

Application of Raw Moroccan Clay as a Potential Adsorbent for the Removal of Malachite Green Dye from an Aqueous Solution: Adsorption Parameters Evaluation and Thermodynamic Study

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Abstract. This study uses raw clay from the Es-sifa (REC) territorial commune in the region of Draa-Tafilalet, Morocco, for malachite green (MG) adsorption from an aqueous medium. The characterization of clay was ensured by Fourier Transform Infrared (FTIR) spectroscopy, X-ray diffraction (XRD), and determining the Point of Zero Charge pH. Moreover, five parameters were considered to regulate the adsorption process, including time of contact, initial dye concentration, mass of the adsorbent, stirring speed, and temperature. The finding displayed that equilibrium was reached after only 40 minutes of contact. The maximum adsorption amount achieved was 89.61 mg/g for a dye concentration of 10^{-4} M at 25 °C, using a REC mass of 0.10 g. According to the thermodynamic study, the endothermicity and spontaneity of MG adsorption were disclosed. Malachite green's fixation on the REC surface was verified by comparing the clay FTIR spectra before and after adsorption.

Introduction

Clay is a material that is abundant and cost-effective and is known for its unique properties. Its applications range from producing cement to manufacturing raw or fired building bricks, cosmetics, and therapeutics. Clays are fine-grained minerals that can harden when dried or fired, making them ideal for building bricks. Clays typically contain phyllosilicates and other substances like quartz and calcite, which impart plasticity or hardening properties when dried or fired [1]. Most natural clays are a blend of different mineralogical phases, and their distinct properties arise from differences in structure and charge. Fine-grained silicate minerals found in clays have a negative charge on their structure, which enables them to adsorb positively charged cations like cationic dyes on their surfaces. Generally, clays are characterized by a notable adsorption capacity, given their specific surface area, which may reach up to 800 m²/g [2].

This work investigates the potential use of Raw Es-sifa Clay (REC) as an adsorbent for treating malachite green polluted solutions. Es-sifa is a Moroccan commune in the Errachidia province, in the Drâa-Tafilalet region.

It is important to note that malachite green (MG) is a harmful pollutant that can cause cancer and mutations in organisms [3, 4]. Therefore, it is essential to remove it from the environment. In

this respect, the impact of various reactional parameters on MG uptake onto REC was studied. That includes contact time, quantity of clay, MG initial concentration, stirring speed, and temperature. The clay underwent XRD, FTIR, and pH_{pzc} characterization to evaluate its properties. Additionally, the FTIR analysis was conducted before and after adsorption to study any changes that occurred.

Experimental study

Adsorbate

The malachite green oxalate, which has the molecular formula $\text{C}_{52}\text{H}_{54}\text{N}_4\text{O}_{12}$, was provided by VWR Chemicals and used without any additional purification. Fig. 1 depicts its chemical structure. The dye powder was weighed accurately and dissolved in demineralized water to create a dye stock solution. From this solution, a series of well-defined concentrations were prepared.

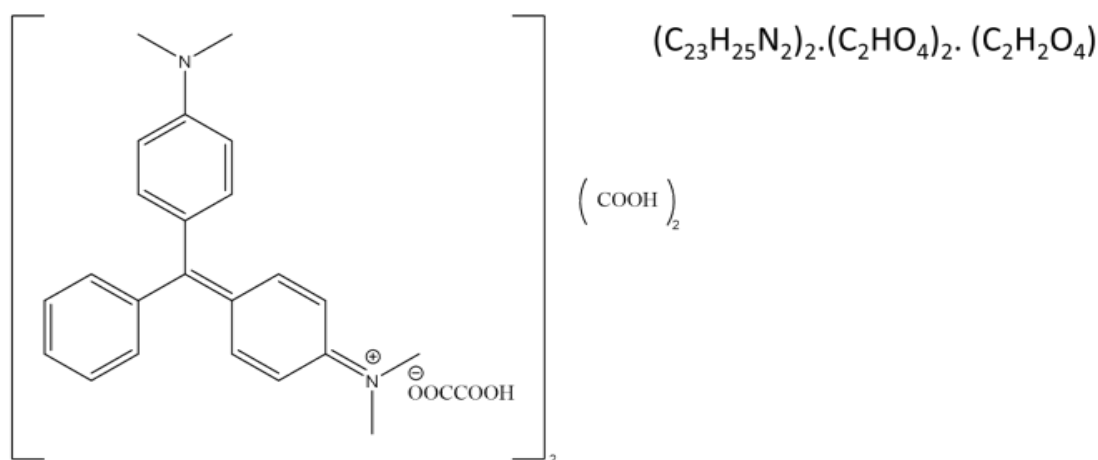


Figure 1: Malachite green oxalate chemical structure

Clay preparation

The clay used in this work comes from Es-sifa, Morocco. The clay is ground and sieved using ISO standard mesh sieves. Only a portion of particles smaller than $315 \mu\text{m}$ is kept for adsorption experiments.

