Preparation and characterization of a chitosan/MgO composite for the effective removal of reactive blue 19 dye from aqueous solution

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ABSTRACT

We developed a multi-functional adsorbent with excellent adsorption capacity and low contact time for reactive blue (RB) 19 dye removal. A multi-functional film based on chitosan (CS) combined with nanosized MgO was prepared by solvent casting with mild drying. The CS/MgO composite product was characterized by Fourier transform infrared spectroscopy, X-ray diffractometry, Field emission-scanning microscopy, and thermal gravimetric and differential thermal analyses. The adsorption properties of the CS/MgO film for RB 19 removal, including effects of key factors (i.e., adsorbent dosage, contact time, pH, initial dye concentration), adsorption equilibrium, and adsorption kinetics, were then investigated. Results showed that the adsorption performance of the CS/MgO film for RB 19 removal was strongly dependent on these factors. The optimal contact time for RB 19 removal by the CS/MgO film was 120 min, which is shorter than that required by other CS adsorbents. Moreover, the maximum adsorption capacities of the adsorbent were generally high (408.16, 485.43, and 512.82 mg g⁻¹ at 18, 28, and 38 °C, respectively). The equilibrium adsorption data could be best described by the Langmuir isotherm model, and the adsorption kinetics followed a pseudo second-order reaction. Thermodynamic parameters, such as changes in free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), indicated that adsorption by the CS/MgO film was spontaneous and endothermic.

1. Introduction

Reactive dyes are the most widely used dyes in the textile industry because they show typical characteristics, such as easy formation of covalent bonds with fibers and high color stability [1]. However, these dyes are also characterized by high solubility (i.e., they are easily hydrolyzed in water) and low degradability; thus, large amounts of dyes are often released into and persist in the environment [2]. The exact amount of the dyes wasted into the environment is unknown; however, up to 50% of reactive dyes may be lost to the effluent after their use in dyeing units, and the dye concentration in wastewater outlets may be as high as 10–200 mg L⁻¹ [3,4]. The existence of dyes in wastewater can cause environmental and health problems due to the high molecular weight, resistance, and toxicity of these colorants; moreover, they are highly toxic to aquatic organisms and pose a serious health risk to humans. Hence, the removal of the dyes from wastewater is a major problem that must be addressed for environmental protection.

Various methods have been investigated to remove dyes from textile wastewaters, and these methods can generally be classified as physical, chemical, biological, radiation, or electrochemical processes [1,4]. Unfortunately, most of these methods have low efficiency because reactive dyes are stable to light, chemicals, and biological degradation [5]. Adsorption is one of the most effective methods for dye treatment of textile wastewaters because of its simplicity, ease of operation, and high efficiency for dye removal [4,5]. Thus far, several types of synthetic and natural adsorbents, such as activated carbon [6], MgO [4,7], zeolite [8], bentonite [9], and chitosan (CS) [10], have been employed for dye removal from aqueous solutions. Each adsorbent has advantages and disadvantages. For instance, activated carbon is one of the most efficient adsorbents for dye removal from textile wastewaters, but its disadvantages include high production, regeneration, and reactivation costs [11]. Natural adsorbents, such as zeolite and bentonite, are used as alternative adsorbents for dye treatment, but they show
relatively low adsorption capacity [2]. CS is a cationic biopolymer produced from the deacetylation of chitin found in the exoskeletons of shrimps, crabs, and crustaceans [12]. CS is widely used as an adsorbent for contaminant removal in wastewaters due to its distinct advantages of non-toxicity, cost-effectiveness, biodegradability, and super-high adsorption capacity [12,13]. However, previous studies [14,15] have demonstrated that CS requires long contact times for dye degradation, which limits its use in practical applications. Therefore, CS is often combined with inorganic materials, such as metal oxides, to improve its application to adsorption processes [16–18]. MgO is a promising material for water purification due to its non-toxicity and chemical stability [19]. Previous studies have reported that MgO nanoparticles show much a lower adsorption capacity but substantially shorter contact time for dye adsorption compared with CS [4,7].

In the present work, we aimed to fabricate a multi-functional material that combines CS and nanosized MgO into a composite film to produce an effective adsorbent with high adsorption capacity and low contact time for reactive blue (RB) 19 dye removal. To this end, a CS/MgO composite film was prepared by solvent casting combined with mild drying and characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), Field-emission scanning electron microscopy (FE-SEM), and thermal gravimetric and differential thermal analyses (TGA/DTA). The effect of several factors (i.e., adsorbent dosage, solution pH, reaction time, initial dye concentration) on the removal of RB 19 was then determined, and the adsorption equilibrium of the CS/MgO composite film was evaluated via the Langmuir and Freundlich models. Finally, the adsorption kinetics and thermodynamics of the reaction system were investigated.

