

Article

Eco-Friendly Dye Removal Using Chitosan: Characterization and Kinetic Modeling of Methylene Blue and Methyl Orange Adsorption

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Abstract

This study investigates the potential of pure chitosan powder as an effective, sustainable, and low-cost adsorbent for the removal of synthetic dyes from aqueous media. The work demonstrates the potential of pristine chitosan for practical wastewater treatment applications by adsorbing two commonly used textile dyes, methyl orange (MO) and methylene blue (MB). To elucidate the adsorption mechanism, chitosan was comprehensively characterized using zeta potential analysis, Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscopy coupled with Energy-Dispersive X-ray Spectroscopy (SEM–EDX), Thermogravimetric Analysis (TGA), Brunauer–Emmett–Teller (BET) surface area analysis, and point of zero charge (pHpzc) determination. FTIR analysis revealed notable shifts in $-NH_2$ and $-OH$ functional groups after dye adsorption, confirming their involvement in electrostatic interactions and hydrogen bonding with MO and MB. SEM images demonstrated significant surface morphological changes following adsorption, while EDX spectra confirmed successful dye uptake through the appearance of sulfur and nitrogen signals characteristic of MO and MB, respectively. Zeta potential and pHpzc results explained the strong pH-dependent adsorption behavior, highlighting favorable electrostatic attraction between chitosan and the ionic dyes. The optimum adsorption conditions were achieved at adsorbent dosages of 0.5 g for MO and 1.0 g for MB, a contact time of 30 min, initial dye concentrations of 20 and 100 mg/L, and solution pH values of 3 for MO and 9 for MB at room temperature. The adsorption data fit the Langmuir isotherm model, indicating monolayer adsorption on a homogeneous chitosan surface, with maximum adsorption capacities of 7.843 mg/g for MO and 7.605 mg/g for MB. Kinetic studies showed that adsorption followed the pseudo-second-order model, suggesting chemisorption as the dominant mechanism. Thermodynamic analysis indicated that the adsorption process was endothermic and non-spontaneous under the investigated conditions. In conclusion, these findings demonstrate that unmodified chitosan is a practical, eco-friendly adsorbent for dye removal, achieving removal efficiencies comparable to many modified chitosan composites, and represents a promising candidate for sustainable wastewater treatment.



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1. Introduction

Textile dyeing, papermaking, plastics processing, and cosmetics manufacturing are all industrial activities that generate significant wastewater containing synthetic dyes. These dyes are very harmful to aquatic ecosystems and human health [1]. Methylene blue (MB), a cationic thiazine dye, and methyl orange (MO), an anionic azo dye, are two of the most common contaminants found in industrial effluents. This is because they are widely used and highly chemically stable [2–6]. These dyes are not very biodegradable and are very resistant to natural processes that break them down. This means they stay in water bodies, where they block light from penetrating, inhibit photosynthesis, and are toxic, mutagenic, and carcinogenic to living things [7–10]. So, it is still essential to find practical, long-lasting, environmentally friendly ways to remove dyes from wastewater before it is released into the environment [11].

Adsorption has become one of the most effective methods for removing dyes because it is easy to use, inexpensive, and effective [12]. In this context, chitosan, a naturally derived polysaccharide obtained by deacetylation of chitin, has garnered significant attention as a bioadsorbent due to its biodegradability, non-toxicity, and high density of amino ($-NH_2$) and hydroxyl ($-OH$) functional groups [13–16]. These functional groups create active binding sites for dye molecules through hydrogen bonding, electrostatic attraction, and chelation, which is why chitosan is so helpful for treating wastewater.

In the last ten years, most studies on chitosan-based adsorption have focused on chemical modification or composite formation to address problems with pure chitosan, such as its low surface area, limited mechanical stability, and sensitivity to acidic environments [14]. There have been reports of various methods, such as chemical grafting, crosslinking, and the addition of inorganic or carbon-based fillers. For instance, amino-ethyl chitosan hydrogels [17], chitosan–graphene oxide aerogels [18], magnetic Fe_3O_4 /chitosan composites [19], ZnO–chitosan photocatalytic composites [20], and chitosan–lignin membranes [21] have all been made to make dyes stick better and be used more than once. Chitosan–MOF composites and chitosan–biochar systems [22], which are more recent examples of advanced hybrid materials, have been shown to have high adsorption capacities for both MB and MO. While these modified materials often have better adsorption properties, they also pose significant challenges, including complicating the synthesis process, increasing production costs, reducing biodegradability, and making large-scale use more difficult. Because of this, the growing use of chemical modification has raised questions about the practicality and environmental friendliness of these adsorbents for treating wastewater in the real world.

Even though extensive research has examined modified chitosan adsorbents, very few have questioned whether chemical modification is essential. Specifically, insufficient attention has been paid to elucidating whether adsorption enhancement can be achieved through functional optimization and mechanistic regulation of pristine chitosan, rather than material modification. Furthermore, systematic evaluations of pristine chitosan's efficacy against both anionic and cationic dyes, underpinned by thorough physicochemical characterization and adsorption modeling, are limited. This gap has led to an unspoken belief in the field that altering the chemical structure is necessary to achieve high adsorption efficiency. This belief lacks sufficient mechanistic support.

In this context, the current study contests the dominant paradigm by reassessing pristine chitosan as a competitive bio-adsorbent through functional optimization rather than chemical alteration. Chitosan was synthesized from shrimp shell waste under controlled processing conditions to maintain functional group accessibility and surface reactivity. The adsorption behavior towards MB and MO was systematically examined to clarify the influences of surface chemistry, surface charge dynamics, and pH-dependent electrostatic interactions.

The main goal of this study is to examine how well unmodified chitosan adsorbs cationic and anionic dyes from water, how quickly it does so, how it behaves at equilibrium, and how many times it can be reused. This study seeks to elucidate the mechanistic aspects of dye–chitosan interactions by combining extensive physicochemical characterization with adsorption modeling. It aims to demonstrate that unmodified chitosan can serve as a cost-effective, scalable, and environmentally sustainable adsorbent.

2. Materials and Methods

2.1. Materials

The raw material used in this study for chitosan extraction was shrimp shell waste, obtained from a local seafood processing facility. Shrimp shells were selected due to their high content of chitin, a naturally occurring polysaccharide and the primary precursor for chitosan synthesis. Before processing, the shells were thoroughly washed with tap water to remove residual organic matter and then rinsed with distilled water. They were subsequently air-dried and stored in sealed containers at room temperature until further use.

All reagents and solvents used were of analytical grade. They purchased from Sigma-Aldrich (St. Louis, MO, USA), including hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, pellets), glacial acetic acid (CH₃COOH), and ethanol (C₂H₅OH, 99%). Two synthetic dyes, methyl orange (MO) and methylene blue (MB), were employed to evaluate the adsorption performance of chitosan as a model anionic and cationic adsorbent, respectively. Deionized water (resistivity $\geq 18.2 \text{ M}\Omega\cdot\text{cm}$) was used in the preparation of all aqueous solutions.

2.2. Using Shrimp Shells to Prepare Chitosan

Chitosan was prepared from shrimp shell waste using a well-established three-step chemical process involving demineralization, deproteinization, and deacetylation. These steps were sequentially performed to isolate chitin from the biomass and convert it to chitosan under alkaline conditions. Demineralization was performed to eliminate inorganic components, primarily calcium carbonate (CaCO₃), from the shrimp shell matrix. Shell powder was soaked in 1 M HCl at a solid-to-liquid ratio of 1:15 (*w/v*) and continuously stirred at room temperature for 24 h. This treatment produced effervescence due to CO₂ release, confirming the removal of carbonates. Using distilled water, the residue was thoroughly cleaned until the filtrate's pH was neutral, then air-dried. The acid-treated shells were subjected to alkaline hydrolysis to remove proteinaceous materials. The demineralized mass was treated with 1 M NaOH at 90 °C for 4 h under reflux, maintaining a solid-to-liquid ratio of 1:10 (*w/v*). After treatment, the mixture was cooled, filtered, and the residue was repeatedly rinsed with distilled water until the filtrate reached neutrality (pH ≈ 7). This step yielded crude chitin, which was then dried overnight at 60 °C. To convert chitin to chitosan, deacetylation was performed using concentrated alkali. The dried chitin was refluxed in 50% (*w/v*) NaOH at 100 °C for 5 h, facilitating the removal of acetyl groups from the N-acetylglucosamine backbone. The product was then filtered and washed extensively with both distilled water and ethanol until the washings reached neutral pH. An oven was used to dry the finished chitosan at 60 °C for 24 h, and the dried chitosan was stored in airtight containers [23].

2.3. Characterization of Chitosan

To assess the suitability of the prepared chitosan for adsorption applications, a series of physicochemical and structural characterizations was performed. Each technique provided

insight into different functional aspects of the material, including surface area, morphology, surface charge, crystallinity, thermal stability, and chemical functionality.

The textural properties, including surface area and pore characteristics of the chitosan, were determined using nitrogen adsorption–desorption isotherms interpreted via the Brunauer–Emmett–Teller (BET) method. The BET surface area of the chitosan was found to be $4.076 \text{ m}^2/\text{g}$, consistent with values reported for biopolymeric adsorbents without extensive modification [24]. Although relatively modest, the surface area is complemented by active amine and hydroxyl groups, which facilitate strong chemical interactions during adsorption. To further evaluate the pore size distribution, the Barrett–Joyner–Halenda (BJH) model was applied, providing valuable insights into the material's mesoporous structure.

The point of zero charge (pHpzc) of chitosan was determined using the pH drift method, in which 0.05 g of chitosan was added to 50 mL of 0.01 M NaCl solution, with the initial pH adjusted from 2 to 12. After 24 h of equilibration under stirring, final pH values were measured, and the pHpzc was identified at the intersection point ($\Delta\text{pH} = 0$). A pHpzc value of 7.0 was recorded, indicating that the surface of the substance is negatively charged under basic conditions and positively charged under acidic conditions [25,26].

Particle size and zeta potential were assessed utilizing a dynamic light scattering (DLS) with a Malvern Zetasizer Nano ZS instrument manufactured by Malvern Panalytical and headquartered in Malvern, United Kingdom.

The average hydrodynamic diameter of the chitosan particles was 508.6 nm, suggesting good dispersion and nanoscale structuring, both of which are favorable for adsorption. Zeta potential was measured as -22.6 mV , indicating sufficient electrostatic repulsion to maintain colloidal stability and prevent particle aggregation, a key attribute for enhanced surface accessibility [27].

To identify the functional groups responsible for dye adsorption, Fourier Transform Infrared Spectroscopy (FTIR) was conducted. For this analysis, chitosan powder was homogenized with potassium bromide (KBr), then dried at 100°C for at least 6 h before being scanned over a wavenumber range of $500\text{--}4000 \text{ cm}^{-1}$. This technique enabled the detection of surface functional groups before and after exposure to dye, revealing changes associated with adsorption interactions.

The crystallographic structure of the prepared chitosan was investigated using X-ray diffraction (XRD) to evaluate its phase composition and degree of crystallinity, which influence polymer chain organization, functional group accessibility, and adsorption performance. The degree of crystallinity of the prepared chitosan was estimated from the XRD pattern using the Segal method. The crystallinity index (CrI) was calculated based on the relative intensities of the central crystalline peak at $2\theta \approx 20^\circ$ (I_{110}) and the amorphous background at $2\theta \approx 16^\circ$ (I_{am}), according to the following equation: $\text{CrI (\%)} = ((I_{110} - I_{\text{am}}) / I_{110}) \times 100$. This method is commonly used to evaluate the relative proportions of crystalline and amorphous domains in semi-crystalline polysaccharides, such as chitosan.

To examine the surface morphology and elemental composition, the material was further characterized using Scanning Electron Microscopy (SEM) with Energy-Dispersive X-ray Spectroscopy (EDX), JEOL Ltd. (Tokyo, Japan). This dual technique facilitated the visualization of microstructural features and the spatial distribution of elements involved in dye uptake.

Thermal behavior and material stability of the material were evaluated using Thermogravimetric Analysis (TGA) with an SDT Q600 instrument. The manufacturer of the SDT Q600 Thermogravimetric Analyzer is TA Instruments - Waters LLC. The company is headquartered in New Castle, DE, USA. The chitosan was heated gradually from ambient temperature to 700°C at a controlled rate of $10^\circ\text{C}/\text{min}$. The resulting thermograms

provided insight into the chitosan's decomposition profile and overall thermal resilience. Altogether, this multifaceted characterization underscores the potential of chitosan powder as an effective, thermally stable biosorbent for the removal of dye pollutants from contaminated water systems.

2.4. Batch Adsorption Experiments

To investigate the adsorption performance of chitosan for the removal of dye pollutants, a series of controlled batch experiments was conducted using MO and MB as representative anionic and cationic dyes, respectively. These studies aimed to assess the impact of different operational indicators, including pH, adsorbent dosage, initial dye concentration, contact time, and temperature, on the efficiency of dye removal.

All adsorption trials were carried out in 25 mL Erlenmeyer flasks. The flasks were agitated in an orbital shaker at a constant speed of 300 rpm to ensure homogenous mixing. After the designated contact periods, solutions were filtered through Whatman No. 1 filter paper, and the residual dye concentrations were determined spectrophotometrically at their respective maximum absorbance wavelengths (464 nm for MO and 665 nm for MB) using a UV-Vis spectrophotometer (Shimadzu UV-1800, manufactured by Shimadzu Corporation, headquartered in Kyoto, Japan).

The pH-dependent behavior of dye adsorption was evaluated over a pH range of 3–11, adjusted using either 0.1 M NaOH or 0.1 M HCl. The influence of pH on adsorption is critical because it affects the ionization of both the dye molecules and the functional groups on chitosan, such as amino and hydroxyl groups. Optimal pH values were identified based on the highest removal efficiency for each dye.

To examine the effect of adsorbent dosage, varying amounts of chitosan (0.1–2.0 g) were added to fixed-volume dye solutions. This assessment helped establish the minimum effective dose to achieve near-complete dye removal while maintaining cost-efficiency and minimizing material use.

Contact time was systematically varied from 10 to 150 min to identify the minimum duration required to reach adsorption equilibrium. Time-dependent data were later fitted to kinetic models to elucidate the mechanism and rate-controlling steps of the adsorption method.

