Development, Characterization of Non-crosslinked Tetravalent Cerium Ion-Imprinted Polymer Network for the efficient removal of Ce (IV) ions from aqueous solutions and its Antimicrobial Study

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Abstract

Water pollution is a growing concern around the world, and recent advances in materials science have led to the development of metal ion-imprinted polymers that can selectively capture and remove cerium ions from water. The study reveals the synthesis and characterization of a novel tetravalent cerium selective sorbent by an imprinting strategy that shows greater affinity towards Ce (IV) ions in aqueous solutions. The tetravalent Ce (IV) Ion-Imprinted Polymer Network (Ce (IV)-IIPN) was synthesized with monomers acrylamide, alginic acid, and with potassium persulphate, as initiator and was characterized by Fourier Transform IR, UV-Visible spectroscopic studies, Powder X-ray diffraction studies, Scanning Electron Microscopy, and Energy Dispersive X-ray Analysis. The effect of various conditions of sorption such as initial concentration of Ce (IV) ion, contact time, and weight of polymer on Ce (IV) ion binding to the prepared IIPN was studied and results showed an increase in the uptake of Ce (IV) ion with an increase in the parameters stated above. The developed Ce (IV)-IIPN showed good swelling ability and has been investigated by determining the Equivalent water content percentage value. A remarkable affinity towards the Ce (IV) ion was also observed, as verified by the results of cross-adsorption studies with other interfering metal ions. Also, the polymer was found to be effective against the microbial species Staphylococcus aureus.

1. Introduction

Cerium pollution in water is a growing concern due to its potential impact on human health and the environment [1]. Cerium is a rare earth element widely used in various industrial applications, including catalytic converters, glass polishing, and as a fuel additive [2]. The presence of cerium in water can lead to various health problems, including liver and kidney damage, and it can also have adverse effects on aquatic life [3]. Research has shown that cerium can be removed from water using various methods, including phytoremediation, adsorption, and photocatalysis [3-5]. Hao et al. (2016) found that floating aquatic plants can be used to remove heavy metals, including cerium, from polluted water [2]. Ali et al. (2018) developed a novel adsorbent by loading cerium and manganese oxide onto wheat straw-modified biochar, which was found to be effective in removing arsenic from polluted water [4]. Separation of cerium ions in their various oxidation states, from their aqueous solutions can be achieved by nanofiltration using NF 300 membrane, by oxidative precipitation method, and so on [6,7]. However, adsorptive removal using ion-imprinted polymers emerged as an efficient approach due to its high efficiency, selectivity, and ease of operation.

Metal Ion-Imprinted Polymer (MIIP) shows great potential for the removal of metal ion pollutants from water with excellent selectivity and reusability. They are synthetic polymers that are designed to selectively absorb specific metal ions from water based on their chemical properties [8,9]. In the synthesis process, a template metal ion, a functional monomer, and a cross-linker are self-assembled and polymerized to create a network of cavities that match the size, shape, and chemical functionality of the template metal ion [8,10]. The resulting MIIP exhibits high selectivity and affinity for the template ion making them an effective absorbent for the water remediation.

In this regard, a novel Ce (IV)-IIPN as a Ce (IV) ion-selective sorbent using a natural biosorbent alginic acid and template Ce (IV) ion is developed. The advantage of the newly prepared IIPN is that it showed high sorption capacity and remarkable selectivity in Ce (IV) ion separation from a mixture of metal ions. The method of preparation of Ce (IV)-IIPN is simple, rapid, economical, and eco-friendly due to the use of the aqueous medium. The prepared Ce (IV)-IIPN was used for the molecular recognition-based sorption of the Ce (IV) ion from the mixture of metal ions. Characterization of polymer networks, rebinding studies, and investigation of the effect of various parameters on rebinding were done. Selectivity, specificity, and antimicrobial study of the IIPN were also investigated.

2. Materials and Methods

2.1. Materials

All the reagents used were of analytical and spectral grade. The monomers used in this study, namely acrylamide, alginic acid; the template ion source ceric ammonium nitrate; and the initiator potassium persulfate were obtained from NICE, India. Fourier transforms infrared (FT-IR) spectra of the Ce (IV)-IIPN and its Ce (IV) ion-bound complex were recorded between 4000-400cm^{-1} using a Perkin Elmer 400 FT-IR spectrophotometer. UV-Visible spectrophotometric measurements were carried out using Shimadzu 1200 UV-Visible spectrophotometer. The amount of metal ion adsorbed before and after the binding was determined by UV-Vis spectrophotometric method. SEM images and EDX spectrum of the synthesized IIPN and Ce (IV) ion-bound complex of IIPN were taken using the JEOL JSM-6390 instrument. XRD data of the samples were obtained using an Aeris Research benchtop X-Ray Diffractometer. The antimicrobial study was carried out by the microtiter broth dilution method according to the Clinical and Laboratory Standards Institute (CLSI) guidelines.

