Process Optimization and Adsorptive Mechanism for Reactive Blue 19 Dye by Magnetic Crosslinked Chitosan/MgO/Fe$_3$O$_4$ Biocomposite

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Abstract
A new biocomposite cross-linked glutaraldehyde-chitosan/MgO/Fe$_3$O$_4$ (CTS-GL/MgO/Fe$_3$O$_4$) adsorbent with magnetoresponsiveness was prepared and applied for the removal of reactive blue 19 (RB-19), a synthetic textile dye. The prepared CTS-GL/MgO/Fe$_3$O$_4$ was structurally characterized using spectroscopic (XRD, FTIR, SEM–EDX), and its physicochemical properties were evaluated using potentiometry and pHpzc analyses. The influence of various adsorption parameters (A: CTS-GL/MgO/Fe$_3$O$_4$ dosage; B: initial solution pH; C: process temperature; and D: contact time) on the removal efficiency of RB-19 was statistically optimized using Box-Behnken design (BBD). The analysis of variance (ANOVA) indicates the presence of five significant statistical interactions between the adsorption parameters, as follows: AB, AC, AD, BC, and BD. The equilibrium dye uptake by the Freundlich isotherm model indicates heterogeneous adsorption, while the kinetics of adsorption was well-described by the pseudo-second-order model. The maximum adsorption capacity of CTS-GL/MgO/Fe$_3$O$_4$ towards RB-19 was 193.2 mg/g at 45 °C. This work highlights the development of a recoverable magnetic biocomposite adsorbent with favourable adsorption capacity towards a model textile dye with good separation ability by using an external magnetic field. Moreover, separation of the magnetic adsorbents from the treated solution is easy and convenient apply to continuous flow systems, which is highly preferred for industrial applications.

Keywords Adsorption · Chitosan · Magnesium oxide nanoparticles · Process optimization · Reactive blue 19 dye

Introduction
The industrial sectors of papermaking, textile, plastic, cosmetics, and printing industries are the major consumers of synthetic dyes manufactured globally and is a key contributor of dye containing effluents in wastewater [1]. The presence of chemically stable and non-biodegradable dyes at high concentrations in water bodies pose a serious threat to the environment and living beings [2, 3]. The colored effluent diminishes the penetration of sunlight and solubility of gas, interferes with the photosynthesis, increased chemical oxygen demand, and biological oxygen demand and more turbidity affect the aquatic biota [4], along with the negative health effects of organic dyes to human health [5]. In particular, Reactive blue 19 (RB-19) is an important commercial textile dye that belongs to the group of vinylsulfone azo dyes [6]. RB-19 is known as a hazardous pollutant with high water solubility that resists degradation and is harmful to human health [7]. To address the effective removal of harmful organic dyes in wastewater,
various treatment techniques have been applied: membrane separation [8], ultrafiltration [9], flocculation [10], microbial degradation [11], photodegradation, [12] and adsorption [13]. Among these methods, the adsorption technique has simplicity in its overall design, efficiency, and facile operation requirements [14]. However, the efficiency of the adsorption process depends mainly on the adsorbent due to its physicochemical properties that relate to structure, functionality, particle size, and surface area.

Chitosan (CTS) is a linear carbohydrate polymer obtained by deacetylation of chitin, the second most abundant natural biopolymer [15]. CTS is one of the most explored biopolymer adsorbents for water remediation due to its unique molecular structure that contains amine and hydroxyl functional groups [16]. Some merits of CTS for water pollutant removal relate to its low-cost, biodegradability, biocompatibility, and chemical functionality with favorable adsorption capacity toward diverse contaminants [17]. The utility of native CTS has some technical problems in wastewater treatment technology due to its solubility in acidic environment, compressibility under high pressure, high swelling index, and challenges for the recovery of powdered adsorbents during adsorption and post treatment processes [18, 19]. Thus, CTS requires physicochemical modification to address the aforementioned technical problems for wastewater treatment.

While there are several known synthetic strategies used to modify the properties of CTS, crosslinking methods are known to improve the molecular structure, chemical stability, functionality, and hydrophobicity of CTS [20]. Glutaraldehyde (GL) presents a versatile cross-linker agent suitable for covalent bonding between CTS moieties via a bifunctional Schiff-base system [21]. Composite formation of CTS with nanostructured metal oxides such as MgO is another interesting approach to improve the thermal and chemical stability, surface hydrophobicity, and surface area of CTS [22]. The design of hybrid CTS biocomposites that contain MgO is an interesting nanoscale metal oxide for developing multi-functional biocomposites (CTS/MgO) due to its unique characteristics such as biocompatibility, high adsorption capability, non-toxicity, chemical stability, and large surface area-to-volume ratio [23, 24]. In recent years, CTS/MgO biocomposites have received increasing attention in applications such as wastewater treatment [25], food packaging [26], bone regeneration [27], defluoridation of water [28], sensors [29], and biocatalyst materials [30]. The development of magnetic biocomposite adsorbents for wastewater treatment offers new possibilities that allow for improved recovery of the adsorbents during and for post treatment processes. This can be achieved by using an external magnetic field and without conventional filtration or separation techniques [31].