2. Experimental

2.1. Preparation and characterization of the CS/MgO composite film

All reagents were of analytical grade and used as received without further purification. MgCl$_2$·6H$_2$O, cetyltrimethylammonium bromide (CTAB), and RB 19 ($C_22H_{16}N_2Na_2O_11S_3$, molecular weight) were purchased from Sigma-Aldrich. CH$_3$COOH, NaOH, and HCl were obtained from Merck. CS (degree of deacetylation; low m) was obtained from Sigma–Aldrich. CH$_3$COOH, NaOH, and HCl were obtained from Merck. CS flakes (85% degree of deacetylation; low molecular weight) were purchased from Nha Trang Aquatic Institute (Vietnam). Double-distilled water was used for preparing all solutions and reagents.

MgO nanoparticles were prepared through the hydrothermal method assisted by the cationic surfactant CTAB at optimal conditions following our previous work [7]. Briefly, 2.2 g of CTAB was added to 40 mL of 0.2 M MgCl$_2$ solution, and 80 mL of 0.2 M NaOH was slowly added to this solution. The obtained mixture was stirred well with a magnetic stirrer for 4 h at 40 °C to obtain a white suspension, which was then placed in a 200 mL Teflon-lined stainless-steel autoclave and maintained for 24 h at 180 °C. The resulting white precipitate was collected, washed several times with double-distilled water, dried for 10 h at 50 °C, and calcined at 450 °C for 3 h to produce MgO powder.

The obtained MgO powder was used to synthesize the CS/MgO composite film. Briefly, 0.6 g of CS was dissolved in 30 mL of 2% (v/v) CH$_3$COOH on a magnetic stirrer for 3 h at room temperature to generate a 2% (w/v) CS solution. The resulting CS solution was brought to the pH range of 6–7 by an addition of 1 M NaOH solution. A suspension of 0.2 g of MgO in double-distilled water was added dropwise to the CS solution. The mixture was further stirred for 1 h at room temperature, cast into a 100 mm Petri dish, and then dried at 60 °C for 10 h to remove the CH$_3$COOH. The CS/MgO film obtained was detached, washed gently several times with distilled water, and dried at 40 °C to ensure that the solvent evaporated completely from the CS/MgO film. The film was stored in a desiccator for further experiments.

X-ray analyses of the CS/MgO film were performed on a Siemens D5005 diffractometer. The XRD patterns of the CS/MgO film and CS and MgO nanoparticles (for comparison) were recorded in the range of 20 ($10^{-70}$°) at a scan rate of 0.02°/s by using CuK$_\alpha$ radiation ($\lambda = 0.15406$ nm). FTIR spectra were measured on a Nicolet iS10 spectrometer using the KBr pellet technique in the range of 4000–400 cm$^{-1}$ and a resolution of 4 cm$^{-1}$. All measurements were performed at room temperature. The morphology of the CS/MgO film and the presence of MgO nanoparticles were examined by FE-SEM imaging at different magnifications (Nova NanoSEM 450, FEI). The thermal behavior of the CS/MgO composite film was determined by TGA/DTA analyses from 25 °C to 700 °C at a heating rate of 10 °C/min under nitrogen flow using a TG 209F1 Libra NETZSCH thermal analyzer.

2.2. Dye adsorption studies

Batch adsorption experiments were carried out to investigate the RB 19 adsorption capacity of the CS/MgO film. The effect of key factors, namely, adsorbent dosage, contact time, initial dye concentration, and solution pH, on the adsorption of RB 19 by the CS/MgO film was examined under the following conditions at room temperature (30 °C): adsorbent doses from 0.02 g to 0.16 g, contact times from 30 min to 180 min, initial dye concentrations from 100 mg L$^{-1}$ to 700 mg L$^{-1}$, and pH from 3 to 9 (adjusted by addition of 0.1 M HCl or 0.1 M NaOH). In a typical experiment, a desired amount of adsorbent was added to a closed glass flask containing 15 mL of the dye solution of a predefined concentration and stirred at a constant speed of 150 rpm. After stirring, the adsorbent sample was removed, and the dye concentration remaining in the supernatant was determined using a UV-vis spectrophotometer (Agilent 8453, USA) at a wavelength of 592 nm. The dye concentration was determined using a linear regression equation obtained by plotting a calibration curve of RB 19 within a range of known concentrations. The percentage of dye removal was determined using the following expression:

Percentage of dye removal (%) = \[ \frac{(C_0 - C_t)}{C_0} \times 100 \]  

where $C_0$ and $C_t$ represent the initial and final (i.e., after adsorption) dye concentrations, respectively. All tests were performed in triplicate, and the data reported reflect the average of triplicate measurements.

