Adsorption using chitosan and nano zerovalent iron composite material for sustainable water treatment

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Abstract

The growing global population and rapid urbanization have led to a water crisis. Current environmental issues emphasize the exploration of advanced materials and economical methods for purification of wastewater. The present work focuses on using advanced composite material made up of chitosan, activated carbon, zerovalent iron nanoparticles for adsorption of Congo red dye. The adsorbent was characterized using SEM, XRD and FTIR. An investigation was conducted on the critical parameters such as pH, the effect of initial dye concentration, temperature and the adsorbent dosage. The optimum dye to adsorbent ratio was analyzed. The composite material proposed as adsorbent was found to be very effective in adsorption of the Congo red dye. 100% adsorption was noted in 70 min under room temperature for the dye concentration of 100 ppm using 1 g of the adsorbent at pH 7. The efficacy of adsorption increased with the increase in temperature and found to increase under acidic pH. The optimum dye to adsorbent dosage is found to be 1:10. 100% of degradation is achieved within 50 min at a temperature of 80 °C and pH 1. The optimization studies were incorporated to investigate the effects of the variables on the process of adsorption using Box-Behnken design of experiments. The inquest of the present study provides an economical and efficient method for water treatment which can be easily adapted for the wastewater purification.

1. Introduction

The scarcity of good quality water would lead to several problems affecting humankind and the other living entities, causing a threat to the balanced ecosystem. It is very much essential to control water pollution by treating polluted water. Presence of dyes (colouring substances) is one of the major contaminants present in wastewater. Dyes are extensively employed in various industries like the textile industry, paper and pulp industry, pharmaceutical, food industry, cosmetics, dyestuffs, etc, which are discharged in wastewater [1–3]. The discharged untreated textile industry effluent, which consists of residual dyes and auxiliary chemicals is the major contributors of water pollution [4]. The presence of dye in water bodies even at lower concentrations harms the environment, especially the aquatic biota. It also possesses a mutagenic and carcinogenic effect on mankind. The aromatic amine compounds obtained as by-products during the degradation of azo dyes also cause a serious threat to the environment as the amine compounds are toxic and possess meagre rate of removal during aerobic treatment [5–9]. Dye effluent treatment is a difficult and tedious task owing to the stability of dye to heating, light and oxidizing agents and also due to resistance to aerobic digestion [10, 11]. Like most of the azo dyes, Congo red dye is found to be toxic, mutagenic and carcinogenic. The complex aromatic structure of the dye hinders the biodegradation process of the dye [12]. Therefore, it is necessary to develop a novel method and low-cost processes for dye degradation. Several processes such as adsorption, coagulation-flocculation; reverse osmosis, filtration (physical methods), ion exchange, electrochemical methods, oxidation using chemical agents, ozonation (chemical methods), aerobic and anaerobic digestion (biological methods) are used to remove the dye molecules from water. The processes possess several pros and cons with respect to cost-effectiveness, efficacy and environmental impacts [6, 13, 14]. One of the most simple and highly efficient processes is
adsorption using various adsorbents. This process helps in complete removal of dye without leaving any trace of dye in wastewater. In recent years, the usage of nanocomposite for adsorption of dye has attracted much attention from the research community. Among the wide range of adsorbents used, activated carbon and zerovalent iron nanoparticles stand out to be the most widely used adsorbent owing to the excellent adsorption capacity of both the composites [15–22]. The various other new adsorbents employed for Congo red dye removal are CNT and Mg(Al)O nanoparticles [23], starch–AlOOH–FeS2 [24], chitosan/montmorillonite [25], mixed iron and aluminium oxide (Fe2O3–Al2O3) [26], gold-magnetic nanocomposite (Au–Fe3O4–NPs–AC) [27], xanthan gum/silica hybrid nanocomposite (XG-g-PAM/SiO2nanocomposite) [28], guar gum-graft-poly(acrylamide)/silica (g-Gg/SiO2) hybrid nanocomposite [29], ZnO–ZnFe2O4-poly pyrrole magnetic nanocomposite [30], magnetic Fe3O4@graphene composite [31], polypyrrole and polyaniline nanoparticles [32], NiO–Al2O3 nanocomposites [33], exfoliated graphite-decorated MnFe2O4 nanocomposite [34], polyaniline/bismuth tungstate (PANI/Bi2WO6) [35], polyaniline/carboxymethyl cellulose/TiO2 nanocomposite (PAN/CMC/TiO2) [36]. The present work focuses on effective dye removal using advanced nanoengineered adsorbent. The composite of chitosan activated carbon and nano zerovalent iron beads CH-AC-nZVI is employed as an adsorbent for removal of Congo red dye from water. The chitosan is chosen in the proposed composite owing to the wide availability, low cost, good effectiveness in adsorption of dyes, non-toxic and biodegradable nature [37, 38]. Activated carbon is used as it is excellent adsorbent, abundantly available and cost-effective. The major disadvantage of using only activated carbon in adsorption of dye is the low reaction rate, difficulty in separation of the adsorbent from dye and regeneration immobilizing it on the chitosan support helps in overcoming the disadvantages [15]. Nano zerovalent iron (nZVI) is chosen owing to the high surface reactivity, large specific surface area, particle size and ease in using in the water system. nZVI tends to agglomerate, which decreases its reactivity specific surface area and dispersibility. In order to overcome the problem of agglomeration, it is essential to use support materials to decrease the agglomeration of nZVI. Immobilization of nZVI particles onto chitosan leads to an increase in the reactivity and dispersity of the nZVI. On the other hand, nZVI renders strength to the chitosan-activated carbon and nZVI(CH-AC-nZVI) composite and also helps in magnetic separation of the adsorbent from the aqueous system [39, 40]. The CH-AC-nZVI composite synthesized was subjected to characterization using SEM, XRD, and FTIR. Experiments were carried out to understand the effect of parameters such as solution pH, catalyst loading, initial concentration of dye and temperature on adsorption. Kinetic studies were carried out to understand the reaction mechanism.