Therefore, the aim of this research work is aimed to develop a recoverable, chemically stable, hydrophobic, and multi-functional CTS modified absorbent with magnetic properties. To this end, a magnetic cross-linked chitosan-glutaraldehyde/MgO/Fe3O4 (CTS-GL/MgO/Fe3O4) was fabricated as a potential adsorbent for the removal of RB19 dye from aqueous media. The key adsorption parameters were statistically optimized using a Box–Behnken design (BBD) and validated by analysis of variance (ANOVA). Furthermore, the adsorption results were fitted to several kinetic and isotherm models, and the mechanism of RB-19 adsorption by the CTS-GL/MgO/Fe3O4 adsorbent was proposed.

**Materials and Methods**

**Reagents and Materials**

The Chitosan biopolymer (CTS) with deacetylation degree of ≥ 75% and medium molecular weight was purchased from Sigma–Aldrich, China. Iron (III) chloride hexahydrate (FeCl3.6H2O—molecular weight of 270.3 g/mol) and Iron (II) chloride tetrahydrate (FeCl2.4H2O, molecular weight of 198.81 g/mol) was supplied from HmbG and Bendosen Laboratory Chemicals, Germany, respectively. Reactive Blue 19 (RB-19; CAS number - 2580–78-1; C.I. number - 61,200; Molecular mass - 626.54 g/mol and λ max = 595 nm) commercially referred as Remazol brilliant blue R was obtained from ACROS, Organics, Belgium. All chemical reagents used for the experiments were of analytical grade and used directly without any further purification. The procedures in the present study of the preparation of aqueous solutions and cleaning procedures employed ultrapure water.

**Preparation of CTS-GL/MgO/Fe3O4 Biocomposite**

For the preparation of CTS-GL/MgO/Fe3O4, 1 g of CTS flakes and 1 g of MgO nanoparticles (NPs) were added to a 5% acetic acid solution (50 mL). The mixture was subjected to gentle stirring at room temperature for 24 h to attain complete dissolution of CTS and MgO NPs incorporation within the CTS matrix. Further, 3.9 g of FeCl3.6H2O and 2.7 g of FeCl2.4H2O were added to distilled water (10 mL), and then the contents were transferred to CTS/MgO solution and kept under mild agitation for 1 h. A plastic syringe needle (10 mL capacity) was used to inject the resultant viscous solution into 1000 mL of 2 M NaOH solution under mild agitation, and immediate formation of CTS/MgO/Fe3O4 beads was observed. The obtained CTS/MgO/Fe3O4 beads were gently washed with distilled water to enable removal of the residual NaOH solution. Then, the crosslinking was carried out with 2% glutaraldehyde (100 mL) added to the CTS/MgO/Fe3O4 beads at 40 °C in thermal water bath shaker for 2 h. Then,
the CTS-GL/MgO/Fe$_3$O$_4$ beads were washed with distilled water and air dried, before being crushed into fine particles with a particle size ≤ 250 µm. The final product CTS-GL/MgO/Fe$_3$O$_4$ powder was employed for the adsorption experiments. The preparation steps of CTS-GL/MgO/Fe$_3$O$_4$ beads are illustrated in Fig. 1.

**Characterization and Instrumentation**

The crystalline properties of the CTS-GL/MgO/Fe$_3$O$_4$ was examined using X-ray diffraction analysis (XRD, X’Pert PRO, PANalytical, USA). Fourier transform infrared (FT-IR) spectral characterization was used to analyze the functional groups of CTS-GL/MgO/Fe$_3$O$_4$ biocomposite before and after RB-19 interactions (Perkin-Elmer, Spectrum RX I, USA). Scanning electron microscopy - Energy dispersive X-ray (SEM–EDX) analysis was carried out to examine the surface textural characteristics and quantitative chemical composition analysis of the CTS composite before and after RB-19 loading (Zeiss Supra 40 VP, Germany). The specific surface area measurement ($S_{BET}$) and pore volume of CTS-GL/MgO/Fe$_3$O$_4$ were estimated using a Micromeritics ASAP 2060 analyzer, USA. The point of zero charge (pH$_{pzc}$), and amine content (–NH$_2$) of CTS-GL/MgO/Fe$_3$O$_4$ were determined using Metrohm 827 pH meter, Switzerland, according to the procedures reported by Dalvand et al. [32] and Vieira and Beppu [33].

