



Boron adsorption from water using titanium dioxide nanoparticles and modified titanium dioxide by cationic surfactant (CTAB): kinetics, isotherms, and thermodynamics

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ABSTRACT

Boron, an essential micronutrient, has gained significant attention due to its potential adverse effects on water quality and ecosystems when present in both natural and anthropogenic discharges. High boron concentrations exceeding defined limits in waters can lead to detrimental impacts on various agricultural crops. This thesis investigates the feasibility of employing adsorption processes to remove boron from aqueous solutions spanning concentrations from 1.5 to 16.5 ppm. The study utilizes both of bare TiO₂ (NPs) and chemically surfactant modified for bare TiO₂ using cationic surfactant via cetyltrimethylammonium bromide to produce CTAB-TiO₂ (NPs). The synthesized adsorbent CTAB-TiO₂ (NPs) was meticulously characterized through Fourier-transform infrared spectroscopy tests and Brunauer–Emmett–Teller surface area analysis. Batch adsorption experiments were conducted to examine the influence of operational parameters such as initial boron concentration, pH value, contact time, adsorbent dosage, and temperature on the efficiency of boron removal for each material. The outcomes revealed that bare TiO₂ (NPs) exhibited limited boron adsorption efficiency, reaching a maximum of 40.6% at pH 4, while CTAB-TiO₂ (NPs) displayed more promising results with a maximum removal efficiency of 62.70% at pH 4. To optimize the removal of boron for each synthesized adsorbent, a 2³ factorial experimental design was employed, aided by the statistical software Minitab 18.0, which facilitated both the design and optimization of factors while evaluating their significance. Thermodynamic parameters, including enthalpy, entropy, and Gibbs free energy change, were computed for each adsorbent, providing insights into the underlying mechanisms. Furthermore, the isotherm analysis indicated a commendable fit with either the Langmuir or Freundlich model, suggesting favorable adsorption behavior. The kinetic data aligned well with either the pseudo-first-order or pseudo-second-order model. In conclusion, based on the research findings, CTAB-TiO₂ (NPs) emerged as an effective adsorbent for boron removal. This material represents environmentally friendly alternative for boron removal during real water treatment processes, ensuring that the resulting water complies with accepted limits for agricultural purposes.

Keywords: Boron removal; CTAB-TiO₂; Factorial design; Adsorption models

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1. Introduction

Boron, a naturally occurring element, is a trace element found in earth's crust and is essential for the growth of plants in minute quantities. However, its presence in water sources at elevated levels can have detrimental effects on both ecosystems and human health [1]. The critical range of boron concentration in water varies depending on the specific application. For instance, in drinking water, the World Health Organization (WHO) recommends a boron concentration of less than 2.4 mg/L to prevent health risks [2]. Excessive boron levels can lead to issues such as impaired reproductive function in aquatic organisms and toxicity in humans [1].

Several technologies have been developed to remediate boron from natural water sources due to its widespread presence and potential adverse effects. These methods encompass a range of approaches, including membrane bioreactors, ion exchange, chemical precipitation, and reverse osmosis. While these techniques have proven effective in boron removal, they come with significant drawbacks. They often require expensive equipment, consume high levels of energy, and generate unwanted waste materials during the treatment process [3]. In contrast, adsorption is considered one of the most advantageous methods for removing boron from water due to its simplicity, ease of design, and cost-effectiveness [4]. The removal of boron from water by adsorption is a widely studied and effective method for mitigating boron contamination in water sources. Adsorption is a process in which boron ions in water adhere to the surface of a solid adsorbent material, thereby reducing their concentration in the aqueous phase [5–7]. The mechanism of this approach has highlighted the importance of factors like pH, temperature, initial boron concentration, and adsorbent dosage in optimizing the adsorption process for efficient boron removal [8,9].

Numerous boron adsorbent materials have been developed and explored for their potential in this regard. These materials encompass a wide spectrum, including activated carbon, layered double hydroxides, industrial waste materials like concrete particles, natural substances such as eggshells, metal-organic frameworks, porous aromatic frameworks, and other novel materials like zirconium-chitosan hydrogel beads [10,11].

The need to find an affordable, environmentally responsible, and efficient adsorbent material for boron removal remains crucial in addressing the challenges associated with boron-contaminated water sources. This research aims to contribute to this endeavor by investigating the use of titanium dioxide (TiO_2) and modified titanium dioxide by cationic surfactant of cetyltrimethylammonium bromide (CTAB) as potential adsorbents for boron removal from water. The presence of CTAB on the surface of titanium dioxide introduces positive charges, which attract the negatively charged boron ions and enhance the nanoparticles' affinity for boron ions. These modifications can also improve the stability of the nanoparticles during the boron removal process.

2. Materials and methods

2.1. Materials

Titanium dioxide nanoparticles were purchased from Sigma-Aldrich. Anhydrous boric acid (H_3BO_3), hydrochloric

acid (HCl 33%), sodium hydroxide (NaOH 10%) and CTAB were purchased from HiMedia Company. Other analytical grades including potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), silver nitrate (AgNO_3) were obtained from Merck Chemicals. Distilled and de-ionized water were used in all experimental work.

2.2. Preparation of water solutions

The stock solution of boron (measured as 50 mg/L) was prepared from analytical grade H_3BO_3 . Suitable solutions were freshly prepared by using H_3BO_3 stock solution with distilled water before conducting the adsorption experiments. The concentration of present boron in these solutions was measured by an inductively coupled plasma-optical emission spectrometry (ICP-OES) (Thermo Scientific, iCAP 6300, ICP-OES CID Spectrometer).

2.3. Preparation of modified titanium dioxide by cationic surfactant (CTAB)

To create surfactant-modified titanium dioxide (CTAB- TiO_2), 5 g of untreated titanium dioxide was combined with 250 mL of a 20 mmol CTAB solution. The mixture was stirred for 5 h at 70°C on a table shaker. Subsequently, it was left to allow the CTAB-titanium dioxide particles to settle. The remaining substances were washed with distilled water multiple times to eliminate all bromide ions from the solution. The presence of bromide ions was indicated by the formation of a white precipitate when AgNO_3 was introduced. Next, the obtained CTAB-titanium dioxide residues were filtered and subjected to oven drying at 105°C for 6 h. Finally, this new modified titanium dioxide material was crushed into fine powder particles using a mortar and pestle.

2.4. Characterization of the adsorbent

The bare titanium dioxide and modified titanium dioxide by cationic surfactant was tested and recorded using Fourier-transform infrared spectroscopy (FTIR Spectrometer Frontier/TGA 4000-PerkinElmer) and the measurements were performed over 4,000–400 cm^{-1} . Furthermore, nitrogen adsorption measurements were used at liquid nitrogen temperature, 77 K to determine the surface area and the pore size distribution of the adsorbents using the Brunauer-Emmett-Teller (BET) equation.

2.5. Batch adsorption and isotherm study

Batch adsorption method was used during the experiments to get information about the boron equilibrium data and studying the variable parameters such as adsorbent dosage (0.10, 0.20, 0.30, 0.40, 0.50) g, pH (2, 4, 6, 8, 10 and 12), initial boron concentration (1.50, 4.50, 8.50, 12.50, 16.5) mg/L and temperature of (15°C, 25°C, 35°C and 45°C). A mass of each adsorbent was mixed with 50 mL of stock solutions in 100 mL cleaned polythene bottles using a mechanical shaker (Innova 2100 Platform Shaker) for a various programmed time interval at a constant speed of 150 RPM at various temperatures for a certain contact time and the pH was adjusted by 0.1 M HCl and 0.1 M NaOH.

