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# $Fe^{3+}$-Imprinted Polymeric Systems

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## Abstract

The ion-imprinting is a technique which is prepared using metal ions and binding with high crosslinking for the preparation of adsorbents for the separation of metal ions. Ion-imprinted materials are easy to prepare, stable, inexpensive and capable of molecular recognition. The aim of this study is to prepare an ion-imprinted polymer, which can be used for the selective removal of $Fe^{3+}$ ions. Chitosan-succinate was chosen as the complexing monomer, $Fe^{3+}$ as template and epichlorohydrin was chosen as crosslinking agent. In the first step, chitosan was modified with succinic anhydrides and complex formation occured between carboxylic acid functional groups and $Fe^{3+}$ ions. Secondly, $Fe^{3+}$-chitosan-succinate polymer was crosslinked with epichlorohydrin. After that, the template ($Fe^{3+}$ ions) was removed using 0.1 M HCl solution and the $Fe^{3+}$-imprinted polymer was used in the adsorption-desorption process. Molecular cavity for the $Fe^{3+}$ ion was obtained in the $Fe^{3+}$-imprinted polymer. The maximum adsorption capacity has found to be 78.2 mg/g. Adsorption equilibrium was achieved in about 60 min. The relative selectivity coefficients of imprinted polymers for $Fe^{3+}/Al^{3+}$ and $Fe^{3+}/Mn^{2+}$ were 5.13 and 4.0 times greater than non-imprinted matrix, respectively. It should be noted that the $Fe^{3+}$-imprinted polymer could be used many times without decreasing the adsorption capacity significantly.

**Key Words:** Ion-imprinting, $Fe^{3+}$, chitosan, ICP-AES, molecular recognition

## INTRODUCTION

Molecular imprinting is a technique for preparing polymeric materials that are capable of high molecular recognition. In molecular imprinting, a molecular “memory” is imprinted on the polymer. Molecular imprinting polymers (MIPs) are capable of recognizing and binding the desired molecular target with a high affinity and selectivity [1]. 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 [2]. Ion-imprinted polymers (IIPs) are similar to MIPs, but they can recognize metal ions after imprinting and retain all the virtues of MIPs [3,6]. IIPs have outstanding advantages such as predetermined selectivity 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 [7]. One of the first ionic template effects in the synthesis of chelating polymers was reported by Nishide and Tsuchida [8] in the mid-1970s. Recently, Takagi and co-workers [9] introduced a novel imprinting technique called surface template polymerization. Surface molecular imprinting is one of the important types of molecular

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imprinting. Surface molecularly imprinted polymer not only possesses high selectivity but also avoids problems with mass transfer [10].

For metal ions, molecular imprinting can be interpreted as ionic imprinting exactly. So far there are a lot of metal ions, imprinted polymers have been prepared, including $Pb^{2+}$. [11], $Ni^{2+}$ [12-13], $Pd^{2+}$ [14], $Dy^{3+}$ [15], $UO^{2+}$ [16], $Cd^{2+}$ [17], $Th^{4+}$ [18] $Ca^{2+}$ [19] and $Mg^{2+}$ [20] imprinted polymers. However, few people developed procedure to research $Fe^{3+}$. In this study, a new $Fe^{3+}$-imprinted amino functionalized silica gel sorbent was synthesized by combining a surface molecular imprinting technique for selective extraction or preconcentration of $Fe^{3+}$. In this study, the $Fe^{3+}$-imprinted polymer was prepared and it was used for the selective binding of $Fe^{3+}$ ion from complex matrices. Chitosan-succinate was synthesized as the metal complexing monomer, with the goal of preparing a solid-phase that has the high selectivity for $Fe^{3+}$. Chitosan-succinate was reacted with $Fe^{3+}$ ions and then was crosslinked with epichlorohydrin. After removal of $Fe^{3+}$ ions, $Fe^{3+}$- imprinted polymer was used for the binding of iron from complex matrices. $Fe^{3+}$ binding from complex matrices containing different amounts of metal ions, and selectivity studies of iron versus other interfering metal ions mixture, $Al^{3+}$ and $Mn^{2+}$, were reported here.