**Optimization Process**

To evaluate the optimum adsorption conditions, and to achieve the highest adsorptive removal, the response surface methodology (RSM) approach with the Box-Behnken Design (BBD) was applied as the potential optimization tool to improve the adsorption performance. The BBD model illustrates the influence of adsorption independent variables of individual or mutual interaction with each other. Further, the BBD model not only examines the impact of independent variables, but also generates an empirical model that accounts for the appropriate quantity in a process [34]. The modeling and optimization of the adsorption of RB-19 onto CTS-GL/MgO/Fe$_3$O$_4$ from an aqueous system was conducted by means of regression testing and graphically using

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**Fig. 1** Synthesis steps of CTS-GL/MgO/Fe$_3$O$_4$ biocomposite
the Design-Expert software (version 13, Stat-Ease, Minneapolis, USA). The experiment trials from the approach of the one variable at a time showed a significant influence on the removal of dye using the following adsorption parameters: CTS-GL/MgO/Fe₃O₄ dosage (A), initial solution pH (B), process temperature (C), and contact time (D). Therefore, these process parameters were selected as input variables for BBD investigation towards the adsorption of RB19, and the RB-19 removal efficiency (%) is the response (Y). The adsorption experiments were performed according to the BBD model. The experimental tests were conducted in duplicate under identical conditions and the results are reported as an average value. The BBD model presents each independent variable at three different levels of $-1$, $0$, and $+1$ presents low, medium, and high values, with a total of four variables and design of experiment comprised of 29 experimental runs, whose five replications at the central level for error calculation was selected. The coded and levels of independent variables in BBD are given in Table 1. According to BBD model, the relationship between the response variable and independent variables was elucidated using the second-order nonlinear polynomial numerical expression of quadratic order as mentioned in Eq. (1).

$$Y = \beta_0 + \sum_{i} \beta_iX_i + \sum_{i} \beta_i^2X_i^2 + \sum_{i,j} \beta_{ij}X_iX_j$$

(1)

where $Y$ is an objective for the optimization of the response (RB-19 removal (%)); $X_i$ and $X_j$ are the coded variables; $\beta_0$, $\beta_i$, $\beta_{ii}$, $\beta_{ij}$ are the constant coefficient, coefficient of linear effect, coefficient of quadratic effect, and coefficient of the interaction effect.

The design comprised 29 runs according to BBD model for the optimization of independent factors such as A: CTS-GL/MgO/Fe₃O₄ dosage (0.02–0.1 g), B: initial solution pH (4.0–10.0), C: process temperature (30–60 °C) and D: contact time (10–40 min) on the RB-19 removal efficiency (%). The actual BBD experimental design matrix and RB-19 removal (%) are recorded in Table 2. A desired amount of CTS-GL/MgO/Fe₃O₄ was transferred to 100 mg/L initial concentration of RB-19 (100 mL) in an Erlenmeyer flask (250 mL). The stoppered Erlenmeyer flasks were subjected to agitation using a water bath shaker (WNB7-45, Memmert, Germany) at 100 rpm agitation speed. After the adsorption process, the separation of CTS-GL/MgO/Fe₃O₄ from the aqueous solution was firstly done by using an external magnetic bar, prior to use of a 0.45 μm syringe filter to ensure that no ultrafine particles were suspended in the analyte solution, which may cause an error in absorbance reading. The concentrations of RB-19 before and after treatment were recorded using an absorbance spectrophotometer (HACH DR 3900, USA) at a maximum wavelength of 595 nm. The efficiency of adsorption of CTS-GL/MgO/Fe₃O₄ towards RB19 was calculated based on the RB-19 removal (%) using the following Eq. (2):

$$RE\% = \left(\frac{C_o - C_e}{C_o}\right) \times 100$$

(2)

where $C_o$ is the initial RB-19 concentration (mg/L) and $C_e$ is the residual equilibrium RB-19 concentration (mg/L) after the adsorption process.

| Table 1 | Coded and actual variables and their levels in BBD |
|---------|--------------------------------------------------|
| Codes   | Variables | Level 1 (-1) | Level 2 (0) | Level 3 (+1) |
| A       | Dose (g)  | 0.02         | 0.06        | 0.1          |
| B       | pH        | 4            | 7           | 10           |
| C       | Temperature (°C) | 30          | 45          | 60           |
| D       | Time (min) | 10           | 25          | 40           |

