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Cobalt (II) imprinted chitosan for selective removal of cobalt during nuclear reactor decontamination

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ABSTRACT

The selectivity of chitosan has been modified through metal ion imprinting technique for its potential application in nuclear industry. Considerable reduction in radioactive waste volume, generated during the chemical decontamination of nuclear power plants, can be achieved through the selective removal of the radionuclides. In this context, a Co(II) imprinted chitosan was synthesized using epichlorohydrin as the crosslinker. The selective removal of Co(II) in presence of Fe(II), which is the major non-radioactive ion present in excess during decontamination, was studied. The imprinted chitosan showed selective sorption of Co(II) over Fe(II), while the raw chitosan was selective to Fe(II) over Co(II). The imprinted chitosan was found to retain the enhanced selectivity towards Co(II) under various solution conditions, including typical nuclear reactor decontamination formulations containing strong complexants. The highest uptake by the imprinted chitosan, with maximum selectivity for Co(II) over Fe(II), was obtained in citrate medium at pH 4.8.

1. Introduction

Structural materials like carbon steel, monel, incoloy, stainless steel, stellite, etc., which are largely used in the coolant channels of Nuclear Power Plants (NPPs), undergo corrosion because of the high temperature coolant interaction with these structural materials. The corrosion products thus formed get activated by the neutrons while they pass through the reactor core. The protective oxide layer (e.g., Fe_3O_4 in case of carbon steel) formed on the walls of the coolant channels trap these activated corrosion products (e.g.^{60}Co) in their lattices. Activation followed by deposition of these corrosion products in the outer core surfaces during the reactor operation leads to radiation field build-up in the outer core surfaces (Lin, 2009). Hence, periodic cleaning campaigns, called decontamination campaigns, are carried out to remove the oxide layer along with the deposited radioactive metal ions for reducing the radiation field (Ocken, July 1999).

In a typical nuclear reactor decontamination campaign, formulation containing chemicals such as NTA, citric acid and ascorbic acid is circulated, in a regenerative mode, through the reactor coolant system. The strong complexants such as NTA and citric acid present in the formulation dissolve the corrosion products and remove the metal ions as the corresponding metal complexes. The metal loaded formulation is then sent through cation resin beds, wherein all the metal ions – radioactive and non-radioactive – are trapped, and complexants released for further circulation through the reactor system. At the end of the process, the formulation is sent through a mixed bed for removal of the complexants and the left over metal ions (Rufus, Velmurugan, Sathyaseelan, & Narasimhan, 2004). Radioactive cobalt, the major contributor towards the radiation field build-up in Pressurized Heavy Water Reactors (PHWRs), is generated by the activation of the non radioactive cobalt present in the corrosion products originating from various metal surfaces containing traces of cobalt impurity (especially nickel alloys and to some extend carbon steel), and from alloys such as stellite (a hard material used in the internals of valves, pumps, etc.,) which have cobalt as one of the constituents. The ^{60}Co is of a major concern because of its fairly long half life ($t_{1/2}$ 5.27 years) and high energy (2.5 MeV) gamma emission (IAEA, June 1981). The main corroding surface in primary cooling water circuits of PHWRs is of carbon steel. Hence, the major amount of the metal ions removed during decontamination will be the largely non radioactive ferrous ions (Velmurugan et al., 2010), while the physical quantity of radioactive metal ions will be very minimal. Use of conventional non-selective cation exchange resin alone, for removing the metal ions during chemical decontamination, leads to generation of large volume of radioactive resin

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waste, which require expensive special procedures for their storage/remediation. The segregation of active cobaltous ions using selective resins by excluding the excess non-radioactive ferrous ions can lead to significant reduction in the volume of the radioactive resin waste generated. This can be achieved by passing the metal ion loaded decontamination formulation through a cobalt selective resin bed before the formulation reaches the conventional organic resin bed (Bhaskarapillai, Sevilimedu, & Sellergren, 2009). The cation beds, thus would be predominantly loaded with the non-radioactive ferrous ions, while the radioactive cobaltous ions would be concentrated within the small volume of the selective resin. If, for some reasons (such as slow kinetics), such an online incorporation of the selective resin in the decontamination circuit is not feasible, the radioactive cobaltous ions can be concentrated within this resin through offline process post the decontamination campaign.

Molecular imprinting (Sellergren, 2001) has been reported widely for synthesizing selective sorbents for various molecules and metal ions. These are highly crosslinked polymers synthesized in presence of a chosen molecule or metal ion as the template. The template is subsequently removed to get the molecularly/metal ion imprinted polymer (MIP). We have earlier successfully demonstrated the possibility of reducing the volume of radioactive resin bed generated during decontamination using cobalt imprinting on organic polymers, where there was complete exclusion of ferrous ions (Bhaskarapillai, Sevilimedu, et al., 2009). Designing biosorbents with similar selectivity can make the process more economical and environment friendly. The present study is an attempt towards realizing the possibility of modifying a biosorbent, using metal ion imprinting procedure, to be cobalt selective in presence of excess ferrous ions.

