



Nitrate removal from aqueous solutions by cross-linked chitosan beads conditioned with sodium bisulfate

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ABSTRACT

The investigation of adsorption of nitrate onto chitosan beads modified by cross-linking with epichlorohydrin (ECH) and surface conditioning with sodium bisulfate was performed. The results indicated that both cross-linking and conditioning increased adsorption capacity compared to normal chitosan beads. The maximum adsorption capacity was found at a cross-linking ratio of 0.4 and conditioning concentration of 0.1 mM NaHSO₄. The maximum adsorption capacity was 104.0 mg g⁻¹ for the conditioned cross-linked chitosan beads at pH 5, while it was 90.7 mg g⁻¹ for normal chitosan beads. The Langmuir isotherm model fit the equilibrium data better than the Freundlich model. The mean adsorption energies obtained from the Dubinin-Radushkevich isotherm model for all adsorption systems were in the range of 9.55–9.71 kJ mol⁻¹, indicating that physical electrostatic force was potentially involved in the adsorption process.

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1. Introduction

Nitrate is one of the most common groundwater contaminants in rural areas and can create serious problems, such as eutrophication and outbreaks of infectious disease, when released into the environment [1]. Contamination of drinking water by nitrates can cause potential hazards to human health. Excess nitrate in drinking water may cause blue-baby syndrome, which results from the conversion of haemoglobin into methaemoglobin, which cannot carry oxygen [2].

Traditional methods for removal of nitrates from water include two main groups of treatment processes: biological and physico-chemical. Biological denitrification is an eco-friendly and cost-effective method by which facultative anaerobic denitrifying bacteria reduce nitrate or nitrite into harmless nitrogen gas in the absence of oxygen [3]. The biological denitrification process is slow, particularly for industrial wastewater containing high concentrations of nitrate and for low temperatures. The most conventional physico-chemical processes for nitrate removal are ion exchange [4], reverse osmosis [5], electrodialysis [6], metallic iron-aided abiotic nitrate reduction [7] and adsorption [8]. Comparing these methods, ion exchange seems to be the most suitable because

of its simplicity and effectiveness [4]; however, the main problem is that the ion exchange resin is quite expensive. In recent years, considerable attention has been given to different low cost adsorbents, such as modified wheat residue [9] and red mud [10], for the removal of nitrate.

Chitosan, a linear copolymer of glucosamine and N-acetyl glucosamine, is obtained by thermo-chemical deacetylation of crustacean chitin [11]. Recently, chitosan beads have become effective biosorbents for the removal of dyes [12] and heavy metals [11] due to its high content of amino and hydroxyl functional groups. The poor acid stability and mechanical strength are the main disadvantages of using chitosan beads [11]. Several chemical modification methods, such as chemical cross-linking of the surface of the chitosan beads with cross-linking agents [13], have been performed to improve acid stability, mechanical strength, pore size, hydrophilicity and biocompatibility. To improve adsorption capacity, several chemical modifications such as cross-linking [14], insertion of new functional groups [15], or conditioning [16] of chitosan beads or resins are performed. Conditioning of the chitosan hydrobeads with ammonium sulphate reduces the pH sensitivity of the process and maintains the maximum sorption capacity near pH 8 [16]. In our previous study, sodium bisulphate (NaHSO₄) was found to be the most effective conditioning agent, even though the study was performed for coagulation of soil particles in aqueous solutions [17].

In our previous study, normal chitosan bead was applied to nitrate removal from aqueous solutions [18]. We investigated the

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effects of NaHSO_4 conditioning for non-cross-linked and cross-linked chitosan beads for the removal of nitrate from aqueous solution in this study. Epichlorohydrin (ECH) was selected as a cross-linking agent because ECH does not interact with cationic amine groups of chitosan during cross-linking. The effect of pH and of the ratio of cross-linking agent, and equilibrium isotherm of nitrate ions on these beads were investigated.

2. Materials and methods

2.1. Preparation of chitosan beads

Chitosan and all other chemicals used in this study were purchased from Sigma Chemical Co., USA. To prepare the chitosan beads, 10.0 g of chitosan powder was dissolved in 300 mL of 5% (v/v) acetic acid solution. After dilution to 1 L with deionized water, it was left overnight in stirring condition. It was kept standing for another 6 h to ensure that the chitosan was completely dissolved. The chitosan solution was then added drop-wise into a precipitation bath containing 1 L of alkaline coagulating mixture ($\text{H}_2\text{O}:\text{MeOH}:\text{NaOH}$ 4:5:1, w/w) to form chitosan beads [19]. The wet chitosan beads were filtered and extensively washed with deionized water to remove any NaOH. Before use, the chitosan beads were kept for 30 min in the pH adjusted aqueous solution required for different experimental conditions.

