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Effective removal of nitrate and phosphate anions from aqueous solutions using functionalised chitosan beads

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ABSTRACT

Adsorption of nitrate and phosphate from aqueous solution on both the protonated cross-linked chitosan beads (PCB) and carboxylated cross-linked chitosan beads (CCB) was investigated in batch mode. Effects of various parameters such as contact time, dosage of adsorbent, pH of the aqueous solutions, competitive co-anions and temperature on the sorption capacity of the sorbents were studied. The reuse of sorbents was evaluated by sequential sorption–desorption cycles using 0.1 M NaOH as regenerant. Three isotherms namely Langmuir, Freundlich and Dubinin–Radushkevich were used to fit the equilibrium data, whereas the pseudo-second-order equation was used for the kinetic data. The E values obtained from the D–R isotherm at 303 K for nitrate and phosphate adsorption on PCB were 0.036 and 0.107 kJ/mol, respectively, and on CCB were 0.029 and 0.114 kJ/mol, respectively, which confirms the physical adsorption between the anions and functional moieties in PCB and CCB. ΔH° values revealed that the adsorption of nitrate is exothermic process and adsorption of phosphate is endothermic process. The sorbents were characterised by SEM and FTIR.

Keywords: Nitrate; Phosphate; Chitosan beads; Isotherms; Regeneration; Kinetics

1. Introduction

Nowadays, the amount of nitrate and phosphate in the water bodies has exceeded the drinking water limit as a result of wastewaters generated from industrial, agricultural and house hold sources. Presence of these nutrients, especially phosphate, more than required for the normal aquaculture activity can lead to significant growth of aquatic plants including harmful algal blooms, as well as depletion of oxygen that subsequently results in the decline of aquatic life which is known as eutrophication [1]. In many countries, stringent regulations limit phosphorous level to 0.05 mg/L to prevent increased algae growth [2]. A high concentration of nitrate in drinking water leads to the production of nitrosamine, which is related to cancer [3]. Concentration of nitrate higher than 45 mg/L in drinking water is hazardous to health, especially for infants and pregnant women [4].

Generally, the removal of dissolved nutrients from water and wastewaters has been possible by numerous physicochemical processes such as ion exchange [5,6], chemical precipitation [7], electro coagulation [8,9], membrane process [10,11] and adsorption method [12,13] as well as biological processes [14]. Adsorption is one of the techniques that would be comparatively more useful and economical for

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phosphate and nitrate removal. Adsorption has found to be superior to other techniques for water reuse in terms of initial cost, flexibility and simplicity of design, and ease of operation.

Chitosan, a linear copolymer of glucosamide and N-acetyl glucosamine, is obtained by thermo-chemical deacetylation of most abundant crustacean chitin and is unique in its applications in wide fields as a biomaterial [15,16]; as it is biodegradable, biocompatible and non-toxic. Several chemical modification methods, such as chemical cross-linking of the surface of the chitosan beads with cross-linking agents and insertion of new functional groups of chitosan beads have been performed to improve its stability and applicability [17–19].

The present study investigates the effectiveness of protonated chitosan and carboxylated chitosan beads for the removal of nitrate and phosphate from aqueous solutions and also the role of factors like contact time, dosage of sorbent, pH, temperature on the adsorption, dynamics of equilibrium and nature of adsorption. This study also envisaged to establish the isothermal behaviour of adsorption process.

2. Materials and methods

2.1. Materials

All the chemicals used were of analytical reagent grade. Chitosan was supplied by Pelican Biotech and Chemicals Labs Kerala (India). Working solution of nitrate and phosphate were prepared by dissolving respective KNO_3 and KH_2PO_4 (Supplied by Merck) in deionised water. The reagents HCl, NaOH, NaCl, $NaHCO_3$ and Na_2SO_4 used were of analytical grade. Doubly distilled water was used throughout the study.

2.2. Preparation of protonated cross-linked chitosan beads and carboxylated cross-linked chitosan beads

Protonated cross-linked chitosan beads (PCB) and carboxylated cross-linked chitosan beads (CCB) were prepared as reported in the earlier studies [19–21]. Chitosan (20 g) was dissolved in 1,000 mL of 2.0% glacial acetic acid solution. The viscosity of the solution was measured as 480 mPas. The chitosan solution was dropped into a 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 a neutral pH. The wet beads were cross-linked with 2.5 wt.% gluteraldehyde solution and the ratio of gluteraldehyde to chitosan beads was approximately 1.5 mL/g of wet beads. The cross-linking reaction occurred for 48 h and then the cross-linked beads were washed with distilled water to remove any free gluteraldehyde. From the cross-linked chitosan beads, the PCB and CCB were prepared. The cross-linked chitosan beads were treated with concentrated HCl for 30 min for protonation of the amine group in the chitosan beads. The resulting PCB was washed with distilled water to neutral pH, dried at room temperature and used for the sorption studies. The CCB was prepared by treating cross-linked chitosan beads with 0.5 M chloroacetic acid maintained at pH 8.0 using 0.1 M NaOH for 10 h at room temperature to convert the hydroxyl groups to carboxyl group. Then, the CCB was washed with distilled water to neutral pH, dried at room temperature and used for sorption studies.

