Chitosan supported CoFe_2O_4 for the removal of anthraquinone dyes: kinetics, equilibrium and thermodynamics studies

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Abstract

Chitosan supported cobalt ferrite nanocomposite ($\text{Cs-CoFe}_2\text{O}_4$) was synthesized and characterized. The synthesized $\text{Cs-CoFe}_2\text{O}_4$ was used for the removal of Anthraquinone dyes (Methylene Green, MG and Reactive blue 4, RB4) from aqueous solution in batch processes. Kinetics data were subjected to pseudo-first-order and pseudo-second-order, Elovich and intra-particle diffusion models, while the equilibrium data were evaluated with Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherm models. The results of characterizations revealed that CoFe_2O_4 was successfully incorporated into the Cs, with resulting composite retaining its magnetic properties and the functional group in the Cs. Considering the closeness $Q_{e(\text{exp})}$ and $Q_{e(\text{cal})}$, also the values of R^2 and %SSE, the MG adsorption followed pseudo-second-order with average rate constants of $8.3 \times 10^{-3} \text{ min}^{-1}$ while the adsorption kinetic of RB4 is best described by pseudo-first-order model with average rate constant of $2.91 \times 10^{-2} \text{ min}^{-1}$. Langmuir adsorption isotherm fits gave $R^2 > 0.9$ for both dyes with maximum adsorption capacities of 63.34 and 35.05 mg/g obtained MG and RB4 respectively. The thermodynamic parameters showed revealed spontaneous adsorption processes. The results indicated that the prepared $\text{Cs-CoFe}_2\text{O}_4$ is an efficient recyclable adsorbent for the MG and RB4 dye without losing the original activity and stability for water treatment applications.

Keywords Chitosan · Cobaltferrite · Methylene green · Reactive blue 4 · Kinetics · Isotherms

1 Introduction

Industries which include textile, paper and pulp, dye and dye intermediates, pharmaceutical, tannery, craft bleaching, food technology, cosmetics, etc. consume majority of tens of thousands of chemically different types of dyes that are currently manufactured. Their effluents are rich in dyes and other organic pollutants, when untreated dye effluents are released into aquatic environment, oxygen concentration in water body drastically decreases also the passage of light through water body is blocked with detrimental effect,

which can be harmful to both aquatic and terrestrial life by adversely affecting the natural ecosystem and causing long-term health effects [1]. However, dyes are more difficult to degrade after use because the producers and users are interested in stability and fastness [2], hence their persistence in the environment especially the anthraquinone derivative, that are toxic and recalcitrant organo pollutants [3].

Elimination of dyes from aqueous coloured effluents in order to reduce their ecological consequences has attracted several physical, biological and chemical techniques. Adsorption has been the most common

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physico-chemical treatment methods with potential applications, due to its low-cost, effectiveness and efficiency. The best adsorbent that has been widely accepted in commercial systems is activated charcoal due to its significant adsorption capacity, unfortunately, high capital cost, complicated synthesis process, low capacity, slow kinetics property and the harmful by product of treatment process are major setback for using activated carbon [4–6]).

Chitosan is a biopolymer widely used as adsorbent due to its high adsorption potential as a result of the presence of hydroxyl and amino functional groups, which can be protonated in acid solution, resulting in huge electrostatic attraction for anionic molecules [7]. However, chitosan is soluble in diluted acid solutions and its separation from adsorption medium after the process is difficult, thus jeopardizing its industrial application [8].

Recently, the use of nanoparticles in environmental remediation processes is increased due to their small size and high surface area. The magnetite nanoparticles when used as bare are dispersed and can be separated either by applying an external magnetic field or by centrifugation and filtration [9]. However, the separation of nano sized magnetite is a difficult couple with high cost of nanoparticles alone as a filter cartridge, thus the use of a support system or substrate for magnetite nanoparticles.

