



Preparation of microspheric Fe(III)-ion imprinted polymer for selective solid phase extraction

Behisht Ara^{1,2} · Mian Muhammad¹ · Muhammad Salman¹ · Raees Ahmad¹ · Noor Islam¹ · Tanveer ul Haq Zia^{3,4}

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Abstract

In this research work, an Fe(III)-IIP was prepared using methacrylic acid as monomer, divinylbenzene as cross-linker, azobisisobutyronitrile as initiator. The ion imprinted polymer was functionalized with Fe(III)-8-hydroxy quinolone complex under thermal conditions by copolymerization with the monomer and the cross-linker. The prepared Fe(III)-ion imprinted polymer (IIP) and non-ion imprinted polymer (Non-IIP) were characterized with fourier transform-infrared spectroscopy, scanning electron microscopic analysis and thermal gravimetric analysis. The polymer showed a good stability to thermal analysis up to a temperature of 500 °C. The size of the polymer obtained was 1 μm, large enough to be filtered easily. At pH 2.5 more affinity was observed with ion imprinted polymer in comparison to non-ion imprinted polymer. For the kinetic study, the most linear and rhythmical relation were seen in pseudo second order. The maximum sorption capacity of Fe(III) ions on Fe(III)-IIP and non-IIP was 170 and 30.0 μmolg⁻¹, respectively. The relative selectivity factor (α_r) values of Fe(III)/Fe(II), Fe(III)/Al(III) and Fe(III)/Cr(III) were 151.0, 84.6 and 91.9, respectively. The preconcentration factor was found to be 240. The developed method was successfully applied to the determination of trace Fe in the drinking water.

Keywords Ion imprinted polymer · Polymerization · Fe(III) · Methacrylic acid · 8-Hydroxyquinoline · Divinylbenzene · Azobisisobutyronitrile

Introduction

Iron (Fe) is one of the most important essential macro-nutrient and also a heavy metal. It occurs freely, or in the compound containing Fe when in solid form. It exists as Fe²⁺, the ferrous form, and Fe³⁺, the ferric form in aqueous solution. The element is known for its high redox potential in solution (Coplin et al. 1991; Frykman et al. 1994; Hallberg et al. 1996; Liguori 1993; Lokken and Birkeland 1979; Greenwood 1995; Reddaiah et al. 1989). Fe(III), the stable form of Fe in nature, depicts its stability in the prevalence

of rust, an absolutely insoluble Fe(III) (Boyd et al. 2000; Berg and Lippard 1994). Ferric forms insoluble compounds in water, near pH 7. Salt of ferric Fe hydrolyzes water and produces Fe(III) oxide-hydroxides thus contributing hydrogen ions to the solution and ultimately pH is decreasing. This behavior of ferric form reflects the effect of charge: water when attached to Fe³⁺ ions in highly acidic solutions, forming Fe(III) hydroxides. Ferric is present transiently in Fe containing proteins. Its biological functions in living systems rely on its more redox potential. The deficiency of Fe develops slowly, is not clinically apparent until the stored Fe is exhausted and its supply in the body is compromised. On the other hand, large amount of Fe ingested can result in its high levels in the blood. Its high level in blood produce more reactive free radicals from peroxides that damage DNA, protein, lipids. When gastrointestinal tract cells are damaged, it can also stop Fe absorption resulting in its further increase in blood levels. Excess Fe may cause harmful effects such as shock, coma, adult respiratory distress syndrome, liver failure, coagulopathy, metabolic acidosis, long-term organ damage, and even death. For every kg of Fe, humans experience Fe toxicity above 20 mg, and 60 mg/Kg

✉ Behisht Ara
bahishtara@gmail.com

¹ Department of Chemistry, University of Malakand, Chakdara Dir Lower, Khyber Pukhtunkhwa 18800, Pakistan

² Institute of Chemical Sciences, University of Peshawar, Peshawar, Khyber Pukhtunkhwa 25000, Pakistan

³ School of Chemical and Materials Engineering, National University of Science and Technology, Islamabad, Pakistan

⁴ Department of Chemistry, Sarhad University of Science and Information technology, Peshawar, Pakistan

is considered a fatal dose. The dietary reference intake lists the tolerable upper intake level for adults as 45 mg/day. For children under 14 years old the upper intake level is 40 mg/day (Pospiech and Walkowiak 2010).

For the extraction of Fe(III), among the various methods listed in literature, solvent extraction is one of the earliest approach and is widely studied. The solvent extraction of Fe(III) had been investigated with neutral extracts, such as ethers, ketones, amines and tributylphosphate and also with cationic reagents, such as quaternary ammonium ions. A survey of literature showed that neutral solvating extracts such as methylisobutyl ketone and tributylphosphate and acidic organophosphorus extractants such as di-(2-ethylhexyl)phosphoric acid have been widely used for the removal of Fe(III) from acidic chloride solutions. The use of acidic organophosphorus extracts for the removal of Fe(III) have some demerits such as slow kinetics and requires high mineral acid concentration for the recovery of Fe(III) from the loaded organic phase. On the other hand, neutral organophosphorus extracts such as tributylphosphate, when used for the extraction of Fe(III) resulted in third phase formation and poor phase disengagement. Hence, a modifier in the organic phase has to be introduced. To get complete extraction of Fe(III) with methylisobutyl ketone very high concentration of HCl is needed (Akl 2003; Soledade et al. 2014; Fernandes et al. 2012).

The conventional solid phase extraction methods used for the extraction of Fe(III) typically contain an ion exchange material such as chelating resins (Rubi et al. 1997; Filik et al. 1997), modified C18 phase column (Blain and Tréguer 1995), and modified silica gel (Mahmoud and Al Saadi 2001) to remove the major ions as well as to concentrate Fe. In several environments these materials can function, can exhibit more affinity for the analyte and can be readily regenerated. Solid phase extractants such as IIP offer selective solid phase extraction of analytes present in low concentration or the separation from other coexisting ions or complex matrix. Thus, imprinting for solid-phase extraction is a rapid developing area for its wide applications (Fu et al. 2015; Khan and Park 2006; Khan et al. 2008).

The present method is simple and convenient for the preparation of ion imprinted polymer for Fe(III), following the

thermal copolymerization of the ternary complex of Fe(III) with methacrylic acid and divinyl benzene. The inconvenient of extra step in its preparation, such as preparing its composite with magnetic particles or with silica particle is being avoided. Not only is the preparation easy but when compared to the literature, it gives results comparable to the already reported IIP. The size of polymer is in micrometer, can easily to be filtered by simple batch filtration method, and does not require high speed centrifugation or modification by introducing magnetic properties. For the preparation of IIP, ligands used for other metal ions in general are dithiocarbamate for Sr(II), vinylbenzyl iminodiacetic acid for Ni(II), 1,10-phenanthroline for Ag(II), N,N'-o-phenylene bis (salicylideneimine) for Zn(II), 4-(2-thiazolylazo) for Hg(II) and 5-methyl-2-thiozymethacrylamide for Cu(II) (Rajabia et al. 2005; Lenoble et al. 2015; Liu et al. 2015; Shamsipur et al. 2014; Yilmaz et al. 2013; Singh and Mishra 2010a, b, c). For Fe(III) ion imprinted polymer very little had been studied. The already reported polymerization techniques (Table 1) and chelating agents used for are amino-functionalized silica gel sorbent, chelating diamines and p-nitrobenzyl alcohol, respectively (Changa et al. 2007; Xie et al. 2012; Sun et al. 2013, Sing and Mishra 2010a, b, c).

