

Preconcentration of Fe(III) Using Fe(III)-Ion Imprinted Polymeric Traps and Its Analytical Performance for FAAS

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Abstract

Novel Fe(III)-imprinted beads were prepared by molecular imprinting technique for selective solid-phase extraction (SPE) of Fe(III) ions prior to its determination by flame atomic absorption spectrometry (FAAS). The functional metal-complexing monomer and crosslinking monomer used were methacrylamidoantipyrine (MAAP) and ethyleneglycol dimethacrylate (EGDMA), respectively. MAAP was synthesized using methacryloylchloride, 4-aminoantipyrine and pyridine. Fe(III) ions were complexed with MAAP and the Fe(III)-imprinted poly(MAAP-EGDMA) beads were synthesized by suspension polymerization. After that, the template ions (i.e., Fe(III) ions) were removed using 4.0 M HNO₃ solution. The specific surface area of the Fe(III)-imprinted and non-imprinted poly(MAAP-EGDMA) beads was found to be 1181.45 m²/g and 437.94 m²/g, respectively. The swelling ratio was 60% and 47% for imprinted and non-imprinted beads, respectively. According to the elemental analysis results, the beads contained 119.0 μmol MAAP/g polymer. The maximum adsorption capacity, optimum pH and equilibrium binding time were 29.32 mg/g, 4.0 and 80 min, respectively. Selectivity coefficients for Al(III), Cu(II), Zn(II) and Co(II) ions were compared with Fe(III) ion. Fe(III)-imprinted beads showed the following order of metal ion affinity: Fe(III)>Zn(II)>Cu(II)>Co(II)>Al(III). The Fe(III)-imprinted poly(MAAP-EGDMA) beads could be used many times without decreasing their adsorption capacities significantly.

Key Words: Ion imprinting (IIP), FAAS, Fe(III) ion, preconcentration, solid phase extraction.

Introduction

Iron is the most abundant trace mineral in the body and is an essential element in most biological systems (1,2). It is likely that iron was essential for developing aerobic life on Earth (3). But iron is toxic to cells in excessive amounts. Acute iron poisoning is common and potentially lethal in dogs, cats, and many other animals. Iron is also a leading cause of unintentional poisoning deaths in children less than 6 years old (4). The toxicity of iron is related to its ability to induce oxidative stress in cells (5). In an occupational setting, inhalation exposure to iron oxide may cause siderosis. In the nonoccupational population, ingestion of large quantities of iron salts may cause nausea, vomiting, and intestinal bleeding. There is accumulating evidence suggesting that an increase in iron storage may be associated with an increasing risk of developing cancer (6). For these reasons, separation of iron ions is very important. In recent years, continuous progress in analytical chemistry have produced an important development of new chemical separation/preconcentration techniques for metal ions such as ion exchange (7), precipitation and coprecipitation (8), sol-

vent extraction (9), chemical and biosorption (10-12), cloud-point extraction (13), solid phase extraction (14), and on-line flow injection (15). Of all the preconcentration methods, solid-phase extraction (SPE) method is one of the most effective multielement preconcentration methods because it can provide more flexible working conditions and simple operation (16-19), and become known as a powerful tool for separation and enrichment of various inorganic and organic analytes (20-22). Numerous substances have been used as solid-phase extractants, such as XAD resins (19), ion exchange resins (23), silica gel (24), cellulosic derivatives (25), polyurethane foam (26), C18 (27), active carbon (28), and molecular imprinted polymer (29-32).

Molecular imprinting is a technique for preparing polymeric materials that are capable of high molecular recognition. In molecular imprinting, a molecular "memory" is introduced on the polymer. Molecular imprinted polymers (MIPs) are capable of recognizing and binding the desired molecular target with a high affinity and selectivity (33). Because of the highly crosslinked polymeric nature of MIP materials, they are intrinsically stable and robust. Moreover, MIP materials are low cost to produce and can be stored in a dry state at room temperature for long periods of time (34). Ion-imprinted polymers (IIPs) are similar to MIPs, but they can recognize metal ions after imprinting and retain all the virtues of MIPs (35,36). IIPs have outstanding advantages such as predetermined se-

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lectivity in addition to being simple and convenient to prepare. A particularly promising application of IIPs is the solid-phase extractive preconcentration of analytes present in low concentration or the separation from other coexisting ions or complex matrix. Thus, ion-imprinted polymers for solid-phase extraction is a fast developing area for the application of ion imprinting technology (37).