Because of its natural abundance and high sorption capacities; chitosan and its derivatives have gained wide attention as effective biosorbents for the removal of various metal ions, including radioactive metal ions such as uranium, and other pollutants (Muzzarelli, 2011; Varma, Deshpande, & Kennedy, 2004). Chitosan's resistance to radiolysis, and its applicability in the nuclear field, also has been investigated as early as in 1972 (Muzzarelli & Tubertini, 1972). The complexing nature and chemical reactivity of the amine and hydroxyl functional groups of the chitosan make it a suitable sorbent for the removal of metal ions (Bhatnagar & Sillanpää, 2009). The use of chitosan in acidic solutions, however, is limited because of its solubility in dilute organic and mineral acids (except H_2SO_4) (Pillai, Paul, & Sharma, 2009). Crosslinking of chitosan can reduce its solubility in dilute acids and also can impart improved physical and mechanical properties. However, crosslinking decreases the amount of complexing groups in chitosan, which are primarily responsible for the sorption, and thus negatively affects the uptake capacity of chitosan (Wan Ngah, Endud, & Mayanar, 2002). Such crosslinking, however, do not always lead to enhanced selectivity (Webster, Halling, & Grant, 2007), whereas preparation of crosslinked chitosan through metal ion imprinting method can lead to enhanced selectivity towards the target ion of interest (Chen, Yang, Chen, Chen, & Chen, 2009; Dhakal, Oshima, & Baba, 2008). Though there are reports on use of chitosan (Minamisawa, Iwanami, Arai, & Okutani, 1999) and cobalt imprinted chitosan (Liu et al., 2010) for cobalt sorption, they do not address the selective removal of Co(II) in presence of the close competitor Fe(II) from complexing medium. The main focus of this study is to modify the sorption properties of the biosorbent in order to make it suitable for the nuclear industry application, which demands selective sorption of Co(II) in presence of excess Fe(II) under complexing conditions.

The Co(II) imprinted chitosan was synthesized using epichlorohydrin as the crosslinker. Its sorption properties were studied vis a vis those of non-imprinted and raw chitosan. The applicability of the imprinted chitosan under typical decontamination conditions, in particular, was investigated in detail.

2. Experimental details

2.1. Materials and methods

Chitosan from shrimp shells with ≥75% deacetylation was obtained from Sigma–Aldrich. $Co(NO_3)_2{\cdot}6H_2O$ (G.R grade) was purchased from SD fine-chem, India. $(NH_4)_2Fe\ (SO_4)_2$ and Sodium hydroxide (A.R grade) were obtained from Ranbaxy fine chemicals Limited, India. Citric acid anhydrous (A.R grade) was obtained from Lab-Chemie Industries, India. Trisodium citrate (G.R grade) and nitrilotriacetic acid (G.R grade) were obtained from Loba Chemie, India. All the Metal ion/sample solutions were prepared in ultra pure water (Sartorius Arium®611). All the chemicals were used as supplied without further purification.

2.2. Synthesis of Co(II) imprinted polymer

Co(II) imprinted chitosan was synthesized according to the reported literature procedure (Chen et al., 2009) with some modifications (Fig. 1). Chitosan (0.5 g, 2.33 mmol of $-NH_2$ for a 75% deacetylated chitosan) was dissolved in 25 mL acetic acid solution (3% w/w) with stirring on a magnetic stirrer. To this homogeneous solution; $Co(NO_3)_2{\cdot}6H_2O$ (0.335 g, 1.157 mmol) was added and pH of the solution was raised to 6 by drop wise addition of 0.25 M aqueous NaOH solution under stirring. The precipitated Co(II) complexed chitosan gel was separated, washed with ultra pure water, and transferred to a solution of epichlorohydrin (1.23 mL, 15.5 mmol). The crosslinking was initiated by increasing the solution pH to 11 with 0.25 M NaOH and the crosslinking reaction was continued for 24 h. The precipitate (polymer) formed was separated, washed with ultra pure water and dried in air. The complexed Co(II) from the dried polymer was removed by extraction with 1 M H_2SO_4 (100 mL). The polymer was then washed with excess water and treated with 0.05 M NaOH (50 mL) for regenerating the binding sites ($-NH_2$ groups in chitosan backbone). The polymer was again washed several times with ultra pure water and ethanol, and dried under vacuum to obtain the metal ion (Co(II)) imprinted chitosan (MIP). A non imprinted chitosan (NIP) was prepared in the same way as the MIP, but in the absence of the template ion, Co(II). The NIP was also subjected to similar chemical treatments as the MIP to ensure identical preparation conditions.

