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Selective Preconcentration of Fe^{3+} Using Ion-Imprinted Thermosensitive Particles

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Abstract

Molecular imprinting is a form of template polymerization which has been used to produce artificial binding sites in porous polymer particles that exhibit selective rebinding of the imprint or template molecules used in the fabrication. In this study, thermosensitive ion-imprinted polymers (TIIP) were prepared for selective preconcentration of Fe^{3+} ions. Langmuir and Freundlich adsorption models for TIIP were applied to describe the experimental isotherm and isotherm constants. Equilibrium data fit very well to the Langmuir model in the entire concentration range (5-40 mg/L). Furthermore, the selective adsorption of Fe^{3+} ions was confirmed by comparing the adsorption amount of other metal ions, Al^{3+}, Zn^{2+}, Co^{2+}, Cu^{2+} and Mn^{2+}.

INTRODUCTION

Molecular imprinting is becoming an established technique for the preparation of polymeric materials with recognition properties for small molecules [1-6]. The main thrust of research in this field has included separation processes (chromatography, capillary electrophoresis, solid-phase extraction, membrane separations), immunoassays and antibody mimics, biosensor recognition elements, and catalysis and artificial enzymes [7,8]. Molecular imprinting involves forming a pre-polymerization complex between the template molecule and functional oligomers (or polymers) [9], with specific chemical structures designed to interact with the template either by covalent [10-12] or non-covalent chemistry (self-assembly) [13,14] or both [15,16]. Once the pre-polymerization complex is formed, the polymerization reaction occurs in the presence of a crosslinking monomer and an appropriate solvent, which controls the overall polymer morphology and macroporous structure. Once the template is removed, the product is a heteropolymer matrix with specific recognition elements for the template molecule. Several reviews describe the evolving field of molecular imprinting and designed molecular recognition [7,10,13,14,17-20].

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Molecular imprinted polymers (MIPs) with a backbone polymer that is responsive to stimuli, such as temperature, light, pH and so on, have recently been developed [21,22]. MIPs express their unique function as a result of the stimuli. Oya et al. [21], reported an imprinted hydrogel using N-isopropyl-acrylamide (NIPA) and methacrylamidopropyl-trimethylammonium chloride, in which the template molecules are adsorbed in a thermosensitive manner. It is well known that the NIPA hydrogel has thermosensitive properties, that is, it reversibly swells/shrinks in water at a temperature around 305 K due to a hydrophilic/hydrophobic transition [23]. Tokuyama et al. [24] studied the preparation of the imprinted N-isopropylacrylamide-N-(4-vinyl) benzyl-ethylene diamine (NIPA-VBEDA) gel adsorbent and the adsorption/desorption performances. Several studies of imprinted thermosensitive gels, which adsorb metal ions via the formation of an ionic bond have been reported [25-27].

Thermosensitive polymers with different functionalities have been widely used in different applications like enzyme immobilization, antibody-antigen interactions, gene transfection, medical, pharmaceutical science [28], drug delivery systems, sensor, actuator [29], molecular separation, enzyme activity controlling systems, materials for improved biocompatibility [30], removal of heavy metal ions from waste water [24] and so on.

In this study, the preparation of a novel ion-imprinted thermosensitive polymer was investigated for selective preconcentration of Fe^{3+} ions. The Fe^{3+}-imprinted thermosensitive poly(methacryloyl antipyrine-Fe^{3+}-N-isopropylacrylamide [poly(MAAP-Fe^{3+}-NIPA)] was produced by bulk polymerization. Adsorption/desorption of the Fe^{3+} ions by temperature change were examined.

EXPERIMENTAL

Reagents

Methacryloyl chloride was supplied by Sigma (St.Louis, MO, USA) and used as received. N-isopropylacrylamide (NIPA), N,N,N',N'-tetra-methylenediamine (TEMED), 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 analytical reagent grade and were purchased from Merck (Darmstadt, Germany). Laboratory glassware was kept overnight in a 5% nitric acid solution. The glassware was rinsed with deionized water and dried in a dust-free environment. Stock solution of 1000 mg/L Fe^{3+} was prepared by dissolving iron nitrate ($Fe(NO_3)_3.9H_2O$) (Merck, Darmstadt, Germany) in H_2O. Standard iron solutions were prepared daily by dilution of the stock Fe^{3+} solutions. 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 (Bamstead D2731), Barnstead D3804 Nanopure organic/colloid removal and ion-exchance packed-bed system.

Apparatus

Perkin Elmer A Analyst 800 atomic absorption spectrophotometer with deuterium background correction was used for the determination of Fe^{3+} and other investigated metals. Fe^{3+} absorbance measurements were made at 248.3 nm using spectral bandwidth of 0.5 nm. Perkin Elmer Lumina Lamp operating at 7.5 mA. A Fisher Scientific, Accumet Basic AB15 pH-meter was used to measure pH. Surface morphology of the particles was examined using transmission electron micro-scopy (TEM) (Zeiss Eva 50 ED). To evaluate the degree of MAAP incorporation, the TIIP particles were subjected to elemental analysis using a leco Elemental Analyzer (Model CHNS-932). The Fourier Transform Infrared Spectroscopy (FTIR) was used

in the range of 4000-400 cm^{-1} to clarify structures of MAAP monomer, MAAP-Fe^{3+} complex and TIIP particles in the solid state (FTIR 100 series, Perkin Elmer, USA).

