Nickel Adsorption from Environmental Samples by Ion Imprinted Aniline -Formaldehyde Polymer

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ABSTRACT: *In this study, aniline-formaldehyde polymer was synthesized and then modified with extra aniline as cross-linker in the presence and absence of Ni(II) as the template to produce Ion Imprinted Poly(Aniline-Formaldehyde) (IIPAF) and Non Imprinted Poly(Aniline-Formaldehyde) (NIPAF). The IIPAF was subjected to adsorption, preconcentration and determination of Ni(II) ion in environmental samples. The effect of pH, contact time, interfering ions and other parameters on adsorption of Ni(II) was investigated. The optimum pH was found to be 8.0 with a recovery of 97.5%. Elution was performed with 0.5 M nitric acid. The sorption polymer capacity was found to be 59.4 $mg.g^{-1}$. The concentration of the metal ion was detected with flame atomic adsorption spectrometry. The prepared ion imprinted sorbent showed high adsorption capacity, significant selectivity, good site accessibility and fast binding kinetics for Ni(II) ion. Scatchard analysis revealed that the homogeneous binding sites were formed in the polymers. The equilibrium adsorption data of Ni (II) on synthetic polymer were analyzed by Langmuir, Freundlich and Temkin models. The method was successfully applied for determination of Ni(II) ions in environmental water sample.*

KEY WORDS: *Solid phase extraction, Ion imprinted polymers, Poly(aniline-formaldehyde), Nickel.*

INTRODUCTION

Nickel is considered an essential element, which acts as an activator of several enzymes beyond to enhance the insulin activity, excessive nickel amount in the organism is very toxic, which can be manifested by affecting the activity of natural killer cells. In addition, the chronic exposition at high nickel concentration can cause cancer.

Another common disease caused by skin disorder is known as nickel-eczema. It is used in a wide variety of industries such as plating and cadmium–nickel battery, phosphate fertilizers, mining, pigments, stabilizers and alloys, and find its way to the aquatic environment through wastewater discharge. Toxic metal compounds

coming to the earth's surface not only reach the earth's waters (seas, lakes, ponds and reservoirs), but can also contaminate underground water in trace amounts by leaking from the soil after rain and snow. Therefore, the earth's waters may contain various toxic metals.

The direct determination of trace elements like nickel real samples are a difficult task. The main restrictions come from the complexity of the matrix and the extremely low concentrations of analytes in those samples, which are often below the detection limits of available techniques [1- 4]. Preconcentration is a very important issue for achievement of low detection limits [5-7]. There are many methods of preconcentration and separation such as liquid-liquid extraction [8] ion exchange techniques [9], coprecipitation [10, 11], membrane filter techniques [12], cloud point extraction [13, 14] and other methods [15, 16].

The purpose of this study was to investigate the removal of Ni(II) from aqueous solution by adsorption, to determine the optimum removal condition by using Ion Imprinted Aniline -Formaldehyde Polymer. (IIPAF) is widely used as an adsorbent in industry due to its high adsorption capacity. Trace Ni(II) can be selectively retained on the surface of Ion Imprinted Aniline - Formaldehyde Polymer and then desorbed with 0.5M nitric acid prior to determination by Flame Atomic Adsorption Spectrometry (FAAS).

EXPERIMENTAL SECTION
Materials

Aniline, formaldehyde, hydrochloric acid, sulfuric acid, nitric acid, sodium hydroxide, acetic acid, sodium acetate, sodium dihydrogen phosphate, di-sodiumhydrogen phosphate, nickel nitrate, acetone, ethanol and other materials were products of Merck (Darmstadt, Germany).

All the solutions were prepared in deionized water using analytical grade reagents.

The stock solution (500 mg. L^{-1}) of Ni(II), were prepared by dissolving appropriate amounts of $Ni(NO_3)_2$, in deionized water. 0.1 M acetic acid - acetate buffer (pH 3 - 6.5), 0.01 M phosphate buffer (pH 6.5 - 9) was used to adjust the pH of the solutions, wherever suitable. Ni(II) concentration of the samples were measured using a Atomic Adsorption Spectrophotometer, Varian, (Palo Alto, CA, USA) AA240, equipped with air-acetylene flame (air and acetylene flow rate: 8 and 1.7 $L.min^{-1}$, respectively), after filtration with Whatman 42 filters.

