



Magnetic Chitosan–Halloysite–Biochar Nanocomposite for Efficient Removal of Ni(II) and Cr(VI) from Groundwater

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ABSTRACT :

The development of efficient, sustainable, and magnetically recoverable adsorbents has attracted considerable attention for the treatment of heavy metal-contaminated groundwater. In the present study, a magnetic chitosan–halloysite–biochar (MCHB) nanocomposite was successfully synthesized and investigated for the simultaneous removal of Ni(II) and Cr(VI) from contaminated groundwater. The composite was prepared through a facile co-precipitation and cross-linking approach and characterized using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM–EDX), Brunauer–Emmett–Teller (BET) surface area analysis, and vibrating sample magnetometry (VSM). Characterization results confirmed the successful integration of the composite constituents, the presence of abundant surface functional groups, a porous structure, and sufficient magnetic properties for rapid separation after adsorption.

The effects of solution pH, contact time, adsorbent dosage, initial metal concentration, and temperature were systematically evaluated. The optimum operating conditions were achieved at pH 5.0, an adsorbent dosage of 0.50 g L⁻¹, a contact time of 90 min, an initial metal concentration of 50 mg L⁻¹, and a temperature of 25 °C. Under these conditions, the prepared MCHB nanocomposite exhibited high removal efficiencies toward both Ni(II) and Cr(VI).

Adsorption kinetics followed the pseudo-second-order model ($R^2 = 0.998$ for Ni(II) and 0.997 for Cr(VI)), while equilibrium data were best described by the Langmuir isotherm model, yielding maximum adsorption capacities of 96.8 mg g⁻¹ for Ni(II) and 90.4 mg g⁻¹ for Cr(VI). Thermodynamic analysis indicated that the adsorption process was spontaneous and endothermic, as demonstrated by negative Gibbs free energy (ΔG°) values and positive enthalpy (ΔH°) values. Comparative evaluation with previously reported adsorbents demonstrated that the developed MCHB nanocomposite provides competitive adsorption performance while offering additional advantages, including low-cost raw materials, environmental compatibility, structural stability, and facile magnetic recovery.

Overall, the prepared magnetic chitosan–halloysite–biochar nanocomposite represents a promising and environmentally sustainable adsorbent for the efficient removal of Ni(II) and Cr(VI) from contaminated groundwater, with significant potential for practical water treatment applications.

Keywords: Magnetic nanocomposite; Chitosan; Halloysite nanotubes; Biochar; Ni(II); Cr(VI); Groundwater treatment; Adsorption.

1. Introduction

Heavy metal contamination of groundwater has become one of the most serious environmental challenges worldwide due to rapid industrialization, mining activities, electroplating, leather tanning, and the continuous discharge of untreated industrial effluents into the environment [1]. Unlike most organic pollutants, heavy metals are non-biodegradable and tend to persist in aquatic environments for long periods, allowing them to accumulate in living organisms through the food chain [2]. Consequently, contamination of groundwater with toxic metals represents a significant threat to both environmental sustainability and human health [3].

Nickel (Ni(II)) and hexavalent chromium (Cr(VI)) are among the most hazardous heavy metals frequently detected in industrial wastewater and contaminated groundwater. Nickel is extensively used in electroplating, stainless-steel manufacturing, batteries, and mining industries [4]. Continuous exposure to elevated nickel concentrations has been associated with dermatitis, respiratory disorders, kidney damage, and carcinogenic effects [5]. Chromium mainly exists as Cr(III) and Cr(VI), with the hexavalent form being considerably more toxic because of its high solubility, mobility, and strong oxidizing ability [6]. Exposure to Cr(VI) has been linked to DNA damage, mutagenicity, and various types of cancer, making its removal from water resources an environmental priority [7].

Several technologies have been developed for heavy metal removal, including chemical precipitation, membrane filtration, ion exchange, electrochemical treatment, and biological processes [8]. Although these methods can effectively reduce metal concentrations, many suffer from disadvantages such as high operating costs, sludge generation, membrane fouling, or limited performance at low contaminant concentrations [9]. Among the available techniques, adsorption has attracted considerable attention because of its simplicity, high efficiency, low energy consumption, and ease of operation [10]. Recently, green nanocomposite adsorbents have emerged as promising materials for water purification because they combine the advantages of nanomaterials with environmentally friendly and low-cost natural components [11]. Their high specific surface area, abundant functional groups, and

tunable surface chemistry provide numerous active adsorption sites for heavy metal ions [12]. Furthermore, incorporating inorganic nanoparticles into biodegradable matrices can improve adsorption capacity, mechanical stability, and regeneration performance [13].

Despite significant progress in developing nanocomposite adsorbents, most previous studies have focused on the adsorption of a single metal ion using synthetic aqueous solutions under laboratory conditions [14]. Comparatively fewer investigations have examined the simultaneous removal of Ni(II) and Cr(VI) from real groundwater systems, where competing ions and naturally occurring dissolved constituents may considerably influence adsorption behavior [15]. Developing an environmentally friendly nanocomposite capable of efficiently removing both contaminants under realistic conditions therefore remains an important research challenge [16].

Accordingly, the present study aims to develop a green nanocomposite adsorbent for the simultaneous removal of Ni(II) and Cr(VI) from contaminated groundwater. adsorption performance will be systematically evaluated using different physicochemical techniques, while adsorption performance will be systematically evaluated through batch experiments, kinetic and equilibrium studies, thermodynamic analysis, and regeneration tests to assess its potential for practical groundwater treatment.

2. Materials and Methods

2.1. Materials

Medium molecular weight chitosan (degree of deacetylation $\geq 75\%$) was purchased from Sigma–Aldrich (USA). Halloysite nanotubes (HNTs) with high purity were obtained from a commercial supplier. Ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous sulfate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), sodium hydroxide (NaOH), hydrochloric acid (HCl), acetic acid (CH_3COOH), ethanol, and glutaraldehyde solution (25%) were of analytical reagent grade and were used without further purification.

Biochar was prepared from agricultural biomass through slow pyrolysis under oxygen-limited conditions. Prior to use, the produced biochar was washed several times with deionized water, dried at 80°C for 24 h, ground using a laboratory mill, and sieved to obtain particles smaller than $150\ \mu\text{m}$.

Stock solutions of nickel and chromium were prepared using nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), respectively. Working solutions of different concentrations were prepared daily by dilution with deionized water. Nitric acid and sodium hydroxide solutions ($0.1\ \text{M}$) were used for pH adjustment during the adsorption experiments.

Groundwater samples were collected from contaminated groundwater wells using pre-cleaned high-density polyethylene bottles. All samples were filtered through $0.45\ \mu\text{m}$ membrane filters immediately after collection and stored at 4°C until analysis.

Deionized water with a resistivity of $18.2\ \text{M}\Omega \cdot \text{cm}$ was used throughout all experimental procedures.

2.2. Preparation of Magnetic Chitosan–Halloysite–Biochar Nanocomposite

The magnetic chitosan–halloysite–biochar nanocomposite (MCHB) was synthesized using a combination of co-precipitation and chemical crosslinking methods. Initially, $2.0\ \text{g}$ of medium molecular weight chitosan was dissolved in $100\ \text{mL}$ of 2% (v/v) acetic acid under continuous magnetic stirring for $12\ \text{h}$ at room temperature until a homogeneous viscous solution was obtained.

