OPEN ACCESS

Scholars International Journal of Chemistry and Material Sciences
Abbreviated Key Title: Sch Int J Chem Mater Sci
ISSN 2616-8669 (Print) |ISSN 2617-6556 (Online)
Scholars Middle East Publishers, Dubai, United Arab Emirates
Journal homepage: http://saudijournals.com

Original Research Article

Synthesis of Chitosan-Based Nanocomposites from Crab Shells for Optimized Cadmium (II) Removal in Aqueous Solution

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DOI: https://doi.org/10.36348/sijcms.2025.v08i05.001 | **Received:** 23.06.2025 | **Accepted:** 25.08.2025 | **Published:** 03.09.2025

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Abstract

Heavy metal pollution especially that of cadmium (II), poses serious threats to the environment and human health because of its toxicity and endurance. The synthesis of chitosan from crab shells, a fisheries waste, and its effectiveness as a biosorbent for the removal of Cd^{2+} from aqueous solutions are the subjects of this work. Crab shells were demineralised, deproteinised, and deacetylated to create chitosan, which was then characterised using FTIR to verify the functional groups ($-NH_2$, -OH) in charge of metal binding. The effects of pH, adsorbent dosage, beginning Cd^{2+} concentration, and contact time with adsorption behavior analyzed using Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models, alongside kinetic and thermodynamic studies. The chitosan exhibited a maximum adsorption capacity of 714.3 mg/g at pH 8, with 92.5% removal efficiency, as described by the Langmuir isotherm model ($R^2 = 0.99$). Pseudo-second-order kinetics ($R^2 = 0.9995$) confirmed chemisorption as the dominant mechanism. Thermodynamic studies revealed an endothermic ($\Delta H° = 14.8$ kJ/mol) and spontaneous ($\Delta G° = -6.1$ to -8.2 kJ/mol) process, with efficiency increasing from 85.3% to 94.7% at 303–333 K. Compared to commercial chitosan, the crab shell-derived chitosan offers a cost-effective, sustainable alternative, aligning with circular economy principles. These results demonstrate its potential for large-scale wastewater treatment in areas affected by heavy metal contamination, and further study is advised to improve chitosan regeneration and modification for industrial use.

Keywords: Heavy metal, adsorption, chitosan, cadmium, kinetics, thermodynamics.

INTRODUCTION

Rapid industrial growth, urbanization, and extensive farming practices have made environmental harm, particularly the poisoning of water sources, a global concern in recent decades. Despite being necessary for economic expansion, these advancements have resulted in the extensive discharge of pollutants into both terrestrial and aquatic habitats, including hazardous organic and inorganic substances (Adriano, 2001). Heavy metals are a particularly hazardous class of these contaminants, distinguished by their bio accumulative nature, extended environmental persistence, and significant health concerns even at low doses (Mitra *et al.,* 2022).

Heavy metals have been removed from contaminated surroundings using a variety of methods. The adsorption method is superior to the others among these techniques in many ways, this method is a surface phenomenon during which contaminants are adsorbed in the adsorbent surface with physical forces. Adsorption depends on many factors such as temperature, pH, concentration of contaminants, time of adsorption phase contact with contaminants, particle size of adsorbent phase and contaminants and temperature and nature of pollutants and adsorption (Saheed, Azeez & Suah 2022).

Both natural and man-made sources can release heavy metals into the environment, including cadmium (Cd), lead (Pb), mercury (Hg), chromium (Cr), and arsenic (As). Naturally, little amounts of these metals are released into ecosystems through processes like volcanic eruptions and the weathering of rocks that are heavy in metals (Tchounwou *et al.*, 2012). However, human

Citation: Nwokoma Patience C., Okeke Chibuzor O., Onyeocha Veronica, Okoronkwo Joseph C., Nwachukwu Oluebube U., Onukwufor Gifty A. (2025). Synthesis of Chitosan-Based Nanocomposites from Crab Shells for Optimized Cadmium (II) Removal in Aqueous Solution. *Sch Int J Chem Mater Sci, 8*(5): 183-191.

activities like mining, metal refining, burning fossil fuels, electroplating, using phosphate fertilizers, manufacturing paints and batteries, mishandling municipal and industrial wastewater, and industrial waste are the main source of input (Oladimeji *et al*, 2024; Rashid *et al*., 2023).

