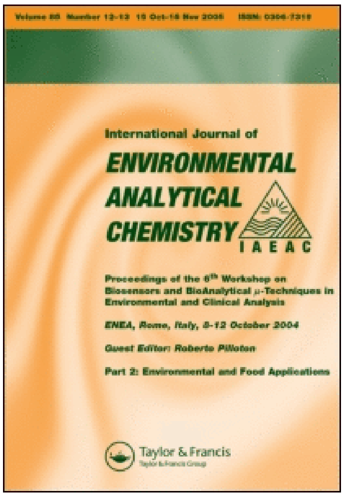

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Preparation and evaluation of an ion imprinted sol-gel material for selective solid-phase extraction of Ni(II)

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To cite this Article Saraji, Mohammad , Yousefi, Hamideh and Meghdadi, Soraia(2009) 'Preparation and evaluation of an ion imprinted sol-gel material for selective solid-phase extraction of Ni(II)', International Journal of Environmental Analytical Chemistry, 89: 5, 305 — 317

To link to this Article: DOI: 10.1080/03067310802610268

URL: http://dx.doi.org/10.1080/03067310802610268

Intern. J. Environ. Anal. Chem.
Vol. 89, No. 5, 20 April 2009, 305–317

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Preparation and evaluation of an ion imprinted sol–gel material for selective solid-phase extraction of Ni(II)

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(*Received 21 August 2008; final version received 7 November 2008*)

An ion imprinted silica sorbent was prepared using a sol–gel process for selective extraction of Ni(II) ions from water samples. *Bis*(dibenzoylmethanto)nickel(II) complex was used as template; phenyltrimethoxysilane and 3-aminopropyltriethoxysilane as functional monomers and tetraethylorthosilicate as reticulating agent. The material was packed in solid-phase extraction (SPE) column. The effect of sampling volume, elution conditions, sample pH and sample flow rate on the extraction of Ni ions from water samples were studied. The relative selectivity coefficients of imprinted sorbent for Ni(II)/Co(II), Ni(II)/Cu(II) and Ni(II)/Cd(II) were 23.7, 30.3 and 24.4, times greater than non-imprinted sorbent, respectively. The relative standard deviation of the eight replicate determinations of Ni(II) was 4.2%. The detection limit was $0.9\,\mu g\,L^{-1}$ using flame atomic absorption spectrometry. The developed method was successfully applied to the determination of trace nickel in water samples.

Keywords: ion imprinted silica sorbent; sol–gel process; solid-phase extraction; nickel ion; atomic absorption spectrometry

1. Introduction

Materials with molecular recognition ability are of great importance in fields such as separation, sensors, drug delivery, and catalysis. Molecular imprinted polymers (MIPs) are synthetic materials produced by the cross-linking of functional monomers or polymers in the presence of a template molecule. Extraction of the template molecules leaves a predetermined arrangement of ligands and a tailored binding pocket [1]. Such an imprinted polymer shows an affinity for the template molecule over other structurally related compounds. Most imprinted polymers were produced with pure organic polymers and there are very limited reports on inorganic molecularly imprinted polymers.

Recently, molecularly imprinted sol–gel materials have been extensively studied [2–6]. These materials are fabricated by a conventional sol–gel process and incorporation of the template molecules into rigid inorganic or inorganic–organic networks. The inorganic matrix is formed by sequential hydrolysis and condensation of metal alkoxides in aqueous acid or base with a mutual cosolvent. Sol–gels possess several physical properties, as they exhibit porous, rigid, good optical and mechanical properties and chemically inert. The advantages of templating using sol–gels rather than acrylic systems were reviewed by Collinson [7].

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067310802610268
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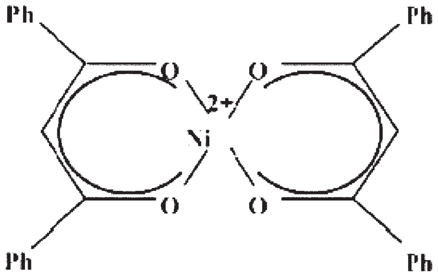

Figure 1. Structure of *bis*(dibenzoylmethanto)nickel(II) complex.