Synthesis of MAAP

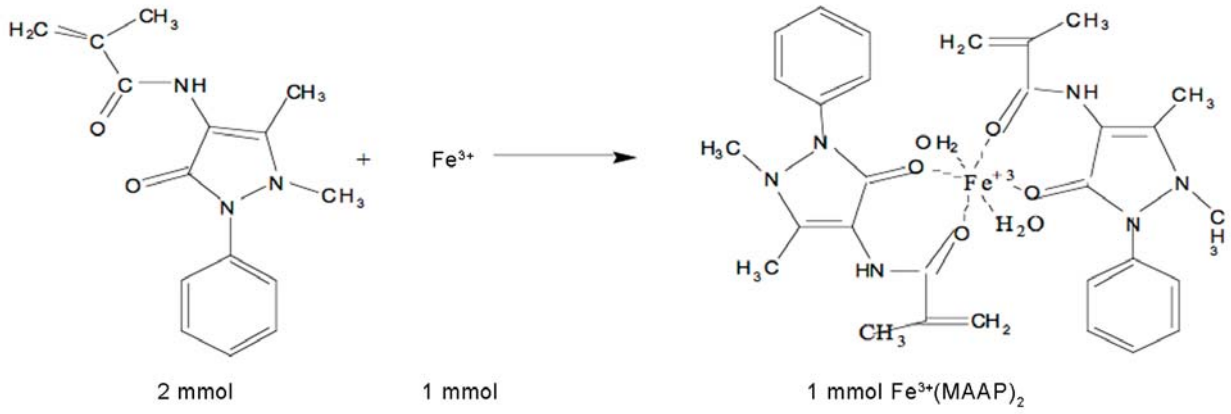
The following experimental procedure was applied for the synthesis of MAAP [31]; 4-amino antipyrine (0.5 g; 2.46 mmol) and pyridine (0.2 mL; 2.46 mmol) were dissolved in 100 ml of dry chloroform and the mixture was cooled to 0°C. Then, methacryloyl chloride (0.26 ml; 2.46 mmol) was poured slowly into the mixture being stirred magnetically at room temperature for 2 h. At the end of the reaction, the solution was sequentially washed with 50 ml of dilute HCl and 50 ml of dilute NaOH solutions. Then, the organic phase was evaporated in a rotary evaporator. The residue was recrystallized in petroleum benzene-ethyl acetate mixture.

FT-IR spectrum of MAAP is as following: FTIR (KBr, cm^{-1}): 1667 cm^{-1} amide carbonyl band, 3444 cm^{-1} N-H band, 3528 cm^{-1} N-H band. ^1H NMR spectrum was recorded to determine the structure of synthesized MAAP. ^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 (-C=C-CH_3, vinyl methyl), 3.0 ppm 3 singlet (-C-CH_3), 3.35 ppm 3H singlet (-N-CH_3), 5.5 ppm 1H singlet (-CH_a-C), 5.8 ppm 1H singlet (-CH_b-C), 7.25–8.80 ppm 4H multiplet (aromatic, $CDCl_3$ peak is also observed at 7.3 ppm with aromatic peaks), 8.80 ppm 1H singlet (aromatic), 9.1 ppm 1H singlet (N-H).

Preparation of Fe^{3+}-MAAP preorganized complex

In order to prepare MAAP-Fe^{3+} complex, MAAP (0.552 g, 2.0 mmol) was added slowly into 20 mL of methanol and then treated with iron nitrate ($Fe(NO_3)_3.9H_2O$) (0.404 g, 1.0 mmol) at room temperature with continuous stirring for 3 h. Then, the formed metal-monomer complex was filtered, washed with 96% ethanol (250 ml), and dried 2 days in a vacuum oven. The structure for MAAP-Fe^{3+} complex was given in Scheme 1.

Detailed FT-IR spectrum of MAAP and MAAP- Fe^{3+} complex is given below (Figure 1): 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). As a result, when the possible interactions between Fe^{3+} ions and "O" atoms were considered, it was concluded that Fe^{3+} 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.



Scheme 1. The structure of MAAP-Fe^{3+} complex.

