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# Effective utilization of the functional groups in chitosan by loading Zn(II) for the removal of nitrate and phosphate

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ABSTRACT

Chitosan beads cross-linked with glutaraldehyde were loaded with Zn(II) for the removal of nitrate and phosphate. The Zn(II) was bound by the free amino groups in the cross-linked chitosan beads. In order to utilise the hydroxyl groups on cross-linked chitosan, it was carboxylated with chloroacetic acid and then loaded with Zn(II). Both the sorbents viz. zinc-loaded cross-linked chitosan beads (ZnCB) and zinc-loaded carboxylated cross-linked chitosan beads (ZnCCB) were characterised by SEM, EDAX, X-ray diffraction and FT-IR. Adsorption studies were carried out in batch mode. The maximum adsorption capacity of ZnCB and ZnCCB for nitrate was 27.56 and 59.00 mg/g, respectively and for phosphate it was 31.45 and 67.50 mg/g, respectively. The suitability of the Freundlich, Langmuir and Dubinin–Radushkevich adsorption models to the adsorption equilibrium data was investigated. The equilibrium data obtained for nitrate and phosphate removal using ZnCCB were found to follow Freundlich adsorption isotherm. The thermodynamic parameters were evaluated. The results showed that the adsorption process was spontaneous, endothermic and entropy driven.

*Keywords:* Zn(II)-loaded chitosan beads; Nitrate; Phosphate; Adsorption; Regeneration

## 1. Introduction

Chitosan, a biopolymer having both amino and hydroxyl groups in its skeleton is a derivative of chitin, the second most available natural biopolymer on earth [1]. In the water purification point of view, the material used for purification should be non-toxic and compatible to suitable modifications. Chitosan is non-toxic and biodegradable [2]. Moreover, it is compatible since it is bifunctional. The only one drawback of pure chitosan is its poor mechanical strength, but it is lucratively improved using cross-linking process by the chemists. Various pollutants have been removed from water using chitosan and its modified forms [3–6].

Nitrate and phosphate are necessary nutrients for biological organisms, but it comes under the category of water pollutants if it exceeds the limit. Excess phosphate and nitrate induce eutrophication in water bodies [7]. Eutrophication indirectly affects human beings also though food chain. Nitrate consequences methemoglobinemia for newborn infants which engulf the oxygen-carrying ability of haemoglobin [8]. Thus, definitely there is a need for the removal of these excess nutrients from water. Among the methods developed

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for this purpose, adsorption seems to be the best method due to its simplicity and ease of operation [9].

The application of chitosan-based materials as adsorbent for these nutrients is a good choice. Positive sites should be there for the adsorption of these oxy anions. Modified chitosan beads were used by Jaafari et al. [10], Chatterjee et al. [11,12], Meenakshi et al. [13,14] and Dai et al. [15] for the removal of nitrate and phosphate. A few chitosan-modified materials were also reported for the removal of nitrate and phosphate [16,17]. Composites of chitosan and metal-based materials also gathered attention [18,19].

Hassan et al. utilised the Zr(IV)-loaded sugar beet pulp [20] for the removal of nitrate anion. Zr(IV)-loaded activated carbon [21], fibrous synthetic polymeric adsorbent [22]; Fe(III)-loaded functionalised sugarcane bagasse fibres [23], diamino-functionalised mesoporous silica [24], diamino-functionalised SBA-15 [25], iminodiacetic acid modified non-woven fabric [26]; La(III)-loaded chelex resin [27]; Cu(II)-loaded chelating resin functionalised with polyethylenimine [28] and Al(III)-loaded functionalised macroporous-mesoporous silica [29] were the various metal ion-loaded adsorbents reported so far for the removal of phosphate ions.

In the current study, Zn(II) was loaded in cross-linked chitosan beads as well as cross-linked carboxylated chitosan beads. The efficiency of adsorption was compared using batch studies. The adsorption mechanism was illustrated. The modification of chitosan with zinc for the removal of nitrate and phosphate was not reported elsewhere.

## 2. Materials and methods

### 2.1. Chemicals used

Chitosan with its deacetylation degree of 85% was supplied by Pelican Biotech and Chemicals Labs, Kerala (India). Analytical grade $KNO_3$ and $KH_2PO_4$ were used as the source of nitrate and phosphate anions, respectively. $ZnCl_2$, NaOH, HCl, glacial acetic acid and glutaraldehyde were also of analytical grade. Double distilled water was used throughout the study.