Under specified conditions of pH many metals (e.g. aluminium, copper, cadmium, Fe, nickel, cobalt, manganese, magnesium and zinc) give well-defined crystalline precipitates with 8-hydroxyquinoline. The general formula these precipitates is $M(C_9H_6O N)_n$, where n shows the charge on the metal M ion. This present method under specified pH is based on the fact that in the IIP, the use of 8-hydroxyquinoline as a functionalizing agent offers a control and selective extraction of Fe(III).

The objective of this study is to provide a process which can completely and selectively separate Fe(III) from a solution mixture of ferric ion and many other metal ions. Another objective of this study is to provide a simple and economical process for treating a Fe(III)-containing aqueous solution. In this work, Ion Imprinted Polymers (IIP) for selective binding of Fe^{3+} are synthesized using divinylbenzene (DVB) as cross-linker, methacrylic acid (MAA) as monomer azobisisobutyronitrile (AIBN) as initiator, and 8-hydroxy quinoline as a binding site for the metal ion. Results showed that this IIP have

Table 1 Comparison of the sorbent characteristic of various Fe(III)-imprinted polymer with present study

Ligand	Method of polymerization	Technique	Relative selectivity coefficient	Sorption capacity (mg/g)
Cetyl trimethyl ammonium bromide	Sol-gel	FAAS	68.9	36.90
3-aminopropyltrimethoxysilane	Surface imprinting	ICP-AES	49.9	25.21
	Thermal co-polymerization	Spectrophotometer	–	62.4
Acrylic acid 8-hydroxy quinolone (present method)	Thermal co-polymerization	FAAS	84.6	170

a good binding capacity for the target ion in both control and environmental samples, respectively.

Experimental

Instruments

Ultraviolet–Visible spectrophotometer (Model SP-300 plus, Optima, Japan) with matched 1.0 cm quartz cells was used for the optimization studies. Flame Atomic Absorption Spectrometer (AA 240, Varian, USA) was used for Fe(III) determination in real water samples, its selectivity study and study of foreign ion effect. For heating of solutions, an electrical thermostatic water bath (model DSB-1000T, Taiwan) was used. A ks300 KUM SUNG ultrasonic (Korea) sonicator was used for the desorption of Fe(III). For binding experiments of the Fe(III) to the polymer, Orbital Shaker (Model OS-340C, Taiwan) was used. These polymers were characterized by 20 kV Scanning electron microscope. The powdered samples were mounted on standard specimen stubs with double adhesive carbon tape. Fourier transform infrared spectroscopy (Nicolet 6700) was used to study for functional group determination. Thermal degradation of the microspheres was examined by Perkin Elmer diamond Thermal gravimetric analysis/Differential thermal analysis.

Chemicals

Ferric chloride 99% (scharlau), 8-hydroxyquinoline 99% (scharlau), methacrylic acid $\geq 99\%$ (Sigma–Aldrich), azobisisobutyronitrile 98% (Sigma–Aldrich), chloroform $\geq 99.8\%$ (Sigma–Aldrich), hydrochloric acid 36.5–38.0% (Riedel–de Haen), acetic acid $\geq 99.85\%$ (Sigma–Aldrich), sodium acetate $\geq 99\%$ (Sigma–Aldrich), divinyl benzene 80% (Sigma–Aldrich).

8-Hydroxyquinoline (oxime): oxime is a flexible organic reagent and can make chelates with various metallic ions. The general formulae of chelates of doubly and triply charged metal ions are the $M(C_9H_6ON)_2$ and $M(C_9H_6ON)_3$, respectively. Normally 1 per cent (0.07 M) solution of oxime in chloroform is used. 8-Hydroxyquinoline is amphoteric in aqueous solution, having both a basic nitrogen atom and a phenolic hydroxyl group; at $pH < 5$ and $pH > 9$ it is completely extracted from aqueous solution by chloroform; the distribution coefficient of the neutral compound between chloroform and water is 720 at 18 °C (Jeffery et al. 1989).

Fe-8 hydroxyquinolone complex

Procedure

A weighed amount of Fe(III) chloride (0.0226 g) was dissolved in 1 Litre of distilled water (pH 2.5) in a graduated

flask. 50.0 mL of the solution was placed in a 100 mL separatory funnel, followed by addition of 10 mL of a 1% oxime solution in chloroform. It was shaken for 1 min. The dark red colored chloroform has the Fe(III)8-hydroxyquinolone complex. Fe(III) (50–200 μg) can be extracted from aqueous solution with 1% solution of 8-hydroxyquinoline in chloroform by double extraction when the pH of the aqueous solution is between 2 and 10. At a pH of 2–2.5 nickel, cobalt, cerium(III), and aluminium do not interfere.

For the preparation of Fe(III)-IIP, chloroform extract was used.

