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Outstanding Performance of a New Exfoliated Clay Impregnated with Rutile TiO₂ Nanoparticles Composite for Dyes Adsorption: Experimental and Theoretical Studies

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Abstract: Pure rutile TiO₂ nanoparticles (Rt) were combined with exfoliated black clay (BC) to prepare a new composite for water decontamination, in particular, for the uptake of methylene blue (MB) and methyl orange (MO) dyes. The as-prepared Rt/BC was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and Field emission scanning electron microscopy (FESEM) techniques, and the dyes' adsorption isotherms at three temperatures (i.e., 25, 40, and 50 °C) were studied. The results indicated that Rt/BC displayed a high removal performance for MO (96.7%) and MB (91.4%) at pH 3.0 and 8.0, respectively. Adsorption data of MB and MO were adjusted by a double layer model at all temperatures. The theoretical parameters of this statistical physics model were interpreted to understand the MO and MB adsorption mechanisms at the molecular level. The removed molecules per active site (*n*) of Rt/BC ranged from 1.12 to 1.29 for MB and 1.47 to 1.85 for MO, thus representing parallel orientation and multi-interactions mechanisms (i.e., van der Waals forces, hydrogen bonding, and electrostatic interactions were involved). The Rt/BC composite had a density of surface adsorption sites of 100 mg/g. The aggregation of MO molecules was high and increased their adsorption capacities ($Q_{sat} = 294\text{--}370$ mg/g) compared to that of MB ($Q_{sat} = 214\text{--}249$ mg/g). Adsorption energies were 9.70–20.15 kJ/mol, and these values indicated that MO and MB adsorption processes were endothermic and occurred via physical interactions. Overall, the low cost, high regeneration performance, and stability of Rt/BC support its application as a promising adsorbent for organic pollutants from wastewaters.

Keywords: black clay; rutile nanoparticles; dyes; adsorption; advanced statistical physics models; regeneration

1. Introduction

Different industrial activities, such as textiles, printing, food, and cosmetics, use organic dyes as coloring materials to supply products with distinctive colors [1–4]. In particular, anionic methyl orange (MO) and cationic methylene blue (MB) are documented as stable dyes under a wide range of light, heat, and chemical reagents, and thus, MO and

MB are involved in varied industries [1,5,6]. The discharge of effluents containing MB and MO into water resources without any treatment generates ecological impacts and human health risks. Accordingly, it is critical to find an effective manner to clean wastewaters containing MB and MO for attaining a healthy natural environment.

Numerous procedures, including biological treatment, advanced oxidation, adsorption, coagulation, ultrafiltration, or precipitation, were used to remove organic dyes from aqueous solutions [7–9]. The adsorption method is most common and preferred in water remediation due to its simple design, high efficiency, non-toxicity, and low cost [10–15]. However, the high cost of various adsorbents (e.g., carbon nanotubes and graphene oxide) usually inhibits their broad applications, and consequently, finding an eco-friendly adsorbent with high removal efficiency and low cost has become a required target.

Clays as accessible natural materials are characterized by high thermal and chemical stabilities, non-toxicity, and low cost [5]. Thus, clay-based adsorbents, such as smectite [16], kaolin [17], red mud [18], fibrous clay minerals [19], and Fe_3O_4 /serpentine [6], were utilized to MB uptake from contaminated water. Conversely, activated volcanic mud [7], bentonite-supported zero-valent iron [20], and surfactant-modified clay [5] were utilized for the uptake of MO dye. Furthermore, the activation of black clay using hydrogen peroxide resulted in being an adequate strategy to facilitate the insertion of different organic and/or inorganic modifiers in its structure, generating new effective adsorbents [5,21]. Moreover, TiO_2 nanoparticles are widely employed in decreasing the concentrations of dyes through degradation and adsorption techniques because of their chemical inertness, non-toxicity, and high capability of interaction with organics in waters [21–27]. Furthermore, the utilized TiO_2 nanoparticles were related to rutile (Rt) extracted with high purity by thermo-chemical activation of ilmenite ore (FeTiO_3) [28]. Consequently, the interface between the treated black clay and Rt nanoparticles is promising to prepare a new eco-friendly composite with abundant active adsorption sites for different environmental applications.