Isotherms describing the adsorption of RB 19 onto the CS/MgO adsorbent were studied at various temperatures. Dye solutions with various initial dye concentrations in the range of 100–700 mg L$^{-1}$ were stirred for 24 h at constant temperature (18, 28, and 38 °C) to attain equilibrium. Afterward, the residual dye concentration in the solutions was analyzed. Adsorption kinetics was then conducted for the initial dye concentration of 100 mg L$^{-1}$ at 27 °C and pH 7.76. The amount of dye adsorbed onto CS/MgO was calculated using the mass balance equation:

\[ q_e = \frac{(C_0 - C_e)}{m} V, \quad q_t = \frac{(C_0 - C_t)}{m} V \]  

where $C_0$, $C_e$, and $C_t$ are dye concentrations at initial, equilibrium, and t (mg L$^{-1}$), respectively; $V$ is the solution volume (L), and $m$ is the mass of the adsorbent used (g).
3. Results and discussion

3.1. Characterization of the CS/MgO composite film

The structures of the CS/MgO nanocomposite film were analyzed using FTIR and XRD. Fig. 1 shows the FTIR spectra of the CS–MgO composite film and pure MgO. The FTIR spectrum of the MgO powder (Fig. 1a) exhibited characteristic bands at 3696, 3433, and 1639 cm$^{-1}$, which are attributed to the O–H stretching and bending vibrations of water molecules [20,21]. The bands at 1446 and 864 cm$^{-1}$ were assigned to carbonate species chemisorbed on the surface of MgO [21], and the major bands at 666 and 409 cm$^{-1}$ indicated the Mg–O vibrations of MgO [20]. The FTIR spectrum of the CS/MgO film (Fig. 1b) showed visible bands at 3697, 3359, 3292, 2878, 1649, 1557, 1418, 1377, 1148, 1062, 1029, 894, 667, 591, and 553 cm$^{-1}$. The bands at 3697 and 1649 cm$^{-1}$ indicated the O–H stretching vibrations of water molecules, while the bands at 3359 cm$^{-1}$ were assigned to the N–H stretching vibrations of –NH$_2$ of CS. The band at 1557 cm$^{-1}$ indicated N–H bending vibrations. The band observed at 2878 cm$^{-1}$ and those observed at 1418 and 1377 cm$^{-1}$ could respectively be attributed to the C–H stretching and bending vibrations of –CH$_2$ or –CH$_3$. Three bands at 1148, 1062, and 1029 cm$^{-1}$ indicated the asymmetric and symmetric C–O stretching vibrations of the C–O–C linkage [14], and the small band at 894 cm$^{-1}$ was attributed to the vibrations of the saccharide structure of CS [22]. The characteristic bands at 667, 591, and 553 cm$^{-1}$ shifted toward higher wavenumbers compared with those in the FTIR spectrum of MgO and verify the Mg–O vibrations of the CS/MgO composite. These results confirm that the CS phase serves as a matrix on which the MgO nanoparticles assemble and indicate that some intermolecular interactions may occur between CS and MgO in the composite.

The structural phases of the CS/MgO film were determined by XRD analyses. Fig. 2 compares the XRD patterns of CS/MgO, MgO powder, and CS. The XRD pattern of CS (Fig. 2b) was characterized by a broad peak at 20 = 19.92°, thus revealing that the polymer is amorphous. The XRD pattern of the CS/MgO film (Fig. 2c) shows a broader peak at about 20 = 20°, which is assigned to amorphous CS in the CS/MgO composite film. In addition to the broad peak at 20 = 20°, the diffraction peaks at 20 of 39.97°, 58.91°, and 62.15° in the XRD pattern of the CS/MgO film matched the cubic lattice of MgO (ICPD No. 4-829) well and could be indexed to the (111), (110), and (220) planes, respectively, of the oxide. The XRD pattern of pure MgO powder (Fig. 2a) showed typical crystalline peaks with high intensity at 20 of 37.72°, 42.76°, 58.81°, and 62.08°. Compared with those in the XRD pattern of pure MgO powder, the characteristic peaks of MgO shifted toward higher 20, and the peak at 42.76° was not observed in the XRD pattern of the CS/MgO film. Moreover, the intensity of the characteristic peaks of MgO considerably decreased in the CS/MgO film compared with those of pure MgO (Fig. 2a,c). These results suggest that MgO nanoparticles were successfully dispersed into the CS matrix to produce the CS/MgO composite.

The surface morphology of the CS/MgO film and the existence of MgO nanoparticles in the film were investigated by FE-SEM. The FE-SEM images of the CS/MgO chitosan film at low and high magnifications are presented in Fig. 3. The FE-SEM image at low magnification of 20 k (Fig. 3a) illustrates the CS/MgO film was characterized by rough and folded morphology, containing numerous small openings and slit-shaped holes on the surface. From Fig. 3a, it can also be seen that MgO nanoparticles were dispersed on the film surface. The insert in Fig. 3b indicated that MgO nanoparticles were hexagonal-like platelets with average sizes of 75 nm in diameter and 27 nm in thickness. It is noticeable that edges of numerous MgO nanoparticles can be observed from the FE-SEM image at a higher magnification of 50 k (Fig. 3b), which confirmed that the MgO nanoparticles were embedded in the CS matrix. The thermal stability of the CS/MgO composite film was shown in Fig. 3c. A small mass loss within the temperature interval of 25–100 °C could be attributed to the removal of adsorbed water on the surface. At the temperature region of 250–350 °C, the weight loss of 36% was due to the thermal decomposition of –NH$_2$ and –CH$_2$OH groups of CS, while the weight loss of 24% in the region of 350–600 °C could be due to the degradation of saccharide ring of CS. The previous study reported that the degradation of pure CS film occurred in the temperature range of 210–360 °C during which the weight loss was about 50% [23]. Our results indicated that the incorporation of MgO nanoparticles has improved the thermal stability of the composite film, which could be due to the high thermal stability of MgO and the distribution of MgO. The dispersion of MgO within the CS matrix can act as a barrier to prevent the diffusion of thermally degraded products of CS, which results in a delay of mass transport.