## EXPERIMENTAL

### *Materials*

Chitosan, succinic anhydride and epichlorohydrin were supplied from Aldrich Chemical (USA). All other chemicals were analytical reagent grade and purchased from Merck (Darmstadt, Germany).

### Intrumentation

ICP-AES was used for the determination of iron and other metals which are studied. Jenway 3100 pH-meter was used to measure pH values.

### Preparation of chitosan succinate

Chitosan-succinate was synthesized according to the procedure reported in the Aiedeh and Taha's work [21]. Chitosan (1.00 g, corresponding to approximately 6.20 mmols glucoseamine) was dissolved in the acetic acid aqueous solution (1%, 100 mL) at ambient temperature, and a solution of the succinic anhydride (6.25 mmol) in pyridine (5 mL) was added dropwise with vigorous stirring. The reaction pH was maintained at 7.0 by the dropwise addition of NaOH solution (1.0 M). NaOH addition was continued till the pH was stabilized. After 40 min the reaction was terminated by the addition of NaCl aqueous solution (20%, 200 mL). The resulting precipitate was filtered, washed with acetone and diethyl ether, and desiccated to give chitosan succinate conjugates.

The IR spectra of the chitosan-succinate showed amide carbonyl band at 1650 $cm^{-1}$, carboxylic carbonyl band at the 1735 $cm^{-1}$, indicating the formation of amide links with succinate [21].

### Preparation of $Fe^{3+}$- imprinted polymer

Chitosan succinate (1 g) was dissolved in the acetic acid (5%) and $Fe(NO_3)_3.9H_2O$ (2 g) was added slowly to this solution with continuous stirring at room temperature. The mixture solution was slowly dropped into 150 mL of 1 N aqueous sodium hydroxide for 1 h. The suspended solution was stirred at 200 recycle/min for 12 h. After filtering this reddish-brown suspended solution and drying in vacuum, the obtained $Fe^{3+}$-complexed chitosan succinate was crosslinked by 5 mL of epichlorohydrin in 250 mL of the acetic acid (5%) under refluxing conditions in an oil bath (ca. 110°C) for 1 h. Then, 250 mL of 0.1 N aqueous sodium hydroxide solution was added to complete the crosslinking reaction. After vacuum filtration, the clearly orange product of crosslinked $Fe^{3+}$-complexed chitosan succinate was washed with 1 N $HNO_3$ and deionized water several times. Clearly orange product was obtained, after the removing of $Fe^{3+}$ ions from the $Fe^{3+}$-complexed chitosan succinate using 1 N $HNO_3$.

The IR spectrum of the $Fe^{3+}$-chitosan-succinate polymeric matrix shows principal complex absorption bands at around 1640 $cm^{-1}$ and 1565 $cm^{-1}$, in contrast, the IR spectrum of chitosan succinate shows a carboxyl band at 1735 $cm^{-1}$ and an amide band at 1650 $cm^{-1}$. Accordingly, one can conclude that both carboxyl and amide were shifted to lower frequencies upon complexation to iron, i.e. from 1650 $cm^{-1}$ to 1565 $cm^{-1}$ for amide carbonyls and from 1735 $cm^{-1}$ to 1640 $cm^{-1}$ for carboxyl groups.

## Adsorption studies

Effects of the medium pH and the initial concentrations of $Fe(NO_3)_3.9H_2O$ on the adsorption rate and capacity were used in batch adsorption-equilibrium experiments. The effect of pH on the adsorption rate of the $Fe^{3+}$-imprinted polymer with $Fe^{3+}$ ions was investigated in the pH range 2.0-4.0 at 25°C. 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. In all the experiments, polymer concentration was kept constant at 25 mg/25 mL. Ions was treated with the $Fe^{3+}$-imprinted polymer at room temperature, in the flask stirred magnetically at 600 rpm.The concentration of the ions in the aqueous phase after desired treatment periods was measured by using ICP-AES.

