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Cr(III)-imprinted polymeric beads: Sorption and preconcentration studies

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Abstract

The purpose of this study is to prepare a novel molecular imprinted adsorbent to Cr(III) analysis with high selectivity. Initially, chromium (III)-methacryloylhistidine (MAH/Cr(III)) complex monomer was synthesized and then Cr(III) ion imprinted ethyleneglycoldimethacrylate–methacryloylhistidine (poly(EDMA-MAH/Cr(III))) was polymerized. Cr(III) ions were removed from the Cr(III)-imprinting polymer. Selective cavity for the chromium (III) ions was obtained in the (poly(EDMA-MAH/Cr(III))) beads. These Cr(III)-imprinted beads were used in the sorption-desorption process. The effect of initial concentration of metal, the sorption rate and the pH of the medium on sorption capacity of Cr(III)-imprinting sorbents were studied. Sorption equilibrium time was achieved in about 30 min. The maximum sorption of Cr(III) ions onto imprinted beads was about 69.28 mg/g. Sorption studies of Co(II), Ni(II), Cr(III) and Cr(VI) ions were also investigated using Cr(III)-imprinting polymers. The obtained results show that selectively adsorbed amount of Cr(III) ion on Cr(III)-imprinting polymers is higher than all other studied ions. When the beads were used repeatedly, their adsorption capacity was showed feasibility.
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1. Introduction

The extraction and determination processes of trace metal ions or species from different matrices especially water sample are mainly based on the utilization and application of a number avaliable preconcentration techniques. The preconcentration procudure is an essential step for the accurate measurement and analysis of the various metal species, especially those present in trace level (μg/L and ng/L) in order to match with the detection limits of the major instrumentations (AAS and ICP-OES). [1].

Chromium is one of the essential elements for all vertebrates, as it appears to play a role in the metabolism of glucose and some lipids such as cholesterol. Chromium in natural waters exits mainly in two different oxidation states, chromium (III)

and chromium (VI). Chromium (VI) is known to be more toxic to humans, animals and plants and is more mobile in the environment than Cr(III) [2].

Some methods have been developed for the determination of Cr(III) and Cr(VI) since the determination of elemental species provides a more accurate and reliable evaluation of water quality than that of total element content. One of common ways for chromium speciation analysis is the determination of Cr(VI) or Cr(III), and total chromium in samples. During the determination, two different methods were employed, such as molecular spectrophotometry for Cr(VI) and atomic spectrometry for total chromium. Another common way for chromium speciation analysis is performed by using separation procedures. Several separation methods have been reported for Cr(III) and Cr(VI) simultaneous determination, such as inductive coupled plasma-atomic emission spectrometry (ICP-AES) [3] and chemiluminescence (CL) [4] with ion chromatography (IC) separation.

Three main strategies can be considered for Cr(VI) removal from wastewaters: (i) reduction of hexavalent chromium to trivalent with subsequent immobilization as the hydroxide [5], (ii)

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sorption onto various materials [6–14] and recently also (iii) membran filtration [15,16].

Sorption is one of more popular methods for the removal of chromium from the wastewaters. The pollutant is adsorbed onto the solid adsorbent surface from the effluent with the quantity of the removed pollutant depending on the adsorption capacity of the sorbent [17]. The need of more selective system for separation of metal ions has been increased the development of the synthesis of new extractants and sorbents [18–25]. One of the recently developed tecniques for the preparation of solid phase is the ion-selective imprinting technique that could be used for selective separation and preconcentration of trace metals [26–28]. Molecular imprinting is a method for tailor-made preparation of highly selective synthetic polymer receptors for given molecules. The principle of the molecular imprinting is that a target molecule (template) and functional monomers are polymerized with a crosslinking reagent. After removal of the template, the functional groups in the resulting binding sites should be arranged in position suitable for interaction with the template molecule [29–32].