These metals often remain in the environment for a long period after being released, damaging surface water, groundwater, and soil. Cadmium is one of the most hazardous heavy metals because of its high mobility in land and water systems, propensity to cling to organic materials, and high probability of getting into the food chain. Cadmium is easily absorbed by organisms and tends to accumulate in various tissues, but unlike essential trace elements, it has no recognized biological role in humans or animals (Genchi *et al*., 2020; Farias *et al*., 2024). Chronic exposure to cadmium, whether via contaminated food, water, or air, has been linked to serious health complications, such as osteoporosis, lung illness, heart problems, renal failure, and even cancer (Lalor, 2008).

The "Itai-itai" sickness outbreak in Toyama Prefecture, Japan, is a historical example of the dangers of cadmium toxicity. It resulted in excruciating kidney and skeletal problems after long-term consumption of rice and water contaminated with cadmium from mining (Sasaki *et al*., 2024). In order to lessen the risks associated with heavy metal pollution, this incident highlighted the significance of ongoing environmental monitoring and remediation strategies. The accumulation of heavy metals in the environment necessitates the development of efficient, sustainable, and economical cleanup techniques because of their toxic and non-biodegradable nature. Although helpful, conventional treatment methods include chemical precipitation, ion exchange, reverse osmosis, membrane filtration, and electrochemical procedures have a number of disadvantages (Qasem, Mohammed & Lawal 2021).

These include the creation of hazardous sludge, high operating costs, managerial complexity, and poor efficacy in treating low metal ion concentrations (Razzak *et al*., 2022). Furthermore, these approaches frequently lack selectivity and might not be economically feasible in underdeveloped or rural locations with inadequate infrastructure. The scientific community has embraced biosorption—a technique that employs biological materials for the passive absorption of contaminants from water—in response to these difficulties. Because of its simplicity, affordability, environmental friendliness, and potential for reuse and regeneration, this strategy has attracted a lot of attention (Torres, 2020).

The ability of natural biosorbents, including bacteria, fungi, algae, agricultural waste, and biopolymers, to absorb heavy metals has been thoroughly studied. Because of its abundance, useful properties, and compatibility with the environment, chitosan has become one of the most promising biosorbents (Dehghani *et al*., 2023). The natural polymer chitin, which is mostly present in the shells of crustaceans such as shrimp, crabs, and lobsters, is the source of chitosan. Chitosan, which is created by deacetylating chitin with alkaline solutions, has a high density of reactive amino ($-NH_2$) and hydroxyl (-OH) groups that can bind to heavy metal ions efficiently using chelation, electrostatic interaction, and ion exchange (Iber *et al*., 2021).

Numerous studies have examined the capacity of natural biosorbents, such as bacteria, fungi, algae, agricultural waste, and biopolymers, to absorb heavy metals (Nleonu *et al*., 2017). Chitosan has emerged as one of the most promising biosorbents due to its abundance, practical qualities, and environmental friendliness. Chitosan is derived from the natural polymer chitin, which is mostly found in the shells of crustaceans including shrimp, crabs, and lobsters (Basem *et al*., 2024). A high density of reactive amino ($-NH_2$) and hydroxyl (-OH) groups makes up chitosan, which is produced by deacetylating chitin with alkaline solutions. These groups can effectively bind to heavy metal ions through chelation, electrostatic interaction, and ion exchange (Gamage *et al.,* 2023; Gamage & Shahidi 2007). Chitosan, a marine by-product that is frequently disregarded, was made in this study from locally acquired crab shells and utilized as a biosorbent to remove cadmium (II) ions from aqueous medium (Elgarahy *et al*., 2021).

In this work, crab shell chitosan was synthesised, and its ability to adsorb cadmium (II) ions in aqueous solutions under varied pH, temperature, initial metal concentration, and contact time conditions was assessed. To clarify the methods and effectiveness of Cd^{2+} removal, the adsorption behaviour was examined using kinetic and thermodynamic studies in conjunction with Langmuir, Freundlich, Tempkin, and Dubinin-Radushkevich isotherm models. The results seek to establish chitosan as an economical, environmentally friendly biosorbent for treating wastewater, especially in areas where industrial and agricultural pollutants are prevalent. This study contributes to the development of scalable, environmentally friendly biosorption technologies for environmental remediation by expanding the concepts of green chemistry and the circular economy through the use of fishing waste.