The effect of the initial ion concentration on the adsorption was examined as described above except that the concentration of $Fe^{3+}$ ions in the adsorption medium was varied between 20 and 250 mg/L.

Competitive adsorptions of $Al^{3+}/Fe^{3+}$ and $Mn^{2+}/Fe^{3+}$ from their mixture were also investigated in a batch system. A solution (25 mL) containing 25 mg/L from each ions was treated with the $Fe^{3+}$ imprinted polymer at a pH of 2.0 at room temperature, in the flask stirred magnetically at 600 rpm. After adsorption equilibrium, the concentration of ions in the remaining solution was measured by a ICP-AES.

The amount of adsorbed ions was obtained using the expression.

$$Q=[(C_o-C).V]/M \tag{1}$$

Q is the amount of ions adsorbed onto the unit amount of the polymer (mg/g); $C_o$ and C are the concentrations of the ions in the initial solution and in the aqueous phase after adsorption, respectively (mg/L); V is the volume of the aqueous phase (mL); and M is the amount of polymer (g).

## Desorption and reuse

Desorption of $Fe^{3+}$ ions was performed using 1 N $HNO_3$. The $Fe^{3+}$-imprinted chitosan succinate was placed in this desorption medium and stirred continuously (at a stirring rate of 600 rpm) for 2 h at room temperature. The final $Fe^{3+}$ ions concentration in the desorption medium was measured by ICP-AES.

In order to investigate the reusability of the $Fe^{3+}$-imprinted polymers, adsorption-desorption cycle was repeated five times by using the same sorbent. Adsorption conditions were as follows: initial concentration of the metal ions: 20 ppm; amount of the imprinted polymers: 25 mg; volume of the adsorption medium: 25 mL; pH: 2.0 temperature: 25°C; and adsorption time: 60 min. The imprinted polymer was washed few times with 1 N $HNO_3$ solution and deionized water.

## RESULT AND DISCUSSION

### Adsorption capacity of $Fe^{3+}$-imprinted polymer

### Adsorption rate

Figure 1 shows adsorption rates $Fe^{3+}$ ions onto the $Fe^{3+}$-imprinted polymer from the aqueous solutions containing 10 mg/L of $Fe^{3+}$ ions at a constant pH of 2.0. Note that the ordinate values on this were calculated by using the expression given in eq. (1). As seen here, $Fe^{3+}$ adsorption increase with the time during the first 60 min and then levels off as equilibrium is reached. This fast adsorption equilibrium is most probably due to high complexation and geometric shape affinity (or memory) between $Fe^{3+}$ ions and $Fe^{3+}$ cavities in the polymeric structure.

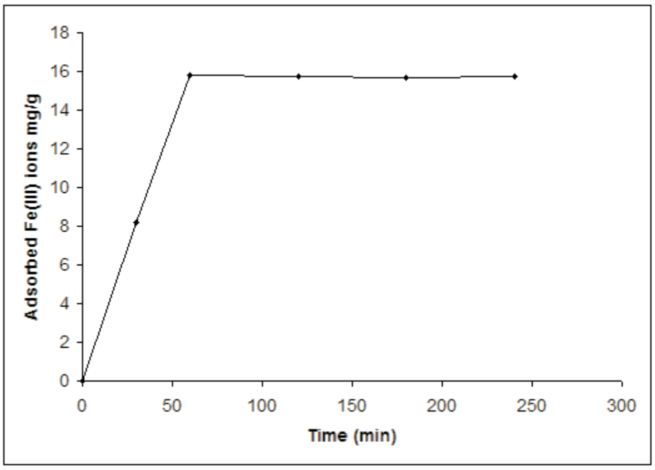

Figure 1. Adsorption rates of $Fe^{3+}$ ions on the $Fe^{3+}$-imprinted polymer; pH, 2.0; T, 25°C.