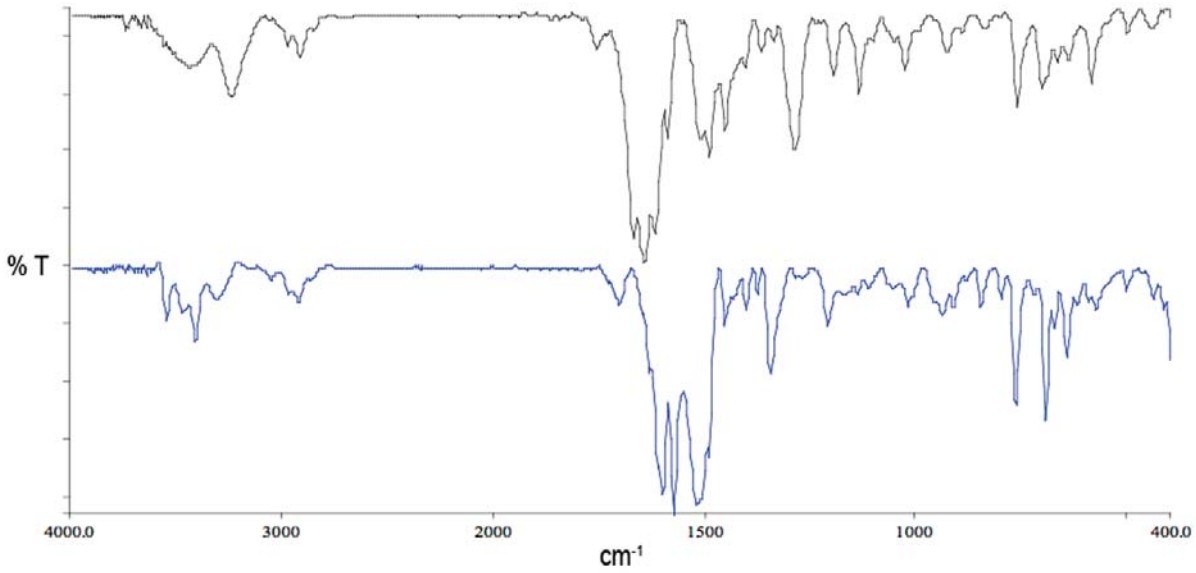


Figure 1. FTIR spectra of (A) MAAP; (B) $(MAAP)_2$-Fe^{3+}.

Synthesis of ion-imprinted thermosensitive polymer

NIPA and $(MAAP)_2$-Fe^{3+} complex were polymerized in bulk polymerization by using azobisisobutyronitrile (AIBN) as the initiator. N,N'-methylenebis-acrylamide (MBAA) was included in the polymerization recipe as the cross-linker. N,N,N´,N´-tetraethyldietyhlenetriamine (TEMED) was used as an activator. The polymerization mixture containing 25 mmol $(MAAP)_2$-Fe^{3+} complex, 200 mmol NIPA, 10 mmol MBAA, 1 mmol TEMED and 0.06 g AIBN was poured into a glass tube and sealed after purging with nitrogen for 2 min. Polymerization reaction was completed in 12 h at 50°C. At the end of the polymerization, soluble components were removed from the polymer by repeated decantation with water and methanol. Fe^{3+} imprinted thermosensitive, TIIP, bulk polymer was grounded in a mill after drying and washed several times with methanol and water to remove any nonreacted components completely. Washed particles were ground again and sieved through 100 µm sieves (Retsch Standard Sieves-Model AS200, Retsch Gmbh & Co, KG, Haan, Germany). Non-imprinted particles (NIP) were prepared in the same manner only without using Fe^{3+} as template.

Removal of the Fe^{3+} template ions

TIIP particles were extensively washed with methanol/water solution (60/40, v/v) for 24 h at room temperature in order to remove nonreacted monomers and other ingredients. After the cleaning procedure, the template was removed from the polymer particles using 4 M HCl aqueous solution. The template free particles were cleaned with ethanol and water with magnetic stirring at room temperature for 12 h. After that the thermosensitive imprinted polymer was dried in a drying oven at 45°C for 4 days.

Characterization studies

Porosity of the particles was measured by the nitrogen sorption technique, performed on Flowsorb II, (Micromeritics Insrument Corporation, Norcross, USA). The specific surface area of particles in dry state was determined by multipoint Brunauer-Emmett-Teller (BET) apparatus (Quantachrome, Nova 2200E, USA). 0.5 g of particle was placed in a sample holder and degassed in a N_2-gas stream at 150°C for 1 h. Adsorption of the gas was performed at -210°C and desorption was performed at room temperature. Values obtained from desorption step was used for the specific surface

area calculation. The pore volume and average pore diameter were determined by BJH (Barrett, Joyner, Halenda) model on adsorption. The average size and size distribution of the particles were determined by screen analysis performed using standard sieves (Model AS200, Retsch Gmb & Co, KG, Haan, Germany).

Water uptake properties of polymeric particles were determined by volumetric method. In this method, 100 mg of the dry particles were placed in a cylindrical tube and the top point of the tube was marked. Then, the tube was filled with distilled water and the particles were allowed to swell at room temperature. The height of the particles were marked every 30 min. The height of swollen particles in the tube was used to calculate the swelling ratio by using the Equation 1:

$$\text{Water uptake (\%)} = [(h_{swollen} - h_{dry}) / h_{dry}] \quad (1)$$

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

The surface morphology of the particles was examined using Transmission electron microscopy (TEM) FEI Company-Tecnai^{Tm}.G^2 Sipirit/Biotwin 20-120 kV Hig res. 11 Megapixel. The surface of the sample was scanned at the desired magnification. To evaluate the degree of MAAP incorporation for both leached and unleached particles, the elemental analysis (Leco Elemental Analyzer, Model CHNS-932) was used. The Fourier transform infrared spectroscopy (FTIR) (Perkin-Elmer Model 2000) was used for the characterization of polymer samples.

Adsorption studies

The adsorption experiments were carried out by a batch method. Effects of the medium temparature, pH, the initial concentration of Fe^{3+} ions on the adsorption rate and capacity were investigated. The effect of temperature on the adsorption rate of the thermosensitive-imprinted polymer was investigated at temperature range of 4-50°C. The suspensions were brought to the desired pH by adding NaOH and HNO_3. The pH was maintained in a range of ± 0.1 unit until equilibrium was attained. Polymeric particles were incubated with the TIIP particles, in a flask stirring magnetically at 400 rpm. The concentration of the Fe^{3+} ions in the aqueous phase was measured using a flame atomic absorption spectrophotometer (FAAS, Analyst 800/Perkin Elmer, USA). The adsorption experiments were performed in replicates of three and the samples were analyzed in replicates of three as well. For each set of presented data, 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. The amount of Fe^{3+} adsorption per unit mass of the particles was evaluated by using a mass balance.