Ion imprinted materials are similar to MIPs but recognise inorganic ions after imprinting [8–13]. Due to the popularity of solid-phase extraction (SPE), imprinted materials have appeared as alternatives to conventional SPE sorbents with the aim of achieving a more selective preconcentration of analytes [10–21]. Rao *et al.* [22,23] have reviewed various ion-imprinted materials as SPE sorbents for enrichment–separation of inorganic materials.

There are a few previously published papers dealing with the preparation and use of ion imprinted polymers (IIPs) for extraction and determination of nickel(II) ion [24,25]. Say *et al.* [24] have developed IIPs based on poly(ethyleneglycoldimethacrylate/Ni(II)–methacryloylhistidinedihydrate microparticles through dispersion polymerisation technique. The competitive adsorption capacity of Ni(II)-imprinted microbeads for Ni(II) ions was higher than non-imprinted microbeads. They reported higher selectivity coefficients compared to non-imprinted polymers for Ni(II) over Zn(II), Co(II) and Cu(II) ions. Chang *et al.* [25] have also prepared a Ni(II)-imprinted amino-functionalised silica gel sorbent with excellent selectivity for nickel(II) by an easy one-step reaction by combining a surface imprinting technique for selective SPE of trace Ni(II) in water samples prior to its determination by inductively coupled plasma atomic emission spectrometry. The distribution ratio (*D*) values of the Ni(II)-imprinted polymer for Ni(II) were greatly larger than that for Cu(II), Co(II), Zn(II) and Pd(II).

In our knowledge, synthesis of Ni(II)-imprinted sol–gel sorbent and preconcentration by packed bed column have not been employed previously for the separation and preconcentration of Ni(II) from aqueous solution. The aim of this work was to utilise sol–gel process to fabricate a stable and rigid host matrix via the hydrolysis and condensation of suitable organosilicon and silicon alkoxide precursors for the creation of Ni(II)-ion imprinted sorbent. *Bis*(dibenzoylmethanto)nickel(II) complex (Figure 1) was used to encapsulate into the sol–gel matrix. The experimental parameters that affect the extraction efficiency of this imprinted silica sorbent and its applicability to selective solid-phase extraction of Ni(II) from water samples were described and discussed.

2. Experimental

2.1 *Reagents*

Standard stock solutions of Ni(II), Co(II), Cu(II) and Cd(II) (1000 mg L^{-1}) were prepared by dissolving the required amounts of the metals in a small volume of concentrated nitric acid. Stock solutions were diluted to 1 L with distilled water. More dilute standards were prepared daily by dilution of these solutions.

Bis(dibenzoylmethanto)nickel(II) complex [Ni(DBM)$_2$] was synthesised from nickel acetate tetrahydride (Merck, Darmstadt, Germany) and dibenzoylmethane (Aldrich, St. Louis, MO, USA) according to the previous procedure [26]. Phenyltrimethoxysilane (PTMOS), 3-aminopropyltriethoxysilane (APTES), and tetraethylorthosilicate (TEOS) were purchased from Fluka (Buchs, Switzerland). HPLC grade methanol, isopropyl alcohol, and tetrahydrofuran (THF) were obtained from Caledon (Georgetown, Canada). The sample pH was adjusted with the NH_3/NH_4Cl buffer solution. Other reagents were purchased from Merck.

2.2 *Apparatus*

A Perkin-Elmer model 2380 atomic absorption spectrometer (Waltham, Massachusetts, USA) was used to measure the concentration of metal ions (Ni, Cd, Cu and Zn) in aqueous solution. The instrumental parameters were those recommended by the manufacturer. Hollow cathode lamps were used as the radiation sources. The wavelengths selected were as follows: Ni 232.0, Cu 324.8, Co 240.7 and Cd 228.8 nm. A digital pH meter (Tajhizat Sanjesh, Iran) model pH-462, equipped with a glass electrode (Sentek, Braintree, UK), was used for pH measurements.

A peristaltic pump model 444 (Ismatec, Glattbrugg, Switzerland) was used in the SPE process. Tygon pump tube with 1.524 mm i.d. was used for aspirating/delivering the solutions. A 3 mL polypropylene SPE column was obtained from IST (Cambridge, UK). Porous polyethylene frits (20 µm porosity, IST) were used to fit the SPE column.