2. Materials and methods

2.1. Materials

Chitosan (C6H12NO6), procured from HiMedia, India. Acetic acid (CH3COOH), sodium hydroxide (NaOH) procured from Merck, India. Glutaraldehyde [CH2(CH2)CHO] from Nice Chemicals, India. Sulfuric acid (H2SO4), sodium borohydride (NaBH4), ferrous sulfate (FeSO4), ethylenediaminetetraacetic acid, EDTA (C10H14Na2O8N2·2H2O) procured from Thomas Baker, India. All chemicals were of AR grade. Distilled water was used in all the experiments.

2.2. Preparation of nano zerovalent iron (nZVI)

The nZVI nanoparticles were synthesized using disodium salt of EDTA based on the procedure proposed by Allabaksh et al [41] without further modification. 150 ml of 0.1 M FeSO4 solution was mixed with 100 ml of 0.05 M EDTA solution with continuous stirring along with the dropwise addition of 100 ml of 0.1 M NaBH4 solution. The solution eventually turned brown in colour, precipitating zerovalent iron which was allowed to settle. The particles were washed thrice with absolute ethanol, filtered, dried and pulverized.

2.3. Preparation and characterization of adsorbent

Chitosan-activated carbon and nano zerovalent iron (CH-AC-nZVI) composite beads were synthesized as suggested by Ngah et al [2002] [42] without any modification. One gram of chitosan flakes was dissolved in 50 ml of 5% (v/v) acetic acid solution. The required amounts of nZVI and activated carbon were added to the chitosan solution. The 250 ml of 1 mol NaOH solution was cross-linked with 1 ml glutaraldehyde. The viscous chitosan-nZVI and activated carbon solution were added dropwise into the NaOH and glutaraldehyde solution. The beads were allowed to remain in the solution for about 3 h for hardening. The hardened beads were removed and washed with distilled water to remove NaOH residues. The adsorbent synthesized was subjected to characterization using SEM, XRD and FTIR. Scanning electron microscope (SEM), Vega3 Tescan was employed to understand the surface morphology of the composite. The adsorbent composites before adsorption and after adsorption were subjected to gold sputtering and the images of the surface were captured at accelerating voltage of 25 kV. X-ray diffraction (XRD) studies were performed
using Rigaku diffractometer with Cu-Kα source of 1.54 Å wavelength at the scan rate of 1°/min and a 2θ range from 10° to 90°. The FTIR spectroscopy was used to obtain spectra ranging from 4000 to 650 cm⁻¹ which was recorded on the Frontier FT-NIR/MIR spectrometer (Perkin Elmer).

2.4. Experimentation
The Congo red dye adsorption on the proposed adsorbent was carried out in the batch process. The dye solution of 100 ml of various concentrations was employed as the reaction mixture along with the appropriate quantity of adsorbent which was placed in the shaker rotating at the speed of 120 rpm for 1 h 40 min. At regular intervals (10 min), 3 ml of the sample was taken out and subjected to analysis using UV spectrophotometer at 497 nm to estimate dye concentration in solution. Further, the Congo red removal percentage was calculated using the following equation (1) [43]

\[
\text{% removal} = \frac{(\text{initial dye concentration} - \text{dye concentration at specific time})}{\text{initial dye concentration}} \times 100
\]

The adsorbent material, CH-AC-nZVI composite beads was employed to study the effect of various parameters such as pH, temperature, initial dye concentration and adsorbent dosage on adsorption of Congo red dye. The effect of pH on Congo red dye adsorption was studied at several pH values (pH 1, pH 3, pH 5, pH 7 and pH 12). The pH adjustment was made using 1 M of HCl and 1 M NaOH solutions. Following experimental conditions were used: initial Congo red dye concentration of 100 ppm, temperature maintained at room temperature (25 ± 3 °C) and the adsorbent dosage of 1000 mg l⁻¹.