3.2. Dye adsorption properties

3.2.1. Effect of some key factors on RB 19 adsorption by the CS/MgO film

Adsorbent dosage is an important factor that must be carefully adjusted in wastewater treatment. The effect of adsorbent dosage
on the adsorption of RB 19 was studied by varying the dosage of the CS/MgO film from 0.02 g to 0.16 g while maintaining all other conditions constant (i.e., initial dye concentration $C_0 = 100 \text{ mg L}^{-1}$, contact time $= 60 \text{ min}$, natural pH, temperature $= 30^\circ \text{C}$). Fig. 4a shows that the percentage of RB 19 removal increased from 18.67% to 58.70% as the adsorbent dosage increased from 0.02 g to 0.14 g. This increase is attributed to the increased adsorbent surface area and greater availability of adsorption sites as the adsorbent dosage is increased. However, further increases in adsorbent dosage up to 0.16 g had minimal effects on dye removal. Specifically, the percentage of dye removal increased only slightly from 58.70% to 59.82% as the adsorbent dosage increased from 0.14 g to 0.16 g. Hence, the optimum dosage of the CS/MgO film for RB 19 removal is 0.14 g.

The contact time between the adsorbent and adsorbate is another parameter that plays a vital role in adsorption processes. The effect of contact time on the performance of the CS/MgO film in adsorbing RB 19 was investigated while all other parameters were fixed (i.e., initial dye concentration of 100 mg L$^{-1}$, optimal value of adsorbent dosage, and natural pH). Fig. 4b shows that the percentage of dye removal increased only slightly from 58.70% to 59.82% as the adsorbent dosage increased from 0.14 g to 0.16 g. The contact time between the adsorbent and adsorbate is another parameter that plays a vital role in adsorption processes. The effect of contact time on the performance of the CS/MgO film in adsorbing RB 19 was investigated while all other parameters were fixed (i.e., initial dye concentration of 100 mg L$^{-1}$, optimal value of adsorbent dosage, and natural pH). Fig. 4b shows that the percentage of dye removal increased only slightly from 58.70% to 59.82% as the adsorbent dosage increased from 0.14 g to 0.16 g. Further increases in adsorbent dosage up to 0.16 g had minimal effects on dye removal. Specifically, the percentage of dye removal increased only slightly from 58.70% to 59.82% as the adsorbent dosage increased from 0.14 g to 0.16 g. Hence, the optimum dosage of the CS/MgO film for RB 19 removal is 0.14 g.

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The effect of solution pH on dye removal by the CS/MgO film was studied at pH ranging from 3 to 9 (Fig. 4c). Adsorption of RB 19 on the CS/MgO film was pH dependent. The results in Fig. 4c show that the percentage of dye removal fluctuated as pH increased from 3 to 7. The dye removal percentage remained high (66%–77.62%) within pH 3–7, and the maximum adsorption of RB 19 (77.62%) was observed at pH 7. This result may be due to the predominance of electrostatic interactions between the negatively charged $-\text{SO}_3^-$ groups of the dye molecules and the positively charged $-\text{CS/MgO}$ composite at pH 3–7. Further increases in pH caused a dramatic decrease in dye removal efficiency, and the removal percentage of RB 19 decreased to 71.48% at pH 9. Conversely, at high pH, hydroxyl ($-\text{OH}^-$) ions compete with the dye for adsorption sites on the surface of the CS/MgO composite and lead to decreased RB 19 removal. These results thus suggest that the optimum pH for dye removal is 7.

The initial dye concentration is an important parameter affecting the adsorption of dye molecules. In this study, the effect of various initial dye concentrations from 100 mg L$^{-1}$ to 700 mg L$^{-1}$ on dye removal by the CS/MgO film was evaluated, and the results are shown in Fig. 4d. When the concentration of RB 19 was increased from 100 mg L$^{-1}$ to 700 mg L$^{-1}$, the percentage of dye removal decreased gradually from 77.07% to 58.86%. However, the dye concentration in textile wastewater normally ranges from 100 mg L$^{-1}$ to 200 mg L$^{-1}$. Thus, 100 mg L$^{-1}$ was selected as the optimal dye concentration.