2.2. Methods

Synthesis of Ce (IV)-IIPN

Alginic acid (14.5 g) was mixed with ceric ammonium nitrate (2 g) in an aqueous medium. This mixture was added to acrylamide (10.6 g), and potassium persulphate (0.3 g) is added as an initiator. The polymerization was carried out at 70 ℃ with constant stirring in a water bath. The polymer obtained was washed with water to remove the unreacted monomer. The polymer was dried, sieved, and weighed. Non-Imprinted Polymer Network (NIPN) was also prepared using the same procedure without cerium ion.
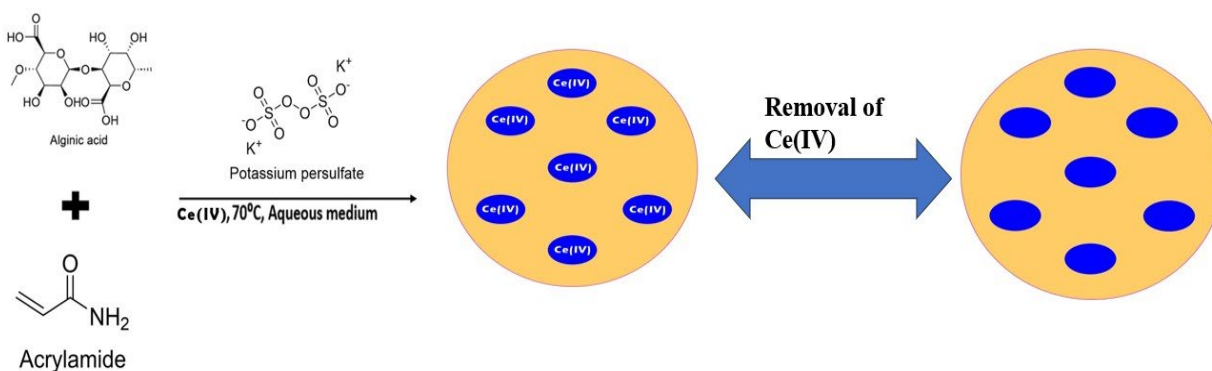
Scheme 1: Synthesis of Ce (IV)-IIPN

2.4. Experimental techniques

Ce (IV) ion binding studies

By batch equilibration method, certain factors affecting rebinding such as weight of the polymer, concentration, and contact time of the Ce (IV) ion solution on binding were investigated.

Effect of concentration on Ce (IV) binding

To investigate the effect of concentration on binding, batch-wise metal ion binding was carried out at various concentrations. 100mg of the Ce (IV)-IIPN and NIPN were equilibrated with (20 mL,

0.009-0.04N) Ce (IV) ion solutions, and from the difference in concentration of template metal ion solution before and after incubation, the amount of metal ion bound was determined by UV-Vis spectrophotometric method.

Effect of time of contact on Ce (IV) binding

The effect of time of contact on Ce (IV) ion binding was determined by the batch equilibration method using Ce (IV) ion solution. 100mg of Ce (IV)-IIPN and NIPN were shaken with (20 mL, 0.04N) Ce (IV) ion solution, and was followed at regular intervals of time by UV-Vis spectrophotometric method.

Effect of the weight of the polymer

The effect of the weight of IIPN, on the binding of Ce (IV) ion, is investigated by equilibration of different weights of polymer with Ce (IV) ion solution. Different weights of Ce (IV)-IIPN to (20 mL, 0.04 N) of Ce (IV) ion solution and shaken for about 35 min (Figure: 3), the optimum time for efficient binding. The concentration of Ce (IV) ions before and after is estimated by the UV-Vis spectrophotometric method.

