

A GREEN METHOD FOR THE REMOVAL OF ZINC(II) IONS FROM WASTEWATER USING MODIFIED BIOPOLYMERS

Christine Jeyaseelan,^{1*} Antil Jain,¹ Ravin Jugade²

¹*Amity Institute of Applied Sciences, Amity University,
Noida-201303 (UP), India*

²*Department of Chemistry, Rashtrasant Tukadoji Maharaj Nagpur University,
Nagpur-440033, India*

* e-mail: cjeyaseelan@amity.edu

Abstract

Zinc pollution in wastewater is a global problem because it is highly toxic. Zinc is commonly used in industries that transfer the water containing zinc directly into water sources, leading to pollution. Exposure to a high level of zinc causes major health problems. This study evaluated the adsorption of zinc ions from aqueous system using modified biopolymers of chitosan by crosslinking with sulphates using the batch adsorption method; the concentration was determined using atomic absorption spectrophotometry. The sulphate cross-linked chitosan (SCC) was characterised by several method. The effects of various experimental parameters such as pH, contact time, concentration, adsorbent dosage and temperature were investigated. Under the optimised conditions, the percentage efficiency for the removal of zinc(II) was up to 85%. Freundlich and Langmuir isotherms were used to analyse the equilibrium adsorption data along with kinetic studies. Various thermodynamic parameters have also been reported.

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1. Introduction

Zinc (Zn) is an essential metal for humans and not considered toxic for humans at lower concentrations. Zn is essential for the function of more than 300 enzymes and enhances cell growth and protein metabolism, among other processes [1]. Zn deficiency in pregnant women can deteriorate the health of the child. The recommended dietary allowances for Zn are 11 and 8 mg/day for men and women, respectively. Concentrations of Zn are homeostatically synchronised in tissues, but when present beyond a certain concentration, its toxic effects become apparent, especially in aquatic organisms. If ignored, the metal can affect the gill surfaces [2]. In humans, long-term exposure to Zn can cause liver as well as pancreatic damage; decrease the immune system; slow the healing of skin sores and wounds; and cause stomach cramps, vomiting or nausea [3]. Zn is not easily metabolised; therefore, it is used in drug industries as sun blocks, ointments, deodorants and stabilisers.

Several methods have been developed to regulate Zn pollution, such as ion exchange, adsorption and precipitation, among others. Adsorption through naturally occurring bioadsorbents has proved to be one of the most sustainable methods because it is cost effective and eco-friendly. Hence, they could be adapted for removal of contaminants from water [4].

Chitosan is the deacetylated form of chitin obtained from shrimp, crab shells and other crustacean sources. Chitin is the most abundant form of natural amino polysaccharide and has advantages like biodegradability, non-toxicity, accessibility and antifungal and antibacterial properties [3]. Various chemical modifications have been studied to improve the absorption of metal ions from wastewater, including the use of *n*-butyl acrylate, 3,4-dimethoxybenzaldehyde, cross-linking with glutaraldehyde, further modification using tetra ethylene, sulphate cross-linking and ammonium hydroxide. However, chelation has shown greater chemical reactivity and utility compared with other methods [4-6]. In previous studies, the application of sulphate cross-linked chitosan (SCC) has been reported for the effective removal of chromium(VI) ions and dyes like Congo red and rhodamine B [7-11]. In the current study, we aimed to examine the applicability of SCC in the removal of Zn(II) by batch adsorption. Various thermodynamic and equilibrium parameters were evaluated to determine the rate and mechanism of adsorption for the removal of Zn ions. Moreover, the influence of pH, contact time, adsorbent dose and solution concentration were studied regarding their effects on metal uptake applications.

2. Material and Methods

2.1. Chemicals

Chitosan with an 85% deacetylation degree was obtained from Uniloid Bio-chemicals India Ltd. (Hyderabad, India). Zinc chloride monohydrate was obtained from Sigma-Aldrich (India). Hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Chemical Drug House Ltd. (India). Double distilled water was used to prepare all the aqueous solutions.

2.2. Preparation of Adsorbent

To prepare the modified chitosan adsorbent, chitosan flakes were weighed accurately. Then, 100 ml of dilute sulphuric acid (1:1) solution was added and the components were stirred using a magnetic stirrer for 1 h at room temperature. The reaction mixture was filtered and the residue was washed with distilled water. The washing was tested for complete removal of sulphate ions using an ultraviolet (UV) spectrometer to give a solid residue of SCC. The residue was dried at 60°C in a hot air oven for 1 h [7] and used for further experiments.