Clay particles characterization

The REC was analyzed using X-ray diffraction and IR spectroscopy, as well as by determining pH_{pzc} .

The clay mineralogy was described using the X-ray powder diffraction method. The X-ray diffraction pattern was captured by an X'Pert PRO MPD wide-angle powder diffractometer equipped with a diffracted beam monochromator and Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$). To take the measurement, the 2θ angle was scanned in increments of 0.02° for 2 seconds, ranging from 10° to 30° .

The clay's vibrational spectra were analyzed with a VERTEX70 model instrument using the Attenuated Total Reflectance method for FTIR, in the $4000\text{-}400 \text{ cm}^{-1}$ region.

The charge on the surface of clay changes based on the solution pH. Thus, when pH equals pH_{pzc} , it is zero. In order to measure the pH_{pzc} , a series of 50 mL of NaCl solution at the concentration of 0.1 M was prepared, and their pH was adjusted with NaOH or HCl to values between 2 and 12. The sample was then added to each solution at an amount of 0.1 g. The suspensions were agitated at 25°C for 72 hours. The mixtures were then filtered, and the filtrate's equilibrium pH was measured using Accumet AB15 Basic pH meter. The pH_{pzc} is determined by

finding the intersection of bisector ($pH_f = pH_i$) with the curve of the final pH against the initial pH [5].

Batch adsorption experiments

This work aims to study the main adsorption parameters that may affect MG uptake on the REC: time of contact, temperature, stirring speed, initial concentration of adsorbent, and mass of adsorbate.

To examine the impact of the adsorption time on MG removal, a series of experiments was conducted. The experiment involved stirring 0.10 g of REC in 100 mL of a $5 \cdot 10^{-5}$ M MG solution at 250 rpm and 25 °C. The experiments were conducted within a time interval of 5 to 60 minutes. to determine the impact of adsorbent mass, the experiments were performed at 25 °C with a stirring speed of 250 rpm by varying the adsorbent mass from 5 to 25 mg at a concentration of $5 \cdot 10^{-5}$ M.

A number of tests were carried out at 25°C to look into the impact of the initial concentration of malachite green solution. 100 mL of MG solution was mixed with 0.10 g of clay was added to for each experiment, and the mixture was agitated at 250 rpm. The initial concentration was varied between $5 \cdot 10^{-6}$, and 10^{-4} M.

The effect of stirring speed was evaluated a three speeds 250, 500, and 750 rpm with an MG concentration of $5 \cdot 10^{-5}$ M, using a dose of 1 g/L at 25 °C.

Furthermore, experiments were conducted at 25, 35, and 45°C using 0.10 g adsorbent per 100 mL adsorbate of $5 \cdot 10^{-5}$ M MG concentration with 250 rpm stirring to study the temperature effect.

After each experiment, the mixture is filtrated, and the residual dye concentration is determined with Shimadzu, UV-160 UV/Visible spectrometer at 620 nm.

For calculated the adsorbed amount and adsorption efficiency, the following equations were utilized:

$$q_t = \frac{C_0 - C_t}{m} \times V_{MG} \quad (1)$$

$$R = \frac{C_0 - C_t}{C_0} \times 100 \quad (2)$$

Where R represents the adsorption efficiency (%), q_t , corresponds to the adsorbed amount of dye at t time (mg/g), C_e and C_0 reveal the t time residual and initial concentrations (M), respectively, m refers to the clay mass (g), V_{MG} is the malachite green solution volume (L).

Results and Discussion

Clay particles characterization

Fig. 2 depicts the REC diffractogram, which indicates the presence of several mineral phases. These include silica in the form of quartz (Q), kaolinite (K), dolomite (D), and calcite (C) [6–10].

