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Magnetic Chitosan-Glutaraldehyde/Zinc Oxide/Fe₃O₄ Nanocomposite: Optimization and Adsorptive Mechanism of Remazol Brilliant Blue R Dye Removal

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Abstract: A magnetic Schiff's base chitosan-glutaraldehyde/Fe_3O_4 composite (CHT-GLA/ZnO/Fe_3O_4) was developed by incorporating zinc oxide (ZnO) nanoparticles into its structure to prepare an efficient adsorbent for the removal of remazol brilliant blue R (RBBR) dye. The CHT-GLA/ZnO/Fe_3O_4 was characterized by the following methods: CHN, BET, FTIR, XRD, SEM-EDX, pHpzc, and potentiometric titrations. Box-Behnken design based on response surface methodology was used to optimize the effects of the A: ZnO nanoparticles loading (0-50%), B: dose (0.02-0.1 g), C: pH (4-10), D: temperature (30-60 °C), and time E: (10-60 min) on the synthesis of the magnetic adsorbent and the RBBR dye adsorption. The experimental data of kinetics followed the pseudo-second order model, while isotherms showed better fit to Freundlich and Temkin models. The maximum adsorption capacity of the target nanocomposite (CHT-GLA/Fe_3O_4 containing 25% ZnO or CHT-GLA/ZnO/Fe_3O_4-25) was reached of 176.6 mg/g at 60 °C. The adsorption mechanism of RBBR onto CHT-GLA/ZnO/Fe_3O_4 nanocomposite can be attributed to multi-interactions including electrostatic attractions, hydrogen bonding, Yoshida H-bonding, and n-π interactions. This study offers a promising hybrid nanobiomaterial adsorbent in environmental nanotechnology to separate and remove the contaminants such as organic dyes from wastewater.

Keywords: Magnetic chitosan; Zinc oxide nanoparticles; Remazol brilliant blue R dye; Glutaraldehyde; Response surface methodology

1. Introduction

Synthetic dyes are widely used in many industrial activities including paper, plastics, textile, cosmetic, leather, and pharmaceutical, which generate massive volumes of wastewaters [1]. Discharging of the organic dyes directly into surface water can cause serious water pollution, i.e. reducing photosynthesis activity, disordering the ecological balance of aquatic systems, and toxic effects on biota [2]. Moreover, several dyes can cause a series of adverse effects on human health [3]. Remazol brilliant blue R (RBBR) dye is a typical reactive dye, which is extensively used in the industrial for synthesis of polymeric dyes [4]. RBBR is considered as recalcitrant organic pollutants, which can cause several health problems [5]. Therefore, the treatment of the effluents containing dyestuffs before being fluxed into water streams is environmentally important. Several methods have been documented for the treatment of the effluents containing dyestuffs such as adsorption [6], membrane separation [7], photodegradation [8], and coagulation [9]. Adsorption is regarded as one of an effective and eco-friendly method due to its exceptional benefits such as operational ease, high regeneration, low-cost, high removal efficiency, and harmless of the treated water [10].

Chitosan (CHT) is a linear biopolymer, and it is one of the most efficient and environmentally friendly adsorbents applied in adsorption method for the adsorption of dyes [11]. CHT shows several outstanding properties such as high hydrophilicity, ease of modification, biodegradability, nontoxicity, and super absorbency [12]. It is characterized by availability a large number of amino and hydroxyl groups, making it an excellent adsorbent for the removal of pollutants such as dyes and heavy metals [13]. However, applying of CHT in adsorption technology is limited due to high swelling index, low chemical stability in acidic environment, weak mechanical strength, and low surface area [4, 14].

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Various procedures have been applied to pass these hurdles and enhance the physical and chemical properties of CHT such as crosslinking reaction [15], functionalization by organic groups [16], composition with inorganic materials [17], and grafting with carbon materials [18]. The cross-linking character is one of the most common procedures, which is commonly used to increase the stability of CHT in an acidic medium and to improve mechanical strength [19]. CHT crosslinked absorbent materials have been vastly used for removal of dyes from water [20]. Furthermore, the CHT-based nanocomposites have been attracted significant interest due to its outstanding properties such as specific surface area, chemical stability, adsorption capacity, and thermal stability l [21]. Various inorganic nanomaterials such as copper oxide (CuO) [22], nickel oxide (NiO) [23], and zinc oxide (ZnO) [24] have been introduced in preparation CHT nanocomposites to improve and enrich its properties. Among these, ZnO nanoparticles is one of the interesting inorganic materials for the development of CHT-based adsorbents due to its exceptional properties such as biocompatibility, safe to use, inexpensive, high surface area, preferable adsorption capacity, antimicrobial activity, chemical stability, and photo activity [25].

Recently, CHT/ZnO nanocomposites have received great attention as a key material in many applications such as food packaging [26], wastewater treatment [27], antibacterial [28], and biosensor [29]. Currently, magnetic adsorbents are receiving great attention from researchers due to its easy collection from an aqueous solution by magnetic tool after adsorption process. In same regard, magnetite (Fe_3O_4) is one of the most magnetic particles used in preparation of magnetic adsorbents for water remediation application owing to its small particle size, biodegradability, high surface area, and temperature stability [30]. In fact, modifying CHT with nano scale materials is an effective strategy to enhance the physical property, thermal stability, and surface area, and surface functionality of CTS. Moreover, the chemical modification of chitosan by dialdehyde

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crosslinking agent and formation of Schiff's base CHT's derivatives is another effective strategy to enhance the chemical stability, prevent high level of swelling in aqueous environment, and reduce leachability in acidic environment.

Therefore, the main aim of this study is to develop a chemically stable Schiff's bases derivate of magnetic chitosan-glutaraldehyde/Fe$_3$O$_4$ composite (CHT-GLA/ZnO/Fe$_3$O$_4$). To achieve this goal, zinc oxide (ZnO) nanoparticles was loaded into its polymeric structure of CHT and followed by crosslinking step via Schiff's base reaction using glutaraldehyde to obtain an effective adsorbent of magnetic chitosan-glutaraldehyde/ZnO/Fe$_3$O$_4$ nanocomposite (CHT-GLA/ZnO/Fe$_3$O$_4$). The effectiveness of CHT-GLA/ZnO/Fe$_3$O$_4$ was tested for the removal of remazol brilliant blue R (RBBR) dye from aqueous environment. The effect of the ZnO nanoparticles loading, dose, pH, temperature, and time on the synthesis of the adsorbent and the RBBR dye adsorption were evaluated and optimized by Box-Behnken design (BBD). Additionally, several kinetic and isotherm models were used to describe the adsorption mechanism and to determine the adsorption capacity of the synthesized nanocomposite. Finally, a proposed adsorption mechanism for RBBR onto CHT-GLA/ZnO/Fe$_3$O$_4$ was discussed.

2. Materials and methods

2.1 Materials

CHT ($\geq$75 % degree of deacetylation), ZnO nanopowder, GLA solution, and RBBR (C$_{22}$H$_{16}$N$_2$Na$_2$O$_{11}$S$_3$; MW: 626.54; g/mol λ_{max} = 592 nm) were supplied by Sigma–Aldrich. Iron (III) chloride hexahydrate (FeCl$_3$.6H$_2$O, MW: 270.30 g/mol), and Iron (II) chloride tetrahydrate (FeCl$_2$.4H$_2$O, MW:198.81 g/mol) were supplied from HmbG Chemicals and Bendosen Laboratory

Chemicals, respectively. Acetic acid (CH_3COOH), sodium chloride (NaCl), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were ordered from R&M Chemicals.