2.3. Analytical instrumental techniques

SEM was taken for the adsorbents on VEGA3TESCAN, Germany. The structure of sorbents before and after sorption of nitrate and phosphate was analysed using FTIR spectra recorded with JASCO-460 plus model. The viscosity of the dissolved chitosan was analysed by Brookfield Dial Reading Viscometer using electronic drive-RVT mode (USA). The analysis of nitrate and phosphate was carried out using UV/VIS Spectrophotometer (Spectroquant Pharo 300, Merck), 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. Adsorption and regeneration studies

Adsorption experiments were carried out by batch equilibration method in duplicate. The effect of contact time on nitrate and phosphate removal was investigated in the range of 15–180 min using 200 mg/L of nitrate solution and 50 mg/L phosphate solution, respectively, at room temperature in a mechanical shaker having 120 rpm. The concentrations of nitrate and phosphate solutions were varied between 50 and 250 mg/L to study the effect of initial concentration. Dosage effect of PCB and CCB was investigated by varying the dose between 0.1 and 0.5 g. To investigate the pH effect, adsorption studies were carried out after adjusting the pH of nitrate and phosphate solutions as 3, 5, 7, 9 and 11 using concentrated HCl and NaOH. The effect of sorption of nitrate and phosphate in the presence of some of the anions which are commonly present in water, like Cl^-, HCO_3^- and SO_4^{2-} were studied. Standard solutions of these ions were prepared and calculated amount was added to the nitrate and phosphate solutions. The sorption capacities were compared with blank experiment. Adsorption isotherm and kinetic studies were carried out at 303, 313 and 323 K at various concentrations.

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 [22] in a UV–Visible spectrophotometer. The sorption studies from the nitrate/phosphate binary coexisting system were also carried out at various concentrations and the nitrate and phosphate were analysed using 883 Basic IC Plus Ion Chromatogram, Metrohm.

Regeneration of PCB and CCB after the adsorption studies of both nitrate and phosphate were carried out using 25 mL of 0.1 M NaOH at various contact times like 5, 10, 15, 30 and 60 min. The minimum required time for the regeneration was fixed and the efficiency of the regenerated samples was checked up to fifth cycle.

3. Results and discussion

3.1. Characterisation of the adsorbents

The SEM image of PCB and CCB surface is given in Fig. 1. The FTIR spectra of raw and nitrate/phosphate-adsorbed PCB and CCB are given in Fig, 2(a) and (b). The strong band in PCB and CCB at the region of 3,400–3,500 cm^{-1} is the characteristics of –OH and $-NH_2$ stretching vibrations. Further, 2,935 and 2,857 cm^{-1} correspond to the presence of aliphatic C–H stretching. The bands at 1,635 and 1,380 cm^{-1} are due to the presence of $-NH_2$ bending vibrations and –CH symmetric bending vibrations in –CHOH [19–21]. The peak at 1,027 cm^{-1} in PCB and the bands at 1,068 cm^{-1} in CCB could be attributed to C–O stretching of C–O–H groups. Strong band at 1,716 in CCB cm^{-1}

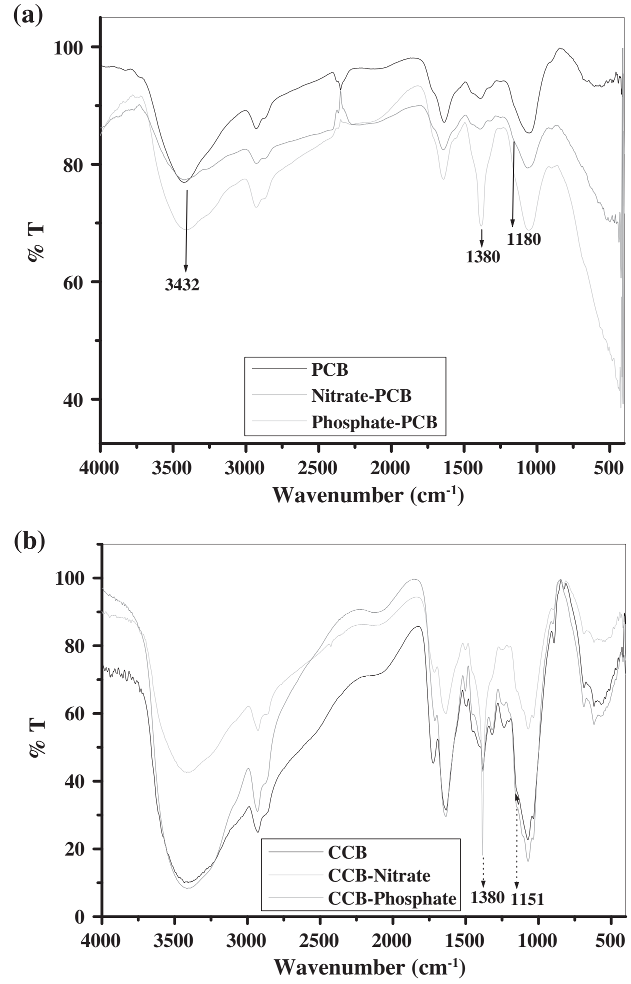

Fig. 2. (a) FTIR spectra of PCB before and after the adsorption of nitrate and phosphate (b) FTIR spectra of CCB before and after the adsorption of nitrate and phosphate.