Preparation of Fe(III)-IIP by precipitation polymerization

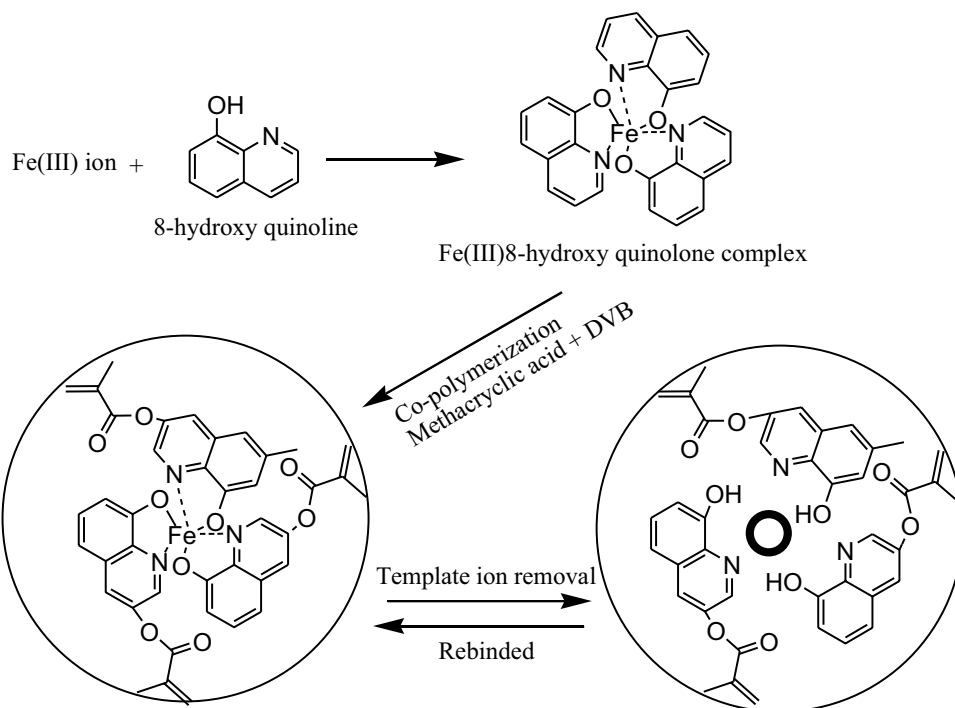
Procedure

IIP was synthesized by precipitation polymerization in which functional monomer and a cross-linker with Fe(III)8-hydroxyquinolone complex was co-polymerized. IIP microspheres was prepared by precipitation polymerization under the conditions mentioned in Table 2. The complex was kept in glass tube which was extracted in 10 mL of chloroform. Then methacrylic acid, divinylbenzene and azobisisobutyronitrile were added. Nitrogen was moderately flowed for 5 min to remove the solution and then it is covered. In water bath at temperature of 60 °C the glass tube was kept vertically for 24 h. Then it is filtered to collect the solid particles. The mechanism of reaction is shown in (Fig. 1). An electron deficiency is caused by the electronegative nitrogen atom at the 2- and 4- position of the pyridine ring of the Fe(III)8-hydroxyquinolone complex, that permits the nucleophilic reagent (MAA) to be added at position 2- and not at 3-of this ring. This interaction is further stabilized when the cross-linker links up the monomer, finally a polymer is formed that has iron embedded inside. The Fe(III) is washed off and the leached Fe(III)-IIP is further used in the studies.

Table 2 Optimization of the amounts of cross linker, monomer and porogen volume for the preparation of Fe(III)-IIP (Temp 60 °C, synthesis time 24 h, complex 0.5 mmol)

Parameter studied	Range studied	Optimized value
Methacrylicacid (monomer)	0.25–1.0 mmol	1.0
Divinylbenzene (cross linker)	0.5–2.5 mmol	2.5
Chloroform (volume)	6–20 mL	10

Fig. 1 Proposed reaction mechanism for the preparation of Fe(III)-IIP showing binding sites for Fe(III) ions



Filtration

The polymer formed was filtered by filter paper. With the help of washing solvent the polymer was washed and the filtrate was wasted.

Washing of the polymer

Detachment of template is needed which is present inside the polymer. Polymer is thoroughly washed with an electrolyte to detach the template. The template ion leaves cavities of its own shape and size. 1 N HCl solution was used for the removal of template from the polymeric microspheres through sonication for 30 min (three times). Then it is filtered to remove the washing solvent and placed in vacuum chamber for drying of polymer. Further studies were carried out for dried polymer.

Only Ligand was added in place of complex to prepare the Non-IIP by the discussed method, the rest of the procedure is same.

Method of ion imprinted polymer for binding study

Fe(III) standard solution was prepared using distilled water as solvent. 15 mL plastic tubes was used in which 0.005 g of polymer was taken. To each tube, 10 mL of the $100 \mu\text{g mL}^{-1}$ Fe(III) standard solution was added. Briton Robinson buffer (0.1 M) was used to fix the pH at 2.5. The

sample was kept for shaking for 2 h at room temperature. Then it was filtered through a 13 mm PTFE syringe filter having pore size of $0.2 \mu\text{m}$. While optimizing the different components of the Fe(III)-IIP, Fe(III) ions determination in batch analysis was carried by a simple spectrophotometric method reported in the literature (Jeffery et al. 1989). In batch analysis, hydroxylamine hydrochloride was added to the free Fe(III) in the filtrate to reduce it to Fe(II). Then 1,10-phenanthroline solution was added to the Fe(II) in the presence of mL buffer, a colored complex was formed, the absorbance of it was measured with spectrophotometer at a wavelength of 510 nm. The free Fe(III) concentration was deducted from the starting amount of Fe(III) concentration to find the amount of Fe(III) bound to Fe(III)-IIP.

Column method

Borosilicate glass burette of 5 mL was used as a column (Z306843 Aldrich Volac[®] burette volume 5 mL, accuracy: 0.01 mL, subdivision, 0.02 mL, class A with certificate) for sorption studies of the Fe(III) ions. 0.3 g of Fe(III)-IIP was packed in the column. To equilibrate the column, 10 mL of water was added. The column was then loaded with solution of Fe(III) solution for 10 min. The solutions were then collected when the equilibration time was completed. Glass syringe fixed with nylon membrane filters having pore size of $0.45 \mu\text{m}$ was used to filter the solutions and finally analyzed by flame atomic adsorption spectroscopy.

Collection of drinking water

In high density polyethylene bottles, 1 L drinking water samples were collected from Shang valley of Besham in District Shangla. A convenient sampling plan was applied for collecting the samples from wells where as rapidly flowing shallow streams and rivers, and shallow (< 5 m) lakes are usually well mixed depth. Grab samples were conveniently collected by submerging a capped polyethylene bottles below the surface and removing the cap. After the sample bottle was filled, the cap was replaced and the bottle removed. 0.45 μm polycarbonate membrane Nucleopore filters (Millipore) was used to filter the water samples and then pH 2.5 was retained.

Results and discussion

Outcomes of the different amounts of components involve in the preparation of Fe(III)-imprinting polymer

pH effect for binding of Fe(III) ions

From the study of effect of the pH, it was found that the binding of Fe(III) to Fe(III)-IIP only takes place under acidic medium. Using 0.2 M Britton Robinson buffer, the pH was maintained in a range from 2 to 8 for the binding solutions.

50 mg of Fe(III)-IIP and 10 mL of the buffer solution that contains 1.0 gmL^{-1} of Fe(III) ions was equilibrated under varying pH condition for testing the effect of pH. From Fig. 2, it is clear that when the pH gets lower than 2.3 than the sorption quantity of iron (III) become very low due to protonation, but intensively increased with pH. The sorption quantity was quite constant after pH 2.5. Further experiments were carried out at pH 2.5 to evade hydrolyzing at greater pH values.

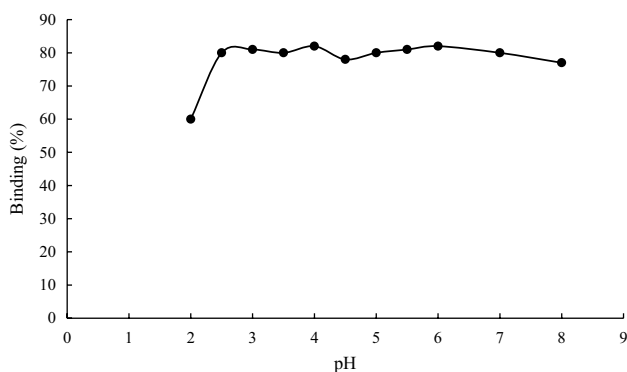


Fig. 2 Effect of pH on the retention of Fe(III) by Fe(III)-IIP

Cross-linker effect on synthesis of ion imprinting polymer of Fe(III)

Divinylbenzene was used as cross-linker for synthesis of Fe(III)-IIP in this work. The divinylbenzene was selected for using as cross-linker due to two reasons: first the size of poly divinylbenzene particle is commonly 1 μm in size when prepared in different solvent and, furthermore, it is suitable for solid phase extraction columns packing, second there is an additional p-p interaction of divinylbenzene with complex, thus efficiency of imprinting polymer has been increased (Jeffery et al. 1989; Singh and Mishra 2010a, b, c; Cui et al. 2013; Yilmaza et al. 2014). For cross-linker optimization, monomer amount and the Fe(III)-complex amount were kept as 0.5 mmol, and initiator amount was kept 20 mg. Cross-linker concentration (Fig. 3) was investigated in the range of (0.5–2.5 mmol). The optimum cross-linker amount was concluded as 2.5 after performing the binding experiments.