2.2 Synthesis of CHT-GLA/ZnO/Fe$_3$O$_4$

1 g of CHT flakes were poured in 60 mL of CH_3COOH acid solution (5% v/v) and agitated at 550 rpm on a magnetic stirrer for 24 h at 25 °C to dissolute of CHT flakes. Subsequently, 10 mL aqueous solution of Fe^{3+}/Fe^{2+} ions (3.9 g $FeCl_3.6H_2O$ and 2.7 g $FeCl_2.4H_2O$) was added to CHT solution with stirring for 1 h. The magnetic CHT/Fe_3O_4 beads were obtained by dropping of the mixture solution as drops into 1000 mL of NaOH solution (2 M). The resulting magnetic CHT hydrogel beads were washed with distilled water until become neutral. Cross-linking process of the magnetic beads was accomplished by adding them into flask containing 80 mL GLA (2 %) with mild stirring in shaker bath incubator at 40 °C for 2 h. The resultant was washed and then dried at 60 °C overnight in oven to get the final $CHT-GLA/Fe_3O_4$ composite. For the purpose of comparison, chitosan-glutaraldehyde/ZnO/Fe_3O_4 nanocomposite was prepared by mixing different ratios (wt.%) of ZnO nanoparticles with chitosan before adding to CH_3COOH solution, i.e. 25:75 wt.% (ZnO:CHT), which was named as CHT-GLA/ZnO/ Fe_3O_4-25 and 50:50. wt.% (ZnO:CHT), which was named as CHT-GLA/ZnO/Fe_3O_4-50. Ultimately, the synthesized composites were pulverized and then sieved at a particle size (≥250 μm) for further use. Fig. 1 demonstrates the fabrication steps of the CHT-GLA/ZnO/Fe_3O_4 nanocomposite.

2.3 Characterization

The specific surface area, and average pore width of the synthesized composites were analyzed by Brunauer-Emmett-Teller (BET) approach (Micromeritics ASAP 2060). The textural

and morphological characteristics of the synthesized composites and target composite (CHT-GLA/ZnO/Fe$_3$O$_4$-25) after RBBR adsorption were observed by scanning electron microscope (SEM, Zeiss Supra 40 VP). The chemical qualitative analysis was also performed for the synthesized composites with energy dispersive X-Ray analysis (EDX). The phase determination of the synthesized composites was characterized by X–ray powder diffractometry (XRD, X'Pert PRO, PAnalytical). The surface chemical characteristics of the synthesized composites and the target composite (CHT-GLA/ZnO/Fe$_3$O$_4$-25) after RBBR adsorption were defined by Fourier Transforms infrared (FTIR) spectra (Perkin-Elmer, Spectrum RX I). The amine group content of the synthesized composites was identified by pH-potentiometric titration mode [31]. The surface charge of the CHT-GLA/ZnO/Fe$_3$O$_4$-25 was estimated by zero point of charge (pH$_{pzc}$) analysis [32]. The C, H, and N contents in the synthesized composites were determined by a CHN analyzer (Thermo Scientific).

2.4 Experimental setup

In this study, BBD was used as an efficient and preferable statistical tool for generating the RBBR removal efficiency (%) as the response regarding response-dependent factors including ZnO loading, dose, pH, temperature, and time. Stat-Ease Design-Expert (Version 11) software was appointed to statistical analysis and mathematical modeling of the experimental data. Table 1 shows the experimental levels of independent variables and their codes. A polynomial equation (Eq. 1) was employed to fit the experimental data and predict the RBBR removal efficiency.

$$Y = \beta_0 + \sum \beta_i X_i + \sum \beta_{ii} X_i^2 + \sum \sum \beta_{ij} X_i X_j \qquad (1)$$

where Y, and (X_i and X_j) denote the predicted response, and coded values of factors. β_0, β_i, β_{ii} and β_{ij} indicate the regression coefficients of intercept, the linear, quadratic, and the interaction effects, respectively. Forty-six experiments were obtained through BBD model to investigate the impacts of the five variables: A: ZnO loading (0-50%), B: dose (0.02-0.1 g), C: pH (4-10), D: temperature (30-60 °C), and E: time (10-60 min) on the RBBR removal efficiency. Table 2 displays the experiments for the optimization as per BBD and their experimental responses. A known mass of adsorbent was added to 250 mL conical flasks, which contained a 100 mL of RRBR solution. The flasks were sealed and shaken by a shaker bath incubator (WNB7-45, Memmert) at shaking speed of 100 strokes/min. After adsorption, the adsorbent material was magnetically separated by external magnetic field, and the resulting solution was filtered with a 0.45 µm syringe filter. The RBBR concentrations in solution were calculated spectrophotometrically at λ_{max} 592 nm by UV-Vis spectroscopy. Eq. (2) shows the relationship for calculating the RBBR removal efficiency (RE %).

$$RE \% = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (2)$$

where C_o (mg/L) and C_e (mg/L) denote the RRBR concentrations at initial and at equilibrium, respectively.

2.5 Adsorption study of RBBR on CHT-GLA/ZnO/Fe₃O₄

Batch experiments were performed to calculate the adsorption capacity of CHT-GLA/ZnO/Fe$_3$O$_4$-25. According to Table 2, the greatest removal of RBBR was recorded in experiment seven under these conditions: ZnO loading = 25%, dose = 0.06 g, pH = 4, temperature = 60 °C, and time = 35 min. Thus, the experiments of the RBBR dye adsorption were conducted

with these conditions stated above at different initial RBBR concentrations (50-250 mg/L) and contact time (0-540 min). The batch adsorption experiments were accomplished by following the same procedure stated above (section 2.4). Eq. (3) gives the relationship for calculating the adsorption capacity, q_e (mg/g) of RBBR onto CHT-GLA/ZnO/Fe$_3$O$_4$ at equilibrium.

$$q_e = \frac{(C_o - C_e)V}{W} \qquad\qquad (3)$$

where W and V denote the mass of the used composite (g) and the volume of the RRBR solution (L), respectively.

3. Results and Discussion

3.1. Characterization of the prepared magnetic adsorbents

The physicochemical characteristics, namely, elemental composition, amine group content, surface areas properties of the CHT-GLA/Fe$_3$O$_4$, CHT-GLA/ZnO/Fe$_3$O$_4$-25, CHT-GLA/ZnO/Fe$_3$O$_4$-50 are presented in Table 3. CHN-O analysis of the elemental composition demonstrated that the CHT-GLA/ZnO/Fe$_3$O$_4$-25 and CHT-GLA/ZnO/Fe$_3$O$_4$-50 had lower carbon content, and higher oxygen content than CHT-GLA/Fe$_3$O$_4$. This finding can be attributed to the incorporation of metal oxide (ZnO) nanoparticles into the molecular structure of CHT-GLA. The results of the pH-potentiometric titration clarified that the amine group content (%) in CHT-GLA/ZnO/Fe$_3$O$_4$-25 and CHT-GLA/ZnO/Fe$_3$O$_4$-50 was gradually decreased with additional loading of ZnO nanoparticles in the molecular structure of CHT-GLA. This observation can be assigned to the physical mixing of CHT with ZnO nanoparticles. In another word, more loading of ZnO nanoparticles will lead to less content of CHT in the whole molecular structure of the composite material as a result less amine group content will be obtained [15]. Another possible

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reason is the coordination of zinc ions with the amino and hydroxyl groups, which may lead to reduce the free amino group content [28].

The results of BET analysis showed that the surface area of CHT-GLA/Fe_3O_4, CHT-GLA/ZnO/Fe_3O_4-25, and CHT-GLA/ZnO/Fe_3O_4-50 are 4.17, 9.92, and 6.67, respectively. These results are probably because the ZnO nanoparticles possessing a high surface area were scattered on the CHT-GLA/Fe_3O_4 matrix and enlarged its surface [33]. It was clearly observed from Table 3 that the CHT-GLA/ZnO/Fe_3O_4-25 has a higher surface area compared to CHT-GLA/ZnO/Fe_3O_4-50, although CHT-GLA/ZnO/Fe_3O_4-50 has a higher loading of ZnO nanoparticles. These results can be attributed to the fact that a high loading of ZnO nanoparticles may cause depositing of some of them within the larger pores of the CHT-GLA matrix [34]. Depending on the classification of IUPAC, all the prepared composites (CHT-GLA/Fe_3O_4, CHT-GLA/ZnO/Fe_3O_4-25, and CHT-GLA/ZnO/Fe_3O_4-50) are a mesoporous [35].