### 2.2. Preparation of ZnCB and ZnCCB

Chitosan (20 g) was dissolved in 1,000 mL of 2.0% glacial acetic acid solution. The chitosan solution was added into 0.5 M NaOH aqueous solution to form uniform chitosan beads. After gelling for a minimum of 16 h in 0.5 M NaOH solution, the beads were washed with distilled water to neutral pH. The wet beads were cross-linked with 2.5 wt.% glutaraldehyde solution and the ratio of glutaraldehyde to chitosan beads was approximately 1.5 mL/g of wet beads. The cross-linking reaction occurred for 48 h and then cross-linked beads (CB) were washed with distilled water to remove any free glutaraldehyde [30,31]. About 5.0% of $ZnCl_2$ aqueous solution was prepared and the cross-linked chitosan beads were immersed in it for 24 h to load Zn(II). Then, the beads were washed thoroughly with distilled water to remove the free ions and dried in room temperature to get zinc-loaded cross-linked chitosan beads (ZnCB).

The wet cross-linked chitosan beads were treated with 0.5 M chloroacetic acid maintained at pH 8 for 10 h at room temperature to introduce carboxylic groups at the hydroxyl groups of chitosan. Then, the beads were washed with distilled water to neutral pH. Then, Zn(II) was loaded as per the procedure followed for ZnCB to get zinc-loaded carboxylated cross-linked chitosan beads (ZnCCB).

### 2.3. Analytical instrumental techniques

SEM and EDAX were taken for the adsorbents on VEGA3TESCAN fitted with Bruker Nano GmbH, Germany. FT-IR spectra were collected on JASCO-460 plus model. X-ray diffraction (XRD) measurements were obtained using Rigaku UltimaIII X-ray Diffractometer. The analysis of nitrate and phosphate was carried out using UV/VIS spectrophotometer (Spectroquant Pharo 300, Merck) and Ion Chromatogram, 883 Basic IC Plus, Metrohm. The pH of the samples was determined using Expandable Ion Analyzer (Orion EA 940 USA) with pH electrode.

### 2.4. Water regain property

To investigate the maximum water absorption property, accurately weighed ZnCB and ZnCCB were immersed in distilled water for fixed time (0.5, 2, 24 and 48 h) to swell. After the suitable time, the beads were taken out, removed the excess water and weighed the swollen resin. The degree of swelling in percentage was calculated using the formula (Eq. (1)):

$$Q = [(W_2 - W_1)/W_1] \times 100 \tag{1}$$

where $W_1$ is the weight of the dry beads and $W_2$ is the weight of the swollen beads.

### 2.5. Batch experiments

Batch adsorption studies have been carried out in a flask containing 50 mL of respective nitrate and phosphate solutions (100 mg/L) and 0.1 g of each adsorbents (ZnCB and ZnCCB) at solution pH separately. Then, the reaction mixture was shaken in mechanical shaker (120 rpm) at room temperature followed by filtration. Nitrate was analysed by Ultraviolet Spectrophotometric Screening method in which the absorbance was measured at wavelength of 202 nm and phosphate was analysed by Vanadomolybdophosphoric Acid Colorimetric method in which the absorbance was measured at wavelength of 400 nm [32]. The adsorption capacity was calculated from (Eq. (2)) where $q_e$ is the anion adsorbed (mg/g), $C_0$ is the initial concentration of anion (mg/L), $C_e$ is the concentration of anion in solution at equilibrium time (mg/L), $V$ is the solution volume (L) and $m$ is the adsorbent dosage (g). To optimise the adsorption process the influence of specific parameters such as equilibration time, pH (adjusted to a definite value using HCl and NaOH solutions) and adsorbate concentrations were investigated by changing one parameter and keeping other parameters as constant. Temperature studies (303, 313 and 323 K) were restricted to the adsorption of anions on ZnCCB only since it possessed higher efficiency. The regeneration of ZnCB and ZnCCB after the adsorption studies of both nitrate and phosphate was carried out using 0.025 M NaCl at various contact times. The efficiency of the regenerated samples was checked up to fifth cycle.

$$q_e = (C_0 - C_e) \quad \mathrm{V/m} \tag{2}$$

## 3. Results and discussion

### 3.1. SEM and EDAX analysis

SEM images of ZnCCB surface is given in Fig. 1. The surface was not even and it consists of many pits and pores. ZnCB also showed similar images. Respective EDAX spectrum of ZnCB and ZnCCB were given in the Fig. 2(a) and (b). The wt.% of Zn in ZnCB was 0.78 wt.% while in ZnCCB the wt.% of Zn was 2.10. The higher wt.% of oxygen in ZnCCB was due to the carboxylic group introduced in it. In both the beads, chloride (provided by the salt of zinc) was present which is attached to Zn(II).

### 3.2. XRD of CB, ZnCB and ZnCCB

The cross-linked chitosan beads showed well-defined peaks at $2\theta = 20.44^\circ$, 30.06°, 40.06°, 42.66°, 52.8° and 57.54° (Fig. 3). After loading of ZnCB some of the peaks corresponding to chitosan were slightly modified as 19.6°, 28.8°, 40.1° and 59.7° and new peaks were appeared at 39.46°, 47.08°, 55° and 75.2°. The newly appeared peaks were correspond to Zn(II) in ZnCB. The peaks in ZnCCB were at 20.26°, 24.06°, 26.68°, 37.68°, 47.48°, 55.1°, 60.9° and 75.4° which were contributed by chitosan and Zn(II) present in ZnCCB. XRD data revealed that zinc was bounded with both cross-linked chitosan and carboxylated chitosan beads.