The solutions were agitated until equilibrium and then filtered by Whatman membrane filter paper of pore size 0.45 μm . Finally, the absorbance of residual boron concentration was determined using an inductively coupled plasma-optical emission spectrometry (ICP-OES) (Thermo Scientific, iCAP 6300, ICP-OES CID Spectrometer)

The removal percent and the amount of adsorbed boron ions by the adsorbents were calculated using relations shown in Eqs. (1) and (2).

$$R(\%) = \frac{(A_i - A_t)}{A_i} \times 100 \quad (1)$$

$$q_t = \frac{(C_i - C_e)}{m} \times V \quad (2)$$

where R represents the removal percent of boron ions, A_i shows initial concentration of boron and A_t is absorbance of boron at a time t , q_t is the amount of adsorbed boron per gram of adsorbent (mg/g), C_i displays the initial boron concentration (ppm), C_e is the equilibrium boron concentration (mg/L) in solution after adsorption process, V is the volume (L) of solution and m is the mass (g) of chemically modified bare TiO_2 .

2.6. Kinetic study

The contact time at different intervals (30, 60, 90, 120, 150, 180, 210, 240 and 270) min and adsorbents weight of (0.10, 0.20, 0.30, 0.40 and 0.50) g/50 mL for bare TiO_2 and CTAB- TiO_2 were applied for each experiment to enable the system to approach the equilibrium. Different kinetic models, particularly Lagergren's pseudo-first-order and pseudo-second-order, were applied to the experimental data.

3. Results and discussions

3.1. Performance characterization of bare TiO_2 and CTAB- TiO_2

3.1.1. FTIR analysis

FTIR analysis of bare TiO_2 nanoparticles can reveal the chemical composition and surface functional groups of the material. Fig. 1 shows that the broad band around

3,200–3,600 cm^{-1} corresponds to the stretching vibration of hydroxyl (OH) groups, which are often present on the surface of TiO_2 nanoparticles due to adsorbed water or hydroxyl species. The strong absorption peak around 600–800 cm^{-1} represents the stretching vibration of titanium-oxygen (Ti–O) bonds, indicating the presence of TiO_2 . Additional peaks in the range of 1,000–1,800 cm^{-1} may indicate the presence of surface adsorbed species, such as carboxylic acids, amines, or other organic molecules. These peaks can help determine the nature of the surface modification or surface interactions with other molecules. When titanium is modified with CTAB, the FTIR analysis can provide insights into the interactions between CTAB molecules and the titanium surface. The presence of CTAB may introduce new peaks or shifts in the FTIR spectrum compared to bare TiO_2 nanoparticles. FTIR spectrum of CTAB typically shows peaks around 2,850–3,000 cm^{-1} (C–H stretching), 1,470–1,500 cm^{-1} (C–H bending), and 1,300–1,400 cm^{-1} (C–N stretching). In addition, the modification with CTAB might affect the Ti–O bonding, leading to shifts in the Ti–O stretching peaks observed in the bare TiO_2 spectrum. New peaks or changes in peak intensities in the range of 1,000–1,800 cm^{-1} can indicate the interaction between CTAB and the TiO_2 surface. These changes may suggest the formation of new chemical bonds or adsorption of CTAB onto the titanium surface.

3.1.2. BET analysis

A set of nitrogen gas adsorption isotherm tests was carried out to evaluate the specific surface area, pore size distribution, and total pore volume for bare TiO_2 , CTAB- TiO_2 modified material using BET method. The specific surface area of bare TiO_2 was determined to be 36.420 m^2/g with pore volume of 0.016 m^3/g . The CTAB- TiO_2 sample showed around 40% increase in specific surface area (50.853) m^2/g with pore volume of 0.023 m^3/g as per shown in Table 1.

3.2. Adsorption study of boron

3.2.1. Effect of pH value on boron adsorption process

Fig. 2 displays the effect of pH on boron removal (%) by bare TiO_2 and modified CTAB- TiO_2 . The maximum removal (%) of boron is higher at a low pH of 4.

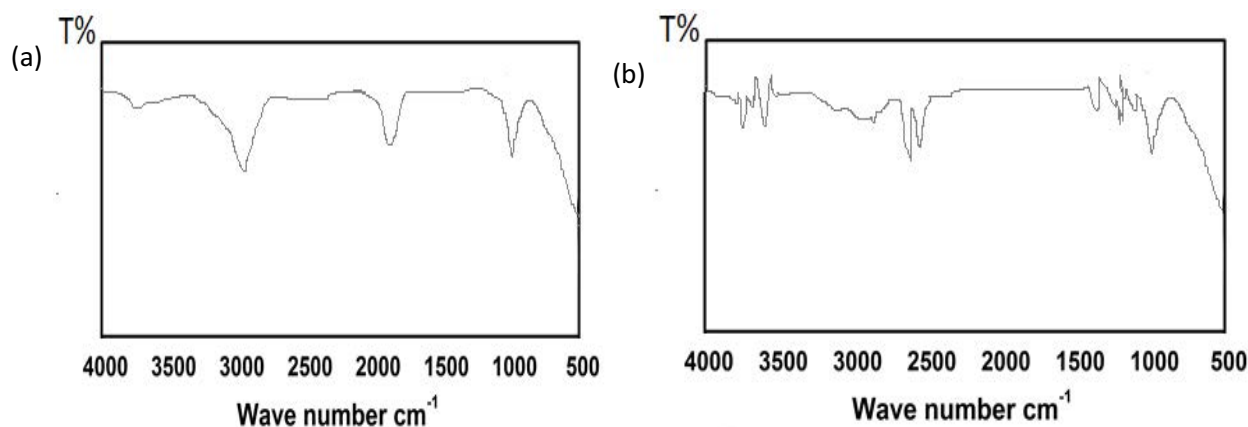


Fig. 1. Fourier-transform infrared spectra of (a) bare TiO_2 and (b) CTAB- TiO_2 .

The surface charge of bare TiO_2 is influenced by the pH of solution due to the presence of hydroxyl groups on its surface. The pzc of bare titanium dioxide (TiO_2) is at pH of 6. Therefore, at a low pH value (4), the surface of TiO_2 tends to be positively charged due to the protonation of the hydroxyl groups. Under these conditions, boron is usually in the form of boric acid which is a Lewis acid with a pKa of (8.92–9.24) or borate ions, can interact electrostatically with the positively charged surface. This electrostatic attraction enhances the adsorption of boron on bare TiO_2 at low pH. As the pH of the solution increases (becoming more basic), the hydroxyl groups on the TiO_2 surface undergo deprotonation, resulting in a negatively charged surface. This change in surface charge reduces the electrostatic attraction between the surface and boron species, leading to decreased boron adsorption on bare TiO_2 .

Similarly, the pzc of modified bare titanium dioxide (TiO_2) by CTAB is calculated at lab using salt addition method and found at pH of 6.70. Therefore, at a low pH value (4), the positively charged CTAB molecules adsorb onto the surface of TiO_2 , resulting in a positively charged surface. This positive charge can enhance the adsorption of boron species through electrostatic interactions, similar to bare TiO_2 under acidic conditions.

However, as the pH increases, the negatively charged hydroxyl groups on the TiO_2 surface start to deprotonate, resulting in a negatively charged surface. The negatively charged surface repels boron species, and the adsorption of boron on CTAB- TiO_2 decreases as the pH becomes more basic. Generally, both bare TiO_2 and CTAB- TiO_2 exhibit increased boron adsorption at a low pH value, which is 4

(acidic conditions), while adsorption decreases as the pH becomes more basic.

