Synthesis, Characterization, and selectivity study of a Fe(III)-Imprinted Selective Ferric Ion Sequestration from Water Sources

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Synthesis, Characterization, and selectivity study of a Fe(III)-Imprinted Selective Polymer for Effective Ferric Ion Sequestration from Water Sources

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Abstract

In the vast aqueous expanse that sustains life, an invisible intruder silently corrodes the purity of our precious resource. Once celebrated for their role in essential biochemical processes, Ferric ions have now emerged as an alarming source of water pollution. With their ability to infiltrate aquatic ecosystems undetected, these iron warriors wreak havoc on the delicate balance of nature. This work embarks on the preparation of a Fe(III)-Imprinted Selective Polymer(Fe(III)-ISP)for removing ferric ions from various water samples. The polymer network was synthesized from Ferric Nitrate, Alginic acid, and Acrylamide using potassium persulphate as initiator and crosslinking agent N, N′-Methylenebisacrylamide. The polymer network was characterized by Fourier Transform IR, UV-Visible spectroscopy, Scanning Electron Microscopy, and SEM-EDS spectrum. The effect of different parameters like PH, Concentration, amount of polymer added, and time on ferric ion uptake was investigated. The method was applied for the adsorptive removal of ferric ions from different real water samples collected from the environment.
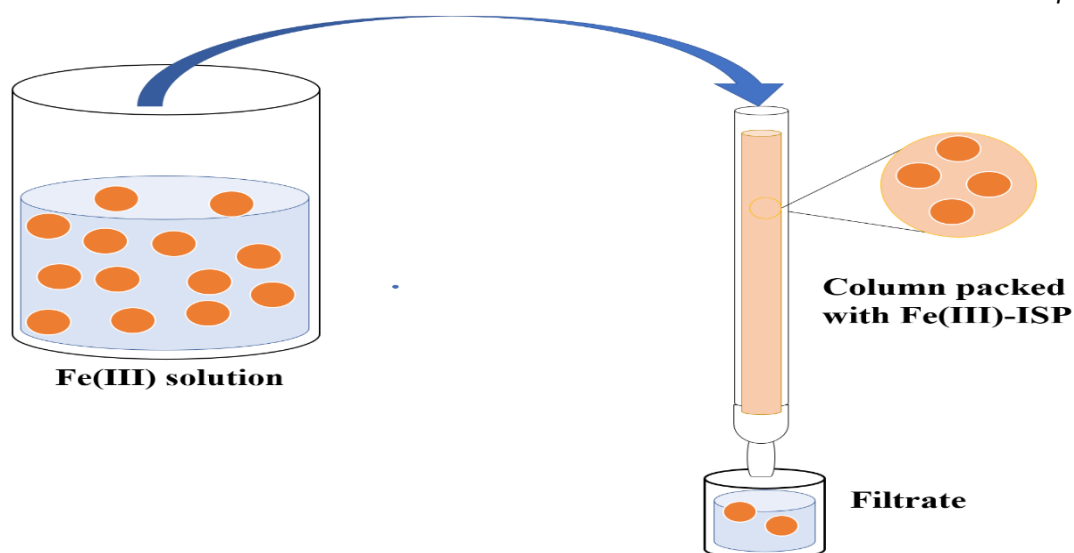
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Figure 1: Fe(III) ion removal using Fe(III)-ISP

Keywords - Ferric ion, Polymer network, Alginic acid, Uptake

1. Introduction

The presence of ferric ions, once hailed for their crucial role in natural processes, has now become a growing concern in our aquatic ecosystems. Seeping into rivers, lakes, and oceans, this insidious form of contamination silently corrodes the delicate balance of aquatic life and endangers human health. With its far-reaching consequences, understanding the origins, impacts, and potential mitigation strategies of ferric ion pollution is of paramount importance. Ferric ions can be found as a common chemical in environmental waterbodies. Iron is one of the earth's most plentiful resources. Iron is rarely discovered in drinking water at levels exceeding 10 milligrams per liter (mg/L) or 10 parts per million. The presence of 0.3 mg/l of ferric ions can cause water to turn a reddish-brown color.

