



## Water Pollution Treatment Using Eco-Friendly ZnO–Chitosan Bio-Composites

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### ABSTRACT

Natural organic matter, particularly humic acid (HA), is a major water contaminant due to its complex structure, strong metal-binding ability, and role as a precursor of toxic disinfection by-products formed during chlorination. This study developed a green and biodegradable ZnO–chitosan bio-composite (ZnO@Cs BC) for efficient HA removal from aqueous solutions. The composite was synthesized by dispersing ZnO within a chitosan matrix and characterized using FTIR, XRD, SEM/EDX, and TGA-DSC, confirming successful ZnO incorporation and enhanced structural and thermal stability compared with pristine chitosan. Batch adsorption experiments evaluated the effects of pH (3–11), contact time (10–180 min), adsorbent dosage (0.05–1.0 g), initial HA concentration (5–100 mg L<sup>-1</sup>), and temperature (20–60 °C). The ZnO@Cs BC achieved over 90% HA removal across a broad pH range and a maximum removal efficiency of 99.8% under optimum conditions (pH 7, 25 °C, 120 min, 0.05 g adsorbent, and 5 mg L<sup>-1</sup> HA). Adsorption kinetics followed the pseudo-second-order model ( $R^2 \approx 1$ ), indicating chemisorption, while equilibrium data were best described by the Langmuir isotherm ( $R^2 = 0.99$ ), with a maximum adsorption capacity of 4.535 mg g<sup>-1</sup>. Thermodynamic analysis confirmed that adsorption was spontaneous ( $\Delta G^\circ < 0$ ) and endothermic ( $\Delta H^\circ > 0$ ). The composite retained approximately 85% of its adsorption capacity after five regeneration cycles, demonstrating excellent reusability. These results highlight ZnO@Cs BC as an effective, sustainable, and cost-efficient adsorbent for removing HA from water.

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## INTRODUCTION

Water pollution remains one of the most significant environmental challenges worldwide, driven by rapid urbanization, industrialization, and agricultural activities that release heavy metals, pharmaceuticals, pesticides, and organic contaminants into aquatic environments (Tella et al., 2025). Among these pollutants, natural organic matter (NOM) is of particular concern because of its abundance, complex composition, and interference with water treatment processes (Nishmitha et al., 2025). Increasingly stringent discharge regulations have promoted hybrid treatment systems for efficient wastewater purification (Kalash et al., 2025). Humic acid (HA), the major fraction of NOM, contains aromatic, carboxylic, phenolic, and quinone functional groups that strongly bind metal ions, influence contaminant transport, and deteriorate water quality through color, taste, and odor problems (Wiercik et al., 2024). More

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importantly, HA acts as a major precursor of carcinogenic disinfection by-products, including trihalomethanes and haloacetic acids, formed during chlorination of drinking water (Ma et al., 2025). Consequently, efficient HA removal before disinfection is essential for safe drinking-water production. Several technologies have been investigated for HA removal, including coagulation–flocculation, membrane filtration, advanced oxidation, and adsorption (Hilmioglu and Yumat, 2024). Advanced oxidation processes, including electrochemical oxidation, are effective for removing recalcitrant organic pollutants from industrial wastewater (Habl et al., 2024). Among these, adsorption is particularly attractive because of its simplicity, high efficiency, and potential for adsorbent regeneration. However, its performance depends largely on the properties of the adsorbent. Biological and hybrid physicochemical processes have also shown promise for removing organic pollutants from wastewater (Al-Amshawee et al., 2022; Mohammed et al., 2022). Chitosan (Cs), a renewable biopolymer derived from chitin, has received considerable attention because its amino and hydroxyl groups promote electrostatic attraction and hydrogen bonding with HA (Kaczorowska and Bożejewicz, 2024). Nevertheless, pristine chitosan suffers from poor mechanical strength, limited thermal stability, and pH-dependent solubility, restricting its practical application (Queiroz et al., 2015). Incorporating zinc oxide (ZnO) nanoparticles into chitosan offers an effective strategy to overcome these limitations by increasing surface area, improving structural stability, and providing additional active adsorption sites (Nawaz et al., 2024). ZnO–chitosan composites have shown promising performance for removing dyes and heavy metals, while maintaining good reusability and stability (Hosseini et al., 2023). Recent reviews highlight metal oxide and biopolymer-based nanocomposites as effective adsorbents and photocatalysts for wastewater treatment. Among them, ZnO-based nanomaterials are particularly attractive because of their high surface activity and structural stability (Alalwan et al., 2022; Mohammed et al., 2021). Despite these advances, the application of ZnO–chitosan composites for HA removal remains insufficiently investigated. Most previous studies have focused on dye adsorption, heavy-metal removal, or photocatalytic degradation of simpler organic pollutants, whereas the adsorption behavior of macromolecular HA and the synergistic interactions between ZnO and chitosan have received limited attention. In particular, the relative contributions of electrostatic attraction, hydrogen bonding, coordination interactions, and surface complexation to HA adsorption remain poorly understood.

Therefore, this study aimed to synthesize and characterize an environmentally friendly ZnO–chitosan biocomposite (ZnO@Cs BC) and evaluate its efficiency for HA removal from water. Adsorption performance was investigated under different operating conditions, and the adsorption mechanism was elucidated using kinetic, isotherm, and thermodynamic models. The reusability of the composite was also assessed. The novelty of this work lies in developing a synergistic ZnO–chitosan adsorbent with enhanced stability, adsorption performance, and regeneration potential for water treatment.

## MATERIALS AND METHODS

### *Chemicals and Reagents*

Chitosan was supplied by PioChem (Laboratory Chemicals, Egypt). Zinc acetate dihydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ ) was used as the zinc precursor for the synthesis of ZnO nanoparticles and the ZnO–chitosan composite. Sodium acetate ( $\text{CH}_3\text{COONa}$ ) and sulfuric acid ( $\text{H}_2\text{SO}_4$ ) were used for buffer preparation, while sodium hydroxide ( $\text{NaOH}$ ) was employed for pH adjustment during adsorption experiments. Humic acid was purchased from Sigma-Aldrich® (USA). A stock solution of HA ( $1000 \text{ mg L}^{-1}$ ) was prepared by dissolving an accurately weighed amount in distilled water under continuous stirring to ensure complete dissolution. Working solutions of lower concentrations were then prepared by appropriate dilution of the stock solution. Residual

HA concentrations were determined spectrophotometrically at the maximum absorption wavelength ( $\lambda_{\max} = 355$  nm). All reagents used in this study were of analytical grade.