In this paper, we prepared ion-imprinted polymer beads, which were used for the molecular recognition based removal of Fe(III) ions from water sample. We used molecular imprinting approach to achieve specific metal binding utilizing methacrylamidoantipyrine (MAAP) as a metal-complexing ligand. After removal of Fe(III) ions, Fe(III)-imprinted beads (IIPs) were used in adsorption and desorption process. Maximum binding capacity, optimum pH, and equilibrium binding time were studied. Fe(III) adsorption on IIP beads, selectivity studies of Fe(III) ion versus other interfering metal ions mixture (Al(III), Cu(II), Co(II), and Zn(II)) were reported. Finally, repeated use and adsorption isotherm of the IIP beads were also discussed.

Materials and Methods

Materials

Methacryloylchloride was supplied by Sigma (St. Louis, USA) and used as received. Ethyleneglycoldimethacrylate (EGDMA) and α,α' -azobisisobutyronitrile (AIBN) were obtained from Fluka (Buchs, Switzerland). Poly(vinyl alcohol) (PVA; MW:10,000, 98% hydrolyzed) was supplied by Aldrich (USA). All other chemicals were of reagent grade and were purchased from Merck (Darmstadt, Germany). Laboratory glassware was kept overnight in a 5% nitric acid solution. Before use, the glassware was rinsed with deionized water and dried in a dust-free environment. Stock solution of 1000 mg/L Fe(III) was prepared by dissolving iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (Merck, Darmstadt, Germany) in deionized water. Standard iron solutions were prepared daily by dilution of the stock solution. All water used in the experiments was purified using a Barnstead D2731 (Dubuque, IA, USA) ROpure LP reverse osmosis unit with a high flow cellulose acetate membrane (Barnstead D2731) followed by a Barnstead D3804 NaNO_2 pure organic/colloid removal and ion-exchange packed-bed system.

Preparation of Fe(III)-Imprinted Beads

Synthesis of Methacrylamidoantipyrine (MAAP) Monomer

The following experimental procedure was applied for the synthesis of MAAP (38). 4-aminoantipyrine (0.5 g; 2.463 mmol) and pyridine (0.2 mL; 2.46 mmol) were dissolved in 100 mL of dry CHCl_3 and the solution was cooled to 0°C. Then, methacryloylchloride (0.26 mL; 2.46 mmol) was poured slowly into this solution while stirring magnetically at room temperature for 2 h. At the end of this chemical reaction period, the mixture was washed with 50 mL of dilute HCl solution and 50 mL of dilute NaOH solution. Then, the organic phase was evaporated in a rotary evaporator and the residue was crystallized in

petroleum benzene ethylacetate.

The ^1H NMR spectrum of MAAP monomer was taken in CDCl_3 on a Bruker-Spectrospin Avance DPX 400 ultra-shield instrument (USA). The residual non-deuterated solvent (CHCl_3) served as an internal reference. Chemical shifts are reported in ppm (d) downfield relative to CHCl_3 . ^1H NMR spectrum indicates the characteristic peaks from the groups in MAAP monomer. These characteristic peaks are as follows: ^1H NMR (CDCl_3): 2.05 ppm 3 singlet ($-\text{C}=\text{C}-\text{CH}_3$, vinyl methyl), 3.0 ppm 3 singlet ($-\text{C}-\text{CH}_3$), 3.35 ppm 3 H singlet ($-\text{N}-\text{CH}_3$), 5.5 ppm 1 H singlet ($-\text{CH}_a-\text{C}$), 5.8 ppm 1 H singlet ($-\text{CH}_b-\text{C}$), 7.25–8.80 ppm 4 H multiplet (aromatic, CDCl_3 peak is also observed at 7.3 ppm with aromatic peaks), 8.80 ppm 1 H singlet (aromatic), 9.1 ppm 1 H singlet (N-H).

Synthesis of MAAP-Fe(III) Preorganized Complex

In order to prepare MAAP-Fe(III) complex, solid MAAP (0.552 g, 2.0 mmol) was added slowly into 20 mL of methanol and then treated with iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) (0.404 g, 1.0 mmol) solution at room temperature with continuous stirring for 4 h. At the end of this period, the MAAP-Fe(III) complex was filtered, washed with 96% ethanol and then dried 2 days in a vacuum oven.