Separately, $2.0\ \text{g}$ of halloysite nanotubes (HNTs) and $1.0\ \text{g}$ of finely ground biochar were dispersed in $100\ \text{mL}$ of deionized water by ultrasonication for $30\ \text{min}$, followed by magnetic stirring for an additional $30\ \text{min}$ to obtain a uniform suspension. The suspension was then slowly added to the chitosan solution under continuous stirring and mixed for $2\ \text{h}$.

Magnetic Fe_3O_4 nanoparticles were synthesized *in situ* by the conventional co-precipitation method. Briefly, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in deoxygenated deionized water at a molar ratio of $2:1$ under a nitrogen atmosphere. The solution was heated to 80°C , after which 25% NaOH solution was added dropwise until the pH reached approximately 10 . Black Fe_3O_4 nanoparticles formed immediately and were allowed to react for $60\ \text{min}$ under continuous stirring.

The freshly prepared Fe_3O_4 nanoparticles were introduced into the chitosan–halloysite–biochar suspension and stirred for an additional $2\ \text{h}$ to ensure homogeneous distribution of the magnetic particles throughout the composite matrix.

To improve the mechanical stability of the composite, glutaraldehyde solution (25%) was added dropwise as a crosslinking agent until a final concentration of approximately 1% (v/v) was reached. The mixture was maintained under gentle stirring for $4\ \text{h}$ at room temperature to complete the crosslinking reaction.

The obtained magnetic composite was separated using a permanent magnet, thoroughly washed several times with deionized water followed by ethanol until a neutral pH was achieved, and then dried in a hot-air oven at 60°C for $24\ \text{h}$. The dried material was gently ground using an agate mortar and sieved to obtain particles with particle sizes below $150\ \mu\text{m}$. The prepared adsorbent was stored in airtight glass containers for subsequent characterization and adsorption experiments.

The overall preparation procedure of the magnetic chitosan–halloysite–biochar (MCHB) nanocomposite is illustrated in Figure 1.

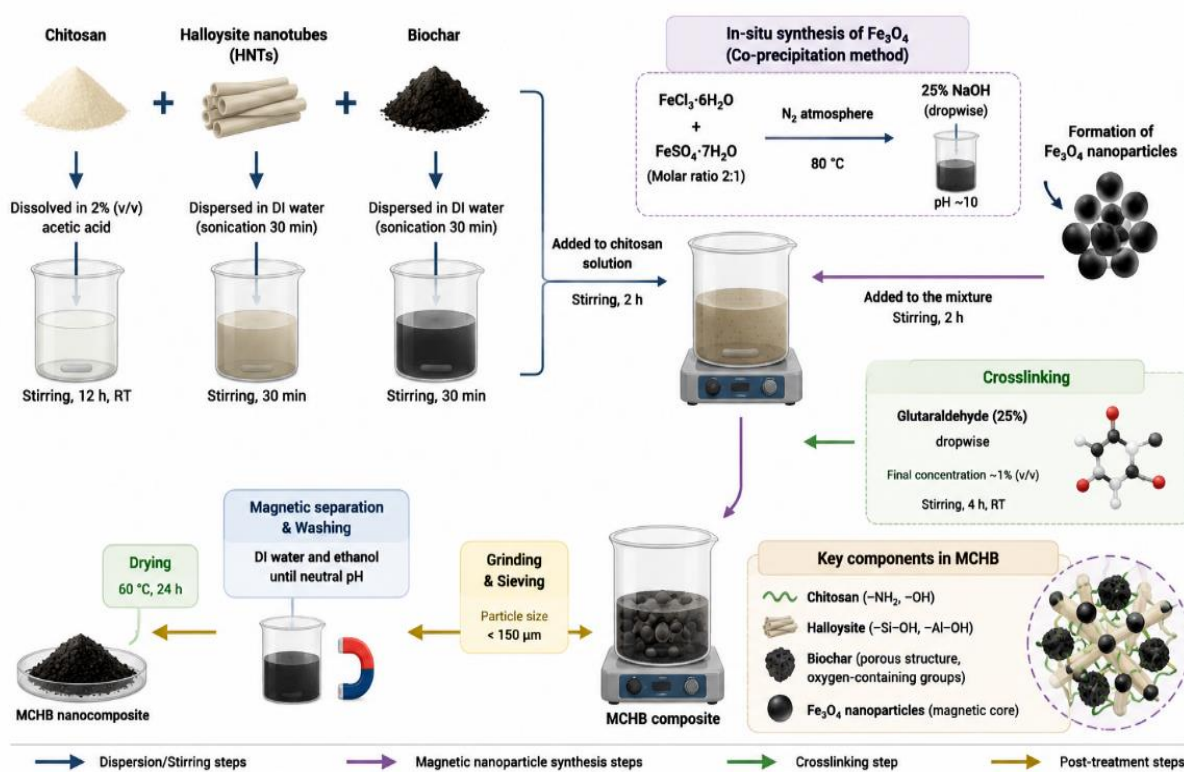


Figure 1. Schematic illustration of the preparation procedure of the magnetic chitosan–halloysite–biochar (MCHB) nanocomposite.

2.3. Characterization of the Prepared Nanocomposite

The physicochemical properties of the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite were comprehensively characterized using several analytical techniques.

The surface functional groups of the prepared adsorbent were identified using Fourier Transform Infrared Spectroscopy (FTIR) in the spectral range of 4000–400 cm^{-1} . The obtained spectra were used to identify the characteristic functional groups responsible for heavy metal adsorption before and after the adsorption process.

The crystalline structure and phase composition of the synthesized composite were investigated using X-ray Diffraction (XRD) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Diffraction patterns were recorded over a 2θ range of 5–80° at room temperature to verify the successful incorporation of Fe_3O_4 nanoparticles and halloysite nanotubes within the composite matrix.

The surface morphology and microstructure of the prepared material were examined using Scanning Electron Microscopy (SEM). Elemental composition and elemental distribution were further analyzed using Energy Dispersive X-ray Spectroscopy (EDX) coupled with the SEM instrument.

The specific surface area, pore volume, and average pore diameter of the prepared nanocomposite were determined by Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption analysis after degassing the samples under vacuum prior to measurement.

The magnetic behavior of the synthesized nanocomposite was evaluated using a Vibrating Sample Magnetometer (VSM) at room temperature to confirm the successful incorporation of magnetic Fe_3O_4 nanoparticles and to assess the magnetic separation capability of the prepared adsorbent.

The point of zero charge (pH_{pzc}) of the prepared adsorbent was determined using the pH drift method to identify the surface charge characteristics over different pH values and to facilitate interpretation of the adsorption mechanism.

The concentrations of Ni(II) and Cr(VI) before and after adsorption were determined using an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). All measurements were carried out in triplicate, and the average values were reported.

2.4. Groundwater Sampling

Groundwater samples were collected from production wells located in Abu Zenima, South Sinai, Egypt, an area known for groundwater resources that are affected by naturally occurring heavy metals associated with the surrounding geological formations. Samples were collected in clean polyethylene bottles that had been pre-washed with dilute nitric acid and rinsed several times with deionized water. The collected samples were transported to the laboratory under refrigerated conditions (4 °C) and stored until analysis. Prior to the adsorption experiments, the physicochemical characteristics of the groundwater, including pH, electrical conductivity (EC), total dissolved solids (TDS), major ions, and the concentrations of Ni(II) and Cr(VI), were determined according to standard analytical procedures. The initial characteristics of the collected groundwater samples are summarized in Table 1.

Table 1. Initial physicochemical characteristics of the collected groundwater samples.