Swelling studies

One hundred milligrams of Ce (IV)-IIPN and NIPN were allowed to swell in 10 mL water for 24h. After 24h the polymers were filtered, the surface water was wiped off, and the final swollen weight was determined. From the swollen and the dry weights of the sample, the equivalent water content % was calculated, using the equation 1 [11].

$$\text{Equivalent water content}\% = \frac{(\text{weight of swelled sample} - \text{weight of dry sample})}{\text{weight of dry sample}} \times 100\% \quad \ldots\ldots\ldots (1)$$

Selective sorption studies

Selective sorption of Ce (IV) ions on the Ce (IV)-IIPN was investigated by equilibrating IIPN with a mixture of Ce (IV) ion and Zn (II), Mg (II), Cr (VI), and V(V) ion solutions. The amount of metal ions adsorbed by IIPN was determined by UV-Visible spectrophotometry.

Antimicrobial study of Ce (IV)-IIPN and its Ce (IV) ion-bound complex

The antimicrobial activity of Ce (IV)-IIPN and its Ce (IV) ion-bound complex against the bacterial species *Staphylococcus aureus* (ATCC 33591), were investigated and Minimum Inhibitory Concentration (MIC) values are determined by the microtiter broth dilution method according to the Clinical and Laboratory Standards Institute (CLSI) guidelines. The stock solutions of samples were prepared in DMSO such that the concentrations of Ce (IV)-IIPN and its Ce (IV) ion-bound complex is 81.33 and 102 mg/ml respectively. The overnight bacterial suspension (*Staphylococcus aureus)* was adjusted to 0.5 McFarland standard and then diluted to 1×10^6 CFU/ml. From this suspension, 100 µl of stock solutions of polymers were inoculated into each well. 100 µl of each compound (81.33 mg/ml and 102 mg/ml) was prepared in Muller Hinton broth and added to the well of the first row, and 2-fold serial dilution was obtained vertically (from row A to H) to obtain 5×10^5 CFU/ml in each test well (Figure: 8). The wells for the positive control contained 5×10^5 CFU/ml, and the negative control well contained 100 µl of media alone. The microtitre plates were incubated overnight at 37 °C. MIC values were visually determined and interpreted as the lowest concentration of compounds displaying no visible growth.

3. **Results and Discussion**

UV-vis spectral studies

UV-Vis spectral study is an important tool to characterize a polymer. The reflectance spectra of Ce (IV)-IIPN and Ce (IV) ion-bound complex of IIPN were different. The UV-Visible spectra of

Ce (IV)-IIPN gel showed maximum absorption at 203 nm while that of Ce (IV) ion-bound IIPN was at 278 nm. This bathochromic shift in the absorption band before and after Ce (IV) ion sorption is strong evidence that reveals the binding of metal ions in IIPN [12].

IR Spectral studies

FTIR spectral study is a significant method to analyze the structure of a polymer at the molecular level. The FTIR spectrum of Ce (IV)-IIPN (Figure: 1(a)) showed absorption at 3346.42 cm^{-1} due to the -OH stretching of alginic acid and is shifted to 3341.62 cm^{-1} in the Ce (IV) ion-bound complex of IIPN (Figure: 1(b)). Also, C=O stretching which is observed at 1599.56 cm^{-1} for Ce (IV)-IIPN was found to be shifted to 1584.95cm^{-1}. These observations indicate that the alginate's carboxyl group participates in Ce (IV) ion sorption process. The peaks in the region below 1000 cm^{-1} are due to the metal-oxygen stretching of the metal-carboxyl bonds in the Ce (IV) ion-bound complex of IIPN [13].
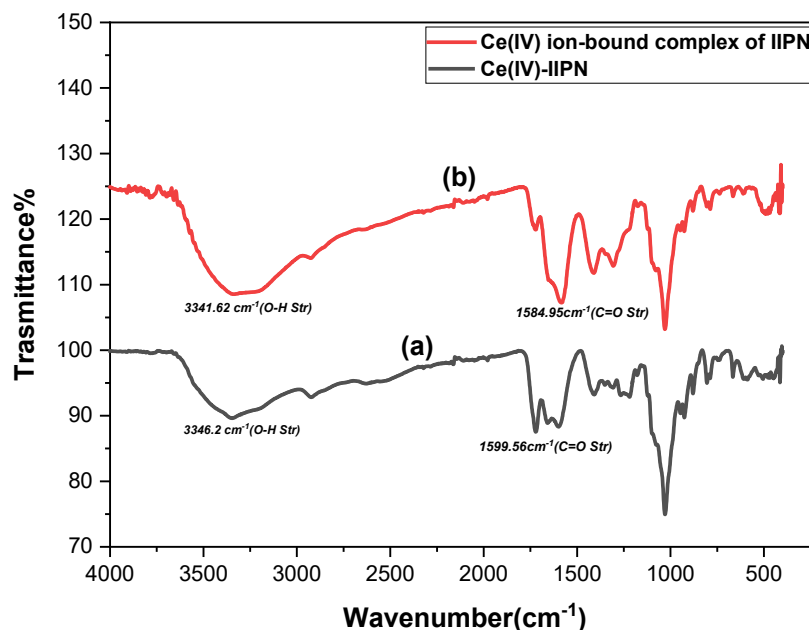