The crystallinity of the CHT-GLA/Fe_3O_4, CHT-GLA/ZnO/Fe_3O_4-25, and CHT-GLA/ZnO/Fe_3O_4-50 were investigated by XRD analysis. The XRD patterns of CHT-GLA/Fe_3O_4, CHT-GLA/ZnO/Fe_3O_4-25, and CHT-GLA/ZnO/Fe_3O_4-50 are exhibited respectively in Fig. 2a-c. The XRD result of CHT-GLA/Fe_3O_4 (Fig. 2a) exhibits several crystalline peaks at $2\theta = 30.1°$, 35.2°, 43.1°, 53.2°, 57.3°, and 62.1°, which are assigned to (220), (311), (400), (422), (511), and (440) of Fe_3O_4 particles, respectively (JCPDS card No. 19-629) [36]. The broad peak observed at 20.3° in Fig. 2a is ascribed to the semicrystalline nature of CHT [37]. The XRD patterns of CHT-GLA/ZnO/Fe_3O_4-25 (Fig. 2b) and CHT-GLA/ZnO/Fe_3O_4-50 (Fig. 2c) shows a typical crystalline peak at 31.80, 34.45, 36.27, 47.59, 56.66, 62.91, and 68.0 belonging to the crystalline phases (100), (002), (101), (102), (110), (103), and (112), respectively of ZnO nanoparticles (JCPDS card no. 36–1451) [37]. These results confirm the strong interaction between the -NH_2 and -OH groups of

CHT with Zn ions and reinforce a good compatibility between the polymer matrix of CHT-GLA and the ZnO [38]. Furthermore, it was noticed that all the peaks of CHT-GLA/ZnO/Fe$_3$O$_4$-50 had a higher intensity compared to CHT-GLA/ZnO/Fe$_3$O$_4$-25 due to the increased loading of ZnO nanoparticles in the polymer matrix of CHT-GLA.

The typical functional groups of the CHT-GLA/Fe$_3$O$_4$, CHT-GLA/ZnO/Fe$_3$O$_4$-25, and CHT-GLA/ZnO/Fe$_3$O$_4$-25 after RBBR adsorption were obtained by FTIR analysis. The FTIR spectra of CHT-GLA/Fe$_3$O$_4$, CHT-GLA/ZnO/Fe$_3$O$_4$-25, and CHT-GLA/ZnO/Fe$_3$O$_4$-25 after RBBR adsorption are presented respectively in Fig. 3a-c. The bands observed (Fig. 3a) at 3430 cm^{-1}, 2910 cm^{-1}, 1640 cm^{-1}, 1370 cm^{-1}, 1060 cm^{-1}, and 550 cm^{-1} are ascribed to O-H and N-H stretching, C-H symmetric stretching, N-H bending vibration, C-N stretching of residual N-acetyl group, C-O-C stretching vibration, and Fe-O bond, respectively [39]. The peak at 1660 cm^{-1} also corresponding to the C=N stretching vibration arising from Schiff base reaction between amino groups of CHT and carbonyl groups of GLA [15]. In FTIR spectrum of CHT-GLA/ZnO/Fe$_3$O$_4$-25, it was clearly observed the bands of -NH$_2$ and –OH groups were shifted and became stronger, signifying the strong interaction between -NH$_2$ and –OH groups and ZnO [37]. In same context, the peak observed at 540 cm^{-1} corresponding to metaloxygen linkage (Zn-O) [40]. The spectrum of the CHT-GLA/ZnO/Fe$_3$O$_4$ nanocomposite after RRBR adsorption appeared a remarkable shift in the -OH and N-H bands, signifying the contributing of the -OH and NH$_2$ groups in the RBBR adsorption.

The surface morphology and chemical composition of CHT-GLA/Fe$_3$O$_4$, CHT-GLA/ZnO/Fe$_3$O$_4$-25, CHT-GLA/ZnO/Fe$_3$O$_4$-50, and CHT-GLA/ZnO/Fe$_3$O$_4$-25 after RBBR adsorption were examined by SEM-EDX. The SEM images and EDX analysis of CHT-GLA/Fe$_3$O$_4$, CHT-GLA/ZnO/Fe$_3$O$_4$-25, CHT-GLA/ZnO/Fe$_3$O$_4$-50, and CHT-GLA/ZnO/Fe$_3$O$_4$-

25 after RBBR adsorption are presented respectively in Fig. 4a-d. As depicted in Fig. 4a, the CHT-GLA/Fe$_3$O$_4$ nanocomposite owned an irregular, wavy, and uneven structure. The EDX analysis of CHT-GLA/Fe$_3$O$_4$ composite detects the presence of C, O, N and Fe. Fig. 4b and Fig. 4c corresponding to 25% ZnO and 50 % ZnO nanoparticles loaded into molecular structure of CHT-GLA show that the nanocomposite's surface contains small fractures and holes due to the embedded and well-dispersed ZnO nanoparticles into polymer matrix of CHT-GLA. According to EDX analysis, the main elements present in CHT-GLA/ZnO/Fe$_3$O$_4$-25 and CHT-GLA/ZnO/Fe$_3$O$_4$-50 nanocomposites are C, N, O, Fe and Zn. The presence of peak for Zn element in the EDX spectrum confirms that the ZnO nanoparticles were successfully loaded into the structure of CHT-GLA. After RRBR adsorption, CHT-GLA/ZnO/Fe$_3$O$_4$ nanocomposite surface was remarkably changed into smooth, compact, and homogenous surface in agreement with the covering by RBBR molecule. This finding was confirmed by EDX, which indicated the existence S element.

3.2 Statistical analysis and model fitting

The statistical analysis and specification the important impacts of the parameters and their interactions for the RBBR removal data was achieved by the variance analysis (ANOVA). Table 4 displays ANOVA results of the RBBR removal. The model F value of 16.37 (p-value < 0.0001) indicates that the model for the RBBR removal is significant [41]. The value of correlation coefficient (R^2) for this model is 0.93, which indicates that the accuracy of the fitting of the model, and good correlation between predicted and experimental RBBR removal values [21]. Statistically, the model terms are significant with P-value less than 0.05. In this case A, B, C, E, AB, BC, BE, A^2, and B^2 are significant terms in the RBBR removal process. Thus, the experimental relationship

between RBBR removal efficiency and the examined variables was correlated by quadratic polynomial model as expressed in Eq. (4).

RBBR removal efficiency (%) $= +45.87 + 7.63A + 12.94B - 13.46C + 2.83E - 5.93AB - 6.95BC + 6.88BE - 6.86A^2 - 4.07B^2$ (4)

Moreover, the verification of experimental results can be achieved by the analysis of the obtained graphics from BBD model such as actual versus predicted, normal probability of the residuals, and externally studentized residuals versus predicted. Fig. 5a displays the actual versus predicted plot of RBBR removal efficiency values. According to Fig. 5a, the points of actual were mostly close to the points of predicted, signifying that the BBD model can adequately optimize the adsorption process of RBBR dye. Fig. 5b demonstrates the normal probability plot of residuals. As per Fig. 5b, all points are normally distributed around the straight-line, elucidating that the independence of the residuals [36]. Fig. 5c shows the plot of externally studentized residuals of the experimental versus predicted values. It can be noticed from Fig. 5c the points are scattered around the horizontal line, indicating that no significant variation between actual and predicted [42].

3.3 Optimization of RBBR removal

Three-dimensional (3D) response surfaces are important graphical plots to explain the interaction effects of two operational factors on the RBBR removal efficiency. Fig. 6a presents the 3D surface plot of the combined effect of ZnO loading and dose on the RBBR removal efficiency at a constant pH (7), temperature (45 °C), and time (35 min). The obtained results from Fig. 6a demonstrate that the RBBR removal efficiency was improved by increasing both adsorbent dose and ZnO loading. This finding relates to the high surface area resulted from ZnO nanoparticles

and the higher number of active binding sites of the CHT-GLA/ZnO/Fe$_3$O$_4$, which are readily available to adsorb RBBR dye [34].

Fig. 6b presents the 3D surface plot of the combined effect of dose and pH on the RBBR removal efficiency at a constant ZnO loading (25%), temperature (45 °C), and time (35 min). It can be seen from Fig. 6b, the RBBR removal efficiency (%) increased by decreasing the pH value from basic environment (pH=10) towards acidic environment (pH=4). The value pH$_{pzc}$ of the CHT-GLA/ZnO/Fe$_3$O$_4$ is 7.4 as illustrated in Fig. 6c. This finding signifies that the CHT-GLA/ZnO/Fe$_3$O$_4$ surface at pH value greater than pH$_{pzc}$ acquires a negative charge. Thus, the CHT-GLA/ZnO/Fe$_3$O$_4$ surface at acidic environment (pH =4) turns to a positive charge due to the increase of H$^+$ concentration in the solution [43]. Accordingly, electrostatic attractions will be formed between the surface cationic groups of the CHT-GLA/ZnO/Fe$_3$O$_4$ and the RBBR molecules as outlined in Eq. (5).

$$CHT - GLA/ZnO/Fe_3O_4^+ \ + \ RBBR^- \ \leftrightarrow \ CHT - GLA/ZnO/Fe_3O_4^+ \ ... \ ^-RBBR \qquad (5)$$
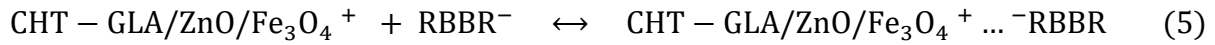
The combined effect of dose and time on the RBBR removal efficiency was important. Fig. 6d presents the 3D surface plot of the important combined effects of dose and time on the RBBR removal efficiency at a constant ZnO loading (25%), pH (7), and temperature (45 °C). As can be shown from Fig. 6d that the RBBR removal efficiency did not improve significantly by increasing the contact time up to 60 min, indicating that the occupancy of the active sites on the adsorbent with RBBR molecules was extremely fast, and reached the equilibrium absorption of RBBR dye within a short period of time.

