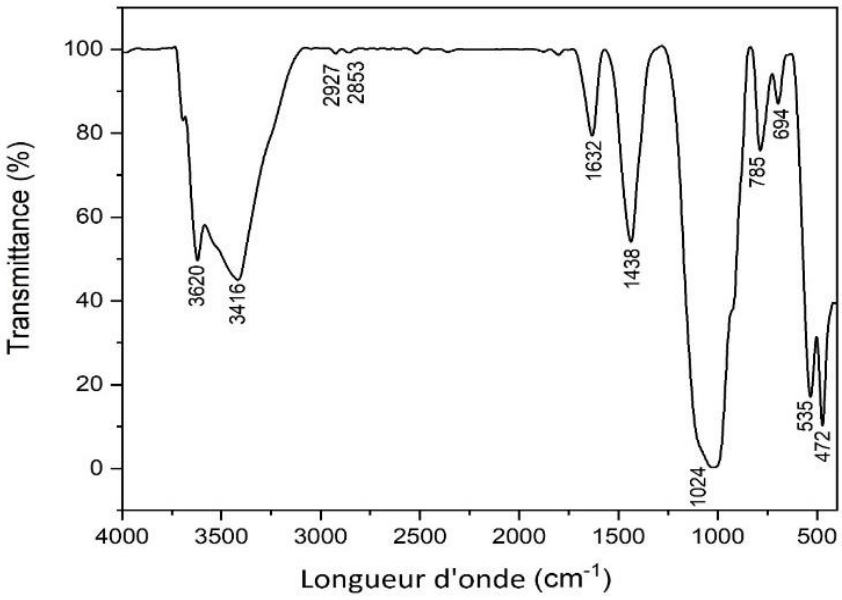


Figure 3. Infrared spectrum of clay.

The results obtained by scanning electron microscopy clearly show the difference in appearance and roughness and the fact that before adsorption, the clay particles as well as the interstices were clearly visible aggregates (**Figure 4**). On the other hand, after adsorption, the roughness is masked by a thin film covering the sample (**Figure 5**). These results indicate the total pore volume and average pore width of clay are important parameters that can indicate its adsorption capacity and the types of substances it can effectively adsorb. Many authors found similar results[11,12,15], According to the results, these properties make clay minerals valuable in various applications, including environmental remediation, water treatment, and the production of adsorbents and catalysts.