Synthesis of aniline -formaldehyde polymer

Commercial grade aniline for synthesizing polymers was purified by distilling over KOH pellets at 180 °C. Poly(aniline-formaidehyde) was synthesized by reacting formaldehyde with aniline as described in the literature [17]. In a 100 mL reaction vessel, 5 mL of formaldehyde (37%) was added to a mixture of 9.3g of aniline and 3 mL of HCl (37%). Condensation was carried at 100 °C for 2 h. The temperature was then decreased to 60 °C and the mixture was neutralized with 4mL of 30% NaOH, resulting in an insoluble liquid resin. The resin was then washed with warm water three times and separated from the aqueous layer. The resin was kept at 80 °C under a reduced pressure of 10 kPa for 1h to remove any unreacted aniline and/or formaldehyde.

IIPAF preparation

The chemical polymerization of aniline was performed as described in the literature; [17-19], however, in this work; ammonium persulfate was used as the initiator. In a 150 mL reaction vessel, 0.5 g Poly(aniline-formaldehyde) was dissolved in minimum amount of 1 M HCl, and then 100 mg L^{-1} of Ni(II) (20 mL) was added dropwise to the solution as a template. Then 0.5 mL of aniline was added to the solution as a cross-linker with vigorous stirring. After polymerization for 1h at 25°C, a dark polymer powder was obtained. The IIPAF kept in the water bath at 0 °C for 2h. The powder was washed with 0.5 M HNO_3 to remove the template and obtain IIPAF. The Non-Imprinted Polymer (NIP) was prepared as the same protocol in the absence of the template ion.

Recommended procedure for separation and Preconcentration

A sample solution (100 mL) containing (0.5 µg.mL^{-1}) of Ni(II) was taken in a glass stopperd bottle, after adjusting its pH to the optimum value. The 0.1 g of ion imprinted aniline-formaldehyde was added to the bottle and then mixture was shaken for optimum time. The resin was filtered and sorbed metal ion was eluted with 0.5 M HNO_3 (10 mL). The concentration of metal ion in the eluate was determined by FAAS.

Isotherm studies

Isotherm studies were carried out by adding a fixed amount of adsorbent (0.05 g) to a series of beakers filled

with 50 mL diluted solutions of Ni(II) (10-100 μg. mL^{-1}). The beakers were then sealed and placed in a water bath shaker and shaken at 200 rpm with a required adsorbent time (3 h) at 25 °C and optimum pH=8. pH adjustments have been done using 0.01 M phosphate buffer. The beakers were then removed from the shaker, and the final concentration of Ni(II) in the solution was measured by FAAS. The amount of Ni(II) at equilibrium q_e (mg g^{-1}) on ion imprinted aniline-formaldehyde was calculated from the following equation:

$$q_e = (C_0 - C_e) \, V/W \tag{1}$$

Where C_0 and C_e (mg/L) are the liquid phase concentrations of Ni (II) at initial and equilibrium, respectively, V (L) the volume of the solution and W (g) is the mass of adsorbent used.

RESULTS AND DISCUSSION

Characterization of polymers

IR Spectrum

Structure of ion imprinted aniline-formaldehyde was elucidated by IR spectra.

IR (NaCl, cm^{-1}) 3413 (OH) and (NH$_2$), 1463 and 1627(C=C) aromatic, 2922 and 2854 (C-H) and 1041 (C-N).

IR spectrum of ion imprinted aniline-formaldehyde loaded Ni(II) demonstrates similar structure. The bands observed in the ion imprinted aniline-formaldehyde at 3413 and 1627 cm^{-1} can be assigned to (NH$_2$) and aromatic ring shift to down for ion imprinted aniline-formaldehyde loaded Ni(II) and confirm the formation of ion imprinted aniline-formaldehyde-Ni(II) complexes (see Fig. 1).