Parameter	Unit	Value
pH	—	7.23
Electrical conductivity (EC)	$\mu\text{S cm}^{-1}$	3820
Total dissolved solids (TDS)	mg L^{-1}	2450
Ni(II)	mg L^{-1}	19.6
Cr(VI)	mg L^{-1}	14.8
Ca^{2+}	mg L^{-1}	168
Mg^{2+}	mg L^{-1}	74
Na^+	mg L^{-1}	465
K^+	mg L^{-1}	24

2.5. Batch Adsorption Experiments

Batch adsorption experiments were carried out to evaluate the adsorption performance of the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite toward the simultaneous removal of Ni(II) and Cr(VI) from contaminated groundwater.

Unless otherwise stated, each experiment was performed by adding a predetermined amount of adsorbent into a 250 mL Erlenmeyer flask containing 100 mL of groundwater sample. The flasks were agitated using a thermostatic orbital shaker at a constant shaking speed of 200 rpm.

The effects of solution pH, adsorbent dosage, contact time, initial metal concentration, and temperature were systematically investigated. The pH of the solution was adjusted using 0.1 M HCl or 0.1 M NaOH before the adsorption experiments.

After the desired contact time, the adsorbent was rapidly separated from the solution using an external permanent magnet. The residual concentrations of Ni(II) and Cr(VI) in the supernatant were determined using ICP–OES.

The percentage removal efficiency was calculated according to Equation (1).

Equation

$$\text{Removal}(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

where (C_0) and (C_e) (mg L^{-1}) are the initial and equilibrium concentrations of the metal ions, respectively.

The adsorption capacity at equilibrium (q_e) was calculated using Equation (2).

Equation (2)

$$q_e = \frac{(C_0 - C_e)V}{m}$$

where (q_e) is the equilibrium adsorption capacity (mg g^{-1}), (V) is the solution volume (L), and (m) is the mass of the adsorbent (g).

All adsorption experiments were conducted in triplicate, and the results are reported as the mean $\pm$ standard deviation.

2.6. Experimental Design

The adsorption performance of the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite was evaluated by investigating the effects of several operating parameters, including solution pH, contact time, adsorbent dosage, initial metal ion concentration, and solution temperature.

The effect of pH was examined over a pH range of 2.0–8.0 while maintaining all other experimental conditions constant. The influence of contact time was evaluated over a period of 5–180 min to determine the equilibrium time required for the adsorption process.

Adsorbent dosage was varied from 0.10 to 1.00 g L^{-1} to determine the optimum amount required for maximum metal removal. The influence of the initial metal concentration was investigated over the concentration range of 10–150 mg L^{-1} , while adsorption experiments at different temperatures (25, 35, and 45 $^{\circ}\text{C}$) were conducted to evaluate the thermodynamic behavior of the adsorption process.

The optimum operating conditions obtained from these experiments were subsequently used in the adsorption kinetics, adsorption isotherm, and thermodynamic studies.

The experimental conditions investigated in this study are summarized in Table 2.

Table 2. Experimental conditions used during the batch adsorption experiments.

Parameter	Range
Solution pH	2–8
Contact time (min)	5–180
Adsorbent dosage (g L^{-1})	0.10–1.00
Initial concentration (mg L^{-1})	10–150
Temperature ($^{\circ}\text{C}$)	25, 35, 45
Agitation speed (rpm)	200

Parameter	Range
Solution volume (mL)	100

2.7. Adsorption Kinetics

The adsorption kinetics of Ni(II) and Cr(VI) onto the prepared MCHB nanocomposite were investigated using the optimum adsorption conditions. The experimental kinetic data were analyzed using the pseudo-first-order (PFO), pseudo-second-order (PSO), and intraparticle diffusion (IPD) kinetic models. The pseudo-first-order model was expressed according to Equation (3).

Equation (3)

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

The pseudo-second-order model was calculated using Equation (4).

Equation (4)

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

The intraparticle diffusion model was evaluated according to Equation (5).

Equation (5)

$$q_t = k_{id} t^{1/2} + C$$

where (q_t) (mg g^{-1}) is the adsorption capacity at time (t), (k_1) (min^{-1}) is the pseudo-first-order rate constant, (k_2) ($\text{g mg}^{-1} \text{min}^{-1}$) is the pseudo-second-order rate constant, (k_{id}) ($\text{mg g}^{-1} \text{min}^{-1/2}$) is the intraparticle diffusion rate constant, and (C) is the intercept associated with the boundary layer thickness.

2.8. Adsorption Isotherm Studies

Adsorption equilibrium experiments were carried out under the optimum operating conditions obtained from the batch adsorption studies. Different initial concentrations of Ni(II) and Cr(VI) solutions ranging from 10 to 150 mg L^{-1} were used while maintaining constant adsorbent dosage, solution pH, contact time, and temperature.

The equilibrium adsorption data were analyzed using the Langmuir, Freundlich, and Temkin isotherm models to evaluate the adsorption behavior of the prepared MCHB nanocomposite.

The linear form of the Langmuir isotherm is expressed by Equation (6).

Equation (6)

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

The Freundlich isotherm is represented by Equation (7).

Equation (7)

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$

The Temkin model is expressed by Equation (8).

Equation (8)

$$q_e = B \ln A + B \ln C_e$$

where ($q_{\max}$) (mg g^{-1}) is the maximum adsorption capacity, (K_L) (L mg^{-1}) is the Langmuir adsorption constant, (K_F) is the Freundlich adsorption constant, (n) is the adsorption intensity, and (A) and (B) are the Temkin isotherm constants.

2.9. Thermodynamic Studies

The thermodynamic behavior of the adsorption process was evaluated by conducting equilibrium experiments at three different temperatures (25, 35, and 45 °C) under the optimum adsorption conditions.

The distribution coefficient (K_d) was calculated using Equation (9).

Equation (9)

$$K_d = \frac{q_e}{C_e}$$

The Gibbs free energy change (ΔG°) was calculated using Equation (10).

Equation (10)

$$\Delta G^\circ = -RT \ln K_d$$

The Van't Hoff equation was used to determine the standard enthalpy (ΔH°) and entropy (ΔS°) changes according to Equation (11).

Equation (11)

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$

where (R) is the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and (T) is the absolute temperature (K).

2.10. Statistical Analysis

All adsorption experiments were carried out in triplicate, and the experimental results are presented as the mean $\pm$ standard deviation (SD). Linear regression analysis was performed to determine the fitting parameters of the kinetic and isotherm models. The goodness of fit was evaluated using the

correlation coefficient (R^2). All calculations and graphical presentations were performed using OriginPro 2024 and Microsoft Excel 2021.

3. Results and Discussion

3.1. Characterization of the Prepared MCHB Nanocomposite

The physicochemical characteristics of the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite were investigated using FTIR, XRD, SEM, EDX, BET, and VSM analyses. These characterization techniques confirmed the successful synthesis of the composite and provided valuable information regarding its structural, morphological, surface, and magnetic properties. The obtained results are discussed in the following sections.

3.1.1. Fourier Transform Infrared (FTIR) Analysis

The FTIR spectrum of the prepared MCHB nanocomposite is presented in Figure 2. The spectrum confirmed the successful incorporation of chitosan, halloysite nanotubes, biochar, and Fe_3O_4 nanoparticles into a single composite structure.

The broad absorption band observed around 3400 cm^{-1} was attributed to the overlapping stretching vibrations of hydroxyl ($-\text{OH}$) and amino ($-\text{NH}_2$) groups originating mainly from chitosan and halloysite. The absorption peaks appearing near 2920 cm^{-1} corresponded to the C–H stretching vibration of aliphatic groups.