To study the effect of temperature on adsorption, experiments were performed at various temperature (20 °C, 40 °C, 60 °C and 80 °C) in the shaker using temperature control knob of the shaker. The initial Congo red dye concentration of 100 ppm, pH 7 and the adsorbent dosage of 1000 mg l⁻¹ was maintained constant throughout the experiments. In order to study the effect of initial dye concentration on adsorption, the initial concentration of the dye was varied (10 ppm, 25 ppm, 50 ppm, 100 ppm and 200 ppm). The other parameters, pH 7, temperature (25 ± 3 °C), and the adsorbent dosage of 1000 mg l⁻¹ were maintained constant for all the trials.

The study the effect of adsorbent dosage on adsorption, the experiments were performed with 100 ppm of initial dye concentration at room temperature, pH 7 by varying the adsorbent dosage of 100, 500, 1000, 1500 and 2000 mg l⁻¹ of the dye solution.

The results obtained were used to design the BBM experimental chart for Congo red dye adsorption on the proposed adsorbent. Twenty-seven sets of experiments were obtained from BBM method. All the experiments were performed by varying the parameters, as mentioned in the BBM experiments. The results obtained are used to understand the adsorption process and to compare the experimental values with the predicted values.

3. Results and discussion
3.1. Control trials
The 100 ppm dye solution was placed in the shaker without adding adsorbent. It was found that there was no noticeable change in dye concentration after subjecting the dye solution for shaking for 2 h.

3.2. Characterization of composite material
3.2.1. SEM
Figures 1(a) and (b) represent the SEM images of the CH-AC-nZVI composite before adsorption and after adsorption, respectively. The SEM image figure 1(a) of the CH-AC-nZVI composite at the magnification of 3KX before adsorption shows porous and coarse surface, which facilitate the adsorption process. Precisely, the pores are seen to be macropores, and the surface is found to be heterogeneous, which are preferential for adsorption. The SEM image of the composite after adsorption (3KX magnification) shows that the surface of the adsorbent after adsorption is covered by the particles which may be attributed to the Congo red dye adsorbed on the surface. The modification of the surface after adsorption, possibly due to the dye molecules seen as clusters on the surface, as shown in figure 1(b).

3.2.2. XRD
XRD provides important data about the physical characteristics and chemical characteristics of the chitosan-activated carbon-nZVI. The spectra of XRD (figure 2) in the 2θ range of 10 to 90° at 25 °C (λ = 1.54 Å) is represented in figure 2. The broad diffraction peak at 2θ = 42° was observed belongs to nZVI crystal. A peak between 2θ = 10 and 20° belongs to chitosan, and the peak at 27° corresponds to activated carbon. It confirms that the iron nanoparticles and activated carbon were successfully loaded to chitosan beads [44, 45].
3.2.3. FTIR

The FTIR pattern of the composite is shown in figure 3. The adsorption peak at a wavenumber of 3295 cm$^{-1}$ indicates the existence of O–H and N–H bond stretching. The peaks at 2918 cm$^{-1}$ may be due to C–H stretching of the –CH$_2$ groups in chitosan. The peak at 1564 cm$^{-1}$ is due to the N–H bending vibration indicating the presence of amide (II) and hydroxy groups in Chitosan. The band at 1283 cm$^{-1}$ can be attributed to C–N stretching vibration. The peaks at 1710 cm$^{-1}$ for C=O of –NH=–C=O bond stretching; 1017 cm$^{-1}$ for C–OH.
bond stretching: 669 cm\(^{-1}\) for the Fe–O stretching vibration group and 2918 cm\(^{-1}\) could be assigned to aliphatic C–H group [44, 45].

3.3. Effect of pH on adsorption of Congo red dye using CH-AC-nZVI adsorbent

Figure 4 represents the variation in percentage removal with different pH for adsorption of the dye. It can be found that 100% removal of Congo red dye occurred in 50 min of adsorption at pH 1. A similar result was obtained with pH 3.97%, 91.87% and 85.95% removal were observed at pH 5, pH 7 and pH 12, respectively. The acidic pH is favourable for Congo red dye adsorption when compared to basic pH. As the pH decreases the adsorption increases at a much faster rate. The zero point charge of the adsorbent was reported to be pH\(_{ZPC}\) = 6.4 [46]. The surface of the adsorbent becomes negatively charged above pH 6.4 and becomes positively charged at pH below 6.4. The acidic pH was more favourable for adsorption of the dye due to the increase in protonation with respect to an amine group (-NH\(_3^+\)). The acidic dye (Congo red) possess sulfonated group (R-SO\(_3^-\)) which is negatively charged. The electrostatic force of attraction among positively charged amine group present in chitosan and negatively charged dye molecule exist at lower pH facilitating the adsorption process. At pH greater than 6.4 the surface of chitosan is negative, which leads to electrostatic repulsion of positively charged adsorbent and negatively charged dye molecules which is similar to the works reported elsewhere [46–48].