Scanning electron microscopy

To analyze the surface morphology of aniline-formaldehyde scanning electron microscopy images were investigated. There are clusters on the surface of polymer. The size of clusters are about 1-3 μm and the size of each bead on the cluster is about 100-300 nm (Fig. 2). Energy dispersive x-ray (EDX) microanalysis was employed to further confirm the adsorption of Ni(II). Fig. 3 (a) demonstrates the Ni(II) in the polymer matrix. It also shows the efficient elution by nitric acid (Fig 3 b).

Thermogravimetry analysis

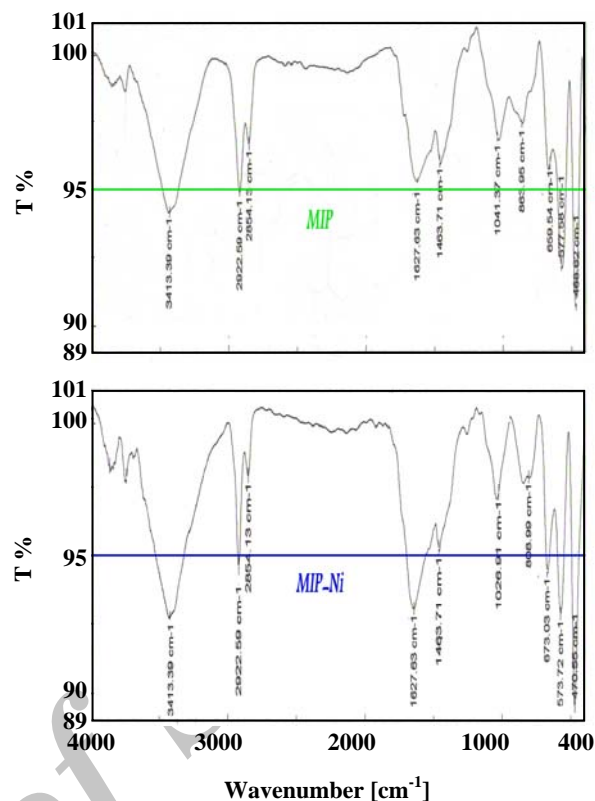The TGA of poly(aniline-formaldehyde) was compared with cross-linked aniline-formaldehyde (IIPAF).

Fig. 1: FTIR spectrum of a) IIPAF and b) IIPAF loaded Ni(II).
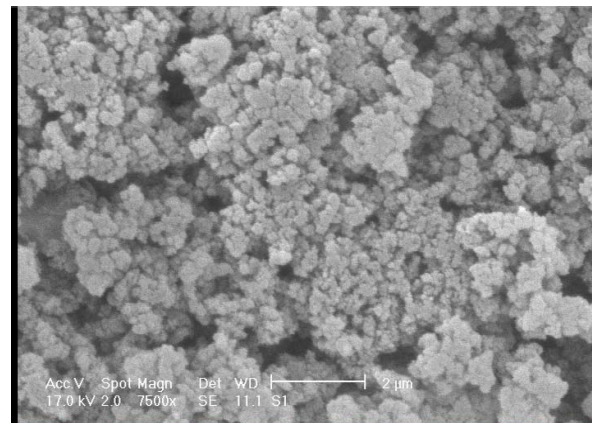

Fig. 2: Scanning electron microscopy photograph of IIPAF.