2.0 EXPERIMENTAL

2.1 Chemicals and Reagents

All reagents and chemicals used in this study were of analytical grade and were used without further purification. Cadmium chloride ($CdCl_2 \cdot 2.5H_2O$) was obtained from Merck (Germany) and used for preparing cadmium ion solutions. Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were used for pH adjustments. Deionized water was used for all solution preparations and dilutions. A commercial chitosan sample was obtained from Sigma-Aldrich (St. Louis, Missouri, USA) and was used as a standard for comparison with the locally synthesized chitosan.

2.2 Preparation of Cadmium Stock and Standard Solutions

standard solution of cadmium ion was prepared by dissolving 2.033 g cadmium chloride ($CdCl_2.5H_2O$) in 1000 ml of deionized water to create a 1000 mg/L cadmium stock solution. Following serial dilution, standard working solutions with different concentrations (0.01, 0.05, 0.10, 0.50, and 1.00 mg/L) were prepared via a serial dilution for atomic absorption spectroscopy (AAS) calibration using a Shimadzu Buck Scientific Model 210VGP. For adsorption experiments, working solutions of 80, 160, 240, and 300 mg/L were prepared by diluting the stock solution with deionized water, and pH was adjusted using 1M HCl or NaOH.

2.3 Preparation of chitosan from crab shells

The following conventional approach was used to turn crab shells from nearby seafood dealers into chitosan (Toan, 2009):

Crab shells were collected from the local market in Nigeria's Akwa-Ibom State. After being cleaned with tap water, the shells were crushed using a mortar and pestle. To aid in the chemical extraction of chitosan and enhance its quality, it was crushed using a mortar and pestle and kept in polyethylene bags at room temperature (28±2℃) for 24 hours to allow for partial autolysis.

2.3.1 Isolation of chitosan

Chitosan was isolated through three steps: demineralization, deproteinization and deacetylation, as outlined below (Figure 2.1).

2.3.2 Demineralization

Crushed crab shells were treated with 2%, 3%, or 4% HCI at ambient temperature (28±2℃) at a solid - to- solvent ratio 1:5 (w/v) for 16 hours (Toan, 2009). The residue was washed and soaked in tap water until neutral pH.

2.3.3 Deproteinization

The demineraized shells were treated with 4% NaOH at ambient temperature (28±2℃) at a solid- to- solvent ratio of 1:5 (w/v) for 20 hours (Toan, 2009). The residue was washed to neutral pH, dried until crispy, and ground into small particles to facilitate deacetylation.

2.3.4 Deacetylation

Chitin was treated with NaOH (30%, 40%, 50%, 60%) at 65°C temperature at a solid- to- solvent ratio 1:10 (w/v) for 20 hours. (Toan, 2009). The resulting chitosan was washed to neutral pH with tap water, dried in a cabinet dryer for 4 hours at 65±50°C and prepared for characterization.

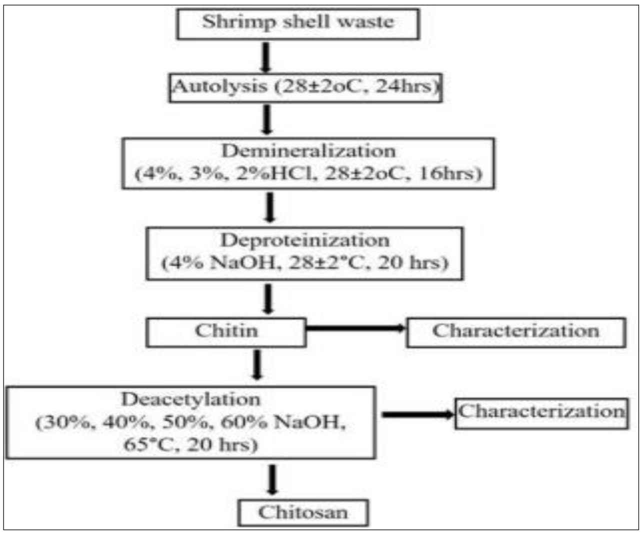

Figure 2.1: Traditional shrimp Chitin and Chitosan production Flow Scheme (Modified from Toan, 2009)

2.4 Characterization of Chitosan

The Characterization of adsorbent was carried out to determine some properties of the adsorbent. Fourier Transform Infrared Spectroscopy (FTIR) was used to characterize the extracted chitosan in order to confirm its chemical identity and identify any functional groups that were present. FTIR spectra were captured between 4000 and 500 cm^{-1}. Chitosan and KBr were combined to create the samples, which were then pressed into pellets for examination.