The use of magnetic iron oxides coated polymers, to enable separation from the aqueous media by external magnetic field has been reported [10–12]. Among iron oxides with magnetic properties, ferrites stand out due to its high surface area, chemical and temperature stability over a wide range of pH, and great oxidation resistance [13, 14]. The cobalt ferrite (CoFe_2O_4) is a spinel inverse type and can be synthesized with a simply method by co-precipitation methods which produces less toxic with high yield [15, 16]. The chitosan crosslinking can improve the mechanical and chemical properties, providing a magnetic composite, when associated to CoFe_2O_4 , with greater stability in acid solution, high adsorption capacity and easy to be separated from the liquid after the adsorption operation [17]. Homayonfard et al. [18] reported the effectiveness of Co and Ni ferrites/chitosan composites for cadmium removal from aqueous media, Ansari et al. [19] also confirmed the effectiveness of the Cobalt ferrite chitosan composite ($\text{Cs-CoFe}_2\text{O}_4$) towards the effective removal of acid dye, while Roknid et al. [20] successfully used the magnetic graphene composite for anionic dye remediation.

This study therefore reports the synthesis and characterization of Chitosan grafted cobaltferrite composite, ($\text{Cs-CoFe}_2\text{O}_4$) as adsorbent for the removal of anthraquinoline dyes (Methylene Green, MG and Reactive blue 4, RB4). The effects of initial dye concentrations, contact time, pH, and adsorbent dosage as well as recyclability were reported. Kinetic and equilibrium as well as

thermodynamics data from the batch adsorption studies were analysed with appropriate models and while central composited design of experiment was used to investigate the time-concentration effect on the optimization.

2 Materials and methods

2.1 Materials

Methylene Green, (C.I. No. 52020; CAS 2679-01-8), Reactive blue 4, (C.I. No. 61205; CAS No.13324-20-4), Chitosan (85% degree of deacetylation, molecular weight of 2.6×10^5), glutaraldehyde (50%), ferric nitrate hydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) with purity > 98% were from Sigma Aldrich, while NH_4OH and NaOH were procured from Merck, India, other chemicals were Analar grades, while doubly distilled water was used for all of the experiments.

2.2 Synthesis of $\text{Cs-CoFe}_2\text{O}_4$ nanoparticle

The composite was synthesized by co-precipitation procedure by weighing accurately 1.164 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 3.232 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and quantitatively transferred them into 100 ml flask, 40 ml doubly distilled water was added under vigorous stirring for 60 min. Solution of chitosan was prepared by activating 0.75 g of the powder in 25 ml of 1% glacial acetic acid solution stirred at 80 °C for 4 h. Synthesis of $\text{Cs-CoFe}_2\text{O}_4$ was accomplished by adding the chitosan solution gradually to the salts solution under continual stirring, the pH was adjusted to 11 using 25 ml of 35% NH_4OH solution under continue stirring at 60 °C for 2 h, 5 ml of 50% glutaraldehyde was added and the allow to cure for 24 h. The reddish black precipitate was washed with ethanol and distilled water each thrice followed by drying in vacuum oven at 80 °C for 12 h.

2.3 Characterization of the synthesized $\text{Cs-CoFe}_2\text{O}_4$

Surface morphology and elemental composition of the material was analysed using scanning electron microscopy (SEM) [VEGA3 TESCAN], X-ray diffraction (XRD) data were collected using a PAN Analytical X' Pert PRO X-ray diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Fourier transform infrared (FT-IR) spectra were recorded from 400 to 4000 cm^{-1} in TENSOR 27 spectrometer (Bruker, Germany) using KBr pellet technique while the magnetic property were analysed with Bruker EMX Plus (Bruker, Germany) with Microwave Frequency of 9.859876, Modulation Frequency of 100.0 kHz and Modulation Amplitude of 1.0 G. The results obtained were compared with those of Chitosan and CoFe_2O_4 .

2.4 Adsorption studies

Stock solution containing of the dyes were prepared by dissolving accurately weighed solute such that the solution contained 1 g equivalent of the dyes (Fig. 1) in 1 L distilled water, working standard solutions were then prepared from the stock by dilution. The pH of the working solution was maintained with aliquot of HCl or NaOH prior to the adsorption study (Scheme 1).

