



Removal of Reactive Blue 4 Dye from Aqueous Solution with Magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ Beads

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Received: 12 August 2025 / Accepted: 2 January 2026 / Published online: 9 February 2026
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Abstract

In this study, magnetic iron oxide@neodymium/alginate ($\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$) beads were prepared by ionic crosslinking with neodymium (Nd) ions, then subjected to heat treatment, and for the first time, effective removal of Reactive Blue 4 (RB 4) dye from aqueous solution was achieved with these beads. For this purpose, ideal adsorption conditions that significantly affect the removal of this dye were determined. The ideal adsorption conditions were determined as pH:5, contact time (t):60 min, amount of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ bead (m):10 mg, initial RB 4 dye concentration (C_0):25 mg/L, temperature (T): 25 °C. Adsorption isotherm, kinetic and thermodynamic studies were carried out under the ideal adsorption conditions. The adsorption data was found to completely follow Langmuir model for RB 4 dye and the maximum adsorption capacity of RB 4 was found to be 263.16 mg/g. The adsorption kinetic data was found to be compatible with pseudo-second order and adsorption processes were explained by intraparticle diffusion. In adsorption thermodynamics studies, it has been determined that the nature of the adsorption reaction is spontaneous, endothermic and with increasing randomness. Furthermore, reuse studies of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads were carried out and it was determined that these beads could be used successfully up to 10 adsorption/desorption cycles.

Keywords Reactive blue 4 · Neodymium · Adsorption · Wastewater · Adsorption condition

Introduction

One of the biggest environmental problems is wastewater in many industries such as textile, food, paper, printing, carpet and mineral processing, and this problem is increasing day by day. Dyes and pigments used to color the products of these industries pose a threat to the environment due to their toxic and carcinogenic effects [1]. The textile industry is one of the important sources of colored and aromatic pollutants, and it is known that more than 100,000 synthetic dyes are used commercially in this industry [2]. The aquatic ecosystem is adversely affected, especially due to the textile

dyes used in the textile industry. Even in the presence of a small amount of dye, the appearance of the water ecosystem changes because of the release of the wastewater formed. As the color of the dye-contaminated wastewater changes, photosynthetic events in the water are adversely affected and as a result, aquatic life is adversely affected. Moreover, it can be detrimental to some aquatic flora and fauna. In wastewater, not only dyestuffs, but also toxic wastes, aromatics, metals, chemicals such as chlorides can be found. Since these polluting factors do not break down in the water, cleaning the polluted water is very important [3].

Many chemical, physical and biological methods have been developed for the removal of dyes commonly used in the textile industry from wastewater. Methods such as adsorption, biodegradation, coagulation-flocculation, photocatalysis (heterogeneous photocatalysis) are used in the treatment of wastewater containing dyes. Biological degradation is applied as aerobic and anaerobic methods and, in these methods, dye removal is achieved by adsorption of bacteria. The coagulation-flocculation method is preferred for the removal of dissolved substances and colloids in wastewater. Heterogeneous photocatalysis is a low-cost and

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environmentally friendly method used for the removal of many dyes [4]. Among these methods, due to its features such as easy operation, reusability of the adsorbent, and low initial value, the adsorption process is generally preferred for the removal of dyes wastewater [5]. New studies on the removal of dyestuffs, which are used extensively in the textile industry, in aqueous media are continuing. For this purpose, biosorbents that do not harm nature and do not require chemicals have been used recently. While food shells and food wastes are used, the use of natural polymers and adsorbents such as alginate, chitosan, and clay are also preferred [6–19].

Alginate, a salt of alginic acid, is a natural polymer obtained from algae. It has many advantages such as being biocompatible, easy to find, low cost, and non-toxic. Alginate, which has an ionic structure, reacts with polyvalent cations to obtain polymer beads. Recently, rare earth elements (REE) have been preferred in the preparation of alginate-based beads due to their special electronic layer structures and coordination with oxygen. There are studies on the use of alginate beads for adsorption purposes, but there are a limited number of studies on the removal of dyestuffs with alginate beads containing rare earth elements [9, 15, 20–24]. In these studies, dye and fluoride removal studies were carried out in aqueous solutions with alginate-containing adsorbents using lanthanum, cerium, and yttrium from REE elements [9, 20–24]. Removal of different dyes in aqueous solutions with Nd/Alg beads obtained using Nd, one of the REE elements, has been reported [15]. In this study, an improvement in adsorbent capacity was predicted by activating the adsorbent surface with magnetic Nd/Alg beads.

Reactive Blue 4 is a tri-azine dye, and the components of such dyes are resistant to much photochemical and chemical degradation. The dye is used generally to color natural fibers in textile industries. It is known that this dye is toxic, carcinogenic, mutagenic and allergenic. Because of these negative reasons, wastewater containing RB 4 dye must be treated [1]. In this study, magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads were prepared using alginate having biocompatible, easy to find, low cost, and non-toxic and the removal of Reactive Blue 4 in aqueous solutions was investigated for the first

time with these beads. For removing RB 4 dye with magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads, different adsorption conditions were examined, ideal adsorption conditions were determined. The reusability of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads and their application in real water samples were evaluated under ideal adsorption conditions. Additionally, isothermal, kinetic and thermodynamic parameters were determined for RB 4 dye under ideal adsorption conditions.

Experimental

Materials

Reactive Blue 4 (RB 4, $\text{C}_{23}\text{H}_{14}\text{Cl}_2\text{N}_6\text{O}_8\text{S}_2$, 637.44 g/mol) from Alfa Aesar (Table 1), $\text{NdNO}_3 \cdot 6\text{H}_2\text{O}$ (99.9%, 438.35 g/mol) from ABCR and sodium alginate, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (≥ 99), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (≥ 98) from Sigma-Aldrich were supplied. Deionized water was used in all experimental studies (Millipore Direct Q, Bedford, MA, USA). 1000 mg/L stock RB 4 dye solution was prepared, and then the standard solutions (0.5–50 mg/L) at different concentrations using the stock solution were prepared. The calibration graph belongs to RB 4 dye and was drawn with the standard solutions. The regression equation of the standard curve of RB 4 dye was found as $y = 0.0095x - 0.0075$; $R^2 = 0.9990$.

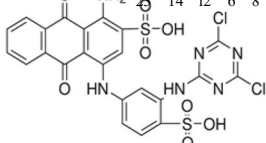
Apparatus

UV-Vis spectrophotometer (Shimadzu 1800, Japan) was used for the adsorption measurements of RB 4 dye, and the measurements were carried out at 598 nm (Table 1). Fourier transform infrared spectrophotometer (FTIR, JASCO 6700, Japan), scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS, Hitachi S-3500, Japan), thermogravimetric and differential thermal analyzer (DTG-60, Shimadzu Inc., Japan) for characterization studies. The variation of zeta potential with respect to pH for magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads was measured with particle size analyzer (Malvern zeta sizer Nano-ZS).