During polymerization experiments, by changing the concentration of cross-linker, the selectivity of the polymer was optimized for Fe(III) ions by varying the micro pore size. Concentration of cross-linker less than 2.5 mmol form larger size cavities in which the Fe(III) ions will bind loosely and hence can be detached easily. And when the cross-linker concentration is greater than 2.5 mmol the cavities formed are too small in which the Fe(III) cannot be sorbed easily.

Monomer effect on synthesis of ion imprinting polymer of Fe(III)

Methacrylic acid was used as monomer for the preparation of Fe(III)-IIP in this work. Methacrylic acid is known for narrow size distribution of the microspheres ultimately displaying a high ion recognition specificity. For the optimization of the amount of monomer, 2.5 mmol of cross-linker with 20 mg of initiator and 0.5 mmol of Fe(III)-complex

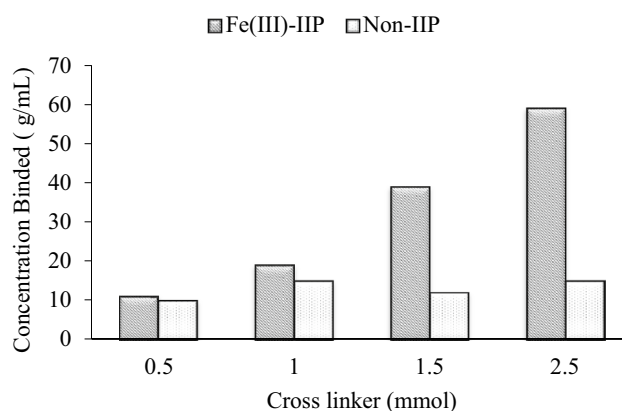


Fig. 3 Optimization of cross-linker for the preparation of ion imprinting polymer of Fe(III)

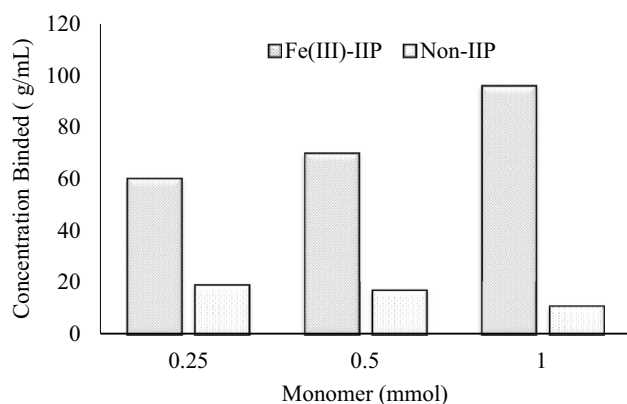


Fig. 4 Optimization of the amount of monomer for the preparation of IIP of Fe^{3+}

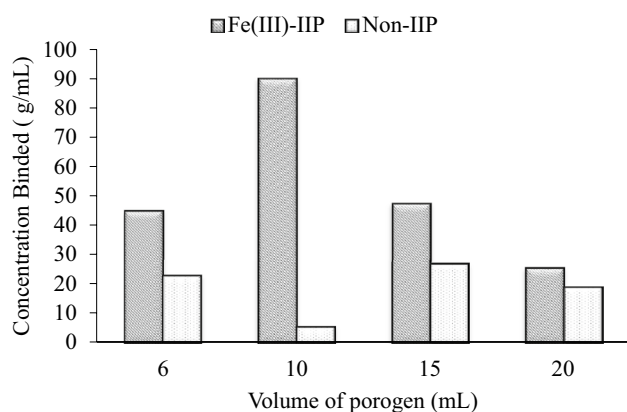


Fig. 5 Optimization of volume for the preparation of ion imprinting polymer of Fe^{3+}

was used. Monomer amount was investigated in the range of 0.25–1 mmol. The optimized value for monomer was concluded as 1 mmol after binding experiments (Fig. 4).

Porogen volume effect on the synthesis of Fe(III)-IIP

Due to the non-polarity of chloroform, a better imprinting was expected due to strong interaction of functional monomer with the Fe(III)-complex. By keeping the amounts of monomer, cross-linker and template (1, 2.5 and 0.5 mmol), respectively, chloroform effect was investigated in the range of (6–20 mL). From the results it was concluded that greater binding capacity was observed in polymer prepared in 10 mL of chloroform (Fig. 5).

The binding capacity of Fe(III) is higher in the polymer formed in 10 mL of porogen due to enough swelling of the polymer pores which resulted in the proper attachment of the Fe(III) ions. When the volume of porogen decreases

than 10 mL, the polymer pores shrined and the analyte was unable to get attached properly.

Polymers characterization

1 N HCl solution was used for washing the IIP and Non-IIP. Infrared spectroscopy, scanning electron microscope, thermogravimetric analysis was used to examine the dried powdered polymer.

Infrared analysis of Fe(III)-IIP and Non-IIP was done by KBr pellet method. The absorptions showed due to $\text{C}=\text{O}$ (1698 cm^{-1}) in the Infrared spectra confirmed the carbonyl group of the monomer, the $\text{C}-\text{H}$ stretching vibrations is shown by peaks at around (3000 cm^{-1}), also by broad band in the area of (2924 cm^{-1}). The strong $\text{C}=\text{C}$ bands (1458 cm^{-1}) corresponds to the aromatic ring of the cross-linker and the quinolone ring of the ligand. The di-substituted aromatic ring of divinylbenzene cross-linker is expressed by the bending absorption bands at (830 and 904 cm^{-1}). The mono-substituted aromatic ring of the 8-hydroxyquinoline ligand is shown by the bending bands at (709 and 796 cm^{-1}). The fact that Fe(III)-IIP and Non-IIP have comparable backbone [since the chemical composition of the leached Fe(III)-IIP and Non-IIP is same] is supported by similarity of fourier transform infrared spectra of the two polymers (Fig. 6).

Morphology of the polymers

Scanning electron microscopy was used to study morphology of the Fe(III)-IIP and Non-IIP. The average diameter of $1.0\text{ }\mu\text{m}$ was observed for the Fe(III)-IIP and Non-IIP. Micro particles are dispersed in a regular semi cluster pattern (Fig. 7).

Thermal stability of the polymer particles was also studied (Fig. 8). At $500\text{ }^\circ\text{C}$, about 85% of weight was lost in thermogravimetric plots. It shows the stability and strength of polymer.

Thermodynamic study

For thermodynamic study, from $100\text{ }\mu\text{g mL}^{-1}$ of Fe(III) solution, 10 mL was added to 0.5 mg of Fe(III)-IIP taken in glass tubes. By varying the temperature from 40 to $90\text{ }^\circ\text{C}$, these tubes were kept in water bath. With gradual increase in temperature the binding capacity decreases. For sorption process determination, thermodynamics parameters were calculated (Table 3). From the negative values of change in Free Energy and change in Enthalpy, it is concluded that the process is spontaneous and the reaction is exothermic. The positive value of change in Entropy support the exothermic spontaneous nature of sorption process and confirming the results.