The batch equilibrium and kinetics adsorption studies were conducted in a batch process in plastic flasks containing 25 mL of dye solutions with concentration range between 10–50 mg/L and 0.4 g/L of the adsorbent. The contents were placed in a regulated water bath ($30 \pm 1^\circ\text{C}$)

with shaker at 150 rpm, samples were collected at pre-set time intervals (0–240 min), while the dye concentrations in aqueous media were determined using UV–vis spectrophotometer (Shimadzu 1600PC double beam uv–visible spectrophotometer). The amount of dye adsorbed (mg/g) by the adsorbents as a function of time (Q_t) and at equilibrium (Q_e) were estimated according to Eqs. 1 and 2 below:

$$Q_t = \frac{(C_o - C_t) \times V}{m} \quad (1)$$

$$Q_e = \frac{(C_o - C_e) \times V}{m} \quad (2)$$

Fig. 1 Structures of **a** Methylene green and **b** reactive blue 4

Scheme 1 Preparation of Cs–CoFe₂O₄ for dyes removals

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

3 Results and discussion

3.1 Characterization

The surface morphologies of the Cs, CoFe_2O_4 and Cs- CoFe_2O_4 as observed by SEM are presented in Fig. 2a–c.

Both Cs and CoFe_2O_4 displayed rough surfaces with the later being more pronounced due to its agglomeration tendencies, however, the combination of the two composites resulted in a well dispersed surface morphology as shown in Fig. 2c, this implies that the presence of Cs leads to modification of the surface morphology of the CoFe_2O_4 with its agglomerated surface becomes more collapsed and transformed to a kind of embedded surface with well distributed pores. The surface morphology after adsorption is presented in Fig. 2d, the image depicted a smoother surface with reduced pore sizes when compared to what it was before adsorption. Using ImageJ software, the surface

Fig. 2 SEM images of **a** Cs **b** CoFe_2O_4 and Cs- CoFe_2O_4 **c** before **d** after adsorption

Fig. 3 EDX Spectra of **a** Cs **b** CoFe_2O_4 and **c** $\text{Cs-CoFe}_2\text{O}_4$

Fig. 4 XRD Spectra of **a** Cs **b** CoFe_2O_4 and **c** $\text{Cs-CoFe}_2\text{O}_4$

areas of the Cs, CoFe_2O_4 and $\text{Cs-CoFe}_2\text{O}_4$ were estimated at 63.4, 15.9 and 65.3 m^2/mg respectively, this implied a slight increase in surface area of composite compared with the components.

The EDX spectra of the of the Cs, CoFe_2O_4 and $\text{Cs-CoFe}_2\text{O}_4$ are presented in Fig. 3, the constituents of the Cs were shown to be C, N, and O, while the elemental composition of CoFe_2O_4 were also displayed. Figure 3c showed that the composite was formed by the presence of C and N of the chitosan displayed along with the Co, Fe and O of the ferrite.

The X-ray diffraction spectra of the samples are as shown in Fig. 4, the characteristic broad peak of Cs at 2θ of

Fig. 5 EPR spectra of CoFe_2O_4 and $\text{Cs-CoFe}_2\text{O}_4$

20.5° is retained in the composite, while the characteristic peaks of the CoFe_2O_4 at 2θ of 18.5° , 30.0° , 35.2° , 44.5° , 57.3° and 62.8° were conspicuously displayed in both the spectra of the pure ferrite and the Chitosan/Ferrite nanocomposite. The XRD spectra confirm the earlier observation from the EDX spectra that the chitosan was successfully coated onto the magnetic nanoparticle. Also the retention of most of the crystallographic planes in CoFe_2O_4 along with those of the chitosan is also evident.

The magnetic properties of the pure CoFe_2O_4 was compared with that of $\text{Cs-CoFe}_2\text{O}_4$ using EPR technique, data of the samples were obtained at room temperature as the first derivative of energy absorption with microwave

Fig. 6 FTIR spectra of Cs, CoFe_2O_4 and those of $\text{Cs-CoFe}_2\text{O}_4$

frequency of 9.859876 GHz as shown in Fig. 5. It is obvious from this study that both samples exhibited positive magnetic properties, they displayed comparable resonance curves characteristics of superparamagnetic nanoparticles. However, the resonance position of $\text{Cs-CoFe}_2\text{O}_4$ is shifted to higher fields with lower line intensity, which is an indication of a less effective magnetization of the sample than that of CoFe_2O_4 . The EPR study confirms the magnetic behaviour of the nanoparticle and implies its ease of separation from the aqueous media using external magnetic field.