The impact of initial dye concentration was evaluated across a range of 5 to 100 ppm. These experiments provided insights into the saturation behavior of chitosan and helped determine whether adsorption followed a monolayer or multilayer mechanism. Additionally, the data supported the calculation of adsorption capacities under varying loading conditions.

Temperature-dependent studies were performed at 25, 35, 45, and 55 °C to explore the thermodynamic feasibility of the adsorption process. Temperature effects are crucial for determining whether a process is endothermic or exothermic and for understanding the role of thermal energy in enhancing or diminishing adsorption capacity.

All batch experiments were conducted in triplicate to ensure reproducibility, and average values were used for further analysis. The percentage removal of dye was calculated using the equation:

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

where C_o is the initial dye concentration (mg/L), and C_e is the equilibrium concentration (mg/L). The amount of dye adsorbed per unit mass of chitosan at equilibrium, q_e (mg/g), was determined using:

$$\text{Adsorption capacity}(q_e) = \frac{(C_o - C_e) \times V}{m}$$

Here, V is the volume of the solution in liters, and m is the mass of the adsorbent in grams.

2.5. Adsorption Models

To gain deeper insight into the mechanisms underlying chitosan-mediated dye uptake, experimental data were analyzed using both equilibrium and kinetic models. These mathematical frameworks allow for the quantitative description of adsorption behavior and the identification of interaction types between the dye molecules and the adsorbent surface. All adsorption isotherm models and kinetic models were applied in their linearized forms. Model parameters were determined using linear regression analysis, and the goodness of fit was evaluated based on the correlation coefficient (R^2) and agreement between experimental and calculated adsorption capacities.

2.5.1. Adsorption Isotherms

Three frequently applied isotherm models, the Freundlich, Langmuir, and Temkin, were used to describe the distribution of MO and MB dye molecules between the aqueous phase and the chitosan surface at equilibrium (Table 1).

The Langmuir model assumes monolayer adsorption on a homogeneous surface with a finite number of identical binding sites. It also implies that there is no interaction between adsorbed molecules. This model is beneficial for estimating the maximum adsorption capacity ($q_{\max}$) and the affinity constant (K_L), which reflect how strongly the adsorbate binds to the surface.

The Freundlich isotherm, an empirical model, accounts for heterogeneous surface energies and multilayer adsorption. Constants K_F and n provide information on adsorption capacity and intensity, respectively. A value of $1/n$ between 0 and 1 generally indicates favorable adsorption.

The Temkin isotherm accounts for adsorbent–adsorbate interactions and assumes that these interactions cause the heat of adsorption to decrease linearly with coverage. It provides constants A_T and B_T , representing the binding energy and adsorption potential, respectively.

Each model was linearized and fitted to the experimental data using least-squares regression to evaluate the best-fitting representation.

2.5.2. Adsorption Kinetics

To evaluate the rate and mechanism of dye adsorption, two kinetic models were applied: the pseudo-first-order and pseudo-second-order models. The pseudo-first-order model, proposed by Lagergren, assumes that the rate of adsorption is directly proportional to the number of unoccupied sites. It is often used for systems where physisorption is dominant. In contrast, the pseudo-second-order model assumes that chemisorption is the rate-limiting step, involving valence forces via electron sharing or exchange between the adsorbate and the adsorbent. This model typically yields better fits for systems in which chemical bonding governs adsorption. Model fitting was assessed by comparing the linear regression coefficients (R^2) and the agreement between experimental and calculated equilibrium values (Table 1).

2.5.3. Thermodynamic Analysis

To evaluate the feasibility, nature, and energy changes associated with the adsorption of MO and MB onto chitosan, a thermodynamic study was conducted by analyzing the temperature dependence of the adsorption equilibria. Adsorption experiments were conducted at four variable temperatures (25 °C, 35 °C, 45 °C, and 55 °C) under otherwise identical conditions, and the corresponding distribution coefficients (K_d) were calculated for each

dye. The distribution coefficient was determined using the relation in Table 1. To obtain thermodynamic parameters, the Van't Hoff equation was applied in its linearized form as shown in Table 1. By plotting $\ln(K_d)$ against $1/T$, a straight line was generated, from which the enthalpy change (ΔH°) and entropy change (ΔS°) were obtained from the slope and intercept, respectively. The Gibbs free energy change (ΔG°) for each temperature was calculated using the equation in Table 1. The sign and magnitude of these thermodynamic parameters offer essential insights into the adsorption process. A negative ΔG° indicates spontaneity, while a positive ΔH° suggests an endothermic adsorption process, typically associated with chemisorption or swelling-facilitated interactions. A positive ΔS° reflects increased randomness at the solid–solution interface, often due to the release of water molecules during dye binding. All experiments were performed in triplicate, and mean values were applied to ensure consistency in thermodynamic modeling [28].

Table 1. Mathematical Expressions of Isotherm, Kinetic, and Thermodynamic Models Used in this Study.

Adsorption Model	Linear Form of Equation	Parameters	Description	References
Isotherm				
Langmuir	$\frac{1}{q_e} = \frac{1}{q_{\max}} + \left(\frac{1}{q_{\max}K_L}\right)\left(\frac{1}{C_e}\right)$ (1)	✓ ✓ ✓ ✓ C_e: the equilibrium concentration of dye (mg/L), q_e: the equilibrium adsorption capacity (mg/g). K_L: The Langmuir isotherm constant.	Monolayer adsorption on a uniform surface	[29]
Freundlich	$\ln q_e = \ln K_f + \frac{1}{n_f} \ln C_e$ (2)	✓ ✓ ✓ K_f: Freundlich isotherm constant. q_{max}: the maximum adsorption capacity (mg/g). n: the adsorption intensity.	Heterogeneous surface and multilayer adsorption	[30]
Temkin	$q_e = B_T \ln A_T + B_T \ln C_e$ (3)	✓ ✓ A_T: equilibrium binding constant (L/min) B_T: the adsorption free energy constant (J/mol)	Accounts for adsorbate–adsorbate interactions	[31]
Kinetics				
Pseudo-First-Order	$\ln(q_e - q_t) = \ln q_e - k_1 t$ (4)		Physical adsorption; rate depends on unoccupied sites	[32,33]
Pseudo-Second-Order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ (5)		Chemisorption; rate depends on adsorbate and adsorbent interaction	[34,35]
Thermodynamics				
Gibbs free energy change	$\Delta G^\circ = -RT \ln K_d$ (6)	✓ ✓ ✓ ✓ ΔH°: enthalpy change ΔS°: entropy change ΔG°: Gibbs free energy K_d: distribution coefficient	Indicates spontaneity; negative values suggest spontaneous adsorption	
Distribution Coefficient	$K_d = q_e / C_e$ (7)	✓ ✓ q_e: equilibrium adsorption capacity and C_e: equilibrium concentration R: universal gas constant (8.314 J/mol·K) T: temperature in Kelvin	Ratio of adsorbed to free dye at equilibrium	
Van't Hoff equation	$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$ (8)	✓	Relates temperature to equilibrium constant	

2.6. Desorption Experiments

Desorption experiments were performed to evaluate the regeneration and reusability potential of the prepared chitosan biosorbent after adsorbing the dye. Following the

adsorption equilibrium, the spent chitosan was separated by filtration and thoroughly washed with deionized water to remove residual dye molecules. Desorption was then carried out by agitating the dye-loaded chitosan in various desorbing agents (0.1 M HCl, 0.1 M NaOH, 0.1 M NaCl, ethanol, and distilled water) at a solid-to-liquid ratio of 1:20 (*w/v*) for 2 h at room temperature. After desorption, the chitosan was again separated and washed with deionized water [36]. The amount of dye desorbed was quantified by measuring the concentration of dye in the desorption solution utilizing a UV-Vis spectrophotometer at the respective wavelength for each dye. The desorption efficiency (%) was calculated as:

$$\%R = \left(\frac{A_{de}}{A_{ad}} \right) \times 100 \quad (9)$$

where A_{de} (mg g^{-1}) is the amount of metal desorbed, and A_{ad} (mg g^{-1}) is the amount of metal initially adsorbed. This metric allowed for a quantitative comparison of desorption performance across the different agents. This procedure was repeated at least 3 times to assess the biosorbent's stability and regeneration capacity.

3. Results and Discussions

3.1. Characterizations

3.1.1. Fourier Transform Infrared Spectroscopy (FT-IR) Analysis

FTIR was used to investigate the functional groups in chitosan before and after adsorption of MO and MB, thereby elucidating the interaction mechanisms between the dye molecules and the chitosan adsorbent (Figure 1). The FTIR spectrum of raw chitosan (black line) displays a broad absorption band around 3430 cm^{-1} , which corresponds to the overlapping O–H and N–H stretching vibrations, characteristic of hydroxyl and amino groups in chitosan [37]. A peak at $\sim 2920 \text{ cm}^{-1}$ corresponds to aliphatic C–H stretching, while the band near 1650 cm^{-1} represents the C=O stretching vibration of amide I groups, typically attributed to residual N-acetyl groups in chitosan. The band at $\sim 1590 \text{ cm}^{-1}$ can be linked to N–H bending of primary amines, and the peak at $\sim 1380 \text{ cm}^{-1}$ is due to C–H bending. The region between 1150 and 1020 cm^{-1} shows C–O–C stretching vibrations, indicative of the polysaccharide backbone [38]. These spectral features confirm the semi-crystalline structure of chitosan and the presence of reactive functional groups capable of binding dyes.

After MO adsorption (red line), significant spectral shifts and intensity changes were observed. The broad band at 3430 cm^{-1} slightly decreased in intensity, suggesting the involvement of hydroxyl and amino groups in hydrogen bonding with MO molecules [39]. The amide I band near 1650 cm^{-1} shifted slightly and broadened, indicating potential electrostatic interaction between the negatively charged sulfonic acid groups of MO and the protonated –NH_3^+ groups of chitosan [37]. Additional new or intensified bands observed between 1140 and 1000 cm^{-1} are attributed to the aromatic sulfonate groups in MO, confirming the presence of dye molecules on the chitosan surface [40]. These spectral modifications are consistent with previously reported findings, which confirmed that MO binds to chitosan mainly via electrostatic interactions and hydrogen bonding involving functional groups such as –OH and –NH_2 [39].

The FTIR spectrum of Chitosan-MB (blue line) reveals similar trends. The decrease in intensity of the 3430 cm^{-1} band again suggests the participation of hydroxyl and amino groups in bonding. Additionally, a shift in the amide I region and the emergence of distinct peaks around 1600 and 1400 cm^{-1} correspond to the aromatic amine vibrations in MB [41]. These bands confirm the adsorption of MB onto chitosan, likely through electrostatic interactions between the positively charged MB molecules and the negatively charged sites or lone pairs on the amino groups of chitosan. Furthermore, π – π interactions between the aromatic rings of MB and chitosan have also been suggested as a secondary adsorption

mechanism [37]. The overall changes indicate successful dye binding and are supported by other studies, which report similar spectral transformations upon MB adsorption onto amine-rich biopolymers [42].

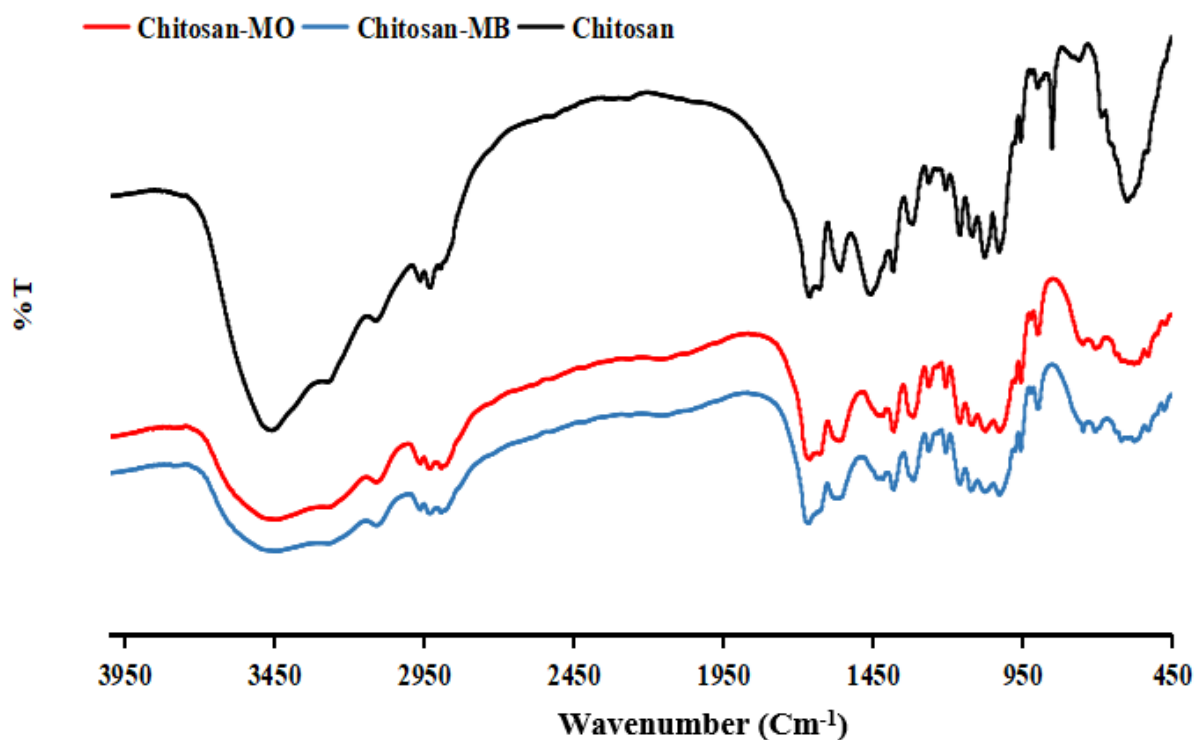


Figure 1. FTIR spectra of pure Chitosan (black), Chitosan modified with Methyl Orange (Chitosan-MO, red), and Chitosan modified with Methylene Blue (Chitosan-MB, blue).