Analysis of the uptake data via equilibrium models is mandatory in understanding the physicochemical parameters that could control the adsorption mechanism [1,9,12,13,29–31]. Generally, the adsorbents-adsorbates interactions are commonly considered by applying classical models such as Langmuir, Freundlich, Sips, and others [1]. However, the parameters of these traditional models cannot offer a complete description and understanding of the adsorption mechanism of the adsorption system at hand [1,13,31]. For instance, the traditional classical isotherm models are inadequate to define the horizontal or vertical geometry of the removed chemical species [12,30].

Conversely, the energetic and steric parameters related to the advanced statistical physics models (ASPMs) can delineate the adsorption interactions between the investigated dyes and the adsorbent surface at a molecular scale [9,13]. Furthermore, the adsorption modeling with ASPMs can provide different parameters related to the removal mechanism, such as the number of molecules removed by one active site of the adsorbent (n), the active sites density of the adsorbent (D_M), the number of the removed layers of the adsorbate (N_t) and the adsorption capacity at saturation (Q_{sat}). Additionally, the adsorption energy (ΔE) can be determined via the ASPMs [1,13,31]. Therefore, in-depth and interesting results can be obtained from applying these ASPMs to fit the experimental data. The novelty of this research article was to prepare a promising adsorbent for the removal of MB and MO dyes via the combination between rutile (TiO_2) nanoparticles (Rt) and H_2O_2 -activated black clay (BC). Numerous techniques (e.g., XRD, FTIR, and FESEM) were used to study the physicochemical characteristics of this Rt/BC composite. In addition, the steric and energetic parameters from the advanced statistical physics models were employed to clarify the performance of Rt/BC for MB and MO dyes' removal and provide new insights on the adsorption mechanisms considering the molecular level.

2. Experimental

2.1. Reactants and Clay

The used black clay (BC) sample was collected from the Qalmasha area in Fayum governorate, Egypt. A mass (200 g) of the representative crushed BC was ground to obtain a sample size of less than 100 μm . Rutile nanoparticles (Rt) were attained via a thermochemical process, with at least 96% purity [28]. The tested adsorbates were: Methylene blue (MB, $\text{C}_{16}\text{H}_{18}\text{ClN}_3\text{S}$, λ_{max} 664 nm, 319.85 g/mol (Merck, Darmstadt, Germany), methyl orange (MO, $\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}$, λ_{max} 464 nm, 327.33 g/mol (Merck, Darmstadt, Germany). In addition, the next reactants were employed: H_2O_2 (30%), aqueous solutions of HCl, and NH_4OH . The molecular structures of studied dyes (MB and MO) are shown in Scheme 1.

Scheme 1. The molecular structures of the studied dyes.

2.2. Preparation of Rt/BC Adsorbent

The following process was used to modify the investigated clay with H_2O_2 : 3 g of the BC was added to a beaker containing 30 mL of deionized water with continuous stirring for 60 min. Then, 20 mL of 30% H_2O_2 was added to this BC/ H_2O mixture, stirring for 120 min at 40 $^\circ\text{C}$. First, H_2O_2 was used in oxidizing the organic carbon of the black clay, thus producing purified and exfoliated BC with open pits and cavities. Then, 1.0 g of the white Rt nanoparticles powder was introduced to the BC slurry, and the contents were magnetically agitated for 3 h at 45 $^\circ\text{C}$. Subsequently, centrifugation at 6000 rpm was used to separate the solid phase from the liquid phase. Next, the material was washed with distilled water before drying for 24 h at 65 $^\circ\text{C}$. Finally, the dried powder Rt/BC adsorbent was homogenized using a mortar.

2.3. Adsorbent Characterization

The Rt/BC adsorbent structure was determined by X-ray diffraction analysis (XRD) in the 2θ range of 5 $^\circ$ –80 $^\circ$ using a Philips diffractometer (APD-3720, Amsterdam, The Netherlands).