Preparation of Magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ Beads

Magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads were prepared by making minor changes in our study reported in the literature [9]. Magnetic iron oxide particles were obtained as reported in the study [9]. To obtain magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads, Fe_3O_4 particles were added to 2% (w/v) alginate solution and mixed for 24 h. The prepared homogeneous solution

Table 1 Chemical properties of RB 4

Dye	Molecular structure	Molecular formula	Molecular Weight, MA (g/mol)	Wave-length, λ_{max} (nm)
Reactive Blue 4		$\text{C}_{23}\text{H}_{14}\text{Cl}_2\text{N}_6\text{O}_8\text{S}_2$	637.44	598

was added dropwise to 1% Nd (w/v) solution using a syringe to perform ionic crosslinking. The resulting magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads were continued to be mixed for 2 h. Magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads were filtered, washed with deionized water and left to dry in the oven. Magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads were heat treated at 450°C to be used in the removal of RB 4 dye. The experimental process is summarized in Fig. 1.

RB 4 Dye Adsorption Studies

Magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads were used for adsorption experiments of RB 4 dye. pH (3.0–11.0), contact time (20–120 min), amount of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads (5–20 mg), initial RB 4 dye concentration (5–50 mg/L) and temperature ($25\text{--}45^\circ\text{C}$) parameters for ideal adsorption conditions of RB 4 dye were investigated. 0.1 mol/L HCl and 0.1 mol/L NaOH solutions were used to adjust the pH of dye solutions. Ideal adsorption conditions were evaluated by considering dye removal efficiencies (R%). Experiments were repeated at least three times for each adsorption condition. The amount of dye absorbed (mg/g) under equilibrium q_t (mg/g) and removal efficiency of dye at equilibrium was calculated from Eqs. (1)–(2) given below [25, 26]:

$$Q_t = (C_0 - C_t) / V \times m \quad (1)$$

$$R\% = (C_0 - C_t) / C_0 \times 100 \quad (2)$$

where C_0 and C_t initial dye concentration and equilibrium dye concentration (mg/L), V (L) is volume of dye solution and m (g) is adsorbent dosage.

Reusability of Magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ Beads

The adsorption/desorption cycles of RB 4 dye were carried out using the same magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads. The reusability of the beads was tested by repeating the adsorption/desorption cycles 10 times. Desorption was carried out in each cycle using ethanol/acetic acid (5 mL) solution [9].

Application of Dye to Real Water Samples

To determine the accuracy of the method used, real water samples (tap water, dam water, river water supplied from Tunceli province, Turkey) were used, a model solution was created by adding RB 4 dye at different concentrations to the water samples and a recovery test was applied.

Results and Discussion

Characterization Studies

FTIR spectra for magnetic Fe_3O_4 particles and Alg are presented in our study reported in the literature [9]. FTIR spectra of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads are presented in Fig. 2 (a). When the FTIR spectrum presented for magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads in the figure is examined, the peak formed around 522.61 cm^{-1} indicates the stretching vibration where the iron oxide bond interacts with Nd/Alg [20]. Thermogravimetric analyses were carried out under nitrogen gas between 25°C and 600°C with a heating rate of $10^\circ\text{C}/\text{min}$. The thermal decomposition curves of magnetic Fe_3O_4 particles and Alg were reported in our study in the

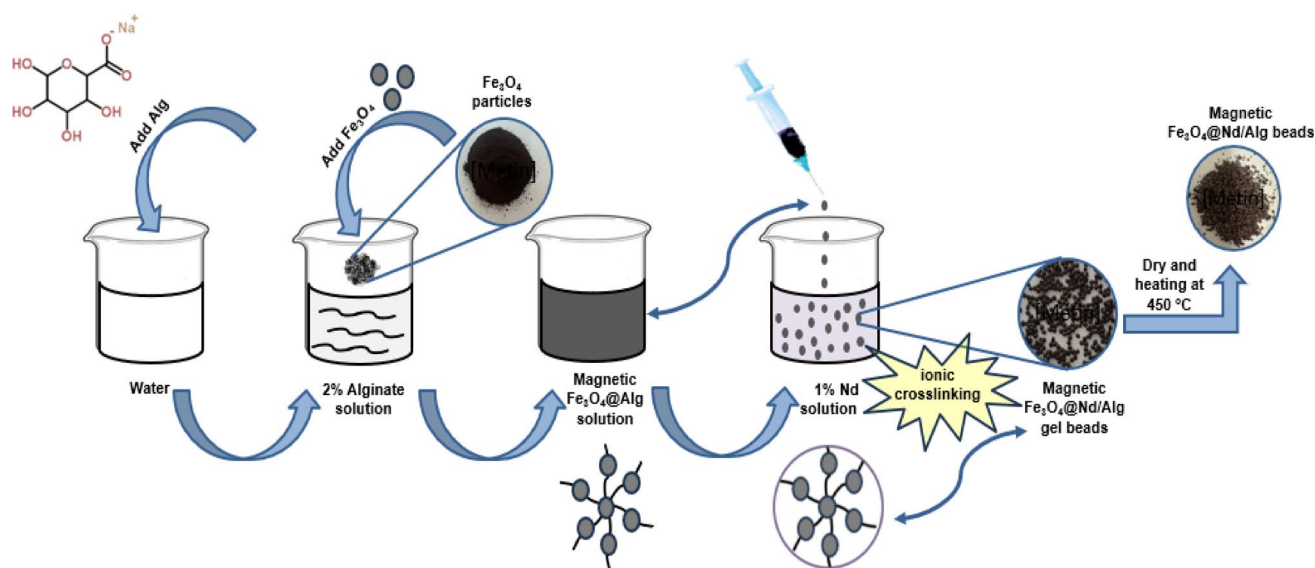


Fig. 1 The experimental preparation process of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads

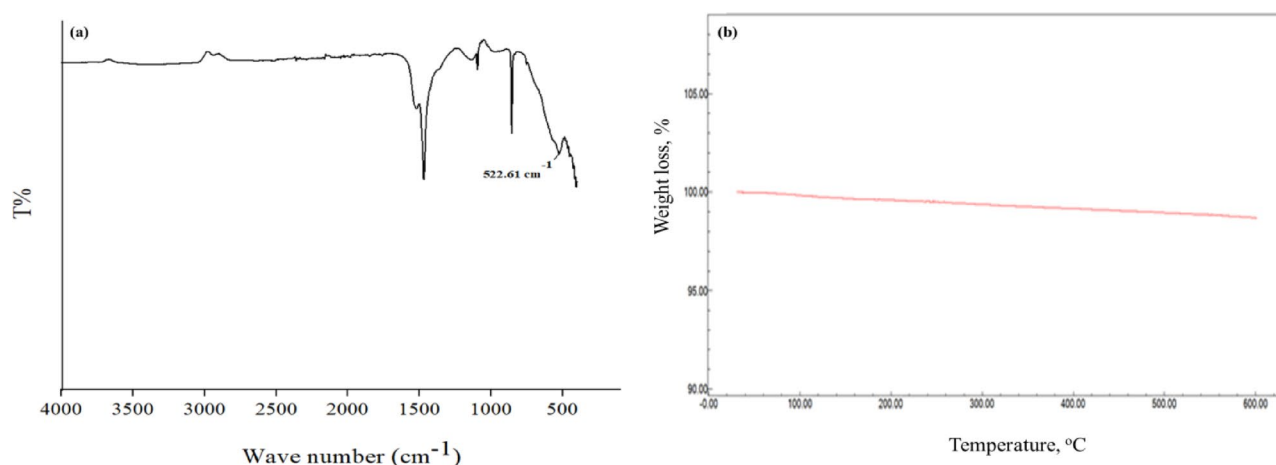


Fig. 2 (a) FTIR spectra of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads (b) TGA analysis of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads

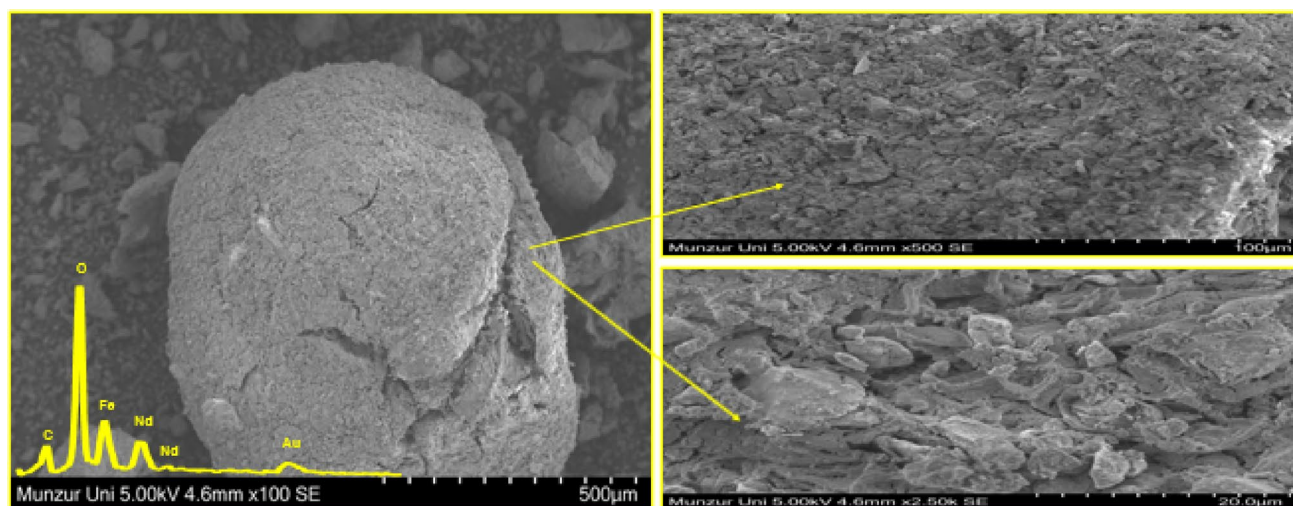


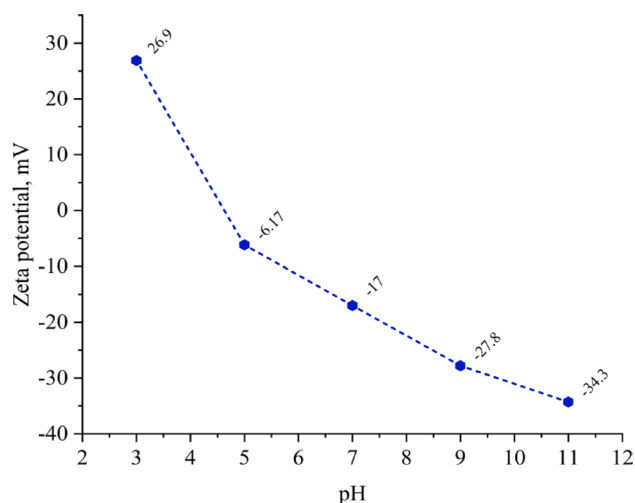
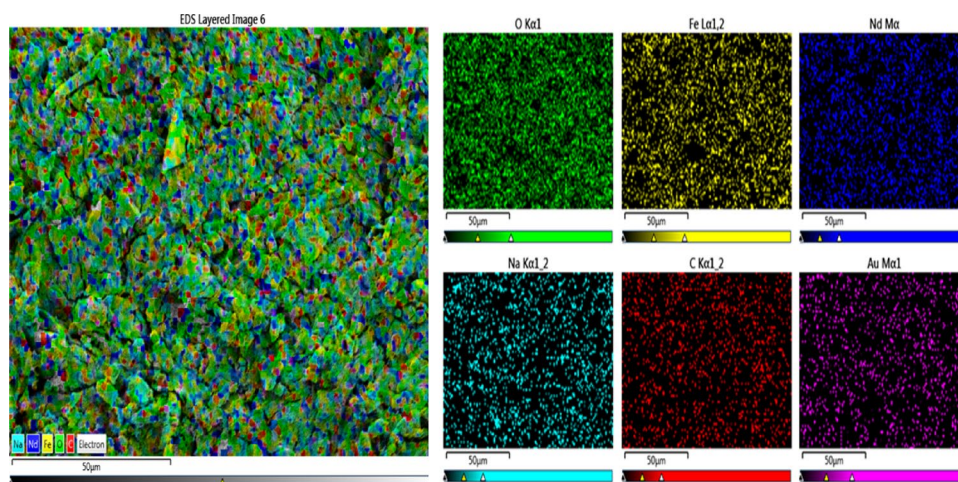
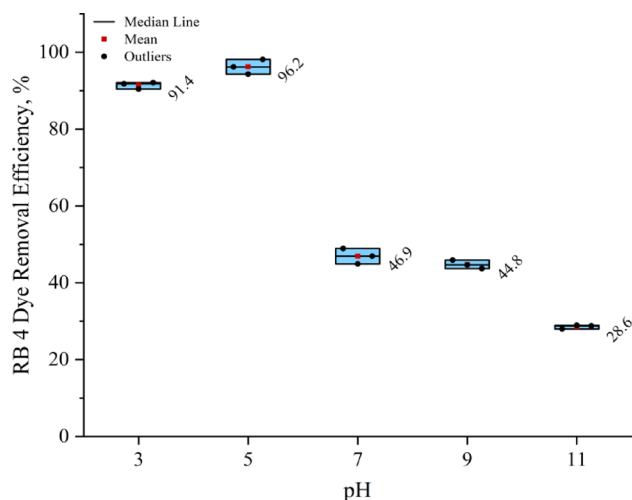
Fig. 3 SEM images (mode: SE, energy: 5 kV, magnification power 100X, 500X, 2500X) and EDS spectra of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads

literature [9]. The thermal decomposition curve of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads is presented in Fig. 2(b), and no weight loss was observed. This was due to the preheating process applied during the production of the beads, which destroyed the alginate skeleton [9]. It can also be stated that magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads have good thermal stability and are suitable for long-term storage.