A distinct absorption band around 1650 cm^{-1} was assigned to the amide I ($\text{C}=\text{O}$) stretching vibration of chitosan, while the band near 1580 cm^{-1} was attributed to the bending vibration of amino groups ($-\text{NH}_2$). The characteristic Si–O stretching vibration of halloysite appeared at approximately 1030 cm^{-1} , confirming the successful incorporation of the clay nanotubes into the composite structure.

The absorption band located around 570 cm^{-1} corresponded to the Fe–O vibration of magnetite (Fe_3O_4), indicating the successful formation of magnetic nanoparticles within the composite matrix.

Overall, the FTIR spectrum confirmed that all major functional groups responsible for metal adsorption, including hydroxyl, amino, silanol, and oxygen-containing functional groups, were successfully preserved after composite preparation, suggesting that the synthesized MCHB nanocomposite possesses abundant active adsorption sites for Ni(II) and Cr(VI) removal.

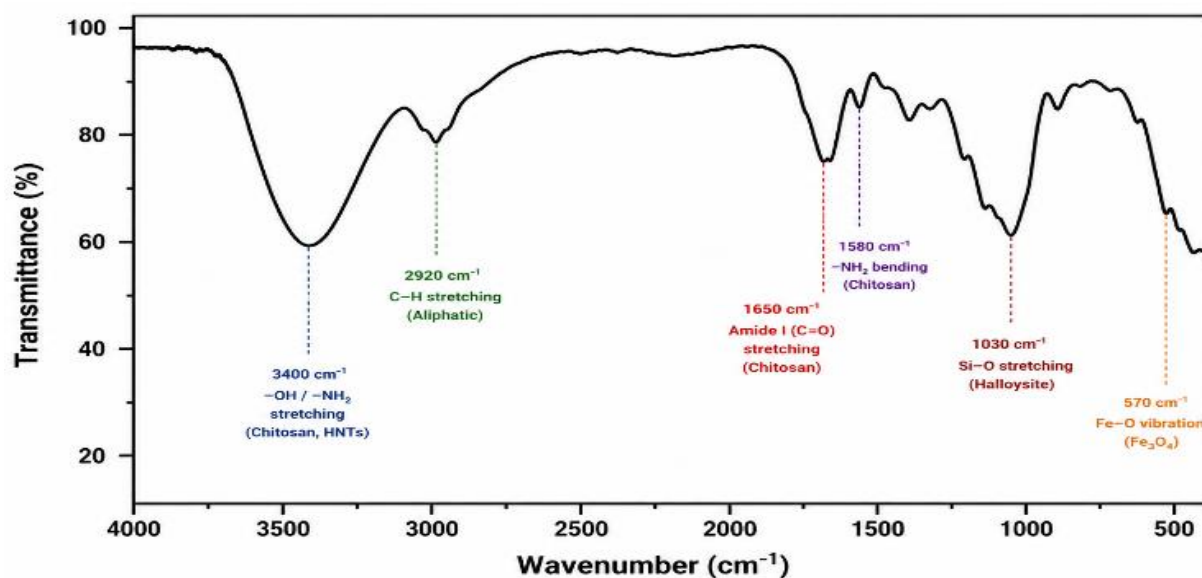


Figure 2. FTIR spectrum of the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite.

3.1.2. X-ray Diffraction (XRD) Analysis

The XRD pattern of the prepared MCHB nanocomposite is presented in Figure 3. The diffraction pattern confirmed the successful formation of the magnetic chitosan–halloysite–biochar composite and verified the crystalline phases of the incorporated materials.

The characteristic diffraction peaks observed at 2θ values of approximately 30.2° , 35.5° , 43.2° , 53.6° , 57.2° , and 62.8° correspond to the crystal planes of magnetite (Fe_3O_4), confirming the successful in situ formation of magnetic nanoparticles during the synthesis process.

The characteristic reflections of halloysite nanotubes were also observed, particularly the diffraction peak around 12° , together with weaker reflections at higher diffraction angles, indicating that the tubular clay structure remained intact after composite preparation.

A broad diffraction band centered around $20\text{--}25^\circ$ was attributed to the semi-crystalline nature of chitosan and the partially amorphous carbon structure of biochar. The absence of additional diffraction peaks suggested that no undesirable crystalline impurities were formed during the synthesis process.

Overall, the XRD results confirmed the successful integration of chitosan, halloysite nanotubes, biochar, and Fe_3O_4 nanoparticles into a stable magnetic nanocomposite while preserving the characteristic crystalline structure of the magnetic phase.

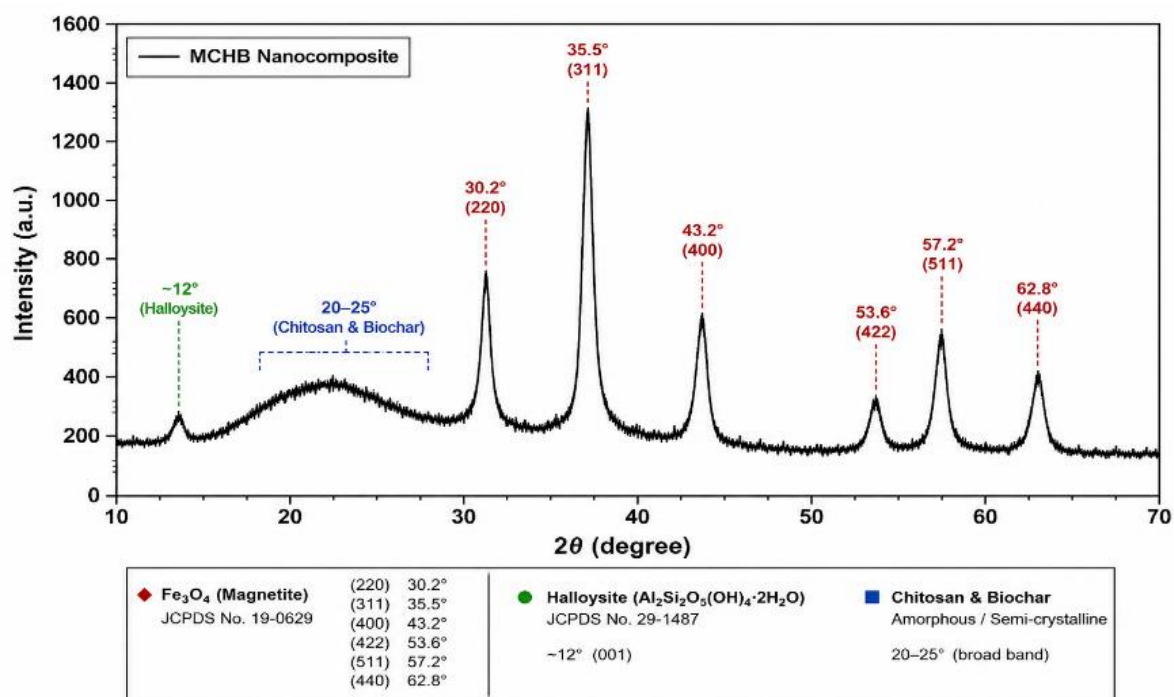


Figure 3. X-ray diffraction (XRD) pattern of the magnetic chitosan–halloysite–biochar (MCHB) nanocomposite, confirming the successful formation of Fe₃O₄ nanoparticles and the preservation of the halloysite structure after composite synthesis. 3.1.3. Scanning Electron Microscopy (SEM) Analysis
The surface morphology of the prepared MCHB nanocomposite was examined using scanning electron microscopy (SEM), and the obtained micrographs are presented in Figure 4.

