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Research Article

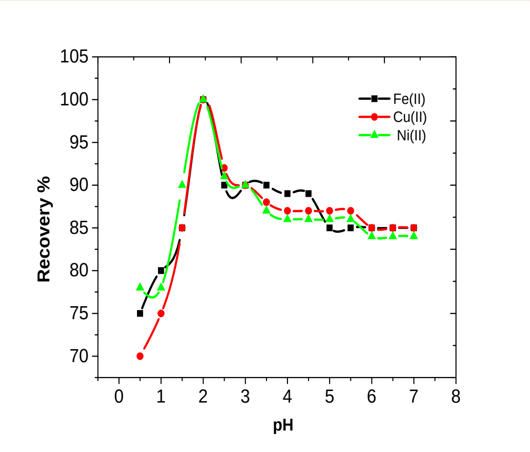
Determination of Fe (II), Cu (II), Ni (II) in Water and Soil Samples by using Amberlite XAD-2 by FAAS Method

A. Saranga Pani[1*], R. Kishore Kumar[1] and N. Venkatasubba Naidu[2]

[1]Department of Chemistry, S.V.Arts College, Tirupati, India -517502
[2]Enviro analytical Laboratories, Department of Chemistry, S.V.University, Tirupati, India -517502

Abstract

This work describes a procedure for the preconcentration of of Fe(II), Cu(II) and Ni(II) from water and soil samples using a column-filled Amberlite XAD -2 resin. The analytes in the effluent were determined by Flame Atomic Absorption Spectrometry (FAAS). Several parameters governing the efficiency of the method were evaluated including pH, resin amount, sample volume, flow rates, eluent type and diverse ions. The method was developed for the determination of Fe (II), Cu (II) and Ni (II) metal ions in different water and soil samples. 3-BPANPC was used as a reagent to determine the metal ions. In this study showed that metal ions were completely adsorbed on the adsorbent over the pH range of 2.0-4.0.Therefore, pH 2 was selected as the optimum pH for further studies.



Keywords: Metal ions, Amberlite XAD -2, FAAS, 3-BPANPC, water and soil samples

***Correspondence**
A. Saranga Pani,
Email: rayanuthalakishore@gmail.com

Introduction

Trace metal ions such as Fe (II), Cu (II), Ni (II) are increasingly important indicators for monitoring environmental pollution. Many studies have been conducted for the investigation of these trace metals in various environmental samples like sediments, soils, geological samples and natural water samples etc. Among these samples, water and soil are existing and essential to all known forms of life. On the other hand, at higher concentrations all of the metals are recognized as potentially toxic. Several instances of metal ion toxicity to humans and aquatic lives have been reported. Hence it requires a time-to-time analysis of trace metals in environmental samples in order to sustain and preserve the ecosystem. But the determination processes are not that simple because the concentration of metals in natural water and soil samples has often been is less than the detection limit of instrumental methods and the metal ions are surrounded and encapsulated by a variety of complex matrix species which may interfere in the direct analysis of metal ions. However, preconcentration techniques provide both separation of analyte from matrix interference and low detection limits. The best way to solve this problem, separation and preconcentraion techniques are needed for the determination of analytes by FAAS.

Many separation methods used for the enrichment and separation of heavy metal ions including copreciptation [1-3], cloud point extraction [4-6] and membrane filtration [7] have been carried out. Among these techniques solid phase extraction is an attractive technique based on the use of the sorbent that retains the analytes. The retained analytes are eluted from the sorbent using relatively small volume of a suitable solvent. These features provide a high preconcentration factor for large volume samples and short time extraction [8-9] . Various sorbents such as activated carbon [10-11], silica gel [12-14], naphthalene [15] , alumina [16-17] and amberlite XAD [15-16] resins have been used for the solid phase extraction of metal ions from different matrices. The potential of chelating ion-exchange resins for separation of metal ions has been very well established [17-20]. Azothiopyrine disulphonic acid [21] has been incorporated into an anion-exchange resin and the product have been used for uptake of mercury, copper, and cadmium from aqueous solutions. Similar use of pyrogallol sulfonic acid [22] enabled the separation and enrichment of Mo(VI), and Fe (III). Dowex 1-X 8 containing adsorbed sulphonated azo dyes [23] have been found useful for separation of copper and nickel.