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3.2.2. Adsorption isotherms

Adsorption isotherms are functional expressions correlating the amount of solute adsorbed per unit weight of the adsorbent and the concentration of adsorbate in bulk solution at a given temperature under equilibrium conditions. Adsorption isotherms provide useful data representing the adsorption characteristics of a particular adsorbent and are very important for modeling and designing adsorption processes [24]. Several models have been suggested to interpret adsorption equilibrium, among which the Langmuir and Freundlich isotherm models are most commonly used to describe this state. The Langmuir isotherm model assumes a monolayer coverage of adsorbate on a homogeneous adsorbent surface, and adsorption occurs at a specific site of the adsorbent. The linear form of the Langmuir can be described with the following equation [25]:

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_{\text{max}}} + \frac{C_e}{q_{\text{max}}}
\]

where \(q_{\text{max}}\) is the maximum adsorption capacity with complete monolayer coverage on the adsorbent surface (mg g\(^{-1}\)), \(K_L\) (L mg\(^{-1}\)) is a Langmuir constant related to the affinity of binding sites of the adsorption, and \(q_{\text{max}}\) and \(K_L\) are determined from the linear plot of \(C_e/q_e\) versus \(C_e\).

The Freundlich isotherm is used to describe a multilayer coverage of adsorbate on a heterogeneous adsorbent surface. The logarithmic form of the Freundlich isotherm is provided in the following equation [27]:

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

where \(K_F\) (L mg\(^{-1}\)) and \(n\) are Freundlich constants related to the capacity of the adsorbent for the adsorbate and adsorption intensity.

In this study, the adsorption isotherms were studied at different temperatures (18, 28, and 38 °C) and various dye concentrations ranging from 100 mg L\(^{-1}\) to 700 mg L\(^{-1}\) to evaluate the adsorption characteristics of the CS/MgO composite film. The equilibrium data of RB 19 adsorption onto the CS/MgO film were then analyzed by using the Langmuir and Freundlich isotherm models. Fig. 5(I)/(II) show Langmuir and Freundlich isotherm plots for the adsorption of RB 19 onto the CS/MgO film at various temperatures. The constants and correlation coefficients (\(R^2\)) obtained from these plots are listed in Table 1. The obtained adsorption data could be successfully fitted to both models because the \(R^2\) values of these models are consistently higher than 0.95 (except for the Langmuir isotherm at 38 °C, \(R^2 = 0.9154\)). Table 1 shows that \(q_{\text{max}}\) and \(K_L\) obtained from the Langmuir isotherm increases with increasing adsorption temperature from 18 °C to 38 °C and that the values of \(R_l\) in the range of 0 < \(R_l\) < 1, thereby indicating that the adsorption of RB 19 by the CS/MgO composite film is favorable at all temperatures.

Fig. 4. Effect of some key parameters on the dye adsorption by the CS/MgO film at 30 °C: (a) Effect of the adsorbent dosage (Conditions: Initial dye concentration = 100 mg L\(^{-1}\), contact time = 60 min, and natural pH); (b) Effect of contact time (Conditions: Initial dye concentration = 100 mg L\(^{-1}\), adsorbent dosage = 0.14 g, and natural pH); (c) Effect of pH (Conditions: Initial dye concentration = 100 mg L\(^{-1}\), adsorbent dosage = 0.14 g, and contact time = 120 min), and (d) Effect of initial dye concentration (Contact time = 120 min, adsorbent dosage = 0.14 g, and pH = 7).
film is favorable within the range of 18°C–38°C. The results of the Freundlich model reveal the same trend for KF, i.e., KF values also increased with increasing adsorption temperature, indicating a corresponding increase in the adsorption capacity of the CS/MgO film with increasing temperature. The parameter n or 1/n is related to the degree of heterogeneity. When the value of 1/n is close or equal to 1, the adsorbent has a large number of homogeneous binding sites [28]. The values of 1/n obtained for the adsorption of RB 19 by the CS/MgO film at 18, 28, and 38°C were 0.917, 0.925, and 0.934, respectively. These values are very close to 1 and reveal the homogeneous nature of the binding sites of the CS/MgO. The results obtained thus far suggest that the adsorption of RB 19 onto the CS/MgO film could be better described by the Langmuir model than by the Freundlich model.

Table 2 compares the adsorption capacities of the prepared CS/MgO film with those of previously reported CS beads, CS films, nanosized MgO, and other metal oxides. The reported CS films and beads showed very high adsorption capacities. For example, the CS films showed extremely high adsorption capacity for RB 19 [14], while the CS beads revealed very high adsorption capacity for RB 4 [15]. However, CS materials require very long adsorption times to remove reactive dyes (about 150 and 300 min for CS films and CS beads, respectively). The nanosized MgO materials [4,7] exhibited substantially lower adsorption capacities for the reactive dye compared with the CS materials, but the adsorption time required by the former was shorter than that of the latter. Moreover, recent works reported that nanoflakes CuO and NiO [29], and nanocomposite graphene oxide/ZnO [30] also showed much lower adsorption capacities for dyes than those of the CS materials. In the present work, the CS/MgO composite film showed a larger adsorption capacity for RB 19 compared with that of the nanosized MgO and a shorter adsorption time compared with that of the CS material. Such excellent adsorption performance could be attributed to the presence of numerous functional groups on the CS material, and the short adsorption time observed may be due to the presence of MgO nanoparticles, which hasten the internal diffusion rate of dye molecules into the pores of the adsorbent and improve the adsorption rate of the adsorbate on the CS/MgO film.