Both thermograms showed a weight loss up to 100 °C was due to the desorption of water molecules from the surface. After 150 °C two different polymers showed a different thermal behavior due to the decomposition polymeric matrix. The aniline-formaldehyde was decomposed with higher slope rather than cross-linked aniline-formaldehyde.
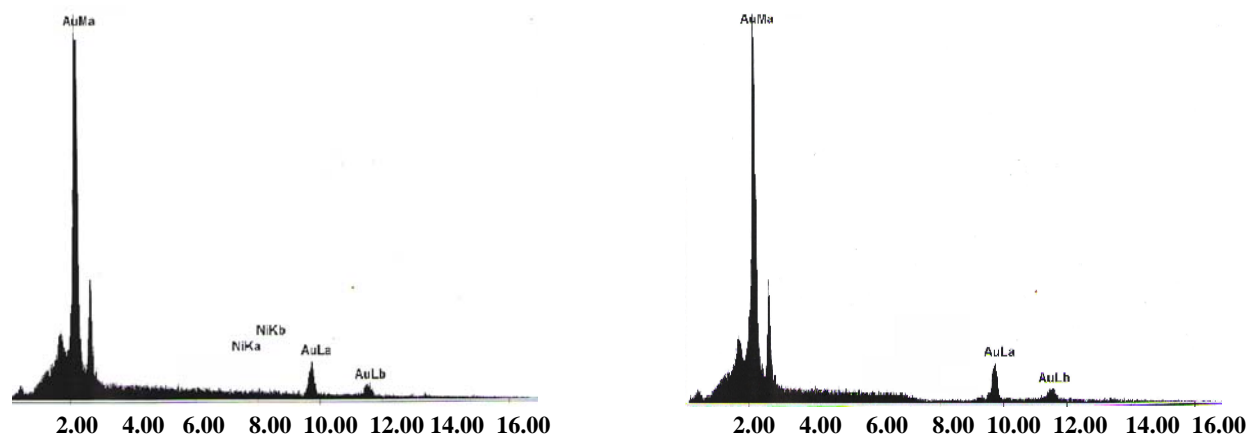
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Fig. 3: Energy dispersive x-ray of a) IIPAF loaded Ni(II) and b) IIPAF loaded Ni(II) after elution with nitric acid 0.5 M.
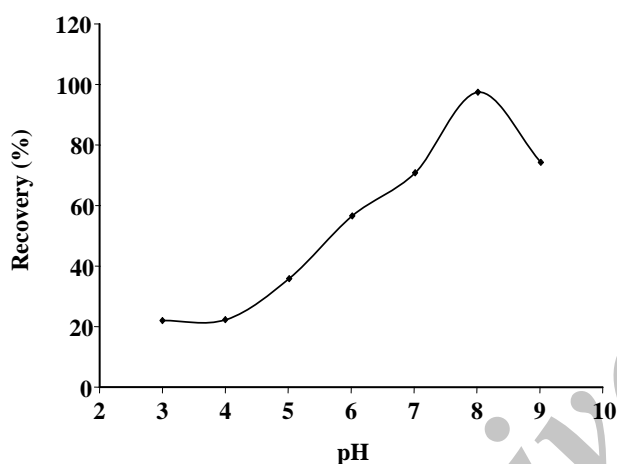

Fig. 4: Effect of pH sorption of Ni(II) onto IIPAF. Volume of each 100 mL containing 0.5 µg mL^{-1} of Ni(II) ions. Their pH values were adjusted with buffer solutions. The 0.1 g of IIPAF was added to each solution and the mixture was shaken for 3 h.

Metal sorption as a function of pH

The degree metal sorption at different pH values was determined by batch equilibration technique. The optimum pH values for quantitative uptake of metal ions were ascertained by measuring the Ni(II) content (by FAAS) in supernatant liquid and in the eluate obtained by desorbing the metal ion from ion imprinted aniline-formaldehyde with 0.5M nitric acid (10 mL). The optimum pH range for the sorption of the metal ion is shown in Fig. 4. The maximum recovery is 97.5 % at pH 8.

The degree metal desorption with different eluting agents after Ni(II) adsorption at optimum pH value was determined in batch experiments (Table 1). Nitric acid at 0.5 M provided the best recovery.