Figure 1: FTIR spectra of (a) Ce (IV)-IIPN (b) Ce (IV) ion-bound complex of IIPN

Adsorption studies and optimization of sorption conditions

The conditions influencing the rebinding of Ce (IV) ion on both IIPN and NIPN were investigated by equilibrating the polymers with Ce (IV) ion solution at different conditions viz. initial concentration, contact time, and weight of the polymer and were optimized.

Effect of concentration

The effect of the initial concentration of Ce (IV) metal ion solution on the sorption was investigated by varying the initial concentration of the Ce (IV) metal ion solution.100 mg of the Ce (IV)-IIPN and NIPN were equilibrated with (20 mL, 0.009-0.04 N) Ce (IV) ion solutions and the concentration of Ce (IV) ion before and after were determined by UV-Vis spectrophotometric method (Figure: 2). Mass transfer that formed due to the difference between the concentration of Ce (IV) ion in bulk solution and around the surface of Ce (IV)-IIPN increases with the increase of initial Ce (IV) ion concentration, can be the driving force which significantly increases the equilibrium adsorption capacity [14]. Also as suggested by Jerzy et al. the concentration of the solution increases, the population of ions increases, and as a result, the competition for vacant sites increases [15]. This reason for the increase in ion uptake with an increase in concentration. Due to the lesser availability of vacant cavities suitable for Ce (IV) ions on the surface of the NIPN, sorption was not achieved effectively with an increase in concentration on the comparison.
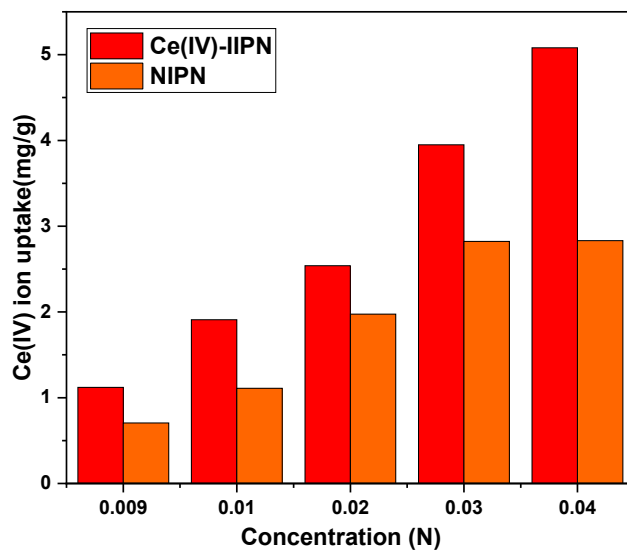
Figure 2: Effect of concentration on Ce (IV) binding on IIPN.