In this study, an ion-imprinting polymer prepared with methacryloylamidohistidine (MAH) was used for selective separation of Cr(III) ions from aqueous solutions. We selected methacryloylamidohistidine (MAH) as the metal complexing monomer by template polymerization, with the goal preparing a solid phase which has the high selectivity for Cr(III) ions. The Cr(III) imprinted poly(ethylene glycol dimethacrylate–methacryloylhistidine/Cr(III)) [poly(EDMA-MAH/Cr(III))], metal complexing beads were produced by a dispersion polymerization technique. After removal of Cr(III) ions, chromium sorption on the Cr(III) ion-imprinted beads from aqueous solutions containing their different amount at different pHs and selectivity studies were investigated. Finally, repeated use of the Cr(III) imprinted polymeric beads from aqueous solutions was also discussed.

2. Experimental

2.1. Materials

Histidine and metacryloylchloride were supplied by Sigma (St. Louis, MO, USA) and used as received. Ehylene glycol dimethacrylate (EGDMA) was obtained from Fluka (Buchs, Switzerland), distilled under reduced pressure in the presence of hydroquinone inhibitor and stored at $4\,^{\circ}C$ until use. Azobisisobutyronitrile (AIBN) was also obtained from Fluka. Poly(vinylalcohol) (PVAL; M_w: 10,000, 98% hydrolyzed) was supplied from Aldrich Chemical (USA). All other chemicals were reagent grade and purchased from Merck (Darmstadt, Germany).

2.2. Intruments and analytical methods

Unicam UV–vis scanning spectrophotometer was used for the determination of chromium (VI). For the colorimetric determination of Cr(VI) by diphenylcarbazide,

chromium (VI) absorbance mesaurements were made at 540 nm.

A Hitachi 180-70 polarized Zeeman atomic absorption spectrophotometer with deuterium background correction was used for the determination of total chromium, and chromium (III).

Chromium absorbance mesaurements were made at 357.9 nm. A Hitachi hollow cathode lamp operating at 7.5 mA.

Jenway 3100 pH-meter was used to mesaure pH values.

2.3. Synthesis of 2-methacryloylamidohistidine (MAH) and chromium (III) methacryloylhistidine

2-Methacryloylamidohistidine (MAH) was synthesized according to the procedure reported in the previous work [26,33]. For synthesis of chromium (III)-methacryloylhistidine, methacryloylhistidine (0.540 g) was dissolved in the 15 mL of ethyl alcohol. $Cr(NO_3)_3 \cdot 9H_2O$ (0.135 g) was added slowly to this solution with continuous stirring at room temperature. The solution was allowed to stir for 3 h and turned to clear green. Solvent was then removed on rotovap to yield a green solid, which was recrystallized from ethanol/acetonitrile to give grey crystalline solid. FTIR (KBr, cm^{-1}); 1724 cm^{-1} (C=O stertch); 1505 cm^{-1} (C–N stertch); 495 cm^{-1} (Cr–N stretch).