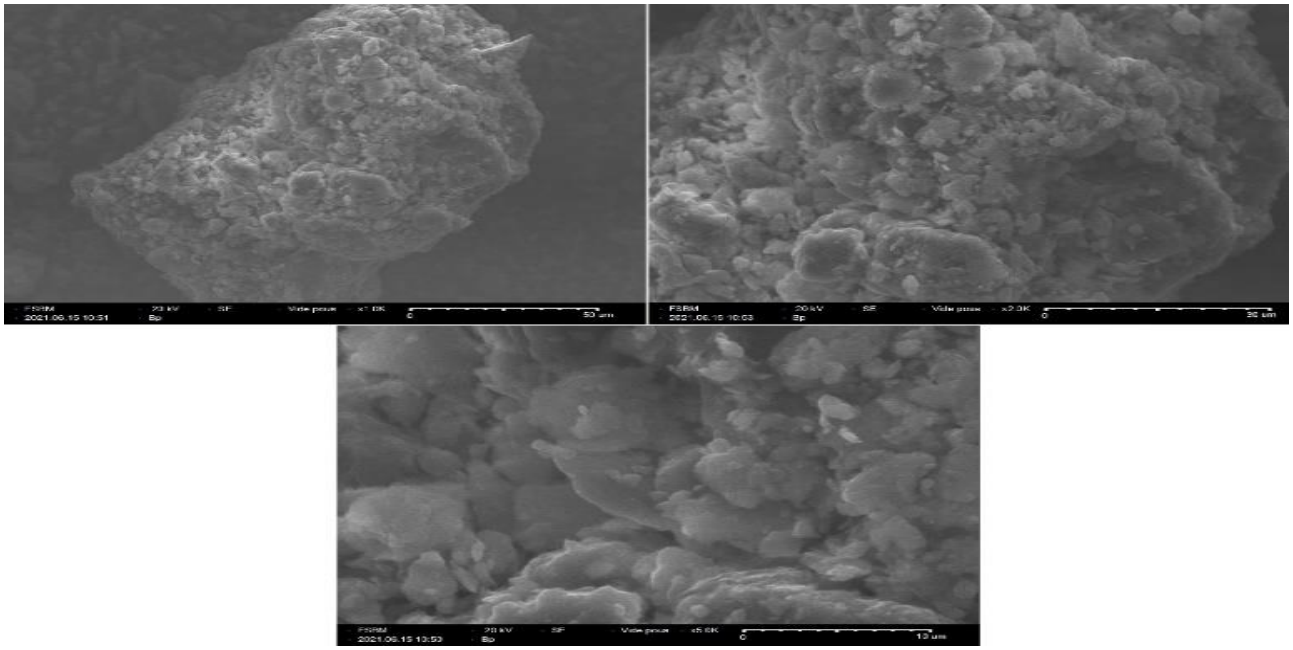


Figure 4. SEM image of the adsorbent (×50, ×30, and ×10) before adsorption.

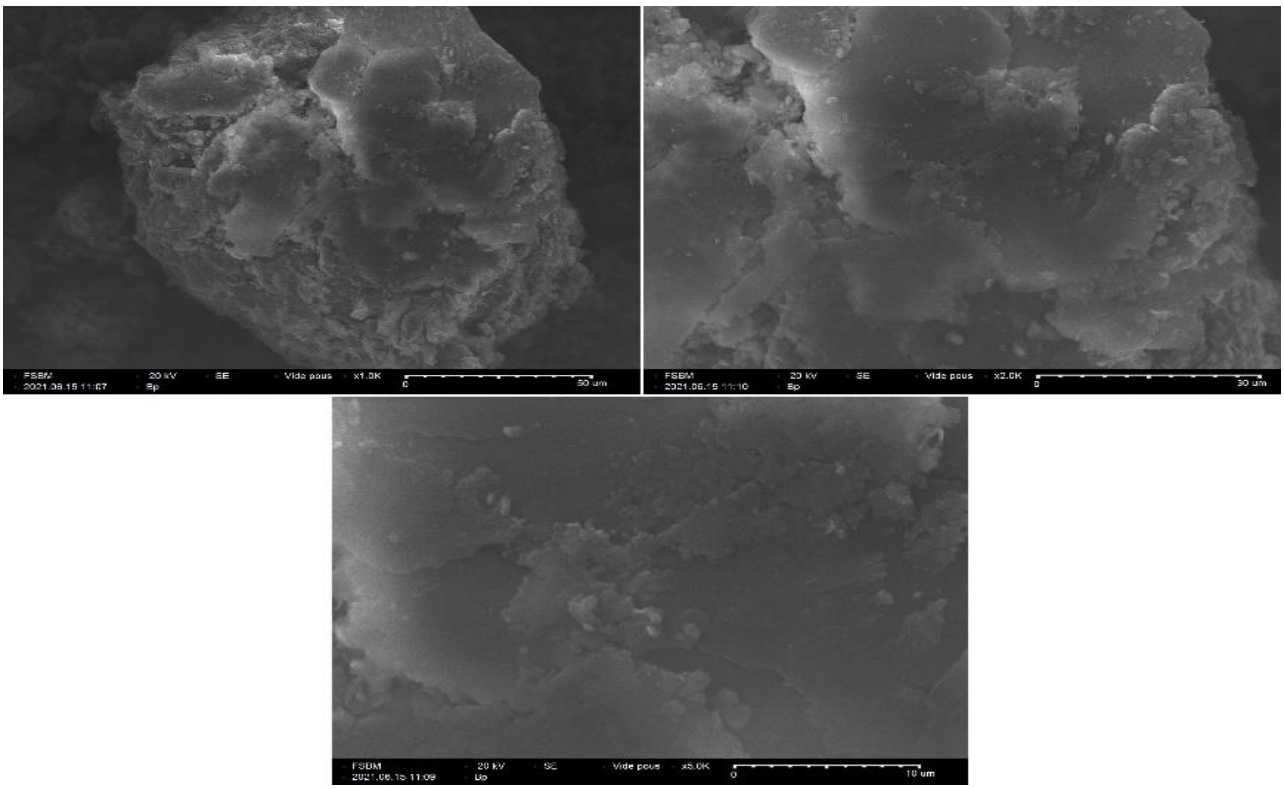


Figure 5. SEM image of the adsorbent (×50, ×30, and ×10) after adsorption.