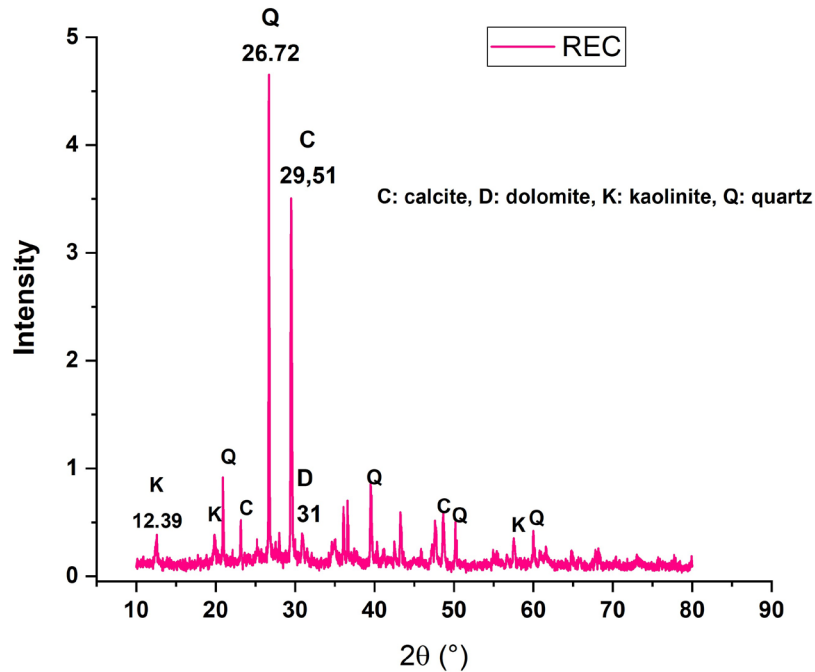


Figure 2: XRD pattern of REC

Fig. 3 presents the infrared spectrum of REC, which displays several absorption bands. The stretching vibration of the hydroxyl group in various settings (Al, AlOH), (Al, MgOH), or (Al, FeOH) is responsible for a band at 3619 cm^{-1} [11,12]. An additional band at 3420 cm^{-1} could be associated with the stretching and bending vibrations of H_2O that are adsorbed on the clay's surface and between its layers [13,14]. The deformation and elongation vibration of the calcite (CaCO_3) is responsible for the bands at 1799 , 1434 , 874 , and 713 cm^{-1} [15]. The deformation and elongation vibrations of the quartz are allocated for the bands at 778 and 692 cm^{-1} [16]. The bonds that characterize the deformation of the Si-O bond in quartz are respected in environments of 517 and 471 cm^{-1} [17,18].

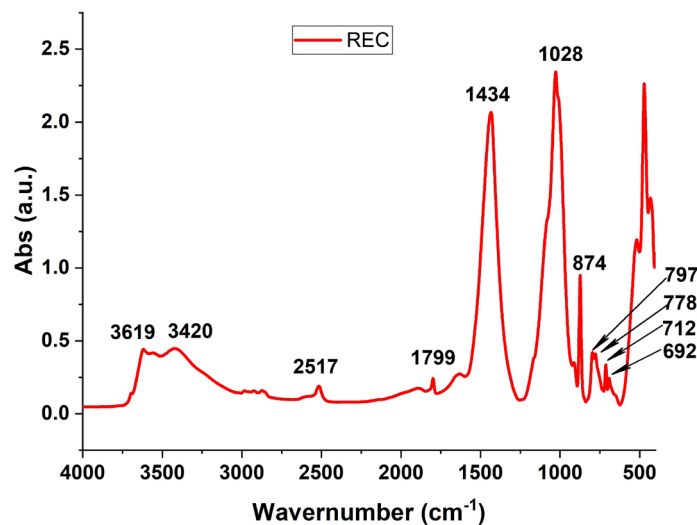


Figure 3: FTIR spectrum of REC

Fig. 4 shows that the pH at which the REC reaches zero charge, also known as pH_{pzc} , is 8.41. Below this pH, the REC surface is charged positively, while above it, the surface becomes

negatively charged. When malachite green is dissolved in water, it releases positively charged malachite green ions and negatively charged oxalate ions. The elimination of these ions can occur at pH both lower and higher than pH_{pzc} , but with different affinities. At a pH higher than pH_{pzc} , retention occurs due to the electrostatic interactions between the cations of malachite green and the negatively charged surface of the adsorbent. Additionally, hydrogen bonds form between the oxalate ions and the OH groups of the adsorbent. However, at a pH lower than pH_{pzc} , elimination takes place due to the hydrogen bond formation between the malachite green ion and the OH groups of the clay. The fixation of the oxalate ion can be done through electrostatic interactions with the surface and/or the formation of hydrogen bonds with the OH groups.