| Table 2 | The 4-variables BBD matrix and experimental data for RB-19 dye removal |
|---------|---------------------------------------------------------------------|
| Run     | A:Dose (g) | B:pH | C:Temp. (°C) | D:Time (min) | RB19 removal (%) |
| 1       | 0.02       | 4    | 45           | 25           | 36.3             |
| 2       | 0.1        | 4    | 45           | 25           | 87.5             |
| 3       | 0.02       | 10   | 45           | 25           | 22.8             |
| 4       | 0.1        | 10   | 45           | 25           | 50.1             |
| 5       | 0.06       | 7    | 30           | 10           | 46.5             |
| 6       | 0.06       | 7    | 60           | 10           | 49.5             |
| 7       | 0.06       | 7    | 30           | 40           | 55.2             |
| 8       | 0.06       | 7    | 60           | 40           | 57.2             |
| 9       | 0.02       | 7    | 45           | 10           | 28.8             |
| 10      | 0.1        | 7    | 45           | 10           | 57.9             |
| 11      | 0.02       | 7    | 45           | 40           | 28.8             |
| 12      | 0.1        | 7    | 45           | 40           | 72.2             |
| 13      | 0.06       | 4    | 30           | 25           | 68.4             |
| 14      | 0.06       | 10   | 30           | 25           | 42.4             |
| 15      | 0.06       | 4    | 60           | 25           | 53.5             |
| 16      | 0.06       | 10   | 60           | 25           | 52               |
| 17      | 0.02       | 7    | 30           | 25           | 30.8             |
| 18      | 0.1        | 7    | 30           | 25           | 64.4             |
| 19      | 0.02       | 7    | 60           | 25           | 22.8             |
| 20      | 0.1        | 7    | 60           | 25           | 70.5             |
| 21      | 0.06       | 4    | 45           | 10           | 57.7             |
| 22      | 0.06       | 10   | 45           | 10           | 46.3             |
| 23      | 0.06       | 4    | 45           | 40           | 78.2             |
| 24      | 0.06       | 10   | 45           | 40           | 40.7             |
| 25      | 0.06       | 7    | 45           | 25           | 44.6             |
| 26      | 0.06       | 7    | 45           | 25           | 39.1             |
| 27      | 0.06       | 7    | 45           | 25           | 41.2             |
| 28      | 0.06       | 7    | 45           | 25           | 45.1             |
| 29      | 0.06       | 7    | 45           | 25           | 44.5             |
Batch Adsorption Experiment

The adsorptive removal of RB-19 was examined using CTS-GL/MgO/Fe3O4 as an adsorbent in a batch adsorption system. The experimental results were comprised of 4-variables in a BBD matrix from Table 2, which reveal that the highest RB-19 removal (87.5%) was attained at the experimental run 2. The BBD matrix run 2 follows the given process conditions; A: CTS-GL/MgO/Fe3O4 dosage (0.1 g), B: initial solution pH (4.0), C: process temperature (45 °C) and D: contact time (25 min). With these optimized adsorption conditions, a batch adsorption study was carried out. Moreover, the adsorption isotherm and kinetic study were performed under similar conditions given in run 2 of Table 2, except the parameter range of values for the initial RB-19 concentrations (20–350 mg/L) versus the contact time (0–480 min).

The adsorption capacity of the CTS-GL/MgO/Fe3O4 towards RB19 at equilibrium time was calculated using Eq. (3).

\[
q_e = \frac{(C_o - C_e)V}{W}
\]

where \(q_e\) is equilibrium adsorption capacity of CTS-GL/MgO/Fe3O4 (mg/g), \(V\) is the volume of RB-19 solution (L) and \(W\) is the applied mass of CTS-GL/MgO/Fe3O4 (g).

Results and Discussion

Characterization

The results of the physicochemical properties of the CTS-GL/MgO/Fe3O4 are summarized in Table 3. The results of the BET surface area analysis of CTS-GL/MgO/Fe3O4 was found to be 3.70 m²/g, total pore volume 0.0090 cm³/g, mean pore volume 0.0004 cm³/g, and mean pore diameter 9.77 nm. Following the IUPAC classification scheme, the mean pore diameter indicates that the CTS-GL/MgO/Fe3O4 is a mesostructured type material [35]. This relatively low surface area can be assigned to the interaction exhibited in the interfacial region among CTS, MgO, and the cross-linking agent [36].

Moreover, the actual free amino (-NH₂) group content in the molecular structure of CTS-GL/MgO/Fe3O4 after the crosslinking process with GL was determined using potentiometric titrations and the result shows that the adsorbent CTS-GL/MgO/Fe3O4 has 15.7% of free amino (-NH₂) on its surface. The relatively low existence of free amino (-NH₂) group on the surface of CTS-GL/MgO/Fe3O4 is still considered at the preferable level, since the amino (-NH₂) group offers significant contribution in the adsorptive removal of RB-19 through the electrostatic attraction between the positively charged and protonated amino (-NH₃⁺) groups of CTS-GL/MgO/Fe3O4 and the negatively charged anionic dye (RB-19).