### 3.3. FT-IR studies

ZnCB and ZnCCB exhibited similar peaks at the regions 3,660–3,200 (O–H and N–H stretching in chitosan, moisture content present in beads also contributes at this wave number), 2,935, 2,857 (aliphatic C–H stretchings), 1,635 (N–H bending) and 1,068 $\mathrm{cm^{-1}}$ (C–O stretching) [31]. The sharp peak corresponding to C–H symmetric bending vibrations in CHOH at 1,380 $\mathrm{cm^{-1}}$ in ZnCB is modified in ZnCCB which is the indication of the modification of O–H in chitosan during carboxylation (Fig. 4). But the specific peaks corresponding to carboxylic groups at 1,716 (C=O stretching in carboxylic group), 1,320–1,210 (C–O stretch) and 883 $\mathrm{cm^{-1}}$ (O–H out-of-plane bending) [14] were absent in ZnCCB which indicates that Zn was loaded at the carboxylic group by involving both of its O–H and C=O groups. Sharp peak at 1,382 $\mathrm{cm^{-1}}$in the nitrate adsorbed ZnCCB was contributed by N–O stretching [33]. At 1,090 $\mathrm{cm^{-1}}$ a slight broadening was there in the phosphate adsorbed ZnCCB due to the presence of phosphate [34].

### 3.4. Water regain property

The swelling behaviour of the ZnCB and ZnCCB was carried out in aqueous media. The swelling values of ZnCB at 0.5, 2, 24, 48 h were 12.5, 15.6, 15.8 and 15.8%, respectively. The maximum swelling ratio of ZnCB was 15.8%. The swelling values of ZnCCB at above mentioned time were 13.4, 16.5, 16.5 and 16.7%. It is evident that the beads gain its maximum swelling capacity within 2 h.

### 3.5. Batch studies

The variation in adsorption capacities of ZnCB and ZnCCB towards nitrate and phosphate with time was studied by varying the time from 10 to 150 min (Fig. 5). On increasing the contact time, the adsorption capacity was found to gradually increase till 60 min for both the anions. The adsorption capacities of ZnCB for nitrate

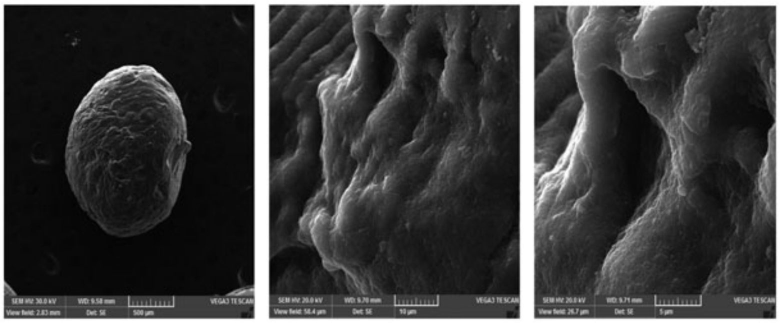
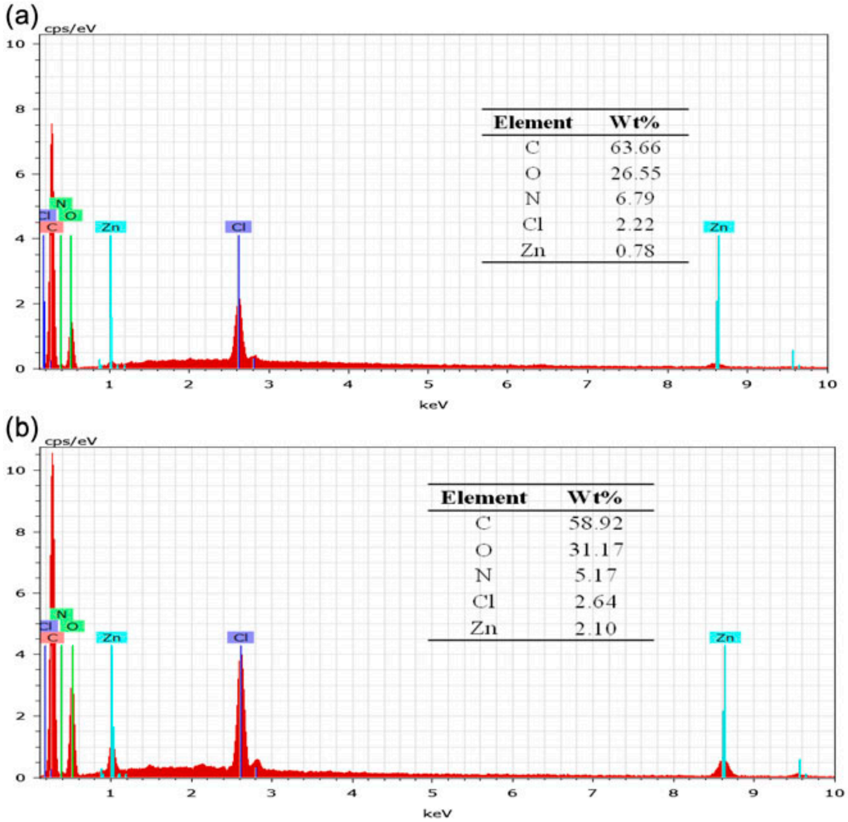