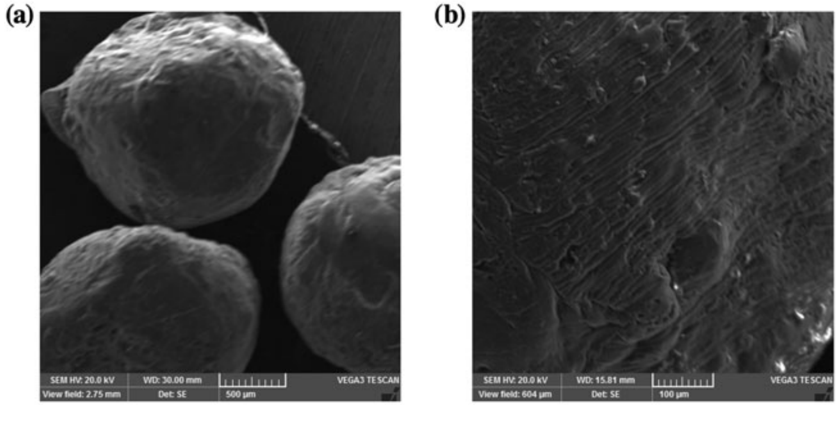

Fig. 1. (a) SEM image of PCB and (b) SEM image of CCB surface.

corresponds to the C=O stretching in carboxylic group. Also, peaks at 1,320–1,210 cm^{-1} (C–O stretch) and 883 cm^{-1} (O–H out-of-plane bending) correspond to carboxylic group.

After the sorption of nitrate and phosphate broadening of band at 3,432 cm^{-1} in PCB was observed, this indicates the adsorption of nitrate and phosphate. In the IR spectra of nitrate-sorbed PCB and CCB, sharp band at 1,380 cm^{-1} which overlapped with –CH symmetric bending vibrations was due to N–O in the nitrate [23]. Phosphate ion usually gives band at 1,100–1,000. Small broadening of the bands at 1,195 and 1,151 cm^{-1} in the IR spectra of phosphate-sorbed PCB and CCB [3] may be due to the presence of phosphate ions.

3.2. Effect of contact time, adsorbate concentration and dose of the adsorbent

The effect of contact time, effect of dosage of PCB and CCB and effect of initial concentration of nitrate and phosphate on sorption capacities of the sorbents were investigated. The sorption capacity of PCB and CCB towards nitrate and phosphate reached saturation after 90 min (Fig. 3). The percentage removal of nitrate and phosphate significantly increased with increase in sorbent dosage because of the increase in number of active sites (Fig. 4). The sorption capacity of adsorbents was found to increase as the concentration of nitrate and phosphate solutions increased from 50 to 250 mg/L as given in Fig. 5.

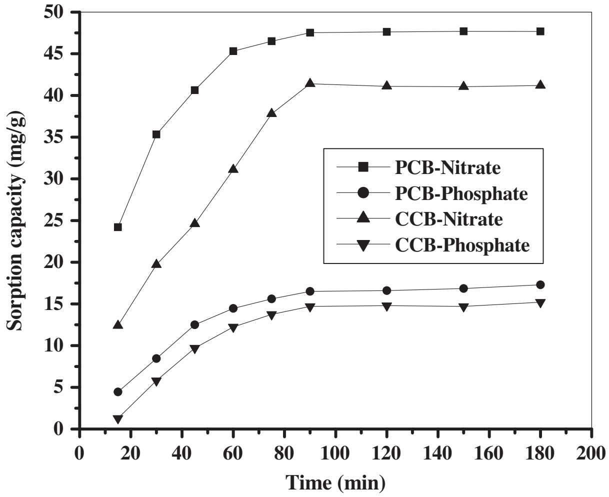

Fig. 3. Effect of contact time on removal of nitrate and phosphate.

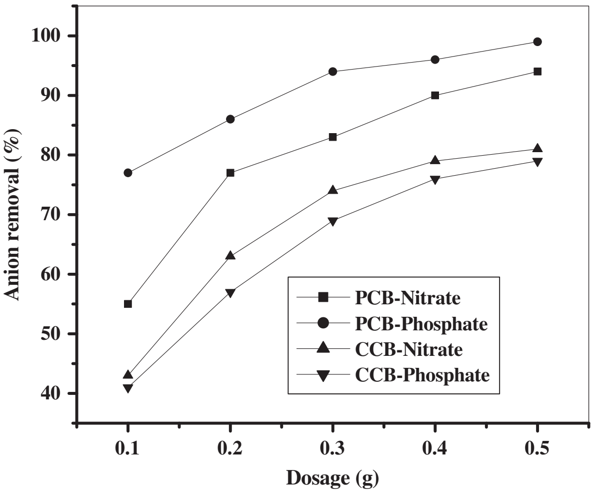

Fig. 4. Effect of dose of sorbents on removal of nitrate and phosphate.