3.2. Effect of different parameters on adsorption

3.2.1. Effect of contact time

Figure 6 shows the curves of evolution of the adsorbed quantity of the dyes as a function of the contact time. We note that the equilibrium time is independent of the type of dye and that the adsorbed quantity of the dyes increases with the contact time in the following two slopes: At the beginning, in the first 10 min the adsorption is very rapid, but afterward it continues at a very slow rate to finally reach an equilibrium within 80 min for MB biosorption onto clay and 90 min for GM/clay. Similar results have been found by Denga et al.[14] and Miyah et al.[16]. This can be explained by the fact that at the start of adsorption all the sites on the surface of the adsorbent are free and the concentration gradient of the solute is relatively high. Consequently, the stabilization of dye removal by clay depends on the number of vacant sites on the clay surface.

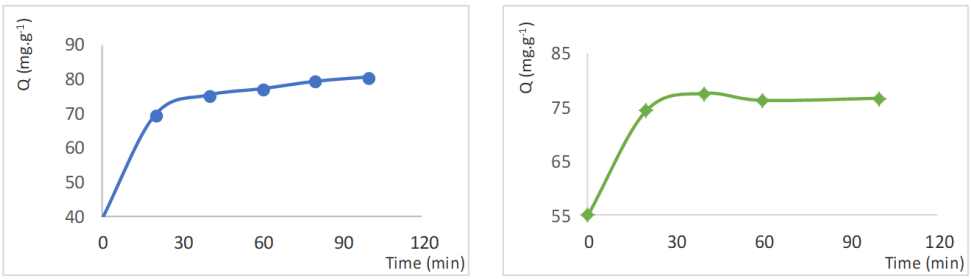


Figure 6. Effect of contact time on the elimination of BM and GM.

3.2.2. pH effect

The results (**Figure 7**) reveal that there is an increase in the amount of adsorption by increasing the pH considerably. This behavior is consistent with several works cited in the literature[17,18]. It has been attributed to the change in the surface charge of materials as a function of pH, which becomes increasingly negative. This may be due to the fact that the addition of H+ protons leads to the neutralization of the negative charge

of the material, which disadvantages the adsorption of cationic dyes in a very acidic medium and conversely favors it in a basic medium.

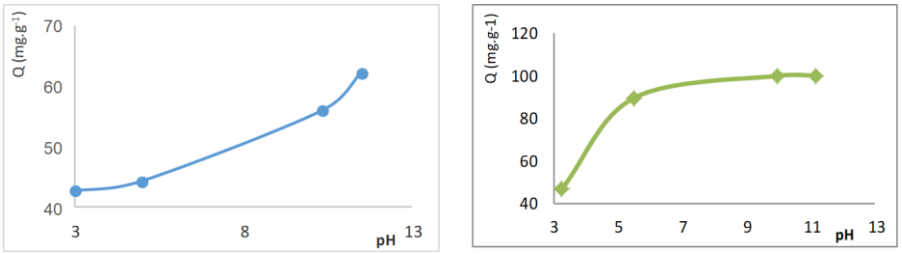


Figure 7. Effect of medium pH on the elimination of BM and GM.

3.2.3. Effect of initial concentration

Figure 8 represents the curve of evolution of the quantity of dyes adsorbed by the clay. The results reveal that the equilibrium time is independent of the concentration and that the quantity adsorbed at equilibrium increases with the concentration. We also note that the quantities adsorbed increase with the increase in the concentration in a linear manner. Indeed, at a higher concentration of dye, the adsorbate/adsorbent ratios are high, this is due to the fact that the diffusion of the dye molecules from the solution to the surface of the adsorbent is accelerated by the increase in the concentration of dye[19].

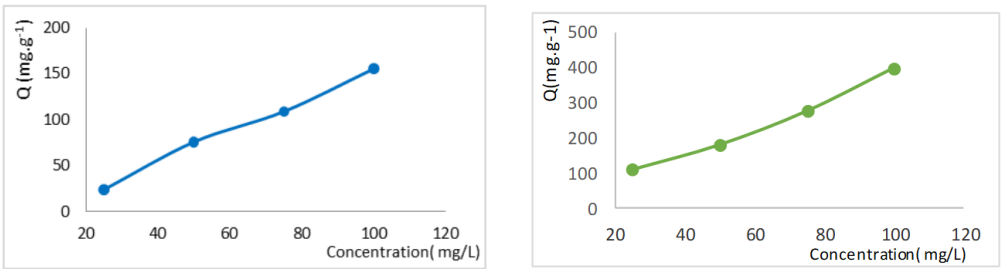


Figure 8. Effect of initial concentration on the elimination of BM and GM.