Synthesis of Fe(III)-Imprinted Beads

MAAP was chosen as functional monomer, Fe(III) ion as template, EGDMA as crosslinker and AIBN as initiator for the synthesis of Fe(III) imprinted poly(MAAP-EGDMA) (IIP) beads. IIPs were prepared by suspension polymerization technique. In a typical procedure the dispersion medium was prepared by dissolving 0.2 g polyvinylalcohol in 60 ml of distilled water. $(\text{MAAP})_2\text{-Fe(III)}$ complex was dissolved in 6.0 ml of ethyl alcohol. Then, this solution was mixed with 8.0 ml/12.0 ml EGDMA/toluene mixture and 0.06 g of AIBN was dissolved within this monomer mixture. The organic phase was dispersed in the aqueous medium by stirring the mixture magnetically (650 rpm) in a glass polymerization reactor (volume: 100 ml). The reactor was flushed by bubbling nitrogen gas and then sealed. The reactor content was heated to polymerization temperature (i.e. 70°C) and the polymerization was conducted for 7h. Then, temperature was increased to 90°C and the polymerization was conducted for further 4h. Final beads were extensively washed with ethanol and water to remove any unreacted monomer or diluent and then stored in distilled water at 4°C. Non-imprinted poly(MAAP-EGDMA) beads (NIP) were prepared in the same way, but without addition of template ions into polymerization medium.

After the cleaning procedure, the template Fe(III) ions were removed from the polymer beads using 4.0 M HNO_3 solution. The IIP beads were added into the 4 M HNO_3 solution for 24 h at room temperature. This procedure was repeated several times until the template molecule (i.e. Fe(III)-ions) could not be detected in the filtrate with a flame atomic absorption spectrophotometer (FAAS). The template free beads were washed with

cleaning solution (1:1 water-ethanol mixture, v/v) and deionized water and then dried for 2 days in a vacuum oven.

Characterization of IIP Beads

The specific surface area of the beads was measured by Brunauer-Emmett-Teller (BET) model using single point analysis and a Flowsorb II 2300 from Micromeritics Instrument Corporation (Norcross, USA). Water uptake properties of the IIP and NIP beads were determined by volumetric method. In this method, the dry beads of 100 mg were placed in cylindrical tubes and the top point of the tube was marked. Then, the tubes were filled with distilled water and the beads were allowed to swell at room temperature. The height of the beads were marked every 30 min. The height of swollen beads in the tube was used to calculate the swelling ratio by using the following equation (1):

$$\text{Swelling ratio (\%)} = [(h_{\text{swollen}} - h_{\text{dry}}) / h_{\text{dry}}] \times 100 \quad (1)$$

where h_{swollen} is the height of the swollen beads and h_{dry} is the height of the dry beads.

To evaluate the degree of MAAP incorporation poly(MAAP-EGDMA) beads were subjected to elemental analysis using a Leco Elemental Analyzer (Model CHNS-932). FTIR spectroscopy was used in the 4000-400 cm^{-1} range to investigate the chemistry of MAAP monomer, MAAP-Fe(III) complex and IIP beads in the solid state (FTIR 100 series, Perkin Elmer, USA). Surface morphology and internal structure of the poly(MAAP-EGDMA) beads were investigated by scanning electron microscope (JEOL, JEM 1200EX, Tokyo, Japan). The samples were dried at room temperature and coated with a thin layer of gold (about 100 Å) in vacuum and photographed in the electron microscope with x1000 magnification.

Adsorption studies

The batchwise adsorption tests of Fe(III) ions were studied for the IIP and NIP beads. Nitrate salt ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was used as the source of Fe(III) ions. Effects of pH (2-5) and initial concentration of Fe(III) (5-40 mg/L) on the adsorption rate and capacity were investigated. The suspensions were brought to the desired pH by adding sodium hydroxide and nitric acid. The pH was maintained in a range of ± 0.1 U until equilibrium was attained (Fisher Scientific, Accumet Basic AB15 pH meter). Solutions were treated with IIP and NIP beads at 25°C, in the flasks stirring magnetically at 400 rpm. The concentration of the metal ions in the aqueous phases after desired treatment periods were measured by using FAAS. Perkin Elmer A Analyst 800 atomic absorption spectrophotometer with deuterium background correction was used for the determination of iron and other metals studied. Iron absorbance measurements were made at 248.3 nm using spectral bandwidth of 0.5 nm with Perkin Elmer™ Lumina™ Lamp operating at 7.5 mA.