FTIR research reveals that the adsorption of both MO and MB onto chitosan is predominantly influenced by electrostatic interactions, hydrogen bonding, and possibly π - π stacking. The reduction in shift and intensity at 3430 cm^{-1} indicates that the hydroxyl and amino groups on chitosan are involved in binding. The pH-dependent surface charge of chitosan, as evidenced by the pHpzc, elucidates these interactions. At $\text{pH} < 7.2$, the protonated $-\text{NH}_3^+$ groups attract the negatively charged sulfonate groups of MO, as evidenced by changes in the amide I band and the emergence of new peaks at $1140\text{--}1000\text{ cm}^{-1}$. Conversely, at $\text{pH} > 7.2$, the diminished protonation of chitosan enhances the adsorption of MB through electrostatic interactions, complemented by π - π stacking between the aromatic rings of MB and chitosan. The findings underscore the essential role of surface charge dynamics in the selective adsorption of anionic and cationic dyes, together with the varying affinities of chitosan for each dye type, as evidenced by the zeta potential and pHpzc data.

3.1.2. SEM and EDX Analysis

The interaction of chitosan with MO and MB was investigated using scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX), providing a detailed view of the surface structure and elemental composition before and after dye adsorption (Figure 2). Initially, the SEM image of unmodified chitosan revealed a relatively clean surface with fine, fibrous textures and linear features. These patterns suggest a semi-crystalline structure typical of chitosan films formed through drying techniques that allow polymer chains to align. Such a structure, featuring moderate porosity and surface roughness, offers ideal conditions for adsorbing contaminants from solution. Previous reports by [43] have described similar morphologies in native chitosan, emphasizing its suitability as a biosorbent due to its reactive surface groups and stable, film-like structure.

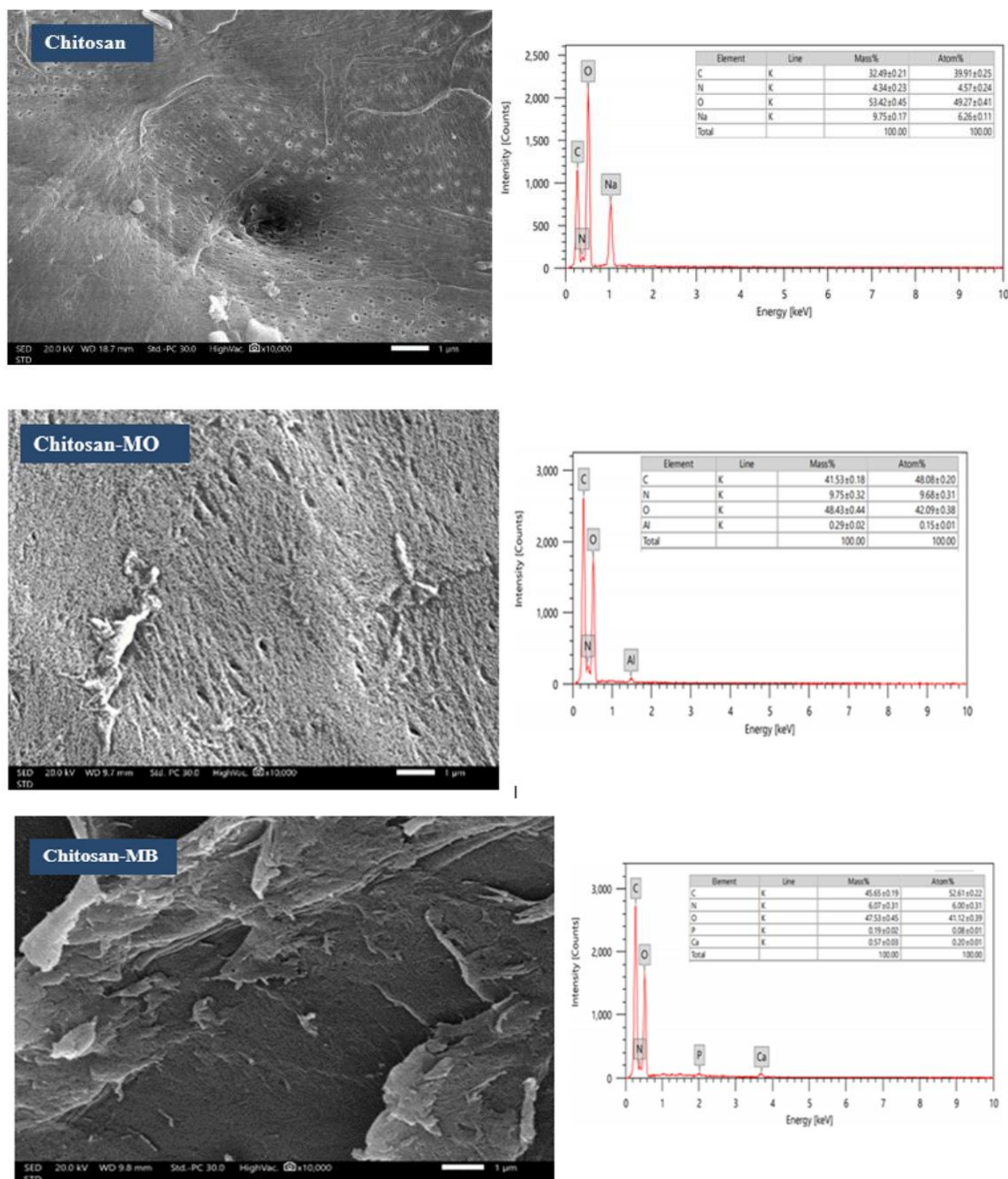


Figure 2. Combined SEM and EDX analysis of chitosan before and after methyl orange (MO) and methylene blue (MB) adsorption.

After exposure to MO, noticeable changes in the chitosan surface were observed. The SEM image of the chitosan-MO sample showed the formation of grooves, ridges, and irregular surface pits, indicating that the dye had interacted with and disrupted the

polymer surface. The appearance of lighter patches may be due to accumulated dye residues or surface-level complexes formed during adsorption. These physical alterations suggest that MO molecules successfully bonded to the chitosan, causing slight degradation or rearrangement of the surface layer. This is further confirmed by the EDX spectrum, which showed the emergence of a sulfur peak, a clear marker of the sulfonate groups in methyl orange. Since sulfur is not part of the original chitosan structure, its presence confirms dye uptake. Studies by [44] reported similar findings, noting that sulfur detection by EDX is a reliable indicator of MO adsorption and that surface roughening typically accompanies strong electrostatic interactions between the dye and chitosan's positively charged amine groups.

The structural response of chitosan to MB was even more pronounced. SEM images of the chitosan-MB sample displayed a fragmented, brittle appearance with flake-like layers, visible cracks, and sharp-edged features. This kind of surface damage is often associated with swelling and shrinking cycles that occur during dye adsorption and subsequent drying. These changes suggest a more aggressive interaction between MB and chitosan, likely involving electrostatic forces, hydrogen bonding, and possibly π - π stacking between MB's aromatic rings and the polymer matrix. The EDX analysis supported this, revealing an increased nitrogen signal on the surface. Since methylene blue is rich in nitrogen, this elemental signature provides direct evidence of its successful adsorption. Occasionally, sulfur peaks may also be seen due to the dye's molecular structure. These findings are consistent with reports by [45], who observed similar elemental changes and surface damage when chitosan was used to adsorb cationic dyes like MB.

3.1.3. Brunauer-Emmett-Teller Surface Area

The adsorption performance of a solid adsorbent is generally associated with its specific surface area, as this factor determines the number of available binding sites for pollutant adsorption. Nitrogen adsorption-desorption tests done at 77 K showed that the chitosan we made has a BET surface area of only $4.076 \text{ m}^2 \text{ g}^{-1}$. This number is precisely what you would expect from pure, unmodified biopolymeric adsorbents. It shows that chitosan-based materials have a dense molecular packing and very few pores through which gas can enter [24]. In Figure 3, the N_2 adsorption-desorption isotherm shows that nitrogen uptake is slow and weak over the entire range of relative pressures. There is no clear adsorption knee at low P/P_0 values. This behavior indicates that there is no accessible microporosity and that nitrogen adsorption is mainly controlled by surface coverage rather than pore filling. A weak hysteresis loop shows up only at high relative pressures ($P/P_0 > 0.8$). This is usually associated with capillary condensation in interparticle voids, not in real mesoporous channels. Isotherm characteristics like these are often seen in chitosan and other natural polymers. This is because the polymer chains prevent nitrogen from entering the internal structure.

The BJH pore size distribution analysis (Figure S1) provided additional information on the pore structure. The BJH plot shows that pore sizes span a wide range, with the most important ones between 30 and 40 nm. This pore size range is mainly composed of macroporous or interparticle spaces that form when particles come together and dry, rather than from the chitosan matrix itself. The lack of sharp, well-defined mesopore peaks further supports the idea that chitosan's textural porosity is limited and mainly on the outside. These results corroborate SEM observations, which reveal a dense polymeric structure with restricted internal pore formation.

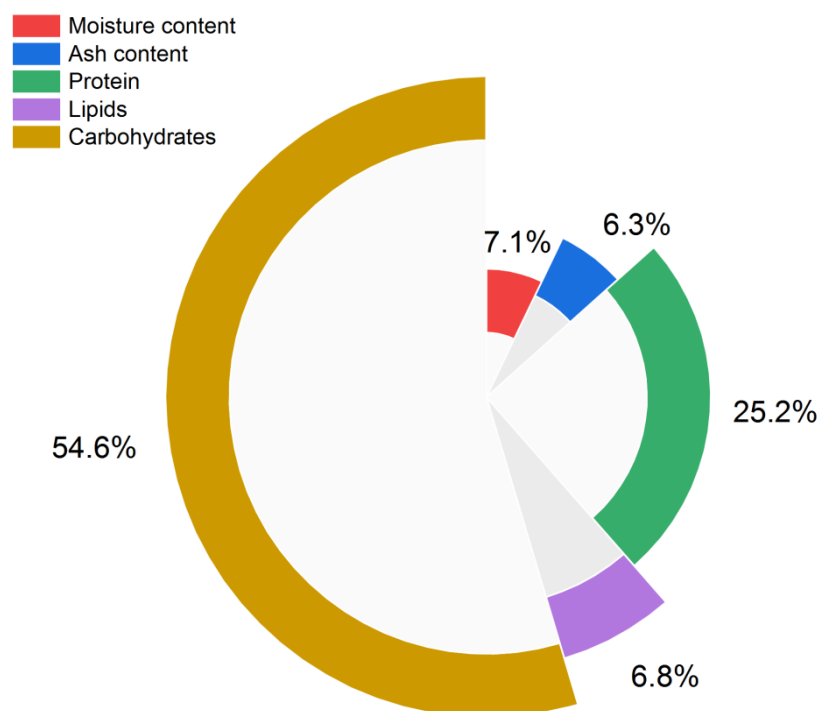


Figure 3. The bar diagram reveals the composition of Chitosan.

The BET surface area of chitosan is not very large compared to highly porous inorganic adsorbents. Still, surface area alone does not tell the whole story about how well it adsorbs. Chitosan's adsorption capacity is primarily determined by its chemical properties, not by the surface area available to gases. As shown by compositional analysis (Figure S1), chitosan contains many polysaccharides, indicating it has many reactive amino ($-NH_2$) and hydroxyl ($-OH$) groups. These functional groups serve as robust, selective binding sites, facilitating adsorption via electrostatic interactions, hydrogen bonding, and chelation. As a result, chitosan's adsorption capacity is much higher than would be expected based solely on its BET surface area.

This combination of low textural porosity and abundant surface functional groups explains why pure chitosan can adsorb ionic contaminants effectively, despite its low BET surface area. The results clearly show that surface chemistry and surface interactions, not pore-driven physical adsorption, control adsorption. This indicates that chitosan is a good bioadsorbent for wastewater treatment.

Consequently, the material's modest surface area does not limit its overall adsorption efficacy. The high removal efficiencies achieved for both methyl orange and methylene blue are governed by chemisorption, driven by the abundant and accessible functional groups on the chitosan surface. In this context, the adsorption capacity is a function of the density and reactivity of these binding sites rather than the material's textural porosity, confirming that unmodified chitosan's performance is dictated by its surface chemistry rather than its physical surface area.

3.1.4. Zeta Potential and Particle Size

The data shown in Figure 4 illustrates the particle size distribution (A) and zeta potential (B) of chitosan nanoparticles. The average particle size of chitosan was 508.6 nm, which is ideal for ensuring both dispersion stability and high surface reactivity. As shown in Figure 4A, the size distribution indicates a predominant population of particles within a narrow range, ensuring consistent, uniform interaction with external agents.

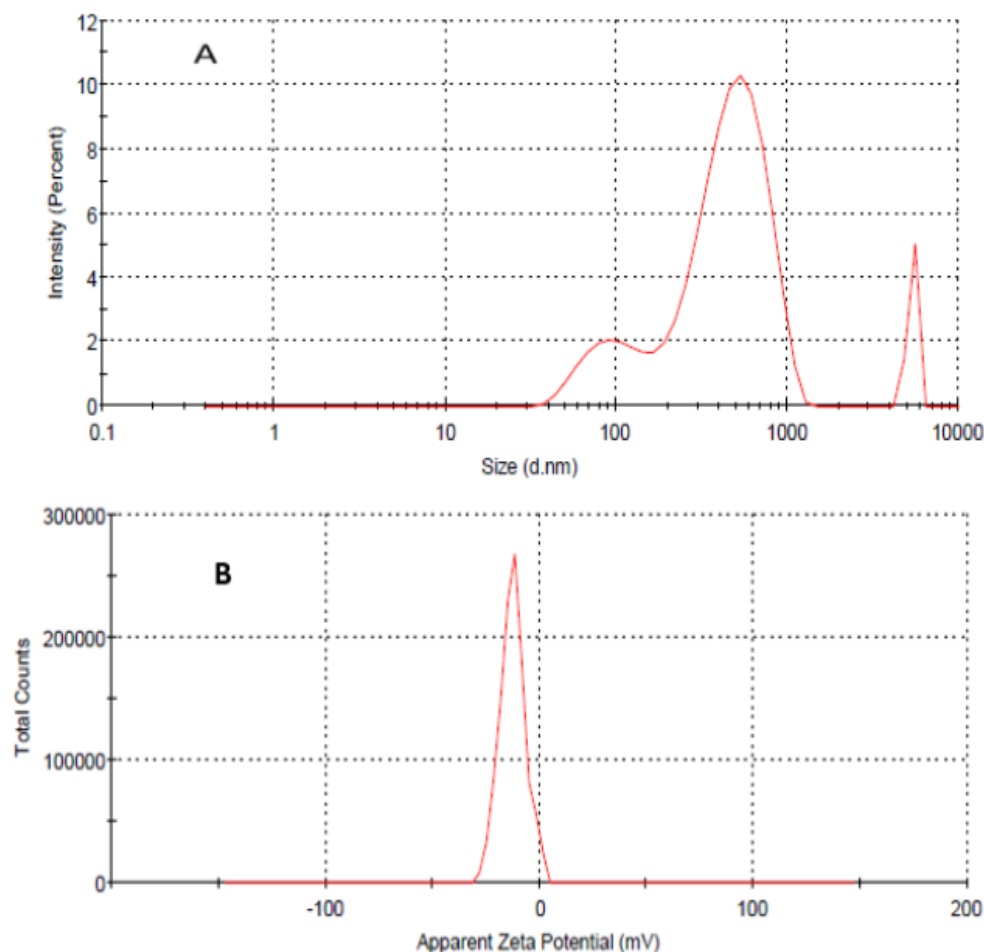


Figure 4. Particle size (A) and zeta potential (B) distribution of the chitosan. The Size average is 508.6 nm.