The presence of ferric ions in water is not harmful to health, but it is considered a secondary or aesthetic contaminant. Ferric ion is an essential element for maintaining good health and plays a crucial role in oxygen transportation within the bloodstream. However, the extraction of metal ions from water is a significant concern due to their toxic nature[1,2]. To address this issue, Interpenetrating Polymer Networks (IPNs) utilize a combination of two different polymers to selectively remove specific ions, while allowing harmless ions to remain in the environment. This approach is highly advantageous as it focuses on removing only the metal ions while leaving the others unaffected. Among the various IPN systems, polysaccharides have emerged as one of the most effective options. They possess the ability to significantly reduce metal ion concentrations to extremely low levels (parts per billion) and are readily available without causing harm to the environment. Polysaccharides like cellulose, alginates,

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Carrageenan, lignin, and chitin derivatives are examples of such compounds[3]. Additionally, these polysaccharides offer several functional groups, viz. as hydroxyls and amines, that can be modified chemically to increase the efficiency of metal ion sorption and increase the maximum chemical loadings[4]. Polymer networks have widespread applications in modern technology[6].

Behisht Ara et al. reported a Ferric ion-imprinted polymer for selective sorption of Fe(III) ions having a sorption capacity maximum of $170\mu molg^{-1}$ and with excellent relative selectivity to other metal ions[7]. Mariya Mitreva et al. synthesized Fe(II)-IIP as a sorbent for Fe(II) ions using crosslinked precipitation polymerization with 2,2'-bipyridyl as the functional ligand[8]. Mahmoud Roushani et al. prepared Fe(III) imprinted polymer for the adsorption and preconcentration of ferric ions from real water sources and food samples[9]. D K Singh et al. reported the preparation and characterization of a Ferric ion-imprinted polymer for the recovery of ferric ions from water samples using thermal copolymerization[10].

2. Materials and methods

Analytical and spectral-grade reagents are used in all experiments. Alginic acid and acrylamide monomers; the free radical initiator Potassium persulphate and the crosslinking agent NNMBA were purchased from NICE Chemicals, India. FTIR spectra of the Fe(III)-ISP and that of Fe(III) ion-adsorbed ISP were recorded using a Perkin Elmer 400 FTIR spectrophotometer between $4000\text{-}400 \ cm^{-1}$. Shimadzu 1200 UV-Visible Spectrophotometer was used for taking UV- vis spectrophotometric measurements for following the effect of sorption conditions on Fe(III) ion adsorption on Fe(III)-ISP. SEM and EDS spectra were taken with the help of the JEOL-JSM-840 Scanning Electron Microscope

3. Experimental

3.1. Preparation of Fe(III)-Imprinted Selective Polymer

7.5g of Alginic acid was mixed with 0.9 g of the template ion source Ferric Nitrate using water as the medium. This mixture was then added to another mixture of 10.66 g acrylamide, and the crosslinking agent NNMBA 7.71g and kept in a water bath at a temperature of 70° C with continuous stirring, in the presence of the required amount of potassium persulphate as initiator. The obtained polymer was washed with distilled water repeatedly to remove unreacted monomers and with 2N HCl solution to leach Fe(III) ions. Then it was dried, sieved, and weighed.

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3.2. Water adsorption studies

100mg of dried Fe(III)-ISP and its Fe (III) ion-adsorbed ISP were allowed to get swelled in 10 ml water for a period of 24 hours. After the specific time of swelling, the ISP and Fe(III) ion-adsorbed ISP were filtered and carefully wiped off the surface water. Thereafter the final weight after swelling was determined. From the difference in weights of the swollen and the dry polymer samples, the Equivalent Water Uptake (EWU%) values for both polymers were calculated, using the equation(1)

$$EWU\% = \frac{\text{Weight of swelled ISP - Weight of dry ISP}}{\text{Weight of dry ISP}} \times 100\% \quad \text{---------------------(1)}$$

3.3. Effect of different physicochemical parameters on Fe(III) ion rebinding

Effects of different physicochemical parameters on the adsorption of ferric ions were investigated by equilibrating Fe(III)-ISP with ferric ion solutions at various conditions and the ferric ion uptake is determined using the UV-Vis method.

3.3.1. Effect of concentration on Fe(III) ion uptake

The impact of the initial concentration of ferric ion solution on ion uptake on ISP was assessed through batch metal ion binding experiments. The experiments involved varying the initial concentration within the range of 0.001N to 0.005N, and the uptake of Fe(III) ions was analyzed using the UV-Vis method.