The equilibrium adsorption of Fe(III) on the microbeads, q_e , was determined from the difference in equilibrium

concentration of Fe(III) in the solution at the end of each period, C_e , and the initial concentration of Fe(III), C_0 , according to the following equation:

$$q_e = (V_L / W_G)(C_0 - C_e) \quad (2)$$

where V_L and W_G are the volume of solution (25 mL) and the weight of the dry microbeads (0.025 g), respectively. The experiments were performed in replicates of three and the samples were analyzed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean values and standard deviations. Confidence intervals of 95% were calculated for each set of samples in order to determine the margin of error.

For the preconcentration of Fe(III) ions, 100 mL of the aqueous solution containing 1.0 ng/mL of Fe(III) was treated with 25 mg IIP beads (pH 4.0) for 80 min at 25°C. Finally, IIP beads were separated from the adsorption media by filtration and 0.1 M 10 mL HNO_3 solution was added. IIP beads were separated from the desorption media and the samples from the desorption media was injected to FAAS system.

Desorption and Reusability

Desorption of Fe(III) ions was performed with 0.1 M HNO_3 solution. The Fe(III)-imprinted beads were placed in this desorption medium and stirred continuously (at a stirring rate of 600 rpm) for 1 h at room temperature. The final Fe(III) ions concentration in the desorption medium was measured by FAAS. The desorption ratio was calculated from the amount of Fe(III) adsorbed on the beads and the final Fe(III) ions concentration in the desorption medium. In order to test the reusability of the IIP beads Fe(III) ion adsorption-desorption procedure was repeated ten times using the same beads.

Selectivity Experiments

In order to show Fe(III) specificity of the IIP beads, competitive adsorption experiments of Al(III), Zn(II), Co(II), and Cu(II) ions were also studied with IIP and NIP beads. The beads (25 mg) were added to 25 ml of aqueous mixture solution of containing 5 mg/L of Fe(III), Al(III), Zn(II), Co(II), and Cu(II) (pH: 4.0) placed in a reaction vessel stirring magnetically (600 rpm) at 25°C. After adsorption equilibrium, the concentration of each ions in the remaining solution was measured by FAAS.

Distribution and selectivity coefficients of each ion with respect to Fe(III) were calculated by the following equation:

$$K_d = [C_i - C_f / C_f] \times V / m \quad (3)$$

where K_d is distribution coefficient, C_i and C_f are the initial and final solution concentrations, respectively, V the volume of solution used for the extraction (mL) and m is the weight of beads used for extraction (g).

The selectivity coefficient (k) for the binding of a specific

metal ion in the presence of competitor species can be obtained from equilibrium binding data according to equation 4:

$$k = K_{d(\text{template metal})} / K_{d(\text{interferent metal})} \quad (4)$$

A comparison of the k values of the imprinted beads with those metal ions allows an estimation of the effect of imprinting on selectivity. A relative selectivity coefficient k' can be defined as:

$$k' = k_{\text{imprinted}} / k_{\text{control}} \quad (5)$$

Results and Discussion

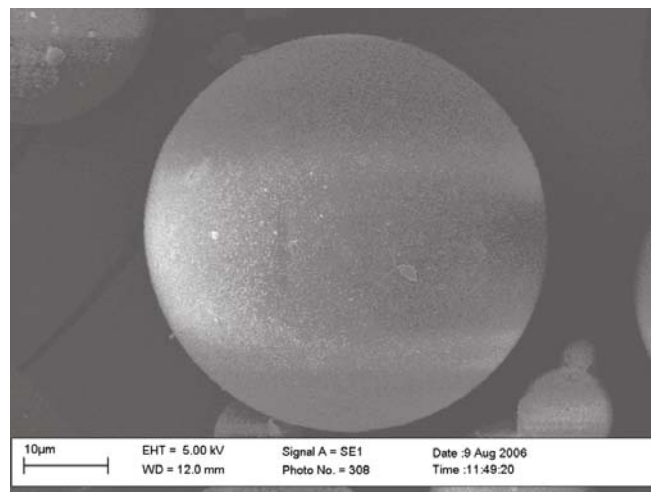
Characterization of Fe(III)-Imprinted Beads