Total sorption capacity

At this point, 0.05 g of ion imprinted aniline-formaldehyde was stirred for 3 h. with 50 mL solution containing 10-100 µg.mL^{-1} of Ni(II) at optimum pH and 25 ºC. The metal ion concentration in the supernatant liquid was estimated by FAAS. The sorption capacity of the sorbent for the metal ion was ascertained from the difference between the metal ion concentrations in solution before and after the sorption. The saturated adsorption capacity of the resin was shown in Fig. 5. This Figure indicates the effect of initial concentration of the Ni(II) in the solution and temperature on capacity sorption of Ni(II) by ion imprinted aniline-formaldehyde. The capacity increases with increasing initial concentration of the Ni(II) in the solution and reaches a constant value after 100 µg.mL^{-1} concentration of Ni(II) (59.4 mg g^{-1}).

Optimization of sorption and desorption time of Ni(II)

Ion imprinted aniline-formaldehyde (0.05g) was shaken with 50 mL of solution containing 40 µg mL^{-1} of Ni(II) for different length of time (2-180 min) under optimum pH. After filtration of the sorbent, the concentration of Ni(II) in solution was determined with FAAS using the recommended batch method. The sorption as a function of contact time for all the metal ions is shown in Fig. 6. About 2min shaking was required for 95% sorption. The profile of Ni(II) uptake on this sorbent reflects good accessibility of the chelating sites in the ion imprinted aniline-formaldehyde.

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Table 1: Effect of eluting agent on Ni(II) recovery.

Elution agent	Preconcentration factor	Concentration	Recovery (%)
H_2SO_4 (0.5 mol L^{-1})	10	2.85	57
HCl (0.5 mol L^{-1})	10	3.75	75
HNO_3 +HCl (0.5 mol L^{-1})(3:1)	10	4.05	81
HNO_3 (0.5 mol L^{-1})	10	4.88	97.5
HNO_3 (0.02 mol L^{-1})	10	0.70	14
HNO_3 (0.1 mol L^{-1})	10	3.65	73
HNO_3 (1 mol L^{-1})	10	4.88	97.5
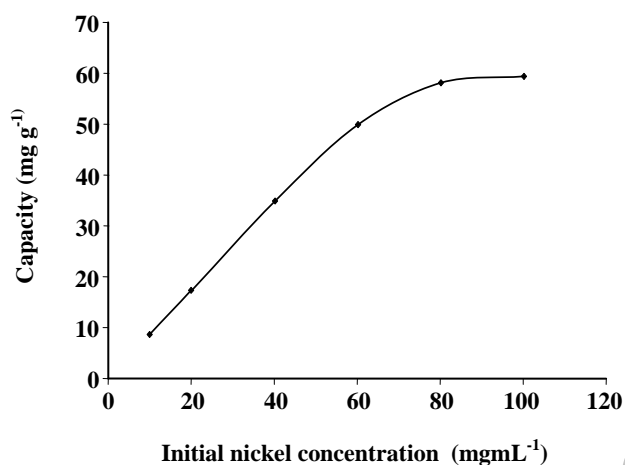
Fig. 5: Effect of initial concentration on capacity sorption of Ni(II) onto IIPAF.

Fig. 6: Kinetics of Ni(II) sorption on IIPAF.

Ascertaining optimum sorption time, the same procedure was carried out for optimization of desorption time. This time 50 mL of solution containing 0.5 μg.mL^{-1} of each metal ion with 0.05g sorbent was shaken for 240 min under optimum pH. Desorption process was taken place by nitric acid for different time (5, 15, 30, 60 and 120 min). Desorption as a function of time for the metal ion is shown in Fig. 7. It seems, shaking for 15 min is required for 95% desorption.

Adsorption isotherms

The Langmuir equation was given in the following form [20]:

$$q_e = q_{max}.K_L. C_e/ (1+K_L.C_e) \qquad (2)$$

where q_{max} is the maximum adsorption capacity corresponding to complete monolayer coverage on the surface (mg g^{-1}) and K_L is the Langmuir constant (L mg^{-1}). The equation (2) can be rearranged to a linear form:
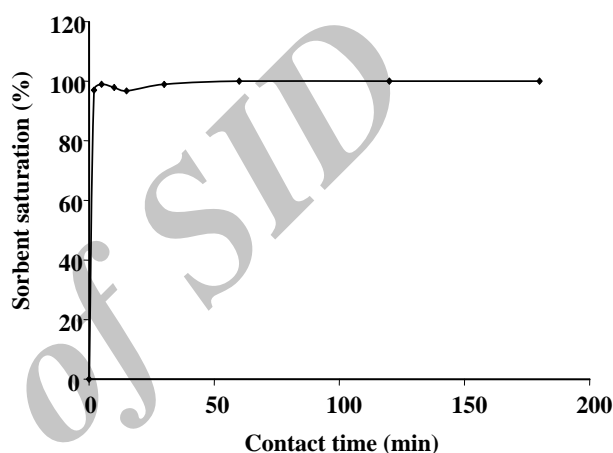
$$C_e/q_e = (1/q_{max}.K_L) + (C_e/q_{max}) \qquad (3)$$

The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e versus C_e.

Conformation of the experimental data in to Langmuir isotherm model indicates the homogeneous nature of ion imprinted aniline-formaldehyde surface. Langmuir parameters calculated from Equation (3) are listed in Table 2.

The essential characteristics of the Langmuir equation can be expressed in term of a dimensionless separation factor, R_L, defined as [21]:

$$R_L = 1 / (1+K_L.C_0) \qquad (4)$$

Table 2 shows the value of R_L (0.066) is in the range of 0-1 at optimum pH which confirms the favorable uptake of Ni (II).

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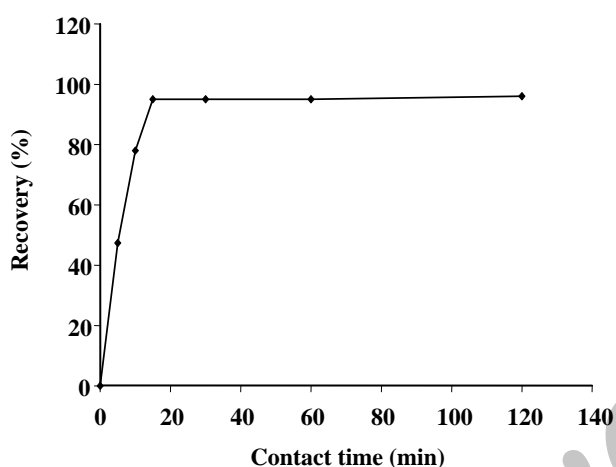| Langmuir isotherm model			
q_{max} (mg/g)	K_L (L/mg)	R_L	R^2
71.94	0.142	0.066	0.978
Frendlich isotherm model			
K_F (mg/g) (L/mg)$^{1/n}$	n		R^2
10.003	1.768		0.868
Temkin isotherm model			
A (L/g)	B (J/mol)	b(J/mol)	R^2
1.394	16.292	152.15	0.947

Fig. 7: Kinetics of Ni(II) desorption on IIPAF.

The Freundlich equation is an empirical equation employed to the described heterogeneous systems, in which it is characterized by the heterogeneity factor 1/n. Hence, the empirical equation can be written as [22]:

$$q_e = K_F . C_e^{1/n} \qquad (5)$$

where K_F is the Freundlich constant (mg/g) (L/mg)$^{1/n}$ and 1/n is the heterogeneity factor. A linear form of the Freundlich expression can be obtained by taking logarithms of the Equation (5):

$$\ln q_e = \ln K_F + 1/n \ln C_e \qquad (6)$$

Therefore, a plot of ln q_e versus ln C_e enables the constant K_F and exponent 1/n to be determined. The Freundlich equation predicts that the Ni(II) concentration on the adsorbent will increase as long as there is an increased in the Ni(II) concentration in the liquid.

The Temkin equation suggests a linear decrease of sorption energy as the degree of completion of the sorptional centers of an adsorbent is increased.

The Temkin isotherm has been generally applied in the following form:

$$q_e = \frac{RT}{b} \ln(AC_e) \qquad (7)$$

and can be linearized:

$$q_e = B \ln A + B \ln C_e \qquad (8)$$

Where B=RT/b and b is the Temkin constant related to heat of sorption (J/mol). A is the Temkin isotherm constant (L/g), R the gas constant (8.314 J/mol. K) and T is the absolute temperature (K). Therefore plotting q_e versus ln C_e enables one to determine the constants A and B. Temkin parameters calculated from Eqs. (7) , (8) are listed in Table 2.