### Preparation of Adsorbents

**ZnO nanoparticles** were synthesized via a chemical precipitation method using  $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  as a precursor. An aqueous zinc acetate solution was prepared and stirred at room temperature, followed by the gradual addition of NaOH until pH  $\sim 11$ . The resultant precipitate was allowed to mature under controlled conditions, subsequently separated by centrifugation, thoroughly rinsed with distilled water followed by ethanol, oven-dried at  $60^\circ\text{C}$  for 12 h, and finally subjected to thermal calcination at  $500^\circ\text{C}$  for 2 h to yield crystalline ZnO nanoparticles (Rajendran et al., 2022). **Chitosan (Cs)** solution (2% w/v) was prepared by dissolving 2 g chitosan in 100 mL of 1% acetic acid under stirring for 4–6 h at room temperature until a homogeneous solution formed (Al-Rajhi et al., 2024). **ZnO–chitosan composite (ZnO@Cs BC)** was synthesized by dispersing 0.2 g ZnO in 20 mL of 1% acetic acid containing dissolved chitosan. The mixture was stirred at  $60^\circ\text{C}$  for 3 h to enhance the interaction between ZnO and chitosan functional groups, then centrifuged, washed, and dried at  $60^\circ\text{C}$  for 4 h.

### Optimum Conditions Experiments

Batch adsorption experiments were performed to evaluate HA removal using Cs, ZnO, and ZnO@Cs under varying conditions, including pH, contact time, adsorbent dose, initial HA concentration, and temperature. All experiments were conducted in triplicate ( $n = 3$ ).

The effect of **pH** (3–11) was studied using 25 mL HA solutions (5, 20, and 40 mg/L) with 10 mg adsorbent at  $25^\circ\text{C}$ , 120 rpm, and 30 min contact time. **Contact time** experiments were performed from 10–180 min using 25 mL HA solutions under optimal pH at  $25^\circ\text{C}$  and 300 rpm. **Adsorbent dose** (0.05–1 g) was evaluated using 25 mL HA solution at optimal pH, time,  $25^\circ\text{C}$ , and 300 rpm. The effect of **initial concentration** (5–100 mg  $\text{L}^{-1}$ ) was studied at pH 7,  $25^\circ\text{C}$ , and 300 rpm. **Temperature effects** were investigated between  $20$ – $60^\circ\text{C}$  under optimized conditions. After adsorption, solutions were filtered and residual HA was measured by UV–Vis spectroscopy at 355 nm. Removal efficiency and equilibrium adsorption capacity ( $q_e$ ) were calculated using:

$$q_e = \frac{(C_o - C_e) \times V}{m} \quad (1)$$

$$\% \text{Removal} = \left( \frac{C_o - C_e}{C_o} \right) \times 100 \quad (2)$$

where  $C_o$  (mg  $\text{L}^{-1}$ ) and  $C_e$  (mg  $\text{L}^{-1}$ ) represent the initial and equilibrium HA concentrations, respectively;  $V$  (L) denotes the solution volume; and  $m$  (g) corresponds to the adsorbent mass.

### Adsorption Models

The adsorption behavior of HA on Cs, ZnO nanoparticles, and ZnO@Cs bio-composite was investigated using kinetic, equilibrium isotherm, and thermodynamic models. Equilibrium data were analyzed using Langmuir, Freundlich, and Temkin thermal equilibrium models, including Langmuir, Freundlich, and Temkin models, to describe the relationship between equilibrium HA concentration in solution and adsorption capacity. Model parameters were obtained from linear regression of experimental equilibrium data, as summarized in Table 1. Adsorption kinetics were evaluated using pseudo-first-order (PFO), pseudo-second-order (PSO), intraparticle diffusion, and film diffusion models to describe adsorption rate mechanisms. Thermodynamic parameters were calculated to assess feasibility and temperature dependence. Gibbs free energy ( $\Delta G^\circ$ ) was

Table 1. Adsorption equations and definitions of fitting parameters used to evaluate HA adsorption mechanisms.

| Models                  | Linear Equation                                                                                     | Eq. No | Parameters Definition                                                                                                                                                                      | References                  |
|-------------------------|-----------------------------------------------------------------------------------------------------|--------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------|
| Kinetic                 |                                                                                                     |        |                                                                                                                                                                                            |                             |
| Pseudo-first-order      | $\ln(q_e - q_t) = \ln q_e - k_1 t$                                                                  | Eq.3   | $q_t$ (mg g <sup>-1</sup> ), $q_e$ (mg g <sup>-1</sup> ) are the adsorption at time $t$ (min) and at equilibrium, respectively.                                                            | (Lagergren, 1898)           |
| Pseudo-second-order     | $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$                                               | Eq.4   | $k_1$ (min <sup>-1</sup> ) : PFO rate constant. $k_2$ (min <sup>-1</sup> ): PSO rate constant, $k_p$ (mg g <sup>-1</sup> min <sup>-1/2</sup> ): the intraparticle diffusion rate constant, | (Ho and McKay, 1999)        |
| Intraparticle diffusion | $q_t = k_p t^{1/2} + C$                                                                             | Eq.5   | C: represents the boundary layer thickness. $F=q_t/q_e$ . $k_f$ : indicates film diffusion rate constant.                                                                                  | (Weber Jr and Morris, 1963) |
| Isotherm                |                                                                                                     |        |                                                                                                                                                                                            |                             |
| Langmuir                | $\frac{1}{q_e} = \frac{1}{q_{max}} + \left(\frac{1}{q_{max} K_L}\right) \left(\frac{1}{C_e}\right)$ | Eq.6   | $K_L$ : Langmuir affinity constant (L/mg). $q_{max}$ : monolayer adsorption capacity                                                                                                       | (Langmuir, 1918)            |
| Freundlich              | $\log q_e = \log K_f + \frac{1}{n_f} \ln C_e$                                                       | Eq.7   | $K_f$ : adsorption capacity<br>$n_f$ : adsorption intensity                                                                                                                                | (Freundlich, 1906)          |
| Temkin                  | $q_e = B_T \ln A_T - B_T \ln C_e$                                                                   | Eq.8   | $A_T$ : Temkin equilibrium binding constant                                                                                                                                                | (Temppin and Pyzhhev, 1940) |