FT-IR spectrum of MAAP monomer includes the following characteristic peaks; FT-IR (KBr, cm^{-1}): 1667 cm^{-1} amide carbonyl band, 3444 cm^{-1} N-H band, 3528 cm^{-1} N-H band. FT-IR spectra of the MAAP-Fe(III) complex is given below: FT-IR (KBr, cm^{-1}): 1603 cm^{-1} (amide carbonyl band), 3313 cm^{-1} (N-H band), 2975 and 2925 cm^{-1} (C-H band), 3553 cm^{-1} (-OH band), 472 and 647 cm^{-1} (Fe-O band). When the possible interactions between Fe(III) and "O" atoms were considered, it has been concluded that Fe(III) ion has mainly coordinated to the "O" atom of the carbonyl (C=O) groups of MAAP; because the considerable changes in the infrared frequencies were observed only for those bands containing (C=O) groups.

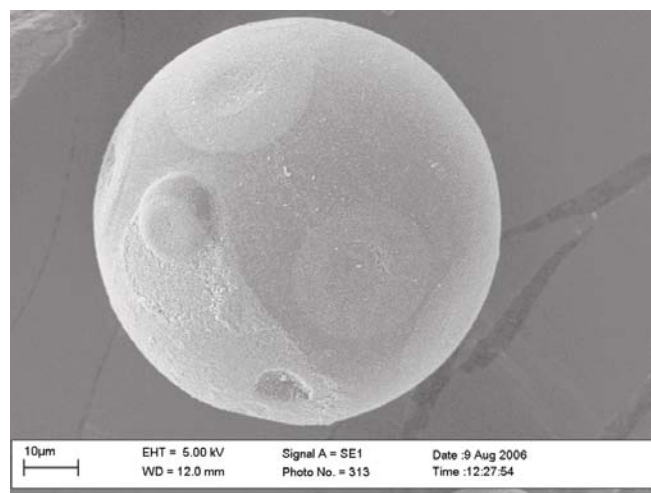
FT-IR spectra of IIP beads have the following peaks; FT-IR (KBr, cm^{-1}): 1639 cm^{-1} (amide carbonyl band), 3469 cm^{-1} (CONH band), 2992 and 2959 cm^{-1} (C-H band), and 655 cm^{-1} (Fe-O band).

The specific surface area of the beads in dry state was determined by the multi-point BET method with nitrogen as sorbate with experimental error $\pm 0.2 \text{ m}^2/\text{g}$. The specific surface area of the NIP and IIP beads which are crosslinked matrices was found to be 437.94 m^2/g and 1181.45 m^2/g , respectively. The equilibrium swelling ratios of the NIP and IIP particles were found as 47% and 60%, respectively. Compared with the NIP beads, both the surface area and the water uptake ratio of the IIP beads increases due to formation of metal ion cavities in the polymer structure. These cavities in the polymer structure introduce more hydrodynamic volume into the polymer chains, which can result in uptake of more water molecules by polymer matrix. The porous character of the beads are exemplified by the scanning electron micrographs in Figure 1.

According to the results of elemental analysis, MAAP incorporation was found to be 119.0 μmol MAAP/g polymer by using nitrogen stoichiometry. This nitrogen amount determined by elemental analysis comes from only incorporated MAAP groups into the polymeric structure.



(a)



(b)

Figure 1. SEM photograph of a) IIP b) NIP beads.

Adsorption Studies of Fe(III)-Imprinted Beads

Effect of pH

The metal ion complexation of polymeric ligands is highly dependent on the equilibrium pH of the medium. In the absence of complexing agent, the hydrolysis and precipitation of metals ions are affected by the concentration and formation of soluble metals species. Iron hydroxide precipitation occurs above pH 4.5 which also depends on the concentration of iron in the medium. In the present study, we changed the pH between 2.0 and 5.0. The effect of pH on the Fe(III) binding onto IIP beads was shown in Figure 2. The IIP beads exhibited low affinity in hard acidic conditions (pH 2.0), somewhat higher affinity at pH 4.0. The increasing pH of the solution favors complex formation between the carbonyl groups of MAAP in the ion cavities and iron ions.