2.3. Sorption studies

All the sorption experiments were carried out in batch mode by equilibrating a fixed amount of the MIP, NIP or chitosan (20 mg) with a fixed volume (2 mL) of the test solution. The same adsorbent to solution ratio was maintained in all the experiments. Experiments were conducted in triplicate and the mean value was used. Metal ion concentrations were measured using an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES, Ultima2 Horiba Jovin Yvon, France) and pH measurements were done using a Hach, Sension 378 pH meter. Nirilotriacetic acid (NTA) concentrations were determined using a UV–Visible spectrophotometer (Evolution 500, Thermo Scientific) by dual wave length method (Bhattacharyya & Kundu, 1971) modified for NTA estimation.

The amount of metal ion sorbed, q_t (μmol/g) during equilibration for time t, was obtained as

$$q_t = (C_o - C_f)\frac{V}{W} \tag{1}$$

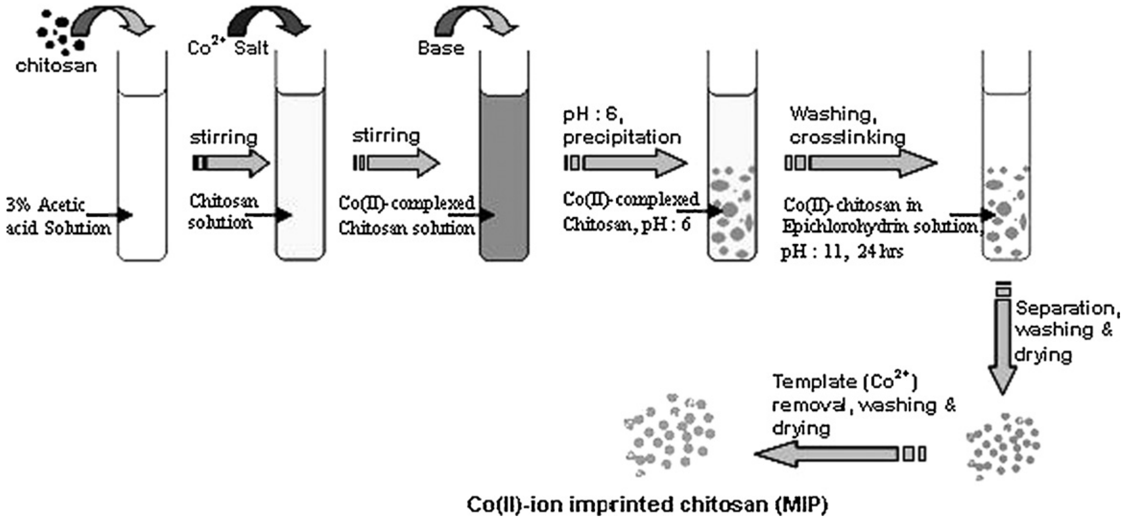

Fig. 1. Schematic showing the procedure used for the synthesis of Co(II) imprinted chitosan.

where, C_0 and C_f are the initial and final liquid phase concentration (μmol/L) of the metal ions, respectively; V is the volume of the solution in litre, and W is the weight of the sorbent used in gram.

Imprinting factor (I.F.), which is a measure of the selectivity induced by imprinting, was obtained as

$$\text{I.F.} = \frac{Q_{\text{MIP}}}{Q_{\text{NIP}}} \tag{2}$$

where, Q_i is the ratio of the capacity for Co(II) over the capacity for the competitor ion Fe(II), on equilibration of the sorbent with a solution containing both the ions (Eq. (3))

$$Q_i = \frac{q_{\text{Co(II)}}}{q_{\text{Fe(II)}}} \tag{3}$$

3. Results and discussions

3.1. Synthesis of the polymer

There are many reports on synthesis of metal ion imprinted chitosans for different metal ions using various crosslinking agents namely, gluteraldehyde (Chen et al., 2009), epichlorohydrin (Chen, Yang, & Chen, 2011) and ethylene glycol diglycidyl ether (Tianwei, Xiaojing, & Weixia, 2001). We have adopted a two step process in preparing the MIP, which involved synthesis of cobalt (II) complexed chitosan followed by freezing the complex configuration through its crosslinking polymerization with epichlorohydrin. Epichlorohydrin is known to be crosslinking through the hydroxyl groups of chitosan (Baroni, Vieira, Meneghetti, da Silva, & Beppu, 2008). Thus, the amino groups, the most important complexing groups of the chitosan, remain available for the metal ion binding at the imprinted sites. Acid extraction of the cobalt ions (template) from the crosslinked chitosan gave the metal ion imprinted chitosan (MIP). The amount of cobalt in the extracted solutions was measured by ICP-AES. The maximum theoretical capacity that can be attained by the MIP could thus be calculated, and was found to be 500.3 μmol/g.