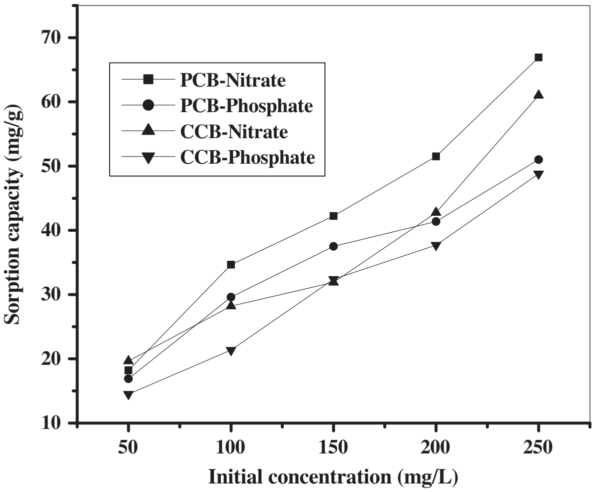

Fig. 5. Effect of initial concentration of nitrate and phosphate.

3.3. Effect of pH

pH is an important parameter which influences the nature of the adsorbent as well as the adsorbate. In case of nitrate adsorption, the pH dependency was related to the surface charge of the PCB and CCB. The nitrate sorption capacity was high at acidic pH on both the adsorbents. The pH at zero point charge for the PCB and CCB determined by drift method was 2.8 and 3.2, respectively. At acidic pH, the surface of the PCB and CCB acquires more positive charge and hence more nitrate ions could get electrostatically attracted by the adsorbents. The nitrate adsorption capacity slightly decreased at pH near 7 and significantly decreased at basic pH. This is because at higher pH the surface of the adsorbents acquires more negative charge which repels nitrate ions (Fig. 6). In contrast, pH dependency of the phosphate adsorption was related to both surface charge of the adsorbent and to the polyprotic nature of phosphate [24]. There was a small decline in adsorption capacity of phosphate at pH 3. Adsorption capacity was high at the pH range of 5–7 and beyond that decreasing trend was observed. Since 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 [25], slight amount of H_3PO_4 may be there at pH 3 and this cannot be electrostatically attracted by the positive surface. At pH 5–7 more dihydrogen phosphate ($H_2PO_4^-$) was there in the solution which electrostatically adsorbs on the positive surface. Beyond pH 7, phosphate exists as HPO_4^{2-} which could be attracted well by PCB and CCB, however, the increase in pH makes the surface to acquire negative charge which repels phosphate ions and hence the reduction in sorption capacity (Fig. 6) was observed.

3.4. Effect of co-ions

Anions such as Cl^-, HCO_3^- and SO_4^{2-} are mostly found in natural fresh water as well as in effluents. The adsorption abilities of the PCB and CCB for nitrate and phosphate removal in the presence and absence of Cl^-, HCO_3^- and SO_4^{2-} ions are shown in Fig. 7. It can be seen that sulphate ion significantly altered the sorption capacity of PCB and CCB towards nitrate and phosphate. Higher influence of sulphate on the adsorption may be due to its higher ionic charge than nitrate and phosphate ions [26]. Sorption studies were also carried out from the binary coexisting solutions of nitrate and phosphate having initial concentration of 50 and 200 mg/L of both the anions. The nitrate and phosphate sorption capacities of PCB from 50 mg/L binary nitrate/phosphate solutions were 23.5 and 11.5 mg/g, respectively, and from 200 mg/L were 45 and 16 mg/g, respectively. The nitrate and phosphate sorption capacities of CCB from 50 mg/L binary solution were 22 and 7.5 mg/g, respectively, and from 200 mg/L the sorption capacities were 35.5 and 28.5 mg/g, respectively.

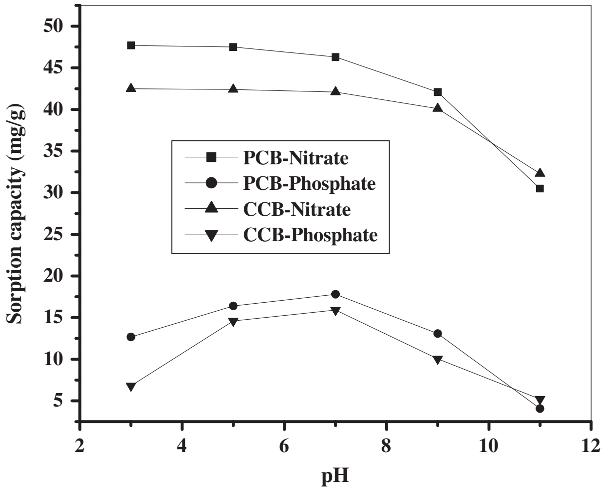

Fig. 6. Effect of pH on removal of nitrate and phosphate.