2.3. Preparation of Stock Solution

A stock solution of zinc chloride monohydrate was prepared in deionised water by weighing the required quantity of salt; the stock was used for further dilutions. The initial concentrations of metal ions were checked using atomic absorption spectrometry at 283.31 nm and a slit width of 2.7/1.05 mm. The other parameters were optimised by studying the effect of pH (1-10), adsorbent dosage (0.1-1.0 g), concentration of Zn(II) ions (10-300 mg/l) and contact time (20-200 min). Each parameter was studied by keeping all other parameters constant.

2.4. Batch Adsorption Method

The equilibrium method was used to Zn(II) ions for SCC batch adsorption. For each experiment, a 250-ml conical flask with 50 ml of Zn(II) ions contained the appropriate concentration of SCC.

The removal of Zn from the solution after each parameter was calculated by using Eq. (1):

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100, \quad (1)$$

where C_0 represents the initial Zn(II) concentration and C_e represents the equilibrium Zn(II) concentration in the solution in mg/l.

The equilibrium adsorption capacity q_e (mg/g) was calculated by using Eq. (2):

$$q_e = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where V is the volume of the solution (l) and m is the mass of the adsorbent (g).

3. Results and Discussion

3.1. Characterisation of SCC

Fourier-transform infrared (FT-IR) spectroscopy showed broad peaks in the region of 3350 cm^{-1} for O-H stretching vibrations, 3550 cm^{-1} for N-H stretching vibrations, 1588 cm^{-1} for N-H bending vibration and 1375 cm^{-1} for C-N bending vibrations. There were also peaks corresponding to C-O and C-H stretching peaks at 2880 cm^{-1} and 1070 cm^{-1} . The sulphate peaks were observed at 620 and 1110 cm^{-1} (Figure 1).

Figure 2 shows the X-ray diffraction (XRD) patterns for chitosan and SCC. SCC showed peaks at 10.428° and 19.69°. On cross linking with sulphuric acid, new peaks were observed at 11.55° and 18.26°, which indicate that SCC was formed.

Scanning electron micrographs revealed that chitosan had irregularly shaped particles while SCC showed a regular arrangement (Figure 3).

The peaks of C, H and N were observed in the energy dispersive X-ray (EDX) spectra and after treatment with sulphuric acid; the peak for S was also clearly observed (Figure 4) [7].

3.2. pH_{pzc}

The parameter pH_{pzc} is the pH at which the surface of the adsorbent is zero. The pH of the zero-point charge affects the process of adsorption. To measure this, 50 ml of 0.01 M NaCl was placed in flasks numbered 1-10 and the initial pH was adjusted using NaOH or HCl (0.1 N). Then, 0.1 g of the prepared adsorbent was added to each flask and incubated overnight. The final pH was recorded and a graph was plotted along with the initial pH. The point at which the curve crosses the line – that is, initial pH = final pH – is recorded as the pH_{zpc} . For SCC, the value was 4.6.

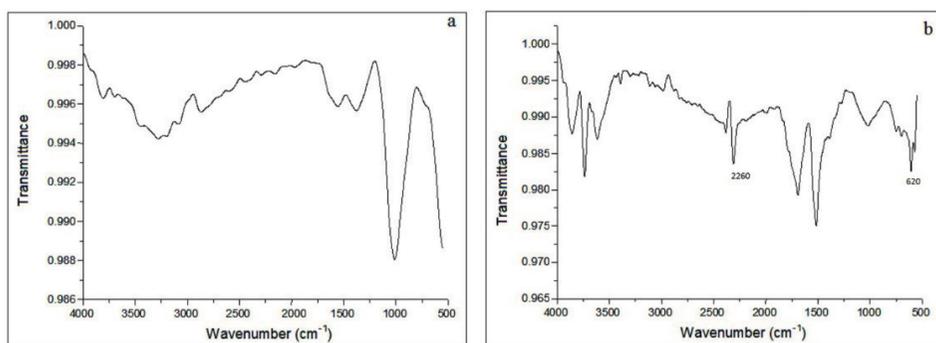


Figure 1. Fourier-transform infrared spectra of (a) chitosan and (b) sulphate cross-linked chitosan