3.4 Adsorption study

The time dependence of RBBR uptake by CHT-GLA/ZnO/Fe$_3$O$_4$-25 nanocomposite was monitored for better understanding to the adsorption process. In this regard, the influence of different initial RBBR concentration (range: 50-250 mg/L) on adsorption behaviour of RBBR by CHT-GLA/ZnO/Fe$_3$O$_4$-25 nanocomposite was investigated at fixed dose of CHT-GLA/ZnO/Fe$_3$O$_4$-25 (0.06 g), temperature (60 ^{o}C), solution pH (4), and solution volume (100 mL). The adsorption capacity values of CHT-GLA/ZnO/Fe$_3$O$_4$-25 as a function of contact time were presented in Fig. 7a. As can be seen, rapid q_t increases at the beginning of the adsorption process for all studied concentrations which can be attributed to the existence of the adsorption active groups on the surface of CHT-GLA/ZnO/Fe$_3$O$_4$-25, indicating CHT-GLA/ZnO/Fe$_3$O$_4$-25 could be utilized as a promising adsorbent in textile dye removal. Moreover, the adsorption capacity of CHT-GLA/ZnO/Fe$_3$O$_4$-25 was found to increase from 60.6 to 179.7 mg/g by increasing the initial RBBR concentration from 50 to 250 mg/L. This result may be due to the higher RBBR concentration gradient, which enhances the moving of RBBR molecules to the active sites available onto the CHT-GLA/ZnO/Fe$_3$O$_4$-25 surface [13, 44].

3.5 Kinetic study

To determine the controlling mechanism of the adsorption process of the RBBR on the CHT-GLA/ZnO/Fe$_3$O$_4$ surface. The dynamical experimental data were fitted to two kinetic models: pseudo-first order (PFO) [45] and pseudo-second order (PSO) [46]. The parameters of the kinetic models were obtained by the non-linear equations of PFO and PSO given in Eqs. (6) and (7) respectively.

$$q_t = q_e (1 - \exp^{-k_1 t})$$ (6)

$$q_t = \frac{q_e^2 k_2 t}{1 + q_e k_2 t}$$ (7)

where q_e and q_t are the adsorption capacities (mg/g) at adsorption equilibrium and time (t), respectively. k_1 (1/min) is the PFO adsorption rate constant and k_2 (g/mg min) is the PSO adsorption rate constant. The calculated parameters of the kinetic models are listed in Table 5. It can be seen from Table 5 that the R^2 values of the PSO was higher than the PFO. Moreover, the calculated q_e of the PSO was closer to the experimental q_e compared to the values of calculated q_e for the PFO. The obtained results clarified that the adsorption of RBBR dye onto CHT-GLA/ZnO/Fe$_3$O$_4$ surface is a chemisorption process including electrostatic interactions, which are happened between the positive charges and cationic groups available on the CHT-GLA/ZnO/Fe$_3$O$_4$ nanocomposite surface with the negative charges (-SO$_3^-$) of the RBBR dye [47].

3.6 Isotherm study

The adsorption isotherms are applied to understand the relationship between equilibrium adsorption capacity of the CHT-GLA/ZnO/Fe$_3$O$_4$ nanocomposite and initial concentration of RBBR [13]. The equilibrium adsorption is crucial parameter in the describing and explaining the correlation between CHT-GLA/ZnO/Fe$_3$O$_4$ nanocomposite and RBBR molecules. The affinity and adsorption capacity of CHT-GLA/ZnO/Fe$_3$O$_4$-25 nanocomposite to adsorb RBBR dye from aqueous solution were elucidated by fitting the experimental data to Langmuir [48], Freundlich [49], and Temkin [50] isotherm models. The Langmuir model indicates that all adsorption sites are equivalent and a monolayer adsorption towards pollutants is occurred on a homogeneous

surface of adsorbent [13]. The Freundlich model is generally used to describe a multilayer adsorption towards pollutants is occurred on a heterogeneous surface of adsorbent [18]. Moreover, the Temkin model assumes there is a linear relationship between adsorption heat and coverage by taking into consideration the temperature effect [17]. The parameters of the isotherms were obtained by the non-linear equations of Langmuir, Freundlich, and Temkin as presented in Eqs (8), (9), and (10) respectively.

$$q_e = \frac{q_{max}K_aC_e}{1+K_aC_e} \qquad (8)$$

$$q_e = K_fC_e^{1/n} \qquad (9)$$

$$q_e = \frac{RT}{b_T}\ln(K_TC_e) \qquad (10)$$

where q_{max} (mg/g) is the calculated adsorption capacity of the CHT-GLA/ZnO/Fe$_3$O$_4$, and K_a (L/mg) is the Langmuir equilibrium constant. K_f (mg/g) (L/mg)$^{1/n}$ and n are constants related to the Freundlich model. K_T (L/mg) and b_T (J/mol) are Temken constants related to the equilibrium binding, and adsorption heat. T (K) and R (8.314J/molK) represents the temperature and gas constant, respectively. Fig. 7b and Table 6 show the fitting parameters and curves of isotherms, respectively. As per the correlation coefficient (R^2) of models, the Freundlich model ($R^2 = 0.97$) and Temkin model ($R^2 = 0.97$) are higher than that of the Langmuir model ($R^2 = 0.94$), Thus, the adsorption process of RBBR by CHT-GLA/ZnO/Fe$_3$O$_4$ is more in line with the Freundlich and Temkin models, indicating the heterogeneous character of the RBBR physical and chemical adsorption onto CHT-GLA/ZnO/Fe$_3$O$_4$ surface [51]. The q_{max} of RBBR on CHT-GLA/ZnO/Fe$_3$O$_4$-25 was found as 176.6 mg/g at 60 °C. Table 7 summarizes the comparison the q_{max} of the CHT-GLA/ZnO/Fe$_3$O$_4$-25 with other adsorbents reported in previous works toward

RBBR. These results of Table7 demonstrate that the CHT-GLA/ZnO/Fe$_3$O$_4$-25 had favorable adsorption ability for the removal of organic dyes from wastewater.

3.7. Adsorption mechanism of RBBR

The adsorption mechanism of RBBR on the CHT-GLA/ZnO/Fe$_3$O$_4$ nanocomposite surface was sketched depending on of the presence of active adsorption sites such as hydroxyl (-OH), amino (-NH$_2$) and Zn (OH)$^+$, as shown in Fig. 8. At first, CHT-GLA/ZnO/Fe$_3$O$_4$ nanocomposite surface can obtain positive charges in an acidic solution due to pH$_{acidic}$ < pH$_{pzc}$. The positive charges of the CHT-GLA/ZnO/Fe$_3$O$_4$ nanocomposite surface can be obtained from different sources such as hydroxyl (-OH), and amine (-NH$_2$) protonated groups, as well as positive charges formed from ZnO nanoparticles. Electrostatic interactions are prime character for the RBBR adsorption because of the plenty of positive charges and cationic groups on the CHT-GLA/ZnO/Fe$_3$O$_4$ nanocomposite surface, which are attracted with the negative charges (-SO$_3^-$) of the RBBR dye. Various studies have been reported using positive charges of ZnO nanoparticles formed in the acidic medium to adsorb organic dyes through electrostatic interactions [60, 61]. Hydrogen interactions designated by H-bonding and Yoshida H-bonding from significant interactions that could be played an important role in adsorption of RBBR dye. These interactions (H-bonding) and (Yoshida H-bonding) are formed between the free H and H-OH (hydrogen of hydroxyl) available on the CHT-GLA/ZnO/Fe$_3$O$_4$ nanocomposite surface with N and O groups and the aromatic system of the RBBR dye, respectively [62]. Lastly, n-π interactions occur between the electron-donating system represented by groups containing N and O in the CHT-GLA/ZnO/Fe$_3$O$_4$ nanocomposite and the electron-accepting system represented by the aromatic rings of the RBBR dye [39].