The functional groups related to the Rt/BC composite surface were identified in the 400–4000 cm^{-1} range via Fourier transmission infrared spectroscopy (FTIR) analysis using a Bruker spectrophotometer (Billerica, MA, USA).

Field-emission scanning electron microscopy (FESEM, Carl Zeiss, Jena, Germany) images of the Rt/BC material were recorded using a Sigma 500 VP, FESEM microscope.

The pH of the point of zero charge (pH_{PZC}) was determined as follows [9]: 50 mL of 0.1 M KCl was taken in a clean glass Erlenmeyer. The initial pHs (pH_i) of these solutions were adjusted at pH values ranging from 2.0 to 10.0. Then, an amount of 100 mg of Rt/BC material was introduced into 50 mL of 0.1 M KCl with previously adjusted pH values, and the slurries were stirred at 150 rpm for 24 h. Finally, the final solution pH (pH_f) was determined, and the relation between pH_f – pH_i versus pH_i was used to determine the pH_{PZC} (i.e., $\Delta\text{pH} = 0$).

2.4. Isotherm Studies of MB and MO Adsorption

Standard 25–250 mg/L MB and MO solutions were prepared from stock dye solutions (1000 mg/L). Isotherm studies of MB and MO adsorption were performed at pH 8.0 and 3.0, respectively, and three temperatures (25, 40, and 50 $^\circ\text{C}$) using 25 mg of Rt/BC adsorbent.

In the equilibrium experiments, the dye–Rt/BC suspensions were shaken at 150 rpm for 4 h using an orbital shaker. The following equation was used to obtain the dye adsorption capacities (q_e , mg/g) at equilibrium.

$$q_e = (C_0 - C_e) \frac{V}{m} \quad (1)$$

where m is the Rt/BC material mass (g), V is the dye (MB or MO) solution volume (L), C_e and C_0 (mg/L) are the equilibrium and initial dye concentrations, respectively. All MO and MB removal experiments were performed by duplicate, and the results were averaged for data analysis finding standard deviations less than 5.0%.

2.5. MB and MO Adsorption Modeling

This research paper applied different advanced statistical physics models (i.e., monolayer, double layer, and multilayer) to assess the interactions between dyes and Rt/BC. The appropriateness of these advanced models to fit MB and MO adsorption data was compared, and the best one was identified according to the determined coefficient R^2 values [13]. These advanced models are described as follows [9,13,31]:

- Advanced monolayer model (AMM)

In the AMM, the dyes adsorption on Rt/BC results in the formation of a single layer linked to a given interaction energy (ΔE) (i.e., Rt/BC adsorption sites have the same energy).

$$Q_e = \frac{nD_M}{1 + \left(\frac{C_{1/2}}{c}\right)^n} \quad (\text{advanced monolayer model}) \quad (2)$$

where $C_{1/2}$ is the concentration at half-saturation of the removed MB or MO layer.

- Advanced double layer model (ADM)

This model suggests that the removal of the tested dyes occurs due to the formation of two layers with two dissimilar adsorption energies (i.e., ΔE_1 for dye–Rt/BC interaction and ΔE_2 for dye–dye interface).

$$Q_e = nD_M \frac{\left(\frac{c}{c_1}\right)^n + 2\left(\frac{c}{c_2}\right)^{2n}}{1 + \left(\frac{c}{c_1}\right)^n + \left(\frac{c}{c_2}\right)^{2n}} \quad (\text{advanced double model}) \quad (3)$$

For ADM, two layers of each investigated dye were involved with two dye concentrations at half-saturation that were recognized as C_1 and C_2 , respectively.

