



Sorption behaviour of Co(II) and Cu(II) on chitosan in presence of nitrilotriacetic acid

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ABSTRACT

Separation and isolation of radioactive cobalt (^{60}Co), one of the main contributors towards the activity build up in nuclear reactors, is essential for radioactive waste volume reduction during nuclear reactor decontamination procedures. In this context, sorption of free and complexed Co(II), Cu(II) and nitrilotriacetic acid (NTA) on the biosorbent, chitosan was studied. A detailed investigation on the role of pH on sorption of Co(II), Cu(II) and NTA was done. Uptake capacities of the metal ions and NTA were measured within pH range of 2.0–7.0. At pH above 5, the NTA uptake capacities were found to be higher in presence of the metal ions than in their absence. Effect of NTA was found to be more pronounced on copper uptake than on cobalt uptake. Significant change in selectivity of chitosan towards metal ion uptake from NTA medium was observed with respect to change in pH. At pH 2.9, the uptake of cobalt was found to be more than that of copper, while the selectivity was reversed at pH 6.0. The respective selectivity coefficient ($k_{\text{Co/Cu}}$) values were found to be 2.06 and 0.072.

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1. Introduction

Various biosorbents have been used for the removal of hazardous metal ions and organic materials like dyes with varying degrees of success [1–3]. Chitosan, a partially acetylated D-glucosamine biopolymer obtained by the deacetylation of chitin extracted mainly from the crustacean shells, is one of the well studied biosorbents [4,5] with sorption properties for a wide range of metal ions e.g., Hg^{2+} , Cd^{2+} , Cr^{6+} , Pb^{2+} , Cu^{2+} , Zn^{2+} , etc. [6–10]. There has also been reports on the use of chitosan as a sorbent for removal of anionic dyes [11–13] and complexing agents [14] such as EDTA, citrate, etc., which are routinely used in many industries, including nuclear. However, there are only limited studies on the sorption of metal ions from a medium containing complexing agents. The most studied metal ion in this regard, as is with most sorbents, is copper (II) [15–19]. Juang et al. [15] studied the removal of Cu(II) from solutions containing chelants EDTA, citrate, tartaric acid and gluconate and found an optimum pH range for each complexing agent based on metal ion sorption results. Lu et al. [16] modeled the sorption of copper–citrate on chitosan through theoretical calculations to develop a mathematical model to predict the copper adsorptions

at varying pH values and copper to citrate ratios. But, in these studies, the sorption of the complexing ligands was not monitored and the conclusions were drawn based on the results obtained from the metal ion sorption. Thus, the nature of metal ion sorption namely as complex or as free metal ion on chitosan has not been addressed. Cu(II)–EDTA sorption on to chitosan and its regeneration through electrolysis was also reported wherein possible mechanisms for the uptake of Cu(II) and EDTA in acidic and alkaline conditions were discussed [18]. Similarly, Ni(II)–citrate sorption by chitosan and its subsequent regeneration through electrolysis for reuse was reported wherein both nickel and citrate uptake was monitored [20]. However, there are not many reports on the sorption of the ligand nitrilotriacetic acid (NTA) and its metal ion complexes by chitosan except for a report by Jeon et al. [21], where the effect of NTA on mercury-ion removal, and the preparation of chitosan–NTA conjugate for application in drug delivery systems were studied [22,23].

Formation and deposition of the radioactive cobalt (^{60}Co) is one of the main contributors towards activity build-up in nuclear reactor coolant circuits, which gives a higher MAN-REM dose to the maintenance personnel. Removal of ^{60}Co along with other radioactive nuclides is done through decontamination procedures where corrosion products deposited over nuclear reactor coolant circuit surfaces are dissolved using chemical formulations containing complexants such as NTA [24]. Both radioactive elements (extremely small quantity as chemical species) and non-radioactive elements are dissolved by the decontaminant formulations. Selec-

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tive removal of the ^{60}Co from the solution so obtained can lead to reduction in the High Level Waste (HLW) volume generated during such decontamination procedures. Recently, we have successfully developed an organic resin towards such application using metal ion imprinting method [25]. However, there are growing concerns about storage/disposal of organic resins used in nuclear reactors. Decomposability of sorbents, post-stripping of active ions, can play a major role in making the process more environmental friendly. At present, techniques like high energy UV irradiation are used in decomposing the organic resin material. Use of bio-degradable sorbents thus becomes a better option if they can match the sorption properties of the organic resins. The present report is a part of our studies directed towards this objective. The ease of availability and versatility of chitosan makes it an important biosorbent to be considered for such applications. Though there are many reports on sorption properties of chitosan towards various metal ions, studies regarding its use for the removal of cobalt and other radioactive nuclides is very limited. Liu et al. [26] synthesized a surface grafted Co(II) imprinted polymer using chitosan for the selective removal of cobalt and studied its adsorption performances. Sorption behaviour of ^{60}Co and $^{152+154}\text{Eu}$ radionuclides onto chitosan derivatives was studied by Metwally et al. [27]. Also Mizera et al. [28] studied the sorption of Cs, Co and Eu on oxidized coals in mixture with chitosan using radiotracer method. Investigations on sorption of metal ion as along with complexants can give indications about the speciation and mechanisms involved during sorption from complexing media. In this context, it is important to understand the sorption properties of the biosorbent, chitosan, especially towards cobalt from complexing medium. Since most of the reported studies regarding the sorption of metal ions in presence of complexing media were done with Cu(II), sorption characteristics of Cu(II) in presence of NTA was also studied for comparison with Co(II) sorption. Possibilities on the selective sorption of either of the metal ions in the presence of the other using chitosan have also been addressed.

2. Experimental

2.1. Chemicals and reagents

Chitosan from shrimp shells with $\geq 75\%$ deacetylation was obtained from Sigma–Aldrich. Sodium hydroxide (A.R. grade) was obtained from Ranbaxy fine chemicals Limited, India. Sulphuric acid (98%, GR grade) was obtained from Merck India. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was obtained from Spunchem, India. $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (G.R. grade) and NTA (G.R. grade) were supplied by Loba Chemie, India. All chemicals were used as such without further purification. The metal ion/complexant solutions were prepared in ultra pure water (Sartorius arium®611). A measured quantity of NaOH solution was added for the dissolution of NTA.

