A sustainable approach to the development and characterization of chitosan thiomer beads for the efficient removal of Cd(II) ions from aqueous effluents

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1. Instrumentation

1.1. Material

Chitosan was produced from crab shell and then modified to glutaraldehyde-crosslinked chitosan (GCC) (refer to the supplementary materials (**SM†**)). NaOH, HCl, CH_3COOH, glutaraldehyde ($HCO(CH_2)_3CHO$) and thiourea (H_2NCSNH_2) are all purchased from Sigma-Aldrich. All reagents, including NaOH (≥98%), HCl (37%), CH_3COOH (≥99%), glutaraldehyde (25% aqueous solution), and thiourea (≥99%), were purchased from Sigma-Aldrich and used without further purification.

1.2. Characterization and instruments

The KBr wafer approach was used to acquire Fourier transform infrared (FTIR) spectra with a Perkin-Elmer-1430 spectrophotometer. A Phillips X-ray radiation unit (Generator PW-1390) was used to capture X-ray diffractograms of the adsorbent using Ni-filtered Cu radiation. A Shimadzu TGA-50H thermogravimetric analyzer was used in a nitrogen environment. A scanning electron microscope (SEM) with a JXA 850 prop micro analyzer was used to assess the morphology. Energy-dispersive X-ray spectroscopy (EDS) was performed with an Oxford Instruments X-MaxN 80 mm^2 detector attached to the JEOL JXA-8500F SEM operated at 15 kV. The concentration of cadmium ions was determined using an atomic absorption spectrometer (AAS, Agilent AA-200).

2. Synthesis of Chitosan

Chitosan synthesis engages three main steps for instance deproteinization, demineralization and deacetylated [S1]. Waste shrimp shells were treated by stirring in 1M NaOH for 90 min at a temperature of 65°C. The alkali was washed-out from the scales and the sample mass was washed with distilled water over and again till the sample reaches neutrality. The deproteinized samples were dried at room temperature and then stirred with 0.75 M HCl (demineralization) for 150 min to yield chitin. The excess HCl present in the chitin sample was removed by thorough washing, with distilled water and the sample was dried at room temperature. Chitin samples were deacetylated by treating with 50 % NaOH for 12 hours at a temperature of 100°C, and then refluxed for 1h at 80 °C to produce chitosan.

1.2.1. Synthesis of glutaraldehyde-crosslinked chitosan (GCC)

A slightly modified version of previously reported protocols (Bui et al., 2020; Taha et al., 2025) was used to prepare the glutaraldehyde-crosslinked chitosan beads. A 5% chitosan solution (w/v) was initially prepared by dissolving chitosan in a 2% CH_3COOH solution (v/v) under magnetic stirring at 500 rpm for 24 h. The resulting solution was centrifuged at 6000 rpm to remove any insoluble substance and subsequently loaded into a syringe (10 mL per instance) equipped with a steel needle of internal diameter 0.33 mm. Using a 1 mL/min flow rate, the CS solution was pushed out of the syringe and mixed with a 1 M NaOH solution. Round beads of coagulated CS formed as soon as the CS-containing droplets came into touch with the NaOH solution. Before being removed from the NaOH solution, the beads were immersed in deionized water (DIW) for many washings until the DIW's pH became neutral. To initiate the crosslinking process, the pre-formed CS beads were introduced to a water-based GA solution (2.5%) at 25 °C. Crucial variables in the GCC formulation were a GA/CS molar ratio of 5:1 and a crosslinking duration of 5 h. Ultimately, the produced GCC beads were removed and thoroughly rinsed with DIW. The final stage was ethanol washing after the DIW washing phase was carried out ten times to get rid of all the unreacted glutaraldehydes in the GCC beads. The purified beads were subsequently dried in an oven for two days at 50 °C.