3.4. Effect of temperature on Congo red dye adsorption using CH-AC-nZVI

The effect of temperature for adsorption of Congo red dye was studied at the initial dye concentration of 100 mg l\(^{-1}\), pH 7 and adsorbent dosage of 1 mg l\(^{-1}\). Figure 5 represents the effect of temperature on the adsorption of Congo red dye. It can be found that 100% removal of Congo red dye was observed at 50 min for 80 °C, 96.19% removal was observed at temperature 60 °C, 93.92% of removal was observed at 40 °C in 50 min. The higher temperature was favourable for the adsorption process. Similar outcomes were reported by Wang et al (2007) [47], using Rhodamine—B onto perlite as adsorbent. The increase in temperature leads to increase in diffusion and attachment of the dye onto the surface of the adsorbent and also causes a swelling effect in the internal hydrogel structure, thus facilitating the adsorption of the dye molecules.

3.5. Effect of initial dye concentration of Congo red dye on adsorption on CH-AC-nZVI

In order to analyse the effect of initial dye concentration on adsorption experiments were carried out using the adsorbent dosage of 1000 mg l\(^{-1}\) under room temperature. The Congo red dye concentrations were varied from 10 to 100 ppm. Figure 6 depicts the variation in percentage removal with a different initial dye concentration of Congo red dye. It can be found that 100% removal of the dye was noticed within 30 min for 10 ppm dye, 100% removal of the dye was observed within 40 min for 25 ppm dye and within 60 min for 50 ppm dye. The percentage of adsorption decreased as the Congo red dye concentration increased. Lower initial dye concentration had access to the adsorption sites, and good adsorption was noticed at the lower concentration of the dye. The adsorption tends to decrease with the increase in dye concentration. Similar results were obtained by Chiu et al (2004) [48] employing cross-linked chitosan beads.
3.6. Effect of adsorbent dosage (CH-AC-nZVI) on the adsorption of Congo red dye

The effect of dosage of CH-AC-nZVI composite on Congo red dye adsorption was analyzed by varying the adsorbent dosage from 0.1 to 2 g, initial Congo red dye concentration of 100 mg l\(^{-1}\) was maintained for 100 ml dye at ambient temperature condition and pH 7. Figure 7 shows the effect of adsorbent dosage on the adsorption of the dye. After 80 min, 54.08% and 65.14% removal occurred for 0.1 g and 0.5 g, respectively. 100% removal was noticed in 70 min for the adsorbent dosage of 1 g, 60 min for 1.5 g of adsorbent and 60 min for 2 g of the adsorbent dosage. It was found that with the increase in adsorbent dosage the percentage of degradation also increases. The maximum adsorption of 100% was found for the 1.5 g and 2 g CH-AC-nZVI dosage. The increase
in adsorption dosage led to an increase in adsorption as the amount of surface area available for adsorption increases with an increase in adsorption dosage. The increase in the adsorbent surface area leads to an increase in the number of active sites for adsorption, which increases the adsorption of dye molecules onto the adsorbent. Similar results were reported by Jiang et al. (2011) [49] upon using a chitosan nanocomposite for the adsorption of methyl orange, and Jumadi et al. (2019) [50] observed the similar result for Congo red dye adsorption using magnetic chitosan composite.

3.7. Chemical kinetics
The studies on adsorption isotherms assist in optimizing the usage of CH-AC-nZVI as an adsorbent. The predictions and interpretation of data were carried out using empirical equations.
| Adsorbent                                                        | Langmuir Isotherm | Freundlich Isotherm | References |
|-----------------------------------------------------------------|-------------------|---------------------|------------|
|                                                                | Qm (mg/g)         | b L/mg              | R² (Langmuir) | Kf (mg/g (L/mg)^1/n) | n | R² |
| Cabbage waste powder                                            | 2.313             | 2.355               | 0.992       | 1.814              | 1.568 | 0.978 | [13] |
| Terephthaloyl thiourea cross-linked chitosan (TTU-chitosan) hydrogels | 42.735            | 0.8770              | 0.9670      | 1.9570             | 1.91 | 0.671 | [37] |
| Diammonium modified chitosan                                    | 1632              | 0.06                | 0.98        | 433.7              | 8.9  | 0.67  | [43] |
| Carbon fiber-based bimetallic oxide nanocomposite C/ NiO-ZnO | 613               | 0.574               | 0.997       | 228                | 3.14 | 0.963 | [51] |
| Bentonite/chitosan@cobalt oxide composite                       | 303               | 0.0263              | 0.984       | 1.3821             | 2.138 | 0.835 | [52] |
| Magnetic chitosan nanocomposite                                 | 1.8257            | 13.906              | 0.99        | 1.6429             | 20.756 | 0.0569 | [50] |
| Delonix regia Pod-Derived Activated Carbon                      | 17.12             | 0.0022              | 0.9951      | 0.084              | 1.28 | 0.9848 | [53] |
| FeₓCoₓ₋₅₋₅₋₅ O₄ nanoparticles                                    | 160.3             | 0.16                | 0.998       | 23.1               | 1.44  | 0.996 | [54] |