Fig. 1. SEM images of ZnCCB.



| Element | Wt% |
|---|---|
| C | 63.66 |
| O | 26.55 |
| N | 6.79 |
| Cl | 2.22 |
| Zn | 0.78 |

| Element | Wt% |
|---|---|
| C | 58.92 |
| O | 31.17 |
| N | 5.17 |
| Cl | 2.64 |
| Zn | 2.10 |

Fig. 2. (a) EDAX spectra of ZnCB. (b) EDAX spectra of ZnCCB.

and phosphate were 11.30 and 17.75 mg/g, respectively, and of ZnCCB were 26.30 and 27.41 mg/g, respectively. In order to know the maximum adsorption capacity of 0.1 g of adsorbents, the concentration of nitrate varied reasonably in the range of 10–1,000 mg/L. The adsorption capacity worthily increased with increasing initial concentration of anionic solutions. The nitrate and phosphate adsorption capacity of ZnCB was 27.56 and 31.45 mg/g, respectively, and of ZnCCB were 59.00 and 67.50 mg/g, respectively, from 1,000 mg/L of respective aqueous solutions. Zn(II) ions were chelated by the amino groups of cross-linked chitosan beads in ZnCB. But in ZnCCB, Zn(II) ions were chelated in the amino groups as well as carboxylic groups in chitosan. Thus, ZnCCB owed higher percentage of Zn(II) than the percentage of Zn(II) in ZnCB and hence the evidenced increase in the anion removal efficiency of ZnCCB. The Zn(II) loaded at the various functional sites adsorbs nitrate and phosphate by electrostatic attraction. $Cl^-$ ions pres-

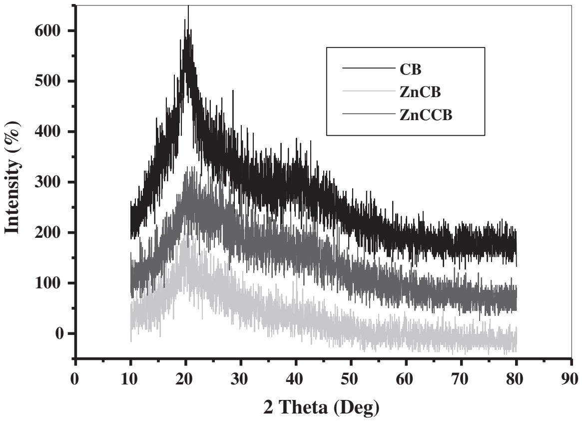


Fig. 3. XRD patterns of CB, ZnCB and ZnCCB.

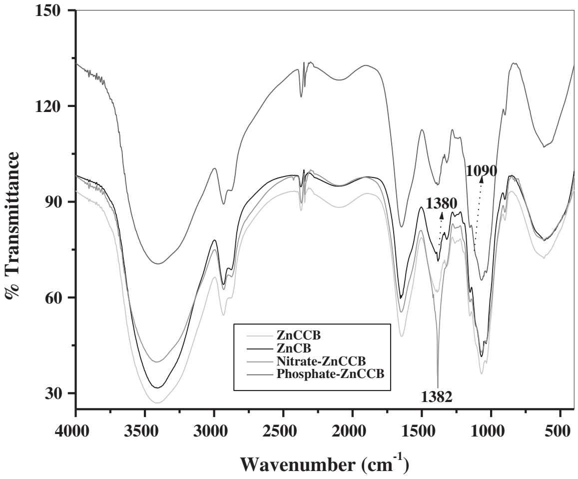


Fig. 4. FT-IR of adsorbents.