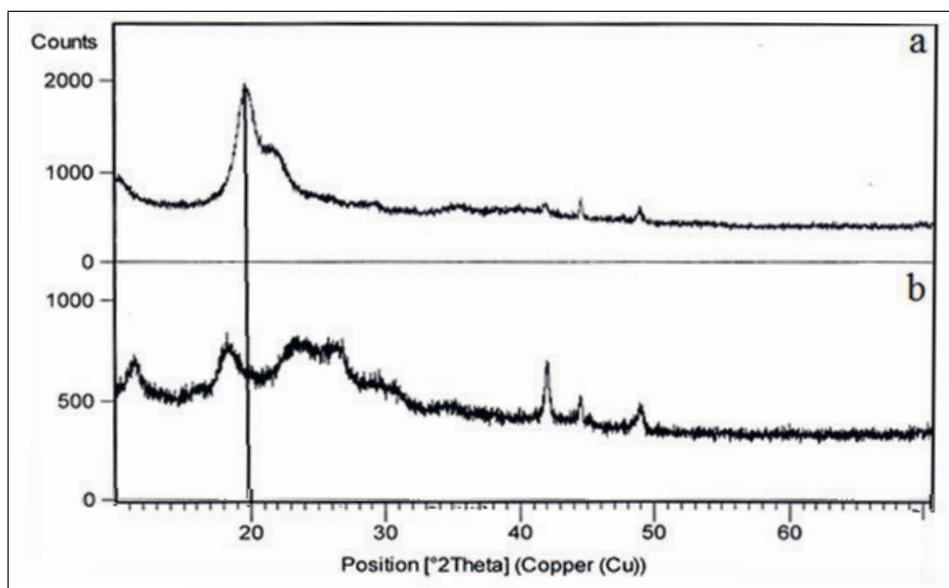


Figure 2. X-ray diffraction patterns of (a) chitosan and (b) sulphate cross-linked chitosan

3.3. Effect of pH

The pH of the solution plays a major role because it affects the surface area as well as the adsorption of Zn ions present in the solution, as most of the surface phenomena are pH dependent. These experiments were carried out using 50 ml of 50 mg/l Zn(II) solution with pH from 1.0 to 10.0. To each solution, 200 mg of SCC was added and stirred for 60 min (only for pH optimisation) at 25°C. The solution was filtered and the final Zn(II) concentration was estimated. The maximum adsorption occurred at pH 5.0 (Figure 5a). This outcome could be due to SCC acquiring a maximum negative charge at this pH. Moreover, between pH 4 and 6, the adsorption was at the maximum, a finding that could be attributed to the existence of electrostatic force of attraction between SCC and metal ions. Hence, pH 5.0 was used for all further studies.

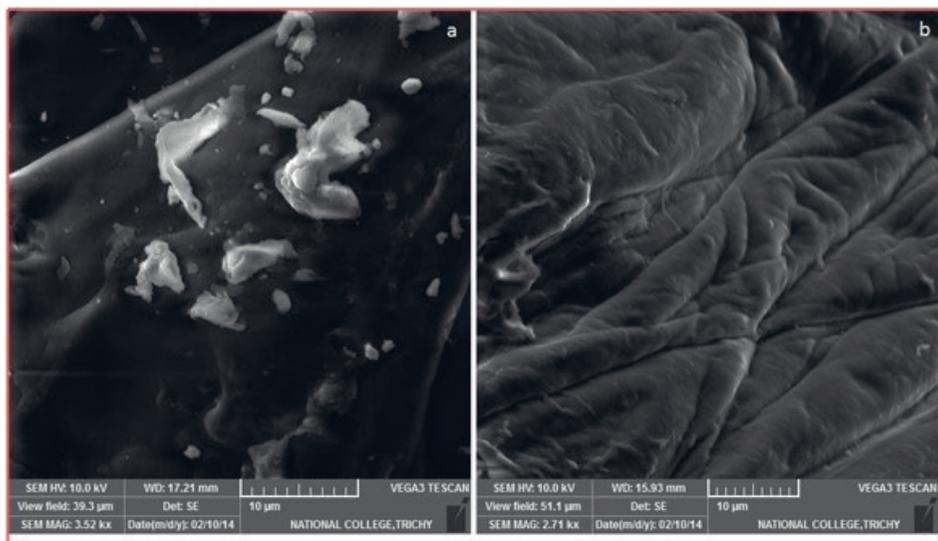


Figure 3. Scanning electron micrographs of (a) chitosan and (b) sulphate cross-linked chitosan