The zeta potential of -22.6 mV reflects the electrostatic charge on the chitosan particles. This value, displayed in Figure 4B, suggests that the colloidal system remains stable, with sufficient repulsive forces to prevent particle aggregation. A stable dispersion is crucial for maintaining optimal adsorption properties, especially in environmental and biomedical applications where uniform particle distribution is needed to maximize surface-area interaction with contaminants or targets [27].

The combination of these two properties, an appropriate particle size and negative surface charge, ensures the chitosan nanoparticles remain suspended over time without agglomerating. This enhances the nanoparticles' ability to interact with various substances, a feature essential for applications requiring efficient, prolonged adsorption [46].

3.1.5. X-Ray Diffraction (XRD)

The structural nature of the extracted chitosan was investigated by X-ray diffraction, and the resulting diffractogram is shown in Figure 5. The pattern reveals the characteristic semicrystalline structure of chitosan, defined by the coexistence of ordered crystalline domains and disordered amorphous regions. This dual nature is evidenced by the presence of both sharp, well-defined diffraction peaks superimposed on a broad, underlying hump.

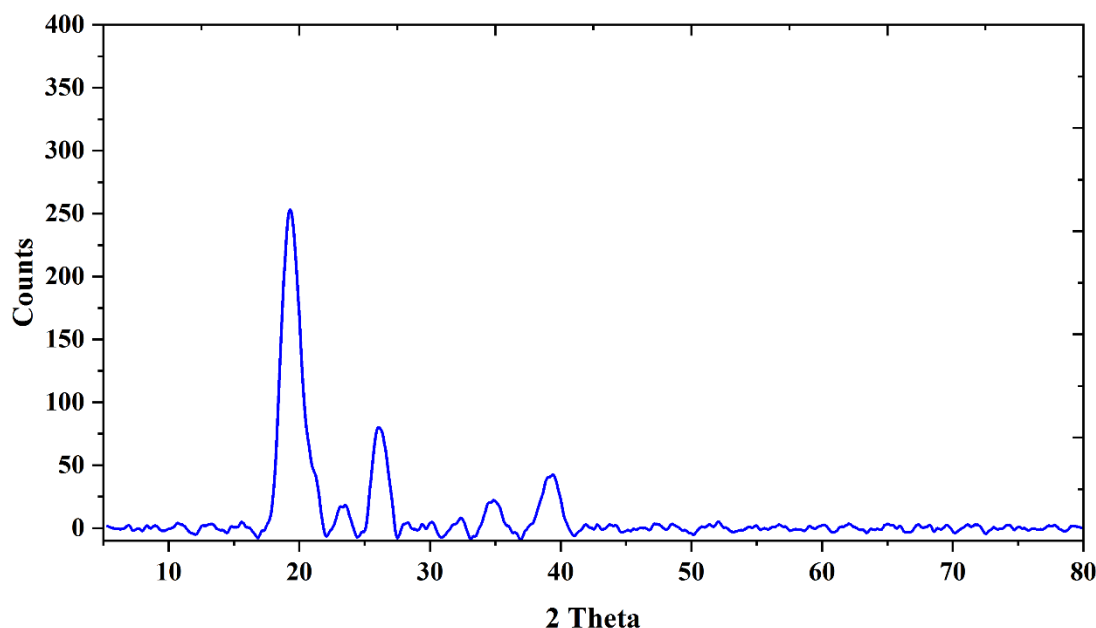


Figure 5. X-ray diffraction pattern of chitosan extracted from shrimp shell powder.

The most prominent feature in the diffractogram is a sharp, strong peak at a diffraction angle (2θ) of approximately 19.38° . This peak is widely recognized in the literature as corresponding to the (110) lattice plane of the hydrated crystalline polymorph of chitosan. Its presence confirms a significant degree of structural order arising from the extensive network of inter- and intramolecular hydrogen bonds between the polymer chains. This ordered arrangement is further substantiated by additional, well-defined peaks located at 26.26° and 29.84° , which are also characteristic of chitosan's crystalline conformation.

Underpinning these sharp peaks is a broad, diffused hump spanning a wide angular range from approximately 10° to 35° . This feature indicates the amorphous domains within the material, where the polymer chains lack long-range order. The coexistence of these crystalline and amorphous features is a hallmark of semi-crystalline polymers. The degree of crystallinity in chitosan is known to be highly dependent on its origin and processing history, particularly the degree of deacetylation (DDA) and any subsequent chemical modifications.

Furthermore, several minor yet distinct peaks at 22.18° , 38.95° , and 44.19° suggest the presence of additional, smaller domains of crystalline order within the polymer matrix. This complex pattern reinforces the semi-crystalline model of the prepared chitosan. It is well established that native chitosan exhibits some degree of crystallinity, which chemical modifications, such as cross-linking or grafting, can intentionally disrupt. Such processes often lead to a reduction in peak intensity and a more pronounced amorphous halo, as they disturb the polymer chain packing required for crystallization. This ability to modulate the crystalline-to-amorphous ratio is critical for tailoring chitosan's physicochemical properties, including swelling behavior, degradation rate, and mechanical strength, making it a highly versatile biomaterial for advanced applications, including controlled-release drug delivery systems.

Using the Segal method, the XRD pattern was used to determine the crystallinity of the chitosan. Because this method is only semi-quantitative and it is known to overestimate crystallinity in polysaccharides, the results were taken with a grain of salt. The produced chitosan has a moderate degree of crystallinity (about 55%), indicating a semicrystalline structure. This range of crystallinity is consistent with reports in the literature on chitosan derived from shrimp shells and aligns well with our thermal behavior. The presence of large

amorphous regions promotes carbonization and char formation at elevated temperatures, accounting for the significant residual mass observed in TGA, while still offering accessible amino and hydroxyl functional groups that facilitate efficient adsorption.

3.1.6. Point of Zero Charge (pHpzc)

Using the pH drift method, we found the point of zero charge (pHpzc) of the produced chitosan. This is shown in Figure 6. The pHpzc is the pH level at which the adsorbent's net surface charge is neutral. This is the point where ΔpH equals zero. The pHpzc of the unmodified chitosan was determined to be about 7.2, which is in line with values reported in the literature for chitosan derived from shrimp shells. In the acidic region ($\text{pH} < 7.2$), positive ΔpH values were observed, indicating that the solution's pH at the end was higher than its original pH. This happens because amino groups ($-\text{NH}_2$) on the chitosan surface become protonated, forming $-\text{NH}_3^+$ species that deprotonate the solution. This proton uptake indicates that chitosan is basic and can buffer well in acidic environments. In alkaline media ($\text{pH} > 7.2$), however, ΔpH readings became negative, indicating that the final pH was lower than the starting pH. This tendency occurs because surface functional groups lose protons, releasing them into the solution and making the surface negatively charged. This amphoteric behavior is typical of amino-functionalized biopolymers and demonstrates how chitosan naturally reacts with acids and bases.

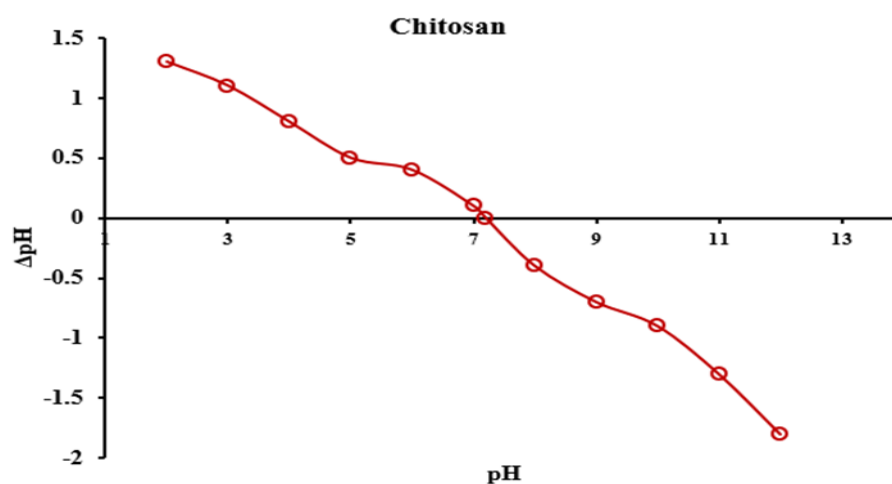


Figure 6. Zero-point charge (pH_{pzc}) of chitosan.

The pHpzc value obtained is significant for controlling electrostatic interactions during adsorption. When the pH is below 7.2, the positively charged chitosan surface facilitates binding of anionic species. When the pH is greater than 7.2, reduced protonation and a partial negative charge make it easier for cationic species to bind to it. The pHpzc of pristine chitosan thus provides a basis for elucidating the pH-dependent adsorption behavior of ionic dyes in the following investigations.

3.1.7. Thermal Profile of Chitosan

The thermal stability of the prepared chitosan was thoroughly investigated using Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC), which together provide a detailed picture of its behavior under increasing temperatures (Figure 7). The TGA results revealed a multi-stage decomposition process, beginning with an initial, minor weight loss of 4.23% up to 67.23 °C, a change attributed to the evaporation of loosely bound surface moisture as the temperature continued to rise to 130.63 °C, a further loss of 2.38% occurred, corresponding to the removal of more integral, tightly bound water

molecules. This initial resilience to weight loss suggests a high degree of thermal stability at lower temperatures.

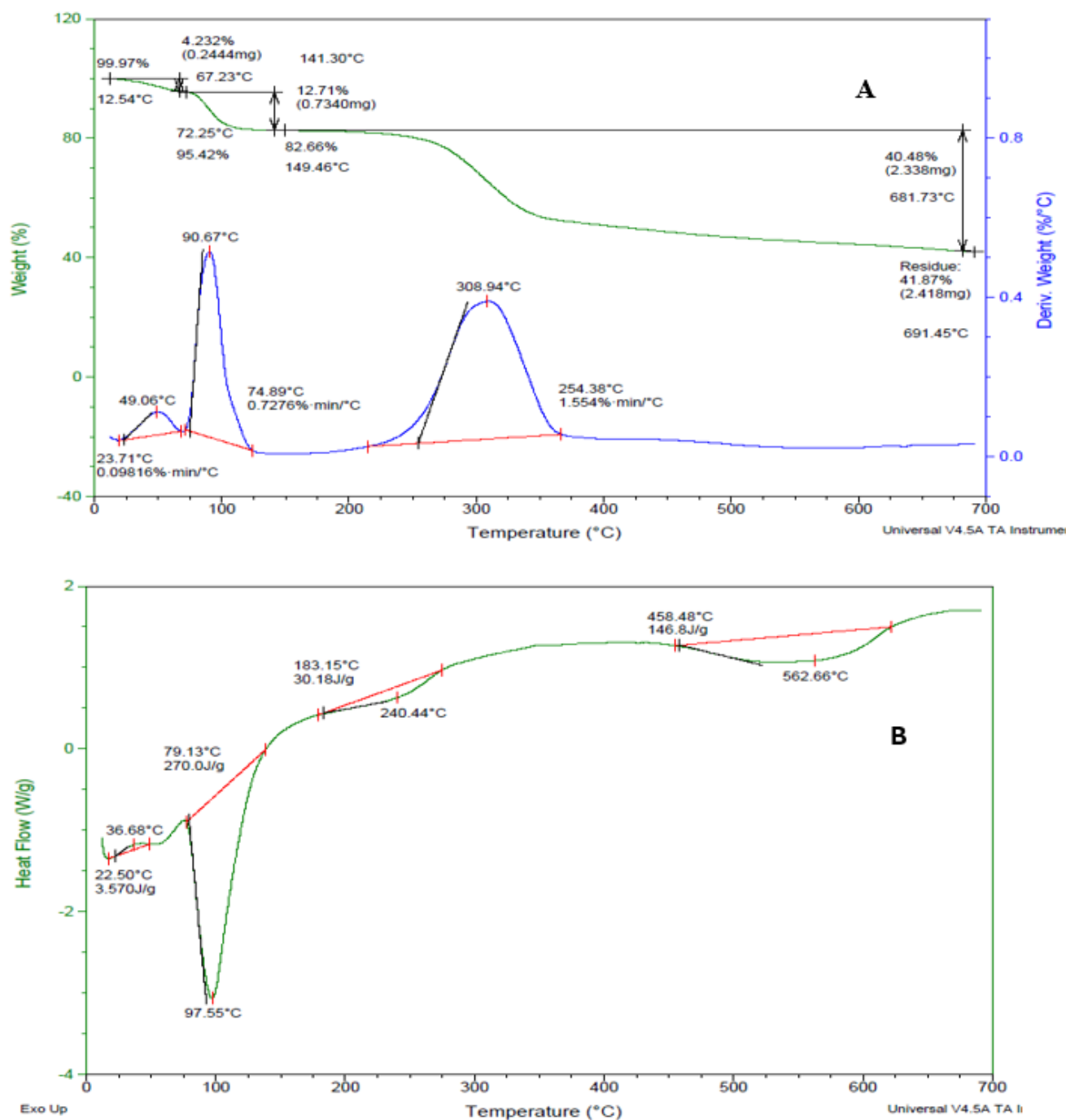


Figure 7. Thermogravimetric analysis for Chitosan ((A) TGA and (B) DSC).