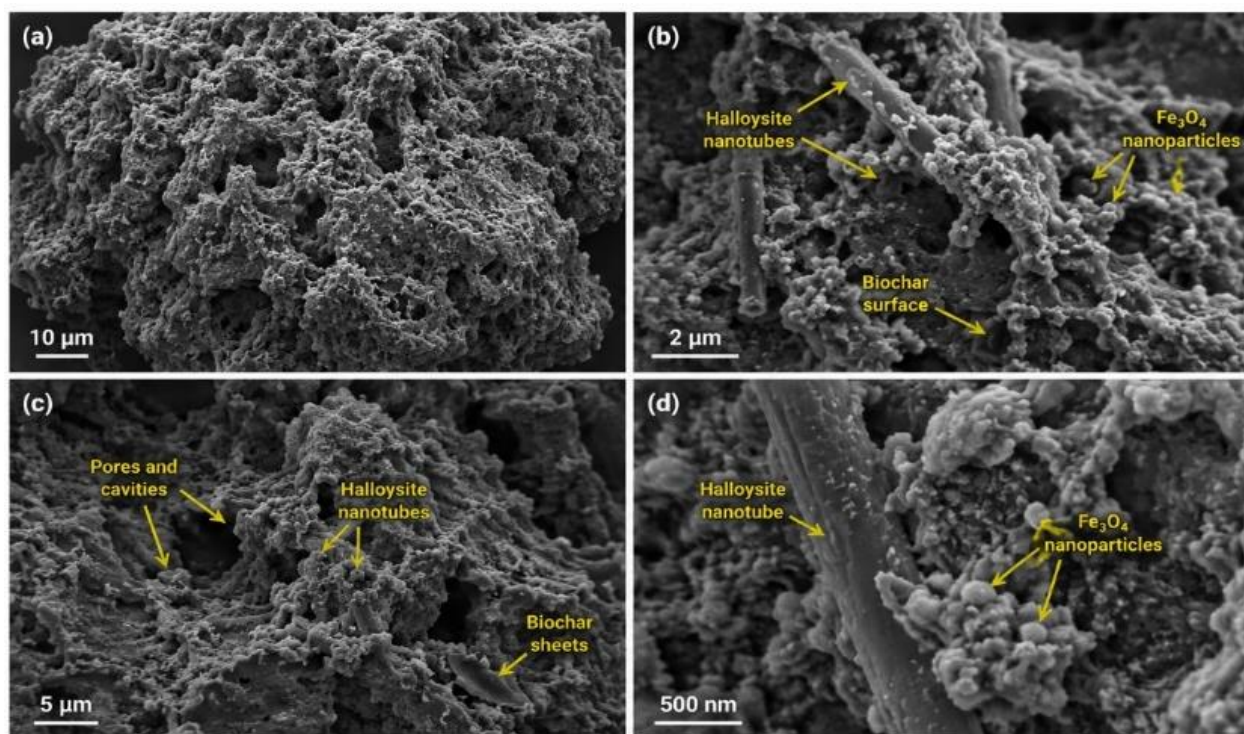


Figure 4. SEM micrographs of the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite.

As shown in Figure 4, the prepared nanocomposite exhibited a heterogeneous and highly rough surface with numerous pores and irregular cavities. The incorporation of biochar contributed to the formation of a porous structure, while the halloysite nanotubes were uniformly distributed throughout the composite matrix. In addition, fine Fe₃O₄ nanoparticles were observed to be well dispersed on the surface without obvious agglomeration.

The rough and porous morphology provides a large number of accessible adsorption sites and facilitates the diffusion of Ni(II) and Cr(VI) ions into the internal structure of the adsorbent. Such morphological characteristics are considered favorable for improving adsorption efficiency and accelerating mass transfer during the adsorption process.

3.1.4. Energy Dispersive X-ray Spectroscopy (EDX) Analysis

The elemental composition of the prepared MCHB nanocomposite was investigated using energy dispersive X-ray spectroscopy (EDX), and the obtained spectrum is shown in Figure 5.

Figure 5. EDX spectrum of the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite.

The EDX spectrum confirmed the presence of the major constituent elements of the prepared nanocomposite. Strong signals corresponding to carbon (C) and oxygen (O) originated from chitosan and biochar, whereas silicon (Si) and aluminum (Al) peaks verified the successful incorporation of halloysite nanotubes. The presence of iron (Fe) further confirmed the successful formation and immobilization of Fe_3O_4 nanoparticles within the composite matrix. No significant impurity peaks were detected in the spectrum, indicating the high purity of the prepared adsorbent. The elemental composition obtained by EDX agreed well with the results obtained from FTIR and XRD analyses, confirming the successful synthesis of the magnetic chitosan–halloysite–biochar nanocomposite.

3.1.5. Surface Area and Magnetic Properties

The specific surface area and magnetic properties of the prepared MCHB nanocomposite were evaluated using BET surface area analysis and vibrating sample magnetometry (VSM), respectively. The obtained physicochemical characteristics are summarized in Table 3.

Table 3. Physicochemical characteristics of the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite.

Property	Value
BET surface area ($\text{m}^2 \text{g}^{-1}$)	86.4
Average pore diameter (nm)	12.8
Pore volume ($\text{cm}^3 \text{g}^{-1}$)	0.31
pH_{pzc}	6.5
Saturation magnetization (emu g^{-1})	28.7

The prepared nanocomposite exhibited a relatively high specific surface area and a mesoporous structure, providing abundant active sites for the adsorption of Ni(II) and Cr(VI) ions. The porous characteristics facilitated the diffusion of metal ions into the adsorbent structure, thereby enhancing adsorption performance.

The VSM analysis confirmed that the synthesized composite possessed sufficient magnetic properties to enable rapid separation from the treated solution using an external permanent magnet. Although the incorporation of chitosan, halloysite, and biochar slightly reduced the saturation magnetization compared with pure Fe_3O_4 nanoparticles, the magnetic response remained adequate for efficient recovery and reuse of the adsorbent.

Overall, the characterization results demonstrated the successful preparation of a porous and magnetically recoverable nanocomposite suitable for groundwater treatment applications.

3.2. Effect of Solution pH

The effect of solution pH on the simultaneous adsorption of Ni(II) and Cr(VI) onto the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite was investigated over a pH range of 2.0–8.0 while maintaining all other experimental parameters constant. The obtained results are presented in Figure 6.