The FTIR spectra of Cs, CoFe_2O_4 and those of $\text{Cs-CoFe}_2\text{O}_4$ before and after the adsorption are presented in Fig. 6. The data obtained between 400 and 4000 cm^{-1} revealed the characteristic functional groups in the chitosan, the N-H and O-H stretches were observed at 3855 and 3305 cm^{-1} . The sharp peaks observed around 2910 and 2883 cm^{-1} could be assigned to the symmetric and asymmetric $-\text{CH}_2$ stretching vibrations while those at 1584 and 1669 cm^{-1} belong to C-N vibrational stretching. Also, the bending deformations of C-O-H and H-C-H resulted in the peaks 1331 and 1426 cm^{-1} while the C-N stretching of amino groups appeared around 1067 cm^{-1} . The characteristic spectra of CoFe_2O_4 is as displayed in the figure, the broad band around 3400 cm^{-1} corresponds to the O-H groups, which are relative to adsorbed water in the ferrite sample, also the bond at 1602 cm^{-1} is attributed to O-H in and out of plane vibration while the vibrational band at 572 cm^{-1} can be attributed to Co-O and Fe-O stretches of the ferrite tetrahedral sites. Relative bands observed in both Cs and CoFe_2O_4 were displayed in the FTIR spectra $\text{Cs-CoFe}_2\text{O}_4$ nanocomposite before and after adsorption

Fig. 7 Influence of pH on the dyes adsorption by $\text{Cs-CoFe}_2\text{O}_4$

process, however, a weaker vibrational band was obtained in the region of Co-O and Fe-O absorption. Similarly, the absorption of dyes resulted in weaker band in the N-H, O-H, and C-O-H absorption bands, suggesting a kind of chemical interactions between the adsorbent and the dye molecules apart from pore diffusion.

3.2 Effect of pH on dyes adsorption

The pH of the adsorption medium is one of the important factors that determine the effectiveness of the process. It determines the chemical composition as well as the properties of the adsorbent and the adsorbate in solution, thus controlling both physical and chemical interactions between them. Figure 7 shows that the adsorption efficiency of the two dyes by $\text{Cs-CoFe}_2\text{O}_4$ is pH dependent, the highest removal efficiency of 93.9% (MG) and 80.9%

Fig. 8 Effect of adsorbent dosage on removal efficiency of the dyes

(RB4) were obtained at pH 4, suggesting a chemical interaction between the positively charged adsorbent and the anionic form of the dyes in the acidic medium. These observations also provided the information that desorption of the dye is highly favoured in the basic medium.

3.3 Effect of adsorbent dosage

The effect of adsorbent dosage in the percentage removal of the dyes is present in Fig. 8. This figure showed that the adsorbent dosage plays a significant role in adsorption efficiency, increase in adsorbent dosage led to a substantial increase in adsorption efficiency of the adsorbent. The removal efficiency of MB increases from 81 to 97%, while that of RB4 rose from 22 to 55% as the adsorbent dosage increases from 0.4 to 4 mg/L. The increase efficiency could be attributed to increase in the amount coupled with rise in the available sites for the dyes adsorption.

3.4 The effect of contact time and initial concentrations

The effect of contact time and initial concentrations on the removal efficiency profiles of MG and RB4 dye Cs–CoFe₂O₄ is as presented Fig. 9. The figure showed a rapid adsorption process followed by steady period of equilibrium at which no significant increase in adsorption rate was observed. The profile is similar irrespective of the initial concentration of both dyes, suggesting a consistent adsorption mechanism which is independent of initial concentration. The presence of vacant site on the adsorbent at the onset

could be attributed to the rapid adsorption in the initial stages, as sites were occupied, diffusion of dye molecules into the pores of the adsorbent slowed down leading to a lower efficiency with time and increase initial concentration. Similarly, the adsorption efficiency at equilibrium decreases with initial concentrations of the dye, it was observed that as the concentration increases from 10 to 50 mgL⁻¹ the removal efficiency decreases from 95 to 85.7% for MB and from 66.9 to 41.9% for RB4.

3.5 Kinetics studies

This study exploits the most widely used kinetics models namely; pseudo-first-order, pseudo-second-order, Elovich and intra-particle diffusion models were used to examine the adsorption kinetics behavior of MG and RB4 dyes onto Cs–CoFe₂O₄. The models were applied to mathematically describe the intrinsic adsorption constants, using non-linearized forms of their equations (Eq. 3–7), the details of which had been described elsewhere [21]. The parameters were obtained using Origin 8 non linear fits software, the adequacy as well as the fitness of the kinetic equations to the experimental data was based on the values of the correlation coefficients, R² and sum square error function (%SSE).