The most significant thermal event occurred between 141 °C and 681 °C, during which the primary decomposition of the chitosan polymer occurred. During this stage, the material experienced a 40.48% weight loss [2]. The derivative Thermogravimetric (DTG) curve, which tracks the rate of weight change, identified the peak decomposition rate at 254.38 °C, pinpointing the precise temperature at which the polymer structure breaks down most rapidly. Even after this extensive degradation, a remarkable 41.87% of the initial mass remained as a stable char residue at the final temperature of 691.45 °C. This high residual

mass underscores the material's notable thermal integrity, suggesting the formation of a stable carbonaceous structure that can withstand extreme heat.

This relatively high residual mass, although higher than that reported for some commercial chitosan samples, is consistent with previously reported thermal behavior of chitosan analyzed under inert atmospheres. Under nitrogen conditions, chitosan undergoes dehydration and depolymerization at intermediate temperatures, followed by progressive carbonization and char formation at higher temperatures. The abundance of amino ($-\text{NH}_2$) and hydroxyl ($-\text{OH}$) groups promotes extensive intermolecular hydrogen bonding, which facilitates the development of a thermally stable carbonaceous structure and limits complete volatilization at elevated temperatures. Similar char yields of approximately 40–45% at temperatures above 650 °C have been reported for chitosan with high structural integrity and degree of deacetylation, particularly when derived from natural sources such as shrimp shells [15]. Therefore, the observed residue in this study reflects intrinsic carbonization behavior rather than experimental anomaly.

Complementing the TGA findings, the DSC analysis provided insight into the energetic transitions occurring within the material. The study identified a major endothermic event between 79.13 °C and 97.55 °C, characterized by a very large enthalpy of 270.0 J/g. This significant energy absorption is likely associated with a major structural rearrangement and the energy-intensive process of releasing bound water from the polymer matrix. Further heating revealed a secondary exothermic transition between 183.15 °C and 240.44 °C (30.18 J/g), possibly indicating a crystallization event or molecular cross-linking just before the onset of primary decomposition. Finally, a significant exothermic peak from 458.48 °C to 562.66 °C, with an enthalpy of 146.8 J/g, corresponds to the high-temperature degradation and backbone breakdown of chitosan, aligning with the primary weight loss observed in the TGA. Taken together, these analyses demonstrate that chitosan is a structurally robust biopolymer. It maintains its integrity up to approximately 140 °C, undergoes its most significant decomposition around 255 °C, and ultimately leaves a substantial stable residue [47].

3.2. Optimum Conditions

3.2.1. pH Effect

The influence of pH on the adsorption efficiency of chitosan for two model dyes, MO (an anionic dye) and MB (a cationic dye), was systematically examined over a pH range of 3–11. The results reveal distinct, opposing trends for the two dyes, highlighting electrostatic interactions as a major governing factor in the adsorption process (Figure 8 and Table S1). This divergence is primarily due to the ionic nature of the dyes and the pH-dependent charge distribution on the chitosan surface.

For methyl orange, the adsorption capacity was highest at pH 3, with a removal efficiency of approximately 79.76%, and declined steadily to 29.46% at pH 11. This trend is attributed to the electrostatic interactions between the chitosan surface and the anionic dye molecules. At lower pH values, the amino groups on chitosan become protonated, forming $-\text{NH}_3^+$, thereby imparting a strong positive surface charge. This facilitates attraction to the negatively charged sulfonate groups of MO, promoting effective adsorption. As pH increases, the extent of protonation decreases, thereby diminishing electrostatic attraction and reducing dye uptake. These findings are consistent with previous studies that reported enhanced adsorption of anionic dyes by chitosan in acidic environments [15,16,48]. Moreover, a similar pH-responsive adsorption mechanism was reported by [49], who demonstrated that low pH enhances the binding of acidic dyes due to favorable electrostatic attraction. More recent work by [50] on chitosan-functionalized graphene oxide composites also confirmed that anionic dye removal peaks in acidic media due to strong electrostatic forces and

hydrogen bonding. Additionally, Priyadarshi et al. (2022) [51] observed that the removal efficiency of MO using cross-linked chitosan beads was highest at pH < 4, supporting the assertion that surface charge manipulation is key in optimizing anionic dye uptake.

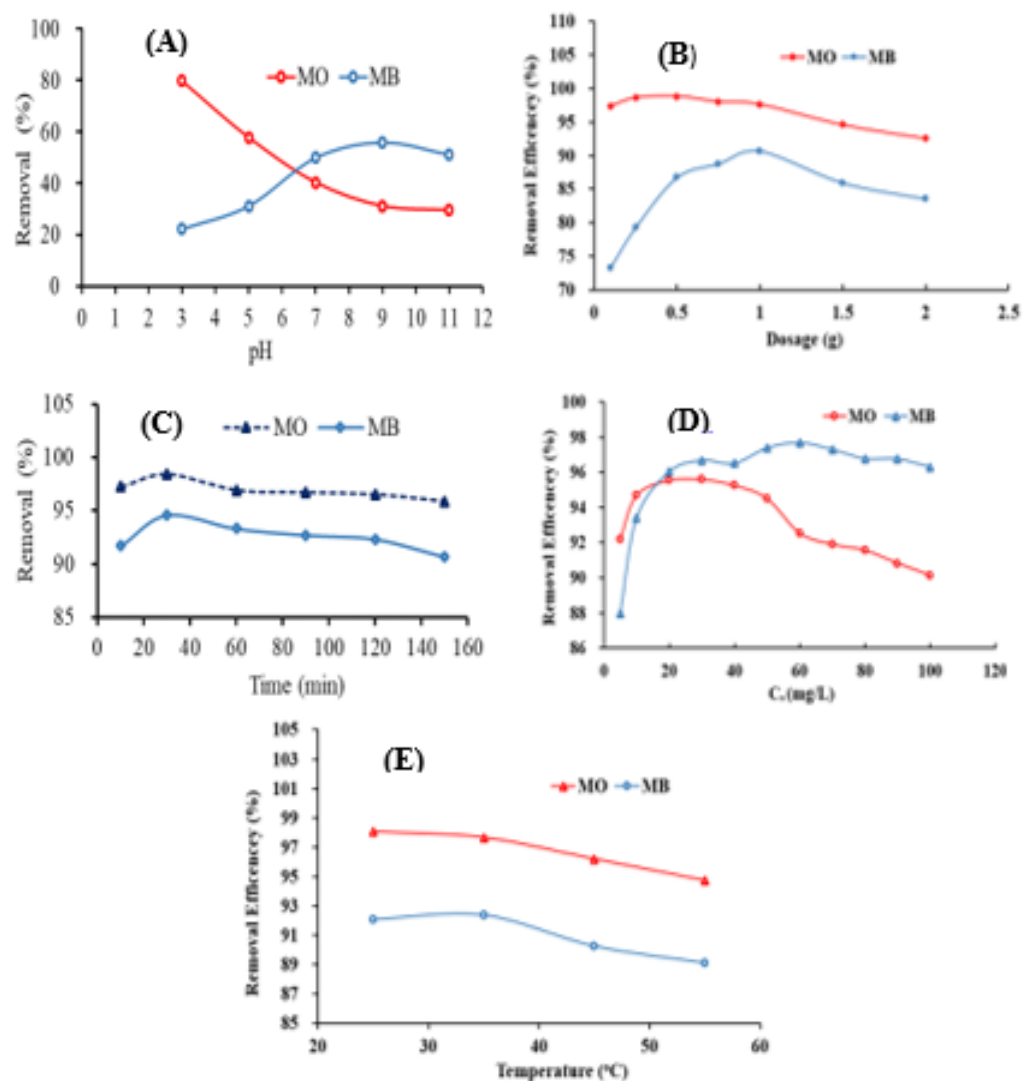


Figure 8. Effect of different parameters on the removal efficiency of MO and MB using chitosan: (A) pH ($C_0 = 20$ mg/L, dosage = 0.5 g for MO and 1.0 g for MB, contact time = 30 min, $T = 25^\circ\text{C}$); (B) adsorbent dosage (pH = 3 for MO and 9 for MB, $C_0 = 20$ mg/L, contact time = 30 min); (C) contact time (pH = 3 for MO and 9 for MB, dosage = optimum, $C_0 = 20$ mg/L); (D) initial dye concentration (pH = 3 for MO and 9 for MB, dosage = optimum, contact time = 30 min); (E) temperature (pH = optimum, dosage = optimum, contact time = 30 min).

For methylene blue, the removal profile follows an opposite trend. The lowest removal efficiency, approximately 22.18%, was observed at pH 3, while maximum adsorption occurred at pH 9, reaching 55.82%, followed by a slight decrease at pH 11. Under acidic conditions, the protonated chitosan surface repels the cationic MB molecules, reducing the likelihood of adsorption. However, as the solution becomes more alkaline, deprotonation of the amine groups reduces surface charge, possibly generating weakly negative surface sites that can attract cationic dyes. This shift results in increased MB uptake under basic conditions.

Additionally, higher pH levels may also enhance pore availability and reduce competition with hydrogen ions for active sites, further improving adsorption. Comparable outcomes have been observed in prior studies; for instance, [52] reported enhanced re-

removal of basic dyes at elevated pH due to reduced electrostatic repulsion. More recent work by [53] supports this explanation, demonstrating that chitosan-based beads exhibit optimal MB uptake in alkaline conditions owing to improved interaction between the dye and the adsorbent surface. Recent literature has further corroborated this behavior. For instance, [54] demonstrated that chitosan-activated carbon composites exhibited maximum MB adsorption above pH 8 due to enhanced negative surface charge. [55] also reported that alkaline pH enhances the accessibility of chitosan adsorption sites by decreasing intramolecular hydrogen bonding and increasing pore exposure. Moreover, [56] showed that modification of chitosan with functional groups (carboxyl or hydroxyl) can further enhance MB binding in basic environments, particularly through hydrogen bonding and cation exchange mechanisms.

3.2.2. Dosage Effect

The adsorbent dosage plays a pivotal role in adsorption performance, as it directly influences the number of active sites available for binding dye molecules. In this study, the effect of varying chitosan dosage (0.1–2.0 g) on the removal efficiency of MO and MB was evaluated. The results are shown in Figure 8 and summarized in the accompanying Table S1. For MO, the removal efficiency increased sharply from 97.39% at 0.1 g to 98.80% at 0.5 g. After reaching this peak, the efficiency gradually declined to 92.59% at 2 g. MB removal followed a similar trend but with a slightly shifted optimum. At the lowest dosage (0.1 g), MB removal was only 73.32%, indicating insufficient adsorption sites.

As the dosage increased, removal improved significantly, reaching a maximum of 90.65% at 1 g. Beyond this point, MB removal efficiency showed a mild reduction, then leveled off at 83.517% at the highest dosage tested. Two main phenomena can explain this behavior. First, the initial increase in dye removal with higher dosage is attributed to the increased availability of adsorption sites. Chitosan is rich in amino and hydroxyl functional groups that interact with dye molecules via electrostatic attraction, hydrogen bonding, and van der Waals forces. As more chitosan is introduced, more surface area and functional groups become available for dye uptake. However, once an optimal dosage is reached, further increases do not enhance removal and may even reduce it. This can occur due to particle agglomeration at high concentrations, which effectively reduces the surface area accessible for adsorption. Moreover, overlapping adsorption sites and increased solution viscosity can hinder dye diffusion and lower the overall adsorption rate. This trend has been reported in various studies. For instance, [57] observed similar saturation behavior when using modified chitosan for azo dye removal, where excessive adsorbent hindered dye accessibility to active sites. Another contributing factor may be the shielding of internal surface sites by multilayered chitosan particles in suspension. At higher dosages, the adsorbent particles may clump, preventing dye molecules from penetrating deeper pores and decreasing overall efficiency. This is particularly critical in the case of MB, a cationic dye with a slightly larger molecular structure compared to MO [58,59].

In practical applications, these findings emphasize the importance of optimizing adsorbent dosage not only to achieve high removal efficiency but also to ensure cost-effectiveness. Using more adsorbent than necessary adds to operational costs and may reduce process efficiency. Based on this study, the optimal dosages are 0.5 g for MO and 1 g for MB, which offer the best trade-off between performance and resource utilization. These results are consistent with findings from recent literature. For example, [60] demonstrated that while increasing biosorbent dosage initially improves dye uptake, excessive amounts reduce efficiency due to saturation effects and reduced driving force for mass transfer. Similarly, [61] showed that for chitosan-based composites, optimal dosages yield maximum performance, beyond which dye removal rates plateau or decrease.

3.2.3. Effect of Shaking Time

The influence of shaking time on dye adsorption was assessed over a range of 10 to 150 min. The results indicate that MO removal efficiency rapidly reaches over 97% within the first 10 min, peaking at 98.45% at 30 min. A slight decline is observed by 60 min, after which the efficiency stabilizes around 96%. In contrast, MB exhibits a modest downward trend. It achieves 91.72% removal at 10 min, with a peak efficiency of 94.61% at 30 min, followed by a gradual decline. From 60 to 150 min, MB removal efficiency decreases from 92.74% to 90.70%, suggesting that prolonged shaking has a limited or slightly negative impact on MB adsorption.

This rapid initial adsorption is likely due to the abundance of available active sites on chitosan particles, which enables swift binding of dye molecules. As time progresses, surface sites become saturated, and intraparticle diffusion into pores becomes more significant, leading to slower uptake, a phenomenon commonly observed in batch adsorption systems. Comparable studies report that dye removal by chitosan-based adsorbents follows pseudo-second-order kinetics, characterized by a rapid initial phase followed by a gradual approach to equilibrium [62,63].

Interestingly, the dip observed at around 60 min for both dyes may be attributed to a dynamic adsorption–desorption equilibrium. As dye molecules diffuse deeper into particle pores, some previously adsorbed at the surface may desorb. However, this state appears transient, as adsorption levels recover and remain steady at later time points. A similar phenomenon was reported by, who noted minor fluctuations around equilibrium time due to boundary-layer and intraparticle diffusion interactions in chitosan hydrogel systems [64].

Overall, the average removal percentages (96.61% for MO and 92.57% for MB) indicate that a contact time of 30–90 min is sufficient to achieve near-optimal dye removal, beyond which prolonged shaking does not confer significant benefits and may even slightly reduce efficiency. From a practical standpoint, maintaining an equilibrium period of approximately 60 min is both time- and energy-efficient for dye-laden water treatment, aligning well with processing requirements in both continuous-flow and batch adsorption systems.