Effect of contact time on Ce (IV) ion sorption

The effect of contact time on the sorption of Ce (IV) ion on the IIPN and NIPN was investigated by equilibrating 100 mg of both the polymers by batch with (20 mL,0.04 N) Ce (IV) ion solution, and the sorption capacities were determined concerning time by UV-Visible spectrophotometric method. The results show that the sorption of Ce (IV) ion on both IIPN and NIPN increases with an increase in contact time and remains independent after a particular time. Initially, adsorption occurs at a faster rate due to the greater availability of vacant sites for sorption and increased kinetics of ions with time due to reducing boundary layer resistance to mass transfer [16]. But due to the absence of specific cavities for the sorption of Ce (IV) ions, the rate of sorption and its efficiency were low for NIPN [17]. The time at which equilibrium is attained can be considered as the optimum time for adsorption studies and was found as 35 min for IIPN and NIPN (Figure: 3). After the optimum time of contact, the unavailability of no more vacant sites reason for the leveling off the sorption of ions.
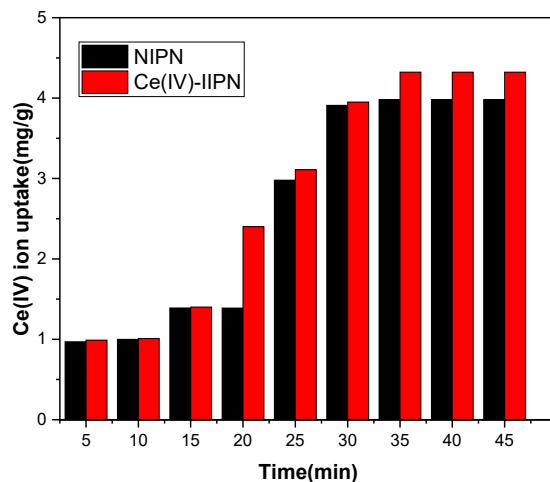
Figure 3: Effect of time on Ce (IV) binding on IIPN

Effect of the weight of Ce (IV)-IIPN dosage on Ce (IV) ion uptake

The effect of the weight of the polymer on Ce (IV) ion binding on the Ce (IV)-IIPN was investigated by batch equilibration method. Different weights of both Ce (IV)-IIPN were equilibrated with (20 ml,0.03 N) Ce (IV) ion solution, and the concentration of Ce (IV) ion in solution before and after the binding was determined by UV-Visible spectrophotometric method. From the observations of the study, it is clear that the Ce (IV) ion uptake decreases with an increase in the weight of the polymer and becomes independent above a particular weight (Figure: 4); because the total available surface area of the IIPN is decreased as binding sites aggregates and also binding path-length is increased with an increase in the amount of polymer loaded [18].
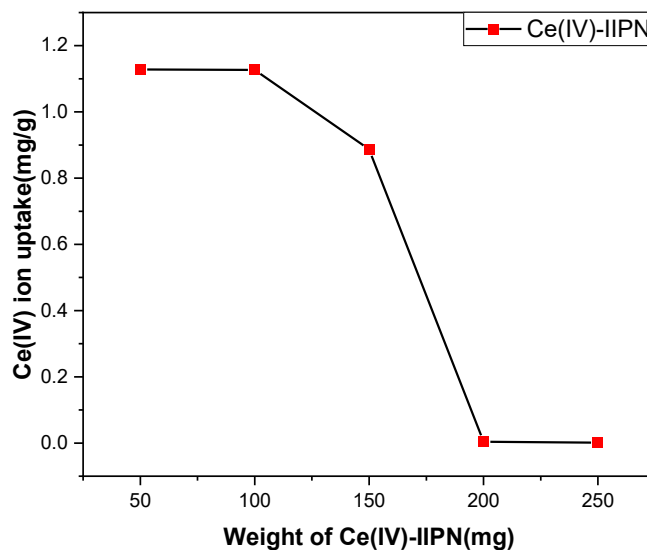
Figure 4: Effect of the weight of Ce (IV)-IIPN dosage on Ce (IV) binding on IIPN

Swelling studies

A polymer's swelling ability depends on its polymer backbone's nature and chemical character. The swelling behavior of the Ce (IV)-IIPN and NIPN was investigated by making a time-bound study of its swelling and determining its Equivalent water content percentage values. Maximum swelling was obtained for Ce (IV)-IIPN and it may be due to the adsorption of water molecules into the cavities vacated by Ce (IV) ions (Table 1) [19]. Due to the non-availability of such vacated cavities, swelling decreases for NIPN.

Table 1: Equivalent water content % values

Polymer used	Equivalent water content %
Ce (IV) ion selective IPN gel	75.83
Non-imprinted IPN gel	54.51