3.3.2. Time dependence on Fe(III) ion uptake

The time required by a specific amount of ISP for maximum uptake was determined by batch-wise equilibration method using 0.005N Fe(III) ion solution**.** 100mg of the polymer was added to (10 ml/0.005N) Ferric ion solution and the Fe(III) ion uptake was determined at regular intervals of time using the UV-Vis method.

3.3.3. Effect of pH of the solution on Fe(III) ion uptake

100 mg of the ISP was subjected to rebinding using 0.005 N Fe(III) ion solution at varying pH. The amount of ferric ions uptaken at different pHs of the solution was determined using the UV-Vis method.

3.3.5. Effect of variation of quantity of polymer on Fe(III) ion uptake

The effect of the quantity of ISP added on Ferric ion uptake was examined by varying the amount of polymer and ferric ion uptake was determined. 10mg-100mg of the

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polymer was subjected to rebinding using 0.005 N Fe(III) ion and the ferric ion uptake was determined using the UV-Vis method.

3.4. Recyclability studies

The reusability of the polymer was investigated by subjecting ISP to several loading-elution operations with (50mg/10mL) of Fe(III) ion solution. Elution was carried out using 4 mL of 3N HCl.

3.5. Selective sorption studies

Selective sorption studies of the polymer were carried out by column experiment. 1 g of the polymer was made into a slurry with demineralized water and is then poured into a Pyrex glass column with a small portion of glass wool plucked at the bottom. The column was pre-conditioned by passing demineralized water and then the mixture of Ferric ion solution (1×10^{-3} M, 10 ml) was passed through the column at a flow rate of ~ 0.5 ml min^{-1}. The eluted solution was collected and the amount of metal ions bound was determined by the AAS method.

4. RESULTS AND DISCUSSIONS

4.1. Synthesis of Fe(III) Imprinted Selective Polymer

The Fe(III)-ISP was synthesized by free radical polymerization of monomers acrylamide and Alginic acid in the presence of Potassium persulphate using NNMBA as the crosslinking agent. The polymerization was carried out at a temperature of 70°C in aqueous medium. The obtained ISP was washed with distilled water repeatedly to remove unreacted monomers and with 2N HCl to leach Fe(III) ions.

4.2. FTIR Spectral Analysis

The Fe(III)-ISP and its Fe(III) ion-adsorbed ISP were analyzed using FTIR spectroscopic technique. The spectrum of Fe(III)-ISP shows a peak around 1640 cm^{-1} for C=O stretching and at 3280.72 cm^{-1} for O-H stretching due to the carboxyl group of the alginate which is found to be shifted to a higher wavelength region on 1645 cm^{-1} and 3290.02 cm^{-1} on ferric ion binding on ISP. It reveals that the carboxyl group of alginate participates in the ferric ion binding process onto the polymer. Also, there are peaks below 1000 cm^{-1} in Fe(III) ion-adsorbed ISP which can be due to the Fe-O bond.

4.4 Scanning Electron Microscopy and EDX Analysis

SEM studies were employed to determine the surface properties of the Fe(III)-ISP and its Fe(III) adsorbed ISP. SEM images of the ISP and its Fe(III) ion-adsorbed ISP

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show the difference in surface morphology. The SEM micrographs and EDX spectra of the Fe(III)-ISP and Fe(III) ion-adsorbed ISP are shown in Fig.2 and Fig.3 respectively. From the images, it is observed that the surface of the Fe(III)-ISP is fairly rough and the surface became smooth after the adsorption of Fe(III) ions onto the ion-specific cavities on the ISP surface[11]. The EDX analysis shows no presence of Fe(III) ions in the Fe(III)-ISP but has Fe(III) ion peaks in the Fe(III) ion-adsorbed ISP, revealing that the desired function of the polymer synthesized is accomplished.
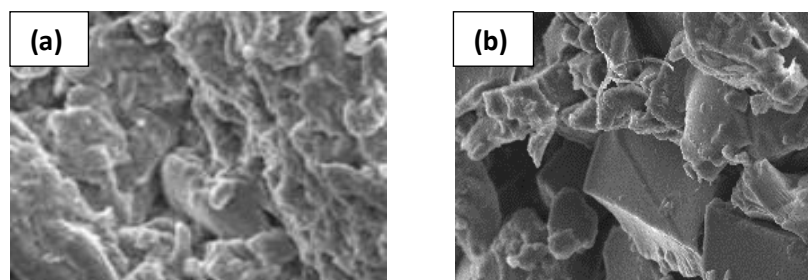