2.2. Sorption experiments

All the sorption experiments were carried out in batch mode at room temperature by equilibrating a fixed amount of chitosan (0.1 g) with a fixed volume (15 mL) of experimental solution. The adsorbent to solution ratio was maintained same in all the experiments unless specified otherwise. The solutions were kept under stirring with constant stirring speed in all sorption experiments. During sorption, pH and concentrations were monitored at fixed time intervals. All the sorption experiments were conducted in triplicate and the mean value reported.

Metal ion concentrations were measured using an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Ultima-2, Horiba Jovin Yvon, France). NTA concentrations were determined by the dual wavelength method [29] modified for NTA estimation

using a UV–visible spectrophotometer (Evolution 500, UV–Visible Spectrophotometer). A Hach (sension 378) pH meter was used for pH measurements.

The amount of metal ion (or ligand) adsorbed (q) in $\mu\text{mol/g}$, was obtained as

$$q = \frac{(C_0 - C_f)V}{W} \quad (1)$$

where, C_0 and C_f are the initial and final liquid phase concentrations ($\mu\text{mol/L}$) of metal ion (or ligand), respectively; V is the volume of the solution (L) and W is the weight (g) of the dry chitosan used.

3. Results and discussions

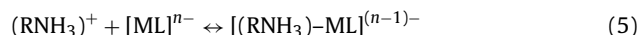
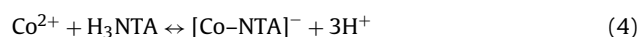
There are numerous reports on metal ion interactions with chitosan [30]. For metal ion sorption, though the hydroxyl groups (especially of the C-3 position) (Fig. 1) on chitosan also can contribute to metal ion sorption [31], it is known that the uptake of transition metals is mainly effected via coordination with the amine (NH_2) groups on chitosan [32]. When a solution containing metal ions/ligands is equilibrated with chitosan, the sorption can occur through the following three different modes of interaction (where, 'R' is the chitosan backbone).

- (i) *Chelation*: Chelation of metal ions by the NH_2 and OH groups of the chitosan (Eq. (2)). This mode of metal ion sorption is favored by the presence of non-protonated NH_2 groups and non-complexing environment in the solution.



This mode of sorption leads to reduction in just the metal ion concentration in the solution. Though not proven, the possibilities of a "bridge model", where metal ion chelates with several amine groups from the same chain (intramolecular) or from different chains of chitosan (intermolecular) have also been proposed in the literature [10,30]

- (ii) *Electro-static attraction*: Chitosan, with 87% deacetylation, is reported to have a pK_a of 6.5 for amine protonation [19]. Protonated NH_2 groups of the chitosan (i.e., NH_3^+ , Eq. (3)) can sorb the negatively charged metal ion complexes (i.e., $[\text{M}-\text{L}_x]^{n-}$, e.g., Eq. (4)) in a complexing medium through electrostatic attraction (Eq. (5)). This leads to uptake of the anionic complex and repulsion of free metal cations by the positively charged chitosan.



This mode of sorption leads to reduction in metal ion and ligand concentration in the solution.

- (iii) *Amide bond formation*: Covalent bond formation between the carboxylic groups of the ligands in the solution and NH_2 group of the chitosan under favorable conditions leads to the sorption of ligand. Amide bond formation between EDTA and chitosan in acidic pH conditions was proved using FT-IR studies by Gylinè et al. [18]. The amide bond formation between chitosan and NTA is shown in Scheme 1. This can result in the formation of an iminodiacetic acid group (or imino-monoacetic acid group if two NH_2 groups are involved to yield diamide) [23] linked to chitosan. This mode of sorption leads to reduced ligand concentration in solution. However, it is to be noted that these resultant iminoacidic groups are efficient metal ion complexing agents which can in turn complex with the free metal ions present in the solution thereby leading to further metal ion sorption subject to the pH conditions as applicable.

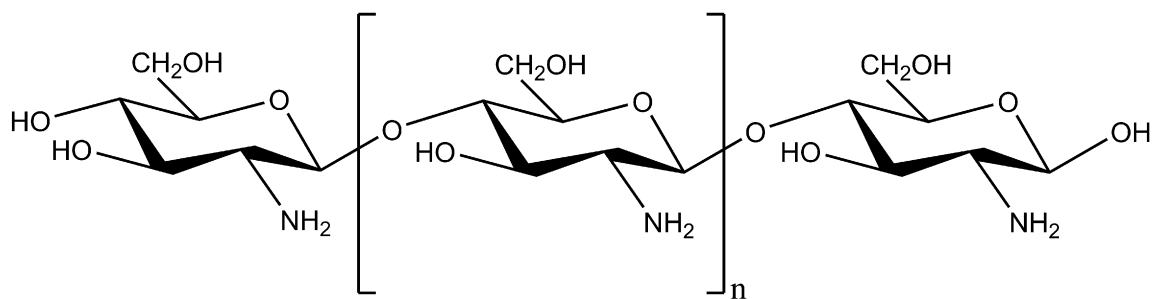
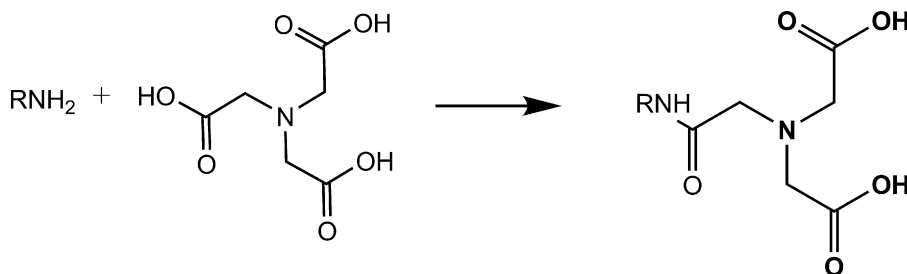


Fig. 1. Structure of chitosan or fully deacetylated chitin.



Scheme 1. Amide bond formation between chitosan and NTA.

Sorption by chitosan, from a solution containing metal ions and complexing agents, involves an interplay of the above three different modes of sorption. The fraction of sorption through each mode is decided by a combination of factors such as the solution pH, stability of the complexes involved and the concentration of the various species present. For example, the reactions (2) and (3) compete during equilibration of chitosan with a metal ion solution in weakly acidic media. Such a complexed interplay of different types of interactions is revealed in the sorption behaviour of chitosan studied under different conditions as discussed below.