4. Conclusion

A Schiff's base magnetic chitosan-glutaraldehyde/zinc oxide/Fe_3O_4 nanocomposite (CHT-GLA/ZnO/Fe_3O_4) was successfully developed to be an effective adsorbent for the removal of RBBR from RBBR dye solutions. The optimum conditions for synthesis of adsorbent and RBBR adsorption were ZnO nanoparticles loading (25%), dose (0.06 g), pH (4), temperature (60 °C), and time (35 min). The obtained results from BBD demonstrated that the highest RBBR removal efficiency (75.8%) was recorded at AB (ZnO loading x adsorbent dosage), BC (adsorbent dosage x pH), and BE (adsorbent dosage x time) interactions. The experimental data of kinetics, isotherms showed that chemisorption and multilayer adsorption of the RBBR on the CHT-GLA/ZnO/Fe_3O_4-25 surface. The maximum adsorption capacity of the target nanocomposite (CHT-GLA/ZnO/Fe_3O_4-25) was reached of 176.6 mg/g at 60 °C. The adsorption mechanism of RBBR onto CHT-GLA/ZnO/Fe_3O_4 nanocomposite was attributed to multi-interactions including electrostatic attractions, hydrogen bonding, Yoshida H-bonding, and n-π interactions. This study presents a promising hybrid nanobiomaterial adsorbent in environmental nanotechnology to separate and remove the contaminants such as organic dyes from wastewater.

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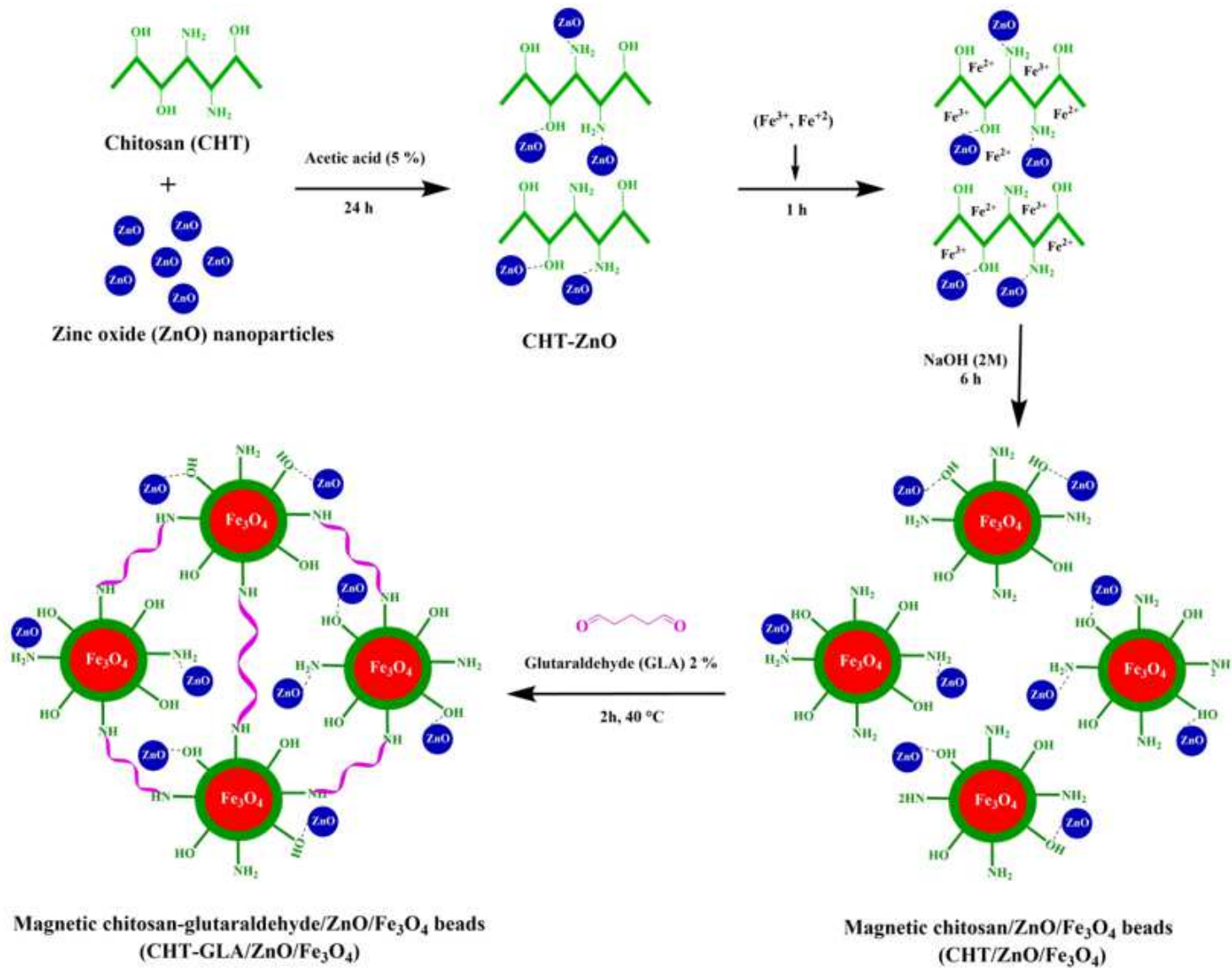
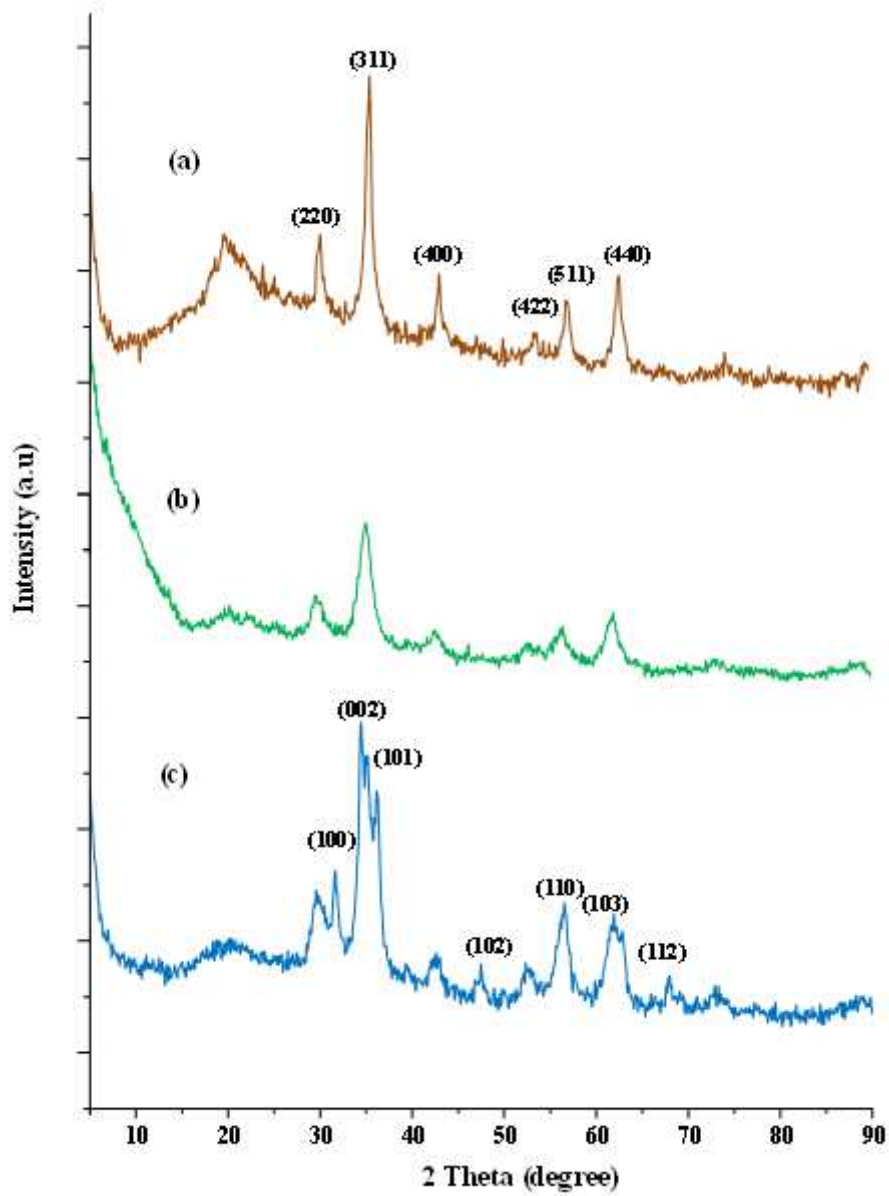# Figures