2.3 *Preparation of the sol–gel Ni(II)-ion imprinted sorbent (IIS)*

Tetraethylorthosilicate (180 mmol, 37.50 g), PTMOS (6.9 mmol, 1.36 g), APTES (3.5 mmol, 0.763 g) and THF (300 mL) were mixed in a beaker. To this homogeneous solution, 46 mL of water and 5.8 mL of ammonium hydroxide (0.025%) as catalyst were added. The resulting mixture was stirred at 25°C for 45 min. The imprint molecule, [Ni(DBM)$_2$] (2.3 mmol, 1.248 g) was dissolved in 45 mL of THF and added to the silica solution. The mixture was stirred for 2 h at room temperature. The reaction vessel was open to air and left to stand for 7 days at 25°C. The resulting solid was grounded in a mechanical mortar and wet-sieved to 53–106 µm particle size. The particulates were washed with 0.1 M HCl solution. Finally, the particles were washed with distilled water and dried at 60°C.

For comparison, blank non-imprinted silica (NIS) that did not contain [Ni(DBM)$_2$] was prepared simultaneously using the same protocol. The dibenzoylmethane ligand (4.6 mmol, 2.226 g) was used as template instead of the [Ni(DBM)$_2$].

2.4 *Solid-phase extraction of Ni(II)*

A total of 200 mg of the sorbent (IIS and NIS) was poured into the SPE column. A polyethylene frit was placed at both ends to prevent loss of the sorbents during the sample loading. At first use of the IIS column, for elimination of the Ni ions, 1 M HCl solution was passed through the column at 0.2 mL min^{-1} for 24 h. Before loading the sample, SPE cartridges were conditioned by passing 10 mL buffer solution (pH 8) at a flow rate of 1.0 mL min^{-1}. Then a solution (pH 8) containing Ni(II) was passed through the column at flow rate of 2.0 mL min^{-1}. The column was washed with 3 mL distilled water and then eluted with 12 mL of 1 M HCl–isopropanol (90 : 10) at a flow rate of 0.4 mL min^{-1}. To access lower detection limits in the sample solution, the final extract was placed in a water bath (60°C) and concentrated to 2.0 mL under a gentle stream of nitrogen. For study of the real samples spiked at concentration of 100 µg L^{-1}, to avoid exceeding data from the linear dynamic range of the method, the volume of final extract was concentrated to 4.0 mL before atomic absorption spectrometer (AAS) determination.

2.5 *Loading capacity*

Loading capacity of IIS was studied in a batch experiment. To investigate the loading capacity, 100 mg of IIS (or NIS) was added to 40 mL solution containing different amounts of Ni ions (from 0.1 to 3 mg) at pH 8. The mixture was shaken at 25°C for 5 h. After centrifugation, the nickel ion in the centrifugate solution was determined by AAS.

2.6 *Selectivity experiments*

For the preconcentration of Ni(II) ions, 300 mL of the aqueous solution (pH 8) containing 20 µg L^{-1} of Cu(II), Co(II), Ni(II) and Cd(II), was passed through the IIS and NIS columns at a flow rate of 2 mL min^{-1}. After passage of the solution, the columns were eluted with 12 mL of the eluent [1 M HCl–isopropanol (90 : 10)] at 0.4 mL min^{-1} and the concentration of metal ions in the eluate was determined by AAS.

3. Results and discussion

3.1 *Ni^{2+} recognition by the Ni(II)-imprinted sorbent*

A general scheme for the sorption and desorption of Ni ion by IIS is illustrated in Figure 2. Soldatov *et al.* [26] have demonstrated that in metal dibenzoylmethanates complex, amine ligands such as 4-vinylpyridine can coordinate to the central metal (Ni or Co) axially. In this work, 3-aminopropyltriethoxysilane acts not only as the axial ligand for the complex but also as functional monomer for the polymerisation. As can be seen in the figure, the Ni^{2+} recognition site contains two dibenzoylmethanate chelate ligands in the equatorial plane and two axial amine ligands.

3.2 *Optimisation of sorption and elution of Ni ions on the ion imprinted sorbent*

To evaluate the capability of the sorbent for selective preconcentration of Ni ions from water samples, the method was optimised for various parameters such as sample pH, sample volume, and elution conditions. The recovery percentage, which was calculated from the amount of Ni ion in the starting sample and the amount of Ni ion eluted from the column, used as the analytical signal.