3.2. Evaluation of sorbents under complexing and non complexing conditions

Uptake of metal ions by chitosan is known to be dependent upon the solution nature and pH (Navarro, Guzmán, Saucedo, Revilla, & Guibal, 2003). The sorption characteristics of the sorbents (MIP, NIP and chitosan) were thus investigated under various solution conditions by batch sorption studies with solutions of Co(II) in water, acetate buffer, citrate buffer and in citrate buffer containing NTA. The respective test solutions used were 4 mM Co(II) in 50 mM acetate buffers (pHs 4.9 and 5.6); 4 mM Co(II) in 50 mM citrate buffer (pH 4.7); and 4 mM Co(II) in 50 mM citrate buffer containing 4 mM NTA (pH 4.5). The experiments were carried out by equilibrating 20 mg of the sorbent with 2 mL of the respective solution. The uptake capacities obtained are tabulated in Table 1. The capacity values indicate reduction in sorption capacity in the MIP and NIP as compared to the chitosan. The reduction in capacity is attributable to crosslinking, which reduces the available free binding sites for metal sorption. The presence of the metal ion template ensures an effective availability of the binding sites in MIP unlike in the case of NIP, which was synthesized in the absence of the template ion. Therefore, among the MIP and NIP, the former exhibits a higher capacity for metal ion uptake.

The metal ion uptake by chitosan from a non complexing medium is expected to increase with increase in pH (Padala, Bhaskarapillai, Velmurugan, & Narasimhan, 2011), and an optimum pH is generally seen for the metal ion uptake from complexing

Table 1
Co(II)-ion uptake by the sorbents from complexing (citrate and NTA) and non complexing aqueous solutions.

Solution	pH_{eqbm}	Capacity (μmol/g)		
		MIP	NIP	Chitosan
4.22 mM Co^{2+} in water	6.0	46.7	16.6	72.5
3.85 mM Co^{2+} in 50 mM Acetate buffer	4.9	3.6	BDL[a]	32.1
5.08 mM Co^{2+} in 50 mM Acetate buffer	5.6	51.0	10.1	117.9
4.08 mM Co^{2+} in 50 mM Citrate buffer	4.7	76.6	16.5	199.6
4.15 mM Co^{2+} and 4 mM NTA in 50 mM Citrate buffer	4.5	92.2	32.8	210.9

[a] BDL: Below detectable level.

medium (Guzman, Saucedo, Revilla, Navarro, & Guibal, 2003; Gyliene, Binkiene, & Butkiene, 2009; Gylienë & Nivinskienë, 2005). In the present study, the uptake of Co(II) by the MIP was found to be very less at pH 4.9 in the non complexing acetate medium (Table 1). The lesser uptake of metal ions in this acidic pH can be attributed to the pKa of the $-NH_2$ groups of the chitosan. The amine protonation pKa for chitosan with a degree of deacetylation $\geq$80% has been reported to be around 6.5 (Navarro et al., 2003). Below this pH, as the amine groups will be largely in the protonated (NH_3^+) form, the metal cations have to compete with the H^+ ions for the binding sites, which leads to the reduced sorption. The effect of pH is further demonstrated by the increased uptake of Co(II) from the acetate solution at pH >5. The increase is due to the enhanced availability of free NH_2 groups at higher pH values. Near similar capacity values in acetate and non acetate medium at similar equilibrium pH values indicate the absence of any significant interference of acetate on cobalt sorption.

The significant increase in uptake capacities of MIP, NIP and chitosan in presence of citrate solution, as compared to the non-complexing solutions, indicates that there is synergistic effect by the citrate during the Co(II) sorption. This is not the case with other metal ions such as Cu (II), wherein the presence of the complexing agents in the solution is known to reduce the metal ion uptake by chitosan (Juang, Wu, & Tseng, 1999). Similar results were obtained in our earlier studies as well, wherein chitosan showed a reduced uptake of Cu(II) and an increased uptake of Co(II) from their respective complexing (NTA) solutions as compared to the uptake from their non complexing solutions (Padala et al., 2011).

This indicates that the uptake mechanism in the citrate medium is different from that in the non complexing medium and that the citrate also plays a role in the enhanced uptake shown by all the three sorbents (MIP, NIP and chitosan). However, in the case of the MIP, the favorable geometry created via imprinting leads to higher selectivity in favor of the cobaltous ion (vide infra). Sorption results obtained in presence of NTA (Table 1) showed that the Co(II) uptake was not affected significantly by the presence of NTA.