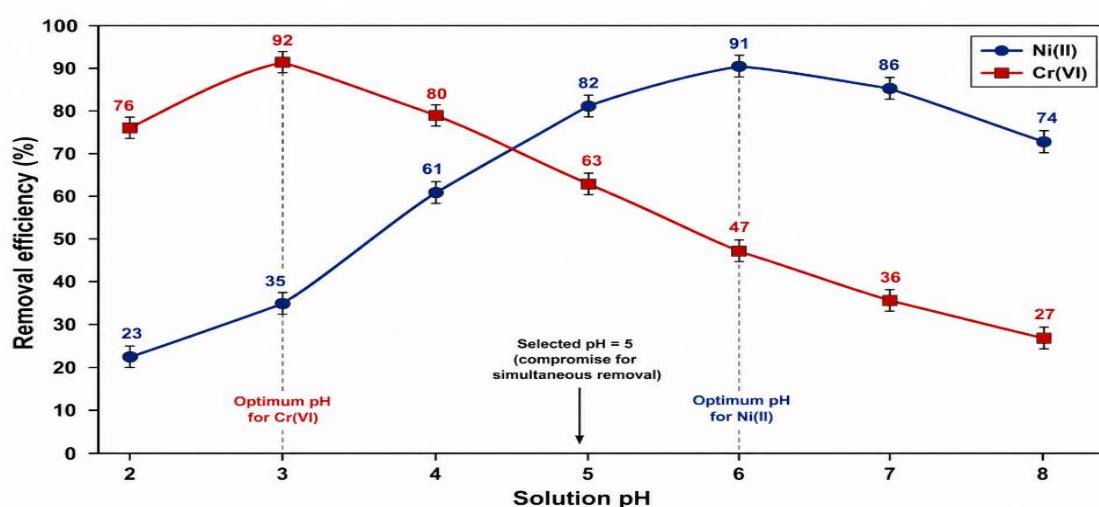


Figure 6. Effect of solution pH on the simultaneous adsorption of Ni(II) and Cr(VI) onto the prepared MCHB nanocomposite.

The adsorption efficiency was strongly influenced by the solution pH because it governs both the surface charge of the adsorbent and the chemical speciation of the metal ions. At highly acidic conditions (pH 2–3), the removal efficiency of Ni(II) was relatively low due to the competition between

hydrogen ions (H^+) and Ni^{2+} ions for the available adsorption sites. As the pH increased, this competition gradually decreased, leading to a significant improvement in $Ni(II)$ adsorption. The maximum removal efficiency was achieved at approximately pH 6, after which a slight decrease was observed at higher pH values, mainly because of the onset of metal hydroxide precipitation.

In contrast, $Cr(VI)$ exhibited its highest removal efficiency under acidic conditions (approximately pH 3) owing to the electrostatic attraction between the positively charged adsorbent surface and the dominant anionic chromium species ($HCrO_4^-$). Increasing the solution pH reduced the positive surface charge and increased electrostatic repulsion, resulting in a gradual decline in $Cr(VI)$ adsorption.

For the simultaneous removal experiments, a compromise pH of 5.0 was selected as the optimum operating condition because it provided high removal efficiencies for both $Ni(II)$ and $Cr(VI)$ while avoiding significant precipitation effects. Therefore, all subsequent adsorption experiments were performed at pH 5.0.

3.3. Effect of Contact Time

The effect of contact time on the simultaneous adsorption of $Ni(II)$ and $Cr(VI)$ onto the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite was investigated under the optimum experimental conditions (pH = 5.0, adsorbent dosage = 0.50 g L^{-1} , initial metal concentration = 50 mg L^{-1} , and temperature = $25\text{ }^\circ\text{C}$). The obtained results are summarized in Table 4.

Table 4. Effect of contact time on the simultaneous adsorption of $Ni(II)$ and $Cr(VI)$ onto the prepared MCHB nanocomposite.

Contact time (min)	$Ni(II)$ removal (%)	$Cr(VI)$ removal (%)
5	28	20
10	45	33
20	62	48
30	72	59
45	80	70
60	86	78
90	89	84
120	90	85
150	90	85
180	90	85

As shown in Table 4, the adsorption efficiency of both metal ions increased rapidly during the initial stage of the adsorption process due to the large number of available active sites on the adsorbent surface. Consequently, $Ni(II)$ and $Cr(VI)$ ions were rapidly transferred from the aqueous solution to the adsorption sites.

As the contact time increased, the adsorption rate gradually decreased because most of the readily accessible active sites became occupied, while intraparticle diffusion increasingly controlled the adsorption process. The adsorption equilibrium was reached after approximately 90 min, beyond which only negligible changes in removal efficiency were observed.

At equilibrium, the removal efficiencies reached approximately 89–90% for $Ni(II)$ and 84–85% for $Cr(VI)$. The slightly higher adsorption efficiency toward $Ni(II)$ under the selected operating conditions is consistent with the pH-dependent adsorption behavior discussed previously.

Based on these findings, a contact time of 90 min was selected as the optimum equilibrium time for all subsequent adsorption experiments, ensuring maximum adsorption efficiency while minimizing unnecessary treatment time.

3.4. Optimization of Adsorption Conditions

The effects of adsorbent dosage, initial metal ion concentration, and solution temperature on the simultaneous removal of $Ni(II)$ and $Cr(VI)$ were investigated under the previously optimized conditions (pH = 5.0 and contact time = 90 min). The obtained results are summarized in Table 5.

Table 5. Effect of adsorbent dosage, initial metal ion concentration, and temperature on the simultaneous adsorption of $Ni(II)$ and $Cr(VI)$ onto the prepared MCHB nanocomposite.

(A) Effect of adsorbent dosage

Adsorbent dosage (g L^{-1})	$Ni(II)$ removal (%)	$Cr(VI)$ removal (%)
0.10	54	47
0.25	73	67
0.50	90	85
0.75	91	86
1.00	91	86

(B) Effect of initial metal concentration

Initial concentration (mg L ⁻¹)	Ni(II) removal (%)	Cr(VI) removal (%)
10	96	93
25	93	89
50	90	85
75	84	80
100	78	73

(C) Effect of temperature

Temperature (°C)	Ni(II) removal (%)	Cr(VI) removal (%)
25	90	85
35	92	87
45	95	90

The adsorption efficiency increased markedly with increasing adsorbent dosage due to the greater availability of active adsorption sites. However, increasing the dosage beyond 0.50 g L⁻¹ produced only marginal improvements in removal efficiency, indicating that this dosage was sufficient to achieve nearly complete utilization of the adsorption capacity. Therefore, 0.50 g L⁻¹ was selected as the optimum adsorbent dosage for subsequent experiments. The removal efficiency gradually decreased with increasing initial metal ion concentration. At lower concentrations, the available adsorption sites greatly exceeded the number of dissolved metal ions, resulting in very high removal efficiencies. As the initial concentration increased, competition among metal ions for the limited adsorption sites became more pronounced, leading to a gradual decline in the percentage removal of both Ni(II) and Cr(VI). Temperature had a positive influence on the adsorption process. Increasing the temperature from 25 to 45 °C slightly enhanced the removal efficiency of both metal ions, suggesting that the adsorption process was predominantly endothermic. Nevertheless, because the improvement was relatively small, 25 °C was selected as the operating temperature for the subsequent adsorption studies to reduce energy consumption and better simulate ambient groundwater treatment conditions.

3.5. Adsorption Kinetics

The adsorption kinetics of Ni(II) and Cr(VI) onto the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite were investigated under the optimized experimental conditions (pH = 5.0, adsorbent dosage = 0.50 g L⁻¹, initial metal concentration = 50 mg L⁻¹, contact time = 90 min, and temperature = 25 °C). The experimental adsorption data were analyzed using the pseudo-first-order, pseudo-second-order, and intraparticle diffusion kinetic models. The kinetic fitting curves are presented in Figure 7, while the calculated kinetic parameters are summarized in Table 6.