3.2.2. Effect of adsorbent dosage on boron adsorption process

The adsorbent dosage plays a significant role in the boron adsorption process using bare TiO_2 and CTAB- TiO_2 . In the case of bare TiO_2 , an increase in the adsorbent dosage generally leads to an increase to removal percentage of boron. This is because a larger quantity of adsorbent provides more surface area for boron adsorption, increasing the chances of interaction between boron ions and TiO_2 particles. However, there is typically a point of diminishing returns, where further increases in the adsorbent dosage may not significantly improve the removal efficiency. The mass of dosage required depends on the initial boron concentration and desired removal percentage.

On the other hand, CTAB- TiO_2 , which is TiO_2 modified with cetyltrimethylammonium bromide, shows improved boron adsorption performance compared to bare TiO_2 . The presence of CTAB on the surface of TiO_2 enhances its adsorption capacity and selectivity for boron ions. With CTAB- TiO_2 , even at lower adsorbent dosages, a considerable removal percentage of boron can be achieved. As with bare TiO_2 , there is a point where further increases in the adsorbent dosage may not lead to significant improvements in removal efficiency. The required mass of dosage for CTAB- TiO_2 is (0.3 g/0.05 L) which is typically lower compared to bare TiO_2 which is (0.5 g/0.05 L) due to its enhanced adsorption properties as per shown in Fig. 3.

3.2.3. Effect of initial boron concentration on the adsorption process

Fig. 4 shows the effect of initial boron concentration on the adsorption capacity of bare TiO_2 and CTAB- TiO_2 . In the case of bare TiO_2 , a higher initial boron concentration generally leads to an increase in the adsorption capacity. This is because the greater concentration of boron provides more opportunities for interaction with the available adsorption sites on the TiO_2 surface. As a result, the adsorption

Table 1
Pore volume, pore size and surface area of adsorbents

	Surface area (m^2/g)	Pore volume (m^3/g)	Pore diameter (nm)
Bare TiO_2	36.420	0.016	2.647
CTAB- TiO_2	50.853	0.023	2.769

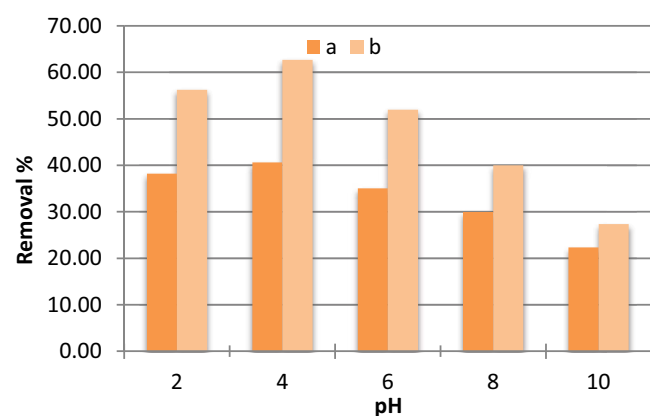


Fig. 2. Effect of pH on the boron removal by (a) bare TiO_2 and (b) CTAB- TiO_2 . (Experimental conditions: solution volume: 50 mL, contact time: 4 h, speed: 150 rpm, adsorbent dosage: 0.5 g, 0.3 g and initial boron conc. 16.5 mg/L, 1.5 mg/L, respectively).

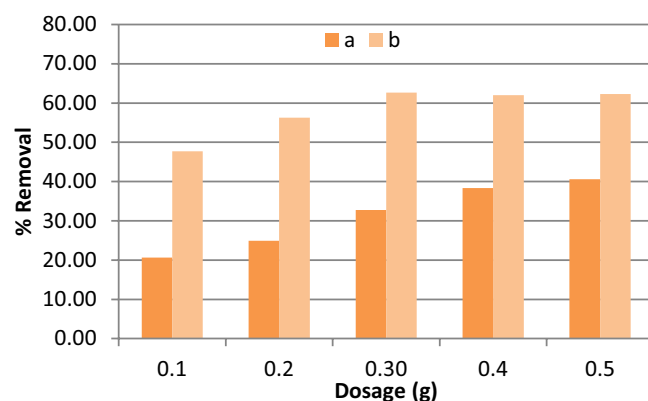


Fig. 3. Effect of adsorbent dosage on the boron removal by (a) bare TiO_2 and (b) CTAB- TiO_2 . (Experimental conditions: solution volume: 50 mL, contact time: 4 h, speed: 150 rpm, pH: 4 and initial boron conc. 16.5 mg/L, 1.5 mg/L, respectively).

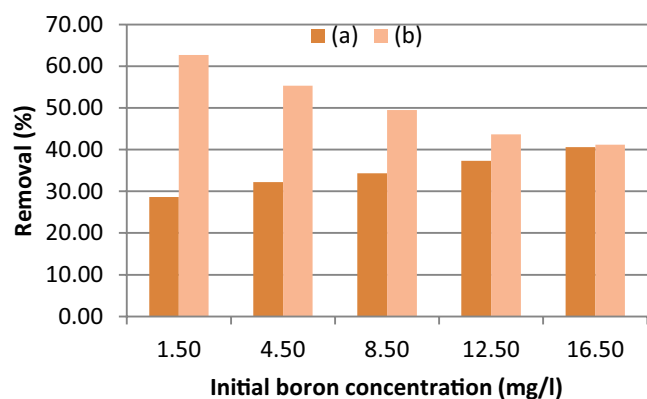


Fig. 4. Effect of initial boron concentration on the boron removal by (a) bare TiO₂ and (b) CTAB-TiO₂. (Experimental conditions: solution volume: 50 mL, contact time: 4 h, speed: 150 rpm, pH: 4 and adsorbent dosage: 0.5 g, 0.3 g, respectively).

efficiency of boron onto bare TiO₂ is enhanced with increasing initial concentration.

On the other hand, when considering CTAB-TiO₂, the effect of initial boron concentration can be more complex. At low initial boron concentrations, CTAB-TiO₂ can exhibit enhanced adsorption capacity compared to bare TiO₂. This can be attributed to the presence of the surfactant, which can create favorable conditions for boron adsorption by promoting electrostatic interactions and improving surface area coverage.

However, as the initial boron concentration increases further, the adsorption capacity of CTAB-TiO₂ may become saturated or even decrease. This is because the surfactant molecules can start to compete with boron for adsorption sites, leading to a reduced availability of active sites for boron binding. Consequently, at higher initial boron concentrations, the adsorption efficiency of CTAB-TiO₂ may not increase proportionally, and a point of diminishing returns or even a decline in adsorption capacity may be observed.

Therefore, bare TiO₂ generally benefits from higher initial boron concentrations due to increased adsorption capacity. The presence of CTAB on TiO₂ can introduce more intricate dynamics. CTAB-TiO₂ may exhibit improved adsorption capacity at low initial boron concentrations, but the presence of the surfactant can result in a saturation or decrease in adsorption efficiency at higher concentrations. In addition, the declining adsorption behavior of the CTAB-TiO₂ adsorbent with the increase in the boron concentration by the fast adsorption of boron on the adsorbent surface, which creates high boron surface concentration and subsequently reduces the boron concentration gradient, the main driving force of the adsorption process, between the liquid phase and the adsorbent solid phase and creates a false equilibrium state. This effect was recognized clearly with the boron ions concentration increase.