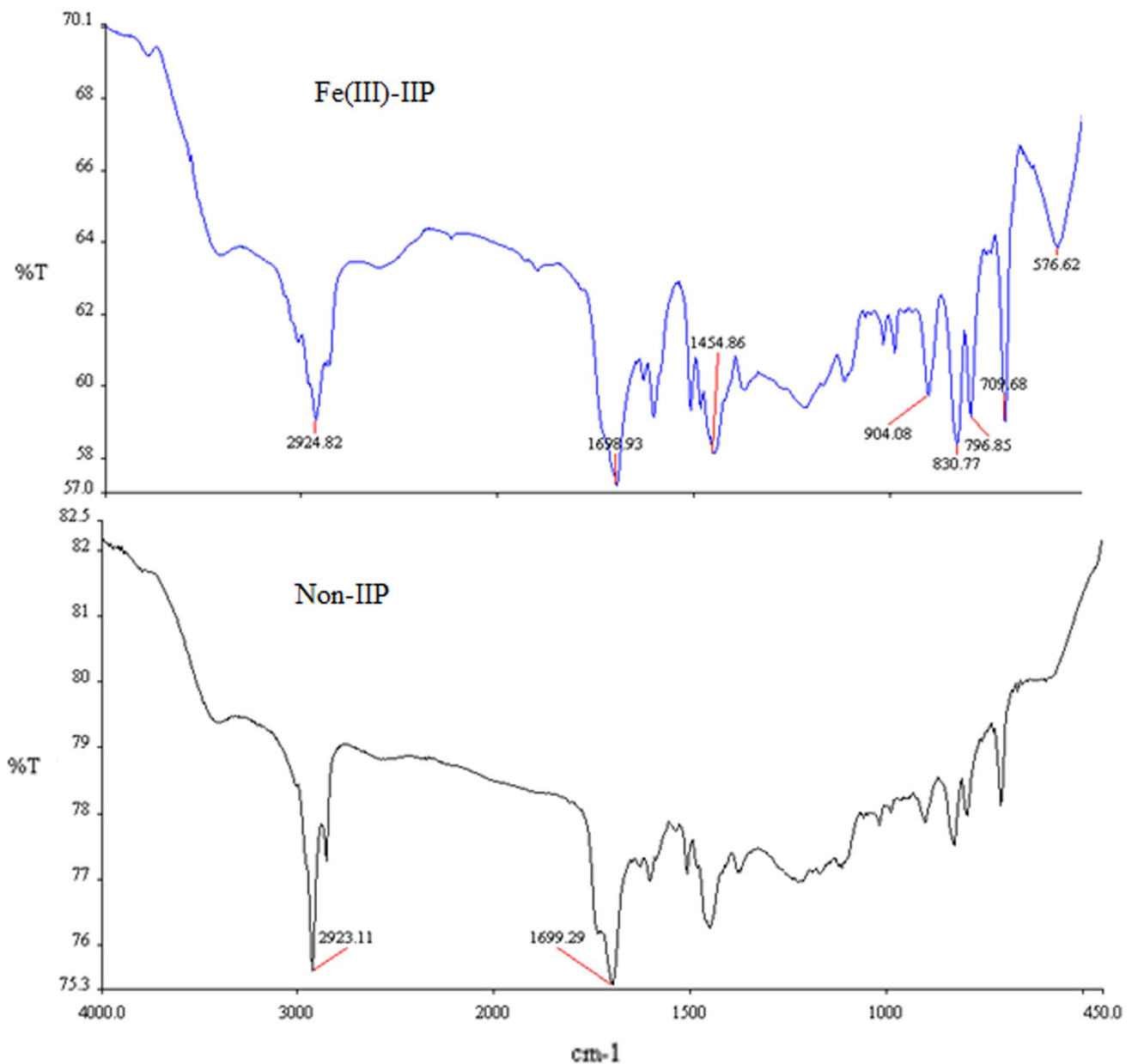


Fig. 6 Fourier transform-infrared spectra of Fe(III)-IIP and non-IIP

Kinetic study

Polymer of 0.015 g was added into 15 mL tube and 10 mL of $100 \mu\text{g mL}^{-1}$ of standard Fe(III) solution was added to the tube. The tubes were kept on shaker for various time interval of 30, 60, 90, 120 and 150 min for the kinetic study and the binding capacity was determined. Equilibration was achieved in 120 min.

The kinetic modeling (pseudo-first-order and pseudo-second-order models) for sorption of Fe(III) ions on the ion imprinted polymers was studied. Pseudo-first-order equation is as follow:

$$\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}, \quad (1)$$

where q_e is the amount of Fe(III) ion binded (mg g^{-1}) to the polymer at equilibrium, q_t is the amount of Fe(III) ion binded (mg g^{-1}) at any given time (min), k_1 is the pseudo-first-order reaction rate constant for the sorption of Fe(III) ions (min^{-1}). Pseudo-second-order equation is expressed as:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{K_2 q_e^2}, \quad (2)$$