3.3. Evaluation of sorption capacities for Co(II) and Fe(II) from their respective citrate solutions

The sorption capacities of the sorbents for the target ion Co(II) and the competitor ion Fe(II) were investigated in complexing citrate medium. It has been reported (Guzman et al., 2003; Gylienë & Nivinskienë, 2005) that the uptake of metal ions on chitosan from the complexing citrate medium is well favored in the pH range of 4.8–5.2, which is also the pH range generally maintained during the chemical decontamination. Thus the sorption studies were done with pH 4.8 citrate buffer (50 mM) solution containing 4 mM Co(II) or Fe(II). Raw chitosan displayed a higher uptake capacity for Fe(II) than Co(II) and the non imprinted chitosan (NIP) showed almost equal capacities for both, whereas the imprinted chitosan (MIP) showed a higher sorption capacity for Co(II) than Fe(II) (Fig. 2). The Fe(II) selectivity showed by the chitosan is in agreement with the Irving–Williams series of complex stability (Cotton & Wilkinson, 1972). In case of the NIP, the capacity values (Co(II):16.5 ± 1.5 μmol/g and Fe(II): 13.3 ± 1.4 μmol/g) were very less as the crosslinking reduces the available functional groups. In case of the MIP, however, the presence of template ion ensures relatively higher availability of the functional groups, which were complexed to the template ion during the MIP synthesis.

The effect of imprinting with Co(II) as the template ion is exemplified by the selectivity shown by the MIP in favor of Co(II) over Fe(II) as compared to the NIP and the raw chitosan. Thus, a complete reversal in the selectivity of chitosan was realized through metal ion imprinting. The viability of imprinting in a chitosan derivative to differentiate two different geometries has been earlier demonstrated (Baba, Oshima, & Kanemaru, 2011) using Pd(II) as the template ion. The report had shown that the palladium imprinted polymer prepared selectively sorbs ions that form a complex with similar geometry as formed by the template, Pd(II), in the imprinted cavity against other ions that form complexes with different coordination geometry. In the present study, however, the competition is between two adjacent transition metal ions, which have similar oxidation state and predominantly form complexes of similar geometry. Despite such similarity, clear differentiation has been realized through imprinting. Our earlier theoretical studies (Bhaskarapillai, Chandra, Sevilimedu, & Sellergren, 2009) on the observed selectivity of an organic cobalt imprinted polymer for cobalt over ferrous have shown that differentiation is feasible due to favorable formation energy for the template ion within the imprinted site even though they form similar complexes in the imprinted site. The results obtained in the present study indicate that such factor must be operating in chitosan as well. However, definite quantitative conclusion would require a separate study involving detailed theoretical calculations for various geometries.

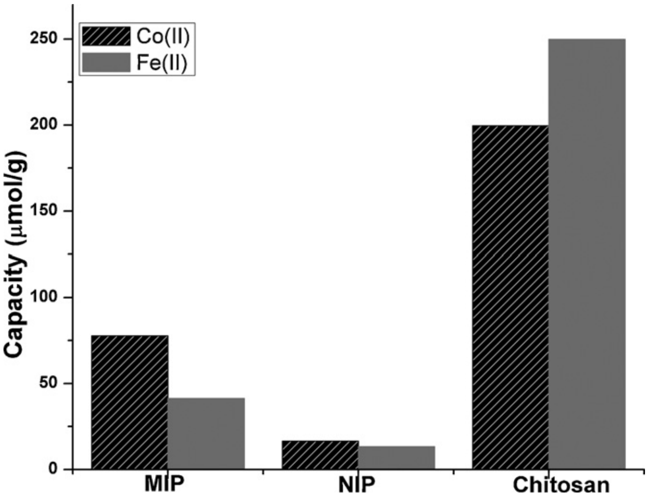

Fig. 2. Uptake capacities of the polymers in citrate medium.

3.4. Competitive sorption of Co(II) and Fe(II) by the sorbents under complexing conditions

For investigating the suitability of the MIP prepared for the intended application in the nuclear industry, the sorbents have been tested for their competitive cobalt sorption ability in presence of ferrous ions under complexing conditions. To study the effect of pH on the uptake capacity and selectivity of the MIP (towards Co(II) in presence of Fe(II)); batch sorption experiments were carried out with MIP, NIP and chitosan with solutions containing 2 mM: 2 mM: 50 mM of Co(II): Fe(II): Citrate, at different pH values.

3.4.1. Uptake capacities

The competitive sorption studies have indicated that both the NIP and chitosan show a higher uptake of Fe(II) than Co(II) in all the pH conditions studied, while the selectivity of the MIP was found to be dependent on the solution pH (Fig. 3a–c). Maximum uptake of Co(II), for the MIP and chitosan, was found to be in the region of pH 4. In the case of NIP, both Fe(II) and Co(II) showed an uptake maximum at around pH 4.8. While there was a peak maximum for the cobalt uptake, there was continuous decrease in the iron uptake capacity by the MIP. As could be seen in the graphs, the trend in change in capacity with respect to pH was found to be different for MIP, NIP and chitosan cases. There was significant decrease in the uptake of both the metal ions by the MIP at pH > 5.