Effect of Time

Figure 3 shows the time dependence of the adsorption capacities of Fe(III) ions on IIP beads. As seen here, iron adsorption increases with the time during the first 50 min and then levels off as equilibrium is reached within 80

min. This fast adsorption equilibrium is most probably due to high complexation and geometric shape affinity (or memory) between Fe(III) ions and Fe(III) cavities in the beads structure. It is well known that removal of the template from the beads matrix leaves ion cavities of complementary size, shape and chemical functionality to the template.

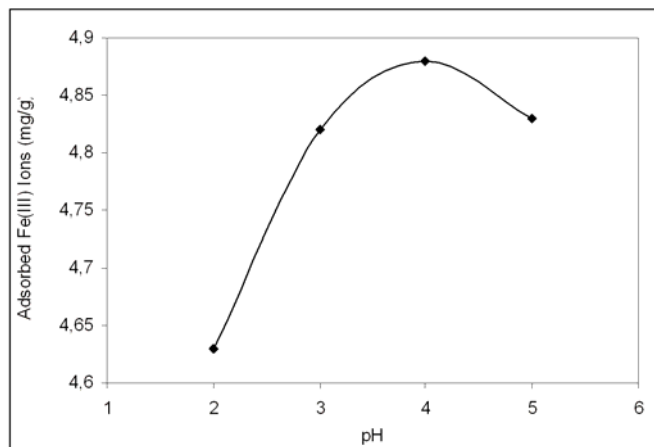


Figure 2. Effect of pH on the Fe(III) binding onto IIP beads. Fe(III) concentration: 5 mg/L; T: 25°C.

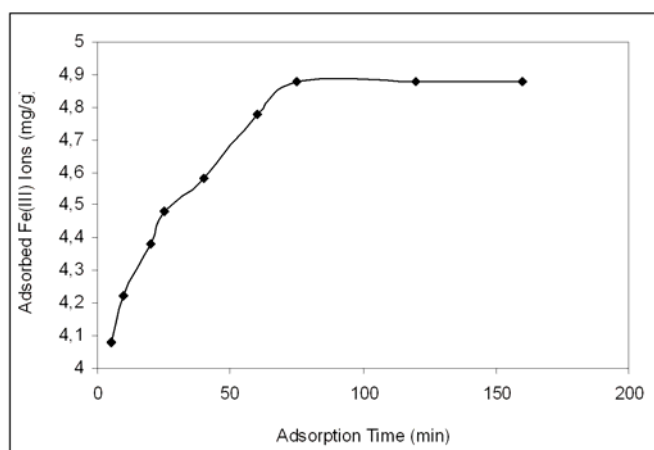


Figure 3. Effect of time on Fe(III) adsorption; Fe(III) concentration: 5 mg/L; pH.4.0, T: 25°C.

Effect of Fe(III) Ion Concentration

Figure 4 shows the equilibrium concentration dependence of the adsorbed amount of Fe(III) onto the IIP beads. The adsorption values increased with increasing concentration of Fe(III) ions, and a saturation value is achieved at ion concentration of 40 mg/L, which represents saturation of the active binding cavities on the IIP beads. Mass transfer limitations were also overcome by high driving force, which was the concentration difference of Fe(III) ions between the liquid and the solid phases, in the case of high Fe(III) concentration. The maximum Fe(III) adsorption capacity of the imprinted beads was 29.32 mg/g.

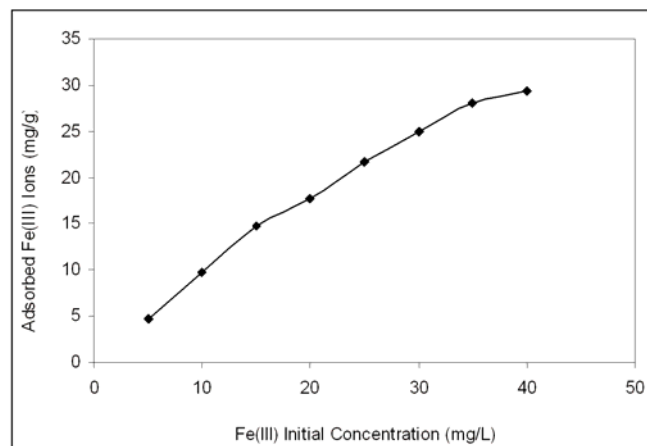


Figure 4. Adsorption isotherm of IIP beads. pH, 4.0; T, 25°C.