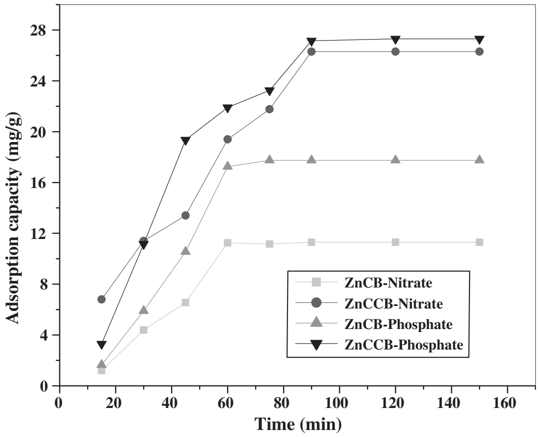


Fig. 5. Effect of contact time on removal of nitrate and phosphate.

ent in the adsorbents (as evidenced from EDAX) would also exchange for nitrate and phosphate anions. The possible mechanism of nitrate and phosphate adsorption on ZnCB and ZnCCB were depicted in Fig. 6(a) and (b).

Nitrate adsorbed well on the ZnCB and ZnCCB at the pH range 2–9 with a maximum adsorption in the range of 4–7 (Fig. 7). The exigent $OH^-$ ions were the reason for the significant reduction of nitrate adsorption after pH 9. Phosphate can exist in the form of $H_3PO_4$, $H_2PO_4^-$, $HPO_4^{2-}$ and $PO_4^{3-}$, respectively, at pH ranges of <2, 2–7, 7–12.5 and >12.5 [18]. Maximum phosphate adsorption on ZnCB and ZnCCB were in the pH range of 4–7. Slight amount of $H_3PO_4$ may be there at pH 2 and 3 which may not get adsorbed on zinc-loaded adsorbents due to the lack of negative sites. $OH^-$ ions compete with phosphate ions also for the Zn(II) sites after the pH 9. The results illustrate that phosphate gets adsorbed well on Zn(II) adsorbents irrespective of charge ($H_2PO_4^-$ or $HPO_4^{2-}$).

### 3.6. Effect of co-anions

$Cl^-$, $SO_4^{2-}$ and $HCO_3^-$ were some of the common anions present in the water sources. The adsorption studies of nitrate and phosphate on ZnCB and ZnCCB were carried out in the presence of the above-mentioned anions (100 mg/L each). As depicted in Fig. 8(a) and (b), the nitrate adsorption capacities were altered by $Cl^-$ and $SO_4^{2-}$ while $HCO_3^-$ has no effect on it. $Cl^-$ ion is a simple anion having ionic radius (1.81 Å) almost similar to that of $NO_3^-$ (1.79 Å). It also has affinity towards the positive Zn(II) sites and hence it competes with nitrate and phosphate. The $SO_4^{2-}$ ion is a simple anion which has similar ionic radius (2.3 Å) to that of phosphate (2.38 Å) and has more negative charge than phosphate and nitrate. So, $SO_4^{2-}$ could also get adsorbed on adsorbents and considerably affect the nitrate and phosphate adsorption to some extent. Results show that, $HCO_3^-$, the simple oxy anion (1.78 Å) does not alter the sorption capacity of both nitrate and phosphate since it is less basic than nitrate and phosphate. The adsorption studies were carried out from the binary coexisting solution of nitrate and phosphate anions (100 mg/L each). Phosphate preferably adsorbed more on the adsorbents than nitrate. The nitrate and phosphate adsorption capacities were 7.8 and 9.9 mg/g, respectively, for ZnCB and 12.8 and 18.5 mg/g, respectively, for ZnCCB.