Images of the surface morphology of magnetic Fe_3O_4 particles and Alg of different sizes visualized by SEM and EDS analysis results are presented in our study reported in the literature [9]. Figure 3 shows the surface morphology of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads of different sizes visualized by SEM. When the images are examined, it can be said that the magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads have deep grooves and rough surfaces, and that magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads with these properties are suitable for dye adsorption. The EDS analysis results for magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads are presented in Fig. 3, and the elemental ratios are 2.2% for

C, 14.3% for O, 13.7% for Fe, 1.0% for Au, and 68.8% for Nd. Mapping images showing the elemental distributions in magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads are also shown in Fig. 4.

Zeta potential measurements of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads were carried out in aqueous solutions with different pH values, including pH 3, 5, 7, 9 and 11. As seen in Fig. 5, it was determined that the zeta potential values of magnetic beads changed between 26.9 mV and -34.3 mV as pH increased from 3 to 11. The zero potential point of pH_{pzc} of magnetic beads is around 4.8 (Fig. 5). As pH increased, the surface of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads became negatively charged. In acidic conditions, the surface of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads is more positive compared to the basic region. Therefore, the electrostatic attraction between magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads and anionic dye RB 4 increased.

Fig. 4 EDS mapping images of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads**Fig. 5** Zeta potential values of magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads at different pH**Fig. 6** Effect of pH (t:60 min, m:10 mg, C_0 :10 mg/L, T:25 °C)

Determination of Ideal Adsorption Conditions

pH

It is one of the most important factors in investigating adsorption conditions. Since pH significantly affects the adsorption mechanism and surface charge of adsorbents [10]. It was investigated at room temperature in the pH range of 3–11 using magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads, contact time:60 min, RB 4 dye concentration:10 mg/L and magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ bead amount:10 mg. When the dye removal efficiencies for different pH values are examined in Fig. 6, the efficiencies were obtained $91.4 \pm 0.88\%$ for pH 3, $96.2 \pm 1.91\%$ for pH 5, $46.9 \pm 0.201\%$ for pH 7, $44.8 \pm 1.10\%$ for pH 9 and $28.6 \pm 0.52\%$ for pH 11. It was determined that the removal efficiencies of RB 4 were higher in the acidic region. Zeta potential measurements at different pHs also support these results (Fig. 6). The surface charge in the acidic region is more positive than in the basic region and therefore the removal of anionic dye RB 4 is higher in the acidic region [4, 27]. In this case, it can show hydrogen bond interactions as well as electrostatic adsorption between the adsorbent and anionic dye molecules present cationically in the solution. Therefore, pH: 5 was selected as the ideal pH value with $96.2 \pm 1.91\%$ efficiency.

Contact time

The removal of RB 4 dye was investigated using magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads with a range of different contact times ranging from 20 to 120 min at pH 5. When the results were examined in Fig. 7, the efficiencies were obtained $85.9 \pm 0.93\%$ for 20 min, $95.5 \pm 0.62\%$ for 40 min, $96.2 \pm 0.91\%$ for 60 min, $96.2 \pm 0.56\%$ for 80 min, $96.2 \pm 0.90\%$ for 100 min and $96.2 \pm 0.91\%$ for 120 min. It was determined that the ideal dye removal was 60 min with $96.2 \pm 0.91\%$ efficiency, and after 60 min, the dye removals were fixed due

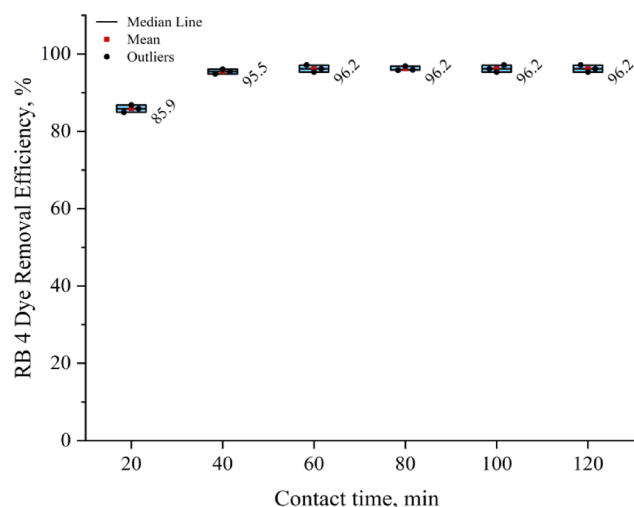


Fig. 7 Effect of contact time (pH:5, m:10 mg, C_0 :10 mg/L, T:25 °C)

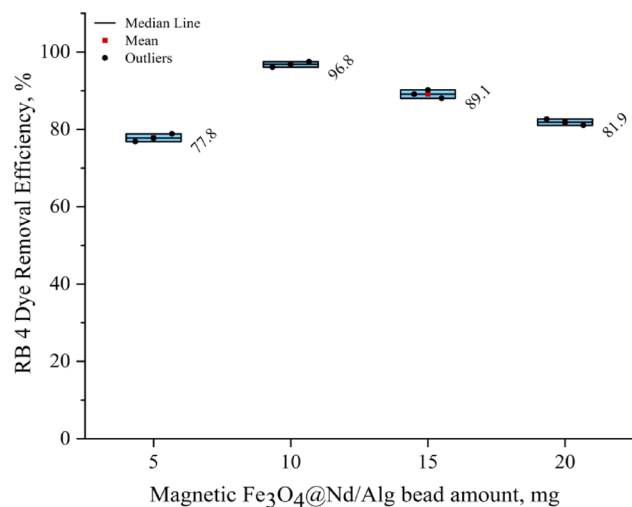


Fig. 8 Effect of the amount of magnetic Fe₃O₄@Nd/Alg beads (pH:5, t:60 min, C_0 :10 mg/L, T:25 °C)

to the saturation of the active sites that are effective in dye adsorption of the magnetic beads [9, 25]. For this reason, 60 min was chosen as the ideal contact time.