Yavuz et al. was studied iron removal from human plasma using imprinted beads and reported 30 min as an equilibrium time [22].

### Adsorption capacity

Figure 2 shows the dependence of the equilibrium concentration on the adsorbed amount of the $Fe^{3+}$ onto the $Fe^{3+}$-imprinted polymer. The adsorption values incrased with increasing concentration of $Fe^{3+}$ ions, and a saturation value is achieved at iron ion concentration of 100 mg/L, which represents saturation of the active binding cavities on the $Fe^{3+}$-imprinted polymer. Maximum adsorption capacity was 78.2 mg/g.

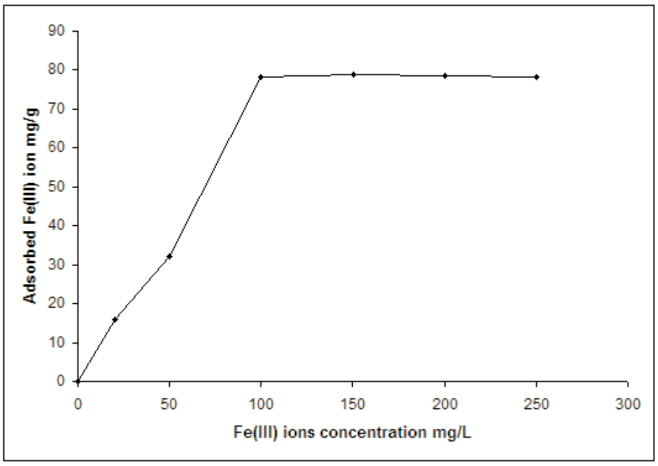

Figure 2. Adsorption capacity of $Fe^{3+}$ ions on the $Fe^{3+}$-imprinted polymers; pH, 2.0; T, 25°C.

### Effects of pH on the adsorption of iron ions

It is well known that heavy metal ions adsorption both on nonspecific and specific sorbents is pH dependent [23-24]. In the absence of complexing agents, the hydrolysis and precipitation of the metal ions are affected by the concentration and form of soluble metal species. The effect of pH on the $Fe^{3+}$ ions adsorption using $Fe^{3+}$-imprinted polymer is shown in Figure 3. As seen in Figure 3, for $Fe^{3+}$ imprinted polymer, the optimum pH for maximum $Fe^{3+}$ binding capacity was found to be between pH

2-4. The $Fe^{3+}$-imprinted polymers exhibited affinity in acidic conditions (pH=2.0) and when the pH of the solution was over 4.0, a precipicate was deposited.

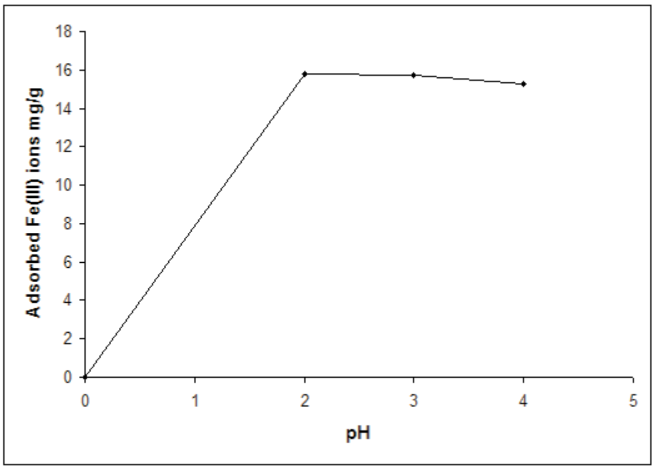

Figure 3. Effects of pH on $Fe^{3+}$ adsorption; $Fe^{3+}$ initial concentration, 10 ppm; T, 25°C.