3.1. Effect of contact time on uptake of metal and NTA from metal–NTA solutions

Variations in metal ion and NTA concentrations and solution pH with time during sorption were studied by equilibrating a 15 mM solution of 1:1 metal–NTA solution with chitosan.

3.1.1. Co(II)–NTA case

The results for Co(II)–NTA sorption are plotted in Fig. 2. It shows a sharp increase in sorption of Co(II) and NTA followed by saturation, indicating fast attainment of equilibrium. The increase in pH is due to the abstraction of free protons present in water by the amine groups of the chitosan. The increase in pH continued until equilibrium was attained. The rate of change in pH was very fast and comparable to that of Co(II)/NTA uptake by chitosan. Hence, the pH also reached a plateau on saturation. Protonation of the amine groups in chitosan enhances the sorption of the anionic complex, while it reduces the uptake of positively charged free metal ions. These two competitive (sorption modes (i) and (ii)) processes play an important role in the sorption of metal ions and charged metal complexes from solutions containing metal ions and chelating agents. The uptake of Co(II) was seen to be comparatively more than NTA. This may be due to sorption of metal ions by both mode (i) (through available free NH_2 and OH groups) and mode (ii), whereas the uptake of NTA is, probably, only as its cobalt complex and not as free NTA.

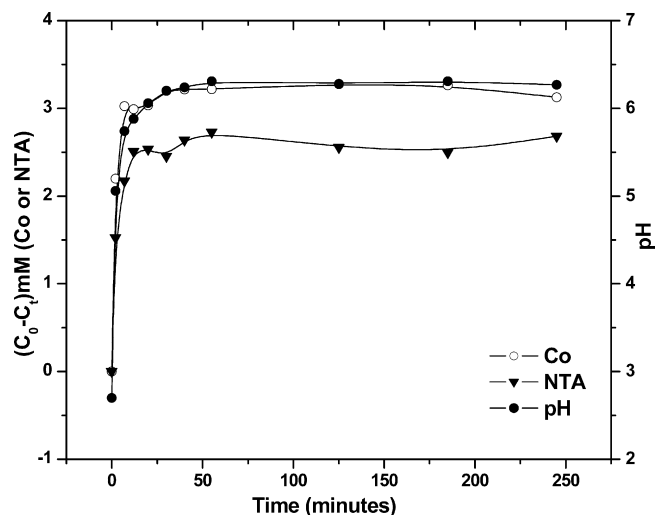


Fig. 2. Change in solution pH and uptake of Co(II) and NTA by chitosan with time on equilibration with Co(II)–NTA (1:1) solution.

3.1.2. Cu(II)–NTA case

In the case of Cu(II)–NTA solution, as shown in Fig. 3, the sorption attained equilibrium quickly in a similar fashion to Co(II)–NTA. But, unlike as in the case of Co(II)–NTA, Cu(II) and NTA were sorbed in a 1:1 ratio which implied that the sorption was predominantly as negatively charged complex, $[\text{CuNTA}]^-$ (mode (ii)). Since Cu(II) forms comparatively more stable complexes with NTA (Table 1), the chitosan amine groups may not be able to compete with NTA for the Cu(II) ions. Also, free NTA may not be available for the amide bond formation with the chitosan amine group as it is largely bound with Cu(II) as $[\text{CuNTA}]^-$. Speciation studies using Visual MINTEQ (Version 2.61) indicated a higher fraction of Cu(II) being present as $[\text{Cu-NTA}]^-$, than Co(II) as $[\text{Co-NTA}]^-$ in the lower pH values.

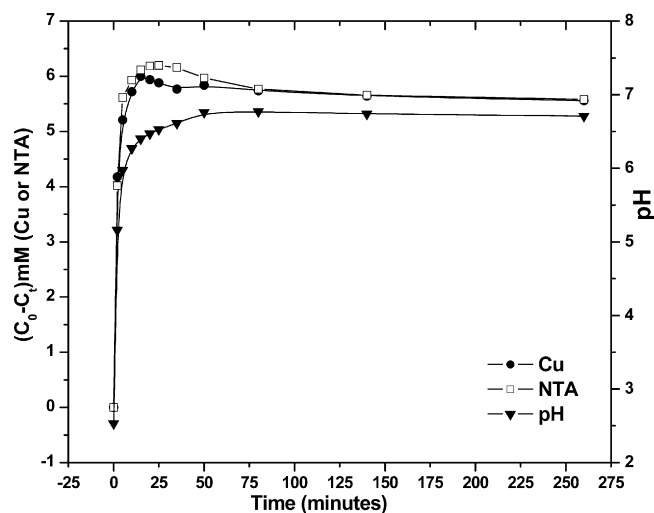


Fig. 3. Change in solution pH and uptake of Cu(II) and NTA by chitosan with time on equilibration with Cu(II)-NTA (1:1) solution.

Table 1

Stability constant values for the NTA complexes of Co(II) and Cu(II).

Reaction	log K ^a
<i>Chelate acidity</i>	
$H^+ + NTA^{3-} = HNTA^{2-}$	10.29
$H^+ + HNTA^{2-} = H_2NTA^-$	2.91
$H^+ + H_2NTA^- = H_3NTA$	2.01
$H^+ + H_3NTA = H_4NTA^+$	1.0
<i>Metal complexes</i>	
$Na^+ + NTA^{3-} = NaNTA^{2-}$	1.86
$Co^{2+} + NTA^{3-} = CoNTA^-$	10.38
$Co^{2+} + 2 NTA^{3-} = Co(NTA)_2^{4-}$	14.33
$Co^{2+} + NTA^{3-} + H_2O = Co(OH)NTA^{2-} + H^+$	10.80
$Cu^{2+} + NTA^{3-} = CuNTA^-$	13.0
$Cu^{2+} + 2 NTA^{3-} = Cu(NTA)_2^{4-}$	17.4
$CuNTA^- + H^+ = CuHNTA$	1.6
$Cu^{2+} + NTA^{3-} + H_2O = Cu(OH)NTA^{2-} + H^+$	9.2

^a From NIST critically selected stability constants of metal complexes, version 8.0.

3.2. Effect of pH on equilibrium uptake of metal and NTA from metal-NTA solutions

To study the variation of the metal ion and NTA uptake capacities with respect to pH, a 15 mM solution of 1:1 metal-NTA solution was used in all the experiments. A constant pH (within ± 0.3 during initial stages of sorption and ± 0.1 towards the end) was maintained throughout the sorption experiments by adding 1 M NaOH or 1 M H₂SO₄ solutions. The change in pH was rapid in initial stages and slow towards the equilibrium.