Desorption and reusability

For desorption procedure, the polymeric particles were treated with deionized water 25 mL at 4°C. The Fe^{3+} adsorbed particles were placed in the desorption medium and stirred continuously at 600 rpm at room temperature for 1 h. The final Fe^{3+} ion concentration in the aqueous phase was determined by FAAS. The desorption ratio was calculated from the difference between the amount of Fe^{3+} ions adsorbed on the TIIP particles and the final Fe^{3+} ions concentration in the desorption medium. In order to test the reusability of TIIP partciles, Fe^{3+} ions adsorption-desorption procedure was repeated 7 times by using the same group of particles.

For the preconcentration of Fe^{3+} ions, 100 mL of the aqueous solution containing 1.0 ng/mL of Fe^{3+} ions was treated with 25 mg TIIP particles at pH 4.0 and 20°C for 30 min. Finally, TIIP particles were separated from the adsorption media by filtration

and stirred in deionized water at 400 rpm and 4°C for 300 min. TIIP particles were separated from the desorption media and the solution of Fe^{3+} ions in the desorption media was injected into the FAAS system.

Selectivity experiments

The batchwise selective adsorption experiments of Al^{3+}, Zn^{2+}, Co^{2+}, Cu^{2+} and Mn^{2+} ions with respect to Fe^{3+} were conducted using TIIP and NIP particles. The particles (0.050 g) were added to 25 mL of aqueous solution of containing 5 mg/L of Fe^{3+}, Al^{3+}, Zn^{2+}, Co^{2+}, Cu^{2+} and Mn^{2+} ions. This solution was incubated in a sealed test tube at pH 4.0 at 20°C, then stirred magnetically at 600 rpm at 45 min. After adsorption equilibrium, the concentration of each ions in the remaining solution was measured by FAAS.

The effect of imprinting on selectivity was defined as Equation 2.

$$K_d = [(C_i - C_f / C_f)] \times V / m \quad (2)$$

where K_d (L/g) is distribution coefficient, C_i and C_f are the initial and final solution concentrations (mg/L), V is the volume of solution used for the extraction (L) and m is the weight of polymer used for extraction (g), respectively. 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 3.

$$k = K_{d(\text{template metal})} / K_{d(\text{interferent metal})} \quad (3)$$

The relative selectivity coefficient (k') was defined in Equation 4 [32,33].

$$k' = k_{\text{imprinted}} / k_{\text{control}} \quad (4)$$

The comparison of the k values of the TIIP particles with NIP particles allows an estimation of the effect of imprinting on selectivity.