3.2.4. Effect of contact time on boron adsorption process

It was perceived that in the case of bare TiO₂, a longer contact time allows for increased interaction, leading to enhanced adsorption. More opportunities for boron ions to

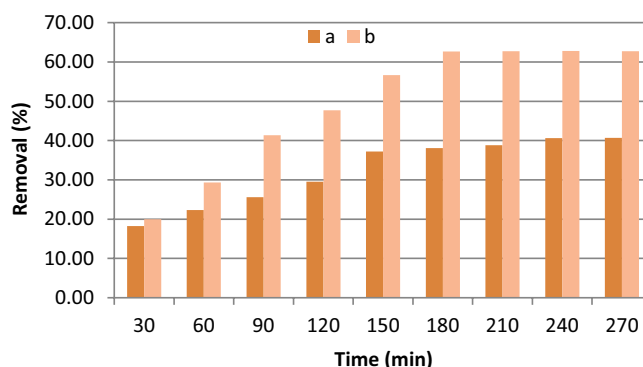


Fig. 5. Effect of contact time on the boron removal by (a) bare TiO₂ and (b) CTAB-TiO₂. (Experimental conditions: solution volume: 50 mL, speed: 150 rpm, pH: 4, adsorbent dosage: 0.5 g, 0.3 g and initial boron conc. 16.5 mg/L, 1.5 mg/L, respectively).

diffuse and attach to the active sites on the TiO₂ surface result in higher removal efficiency. Initially, the adsorption process shows a rapid increase in boron removal due to available active sites. However, as the contact time increases, the adsorption rate gradually decreases, indicating saturation or blockage of active sites by adsorbed boron species. On the other hand, when CTAB-TiO₂ is used, the presence of CTAB improves the surface properties and adsorption capacity of TiO₂. The positively charged CTAB molecules facilitate boron adsorption through electrostatic attraction, leading to higher efficiency compared to bare TiO₂. Consequently, CTAB-TiO₂ exhibits a more sustained adsorption capacity with increasing contact time, indicating its ability to retain boron species even after prolonged exposure. Thus, both bare TiO₂ and CTAB-TiO₂ show improved boron adsorption with increasing contact time, but the presence of CTAB enhances the overall adsorption performance due to the synergistic effect of electrostatic interactions and increased active sites and the boron adsorption within 240 min contact time could be considered as adsorption equilibrium as shown in Fig. 5.

3.2.5. Effect of temperature on boron adsorption process

The effect of temperature on the boron adsorption process can vary for bare TiO₂ and CTAB-TiO₂. In the case of bare TiO₂, an increase in temperature generally enhances the adsorption of boron onto the surface of the material. This can be attributed to the increased kinetic energy of the molecules at higher temperatures, leading to higher collision frequencies and greater chances of boron adsorption onto the TiO₂ surface. The higher temperature can also promote the desorption of water molecules from the surface, providing more available sites for boron adsorption. Therefore, at a temperature of (45°C) boron adsorption was generally enhanced on bare TiO₂ due to increased mobility and diffusion.

On the other hand, in the case of CTAB-TiO₂, the presence of (CTAB) alters the adsorption behavior. At higher temperatures, CTAB molecules may undergo thermal degradation, reducing their adsorption capacity and affecting the overall boron adsorption process. Additionally, the thermal

stability of the CTAB-TiO₂ composite may be affected by temperature, potentially leading to changes in the structure and properties of the material, which could impact boron adsorption. Therefore, at temperature of (25°C) the CTAB-TiO₂ was allowing for increased boron access to the adsorbent surface and enhancing the adsorption process as shown in Fig. 6.

3.2.6. Optimizing boron removal: design of experiments using Minitab program

In research involving the assessment of the significance of factors and their interactions on a response, statistical analysis methods like response surface methodology and factorial design are commonly employed. These techniques help researchers understand the relationship between input factors and the output response. In this study, the statistical software Minitab 18.0 was utilized to facilitate the design and optimization of these factors. The main objective of the statistical analysis was to evaluate the removal percentage of boron, which served as the response variable in the study. Boron removal percentage represents the efficiency of a process in removing boron from a certain system, and the researchers sought to identify the factors and interactions that significantly influenced this response. To assess the reliability and significance of the developed statistical model, the researchers employed *P*-values, often referred to as probability constants. The researchers evaluated both individual effects of the factors and their interactions by analyzing the corresponding *P*-values. In statistical hypothesis testing, a smaller *P*-value suggests stronger evidence against the null hypothesis, indicating that the factor or interaction is likely to have a significant effect on the response. Conversely, a larger *P*-value implies weaker evidence against the null hypothesis, suggesting that the factor or interaction may not have a significant influence on the response. Additionally, the researchers considered the magnitude of the *t*-values associated with the coefficient terms in the statistical model. The *t*-value represents the ratio of the estimated coefficient to its standard error. In the context of regression analysis, a larger absolute *t*-value indicates that the coefficient is more significant, as it suggests that the estimated coefficient is larger relative to its variability [13,14].

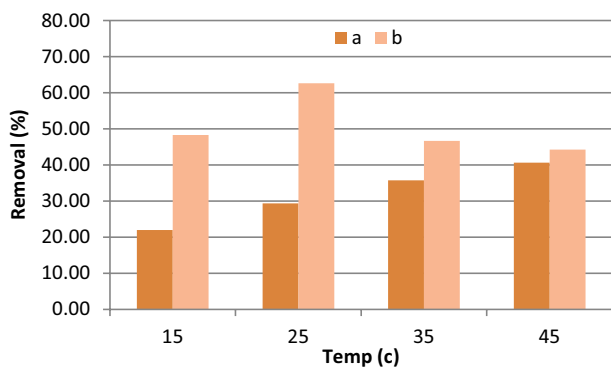


Fig. 6. Effect of temperature on the boron removal by (a) bare TiO₂ and (b) CTAB-TiO₂. (Experimental conditions: solution volume: 50 mL, speed: 150 rpm, pH: 4, adsorbent dosage: 0.5 g, 0.3 g and initial boron conc. 16.5 mg/L, 1.5 mg/L, respectively).

Table 2 illustrates the setup employed in the boron extraction process from solutions. This table contains details regarding factors such as pH, dosage quantity, and boron concentration. The statistical assessment, specifically analysis of variance, concerning the elimination of boron, has been explained in Tables 3 and 4. The assessment was carried out with a 95% confidence level, facilitating the recognition of significant variables. Consequently, this procedure resulted in the development of a regression model that encompasses all these statistically valid parameters.

The regression model was developed as follows:

$$\% \text{Removal} = 65.16 - 1988 \text{ Concentration} - 4.513 \text{pH} + 55.3 \text{ Dosage} + 0.1696 \text{ Concentration} \times \text{pH} \quad (3)$$

Based on the Pareto chart derived from the analysis demonstrated in Fig. 7, several factors were recognized as having statistical significance at a 95% confidence level. These factors include concentration, pH, and concentration × pH.

According to contour plots shown in Fig. 8, the percentage of boron removal exhibited an upward trend as pH and concentration decreased, while dosage was increased up to a certain limit.