2.4. Preparation of chromium (III) imprinted beads

The Cr(III) imprinted beads were prepared by suspension polymerization technique. A typical polymerization procedure of poly(EDMA-MAH/Cr(III)) beads was given as follow: the dispersion medium was prepared by dissolving 0.2 g polyvinylalcohol within 60 mL of distilled water. MAH-Cr(III) complex was dissolved in 4.0 mL of ethyl alcohol, then this solution was mixed into 8.0 mL/12.0 mL EDMA/toluene mixture and 0.06 g of 2,2′-azobisisobutyronitrile (AIBN) was dissolved within this monomer mixture. This solution was then transferred into the dispersion medium placed in a magnetically stirred (at a constant stirring rate of 600 rpm) glass polymerization reactor (100 mL), which was in a thermostatic water bath. The reactor was flushed by bubbling nitrogen and then was sealed. The reactor temperature was kept constant at $70\,^{\circ}C$ for 6 h. Then, the polymerization was completed at $90\,^{o}C$ in 3 h. After polymerization, the poly(EDMA-MAH/Cr(III)) beads were separated from the polymerization medium. The residuals (e.g., unconverted monomer, initiator and solvent) were removed by a suitable cleaning procedure. The resulting beads were treated with 60/40 methanol/water, pH 3, for 24 h to remove the template. The template free polymers were treated with 1 M HNO_3 and 100 mM succinic acid in the shaker bath to remove Cr(III) ions for 72 h. The chromium content of the succinic acid and HNO_3 solutions were determined spectrophotometrically. Briefly, beads were cleaned by water and dried in a vacuum oven at $70\,^{\circ}C$. The mechanism for the molecular recognition was given in the following Scheme. In the same way, non-imprinted beads were also prepared by using MAH and EDMA [26].
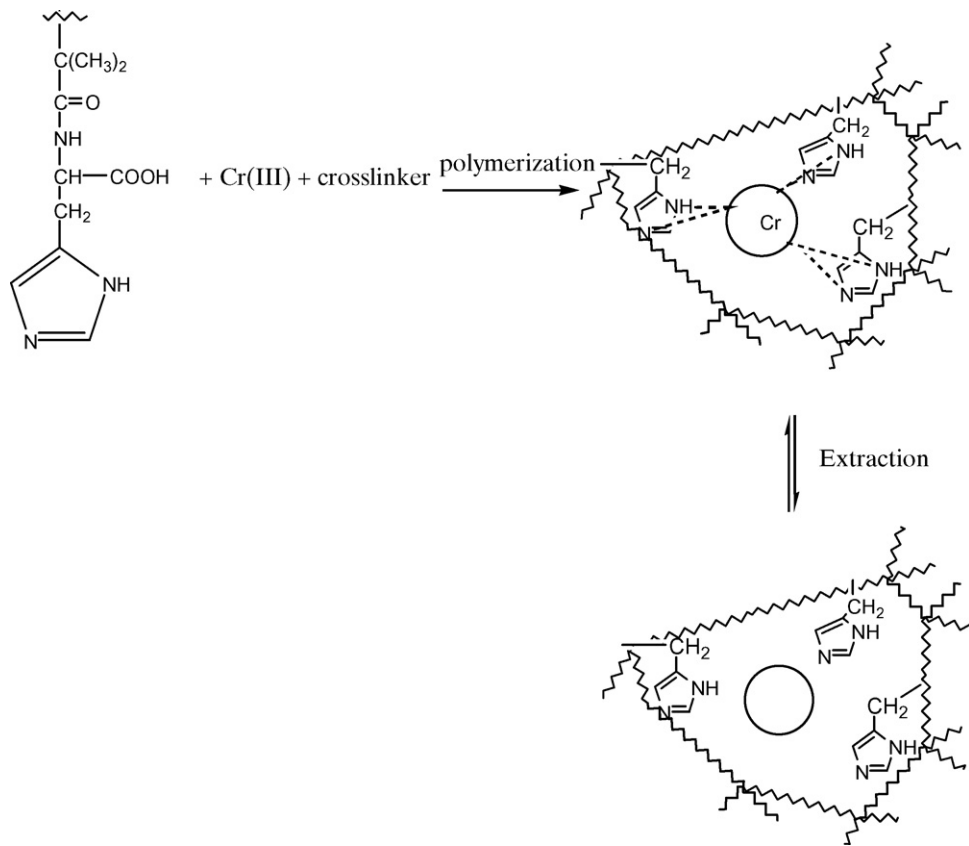
In the suspension polymerization, the yield of spherical beads with a size range of 63–140 μm in diameter was found to be 93% (w/w) based on monomers initially charged in the polymerization reaction. The equilibrium swelling ratio of non-imprinted and Cr(III)-imprinted beads are 37% and 59%, respectively.

2.5. Cr(III) sorption–desorption studies

Sorption of Cr(III) aqueous solutions was investigated in batch experiments. Effects of the initial Cr(III) concentration and pH of the medium on the adsorption rate and sorption capacity were studied. 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 until equilibrium was attained. In all experiments, polymer concentration was kept constant at 25 mg/50 mL. The concentration of the metal ions in the aqueous phases after desired treatmant periods were measured by using a flame atomic absorption spectrophotometer and deuterium background correction was used. The instrument response was periodically checked with known Cr(III) solution standards. The experiments were performed in replicates of three and the sample were analyzed in replicates of three as well. For each set of data present, standard statistical methods were used to determine the mean value and standard deviations. Confidence intervals of 95% were calculated for each set of samples in order to determine the margin error. Sorption values (mg/g) were calculated as the difference in Cr(III) ion concentration of the pre- and post-sorption solutions divided by the weight of dry beads. Competitive sorption of Cr(III), Co(II), Ni(II) and Cr(VI) from their mixture was also investigated in a batch sysytem. A solution (20 mL) containing 50 mg/L from each metal (using $K_2Cr_2O_7$, $Ni(NO_3)_2$, $Co(NO_3)_2 \cdot 4H_2O$ and $Cr(NO_3)_3 \cdot 9H_2O$) ions was treated with the Cr(III) imprinted polymers at a pH 7.0 at room temperature, in the flask stirred magnetically at 600 rpm. After sorption equilibrium, the concentration of metal ions (total chromium, chromium (III), nickel (II), cobalt (II)) in the remaining solution was mesaured by a FAAS system and used UV–vis scanning spectrophotometer for determination of chromium (VI).