3. Adsorption kinetics

Lagergren's 1898 pseudo-first-order model [83] posits a direct relationship between adsorption rate and the quantity of vacant adsorption sites. The model equations are expressed as equation 1:

$$\mathbf{q_t = q_e(1-e^{-K_1 t})} \qquad \mathbf{(1)}$$

Where (q_e), and (q_t) are the amounts of cadmium adsorbed (mg/g) at equilibrium and at time (t), respectively, while K_1, (min^{-1}), is the Pseudo-1st Order rate constant.

Ho and McKay's 1999 pseudo-second-order model [S2] posits a relationship where the adsorption rate is proportional to the squared difference between equilibrium and current adsorption capacities. The model equation is presented by equitation 2:

$$qt = \frac{q_e^2 K_2 t}{1 + q_e K_2 t} \qquad \textbf{(2)}$$

where (K_2) is the rate constant of pseudo-second-order adsorption model (g/mg·min).

The Elovich model [S2] is a realistic equation that describes the adsorption processes involving heterogeneous surfaces and variable activation energies. It is applicable to adsorption processes involving chemical reactions and assumes that the adsorption rate is associated to the extent of the reaction. The model equation is shown by equation 3:

$$q_t = \frac{1}{\beta}\ln(\alpha\beta) + \frac{1}{\beta} ln(t) \qquad \textbf{(3)}$$

Where, α (alpha) is the initial adsorption rate (mg/g·min), and β (beta) is the desorption constant related to surface coverage and activation energy (g/mg).

Especially early in the adsorption process, the Elovich model showed a satisfactory fit to the experimental data. The adsorption process appears to occur on a heterogeneous surface with diverse activation energies. The functionalized nature of the chitosan beads, providing diverse adsorption sites and cadmium ion affinities, supports the use of the Elovich model.

Adsorption, according to Weber and Morris's 1963 intraparticle diffusion model, happens via adsorbate molecule diffusion into the adsorbent particles. The model is expressed as equation 4:

$$\mathbf{q_t = k_{id} t^{1/2} + C} \qquad \textbf{(4)}$$

Where, K_{id} is the intraparticle diffusion rate constant (mg/g·min$^{1/2}$), C is the intercept, related to the boundary layer thickness.

4. Adsorption isotherm models

Adsorption isotherm models describe the relationship between adsorbate quantity on the adsorbent and solution concentration at a fixed temperature, and clarify equilibrium distribution between liquid and solid phases, revealing adsorbent-adsorbate interaction mechanisms. The adsorbent's adsorption capacity, mechanism, and surface properties are critically illuminated by them. Langmuir, Freundlich, Temkin, and

Dubinin-Radushkevich are among the most frequently used isotherm models. Every model possesses unique assumptions and application scopes, offering insights into adsorption mechanisms. This study examines several isotherm models to explain the adsorption behavior of Cd^{2+} on glutaraldehyde cross-linked thiourea-functionalized chitosan beads (CLCTB).

The Langmuir isotherm model [S5] can mathematically represented by equation 5:

$$q_e = \frac{q_{max} * K_L * C_e}{1 + K_L * C_e} \tag{5}$$

Where, K_L Langmuir constant related to the affinity of binding sites (L/mg), q_e is the equilibrium adsorption capacity (mg/g), q_{max} the maximum adsorption capacity (mg/g), and C_e the equilibrium concentration of adsorbate (mg/L)

The Freundlich model [S6] can be represented as in equation 6:

$$q_e = K_f * C_e^{1/n} \tag{6}$$

Adsorption capacity is represented by the Freundlich constant (Kf), while adsorption intensity is represented by the empirical parameter (n). The adsorbent's adsorption capacity is reflected by its (Kf) value. The adsorption intensity is indicated by the value (n); if (n > 1), it indicates favorable adsorption, while (n < 1) suggests unfavorable adsorption.