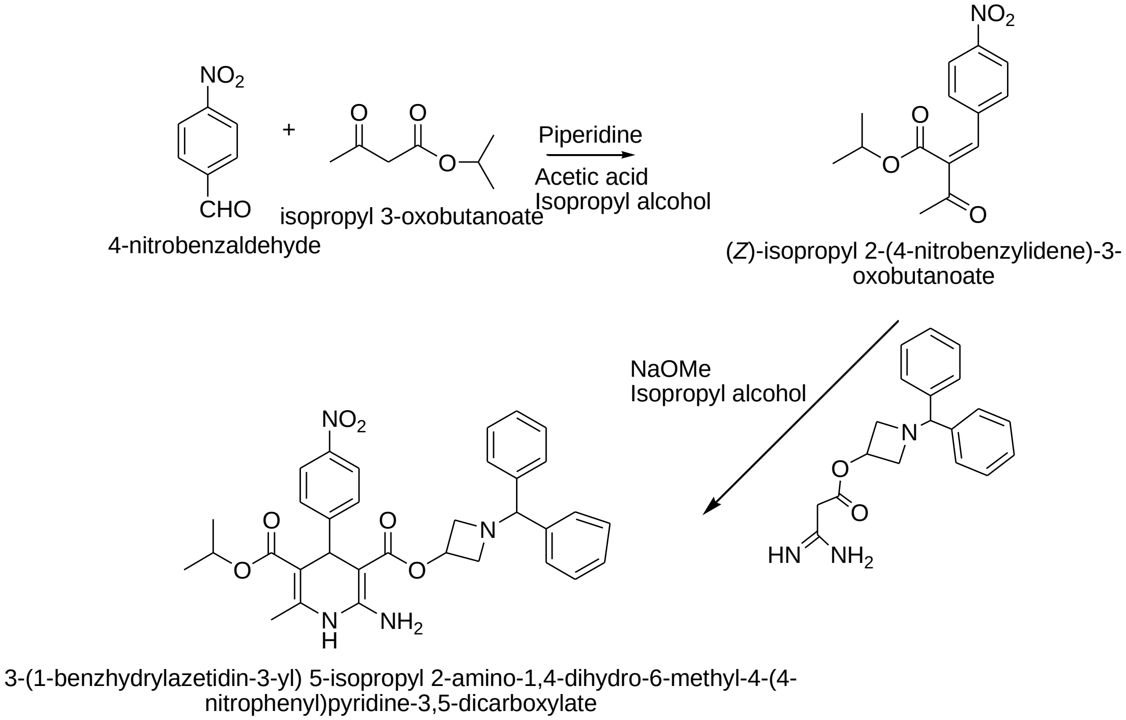
Therefore the present study focusing on 3- bpanpc immobilized with Amberlite XAD -2 using as a new solid phase extractor for determination of Fe (II), Cu(II), and Ni(II) in water and soil samples by FAAS. The parameters were studied include pH of the sample, sample volume, amount of resin, type and volume of eluents and foreign ions effect.

Experimental

Instrumentation and reagents

Preparation of the Ligand (3-BPANPC)

The ligand was prepared by adding of 0.02 mol L^{-1} 4-nitrobenzaldehyde, 9.4g of 30% isopropyl 3-oxobutanoate with acetic acid and piperidine refluxed in the presence of isopropyl alcohol the product is formed is yellow colored crystalline substance. The IR spectra are showed in **Table 1** .The synthesized ligand shown in **Scheme 1.** This mixture was stirred with 1-benzhydrylazetidin-3-yl 2-amidinoacetate in the presence of sodium methoxide and isopropyl alcohol and refluxed for 8 hours. The precipitate obtained was cooled, filtered and washed several times with cold water as well as hot water / ethanol solution to remove unreacted 4-nitrobenzaldehyde. The isolated white product was recrystallized from acetone and finally dried in air for 24 hours. IR and H^1NMR studies of the ligand are shown in (**Table 1, 2).** The IR spectra are shown in **(Figure 1).**