Adsorbed Cr(III) ions were desorbed by treatment with 0.1 M of succinic acid solution. The Cr(III) adsorbed imprinted beads were placed in the desorption medium and stirred continuously at 600 rpm at room temperature for 2 h. The final Cr(III) concentration in aqueous phase was determined by atomic absorption spectrometer. The desorption ratio was calculated from the amount of Cr(III) ions adsorbed on the imprinted beads and final Cr(III) concentration in the desorption medium. In order to test the reusability of Cr(III)-imprinted beads, Cr(III) sorption–desorption procedure was repeated five times by using the same imprinted beads.

For the preconcentration of Cr(III) ions, 100 mL of the aqueous solution containing 1.0 ng/mL of chromium (III) was treated with 25 mg imprinted beads at pH 7.0 for 30 min. Finally, Cr(III)-imprinted beads were separated from the adsorption media by filtration and 10 mL of succinic acid solution was

added and stirred at 200 rpm for 3 h. Imprinted beads were separated from the desorption media and the concentration of Cr(III) ions in the desorption media was injected to FAAS system.

3. Result and discussion

3.1. Sorption

3.1.1. Sorption rate

Fig. 1 shows the amount of Cr(III) ions adsorbed on poly(EDMA-MAH/Cr(III)) beads as a function of time. High adsorption rates are observed at the beginning of adsorption and saturation values are reached wihtin 30 min. Adsorption of Cr(III) ions was quite fast. This fast adsorption equilibrium time is most probably due to high complexation rate groups onto the beads structure.

3.1.2. Sorption capacity

Fig. 2 shows the sorption capacity of Cr(III) ions on the Cr(III)-imprinted beads and Fig. 3 shows Langmuir adsorption isoherm of Cr(III)-imprinted beads. The amount of Cr(III) ions adsorbed per unit mass of the imprinted beads (i.e. sorption capacity) increased almost linearly with the initial concentration of Cr(III) ions. The amount of Cr(III) ions adsorbed on beads was 69.28 mg/g. For the systems considered, the Langmuir model was found to be applicable in interpreting Cr(III) adsorption on the Cr(III)-imprinted beads. The Langmuir adsorption model can be applied in this affinity system and the correlation coefficients (R^2) was 0.9158.
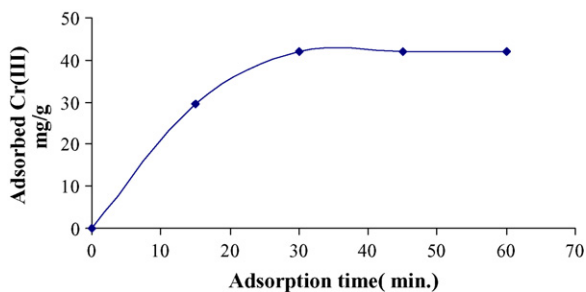

Fig. 1. Sorption rates of Cr(III) ions on the Cr(III)-imprinted microbeads; pH: 6.0; T: 25 °C.
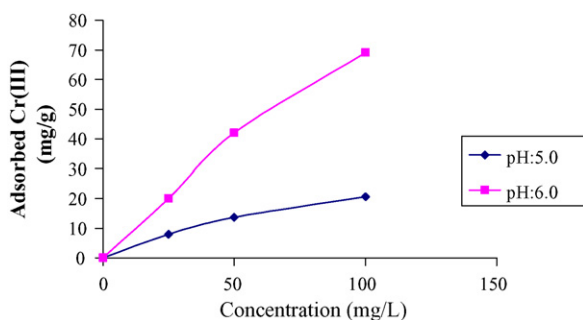