3.2.4. Effect of Initial Dye Concentration (C_0)

The study investigated how varying initial dye concentrations (5–100 mg/L) affected the removal efficiency of MO and MB using chitosan. The data reveal distinct patterns for each dye: MO removal began at 92.18% for 5 mg/L and peaked at 95.54% at 20 mg/L. After that, a gradual decline was observed, dropping to 90.81% at 90 mg/L, followed by a slight rebound at 100 mg/L (90.13%). In contrast, MB showed a rising trend across the concentration range, from 87.94% at 5 mg/L to 96.28% at 100 mg/L, with minor fluctuations between 20 and 100 mg/L. These trends align with typical adsorption behavior. At low initial concentrations, chitosan's abundant active sites allow efficient dye uptake. As concentration increases, more dye molecules compete for those sites, leading to saturation and diminishing removal percentages, especially for MO. Such saturation-based decline is common and often modeled by Langmuir adsorption isotherms, reflecting monolayer coverage and finite active sites [65]. The MB rising trend, even at high concentration, suggests strong affinity and favorable interactions with chitosan, likely due to its cationic structure and size, which fit well with chitosan's negatively charged active groups. Similar outcomes have been reported in studies using chitosan-biochar composites, where MB removal efficiency increased with concentration due to stronger driving forces and reduced repulsion at elevated dye loading [62]. The depression in MO adsorption beyond 20 mg/L reflects competition and site saturation, typical of dye systems with limited adsorption capacity. A spike at 100 mg/L may be attributed to multilayer adsorption or aggregation-

induced retention, phenomena discussed in the adsorption literature. Generally, the average removal efficiencies of 93.18% for MO and 96.12% for MB highlight that chitosan is more effective for MB removal across the tested concentration range.

3.2.5. Different Temperature Effect

The removal efficiency of MO and MB using chitosan was evaluated at four different temperatures: 25, 35, 45, and 55 °C (Figure 8 and Table S1). For MO, the highest removal (98.05%) occurred at 25 °C, followed by a dip at 35 °C (97.65%), a slight decrease at 45 °C, and a modest decline at 55 °C (94.74%). MB showed a gradual reduction in removal efficiency with increasing temperature, from 92.06% at 25 °C to 89.08% at 55 °C, yielding an average removal efficiency of 90.93%.

These results suggest that MO adsorption is moderately endothermic at lower temperatures but becomes less favorable at higher temperatures. The depression observed at 35 °C may be due to competition between increased molecular motion and reduced adsorbent–adsorbate interactions at that temperature. MB, on the other hand, seems to respond negatively to temperature increases, likely because elevated temperatures disrupt hydrogen bonding and electrostatic attractions between the cationic dye and chitosan's amino groups.

Findings from the literature offer comparable trends. For instance, studies on carboxymethyl chitosan hydrogels report that MB adsorption is endothermic, with adsorption capacities increasing slightly as temperature rises from 25 to 55 °C [66]. This behavior is often attributed to increased swelling of the adsorbent matrix at higher temperatures, allowing deeper dye penetration. Similarly, [67] demonstrated modest increases in MO adsorption with temperature, but beyond a specific point, adsorption plateaued or decreased due to weakened chitosan–dye binding forces.

Additionally, research on chitosan-biochar and chitosan–silica composites by [18] confirmed that MO adsorption exhibited a mild temperature dependence, with optimal performance often between 25–45 °C. These dynamics reinforce the idea that moderate thermal conditions are ideal for maximizing chitosan-mediated dye removal, thereby avoiding the counterproductive effects of excessive heat.

From an application perspective, operating at room temperature (~25 °C) appears most effective and energy-efficient, with MO removal approaching 98%. Slight temperature increases may not significantly improve adsorption, and in the case of MB, may even diminish efficiency. Thus, maintaining ambient or slightly elevated temperatures would be optimal for practical wastewater treatment using chitosan-based adsorbents.

3.3. Isotherm Modeling

3.3.1. Dye Adsorption onto Chitosan

Our investigation into the removal of MO and MB using chitosan as an adsorbent revealed compelling insights into the underlying adsorption mechanisms, as elucidated through various isotherm models (Figure 9). The experimental data were rigorously analyzed using the Langmuir, Freundlich, and Temkin isotherm models, with the derived parameters providing a quantitative understanding of the adsorption process. A summary of these critical parameters is presented in Table 2.

For methyl orange adsorption, the Langmuir isotherm model provided an exceptional fit to the experimental data, as evidenced by its high correlation coefficient ($R^2 = 0.9973$). This strong correlation suggests that MO molecules predominantly adsorb as a monolayer on a uniform chitosan surface, implying a finite number of identical adsorption sites with no significant interaction between adsorbed molecules [29]. The calculated maximum adsorption capacity ($q_{\max}$) for MO was 7.843 mg/g. This finding is consistent with the

established literature, which shows that the Langmuir model frequently provides the best description of dye adsorption onto chitosan-based materials, often pointing to a chemisorption process or a strong affinity between the adsorbate and adsorbent [68,69]. The Langmuir constant (K_L) of 0.147 L/mg further underscores the favorable nature of this adsorption process.

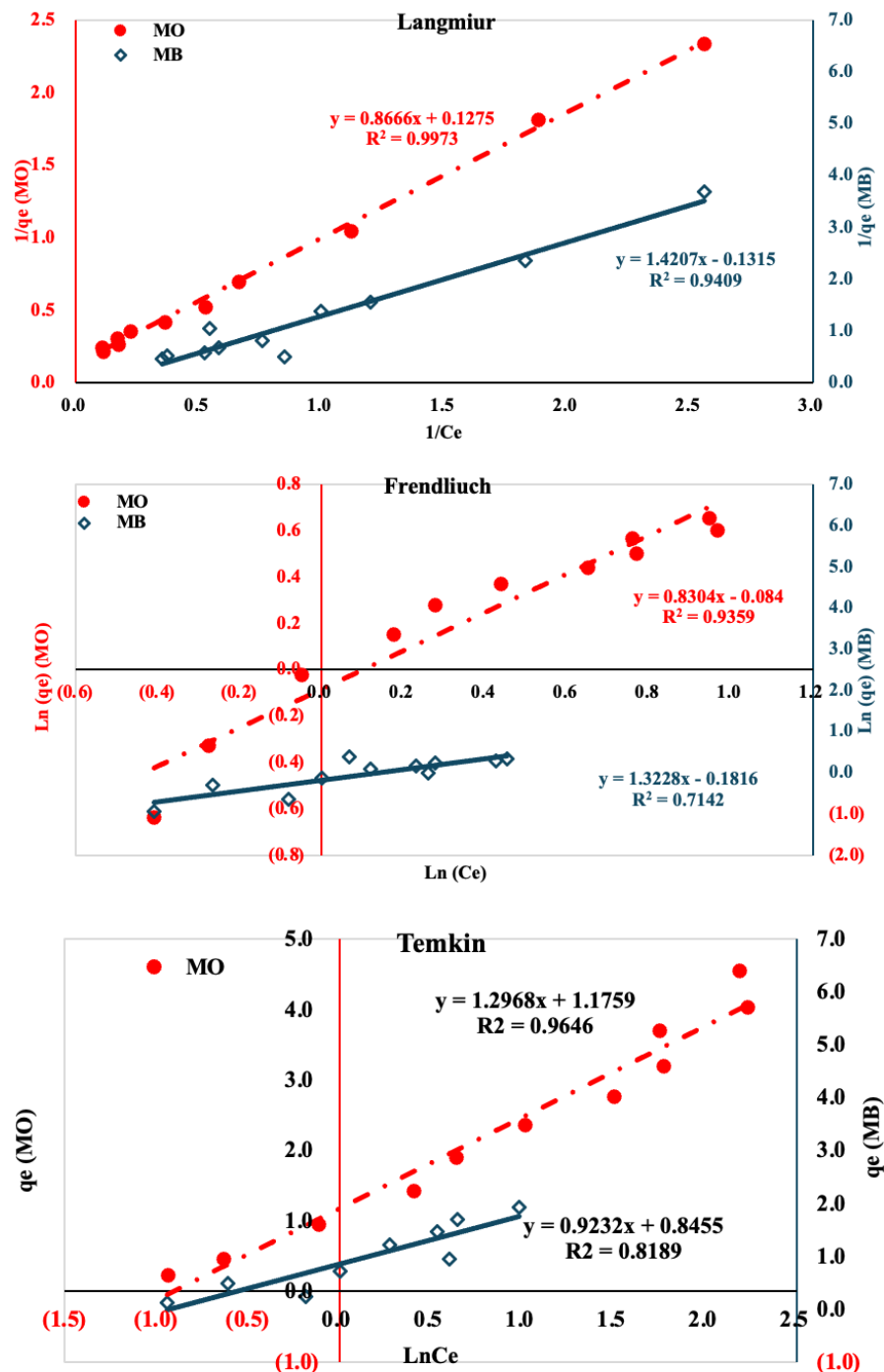


Figure 9. Isotherm Models for the Adsorption of MO and MB onto Chitosan. This figure presents the linear plots of the Langmuir, Freundlich, and Temkin isotherm models for the adsorption of Methyl Orange (represented by red circles and dashed lines) and Methylene Blue (represented by blue diamonds and solid lines) onto chitosan. Each plot includes the corresponding linear regression equation and the coefficient of determination (R^2) for both dyes, illustrating the fit of each model to the experimental adsorption data.

Table 2. Isotherm Parameters for Adsorption of Methyl Orange (MO) and Methylene Blue (MB) onto Chitosan.

Adsorption Model	Parameters	MO	MB
Langmuir	$q_{\max}$	7.843	7.605
	K_L	0.147	0.093
	R^2	0.9973	0.9409
Freundlich	$1/n_f$	0.8304	1.323
	n_f	1.204	0.756
	K_f	1.088	1.199
	R^2	0.9359	0.7142
Temkin	B_T	1.297	0.923
	$\ln A_T$	0.907	0.916
	A_T	2.476	2.499
	R^2	0.9646	0.8189

Similarly, the adsorption of methylene blue (MB) also showed a good fit with the Langmuir isotherm model, yielding an R^2 value of 0.9409. This indicates that monolayer adsorption is a significant mechanism for MB removal by chitosan. The maximum adsorption capacity ($q_{\max}$) for MB was found to be 7.605 mg/g, a value quite comparable to that observed for MO. This similarity in adsorption capacities for both anionic (MO) and cationic (MB) dyes highlights the versatility of chitosan, which possesses both amine and hydroxyl functional groups that can interact with various dye molecules [18]. The K_L value for MB (0.093 L/mg) also indicates favorable adsorption.

While the Langmuir model provided the best fit, it is also essential to consider the insights from the Freundlich and Temkin models. The Freundlich isotherm, which accounts for heterogeneous surface adsorption and multilayer formation [30], yielded an R^2 value of 0.9359 for MO. Although a reasonable fit, it was notably lower than that of the Langmuir model, suggesting that while some heterogeneity might exist, the primary adsorption mechanism for MO is not dominated by multilayer formation. The Freundlich intensity parameter ($1/n_f$) of 0.8304, being between 0 and 1, confirms the favorable nature of the adsorption. For MB, the Freundlich model yielded a lower R^2 of 0.7142, further supporting the notion that MB adsorption on chitosan is better characterized by a monolayer mechanism rather than a heterogeneous, multilayer process. The $1/n_f$ value for MB was 1.323, which is greater than 1, potentially indicating less favorable adsorption or a more complex adsorption mechanism than for MO.

The Temkin isotherm model, which accounts for adsorbate–adsorbate interactions and assumes a linear decrease in the heat of adsorption with increasing surface coverage [31], yielded an R^2 value of 0.9646 for MO. This good fit, albeit slightly less pronounced than the Langmuir model, suggests that while monolayer adsorption is paramount, there might be some degree of interaction between adsorbed MO molecules or a linear reduction in the heat of adsorption as the surface becomes more saturated. The B_T value (related to the heat of adsorption) was 1.297 J/mol, and the A_T value (equilibrium binding constant) was 2.476 L/g. For MB, the Temkin model yielded an R^2 of 0.8189, indicating that adsorbate–adsorbate interactions or the linear decrease in heat of adsorption are less significant for MB than for MO. The B_T value for MB was 0.923 J/mol, and the A_T value was 2.499 L/g.

This finding, particularly the firm adherence to the Langmuir model for both dyes, is well-supported by a substantial body of existing scientific literature. Numerous studies investigating dye adsorption by chitosan and its derivatives consistently report that the Langmuir isotherm provides the best fit, indicating a monolayer adsorption mechanism [70,71]. This phenomenon is often attributed to strong electrostatic interactions

between the protonated amine groups of chitosan and anionic dyes, and between chitosan's hydroxyl groups and cationic dyes, leading to well-defined monolayer coverage [72,73]. The maximum adsorption capacities observed in this study (7.843 mg/g for MO and 7.605 mg/g for MB) fall within the typical range reported for chitosan-based adsorbents. It is important to note that adsorption capacities can vary considerably depending on factors such as the specific chitosan derivative used, the preparation methodology, and the experimental conditions [70,74]. For instance, some chemically modified chitosan materials have demonstrated significantly enhanced adsorption capacities due to increased surface area or improved functionalization [75]. Our results affirm the effectiveness of the chitosan utilized in this study for removing both methyl orange and methylene blue with comparable efficiency.

While the Langmuir model provided the optimal fit, the reasonable R^2 values obtained for the Freundlich and Temkin models, especially for MO, hint that the adsorption process may not be exclusively monolayer. It is conceivable that a combination of mechanisms, including both monolayer and multilayer adsorption, as well as interactions between adsorbed molecules, could contribute to the overall process, particularly at higher dye concentrations [76]. The slight deviation from an ideal Langmuir fit for MB, coupled with the relatively lower R^2 values for the Freundlich and Temkin models, might be explained by differences in the molecular size, charge distribution, or steric hindrance between the two dyes and the chitosan surface [77]. Recent research continues to explore these nuances; for example, one study demonstrated that incorporating polyacrylamide gel with chitosan significantly improved the removal efficiency of Direct Blue 78 dye and dramatically reduced sedimentation time, with the Langmuir isotherm model confirming monolayer adsorption driven by electrostatic forces [78]. In a separate investigation, chitosan-based magnetic sorbents demonstrated exceptional capacity (up to 330.96 mg/g) for removing the basic yellow dye, with the Langmuir model again providing the best fit, reinforcing the ongoing significance of equilibrium modeling in optimizing dye removal systems [79].