3.2.4. Effect of temperature

The effect of temperature was studied at temperatures between (20 °C and 70 °C), using dyes at 30 mg L^{-1}. **Figure 9**, shows an increase in the quantity adsorbed with increasing temperature, we can explain this elevation by the increase in the mobility of the active sites of the particles and the solubility of the dye, which allows us to say that the adsorption reaction is probably endothermic and these same findings have been observed in several works[20], suggested that the interaction of the adsorbent and the adsorbate is endothermic in nature. Generally speaking, increasing the temperature promotes adsorption[21].

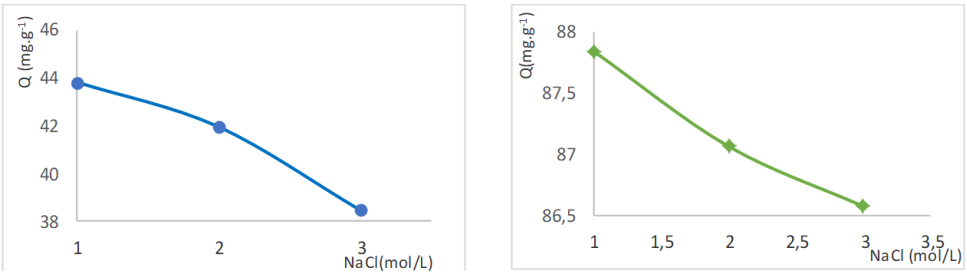


Figure 9. Effect of temperature on the elimination of BM and GM.

3.2.5. Influence of salinity

The effect of salinity on the medium was studied at concentrations varying between (0.1 and 1 mol/L of NaCl), **Figure 10** represents the evolution curve of the quantity of adsorbed dyes, the results show that there is a decrease in the quantity adsorbed by increasing the quantity of NaCl in the solution, we can explain these

results by, the presence of Na+ ions in the medium, the surface of the grains is positively charged, which generates electrostatic repulsions between the cations of the dyes and the surface area of the sorbent and therefore the amount of adsorption will decrease. This is consistent with the research results of Li et al.[17] and Amrhar et al.[20].

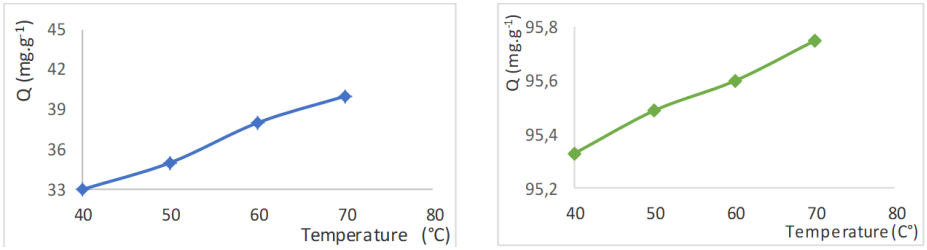


Figure 10. Effect of salinity on the elimination of BM and GM

3.3. Isotherm Modeling

The results found are represented in **Table 3**, the values of the Langmuir and Freundlich constants inferred from the straight lines for these two models; and according to the correlation coefficient found, the R^2 value of the Freundlich isotherm is larger than that of Langmuir, which indicates that the isotherm of adsorption by illitic clay can be satisfactorily described by the Freundlich model, that indicates that the adsorption sites present on the surface are energetically heterogeneous and adsorption occurs in multiple layers[12,16].

Table 3. Parameters of adsorption isotherms of BM & GM on clay.

	Langmuir model				**Freundlich model**		
	Q_m (mg g^{-1})	**K_L (L mg^{-1})**	**R_L**	**R^2**	**K_F (mg/g)(L/mg)$^{(1/n)}$**	**1/n**	**R^2**
BM	44.44	53.04	0.0009	0.883	0.56	0.743	0.953
GM	33.33	0.28	0.7812	0.766	5.720	0.558	0.805

3.4. Kinetic modes

The results of the modeling showed that best linearity was obtained by the pseudo second order model, and according to **Table 4**, the calculated values of the quantity adsorbed at equilibrium Qe-cal of the pseudo-second order model are in agreement with the experimental data Qe-exp whatever the initial concentration of two dyes BM and GM, moreover the values of the correlation coefficients approach unity **Figure 11** (R^2 = 0.999)[16,21].

Table 4. Kinetic constants of the pseudo-second order model.