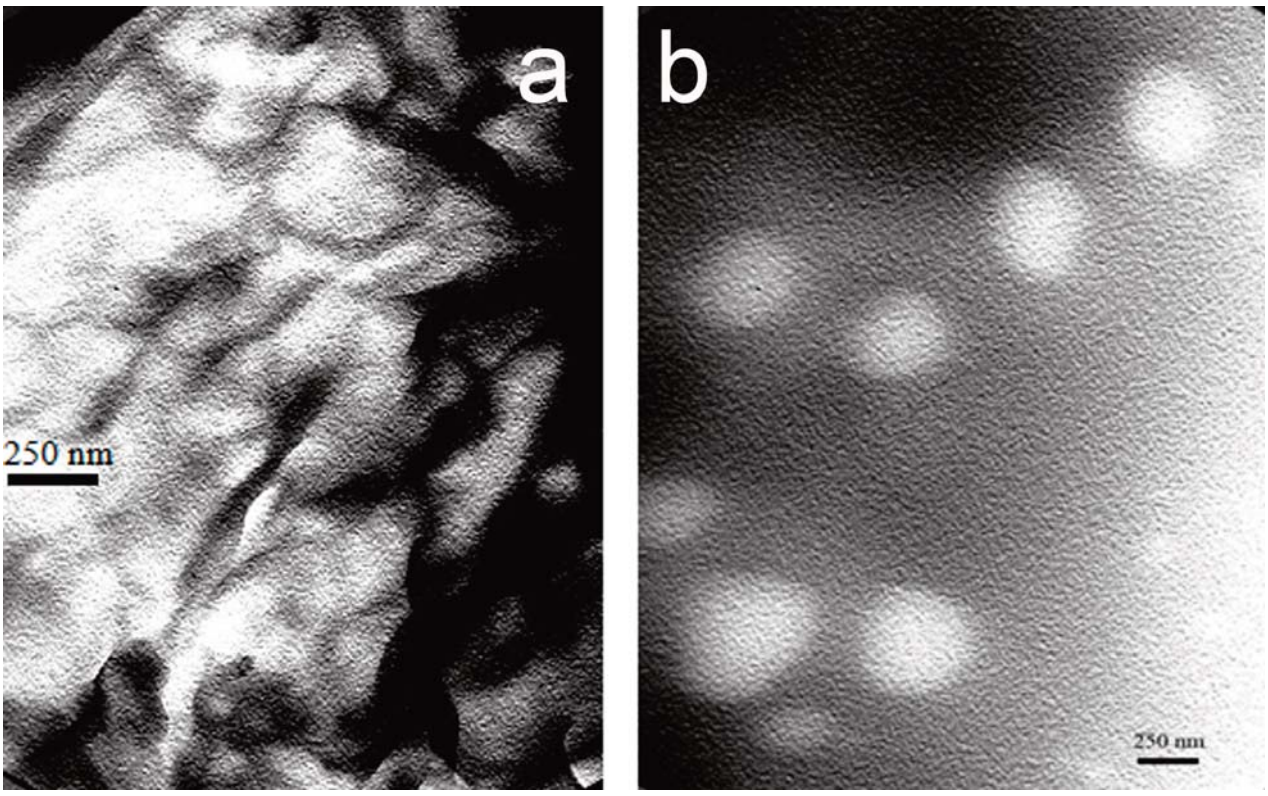


Figure 2. TEM photographs of TIIP particles: (a) unleached particles, (b) leached particles.

RESULTS AND DISCUSSION

Characterization studies

The specific surface area of leached and unleached particles in dry state was determined by the multi-point BET method with nitrogen as adsorbate with experimental error ± 0.2 m^2/g. The specific surface area of the unleached and leached particles which are crosslinked matrices was found to be 11.4 and 39.5 m^2/g, respectively. After removal of Fe^{3+} ions from thermosensitive polymer, the surface area of adsorbent increased. The equilibrium swelling ratios of the leached and unleached particles were found as 425% and 350%, respectively. Compared to the leached particles, the water uptake ratio of the unleached particles increases due to formation of metal ion cavities in the polymer structure. This introduces more hydrodynamic volume into the polymer chain. The surface morphology and internal structure of the TIIP particles are exemplified by the TEM micrographs in Figure 2. As seen in Figure 2b, the leached particles have rough surface and micropores due to the Fe^{3+} ions. It is seen that the unleached particles have no rough surface and micropores, thus they do not have Fe^{3+} ions.

FTIR results of TIIP particles are given below. FT-IR (KBr, cm^{-1}): 1647 cm^{-1} (amide carbonyl band), 3079 cm^{-1} (N-H band), 2976 and 2937 cm^{-1} (C-H band), 3441 cm^{-1} (-OH band), 538 cm^{-1} (Fe-O band). After removal of Fe^{3+} ions from the structure, Fe-O (538 cm^{-1}) band was not observed in the leached polymer structure.

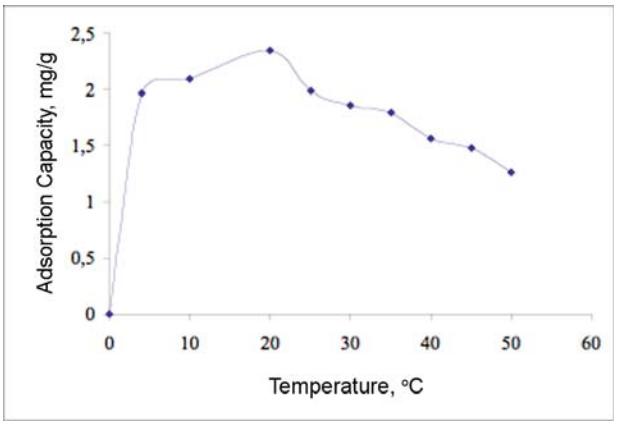


Figure 3. The effect of temperature on the adsorption amount of Fe^{3+} ions onto TIIP particles.

Elemental analysis results are C: 54.12%, N: 10.87%, O: 9.54% for the unleached polymer, C: 57.29%, N:10.19%, O: 11.66% for the leached polymer. Elemental analysis results showed an increase in C, N, H % after the removal of Fe^{3+} ions from TIIP. So, it can be said that the imprinting process has been done successfully.

Adsorption studies

Effect of temperature

Adsorption of Fe^{3+} ions onto the TIIP particles (Figure 3) has been studied from aqueous solutions containing 5 mg/L of Fe^{3+} ions at the temperature range of 4-50°C. The adsorption amount of Fe^{3+} ions on to TIIP particles increased with the increasing temparature, and the peak of the adsorption amount was observed at 20°C. Maximum adsorption was found to be 2.1 mg/g. Kanazawa et al. [34] have investigated adsorption/desorption properties of heavy metal ions by temperature change in molecular imprinted thermosensitive poly(N-isopropylacrylamide-N-4-(vinyl)benzyl ethylenediamine) gel adsorbent and reported optimum temperature as 35°C.

Effect of time

Figure 4 shows the time course of the adsorption amount of Fe^{3+} ions measured using TIIP particles. Adsorption rate of Fe^{3+} ions onto the TIIP particles was studied from aqueous solutions containing 5 mg/L of Fe^{3+} ions. Note that the ordinate values were calculated by using the Equation 2. As seen here, high adsorption rate has been observed at the beginning, and then plateau values (i.e., adsorption equilibrium) have been gradually reached within 30 min.