3.2.1 *Sample pH*

Sample pH plays an important role in the retention of nickel ions on the sorbent because it affects the complexation reaction between metal ion and ligand. The influence of sample pH on the retention of Ni(II) ions on the sorbent was studied at different pH values

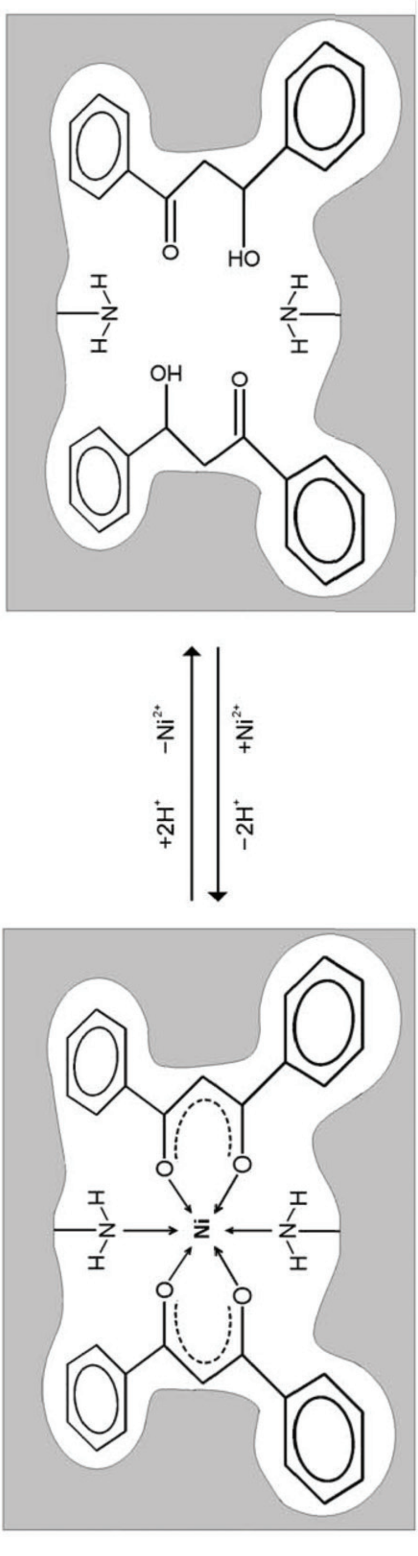

Figure 2. Scheme for Ni^{2+} recognition by the Ni(II)-imprinted sorbent.

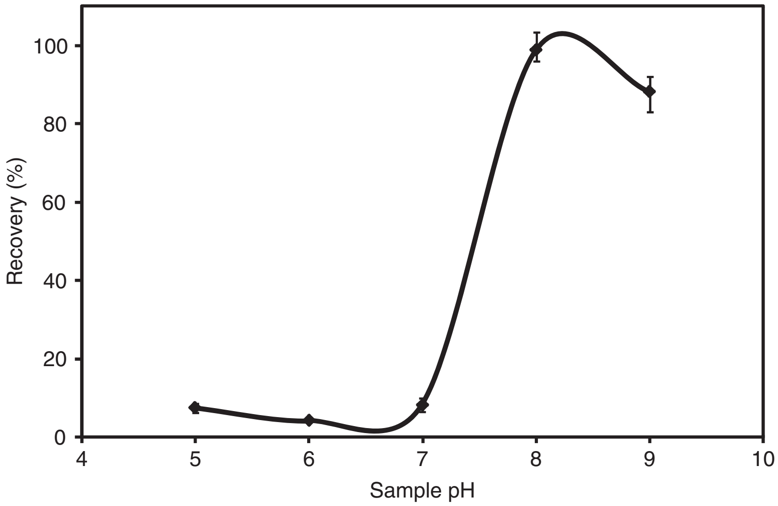

Figure 3. Effect of sample pH on the adsorption of Ni(II) on the Ni(II)-imprinted sorbent. Sample volume: 50 mL, Ni(II) concentration: 0.15 mg L^{-1}, sample flow rate: 1 mL min^{-1}, eluent: 1.0 M HCl–isopropanol (90 : 10), eluent flow rate: 0.4 mL min^{-1}, elution volume: 12 mL.

from 5 to 9. A volume of 50 mL of the sample containing 0.15 mg L^{-1} of Ni ions was passed through the IIS column at 1 mL min^{-1} (Figure 3).