- A multilayer model, as the general form of ASPMs, was also implemented in this study to fit the MB and MO adsorption processes. The following equations (Equations (4)–(9)) are used to determine the parameters of the multilayer model [9]:

$$Q = n D_M \frac{F_1(c) + F_2(c) + F_3(c) + F_4(c)}{G(c)} \quad (4)$$

$$F_1(c) = -\frac{2\left(\frac{c}{c_1}\right)^{2n}}{1 - \left(\frac{c}{c_1}\right)^n} + \frac{\left(\frac{c}{c_1}\right)^n \left(1 - \left(\frac{c}{c_1}\right)^{2n}\right)}{\left(1 - \left(\frac{c}{c_1}\right)^n\right)^2} \quad (5)$$

$$F_2(c) = \frac{2\left(\frac{c}{c_1}\right)^n \left(\frac{c}{c_2}\right)^n \left(1 - \left(\frac{c}{c_2}\right)^{N_2}\right)}{1 - \left(\frac{c}{c_2}\right)^n} \quad (6)$$

$$F_3(c) = -N_2 \frac{\left(\frac{c}{c_1}\right)^n \left(\frac{c}{c_2}\right)^n \left(\frac{c}{c_2}\right)^{n N_2}}{1 - \left(\frac{c}{c_2}\right)^n} \quad (7)$$

$$F_4(c) = \frac{\left(\frac{c}{c_1}\right)^n \left(\frac{c}{c_2}\right)^{2n} \left(1 - \left(\frac{c}{c_2}\right)^{n N_2}\right)}{\left(1 - \left(\frac{c}{c_2}\right)^n\right)^2} \quad (8)$$

$$G(c) = \frac{\left(1 - \left(\frac{c}{c_1}\right)^{2n}\right)}{1 - \left(\frac{c}{c_1}\right)^n} + \frac{\left(\frac{c}{c_1}\right)^n \left(\frac{c}{c_2}\right)^n \left(1 - \left(\frac{c}{c_2}\right)^{n N_2}\right)}{\left(1 - \left(\frac{c}{c_2}\right)^n\right)^2} \quad (9)$$

where the parameter N_2 designates the number of removed dye layers with specified energy of adsorption. Numerous situations were anticipated depending on the multilayer adsorption model as given in Figure 1 [13,31,32]:

Figure 1. The expected situations based on the multilayer adsorption model.

- Langmuir adsorption model: n parameter was fixed at 1, and N_2 was fixed at 0;
- Monolayer adsorption model: n was the fitted parameter, and N_2 was fixed at 0;
- Double-layer adsorption model: n was the fitted parameter, and N_2 was fixed at 1;
- Triple-layer adsorption model: n was the fitted parameter, and N_2 was fixed at 2;
- Multilayer adsorption model: n and N_2 were the fitted parameters.

The multilayer model suggests that the dye-Rt/BC interaction was related to dissimilar adsorption energies [13]. Thus, the primary energy of adsorption corresponds to the interaction between the first adsorbed dye layer and the active sites of the Rt/BC adsorbent. Conversely, the additional energy was linked to the dye-dye interaction. Therefore, the whole number of the removed dye layers is calculated by $N_t = 1 + N_2$ [31].

2.6. Regeneration of Rt/BC Adsorbent

In industrial processes, the use of an adsorbent numerous times is considered an essential concern for decreasing the water purification costs [21]. Therefore, in order to test the recycling of Rt/BC adsorbent, the adsorption-desorption cycle was performed 4 times. Firstly, the Rt/BC (50 mg) loaded adsorbent was thoroughly washed using distilled water and subsequently oven-dried for 24 h at 75 °C. Next, the desorption of the studied dyes was performed using 50 mL of 0.5 M NaOH eluent solution at 25 °C. Finally, a rotatory

shaker (SHO-2D shaker, Germany) agitated Rt/BC adsorbent loaded with MB and MO molecules for 240 min at 120 rpm.

3. Results and Discussion

3.1. Characterization of the Rt/BC Material

The XRD pattern of Rt/BC composite displays diffracting lines corresponding to black clay and titanium oxide rutile nanoparticles (Figure 2a). Montmorillonite (JCPDS 10-0357), in addition to kaolinite (JCPDS 78-2110), were identified as clay minerals [14]. Quartz (SiO_2), with its descriptive diffraction peaks at 3.37 and 4.26 Å (JCPDS 46-1045), was recognized as a common non-clay mineral (Figure 2a). The minor variations in the montmorillonite and kaolinite peaks intensities could be associated with the interface between rutile nanoparticles and H_2O_2 -activated black clay. Moreover, strong peaks were observed in the 2θ range 25° – 70° (Figure 2a), which agreed with TiO_2 Rt [21]. In particular, the three strong peaks detected at nearly 27° , 36° , and 55° indicated TiO_2 in the Rt phase (JCPDS 88-1175) [21].