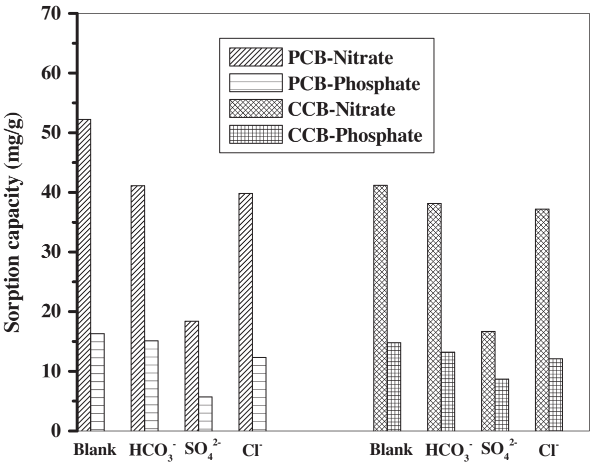

Fig. 7. Effect of co-ions on removal of nitrate and phosphate.

3.5. Isotherms

The equilibrium sorption data of nitrate and phosphate on PCB and CCB were investigated using the adsorption isotherm models viz., Langmuir, Freundlich and Dubinin–Radushkevich (D–R).

The linear form of Freundlich equation [27] is,

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \tag{1}$$

where C_e is the equilibrium concentration (mg/L) and q_e is the amount adsorbed per unit weight of adsorbent. The k_F and n values are calculated from the intercepts and slopes of the linear plots of log q_e vs. log C_e for the removal of both anions using PCB and CCB.

The linear form of Langmuir equation [28] is given as follows:

$$C_e/q_e = 1/Q_0 b + C_e/Q_0 \tag{2}$$

where C_e is the equilibrium concentration (mg/L); q_e is the amount adsorbed at equilibrium (mg/g); and Q_0 and b are Langmuir constants related to energy of adsorption (L/mg) and adsorption capacity (mg/g), respectively.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, R_L [29].

$$R_L = \frac{1}{1 + bC_o} \tag{3}$$

where b is the Langmuir isotherm constant and C_0 is the initial concentration of anion (mg/L).

Linear form of D–R isotherm equation is given as,

$$\ln q_e = \ln\ X_m - \ k_{DR}\varepsilon^2 \tag{4}$$

where X_m is the adsorption capacity (mg/g) and k is the constant related to adsorption energy (mol^2/kJ^2). The values of k and X_m were computed from the slope and intercept of the plot ln q_e vs. ε^2, respectively. Polanyi potential can be calculated by the equation,

$$\varepsilon = RT \ln\left(1 + \frac{1}{C_e}\right) \tag{5}$$

where T is the temperature (K) and R is the gas constant (8.314 J mol^{-1} K^{-1}). The value of k is used to calculate the mean free energy E (kJ/mol) of the sorption:

$$E = -(2k)^{-0.5} \tag{6}$$

To identify the most suitable isotherms for the adsorption of nitrate and phosphate onto PCB and CCB, chi-square analysis was carried out. The mathematical statement of chi-square analysis [30] is

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}} \tag{7}$$

where $q_{e,m}$ is the equilibrium capacity obtained from the model (mg/g) and q_e is the experimental data of the equilibrium capacity (mg/g).

The isotherm parameters, r, SD and chi-square values for the isotherms were given in Tables 1 and 2. The higher r, lower SD and lower chi-square values indicate the applicability of the three isotherms studied. The values of $1 < n < 10$ and R_L values between 0 and 1 indicate favourable condition for the adsorption of both nitrate and phosphate. From the isotherm

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

Isotherms	Parameters	PCB					
		Nitrate			Phosphate		
		303 K	13 K	323 K	303 K	313 K	323 K
Freundlich	$1/n$	0.571	0.409	0.364	0.697	0.735	0.772
	n	1.751	2.447	2.749	1.434	1.361	1.296
	k_F (mg/g) (L/mg)$^{1/n}$	3.432	8.761	14. 205	1.550	1.216	1.129
	r	0.999	0.998	0.999	0.999	0.999	0.999
	SD	0.002	0.005	0.012	0.002	7.7E-04	0.001
	χ^2	0.004	0.021	0.009	1.1E-04	1.6E-05	0.797
Langmuir	Q_0 (mg/g)	113.12	93.72	108.11	58.45	57.14	56.82
	b (L/g)	0.007	0.016	0.023	0.014	0.012	0.009
	r	0.997	0.997	0.993	0.999	0.999	1
	SD	0.034	0.034	0.042	0.004	0.002	1.1E-04
	R_L	0.924	0.848	0.749	0.867	0.885	0.909
	χ^2	0.004	0.021	0.027	0.019	0.244	0.0002
D–R	k_{DR} (mol^2/J^2)	3.8E-04	2.8E-04	1.1E-04	4.3E-05	4.9E-05	5.9E-05
	X_m (mg/g)	63.67	71.25	79.88	22.574	21.451	19.489
	E (kJ/mol)	0.036	0.041	0.071	0.107	0.101	0.092
	r	0.987	0.998	0.951	0.997	0.995	0.996
	SD	0.043	0.012	0.061	0.016	0.019	0.018
	χ^2	0.032	0.003	0.083	0.001	0.002	0.002