An adsorption isotherm is used to characterize the interactions of each molecules with the adsorbents. This provides a relationship between the concentration of the ions in the solution and the amount of ion adsorbed on the solid phase when the two phases are at equilibrium. The Langmuir adsorption model assumes that the molecules are adsorbed at a fixed number of well-defined sites, each of which is capable of holding only one molecule. These sites are also assumed to be energetically equivalent, and distant from each other so that there are no interactions between molecules adsorbed on adjacent sites.

During the batch experiments, adsorption isotherms were used to evaluate adsorption properties. Equation 6 expresses the Langmuir adsorption isotherm:

$$Q = Q_{\max} \cdot b \cdot C_{\text{eq}} / (1 + bC_{\text{eq}}) \quad (6)$$

where Q is the adsorbed amount of Fe(III) (mg/g), C_{eq} the equilibrium Fe(III) concentration (mg/mL), b is the Langmuir constant (mL/mg), and Q_{\max} is the maximum adsorption capacity (mg/g).

The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of the monolayer. This empirical equation takes the form:

$$q = K_F C_{\text{eq}}^{1/n} \quad (7)$$

where K_F and n are the Freundlich constants.

Table 1 shows the kinetic constants of Langmuir and Freundlich isotherms. According to the correlation coefficients of isotherms, Langmuir adsorption model is most favorable.

Selectivity Studies

Adsorption capacities of the IIP and NIP beads for metal ions under competitive conditions (i.e. adsorption from solutions containing 5 mg/L from each of Fe(III)/Al(III), Fe(III)/Zn(II), Fe(III)/Co(II) and Fe(III)/Cu(II) ions) are given Table 2.

Table 1. Langmuir and Freundlich adsorption constants for IIP beads.

Beads	Q_{ex} (mg/g)	Langmuir Constants			Freundlich Constants		
		Q_{max}	b	R^2	K_F	n	R^2
IIP	29.32	28.7	3.3	0.976	14.9	0.343	0.960

Table 2. Competitive adsorption of Fe(III) and interfering metal ions onto IIP and NIP beads.

Metal Ion	Adsorption Capacity (mg/g)	
	IIP Beads	NIP Beads
Fe(III)	4.927	4.369
Al(III)	3.563	4.488
Co(II)	4.486	4.873
Zn(II)	3.342	4.759
Cu(II)	3.697	4.695

The Fe(III) adsorption capacity of the IIP beads was much higher than that of other metal ions. The competitive adsorption capacity of the IIP beads for Fe(III) ions was also higher than NIP beads. When they exist in the same medium, a competition will start for the same attachment sites. Fe(III)-imprinted beads showed the following metal ion affinity order under competitive conditions: Fe(III)>Zn(II)>Cu(II)>Co(II)>Al(III). It should be noted that the imprinted beads showed excellent selectivity for the target molecule (i.e. Fe(III) ions) due to molecular geometry.

The relative selectivity coefficient (k') resulting from the comparison of the k values of the IIP beads with NIP beads allows an estimation of the effect of imprinting on selectivity. The K_D and k values of Fe(III) imprinted beads are significantly larger in comparison to the interfering metal ions. These results show that relative selectivity coefficients for IIP beads for Fe(III)/Cu(II), Fe(III)/Al(III),

Table 3. The effect of imprinting on selectivity

Metal ion	Fe(III)-Imprinted beads		Non-imprinted beads		k'
	K_D	k	K_D	k	
Fe(III)	67627	-	6923	-	-
Al(III)	2479	27.28	8765	0.79	35.5
Co(II)	8727	7.75	38370	0.18	43.1
Zn(II)	2015	33.56	19746	0.35	95.9
Cu(II)	2837	23.83	15393	0.45	52.9

Fe(III)/Zn(II), and Fe(III)/Co(II) were 52.9, 35.5; 95.9; and 43.1 times greater than non-imprinted matrix, respectively (Table 3).