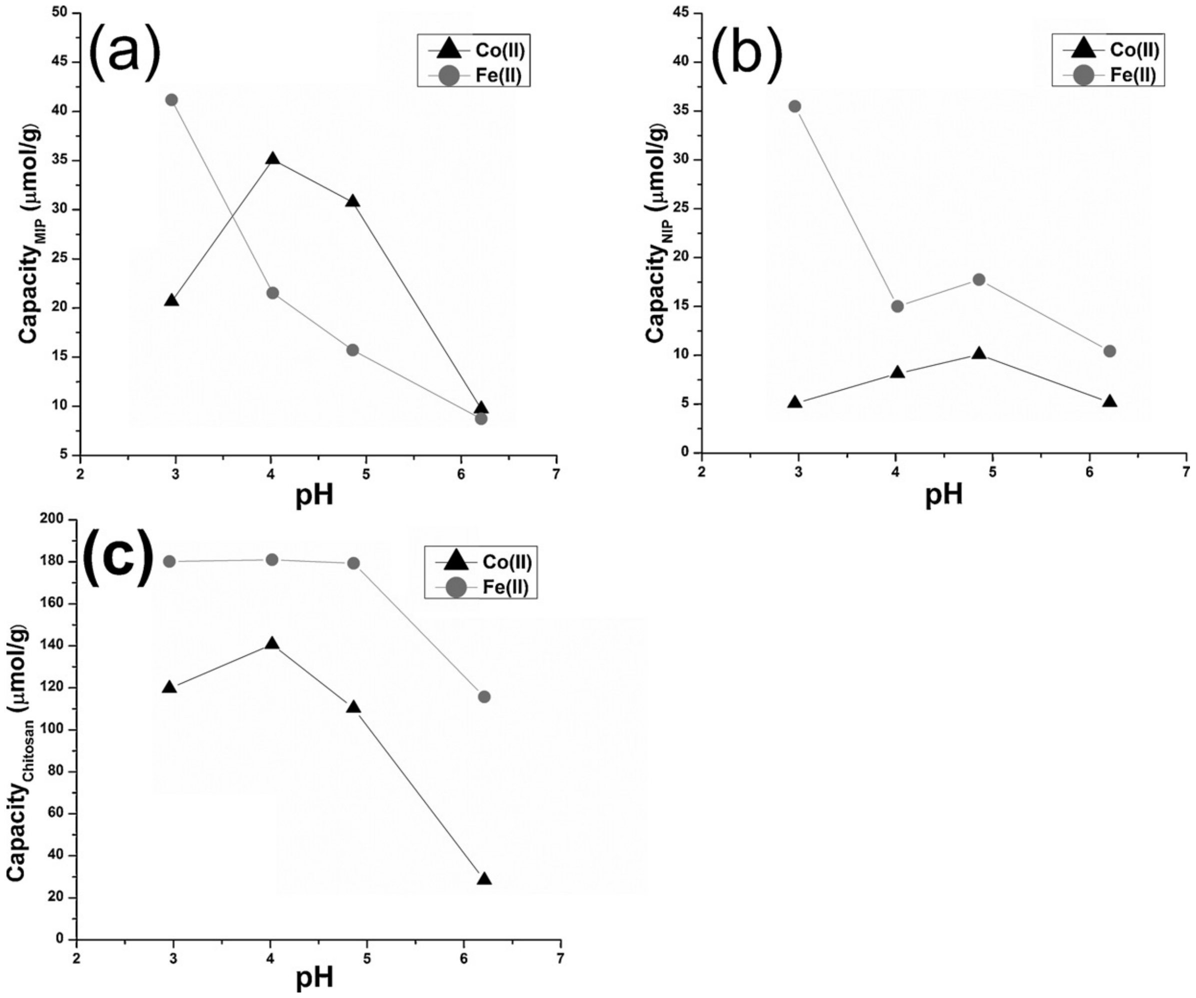

Fig. 3. Dependence of competitive sorption of Co(II) and Fe(II) by (a) MIP, (b) NIP and (c) chitosan on solution pH in citrate medium.

While the increase in uptake is due to the increased availability of free NH2 groups; beyond pH 4, there is increased ionization of citric acid, which leads to higher fraction of the metal ions remaining in solution as stable citrate complexes and thereby reduced uptake.

3.4.2. Selectivity and imprinting factor

The MIP showed maximum selectivity for Co(II) at pH 4.8 (Fig. 4). The imprinting factor, which is a measure of increase in selectivity due to imprinting, was found to be above 2.0, and nearly the same, in the pH conditions studied (Fig. 5). This indicates that the imprinted sites retain the selectivity under all the pH conditions studied. As the optimum pH range obtained is very near to the pH conditions maintained during the decontamination of the PHWRs, the MIP has the potential to be used for the selective removal of Co(II) from the decontamination formulation.