Several experimental data on the adsorption of

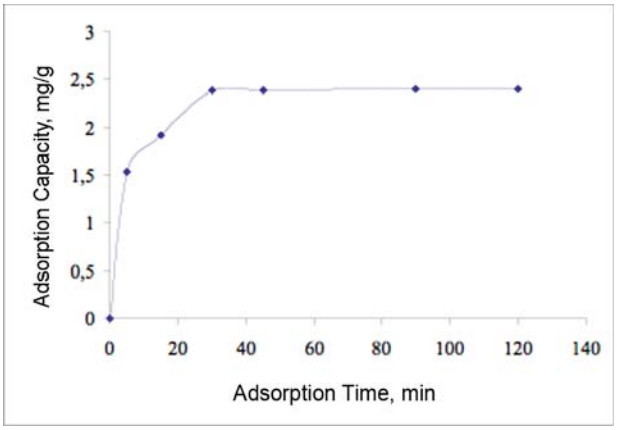


Figure 4. Adsorption rate of Fe^{3+} ions on the TIIP particles; pH, 4.0; Fe^{3+} initial concentration: 5 mg/L; T, 20°C.

various ions by thermosensitive polymer have shown a wide range of adsorption rates. For example, Kanazawa et.al. [34] have studied adsorption/desorption properties of heavy metal ions by molecular imprinted thermosensitive gel adsorbent and they have found adsorption time as 100 h. Tokuyama et al. [24] have investigated the equilibria and kinetics for the adsorption/desorption by a temperature swing of 307/283K for the adsorption of Cu^{2+} on an imprinted N-isopropylacryl-amide-N-(4-vinyl) benzylethylene diamine NIPA-VBEDA gel and have reported 1000 min as an equilibrium time.

Effect of Fe^{3+} ions concentration

Figure 5 shows the effect of Fe^{3+} ions concentration onto the adsorption capacity of the TIIP particles at

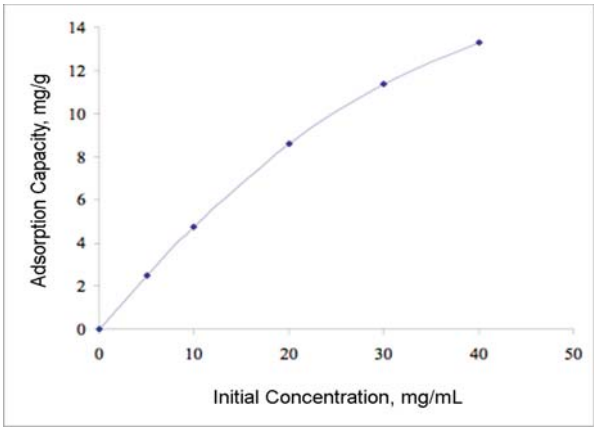


Figure 5. Adsorption capacity of Fe^{3+} ions on the TIIP particles; pH, 4.0; T, 20°C.

Table 1. Langmuir and Freundlich adsorption models for TIIP particles; pH, 4.0; T: 20°C.

Q_{ex}, mg/g	Langmuir Constants			Freundlich Constants		
	Q_{max}, mg/g	b, L/mg	R^2	K_f	n	R^2
13.2	14.23	0.048	0.9983	1.3	0.7703	0.9942

pH 4.0. As seen from the figure, the amount of adsorbed Fe^{3+} ions per unit mass of the polymer (i.e. adsorption capacity) increased with the initial concentration of Fe^{3+} ions. The maximum adsorption (corresponding to 40 ppm Fe^{3+} ion initial concentration), which represents saturation of active points (which are available for Fe^{3+} ions) on the polymers was found to be 13.3 mg Fe^{3+}/g polymer.

An adsorption isotherm is used to characterize the interactions of each molecule with this adsorbent. This provides a relationship between the concentration of the molecules in the solution and the amount of ion adsorbed on the solid phase when the two phases are at equlibrium. 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 far from each other so that there are no interactions between adsorbed molecules on adjacent sites. During the batch experiment, adsorption isotherms were used to evaluate adsorption properties. Table 1 shows the Langmuir and Freundlich adsorption isotherms, n and K_F, and the correlation constants (R^2). According to the correlation coefficients, Langmuir adsorption model is favorable (R^2: 9983) than Freundlich adsorption model.

Effects of pH

It is well known that heavy metal ions adsorption both on nonspecific and specific adsorbents is pH dependent [35-37]. In the absence of complexing agents, the hydrolysis and precipitation of the metal ions are affected by the concentration and form of

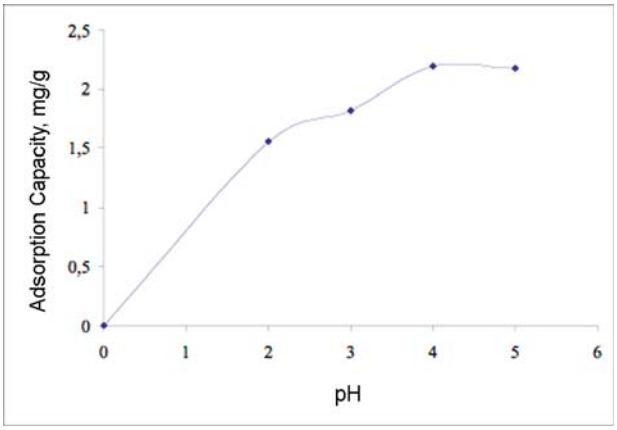


Figure 6. Effects of pH on Fe^{3+} adsorption; Fe^{3+} initial concentration, 5 mg/L; T: 20°C.

soluble metal species. The effect of pH on the Fe^{3+} adsorption using TIIP particles is shown in Figure 6. The optimum pH for maximum Fe^{3+} binding was found between pH 4.0-5.0. The TIIP particles exhibited a low affinity in acidic conditions (pH: 2.0-3.0), a somewhat higher affinity at pH 4.0 was observed and when the pH of the solution was over 5.0, a precipicate was deposited. Because of precipitation, it is dificult to decide whether the affinity is the result of adsorption or precipitation. Thus, the pH values over 5.0 have not been studied.