Elution of the SPE column was performed with 12 mL of 1 M HCl–isopropanol (90 : 10) at 0.4 mL min^{-1} and the concentration of metal ions in the eluate was determined by AAS. At neutral and acidic media, the extraction of Ni ion was $<10\%$. At $pH < 7$ the donating oxygen atoms can be protonated and, therefore, negligible amounts of nickel ions are adsorbed to the sorbent. The percent recovery of Ni ion is sharply increased with increasing pH of solution from 7 to about 8, so that Ni^{2+} ions are quantitatively extracted at a pH 8. After pH 8, the sorption quantity of Ni ion was decreased. At $pH > 8$, concentration of NH_3 is increased and a fraction of Ni ions in the solution remain as Ni–NH_3 complex and as a result, sorbent extraction efficiency is decreased. On the other hand, the hydroxide in a basic solution may precipitate nickel ions.

3.2.2 *Nature and volume of eluent*

A 50 mL volume of the sample containing 0.15 mg L^{-1} of Ni ions at pH 8 was passed through the ion-imprinted column at 1 mL min^{-1}. For elution of Ni ions from the column, various eluents with different elution volumes were tested. The elution flow rate was set at 0.2 mL min^{-1}. The results are shown in Table 1. Addition of isopropanol to the eluent showed an enhancement in the percentage recovery of Ni(II). Hydrophobic nature of the complex on the sorbent surface may inhibit close contact with sample solution. Addition of isopropanol to the HCl solution may decrease both surface tension and polarity of the eluent and would affect the eluting power of the eluent. The results indicate quantitative recovery ($>98\%$) of nickel is achieved with 12 mL mixture of 1 M HCl and isopropanol in the ratio of 9 : 1 (or 8 : 2).

Table 1. Influence of nature and volume of eluent on the percent extraction of nickel ion.

Eluent	Eluent volume (mL)	Extraction (%)[a]
1 M HCl	14.0	84.4
1 M HCl	12.0	85.4
1 M HCl	8.0	74.1
1 M HCl + MeOH (80 : 20) (v/v)	12.0	88.0
1 M HCl + MeOH (60 : 40) (v/v)	12.0	76.8
1 M HCl + isopropanol (80 : 20) (v/v)	12.0	98.1
1 M HCl + isopropanol (90 : 10) (v/v)	12.0	99.9
1 M HCl + isopropanol (90 : 10) (v/v)	10.0	94.1
1 M HCl + isopropanol (90 : 10) (v/v)	8.0	93.9

[a]The relative SDs are between 2.8% and 6.4% ($n = 3$).

3.2.3 *Eluent and sample flow rate*

Eluent flow rate has a great effect on the elution efficiency of Ni(II) from the sorbent. At high eluent flow rate, Ni(II) cannot be desorbed completely and the elution efficiency will be decreased. Influence of the eluent flow rate (0.2, 0.4, 0.6, 0.8 and 1.0 mL min^{-1}) on the value of nickel desorption was studied. Elution of the SPE column was performed with 12 mL of 1.0 M HCl–isopropanol (90 : 10) at different flow rates between 0.2 and 1.0 mL min^{-1}. The results (data no shown) show that the quantitative recovery was observed at flow rates ≤0.4 mL min^{-1}.

As the retention of Ni(II) on the adsorbent depends upon the flow rate of the sample solution, its effect was examined under the optimum conditions (pH, eluent, etc). A 50 mL volume of the sample containing 0.15 mg L^{-1} of Ni ions at pH 8 was passed through the SPE column. Effect of the sample flow rate on the adsorption of Ni ions was studied by changing the flow rate between 1 and 5 mL min^{-1}. Adsorption of Ni ions was quantitatively at flow rates up to 2 mL min^{-1}.