2.2. Chitosan beads cross-linking

After removing the attached surface water, the wet non-cross-linked chitosan beads (containing 1 g chitosan on the basis of dry weight) were inserted into a flask containing 500 mL of a 1 N NaOH solution. Epichlorohydrin was added to the chitosan in five cross-linking ratios (ECH/chitosan: 0.2, 0.4, 0.6, 0.8 and 1), and the cross-linking reaction was allowed to proceed at 60 °C for 6 h with continuous agitation. The cross-linked chitosan beads were then washed several times with deionized water to remove any unreacted ECH and stored in deionized water for further use.

2.3. Chitosan beads conditioning

The non-cross-linked and cross-linked chitosan beads (containing 1 g chitosan on the basis of dry weight) were conditioned with 500 mL sodium bisulphate (NaHSO_4) solution where the concentration of NaHSO_4 was varied from 0.001 to 5 mM. The conditioning of chitosan beads was allowed to proceed at 50 °C for 24 h with continuous agitation.

2.4. Diameter and porosity of chitosan beads

The diameter (D) and porosity (ε) of the chitosan beads were determined by the amount of water within the pores of the chitosan beads [20]. The diameter (D) and porosity (ε) can be calculated using these equations:

$$D = \left[6 \frac{W_D/\rho_{CS} + (W_W - W_D)/\rho_W}{\pi} \right]^{1/3} \quad (1)$$

$$\varepsilon = \frac{(W_W - W_D)/\rho_W}{W_D/\rho_{CS} + (W_W - W_D)/\rho_W} \times 100\% \quad (2)$$

where W_W (g) is the weight of the wet chitosan beads before drying; W_D (g) is the weight of the chitosan beads after drying; ρ_W is the density of water, 1.0 g cm^{-3} ; and ρ_{CS} is the density of chitosan, 0.47 g cm^{-3} . Chitosan density represents the dry weight of chitosan materials in the volume of wet chitosan beads containing water.

2.5. Characterization of chitosan beads

BET specific surface area and pore volume of freeze-dried cross-linked and non-cross-linked chitosan beads were determined on the basis of nitrogen adsorption at 77.3 K by using a surface area analyzer (ASAP 2010, Micromeritics, USA). The surface morphology of freeze-dried chitosan beads after gold coating was obtained using HR FE-SEM (JSM-7401F, JEOL, USA). The specific surface area was calculated according to the Brunauer-Emmett-Teller (BET) method. To estimate the zeta potentials of chitosan beads (conditioned cross-linked, cross-linked, conditioned non-cross-linked or non-cross-linked), the dry powder of chitosan beads (0.1 g) was suspended into 100 mL of deionized water, and the pH of the suspension was adjusted with 0.1N NaOH or HCl to pH 5. The chitosan suspension was sonicated first for 2 h, followed by stirring for 24 h and then allowed to settle for 12 h. The supernatant containing some small particles was used for the zeta potential analysis with the ELS-8000 (Otsuka Elec. Instrument, Japan) and no background electrolyte was added to the sample.

2.6. Preparation of nitrate solution and analytical measurements

A stock solution (1 g L^{-1}) of nitrate was prepared by dissolving potassium nitrate (KNO_3) in deionized water, and experimental solutions of desired nitrate concentrations were obtained by successive dilutions. The concentration of nitrate ions in the experimental solution was determined using a 790 Personal Ion Chromatography (Metrohm Ion Analysis, Switzerland) with a Suppressed CD detector. The analytical column was METROSEP A Supp 5 column ($100 \text{ mm L} \times 4.0 \text{ mm ID}$). Nitrate ion was eluted (Eluent: $3.2 \text{ mM Na}_2\text{CO}_3 + 1.0 \text{ mM NaHCO}_3$) at a flow rate of 0.7 mL/min with retention time of 7.0 min.