**Table 2.** The adsorption capacity of various adsorbents on adsorption of Congo red dye.
Langmuir isotherm is represented by equation (2).

\[ \frac{C_t}{Q_t} = \frac{1}{Q_0 b} + \frac{C_t}{Q_o} \]  

(2)

C_t refers to equilibrium concentration expressed in mg/l, Q_t refers to the amount of dye adsorbed at equilibrium expressed in mg/g, Q_o expressed in mg/g and b expressed in L/mg are Langmuir constants.

Freundlich Isotherm is represented by equation (3).

\[ \ln Q_t = \ln K_f + \frac{1}{n} \ln C_t \]  

(3)

where \( C_t \) represents the concentration of dye at equilibrium expressed in mg/l, \( Q_t \) refers to the amount of dye adsorbed in mg/g and \( K_f \) and \( n \) denotes Freundlich constants.

Scatchard isotherm model

\[ \frac{Q_t}{C_t} = Q_m K_b - K_b Q_t \]  

(4)

where \( Q_t \) represents the amount of dye adsorbed in mg/g, \( C_t \) represents the concentration of the dye at equilibrium in mg/l, \( Q_m \) refers to maximum adsorption capacity, and \( K_b \) is the Scatchhard constant.

The adsorption isotherm is studied to understand the behaviour of adsorbed ions between a solid and liquid phase at the state of equilibrium. Adsorption isotherms are studied using the isotherm models of Langmuir and Freundlich. Langmuir adsorption isotherm model assumes that the dye adsorbs onto the adsorbent with limited active sites, a monolayer of adsorption occurs on the external surface of the adsorbent, and there is no interactivity between adsorbed dye molecules. The slope and intercept of the \( C_t/Q_t \) versus \( C_t \) graph, as shown in figure 8(a) gives the Langmuir constants, which are reported in table 1. The parameter \( R_L \), which is adsorption intensity depicts the mode and quality of the isotherm model. The adsorption is undesirable for \( R_L > 1 \), linear for \( R_L = 1 \) irreversible for \( R_L = 0 \) and desirable for \( 0 < R_L < 1 \). \( R_L \) for adsorption of Congo red dye using CH-AC-nZVI is in the range of 0–1 which shows that the process is desirable. Maximum adsorption capacities of dye were obtained as 6.25 mg g\(^{-1}\).

Freundlich model is based on the heterogeneous and multilayer adsorption onto the surface of the adsorbent. ln \( q_t \) versus ln \( C_t \) graph, as shown in figure 8(b) is plotted to determine the \( K_f \) and \( n \) values. The type of
adsorption in terms of the physical and chemical reaction is depicted by \( n \). \( n < 1 \) indicates the adsorption process is desirable and chemical, the adsorption process is linear, and the adsorption process is desirable and physical, respectively. The \( n \) value obtained for adsorption on Congo red dye onto CH-AC-nZVI is found to be 2.66 (table 1), which shows that the process is desirable and physical. Adsorption capacities for Congo red dye using various adsorbents are presented in table 2 for both Langmuir and Freundlich isotherms. Scatchard isotherm model explains the interaction of the pollutant and active sites of the adsorbent. The deviation in the linearity describes that more than one type of active adsorbent group is present in the adsorption process and if the model shows linearity with a negative slope, it implies that the active sites are identical and independent. The value of \( R^2 \) for adsorption of Congo red dye is 0.675, which shows the deviation from the linearity. This confirms that more than one type of active site is present in the process of adsorption of Congo red dye using CH-AC-nZVI nanocomposite which may be due to the presence of different materials in the adsorbent such as chitosan, activated carbon and nano zerovalent iron. Since the Scatchard isotherm model is derived from the Langmuir isotherm model, the adsorption data is not supposed to be compatible with the Langmuir isotherm model, which can be seen in table 1. The value of the Scatchard constant \( K_b \) for the Congo red dye adsorption process is found to be 0.182 from figure 8(c). High values of \( R^2 \) for both Langmuir isotherm model and the Freundlich isotherm model shows that the adsorption is both monolayer and multilayer [55].