Scheme 1 Preparation of the 3 bpanpc ligand

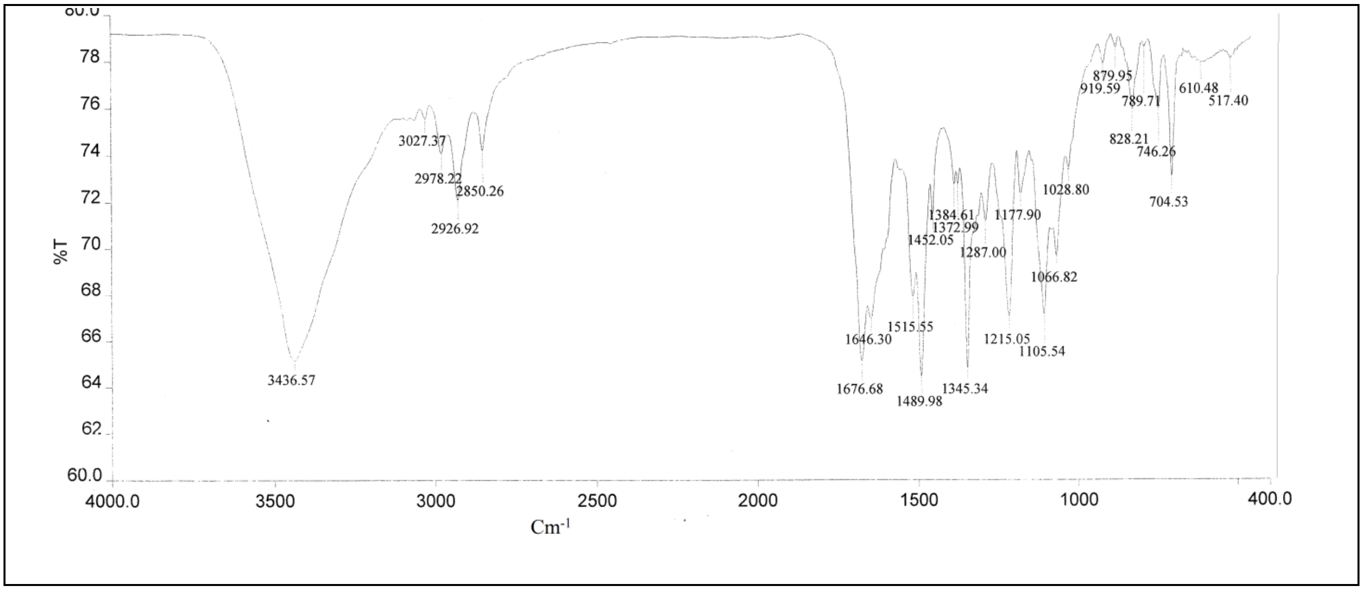
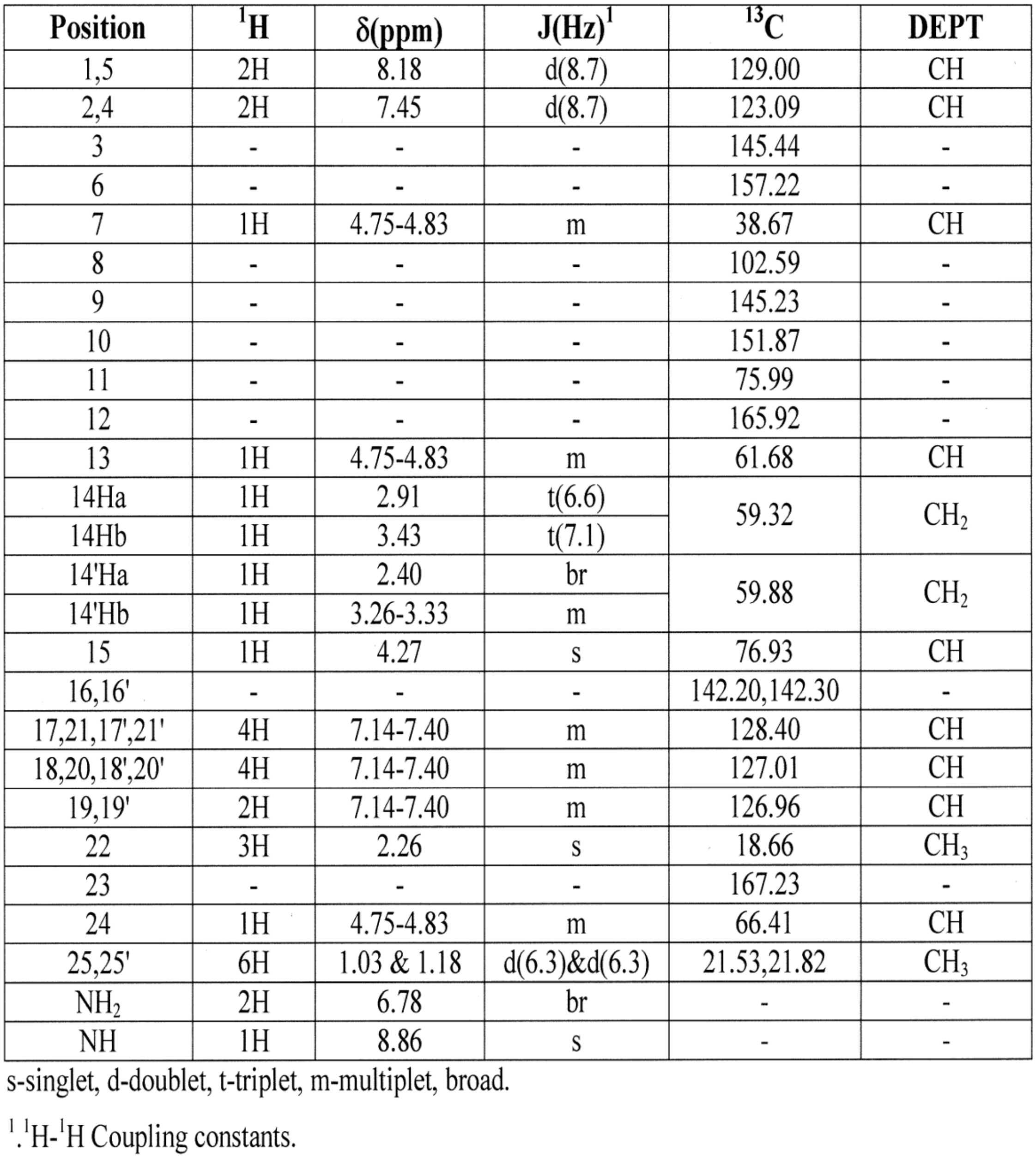