XRD Spectral studies

XRD pattern provides an understanding of the structural properties of the polymer network. The XRD patterns of Ce (IV)-IIPN and its Ce (IV) ion-bound complex are given (Figure: 5). XRD patterns show broad halo peaks in 2θ regions 10 to 80 degrees indicating the amorphous nature of the polymer and its complex [20].
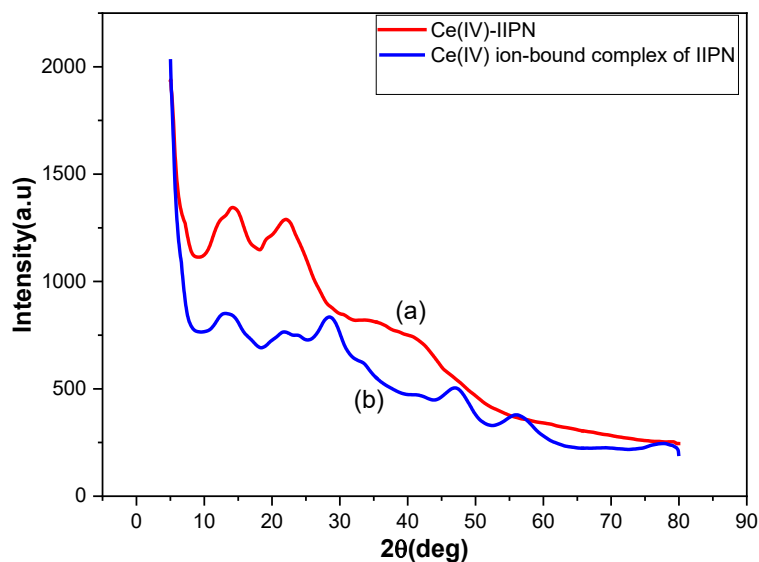

Figure 5: XRD pattern of (a) Ce (IV)-IIPN (b) Ce (IV) ion-bound complex of IIPN

SEM EDAX Spectrum

The composition and successful rebinding of Ce (IV) ions on the Ce (IV)-IIPN is confirmed by SEM EDAX (Figure: 6). The SEM EDAX of the metal ion-bound polymer showed the incorporation of Ce (IV) ions on the supramolecular cavities at its surface. It provides evidence for the successful binding of Ce (IV) ions on the polymer synthesized.
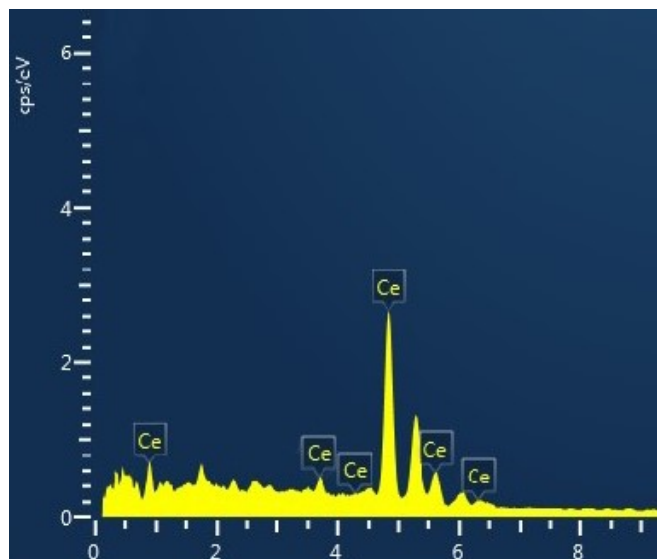
Figure 6: SEM EDAX of Ce (IV) ion-bound complex of IIPN

SEM Analysis

SEM characterization is employed to analyze the surface properties of the polymer network. The SEM images of the Ce (IV)-IIPN and Ce (IV) ion-bound complex of IIPN are given in Figure: 7. From the images it is observed that the unbound ion-imprinted polymer surface morphology is entirely different compared to that of Ce (IV) ion bound complex polymer surface, as the surface sites are more occupied in the complex. It can be considered as a piece of physical evidence for the successful adsorption of Ce (IV) metal ions onto the cavities imprinted by the Ce (IV) ions on the synthesized ion imprinted polymer.
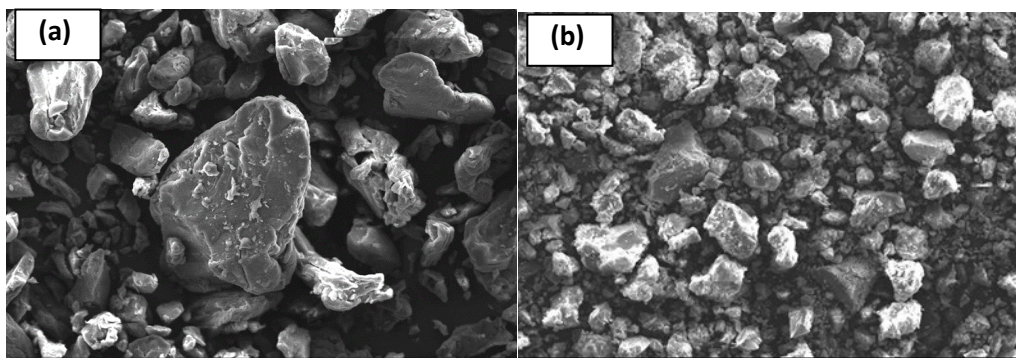
Figure 7: SEM image of (a) Ce (IV)-IIPN (b) Ce (IV) ion-bound complex of IIPN