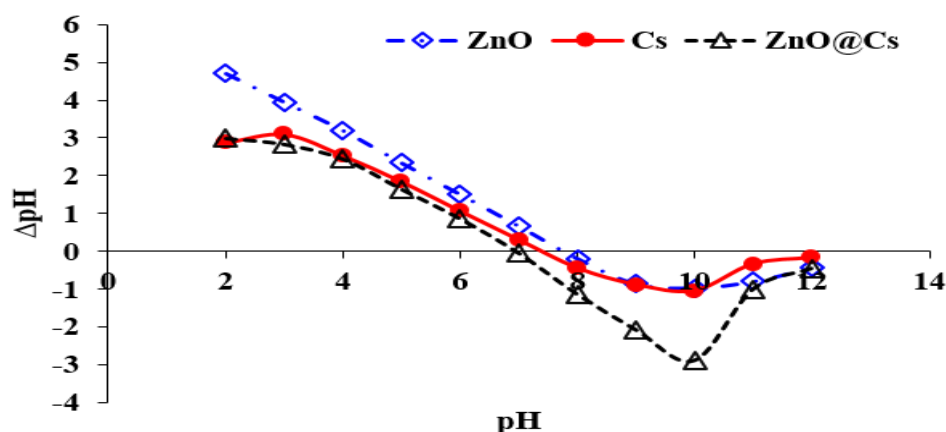


Fig. 1. Variation of  $\Delta\text{pH}$  as a function of initial pH for ZnO, Cs, and ZnO@Cs samples.

derived from  $\Delta H^\circ$ ,  $\Delta S^\circ$ , temperature, and distribution coefficient ( $K_d$ ), using  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ .  $\Delta H^\circ$  and  $\Delta S^\circ$  were obtained from the Van't Hoff plot of  $\ln(K_d)$  versus  $1/T$ , where slope and intercept correspond to  $-\Delta H^\circ/R$  and  $\Delta S^\circ/R$ , respectively.

#### Characterization of Prepared Materials

The synthesized chitosan, ZnO nanoparticles, and ZnO@Cs bio-composite were characterized using Fourier-transform infrared spectroscopy (FTIR), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM–EDX), X-ray diffraction (XRD), and thermogravimetric analysis coupled with differential scanning calorimetry (TGA–DSC). FTIR analysis was used to identify the principal functional groups and assess interactions between ZnO and the chitosan matrix. SEM was employed to examine surface morphology, while EDX was used to determine the elemental composition of the prepared materials. XRD analysis was conducted to evaluate crystallinity and confirm the structural phases of the synthesized components. Thermal behavior and stability were assessed using TGA–DSC. The characterization procedures and interpretation followed approaches reported by Makhoul et al. (2025), Alharbi et al. (2026), Dinarvand and Moradi (2025), and Nandhini et al. (2024).

## RESULTS AND DISCUSSIONS

#### Surface Properties and Point of Zero Charge ( $\text{pH}_{\text{pzc}}$ )

The surface properties of ZnO, Cs, and ZnO@Cs were evaluated using the  $\Delta\text{pH}$ –pH method (Fig. 1). ZnO showed a  $\text{pH}_{\text{pzc}}$  around pH 7–8, reflecting its amphoteric nature, where the surface is positively charged under acidic conditions and becomes progressively negative with increasing pH. Chitosan exhibited relatively stable buffering behavior across the pH range due to its amino and hydroxyl groups, resulting in relatively smaller  $\Delta\text{pH}$  variations. The ZnO@Cs composite displayed a mildly alkaline  $\text{pH}_{\text{pzc}}$  (~8.0–8.2), indicating that ZnO incorporation modifies the surface acid base properties of chitosan. This shift suggests interactions between Zn–OH groups and chitosan functional groups, leading to altered surface charge distribution and overall surface chemistry of the composite. Fig. 1 shows  $\Delta\text{pH}$  variation with initial pH, used to determine  $\text{pH}_{\text{pzc}}$ . The shift in  $\text{pH}_{\text{pzc}}$  after ZnO incorporation confirms surface interaction and surface charge redistribution within the composite.

#### Physicochemical Characterization of Adsorbents

**FTIR Analysis:** Present the characteristic bands of chitosan, ZnO, and ZnO@Cs separately.

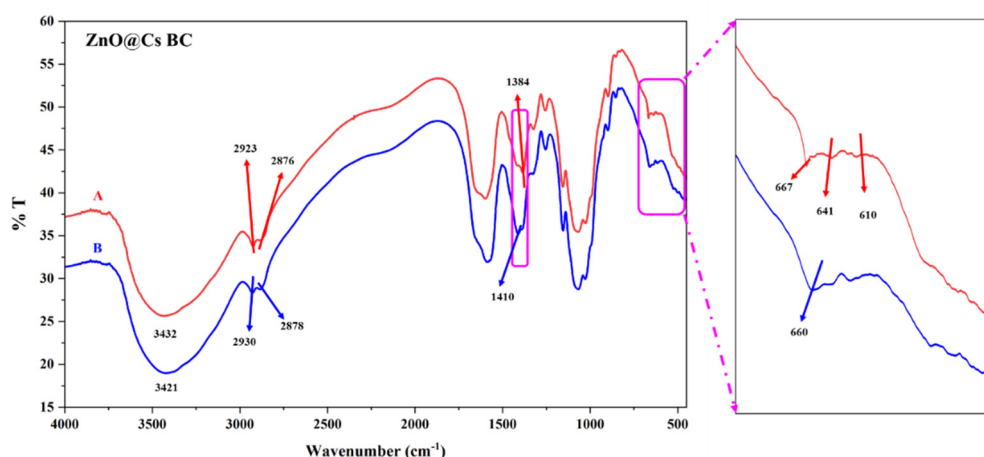


**Fig. 2.** FTIR spectra of ZnO nanoparticles, chitosan, and ZnO@Cs BC showing characteristic functional group vibrations and Zn–O incorporation.

Compare band positions and intensities, particularly the O–H/N–H, amide, and Zn–O regions. Explain how the shifts observed after composite formation confirm interactions between ZnO and the chitosan matrix. Then compare the spectra before and after HA adsorption to identify the functional groups involved in HA binding (Fig. 2).

**SEM Morphological Analysis:** describe the morphology of pure chitosan, ZnO nanoparticles, and the ZnO@Cs composite. Explain how ZnO incorporation changes surface roughness, particle distribution, porosity, or aggregation. Compare images before and after adsorption and interpret the more compact or coated surface as evidence of HA deposition.