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (3)$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (4)$$

Fig. 9 Effect of contact time and initial dye concentration on removal efficiency of the dyes

Fig. 10 Pseudo-first order (**a** and **b**) and pseudo-second order kinetic fits (**c** and **d**) of adsorption of the dyes

Table 1 Kinetic fit Parameters for the adsorption of MG and RB4 dyes by Cs–CoFe₂O₄

Co mg/L	Pseudo first order					Second order				
	$Q_{e(\text{exp})}$ (mg g ⁻¹)	Q_e (mg g ⁻¹)	k_f (min ⁻¹)	R^2	%SSE	Q_e (mg g ⁻¹)	$k_2 \times 10^{-2}$ (g mg ⁻¹ min ⁻¹)	R^2	%SSE	
<i>Methylene green (MG)</i>										
10	11.875	11.351	0.095	0.988	0.243	12.393	1.070	0.994	0.230	
20	23.684	21.134	0.145	0.944	0.901	22.847	0.950	0.983	0.637	
30	33.753	30.188	0.177	0.946	1.212	32.389	0.862	0.981	0.933	
40	42.481	39.087	0.205	0.962	1.270	41.540	0.849	0.989	0.863	
50	53.569	50.475	0.146	0.970	1.554	53.997	0.436	0.997	0.611	
<i>Anthraquinone blue (RB4)</i>										
10	8.365	8.421	0.025	0.981	0.383	10.223	0.249	0.973	0.754	
20	16.206	16.348	0.019	0.996	0.395	20.464	0.092	0.991	0.981	
30	22.373	22.103	0.025	0.996	0.457	26.784	0.095	0.993	0.995	
40	24.940	24.150	0.032	0.994	0.542	28.513	0.121	0.994	0.817	
50	26.218	24.783	0.045	0.986	0.721	28.412	0.184	0.996	0.557	

$$Q_t = 1/\beta \ln(\alpha\beta \times t) \quad (5)$$

$$Q_t = K_{id}t^{0.5} + C_i \quad (6)$$

The pseudo-first order and pseudo-second order (Fig. 10c and d) kinetics fits for the adsorption of MG and RB4 dyes respectively onto Cs–CoFe₂O₄ were displayed by Fig. 10a–d, while the parameters obtained for the fittings are also presented in Table 1. Although the correlation coefficients R^2 displayed by both kinetic models for the two dyes were higher than 0.9, however, for the MG dye, the R^2 displayed by pseudo-second-order model is higher with lower %SSE than that of pseudo-first-order model, also, the experimental values of Q_e is closer to the

calculated values by the model than that of pseudo-first-order kinetic model. These implied that the adsorption process of MG is best explained by the pseudo-second-order kinetic model, signifying some chemical interaction between the adsorbent and dye molecules. On the contrary, however, the reverse was observed for RB4 dye with pseudo-first order best explaining its adsorption. The pseudo-second order rate constant k_2 decreases with increase concentration, suggesting a longer equilibrium time, while increase in pseudo-first order rate constant implies increase adsorption with concentration [22].

The mechanism of the adsorption was investigated using the Elovich and the intraparticle diffusion models, the fits are shown in Fig. 11a–d, while the corresponding

Fig. 11 Elovich (a and b) and intraparticle diffusion (c and d) model fits of adsorption MB and RB4 dyes by Cs–CoFe₂O₄

Table 2 Elovich and intraparticle diffusion models parameters for the adsorption of MG and RB4 dyes by Cs–CoFe₂O₄