3.2.3. Adsorption thermodynamics

The adsorption thermodynamics was studied to determine the effect of temperature on the adsorption of RB 19 onto the CS/MgO film.

**Table 1** Langmuir and Freundlich isotherm constants for the adsorption of RB 19 onto the CS/MgO film at different temperatures.

| Temperature | Langmuir | Freundlich |
|-------------|----------|------------|
|             | $q_{\text{max}}$ (mg.g$^{-1}$) | $K_L$ (L.mg$^{-1}$) | $R^2$ | $R_L$ | $K_F$ (L.mg$^{-1}$) | $n$ | $R^2$ |
| 18°C        | 408.16   | 0.0127     | 0.9544 | 0.1–0.44 | 5.55 | 1.09 | 0.9992 |
| 28°C        | 485.43   | 0.0156     | 0.9602 | 0.083–0.39 | 7.76 | 1.08 | 0.9997 |
| 38°C        | 512.82   | 0.0187     | 0.9154 | 0.071–0.34 | 9.61 | 1.07 | 0.9991 |

**Table 2** Adsorption capacities of dyes on chitosan, MgO, chitosan/MgO composite, and other metal oxides.

| Adsorbents                  | Conditions | Adsorption capacity (mg.g$^{-1}$) | The adsorption time, min | References |
|-----------------------------|------------|-----------------------------------|--------------------------|------------|
| Chitosan films              | 20°C, pH 6.8 | 799                                | 150                      | [14]       |
| Hexagonal nanosized MgO     | 18°C, pH 7.76 | 250                                | 20                       | [7]        |
| Nanosized MgO               | 25°C, pH 8  | 166                                | 5                        | [4]        |
| Chitosan beads              | 30°C, pH 4  | 317                                | 300                      | [15]       |
| Nanoflakes CuO              | 30°C, pH 2  | 158.73                             | 120                      | [29]       |
| Nanoflakes NiO              | 30°C, pH 2  | 158.73                             | 120                      | [29]       |
| Graphene oxide/ZnO          | 30°C, pH 6  | 265.95                             | 90                       | [30]       |
| Chitosan/MgO                | 18°C, pH 7.75 | 408.16                             | 120                      | This work  |
film and the energy change of the adsorption process. Changes in several thermodynamic parameters, such as free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°), were determined using the Van't Hoff equations [31]:

\[ \Delta G^0 = -RT \ln K_L \]  
\[ \ln K_L = \frac{-\Delta H^0}{R T} + \frac{\Delta S^0}{R} \]

where R is the ideal gas constant (8.314 J mol⁻¹.K⁻¹), T is the adsorption temperature (°K), and K_L (L mol⁻¹) is the Langmuir constant. ΔH° and ΔS° are constant within the temperature range studied (18–38 °C), and their values could be obtained from the slope and intercept of the Van’t Hoff linear plot of lnK_L versus 1/T.

![Fig. 6. Van’t Hoff linear plot of lnK_L versus 1/T.](image)

Table 3
Thermodynamics parameters of the adsorption of RB19 onto the CS/MgO film.

| T (°K) | K_L (L mol⁻¹) | ΔG° (kJ mol⁻¹) | ΔH° (kJ mol⁻¹) | ΔS°(kJ mol⁻¹ K⁻¹) |
|-------|---------------|----------------|----------------|-------------------|
| 291   | 7956.55       | -21.73         | 14.56          | 0.125             |
| 301   | 9773.4        | -22.99         |                |                   |
| 311   | 17115.55      | -24.22         |                |                   |

(6.1) R² = 0.999. All of the thermodynamic parameters of RB 19 adsorption onto the CS/MgO film are presented in Table 3. The ΔG° values obtained at adsorption temperatures of 18, 28, and 38 °C were -21.73, -22.99, and -24.22 kJ mol⁻¹, respectively. The negative value of ΔG° reflects the feasibility and spontaneous nature of RB 19 adsorption in the range of temperatures studied. Moreover, the observed increase in the negative value of ΔG° as temperature increases reveals that adsorption occurs more favorably at elevated temperatures. The positive value of ΔH° (14.56 kJ mol⁻¹) confirms that RB 19 adsorption onto the CS/MgO film is an endothermic process. The positive value of ΔS° (0.125 kJ mol⁻¹ K⁻¹) reveals an increase in randomness of the solid/solution interface during RB 19 adsorption onto the CS/MgO film, which is related to an increase in adsorbent surface heterogeneity.