### 3.8. Adsorption kinetics and mechanism of Congo red dye on CH-AC-nZVI

Adsorption kinetics is employed to understand the control mechanism of the adsorption. The kinetic studies on the adsorption of Congo red dye were modelled using equations (5), (6) and (7), which refers to the pseudo-first-order and pseudo-second-order equation and Elovich models, respectively [55, 56].

\[
\ln \frac{Q_t - Q_e}{Q_e} = -K_f t
\]  
(5)

\[
\frac{t}{Q_t} = \frac{1}{K'Q_e^2} + \frac{t}{Q_e}
\]  
(6)

\[
Q_t = \frac{1}{\omega} \ln (\alpha \omega) + \frac{1}{\omega} \ln t
\]  
(7)

\( K_f \) denotes the pseudo-first-order rate constant expressed in \( \text{min}^{-1} \), \( K' \) refers to pseudo-second-order rate constant expressed in \( \text{g/mg min} \), \( Q_e \) denotes the quantity of dye adsorbed in \( \text{mg/g} \) at equilibrium and \( Q_t \) represents the quantity of dye adsorbed at a specific time, \( \alpha \) : initial rate of adsorption (\( \text{mg/g-min} \)), \( \omega \) : desorption value (\( \text{g/mg} \)).

Laguerre proposed first-order rate equation which is employed to study the kinetics of the liquid-solid phase adsorption. According to the pseudo-first-order model, the assumptions are made as the rate of adsorption of the solute is proportional to the variation in the saturation concentration and quantity of adsorbent versus contact time. Pseudo-second-order kinetic model describes that the chemical adsorption is the rate-limiting step and controls adsorption processes. This model is according to solid-phase adsorption, where the rate of active sites is proportional to the square of unoccupied active sites. The parameters and constants of pseudo-first, pseudo-second-order, and Elovich models are obtained using the graph shown in figures 9(a)–(c) respectively and are listed in table 3. The results show that the higher correlation coefficient (\( R^2 \)) is obtained for pseudo-second-order model in comparison with pseudo-first-order and Elovich model confirming that the adsorption of anionic dye by CH-AC-nZVI fits the pseudo-second-order kinetics showing the correlation

| Model               | Parameter                              | Present study |
|---------------------|----------------------------------------|---------------|
| Pseudo-first-order  | \( K_f \): Pseudo-first-order rate constant (\( \text{min}^{-1} \)) | 0.083         |
|                     | \( Q_e \) (\( \text{mg/g} \))          | 33.58         |
|                     | \( R^2 \)                              | 0.680         |
| Pseudo-second-order | \( K' \): Pseudo-second-order rate constant | 0.001716      |
|                     | \( Q_e \) (\( \text{mg/g} \))          | 15.38         |
|                     | \( R^2 \)                              | 0.983         |
| Elovich             | \( \alpha \): initial rate of adsorption (\( \text{mg/g.min} \)) | 0.822         |
|                     | \( \omega \): Desorption value (\( \text{g/mg} \)) | 0.277         |
|                     | \( R^2 \)                              | 0.987         |
Table 4. Comparison of kinetics using different adsorbent for adsorption of Congo red dye.

| Adsorbent                              | Pseudo-first-order | Pseudo-second-order | Elovich equation | References |
|----------------------------------------|--------------------|---------------------|------------------|------------|
|                                        | $Q_e$ (mg/g) | $K_l$ (min)$^{-1}$ | $R^2$           | $Q_e$ (mg/g) | $K$ (g mg$^{-1}$ min$^{-1}$) | $R^2$ | $\alpha$ (mg/(g min)) | $\omega$ (g/mg) | $R^2$ |
| Cabbage waste powder                   | 1.24               | 0.028               | 0.546            | 0.250      | 0.061               | 0.945 | 0.71               | 16.18            | 0.97 |
| C/NiO-ZnO                              | 98                 | 0.006               | 0.672            | 448        | 0.00046             | 0.999 | —                 | —                | —   |
| Delonix regia Pod-derived activated carbon | 1.62              | 0.019               | 0.964            | 1.74       | 0.035               | 0.969 | —                 | —                | —   |
| Walnut shell powder activated carbon   | 14.63              | 0.011               | 0.978            | 19.53      | 0.030               | 0.999 | 0.25               | 2.02              | 0.97 |

References:

[13] Sowmya et al.
coefficient of $R^2 = 0.983$. The value of adsorption capacity, $Q_e$ was found to be 15.38 mg g$^{-1}$ and $K_L$, the rate constant of the pseudo-second-order kinetic model was found to be 0.002 g mg$^{-1}$ min$^{-1}$. The result shows that the adsorption process is due to chemisorptions which occurs by sharing/exchange of electrons between the CH-AC-nZVI and Congo red dye. The Elovich equation fits well with the data as the $R^2$ value for the Elovich model is found to be high. The values of $\alpha$ and $\omega$ are 0.822 mg g$^{-1}$ min$^{-1}$ and 0.277 g mg$^{-1}$, respectively [55, 57]. Adsorption kinetics of Congo red dye using various adsorbents is presented in table 4.