### *Selectivity Studies*

Competitive adsorption of $Mn^{2+}/Fe^{3+}$ and $Al^{3+}/Fe^{3+}$ from their couple mixture was also investigated in a batch system. $Mn^{2+}$ and $Al^{3+}$ were choosen as competitive metal ions. Adsorption capacities of the $Fe^{3+}$-imprinted and non-imprinted polymer for metal ions under competitive conditions (i.e. adsorption from solution containing 20 mg/L from each of $Mn^{2+}/Fe^{3+}$, $Al^{3+}/Fe^{3+}$, are given in Table 1. The $Fe^{3+}$ adsorption capacity of the $Fe^{3+}$-imprinted polymer was higher than that other ions. The compatitive adsorption capacity of the $Fe^{3+}$-imprinted polymer for $Fe^{3+}$ ions was also higher than non-imprinted polymer.

Table 1. Competitive adsorption of $Fe^{3+}$ and anions on the $Fe^{3+}$-imprinted and non-imprinted polymer.

| Couple mixture (20 mg/L) | $Fe^{3+}$-imprinted polymer | | | Non-imprinted polymer | | |
|---|---|---|---|---|---|---|
| | $Fe^{3+}$ | $Al^{3+}$ | $Mn^{2+}$ | $Fe^{3+}$ | $Al^{3+}$ | $Mn^{2+}$ |
| $Fe^{3+}/Al^{3+}$ | 17.50 | 10.80 | - | 12.90 | 12.18 | - |
| $Fe^{3+}/Mn^{2+}$ | 19.51 | - | 15.23 | 15.64 | - | 10.74 |

When they exist in the same medium, a competition will start for the same attachment sites. It can be concluded that the $Fe^{3+}$ imprinted polymer show the following metal ion affinity order under competitive conditions: $Fe^{3+} > Al^{3+} > Mn^{2+}$. It should be noted that the imprinted polymer showed excellent selectivity for the target molecule (i.e. $Fe^{3+}$ ions) due to molecular geometry.

Distribution and selectivity coefficient of $Fe^{3+}$ with respect to, $Al^{3+}$ and $Mn^{2+}$ was calculated as explained below.

$$K_D = [C_i - C_f / C_f] \times V / m \qquad (2)$$

where $K_D$, $C_i$ and $C_f$ represent the distribution coefficient, initial and final solution concentrations, respectively. V is volume of the solution (mL) and m is mass of polymer (g). The selectivity coefficient for the binding of an ion in the presence of competitor species can be obtained from equilibrium data according to the Eqn.3;

$$k' = K_D (Fe^{3+}) / K_D (X) \qquad (3)$$

where k′ is the selectivity coefficient which gives the comparison of the effect of imprinting on selectivity. A relative selectivity coefficient k (Eqn. 4) can be defined as [25];

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

The relative selectivity coefficient ($\kappa'$) results from the comparison of the k values of the imprinted microbeads with non-imprinted microbeads allows an estimation of the effect of imprinting on selectivity. A comparison of the selectivity coefficient of $Fe^{3+}$-imprinted polymers with the selectivity coefficient of non-imprinted polymers showed that the imprinted matrix for $Mn^{2+}/Fe^{3+}$ and $Al^{3+}/Fe^{3+}$ was 4 and 5.13 times greater than non-imprinted matrix, respectively (Table 3). This means that $Fe^{3+}$ ions can

Table 2. The effect of imprinting on selectivity.

| Polymer | $Fe^{3+}$ (mg/L) | $Mn^{2+}$ (mg/L) | $K_D$ ($Fe^{3+}$) | $K_D$ ($Mn^{2+}$) | k | k' |
|---|---|---|---|---|---|---|
| Non-imprinted | 20 | 20 | 3590.31 | 1161.22 | 3.09 | |
| $Fe^{3+}$-imprinted | 20 | 20 | 40382.16 | 3196.39 | 12.63 | 4 |

| Polymer | $Fe^{3+}$ (mg/L) | $Al^{3+}$ (mg/L) | $K_D$ ($Fe^{3+}$) | $K_D$ ($Al^{3+}$) | k | k' |
|---|---|---|---|---|---|---|
| Non-imprinted | 20 | 20 | 1818.88 | 1557.87 | 1.16 | |
| $Fe^{3+}$-imprinted | 20 | 20 | 7003.20 | 1174.62 | 5.96 | 5.13 |

be determined even the presence of $Mn^{2+}$ and $Al^{3+}$ interferences.