2.7. Batch adsorption studies

Batch adsorption studies were carried out by shaking 100 mL conical flasks containing 1 g of wet chitosan beads and 50 mL of nitrate solutions of desired concentration and pH at 150 rpm and 30 °C. In this study cross-linked, non-cross-linked, conditioned cross-linked and conditioned non-cross-linked chitosan beads were used as adsorbents. All the adsorption experiments were conducted in triplicate. For the study on the optimum pH, the initial pH values of nitrate solutions were varied from 3 to 8 by drop-wise addition of 0.1N HCl or NaOH solutions with the initial nitrate concentration fixed at 500 mg L^{-1} . At the end of the adsorption period of 24 h, the supernatant solution was separated by centrifugation at 3000 rpm for 30 min. The supernatant solution was again filtered using a PVDF syringe filter. The amount of nitrate in the solutions before and after adsorption was analyzed by the ion chromatography. Equilibrium isotherm studies were carried out with different concentration of nitrate solutions ($25\text{--}1000 \text{ mg L}^{-1}$) at 30 °C and pH 5. Langmuir and Dubinin-Radushkevich (D-R) isotherms were used to analyze the equilibrium adsorption data. The amount of nitrate adsorbed (mg g^{-1}) was calculated based on a mass balance equation as given below:

$$q = \frac{(C_0 - C_{eq}) \times V}{W} \quad (3)$$

where q is the adsorbent capacity (mg g^{-1}); C_0 is the initial concentration of nitrate in solution (mg L^{-1}); C_{eq} is the final or equilibrium concentration of nitrate in solution (mg L^{-1}); V is the volume of experimental solution (L); and W is the weight of chitosan in the form of hydrobeads (g).

Table 1
Porosity and diameter of different types of chitosan beads.

Chitosan beads	Wet weight (W_w , mg)	Dry weight (W_d , mg)	Porosity (ϵ , %)	Diameter (D , mm)
Conditioned cross-linked	6.42 ± 0.046	0.232 ± 0.0013	92.52 ± 0.060	2.34 ± 0.006
Cross-linked	6.33 ± 0.060	0.232 ± 0.0015	92.42 ± 0.070	2.33 ± 0.005
Conditioned non-cross-linked	6.80 ± 0.066	0.244 ± 0.0011	92.66 ± 0.064	2.39 ± 0.006
Non-cross-linked	6.76 ± 0.061	0.243 ± 0.0012	92.65 ± 0.062	2.38 ± 0.006

Results are average of triplicate experiments \pm standard deviation.

3. Results and discussion

3.1. Characterization of chitosan beads

Table 1 shows the diameter (D) and porosity (ϵ) of the different types of chitosan beads. The slight reduction in the diameter and porosity of chitosan beads was found after cross-linking with ECH. This is related to an increase in the hydrophobicity of the chitosan beads by the addition of an alkyl group in the cross-linking reaction [14].

The BET specific surface area and pore volume of the freeze-dried chitosan beads, as calculated from the nitrogen isotherms, are summarized in Table 2. The value of the BET specific surface area of the cross-linked chitosan beads ($27.35 \pm 1.25 \text{ m}^2 \text{ g}^{-1}$) was a bit smaller than that of the non-cross-linked chitosan beads ($28.52 \pm 0.46 \text{ m}^2 \text{ g}^{-1}$). The total pore volume changed from 0.065 to 0.029 mL g^{-1} after cross-linking the chitosan beads. The value of the median pore diameter of cross-linked chitosan beads (2008 Å) was significantly higher than that of non-cross-linked chitosan beads (1074 Å). According to International Union of Pure and Applied Chemistry (IUPAC), pore diameters are classified by diameter (d) into micropores ($d < 20 \text{ Å}$), mesopores ($20 \text{ Å} < d < 500 \text{ Å}$) and macropores ($d > 500 \text{ Å}$). The value of the median pore diameter indicated that the chitosan beads are macroporous. The micropore

Table 2
Specific surface area and pore volumes of ECH cross-linked and non-cross-linked chitosan beads.

	Cross-linked chitosan beads	Non-cross-linked chitosan beads
S_{BET}^a ($\text{m}^2 \text{ g}^{-1}$)	27.35 ± 1.25	28.52 ± 0.46
V_{tot}^b (mL g^{-1})	0.0290	0.0654
D_p^c (Å)	2008	1074
V_{micro}^d (mL g^{-1})	0.00361	0.00347
A_{micro}^e ($\text{m}^2 \text{ g}^{-1}$)	8.94	8.65
A_{External}^f ($\text{m}^2 \text{ g}^{-1}$)	18.40	19.87

^a BET specific surface area ($\text{m}^2 \text{ g}^{-1}$).