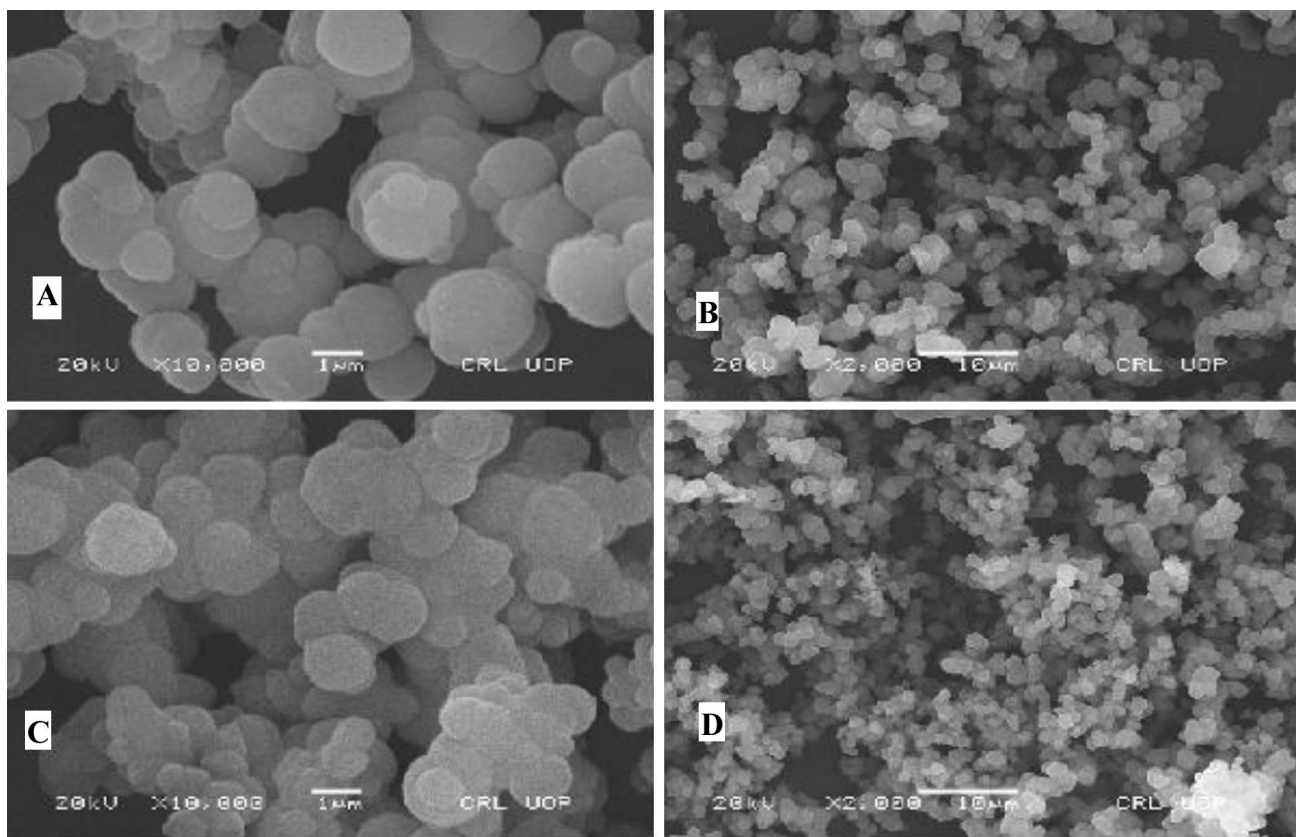


Fig. 7 Scanning electron micrographs of Fe(III)-IIP (a, b) and non-IIP (c, d) at 10,000 and 2000 magnification

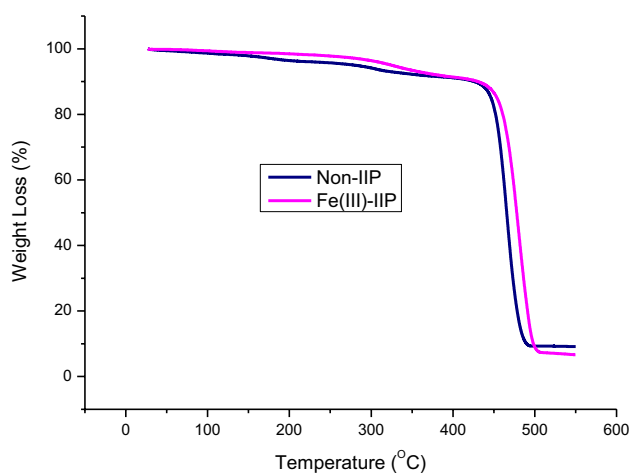


Fig. 8 Thermogravimetric analysis of a non-ion imprinting polymer and b Fe(III)-IIP

where q_e is the amount of Fe(III) ion binded (mgg^{-1}) to the polymer at equilibrium, q_t is the amount of Fe(III) ion binded (mgg^{-1}) at any given time (min), k_2 is the pseudo-second-order reaction rate constant for the sorption of Fe(III) ions (min^{-1}). The reaction follows first order kinetic

Table 3 Thermodynamic parameters studied for ion imprinting polymer (Fe(III)-ion imprinting polymer = 5 mg, volume of binding solvent 10 mL, equilibration time 2 h, pH 2.5)

Temperature (K)	ΔG (KJ/mol)	ΔH (KJ/mol)	ΔS (KJ/mol)
313	-17,617.44	-5.8198×10^7	4.5411×10^4
323	-15951.40		
343	-15,409.60		

mechanism as determined from the correlation values of the plots, thus it was established that the reaction is depending on amount of substrate only (Fig. 9).

Isotherms studies

Sorption behavior of Fe(III) ions on the Fe(III)-IIP is studied, Freundlich, Langmuir, Temkin and Dubinin–Radushkevich sorption isotherm were examined for their ability to model the equilibrium sorption data. The data for these isotherms are given in Table 4.

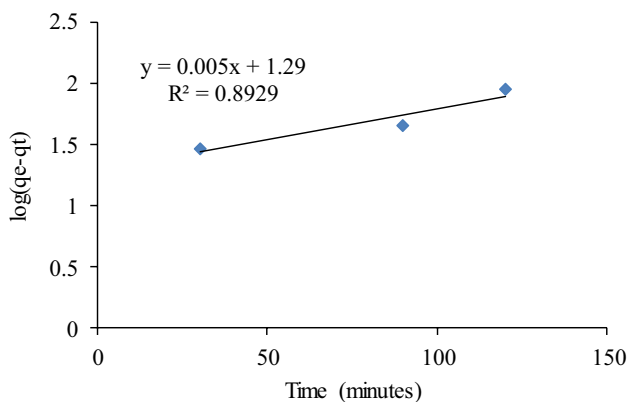


Fig. 9 Pseudo first order kinetic model for the sorption of Fe(III) on Fe(III)-IIP

Table 4 The studied isotherm parameters of Fe(III)-IIP

Parameter	Values
Langmuir	
Langmuir isotherm constant measure of maximum capacity K_L (mg/g)	500
Theoretical monolayer capacity (Q_0) (mg/g)	357.14×10^7
Bonding strength (aL)	1.4×10^{-7}
Correlation coefficient	0.9498
Freundlich	
Freundlich adsorption isotherm constant (K_F)	4×10^4
n	0.0005
Correlation coefficient	1
Temkin	
Temkin isotherm constant (A_T)	1.862×10^{-5}
Temkin constant related to heat of sorption (b_T)	0.2399
Correlation coefficient	0.9818
Dubinin–Radushkevich (D–R)	
Constant of the sorption energy (mol^2/J^2) (β)	0.0002
Theoretical monolayer sorption capacity (q_m)	1.462×10^{10}
Sorption energy E (kJ/mol)	50
Correlation coefficient	0.7345

Freundlich sorption isotherm

Freundlich isotherm depict non-ideal sorption on heterogeneous surfaces and is stated by the following equation:

$$q_e = K_F C_e^{\frac{1}{n}} \tag{3}$$

The logarithmic equation of Freundlich isotherm is given as:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e, \tag{4}$$

where K_F is the Freundlich sorption isotherm constant (mgg^{-1}), $1/n$ (gL^{-1}) is a measure of the sorption intensity of the polymer and q_e is the amount of Fe(III) ion sorbed (mgg^{-1}) and C_e is the equilibrium concentration of Fe(III) ions (μgmL^{-1}).

Freundlich sorption isotherm constant values were determined and are given as under:

$$K_F = 4 \times 10^4 \text{mgg}^{-1},$$

$$R^2 = 1,$$

where R^2 is correlation value from the graph (Fig. 10b).

Langmuir adsorption isotherm

The Langmuir isotherm expresses the monolayer sorption on a homogeneous surface and is given as the following equation:

$$q_e = \frac{K_L C_e}{1 + a_L C_e} \tag{5}$$

The linear form of the equation is as follows:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L C_e}{K_L}, \tag{6}$$

where C_e is the equilibrium concentration (μgmL^{-1}) of Fe(III) ions, q_e is the amount of Fe(III) ions sorbed per gram of polymer; K_L and a_L are the Langmuir sorption isotherm constants referring to the maximum capacity (Lg^{-1}) and bonding strength (Lmg^{-1}), respectively. The theoretical monolayer capacity is Q_0 and is numerically equal to K_L/a_L .

The correlation value of Freundlich adsorption isotherm is higher than Langmuir adsorption isotherm, which indicates there is a multilayer formation on heterogeneous surface (Fig. 10a).