Figure 1 IR data of the 3-BPANPC ligand

Table 1 IR studies of the ligand

Wave number (cm^{-1})	Assignment	Mode of Vibration
3437	N-H	Stretching
3027	Aromatic C-H	Stretching
2978,2927,2850	Aliphatic C-H	Stretching
1677,1646	C=O	Stretching
1516	Aromatic $(N=O)_2$	Asymmetric Stretching
1490	Aromatic C=C	Stretching
1452,1385,1373	Aliphatic C-H	Bending
1345	Aromatic $(N=O)_2$	Symmetric Stretching
1287	C-N	Stretching
1215,1106,1067	C-(C=O)-O	Stretching
828,746,705	Aromatic C-H	Bending

Table 2 NMR studies of the ligand



Position	^{1}H	δ(ppm)	J(Hz)^1	^{13}C	DEPT
1,5	2H	8.18	d(8.7)	129.00	CH
2,4	2H	7.45	d(8.7)	123.09	CH
3	-	-	-	145.44	-
6	-	-	-	157.22	-
7	1H	4.75-4.83	m	38.67	CH
8	-	-	-	102.59	-
9	-	-	-	145.23	-
10	-	-	-	151.87	-
11	-	-	-	75.99	-
12	-	-	-	165.92	-
13	1H	4.75-4.83	m	61.68	CH
14Ha	1H	2.91	t(6.6)	59.32	CH_2
14Hb	1H	3.43	t(7.1)		
14'Ha	1H	2.40	br	59.88	CH_2
14'Hb	1H	3.26-3.33	m		
15	1H	4.27	s	76.93	CH
16,16'	-	-	-	142.20,142.30	-
17,21,17',21'	4H	7.14-7.40	m	128.40	CH
18,20,18',20'	4H	7.14-7.40	m	127.01	CH
19,19'	2H	7.14-7.40	m	126.96	CH
22	3H	2.26	s	18.66	CH_3
23	-	-	-	167.23	-
24	1H	4.75-4.83	m	66.41	CH
25,25'	6H	1.03 & 1.18	d(6.3)&d(6.3)	21.53,21.82	CH_3
NH_2	2H	6.78	br	-	-
NH	1H	8.86	s	-	-

s-singlet, d-doublet, t-triplet, m-multiplet, broad.

^{1}.^{1}H-^{1}H Coupling constants.