The Temkin model is represented as equation 7:

$$q_e = B * \ln(A * C_e) \tag{7}$$

Adsorption capacity and energy are consistently related to A and B, respectively. The Temkin isotherm's A constant (L/g) reflects adsorption capacity; its B constant (J/mol) reflects adsorption energy. The equilibrium amount of adsorbate adsorbed is q_e (mg/g), and C_e (mg/L) signifies its equilibrium concentration in the solution.

$$B = \frac{R * T}{b} \tag{8}$$

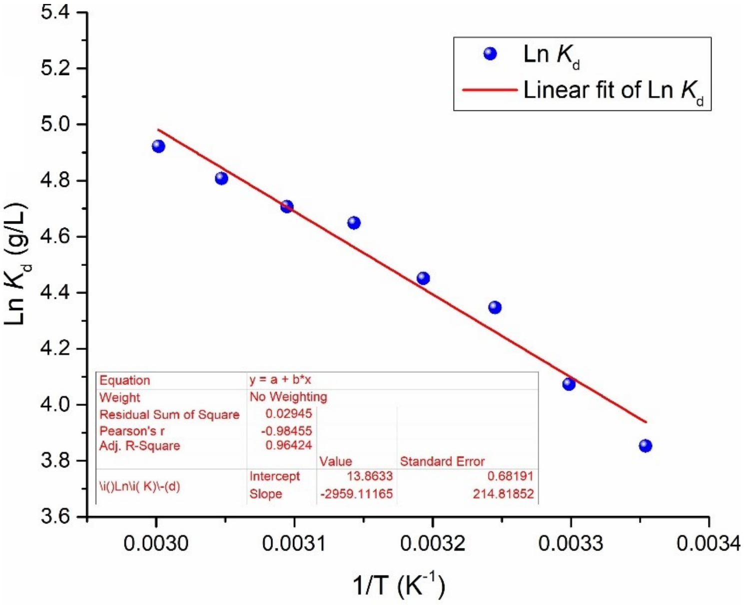
The gas constant (8.314 J/mol·K) is denoted by R, temperature (K) is represented by T, and the Temkin constant associated with adsorption energy (J/mol) is symbolized by b.

This model is particularly useful for systems where the adsorption energy is not constant and varies with the amount of adsorbate on the adsorbent [S7].

Dubinin-Radushkevich (D-R) model [S8] is represented in equation 9:

$$q_e = q_{max} * exp(- K_E * (RT * ln(1 + 1/C\_e))^2) \qquad \textbf{(9)}$$

In this equation, q_e represents the amount adsorbed at equilibrium, q_{max} is the maximum adsorption capacity, K_E corresponds to the Dubinin constant for adsorption energy, R is the universal gas constant (8.314 J/mol·K), T stands for the absolute temperature, and C_e denotes the equilibrium concentration of the adsorbate.



Equation	y = a + b*x		
Weight	No Weighting		
Residual Sum of Square	0.02945		
Pearson's r	-0.98455		
Adj. R-Square	0.96424		
		Value	Standard Error
\i()Ln\i(K)\-(d)	Intercept	13.8633	0.68191
	Slope	-2959.11165	214.81852

Figure S1: Plot of Van't Hoff equation for adsorption of Cd(II) on to CLCTB

Table S1: Thermodynamic parameters of adsorption of Cd^{2+} by CLCTB

Temperature (ºK)	**ΔGº (kJ/mol)**	**ΔHº (kJ/mol)**	**ΔSº (kJ/mol.K)**	***R*²**
298.15	-58968.65	-24602.05	115.27	0.96424
303.15	-59544.98			
308.15	-60121.31			
313.15	-60697.64			
318.15	-61273.97			
323.15	-61850.30			
328.15	-62426.64			
333.15	-63002.97			

Bui, T.H., Lee, W., Jeon, S.-B., Kim, K.-W., Lee, Y., 2020. Enhanced Gold(III) adsorption using glutaraldehyde-crosslinked chitosan beads: Effect of crosslinking degree on adsorption selectivity, capacity, and mechanism. Separation and Purification Technology 248, 116989.

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