Figure 1

Synthesis steps of CHT-GLA/ZnO/Fe3O4

Figure 2

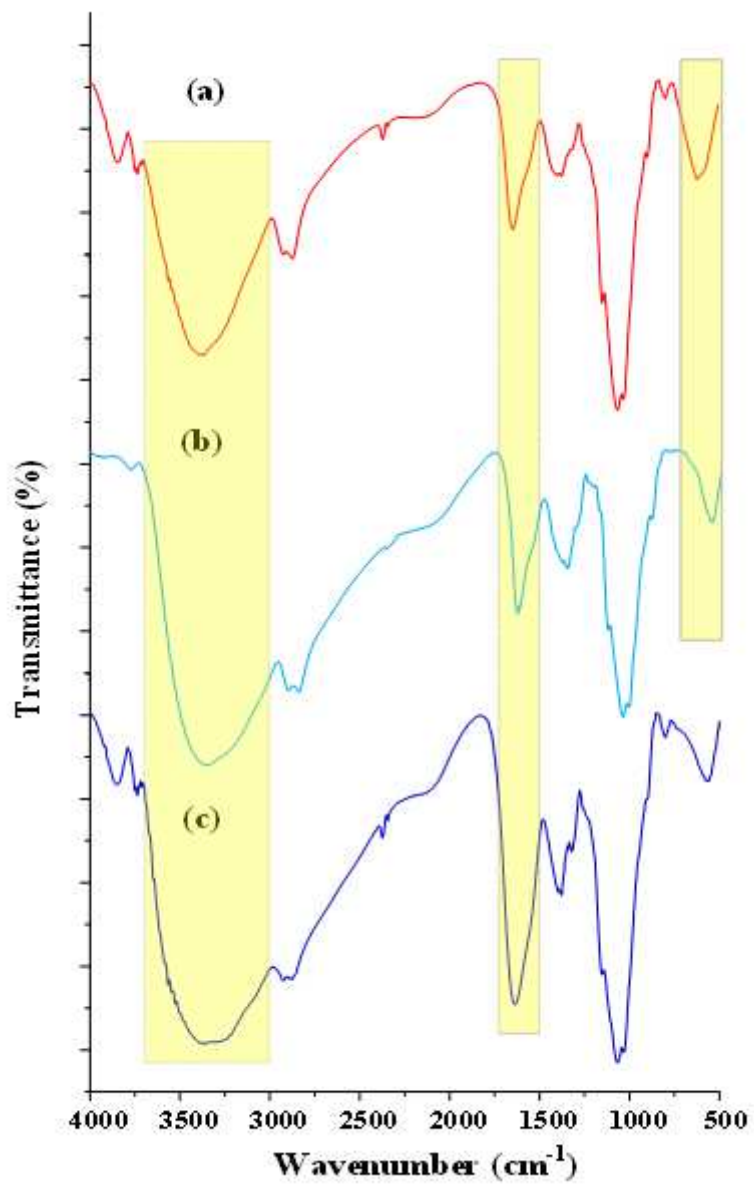XRD patterns of (a) CHT-GLA/Fe3O4, (b) CHT-GLA/ZnO/Fe3O4-25, and (c) CHT-GLA/ZnO/Fe3O4-50

Figure 3

FTIR spectra of (a) CHT-GLA/Fe3O4, (b) CHT-GLA/ZnO/Fe3O4-25, and (c) CHT-GLA/ZnO/Fe3O4-25 after adsorption of RBBR dye
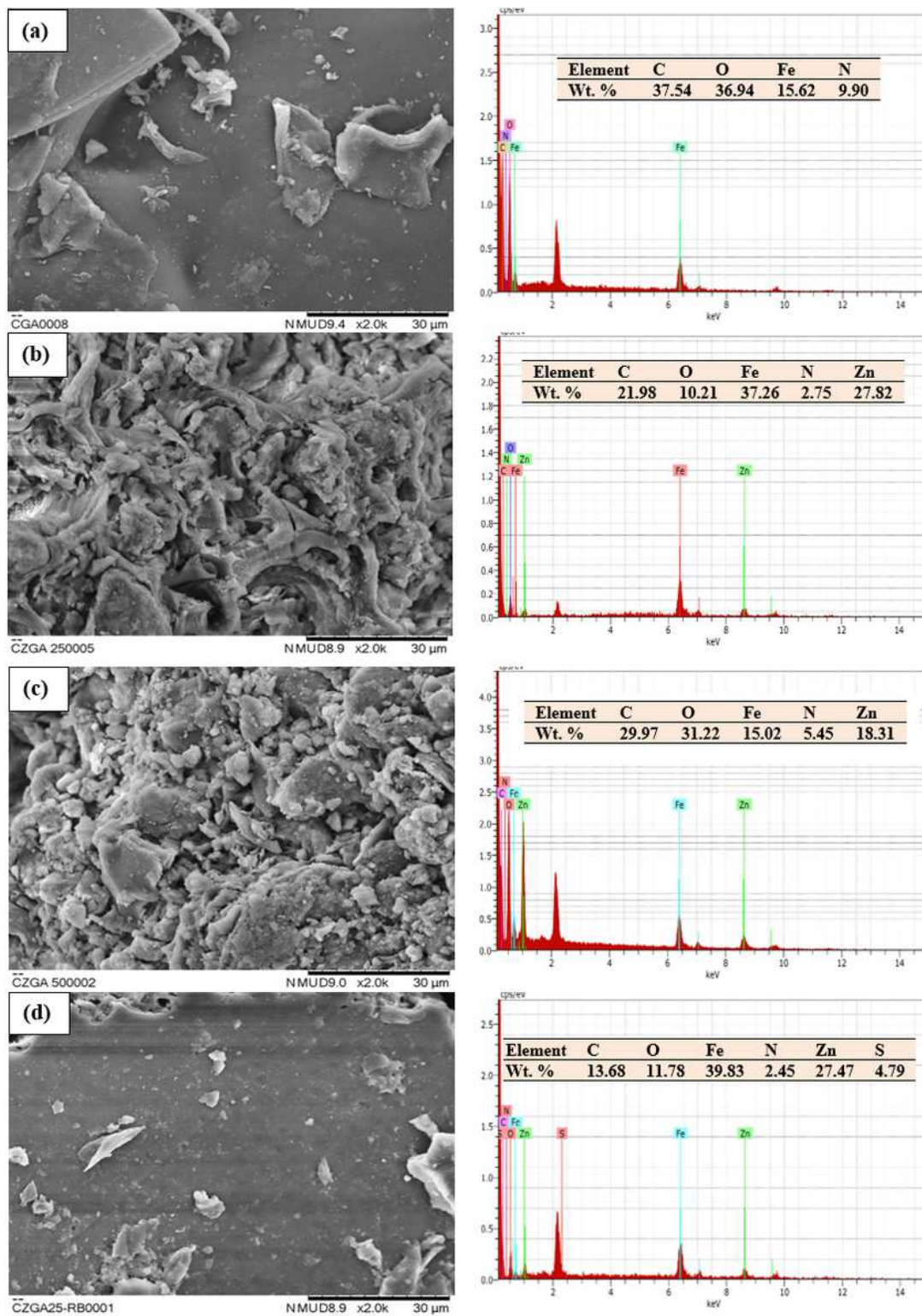
(a)

Element	C	O	Fe	N
Wt. %	37.54	36.94	15.62	9.90

(b)

Element	C	O	Fe	N	Zn
Wt. %	21.98	10.21	37.26	2.75	27.82

(c)

Element	C	O	Fe	N	Zn
Wt. %	29.97	31.22	15.02	5.45	18.31

(d)