Results and Discussion

Effect of pH

The effect of pH on the retention of Fe(II),Cu(II),Ni(II) was studied by passing 50 µg of individual metal ion through the 3 bpanpc coated Amberlite XAD -2 resin (500 mg) loaded columns at different pH values (1.0 to 7.0) and determined as described in general procedure. The data corresponding to each element were shown in (**Table 3)** and graphically presented in **(Figure 2)** The recoveries were in the pH ranges 2.0 to 5.0 for Fe(II),Cu (II), Ni(II). Hence pH 2.0 was chosen for the simultaneous determination of metal ions in various water and soil samples.

Table 3 Effect of pH on the complexation of metals with 3- bpanpc (μg/l)

pH	Fe	Cu	Ni
1.0	80.42	75.78	78.72
2.0	99.98	99.99	99.92
3.0	97.97	92.47	98.89
4.0	89.80	87.69	87.80
5.0	85.49	87.22	86.99
6.0	85.44	85.22	84.15

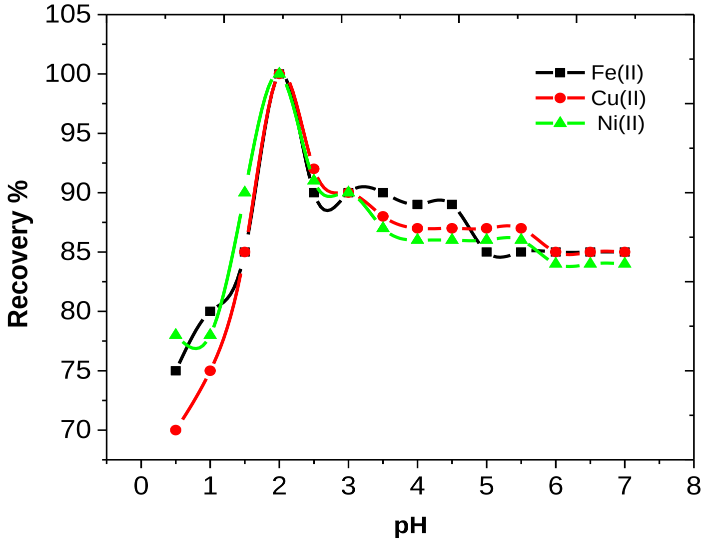


Figure 2 Effect of pH on the complexation of metals with reagent 3 BPANPC

Effect of amount of resin

The Amberlite XAD-2 resin (Milwaukee, USA, Aldrich) with a particle size, 20-60 mesh, pore diameter, $90A^0$ and surface area, 330 m^2 g^{-1} was used. Before use, the resin was washed with methanol 4 M HCl to remove the metal impurities, washed with deionised doubly distilled water until the pH was neutral and then dried at 40 °C for 24 h in a vacuum desiccator. The resin was modified by fictionalization with chelating reagents and used as a matrix for separation and preconcentration of metals.

The amount of Amberlite XAD-2 resin coated with 3 -bpanpc required for effective preconcentration of metals was studied. This was ascertained by taking 100 μg of multi elemental standard solution in 100 ml and passing through a column containing 0.25-1.5 g of 3- bpanpc coated resin. 500 mg of 3 -bpanpc coated resin was enough for quantitative recovery (>96%) of metal ions. So, 500 m g of 3- bpanpc coated resin was recommended for further studies. It is graphically showed in **(Figure 3).**

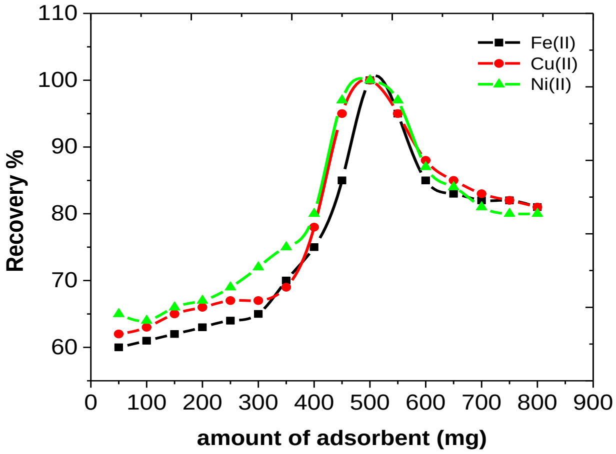


Figure 3 Effect of resin amount on the (%) recovery of metal ions

Batch exchange experiments

For measuring the equilibrium amount of exchange, 500m g of the air-dried resin was used in a batch vessel to which the solution (100 cm3) was poured. The vessel was allowed to shake for 24 h in a temperature-controlled shaker (Firstek, Taiwan, Model B603) at 25 ^{0}C. Preliminary tests had shown that the exchange reaction studied was complete after 4 h. After agitation for 10 h, aqueous samples were taken and the concentrations of metals were analyzed using FAAS (Varian Spectra AA 55, Australia) equipped with a flame ionization detector. The solution pH was measured using a pH meter (a pH meter Elico, Model LI-129, India). The dose of the dry resins was 500 mg/dm^3. Each experiment was performed twice at least under identical conditions. The reproducibility of the measurements was mostly within 4%.