2.5 Batch Adsorption Experiments

Batch adsorption experiments were conducted to evaluate the effects of pH, adsorbent dose, initial cadmium concentration, and contact time on Cd^{2+} removal.

Chitosan produced was crushed and sieved with 250µm mesh size, before using it for the experiment. The batch adsorption studies were carried out at room temperature. Batch mode was chosen because of its simplicity. The batch experiment was performed by adding 0.3g of the adsorbent to 30ml of metal solution in 60ml plastic container at room temperature. The effect of temperature was determined by placing the plastic bottle in a 186 hermos- stated water bath. The effects of operating parameters were carried out on pH, adsorbent dose, initial metal ion concentration, and contact time. Each experiment was performed in duplicate, and the average values were calculated to minimize error. The amount of metal ion adsorbed was calculated from the equation below:

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

% Adsorption = $\frac{(C_o - C_e)\times 100}{C_o}$

qe (mg/g) is the adsorption capacity of adsorbent on the adsorbate at equilibrium. Ce (mg/l) and Co (mg/l) are the equilibrium concentration and initial concentration of the metal ions in solution respectively. V (L) is the volume of solution and m (g) is the mass of the adsorbent used.

Adsorbent Dose

The effect of adsorbent dose was studied using 0.1–0.5 g of chitosan in 30 mL of 250 mg/L Cd^{2+} solution, agitated for 60 minutes at constant pH and temperature

Contact time

The effect of contact time was studied by adding 0.3g of the adsorbent to 30ml of metal solution in 60ml plastic bottle. The sample was agitated at varying time intervals of (10-90mins) after which the samples were withdrawn, filtered and analyzed. Experiments were conducted at constant temperature, pH, and initial metal ion concentration.

pH of Solution

The pH was adjusted from 2 to 8 using 1 M HCl or NaOH, with 0.3 g of chitosan in 30 mL of 250 mg/L Cd^{2+} solution, agitated for 60 minutes.

Initial metal ion Concentration

Initial Cd^{2+} concentrations of 80, 160, 240, and 300 mg/L were tested with 0.3 g of chitosan in 30 mL, agitated for 60 minutes**.**

2.6 Adsorption Isotherm Studies

Adsorption isotherms were analyzed using Langmuir, Freundlich, Tempkin, and Dubinin-Radushkevich models. Experiments used 0.2 or 0.3 g of chitosan in 30 mL of Cd^{2+} solution (80–300 mg/L), agitated for 60 minutes. The Langmuir model is:

2.6.1 Langmiur isotherm model:

Langmuir isotherm model is expressed as (Akpomie and Dawodu, 2014):

$$\frac{C_e}{q_e} = \frac{1}{q_L K_L} + \frac{C_e}{q_L} \qquad (3)$$

Where ql (mg/g) is monolayer adsorption capacity of the adsorbent and KL (L/mg) is the adsorption constant which reflects the affinity between the adsorbent and adsorbate. qL and KL were determined from the slope and intercept of the plots of ce/qe versus Ce. An essential feature of the Langmuir isotherm can be expressed in terms of dimensionless separation factor (RL) defined as:

$$R_L = \frac{1}{(1+bC_O)} \qquad (4)$$

2.6.2 Freundlich isotherm model:

The Freundlich isotherm is based on the assumption that sorption takes place on homogeneous adsorbent surface, where the sorption energy distribution decreases exponentially and can be expressed as:

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (5)$$

Where KF (mg/g) (mg/l)1/n and n are constants for adsorption capacity and intensity respectively. A plot of Log qe versus Log Ce gives a straight line graph of slope 1/n and intercepts Log KF.

2.6.3 Temkin isotherm model:

This is based on the assumption that the free energy of adsorption is a function of the surface coverage, it is expressed as:

$$qe = B\ln A + B\ln Ce \qquad (6)$$

Where B = $\underline{RT}$ (mg/g) is the isotherm constant related to the heat of adsorption, and A (L/g) is the equilibrium binding constant corresponding to the maximum binding energy, R is the gas constant ($8.314 J/molk^{-1}$) and T(k) is the absolute temperature. The constants A and B were calculated from the plot of qe and ln Ce.