Element	C	O	Fe	N	Zn	S
Wt. %	13.68	11.78	39.83	2.45	27.47	4.79

Figure 4

SEM images of (a) CHT-GLA/Fe3O4, (b) CHT-GLA/ZnO/Fe3O4-25 (c) CHT-GLA/ZnO/Fe3O4-50, and (d) CHT-GLA/ZnO/Fe3O4-25 after adsorption of RBBR dye at magnification power 2000x.
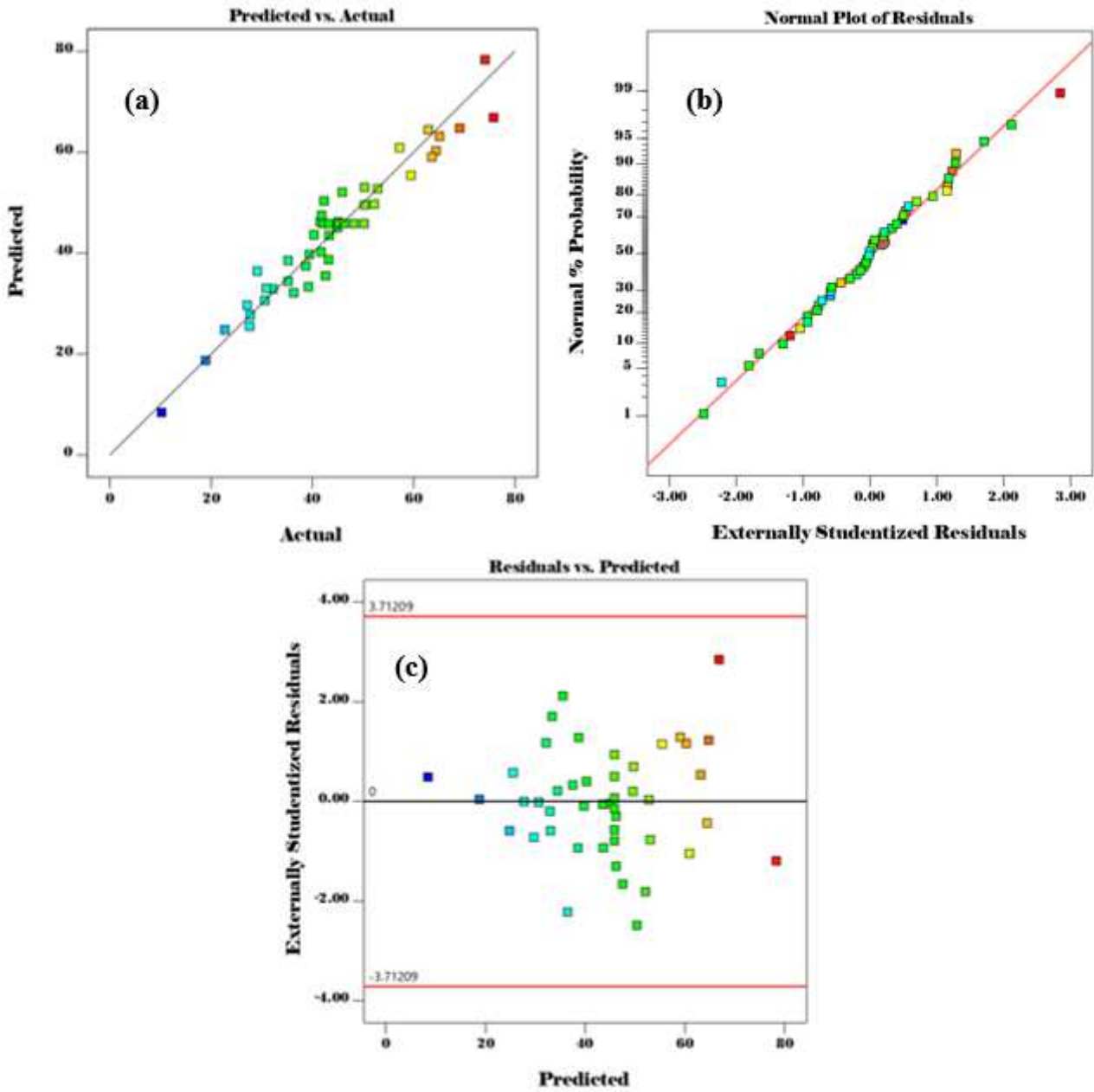
Figure 5

Plots of (a) actual versus predicted, (b) normal probability of the residuals, and (c) externally studentized residuals versus predicted.
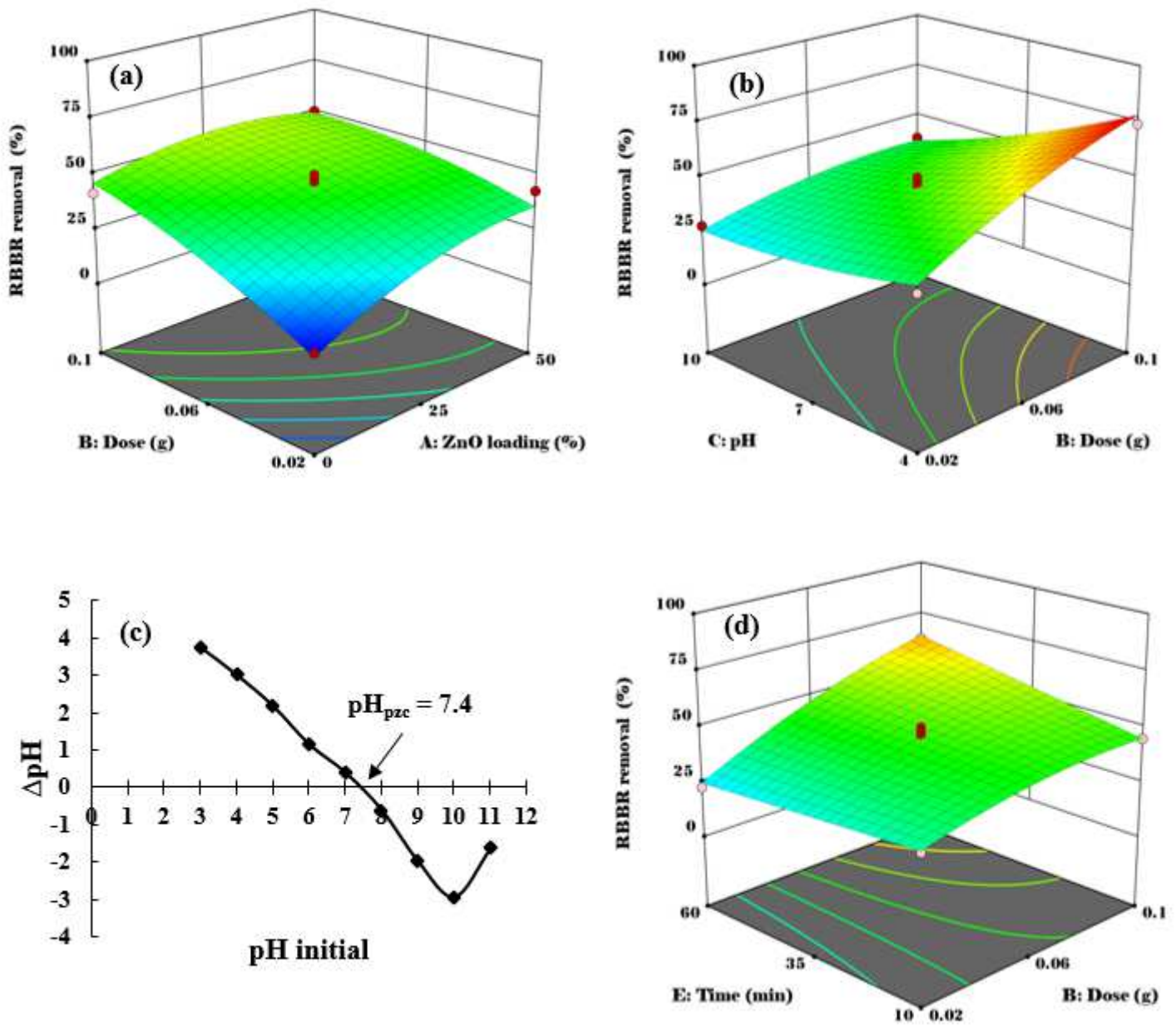
Figure 6