Table 2
Parameters for Freundlich, Langmuir and D–R isotherms for the adsorption of nitrate and phosphate on CCB

Isotherms	Parameters	CCB					
		Nitrate			Phosphate		
		303 K	313 K	323 K	303 K	313 K	323 K
Freundlich	$1/n$	0.578	0.589	0.541	0.344	0.222	0.309
	n	1.731	1.699	1.848	2.907	4.502	3.238
	k_F (mg/g) $(L/mg)^{1/n}$	2.419	2.480	3.223	3.136	4.379	2.675
	r	0.999	0.999	0.999	0.995	0.999	0.999
	SD	0.003	4.0E-04	1.6E-04	0.005	4.1E-04	6.8E-04
	χ^2	7.0E-04	0.001	0.002	5.1E-04	2.9E-05	7.1E-04
Langmuir	Q_0 (mg/g)	90.66	99.41	91.16	16.56	12.75	12.32
	b (L/g)	0.006	0.006	0.008	0.052	0.089	0.053
	r	0.999	0.995	0.998	0.999	0.999	0.999
	SD	0.005	0.053	0.038	0.023	0.011	0.011
	R_L	0.446	0.452	0.399	0.242	0.157	0.238
	χ^2	3.9E-04	0.006	0.003	2.1E-04	2.4E-05	1.4E-05
D–R	k_{DR} (mol^2/J^2)	5.8E-04	4.9E-04	4.2E-04	3.8E-05	2.5E-05	3.8E-05
	X_m (mg/g)	51.23	53.76	54.37	13.02	11.09	9.94
	E (kJ/mol)	0.029	0.032	0.035	0.114	0.142	0.115
	r	0.992	0.989	0.984	0.999	0.994	0.995
	SD	0.032	0.050	0.043	0.002	0.008	0.009
	χ^2	0.015	0.562	0.759	1.4E-05	9.1E-04	0.003

data, the most suitable adsorption isotherm for the sorption of both nitrate and phosphate was found to be Freundlich isotherm and hence it could be concluded that non-ideal adsorption on the heterogeneous surface of PCB and CCB was occurred and multilayer nitrate and phosphate sorption was also possible [5]. The E values obtained from the D–R isotherm at 303 K for nitrate and phosphate adsorption on PCB were 0.036 and 0.107 kJ/mol, respectively, and for nitrate and phosphate adsorption on CCB was 0.029 and 0.114 kJ/mol, respectively. The E values less than 8 kJ/mol confirm that adsorption between the anions and functional moieties in PCB and CCB is favoured by physical forces [5,31,32].

3.6. Thermodynamic parameters

The temperature dependence of adsorption process is associated with the changes in thermodynamic parameters such as standard free energy, enthalpy and entropy of adsorption. These thermodynamic parameters were calculated by the Khan and Singh method [33] and are given in Table 3. The negative values of ΔG° at different temperatures indicate the spontaneous nature of phosphate and nitrate adsorption. The positive values of ΔH° confirm the endothermic nature of nitrate adsorption on both the sorbents. Further, the negative values of ΔH° confirm the exothermic nature of phosphate adsorption on both the sorbents. The positive values of ΔS° indicated a decreased randomness during the adsorption of nitrate and phosphate onto PCB and CCB.

3.7. Pseudo-second order kinetic model

The adsorption kinetics may be described by the pseudo-second order model [34], which is generally given as follows

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e} \qquad (8)$$

where $q_t = \frac{q_e^2 kt}{1+q_e kt}$ is the amount of anions on the surface of the sorbents at any time, t (mg/g); k is the pseudo-second-order rate constant (g/mg min); and q_e is the amount of anions adsorbed at equilibrium (mg/g) and the initial sorption rate, $h = kq_e^2$. The value of q_e (1/slope), k (slope^2/intercept) and h (1/intercept) of the pseudo-second-order equation can be found out experimentally by plotting t/q_t against t. The kinetic data of

Table 3
Thermodynamic parameters for the adsorption of nitrate and phosphate on PCB and CCB

Anion	ΔG° (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° (kJ K^{-1} mol^{-1})
	303 K	313 K	323 K		
PCB					
Nitrate	−13.78	−13.04	−12.70	30.25	0.05
Phosphate	−11.39	−12.30	−13.36	−18.37	0.10
CCB					
Nitrate	−14.22	−14.66	−14.78	5.62	0.03
Phosphate	−10.20	−10.22	−11.05	−2.64	0.04