Effect of flow rate on retention and recovery of Fe(II), Cu(II), Ni(II)

The effect of flow rate on the retention and recovery of Fe(II), Cu(II), Ni(II) on 3 – BPANPC coated Amberlite XAD -2 resin was examined by varying flow rate from 2.0–5.0 ml min^{-1} under optimal conditions. It was found that the optimum flow rate for preconcentration of these metal ions on resin bed was between 1.0 and 8.0 ml min^{-1}. However, at flow rate more than 3.0, a decrease in percentage sorption was observed. Hence 3.0 ml min^{-1} flow rate was used for elution of these metals from resin. The preconcentration of metal ions from water and soil Samples data are presented in **Table 4.**

Table 4 Recovery of metal ions from water and soil samples after preconcentration on 3- BPANPC coated Amberlite XAD -2 resin

Element	Concentration of each element added (µg/ l)	Resin coated with BPANPC		
		Found (µg/l)	Recovery (%)	R.S.D
Fe	25.00	24.98	99.92	1.04
	50.00	49.38	98.76	3.92
Cu	25.00	24.89	99.56	0.88
	50.00	48.34	96.68	4.90
Ni	25.00	24.99	99.96	1.28
	50.00	49.41	98.82	3.12

Effect of HNO_3 concentration on elution

The effect of HNO_3 concentration on elution of metal ions complex on 3 -BPANPC coated Amberlite XAD -2 resin was studied by carrying out the elution with 1.0-6.0 M HNO_3. The results are presented in **Table 5** and in **(Figure 4)**.This data indicate that the highest recoveries for Fe(II), Cu(II), Ni(II) were obtained at HNO_3 concentration of 3 M. Hence 3 M HNO_3 were used for further experimental studies.

Table 5 Effect of HNO_3 concentration on elution of metals from Amberlite XAD -2 resin coated with 3-BPANPC

HNO_3 (M)	**% Recovery(µg/l)**		
	Fe	**Cu**	**Ni**
1.0	87.18	93.09	93.10
2.0	90.47	89.55	90.15
3.0	99.88	99.89	99.98
4.0	90.03	94.03	94.03
5.0	87.06	88.70	87.70
6.0	85.77	87.37	86.38

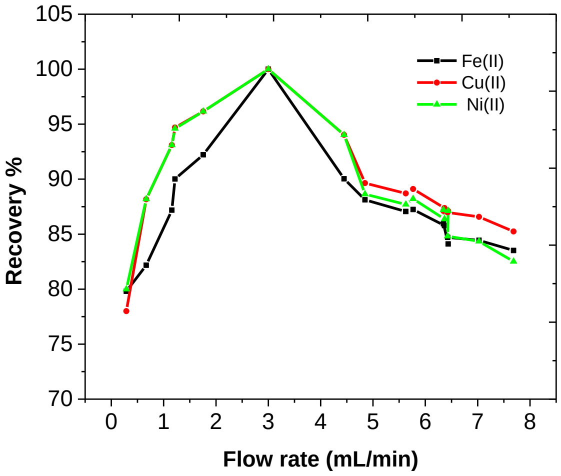


Figure 5 Effect of HNO_3 concentration on elution of metals from Amberlite XAD-2 resin coated with reagent 3-BPANPC.

Kinetics of sorption

The rate of uptake of Fe (II),Cu (II) and Ni (II) on 3-BPANPC coated Amberlite XAD-2 was studied by Batch method. **50 µg** of individual metal ion solutions were added to 500 mg resin and stirred for 2, 5, 10, and 20 minutes at room temperature. The concentration of metal ions in the supernatant was analyzed by FAAS as described in the standard procedure. The results of saturation of resin with time are presented in **Table 6** Indicated results that the time needed to reach 50% of loading capacity ($t_{1/2}$) is less than 10 min for each metal ion for 3- BPANPC coated resin.