Temkin sorption isotherm

Temkin and Pyzhev measured the effects of some indirect sorbate/sorbent interaction on sorption isotherms. They proposed that the heat of sorption of all the ions in the layer would decrease linearly with coverage because of sorbate/sorbent interaction. The general form of Temkin isotherm is as following:

$$q_e = \frac{RT}{b} \ln AC_e, \tag{7}$$

where the linear equation is as follows:

$$q_e = B \ln A + B \ln C_e. \tag{8}$$

In this equation, A is Temkin isotherm constant (L/g), $B = RT/b$, b is a constant related to heat of sorption (J/mol),

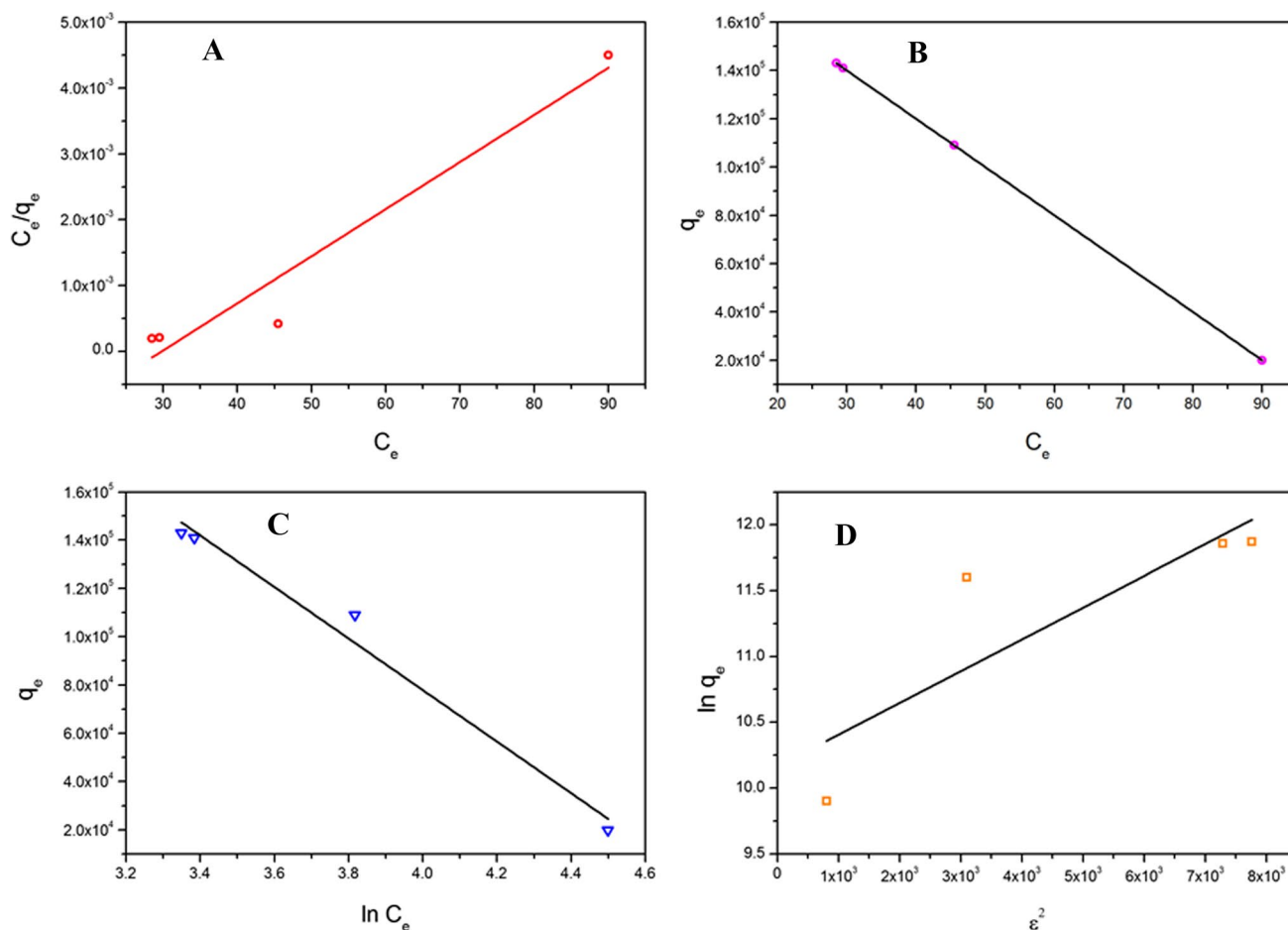


Fig. 10 Sorption isotherm for sorption of Fe(III) on Fe(III)-IIP, Langmuir sorption isotherm (a), Freundlich sorption isotherm (b), Temkin sorption isotherm (c), D–R sorption isotherm (d)

R is 8.314 J/mol K, and T is K. The linear form of the Temkin isotherm was used for analyzing the data and the linear plots are shown in (Fig. 10c). The b value shows that there is enough interaction between sorbate and sorbent for the sorption.

Dubinin–Radushkevich isotherm

The experimental data of sorption was also applied to the D–R model to determine the physical or chemical nature of it. The D–R isotherm in its linear form is presented in the following equation:

$$\ln q_e = \ln q_m - \beta \varepsilon^2, \quad (9)$$

where q_e is the amount of Fe(III) ions sorbed on the polymer (mol g^{-1}), q_m is for the theoretical monolayer sorption capacity of the polymer (mol/g), β is the constant of the sorption energy (mol^2/J^2), which is related to the average energy of sorption per mole of the Fe(III) ions as it is transferred to the

surface of the polymer from infinite distance in the solution, and ε is Polanyi potential, which is described as:

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right), \quad (10)$$

where T is the solution temperature (K) and R (gas constant) is equal to 8.314 J/mol K. The value of mean sorption energy, E (kJ/mol), can be calculated from D–R parameter β as follows:

$$E = \frac{1}{\sqrt{-2\beta}}. \quad (11)$$

The value of mean sorption energy indicates the chemical and physical sorption phenomena. The E value from 1 to 8 kJ/mol depict physical sorption and from 8 to 16 kJ/mol indicates chemical sorption. Values of q_m and β are calculated from the intercept and slope of the plot by plotting $\ln q_e$ versus ε^2 (Fig. 10d) and are listed in Table 4.

The *E* value in the process is investigated as 50 and hence the Dubinin–dushkevich sorption isotherm is not followed for the sorption phenomena of Fe ions on the Fe(III)-ion imprinted polymer. The results are supported by the facts that Dubinin–Radushkevich is suitable only for an intermediate range of ion concentration because it exhibit unrealistic asymptotic behavior.

Maximum sorption capacity

Maximum sorption capacity of the polymer was investigated on a series of concentrations of Fe(III) ions solutions, 5 mg of polymer was taken in conical flasks and 10 ml of Fe(III) solutions of various concentrations was added to it and placed on orbital shaker for 2 h at 100 rpm. The flasks were tightly covered with aluminum foil to avoid solvent evaporation. After 2 h of shaking, the solutions were centrifuged and supernatant was removed and the solutions were filtered with nylon filter paper of pore size 1 μm. Based on three replicate measurements, the maximum sorption capacity of Fe(III) on Fe(III)-IIP and Non-IIP was 170 ± 0.10 and $30.0 \pm 0.16 \mu\text{mol g}^{-1}$, respectively.