Desorption and Repeated Use

The regeneration of the adsorbent is likely to be a key factor in improving process economics. Desorption of the adsorbed Fe(III) ions from the IIP beads was also performed in a batch experimental set up with 0.1 M HNO₃ solution. Various factors are probably involved in determining rates of Fe(III) desorption, such as the extent of hydration of the metal ions and polymer microstructure. However, an important factor appears to be binding strength. In this study, desorption time was chosen to be 1 h. Desorption ratios were high (up to 99%). In order to show the reusability of the IIP beads, adsorption-desorption cycles were repeated 10 times by using the same IIP beads. The adsorption capacity of the recycled IIP beads can still be maintained at 99% of its original value at the 10th cycle (Figure 5). It can be concluded that the IIP beads can be used many times without decreasing their adsorption capacities significantly.

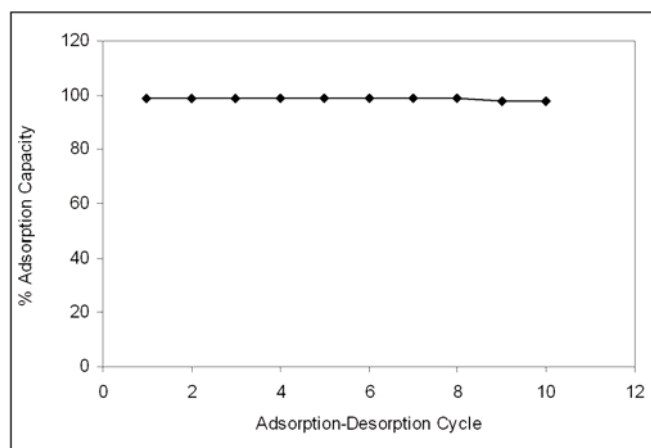


Figure 5. Reusability of IIP beads

Analytical performance of the methods

The characteristic performance data for the off-line pre-concentration procedure were given in Table 4.

Table 4. Performance characteristics of the preconcentration procedure.

Parameters	Fe(III)
Precision (R.S.D)	3.7%
Detection limit (3s)	1.23 ng/mL
Linear calibration range	0.5-25 ng/mL
Regression equation (after preconcentration)	AA=0.0013Fe -0.0001 ng/mL
Conventional regression equation	AA=0.0032Fe + 0.0035 µg/mL
Enrichment factor	0.0013ng/mLx1000mg/mL/0.0032 = 406

The precision of the method for a standart, evaluated as the relative standart deviation (R.S.D: n=7) was 3.7 ng/mL Fe (III) ions. The detection and determination limits, defined as the concentration of analyte giving signals equivalent to three and ten times, respectively, the standart deviation of the blank plus the net blank intensity for 100 mL of sample volume, were 1.23 and 3.92 ng/mL. The preconcentration procedure showed a linear curve within the concentration range from 0.5 to 25 ng/mL. The enrichment factor, defined as the ratio of the slopes of linear section of the calibration graphs before and after the preconcentration was 406.

Giokas et al. studied to single-sample cloud point determination of iron, cobalt and nickel by flow injection analysis flame atomic absorption spectrometry-application to real samples and certified reference materials and was reported to Fe(III) ions dedection limits as 19 µg/L (39). Roldana et al. studied determination of copper, iron, nickel and zinc in gasoline by FAAS after sorption and preconcentration on silica modified with 2-aminotiazole groups and were found Fe(III) ions dedection limit as 3 µg/L (40).

Conclusion

In the present work, Fe(III) ion imprinted (IIP) beads were obtained. For this purpose MAAP was synthesized as metal complexing functional monomer and MAAP/Fe(III) complex monomer was copolymerized with EGDMA by suspension polymerization technique to obtain Fe(III) ion-imprinted poly(MAAP-EGDMA) beads. Template Fe(III) ions were removed from the polymer to have IIP adsorbent. These IIP beads are suitable for repeated use without considerable loss of adsorption capacity. The adsorption was relatively fast and the time required to reach equilibrium conditions was about 80 min. The maximum adsorption capacity for Fe(III) ions was 29.32 mol/g dry weight of beads. This fast adsorption equilibrium is most probably due to high complexation and geometric affinity between Fe(III) ions and Fe(III) cavities in the beads structure. Competitive Cu(II)/Fe(III), Zn(II)/Fe(III), Co(II)/Fe(III) Al(III)/Fe(III) adsorption studies showed that, IIP beads are selective for Fe(III) ions, even in the presence of Al(III), Co(II), Zn(II) and Cu(II) ions.

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