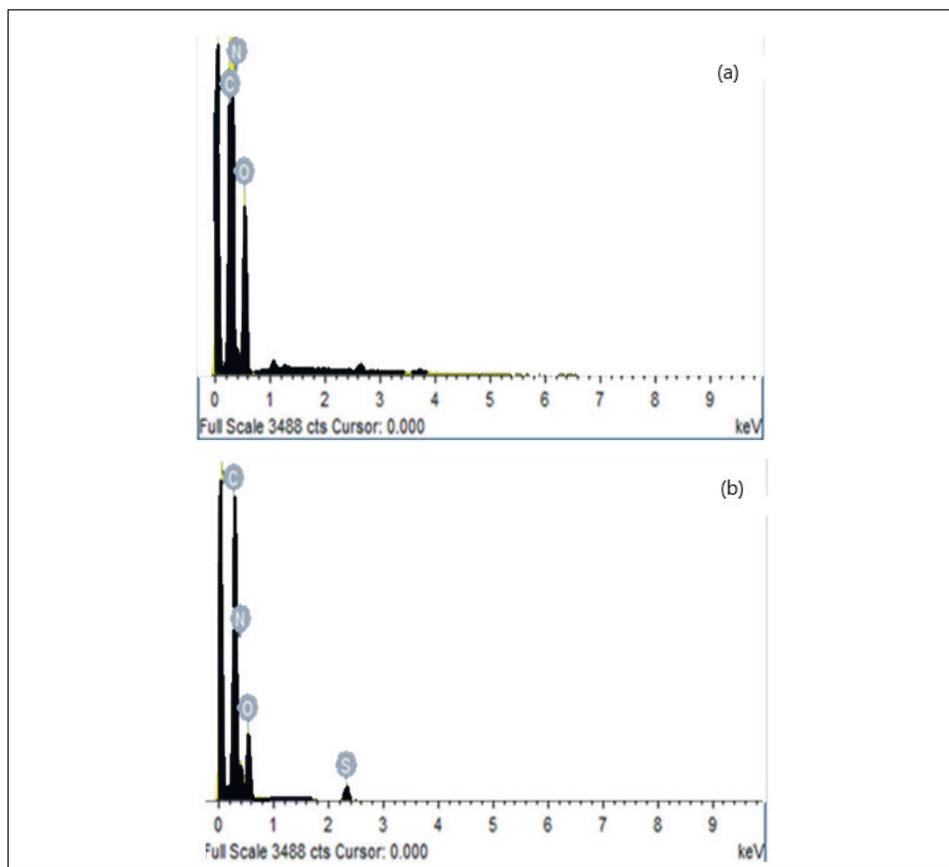


Figure 4. Energy dispersive X-ray spectra of (a) chitosan and (b) sulphate cross-linked chitosan

3.4. Effect of Contact Time

To study the effect of contact time, 50 mg/l Zn(II) solution with adjusted to pH 5.0 and then equilibrated with 200 mg of SCC for 20-200 min at 25°C. As the contact time increased, there was an increase in adsorption of metal ions and adsorption process. The process reached equilibrium in 165 min (Figure 5b). Hence, this time was used in all further studies.

3.5. Effect of Initial Zn(II) Ion Concentration

The initial Zn(II) concentration was varied from 10 to 300 mg/l, keeping other parameters constant (pH 5.0, 200 mg SCC, 20°C and 165-min contact time). The final concentration was determined after filtration. As the metal ion concentration increased, there was a decrease in the adsorption capacity because of an increase in competitive dispersion of metal ions onto active adsorbent sites (Figure 5c). The percentage removal decrease as the Zn(II) concentration increased. With respect to this experiment, the maximum adsorption (85%) was obtained for 50 mg/l. Hence, this concentration was maintained for the subsequent studies.