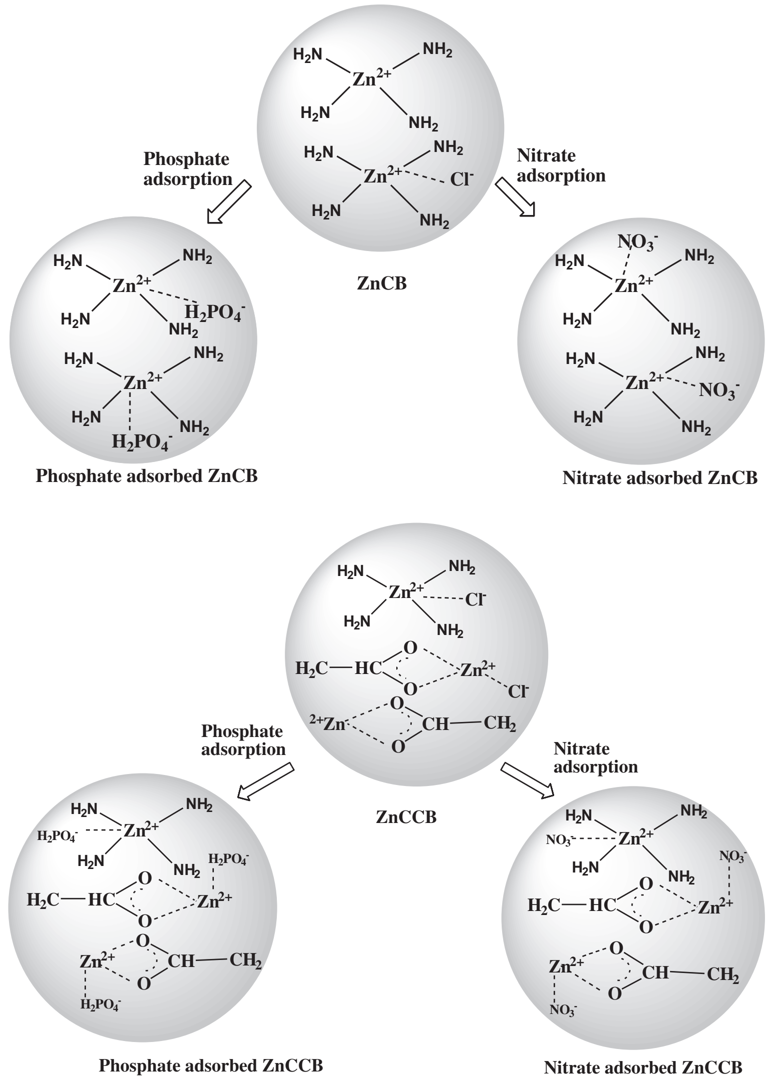


Fig. 6. (a) Possible mechanism of anion adsorption by ZnCB. (b) Possible mechanism of anion adsorption by ZnCCB.

### 3.7. Regeneration of the adsorbents

The nitrate and phosphate adsorbed ZnCB and ZnCCB was collected and regenerated using 0.025 M NaCl solutions. The regeneration was carried out for 30 min of contact time. In the presence of higher concentration of $Cl^-$ ions, the nitrate and phosphate which were electrostatically attached on Zn(II)-loaded beads gets replaced. The regenerated ZnCB and ZnCCB were used for the adsorption studies at the predetermined conditions. The nitrate and phosphate adsorption capacity after first regeneration were 10.8 and 17.1 mg/g, respectively, for ZnCB and 22.5 and 24.6 mg/g, respectively, for ZnCCB. The slight reduction in the adsorption capacity may be due to the incomplete exchange of oxy anions by the regenerant. After fifth regeneration the adsorption capacities were almost retained as shown in Fig. 9.

### 3.8. Adsorption isotherms

Three commonly used adsorption isotherm equations like Langmuir [35], Freundlich [36] and Dubinin–Radushkevich (D–R) [37] were used for fit the equilibrium data obtained for the nitrate and phosphate adsorption using ZnCCB. The linear equations (Eqs. (3)–(5)) and the respective plots were given below.

Freundlich equation:

$$\log\ q_e = \log\ k_F + \frac{1}{n}\log C_e; \quad \log q_e \text{ vs. } \log C_e \tag{3}$$

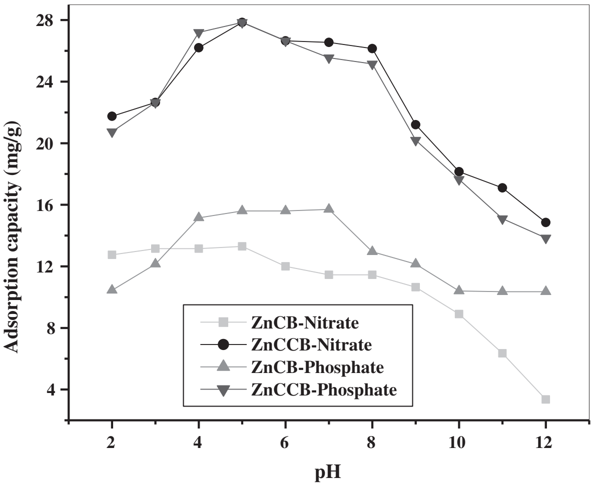


Fig. 7. Effect of pH on removal of nitrate and phosphate.