Magnetic Fe₃O₄@Nd/Alg Bead Amount

Under ideal adsorption conditions for RB4 dye removal, different adsorbent amounts of magnetic Fe₃O₄@Nd/Alg beads were examined in the range of 5–20 mg and the results are presented in Fig. 8. The RB 4 dye removal efficiencies were obtained as $77.8 \pm 0.99\%$ for 5 mg, $96.8 \pm 0.71\%$ for 10 mg, $89.1 \pm 1.07\%$ for 15 mg and $81.9 \pm 0.81\%$ for 20 mg. It is expected that the dye removal will increase with the increase in the amount of absorbent, but as seen in Fig. 8, RB 4 dye removal started to decrease as the adsorption process reached saturation [9, 25, 28]. The ideal amount of

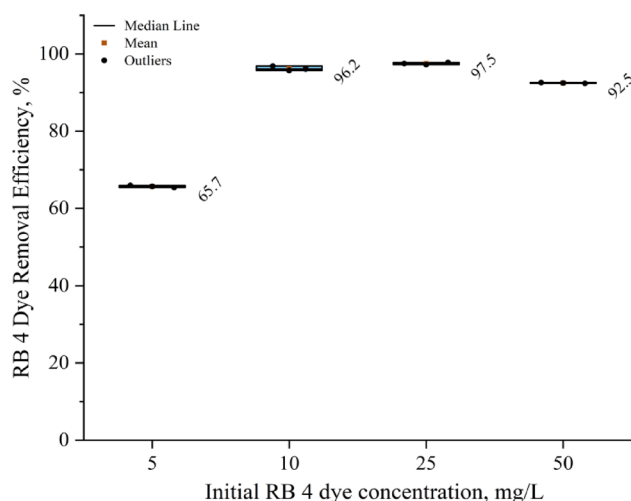


Fig. 9 Effect of initial RB 4 dye concentration (pH:5, t:60 min, m:10 mg, T:25 °C)

magnetic Fe₃O₄@Nd/Alg beads was determined as 10 mg with $96.8 \pm 0.71\%$ efficiency.

Initial RB 4 Dye Concentration

The dye removal efficiencies of four different concentrations of RB 4 dye (5 mg/L, 10 mg/L, 25 mg/L and 50 mg/L) were investigated at the adsorption conditions (pH:5, contact time:60 min, magnetic Fe₃O₄@Nd/Alg bead amount:10 mg). According to the results presented in Fig. 9, the dye removal efficiencies were observed as $65.7 \pm 0.27\%$ for 5 mg/L, $96.2 \pm 0.58\%$ for 10 mg/L, $97.5 \pm 0.26\%$ for 25 mg/L and $92.5 \pm 0.10\%$ for 50 mg/L and the initial RB 4 dye concentration were determined to be 25 mg/L. As seen in the figure, the dye removal efficiency between 5 mg/L and 25 mg/L increased with increasing concentration. However, the dye removal efficiency decreased due to saturation of active sites of magnetic Fe₃O₄@Nd/Alg beads, which are effective in dye adsorption at 50 mg/L. The ideal initial RB 4 dye concentration was determined as 25 mg/L. A graph showing that Q_e increases with increasing initial RB 4 dye concentration is presented in Fig. 10, which expresses the effect of initial dye concentration and adsorption capacity as a function of equilibrium concentration.

Temperature

The ideal temperature was determined at conditions; pH:5, contact time:60 min, magnetic Fe₃O₄@Nd/Alg bead:10 mg, initial RB4 concentration:25 mg/L. For this, 25 °C,

35 °C and 45 °C were investigated and the results are shown in Fig. 11. As seen in Fig. 11, the RB 4 dye removal efficiencies were obtained as $97.5 \pm 0.26\%$ for 25 °C, $93.9 \pm 0.24\%$ for 35 °C and $90.4 \pm 0.29\%$ for 45 °C.

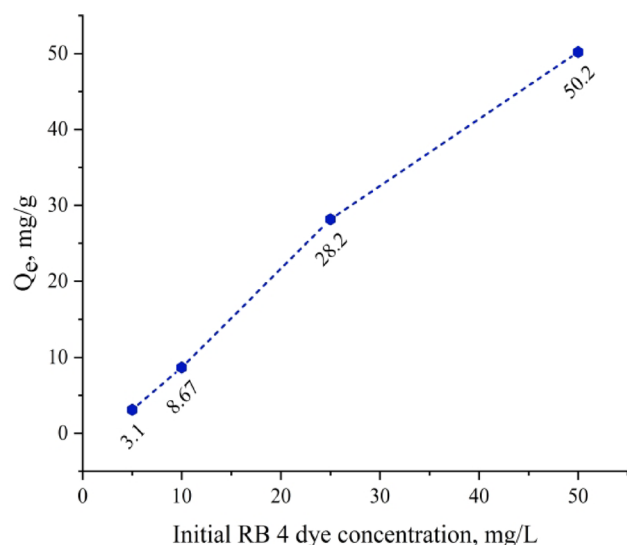


Fig. 10 Adsorption capacity versus initial RB 4 concentration

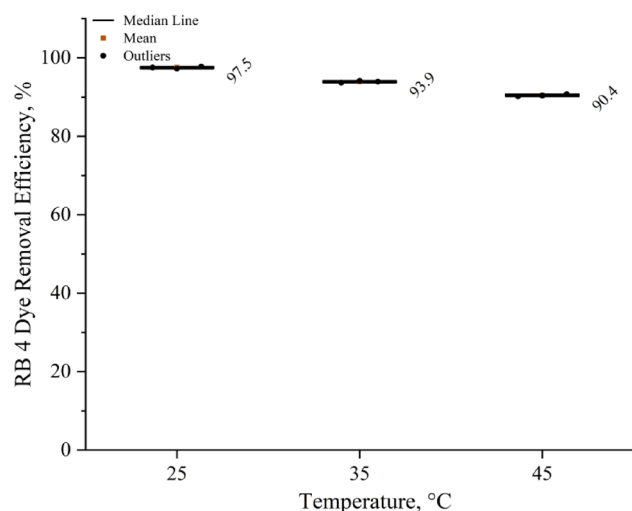


Fig. 11 Effect of temperature (pH:5, t:60 min, m:10 mg, C₀:25 mg/L)

Increasing the temperature caused a decrease in the adsorption of the dye. The optimum temperature with the highest efficiency was determined as 25 °C.