Attainment of stable pH condition was fast for the pH values of 2, 3 and 7 while slow for the pH values of 4, 5 and 6. All the reactions were carried out until the pH stabilized (i.e., no change in the pH for at least 2–3 h) and sampled for the estimation of metal and NTA uptake.

3.2.1. Co(II)-NTA case

The uptake of both cobalt and NTA was found to be increasing with pH with two maxima, one at pH ca. 6 and the other at pH ca. 3.5 (Fig. 4). An interesting observation was the change in ratio of cobalt and NTA sorbed with increase in pH. From pH 3 to 6, the difference between cobalt and NTA sorption decreased and became almost 1:1 sorption at pH 6. Similar 1:1 sorption was observed at pH 2 as well, though the sorption as such was very less. This can easily be explained by the fact that, at a highly acidic pH, there is almost complete protonation of the NH₂ groups of the chitosan [33] and

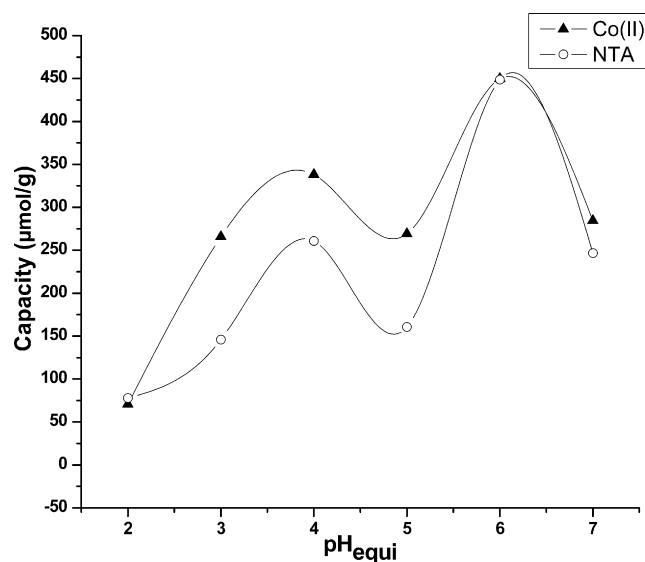


Fig. 4. Change in Co(II) and NTA uptake by chitosan from Co(II)-NTA solution with varying pH.

thereby making electrostatic attraction (mode (ii)) the only mode of sorption. However, since there is only a small fraction of cobalt and NTA which could be present as $[Co-NTA]^-$ complex at this pH, there is very little sorption.

As the pH was increased to 3, the sorption increased and the sorption of cobalt and NTA was not in the 1:1 ratio, as cobalt was sorbed more than NTA. NTA could get sorbed as Co(II)-NTA complex and also by forming covalent linkage through amide bond formation which is favored in this pH range (3–4). The NTA thus bound through amide bond can again complex with the free cobalt ions present in the solution (mode (iii)) [22]. Thus, NTA sorption always leads to cobalt sorption as well. However, cobalt has other avenues of sorption (mode (i)) as well. This resulted in more sorption of cobalt than NTA.

At pH 4, competition by the free hydrogen ions for the chitosan amine groups is further reduced leaving the amine groups relatively more accessible for cobalt and NTA. Also, the amount of complexed NTA (as $Co[NTA]^-$) is more at this pH leading to higher sorption through mode (ii) which is reflected in the reduced difference between NTA and cobalt sorption (as compared to pH 3).

At pH 6.0, there is complete complexation between cobalt and NTA. Thus, all the sorption of NTA and cobalt was as anionic complex (mode (ii)) leading to nearly 1:1 sorption. At pH 7, the reduction in sorption is due to reduced fraction (<20%) of the protonated NH₂ groups in the chitosan [15] and highly reduced fraction of free cobalt and NTA species available in the solution. As all the cobalt and NTA are present as $[Co-NTA]^-$, free cobalt and NTA species do not become easily available for the chitosan NH₂ groups and there are not enough protonated amine groups available in the chitosan for sorption of the anionic complex species. Hence, there was reduced sorption at this pH. The behaviour at pH 5.0, however, is not very easy to explain. One probable reason is that at this pH, chances for the amide bond formation is less (as compared to at pH < 5) leading to reduced uptake of NTA and cobalt through this route and at the same time, the amount of complexed anionic species will be less than at pH higher than 5 leading to reduced avenue for sorption of the complexed species as well. There is also, though small, reduction in the available protonated NH₂ groups leading to further reduction in sorption of any anionic complex species present in the solution. This also explains the widening of the difference between the amount of cobalt and NTA sorbed.

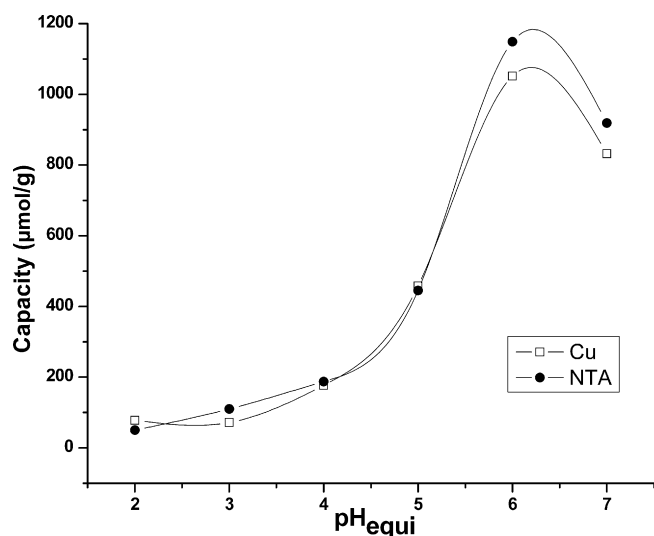


Fig. 5. Change in Cu(II) and NTA uptake by chitosan from Cu(II)-NTA solution with varying pH.

3.2.2. Cu(II)-NTA case

The uptake of copper and NTA increased with increase in pH and gave a maximum sorption capacity near pH 6 (Fig. 5). The uptake of copper and NTA proceeded in a nearly 1:1 ratio, which implies that copper and NTA were taken as the Cu(II)-NTA complex (mode (ii)). The very large log K values (Table 1) for Cu(II)-NTA complex makes it difficult for copper sorption through mode (i). This ensures uptake to be only as $[\text{Cu-NTA}]^-$ complex. But, at pH 6 and beyond, due to availability of an excess amount of free NH_2 groups, there was sorption of free Cu^{2+} ions to some extent. This led to a small difference between copper and NTA sorption.