3D plots of (a) AB, (b) BC, and (d) BE significant interactions on RBBR removal; whereas. (c) pHpzc of CHT-GLA/ZnO/Fe3O4.
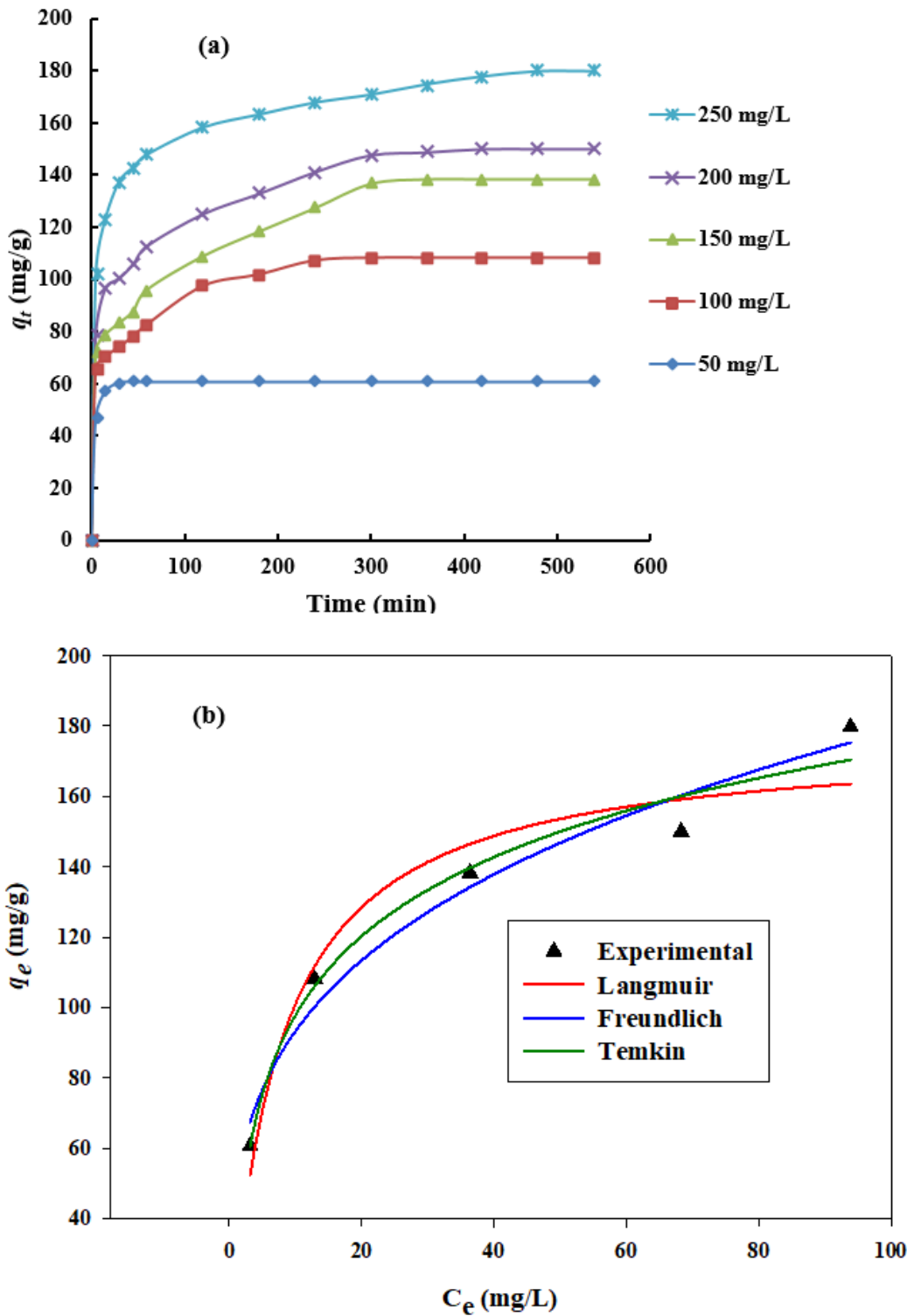
Figure 7

(a) Effect of the contact time on RBBR dye adsorption at different initial concentrations and (b) adsorption isotherms of RBBR by CHT-GLA/ZnO/Fe3O4-25 (dosage 0.06g, pH of solution 4, temperature 60 oC, agitation speed = 100 strokes and volume of solution = 100 mL).
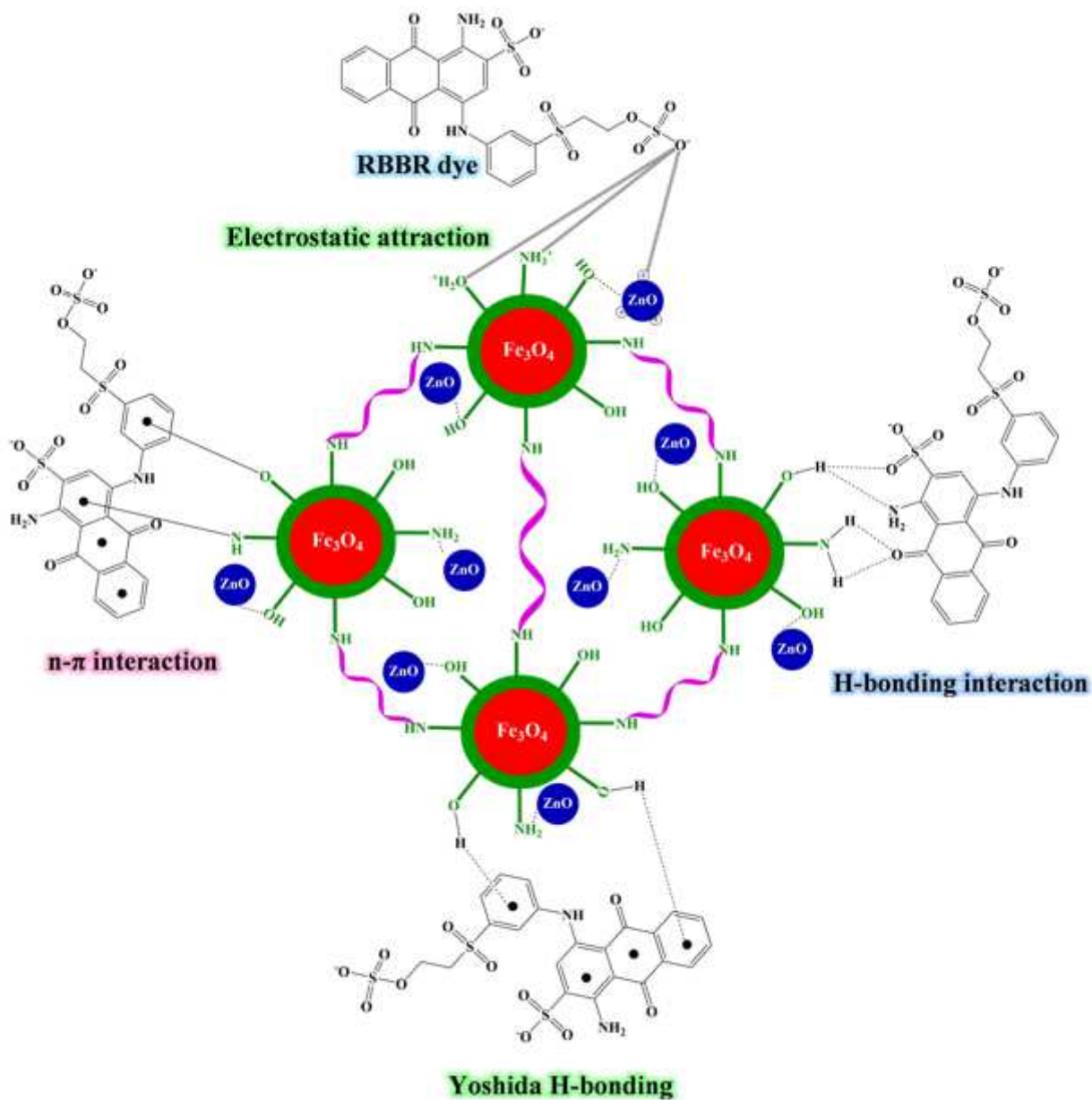
Figure 8

Illustration of the possible interaction between CHT-GLA/ZnO/Fe3O4 nanocomposite surface and RBBR dye including electrostatic attraction, hydrogen bonding interactions, Yoshida H-bonding, and n-π interactions.