Fig. 2. Adsorption capacity of Cr(III) ions on the Cr(III)-imprinted beads; pH: 5.0 and 6.0; T: 25 °C.
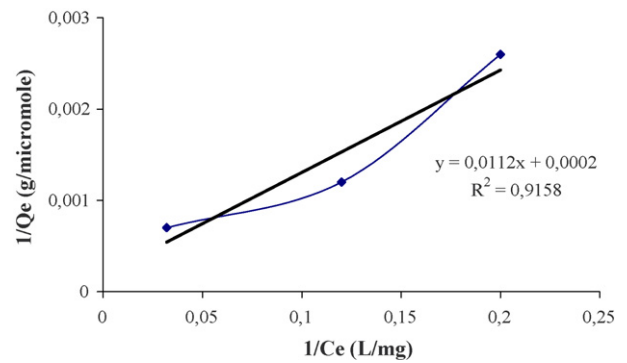

Fig. 3. Langmuir adsorption isoherm of Cr(III)-imprinted beads, pH: 6.0; T: 25 °C.

3.1.3. Effect of pH

The pH is one of the most important parameters controlling the metal ion sorption process. The effect of pH on the chromium (III) and Cr(VI) ion sorption of poly(EDMA-MAH/Cr(III)) beads is shown in Fig. 4. The Cr(III)-imprinted beads for Cr(III) exhibited a low affinity in acidic concentration (pH < 5) and a high affinity at pH.6.0. Sorption capacity was also showed to decrease at pH ≥ 4 for Cr(VI) ions. At pH < 4 the concentration of hydrogen ions caused such amino group protonation that the separation of Cr(VI) ions was almost complete. Cr(VI) is in anionic form and Cr(III) is in cationic form. So, Cr(VI) ions are reacted with protoned amino groups but Cr(III) ions are not reacted with them. With an increase of pH and a decrease in the number of protoned amino groups, retention decreases for Cr(VI) ions but increases for Cr(III).

3.1.4. Selectivity studies

Competitive sorption of Cr(VI)/Cr(III), Ni(II)/Cr(III), Co(II)/Cr(III) from their couple mixture was also investigated in a batch system. Sorption capacities of the Cr(III)-imprinted and non-imprinted beads for metal ions under competitive conditions (i.e. sorption from solution containing 50 mg/L from each of Cr(III), Co(II), Ni(II) and Cr(VI) ions) are given in Table 1. The Cr(III) sorption capacity of the Cr(III)-imprinted beads was much higher than that for other metal ions. The compative sorption capacity of the Cr(III)-imprinted beads for Cr(III) ions was also higher than non-imprinted beads. When they exist in the
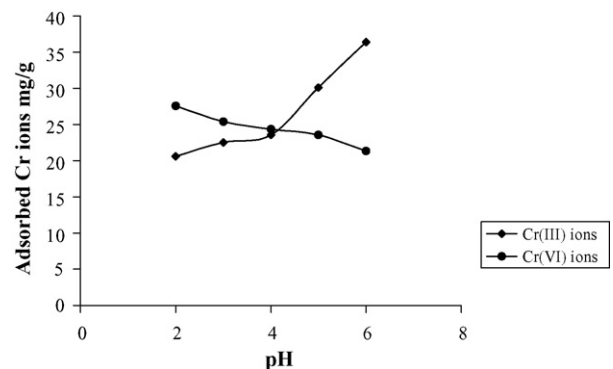

Fig. 4. Effects of pH on Cr(III–VI) sorption; Cr(III–VI) initial concentration, 50 ppm; sorption time: 30 min; T: 25 °C.