^b Total pore volume (mL g^{-1}).

^c Median pore diameter (Å).

^d Micropore volume (mL g^{-1}).

^e Micropore area ($\text{m}^2 \text{ g}^{-1}$).

^f External area ($\text{m}^2 \text{ g}^{-1}$).

volume (0.0036 mL g^{-1}) and area ($8.94 \text{ m}^2 \text{ g}^{-1}$) of the ECH cross-linked chitosan beads were very similar to the micropore volume (0.0035 mL g^{-1}) and area ($8.65 \text{ m}^2 \text{ g}^{-1}$) of the non-cross-linked chitosan beads.

The SEM study of chitosan beads showed that the cross-section of the cross-linked chitosan beads at $100\times$ magnification (Fig. 1A)

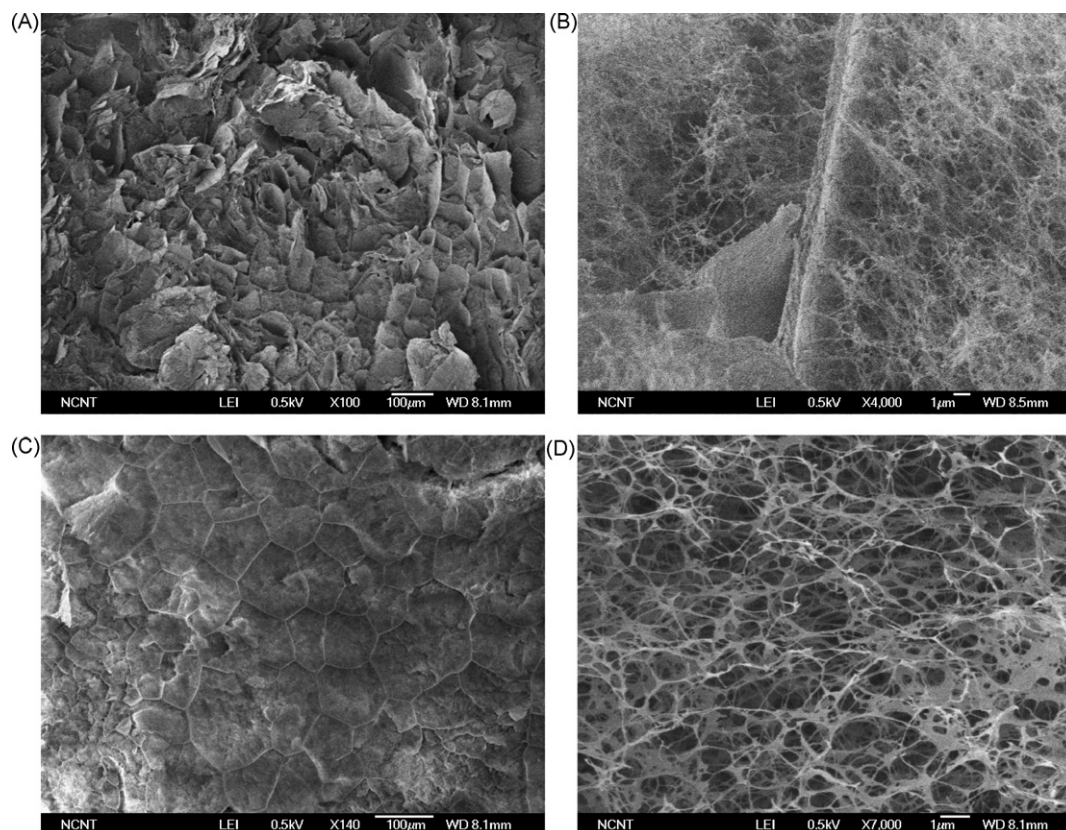


Fig. 1. SEM images of the cross-section of cross-linked chitosan beads at (A) $100\times$ and (B) $4000\times$ and non-cross-linked chitosan beads at (C) $140\times$ and (D) $7000\times$.