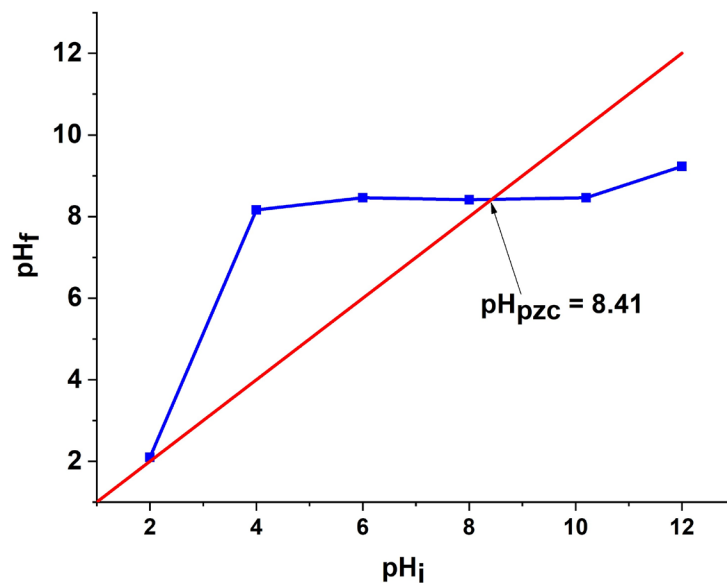


Figure 4: pH_{pzc} determination curve of the REC

Adsorption study

Adsorption is a process where a solute attaches to the surface of an adsorbent. This process is in a dynamic state when it reaches equilibrium. The nature of the adsorbent and the solute, as well as operational factors such as the time of contact, the adsorbate initial concentration, the mass of the adsorbent, the stirring rate, and the temperature of the medium, generally govern adsorption equilibrium. Therefore, it is crucial to study how these operational parameters affect the fixation of malachite green on REC.

Effect of contact time

Fig. 5 illustrate the impact of contact time on the adsorption efficiency of MG onto REC. The adsorbed amount rose rapidly in the first 5 minutes, reaching over 91 %. However, beyond 5 minutes, the adsorption efficiency of MG increased slowly, reaching equilibrium at about 40 minutes. This can be explained by the initial abundance of active sites which gradually became occupied over time, resulting in no significant difference in the adsorption efficiency [19].

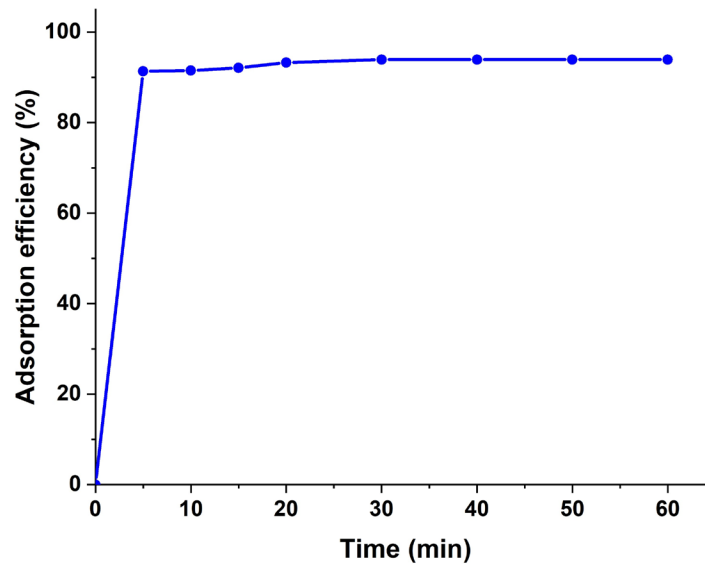


Figure 5: Contact time's impact on MG adsorption onto REC

Effect of adsorbent mass

In order to demonstrate how the adsorbent mass affects the MG retention, three different masses were tested: 0.05, 0.10, and 0.25 g. These masses were added to 100 mL of adsorbate with a concentration of $5 \cdot 10^{-5}$ M at varying contact times. After 40 minutes, equilibrium was reached for all three masses with different responses, as shown in Fig. 6. The results indicate that as the mass of adsorbent increases, the percentage of MG removal also increases. This can be explained by the increase in retention sites [14,20]. Based on these findings, a mass of 0.10 g REC/100 mL MG was determined to be the optimal mass for further parameter studies.