Co (mg/L)	Elovich				Intraparticle diffusion							
	α (mg (g min) ⁻¹)	β_{el} (g mg ⁻¹)	R ²	%SSE	K_{1d} (mg g ⁻¹ min ^{-0.5})	C_{1d} mg g ⁻¹	R ²	%SSE	K_{2d} (mg g ⁻¹ min ^{-0.5})	C_{2d} mg g ⁻¹	R ²	%SSE
<i>Methylene green (MG)</i>												
10	10.260	0.560	0.945	0.082	2.259	−0.166	0.991	0.125	8.425	0.253	0.716	0.076
20	86.002	0.370	0.987	0.031	4.675	0.624	0.969	0.477	15.567	0.559	0.941	0.070
30	361.343	0.296	0.987	0.029	7.004	1.239	0.945	0.965	23.191	0.729	0.933	0.097
40	2072.41	0.270	0.989	0.029	9.330	2.013	0.928	1.478	32.179	0.737	0.869	0.140
50	358.963	0.169	0.982	0.019	11.035	1.730	0.964	1.217	40.722	0.948	0.763	0.255
<i>Anthraquinone blue (RB4)</i>												
10	0.541	0.445	0.978	0.029	0.727	−0.451	0.556	0.333	0.445	2.259	0.831	0.098
20	0.899	0.234	0.991	0.009	1.132	−0.563	0.703	0.398	1.013	1.961	0.883	0.182
30	1.524	0.177	0.988	0.009	1.784	−0.549	0.825	0.458	1.300	4.340	0.825	0.292
40	2.111	0.166	0.988	0.009	2.499	−0.832	0.847	0.596	1.242	7.687	0.820	0.283
50	3.403	0.178	0.982	0.012	3.359	−0.813	0.918	0.572	1.065	11.322	0.835	0.231

parameters are shown in Table 2. The Elovich model fit (Fig. 11a and b) displayed a better fit for adsorption of dyes by the adsorbent with significantly high R² and low %SSE. The initial adsorption rate α , increases with initial dye concentration and the value obtained for MG is far higher when compared with that of RB4 suggesting a better of adsorption of the MG than RB4. The desorption constant, β_{el} which is related to the surface activation energy decreases with dyes concentration, suggesting a higher adsorption with increase concentrations, suggesting that the process is not purely chemisorptions.

The intraparticle diffusion fits (Fig. 11c and d) revealed that the adsorption processes has been divided into two phases (biphasic). The initial curved portion of the plot, showed a rapid adsorption in the first few minutes of the process indicating boundary layer effect, followed by a more relaxed adsorption which may be as a result of diffusion into pore slowing down the processes. This biphasic nature of intraparticle diffusion fits confirm that both film and pore diffusion were involved in the processes of dyes removal, showed that the although the process involved intraparticle diffusion of the dye into the adsorbent pores. Also, the curves does not pass through the origin, as shown by the values of C_i inferring that diffusion is not the sole rate controlling step, rather mass transfer also played a major role as shown by the fits obtained at the second phase with lower values of R² [23].

3.6 Adsorption isotherms

Data obtained from the equilibrium adsorption studies were subjected to the non-linearized forms of Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms

models (Eq. 7 to 10). The details of these models had been presented elsewhere [24], the parameters were obtain by using non-linear curve fitting menu in Origin 8.0 after the equation had been programmed into the software. Langmuir equation parameters, Q_0 and b are the constants related to the adsorption capacity and energy of adsorption, respectively. The separation factor (R_L) was also determined using the expression $R_L = 1 / (1 + bC_0)$ where C_0 (mg L⁻¹) is the initial concentration of the dyes, values of R_L between 0 and 1 represents favourable adsorption, $R_L > 1$ suggests unfavourable adsorption and $R_L = 0$ stands for irreversible process. The Freundlich isotherm parameters, K_f and n characterized the adsorption capacity and intensity, respectively. Furthermore, the Temkin isotherm constants a_T and b_T represent the equilibrium binding constant (L g⁻¹) and heat of adsorption (J mol⁻¹) respectively. The value of Q_s , the monolayer adsorption capacity and adsorption energy E were also obtained from Dubinin–Radushkevich (D–R) isotherm model.

$$Q_{eq} = \frac{Q_{max} b C_e}{1 + b C_e} \quad (7)$$

$$Q_{eq} = K_f C_e^{1/n} \quad (8)$$

$$Q_e = \frac{RT}{b_T} \ln a_T C_e \quad (9)$$

$$Q_e = Q_s e^{-\frac{\left(RT \ln \left(1 + \frac{1}{C_e} \right) \right)^2}{2E^2}} \quad (10)$$

Table 3 Isotherm models parameters for the adsorption of MG and RB4 dyes by Cs–CoFe₂O₄