2.6.4 The Dubinin – Radushkevich isotherm

This isotherm assumes a homogeneous surface or a constant adsorption potential and it is expressed as:

$$\ln qe = \ln qm - \beta\varepsilon 2 \qquad (7)$$

Where qm (mg/g) is the theoretical saturation capacity, β (mol2 /j2) is a coefficient related to the mean free energy of adsorption and ε is the Polanyi expressed as:

$$\varepsilon = RT \ln\left(1 + \frac{1}{Ce}\right) \qquad (8)$$

The constant qm and β were calculated from the intercept and slope of ln qe versus ε2.

2.7 Adsorption Kinetics Studies

The batch adsorption studies were carried out at varying time intervals and were fitted to the Pseudofirst-order and Pseudo –second –order equations. The linear form of the Pseudo –second – order is given as:

$$\text{Log }(qe\text{-}qt) = \text{Log }qe - \frac{(K1t)}{2.303} \qquad (9)$$

Where K1 (min-1) is the rate constant and qt and qe are the amounts of metal ion adsorbed at time t and equilibrium respectively. The constant K1 and qecal were obtained from the slope and intercept of the plot of Log (qe – qt) versus t.

The pseudo –second – order model assumes that the rate of occupation of adsorption sites is proportional to the square of the number of unoccupied sites (Akpomie and Dawodu, 2014). The linear form of the pseudo- second –order equation is:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \qquad (10)$$

K_2 (g/mgmin) is the rate constant. The initial sorption rate h was calculated from the equation: $h = K_2 q_e^2$ If the pseudo –second –order equation is applicable, the plot of t/qt versus t yields a straight line graph. K_2 and qe were to be calculated from the slope and intercept of the plot respectively.

2.8 Thermodynamics Studies

Thermodynamic experiments used 0.3 g of chitosan in 30 mL of 250 mg/L Cd^{2+} solution at 303, 313, 323, and 333 K, agitated for 60 minutes. Thermodynamic parameters were calculated using:

$$Kc = \frac{Ca}{Ce} \qquad (11)$$

$$\Delta G = -RT\ln Kc \qquad (12)$$

$$\ln Kc = -(\Delta H^{O}/RT) + (\Delta S^{0}/R) \qquad (13)$$

Where Kc is the thermodynamic equilibrium constant, Ca (mg/l) is the concentration of metal ions adsorbed at equilibrium, Ce (mg/l) is the concentration of metal ions remaining in solution at equilibrium, R is the ideal gas constant (8.314j/molk) and T(k) is the absolute temperature. The values of ΔH^0 and ΔS^o will be gotten from the slope and intercept of the plot of ln Kc versus 1/T

3.0 RESULTS AND DISCUSSION

The chitosan synthesized from crab shells demonstrated a high adsorption capacity for Cd^{2+} ions, attributed to its functional groups ($–NH_2$, –OH, C=O), which facilitate chelation and ion exchange, as evidenced by Fourier Transform Infrared Spectroscopy (FTIR) shifts. Specifically, the NH_2 peak shifted from 897.5 cm^{-1} to 758.64 cm^{-1}after cadmium adsorption, confirming chemisorptions via coordination with amino groups, consistent with findings by Iber et al. (2021). Slight shifts in OH and C=O peaks further indicate interactions with hydroxyl and carbonyl groups, reinforcing chitosan's role as an effective adsorbent. The shift in the NH_2 peak from 897.5 cm^{-1} to 758.64 cm^{-1} after cadmium adsorption suggests coordination between Cd^{2+} ions and the amino groups, confirming chemisorption as a primary mechanism. The slight shifts in OH and C=O peaks further indicate interactions with hydroxyl and carbonyl groups, consistent with literature finfings that chitosan's amino and hydroxyl groups are key binding sites for heavy metals (Iber *et al.,* 2021). The shift in the NH_2 peak from 897.5 cm^{-1} to 758.64 cm^{-1} after cadmium adsorption suggests coordination between Cd^{2+} ions and the amino groups, confirming chemisorption as a primary mechanism. The slight shifts in OH and C=O peaks further indicate interactions with hydroxyl and carbonyl groups, consistent with literature finfings that chitosan's amino and hydroxyl groups are key binding sites for heavy metals (Iber *et al.,* 2021).