Selectivity studies

Adsorption capacities of the TIIP and NIP particles for metal ions under competitive conditions (i.e. adsorption from solutions containing 5 mg/L from each of Fe^{3+}/Al^{3+}, Fe^{3+}/Zn^{2+}, Fe^{3+}/Co^{2+}, Fe^{3+}/Mn^{2+}, Fe^{3+}/Ni^{2+}, Fe^{3+}/Cu^{2+} ions) are given in Table 2. The Fe^{3+} adsorption capacity of the TIIP particles was much higher than that of the other ions. The competitive adsorption capacity of the TIIP particles for Fe^{3+} ions was also higher than NIP particles. When they exist in the same medium, a competition will start for the same attachment sites. It can be concluded that the TIIP particles show the following metal ion affinity order under competitive conditions: $Fe^{3+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Zn^{2+} > Al^{3+} > Cu^{2+}$. It should be noted that the TIIP particles have been showed excellent selectivity for the target molecule (i.e. Fe^{3+} ions) due to molecular geometry.

Table 2. Competitive adsorption of metal ions on the TIIP and NIP particles.

Metal ion	Adsorption Capacity mg/g	
	Imprinted polymer	Non-imprinted polymer
Fe^{3+}	2.353	1.642
Al^{3+}	1.962	2.188
Co^{2+}	1.632	2.343
Zn^{2+}	1.523	2.210
Cu^{2+}	1.732	1.992
Mn^{2+}	1.861	2.390
Ni^{2+}	1.535	2.356

The relative selectivity coefficient (k') resulting from the comparision of the k values of the TIIP particles with NIP particles allows an estimation of the effect of imprinting on selectivity. The Kd and k values of TIIP particles (i.e., in the presence of surfactant temperatures) are significantly larger in comparison to the TIIP particles. A comparison for the selectivity coefficient of the TIIP particles to the selectivity coefficient of NIP particles showed that the imprinted matrix for Fe^{3+}/Cu^{2+}, Fe^{3+}/Al^{3+}, Fe^{3+}/Zn^{2+}, Fe^{3+}/Mn^{2+}, Fe^{3+}/Co^{2+} and Fe^{3+}/Ni^{2+} was 14.8; 16.3; 41.2; 62.5; 66.4 and 83.4 times greater than the NIP particles, 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^{3+} ions from the TIIP particles was also studied in a batch experimental set up. TIIP particles were treated with 5 mg/L Fe^{3+} solution at pH.4 and 20°C for adsorption process. Desorption rate of adsorbed Fe^{3+} ions was shown in Figure 7. As seen here, high desorption rate is observed at the beginning, and then desorption is gradually completed within 300 min. After the same was polymer filtered, adsorbent was treated with deionized water at 4°C. Amount of Fe^{3+} ions into desorption medium was measured by FAAS.

In order to show the reusability of the TIIP particles, adsorption-desorption cycle was repeated 7 times

Table 3. The effect of imprinting on selectivity.

Metal ion	Thermosensitive-imprinted polymer		Non-imprinted polymer		
	K_D	k	K_D	k	k'
Fe^{3+}	8003.4	-	956.9	-	-
Ni^{2+}	795.4	10.0	8180.6	0.12	83.4
Co^{2+}	940.1	8.5	7461.8	0.13	66.4
Mn^{2+}	1456.2	5.5	10863.6	0.09	62.5
Zn^{2+}	779.4	10.3	3810.3	0.25	41.2
Al^{3+}	1823.4	4.4	3506.4	0.27	16.3
Cu^{2+}	1127.6	7.1	1960.6	0.48	14.8

by using the same groups of particles. The results showed that the adsorption capacity of TIIP particles has not been changed significantly. As an important advantage the particles can be used repeatedly.

Adsorption and desorption by temperature swing

Figure 8 shows the change of the adsorption amount of Fe^{3+} ions by the temperature swing between 4 and 20°C. The adsorption amount (20°C) was almost the same as the desorption amount (4°C) for the each adsorption-desorption cycle. From these results, it can be said that the adsorption and desorption of Fe^{3+} ions can be done repeatedly by temperature swing as expected.

Preconcentration of Fe^{3+} ions in aqueous sample

For the preconcentration of Fe^{3+} ions, 100 mL of the aqueous solution containing 1.0 ng/mL of Fe^{3+} ions was treated with 25 mg of the TIIP particles at pH 4.0 and 20°C for 30 min. Finally, TIIP particles were separated from the adsorption media and 10 mL deionized water was added and stirred at 400 rpm, and 4°C for 300 minutes. TIIP particles were removed from the desorption medium. Desorption solution was determined by FAAS for the determination of the Fe^{3+} concentration. It was observed that the applied preconcentration process improved the results more than 656 times. In the present case, the observed detection limit was 2.26 ng/mL. Janathan et al. [38] have studied the determination of iron in a zirconium-based glass by electrothermal atomic absorption spectrometry and detection limit was found to be 0.04 ng/g. Soares et al. [39] have researched the determination of copper, iron, aluminium, lead and cadmium in cork stoppers by electrothermal atomic absorption spectrometry and linear determination range was reported as 0.8-50 mg/L. Pourreza et al. [40] have studied the simultaneous preconcentration of Cu, Fe and Pb as methylthymol blue complexes on