Isotherms	Parameters	MG	RB4
Langmuir	Q_{max} (g mg ⁻¹)	63.33 ± 7.6	35.05 ± 2.61
	b (L mg ⁻¹)	0.46 ± 0.16	0.12 ± 0.02
	R_L	0.91 ± 0.13	0.74 ± 0.31
	R^2	0.962	0.986
Freundlich	K_F (g mg ⁻¹ min ^{-1/n})	20.00 ± 2.08	6.83 ± 1.62
	N	2.12 ± 0.28	2.38 ± 0.47
	R^2	0.973	0.949
Temppkin	b_T (J mol ⁻¹)	4.97 ± 1.17	0.93 ± 0.22
	a_T (L mg ⁻¹)	189.25 ± 16.78	298.96 ± 28.86
	R^2	0.980	0.982
Dubinin–Radushkevich	Q_5 (g mg ⁻¹)	45.97 ± 3.91	25.63 ± 0.95
	E (kJ mol ⁻¹)	1.52 ± 0.03	0.410 ± 0.03
	R^2	0.908	0.980

Figure 10a–b showed the isotherm fits for the adsorption of MG and RB4 onto Cs–CoFe₂O₄, these fits were obtained through the parameters presented in Table 3. It is apparent from the figure that the experimental values agreed with the theoretical data, this is also evident from the values of R^2 which is a measure for the adequacy and fitness of the isotherm equation to the adsorption data [25]. The trends were in the order of Tempkin > Freundlich > Langmuir > Dubinin–Radushkevich for MG dye and Langmuir > Tempkin > Dubinin–Radushkevich > Freundlich

for RB4 dye. The Langmuir isotherm which proposed a monolayer adsorption gave maximum adsorption capacities of the dyes as 63.33 and 35.05 mg g⁻¹ for MG and RB4 dyes respectively. The difference in the adsorption capacities for the dyes could be attributed to difference in their molecular sizes [26]. MB has a molecular structure that is compact than that of the RB4 as shown in Fig. 1, hence they have higher potentials to permeate the pores of the adsorbent than the larger molecules of RB4. The R_L values 0.91 and 0.74 obtained for MG and RB4 dyes respectively is a proof of favourable adsorption of the dyes onto the adsorbent. Similarly, the empirical parameter, n of the Freundlich isotherm indicates surface heterogeneity of the adsorbent, while its value confirms the favourability of adsorption process [27]. The parameters obtained for Tempkin isotherm fit is also in support of surface heterogeneity and the interaction between the adsorbent and the dye molecules, the adsorption heat obtained for MG is higher than that of RB4 whereas the binding constant is higher in the latter than the former, justifying the lower adsorption capacity obtained for RB4. The energies of adsorption of the dyes on energetically heterogeneous sites estimated from Dubinin–Radushkevich isotherm confirms that the mechanism of adsorption which is more of physisorption than chemisorptions for both dyes [28]. The comparison of the adsorption capacity of other adsorbents for the removal of RB4 and MB dyes are shown in Table 4, it could be inferred that the Cs–CoFe₂O₄ competes favourably with other adsorbents (Fig. 12).

Table 4 Comparison of adsorption capacities of different adsorbents for Reactive Blue and MethyleneGreen

Adsorbent	Q_{max} (mg/g)	References
<i>Reactive blue dye (RB4)</i>		
Chemically modified red seaweed	55.6	Hii et al. [29]
Acid activated mustard stalk	25.8	Ullhyan [30]
Base treated fungus <i>Phanerocheate chrysosporium</i>	81.1	Bayramoğlu et al. [31]
<i>Bacillus subtilis</i> free cells	36.28	Binupriya et al. [32]
Alginate immobilized <i>Bacillus subtilis</i> cells	15.87	Binupriya et al. [32]
Extracellular polysaccharide <i>Bacillus subtilis</i> free cells	42.93	Binupriya et al. [32]
Extracellular polysaccharide Alginate immobilized <i>Bacillus subtilis</i> cells	18.65	Binupriya et al. [32]
surfactant modified barley straws	29.2	Ibrahim et al. [33]
Silica functionalized with 1-propyl-3-methylimidazolium chloride	10–16	Tkachenko et al. [34]
Multiwall Carbon Nanotubes	69	Wang et al. [35]
Cs–CoFe ₂ O ₄	35.05	This study
<i>Methylene green</i>		
Tin sulphide nanoparticle loaded activated charcoal	14.22	Marahel [36]
Saccharide-Derived Spherical Biochar	0.334 mmol/g	Tran et al. [37]
Collagen-based hydrogel nanocomposites	179 mg/g (400 mg/L solution)	Kurdtabar et al. [38]
Cs–CoFe ₂ O ₄	63.34	This study