Efficiency of sorption on 3 - BPANPC coated Amberlite XAD -2 resin

The efficiency of sorption was expressed as the concentration of the analyte retained on the sorbent during preconcentration. The quantitative sorption of Fe (II),Cu(II) and Ni(II) from aqueous solution was studied by taking **50 µg** of each element in 100 ml and passed through the column containing resin coated with 500 mg of each 3 -bpanpc. The elements sorbed on 3 -bpanpc coated resins were eluted with 3 M HNO_3 and determined. The data are presented in **Table 6.**

Detection limits

The detection limits of each element were expressed as the amount of analyte in μg l^{-1} giving a signal to noise ratio of 3. The detection limits of elements Fe(II),Cu (II) and Ni(II) in the range between **0.5 to 1.5 μg l^{-1}** with 3-BPANPC coated Amberlite XAD -2 resin.

Sorption capacity and Preconcentration factor

The sorption capacity of the resin was calculated by passing increasing concentrations of Fe(II),Cu(II) and Ni(II) solutions in 1.0 g of 3-BPANPC coated Amberlite XAD -2 resin containing columns. The sorbed metal ions were eluted with 3 M HNO_3 at a flow rate of **3.0 ml min^{-1} and** determined as described in general procedure. The results are presented **Table 6.**

The preconcentration factor was examined by passing the increasing volumes of Fe (II),Cu (II) and Ni (II) solutions into 500 mg of 3-BPANPC coated resin, keeping the total Fe (II),Cu (II) and Ni (II) amount **20 $μg^{-1}$** are analysed by general procedure. The preconcentration factor for metal ions with 3- BPANPC Amberlite XAD -2 resin is presented in **Table 6.**

Table 6 Sorption capacity, loading time and preconcentration factor of Amberlite XAD -2 resin coated with 3-BPANPC

Metal ion	**Sorption capacity (mg/g)**	**Loading time (min)**	**Preconcentration factor**
Fe(II)	8.42	3.1	100
Cu(II)	8.18	6.3	60
Ni(II)	7.21	5.4	100

Effect of matrix ions

The effect of matrix ions on the sorption of Fe (II),Cu (II) and Ni (II) were studied. Different amounts of various cations and electrolytes were added to the 50 μg of individual metal ion solution in 100 ml and passed this solution into column containing 1.0 g of 3-BPANPC coated Amberlite XAD -2 resin. The concentration which caused ± 2 % error is given in **Table 7.** The results in table demonstrate that the anions and cations do not affect the sorption of Fe(II),Cu(II) and Ni(II) under reported conditions. The alkaline and alkaline earth metals were almost not retained through the column due to low solubility constant of their chelates and the small amounts of retained matrix ions were removed by washing with 10-15 ml of buffer solution as reported by Uzun et al.

Table 7 Effect of matrix ions on the determination trace of metals in water samples

Matrix ion	**Tolerance limit (μg ml^{-1})**
Na^+	60000
K^+	50000
Ca^{2+}	40000
Mg^{2+}	35000
Cl^-	60000
SO_4^{2-}	40000

CH_3COO^-, NO_3^-	4000
HCO_3^-	500
Cr^{6+}	45
Al^{3+}	40

Determination of metal ions in standard reference materials

The accuracy of the proposed method was ascertained by the determination of Fe(II),Cu(II) and Ni(II) in standard reference materials (NIST-SRM) and the data is given in **Table 8,9.** The SRMs are aqueous solutions and the concentration of Fe(II),Cu(II) and Ni(II) were analysed by following the general procedure described in the experimental section. The experimental results are in good agreement with standard reference values.

Table 8 Recovery of metal ions from standard reference materials (NIST-SRM 1643e) after preconcentration on 3-BPANPC coated Amberlite XAD-2 resin

Element	Certified value*	After preconcentration on 3-BPANPC Coated resin
Fe	38.97 ± 0.012	38.49 ± 0.67
Cu	6.57 ± 0.07	6.42 ± 0.41
Ni	19.63 ± 0.21	19.67 ± 0.22

*All values are in ppb. The values reported are the means of five readings ± SD

Table 9 Recovery of metal ions from soil samples standard reference materials (NIST-SRM 2709a)) after pre concentration on 3-BPANPC coated Amberlite XAD-2 resin