Table 1: FTIR Spectra Data for Chitosan Samples

Functional groups	Foreign chitosan (cm^{-1})	Local chitosan (cm^{-1})	Local chitosan with cadmium (II) ion (cm^{-1})
OH	3432.03	3436.81	3433.31
N-H stretching	3432.03	3274	3270
C-H stretching	2877.43	2893	2865.3
C=O stretching	1655.3	1631.17	1630.98
CH_3	1423.76	1429.1	1413.3
C-O-C	1080.01	1073.49	1072
NH_2	889.57	897.5	758.64

3.1 ADSORPTION STUDIES

3.1.1 Effect of pH

As explained in the experimental section, the effect of pH on Cd2+ adsorption was examined over a pH range of 2–8, with the adsorption efficiency increasing with pH and peaking at pH 8 with a remova efficiency of 92.5%. At lower pH values, protonation of amino groups decreased their avaiability for metal binding due to electrostatic repulsion, while at pH 8, deprotonation improves coordination with Cd2+ ions. This pH dependency aligns with studies indicating optimal heavy metal adsorptionby chitosan at neutral to slightly alkaline conditions (Gamage *et al.,* 2023). The adsorption process was highly pH-dependent, with maximum removal efficiency (92.55) at pH 8. At lower pH values (e.g., pH 2), protonation of amino group reduces their availability for metal binding due to electrostatic repulsion. At pH 8, deprotonation enhances coordination with Cd^{2+} ions, aligning with studies by Gamage *et al.,* (2023) that report optima heavy metal adsorption by chitosan in neutral to slightly alkaline conditions. The stability of chitosan at low pH was not compromised, as experiments were conducted within a safe range to prevent dissolution.

3.1.2 Effect of Adsorbent Dose

The influence of adsorbent dose was studied using 0.2 and 0.3 g of chitosan in 30ml of 250 mg/L Cd^{2+} solution. The 0.3g dose achieved a higher removal efficiency (90.2 %) compared to 0.2g (82.7 %), due to the increased availability of binding sites. However, the adsorption capacity (q_e) decreased from 619.5mg/g at 0.2 g to 451.3 mg/g at 0.3g, indicating site saturation at higher doses. Adsorbent dose experiments showed that increasing the dose from 0.2g to 0.3 g in 30 ml of 250 mg/L Cd^{2+} solution improved removal efficiency from 82.7% to 90.2%, due to greater availability of binding sites. However, the adsorption capacity (qe) decreased from 619.5 mg/g to 451.3 mg/g, indicating site saturation at higher doses, a common phenomenon in biosorption studies (Elgarahy *et al.,* 2021). It has been reported in various research that electrostatic interactions between the adsorbent can play a significant factor in the relationship between adsorbent and metal sorption (Nleonu *et al*., 2023; Onyemenonu *et al*., 2015).

3.1.3 Effect of Initial Cadmium Concentration

Adsorption experiments with initial Cd2+ concentrations of 80, 160, 240, and 300 mg/L showed that adsorption capacity increased steadily, reaching 694.2 mg/g at 300 mg/L for 0.3 g chitosan. In contrast removal efficiency declined from 95.1% at 80 mg/L to 69.4% at 300 mg/L, reflecting the saturation of available adsorption sites at higher concentrations. The effect of initial cadmium concentration revealed that qe increased to 694.2 mg/g at 300 mg/L, while removal efficiency decreased from 95.1% at 80 mg/L to 69.4% at 300 mg/L, reflecting saturation of adsorption sites at higher concentrations.

3.2 Adsorption Isotherm Studies

The adsorption data were fitted to Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich isotherm models. The Langmuir model provided thebest fit (R^2 = 0.99), indicating monolayer adsorption on a homogenous surface. The maximum adsorption capacity (q_{max}) was 714.3 mg/g, with a Langmuir constant (K_L) of 0.032 L/mg. the separation factor (R_L) ranged from 0.094 to 0.289, suggesting favorable adsorption. The high q_{max} value suggests that crab shell-derived chitosan is a highly effective adsorbent compared to other biosorbents, such as algae or agricultural waste (Dehghani *et al*., 2023)