3.5. Evaluation of MIP in a typical decontamination formulation (NAC medium)

NAC (NTA–Ascorbic acid–Citric acid) based formulations are normally employed for the dilute chemical decontamination of PHWRs (Rufus et al., 2004). Hence, the ability of the MIP to sorb cobaltous ions present in very low level concentrations, in presence of large excess of ferrous ions, was investigated by conducting batch sorption studies in NAC medium. The typical NAC formulations used contained 1.4 mM NTA, 1.7 mM ascorbic acid and 50 mM citrate. The sorption study was done by equilibrating 20 mg of the sorbent with 2 mL of the test solution containing 4.0 mM (225 ppm) Fe(II) and 10.0 μM (600 ppb) Co(II) ions at pH 4.9. The results (Table 2) show that while the chitosan is selective towards Fe(II), the MIP is selective towards Co(II) in the complexing NAC medium. Percentage removal of Fe(II) by chitosan is seen to be

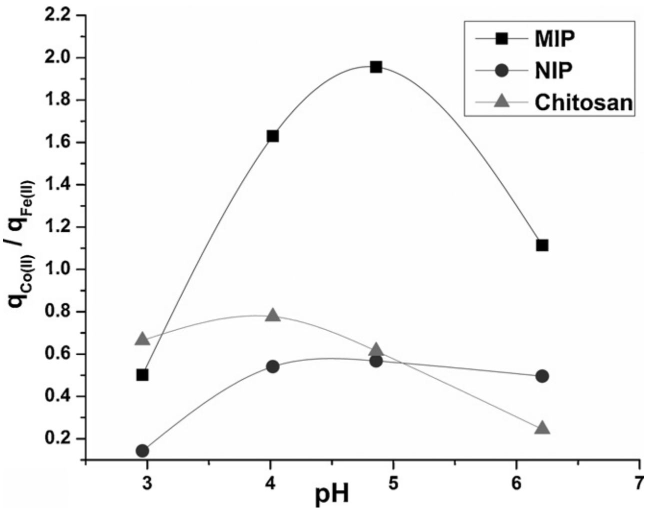

Fig. 4. Dependence of selectivity (ratio of Co(II) capacity over Fe(II) capacity) of MIP, NIP & chitosan on pH.

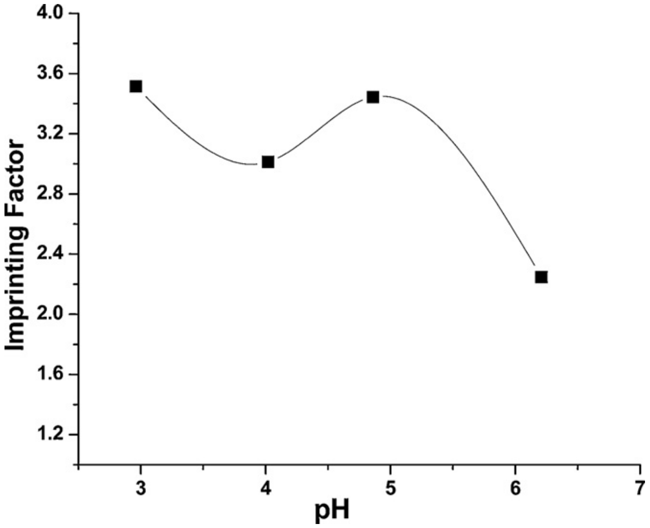

Fig. 5. Variation of imprinting factor (I.F.) with pH.

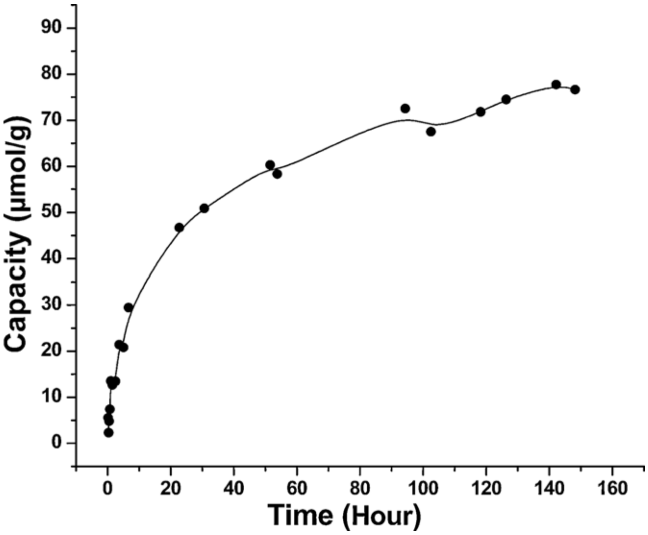

Fig. 6. Effect of equilibration time on cobalt uptake.

almost twice that of cobalt, while for the MIP the Co(II) removal is twice that of Fe(II) removal. Even though 100% exclusion of Fe(II), which would lead to complete separation of Fe(II) and Co(II), was not achieved, significant selectivity could be introduced in chitosan through imprinting. The workability of the MIP with low level cobalt concentrations in the NAC medium indicates its potential for application in nuclear reactor decontamination as a special sorbent for selective removal of cobaltous ions from the decontamination formulation.