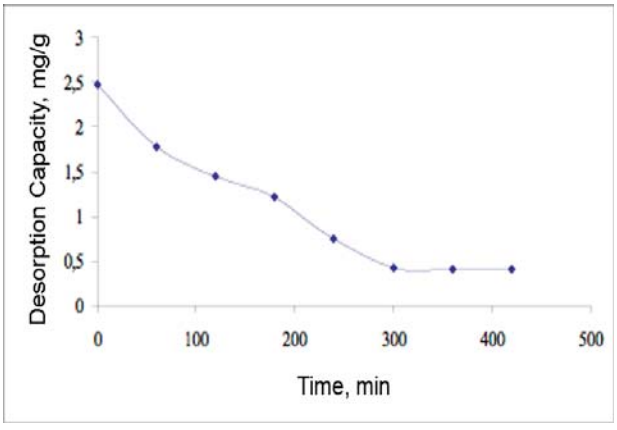


Figure 7. Desorption rate of adsorbed Fe^{3+} ions; T: 4°C.

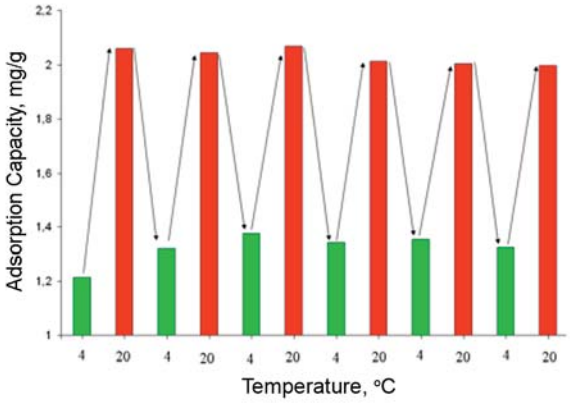


Figure 8. Adsorption amount of Fe^{3+} ions by temperature change.

Table 4. Performance characteristics of the preconcentration procedure.

Parametreler	Fe
Precision (R.S.D)	2.1%
Detection limit (3s)	2.26 ng/mL
Linear calibration range	0.5-20.0 ng/mL
Regression equation (after preconcentration)	AA= 0.0021 Fe + 5 E-05 ng/mL
Conventional regression equation	AA= 0.0032 Fe + 0.0035 µg/mL
Enrichment factor	(0.0021 ng/mL x 1000 mg/mL/ 0.0032 = 656

naphthalene adsorbent using flame atomic absorption determination and detection limits of Fe^{3+} ions were reported as 3.1 ng/mL. Satake et al. [41] have investigated the preconcentration of Fe^{3+} ions with an ion pair of 1,2-dihydroxybenzene-3,5-disulfonate and benzyl- dimethyltetradecylammonium ion supported on naphthalene using flame atomic absorption spectrometry and the linear calibration graph range has found to be 0.5-20 µg of iron in 5 ml of the final DMF solution.

As mentioned above, in our study, detection and determination limits were found as 2.26 ng/mL and 7.5 ng/mL, respectively. The preconcentration procedure showed a linear calibration curve within the concentration range from 0.5 to 20.0 ng/mL. When these results were compared to literature values, the results showed the applicability of preconcentration to FAAS for determination of Fe^{3+} using TIIP.

Analytical performance of the method

The characteristic performance data for the off-line preconcentration procedure were given in Table 4. The precision of method for a standard, evaluated as the relative standard deviation (R.S.D:, n=7) was found to be 2.1 ng/mL Fe^{3+} 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 2.26 and 7.5 ng/mL. The preconcentration procedure has been showed a linear curve within the concentration range from 0.5 to 20 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 found to be 656.

CONCLUSIONS

Molecular imprinting is a technology to create recognition sites in a macromolecular matrix using a molecular template. In other words, both the shape of the target and alignment of the functional moieties to interact with those in the target are memorized in the macromolecular matrix for the recognition or separation of the target during formation of the polymeric materials themselves. By considering this, we have synthesized MAAP-Fe^{3+}-NIPA (TIIP) particles for adsorption/desorption properties of Fe^{3+} ions by temperature swing. The amount of adsorbed Fe^{3+} ions to the gel has been increased with increasing temperature to 20°C. This thermosensitive change in the amount of adsorbed Fe^{3+} was reversible. In the desorption process at 4°C, the thermosensitive polymer, which shrinks extensively as a result of the enhanced metal-chelate interactions compared with the thermosensitive gel-network, expels free water along with Fe^{3+} ions. The adsorption was fast, the required time to reach equilibrium conditions was about 30 min. The maximum adsorption capacity for Fe^{3+} ions was 13.3 mg/g for dry weight of particles. The relative selectivity coefficient is an indicator to express an adsorption affinity of recognition sites to the imprinted Fe^{3+} ions. A significant increase is observed in the selectivity of TIIP particles when the adsorbent is prepared in the presence of the target ion. The desorption time was found to be 300 min. Finally the TIIP particles can be used many times without decreasing their adsorption capacities significantly.

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