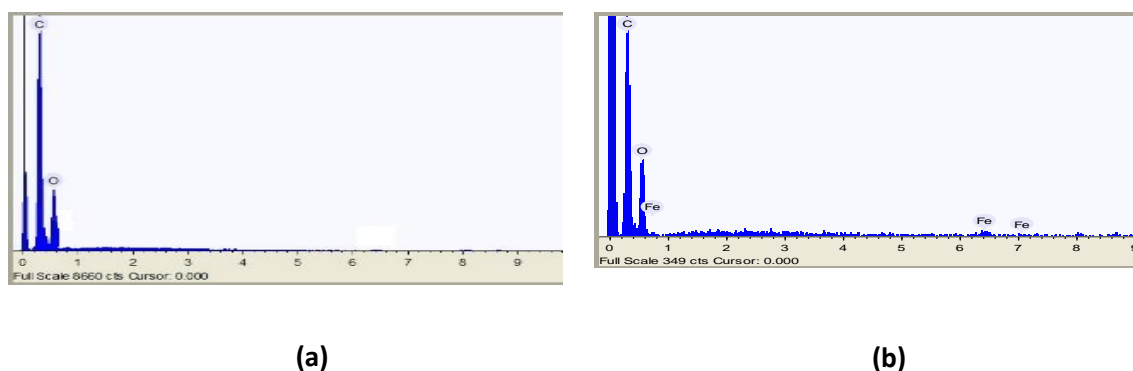**Fig.2: SEM image of (a) Fe(III)-ISP (b) Fe(III) ion adsorbed ISP**

(a)   **(b)**

Fig.3: SEM EDAX of (a) Fe(III)-ISP (b) Fe(III) ion adsorbed ISP

4.5. Water sorption studies

The Ferric ion binding studies of the Fe(III)-ISP and Fe(III) ion-adsorbed ISP in the aqueous medium can be greatly influenced by the swelling behavior of the polymer. The swelling behavior of Fe(III)-ISP and Fe(III) ion-adsorbed ISP at various pH are investigated and tabulated in Table.1. EWU% values are found to be high for Fe(III)-ISP as it possesses more vacant cavities but sites are occupied by ferric ions in the Fe(III) ion-adsorbed ISP. Also, it was found that at neutral PH, the EWU% value for both polymers is low and it increases with an increase in the pH of the medium. This is due to the electrostatic interaction between the

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ferric ion and the ISP, which may depend on the extent of dissociation of the carboxyl group. The dissociation can increase with an increase in pH of the medium of swelling and deprotonation reactions of the carboxyl group occur.

pH	EWU(%) of Fe(III)-ISP	EWU(%) of Fe(III) ion-adsorbed ISP
3.5	54	51
4.5	58	56
5.5	61	59
6.5	64	60
7	68	62

Table 1:Effect of pH on swelling behavior

4.6. Polymer Surface Area Analysis

The surface area of the ISP was measured by the BET method using single-point analysis. The Fe(III)-ISP showed a value of $19.6 \mathrm{m}^2\mathrm{g}^{-1}$ for a specific surface area, from which it can be inferred that the porosity of the polymer network which is formed after ferric ion removal enhances the surface area.

4.7. Effect of different physicochemical parameters on Fe(III) ion rebinding

The effect of different physicochemical parameters on the adsorption of ferric ions was investigated by equilibrating Fe(III)-ISP with ferric ion solutions at various conditions of rebinding.