Table 2
Low and high levels of parameters for optimization of CTAB-TiO₂

Parameters	Low level	High level
pH	4	8
Dosage amount (g/50 mL)	0.1	0.30
B concentration (mg/L)	1.50	16.50

Table 3
Experimental matrix for optimization and responses (25°C, 150 rpm and 4 h)

Run	Experimental parameters			% Removal
	B concentration	pH	Dosage	
1	16.5	8	0.3	33.94
2	1.5	4	0.3	62.67
3	16.5	4	0.3	41.14
4	1.5	4	0.3	62.67
5	1.5	8	0.3	40.00
6	16.5	4	0.1	28.41
7	16.5	4	0.3	44.42
8	1.5	8	0.1	45.33
9	16.5	8	0.1	23.45
10	16.5	8	0.3	33.94
11	16.5	8	0.1	23.45
12	1.5	4	0.1	47.73
13	1.5	4	0.1	47.73
14	1.5	8	0.1	26.67
15	1.5	8	0.3	40.67
16	16.5	4	0.1	28.23

Table 4
Factorial fitness and analysis of variance analysis for boron removal using CTAB-TiO₂

Source	Adj. SS	Adj. MS	F-value	P-value
Model	2,010.78	502.70	21.94	0.000
Linear	1,907.18	635.73	27.75	0.000
Concentration	847.87	847.87	37.01	0.001
pH	570.63	570.63	24.91	0.000
Dosage	488.68	488.68	21.33	0.001
2-Way interactions	103.61	103.61	4.52	0.057
Concentration × pH	103.61	103.61	4.52	0.057

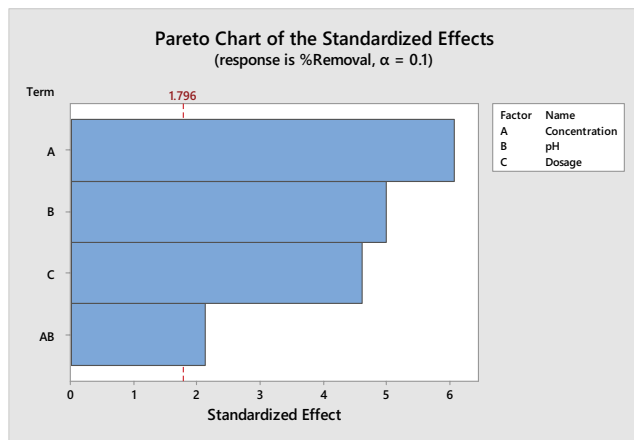


Fig. 7. Pareto chart of analysis using CTAB-TiO₂.

3.3. Data Analysis related to (thermodynamic, isotherm and kinetic models) of boron adsorption using bare TiO₂ (b) CTAB-TiO₂

3.3.1. Thermodynamic analysis

It deals with the study of the energy changes and equilibrium conditions associated with the adsorption process. It provides insights into the interaction between adsorbate molecules and the adsorbent surface, and helps in understanding the factors that influence the adsorption behavior and the nature of adsorption process is it spontaneous or unspontaneous [15].

The Gibbs free energy change (ΔG) is a key thermodynamic parameter that determines the feasibility of an adsorption process. The adsorption process is spontaneous when ΔG is negative, indicating a decrease in free energy of the system. The relationship between ΔG and other thermodynamic quantities, such as enthalpy (ΔH) and entropy (ΔS), is described by the following equations [16].

$$\Delta G = -RT(\ln K) \tag{4}$$

$$\Delta G = \Delta H - T\Delta S \tag{5}$$

$$\ln K = \Delta \frac{S}{R} - \Delta \frac{H}{RT} \tag{6}$$

$$K = \frac{Q_e}{C_e} \tag{7}$$

where T represents the temperature in Kelvin, R is the universal gas constant (8.314 J/mol·K) and $K = (Q_e/C_e)$ is the equilibrium constant in (L/g).

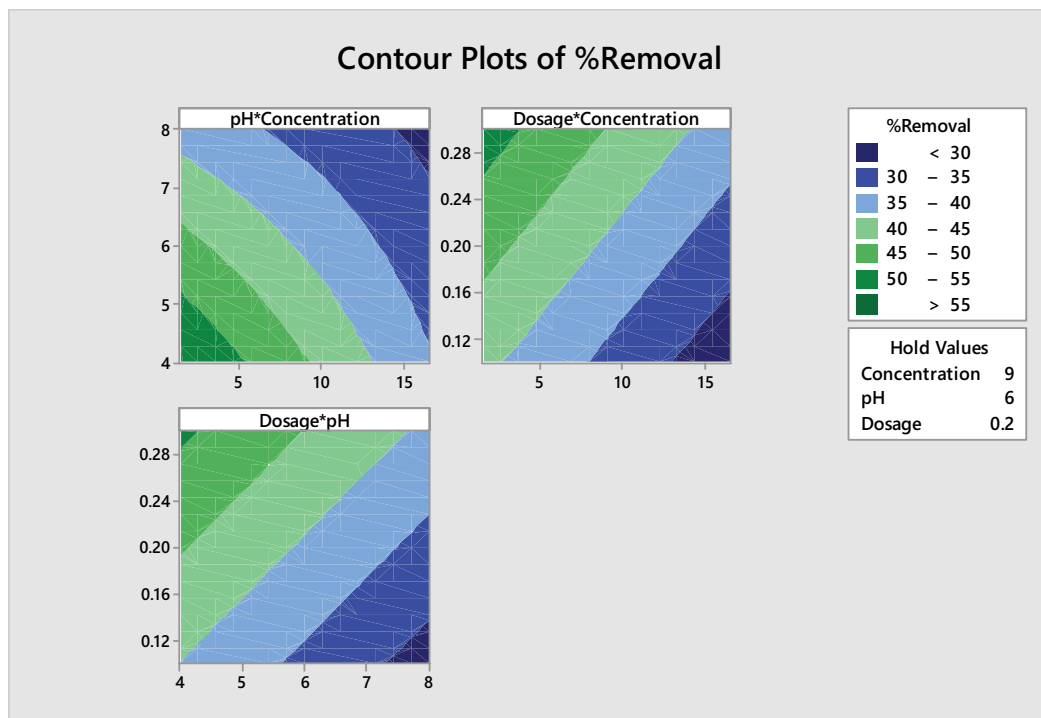


Fig. 8. Surface plots for boron removal using CTAB-TiO₂.

To analyze the thermodynamics of the adsorption process, a plot of $\ln K$ (natural logarithm of the equilibrium constant) against $1/T$ (reciprocal of the absolute temperature) is used. The slope and intercept of this plot provide valuable information about the free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) associated with the adsorption process.

Using the data from Fig. 9, the values of ΔG were calculated at different temperatures (25°C, 35°C, and 45°C). The calculated values for the Gibbs free energy change were 7.883, 7.396, and 7.093 kJ/mol when adsorbed onto TiO_2 , and 3.155, 4.930, and 5.346 kJ/mol when adsorbed onto TiO_2 -CTAB. These values indicate that the adsorption of boron onto both of them are unspontaneous reaction.

The enthalpy change (ΔH) of the boron adsorption process was also determined and found to be 19.687 and -29.704 kJ/mol. The positive value of ΔH indicates an endothermic reaction, meaning that the adsorption of boron requires the input of energy. The negative value of the TiO_2 -CTAB indicates an exothermic reaction, suggesting that the adsorption of boron onto this material releases energy into the surroundings.

Additionally, the entropy (ΔS) of the process was calculated as 39.705 J/mol-K for TiO_2 and -110.978 J/mol-K for modified TiO_2 -CTAB. These values represent the change in entropy associated with the adsorption process.

3.3.2. Adsorption isotherm models

Adsorption isotherm models are mathematical representations that elucidate the connection between the quantity of adsorbate (e.g., gas, liquid, or solute) attached to a solid surface and the concentration of the adsorbate in the surrounding medium at a constant temperature [17]. These models play a crucial role in comprehending the behavior of adsorbent materials during adsorption processes and are instrumental in designing and optimizing such processes [18].

Various adsorption isotherms can be employed to analyze the parameters associated with the adsorption process. Among these, the Langmuir and Freundlich adsorption isotherms, both two-parameter models, are widely used due to their simplicity and ease of interpretation.

The Langmuir isotherm model, one of the most prevalent models, posits that adsorption transpires on a homogeneous surface with a fixed number of adsorption sites (monolayer adsorption) for the contaminants. The linear representation of the Langmuir model equation is expressed as [19]:

$$\frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \tag{8}$$

where C_e is the equilibrium concentration in the liquid phase (mg/L), q_e the amount of adsorbate in the adsorbent at equilibrium (mg/g). q_{\max} is the maximum monolayer converges capacities (mg/g). K_L is the Langmuir isotherm constant (L/mg).