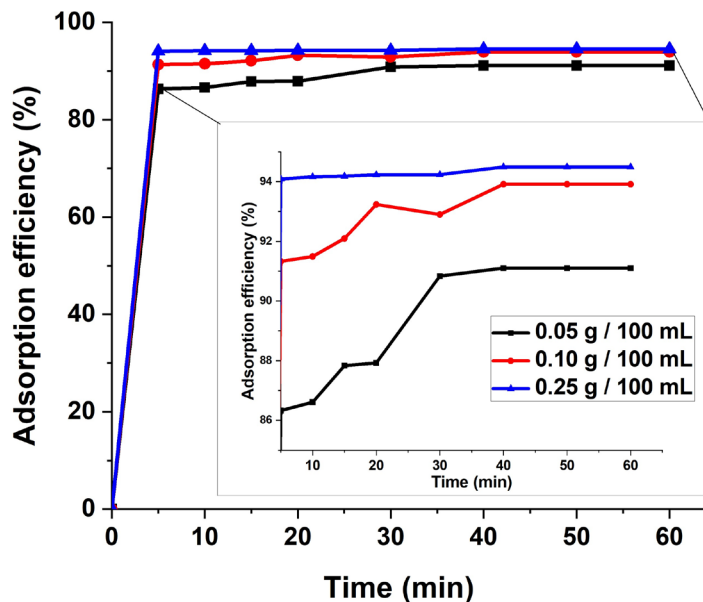


Figure 6: Adsorbent mass's effect on MG adsorption onto REC

Effect of MG initial concentration

The influence of the initial dye concentration on the adsorption of MG onto REC was investigated by altering the concentration within the range of $5 \cdot 10^{-6}$ to 10^{-4} M at various contact times, as illustrated in Fig. 7. The results indicated that an elevation in the concentration of the adsorbate led

to an increased quantity of adsorption. That can be related to the enhancement of driving force due to the concentration gradient [21]. The 10^{-4} M MG initial concentration yielded the highest adsorption capacity, 89.61 mg/g.

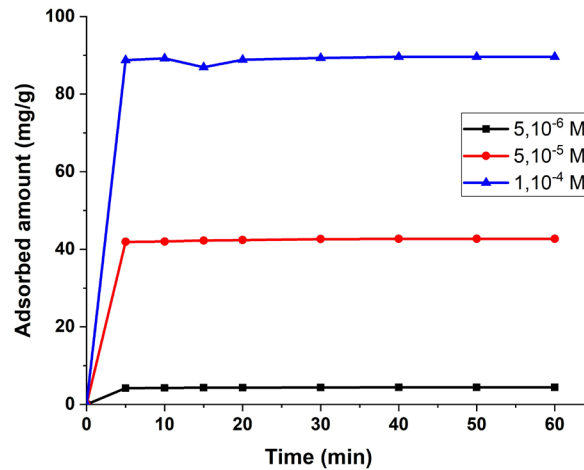


Figure 7: Initial dye concentration's impact on MG adsorption onto REC

Effect of agitation speed

Adsorption experiments were conducted at three different agitation speeds (250, 500, and 750 rpm) to investigate how agitation affects the adsorption of MG by REC. For each experiment, 0.10 g of the clay was added to 100 mL of a $5,10^{-5}$ M adsorbate solution at 25°C. The graphs depicting the variation of the adsorbed amount over time looked similar across all three speeds (Fig. 8). The adsorbed amount slightly increased with higher agitation speed, rising from 42.68 mg/g at 250 rpm to 43.17 mg/g at 750 rpm. This finding indicates that agitation speed does not significantly impact MG adsorption. Therefore, the optimal stirring speed for further parameter studies was selected as 250 rpm since it is sufficient to enhance contact between MG ions and REC particles.