3.3.2. Kinetics of MO and MB onto Chitosan

The kinetic behavior of MO and MB adsorption onto chitosan was investigated to understand the underlying mechanisms and determine the rate-limiting steps. To this end, the experimental data were analyzed using the pseudo-first-order and pseudo-second-order kinetic models. The pseudo-first-order model, proposed by Lagergren, assumes that the rate of occupation of adsorption sites is proportional to the number of unoccupied sites. It is mathematically expressed as:

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

where q_t (mg/g) is the amount of dye adsorbed at time t , q_e is the equilibrium adsorption capacity (mg/g), and k_1 is the rate constant of the pseudo-first-order model (min^{-1}). However, the pseudo-second-order model, which assumes that chemisorption is the rate-limiting step, provided a significantly better fit for both dyes. It is given by:

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

where k_2 is the pseudo-second-order rate constant ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$). For all MO concentrations, the correlation coefficients (R^2) for the pseudo-second-order model were 1, and the calculated q_e values closely matched the experimental values. In contrast, the pseudo-first-order model yielded poor fits, with R^2 values often below 0.05 (Table 3 and Figure S2). These results confirm that the adsorption of MO onto chitosan is governed primarily

by chemisorption, a conclusion supported by similar studies on azo dye removal using biopolymer-based adsorbents [39,80].

Table 3. Kinetic parameters for the adsorption of MO and MB onto chitosan at various initial dye concentrations using pseudo-first-order and pseudo-second-order models.

	C_0 (mg/L)	q_e (exp)	Pseudo-First-Order Kinetics			Pseudo-Second-Order Kinetics		
			K_1	q_e (cal)	R^2_1	K_2	q_e (cal)	R^2_2
MO	5 ppm	1.243	0.036	591.582	0.218	9.849	1.243	1
	10 ppm	2.486	0.007	74.433	0.0097	12.986	2.482	1
	15 ppm	3.724	0.067	6.671	0.4683	80.341	3.719	1
	20 ppm	4.964	0.003	52.300	0.0067	2.292	4.965	1
	25 ppm	6.196	0.027	12.405	0.4084	30.366	6.188	1
	30 ppm	7.432	0.006	32.291	0.009	1.093	7.446	1
MB	5 ppm	1.187	0.039	306	0.5337	0.666	1.111	0.9964
	10 ppm	2.448	0.017	4.507	0.1723	0.224	2.464	0.9941
	15 ppm	3.454	0.025	7.376	0.2453	0.251	3.110	0.992
	20 ppm	4.643	0.004	2.627	0.0332	0.052	3.259	0.9092
	25 ppm	5.760	0.006	1.133	0.0588	0.087	5.482	0.9671
	30 ppm	6.553	0.058	1.344	0.1733	0.248	6.443	0.997

In the case of MB, while the pseudo-second-order model also provided a better fit than the pseudo-first-order model, the correlation coefficients were slightly lower than those observed for MO, ranging from 0.9092 to 0.997 (Table 3 and Figure 10). This suggests that although chemisorption dominates the adsorption process, the mechanism for MB may also involve additional interactions. Unlike MO, which carries a negative charge, MB is a cationic dye. Under acidic conditions, chitosan's amino groups are protonated ($-\text{NH}_3^+$), thereby enhancing its affinity for negatively charged dyes such as MO. For MB, however, electrostatic attraction is less favorable due to like-charge repulsion. As a result, the adsorption of MB likely proceeds via hydrogen bonding, van der Waals forces, and π - π interactions between the aromatic structure of MB and the polysaccharide backbone of chitosan, particularly residual acetylated sites [64,81].

As the initial dye concentration increased from 5 to 30 mg/L, both dyes exhibited an increase in equilibrium adsorption capacity. For MO, q_e increased from 1.243 to 7.432 mg/g, while MB increased from 1.187 to 6.553 mg/g. This trend reflects the greater driving force for mass transfer at higher concentrations, which enhances the probability of collision between dye molecules and active adsorption sites [82]. However, the pseudo-second-order rate constant k_2 generally decreased with increasing concentration, especially for MB. This is likely due to the progressive saturation of available surface sites, as well as the emergence of steric hindrance and internal diffusion resistance at elevated dye loads [83].

Mechanistically, the adsorption of MO is dominated by electrostatic interactions between the dye's sulfonate groups and the positively charged amino groups on chitosan. The exact fit of the pseudo-second-order model and perfect match between theoretical and experimental q_e values reinforce the assumption of monolayer chemisorption. In contrast, the adsorption of MB appears to follow a more complex pathway, potentially involving multilayer formation or dye aggregation at higher concentrations. This is further supported by the increasing deviation between q_e (calculated) and q_e (experimental) values for MB at higher dye concentrations. Such behavior has been previously observed in systems involving surface heterogeneity or cooperative adsorption effects [84].

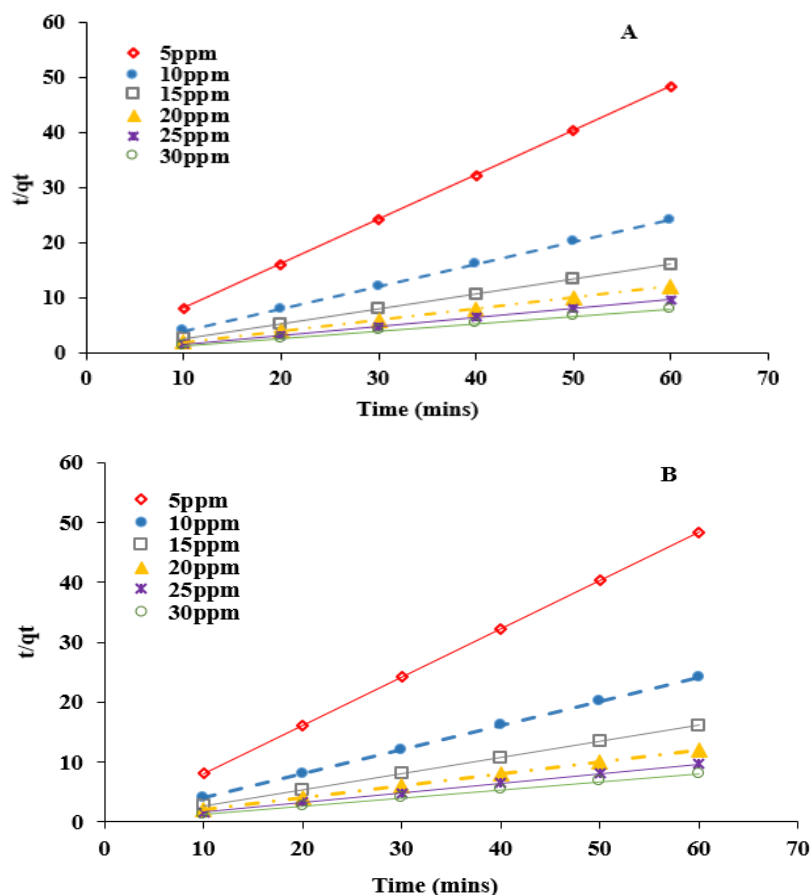


Figure 10. Pseudo-second-order kinetic plots for the adsorption of (A) MO and (B) MB onto chitosan at different initial concentrations (5–30 mg/L) [34,35]. Model fitting indicates a chemisorption-controlled mechanism with excellent agreement between calculated and experimental values.

From a materials science perspective, chitosan remains a compelling adsorbent due to its biodegradability, abundant functional groups, and ease of chemical modification. Its ability to selectively interact with both anionic and cationic dyes, albeit via different mechanisms, underscores its versatility for water treatment applications. The kinetic data derived in this study align closely with the theoretical framework of pseudo-second-order chemisorption and contribute to a broader understanding of biopolymer interaction dynamics. Recent studies support these findings, emphasizing chitosan's adaptability to bind a diverse array of dyes through various physical and chemical pathways [85,86].

3.3.3. Thermodynamics of MO and MB Adsorption onto Chitosan

Understanding the thermodynamic parameters of an adsorption process is crucial for elucidating its feasibility, spontaneity, and the underlying mechanisms involved. These parameters, including the Gibbs free energy change (ΔG^0), enthalpy change (ΔH^0), and entropy change (ΔS^0), provide valuable insights into the energy changes and randomness associated with the adsorption of pollutants onto an adsorbent material. A negative ΔG^0 indicates a spontaneous process, while its magnitude reflects the driving force of the reaction. The ΔH^0 value indicates whether adsorption is exothermic (negative) or endothermic (positive), providing clues about the nature of the adsorption forces (e.g., physical or chemical). Lastly, ΔS^0 includes information on the degree of disorder or randomness at the solid–solution interface during adsorption [87].

The thermodynamic parameters for the adsorption of MB and MO onto chitosan were determined at various temperatures, as presented in Table 4 and Figure 11. These values provide critical insights into the spontaneity and nature of the adsorption processes. For

both dyes, the ΔG^0 values are positive across the studied temperature range (25–55 °C), indicating that the adsorption processes are non-spontaneous under these conditions. This suggests that external energy input might be required for adsorption to proceed effectively, or that the process is more favorable under different conditions not explored in this temperature range [88].

Table 4. Thermodynamic Parameters for MO and MB Adsorption.

	T (°C)	K_d	ΔG^0	ΔH^0	ΔS^0
MO	25	0.590	109.759	333	17.503
	35	0.156	540.260		
	45	0.396	347.011		
	55	0.322	517.629		
MB	25	0.579	113.432	133	9.297
	35	0.604	146.765		
	45	0.462	289.111		
	55	0.408	409.963		

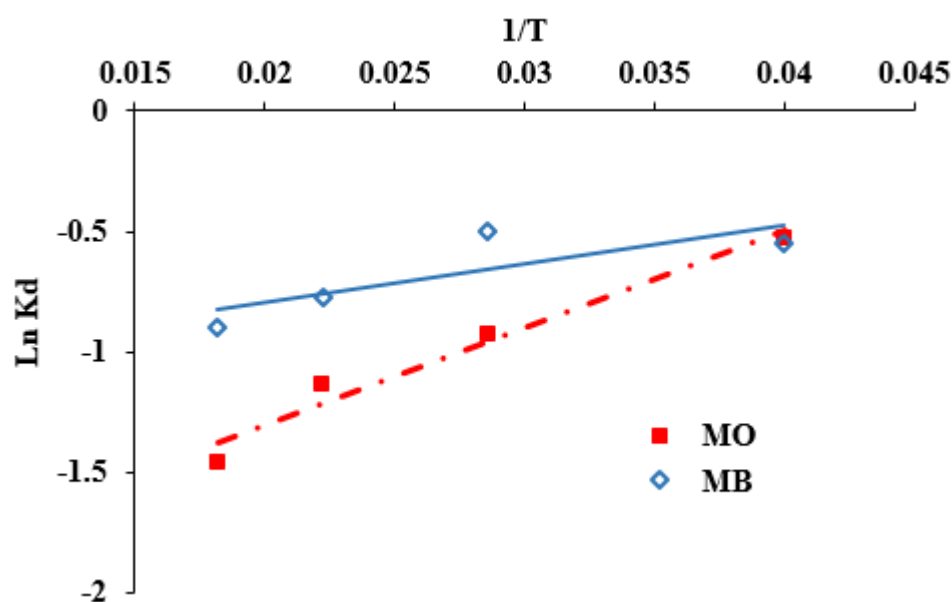


Figure 11. Van't Hoff Plot for MO and MB Adsorption.

The positive ΔH^0 values of 333 for MO and 133 for MB suggest that the adsorption processes are endothermic. This implies that the adsorption of both dyes onto chitosan requires energy input, and higher temperatures generally favor adsorption up to a point where other factors may become dominant. This endothermic characteristic is often observed in chemisorption processes where bond formation occurs, or in physisorption, where the energy required to desorb water molecules from the adsorbent surface or dye molecules from the solution is greater than the energy released during the adsorption of the dye onto the chitosan [66]. Furthermore, the positive ΔS^0 values (17.503 for MO and 9.297 for MB) indicate an increase in randomness or disorder at the solid–solution interface during the adsorption of both dyes. This positive change can be attributed to the displacement of water molecules from the chitosan surface by the adsorbate molecules, thereby increasing the system's degrees of freedom. This phenomenon is commonly observed in adsorption processes, in which adsorbate molecules displace a greater number of solvent molecules from the adsorbent surface [89].

The relationship between the distribution coefficient (K_d) and temperature is often described by the Van't Hoff equation, which can be linearized as:

$$\ln(K_d) = -\Delta H^0/RT + \Delta S^0/R.$$

A plot of $\ln(K_d)$ versus $1/T$ (where T is in Kelvin and R is the ideal gas constant) yields a straight line, from which ΔH^0 and ΔS^0 can be determined from the slope and intercept, respectively. The graph illustrates the adsorption of Methylene Blue and Methyl Orange onto chitosan. The positive slopes observed for both dyes in the $\ln K_d$ versus $1/T$ plot further confirm the endothermic nature of the adsorption processes, consistent with the positive ΔH^0 values presented in the table. This graphical representation visually reinforces the finding that increasing temperature enhances adsorption capacity, as indicated by the rising K_d values with temperature for both dyes. However, the trend for MB appears less pronounced than for MO in the given temperature range [90].

3.4. Comparison with Previously Reported Chitosan-Based Adsorbents

To properly evaluate the adsorption performance of the pristine chitosan used in this study, it is essential to contextualize the results within the broader landscape of chitosan-based adsorbents and other common materials reported in the literature (Table 5). The maximum adsorption capacities ($q_{\max}$) obtained in this work were 7.843 mg/g for methyl orange (MO) and 7.605 mg/g for methylene blue (MB). These values are relatively moderate compared with many modified or composite systems; however, they must be understood within the framework of the material's inherent properties and the specific advantages of unmodified chitosan.

Table 5. Comparison of removal efficiency (%R) of pristine and modified chitosan-based adsorbents.