Table 1
Competitive sorption of chromium and metal ions on the Cr(III)-imprinted and non-imprinted beads (pH: 6.0)

Couple mixture (50 mg/L)	Adsorbed metal ions (mg/g)							
	Imprinted beads				Non-imprinted beads			
	Cr(III)	Co(II)	Ni(II)	Cr(VI)	Cr(III)	Co(II)	Ni(II)	Cr(VI)
Cr(III)–Co(II)	39.91	25.44	–	–	21.2	27	–	–
Cr(III)–Ni(II)	20.1	–	6.57	–	20.4	–	28.9	–
Cr(III)–Cr(VI)	32.7	–	–	18.43	22.4	–	–	29.3

same medium, a competition will start for the same attachment sites. It can be concluded that the Cr(III)-imprinted beads show the following metal ion affinity order under competitive conditions: Cr(III) > Co(II) > Ni(II) > Cr(VI). It should be noted that the imprinted beads showed selectivity for the target molecule (i.e. Cr(III) ions) due to molecular geometry.

Distribution and selectivity coefficient of Cr(III) with respect to Co(II), Ni(II) and Cr(VI) was calculated as explained below.

$$K_d = [C_i - \frac{C_f}{C_f}]$$
$$\times (\text{volume of the solution, mL/mass of beads, g}) \qquad (1)$$

where K_d, C_i and C_f represent the distribution coefficient, initial and final solution concentrations, respectively. The selectivity coefficient for the binding of a nickel ion in the presence of competitor species can be obtained from equilibrium data according to the Eq. (1):

$$k = \frac{K_d(\text{Cr(III)})}{K_d(X)} \qquad (1)$$

where k is the selectivity coefficient and K is the competitive metal ion. A comparison of the k values of imprinted polymers allow an estimation of the effect of imprinting on selectivity. A relative selectivity coefficient k' (Eq. (2)) can be defined [34,35]:

$$k' = \frac{k_{\text{imprinted}}}{k_{\text{control}}} \qquad (2)$$

A comparison of the selectivity coefficient of Cr(III)-imprinted polymers with the selectivity coefficient of non-imprinted polymers showed that the imprinted matrix for Cr(III)/Co(II), Cr(III)/Ni(II) and Cr(III)/Cr(VI) was 6.35, 8.88, 5.66 times

greater than non-imprinted matrix, respectively (Table 2). This means that Cr(III) ions can be determined even in the presence of Co(II), Ni(II), Cr(VI) interferences.

3.1.5. Desorption and repeated use

The repeated use (i.e. regenerability) of the commercial adsorbent is likely to be a key factor in improving wastewater process economics. Desorption of the adsorbed Cr(III) ions from the imprinted microbeads was also studied in a batch experimental set-up. Various factors are probably involved in determining rates of Cr(III) desorption, such as the extent of hydration of the heavy metal ions and polymer microstructure. However, an important factor appears to be binding strength. In this study, the desorption time was found to be 3 h.

Desorption ratios are very high (94%). When succinic acid is used as a desorption agent, the coordination sphere of chelated Cr(III) ions is disrupted and subsequently Cr(III) ions are released from the chromium templates into desorption medium. In order to show the reusability of the Cr(III)-imprinted polymers, sorption–desorption cycle was repeated 5 times by using same imprinted microbeads. Sorption-desorption cycle of Cr(III)-imprinted polymeric sorbents was shown in Fig. 5. The results clearly showed that the Cr(III)-imprinted beads can be used repeatedly without loosing significantly their adsorption capacities.

3.2. Preconcentration

For the preconcentration of chromium ions, 100 mL of the aqueous solution containing 1.0 ng/mL of Cr(III) ions was treated with 25 mg of Cr(III)-imprinted beads at pH 7.0 for 30 min. Finally, polymeric microbeads were separated from

Table 2
The effect of imprinting on selectivity, pH: 6.0

Beads	Cr(III) (mg/L)	Co(II) (mg/L)	K_D (Cr(III))	K_D (Co(II))	k	k'
Non-imprinted	50	50	711.4	1173.91	0.60	
Cr(III)-imprinted	50	50	3955.40	1035.83	3.81	6.35

Beads	Cr(III) (mg/L)	Ni(II) (mg/L)	K_D (Cr(III))	K_D (Ni(II))	k	k'
Non-imprinted	50	50	689.18	1363.2	0.50	
Cr(III)-imprinted	50	50	672.24	151.27	4.44	8.88