3.9. Box-Behnken analysis (BBM)

Compared to the conventional approach, statistical experimental designs are found to be more effective for optimization of parameters in adsorption studies. The effect of four variables considered for the present study using BBM are pH, adsorbent dosage, temperature, and initial dye concentration on % Congo red dye adsorption. BBM designs are the group of rotatable or nearly rotatable second-order models which are based on three-level factorial models used to verify the parameters influencing the removal of the Congo red dye from the solution by adsorption. Three factorial BBM design is employed in the present work. The list of levels of BBM is as shown in table 5.

According to the BBM design, the following specific analysis was formed in order to calculate the percentage adsorption experimentally. Table 5 shows the BBM experimental design parameters with minimum and maximum values for the optimisation of experimental values and the predicted values of Congo red dye for 27 experimental trials. Table 6 represents the design for optimization based on four variables. The % adsorption for

| Variables | Observed—Minimum | Observed—Maximum |
|-----------|-----------------|-----------------|
| pH        | 1               | 13              |
| Temperature (°C) | 20             | 80              |
| Dye Concentration (mg/l) | 50             | 250             |
| CH-AC-nZVI Dosage (g) | 1              | 2               |

Table 6. Box–Behnken method experiments for Congo red dye adsorption on CH-AC-nZVI.

| pH     | Temperature (°C) | Dye Concentration (mg/l) | CH-AC-nZVI Dosage (g) | % Adsorption Predicted |
|--------|------------------|--------------------------|-----------------------|------------------------|
| 1      | 1.00000          | 20.00000                 | 150.0000              | 1.500000               | 33.52                  | 39.99708               |
| 2      | 13.00000         | 20.00000                 | 150.0000              | 1.500000               | 26.43                  | 31.61542               |
| 3      | 1.00000          | 80.00000                 | 150.0000              | 1.500000               | 47.01                  | 52.16375               |
| 4      | 13.00000         | 80.00000                 | 150.0000              | 1.500000               | 34.96                  | 38.82208               |
| 5      | 7.00000          | 50.00000                 | 50.0000               | 1.000000               | 13.98                  | 29.68208               |
| 6      | 7.00000          | 50.00000                 | 250.0000              | 1.000000               | 7.05                   | 6.88708                |
| 7      | 7.00000          | 50.00000                 | 50.0000               | 2.000000               | 70.52                  | 81.02208               |
| 8      | 7.00000          | 50.00000                 | 250.0000              | 2.000000               | 52.11                  | 46.74708               |
| 9      | 7.00000          | 50.00000                 | 150.0000              | 1.500000               | 35.12                  | 35.09667               |
| 10     | 1.00000          | 50.00000                 | 150.0000              | 1.000000               | 12.87                  | 20.12542               |
| 11     | 13.00000         | 50.00000                 | 150.0000              | 1.000000               | 9.15                   | 11.96875               |
| 12     | 1.00000          | 50.00000                 | 150.0000              | 2.000000               | 69.15                  | 68.43042               |
| 13     | 13.00000         | 50.00000                 | 150.0000              | 2.000000               | 60.02                  | 54.86375               |
| 14     | 7.00000          | 20.00000                 | 50.0000               | 1.500000               | 47.37                  | 46.16375               |
| 15     | 7.00000          | 80.00000                 | 50.0000               | 1.500000               | 74.55                  | 68.14542               |
| 16     | 7.00000          | 20.00000                 | 250.0000              | 1.500000               | 21.42                  | 29.92375               |
| 17     | 7.00000          | 80.00000                 | 250.0000              | 1.500000               | 24.01                  | 27.31542               |
| 18     | 7.00000          | 50.00000                 | 150.0000              | 1.500000               | 35.16                  | 35.09667               |
| 19     | 1.00000          | 50.00000                 | 50.0000               | 1.500000               | 78.42                  | 66.25917               |
| 20     | 13.00000         | 50.00000                 | 50.0000               | 1.500000               | 47.42                  | 40.98750               |
| 21     | 1.00000          | 50.00000                 | 250.0000              | 1.500000               | 29.32                  | 23.31417               |
| 22     | 13.00000         | 50.00000                 | 250.0000              | 1.500000               | 27.14                  | 26.86250               |
| 23     | 7.00000          | 20.00000                 | 150.0000              | 1.000000               | 30.82                  | 14.75250               |
| 24     | 7.00000          | 80.00000                 | 150.0000              | 1.000000               | 33.95                  | 24.40417               |
| 25     | 7.00000          | 20.00000                 | 150.0000              | 2.000000               | 63.21                  | 60.31750               |
| 26     | 7.00000          | 80.00000                 | 150.0000              | 2.000000               | 66.41                  | 70.03917               |
| 27     | 7.00000          | 50.00000                 | 150.0000              | 1.500000               | 35.01                  | 35.09667               |
experimental values and predicted values are recorded in table 6. The adsorption was found to be maximum for pH 1, 50 °C, 50 mg l⁻¹ initial dye concentration and 1500 mg l⁻¹ of adsorbent dosage.