3.2.1 The Langmuir Isotherm

From Table 2, the correlation coefficient (R^2) of Cd (II) is 0.99 which indicates a good fit of the monolayer Langmuir to the adsorption of the metal ions unto oil bean seed shell activated carbon. The Langmuir isotherm model provided the best fit (R^2= 0.99), suggesting monolayer adsorption on homogenous binding sites. The maximum adsorption capacity (q_{max}~ 200-5mg/g) or agricultural waste (q_{max} ~ 100-400 mg/g), as reported by Dehghani *et al.,* (2023). The Langmuir constant (K_l = 0.032 L/mg) and separation factor (R_l = 0.094—0.289 for initial concentrations of 80-300 mg/L) indicate favorable adsorption. Also the maximum monolayer adsorption capacity qL (mg/g) for Pb (II) is 34.4483. The value of the separation factor (R_L) provides important information about the nature of the adsorption process. The adsorption is said to be irreversible (R_L = 0), favourable ($0<R_L<1$), linear (R_L =1) or unfavourable ($R_L>1$). For the initial concentration ranging from 80mg/l to 300mg/l, the RL values range from 0.0000968 – 0.000363 indicating a favourable adsorption of Cd (II) onto chitosan.

3.2.2 The Freundlich isotherm model

The Freundlich isotherm model assumes a multilayer adsorption unto a heterogeneous adsorbent surface, where the sorption energy distribution decreases exponentially. From the Table 3, the correlation coefficient (R2) of the Cd (ii) adsorption is 0.93, indicating a good fit of the Freundlich multilayer heterogeneous adsorption model to the adsorption of Cd(ii) using the adsorbent. If the value of n lie between 1 and 10, it indicates a favourable adsorption (Das and Mondal,2011). The values of n obtained for the Cd (ii) adsorption using chitosan is 2.5, indicating a favourable adsorption. The adsorption capacity constant KF (mg/g)(mg/l)1/n for metal ion adsorption is 45.8.

3.2.3 The Temkin Isotherm Model

Temkin considered the effect of the adsorbate interaction on adsorption and proposed the model. From Table 3, the correlation coefficient of the Cd(II) ion adsorption is 0.90 which is lower than that of the Langmuir and Freundlich. This shows that the adsorption of Cd (ii) ion onto chitosanfit well to the model as much as the two models above. The value of equilibrium binding constant A (L/g) is 0.42 and the isotherm constant B (mg/g) which is related to heat of adsorption is 128.6.

3.2.4 Dubinin – Radushkevich Isotherm

The correlation coefficient for the Cd (II) adsorption is given as R^2 = 0.87 in the above table which shows that the model does not fit as much as the first two models above. Also, the constants q_m and β were calculated from the intercept and slope of the plot of lnqe versus ε^2. The values of q_m and β are given as 680.5 and 1.2 X 10^{-8} respectively.

The Freundlich mode (R^2 = 0.93, K_x = 45.8 (mg/g) $(mg/L)^{1/n}$, n = 2.5) suggests multilayer adsorption is less dominant, while Tempkin (R^2 = 0.90) and Dubinin-Radushkevich (R^2 = 0.87, q_m = 680.5 mg/g, β = $1.2 \times 10^{-8} kj^2/mol^2$) models confirm the chemical nature of the adsorption process.

Table 3: Isotherm Parameters for Cd2+ Adsorption

Isotherm model	**Cd (II)**
Langmuir model	
qL (mg/g)	714.3
KL (L/mg)	0.032
R^2	0.99
Freundlich model	
KF (mg/g) (mg/L)1/n	45.8
n	2.5
R^2	0.93
Temkin model	
B (mg/g)	128.6
A (L/g)	0.42
R^2	0.90
Dubinin- Radushkevich model	
q _m(mg/g)	680.5
β(mol2/kj2)	$1.2\ x10^{-8}$
R^2	0.87

3.3 Adsorption Kinetics

Kinetic studies were conducted at contact times of 10-90 minutes. The pseudo-second-order model provided a better fit (R^2 = 0.995) compared to the pseudo-first-order model (R^2 = 0.88), indicating that chemisorptions, involving coordination with functional groups, is the rate-limiting step. The equilibriumadsorption capacity (q_e) was 451.3 mg/g for 0.3g chitosan, with a rate constant (k_2) of 0.00012 g/mg.min. Kinetic studies showed that the pseudo-second-order model (R^2 = 0.9995, q_e = 451.3 mg/g, k_2 = 0.0012 g/mg.min) fit better than the pseudo-first-order model (R^2 = 0.88, q_e = 420.1 mg/g, k_2 = 0.028 g/min^{-1}), indicating that chemisorptions, involving coordination with functional groups, is the rate-limiting step. The initial sorption rate ($h = k_2qe^2 = 2.44$ mg/g.min) reflects rapid surface binding within the first 30 minutes (70% of q_e), followed by slower intraparticle diffusion into chitosan's porous structure.