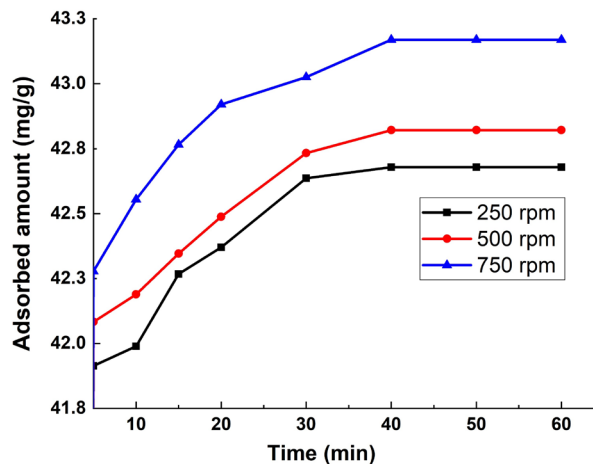


Figure 8: The impact of agitation speed on the MG adsorption onto REC

Effect of temperature

Fig. 9 illustrates how temperature changes affect MG adsorption onto REC. It was found that clay's adsorption capacity marginally increases with temperature. In fact, by raising the temperature from 25 to 45 °C, the amount adsorbed enhanced from 42.68 to 44.43 mg/g. That suggests that the MG adsorption process on REC is endothermic [22].

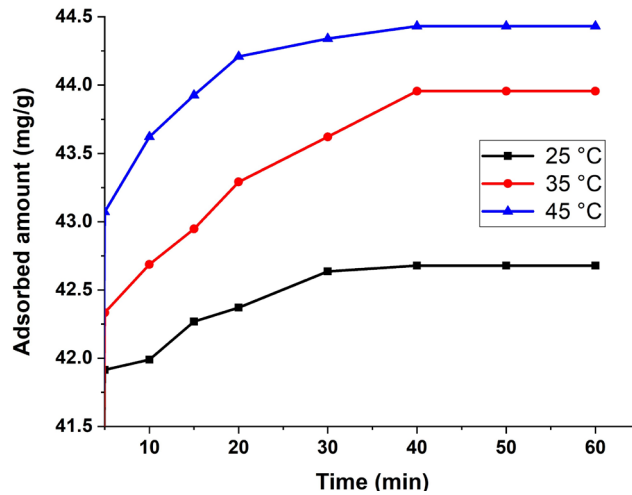


Figure 9: Temperature's impact on MG adsorption onto REC

Thermodynamic study

The thermodynamics of adsorption can be described by three parameters: entropy (ΔS°), standard enthalpy (ΔH°) and standard free energy (ΔG°). The values of ΔS° and ΔH° can be determined through the following equation:

$$\ln K_d = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \tag{3}$$

Where K_d represents the distribution coefficient ($K_d = q_e/C_e$), R (8314 J/mol K) and T (K) correspond to the gas constant and absolute temperature, respectively.

Plotting $\ln K_d$ against the inverse of temperature yields, from the slope and intercept, the values of enthalpy and entropy standards respectively (Fig. 10).

The following formula was used to get the standard free energy, ΔG° :

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{4}$$

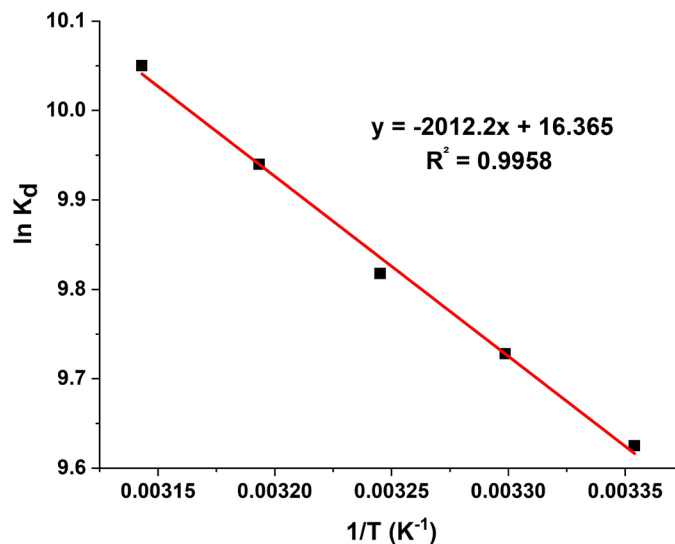


Figure 10: Van't Hoff plot for determining thermodynamic parameters

Table 1: shows the thermodynamic values obtained.