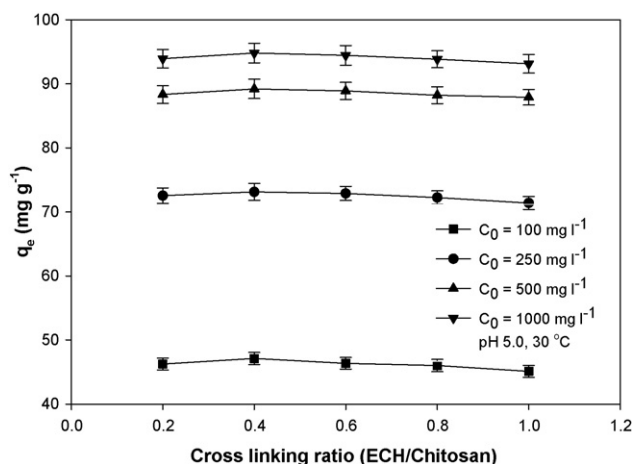


Fig. 2. Effect of the cross-linking ratio on nitrate adsorption onto cross-linked chitosan beads.

has a much more wrinkled and irregular structure than non-cross-linked beads at $140\times$ magnification (Fig. 1C). Both cross-linked (Fig. 1B) and non-cross-linked (Fig. 1D) chitosan beads showed an interconnected flow-through polymeric network with irregular pores at higher magnification, but the cross-linked chitosan beads (Fig. 1B) were noted to have more asperity in their structure.

3.2. Effect of cross-linking

Fig. 2 shows the effect of the cross-linking ratio (ECH/chitosan) on the nitrate adsorption capacity of the chitosan beads at four different initial nitrate concentrations, which were fixed at 100, 250, 500 and 1000 mg L^{-1} . ECH mainly cross-links chitosan beads using the $-\text{OH}$ group of chitosan and does not interact with the cationic amine groups of chitosan during the cross-linking [14]. The maximum value for the equilibrium adsorption capacity (q_e) of cross-linked chitosan beads was found at a 0.4 cross-linking ratio, and further increases in this ratio slightly reduced the q_e value. Thus, an increase in the cross-linking ratio did not reduce the available adsorption sites but increased the steric hindrance for diffusion through the chitosan beads [21].

3.3. Effect of conditioning

Fig. 3 shows the effects of NaHSO_4 conditioning on the adsorption capacity of non-cross-linked and cross-linked chitosan beads

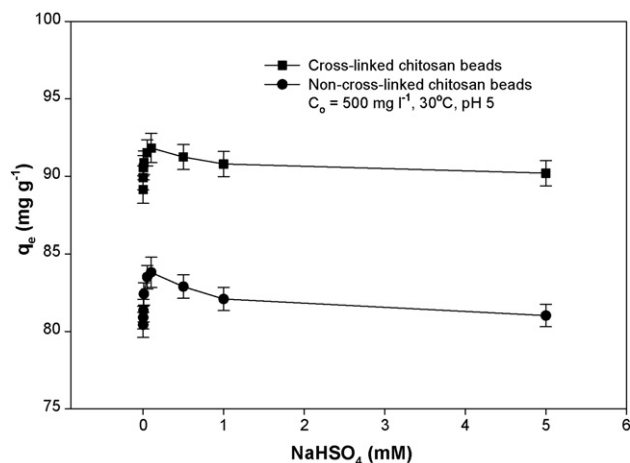


Fig. 3. Effect of conditioning of cross-linked and non-cross-linked chitosan beads on nitrate adsorption.

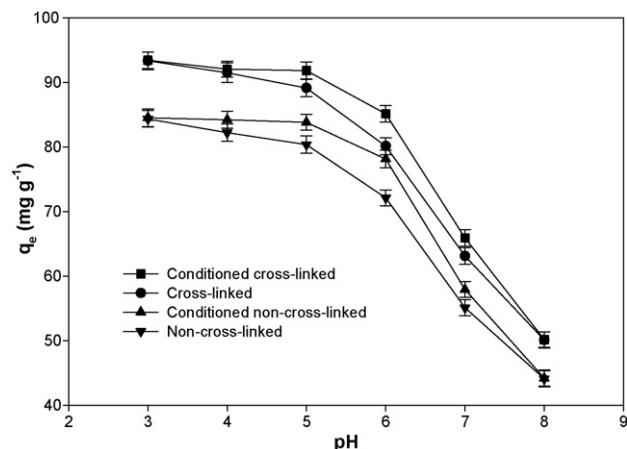


Fig. 4. Effect of pH on nitrate adsorption onto different types of chitosan beads; initial nitrate concentration, 500 mg L^{-1} and at 30°C .