Adsorption Isotherm Studies

Langmuir, Freundlich and Temkin isotherms have investigated the adsorption mechanism of RB 4 dye, and the shape, homogeneity and heterogeneity of the adsorbent surface can be explained using Langmuir and Freundlich isotherms [29, 30]. Temkin isotherm reveals the adsorbent-adsorbate interactions [31]. The correlation coefficients (R^2) for both isotherms were calculated, and the appropriate isotherm was determined for RB 4 dye. Equations (3)-(4)-(5) for Langmuir, Freundlich, Temkin isotherms as follows;

$$1/q_e = (1/q_m b C_e) + (1/q_m) \quad (3)$$

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (4)$$

$$q_e = (RT/b_T) \ln A_T + (RT/b_T) \ln C_e \quad (5)$$

C_e : Equilibrium dye concentration (mg/L)

q_m : Maximum adsorption capacity (mg/g)

b : Langmuir sorption constant (L/mg)

q_e : Equilibrium adsorbed amount (mg/g)

K_f : Freundlich constant (mg/g)

n : Heterogeneity factor

A_T : AT is defined as the Temkin isotherm binding constant

The isotherm constants for Langmuir, Freundlich and Temkin isotherm models were calculated using the ideal adsorption conditions determined for the adsorption of RB 4 dye from aqueous solution. The isotherm constants were obtained from the graphs of three models using magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads at pH:5, t:60 min, m:10 mg, C₀:25 mg/L and T:25 °C. The isotherm graphics and the isotherm data were presented in Fig. 12; Table 2. The basic properties of the Langmuir isotherm were expressed by a dimensionless equilibrium parameter (R_L). R_L values indicate the type of isotherm (unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$)). In our study, the R_L value was calculated as 0.3964 (Table 2). In adsorption studies, the value of $1/n$ in the Freundlich isotherm, which is a measure of heterogeneity, is desired to be between 0 and 1 [25]. In our study, the value of $1/n$ was calculated as 0.9060 (Table 2). The isotherm constant explaining the relationship between the adsorbent and the adsorbent was determined as 16.75 J/mol and it can be stated that the sorption process is suitable for physical adsorption (Table 2).

Correlation coefficients obtained from the graphs of Langmuir, Freundlich and Temkin isotherms for RB 4 dye were compared. The correlation coefficients of Langmuir, Freundlich and Temkin isotherms for the dye were found to be $R^2 = 0.9995$, $R^2 = 0.9986$ and $R^2 = 0.9388$, respectively. Considering the R^2 value obtained from the isotherm curves, it was determined that the Langmuir isotherm for RB 4 dye absorption from aqueous solutions was compatible and the adsorption process was monolayer. The adsorption mechanism was evaluated by characterization studies, and it can be said that the interaction between magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads is guided by electrostatic attraction, hydrogen bonding and complexation [9, 20].

Kinetic Studies

The kinetics of RB 4 dye adsorption on magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads were studied by fitting the data to the model of pseudo-first order (PFO) [32], pseudo-second order

Fig. 12 Langmuir, Freundlich and Temkin isotherms for the adsorption of RB 4 dye

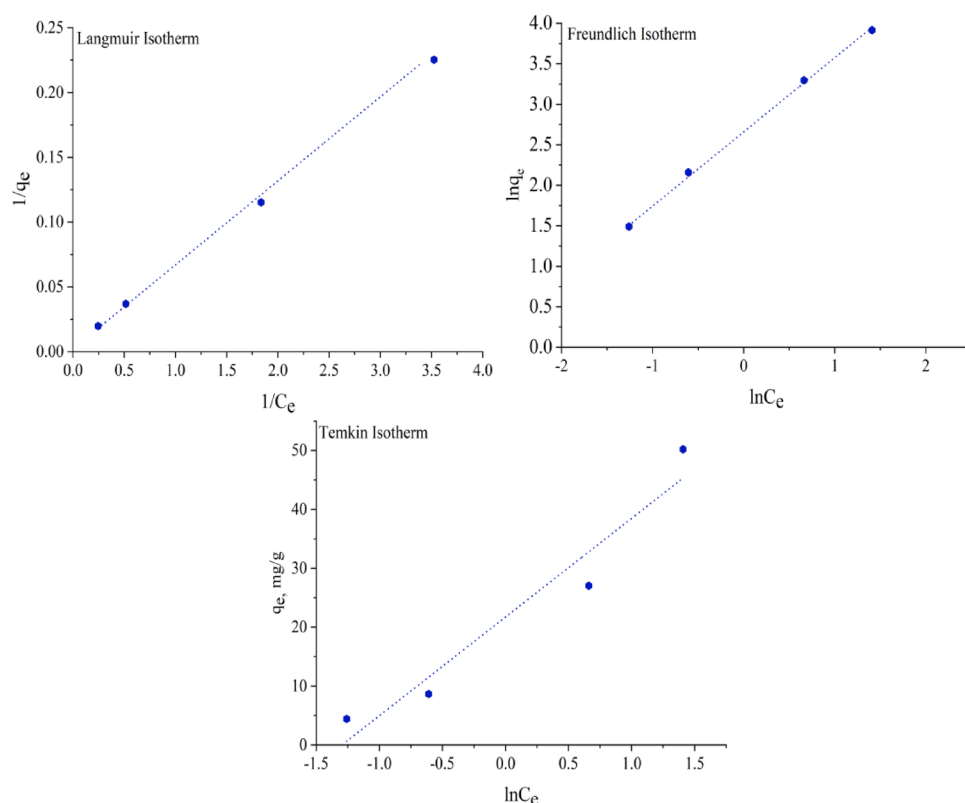


Table 2 Isotherm and kinetic model parameters determined for adsorption of RB 4 dye using magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads (pH:5, t:60 min, m:10 mg, C_0 :25 mg/L, T:25 °C)

Isotherm model	Parameter	Value	Kinetic model	Parameter	Value
Langmuir	q_m (mg/g)	263.16	Pseudo-first order	k_1 (1/min)	0.132
	b (L/mg)	0.061		q_e , cal, mg/g	26.30
	R_L	0.3964		q_e , exp mg/g	28.17
	R^2	0.9995		R^2	0.9920
Freundlich	K_f (L/mg)	14.44	Pseudo-second order	k_2 (g/mg min)	0.007
	$1/n$	0.9060		q_e , cal, mg/g	29.85
	R^2	0.9986		q_e , exp (mg/g)	28.17
				R^2	0.9988
Temkin	B (J/mol)	16.75	Intra-particle diffusion	k_i (mg/g min ^{0.5})	7.543
	K_T (L/g)	3.66		C (mg/g)	3.393
	R^2	0.9388		R^2	0.9910

(PSO) [33] and intraparticle diffusion (IPD) [34]. k_1 and intercept (q_e) is calculated from the graph of $\log(q_e - q_t)$ and t . The Eqs. (6)–(8) are given below.