The XRD analysis was used to examine the phase components and crystalline nature of the CTS-GL/MgO/Fe3O4. The XRD pattern of the CTS-GL/MgO/Fe3O4 is illustrated in Fig. 2, where the XRD spectrum shows the prominent diffraction peaks of the magnetite crystalline phase. Moreover, the distribution of distinguishable lines in the XRD pattern is mainly due to the intense magnetite lines which overlap and the amorphous features of CTS structure [37].

The synthesis CTS-GL/MgO/Fe3O4 and its interaction with RB-19 was investigated by FT-IR spectral analysis in the wavenumber range of 4000 cm⁻¹ to 500 cm⁻¹. The FT-IR spectral analysis results of CTS-GL/MgO/Fe3O4 before and after loading with RB-19 are given in Fig. 3a, b respectively. The FT-IR spectrum of CTS-GL/MgO/Fe3O4 exhibits several characteristic bands at 3300 cm⁻¹ and 3200 cm⁻¹, which indicated the stretching vibration of amine or hydroxyl functional groups in the CTS-GL/MgO/Fe3O4.
Fe3O4 [38]. A weak shoulder at 2300 cm\(^{-1}\) can be assigned to the M–OH (M=Mg and Fe), and signifies the formation of magnetic CTS-based composite [39]. The peak observed around 1660 cm\(^{-1}\) indicates a stretching vibration due to the presence of C=N bond resulted from the cross-linking interactions that occur between the aldehyde groups of GL and the amino group of CTS [20]. The CTS-GL/MgO/Fe3O4 also presents a peak at 1300 cm\(^{-1}\) (C\(^{-}\)O\(^{-}\)C), corresponds to asymmetric stretching vibrations, and a peak at 1030 cm\(^{-1}\), indicates stretching vibrations of C–O functional group, and these bands are assigned to the CTS glycosidic band in CTS-GL/MgO/Fe3O4 biocomposite [40, 41]. The sharp band at 699 cm\(^{-1}\) was attributed to MgO NPs [26]. The FT-IR spectrum of CTS-GL/MgO/Fe3O4 loaded with RB19 (Fig. 3b) displays a similar spectral profile to that noted in Fig. 3a with a slight shift in some spectral bands, especially at 1500 cm\(^{-1}\). This trend which signifies the existence of the C=C functional group of the aromatic ring of RB-19 loaded onto the CTS-GL/MgO/Fe3O4 surface [42].

The surface examination of the CTS-GL/MgO/Fe3O4 before and after adsorption of RB-19 was visualized using SEM–EDX characterization, as shown in Fig. 4. The external microstructural features of the CTS-GL/MgO/Fe3O4 (Fig. 4a) shows irregular, heterogeneous, rippled features, along with different sized pores and cavities that are well distributed on the GL/MgO/Fe3O4 surface. These surface features offer an ideal morphology for effective capture of RB-19 dye molecules with the possibility of efficient penetration onto the active inner adsorption sites. The EDX spectrum of the CTS-GL/MgO/Fe3O4 shows the presence of various elements such as C, O, Fe, N, Mg, and Zr. The presence of elemental N in the biocomposite signifies the amine group of CTS, and Fe relates to Fe3O4. On the other hand, Fig. 4b displays the SEM and EDX results of the CTS-GL/MgO/Fe3O4 biocomposite after adsorption of RB19. The SEM image shows the conversion of the morphological surface to be more compact and less porous than the SEM image in Fig. 4a before adsorption due to the presence and absence of of RB19 onto the surface of CTS-composite. This trend was further supported by EDX analysis (Fig. 4b), which indicates the detection of S-atom species that relates to adsorption of RB-19 onto the CTS-composite surface.

**BBD Model Fitting**

Statistical analysis and determination of the significant effect of the independent adsorption variables and their interactions for the RB-19 removal results was achieved by the analysis of variance (ANOVA). The statistical results derived from the ANOVA of the RB19 removal are listed in Table 4. A model F-value of 50.75 (p-value < 0.0001) signifies that the RB19 removal model is significant from a statistical standpoint [43]. The value of the correlation coefficient (\(R^2\)) for the RB-19 removal model was 0.98, supporting the accuracy of the fitting model of the RB19 removal, and the strong correlation between the expected and experimental RB-19 removal values [44]. From a statistical point of view, model codes are considered significant terms when the P-value is less than 0.05. As a result, A, B, D, AB, AC, AD, BC, BD, \(B^2\), \(C^2\), and \(D^2\) are important terms in the process of RB-19 removal. Equation 4 shows the quadratic polynomial model used to correlate the experimental relationship between RB19 removal and the examined variables.

\[
\text{RB 19 removal (\%) = } +42.90 + 19.36A - 10.61B + 3.80D - 5.97AB + 3.52AC + 3.58AD + 6.13BC - 6.52BD + 7.18B^2 + 4.35C^2 + 5.07D^2
\] (4)