3.6. Effect of Adsorbent Dosage

Variable amounts of SCC (100-1000 mg) were added to 50 mg/l of Zn(II) at pH 5.0 and 25°C. The components were stirred for 165 min and filtered. The removal of metal ions increased as the adsorbent dosage increased (Figure 5d). This indicates that there are sorption active sites available for the removal of Zn(II) metal ions. Moreover, with an increase in adsorbent dosage, there is increase in surface area, which provides better availability of sites. Similar trends have been seen using other biosorbents [7, 8].

3.7. Adsorption Isotherms

To describe the adsorption behaviour and interaction between adsorbent and adsorbate, adsorption isotherm data were obtained by varying the initial metal ion concentration from 10 to 300 mg/l. The equilibrium sorption capacity was calculated using Freundlich and Langmuir isotherms.

3.7.1. Langmuir Isotherm

The Langmuir isotherm represents monolayer adsorption on a set of distinct localised adsorption sites with almost the same energies for adsorption. It assumes that the rate of adsorption is proportional to the uncovered surface area of adsorbent while the rate of desorption to be proportional to the covered surface area. The linearised equation for Langmuir isotherm can be represented as Eq. (3):

$$\frac{C_e}{q_e} = \frac{1}{q_m K} + \frac{C_e}{q_m} \quad (3)$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount adsorbed at equilibrium (mg/g) and q_m and K are Langmuir constants and are calculated from the slope and intercept in Figure 6a.

The essential characteristics of the Langmuir isotherm are expressed in terms of a dimensionless constant separation factor or equilibrium factor R_L , which is indicative of the isotherm and of the nature of the isotherm [12] and is represented according to Eq. (4)

$$R_L = \frac{1}{1 + K_L C_0} \quad (4)$$

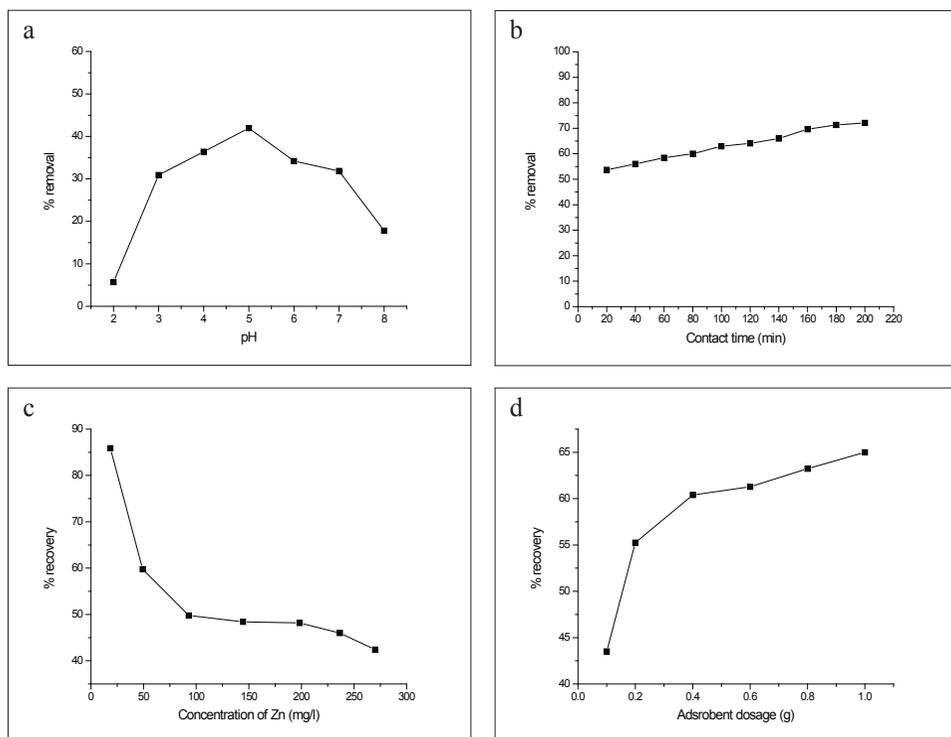


Figure 5. The effect of (a) pH, (b) contact time, (c) concentration and (d) adsorbent dosage on the percentage removal of Zn(II)

A value of R_L below 1 represents favourable adsorption, a value above 1 indicates unfavourable adsorption, a value of 1 indicates linear adsorption and a value of 0 represents irreversible adsorption.