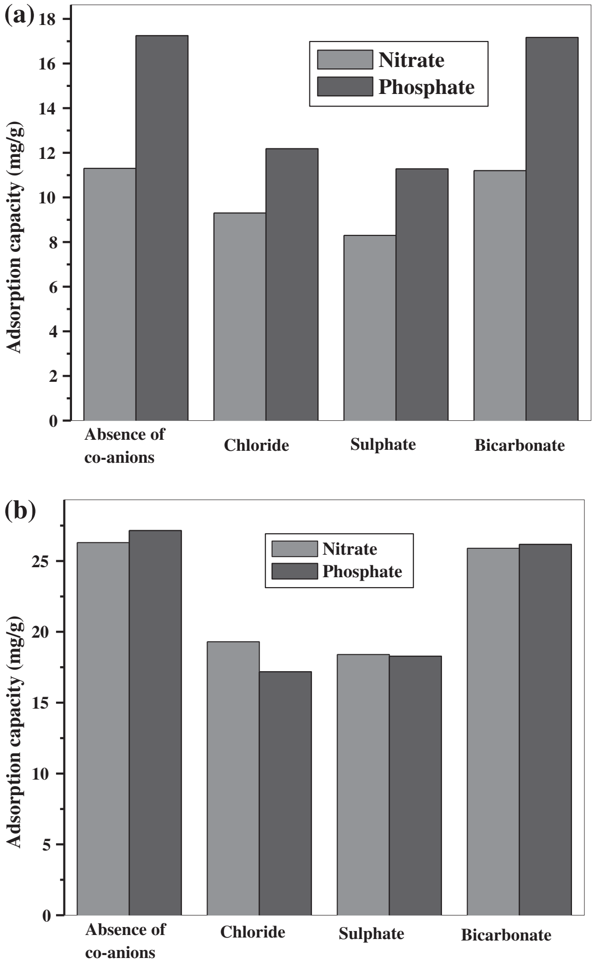


Fig. 8. (a) Effect of co-anions on nitrate and phosphate adsorption by ZnCB. (b) Effect of co-anions on nitrate and phosphate adsorption by ZnCCB.

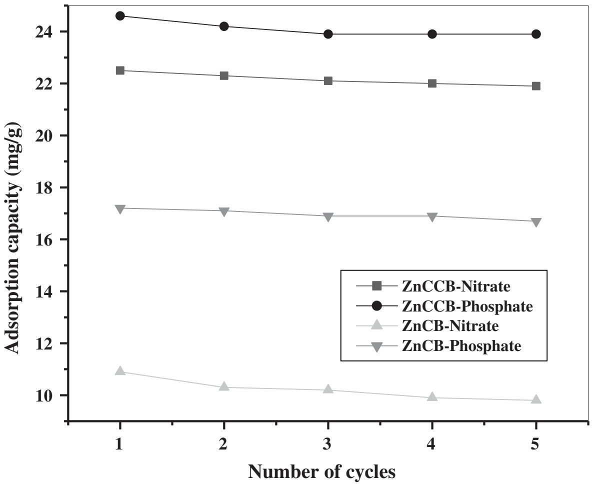


Fig. 9. Nitrate and phosphate adsorption capacity of ZnCB and ZnCCB at various cycles of regeneration.

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{Q^{\circ} b} + \frac{C_e}{Q^{\circ}}; \quad C_e/q_e \text{ vs. } C_e \tag{4}$$

D–R:

$$\ln q_e = \ln X_m - k_{DR}\varepsilon^2; \quad \ln q_e \text{ vs. } \varepsilon^2 \tag{5}$$

where $C_e$ is the equilibrium concentration in solution (mg/L); $q_e$ is the amount of anion adsorbed per unit weight of the sorbent (mg/g), $k_F$ is the Freundlich constant; n(dimensionless) is the heterogeneity factor; $Q^{\circ}$ is the amount of the sorbate sorbed at complete monolayer coverage (mg/g); $b$ is the Langmuir constant (L/mol) and related to the free energy of adsorption. The essential characteristics and the feasibility of the Langmuir model were expressed in terms of a dimensionless constant, commonly known as separation factor ($R_L$) which is expressed by the following equation (Eq. (6)):

$$R_L = \frac{1}{1 + bC_0} \tag{6}$$

where $C_0$ is the initial concentration (mg/L). The suitability of adsorption i.e. unfavourable ($R_L > 1$) or favourable ($0 < R_L < 1$) or linear ($R_L = 1$) or irreversible ($R_L = 0$) was point out by $R_L$ values.

$X_m$ is the adsorption capacity (mg/g) and $k$ is the constant related to adsorption energy ($\text{mol}^2/\text{kJ}^2$) in the

Table 1
Parameters for Freundlich, Langmuir and D–R isotherms for the adsorption of nitrate and phosphate on ZnCCB