T (K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/ mol .K)
298	-23,859	16,729	136,067
308	-25,153		
318	-26,583		

According to Table 1, The MG adsorption process on the examined clay is spontaneous, as indicated by the negative values of ΔG° , and this spontaneity increases with temperature [23]. the positive sign's ΔS° value suggests that adsorption process increases disorder at the interface between the adsorbent and adsorbate. Additionally Values of ΔH° that are positive verify the endothermicity of the adsorption process[21].

FTIR characterization

Fig. 11 shows REC's FTIR spectrum following MG adsorption. Upon analyzing the spectra of the studied clay before and after adsorption (Figs 3 and 11), it was observed that the REC spectra were quite similar. However, after adsorption, the REC spectrum displayed characteristic low-intensity malachite green bands at 1615, 1586, and 1163 cm^{-1} . The first two peaks represent aromatic C-C stretching, while the third is associated with C-N stretching.

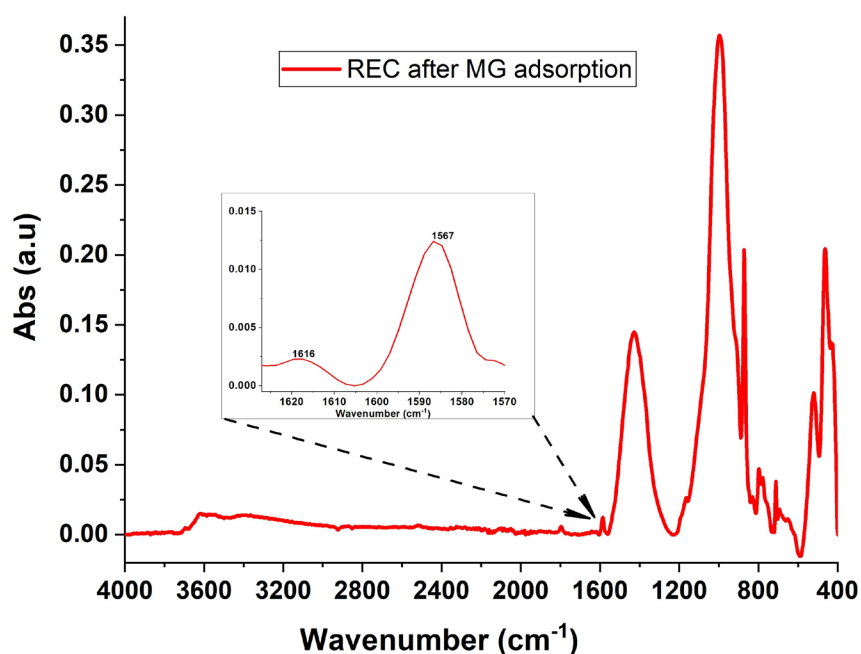


Figure 11: REC's FTIR spectrum following MG adsorption

Comparative study

It would be wise to compare REC's adsorption capacity with other adsorbents studied by other researchers to remove MG. The clay under investigation has a comparatively better adsorption capacity than the others, as indicated in Table 2, which implies that it may be applied as an inexpensive adsorbent for the additional cationic dyes' removal.

Table 2: Analysis of MG adsorption on various adsorbent materials

Adsorbent materials	q_{ads} (mg/g)	Reference
Fly ash	40.65	[24]
Rice husk activated carbon	49.62	[25]
Persian Kaolin	52.91	[26]
Centaurea solstitialis plants	91.00	[27]
Hen feathers	26.10	[28]
Iron humate	19.20	[29]
Bentonite	7.72	[30]
Activated slag	74.20	[31]
Sugar cane dust	4.88	[32]
Raw Es-sifa Clay	89.61	This work

Conclusion

The study shows that raw Es-sifa clay (REC) is effective in adsorbing MG. The adsorption capacity of REC is influenced by various reaction parameters. Among others, time of contact, adsorbent mass, initial concentration of dye, agitation speed, and the temperature of the medium. The MG adsorption process is fast, achieving equilibrium in about 40 minutes at an initial dye concentration of 10^{-4} M and reaching an adsorption capacity of 89.60 mg/g. Furthermore, endothermic and spontaneous adsorption processes are indicated by ΔG° and ΔH° negative values, respectively. A positive result for ΔS° depicted that, during the process, there is more disorder at the interface between the adsorbent and adsorbate. This study highlights that, in comparison to other adsorbents examined by other researchers, REC has a comparatively substantial adsorption capability. That shows that REC has the potential for MG adsorption. Based on these results, REC is a cost-effective option for removing MG dye and other cationic dyes.

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