Another popular adsorption isotherm model is the Freundlich isotherm model, which assumes that the adsorption happens on a heterogeneous surface with adsorption sites of varying energies (multilayer adsorption). The linear form of Freundlich model equation can be written as [20]:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{9}$$

where q_e represents the equilibrium amount of adsorbate in the adsorbent (mg/g), K_f is the Freundlich adsorption constant (mg/g), and C_e is the equilibrium concentration in the liquid phase (mg/L) and $1/n$ is the heterogeneity coefficient. The n value indicates the degree of non-linearity between solution concentration and adsorption. The adsorption will be favorable when $1/n$ is existed within the range of ($0 < 1/n < 1$), but when $1/n > 1$ the adsorption will be unfavorable. On the other hand, when n is equal to 1, it suggests that the adsorption process is linearly related to the equilibrium concentration of the solute. This means that an increase in the concentration of the solute will result in a proportional increase in the adsorption capacity of the adsorbent [21].

The experimental results presented in Figs. 10 and 11 depict the Langmuir and Freundlich isotherm models for both the bare TiO_2 and CTAB- TiO_2 , respectively. For the bare TiO_2 , the experimental data from Tables 5 and 6 indicate that the Freundlich isotherm model fits the boron adsorption process well, as evidenced by the higher R^2 value of 0.994

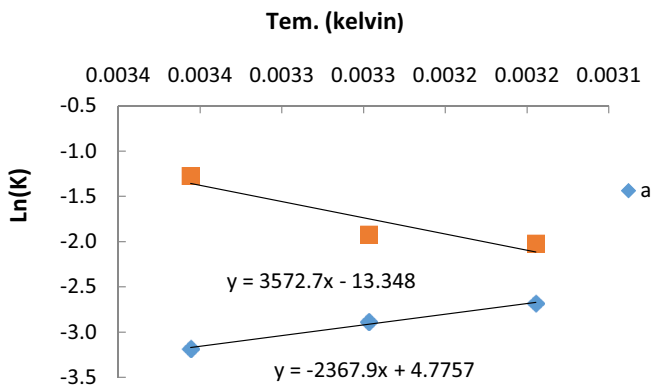


Fig. 9. Thermodynamic analysis of boron adsorption by (a) bare TiO_2 and (b) CTAB- TiO_2 . (Experimental conditions: solution volume: 50 mL, speed: 150 rpm, pH: 4, adsorbent dosage: 0.5 g, 0.3 g and initial boron conc. 16.5 mg/L, 1.5 mg/L, respectively).

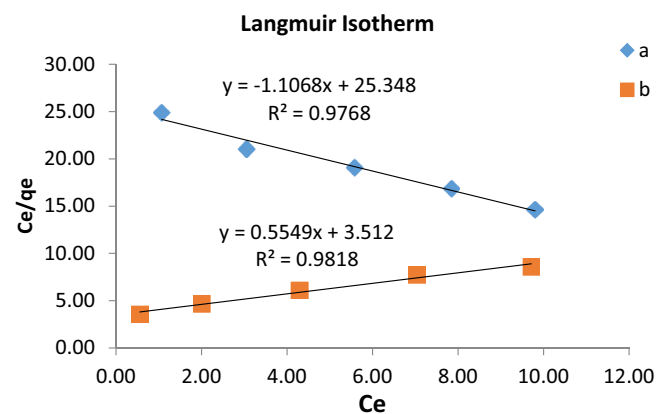


Fig. 10. Langmuir isotherm of boron adsorption by (a) bare TiO_2 and (b) CTAB- TiO_2 .

obtained for the Freundlich isotherm in comparison to the Langmuir model. This suggests that boron adsorption on the bare TiO₂ surface might occur as multilayers, indicating that the adsorbent surface can retain multiple layers of boron.

On the other hand, for CTAB-TiO₂, comparing the two models, Freundlich isotherm model fits the boron adsorption process because it demonstrates a higher R² value of 0.997, indicating a better fit to the experimental data for boron adsorption. This suggests that the Freundlich model provides a more accurate representation of the adsorption process, supporting the hypothesis of a heterogeneous multilayer adsorption where all adsorption sites on the CTAB-TiO₂ surface retain equivalent attraction for the adsorbate (boron).

3.3.3. Adsorption kinetics models

Adsorption kinetic models describe the rate at which adsorption occurs and are utilized to analyze the data of experiments. The two most generally utilized models are

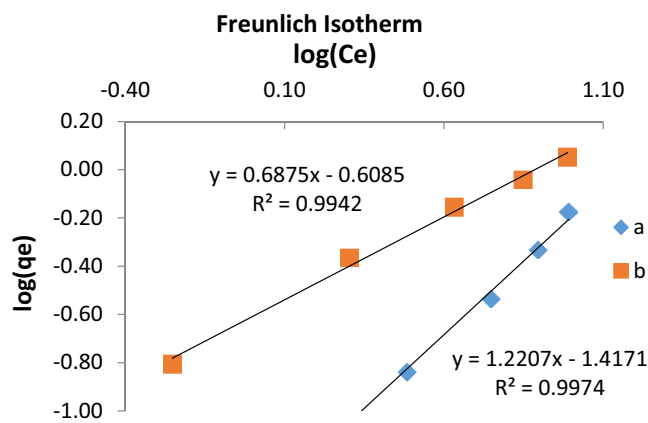


Fig. 11. Freundlich isotherm of boron adsorption by (a) bare TiO₂ and (b) CTAB-TiO₂.

Table 5
Langmuir isotherm parameters for boron adsorption by bare TiO₂ and CTAB-TiO₂

Adsorbent	Parameters		
	q _{max} (mg/g)	K _L (L/mg)	R ²
Bare TiO ₂	-0.90	-22.90	0.976
CTAB-TiO ₂	1.80	6.33	0.982

Table 6
Freundlich isotherm parameters for boron adsorption by bare TiO₂ and CTAB-TiO₂

Adsorbent	Parameters		
	n	K _f (mg ⁿ (L) ^{1/n} ·g ⁻¹)	R ²
Bare TiO ₂	0.82	0.038	0.994
CTAB-TiO ₂	1.45	0.245	0.997

the pseudo-first-order and the pseudo-second-order models. The Lagergren’s pseudo-first-order model assumes that the rate of adsorption is directly proportional to the difference between the equilibrium and the adsorbate concentration on the adsorbent surface. The equation for this model can be expressed as follows [22]:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \tag{10}$$

where q_t is the amount of adsorbate adsorbed at time t, q_e is the amount of adsorbate adsorbed at equilibrium, K₁ is the rate constant of the pseudo-first-order adsorption, and t is the contact time, expressed in min⁻¹. A higher rate constant suggests a faster reaction.

The pseudo-second-order model is another widely used kinetic model for adsorption processes. It assumes that the rate of adsorption is proportional to the square of the difference between the equilibrium and the adsorbate concentration on the adsorbent surface. It depends on the assumption of determining the rate of chemisorption and valency forces throughout the electrostatic interaction between contaminants and surface of adsorbent [23]. The linear form of this model can be represented as follows [22]:

$$\frac{1}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \tag{11}$$

where q_t is the amount of adsorbate adsorbed at time t, q_e is the amount of adsorbate adsorbed at equilibrium, K₂ is the rate constant of the pseudo-second-order adsorption, and t is the contact time.

Figs. 12 and 13 display the adsorption kinetic model plots of log(q_e - q_t) vs. t and t/q_t vs. t for boron adsorption onto TiO₂ and CTAB-TiO₂ using the experimental parameters, (experimental conditions: solution volume: 50 mL, pH: 4, adsorbent dosage: 0.5 g, 0.3 g and initial boron concentration of 16.5 mg/L and 1.5 mg/L, respectively).