Table 4: Kinetic Parameters for Cd^{2+} Adsorption

Kinetic Model	**Parameter**	**Value**	**R^2**
Pseudo-first-Order	k_1(min -1)	0.028	0.88
	q _e (mg/g)	420.1	
Pseudo-Second-Order	k_2 (g/mg.min)	0.00012	0.9995
	q _e (mg/g)	451.3	

3.4 Thermodynamic Studies

Thermodynamic experiments at 303 K, 313 K, 323 K, and 333 K revealed that Cd^{2+} adsorption is endothermic, with increased removal efficiency at higher temperatures (from 85.3%, 88.1%, 91.5% and 94.7%). The negative Gibbs free energy (ΔG°) values indicate a spontaneous process, while the positive enthalpy (ΔH°) and entropy (ΔS°) values suggest an endothermic process with increased randomness at the solid-solution interface. Thermodynamic studies confirmed an endothermic process, with removal efficiency increasing from 85.3% at 303 K to 94.75 at 333 K. negative Giggs free energy (ΔG° = -6.1 to -8.2 kj/mol) indicates spontaneity, while positive enthalpy (ΔH° = 14.8kj/mol) suggest an endothermic process with increased randomness at the solid-solution interface. These findings, derived from the van't Hoff plot (ln Kc vs. 1/T), suggest that higher temperatures enhance molecular mobility and binding site activation, making chitosan suitable for industrial applications where temperature control is feasible. Compared to commercial chitosan, the crab shell-derived from fishery waste, aligning with circular economy principles. The high q_{max} (714.3 mg/g) positions it as a superior biosorbent for cadmium removal, particularly in regions like the Niger Delta, where heavy metal pollution is prevalent. Future studies could explore chitosan modification (e.g., crosslinking or grafting) to enhance adsorption capacity and investigate regeneration potential for repeated use. Scaling up the process for industrial wastewater treatment could address practical challenges in polluted regions.

The pH dependency highlights the importance of optimizing solution conditions, with pH 8 being ideal due to deprotonation of amino groups. The Langmuir isotherm's superior fit suggests monolayer adsorption, consistent with chitosan's homogeneous binding sites. The pseudo-second-order kinetics indicate that chemical interactions dominate, supported by the high q_max (714.3 mg/g), which surpasses many biosorbents reported in the literature (Elgarahy *et al.,* 2021). The endothermic nature of the adsorption process, as confirmed by thermodynamic studies, suggests that higher temperatures enhance molecular mobility and binding site activation, making chitosan suitable for industrial applications where temperature control is feasible.

Thermodynamic Parameters for Cd2+Adsorption

Temperature (K)	**ΔG°(kJ/mol)**	**ΔH°(kJ/mol)**	**ΔS°(kJ/mol)**	**Removal Efficiency (%)**
303	-6.1	14.8	0.069	85.3
313	-6.8			88.1
323	-7.5			91.5
333	-8.2			94.7

4.0 CONCLUSION

This study successfully synthesized chitosan from crab shells and demonstrated its efficacy as a biosorbent for cadmium (II) ions in aqueous solutions. The synthesized chitosan exhibited a high adsorption capacity (q_{max} = 714.3 mg/g), surpassing many biosorbents like algae and agricultural waste, due to its abundant amino ($-NH_2$) and hydroxyl (–OH) groups, which facilitate chemisorption via chelation and ion exchange, as confirmed by FTIR analysis. The adsorption process was optimized at pH 8 (92.5% removal efficiency), with an endothermic nature (ΔH° = 14.8 kJ/mol) and favorable spontaneity (ΔG° = -6.1 to -8.2 kJ/mol) across 303–333 K. The Langmuir isotherm model ($R^2 = 0.99$) and pseudo-second-order kinetics ($R^2 = 0.9995$) indicate monolayer adsorption and chemical interactions as the dominant mechanisms. By using animal waste to address heavy metal contamination and promote the circular economy, crab shell-derived chitosan provides a sustainable and affordable alternative to commercial chitosan. The results demonstrate its potential for treating industrial effluent, especially in areas with cadmium exposure like the Niger Delta. Future studies should concentrate on modifying chitosan (for example, by grafting or crosslinking) to increase capacity, look into regeneration for repurposing, and scale up the procedure for real-world uses. This research advances green chemistry solutions for the world's water pollution problems and advances sustainable environmental remediation techniques.

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