3.2.4. Adsorption kinetics

Adsorption kinetics is one of the most important characteristics describing the adsorption efficiency of an adsorbent for designing and optimizing adsorption systems [32]. In this work, the adsorption kinetics on the CS/MgO film was investigated by using the Lagergren pseudo first- and second-order equations to fit the experimental data; these equations are described in Eqs. (7) and (8), respectively:

\[ \ln(q_e - q_t) = \ln q_e - k_1 t \]  
\[ \frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]

where k_1 is the rate constant of the pseudo first-order adsorption (min⁻¹), k_2 is the rate constant of the pseudo second-order adsorption (g mg⁻¹ min⁻¹), t is the adsorption time (min), and q_t and q_e are the adsorption capacities at time t and equilibrium, respectively (mg g⁻¹).

Linear plots of the Lagergren pseudo first- and second-order kinetic models for RB 19 adsorption onto the CS/MgO film are shown in Fig. 7a,b, respectively, and the kinetic parameters and R² of both models are summarized in Table 4. A good linear plot with an R² of 0.9775 was obtained for the pseudo second-order reaction model; indeed, this R² is higher than that of the pseudo first-order reaction model (R² = 0.7287). Moreover, the calculated adsorption capacities q_e,cal (8.55 mg g⁻¹, Table 4) obtained from the pseudo second-order model were closer to the experimental data q_e,exp (10.47 mg g⁻¹) than those of the Lagergren first-order model.
(Table 4). These results imply that the adsorption rates of RB 19 dye onto the CS/MgO film can be appropriately described by using the pseudo second-order kinetic model. This finding supports the supposition that chemisorption involving valence forces between dye anions and the adsorbent controls the adsorption kinetics of the present system.

4. Conclusion

This work demonstrated the fabrication of a CS/MgO composite film by solvent casting with mild drying. The composite film was investigated as a novel adsorbent for RB 19 removal, and it was found that the adsorption performance of the CS/MgO film during dye removal is higher than those of the CS materials and nanosized MgO reported in the literature. The CS/MgO film exhibited high adsorption capacities (408.16, 485.43, and 512.82 mg g⁻¹ at 18, 28, and 38 °C, respectively) for RB 19 removal. Moreover, the optimal contact time for RB 19 removal by the composite film was 120 min, which is shorter than the time required by other CS adsorbents. This study provides a facile route for the fabrication of an effective adsorbent for dye removal from textile wastewaters.