Figure 2. (a) XRD pattern and (b) FTIR spectrum of Rt/BC material.

The vibrational infrared spectrum of the Rt/BC adsorbent displayed strong absorption bands at nearly 3625 and 3406 cm^{-1} (Figure 2b). These observed bands could be attributed to the stretching vibrations of Al–OH and –OH functional groups [14]. The observed band at 2377 cm^{-1} could be ascribed to the $\text{C}\equiv\text{C}$ of the organic carbon in the studied black clay [33]. The $\text{C}=\text{O}$ stretching band was observed at 1636 cm^{-1} , and the presence of this functional group in the BC sample could improve its removal efficiency for inorganic/organic compounds [34]. The observed band at 1035 cm^{-1} was assigned to the

stretching vibrations of Si–O, while the detected absorption band at 923 cm^{-1} was related to the bending vibrations of –OH groups in the Rt/BC composite [9]. Quartz mineral was identified by the vibration band detected at 790 cm^{-1} [14]. In addition, the broad and intense bands observed at 469, 533, and 679 cm^{-1} could be associated with the Ti–O and Ti–O–Ti stretching and bending vibrations [14]. These functional groups (i.e., active adsorption sites) agreed with the successful preparation of the Rt/BC composite.

The images of FESEM images of the Rt/BC material (Figure 3) displayed the existence of holes and cavities with different sizes and shapes. The observed cracks and fractures in the Rt/BC could be related to the activation of BC via H_2O_2 as an initial stage in the preparation of the Rt/BC adsorbent. This H_2O_2 -modification not only resulted in oxidizing the organic matter but also enhanced the separation of the clay minerals into thin sheets, mainly montmorillonite mineral due to its T–O–T structure (i.e., exfoliated clay); see Figure 3a–d. Furthermore, titanium oxide Rt was observed as an aggregate of several nanoparticles with dissimilar sizes below 100 nm (Figure 3e–f). Obviously, the physical combination between TiO_2 Rt and BC was clearly observed wherein the Rt nanoparticles were connected to the outer surface of BC clay and filled the cracks and holes of the BC sample (Figure 3a–f). Therefore, the existence of spherical-like Rt nanoparticles could be considered as a support to enhance the uptake of MO and MB species because of the improvement of the surface area of Rt/BC [21].

Figure 3. FESEM images of the Rt/BC material at different magnification scales. (a) exfoliated BC; (b,c) Rt/BC composite; (d–f) the aggregated Rt nanoparticles decorated BC sample.

3.2. pH Effect on MB and MO Adsorption by Rt/BC

The pH_{PZC} value of the Rt/BC composite is an important parameter to study the influence of solution pH in the removal of tested dyes. This pH_{PZC} was 5.4 (Figure 4), and therefore, Rt/BC adsorbent displayed different performances towards MO and MB dyes (i.e., at $\text{pH} > 5.5$, MO uptake% increased, while MB removal % decreased). Therefore, MB and MO dyes uptake by Rt/BC adsorbent as a function of pH is shown in Figure 4. At $\text{pH} 2.0\text{--}4.0$, the Rt/BC material was protonated because of the high concentrations of H^+ in pH solutions < 4.0 [5], and thus, the MO uptake % increased, presenting the maximum value (96.7%) at pH 3.0; see Figure 4. On the contrary, the MB removal % improved at $\text{pH} > 6$, reaching the maximum removal value (91.4% at pH 8) due to the deprotonation of Rt/BC functional groups, which could be negatively charged at a pH range of 8.0–10.0. Accordingly, the electrostatic forces (attraction or repulsion) between the Rt/BC functional groups (positively or negatively charged) and dyes were the main factors guiding the

MO and MB adsorption mechanisms. Nevertheless, the Rt/BC composite can capture MB molecules at pH 2.0–6.0 and MO molecules at pH 6–10, which could be related to the interactions with oxygen-functional groups present on the Rt/BC adsorbent [21]. Regarding the components of the investigated adsorbent (i.e., BC and Rt nanoparticles), the presence of $n-\pi$ and $\pi-\pi$ interactions in black clay resulted in increasing its adsorption capacities as compared to Rt TiO_2 nanoparticles because of the involvement of C=O and C=C groups in BC structure; see Figure 4. Therefore, the equilibrium MB and MO uptake experiments were carried out based on the pH results at solutions pH 8.0 and 3.0, respectively.