Comparatively (as compared to in case of Co(II)-NTA) low fraction of the free NTA present in solution under the experimental conditions (as calculated using Visual MINTEQ) might have hindered the sorption mechanism through amide bond formation. These factors make the sorption at acidic pH less for Cu(II)-NTA than for Co(II)-NTA. But, as the pH is increased Cu(II) forms the anionic complex, $[\text{Cu-NTA}]^-$, and gets sorbed through mode (ii). Hence, the capacities increased with increase in pH. At these pH values (beyond 4), the copper complex uptake was more than the case with Co which is due to the well known general higher preference for copper by the sorbent [6,10]. In acidic conditions, amount of the protonated amine groups will be more but at the same time the amount of $[\text{Cu-NTA}]^-$ formed will be less. Moreover, at lower pH, the counter anions SO_4^{2-} can compete with the anionic complex species for the protonated amine groups of the chitosan [33]. So, it is believed that there is an optimum pH where, all the competitive effects would be minimal and adsorption capacities for $[\text{Cu-NTA}]^-$ would be maximum.

The optimum pH range for $[\text{Cu-NTA}]^-$ sorption was found to be around pH 6, which is close to the pK_a of chitosan's amine protonation [19]. At this pH, there will be adequate amount of protonated amine groups and most of the copper and NTA will be present as $[\text{Cu(II)-NTA}]^-$. Above this pH, amine groups in chitosan get deprotonated and it cannot take the anionic complex. The decrease in sorption capacity above pH 6 indicates that the interaction involved in the sorption of copper-NTA is an electrostatic one. The optimum pH range for obtaining the maximum uptake capacities was found to be the same for both Cu(II) and Co(II) in NTA medium. This implies that the optimum pH, for obtaining the maximum uptake, is mainly dependent on the nature of the ligand (NTA) and the chitosan functional group. The report by Juang et al. [15] on the sorption of Cu from solutions containing different complexing

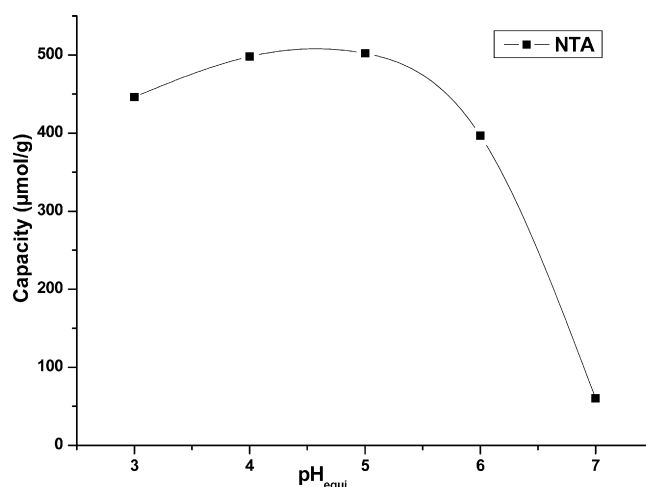


Fig. 6. Change in NTA uptake by chitosan from 7.5 mM NTA solution with varying pH.

agents, which reported different optimum pH range for different complexing agent solutions, also supports this argument.

3.3. Effect of pH on equilibrium sorption of NTA and metal ions

Variation in sorption capacities for Co(II), Cu(II) and NTA from their respective solutions on chitosan was also carried out for comparison.

3.3.1. NTA case

For NTA sorption, a 7.5 mM aqueous solution of NTA was used. A dosage of 50 mg of chitosan per 15 mL of the NTA solution was used in all the experiments so that the number of sorption sites available in chitosan for the uptake of NTA was comparable with the conditions maintained in metal ion/NTA complex studies. The results showed a sharp decrease in NTA sorption after pH 5 (Fig. 6). The maximum sorption was found to be at around pH 4–5 where both the protonated amine groups and the anionic form of NTA (HNTA^{2-}) are in significant amount. The slightly reduced sorption at pH 3 may be, because of the competitive counter anions (Section 3.2.2) and predominant presence of free NTA at this pH. Decrease in sorption capacity above pH 5, even though the fraction of anionic form of NTA increases, is because of the deprotonation of the amine groups. Navarro et al. [33] had plotted the variation in protonation

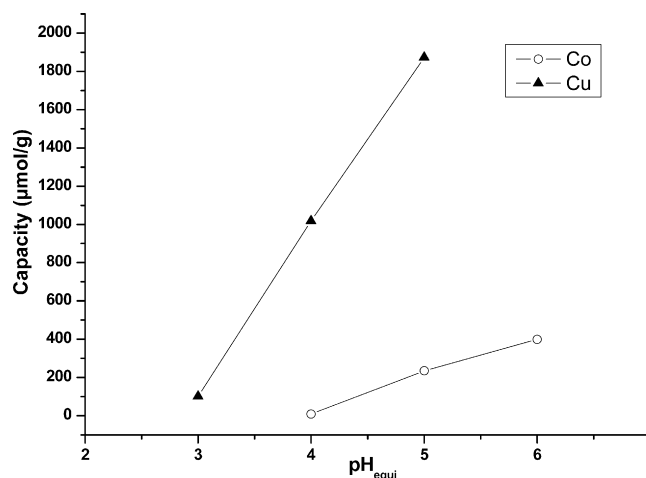


Fig. 7. Change in Co(II) and Cu(II) uptake by chitosan from their respective 15 mM solutions with varying pH.