4.7.1 Effect of concentration on Fe(III) ion uptake

The dependence of the of ferric ion solution concentration on Ferric ion uptake was investigated by varying the initial concentration of the Ferric ion solution. The studies revealed that as the initial concentration increases, ferric ion uptake also increases (Fig.4). The result can be explained based on a high driving force for mass transfer and it is that all available active sites on the polymers will be utilized at higher concentrations[12].
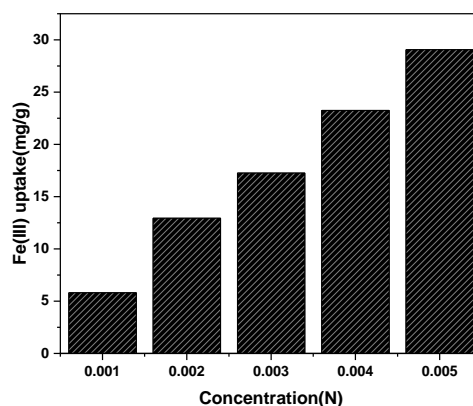
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Fig.4: Effect of concentration on Fe(III) ion uptake

4.7.2. Effect of pH of the solution on ferric ion uptake

The pH of the solution plays an important role in controlling the sorption of metal ions by adsorbent. The effect of the pH of the solution on ferric ion uptake by the ISP was investigated in the pH range of 2-4.5. The PH of the medium was adjusted by using dilute solutions of NaOH and HCl. At low pH ferric ion uptake was found to be in small quantity. The Uptake of Fe(III) ion on ISP increases with an increase in the pH of the Fe(III) ion solution and then falls off as shown in Fig.5. So the maximum uptake can be obtained at a pH between 3.5 and 4.5.
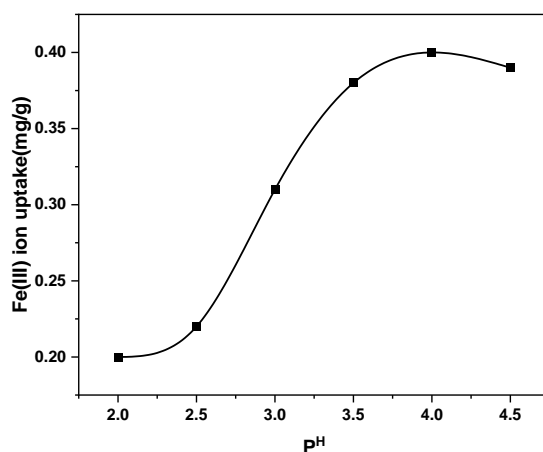

Fig.5: Effect of PH on Fe(III) ion binding

4.7.3. Dependence of time on Fe(III) ion binding

Ferric ion uptake by the ISP was determined as a function of the period. To determine the optimum time of contact of the ISP with a Ferric ion solution for the maximum uptake of Fe

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(III) ion, batch-wise equilibration experiments were carried out. From the data obtained, a period of 90 min was the optimum for the complete recovery of Fe(III) ion by ISP(Fig.6), and after that the uptake levels off.
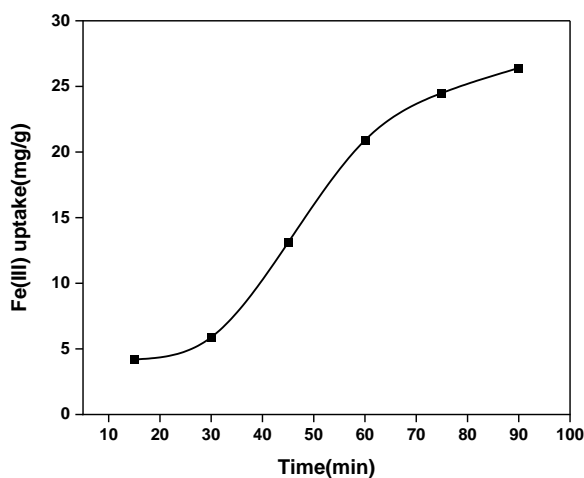

Fig.6: Dependence of time on Fe(III) ion binding

4.7.4. Effect of variation of quantity of polymer on Fe(III) ion uptake

The dependence of the amount of polymer on ferric ion uptake was investigated by varying the quantity of ISP. Fe(III) ion uptake was quantified by the UV-Vis method. The results given in Fig.7 revealed that with an increase in the amount of polymer, ferric ion uptake decreases. This is attributed to the fact that the total available surface area of the polymer network is decreased due to the aggregation of binding sites and an increase in binding path length [13].
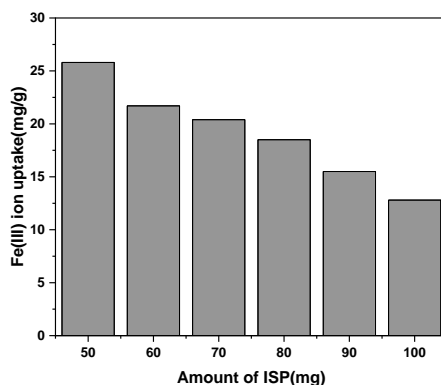