Figure 4. pH_{PZC} of the Rt/BC composite and pH effect on MB and MO dyes adsorption on Rt/BC adsorbent. Rt/BC composite displayed a high removal performance for MO (96.7%) and MB (91.4%) at pH 3.0 and 8.0, respectively.

3.3. MB and MO Adsorption Modeling and Mechanism Interpretation

After checking the advanced statistical physics model parameters, the double layer model was the best choice (i.e., R^2 ranged from 0.98 to 0.99) to describe the adsorption of MB and MO on the Rt/BC adsorbent as shown in Figure 5. Therefore, the adsorption mechanisms of MB and MO on Rt/BC were analyzed via this advanced model. Consequently, the removal efficiency and the adsorption mechanisms associated with dyes-Rt/BC interactions were analyzed by considering the steric and energetic fundamentals of the double layer adsorption model.

3.3.1. Steric Parameters

The steric parameter n represents the connected dyes (MB or MO) molecule numbers per functional group (active site) of the Rt/BC adsorbent. This parameter was utilized to recognize MB and MO molecules' geometry (i.e., horizontal or vertical) on the Rt/BC surface and their aggregation in solutions (i.e., before adsorption). Moreover, the dyes removal mechanism can be clearly identified by determining the value of the n parameter [12,30,31,35]. Thus, this steric parameter is employed to correct the assumption of the classical Langmuir equation, wherein n is equal to unity [12,30]. Overall, numerous scenarios related to the interface geometry between dyes molecules and the Rt/BC active sites can occur [12,30]:

- In the first scenario: $n \leq 0.5$, the molecules of each tested dye were linked to two or more active sites of the Rt/BC adsorbent (i.e., a horizontal adsorption geometry occurred).
- The second scenario: $0.5 < n < 1$, this behavior indicated that Rt/BC could remove MB or MO molecules with both adsorption orientations (i.e., horizontal and vertical) but with various proportions.
- In the last scenario: $n \geq 1$, this suggested that MB or MO dye can be adsorbed on Rt/BC through an entire vertical geometry.

Figure 5. Advanced statistical physics modeling of adsorption isotherms of MO and MB dyes on Rt/BC composite. The double layer model describe well (i.e., $R^2 > 0.98$) the adsorption of MB and MO on the Rt/BC adsorbent.

Furthermore, the MB and MO adsorption mechanisms on Rt/BC could be multi-molecular (i.e., one functional group of Rt/BC can remove numerous dye molecules if $n > 1$) or multi-docking (i.e., several adsorption sites of Rt/BC can capture one dye molecule when $n < 1$) [12,30,31,35]. Figure 6 shows the values of the n parameter at temperatures of 25, 40, and 50 °C, and the results are listed in Table 1. The n values were further than unity at all temperatures (i.e., 1.1–1.3 for MB and 1.5–1.8 for MO). Consequently, the vertical geometry (non-parallel orientation) and the multi-interactions mechanism were implicated in these adsorption systems. Molecules of organic water contaminants such as MB and MO can accumulate in solutions before the adsorption process (i.e., aggregation phenomenon) [21].

Table 1. Steric parameters of the double layer model for the adsorption of MB and MO on the Rt/BC composite.

T (°C)	Dye	n	D_M (mg/g)	Q_{sat} (mg/g)
25	MB	1.12	95.76	214.52
40	MB	1.18	100	235.9
50	MB	1.29	96.66	249.03
25	MO	1.47	100	294.5
40	MO	1.65	100	330.1
50	MO	1.85	100	370.37

Figure 6. Physicochemical parameters n , D_M , and Q_{sat} as a function of temperature for MB and MO adsorption on the Rt/BC adsorbent.