Table 4
Pseudo-second-order kinetic parameters of nitrate and phosphate on PCB and CCB

Model	Parameters	Nitrate			Phosphate		
		150 mg/L	200 mg/L	250 mg/L	50 mg/L	60 mg/L	70 mg/L
PCB							
Pseudo-second-order	q_e	51.55	58.28	67.382	21.584	22.421	22.888
	k	0.0006	0.0008	0.0009	0.0009	0.001	0.002
	h	1.665	2.673	4.071	0.453	0.619	0.975
	r	0.995	0.994	0.996	0.992	0.999	0.999
	SD	0.063	0.058	0.041	0.187	0.034	0.036
CCB							
Pseudo-second-order	q_e	49.48	51.33	59.59	11.71	12.748	13.479
	k	0.0004	0.0007	0.0007	0.005	0.005	0.005
	h	0.971	1.892	2.778	0.655	0.777	0.872
	r	0.999	0.999	0.998	0.998	0.997	0.999
	SD	0.032	0.022	0.033	0.161	0.163	0.075

nitrate and phosphate sorption on PCB and CCB well fitted with the pseudo-second-order model and the parameters are shown in Table 4.

3.8. Regeneration studies

For regeneration, the important aspect is to return the polymeric material to its original state without altering its indented properties in order to reuse the same material which makes the process cost effective. The nitrate- and phosphate-sorbed sorbents PCB and CCB were treated with 0.1 M NaOH [20,21] solution for the time of 5, 10, 15, 30 and 60 min (Fig. 8). Then, the PCB and CCB were washed with deionised water and dried in room temperature and were used again for the adsorption of nitrate and phosphate under predetermined conditions. It is evident that the adsorbents were regenerated using the aqueous solution of 0.1 M of NaOH within 15 min. The regeneration studies were carried out up to fifth cycle (Fig. 9). The first cycle of regeneration showed that the adsorption capacity of PCB for nitrate and phosphate restored to 93 and 86%, respectively, and that of CCB restored to 96 and 87%, respectively. The electrostatic interaction between the nitrate and phosphate anions with the protonated amine (in the case of PCB) and the acidic carboxylic group (in the case of CCB) weakened in the highly basic medium and OH^- ions replaced the nitrate and phosphate anions. As the number of regeneration cycle increased, the regeneration efficiency of the PCB decreased. Na^+ ions may replace some protons from the protonated amines [35] and hence the reduction in the regeneration efficiency. The loss of positive sites on the CCB may be the reason for the decreased regeneration efficiency of CCB.

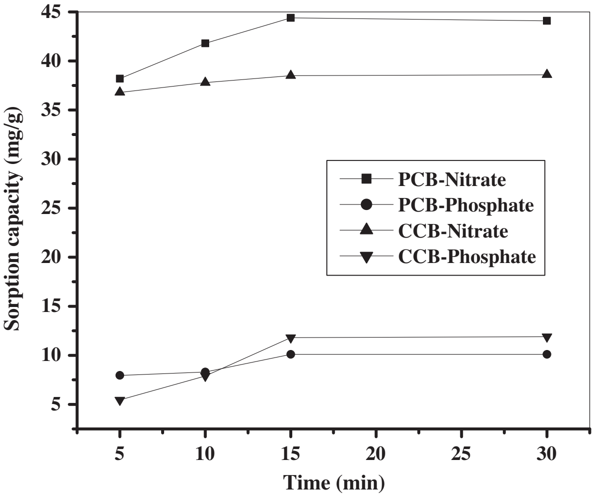

Fig. 8. Effect of desorption time on the regeneration of nitrate- and phosphate-sorbed PCB and CCB.

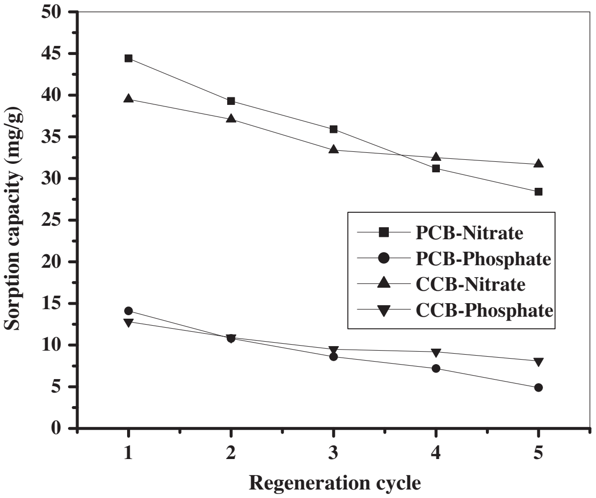

Fig. 9. Sorption capacity of regenerated PCB and CCB on nitrate and phosphate adsorption at various cycles.