## 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 imprinted polymer was also studied in a batch experimental set up. Various factors are probably involved in determining rates of $Fe^{3+}$ desorption, such as the extent of hydration of the heavy metal ions and polymer microstructure. However, an important factor appears to be binding strength. The repeated use of $Fe^{3+}$-chitosan succinate polymer is shown in Figure 4. When $HNO_3$ is used as a desorption agent, the coordination sphere of chelated $Fe^{3+}$ ions is distrupted and subsequently $Fe^{3+}$ ions are released from the $Fe^{3+}$ templates into desorption medium.

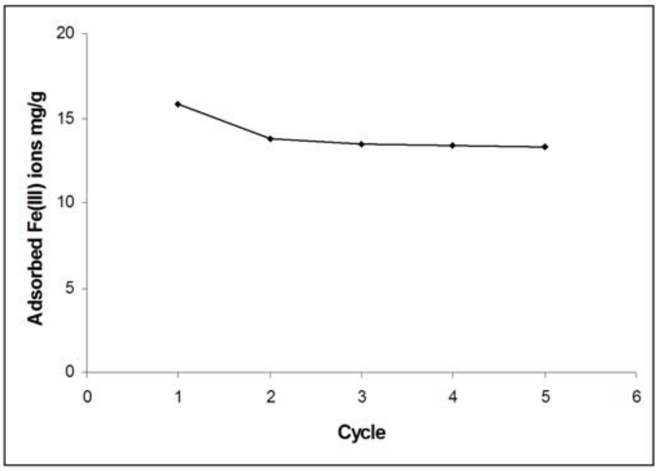

Figure 4. Adsorption-desorption cycle of $Fe^{3+}$-imprinted polymer.

In order to show the reusability of the $Fe^{3+}$-imprinted polymer, adsorption-desorption cycle was repeated 5 times by using the same imprinted polymer. The results showed that the $Fe^{3+}$-imprinted affinity polymer can be used repeatedly without loosing the adsorption capacity significantly.

## CONCLUSION

Molecular imprinting is a technology to create recognition sites in a macromolecular matrix using a molecular template. Molecularly imprinted materials have been demonstrated to posses a very high degree of selectivity towards targeted substance. In this study, we have prepared a novel molecular imprinted adsorbent to remove $Fe^{3+}$ ions with high selectivity. The adsorption was relatively fast and time required to reach equilibrium conditions was about 60 min. The maximum adsorption capacity for $Fe^{3+}$ ions was mg/g dry weight of polymer. This fast adsorption equilibrium is most probably due to high complexation and geometric affinity between $Fe^{3+}$ ions and $Fe^{3+}$ cavities in the polymer structure. The adsorption values increased with increasing concentration of $Fe^{3+}$ ions, and a saturation value is achieved at ion concentration of 100 mg/L, which represents saturation of the active binding cavities on the $Fe^{3+}$-imprinted chitosan succinate. The relative selectivity coefficient is an indicator to express an adsorption affinity of recognition sites to the imprinted $Fe^{3+}$ ions. The results showed that the imprinted polymers for $Fe^{3+}/Al^{3+}$and $Fe^{3+}/Mn^{2+}$ were 5.13 and 4 times greater than non-imprinted matrix, respectively. The $Fe^{3+}$-imprinted polymer can be used many times without decreasing their adsorption capacity significantly.

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