The increment of the n parameter with increasing temperature indicated that the solution's aggregation of MO and MB molecules was endothermic [1]. Additionally, the free movement of MO dye (molecular dimension of 1.2 nm) favored the MO-MO interface, and thus, its molecular aggregation was higher than that of MB dye [36]. Overall, the aggregation of MB and MO with temperature reflected that the uptake processes were energetically activated in aqueous solutions [30].

The D_M parameter signifies the active occupied active sites of the Rt/BC composite by MO and MB dye molecules. The influence of solution temperature on this parameter is described in Figure 5. The temperature effect in changing the value of D_M can be ignored (i.e., D_M was close to 100 mg/g for MB and MO) at all temperatures; see Figure 6 and Table 1. Thus, it can be concluded that the Rt/BC had a given density of surface functionalities, and the number of these adsorption sites did not change with temperature. Additionally, the addition of new active sites in the Rt/BC adsorbent cannot occur with increasing temperature (i.e., the number of adsorption sites was constant).

The adsorption capacities reflect the efficiency of Rt/BC to remove dye molecules at different experimental conditions. The impact of solution temperature on this steric parameter ($Q_{sat} = 2 \times n \times D_M$) is elucidated in Figure 6. The values of adsorption capacities define the performance of Rt/BC adsorbent to remove MB and MO molecules at 25, 40, and 50 °C. These values were 214.5 (25 °C), 235.9 (40 °C), and 249.0 mg/g (50 °C) for MB. On the other hand, the corresponding Q_{sat} values were 294.5 (25 °C), 330.1 (40 °C), and 370.4 mg/g (50 °C) for MO dye (Table 1). Generally, the increment of Q_{sat} values with temperature suggested that the interactions between the considered dyes (MB or MO) and Rt/BC adsorption sites were endothermic processes.

Thus, the temperature supported the adsorption capacities of MB and MO dyes, and this behavior can be associated with the increasing mobility of these dyes with the enhancing temperature, particularly the MO dye. The D_M values were nearly equal at all temperatures for adsorption of MB and MO dyes on Rt/BC; see Figure 6 and Table 1. Accordingly, the activated dyes molecules can interact with identified receptor sites (i.e., selective adsorption positions) in the investigated adsorbent. Therefore, the difference in the adsorption capacity could be related to the number of dye molecules that interact with each functional group. In addition, the diffusion of MO molecules in the Rt/BC pores can play a significant role in increasing the removed amounts of MO dye. This result could be associated with the different molecule sizes between MO and MB dyes and the functional groups of the tested dyes [37]. Moreover, both of the Q_{sat} and n parameters showed an equivalent trend (i.e., the two parameters increased with temperature). Consequently, the n parameter was the key steric factor that enhanced the Rt/BC adsorption performance towards MO dye.

The monolayer adsorption capacities (Q_{max}) resulted from the removal of MB and MO by numerous adsorbents, and their comparison with the performance of the Rt/BC composite is listed in Table 2. Note that MO and MB adsorption capacities were higher than those reported for other materials, such as natural, modified, and fabricated adsorbents. Therefore, the studied Rt/BC composite material presented outstanding adsorption properties for being utilized to remove dyes in aqueous solutions.

Table 2. MB and MO adsorption capacities of different adsorbents.

Adsorbent	Dye	Q_{max} (mg/g)	Reference
Graphene	MB	153	[38]
Kaolin	MB	45	[39]
Zeolite 4A	MB	22	[39]
Polydopamine microspheres	MB	90.7	[40]
Activated rice husk	MB	65	[41]
Ball clay	MB	25	[42]
Fe ₃ O ₄ /montmorillonite	MB	69	[43]
Rt/BC	MB	214.52	This study
Activated clay	MO	16.78	[44]
Treated coal powder	MO	18.52	[45]
Banana peel	MO	21	[46]
Nano-composite films	MO	29.41	[47]
Activated wheat straw	MO	50.4	[48]
CTAB/H ₂ O ₂ -clay	MO	194.3	[5]
Rt/BC composite	MO	294.50	The present study