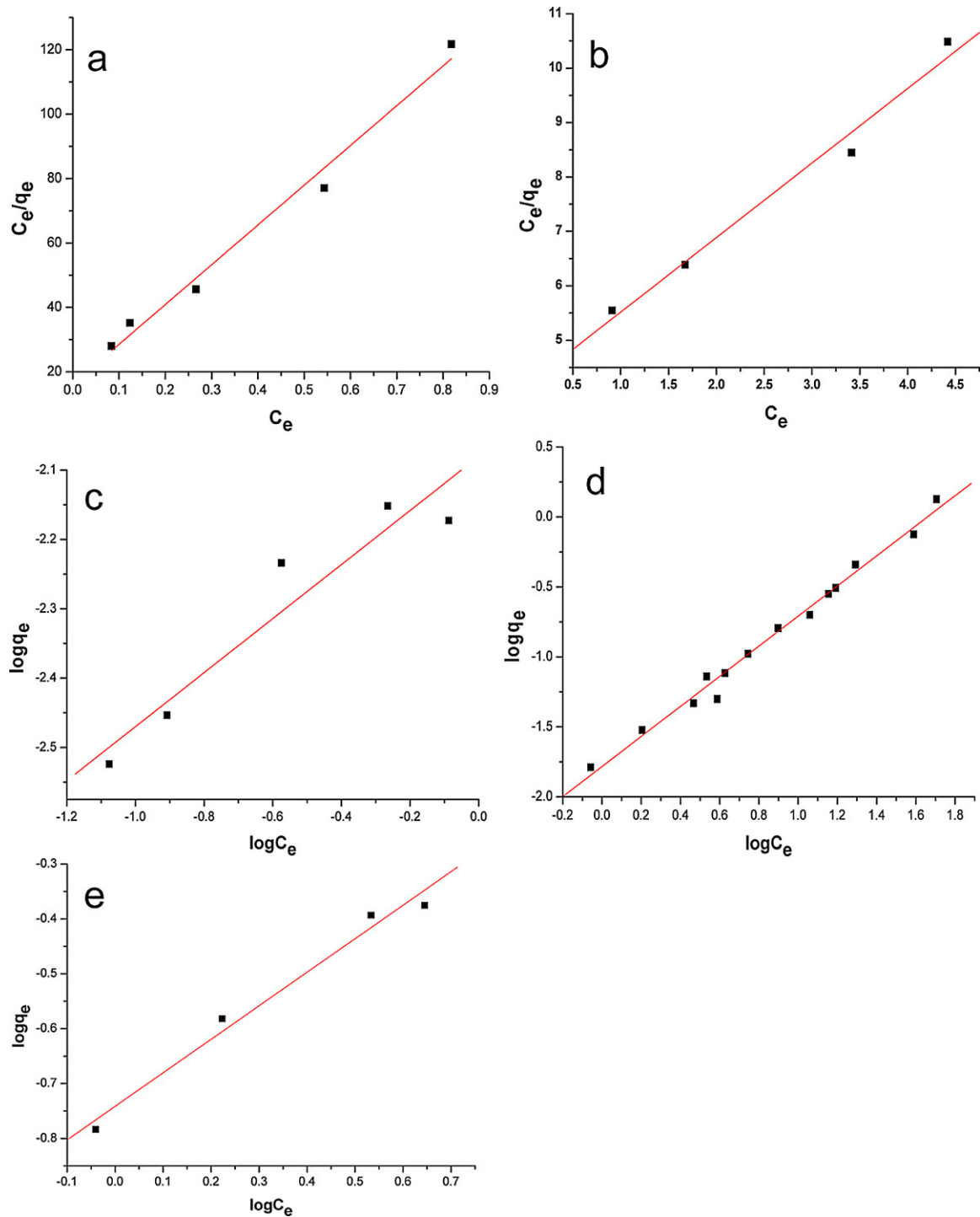


Fig. 8. Isotherm plots: Langmuir plots for (a) Co(II) and (b) NTA; Freundlich plots for (c) Co^{2+} (lower concentration range), (d) Co^{2+} (higher concentration range) and (e) NTA.

of the amine groups with change in pH. Above pH 6.5 most of the amine groups will be in the NH_2 form and hence the NTA uptake capacity decreases drastically above pH 6.

It is interesting to note that there is a drastic reduction in the NTA sorption beyond pH 5 (goes to near zero sorption at pH 7) in this case (Fig. 6) as compared to metal ion/NTA cases (Section 3.2; Figs. 4 and 5). This observation may indicate the possibility of metal ion assisted NTA sorption by chitosan's free NH_2 groups over and above the other modes of sorption. The former occurs when the free (de-protonated) NH_2 groups of the chitosan complex with the metal ion/NTA complex in the solution by replacing the

complexed water molecules. This mode of sorption is not available in NTA alone case and thereby leads to reduced sorption at higher pH as compared to metal ion/NTA cases.

3.3.2. Co and Cu cases

In the case of metal ion solutions (a 15 mM metal ion solution was used for the studies), below pH 6.5, the metal ions have to compete with H^+ ions for sorption by chitosan. At very low pH, the uptake capacity was found to be negligible and then increased with increase in pH (Fig. 7). The uptake capacity for copper was found to be increasing rapidly along with the increase in pH as compared

Table 2
Langmuir and Freundlich isotherm parameters for cobalt and NTA sorption.

Adsorbate	Concentration range (mM)	Langmuir parameters		R^2 (Langmuir)	Freundlich parameters		R^2 (Freundlich)
		Q^0 ($\mu\text{mol/g}$)	b		K_F (L/g)	$1/n$	
Co(II)	0.083–0.82	8.1	7.61	0.985	0.831×10^{-2}	0.39	0.910
	0.82–50.72	–	–		0.165×10^{-1}	1.08	
NTA	0.91–4.42	730.1	0.33	0.983	0.181	0.61	0.980

Table 3
Relative sorption of Co(II) and Cu(II) in NTA medium on chitosan.

pH _{eqbm}	t_{eqbm}	Sorption capacity (q , $\mu\text{mol/g}$ of chitosan)			Selectivity coefficient ($k_{\text{Co/Cu}}$)
		Co(II)	Cu(II)	NTA	
2.9	78 h	145.44	75.57	176.30	2.06
6.0	6 h	92.86	616.93	714.48	0.072

to cobalt. Chitosan was found to be more selective towards copper under all pH conditions as reported in earlier studies [6,7,10]. This observation is in accordance with the Irving–Williams series which gives the stability sequence of high spin octahedral metal complexes for the replacement of water by other ligands. The exothermic enthalpies reported by Lima et al. [34] from calorimetric titration studies of metal ion sorption on chitosan also support the higher sorption of copper.