for removal of nitrate at an initial nitrate concentration 500 mg L^{-1} and the maximum q_e value was obtained when all the samples were conditioned with 0.1 mM NaHSO_4 . The increase in zeta potential of 0.1 mM NaHSO_4 conditioned non-cross-linked chitosan beads from 30.1 to 38.5 mV at pH 5 after conditioning indicated that surfaces of NaHSO_4 conditioned non-cross-linked chitosan beads got a positive potential, which increased the removal of nitrate. The conditioning of chitosan beads with NaHSO_4 increased its equilibrium adsorption capacity because the amine groups of chitosan were protonated by the H^+ produced from the dissociation of NaHSO_4 ($\text{p}K_a = 1.9$) during conditioning.

3.4. Effect of pH

The nitrate adsorption was highly dependent on the pH of the solution, which affects the surface charge of the chitosan beads (Fig. 4). At low pH values (3–6), more protons were available to protonate the amine groups of chitosan, and below pH 5, almost 90% of the total amine groups of chitosan were protonated [22]. The increasing electrostatic interactions between the negatively charged nitrate and positively charged amine groups of chitosan [23] caused an increase in the nitrate adsorption; therefore, the maximum nitrate was removed at pH 3. The cross-linking treatment of the chitosan beads with ECH reinforced its chemical stability in acidic pH, which was reflected in the higher values of equilibrium adsorption capacity of cross-linked chitosan beads especially in acidic pH. At neutral pH, about 50% of the total amine groups remained protonated [11], and the decreasing electrostatic interactions between the negatively charged nitrate and positively charged amine groups of chitosan resulted in less nitrate adsorption. At pH 8, the increased concentration of hydroxide ions in the solution caused the deprotonation of the amine groups of chitosan beads. This resulted in a repulsive effect between the deprotonated amine groups and the negatively charged nitrate, and hence, the adsorption capacity was greatly reduced.

The cross-linked chitosan beads were noted to have higher q_e values than non-cross-linked chitosan beads at all the pH values tested in this study. From the BET specific surface area measurement, the cross-linking of the chitosan beads with ECH did not alter the specific surface area significantly. The increase in the maximum adsorption amount for the cross-linked chitosan beads may be explained by the higher acid stability, as well as the cross-linking property of ECH [14]. The chemical cross-linking of the chitosan beads may cause a reduction in the crystallinity of the cross-linked beads, making the amine groups of chitosan more accessible for adsorption [14]. Conditioning of the non-cross-linked

and cross-linked chitosan beads with 0.1 mM NaHSO₄ increased the maximum adsorption amount at all pH values tested in this study. This was because protonation of the amine groups during conditioning increased the electrostatic interactions between the negatively charged nitrate and the positively charged amine groups of chitosan.

3.5. Adsorption isotherm

Equilibrium adsorption data were analyzed using different isotherm models to understand the adsorbate–adsorbent interaction. The Langmuir isotherm model assumes monolayer coverage on a homogeneous surface without interaction between adsorbed molecules and uniform energies of adsorption onto the surface. The linearized form of the Langmuir model is given as

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \quad (4)$$

where C_e is the equilibrium nitrate concentration (mg L⁻¹) in the solution, q_e is the equilibrium nitrate concentration (mg g⁻¹) on the adsorbent, and a_L (L mg⁻¹) and K_L (L g⁻¹) are the Langmuir constants with a_L related to the adsorption energy. The values of a_L and K_L are calculated from the slope and intercept of the plot of C_e/q_e versus C_e , and q_{\max} [= K_L/a_L] signifies the maximum adsorption capacity (mg g⁻¹).