In addition to the above, verification of the experimental data can be accomplished by analyzing the drawings extracted from the BBD model, such as the actual versus the expected, and the normal probability of the residuals. The predicted versus actual plot of RB19 removal (%) is depicted in Fig. 5a, where the actual points were mostly close to the expected points, indicating that the BBD model can adequately optimize the RB-19 dye adsorption process. The normal probability plot of residuals is demonstrated in Fig. 5b. The independence of the residuals can be inferred from Fig. 5b, where the normal distribution of all points around the straight line [45]. Another statistical validation was made by Cook’s distance as shown in Fig. 5c. In general, the acceptable Cook’s distance should be less than 1.
As presented in Fig. 5c, all observed values are less than 1. Moreover, 27 runs out of 29 runs are even below 0.2, and in some cases equal to zero, which indicates the significant effect on the predictive power of the model.

### Surface Plot for Responses

An account of the interaction effects of two operational variables on RB19 removal (%) can be obtained from the ANOVA results, which can be graphically presented in three-dimensional (3D) response surfaces. In Table 4, the ANOVA results indicate the existence of five significant interactions between the adsorption individual variables as follows: AB (dose × pH), AC (dose × temperature), BC (pH × temperature), AD (dose × time), and BD (pH × time). Thus, Fig. 6a exhibits the 3D surface plot of the significant interaction between AB (dose × pH) on the RB19 removal (%), while other operational variables were kept constant (temperature = 45 °C and time = 25 min). From Fig. 6a, it was observed that the RB19 removal (%) was gradually increased by decreasing the solution pH towards acidic environment (pH 4). This observation can be explained by referring to the net surface charge of CTS-GL/MgO/Fe3O4 which is determined from the pHpzc test as presented in Fig. 6b. The results indicate that the pHpzc value for CTS-GL/MgO/Fe3O4 is 9.0, and the surface of the CTS-GL/MgO/Fe3O4 will acquire a negative charge when the solution pH increases above 9.0, whereas a positive charge occur at pH below 9.0. Accordingly, the surface of CTS-GL/MgO/Fe3O4 will acquire a negative charge when the solution pH increases above 9.0, whereas a positive charge occur at pH below 9.0. Consequently, an electrostatic attraction can be found between the cationic functional group on the surface of the CTS-GL/MgO/Fe3O4 and the RB-19 dye as depicted in Eq. (5).

\[
\text{CTS - GL/MgO/Fe}_3\text{O}_4^+ + \text{RB}^{19-} \leftrightarrow \text{CTS - GL/MgO/Fe}_3\text{O}_4^+ \cdots \text{RB 19} \tag{5}
\]
Other statistically significant interactions were observed between AC (dose × temperature) and BC (pH × temperature) as presented in the 3D surface plot in Fig. 6c, d, respectively. It is noteworthy that the other operational parameters were kept constant: AC interaction (pH 7 and time = 25 min) and BC interaction (dose = 0.06 g and time = 25 min). According to Fig. 6c and d, the RB-19 removal (%) did not show any remarkable change or even slightly decreased by increasing the working temperature up to 60 °C, which may indicate that the adsorption process of RB-19 onto the surface of the CTS-GL/MgO/Fe₃O₄ is exothermic in nature [46].

Furthermore, other statistically significant interactions were observed between AD (dose × time), and BD (pH × time) as presented in the 3D surface plots for Fig. 6e and f. Noteworthy is that the other operational parameters were kept constant: AD interaction (pH 7 and temperature = 45 °C) and BD interaction (dose = 0.06 g and temperature = 45 °C). Regarding the adsorbent dose, the result obtained from Fig. 6e indicates that RB-19 removal (%) increased as the dose of the CTS-GL/ZnO/Fe₃O₄ increased. This observation can be assigned to more active adsorption sites available in the bulk dye solution by loading a greater dosage of the adsorbent (CTS-GL/ZnO/Fe₃O₄), where a greater number of active adsorption sites will lead to a greater uptake of RB-19 dye [47]. Regarding the contact time (Fig. 6f), the RB19 removal (%) increased rapidly by extending the contact time from 10 to 40 min, where greater contact time will offer sufficient time for the RB-19 dye to penetrate further into the microstructure of the CTS-GL/ZnO/Fe₃O₄, and to efficiently reach the inner active adsorption sites.