3.3.2. Energetic Parameters for MB and MO Adsorption

Calculation of adsorption energy is recommended to understand the removal mechanism of MB and MO on Rt/BC composite. At 25, 40, and 50 °C, the adsorption energies (ΔE_1 and ΔE_2) associated with the formation of the two layers on this adsorbent were calculated using the next expressions [30,49,50].

$$C_1 = C_s e^{-\frac{\Delta E_1}{RT}} \quad (10)$$

$$C_2 = C_s e^{-\frac{\Delta E_2}{RT}} \quad (11)$$

where C_1 and C_2 are the half-saturation concentrations, and C_s is the solubility of the utilized dyes. Figure 7 displays the ΔE versus solution temperature, and the results are summarized in Table 3. Surface adsorption energies were positive (i.e., both ΔE_1 and ΔE_2 were positive), indicating that the removal of MB and MO was endothermic, which agreed with the temperature effect on the adsorption capacities. Additionally, the adsorption

energies associated with the removal of the investigated dyes were less than 30 kJ/mol representing physical forces (e.g., hydrogen bindings and van der Waals interactions) [12]. At all adsorption temperatures, values of ΔE_1 were higher than that of ΔE_2 for MB and MO; see Figure 7 and Table 3. This observation is because the ΔE_1 characterized the Rt/BC-dye interaction, while ΔE_2 characterized the dye-dye interaction (i.e., MB-MB or MO-MO) and, therefore, ΔE_1 values were always the highest.

Figure 7. Adsorption energies for (a) MB and (b) MO adsorption on Rt/BC adsorbent.

Table 3. Energetic parameters of the double layer model for the MB and MO uptake on Rt/BC composite.

T (°C)	Dye	C ₁	C ₂	ΔE_1 (kJ/mol)	ΔE_2 (kJ/mol)
25	MB	47.13	99.99	16.93	15.07
40	MB	36.57	99.47	18.44	15.84
50	MB	24.07	99.53	20.15	16.342
25	MO	27.76	100	12.87	9.7
40	MO	20.4	99.39	14.32	10.2
50	MO	12.78	89.61	16.03	10.8

3.4. Regeneration of Rt/BC Adsorbent

After all regeneration cycles, the as-synthesized Rt/BC composite presented removal percentages (%) more than 86% and 75% for MO and MB, respectively (Figure 8). Therefore, this adsorbent can be reused many times to remove both MO and MB dyes without significantly losing its performance, particularly for MO dye molecules. Overall, using accessible and low-cost raw materials to prepare effective adsorbents for the removal of organic/inorganic water pollutants is recommended. Concerning Rt/BC, pure Rt TiO₂ nanoparticles were obtained from Egyptian ilmenite and combined with black clay utilizing

a facile and low-cost method. According to the adsorption/desorption results, it can be suggested that Rt/BC is a prominent and highly stable adsorbent for the remediation of dyes-containing solutions.

Figure 8. Percentage of MB and MO removal during the adsorption/desorption cycles.

4. Conclusions

A composite of rutile TiO₂ nanoparticles (Rt) and exfoliated black clay (BC) was prepared, characterized, and utilized for the removal of dyes (methylene blue and methyl orange). Results of adsorption processes indicated that Rt/BC displayed high efficiency for MO removal compared to MB at the optimum pH value of each tested dye. The theoretical double layer model satisfactorily fitted the experimental data ($R^2 > 0.98$) at 25, 40, and 50 °C. The parallel orientation and multi-interactions mechanisms were involved in these adsorption systems. The aggregation of MO molecules was high, and this behavior was the main reason for enhancing the adsorption capacities of MO dye. MO and MB adsorption energies were less than 30 kJ/mol, suggesting endothermic adsorption processes governed by physical interactions. Overall, the interpretation of the theoretical parameters provided new insights into the MB and MO adsorption mechanisms. Decoration of H₂O₂-activated clay by rutile TiO₂ nanoparticles can be considered a prominent adsorbent for treating water and wastewater contaminated with dyes.

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