**EDX:** report the detected elements and, preferably, their atomic or weight percentages. Demonstrate the presence of Zn in the composite and discuss whether the elemental distribution supports homogeneous ZnO incorporation. Where post-adsorption data are available, explain any changes associated with HA uptake (Fig. 3).

**XRD:** identify the semi-crystalline chitosan peak and assign the principal ZnO reflections to the hexagonal wurtzite structure. Explain that retention of the ZnO peaks in ZnO@Cs confirms structural stability, while changes in the chitosan peak indicate polymer–particle interactions and modification of polymer-chain organization.

**TGA–DSC Thermal:** describe the main degradation stages of chitosan and ZnO@Cs, including moisture loss, polymer decomposition, residual mass, and relevant thermal transitions. Compare the materials quantitatively and explain how the higher residual mass or altered degradation temperature demonstrates improved thermal stability after ZnO incorporation.

Integrate the findings from all techniques explain that ZnO incorporation modifies the chemical environment, morphology, crystallinity, surface properties, and thermal resistance of chitosan. These changes provide accessible –OH, –NH, amide, and Zn–OH/Zn–O sites that promote HA adsorption through electrostatic attraction, hydrogen bonding, and surface complexation. This combined evidence explains the higher adsorption efficiency and wider pH tolerance of ZnO@Cs compared with the individual components.

#### *Influence of pH on HA Adsorption*

The effect of pH (3–11) on HA adsorption was studied at 5 mg L<sup>−1</sup> (Fig. 4). ZnO@Cs showed the highest performance across all conditions, maintaining >92% removal and reaching ~99% at neutral pH. Even at high HA concentration, removal remained stable (≈93–98%), indicating strong pH tolerance. ZnO showed moderate performance (≈75–90% at low concentration), decreasing near neutral pH due to its point of zero charge and increased competition at higher

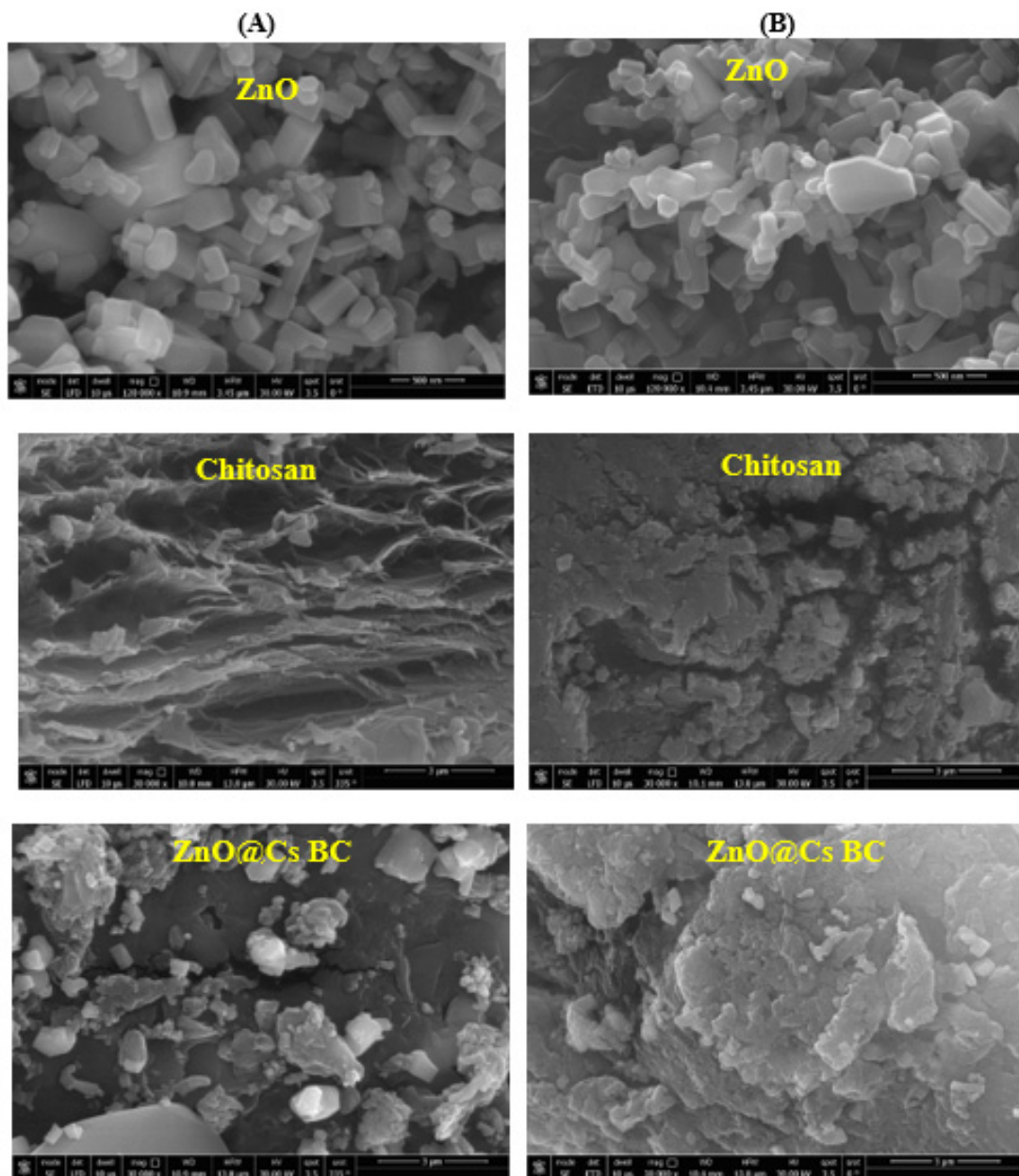


**Fig. 3.** SEM micrographs of ZnO, pure chitosan, and ZnO@Cs BC illustrating morphological differences before (A) and after (B) HA adsorption.

HA levels. Chitosan was highly pH-sensitive, performing well only under acidic conditions and showing strong performance decline at neutral and alkaline pH due to deprotonation of amino groups and site saturation. Overall, ZnO@Cs exhibited superior stability due to synergistic adsorption mechanisms including electrostatic attraction, hydrogen bonding, coordination interactions,  $\pi$ - $\pi$  interactions (if aromatic HA considered) and surface complexation.