$$\log(q_e - q_t) = \log(q_e) - k_1 t / 2.303 \quad (6)$$

$$t/q_t = 1/k_2 q_e^2 + (1/q_e) t \quad (7)$$

$$q_t = k_i t_{1/2} \quad (8)$$

k_1 : Pseudo-first-order kinetics rate constant (1/min)

k_2 : Pseudo-second-order kinetics rate constant (g/mg min)

t : Time (min)

k_i : Intraparticle diffusion constant (mg/g min^{0.5})

The pseudo-first-order, pseudo-second order and intraparticle diffusion values were calculated from the graphs obtained using magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads at pH:5, t:60 min, m:10 mg, C_0 :25 mg/L and T:25 °C. The kinetic graphs and the data were given in Fig. 13; Table 2. The correlation coefficient of PFO and PSO models for RB 4 dye were found to be $R^2=0.9920$ and $R^2=0.9988$. Considering the R^2 value obtained from the kinetic curves, it was determined that the PSO model for RB 4 dye absorption from aqueous solutions was compatible. Also, the q_e obtained with the pseudo-second-order model (experimental) is close to q_e (calculation). It was stated that the adsorption process of RB 4 dye is suitable for the pseudo-second order model (Table 2). As for intraparticle diffusion, if the C value calculated from the intraparticle diffusion equation crosses the zero line ($C=0$), this model is followed. C is the thickness of the limit border formed by the adsorption process. The larger the C , the larger the thickness of the limit border.

Fig. 13 Pseudo-first-order, pseudo-second-order and intra-particle diffusion kinetic models for adsorption of RB 4 dye

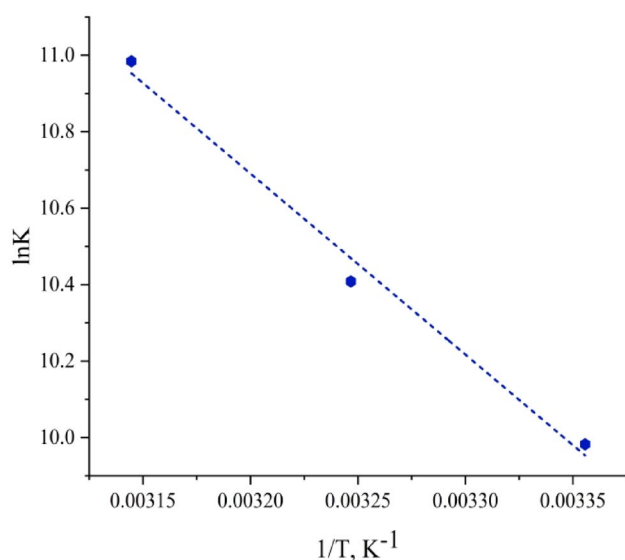
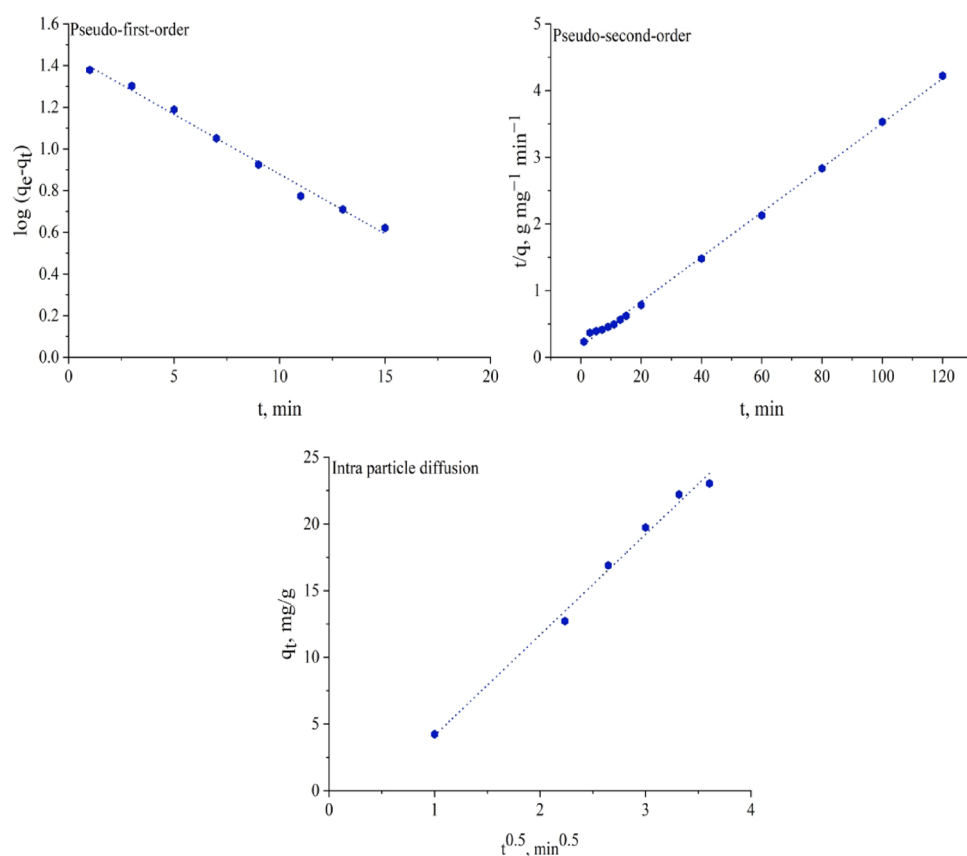


Fig. 14 Variation of $\ln K$ values with $1/T$ for the adsorption of RB 4 dye

In our study, the C value was calculated as 3.393 mg/g (Table 2). In addition, R^2 value was calculated as 0.9910 in the IPD kinetic model used to determine whether the adsorption process was also controlled by the diffusion rate (Table 2).

Thermodynamic Studies

Thermodynamic studies give an idea about the nature of interaction, applicability and spontaneity. For this enthalpy change (ΔH° , kJ/mol), entropy change (ΔS° , kJ/molK) and free energy (ΔG° , kJ/mol) must be calculated. These values are calculated using the following Eqs. (9)–(10).

$$\Delta G^\circ = -R T \ln k \quad (9)$$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (10)$$

k : Equilibrium constant ($k = q_e/c_e$),

R : Universal gas constant (8.314 J/mol K).

T : Temperature (K).