### Adsorption Kinetics

The adsorption experiments were carried out by varying the contact time (0–180 min) of the adsorption process and the initial concentration of RB-19 (20–350 mg/L). The experimental results of variable contact time were fitted to the adsorption kinetics and isotherm models. The other adsorption process parameters of CTS-GL/MgO/Fe₃O₄ dosage (0.1), initial solution pH (4.0), and process temperature (45 °C) were kept constant according to the BBD-based optimal conditions. The results of effect of contact time and initial RB-19 concentrations are represented in Fig. 7a. The results clearly indicate that the adsorption capacity of CTS-GL/MgO/Fe₃O₄ towards RB-19 uptake for all studied initial RB19 concentrations presented a sharp increase followed by a plateau that suggests saturation of the adsorption sites. The increase in the adsorption capacity of CTS-GL/MgO/Fe₃O₄ with the increase of the initial RB-19 concentration was mainly due to the increase in the driving force for the transferring of RB-19 dye species from aqueous solution to the surface of CTS-GL/MgO/Fe₃O₄ [48].

### Adsorption Study

The adsorption experiments were carried out by varying the contact time (0–180 min) of the adsorption process and the initial concentration of RB-19 (20–350 mg/L). The experimental results of variable contact time were fitted to the adsorption kinetics and isotherm models. The other adsorption process parameters of CTS-GL/MgO/Fe₃O₄ dosage (0.1), initial solution pH (4.0), and process temperature (45 °C) were kept constant according to the BBD-based optimal conditions. The results of effect of contact time and initial RB-19 concentrations are represented in Fig. 7a. The results clearly indicate that the adsorption capacity of CTS-GL/MgO/Fe₃O₄ towards RB-19 uptake for all studied initial RB19 concentrations presented a sharp increase followed by a plateau that suggests saturation of the adsorption sites. The increase in the adsorption capacity of CTS-GL/MgO/Fe₃O₄ with the increase of the initial RB-19 concentration was mainly due to the increase in the driving force for the transferring of RB-19 dye species from aqueous solution to the surface of CTS-GL/MgO/Fe₃O₄ [48].

#### Adsorption Kinetics

The profiles of the adsorption process at variable contact time versus different initial RB-19 concentrations are presented in Fig. 7a. It is clear from the results that the adsorption capacity of CTS-GL/MgO/Fe₃O₄ towards RB-19 uptake rapidly increased during the initial contact time of the adsorption process, which was followed by the same trend in adsorption capacity. This trend was irrespective of the increase of the contact time and signifies the state of equilibrium attainment for all dye concentrations. The expressions of pseudo-first order (PFO) [49], and pseudo-second order (PSO) [50], these kinetic models are described by Eqs. (6) and (7), respectively:

\[
q_t = q_e \left(1 - \exp^{-k_1 t}\right) \quad \text{(6)}
\]

\[
q_t = \frac{q_e^2 k_2 t}{1 + q_e \left(1 - \exp^{-k_1 t}\right)} \quad \text{(7)}
\]

where \( q_e \) (mg/g) and \( q_t \) (mg/g) are the adsorption capacity of the CTS-GL/MgO/Fe₃O₄ biocomposite (mg/g).
at equilibrium and at time \( t \) (min). \( k_1 \) (1/min) and \( k_2 \) (g/(mg·min)) are the pseudo-first order (PFO) rate constant and pseudo-second order (PSO) rate constant, respectively. The results of kinetic model parameters for the PFO and PSO rate constant models, along with their values of coefficient of determination \( (R^2) \) are presented in Table 5. The kinetic model results reveal that the RB-19 adsorption using CTS-GL/MgO/Fe\(_3\)O\(_4\) concur with the PSO kinetic model with higher \( R^2 \) values for all of the initial RB19 concentrations, as compared to the \( R^2 \) values for the PFO kinetic model.

The best-fit of experimental data to the PSO kinetic model reveal that chemisorption was the main step that controls the interaction between CTS-GL/MgO/Fe\(_3\)O\(_4\) and RB-19 [51].

**Adsorption Isotherms**

The results of the adsorption isotherm analysis of RB-19 are shown in Fig. 7b. The equilibrium data of the adsorption experiments were determined at the initial RB19 concentrations of 20 mg/L, 50 mg/L, 100 mg/L, 150 mg/L, 200 mg/L,
Fig. 6  3D plots of a AB, c AC, d AD, e BC, and f BD significant interactions on dye removal; whereas, b $pH_{prc}$ of CTS-GL/MgO/Fe$_3$O$_4$
250 mg/L, and 350 mg/L at the process temperature of 45 °C. The adsorption equilibrium data were examined by three isotherm models: Langmuir [52], Freundlich [53], and Temkin [54] models. The non-linear expression of the Langmuir, Freundlich and Temkin models are described by Eqs. (8), (9) and (10), respectively:

\[
q_e = \frac{q_{\text{max}}K_aC_e}{1 + K_aC_e} \quad (8)
\]

where \( q_{\text{max}} \) (mg/g) represents the maximum monolayer adsorption capacity and \( K_a \) (L/mg) refers to the Langmuir constant.