3.6. Sorption kinetics

Studies were undertaken to monitor the variation in uptake of the metal ions and desorption of the loaded metal ion with time, in order to understand the possibilities of the effective use of the sorbents in column/batch experiments and for reusing the same through regeneration.

3.6.1. Variation of cobalt uptake with time

A 4 mM Co(II) solution (10 mL), prepared in 50 mM citrate buffer (pH 4.8), was shaken with 100 mg of the MIP. The variation in cobalt uptake by the MIP with time was monitored. The uptake increased with time and stabilized over a period of 3 days (Fig. 6). The long contact time required for the sorption limits the application of the MIP in online real time applications, but it can be made use of effectively through offline operations.

3.6.2. Desorption and reuse

Desorption of the Co(II) cations loaded on the MIP was carried out in batch mode using 0.25 M H_2SO_4 solution as the eluent. 0.1 g of the Co(II) loaded MIP was treated with 5 mL eluent and the concentration of the cobalt eluted out with time was measured. Desorption was found to be fast and complete. Almost 100% of the bound Co(II) was desorbed in less than 1 h of contact with the eluent. The regenerated MIP (even after multiple times of loading and desorption), when equilibrated with the metal ion solutions, was found to have retained the selectivity and capacity. Therefore, repeated use of the sorbent is feasible.

In case of the raw chitosan, it was found that the sorption saturation was obtained within five minutes of contact time and equally fast desorption was also seen. The long equilibration time required in case of the imprinted chitosan may be because of the very low porosity in the MIP as a result of crosslinking, which makes it relatively difficult to access the binding sites of the MIP as compared to the raw chitosan. Further, the reduction in the concentration of the functional groups in the crosslinked polymer as compared to the raw chitosan also leads to slow kinetics in the former.

Table 2
Evaluation of the sorbent in a typical decontamination formulation (NAC medium) containing NTA, ascorbic acid and citric acid.

Sample	Percentage removal (%)	
	Co(II)	Fe(II)
MIP	26.3	14.7
Chitosan	45.2	83.1

4. Conclusion

The work reported here demonstrates that through metal ion imprinting procedure the selectivity of the biosorbent chitosan could be reversed towards the target ion, namely Co(II), and thus make its application in the nuclear industry for selective concentration of radioactive cobaltous ions during clean up operations feasible. The cobalt uptake and selectivity were found to be high in the pH range 4 to 5, which is the typical pH range encountered during PHWR decontaminations. The sorption of Co(II) by the MIP from strongly complexing media such as NAC formulations indicates its applicability in preferential removal of Co(II) ions from solutions containing mixture of complexing agents. The investigated MIP will be useful in nuclear related applications, wherein the Co(II) ions are found in very low concentration levels and Fe(II) in large excess, as the MIP was shown to retain its cobalt selectivity even under such competitive conditions. Further, fast and easy regeneration of the MIP make the imprinted resin suitable for reuse without notable compromise in capacity and selectivity. Though metal ion uptake capacity is significantly reduced on imprinting, since the physical quantity of cobalt that is to be removed during decontamination is very less – typically in the order of sub ppb levels – the reduced capacity is not an impediment when high orders of selectivity is obtained in favor of the targeted radioactive nuclide. As compared to the imprinted organic resins, these have cost advantage and relatively better degradability. The latter is very beneficial as the concentrated active ions are to be removed from the resin for effective immobilisation and the stripped resin is to be decomposed. The fact that the selectivity could be modified to the point of reversing the preference shows that imprinting can be used as an effective tool for making chitosan suitable, as a replacement for pure organic resins, for various specific applications.

The long contact time needed for obtaining the saturation capacity limits the use of the cobalt imprinted chitosan in online operations during the decontamination process. Nevertheless, it can be effectively used in offline operations, post the decontamination process, for concentrating the radioactive cobaltous ions. In order to make the imprinted resins suitable for online application in column mode during the chemical decontamination of nuclear power plants, the uptake kinetics has to be improved. Also, complete Fe(II) exclusion, which is not achieved by the cobalt imprinting of chitosan, is to be realized for its effective online application. These can possibly be addressed through the imprinting of functionalized chitosan. Our current efforts are directed towards this objective.

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