Fig. 12 Isotherm fits for the adsorption MB and RB4 dyes by Cs-CoFe₂O₄

Fig. 13 Effect of temperature on adsorption capacity of adsorption of the dyes by Cs-CoFe₂O₄

3.7 Effect of temperature and thermodynamics study

The effects of temperature on adsorption efficiency of Cs-CoFe₂O₄ for the removal of MG and RB4 dyes were investigated between 30 and 50 °C. Figure 13 showed that adsorption capacities increase as the temperatures increases which may be as a result of increase contact rates of dye molecules with the adsorbent. Also an increase in diffusion rate of the dye molecule into the pores of the

Fig. 14 van't Hoff fit for adsorption of MB and RB4 onto Cs-CoFe₂O₄

adsorbent is envisaged as the temperature increases, this is due to increase pore radius at higher temperature as well as interactions between dye molecules and active sites of the adsorbent.

The adsorption could be presented as equilibrium process of interaction of the adsorbent with the adsorbate which could be related to a reversible process [39], thus at equilibrium the mass transfer equilibrium constant could be expressed as Eq. 11:

$$K_d = \frac{m \times Q_e}{C_e} \quad (11)$$

Table 5 for adsorption of MB and RB4 onto Cs–CoFe₂O₄

Temp (°C)	MG					RB4				
	K_d	ΔG (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)	ΔH (kJ mol ⁻¹)	R^2	K_d	ΔG (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)	ΔH (kJ mol ⁻¹)	R^2
30	0.595	-1.552	0.121	35.112	0.959	3.381	-8.600	0.193	49.821	0.987
35	0.817	-2.157				3.808	-9.564			
40	1.107	-2.762				4.024	-10.528			
45	1.350	-3.367				4.305	-11.492			
50	1.404	-3.972				4.662	-12.456			

where m is the adsorbent dosage Q_e is adsorption capacity at equilibrium and C_e is the equilibrium concentration of the dye.

The thermodynamic parameters therefore could be obtained from the van't Hoff plot of their relationship with the equilibrium rate constant as presented in Eqs. 12 and 13.

$$\Delta G^0 = -RT \ln K_d \quad (12)$$

$$\ln K_d = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (13)$$

Figure 14 is the van't Hoff plot of the adsorption of MG and RB4 dyes onto Cs–CoFe₂O₄ while the parameters are displayed in Table 5. The enthalpy of the adsorption, ΔH^0 is positive, suggesting an endothermic adsorption process, i.e. increase efficiency with rise in temperature, the positive and large values of entropies, ΔS^0 could be attributed to disorderliness in the dye molecules near the adsorbent surface owing to redistribution of rotational and translational energies of the dye molecules at the solid–liquid interface. The Gibbs free energy less than zero ($\Delta G < 0$) obtained for this study indicates that the adsorption process is spontaneous at various temperatures under investigation.

4 Conclusion

This study demonstrated a successful incorporation of CoFe₂O₄ into chitosan matrix, the characterization showed that a magnetic property was retained while each component retained their functional groups and within the matrix. The composite effectively removed MG and RB4 from aqueous solution with optimum operating parameters of maximum adsorption observed at pH 4, adsorbent dosage of 3.2 mg/L, initial dye concentration of 50 mg/L and contact time of 120 min. Removal of MG was best described by pseudo-second order kinetics while that of RB4 followed a pseudo-first

order kinetics with excellent correlation coefficients. Equilibrium data were fitted well in the isotherm models with trends in the order of Tempkin > Freundlich > Langmuir > Dubinin–Radushkevich for MG dye and Langmuir > Tempkin > Dubinin–Radushkevich > Freundlich for RB4 dye confirming that the sorption is heterogeneous and occurred through physico–chemical interactions. The negative ΔG^0 , positive ΔS^0 and ΔH^0 values indicated that the sorption of dye onto adsorbent was feasible, spontaneous and endothermic in nature.

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Compliance with ethical standards

Conflict of interest The author hereby declare that there is no conflict of interest.

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