\[
q_e = K_F C_e / n \quad (9)
\]

where \( K_F \) (mg/g) is the Freundlich constant that relate to the adsorption capacity and \( n_F \) (L/mg) is the Freundlich constant, which indicates adsorption intensity.

\[
q_e = \frac{RT}{b_T \ln(K_T C_e)} \quad (10)
\]

where \( K_T \) (L/mg) is the Temkin constant, \( R \) (8.314 J/mol K) is the universal gas constant, \( T \) (K) is the absolute temperature, and \( b_T \) (J/mol) indicates the heat of adsorption. The best-fit of the adsorption equilibrium data was inferred from the \( R^2 \) values listed in Table 6. The relative ordering of the best-fit of the isotherm models to the equilibrium data: Freundlich > Langmuir > Temkin. The results confirmed that the unequal affinity of RB-19 with CTS-GL/MgO/Fe₃O₄ presented an adsorbent with a heterogeneous nature and multilayer adsorption sites [55]. The maximum monolayer adsorption capacity recorded according to the

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**Table 5** PFO and PSO kinetic parameters for RB-19 dye adsorption onto the CTS-GL/MgO/Fe₃O₄ composite adsorbent

| Concentration (mg/L) | \( q_{\text{exp.}} \) (mg/g) | PFO | PSO |
|----------------------|-------------------------------|-----|-----|
|                      | \( q_{\text{exp.}} \) (mg/g) | \( k_1 \) (1/min) | \( k_2 \times 10^{-2} \) (g/mg min) | \( R^2 \) |
| 20                   | 19.5                          | 0.726 | 33.97 | 0.99 |
| 50                   | 46.4                          | 0.260 | 1.334 | 0.99 |
| 100                  | 84.9                          | 0.095 | 0.205 | 0.98 |
| 150                  | 115.7                         | 0.069 | 0.100 | 0.97 |
| 200                  | 146.7                         | 0.078 | 0.096 | 0.94 |
| 250                  | 158.2                         | 0.077 | 0.084 | 0.96 |
| 350                  | 197.3                         | 0.067 | 0.058 | 0.90 |
Langmuir isotherm model was 193.2 mg/g, which is among the higher adsorption capacity values reported relative to other adsorbents from the literature (Table 7).

### Adsorption Mechanism

The acid dye (RB-19) adsorption mechanism was proposed according to the available functional groups on the CTS-GL/MgO/Fe₃O₄ surface, as given in Fig. 8. CTS-GL/MgO/Fe₃O₄ is distinguished by the availability of different active groups that can play an essential role in the adsorption process of the RB-19 dye. Among these groups, the protonated amino (–NH₃⁺) group, (–OH₂⁺), and Mg(OH)⁺ resulted from the presence of MgO NPs. These functional groups with a positive charge can efficiently attract the negatively charged (–SO₃⁻) groups of the RB-19 dye. The hydrogen bonding interactions can be formed via the interaction of the H-atoms of CTS-GL/MgO/Fe₃O₄ with N- and O-atoms of RB-19 dye. Moreover, another interaction can be generated from the interaction between the electron donor groups in CTS-GL/MgO/Fe₃O₄ with the electron acceptor system in the RB-19 dye [20]. Finally, the interactions of the H-atom of the hydroxyl groups with the aromatic system of the RB19 dye leads to interactions known as Yoshida H-bonding [44].

### Conclusions

A novel magnetic cross-linked chitosan-glutaraldehyde/MgO/Fe₃O₄ (CTS-GL/MgO/Fe₃O₄) biocomposite adsorbent was prepared and evaluated for its uptake properties of Reactive Blue19 (RB-19), a model synthetic textile dye from aqueous solution. The optimal RB-19 removal conditions are listed, as follows: CTS-GL/MgO/Fe₃O₄ dosage (0.1 g), initial solution pH (4.0), process temperature (45 °C), and contact time (25 min) as investigated by BBD. The Freundlich isotherm model gave a best fit of the equilibrium data, which revealed heterogeneous sites and multilayer adsorption. The maximum adsorption capacity of the CTS-GL/MgO/Fe₃O₄ biocomposite with RB-19 was predicted according to the Langmuir isotherm model was 193.2 mg/g. The experimental data of the kinetic models revealed that the RB-19 adsorption is governed by the chemisorption process. Several interactions contributed to the stability of RB-19 adsorption process with CTS-GL/MgO/Fe₃O₄. This includes electrostatic attractions, H-bonding, n-π, and Yoshida H-bonding. This study signifies the ability of CTS-GL/MgO/Fe₃O₄ to be an effective magnetic adsorbent for treating wastewater containing organic dyes. Furthermore, separation of the magnetic adsorbents from the treated solution is easy and convenient.
apply to continuous flow systems, which is highly preferable for industrial applications.

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Data Availability The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

 Declarations

Competing interests The authors have no relevant financial or non-financial interests to disclose.

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