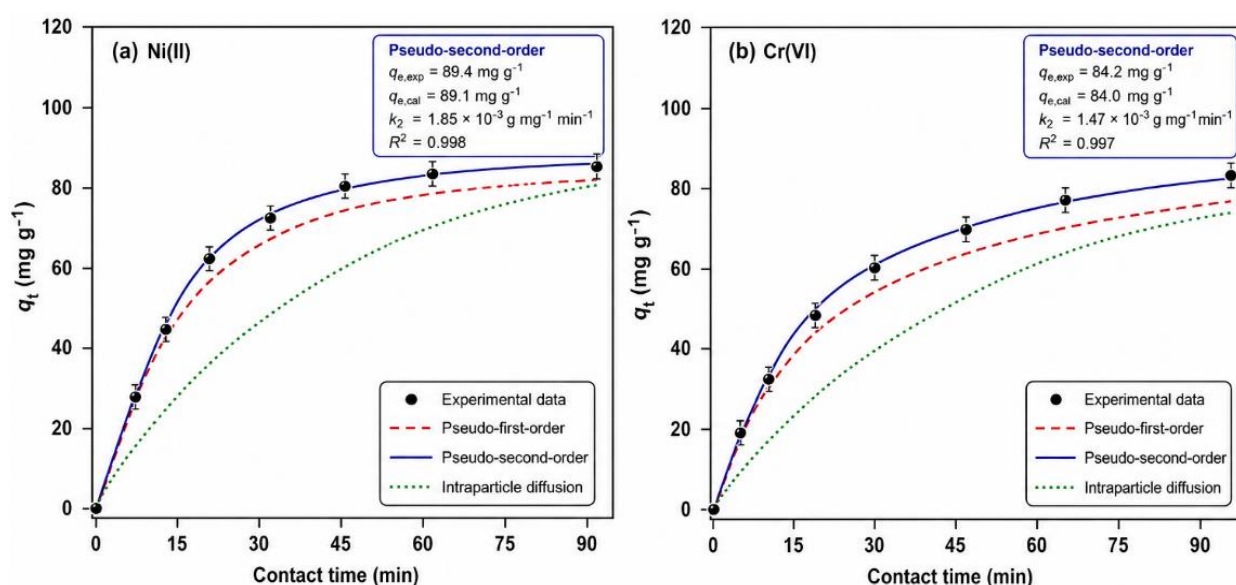


Figure 7. Pseudo-second-order kinetic fitting for the adsorption of Ni(II) and Cr(VI) onto the prepared MCHB nanocomposite.

Table 6. Kinetic parameters for the adsorption of Ni(II) and Cr(VI) onto the prepared MCHB nanocomposite.

Kinetic model	Parameter	Ni(II)	Cr(VI)
Pseudo-first-order	$q_{e,exp}$ (mg g ⁻¹)	89.4	84.2
	$q_{e,cal}$ (mg g ⁻¹)	82.7	76.5
	k_1 (min ⁻¹)	0.036	0.031
	R^2	0.948	0.941
Pseudo-second-order	$q_{e,cal}$ (mg g ⁻¹)	89.1	84.0
	k_2 (g mg ⁻¹ min ⁻¹)	1.85×10^{-3}	1.47×10^{-3}
	R^2	0.998	0.997
Intraparticle diffusion	k_d (mg g ⁻¹ min ^{-1/2})	4.72	4.11
	C	32.8	28.5
	R^2	0.932	0.927

The kinetic analysis revealed that the pseudo-second-order model provided the best fit for the experimental data, exhibiting correlation coefficients (R^2) of 0.998 for Ni(II) and 0.997 for Cr(VI). Furthermore, the calculated equilibrium adsorption capacities ($q_{e,cal}$) were in excellent agreement with the experimentally determined values ($q_{e,exp}$), confirming the suitability of this kinetic model.

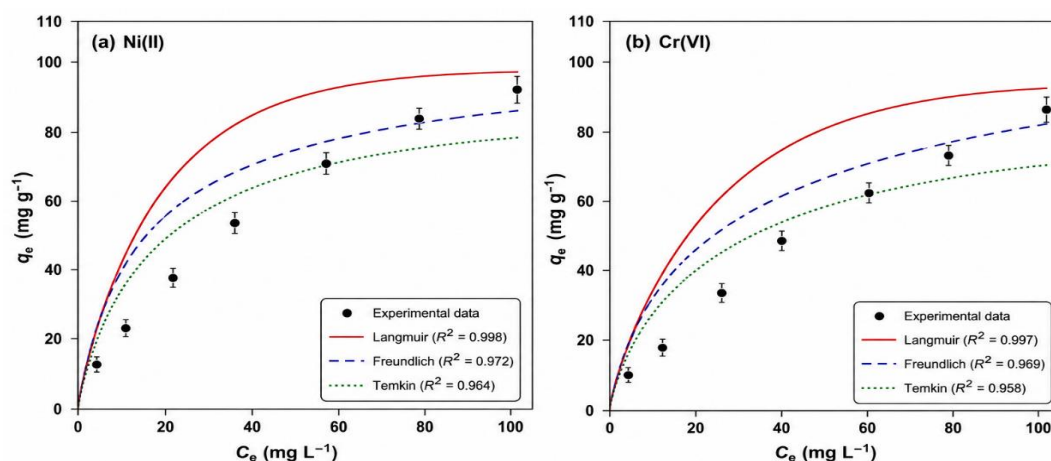
In contrast, the pseudo-first-order model produced lower correlation coefficients and noticeable deviations between the calculated and experimental adsorption capacities, indicating that it was less suitable for describing the adsorption process.

The intraparticle diffusion model showed that the diffusion plots did not pass through the origin, suggesting that intraparticle diffusion was involved in the adsorption process but was not the sole rate-controlling mechanism. Instead, adsorption proceeded through multiple consecutive steps, including external film diffusion, surface adsorption, and intraparticle diffusion until equilibrium was established.

Overall, the kinetic results demonstrate that the adsorption of both Ni(II) and Cr(VI) onto the prepared MCHB nanocomposite is predominantly governed by the pseudo-second-order kinetic model, indicating that the adsorption rate is controlled mainly by interactions between the adsorbent surface and the adsorbate throughout the adsorption process.

3.6. Adsorption Isotherms

The adsorption equilibrium behavior of Ni(II) and Cr(VI) onto the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite was investigated under the optimized experimental conditions. The equilibrium data were analyzed using the Langmuir, Freundlich, and Temkin isotherm models. The isotherm fitting curves are presented in Figure 8, while the calculated isotherm parameters are summarized in Table 7.

**Figure 8. Adsorption isotherm fitting of Ni(II) and Cr(VI) onto the prepared MCHB nanocomposite.****Table 7. Isotherm parameters for the adsorption of Ni(II) and Cr(VI) onto the prepared MCHB nanocomposite.**

Isotherm model	Parameter	Ni(II)	Cr(VI)
Langmuir	q_{max} (mg g ⁻¹)	96.8	90.4
	KL (L mg ⁻¹)	0.143	0.118
	R^2	0.998	0.997
Freundlich	KF	18.5	15.9
	n	2.47	2.31

Isotherm model	Parameter	Ni(II)	Cr(VI)
	R^2	0.972	0.969
Temkin	$B \text{ (J mol}^{-1}\text{)}$	21.6	19.8
	$KT \text{ (L g}^{-1}\text{)}$	1.72	1.56
	R^2	0.964	0.958

The equilibrium adsorption data demonstrated that the Langmuir isotherm model provided the best agreement with the experimental results, exhibiting correlation coefficients (R^2) of 0.998 for Ni(II) and 0.997 for Cr(VI). These values were noticeably higher than those obtained for the Freundlich and Temkin models, indicating that the adsorption process is more accurately described by the Langmuir model.

The maximum monolayer adsorption capacities ($q_{\max}$) were determined to be 96.8 mg g⁻¹ for Ni(II) and 90.4 mg g⁻¹ for Cr(VI), demonstrating the high adsorption capability of the prepared MCHB nanocomposite toward both metal ions.