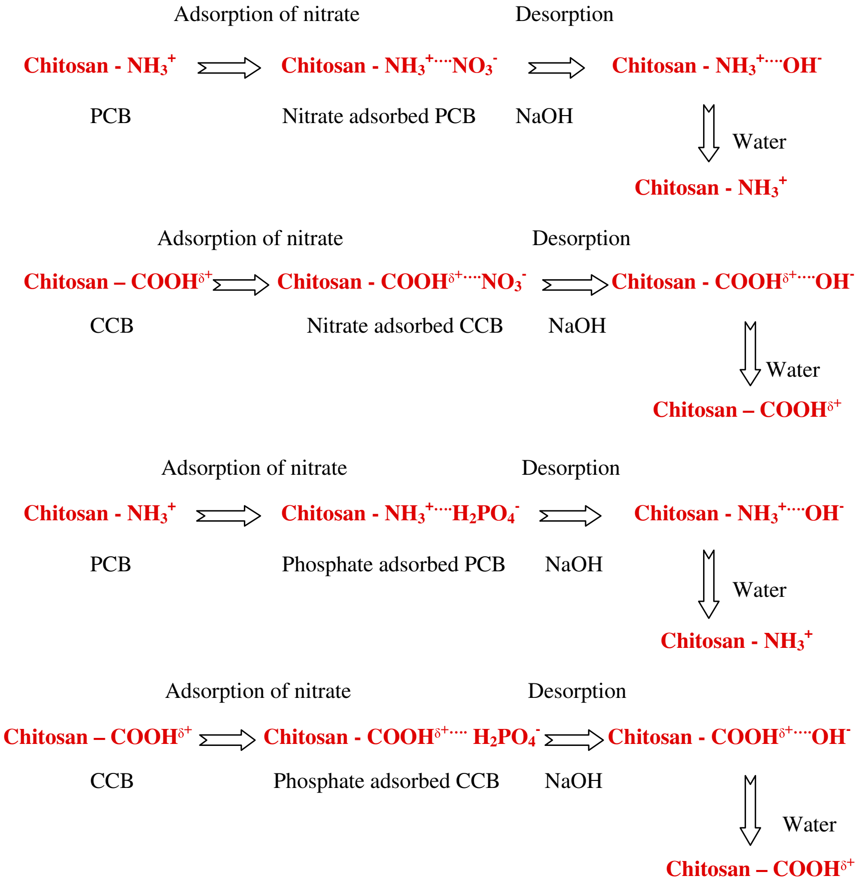

Fig. 10. Mechanism of adsorption and desorption of nitrate/phosphate anions on PCB and CCB.

3.9. Mechanism of sorption/desorption

The protonated amine in the PCB and the acidic carboxylic group in the CCB facilitate the electrostatic attraction with the anions for the effective adsorption. In the regeneration process, the anions adsorbed on PCB and CCB were replaced by OH^-. The adsorbents

Table 5
Chitosan derivatives used for the removal of nitrate and phosphate and maximum adsorption capacities

Adsorbent	Anion	Adsorption capacity (mg/g)	Ref.
Chitosan beads cross-linked with epichlorohydrin	Nitrate	103.1	[36]
Chitosan beads conditioned with sodium bisulphate	Nitrate	93.6	[36]
Chitosan beads cross-linked with epichlorohydrin and conditioned with sodium bisulphate	Nitrate	104.0	[36]
Chitosan beads non-cross-linked	Nitrate	90.7	[36]
Chitosan hydrogel beads	Nitrate	92.1	[37]
Lanthanum carbonate incorporated chitosan microparticles	Phosphate (human serum samples)	97%	[38]
Chitosan-coated zeolite (protonated with HCl) in cold regions	Nitrate	0.74 meq/g	[39]
Chitosan-coated zeolite (protonated with H_2SO_4) in cold regions	Nitrate	0.6 meq/g	[39]
Chitosan hydrogel beads after the adsorption of copper(II)	Phosphate	30.12 mg P/g	[40]
PCB	Nitrate	113.1	Present study
PCB	Phosphate	58.5	Present study
CCB	Nitrate	90.6	Present study
CCB	Phosphate	48.8	Present study

regained their original form after treating with excess of deionised water. The sorption and desorption of anions on PCB and CCB are depicted in Fig. 10. The adsorption capacity for the nitrate and phosphate of a few chemically modified chitosan adsorbents was compared with PCB and CCB and is given in Table 5.

4. Conclusions

The modified chitosan beads PCB and CCB were found to be effective for the removal of nitrate and phosphate. Both the sorbents showed higher sorption capacity at the acidic pH. In adsorption of both phosphate and nitrate studied, sulphate significantly altered the sorption capacity of the adsorbents. The adsorption data were best fitted with the Freundlich adsorption isotherm which indicates the heterogeneous nature of sorption. Physical binding force involved in the sorption of both the anions on PCB and CCB was confirmed from E values calculated from the D–R isotherm. Electrostatic interaction between the anions and the positive functional groups in the sorbents was the mechanism behind the sorption. The kinetic data were well fitted with the pseudo-second-order model. The desorption rate is rapid and occurred within 15 min by using 0.1 M NaOH which would make the process cost-effective and hence the resin could be further employed for the technology development.

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