#### *Impact of Adsorbent Dosage*

The adsorbent dose (0.05-1.0 g) significantly affected the removal of HA, as shown in Fig. 4. Increasing dose improved removal efficiency for all materials due to greater availability of active sites. At low HA concentration (5 mg L<sup>-1</sup>), nearly complete removal (~99%) was achieved by ZnO@Cs using only 0.05 g. At 20 mg L<sup>-1</sup>, performance remained high but slightly

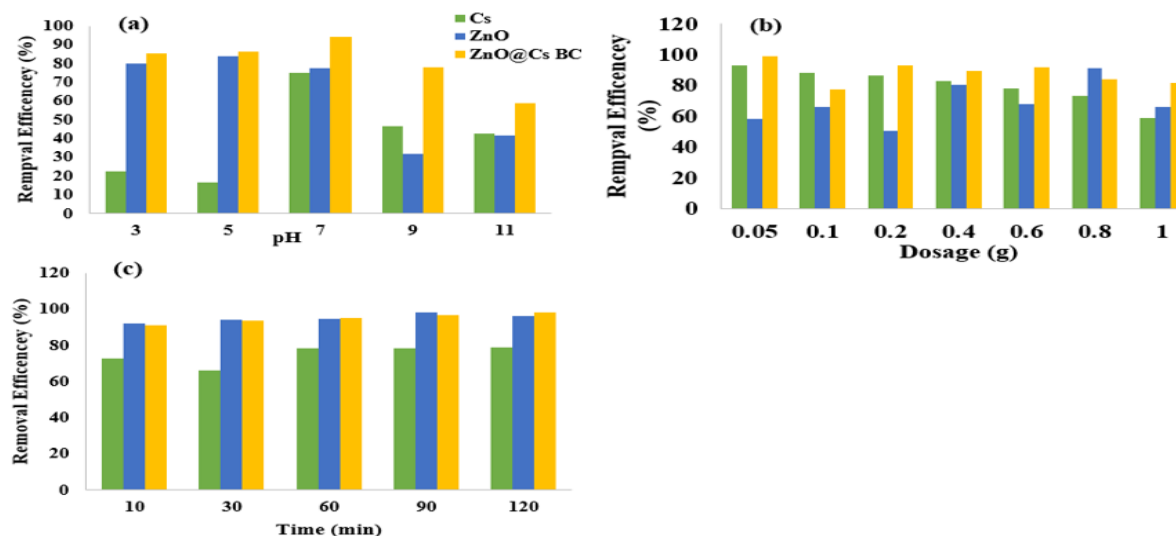


Fig. 4. Humic acid removal (%R) by Cs, ZnO, and ZnO@Cs bio-composite at different (a) pH, (b) dosage and (c) time.

reduced due to increased pollutant loading. At  $40 \text{ mg L}^{-1}$ , adsorption efficiency decreased for all adsorbents due to active-site saturation effects. Chitosan showed limited improvement at low doses, while ZnO exhibited moderate increases with dose but remained less efficient than the composite. ZnO@Cs consistently maintained the highest performance across all conditions, confirming its superior adsorption capacity and high density of accessible active sites.

#### Impact of Contact Duration at Varied Humic Acid Concentrations

The effect of contact time on HA removal was studied for Cs, ZnO, and ZnO@Cs at  $5 \text{ mg L}^{-1}$  (Fig. 4). In all cases, adsorption showed a rapid initial stage (10–30 min) due to abundant active sites, followed by a slower phase until equilibrium at ~100–120 min. ZnO@Cs exhibited the fastest kinetics and highest efficiency. At  $5 \text{ mg L}^{-1}$ , removal increased from ~85–90% initially to ~99–100% at equilibrium. Similar behavior was observed at  $20 \text{ mg L}^{-1}$  (~80–90% to 98–99%) and  $40 \text{ mg L}^{-1}$  (~75–85% to 95–97%), confirming strong performance even at higher pollutant loads. ZnO showed moderate performance, with equilibrium removal decreasing as concentration increased: ~94–95% ( $5 \text{ mg L}^{-1}$ ), ~90–94% ( $20 \text{ mg L}^{-1}$ ), and ~88–90% ( $40 \text{ mg L}^{-1}$ ), reflecting partial site saturation. Chitosan showed the lowest efficiency, particularly at higher concentrations, where removal was limited by faster saturation of adsorption sites.

Kinetic modeling indicated that adsorption capacity increased with HA concentration for all adsorbents. The pseudo-second-order model best described the data ( $R^2 \approx 1$ ), suggesting that adsorption may involve chemical interactions between HA and surface functional groups. Pseudo-first-order fits were slightly weaker. Intraparticle diffusion and film diffusion models revealed multi-step transport involving surface adsorption followed by pore diffusion, with boundary layer effects also contributing.

#### Impact of Temperature and Thermodynamic Evaluation

Temperature influenced HA adsorption slightly, with overall, higher removal efficiencies were observed at 25–45°C for all adsorbents. Chitosan showed a small increase in removal at 5 and  $20 \text{ mg L}^{-1}$  up to 45°C (Fig. 4), followed by a slight decline at higher temperatures. At  $40 \text{ mg L}^{-1}$ , performance remained low but improved modestly with temperature. ZnO also exhibited improved removal with increasing temperature, reaching maximum efficiency around 45°C,