Figure 10. Effect of various parameters on Congo red dye adsorption by BBM. (a) pH and temperature (b) The dye concentration (in mg/l) and adsorbent dosage (c) pH and Congo red dye concentration (in mg/l) (d) pH and CH-AC-nZVI dosage (e) dye concentration (mg/l) and temperature and (f) Temperature and CH-AC-nZVI adsorbent dosage.

Figure 10(a) shows the effect of pH and temperature on Congo red dye adsorption on CH-AC-nZVI composite. It is observed that with the increase in temperature and with a decrease in pH of the solution, adsorption increases. The rise in temperature is found to improve the efficacy of adsorption as an increase in temperature, and the adsorbent surface smoothens, facilitating the dye diffusion onto pores of adsorbent [47]. The binding sites increase with the rise in chitosan-activated carbon–nZVI composite dosage, and the number
of free binding sites tends to decreases as the initial dye concentration increases. Figure 10(b) depicts the influence of initial dye concentration and dosage of adsorbent on adsorption.

Increase in the initial concentration of the dye decreases the adsorption due to unavailability of free sites on the adsorbent. Figure 10(c) shows that the decrease in pH and initial dye concentration leads to an increase in adsorption. Figure 10(d) shows us that under acidic pH, and the higher adsorbent dosage, the rise in percentage adsorption was enhanced. Figure 10(e) clearly shows us that as the temperature increases and the dye concentration decreases, the percentage adsorption increases significantly. From figure 10(f), it is found that with the increase in adsorbent dosage and temperature, the adsorption increases. From figure 11 it is evident that the acidic pH and low initial dye concentration along with maximum adsorbent dosage and the temperature is found to yield maximum adsorption.
Pareto chart (figure 11) represents the contribution and importance of various parameters on Congo red dye removal. From the chart, it can be seen that the influence of adsorbent dosage is more prominent compared to dye concentration, pH and temperature, respectively in that order of importance.

The percentage removal obtained through experiments and predicted values from BBM are compared, and the plot of the predicted v/s experimental values is depicted in figure 12. It is found that the experimental data obtained is in good agreement with the data predicted. The Box- Behnken regression equation is as follows:

\[ Y = 9.58706 - 2.07880X_1 + 0.02808X_1^2 + 0.01062X_2 + 0.00505X_2^2 
- 0.13563X_3 + 0.00032X_3^2 + 24.43250X_4 + 10.95833X_4^2 - 0.00689X_1X_2 
+ 0.1201X_1X_3 - 0.45083X_1X_4 - 0.00205X_2X_3 + 0.00117X_2X_4 - 0.05740X_3X_4 \]

where \( X_1 \) refers to pH, \( X_2 \) refers to temperature (°C), \( X_3 \) refers to initial Congo red dye concentration (mg/l), and \( X_4 \) refers to CH-AC-nZVI dosage (mg/100 ml).

4. Conclusion

The chitosan-activated carbon-zerovalent iron nanoparticles composite is found to be very efficient in the removal of Congo red dye. The SEM images of the composites show the agglomerated structure with the porous and coarse surface, which would favour the adsorption process. The presence of zerovalent iron nanoparticles is found to boost the efficacy of adsorption of Congo red dye onto the CH-AC-nZVI composite and also facilitates easy removal of the adsorbent using a magnetic field. The optimum dye to adsorbent dosage ratio was found to be 1:10. The acidic condition was found to be favourable for adsorption of Congo red dye. Chemical kinetics reveals that equilibrium adsorption isotherm is satisfactorily explained by the Langmuir adsorption isotherm model, which was the best fit for adsorption data. Physical forces, along with ionic interactions, are the parameters vital for the adsorption of the dye. Adsorption is reliant on parameters such as pH, temperature, initial dye concentration and CH-AC-nZVI dosage and follows second-order kinetics. Box-Behnken Method, the statistical technique shows that the adsorbent dosage is the critical parameter in the adsorption of the dye on the proposed composite. The adsorption was found to be maximum for pH 1, 50 ⁰C, 50 mg l⁻¹ initial dye concentration and 1500 mg l⁻¹ of adsorbent dosage. The experimental results are found to be in good agreement with the predicted values of BBM.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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