Element	Certified value* (mg/Kg)	After preconcentration on 3-BPANPC Coated resin (mg/Kg)
Fe	3.39 ± 0.02	3.36 ± 0.07
Cu	34.2 ± 0.07	33.9 ± 0.5
Ni	83.0 ± 0.21	85 ± 2.0

*All values are in ppb. The values reported are the means of five readings ± SD

Application of the method

The preconcentration method was successfully applied to the determination of Fe(II),Cu (II) and Ni(II) in water and soil samples. The treatment and sampling procedure of water and soil samples are given in the experimental section. The results are presented in **Table 8,9.**

Conclusions

Trace metals such as Fe(II),Cu(II) and Ni(II) in water and soil samples were determined by the proposed method. The results indicate that are in good agreement with standard reference values. The statistical results obtained from the present method are in good agreement with the existing methods reported in the literature. The effects of various non-target species were also studied which shows the feasibility of the proposed method.

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References

[1] Safavi . Abdollahi H. Hormozi Nezhad M.R. and Kamali R Spectrochimica Acta Part A:Molecular and Biomolecular Spectroscopy 60(2004) ,2897-2901.

[2] Umith Divrikli ,Asliham Arslan Kartal , Mustafa Soylak, and Latif Elci, Journal of hazardous Materials, 145,(2007), 459-464.

[3] Mustafa Tuzen, Kadriye Saygi O and Mustafa Soylak Journal of Hazardous Materials. 152 (2008), 632-639.

[4] Zhenhua Li, Xijun Chang, Zheng Hu, Xinping Huang, Xiaojun Zou, Qiong Wu and Rong Nie, Journal of Hazardous Material 166(2009), 133-137.

[5] Ghaedi M, Shokrollahi A, Kianfar AH, Pourfarokhi A, Khanjari N, Mirsadeghi AS. And Soylak M J Hazard Mater 162 (2009), 1408-1414.

[6] Celal Duran, Ali Gundogdu, Volkan Numan Bulut, Mustafa Soylak, Latif Elci, Hasan Basri Sentürk and Mehmet Tüfekci Journal of Hazardous Materials 146(2007) ,347-355.

[7] Xie, ZH, Xie, FZ, Guo LQ, Lin XC J. Sep. Sci 5,(2005) ,462-5472.

[8] Sadeghi S, Sheikhzadeh E. J Hazard Mater 163 (2009) ,861-868.

[9] Hatay I. Gup R. Ersöz M Journal of Hazardous Materials 150 (2008) ,546-553.

[10] Gopi Krishna P. Rao, K.S. Biju ,V.M. Prasada Rao, and Naidu G.R.K Chemia analityczna 49(2004), 383-393.

[11] Attinti Ramesh, Bobba Aparna Devi, Hiroshi Hasegaw,a, Teruya Maki, and Kazumasa Ueda Microchemical Journal 86(2007), 124-130.

[12] Ghaedi M, Tavallali H, Shokrollahi A, Zahedi M, Montazerozohori M, Soylak M. Journal of Hazardous Materials 166(2009), 1441-1448.

[13] Sharma R. K, and Pant P. J.Hazard Mater 15(2009) 295-301.

[14] Yong Guo, Bingjun Din, Yongwen Liu, Xijun Chang, Shuangming Meng, Maozhongian Analytica Chimica Acta 504(2004), 319 -324.

[15] Duran C, Senturk, H.B, Elci, L, Soylak M, and Tufekci M J. Hazard. Mater 162(2009), 292-299.

[16] Rao, G.P, Seshaiah ,K, Rao ,Y.K, and Wang M.CJ. Agric, Food Chem 54(2006) , 2868 -2872.

[17] U. Hiroshi, Japan Kokai Tokkyo Koho JP Appl. **155**(1992), 3.

[18] R. Browne and T. Edward Diss. Abstr. Int B **54**(1993), 1524-1527

[19] H.J. Fischer and K.H. Leiser, Fresenius Z. Anal.Chem **335**(1989) 738-742.

[20] H. Hubicka, Hung. J. Ind. Chem. **17** (1989), 355-358.

[21] M. Nakayama, M. Chikuma, and T. Tanaka Talanta **29** (1982), 503-506.

[22] J.L. Pillai and V.N. Siyasankara Analyst **114** (1989), 439-443.

[23] M. Peasvento and A. Profumo Talanta, **35**(1988), 431-437.

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