3.4. Adsorption isotherms for cobalt and NTA sorption

Cobalt and NTA sorption (from their individual solutions) data were fitted with Langmuir and Freundlich sorption isotherm models. Eqs. (6) and (7) represent Langmuir and Freundlich models respectively

$$\frac{C_e}{q_e} = \frac{1}{Q^0 b} + \frac{1}{Q^0} C_e \quad (6)$$

$$q_e = K_F C_e^{1/n} \quad (7)$$

where, q_e is the amount of solute sorbed ($\mu\text{mol/g}$) and C_e , the equilibrium concentration of the solute in the solution (mmol/l). The Langmuir parameters Q^0 (the monolayer adsorption capacity ($\mu\text{mol/g}$)) and b ; and the Freundlich parameters K_F (L/g) and $1/n$ are calculated by least squares method respectively from the plot of C_e/q_e against C_e and $\log q_e$ against $\log C_e$.

Cobalt and NTA sorption was found to be fitting in both Langmuir and Freundlich models in the concentration range of 0.083–0.82 mM for cobalt and 0.91–4.42 mM for NTA. However, cobalt sorption in the concentration range of 0.82–50.72 mM was found to fit in Freundlich model alone. The equilibrium pH for cobalt sorption was 6.0 (± 0.2) and for NTA it was 5.9 (± 0.2). The corresponding plots are shown in Fig. 8. Table 2 gives the Langmuir and Freundlich parameters obtained.

3.5. Relative metal ion sorption by chitosan

The inherent capacity of chitosan for Cu(II) is known to be very high compared to other metal ions [6]. Earlier reports on the competitive sorption of metal cations on chitosan show that it will be difficult to separate other metal ions like Co(II) by chitosan sorption in presence of Cu(II) [35,36]. However, the results discussed above on complexation of these metal ions with NTA and their subsequent sorption with chitosan indicate a possibility that the capacity and hence the selectivity of chitosan for metal cations can be varied by changing the equilibrium pH of the metal–complex solution. To investigate this possibility, competitive sorption study using Co(II) and Cu(II) together in NTA solution with a molar ratio of 1:1:2 (Cu(II):Co(II):NTA) was carried out. The results (Table 3)

showed that cobalt was preferentially sorbed at lower pH compared to copper. Equilibration time needed was found to be more for the lower pH. During the equilibration, Cu(II) is sorbed initially and then slowly replaced by Co(II) before attaining equilibrium. Even though the pH of the solution stabilized within a short period, the metal ion concentration in the solution varied, as was evident from the ICP–AES analysis carried out during the course of the sorption experiment. Solution concentration of Cu(II) increased in the solution while Co(II) decreased, due to desorption/sorption. While at higher pH (pH 6), time required for attaining the equilibrium was very less (less than 2 h), and the amount of copper sorbed was more (Table 3).

The reversal in selectivity is reflected clearly in the selectivity coefficient ($k_{\text{Co/Cu}}$) values [6] obtained at these respective pH conditions as shown in Table 3. Ratio of the total metal ion (Co(II) + Cu(II)) capacity to that of NTA was found to be 1:1 at pH 6, while at pH 3, a more metal ion sorbed chitosan was obtained. As Co(II) was sorbed more at pH 3, the difference in uptake of metal ion and NTA was expected. Visual MINTEQ speciation calculations suggested a higher fraction of free Co(II) as compared to Cu(II) in the solution in the low pH region and a decreasing ratio of free Co(II) to Cu(II) with increasing pH. This explains the higher sorption of Co(II) ions over Cu(II) ions at low pH.

4. Conclusions

Sorption of NTA, Co(II) and Cu(II) on chitosan from their respective individual solutions and from solutions containing metal ions and NTA were studied. It was demonstrated that chitosan can be used for the removal/sorption of the studied metal ions and NTA. It was observed that the relative concentration of metal ion, ligand species and metal–ligand charged complex in solution, and free chitosan, protonated chitosan and chitosan amide in the solid (polymer) phase together with the relative strengths of the interactions between these species decide the sorption capacity and selectivity through operation of different modes of sorption. Sorption of the metal ions (both Co and Cu) was found to increase with increase in pH. An optimum pH range was identified for their maximum uptake from complexing medium, which seemed to be mainly dependent on the nature of complexing agent and independent of the metal ion used. The optimum pH range for NTA uptake from NTA solution was found to be around pH 5 and that for copper and cobalt sorption respectively from Cu(II)–NTA and Co(II)–NTA solutions was found to be around 6. Chitosan was found to be more selective towards copper in general. However, from metal ion–NTA solutions, sorption of Co(II) was found to be favored at lower pH whereas Cu(II) was favored at higher pH. Change in selectivity with pH suggests that the mechanism involved in the sorption of metal ion–NTA com-

plexes varies with pH, as the speciation and conditions favoring the sorption is changed. Such variation of metal ion selectivity with pH can be utilised towards designing selective metal ion sorbents using chitosan.