3.2.4 *Sample volume*

To determine the sample volume that can be concentrated with the acceptable level of recoveries, the effect of sample volume on the retention of metal ions was also investigated. For obtaining breakthrough volume curve, different volumes of aqueous solutions (50, 100, 200, 300, 400 and 500 mL) containing varying amounts of the metal ion (20 µg) were passed through the IIS column. Elution of the SPE column was performed with 12 mL of 1.0 M HCl–isopropanol (90 : 10) at 0.4 mL min^{-1}. Sample volumes up to 300 mL can be applied with quantitative recoveries more than 95% (Figure 4). Therefore, 300 mL sample solution was adopted for the preconcentration of Ni(II) from sample solution. In this study, the final extracted volume was 2 mL, so an enrichment factor of 150 was obtained. The enrichment factor was calculated as the ratio of final concentration of analyte in the extract to initial concentration of analyte in the aqueous solution.

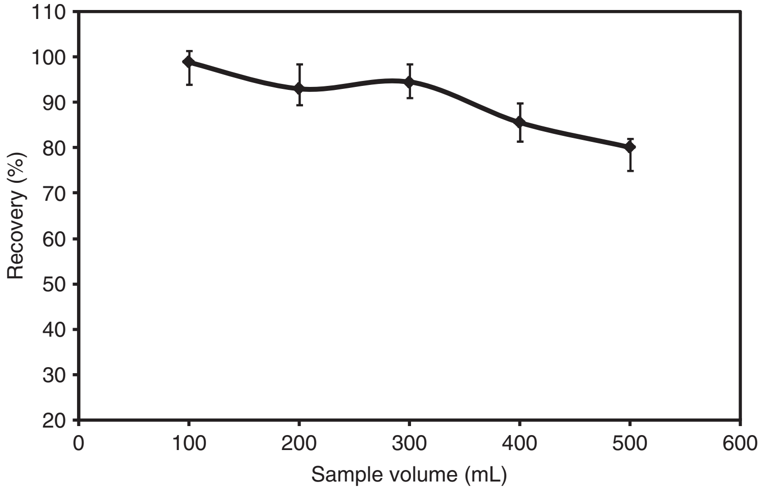

Figure 4. Effect of sample volume on the adsorption of Ni(II) on the Ni(II)-imprinted sorbent. Sample pH 8, sample flow rate: $2\,\mathrm{mL\,min^{-1}}$, eluent: 1.0 M HCl–isopropanol (90 : 10), eluent flow rate: $0.4\,\mathrm{mL\,min^{-1}}$, elution volume: 12 mL.

3.3 *The nickel adsorption capacity value*

The capacity of a sorbent can be defined as maximum amount of metal sorbed per gram of the sorbent [27]. The capacity is dependent on the initial concentration of metal ion. As the concentration of metal ion increases, the capacity value also increases. Loading capacity of the sorbent was calculated by following equation:

$$Q = \frac{(C_0 - C_e)V}{W}$$

where Q is the loading capacity of the sorbent ($\mathrm{mg\,g^{-1}}$); C_0 and C_e are the concentrations of the ions in the initial solution and in the aqueous phase after adsorption, respectively ($\mathrm{mg\,L^{-1}}$); V is the volume of the aqueous phase (mL); and W is the amount of sorbent (g).

Adsorption of Ni(II) from aqueous solution was investigated in batch experiments. 0.2 g of the IIS (or NIS) and different amounts of Ni(II) (from 0.1 to 3 mg) were added into 40 mL of water at pH 8, then these systems were stirred for 5 h. Concentration of the remained Ni(II) in the aqueous phase was determined by AAS. As can be seen in Figure 5, the amount of Ni ions adsorbed per unit mass of the sorbent increased linearly with the initial concentration of Ni(II) ions till a plateau value (adsorption capacity values) was obtained. The maximum adsorption capacity of IIS and NIS for Ni(II) were 3.4 and 1.5 mg Ni(II) $\mathrm{g^{-1}}$ sorbent, respectively.