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References

[1] V.K. Gupta, Suhas, Application of low-cost adsorbents for dye removal – a review, J. Environ. Manag. 90 (2009) 2311–2342.
[2] G. Gok, A.S. Ozcan, A. Ozcan, Adsorption behavior of a textile dye of Reactive Blue 19 from aqueous solutions onto modified bentonite, Appl. Surf. Sci. 256 (2010) 5439–5443.
[3] M. Malakootian, H.J. Mansoorian, A. Hosseini, N. Khajani, Evaluating the ef- ficiency of alumina/carbon nanotube hybrid adsorbents in removing Azo Reactive Red 198 and Blue 19 dyes from aqueous solutions, Process Saf. Environ. Protect. 96 (2015) 125–137.
[4] G. Moussavi, M. Mahmoudi, Removal of azo and anthraquinone reactive dyes from industrial wastewaters using MgO nanoparticles, J. Hazard Mater. 168 (2009) 806–812.
[5] A.S. Ozcan, B. Erdem, A. Ozcan, Adsorption of acid blue 193 from aqueous solutions onto BTMA-bentonite, Colloid. Surface. Physicochem. Eng. Aspect. 266 (1–3) (2005) 73–81.
[6] M. Vallix, W.H. Cheung, G. McKay, Roles of the textural and surface chemical properties of activated carbon in the adsorption of acid blue dye, Langmuir 22 (2006) 4574–4582.
[7] N.K. Nga, P.T.T. Hong, T.D. Lam, T.Q. Huy, A facile synthesis of nanostructured magnesium oxide particles for enhanced adsorption performance in reactive blue 19 removal, J. Colloid Interface Sci. 398 (2013) 210–216.
[8] S. Wang, H. Li, L. Xu, Application of zeolite MCM-22 for basic dye removal from wastewater, J. Colloid Interface Sci. 295 (2006) 71–78.
[9] S.S. Tahir, N. Rauf, Removal of a cationic dye from aqueous solutions by adsorption on bentonite clay, Chromosphere 63 (11) (2006) 1842–1848.
[10] A. Rabbani, M. Oveis, M. Sheikhi, F. Gouarani, Natural polymers as environmental friendly adsorbents for organic pollutants such as dyes: removal from colored wastewater, Curr. Org. Chem. 22 (13) (2018) 1297–1306.
[11] M. Dias, M.C.M. Alvim-Ferraz, F.M. Almeida, J. Rivera-Utrilla, M. Sanchez-Polo, Waste materials for activated carbon preparation and its use in aqueous-phase treatment: a review, J. Environ. Manag. 85 (2007) 833–846.
[12] V.M. Esquerdo, T.R.S. Cadoval Jr., G.L. Dotto, L.A.A. Pinto, Chitosan scaffold as an alternative adsorbent for the removal of hazardous dyes from aqueous solutions, J. Colloid Interface Sci. 424 (2014) 7–15.
[13] D. Liu, Z. Li, Y. Zhu, Z. Li, R. Kumar, Arboil Recycled chitosan nanofibril as an effective Cu(I), Pb(II) and Cd(II) ionic chelating agent: adsorption and desorption performance, Carbohydr. Polym. 111 (2014) 469–476.
[14] N.K. Nga, H.D. Chinh, P.T.T. Hong, T.Q. Huy, Facile preparation of chitosan films for high performance removal of reactive blue 19 dye from aqueous solution, J. Polym. Environ. 25 (2017) 146–155.
[15] M. Yaksi, M. Rafatulilaha, M.H. Ibrahim, A.Z. Abdullah, B. Salamatinac, Z. Gholami, Chitosan hydrogel beads impregnated with hexadeclamyline for improved reactive blue 4 adsorption, Carbohydr. Polym. 137 (2016) 139–146.
[16] H. Haldorai, J.J. Shin, An efficient removal of methyl orange dye from aqueous solution by adsorption onto chitosan/MgO composite: a novel reusable adsorbent, Appl. Surf. Sci. 292 (2014) 454–453.
[17] E. Salehi, M. Arami, N.M. Mahmoodi, H. Bahrami, S. Khorrarnar, Novel biocompatible composite (Chitosan-zinc oxide nanoparticle): preparation, characterization and dye adsorption properties, Colloids Surf. B Biointerfaces 80 (2010) 86–93.
[18] T. Tanhaei, A. Ayati, M. Latinhiz, M. Sillanpaa, Preparation and characterization of a novel chitosan/Al2O3/magnetite nanoparticles composite adsorbent for kinetic, thermodynamic and isotherm studies of Methyl Orange adsorp- tion, Chem. Eng. J. 259 (2015) 1–10.
[19] H.V. Kumar, V. Sivasankar, N. Fayoud, H.A. Ouaid, A.K. Sundramoorthy, Synthesis and characterization of coral-like hierarchical MgO incorporated fly ash composite for the effective adsorption of azo dye from aqueous solution, Appl. Surf. Sci. 440 (2018) 719–728.
[20] W.A. Khaled, S.A. Sadeg, I.A.M. Alani, M.H.M. Ahmed, Magnesium oxide (MgO) thin film as satureable absorber for passively mode locked erbium-doped fiber laser, Optic. Laser, Technol. 115 (2019) 331–336.
[21] N. Suradhar, A. Sinhamahapatra, S.K. Phahri, P. Pal, H.C. Bajaj, I. Mukhopadhyay, A.B. Panda, Controlled synthesis of different morphologies of MgO and their use as solid base catalysts, J. Phys. Chem. 115 (2011) 12308–12316.
[22] C. Paluszkiewicz, E. Stodolak, M. Hasik, M. Blazewicz, Spectrochim Acta. Part. A Mol. Biomol. Spectrosc. 79 (2011) 784.
[23] R. Jayakumar, H. Nagahama, T. Furuike, H. Tamura, Synthesis of phospho- lated chitosan by novel method and its characterization, Int. J. Biol. Macromol. 42 (2008) 335–339.
[24] E. Erdem, C. Colgenro, R. Donat, The removal of textile dyes by diatomite earth, J. Colloid Interface Sci. 282 (2005) 314–319.
[25] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.
[26] Y. Chen, H.A. Abboud, F. He, H. Peng, K. Huang, Magnetic EDTA-modified chi- tosan/SiO2:Fe3O4 adsorbent: preparation, characterization, and application in heavy metal adsorption, Chem. Eng. J. 226 (2013) 300–311.
[27] H.M.F. Freundlich, Trans nanoparticles for removal of malachite green dye from wastewater, J. Phys. Chem. 57 (1906) 385–471.
[28] D. Liu, Y. Zhu, Z. Li, D. Tian, L. Chen, P. Chen, Chitin nanofibrils for rapid and efficient removal of metal ions from water system, Carbohydr. Polym. 98 (2013) 483–489.
[29] K.Y. Kumar, S. Archanaa, T.N. Vinuth Raj, B.P. Prasana, M.S. Raghu, H.B. Muralidhara, Superb adsorption capacity of hydrothermally synthesized copper oxide and nickel oxide nanoflakes towards anionic and cationic dyes, J. Sci. Adv. Mater. Dev. 2 (2017) 183–191.
[30] S. Archanaa, K. Yogesh Kumar, B.K. Jayanna, Sharan Olivera, A. Anand, M.K. Prashanth, H.B. Muralidhara, Versatile graphene oxide decorated by star shaped zinc oxide nanocomposites with superior adsorption capacity and antimicrobial activity, J. Sci. Adv. Mater. Dev. 3 (2018) 167–174.
[31] G.Z. Kyzas, M. Kostoglou, N.K. Lazaridis, Copper and Chromium (VI) removal by chitosan derivatives-equilibrium and kinetic studies, Chem. Eng. J. 152 (2009) 440–448.
[32] K.S. Low, C.K. Lee, Quaternized rice husk as sorbent for reactive dyes, Bio- resour. Technol. 121 (2017) 122–125.