Tables 7 and 8 summarize the final results of applying the linearized pseudo-first-order and pseudo-second-order kinetic model on the boron adsorption.

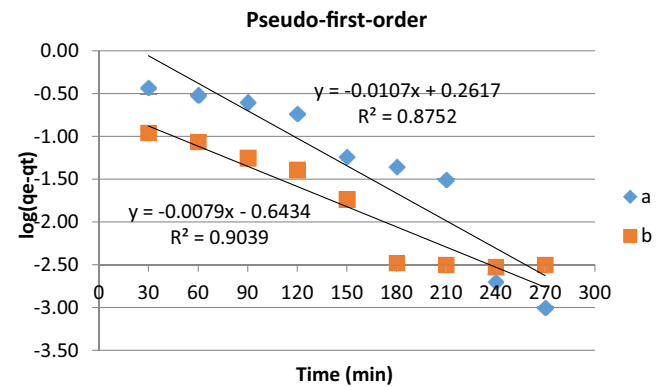


Fig. 12. Pseudo-first-order kinetic model of boron adsorption onto (a) bare TiO₂ and (b) CTAB-TiO₂. (Experimental conditions: solution volume: 50 mL, speed: 150 rpm, pH: 4, adsorbent dosage: 0.5 g, 0.3 g and initial boron conc. 16.5 mg/L, 1.5 mg/L, respectively).

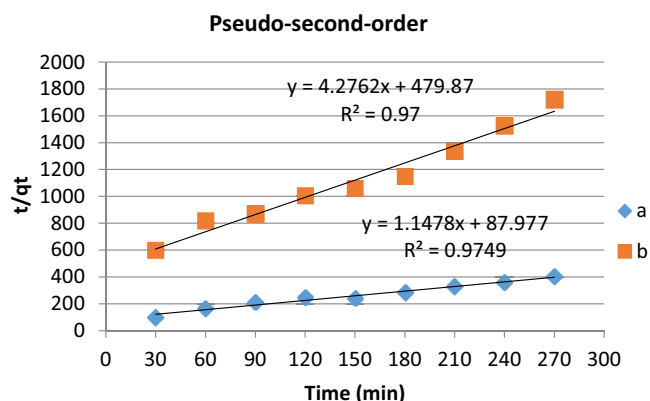


Fig. 13. Pseudo-second-order kinetic model of boron adsorption onto (a) bare TiO_2 and (b) CTAB- TiO_2 . (Experimental conditions: solution volume: 50 mL, speed: 150 rpm, pH: 4, adsorbent dosage: 0.5 g, 0.3 g and initial boron conc. 16.5 mg/L, 1.5 mg/L, respectively).

Table 7

Pseudo-first-order kinetic parameters for boron adsorption by bare TiO_2 and CTAB- TiO_2

Adsorbent	Parameters			
	$q_{e,\text{exp}}$ (mg/g)	$q_{e,\text{cal}}$ (mg/g)	K_1 (min^{-1})	R^2
Bare TiO_2	0.672	1.98	0.025	0.875
CTAB- TiO_2	0.16	0.219	0.018	0.903

Table 8

Pseudo-second-order kinetic parameters for boron adsorption by bare TiO_2 and CTAB- TiO_2

Adsorbent	Parameters			
	$q_{e,\text{exp}}$ (mg/g)	$q_{e,\text{cal}}$ (mg/g)	K_2 (g/(mg·min))	R^2
Bare TiO_2	0.672	0.87	0.015	0.97
CTAB- TiO_2	0.16	0.21	0.038	0.975

Regarding the adsorption of boron onto TiO_2 , and based on the kinetic parameters, the pseudo-second-order kinetic model (with an R^2 value of 0.97) appears to be a better fit for describing the adsorption of boron by bare TiO_2 compared to the pseudo-first-order kinetic model (with an R^2 value of 0.875). The pseudo-second-order model shows a higher correlation with the experimental data, suggesting that it more accurately represents the actual adsorption process. Additionally, the calculated equilibrium adsorption capacity ($q_{e,\text{cal}}$) for the pseudo-second-order model (0.87 mg/g) is closer to the experimental value (0.672 mg/g) than the calculated value for the pseudo-first-order model (1.98 mg/g), further indicating the superiority of the second-order kinetic model in describing boron removal by bare TiO_2 .

On the other hand, in the case of using CTAB- TiO_2 , it appears that the pseudo-second-order kinetic model is more suitable for boron removal in this context. The higher R^2 value (0.975) for the pseudo-second-order model suggests

a better fit to the experimental data compared to the pseudo-first-order model ($R^2 = 0.903$). Additionally, the calculated q_e values ($q_{e,\text{cal}}$) for both models are similar (0.21 mg/g for pseudo-second-order and 0.219 mg/g for pseudo-first-order), but the pseudo-second-order kinetic rate constant (K_2) is also higher (0.038 g/(mg·min)) compared to the pseudo-first-order rate constant (K_1) at 0.018 (min^{-1}). This indicates that the pseudo-second-order model provides a more accurate representation of the boron adsorption process and suggests a better choice for boron removal using the materials and conditions described.

Therefore, the second-order kinetic model seems to be more appropriate for describing the boron removal process using the bare TiO_2 and CTAB- TiO_2 adsorbents. It provides a better fit to the experimental data and shows a faster rate of boron adsorption compared to the first-order model.

3.4. Effect of other competitive ions on boron adsorption process

The experiment aimed to evaluate the impact of these co-existing ions, including Mg^{+2} , Ca^{+2} , Cl^- , NO_3^- , CO_3^{-2} and SO_4^{-2} on the adsorption of boron. These ions can either enhance or inhibit the boron adsorption process, depending on their respective properties and interactions with the adsorbent and boron species. Let's explore the effects of these ions as follows:

- Magnesium (Mg^{+2}) and Calcium (Ca^{+2}) which are positive divalent metal ions can compete with boron for adsorption sites on the surface of the adsorbent. When these metal ions are present at high concentrations in the solution, they may hinder the adsorption of boron by occupying the available binding sites. As a result, the boron adsorption capacity may decrease in the presence of high concentrations of these metal ions.

However, at low concentrations, these ions might enhance boron adsorption due to the formation of surface complexes that facilitate boron binding. These complexes can create additional binding sites or alter the surface charge, making it easier for boron to be adsorbed.

- Chloride ions (Cl^-) showed a negative impact on boron adsorption because can compete with boron for adsorption sites and reduce the overall adsorption efficiency.
- Nitrate ions (NO_3^-) also showed a limited impact on boron adsorption. They do not interfere directly with boron adsorption, and their presence is unlikely to have a substantial impact on the process.
- Carbonate ions (CO_3^{-2}) showed an influence on boron adsorption particularly at low pH, because at low pH, the presence of CO_3^{-2} can compete with boron for adsorption sites and reduce the overall adsorption efficiency. This is because CO_3^{-2} can form complexes with the adsorbent's surface and limit the availability of binding sites for boron.

However, at higher pH levels, CO_3^{-2} can react with the adsorbent and modify its surface properties, potentially increasing boron adsorption.

- Sulfate ions (SO_4^{2-}) have a negative impact on boron adsorption. These ions can compete with boron for binding sites, leading to reduced boron removal efficiency in the presence of high sulfate concentrations. The competition between SO_4^{2-} and boron for adsorption sites can result in decreased boron uptake.