Foreign ions effect and selectivity studies

Common matrix ions, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , SO_4^{2-} and PO_4^{3-} were investigated for their effect on the adsorption of Fe(III) ions. A series of experiments were performed where

Table 5 The effect of foreign ions on the retention of 0.1 mg of Fe(III), pH 2.5

Interfering ions	Concentrations (mgL ⁻¹)	Recovery (%) ± <i>S</i>
Na ⁺	10,000	99 ± 1.15
K ⁺	1000	97 ± 2.32
Ca ²⁺	1000	98 ± 3.51
Mg ²⁺	1000	97 ± 2.25
SO ₄ ²⁻	1000	99 ± 4.01
PO ₄ ³⁻	1000	98 ± 2.57

Values are average ± standard deviation for replicate samples (*n* = 3)

Table 6 The effect of imprinting on the selectivity, recovery (% *R*), distribution ratios (*D*, mgL⁻¹), selectivity coefficients (*α*) and relative selectivity coefficients (*α_r*) for Fe(III)-IIP and NON-IIPr

Element	Fe(III)-ion imprinting polymer			Non-ion imprinting polymer			Relative selectivity coefficients
	Recovery (%)	Distribution ratios	Selectivity coefficient	Recovery (%)	Distribution ratio	Selectivity coefficients	
Fe(III)	99.6	2115	–	28.7	65	–	–
Fe(II)	19.0	14	151.0	31.8	69.9	30.2	5.0
Al	44.1	25	84.6	46.6	80.3	26.3	3.2
Cr	30.7	23	91.9	28.4	69.5	30.4	3.0

the metal ions were added individually to 0.1 mg Fe(III) ions (100 mL solution). The tolerance amount of these metal ions is summarized in Table 5.

From these experiments, it was found that the foreign ions have no significant effects on preconcentration of Fe(III) ions at pH 2.5. Since the method is not affected by relatively high concentrations of alkaline, alkaline earth metals, sulphate and phosphate ions, the presented method can be applied to various natural samples containing Fe(III) ions at even low concentrations. To examine the effect of various competitive cations; sorption of Fe(III)/Al(III), Fe(III)/Fe(II), Fe(III)/Cr(III) from their binary mixture of different concentrations was investigated, it was found that Al(III), Fe(II) and Cr(III) ions have no significant effects on the preconcentration of Fe(III) ions at pH 2.5. The tolerable amounts were defined as the maximum concentration that could cause a change of less than 5% in signal compared to the signal of each ion without any interference. As indicated in Table 5, at pH 2.5, transition metals have no interference and the method is selective toward Fe(III) ions. This high selectivity of the sorbent toward Fe(III) ions could be explained by imprinting techniques which was applied during synthesis of this sorbent. The affinity of the sorbet for Al(III) ions and Cr(III) ions do not show any change in distribution ratio (*D*) on Fe(III)-ion imprinting polymer and the corresponding Non-Ion Imprinting Polymer, suggesting their weak interaction with the sorbent and non-competitiveness for Fe(III)-imprinted sites on Fe(III)-IIP. The results are also supported by literature showing that at a pH of 2–2.5 aluminium (III) do not interfere (Wang and Liu 2014). The distribution ratio (*D*), the selectivity coefficient (*α*) and the relative selectivity coefficient (*α_r*) are shown in Table 6.

These values were calculated using the following equations (Behbahani et al. 2013; Nantasenamat et al. 2016; Yoshimatsu et al. 2007; Ye et al. 2002; Ara et al. 2012; Fu et al. 2015).

$$E(\%) = \left[\frac{C_o - C_e}{C_e} \right] \times \left[\frac{\text{volume of solution (mL)}}{\text{mass of resign(g)}} \right], \tag{12}$$

$$D = \frac{(C_o - C_e)}{C_e}, \tag{13}$$

$$\alpha = \frac{D_{\text{Fe}}}{D_{\text{m}}}, \tag{14}$$

$$\alpha_r = \frac{\alpha_{IIP}}{\alpha_{Non-IIP}} \quad (15)$$

Study of the sequential loading/elution cycles of the Fe-IIP support

Fe(III)-ion imprinting polymer were tested for the number of sequential loading/elution cycles to check the pre-concentration efficiency without prominent loss. Experiments were done by treating aqueous standard solutions containing 0.1 mgL^{-1} of Fe(III), and subjected to flame atomic adsorption spectroscopy measurement. Quantitative Fe recoveries (higher than 98%) were observed within the 15 loading/elution cycles, and analytical recoveries lower than 98% were obtained after that (Table 7). Therefore, ion imprinting polymer can be used at least 15 times without losing of efficiency of the adsorbent ion imprinting polymer for Fe determination.

Study of real drinking water sample

The samples were analyzed using the prepared polymers, these were collected from various sites which include both surface and ground water (such as springs, tube well, hand pumps, open streams and river Indus). The samples were prepared according to the "Collection of drinking water". The pH of the samples was adjusted to 2.5 and spiked with

Fe(III) ions. The amount of Fe(III) was determined as triplicate analysis (Table 8).

Conclusion

Ion imprinted polymers were prepared by taking Fe(III) ions used as template ions, the ligand used was 8-hydroxyquinoline for Fe(III) ions, divinylbenzene as cross-linker, methacrylic acid as monomer, and chloroform was used as porogen. Under specified pH condition 8-hydroxyquinoline has the application of highly selective ligand for iron (III) ions. The results are supported by the study of competitive and foreign ions on iron (III) ion imprinting polymer. Poly(methacrylic acid-co-divinylbenzene) showed strength and high stability with no degradation up to a temperature of $500 \text{ }^\circ\text{C}$. The prepared Fe(III)-ion imprinting polymer were successfully applied for the determination of Fe(III) ions in the drinking water of valley Shang in Besham of District Shangla.

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Table 7 Effect of reused times on the recovery of the Fe(III)-IIP (10 mL of sample: pH 2.5, mean value, $n = 3$)

Cycle number	Recovery (%)	Cycle number	Recovery (%)	Cycle number	Recovery (%)	Cycle number	Recovery (%)
1	99.8	6	99.0	11	98.6	16	97.8
2	99.6	7	98.8	12	98.3	17	97.8
3	99.6	8	98.8	13	98.0	18	97.7
4	99.2	9	98.8	14	98.0	19	97.7
5	99.0	10	98.6	15	98.0	20	97.6

Table 8 Recovery of Fe(III) ions from various samples after its separation on Fe(III)-ion imprinting polymer (100 mL of sample: pH 2.5, mean value, $n = 3$)

Sample no.	Samples	Concentration of Fe(III) found (mgL^{-1})	Concentration of Fe(III) added (mgL^{-1})	Recovery (%)
1	1 (spring)	0.08	100	99.7 ± 2.8
2	2(main reservoir-water tank)	3.40	100	98.4 ± 1.8
3	3 (tube well)	3.72	100	94.5 ± 3.4
4	4 (spring)	2.01	100	97.9 ± 4.9
5	5 (spring)	1.10	100	98.7 ± 2.2
6	6 (stream)	2.47	100	97.1 ± 4.1
7	7(spring)	1.22	100	97.6 ± 5.6

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