3.7.2. Freundlich Isotherm

According to Freundlich isotherm for different concentrations of solution, the ratios of the amount of solute adsorbed on a given mass of adsorbent to its concentration in solution is not constant [13]. The Freundlich isotherm can be represented by Eq. (5):

$$q_e = k_f C_e^{1/n}, \quad (5)$$

where q_e is the amount of dye adsorbed at equilibrium per gram of sorbent (mg/g), C_e is the equilibrium concentration of a dye and n are the Freundlich constants.

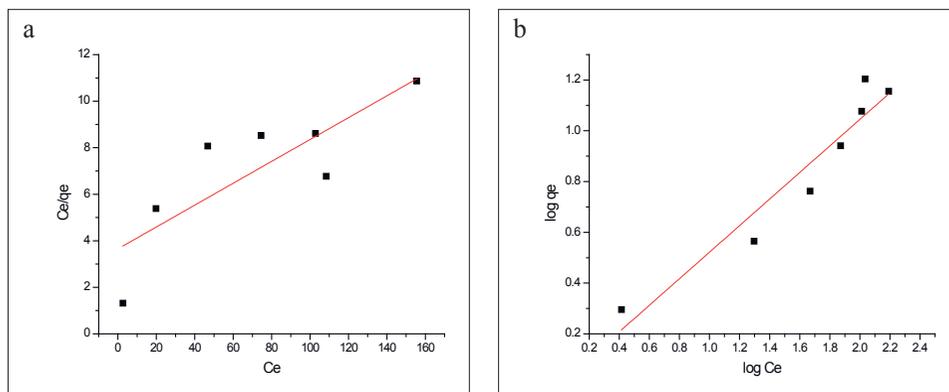
The graph is plotted between q_e and C_e . To determine the constants, a graph can be plotted using $\log q_e$ and $\log C_e$ by linearising and rearranging its form as represented by the following Eq. (6) and shown in Figure 6b:

$$\ln q_e = \ln k_f + \frac{1}{n} \ln C_e. \quad (6)$$

The Langmuir and Freundlich isotherms were verified by using least squares fit and regression analysis (Table 1). The r^2 value shows that the system follows Freundlich adsorption isotherm. Moreover, the R_L between 0 and 1 indicates favourable adsorption.

Table 1. Calculated values of adsorption isotherms

Langmuir isotherm				Freundlich isotherm		
r^2	q_m (mg/g)	K (l/mg)	R_L	r^2	n	K_f
0.6256	21.276	0.0128	0.609	0.9216	1.8793	0.9967

**Figure 6.** (a) Langmuir adsorption isotherm and (b) Freundlich adsorption isotherm

3.8. Adsorption Kinetics

Kinetic models help to interpret the effect of contact time and concentration for the removal of metal ions using SCC. Therefore, to interpret the rate controlling, mass transfer and kinetic mechanism involved for the adsorption process, two kinetic models were adopted, namely pseudo-first order and pseudo-second order.

3.8.1. Pseudo-First-Order Kinetics

The linear form of pseudo-first order kinetics can be expressed as Eq. (7):

$$\text{Log}(q_e - q_t) = \text{log} q_e - \frac{k_{ad} t}{2.303}, \quad (7)$$

where q_e and q_t are the concentrations of metal ions at equilibrium and at time t , respectively. k_{ad} (min^{-1}) is the pseudo-first-order adsorption rate constant, which can be interpreted by the graph shown in Figure 7a.

3.8.2. Pseudo-Second-Order Kinetics

The linear form of pseudo-second-order kinetics has been widely accepted as Eq. (8):

$$\frac{t}{q_t} = \frac{1}{Kq_e^2} + \frac{1}{q_e} t. \quad (8)$$

where k is a second-order kinetic constant and Kq_e^2 is the initial rate constant at time 0. q_e and k can be calculated by plotting t/q_t versus t (Figure 7b).

The r^2 obtained from pseudo-second-order kinetics is higher than for pseudo-first-order kinetics (Table 2). The calculated q_e values for both models are similar. These data indicate the pseudo-second-order kinetic model is the best.