Adsorbent	Pollutants	% R	$q_{\max}$ (mg/g)	Reference
Pristine chitosan	MO	≈85–90	7.84	This study
Pristine chitosan	MB	≈80–88	7.61	This study
Pristine chitosan	Reactive Black 5	90	34.5	[91]
Pristine chitosan	Acid Blue 113	88	-	[3]
Pristine chitosan	Crystal Violet	86	-	[92]
Amino-ethyl chitosan	MO	96	>150	[17]
Chitosan-GO aerogel	MO	>99	180–250	[18]
Chitosan-GO aerogel	MB	98	200–290	[18]
Fe ₃ O ₄ /chitosan	MB	93	93	[19]
ZnO-chitosan	MB	90–95	-	[20]
Chitosan-MOF-235	MB & MO	>95	>200	[22]
Sulfonated chitosan	MB	97–99	-	[93]

Unmodified chitosan from various sources typically exhibits adsorption capacities ranging from approximately 5 to 50 mg/g for different dyes, depending on factors such as the chitosan source, degree of deacetylation, and experimental conditions. For instance, pristine chitosan has been reported to achieve capacities of 5.23 mg/g for Acid Orange 12 [68] and 34.5 mg/g for Reactive Black 5 [91]. Similarly, studies on unmodified chitosan for the removal of Acid Blue 113 and Crystal Violet have demonstrated removal efficiencies of 88% and 86%, respectively, without reporting specific $q_{\max}$ values [3,92]. Our results, therefore, fall well within the expected range for pristine biopolymers and confirm that the chitosan prepared in this study performs comparably to other unmodified chitosan materials reported in the literature.

In contrast, chemically modified chitosan and chitosan-based composites often exhibit substantially higher adsorption capacities due to enhanced surface area, increased porosity,

and the introduction of additional functional groups. For example, amino-ethyl chitosan hydrogels have achieved MO adsorption capacities exceeding 150 mg/g with 96% removal efficiency [17]. Chitosan–graphene oxide (GO) aerogels have demonstrated remarkable capacities of 180–290 mg/g for both MO and MB, achieving removal efficiencies greater than 98% [18]. Magnetic Fe₃O₄/chitosan composites have shown MB adsorption capacities up to 93 mg/g [20], while ZnO–chitosan composites have achieved 90–95% removal of MB [21]. Chitosan–biochar–ZnO composites have reached 112 mg/g for MO with removal efficiencies exceeding 95% [62], and chitosan–MOF composites have demonstrated capacities exceeding 200 mg/g for both dyes [22]. Sulfonated chitosan has also been reported to achieve 97–99% removal of MB [93].

While these modified materials undoubtedly offer superior adsorption capacities, it is essential to recognize that these enhancements come with significant trade-offs. First, the synthesis of modified chitosan and its composites often involves complex, multi-step processes that require specialized equipment, organic solvents, and additional chemicals, thereby increasing production costs and limiting scalability. Second, chemical modification and composite formation can compromise the inherent biodegradability and non-toxicity of natural chitosan, potentially reducing its environmental compatibility. Third, many advanced composites face challenges in large-scale production and real-world application due to issues related to material stability, regeneration efficiency, and cost-effectiveness. These factors must be carefully considered when evaluating the overall suitability of an adsorbent for practical wastewater treatment.

In contrast, the pristine chitosan used in this study offers several distinct advantages, making it an attractive candidate for sustainable wastewater treatment. The material is produced via a straightforward three-step chemical process from shrimp shell waste, a low-cost, abundant resource. This approach embodies the principles of the circular economy and waste valorization, transforming a byproduct of the seafood industry into a valuable biosorbent. The unmodified chitosan retains its inherent biodegradability and non-toxicity, ensuring that its use does not introduce secondary environmental pollution. Despite its moderate adsorption capacity, the material achieves high removal efficiencies exceeding 90% for both dyes under optimized conditions, demonstrating its ability to reduce dye concentrations to acceptable levels effectively. Furthermore, chitosan exhibits excellent reusability, retaining over 75% of its initial adsorption capacity after five cycles, thereby minimizing the need for continuous production of fresh adsorbents and reducing overall operational costs.

The moderate adsorption capacity of unmodified chitosan must therefore be evaluated within the context of its intended application. For decentralized wastewater treatment in resource-limited settings, small-scale operations, or as a preliminary treatment step, the combination of low cost, simplicity, and reasonable performance may be more valuable than maximizing capacity through complex modifications. In such contexts, the ease of material production, the availability of raw materials, and the adsorbent's environmental compatibility are often more critical than achieving the highest possible adsorption capacity. The findings of this study indicate that adsorption efficacy in chitosan-based systems is influenced not only by surface area and porosity but also by the accessibility and reactivity of functional groups, as well as pH-dependent electrostatic interactions. By optimizing these physicochemical parameters, unmodified chitosan can achieve performance levels competitive with those of many real-world applications.

3.5. Desorption and Reusability of the Biosorbent

3.5.1. Efficiency of Desorbing Agents

Desorption experiments were performed to assess the regeneration capability of chitosan after adsorbing MB and MO. Four desorbing agents were tested: 0.1 M hydrochloric acid (HCl), 0.1 M sodium hydroxide (NaOH), 0.1 M sodium chloride (NaCl), and deionized water. Each agent was selected to represent different desorption mechanisms: acid-induced ion exchange (HCl), alkaline disruption of interactions (NaOH), ionic strength-driven displacement (NaCl), and simple physical desorption (deionized water).

As shown in Figure 12, 0.1 M HCl exhibited the highest desorption efficiency for MB, reaching 90.2%. This efficiency is attributed to the protonation of amino groups on chitosan, which promotes electrostatic repulsion and release of the cationic dye. In contrast, 0.1 M NaOH was most effective for MO, with a desorption efficiency of 85.1%. The high alkalinity leads to deprotonation of chitosan's functional groups, weakening the electrostatic interaction with the anionic dye molecules and facilitating their release.

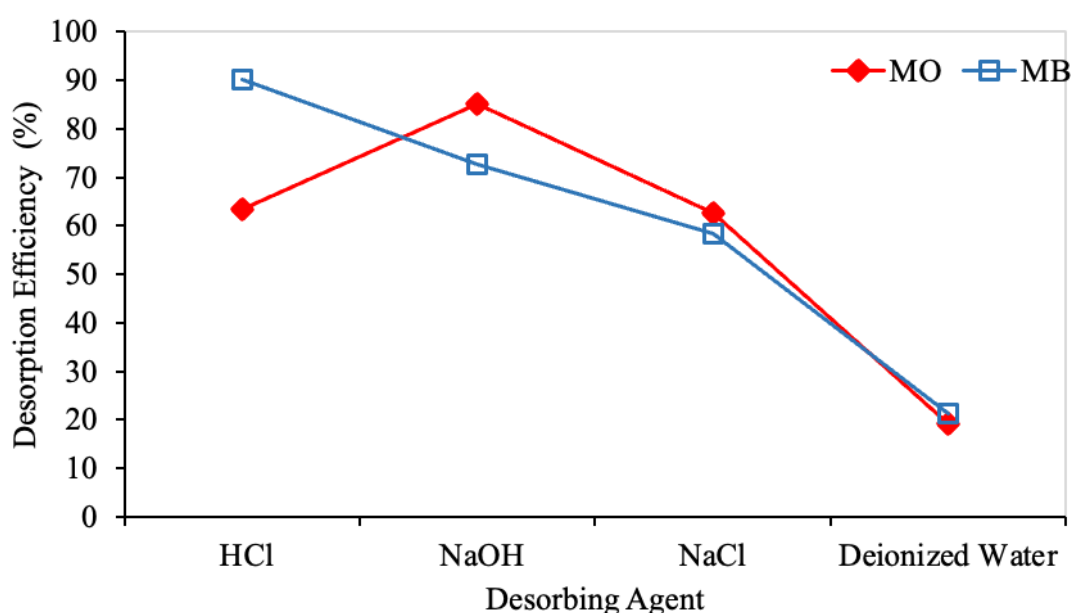


Figure 12. Desorption efficiency of different agents for MB and MO removal.

Sodium chloride showed moderate desorption performance, with 58.3% and 62.7% desorption for MB and MO, respectively. This effect is likely due to competitive ion exchange, where Na^+ and Cl^- ions displace the dye molecules from the active sites. Deionized water exhibited the lowest desorption capacity (<25% for both dyes), indicating that dye retention on chitosan is not solely based on weak physical forces, but is instead dominated by stronger chemisorptive interactions.

The overall results reinforce the conclusion that desorption from chitosan is pH-sensitive and that acidic and alkaline conditions are critical for efficient regeneration. The findings align with prior studies, including those by [86], which emphasized the roles of electrostatic and ionic interactions in dye sorption and desorption on polysaccharide-based materials.

From an environmental and economic perspective, the use of 0.1 M HCl and 0.1 M NaOH as regenerating agents warrants careful consideration. While these reagents are effective, their application on a larger scale would introduce chemical costs and require appropriate handling and neutralization steps to mitigate potential environmental impacts. However, the concentrations employed in this study (0.1 M) are relatively low, minimiz-

ing chemical consumption and associated costs. Furthermore, the ability to reuse the chitosan biosorbent over five cycles with only a 17–18% reduction in adsorption capacity significantly offsets the initial chemical input by reducing the demand for fresh adsorbent material and lowering overall sludge generation. This reusability enhances process economics and aligns with circular-economy principles by extending the useful life of the bio-based adsorbent. Future work could further explore the use of milder, more sustainable desorbing agents, such as organic acids or buffers, to improve the environmental profile of the regeneration step while maintaining acceptable desorption efficiencies. Nonetheless, the current findings demonstrate that chitosan regeneration with dilute acid and base offers a practical balance between performance, cost, and environmental responsibility for wastewater treatment applications.

3.5.2. Reusability of Chitosan over Multiple Cycles

The reusability of chitosan was further evaluated through five successive adsorption–desorption cycles using the most effective desorbing agents identified for each dye: 0.1 M HCl for MB and 0.1 M NaOH for MO. After each cycle, the biosorbent was thoroughly rinsed, dried at ambient conditions, and reused under identical experimental conditions to ensure consistency.

As shown in Table 6, chitosan maintained high dye removal efficiency through the first two cycles, with MO removal decreasing from 98.15% to 94.21%, and MB from 93.76% to 89.58%. From the third cycle onward, a gradual decline in performance was observed. By the fifth cycle, MO and MB removal efficiencies decreased to 81.43% and 77.28%, respectively. This drop corresponds to an approximate 17–18% reduction in adsorption capacity over the five-cycle period.

Table 6. Reusability performance of chitosan over five adsorptions–desorption cycles.

Cycle Number	MO Removal Efficiency (%)	MB Removal Efficiency (%)
1	98.15	93.76
2	94.21	89.58
3	89.87	84.94
4	85.65	81.11
5	81.43	77.28

The decrease in performance can be attributed to several factors. First, partial loss of accessible active sites may occur because dye molecules remain strongly bound and are not fully desorbed during regeneration. Second, repeated exposure to acidic or alkaline desorbing agents may degrade the structural integrity of chitosan, particularly affecting the crystalline domains and weakening the polymer backbone. Third, SEM analysis conducted after five cycles showed visible surface compaction and pore blockage. At the same time, FTIR spectra showed diminished intensities of the -NH_2 and -OH peaks, suggesting partial deactivation of the binding groups.

Despite these limitations, the biosorbent retained over 75% of its original adsorption capacity after five cycles, which supports its applicability for semi-continuous or batch treatment systems. Similar patterns were reported by [85], who showed a gradual but manageable decline in chitosan performance over repeated uses, and emphasized the economic feasibility of its regeneration under controlled conditions.

4. Conclusions

This study systematically evaluated the adsorption performance of unmodified chitosan, derived from shrimp shell waste, for the removal of methyl orange (MO) and methylene blue (MB) from aqueous solutions. The key findings are summarized as follows:

Optimized Removal Efficiency: Under optimized conditions, chitosan achieved high removal efficiencies of 98.80% for MO (at pH 3, 0.5 g dosage) and 90.65% for MB (at pH 9, 1.0 g dosage) within 30 min, demonstrating rapid adsorption kinetics.

Mechanistic Insights via Characterization: Comprehensive characterization (FTIR, SEM-EDX, XRD, TGA, zeta potential, pH_{zpc}) confirmed that adsorption is driven by the abundant amino (–NH₂) and hydroxyl (–OH) functional groups. FTIR analysis revealed their direct involvement through electrostatic interactions and hydrogen bonding, while SEM-EDX provided visual and elemental evidence of successful dye uptake. The pH_{zpc} of 7.2 explained the strong pH-dependent adsorption behavior.

Monolayer Chemisorption: Equilibrium data fitted the Langmuir isotherm model, indicating monolayer adsorption on a homogeneous surface, with maximum adsorption capacities of 7.843 mg/g for MO and 7.605 mg/g for MB. Kinetic studies followed the pseudo-second-order model, confirming chemisorption as the rate-limiting step.

Thermodynamic Profile: Thermodynamic analysis revealed that the adsorption process was endothermic and non-spontaneous under the studied conditions, consistent with energy-dependent surface interactions.

Reusability Potential: Desorption and reusability studies demonstrated that chitosan could be effectively regenerated using 0.1 M HCl for MB and 0.1 M NaOH for MO, retaining over 75% of its initial adsorption capacity after five cycles, which underscores its practical applicability.

Implications for Sustainable Wastewater Treatment:

The findings of this work have significant implications for the development of sustainable, low-cost wastewater treatment technologies. First, by demonstrating that unmodified chitosan—without any chemical grafting or composite formation—can achieve high dye removal efficiencies, this study challenges the prevailing paradigm that modification is always necessary. This simplicity translates directly into reduced material processing costs, lower energy inputs, and more effortless scalability, making it particularly attractive for decentralized treatment facilities or communities with limited technical and financial resources.

Second, the use of chitosan derived from shrimp shell waste embodies the principles of circular economy and waste valorization. Transforming a seafood industry byproduct into a valuable biosorbent not only mitigates waste-disposal issues but also provides an affordable, locally sourced material for water treatment, especially in coastal regions.

Third, the excellent reusability of the biosorbent over multiple cycles minimizes the need for continuous production of fresh adsorbents, thereby reducing the overall material footprint and operational costs of the treatment process. This aligns with the goals of sustainable resource management by extending the material's useful life and reducing sludge generation.

Fourth, the mechanistic understanding gained from this work—particularly the dominance of chemisorption and pH-dependent electrostatic interactions—provides a rational basis for designing treatment protocols tailored to specific dye types. This knowledge enables more efficient use of the adsorbent by simply adjusting operational parameters (such as pH) rather than resorting to complex and costly material modifications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/polym18050546/s1>, Table S1: Showing the average, minimum,

and maximum values for a series of measurements across different categories. The data highlights slight variations in the recorded values, with averages consistently above 90, indicating stable results; Figure. S1: N₂ adsorption–desorption isotherms (77 K) and the corresponding BJH pore size distribution of pristine chitosan.

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