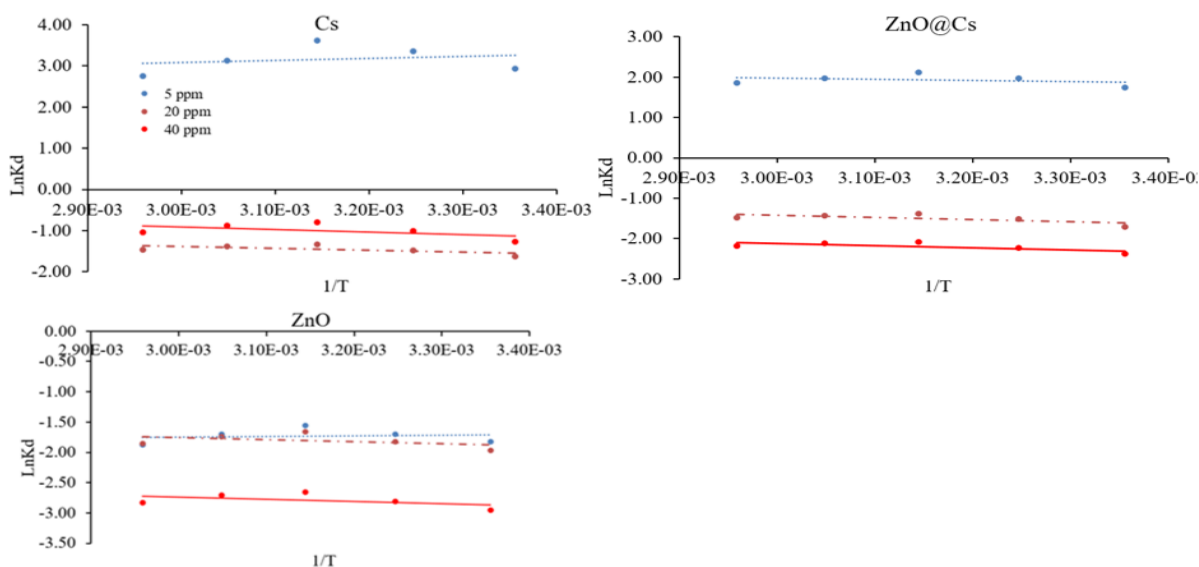


**Fig. 5.** Van't Hoff plots of  $\ln K_d$  as function of  $1/T$  for humic acid adsorbed onto chitosan, ZnO NPs and ZnO@Cs bio-composite at various initial concentrations ( $5 \text{ mg L}^{-1}$ ).

while ZnO@Cs consistently showed the highest performance across all conditions, with only a slight decrease at higher temperatures. Van't Hoff plots ( $\ln K_d$  versus  $1/T$ ) are presented in Fig. 5. Thermodynamic analysis (Van't Hoff plots) showed that adsorption is spontaneous and temperature-dependent. Negative  $\Delta G^\circ$  values for all materials confirm feasibility, becoming more negative with increasing temperature. ZnO@Cs exhibited the most negative  $\Delta G^\circ$  values, indicating stronger adsorption affinity compared to Cs and ZnO. Positive  $\Delta H^\circ$  values confirm that the adsorption process is endothermic, meaning higher temperature enhances HA uptake by improving molecular mobility and overcoming hydration barriers. Positive  $\Delta S^\circ$  values indicate increased randomness at the solid–liquid interface due to displacement of water molecules during adsorption. Overall, thermodynamic results confirm that HA adsorption onto all studied materials

is spontaneous, endothermic, and more favorable at moderate temperatures, with ZnO@Cs showing the strongest thermodynamic performance.

#### *Adsorption Behavior and Equilibrium Modeling*

The effect of initial HA concentration ( $5\text{--}100 \text{ mg L}^{-1}$ ) on adsorption performance was studied for Cs, ZnO, and ZnO@Cs. Adsorption capacity increased with rising HA concentration for all adsorbents. ZnO@Cs showed consistently high removal efficiency ( $>93\%$  at low concentrations) and maintained  $69\text{--}99\%$  at higher concentrations ( $80\text{--}100 \text{ mg L}^{-1}$ ). ZnO showed a gradual increase from  $\sim 21\%$  to  $88\%$ , while chitosan decreased from  $\sim 85\%$  to  $\sim 20\%$  as concentration increased, indicating surface saturation. Equilibrium data were fitted to several isotherm models (Langmuir, Freundlich and Temkin) (Table 2). The Langmuir model provided the best fit for all adsorbents ( $R^2 = 0.92\text{--}0.99$ ), indicating monolayer adsorption on homogeneous sites. ZnO@Cs showed the highest Langmuir constant ( $K_L = 1.91 \text{ L mg}^{-1}$ ), reflecting stronger adsorption affinity. The Freundlich model also showed acceptable fits for Cs and ZnO@Cs ( $R^2 = 0.88\text{--}0.90$ ), while ZnO exhibited weaker adsorption favorability, as indicated by the low Freundlich constant ( $n = 0.27$ ), Temkin results supported moderate agreement.

#### *Structural Characterization and Correlation with Adsorption Efficacy*

FTIR analysis confirmed functional groups of chitosan (O–H, N–H, and amide bands)

**Table 2.** Adsorption isotherm parameters for HA adsorption onto Cs, ZnO, and ZnO@Cs-BC.

| Models     | Parameters | Cs     | ZnO    | ZnO@Cs BC |
|------------|------------|--------|--------|-----------|
| Langmuir   | $Q_{\max}$ | 4.7733 | 0.4749 | 4.5351    |
|            | $K_L$      | 0.2206 | 0.0808 | 1.9074    |
|            | $R^2$      | 0.9913 | 0.9220 | 0.9887    |
| Freundlich | $n_f$      | 2.7315 | 0.2680 | 2.5291    |
|            | $K_f$      | 1.0454 | 2.4576 | 1.2324    |
|            | $R^2$      | 0.8822 | 0.8992 | 0.9006    |
| Tempkin    | $A_T$      | 2.0838 | 4.3867 | 12.5697   |
|            | $B_T$      | 1.0293 | 2.4040 | 0.9923    |
|            | $R^2$      | 0.7089 | 0.6867 | 0.8985    |

and ZnO (O–H and Zn–O vibrations). After HA adsorption, shifts in these bands indicated involvement of hydroxyl and amino groups through hydrogen bonding and electrostatic interactions. Comparable spectrum alterations have been shown for chitosan-based adsorbents interacting with organic compounds possessing oxygenated functional groups (Ghanem et al., 2025). ZnO surface hydroxyl groups also contributed to adsorption via surface complexation.

In the ZnO@Cs composite, band shifts in –OH/–NH and amide regions confirmed strong interactions between ZnO and chitosan, improving dispersion and increasing active adsorption sites. SEM images showed that chitosan had a fibrous structure, ZnO had crystalline morphology, and the composite exhibited well-dispersed ZnO with increased surface roughness, enhancing adsorption efficiency. The alteration in the Zn–O vibration band signifies the involvement of Zn–O–H groups and surface imperfections in the adsorption process (Modrić-Šahbazović et al., 2025).

XRD confirmed that ZnO retained its wurtzite structure after incorporation, while the reduction in chitosan crystallinity suggested increased chain flexibility and more accessible adsorption sites. Thermal analysis (TGA/DSC) showed improved stability of ZnO@Cs compared to chitosan due to reduced polymer mobility and stronger interfacial interactions. These effects are typical of polymer–nanoparticle composites where inorganic fillers enhance thermal resistance and structural stability.

#### *Impact of Operational Parameters and Optimal Adsorption Conditions*

The adsorption of HA on Cs, ZnO, and ZnO@Cs was studied under key operational factors including pH, adsorbent dose, contact time, initial HA concentration, and temperature, all of which influence surface charge, active site availability, and mass transfer.