| Isotherms | Parameters | Nitrate | | | Phosphate | | |
|---|---|---|---|---|---|---|---|
| | | 303 K | 313 K | 323 K | 303 K | 313 K | 323 K |
| Freundlich | $1/n$ | 0.663 | 0.641 | 0.566 | 0.900 | 0.765 | 0.603 |
| | $N$ | 1.506 | 1.558 | 1.767 | 1.111 | 1.307 | 1.658 |
| | $k_F$ (mg/g) (L/mg)$^{1/n}$ | 2.182 | 2.698 | 3.969 | 0.739 | 1.446 | 3.031 |
| | $R$ | 0.999 | 0.997 | 0.997 | 0.999 | 0.999 | 0.998 |
| | SD | 0.005 | 0.010 | 0.009 | 0.005 | 0.005 | 0.008 |
| | $\chi^2$ | 0.001 | 0.004 | 0.004 | 0.001 | 0.001 | 0.003 |
| Langmuir | $Q_0$ (mg/g) | 66.40 | 66.45 | 58.82 | 204.49 | 92.08 | 59.77 |
| | $b$ (L/g) | 0.015 | 0.019 | 0.029 | 0.003 | 0.009 | 0.022 |
| | $R$ | 0.999 | 0.996 | 0.999 | 0.929 | 0.997 | 0.999 |
| | SD | 0.006 | 0.017 | 0.009 | 0.011 | 0.009 | 0.029 |
| | $R_L$ | 0.454 | 0.403 | 0.307 | 0.585 | 0.553 | 0.819 |
| | $\chi^2$ | 0.001 | 0.005 | 0.006 | 0.003 | 0.004 | 0.001 |
| Dubinin–Radushkevich | $k_{DR}$ (mol$^2$/J$^2$) | 5.6E-04 | 4.1E-04 | 2.7E-04 | 6.4E-05 | 3.6E-05 | 9.9E-05 |
| | $X_m$ (mg/g) | 31.55 | 33.63 | 34.52 | 31.09 | 32.29 | 32.64 |
| | $E$ (kJ/mol) | 0.098 | 0.110 | 0.137 | 0.071 | 0.088 | 0.117 |
| | $R$ | 0.993 | 0.996 | 0.994 | 0.985 | 0.994 | 0.994 |
| | SD | 0.036 | 0.028 | 0.032 | 0.059 | 0.036 | 0.032 |
| | $\chi^2$ | 2.141 | 22.150 | 93.488 | 0.027 | 0.024 | 0.044 |

D–R equation. Polanyi potential can be calculated using (Eq. (7)).

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \quad (7)$$

where $T$ is the temperature (K) and $R$ is the gas constant (8.314 J/mol K). The value of $k$ is used to calculate the mean free energy $E$ (kJ/mol) of the sorption using the (Eq. (8)),

$$E = -(2k)^{-0.5} \quad (8)$$

The isotherm parameters, $r$, sd and $\chi^2$ at 303, 313 and 303 K are given in Table 1.

The higher $r$ values and lower sd and $\chi^2$ values revealed that, the best suitable adsorption model was Freundlich isotherm than the Langmuir isotherm. Thus, non-ideal adsorption on the heterogeneous surface of ZnCCB was occurred. The $E$ values obtained from the D–R isotherm were below 8 kJ/mol, which further confirms the physical adsorption between the anions and the adsorbent [37].

### 3.9. Thermodynamic parameters

The temperature dependence of adsorption process is associated with changes in thermodynamic parameters such as standard free energy ($\Delta G^\circ$), enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) of adsorption and were calculated according to the following method.

The Gibbs free energy change ($\Delta G^\circ$) of the adsorption process is related to the equilibrium constant by the classic Van't Hoff equation (Eq. (9)) [38,39].

$$\Delta G^\circ = -RT \ln K_0 \quad (9)$$

Table 2
Thermodynamic parameters for the adsorption of nitrate and phosphate on ZnCCB

| Anion | $\Delta G^\circ$ (kJ mol$^{-1}$) | | | $\Delta H^\circ$ (kJ mol$^{-1}$) | $\Delta S^\circ$ (kJ K$^{-1}$ mol$^{-1}$) |
|---|---|---|---|---|---|
| | 303 K | 313 K | 323 K | | |
| Nitrate | −11.59 | −11.54 | −11.11 | 18.75 | 0.02 |
| Phosphate | −15.06 | −12.99 | −11.68 | 66.50 | 0.17 |

$$\ln K_0 = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (10)$$

The values of change in enthalpy ($\Delta H^\circ$) and entropy ($\Delta S^\circ$) were determined from the slope and intercept, respectively, of the linear Van't Hoff plot (Eq. (10)). The values are presented in Table 2. The negative values of $\Delta G^\circ$ and the positive value of $\Delta S^\circ$ suggests that the adsorption was spontaneous in nature and randomness at the solid/solution interface during the adsorption of nitrate and phosphate on ZnCCB was increased. The negative values of $\Delta H^\circ$ demonstrate the exothermic nature of adsorption.

## 4. Conclusions

Zn(II)-loaded cross-linked chitosan beads and carboxylated cross-linked chitosan beads were prepared. The adsorbents were characterised by the methods like SEM, EDAX, XRD and FT-IR. The ZnCCB exhibited higher nitrate and phosphate adsorption capacity than ZnCB. Nitrate and phosphate adsorption was significant over a wide pH range of 3–9. Presence of co-anions like sulfate and chloride altered the nitrate and phosphate adsorption capacity of ZnCB and ZnCCB. Freundlich isotherm was the most suitable adsorption isotherm for both the adsorption of nitrate and phosphate on ZnCCB. The adsorption of nitrate and phosphate were spontaneous and endothermic in nature. Electrostatic attraction was the major force involved in the adsorption process and $Cl^-$ exchange was also involved in the adsorption process to some extent.

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