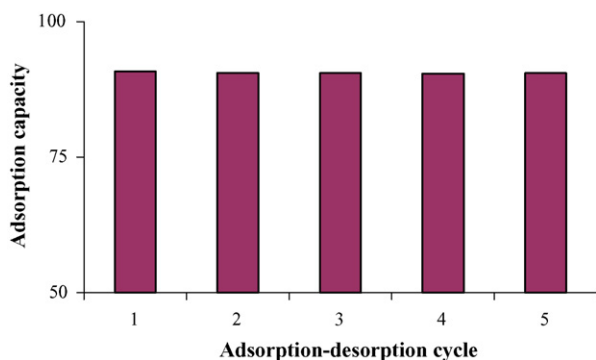| Beads	Cr(III) (mg/L)	Cr(VI) (mg/L)	K_D (Cr(III))	K_D (Cr(VI))	k	k'
Non-imprinted	50	50	811.59	1415.45	0.57	
Cr(III)-imprinted	50	50	1890.17	583.78	3.23	5.66

Fig. 5. Sorption–desorption cycle of Cr(III)-imprinted polymeric sorbents.

the adsorption media and 10 mL of the succinic acid solution was added and stirred at 200 rpm for 3 h. Imprinted beads were removed from the desorption medium and concentration of Cr(III) ions in the desorption medium was determined by FAAS.

It is observed that preconcentration was performed more than 50-folds. In this manner, detection limit of 1.2 ng/mL was reached.

3.2.1. Analytical performance of the methods

The characteristic performance data for the off-line preconcentration procedure were given in Table 3.

The precision of method for a standard, evaluated as the relative standard deviation (R.S.D., $n = 6$) was 1 ng/mL of Cr(III) ions. The detection and determination limits, defined as the concentration of analyte giving signals equivalent to three and ten times, respectively, the standard deviation of the blank plus the net blank intensity for 100 mL of sample volume, were 1.2 and 4 ng/mL. The detection limits were improved by more than an order of magnitude compared with those obtained using single element determination after preconcentration. The improvement in the detection limits is mainly due to beter instrumentation (transverse-heated graphite atomizer and longitudinal Zeeman-effect background corrector). The preconcentration procedure showed a linear curve within the concentration range from 1.2 to 120 ng/mL. The enrichment factor, defined as the ratio of the slopes of the linear section of the calibration graphs before and after the preconcentration, was 267. It was obtained by comparing the analyte signal intensities, submitted to the proposed preconcentration procedure.

Table 3
Performance characteristics of the preconcentration procedure

Parametreler	Cr
Precision (R.S.D.)	2.6
Detection limit (3 s)	1.2 ng/mL
Linear calibration range	1.2–120 ng/mL
Regression equation (after preconcentration)	$AA = 0.0004C_{Cr(III)} + 0.0002C_{Cr(III)}$: ng/mL
Conventional regression equation	$AA = 0.0015C_{Cr(III)} + 0.0005C_{Cr(III)}$: ng/mL
Enrichment factor	267

4. Conclusion

In the present work, we have shown that metal ion-imprinted polymer that contains [poly(EDMA-MAH/Cr(III))] is very selective and has high sorption capacity for Cr(III) ions. The imprinted beads were constructed with the aid of the interaction between Cr(III) ion and imidazole group. A high adsorption rate was observed at the beginning of the sorption process and saturation values were reached within 30 min. The maximum Cr(III) ion sorption capacity of the [poly(EDMA-MAH/Cr(III))] beads was 69.28 mg/g. Competitive Cr(VI)/Cr(III), Ni(II)/Cr(III), Co(II)/Cr(III) sorption studies showed that [poly(EDMA-MAH/Cr(III))] beads are only selective to chromium (III) ion, even in the presence of Cr(VI), Co(II) and Ni(II) ions. The K_d values for the Cr(III)-imprinted beads of [poly(EDMA-MAH/Cr(III))] showed increase in K_d for Cr(III), while K_d decrease for other ions. The cross-linked imprinted adsorbents can be used in harsch mediums such as concentrated acid and high temperature, feature rapid equilibration in absorbing Cr(III) ion and can be used many times without loosing sorption capacity and the Cr(III)-imprinted adsorbent which is highly selective toward Cr(III) ions, therefore, was expected to be useful material for the interference-free adsorbent for the extraction and preconcentration of Cr(III) ions.

Acknowledgement

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