Langmuir equilibrium constant (b) values were used for calculation to ΔG° , ΔH° and ΔS° for this $\ln k$ values and $1/T$ values were plotted, ΔH° and ΔS° values were determined from the obtained equation (Fig. 14). ΔG° values for RB 4 dye adsorption were determined -24.73 kJ/mol for 25 °C, -26.65 kJ/mol for 35 °C and -29.04 kJ/mol for 45 °C. The negative ΔG° values indicate that adsorption of RB 4 dye on magnetic $\text{Fe}_3\text{O}_4@\text{Nd}/\text{Alg}$ beads occurs spontaneously. ΔH° value of RB 4 dye was calculated to be 39.38 kJ/mol and the adsorption of RB 4 dye was endothermic. ΔS° value of RB

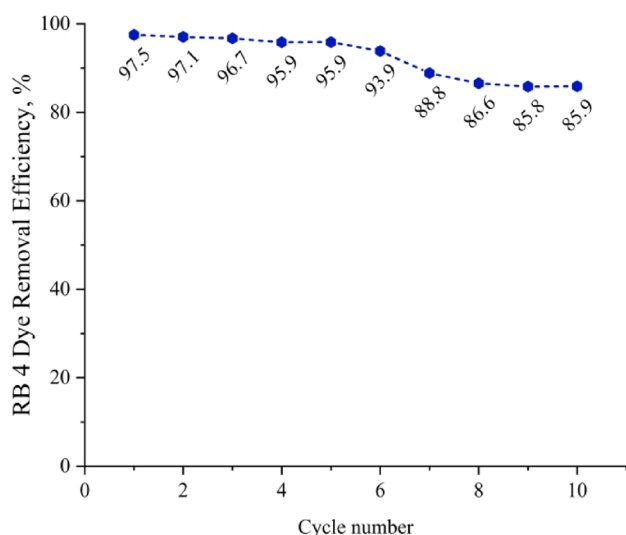


Fig. 15 Reusability of magnetic Fe₃O₄@Nd/Alg beads

4 dye was calculated to be 0.215 kJ/molK. The randomness was increased during the adsorption process.

Reusability of Magnetic Fe₃O₄@Nd/Alg Beads

Adsorption/desorption cycles of RB 4 dye were determined using ideal adsorption conditions; magnetic Fe₃O₄@Nd/Alg beads at pH:5, t:60 min, m:10 mg, C₀:25 mg/L, T:25 °C. Desorption was carried out in each cycle using ethanol/ acetic acid (5 mL) solution [9]. The results obtained with repeated 10 times by using the same magnetic Fe₃O₄@Nd/Alg beads are shown in Fig. 15. While the first use of the beads resulted in 97.5 ± 0.24% RB 4 dye removal, the tenth use of the same bead after desorption resulted in 85.9 ± 0.56% RB 4 dye removal. Magnetic Fe₃O₄@Nd/Alg beads could be used successfully again without any significant reduction.

Application to Real Water Samples

The applicability of the adsorption process developed for the removal of RB 4 dye using magnetic Fe₃O₄@Nd/Alg beads was tested with real water samples. For this, 10 mg/L and 25 mg/L representative RB 4 dye solutions were prepared with tap water, river water and dam water using RB 4 dye. The adsorption process developed was applied to RB 4 dye solutions. An average of over 93% RB 4 dye removal was achieved in tap water samples, and an average of over 91% RB 4 dye removal was achieved in river water and dam water. The results show that the adsorption process developed for RB4 removal using magnetic Fe₃O₄@Nd/Alg beads can be successfully applied to real water samples.

Table 3 Some studies reported in the literature regarding the removal of Reactive Blue 4

Adsorbent	Adsorption capacity, mg/g	pH	Temperature (°C)	References
Hybrid of wood sawdust with 3-Aminopropyl-triethoxysilane-0.5 (AW@APSES-0.5).	415.1	2	50	[5]
Reduced graphene oxide@hydroxyapatite (rGO@HAP-Alg) hybrids	45.56	6–7	30	[35]
Modified husk of agarwood fruit-chitosan (MHAF-CS)	156.25–270.27	3	30–50	[36]
3-aminopropyl triethoxysilane-modified chitosan beads	433.77	4	50	[37]
Single-walled carbon nanotubes (SWCNT)	567.7	2	50	[38]
Multi-walled carbon nanotubes (MWCNT)	502.5			
Chitosan/tannic acid@ ZnFe layered double hydroxide bionanocomposite film	406	5	25–55	[39]
Chitosan@hydroxyapatite nanocomposites	118.4	4	25–55	[40]
Modified microcrystalline cellulose cross-linking with epichlorohydrin	69.79	3	25–65	[41]
Magnetic Fe ₃ O ₄ @Nd/Alg beads	263.16	5	25	This study

Comparison with Other Sorbents of Magnetic Fe₃O₄@Nd/Alg Beads

Adsorption capacity of an adsorbent depends on the surface of the adsorbent used, operating conditions, and the functional groups to which the adsorbent and dye are attached [7, 25]. Studies on dye removal in the literature were examined and evaluated in comparison with this study, and the adsorption capacity of magnetic Fe₃O₄@Nd/Alg beads for RB 4 dye removal was calculated as 263.16 mg/g (Table 3). Considering the current studies, this value shows that magnetic Fe₃O₄@Nd/Alg beads have effective adsorption capacity for the removal of RB 4 dye.

Conclusion

Magnetic Fe₃O₄@Nd/Alg beads were prepared to remove RB 4 dye from aqueous solutions and for the first time RB 4 dye removal was achieved with these magnetic beads. The ideal adsorption conditions determined for the removal of RB 4 dye from aqueous solutions were pH:5, t:60 min, m:10 mg, C₀:25 mg/L, T:25 °C. Under the ideal adsorption conditions, isotherm, kinetic and thermodynamic studies were investigated, and the adsorption process was found to

be suitable for Langmuir isotherm with a maximum adsorption capacity 263.16 mg/g and the adsorption process was found to be suitable for the pseudo-second-order model. In adsorption thermodynamics studies, it has been determined that the nature of the adsorption reaction is spontaneous, endothermic and with increasing randomness. In reuse studies of magnetic $\text{Fe}_3\text{O}_4/\text{Nd}/\text{Alg}$ beads, even after 10 examinations, RB 4 dye removal was achieved with 85.9% efficiency, and it was determined that the beads could be effectively reused. In summary, magnetic $\text{Fe}_3\text{O}_4/\text{Nd}/\text{Alg}$ beads obtained by using alginate, a biodegradable, non-toxic, low cost and natural polymer, have high adsorption potential and can be effective in the treatment of highly concentrated dye wastewater. In addition, the effectiveness of these beads with high adsorption potential in the removal of different dyes can be investigated in future studies.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10924-026-03767-w>.

Author Contributions N.K.A: Conceptualization, investigation, methodology, writing-original draft, writing-review and editing, visualization, formal analysis, supervision, S.S: Investigation, methodology, formal analysis. N.K.A: Conceptualization, investigation, methodology, writing-original draft, writing-review and editing, visualization, formal analysis, supervision.

Funding Open access funding provided by the Scientific and Technological Research Council of Türkiye (TÜBİTAK).

Data Availability No datasets were generated or analysed during the current study.

Declarations

Competing Interests The authors declare no competing interests.

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