Indeed, pH strongly affected adsorption due to changes in both HA ionization and adsorbent surface charge. ZnO@Cs showed excellent stability across a wide pH range (3–11), maintaining >92% removal and reaching ~97% at neutral pH. In contrast, ZnO performance decreased near its point of zero charge (pH<sub>pzc</sub> 8–9), while chitosan showed high adsorption only under acidic conditions due to protonated amino groups. The superior performance of ZnO@Cs is attributed to synergistic interactions (electrostatic attraction, hydrogen bonding, and coordination bonding) (Ghanem et al., 2025). Increasing adsorbent dose (0.05–1.0 g) improved removal due to more available active sites. Nearly complete removal (>99%) was achieved at low HA concentration using only 0.05 g of ZnO@Cs, while at higher concentrations efficiency slightly decreased due to site competition, though it remained ~95%. The high removal efficiency, broad pH tolerance, and reusability observed for ZnO@Cs are consistent with broader trends reported for metal-oxide and biopolymer-based nanomaterials used as adsorbents and photocatalysts in wastewater treatment (Alalwan et al., 2022).

Adsorption followed a two-stage pattern: rapid initial uptake (10–30 min) followed by slower

diffusion-controlled equilibrium at ~90–120 min. ZnO@Cs showed the fastest kinetics due to uniform ZnO dispersion enhancing active site accessibility and mass transfer (Kaczorowska and Bożejewicz, 2024).

Temperature increased adsorption efficiency, confirming an endothermic process supported by positive  $\Delta H^\circ$ . Higher temperatures improve HA mobility and reduce diffusion resistance. Increasing initial HA concentration also enhanced adsorption due to a higher concentration gradient, with ZnO@Cs maintaining >93% removal even at high concentrations because of multiple active binding sites including  $\text{Zn}^{2+}$  and protonated amino groups (Murtaza et al., 2022).

#### *Kinetics and Rate-Controlling Mechanisms*

Kinetic studies using pseudo-first-order, pseudo-second-order, intraparticle diffusion, and film diffusion models showed that the pseudo-second-order model best fit the data ( $R^2 \approx 1$ ), indicating that chemisorption is the dominant mechanism involving electron sharing or exchange.

Although chemisorption governs the process, diffusion also contributes. Intraparticle diffusion plots showed multilinearity, indicating multiple stages: (1) rapid surface adsorption, followed by (2) slower diffusion into pores. Deviation from the origin confirms that intraparticle diffusion is not the sole rate-limiting step. Film diffusion also occurs alongside surface and pore diffusion, explaining the observed two-stage adsorption behavior. Comparable kinetic behavior has been shown for the adsorption of humic compounds onto several metal-oxide and polymer-based composite adsorbents (Habuda-Stanić et al., 2021).

The pseudo-second-order fit alone does not conclusively prove chemisorption; however, together with the FTIR band shifts and SEM changes after adsorption, it supports strong interactions between HA and the  $-\text{OH}$ ,  $-\text{NH}$ ,  $\text{Zn}-\text{OH}$ , and  $\text{Zn}-\text{O}$  sites of ZnO@Cs. These interactions likely involve electrostatic attraction, hydrogen bonding, and surface complexation with the carboxyl and phenolic groups of HA. The Langmuir parameters indicate strong adsorption affinity, although the moderate ( $q_{\text{max}}$ ) suggests that the main advantage of ZnO@Cs is affinity and operational stability rather than exceptionally high capacity.

#### *Thermodynamic Interpretation of the Adsorption Process*

Comparable thermodynamic behavior has been shown for the adsorption of organic contaminants onto chitosan-based composite materials and metal-oxide adsorbents (Hilmioglu and Yumat, 2024). Thermodynamic analysis showed that HA adsorption is spontaneous, as indicated by negative  $\Delta G^\circ$  values, which become more negative with increasing temperature. This confirms enhanced adsorption at higher temperatures. Positive  $\Delta H^\circ$  values indicate an endothermic process, meaning heat facilitates adsorption by weakening hydration layers around both HA molecules and adsorbent surfaces. Positive  $\Delta S^\circ$  values reflect increased randomness at the solid–liquid interface due to water molecule displacement during adsorption. Overall, the adsorption process is driven by both enthalpic and entropic effects, confirming a thermodynamically favorable and structurally dynamic adsorption mechanism.

#### *Real-Water Applicability and Matrix Effects*

Although ZnO@Cs showed excellent HA removal in model solutions, its performance in natural waters may be affected by dissolved ions, suspended solids, and heterogeneous natural organic matter. Therefore, matrix-effect studies are required before practical application. Experiments should be performed under the optimized conditions identified in this study (20 mg  $\text{L}^{-1}$  HA, 0.05 g adsorbent in 25 mL, pH 7.0, 120 min, 25°C, 300 rpm), with all tests conducted in triplicate. The effects of common background ions, including bicarbonate, chloride, calcium, and magnesium, should be evaluated individually and in combination using concentrations representative of drinking water. Bicarbonate is expected to reduce adsorption by increasing

**Table 3.** Comparison of HA adsorption performance of ZnO@Cs BC with other adsorbents.

| Adsorbent                           | $q_{\max}$ (mg/g) | Optimum pH | Reference                |
|-------------------------------------|-------------------|------------|--------------------------|
| ZnO@Cs BC                           | 4.535             | 7.0        | This study               |
| Bare Al <sub>2</sub> O <sub>3</sub> | 0.98 - 1.20       | 6.0        | Al-Mur & Jamal (2026)    |
| Pristine Bentonite                  | 1.12              | 5.0        | Bougdah, et al., (2017)  |
| Activated Biochar (N-AB)            | 1.306             | 7.0        | Chu et al. (2017)        |
| Pumice stone                        | 38.22             | 3.0        | Soleimani et al., (2019) |
| Eggshell powder                     | 101               | 4.0        | Mehri et al., (2022)     |
| DMSO-Bentonite                      | 1.465             | 5.0        | Bougdah, et al., (2017)  |
| Pristine Chitosan                   | 2.50              | 4.0-5.0    | Queiroz et al. (2015)    |

alkalinity and competing with HA for positively charged surface sites, whereas chloride mainly influences ionic strength. Calcium and magnesium may enhance adsorption at low concentrations through cation bridging between HA and ZnO@Cs but reduce adsorption at higher concentrations because of competition for active sites or mineral deposition. Consequently, the overall matrix effect should be determined experimentally. Adsorption performance in complex matrices can be expressed as:

$$\text{Relative performance (\%)} = (q_{e, \text{matrix}} / q_{e, \text{control}}) \times 100$$

where  $q_{e, \text{matrix}}$  and  $q_{e, \text{control}}$  are the equilibrium adsorption capacities measured in matrix-containing and deionized water, respectively. Statistical significance should be evaluated using one-way ANOVA ( $p < 0.05$ ). Competition from natural organic matter should also be investigated by adding dissolved organic carbon (2–10 mg C L<sup>-1</sup>). A decrease in HA removal would indicate competition for the functional groups responsible for adsorption. Because UV–Vis measurements may be affected by other chromophoric compounds, dissolved or total organic carbon analyses should be used to confirm organic matter removal. The influence of turbidity should be examined using kaolin suspensions (0–50 NTU). Matrix blanks should be included, and samples should be filtered or centrifuged before UV–Vis analysis to minimize light-scattering effects. For real-water validation, natural surface or drinking water should be characterized for pH, conductivity, alkalinity, hardness, turbidity, dissolved organic carbon, and major ions before adsorption experiments. Both unspiked samples and samples spiked with HA (5 and 20 mg L<sup>-1</sup>) should be tested, with filtered and unfiltered waters evaluated separately. The practical evaluation involves measuring zinc (Zn) release from the composite material using ICP–OES, and assessing the adsorbent regeneration process over at least five adsorption-desorption cycles, in order to determine the effects of water chemistry on stability and reusability.

#### *Comparative Analysis with Other Adsorbents*

To evaluate the performance of the synthesized ZnO@Cs BC material, its HA adsorption capacity was compared with that of other adsorbents reported in previous studies (Table 3). The ZnO@Cs BC (with a maximum adsorption capacity of  $q_{\max} = 4.535$  mg/g) significantly outperforms many common, low-cost adsorbents; for instance, raw bentonite and certain types of biochar exhibit much lower adsorption capacities and often fail to achieve the high removal rates (exceeding 99%) demonstrated by ZnO@Cs BC at neutral pH.

#### *Economic and Environmental Considerations*

At the optimum dosage of 2.0 kg m<sup>-3</sup>, ZnO@Cs has an estimated material cost of US\$19.8

**Table 4.** Regeneration performance of ZnO@Cs BC over five adsorptions–desorption cycles

| Cycle | Removal efficiency (%R) | Regeneration efficiency (% of initial) |
|-------|-------------------------|----------------------------------------|
| 1     | 100 ± 0.5               | 100                                    |
| 2     | 96.1 ± 0.6              | 96.2                                   |
| 3     | 93.3 ± 0.7              | 93.3                                   |
| 4     | 89.8 ± 1.0              | 89.8                                   |
| 5     | 85.5 ± 1.1              | 85.5                                   |

m<sup>-3</sup> for single use. Reuse over five cycles reduces this to approximately US\$4.3 m<sup>-3</sup>, although energy, labor, regeneration, washing, and disposal costs are excluded. Despite this reduction, the material remains less economical than powdered activated carbon because of its much higher required dosage. Future cost improvements should therefore focus on lowering the adsorbent dose and increasing reuse efficiency. Environmentally, chitosan offers value as a renewable material derived from crustacean waste, but its production still requires chemicals, energy, and water. ZnO enhances performance but introduces impacts from synthesis, calcination, possible Zn<sup>2+</sup> leaching, and nanoparticle release. Regeneration also generates chemical and waste burdens. Continuous-flow studies, leaching tests, durability assessment, and life-cycle analysis are therefore needed before ZnO@Cs can be considered economically and environmentally sustainable.

#### *Reusability and Stability of the Composite Adsorbent*

The reusability of ZnO@Cs BC was evaluated under optimum conditions (pH 7, HA concentration = 20 mg L<sup>-1</sup>, contact time = 120 min, 25°C) over five adsorptions–desorption cycles. After each cycle, the adsorbent was separated by filtration, washed with deionized water, desorbed using 0.1 M NaOH for 30 min at 150 rpm, washed to neutral pH, and dried at 60°C for 4 h (Hilmioglu and Yumat, 2024). Regeneration efficiency (RE%) was calculated as:  $RE (\%) = (q_n / q_1) \times 100$

Where  $q_n$  and  $q_1$  represent adsorption capacities at the  $n$ th and first cycles, respectively. The ZnO@Cs composite exhibited excellent stability and reusability, retaining about 85% of its initial adsorption efficiency after five cycles (Table 4). The slight reduction in performance may be attributed to partial pore blockage, residual HA deposition, and incomplete regeneration of active amino sites after alkaline treatment (Singh et al., 2023). The strong interaction between ZnO nanoparticles and the chitosan matrix likely prevented ZnO leaching while preserving the active functional groups responsible for adsorption. Similar performance reductions have been reported for chitosan-based metal oxide composites after repeated reuse cycles (Li et al., 2025). Overall, the results demonstrate that ZnO@Cs BC is a stable, regenerable, and cost-effective adsorbent for wastewater treatment applications.

## CONCLUSION

A green ZnO@Cs bio-composite was successfully developed as an efficient and sustainable adsorbent for humic acid removal from water. Characterization analyses (FTIR, XRD, SEM/EDX, TGA, and DSC) confirmed the successful incorporation and uniform distribution of ZnO within the chitosan matrix, resulting in improved crystallinity, surface characteristics, and thermal stability. The composite achieved high HA removal efficiencies (>90%) across a wide range of pH values, temperatures, and pollutant concentrations, demonstrating superior operational stability compared with conventional adsorbents. Kinetic studies revealed that adsorption followed the pseudo-second-order model, suggesting adsorption governed by strong

surface interactions involving electrostatic attraction, hydrogen bonding, and coordination interactions between HA molecules and Zn–O, –OH, and –NH functional groups.

-Equilibrium data were best described by the Langmuir isotherm model, suggesting predominant monolayer adsorption on energetically favorable adsorption sites. Thermodynamic analysis confirmed that the adsorption process was spontaneous and endothermic. In addition, the ZnO@Cs composite maintained high adsorption performance after repeated adsorption–desorption cycles, highlighting its good stability and reusability. Overall, the ZnO@Cs bio-composite represents a promising, environmentally friendly, and cost-effective material for HA removal in water purification applications.

## DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## CONFLICT OF INTEREST

The authors declare no conflict of interest.

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