References

- [1] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, *J. Hazard. Mater.* B97 (2003) 219–243.
- [2] Y.S. Ho, G. McKay, Sorption of dyes and copper ions onto biosorbents, *Process Biochem.* 38 (2003) 1047–1061.
- [3] K.M. Shareef, Sorbents for contaminants uptake from aqueous solutions. Part I: Heavy metals, *World J. Agric. Sci.* 5 (2009) 819–831.
- [4] I.B. Rae, S.W. Gibb, Removal of metals from aqueous solutions using natural chitinous materials, *Water Sci. Technol.* 47 (10) (2003) 189–196.
- [5] A. Bhatnagar, M. Sillanpää, Applications of chitin- and chitosan-derivatives for the detoxification of water and wastewater – a short review, *Adv. Colloid Interface Sci.* 152 (2009) 26–38.
- [6] I.M.N. Volda, K.M. Varuma, E. Guibal, O. Smidsrød, Binding of ions to chitosan-selectivity studies, *Carbohydr. Polym.* 54 (2003) 471–477.
- [7] A.-H. Chen, S.-C. Liu, C.-Y. Chen, C.-Y. Chen, Comparative adsorption of Cu(II), Zn(II), and Pb(II) ions in aqueous solution on the crosslinked chitosan with epichlorohydrin, *J. Hazard. Mater.* 154 (2008) 184–191.
- [8] A.J. Varma, S.V. Deshpande, J.F. Kennedy, Metal complexation by chitosan and its derivatives: a review, *Carbohydr. Polym.* 55 (2004) 77–93.
- [9] P. Chassary, T. Vincent, E. Guibal, Metal anion sorption on chitosan and derivative materials: a strategy for polymer modification and optimum use, *React. Funct. Polym.* 60 (2004) 137–149.
- [10] J.R. Rangel-Mendez, R. Monroy-Zepeda, E. Leyva-Ramos, P.E. Diaz-Flores, K. Shirai, Chitosan selectivity for removing cadmium (II), copper (II), and lead (II) from aqueous phase: pH and organic matter effect, *J. Hazard. Mater.* 162 (2009) 503–511.
- [11] A. Kamari, W.S. Wan Ngah, L.K. Liew, Chitosan and chemically modified chitosan beads for acid dyes sorption, *J. Environ. Sci.* 21 (2009) 296–302.
- [12] W.A. Morais, A.L.P. de Almeida, M.R. Pereira, J.L.C. Fonseca, Equilibrium and kinetic analysis of methyl orange sorption on chitosan spheres, *Carbohydr. Res.* 343 (2008) 2489–2493.
- [13] A. Kamari, W.S. Wan Ngah, M.Y. Chong, M.L. Cheah, Sorption of acid dyes onto GLA and H₂SO₄ cross-linked chitosan beads, *Desalination* 249 (2009) 1180–1189.
- [14] O. Gyliene, O. Nivinskiene, T. Vengris, Sorption of tartrate, citrate, and EDTA onto chitosan and its regeneration applying electrolysis, *Carbohydr. Res.* 343 (2008) 1324–1332.
- [15] R.-S. Juang, F.-C. Wu, R.-L. Tseng, Adsorption removal of copper(II) using chitosan from simulated rinse solutions containing chelating agents, *Water Res.* 33 (1999) 2403–2409.
- [16] P.-J. Lu, W.-W. Hu, T.-S. Chen, J.-M. Chern, Adsorption of copper-citrate complexes on chitosan: equilibrium modeling, *Bioresour. Technol.* 101 (2010) 1127–1134.
- [17] O. Gyliene, R. Binkiene, R. Butkiene, Sorption of Cu(II) complexes with ligands tartrate, glycine and quadrol by chitosan, *J. Hazard. Mater.* 171 (2009) 133–139.
- [18] O. Gyliene, O. Nivinskiene, I. Razmute, Copper(II)-EDTA sorption onto chitosan and its regeneration applying electrolysis, *J. Hazard. Mater.* B137 (2006) 1430–1437.
- [19] J. Guzman, I. Saucedo, J. Revilla, R. Navarro, E. Guibal, Copper sorption by chitosan in the presence of citrate ions: influence of metal speciation on sorption mechanism and uptake capacities, *Int. J. Biol. Macromol.* 33 (2003) 57–65.
- [20] O. Gyliene, O. Nivinskiene, Electrochemical regeneration of chitosan after Ni(II)-citrate complex sorption, *CHEMIIJA* 16 (2005) 7–14.
- [21] C. Jeon, K.H. Park, Adsorption and desorption characteristics of mercury(II) ions using aminated chitosan bead, *Water Res.* 39 (2005) 3938–3944.
- [22] V.E. Tikhonov, L.A. Radigina, Y.A. Yamskov, Metal-chelating chitin derivatives via reaction of chitosan with nitrilotriacetic acid, *Carbohydr. Res.* 290 (1996) 33–41.
- [23] A. Bernkop-Schnurch, Chitosan and its derivatives: potential excipients for peroral peptide delivery systems, *Int. J. Pharm.* 194 (2000) 1–13.
- [24] A.L. Rufus, V.S. Sathyaseelan, S. Velmurugan, S.V. Narasimhan, NTA-based formulation for the chemical decontamination of nuclear power plants, *Nuclear Energy* 43 (1) (2004) 47–53.
- [25] A. Bhaskarapillai, N.V. Sevilimedu, B. Sellergren, Synthesis and characterization of imprinted polymers for radioactive waste reduction, *Ind. Eng. Chem. Res.* 48 (8) (2009) 3730–3737.
- [26] Y. Liu, J. Gao, C. Li, J. Pan, Y. Yan, J. Xie, Synthesis and adsorption performance of surface-grafted Co(II)-imprinted polymer for selective removal of cobalt, *Chin. J. Chem.* 28 (2010) 548–554.
- [27] E. Metwally, S.S. Elkholy, H.A.M. Salem, M.Z. Elsabee, Sorption behavior of ⁶⁰Co and ¹⁵²⁺¹⁵⁴Eu radionuclides onto chitosan derivatives, *Carbohydr. Polym.* 76 (2009) 622–631.
- [28] J. Mizera, G. Mizerova, V. Machovic, L. Borecka, Sorption of cesium, cobalt and europium on low-rank coal and chitosan, *Water Res.* 41 (2007) 620–626.
- [29] S.N. Bhattacharyya, K.P. Kundu, Spectrophotometric determination of EDTA, *Talanta* 18 (1971) 446–449.
- [30] E. Guibal, Interactions of metal ions with chitosan-based sorbents: a review, *Sep. Purif. Technol.* 38 (2004) 43–74.
- [31] E. Piron, A. Domard, Interaction between chitosan and uranyl ions. Part 2. Mechanism of interaction, *Int. J. Biol. Macromol.* 22 (1998) 33–40.
- [32] L. Dambies, C. Guimon, S. Yiacoumi, E. Guibal, Characterization of metal ion interactions with chitosan by X-ray photoelectron spectroscopy, *Colloids Surf. A* 177 (2001) 203–214.
- [33] R. Navarro, J. Guzman, I. Saucedo, J. Revilla, E. Guibal, Recovery of metal ions by chitosan: sorption mechanisms and influence of metal speciation, *Macromol. Biosci.* 3 (2003) 552–561.
- [34] I.S. Lima, C. Airoidi, A thermodynamic investigation on chitosan-divalent cation interactions, *Thermochim. Acta* 421 (2004) 133–139.
- [35] M. Rhazi, J. Desbrieres, A. Tolaimate, M. Rinaudo, P. Vottero, A. Alagui, M. El Meray, Influence of the nature of the metal ions on the complexation with chitosan. Application to the treatment of liquid waste, *Eur. Polym. J.* 38 (2002) 1523–1530.
- [36] K. Swayampakula, V.M. Boddu, S.K. Nadavala, K. Abburi, Competitive adsorption of Cu (II), Co (II) and Ni (II) from their binary and tertiary aqueous solutions using chitosan-coated perlite beads as biosorbent, *J. Hazard. Mater.* 170 (2009) 680–689.