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Fig.7: Effect of variation of quantity of polymer on Fe(III) ion uptake

4.8. Selective sorption studies

To find out the selective binding of the Fe(III) ion, Fe(III)-ISP was equilibrated with solutions of metal ions viz. Fe (III), Co(II), Cu(II), and Ni(II) ions. The results indicated that the ISP showed high specificity towards Fe(III) ion (Fig.8). This is by the fact that the coordination geometry of complexation with Fe(III) ions was not disturbed during rebinding, so the polymeric system specifically binds the desorbed metal ion.
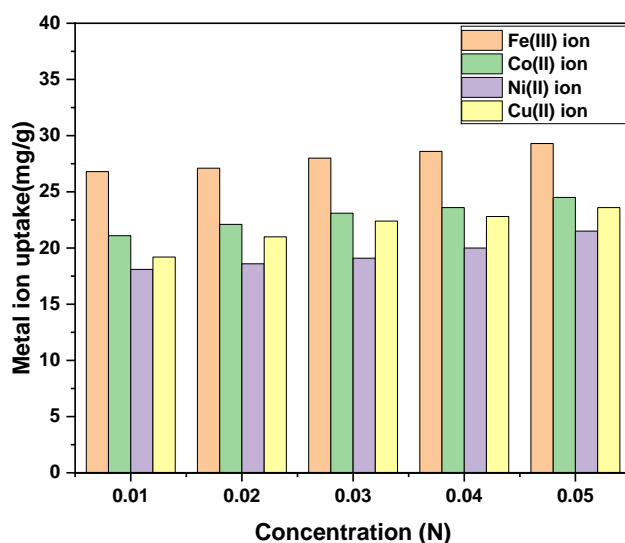

Fig.8: Selectivity of Fe(III)-ISP

4.9. Reusability study

The reusability of Fe(III)-ISP was investigated by the elution process. ISP was subjected to several loading-elution processes with (50mg/10mL) of Fe(III) ion solution and the elution was carried out using 4 mL of 3N HCl. The calculated percentage recovery of the polymer showed no appreciable decrease in efficiency after six cycles of repeated operations. The percentage recovery of the recycled ISP could still be maintained at 96% even after repeated cycles of operations.

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Polymer used	Amount of Fe(III) ion uptaken in each extraction cycle (mg/g)						
	1	2	3	4	5	6	**Recovery(%)**
Fe(III)-ISP	26.6	26.6	26.6	26.4	26.2	26.2	96.0

Table 2: Recycle studies of Fe(III)-ISP

Sequestration of Fe(III) ions from environmental samples

Fe(III)-ISP has been applied for the adsorptive removal with efficient selectivity of Fe(III) ions from natural water samples collected from various sources and analyzed. The obtained removal values described that the prepared polymer network is highly suitable for the sequestration of Ferric ions from collected water samples and can be a suitable sorbent for the adsorptive removal of Fe(III) ions from real water samples. The standard values of Ferric ions found in each source are determined using the AAS method. The results are listed in Table 3.

Real water sources	Found amount (mg/L)	Removed amount (mg/L)	Recovery percentage (%)
lake water	0.39	0.38	97
Tap water	0.61	0.60	98
Borewell water	0.65	0.64	98
Pond water	0.69	0.67	97

Table 3: Application of Fe(III)-ISP on real water remediation

Conclusion

The ferric ion-selective polymer showed effective recovery of Fe(III) ions from solutions of ferric ions. The uptake of ions was maximized by optimizing various physiochemical parameters. The removal Fe(III) from aqueous solution is maximum at pH 4 and at higher pH ferric ion uptake decreases. The optimum time for ferric ion uptake is found to be 90min. Swelling studies proved that the maximum EWU% value is obtained for Fe(III)-ISP and it

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was found that the EWU% value increases with an increase in pH. The recovery of Fe(III) is simple, economical and can be effectively applied for the removal of ferric ions from different environmental water samples.

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