Scatchard analysis

Scatchard analysis was employed to further analyze the binding isotherms, which is an approximate model commonly used in SPE characterization. The Scatchard equation can be expressed as, Q/C= (Q_{max}–Q)/K_d, where C (μmol mL^{-1}) is the equilibrium concentration of Ni(II); Q (μmol g^{-1}) is the equilibrium adsorption amount at each concentration; Q_{max} (μmol g^{-1}) is the maximum adsorption amount; and K_d (μmol mL^{-1}) is the equilibrium dissociation constant at binding sites. Fig. 8 shows the Scatchard plots of the binding of cobalt to the resin. It is clear that the Scatchard plot for resin is a single straight line. The linear regression equation was Q/C= –5.28Q + 7622.3 (R^2=0.9208), suggesting that the

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Table 3: Comparison of recovery, preconcentration and capacities with some literatures.

Sorbent used	R	P	C	D	Ref.
Tungsten Foil	93-103	-	-	0.1	23
Poly(Vinyl Pyrrolidinone)	95	10	11.9	-	24
[1-(2-Pyridylazo)-2-Naphthol] -Naphthalene	-	-	8.9	-	25
Pyrrolidinedithiocarbamate on Cellulose Filters	100	-	-	2.5	26
thiacalix[4]arenetetrasulfonate- loaded Sephadex A-25	97	200	-	-	27
1-(2-Pyridylazo)-2-Naphtol(PAN) Immobilized on Surfactant -Coated Alumina	97	5-300	0.93	0.06	28
chitosan functionalized with 3,4-dihydroxy benzoic acid	-	10	-	0.09	29
Ion imprinted aniline -formaldehyde polymer (Our sorbent)	92.6	10	12.15	0.51	-

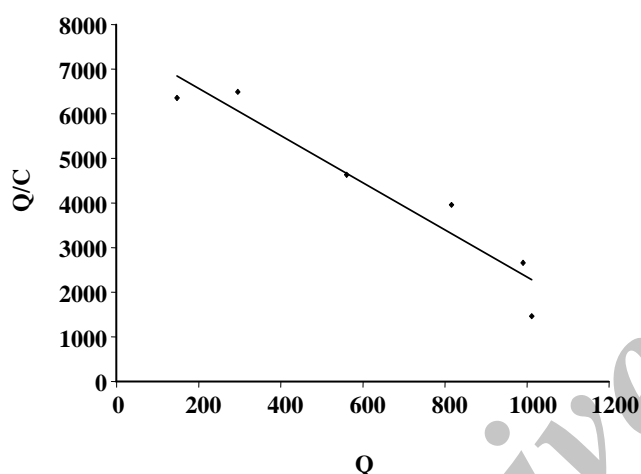*R: Recovery(%), P: Preconcentration factor, C: Capacity (mg. g^{-1}), D: Detection limit : μg.L^{-1}*

Fig. 8: Scatchard plots of Ni(II) adsorption onto IIPAF at 20 ºC.

Fig. 9: Comparison Ni(II) sorption of non cross-linked polymer, IIPAF and NIPAF.

homogeneous recognition sites for Ni(II) were formed in the SPE polymer. From the slope (–5.28 (1/K_d)) and intercept (7622.3 (Q_{max}/K_d)), K_d and Q_{max} for the affinity binding sites were calculated to be 0.189 μmol·mL^{-1} and 1444 μmol·g^{-1}, respectively.