Dyes	**Q_e-exp (mg g^{-1})**	**Pseudo-second-ordre model**		
		Q_e-cal (mg g^{-1})	**k_2 (g mg^{-1} min^{-1})**	**R^2**
GM	77.6	80.56	0.09389	0.999
BM	80.56	81.30	0.00590	0.999

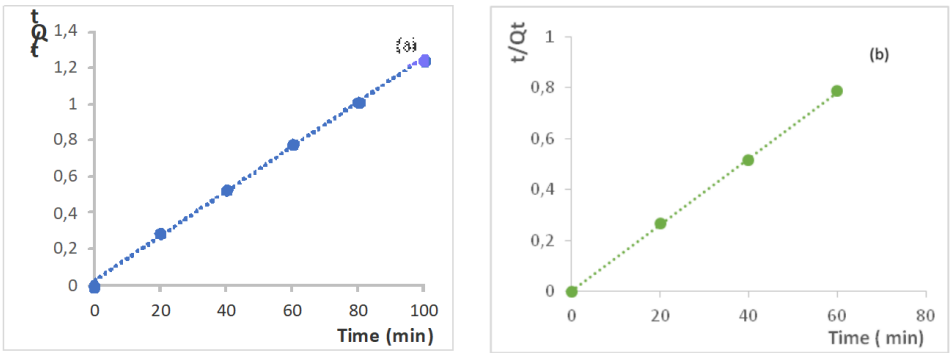


Figure 11. Pseudo-second order model for the adsorption of BM and GM on clay.

3.5. Adsorption thermodynamics

The thermodynamic parameters of the adsorption process of BM and GM on clay, such as the enthalpy $\Delta H°$, the entropy $\Delta S°$ and the free enthalpy $\Delta G°$ were determined by implementing the adsorption at different temperatures. The thermodynamic parameters obtained are grouped in **Tables 5** and **6**. From these results we observe that the free energy is negative, and that the adsorption process of BM and GM by clay is physisorbed since the values of $\Delta G°$ are less than 20 kJ/mol. The free enthalpy is positive, which implies that the adsorption process is endothermic and a higher temperature facilitates adsorption, $\Delta S°$ is positive; this means that the molecules of the BM and GM remain less ordered on the solid/solution interface during adsorption processes[7,22].

Table 5. Thermodynamic parameters of the MB adsorption process on clay.

Temperature (K)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol)	$\Delta G°$ (kJ/mol)
313	12.549	20	−7.124
323			−7.752
333			−8.381

Table 6. Thermodynamic parameters of the GM adsorption process on clay.

Temperature (K)	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol)	$\Delta G°$ (kJ/mol)
293	18.193	65	−0.9571
303			−1.61
313			−2.264
323			−2.917
333			−3.571
343			−4.225

4. Conclusion

The study of adsorption of tow cationic dyes (MB and GM) using natural clay illitic collected in the Safi region of Morocco was carried out to study the effect of initial concentration, of dyes, temperature, contact time, pH and salinity. These effects were studied to evaluate the performance of clay for dye adsorption from aqueous solutions. We found that these variables significantly affect the adsorption kinetics of from the natural clay studied. The results showed that the removal rate increases with increasing adsorbent mass. The contact time effect showed that the equilibrium time is independent of the initial concentration and that adsorption occurred very quickly, reaching 75% within the first 10 min. additionally, increasing temperature accelerates absorption. Linear regression was applied to fit the Langmuir and Freundlich isotherm models, as well as the kinetic models. Based on the study results, the Freundlich isotherm was found to accurately describe the equilibrium behavior of the adsorption of the two dyes. This suggests that

the adsorption process is influenced by factors such as surface heterogeneity and adsorption intensity. Furthermore, the thermodynamic study of adsorption of dye molecules by the natural adsorbent is energetically favorable and occurs without the need for an external energy source. Considering these factors, the illitic clay of Morocco appears to be a promising option for dye removal, as it offers favorable thermodynamics, selectivity, economic efficiency, and environmental friendliness. However, it's important to note that the effectiveness of this adsorbent vary depending on specific conditions, such as the type of dye, concentration, pH, and temperature. Therefore, it's crucial to conduct thorough experimental studies to optimize and validate the performance of this natural adsorbent.

Author contributions

Conceptualization, MB and NB; methodology, SA; software, GRB; validation, MB, BB and NB; formal analysis, SA; investigation, CE; resources, CE; data curation, SA; writing—original draft preparation, CE; writing—review and editing, MB; visualization, NB; supervision, MB; project administration, SEA; funding acquisition, SEA. All authors have read and agreed to the published version of the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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