3.4 *Selectivity of the imprinted sorbent*

Selective recognition to the template ion is an important merit for an IIS sorbent. To assess the recognition performance of the IIS sorbent, selectivity of the IIS and NIS was investigated by competitive adsorption experiment. The distribution ratio (D, $\mathrm{mL\,g^{-1}}$),

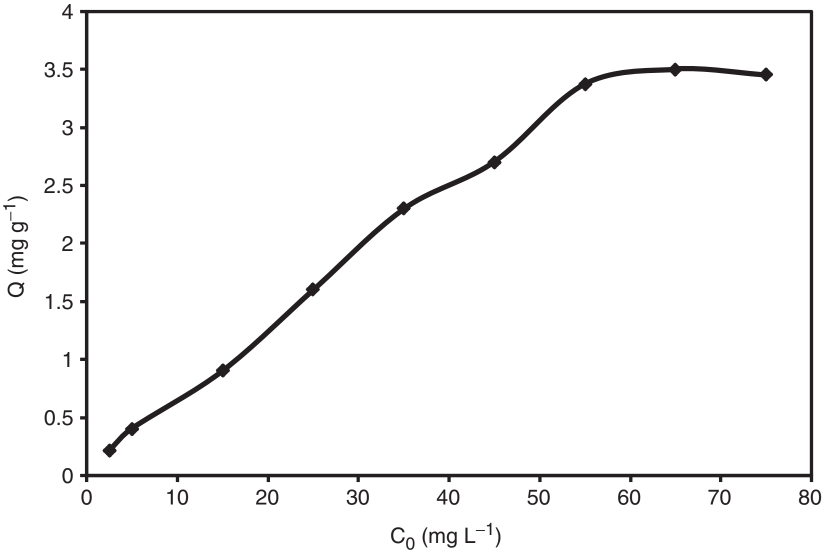

Figure 5. Effect of Ni(II) initial concentration on the adsorption quantity of Ni(II)–IIS. 200 mg of IIS, sample pH 8, 40 mL of Ni(II) solutions, stirring time 5 h.

the selectivity factor of Ni(II) with respect to other ions ($\alpha_{Ni/M}$), and the relative selectivity factor (α_r) were calculated as the following equations [9,11]:

$$D = \frac{Q}{C_e}$$

$$\alpha_{Ni/M} = \frac{D_{Ni}}{D_M}$$

$$\alpha_r = \frac{\alpha_i}{\alpha_n}$$

D_{Ni} and D_M represent the distribution ratios of Ni(II) and other ions. α_i and α_n represent the selectivity factor of IIS and NIS, respectively.

A 300 mL volume of the sample containing 20 μg L^{-1} of each of Ni(II), Cu(II), Co(II) and Cd(II) ions was passed through the IIS and NIS columns at 2.0 mL min^{-1}. After elution of the SPE columns, the metal content of the eluate was determined by AAS. Extraction percentage, distribution ratio, selectivity factor, and relative selectivity factor of Ni(II) with respect to other ions are given in Table 2. As can be seen in the table, the imprinting effect was clearly observed. The D values of present IIS for Ni(II) was large, while decreased significantly for Co(II), Cu(II) and Cd(II). The relative selectivity factors (α_r) are >1. This means that Ni(II) ions can be adsorbed more selective than ions such as Co(II), Cu(II) and Cd(II). The selectivities obtained in this study are comparable with those obtained by previous works [24,25].

3.5 *Effect of matrix ions*

The influence of possible matrix ions in the environmental samples on the recovery of Ni ions on the IIS was examined. A 300 mL portion of sample solution containing analyte and

Table 2. The selectivity parameters of imprinted and non-imprinted sorbents.

Metal ion	E(%) (IIS)	E(%) (NIS)	D_i (mL g^{-1})	D_n (mL g^{-1})	α_i	α_n	α_r
Ni	95.3	47.6	30619.6	1364.8	–	–	–
Cd	50.7	54.7	1662.4	1809.1	18.4	0.754	24.4
Co	49.6	50.9	1474.4	1555.6	20.8	0.877	23.7
Cu	62.7	69.3	2518.2	3390.8	12.2	0.402	30.3

Table 3. Determination of nickel ions in real water samples.