Selective sorption studies of Ce (IV)-IIPN

The selective sorption of Ce (IV) ions on IIPN was investigated by cross-adsorption with Zn (II), Mg (II), Cr (VI), and V(V) ions. Here 0.2 g of the Ce (IV)-IIPN is treated with a (40 mL, 0.04 N) solution containing Ce (IV) ion and an interfering ion. After the equilibrium is reached, the concentration of metal ions is determined by a UV-Visible spectrophotometer. The result (Table: 2) indicates that the surface of the Ce (IV)-IIPN contains cavities with a strict configuration that matches for Ce (IV) ion and the recognition depends on the nature, ionic size, and charge of the metal ions.

Table 2: Selective sorption study of Ce (IV)-IIPN

Metal ions	Ce (IV) uptake(mg/g)	Uptake of coexisting ions(mg/g)
Ce (IV) & V(v)	0.00578	0.002
Ce (IV) & Zn (II)	0.00560	0.001
Ce (IV) & Mg (II)	0.00561	0.001
Ce (IV) & Cr (VI)	0.00564	0.019

Application of the synthesized Ce (IV)-IIPN

Selective sorption of Ce (IV) ions in aqueous solutions by Ce (IV)-IIPN

The synthesized IIPN shows a high affinity towards Ce (IV) ions in aqueous solutions. The polymer network is treated with a mixture of metal ions with Ce (IV) ion in common and other competing ions Zn (II), Mg (II), V(v), and Cr (VI). The result obtained indicates the suitability of the present Ce (IV)-IIPN for the effective sorption of Ce (IV) ions from aqueous solutions. The results are listed in Table: 2.

Antimicrobial activity of polymers

On comparing the antimicrobial activity of Ce (IV)-IIPN and its Ce (IV) ion-bound complex it was found that the former is much more active against American-type cell culture (ATCC), Staphylococcus aureus (ATCC 33591) due to lower MIC value (Table: 3). Staphylococcus aureus is a common human pathogen which causes various infections in a range of severity from common dermatitis to high-risk sepsis, endocarditis, and toxic shock syndrome [21]. From the result, it finds application as an antimicrobial agent against the referred bacterial species.

Table 3: MIC values of Ce (IV)-IIPN and its Ce (IV) ion bound complex

Polymer analyzed	MIC value(mg/ml)
Ce(IV)-IIPN	10.17
Ce(IV) ion-bound complex of Ce(IV)-IIPN	12.75

4. Conclusions

The foregoing studies reveal the importance and applicability of designing a Ce (IV) ion-imprinted polymer network for the selective sorption of Ce (IV) ions from aqueous solutions. In this regard, we developed and characterized a new sorbent for the selective sorption of Ce (IV) ions from aqueous solutions. It shows a high affinity towards Ce (IV) metal ions compared to other competing metal ions. The high binding capacity is obtained as a result of the presence of several -COOH groups in alginic acid as functional groups which leads to an increased surface area and more supramolecular cavities on the imprinted polymer network which can recognize Ce (IV) ions compared to other. This increased surface area than in non-imprinted polymer leads to the increased swellability of the IIPN. The swelling ability decreased for NIPN due to the lesser availability of vacant cavities for the sorption of water molecules. The Ce (IV)-IIPN exhibits higher efficiency in the selective sorption of Ce (IV) ions from other competing metal ions than compared to the NIPN. Antimicrobial studies of Ce (IV)-IIPN and Ce (IV) ion bound complex of IIPN were proved to be active against American type cell culture (ATCC), *Staphylococcus aureus* (ATCC 33591), but due to the lower MIC value of the former, it is considered to be more effective. Based on the above investigations, it can be concluded that the developed Ce (IV) ion-imprinted polymer network, is a very suitable sorbent for efficient sorption and effective recovery of Ce (IV) ions from aqueous solutions and also effective against the bacterial species *Staphylococcus aureus*.

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