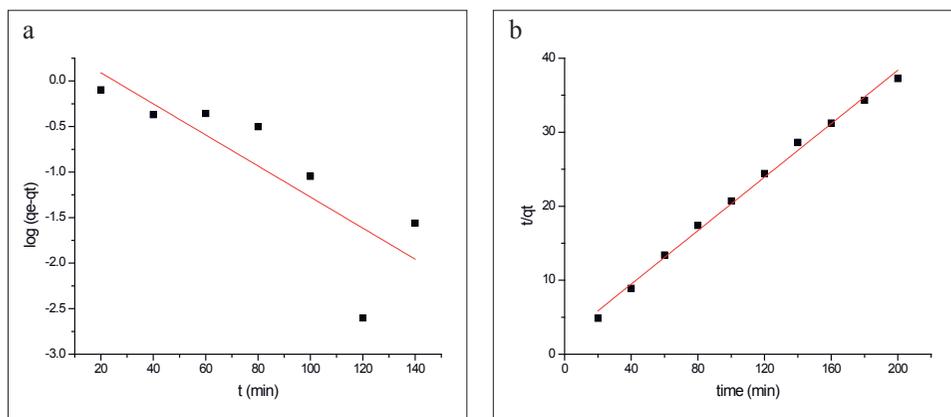


Figure 7. (a) Pseudo-first-order kinetics and (b) pseudo-second-order kinetics

Table 2. Calculated values of kinetic studies

Pseudo first order kinetics			Pseudo second order kinetics		
r ²	K ₁ (min ⁻¹)	q _e (mg/g)	r ²	q _e (mg/g)	k ₂ (min L mg ⁻¹)
0.6887	0.00742	2.6998	0.9954	5.537	0.0144

3.9. Thermodynamic Studies

The effect of adsorption due to change in temperature at 303, 323 and 343 K gives the thermodynamic aspect of the adsorption process, which is given by Eq. (9):

$$\ln k = \left(\frac{\Delta S^0}{R} \right) - \left(\frac{\Delta H^0}{RT} \right). \quad (9)$$

The entropy (ΔS^0) and enthalpy (ΔH^0) changes in the adsorption process are related by the van't Hoff equation (Eq. 10):

$$\Delta G^0 = -RT \ln K. \quad (10)$$

Entropy and enthalpy are calculated by plotting the graph between $\ln K$ versus $1/T$, where T is the absolute temperature and K has been evaluated by the ratio of concentration of Zn(II) adsorbed on SCC to that in the solution. As calculated from the value of slope and intercept of the van't Hoff plot (Figure 8), ΔS is -0.053 kJ/mol and ΔH is -35.241 kJ/mol. A negative free energy indicates the feasibility of a reaction and a negative entropy and enthalpy signify that randomness decreases as the Zn(II) ion moves from the solution to the adsorbed state and the exothermic nature of the adsorption process, respectively.

3.10. Reusability of SCC

The regeneration of SCC was examined using NaOH as described previously [7]. Specifically, SCC was treated with 5% NaOH solution followed by three washings with this solution. The regenerated material was dried in an oven at 60°C. The adsorption capacity of the recycled material for Zn(II) ions was the same as that of the original material. This material was regenerated three times and reused without a change in adsorption efficiency.

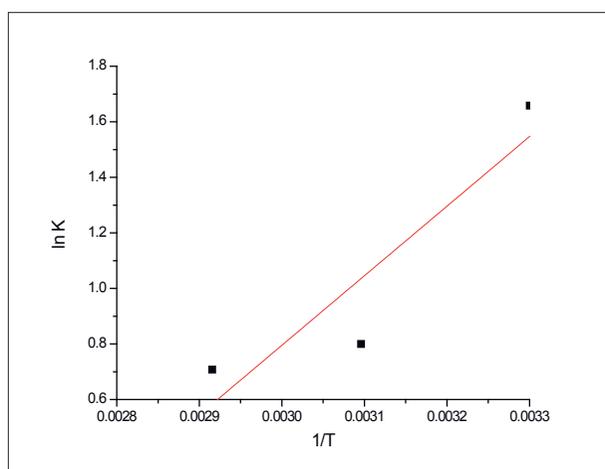


Figure 8. van't Hoff plot

4. Conclusions

Removal of Zn(II) ions using SCC is an efficient and greener way of reducing pollution in water. Its synthesis is much easier, uses fewer resources and is a less time-consuming process, with faster detoxification of up to 85% of Zn ions and a slower deterioration rate. Based on the high correlation coefficients, the Freundlich isotherm is the best model, and the kinetics followed shows chemisorption of the metal ions onto the surface. The process is exothermic, spontaneous and feasible.

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6. References

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