Sample	Ni(II) added (μg L^{-1})	Ni(II) found (μg L^{-1})	Recovery[a] (%)
Zayandeh-rood river water	0.0	13.4	–
	20.0	33.2	99.3
	50.0	66.2	105.7
	100.0	108.5	95.1
Kashkan river water	0.0	10.4	–
	20.0	29.7	96.5
	50.0	60.7	100.6
	100.0	101.9	91.5
Goldaroo wastewater	0.0	17.5	–
	20.0	34.3	94.1
	50.0	67.3	99.7
	100.0	113.7	96.2
Zarinkhodro wastewater	0.0	45.6	–
	20.0	69.4	95.1
	50.0	91.7	92.1
	100.0	134.3	88.7

[a] The relative SDs are between 3.5% and 7.8% ($n = 3$).

a given amount of foreign ions was concentrated. Preconcentration and determination was performed according to the general procedure. The results showed that existence of Na(I) and K(I) at concentration up to 20,000 μg L^{-1}; and Ca(II), Mg(II), Cd(II), Co(II), Pb(II) and Cu(II) at concentration up to 200 μg L^{-1} had no significant interferences with the determination of 20 μg L^{-1} of Ni(II). The extraction recovery of Ni(II) in this study was higher than 96.5%.

3.6 *Reusability of the column*

To test the stability and potential recyclability of the column, the ion imprinted sorbent was subjected to repeated loading and elution operations cycles. The result showed that the column was relatively stable up to at least 10 extraction–elution cycles without obvious decrease in recovery.

3.7 *Analytical performance of the method*

Under the optimum conditions described above, the calibration curve was linear over the concentration range of 3–100 μg L^{-1} of Ni(II) present in 250 mL of solution. A good

Table 4. Comparison of analytical performance data of different Ni(II)-ion imprinted sorbent used in SPE of Ni ion from water.

								Selectivity coefficient, $\alpha_{Ni/M}$						
Ligand used	Preparation method of sorbent	Precon-centration method	Mass of sorbent used (mg)	Adsorption capacity ($mg\,g^{-1}$)	Sample flow rate ($mL\,min^{-1}$)	Break through volume (mL)	Detection system	Cu	Co	Cd	Zn	LOD[c] ($\mu g\,L^{-1}$)	Precision (RSD%)	Reference
MAH[a]	Dispersion polymerisation	SPE	575	≈9	0.5	40	AAS	57.3	17.3	–	53.9	0.3	4.1	[24]
–	Surface imprinting silica gel by amino groups	SPE	20	12.61	1.5	200	ICP[b]	45.9	32.8	–	43.8	0.16	1.48	[25]
Dibenzoyl methane	Sol–gel process	SPE	200	3.4	2	300	AAS	30.3	23.7	24.4	–	0.9	4.2	Proposed method

[a] Methacryloylhistidinedihydrate.
[b] Inductively coupled plasma.
[c] Limit of detection.

linearity with squared correlation coefficient (r^2) 0.9998 was obtained. Reproducibility of the method was assessed by analysing eight spiked distilled water samples ($20\,\mu g\,L^{-1}$). The relative standard deviation was 4.2%. The limit of detection, defined as the concentration equivalent to three times the standard deviation ($n = 8$) of the blank for 250 mL of sample volume was $0.9\,\mu g\,L^{-1}$.

In order to check for possible matrix effects and investigate the applicability of the method to real sample analysis, two river water and two wastewater samples were tested. The results are listed in Table 3. The water samples were spiked with Ni(II) at different concentration levels (20, 50 and $100\,\mu g\,L^{-1}$). Recoveries of nickel were in the range of 88.7–105.7%. These results indicated the suitability of the IIS for selective SPE and determination of Ni(II) in environmental water samples.

4. Conclusions

An ion imprinted silica sorbent was prepared by sol–gel process and evaluated for selective extraction of Ni(II) ions from water samples. The imprinted sorbent has obvious imprinting effect on the imprinting ion. The values of the relative selectivity factor were found to be 23.7, 30.3 and 24.4 for Co(II), Cu(II) and Cd(II), respectively. The maximum adsorption capacity of IIS was $3.4\,mg\,g^{-1}$. This amount is about 3.7 times less than that obtained by surface imprinted silica gel [25]. The lower adsorption capacity may be because of low template/monomer ratio used for the synthesis of IIS in this work. In comparison with other Ni(II) imprinted sorbents for SPE of Ni ion from water samples (Table 4), the proposed method shows comparable results in terms of precision, selectivity, and SPE conditions. The effect of matrix can be overcome by the method, and the results are satisfying. The method has good linearity and reproducibility. The proposed procedure was successfully applied for the determination of Ni in river and wastewater samples.

Acknowledgement

The authors are grateful to the Research Council of Isfahan University of Technology (IUT) for financial support of this project.

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