Overall, the results revealed that the presence of Cl^- , NO_3^- , CO_3^{2-} and SO_4^{2-} negatively affected the percentage of boron removal, indicating that these anions competed with boron species and resulted in a reduced percentage of boron removal. Conversely, the presence of Mg^{+2} , Ca^{+2} slightly increased the percentage of boron removal when using CTAB-TiO₂, which is highly appropriate adsorbent.

Therefore, considering the presence of co-existing ions is crucial when designing boron adsorption processes for water treatment, as it significantly influences the overall efficiency of boron removal.

3.5. Validation experiments for boron removal from real water samples

In order to assess the practical applicability and effectiveness of the developed adsorbent of CTAB-TiO₂ for boron removal process from real-world scenarios, validation experiments on real water samples were conducted at the lab. The findings of the boron removal process from these samples were closely resembled those obtained from the

Table 9
Adsorption isotherms of boron using various adsorbents

Adsorbent	Experimental conditions	Equilibrium ^a /Maximum ^b adsorption capacity	References
CWZ-30	$C_i = 30 \text{ mg/L}$, pH = 6, time = 2 h, adsorbent dose = 20 g/L, $T = 20^\circ\text{C}$	^a 0.294 mg/g	[24]
Cur-AC	$C_i = 1,000 \text{ mg/L}$, pH = 5.5, time = 2 h, adsorbent dose = 40 g/L, $T = 25^\circ\text{C}$	^b 5.0 mg/g	[25]
Fly ash zeolite	$C_i = 50 \text{ mg/L}$, pH = 7, time = 0.5 h, adsorbent dose = 20 g/L, $T = 25^\circ\text{C}$	^a 2.3 mg/g	[26]
Bentonite	$C_i = 120 \text{ mg/L}$, pH = 9, time = 24 h, adsorbent dose = 50 g/L, $T = 25^\circ\text{C}$	^b 0.51 mg/g	[27]
Bentonite-FeCl ₃	$C_i = 120 \text{ mg/L}$, pH = 9, time = 24 h, adsorbent dose = 50 g/L, $T = 25^\circ\text{C}$	^b 0.83 mg/g	[27]
Kaolinite-FeCl ₃	$C_i = 120 \text{ mg/L}$, pH = 9, time = 24 h, adsorbent dose = 50 g/L, $T = 25^\circ\text{C}$	^b 0.80 mg/g	[27]
Waste calcite	$C_i = 120 \text{ mg/L}$, pH = 9, time = 24 h, adsorbent dose = 50 g/L, $T = 25^\circ\text{C}$	^b 1.05 mg/g	[27]
Waste calcite-FeCl ₃	$C_i = 120 \text{ mg/L}$, pH = 9, time = 24 h, adsorbent dose = 50 g/L, $T = 25^\circ\text{C}$	^b 1.60 mg/g	[27]
Zeolite	$C_i = 120 \text{ mg/L}$, pH = 9, time = 24 h, adsorbent dose = 50 g/L, $T = 25^\circ\text{C}$	^b 0.53 mg/g	[27]
Zeolite-FeCl ₃	$C_i = 120 \text{ mg/L}$, pH = 9, time = 24 h, adsorbent dose = 50 g/L, $T = 25^\circ\text{C}$	^b 0.76 mg/g	[27]
Magnesite and bentonite clay composite	$C_i = 20 \text{ mg/L}$, pH = 11, time = 30 min adsorbent dose = 2 g/L, $T = 26^\circ\text{C}$	^b 4 mg/g	[28]
F400 + xylitol	$C_i = 60 \text{ mg/L}$, pH = 7, time = 4 h, adsorbent dose = 20 g/L, $T = 25^\circ\text{C}$	^a 1.45 mg/g	[29]
F400 + sodium gluconate	$C_i = 60 \text{ mg/L}$, pH = 7, time = 4 h, adsorbent dose = 20 g/L, $T = 25^\circ\text{C}$	^a 1.04 mg/g	[29]
Waste tire rubber	$C_i = 17.5 \text{ mg/L}$, pH = 2, time = 48 h, adsorbent dose = 1 g/L, $T = 21^\circ\text{C}$	^b 16.72 mg/g	[30]
CTAB-kaolin	$C_i = 16.5 \text{ mg/L}$, pH = 2, time = 3 h, adsorbent dose = 2 g/L, $T = 25^\circ\text{C}$	^a 3.12 mg/g	[31]
Bare TiO ₂	$C_i = 16.50 \text{ mg/L}$, pH = 4, time = 4 h, adsorbent dose = 10 g/L, $T = 45^\circ\text{C}$	^a 0.672 mg/g	This study
CTAB-TiO ₂	$C_i = 16.50 \text{ mg/L}$, pH = 4, time = 3.5 h, adsorbent dose = 6 g/L, $T = 25^\circ\text{C}$	^a 1.60 mg/g	This study

^aThe equilibrium adsorption capacity is the adsorption capacity when the adsorption rate is equal to the desorption rate.

^bThe maximum adsorption capacity is the ideal adsorption capacity that all adsorption sites are filled with adsorbate.

original tested water samples, indicating that the developed adsorbent is efficient in real-world scenarios and capable of effectively removing boron from real water.

3.6. Comparison with other adsorbents

In this study, Table 9 presents a comprehensive overview of the experimental conditions and the boron adsorption capacity achieved using the produced adsorbents. The researchers compared these results with the capacities reported in the existing literature. The findings clearly indicate that the adsorbents developed in this study demonstrate a highly competitive performance compared to other adsorbents previously reported in the literature.

4. Conclusion

The investigation into boron removal from aqueous solutions using various adsorbent materials has yielded valuable insights into the feasibility and efficiency of this process. boron can become a significant concern when present in concentrations exceeding defined limits in water sources. This study aimed to address this issue by exploring the potential of adsorption processes.

A series of adsorbents, including bare TiO_2 (NPs) and CTAB- TiO_2 (NPs), were synthesized and thoroughly characterized, revealing their distinctive properties and surface characteristics. Batch adsorption experiments provided critical data on the influence of operational parameters, allowing for the optimization of boron removal efficiency. CTAB- TiO_2 (NPs) emerged as the most promising adsorbent, achieving a maximum boron removal efficiency of 62.70% at pH 4, outperforming bare TiO_2 (NPs).

The application of a factorial experimental design and statistical analysis through Minitab 18.0 proved instrumental in optimizing the removal process, identifying key factors, and evaluating their significance. Thermodynamic parameters shed light on the energetics of boron adsorption, while isotherm and kinetic analyses demonstrated a commendable fit with established models, suggesting favorable adsorption behavior.

The experimental data provides a more accurate representation of the adsorption process, as the Freundlich isotherm model fits the boron adsorption process well for both bare TiO_2 and CTAB- TiO_2 . Furthermore, the second-order kinetic model appears to be more appropriate for describing the boron removal process using both the bare TiO_2 and CTAB- TiO_2 adsorbents. It not only offers a better fit to the experimental data but also demonstrates a faster rate of boron adsorption compared to the first-order model.

Moreover, the findings demonstrated that the existence of Cl^- , NO_3^- , CO_3^{2-} and SO_4^{2-} had an adverse impact on the removal of boron, suggesting that these anions vied with boron components, leading to a decreased removal rate of boron. In contrast, the presence of Mg^{2+} , Ca^{2+} marginally enhanced the percentage of boron removal.

In conclusion, CTAB- TiO_2 (NPs) represents a novel and environmentally friendly option for efficiently removing boron from aqueous solutions, particularly in the context of water treatment for agricultural purposes. These findings hold significant promise for addressing boron-related water

quality concerns and ensuring that water resources meet accepted limits for agricultural use, ultimately contributing to sustainable agriculture and ecosystem preservation.

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Compliance with ethical standards

Conflict of interest

The authors declare that there is no conflict of interest.

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