Effect of foreign ions and selectivity

In order to evaluate the selectivity of the sorbent, the effect of Cu(II), Cr(III), Mn(II), Fe(II), Co(II), Zn(II) and Pb(II) (10 mg. L^{-1}) on the sorption behavior of Ni(II) ion (concentration 10 mg.L^{-1}) was investigated. The results indicate that the most effective ions on adsorption of Ni(II) on ion imprinted aniline-formaldehyde are Cu(II), Cr(III) with 6.3% and 5.7% sorption lost, respectively. The most probable possibility for explanation of this effect is high formation constant of these ions with amino
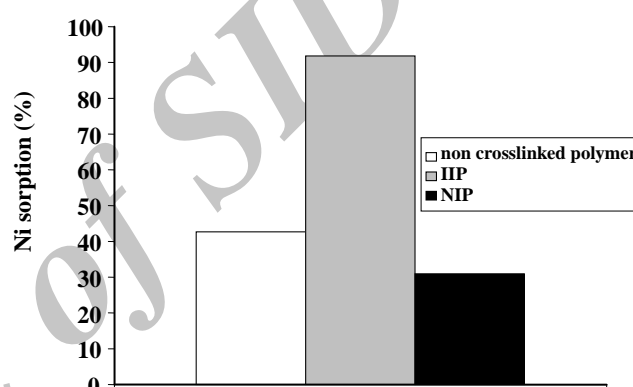
groups of aniline in the polymer. The effect of other mentioned foreign ions at given concentrations are negligible. The adsorption of Ni(II) on the ion imprinted aniline-formaldehyde in presence of all mentioned ions (with each ion having the concentration of 10 mg L^{-1}) shows that the Ni(II) can be determined quantitatively in the environmental samples.

The sorption comparison of Ni(II) on IIPAF, NIPAF and non cross-linked aniline-formaldehyde was investigated. Fig. 9 demonstrates that percentage of Ni(II) sorption by IIP is much higher than the others.

Comparison with other preconcentrating matrices

The sorption capacity, recovery, preconcentration factor, detection limit of ion imprinted aniline-formaldehyde is compared with those of other important matrices in Table 3.

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Table 3: Results obtained for Ni(II) determination in water sample of (I), (II) and (III).

	(I)	(II)	(III)
Found (without spiking of Ni (II))	N.D.	N.D.	N.D.
Added Ni (II) ($\mu g.mL^{-1}$)	0.05	0.1	0.5
Found Ni (II), after preconcentration ($\mu g.mL^{-1}$)	0.48	0.94	4.73
Preconcentration factor	10	10	10
Recovery (%)	96.0	94.0	94.6
Standard deviation	0.008	0.011	0.041
Relative standard deviation (%) [a]	1.6	1.2	0.9

a: For three determinations

The present sorbent exhibits better or comparable capacity values in comparison to most of the metal-matrix combinations. The newly developed method has been successfully applied to the analysis of trace Ni(II) in natural water sample.

Application of method

Ion imprinted aniline-formaldehyde was used to preconcentrate and determine Ni(II) ions in Kosar aqueduct (Omid shahrak, Tehran, Iran). The pH of water sample was adjusted to the optimum pH. Solid phase extraction with ion imprinted aniline-formaldehyde coupled with FAAS was applied to determination of the Co (II) in water sample. Since no Ni(II) was detected in the water sample, 100 mL water sample was spiked with 0.05, 0.1 and 0.5 mg of Ni(II) before subjecting it to the recommended procedure. The results are archive in Table 4. These results demonstrate the applicability of the procedure for Ni(II) determination in samples with high recovery (>94%).

CONCLUSIONS

A selective chelating sorbent is prepared by cross-linking of poly aniline-formaldehyd in presence of Ni(II). The synthesis of the sorbent is simple and economical. The sorbent has a good potential for enrichment of trace amount of Ni(II) from large sample volumes. The resins also present the advantage of high adsorption capacity, good reusability and high chemical stability. The sorption of the investigated metal ions increases by increasing the contact time. Based on the Langmuir isotherm analysis, the monolayer adsorption capacity was determined to be 71.94($mg.g^{-1}$) at 20 °C. The R_L values showed that the ion

imprinted aniline-formaldehyde was favorable for the adsorption of Ni(II). Preconcentration by this sorbent combined with FAAS and ICP- AES can be applied to the determination of trace Ni(II) in water and the mineral reference sample with satisfactory results.

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