The values of the correlation coefficients ($R^2 = 0.999$) obtained from the linearized form of Langmuir isotherm model for all types of chitosan beads used in this study indicated that the adsorption of nitrate on chitosan beads fit well to the Langmuir model. The good correlation also indicated that the adsorption took place at the functional groups/binding sites on the surface of the chitosan beads, which is considered as monolayer adsorption. Table 3 indicates that the conditioned cross-linked chitosan beads were the best adsorbent used in this study, and the q_{\max} value was found at 104.0 mg g⁻¹. Cross-linking the chitosan beads with ECH increased the maximum adsorption capacity (q_{\max}) from 90.7 to 103.1 mg g⁻¹. The measurement of the zeta potential of chitosan beads at pH 5 indicated that the cross-linking of chitosan beads with ECH increased the zeta potential from 30.1 (non-cross-linked) to 41.2 mV (cross-linked) at pH 5. This could be the possible reason for the 13.67% increase in the q_{\max} value for the cross-linked chitosan beads as compared to non-cross-linked chitosan beads. The zeta potential value of the conditioned cross-linked (38.8 mV) chitosan beads was similar to the cross-linked chitosan beads (41.2 mV) at pH 5, and this was reflected in a 0.86% increase in the q_{\max} value after conditioning the cross-linked chitosan beads with 0.1 mM NaHSO₄. The zeta potential value was increased from 30.1 to 38.5 mV after conditioning the non-cross-linked chitosan beads with 0.1 mM NaHSO₄, and this could be the possible reason for the increase in the q_{\max} value from 90.7 to 93.6 mg g⁻¹ after conditioning. Therefore, this process of conditioning was more effective for non-cross-linked chitosan beads. The maximum adsorption capacity of the conditioned ECH cross-linked chitosan beads for nitrate is comparable to several other reported low cost biosorbents [9,10] used for the removal of nitrates from waste water. This suggests the effective-

ness of the conditioned cross-linked chitosan beads as a potential adsorbent for the treatment of water containing nitrates.

The essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor (R_L) [24] given by the following equation:

$$R_L = \frac{1}{(1 + a_L C_0)} \quad (5)$$

where a_L is the Langmuir constant (L mg⁻¹) and C_0 is the initial nitrate concentration (mg L⁻¹). R_L values within the range $0 < R_L < 1$ indicate favourable adsorption. In this study, all the values of R_L were found to lie between 0.063 and 0.072 for the initial nitrate concentration of 1000 mg L⁻¹. This indicated favourable adsorption of nitrate onto the different types of chitosan beads.

The Freundlich isotherm model is an empirical equation employed to describe the multilayer adsorption with a heterogeneous energetic distribution of active sites, accompanied by interactions between adsorbed molecules. A linear form of Freundlich equation is

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

where K_F (L g⁻¹) is the Freundlich adsorption isotherm constant relating to the extent of adsorption and $1/n$ is related to the adsorption intensity, which varies with heterogeneity of the material. The values of K_F and $1/n$ calculated from the intercept and slope of the plot of $\ln q_e$ versus $\ln C_e$ are listed in Table 3. The values of the correlation coefficients (R^2) obtained from the Freundlich model were in the range of 0.905–0.921, indicating better fit to the Langmuir model ($R^2 = 0.999$).

The equilibrium adsorption data were also subjected to the Dubinin–Radushkevich (D-R) isotherm model to determine the nature of the adsorption processes as either physical or chemical. The (D-R) isotherm is used to estimate the adsorption energy. This isotherm model is more general than Langmuir isotherm because it does not assume a homogeneous surface or a constant adsorption potential. The linear form of the (D-R) isotherm equation [25] is given as

$$\ln q_e = \ln q_m - \beta \varepsilon^2 \quad (7)$$

where β is a constant related to the mean free energy of adsorption per mole of the adsorbate (mol² kJ⁻²), q_m is the maximum adsorption capacity (mg g⁻¹) and ε is the Polanyi potential, which is equal to $RT \ln(1 + 1/C_e)$, where R (J mol⁻¹ K⁻¹) is the gas constant and T (K) is the absolute temperature. The values of the correlation coefficients (R^2) obtained from the (D-R) isotherm model were found to vary between 0.951 and 0.962. The values of q_m and β were calculated from the intercept and the slope of the plot of $\ln q_e$ versus ε^2 , and all the values are listed in Table 3. The values of maximum adsorption capacity (q_m) derived from the (D-R) isotherm model for all four types of chitosan beads were higher as compared to the Langmuir isotherm. Fig. 5A and B shows the equilibrium adsorption of nitrate using different types of chitosan beads and the isotherms are plotted in together with the experimental data points. The Langmuir isotherm model only shows good fit to experimental data.

Table 3
Constants of different isotherm models.