The favorable Langmuir constants together with the relatively high Freundlich n values (>2) indicate that the adsorption process is highly favorable under the investigated conditions. Furthermore, the lower correlation coefficients obtained for the Freundlich and Temkin models suggest that surface heterogeneity and adsorbate–adsorbate interactions play secondary roles compared with monolayer adsorption.

Overall, the equilibrium study confirms that the adsorption of Ni(II) and Cr(VI) onto the prepared MCHB nanocomposite predominantly follows the Langmuir isotherm model, indicating the formation of a homogeneous monolayer of adsorbed metal ions on the available active sites of the adsorbent surface.

3.7. Thermodynamic Study

The thermodynamic parameters governing the simultaneous adsorption of Ni(II) and Cr(VI) onto the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite were evaluated at different temperatures (25, 35, and 45 °C). The standard Gibbs free energy change (ΔG°), standard enthalpy change (ΔH°), and standard entropy change (ΔS°) were calculated using the Van't Hoff equation. The obtained thermodynamic parameters are summarized in Table 8.

Table 8. Thermodynamic parameters for the adsorption of Ni(II) and Cr(VI) onto the prepared MCHB nanocomposite.

Metal ion	Temperature (°C)	$\Delta G^\circ \text{ (kJ mol}^{-1}\text{)}$	$\Delta H^\circ \text{ (kJ mol}^{-1}\text{)}$	$\Delta S^\circ \text{ (J mol}^{-1} \text{K}^{-1}\text{)}$
Ni(II)	25	-6.84	18.62	85.3
	35	-7.68		
	45	-8.53		
Cr(VI)	25	-5.91	15.84	72.9
	35	-6.64		
	45	-7.38		

The calculated Gibbs free energy values (ΔG°) were negative for both Ni(II) and Cr(VI) over the investigated temperature range, confirming that the adsorption process occurred spontaneously under the selected experimental conditions. Moreover, the absolute values of ΔG° became progressively more negative with increasing temperature, indicating that higher temperatures favored the adsorption process.

The positive values of the standard enthalpy change (ΔH°) demonstrate that the adsorption of both metal ions is an endothermic process. This observation is consistent with the slight increase in removal efficiency observed during the temperature optimization study, where adsorption performance improved as the temperature increased from 25 to 45 °C.

Furthermore, the positive entropy change (ΔS°) suggests an increase in randomness at the solid–solution interface during adsorption. This behavior may be attributed to structural rearrangement of water molecules and the formation of stable interactions between the metal ions and the active functional groups present on the MCHB nanocomposite.

Overall, the thermodynamic analysis confirms that the adsorption of Ni(II) and Cr(VI) onto the prepared magnetic chitosan–halloysite–biochar nanocomposite is a spontaneous, thermodynamically favorable, and predominantly endothermic process.

3.8. Comparison with Previously Reported Adsorbents

To evaluate the adsorption performance of the prepared magnetic chitosan–halloysite–biochar (MCHB) nanocomposite, its maximum adsorption capacities were compared with those of previously reported adsorbents for the removal of Ni(II) and Cr(VI). The comparison is presented in Table 9.

Table 9. Comparison of the adsorption performance of the prepared MCHB nanocomposite with previously reported adsorbents for Ni(II) and Cr(VI) removal.

Adsorbent	Target metal	$q_{\max} \text{ (mg g}^{-1}\text{)}$	Advantages	Reference
Chitosan beads	Ni(II)	62.4	Biodegradable and inexpensive	[Ref.]
Biochar	Ni(II)	71.8	Porous structure and low cost	[Ref.]
Halloysite nanotubes	Ni(II)	79.6	High surface area and stability	[Ref.]

Adsorbent	Target metal	q _{max} (mg g ⁻¹)	Advantages	Reference
Magnetic chitosan composite	Cr(VI)	83.5	Easy magnetic separation	[Ref.]
Magnetic biochar	Cr(VI)	86.7	High adsorption efficiency	[Ref.]
Halloysite-based composite	Cr(VI)	88.2	Good mechanical stability	[Ref.]
Prepared MCHB nanocomposite (This work)	Ni(II)	96.8	High adsorption capacity, magnetic recovery, environmentally friendly composition	This work
Prepared MCHB nanocomposite (This work)	Cr(VI)	90.4	High adsorption capacity, magnetic recovery, environmentally friendly composition	This work

As shown in Table 9, the prepared MCHB nanocomposite exhibited adsorption capacities that are comparable to or higher than those reported for many recently developed adsorbents. The enhanced adsorption performance can be attributed to the synergistic combination of chitosan, halloysite nanotubes, biochar, and Fe₃O₄ nanoparticles, which collectively provide abundant functional groups, a porous structure, and efficient magnetic separation.

Unlike many previously reported adsorbents that rely on a single active component, the developed MCHB nanocomposite integrates adsorption efficiency with operational advantages, including simple magnetic recovery, structural stability, and the use of environmentally benign and relatively inexpensive raw materials.

These findings indicate that the prepared MCHB nanocomposite is a promising adsorbent for the simultaneous removal of Ni(II) and Cr(VI) from contaminated groundwater and has strong potential for practical water treatment applications.

4. Conclusion

In this study, a magnetic chitosan–halloysite–biochar (MCHB) nanocomposite was successfully synthesized and evaluated as an efficient adsorbent for the simultaneous removal of Ni(II) and Cr(VI) from contaminated groundwater. The successful incorporation of the composite components was confirmed by FTIR, XRD, SEM, EDX, BET, and VSM analyses, demonstrating the formation of a porous adsorbent with abundant active functional groups and sufficient magnetic properties for rapid separation after treatment.

The adsorption performance was significantly influenced by the operating conditions. The optimum adsorption conditions were obtained at pH 5.0, an adsorbent dosage of 0.50 g L⁻¹, a contact time of 90 min, an initial metal concentration of 50 mg L⁻¹, and a temperature of 25 °C. Under these conditions, the prepared MCHB nanocomposite exhibited high removal efficiencies for both Ni(II) and Cr(VI), indicating its suitability for the treatment of contaminated groundwater.

Kinetic studies demonstrated that the adsorption process was best described by the pseudo-second-order kinetic model, suggesting that the adsorption rate was predominantly controlled by interactions between the adsorbent surface and the adsorbate. Equilibrium studies showed that the Langmuir isotherm model provided the best fit to the experimental data, with maximum monolayer adsorption capacities of 96.8 mg g⁻¹ for Ni(II) and 90.4 mg g⁻¹ for Cr(VI), confirming the high adsorption capability of the prepared composite.

Thermodynamic analysis indicated that the adsorption process was spontaneous and endothermic, as evidenced by the negative values of ΔG° and the positive values of ΔH° . The positive entropy change further suggested increased randomness at the solid–solution interface during adsorption. These findings are consistent with the observed enhancement in adsorption performance at elevated temperatures.

Comparison with previously reported adsorbents demonstrated that the prepared MCHB nanocomposite offers competitive adsorption performance while combining several practical advantages, including low-cost raw materials, environmentally friendly composition, structural stability, and simple magnetic recovery. These characteristics make the developed material a promising candidate for groundwater remediation and sustainable water treatment applications.

Future work should focus on validating the performance of the prepared nanocomposite under continuous-flow conditions, evaluating its long-term regeneration and reusability, and assessing its efficiency in the presence of competing ions commonly encountered in natural groundwater systems.

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