Chitosan beads	Langmuir isotherm				Freundlich isotherm			Dubinin–Radushkevich (D-R) isotherm		
	a_L (L mg ⁻¹)	K_L (L g ⁻¹)	q_{\max} [= K_L/a_L] (mg g ⁻¹)	R_L^a	K_F (L g ⁻¹)	$1/n$	β (mol ² kJ ⁻²)	q_m (mg g ⁻¹)	E (kJ mol ⁻¹)	
Conditioned cross-linked	0.0138	1.44	104.0	0.068	6.73	0.424	5.40×10^{-3}	210.6	9.62	
Cross-linked	0.0129	1.33	103.1	0.072	6.34	0.429	5.48×10^{-3}	207.7	9.55	
Conditioned non-cross-linked	0.0148	1.39	93.6	0.063	6.41	0.416	5.34×10^{-3}	190.4	9.71	
Non-cross-linked	0.0143	1.30	90.7	0.065	6.12	0.418	5.38×10^{-3}	184.9	9.64	

^a C_0 is 1000 mg L⁻¹.

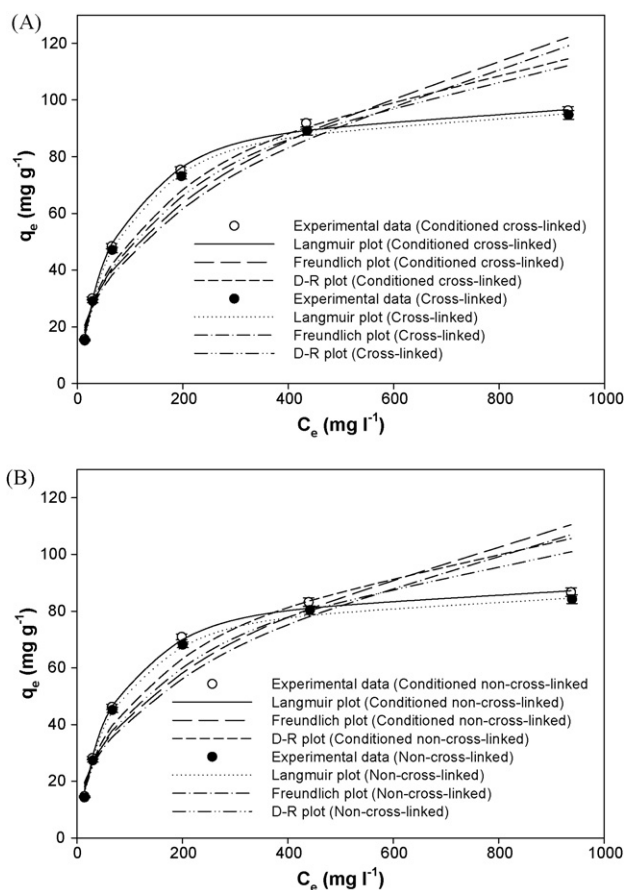


Fig. 5. Plots of q_e vs. C_e for the adsorption of nitrate onto conditioned cross-linked and cross-linked chitosan beads (A), conditioned non-cross-linked and non-cross-linked chitosan beads (B).

The constant β is related to the mean adsorption energy, E (kJ mol⁻¹) [26], as

$$E = \frac{1}{(2\beta)^{1/2}} \quad (8)$$

The range of mean adsorption energy at 2–20 kJ mol⁻¹ could be considered physisorption in nature [27]. The mean adsorption energy (E) values were found to vary between 9.55 and 9.71 kJ mol⁻¹, as shown in Table 3, suggesting that physical means such as electrostatic force played a significant role as an adsorption mechanism for the adsorption of nitrate onto different types of chitosan beads.

4. Conclusions

This study demonstrated that NaHSO₄ conditioning and epichlorohydrin cross-linking could be used as an effective method to improve chitosan beads for the removal of nitrate from aqueous solution. The conditioning of cross-linked and non-cross-linked chitosan beads with 0.1 mM NaHSO₄ increased the adsorption capacities of all adsorbents. The nitrate adsorption was strongly dependent on pH, and the maximum nitrate removal was found at pH 3. The high adsorption capacity values for all adsorption systems in acidic solutions (pH 3–5) were due to the strong electrostatic interactions between its adsorption sites and the nitrate. Equilib-

rium adsorption isotherm data indicated a good fit to the Langmuir isotherm model. The mean adsorption energies obtained from the (D-R) isotherm model indicated that physical electrostatic force was potentially involved in the adsorption process.

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