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Solid phase extraction preconcentration of cobalt and nickel with 5,7-dichloroquinone-8-ol embedded styrene–ethylene glycol dimethacrylate polymer particles and determination by flame atomic absorption spectrometry (FAAS)

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Abstract

This article explores the synthesis of styrene–divinyl benzene (DVB)/ethylene glycol dimethacrylate (EGDMA) polymers embedded with quinoline-8-ol (Q) or its dihalo derivatives by thermal means in the presence and absence of 4-vinyl pyridine (VP). The above-synthesized polymers were found to enrich cobalt and nickel present in admixtures. Of these, 5,7-dichloroquinoline-8-ol (DCQ) embedded styrene–EGDMA polymer particles enrich cobalt and nickel quantitatively from dilute aqueous solutions within 5 min of preconcentration time. Styrene–EGDMA, DCQ embedded styrene–EGDMA particles obtained by bulk polymerization and cobalt/nickel bonded polymers were characterized by FTIR, thermogravimetric analysis (TGA), elemental analysis and surface area studies. The use of these polymer particles obtained by bulk polymerization for the solid phase extractive preconcentration of cobalt and nickel was investigated in detail and explores the possibility of employing this procedure for the analysis of cobalt and nickel in soil and sediment samples using a simple, low cost and readily available flame atomic absorption spectrometric instrument was explored.

Keywords: Solid phase extraction; 5,7-Dichloroquinoline-8-ol embedded polymer particles; Preconcentration; Flame AAS

1. Introduction

Quinoline-8-ol (Q) has been widely used as metal chelate for both analysis and separation of metal ions [1–3]. Use of polymer-bound derivatives of quinoline-8-ol in these two areas is comparatively new. Generally, two approaches, viz. surface sorbed chelating resins and grafted chelating resins have been widely used when compared to nascent and ion-exchange resins [4]. Further, grafting was effected by chemical immobilization or in situ polymerization. The in situ polymerization approach was adopted in the present study to prepare chelating macroporous resins.

Solid phase extraction (SPE) involves the transfer of analytes from aqueous phase to the active sites of the adjacent phase [5,6]. SPE has come to the forefront compared to other preconcentration and/or separation techniques, as it offers several advantages such as flexibility, higher enrichment factors, absence of emulsion, low cost (because of lower consumption of reagents), speed and simplicity, safety with respect to hazardous samples and more importantly environmental friendly [7–9]. Chelate modified macroporous polymeric sorbents have numerous advantages over inorganic oxide and natural organic based sorbents [4,10]. These include (i) hydrolytic stability over a wide pH range, (ii) higher surface area, (iii) greater surface polarity, (iv) regenerability, (v) kinetically faster sorption and desorption mechanisms due to permanent pore structure and (vi) easy accessibility.

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Table 1
Summary of solid phase extractive preconcentration procedures reported for cobalt and/or nickel using polymeric sorbents

S. No.	Metal ion	Polymer sorbent	Chelating agent/s	Mode of functionalization	Preconcentration mode	Detection technique	Application	Detection limit ($\mu g\, l^{-1}$)	References
1	Co, Ni	Styrene–DVB (XE-305)	Quinoline-8-ol	Adsorption	Offline	GFAAS	Seawater	–	[18]
2	Ni	Fiber	–	Coating	Offline	FAAS	Natural waters	–	[19]
3	Co, Ni	Amberlite XAD-2	Chromotropic acid	Chemical immobilization	Offline	FAAS	River waters	–	[20]
4	Co, Ni	Amberlite XAD-2	*o*-Amino phenol	Chemical immobilization	Offline	FAAS	Well water	5.0 and 7.5	[21]
5	Co, Ni	Amberlite XAD-2	Tiron	Chemical immobilization	Offline	FAAS	River water	5.0 and 4.0	[22]
6	Co, Ni	Amberlite XAD-2	Thiosalicylic acid	Chemical immobilization	Offline	FAAS	River and tap water	0.2 and 1.28	[23]
7	Co, Ni	Amberlite XAD-2	Pyrogallol	Chemical immobilization	Offline	FAAS	River water	5.0 and 4.0	[24]
8	Co, Ni	Amberlite XAD-2	Pyrocatechol	Chemical immobilization	Offline	FAAS	River water	0.06 and 0.24	[25]
9	Ni	Amberlite XAD-2	1-(2-Pyridylazo)-2-naphthol	Chemical immobilization	Offline	FAAS	Alkaline salts and table salt	0.1	[26]
10	Ni	Amberlite XAD-2	Eriochrome blue black R	Chemical immobilization	Online	GFAAS	–	0.1	[27]
11	Ni	Amberlite XAD-2	Pyrocatechol violet	Chemical immobilization	Offline	FAAS	Well water	–	[28]
12	Co	Amberlite XAD-2	2-(2-Thiazolylazo)*p*-cresol	Adsorption	Offline	Spectrophotometry	–	–	[29]
13	Co, Ni	Amberlite XAD-4	Ammonium pyrollidine dithiocarbamate (APDC) and oxine	Adsorption	Offline	FAAS	River waters	–	[30]
14	Ni	Amberlite XAD-4	Butane-2,3-dione bis(*N*-pyridinoacetyl hydrazone)	Chemical immobilization	Online	ICP-MS	River reference material	0.01	[31]
15	Co, Ni	Amberlite XAD-4	APDC	Adsorption	Offline	FAAS	Dialysis solutions	–	[32]
16	Co	Amberlite XAD-4	2-(5-Bromo-2-pyridylazo)-5-diethylamino phenol	Adsorption	Online	HPLC–UV–vis	–	1.1×10^{-10} mol l^{-1}	[33]
17	Co, Ni	Amberlite XAD-4	1-Nitroso-2-naphthol	Adsorption	Offline	FAAS	Chemical grade potassium salts	0.06 (Ni)	[34]
18	Co, Ni	Amberlite XAD-4		Adsorption	Offline	GFAAS	Drinking water	–	[35]
19	Ni	Amberlite XAD-4	Diethyldithiocarbamate	Adsorption	Offline	FAAS	Waste waters	–	[36]
20	Co, Ni	Amberlite XAD-4	*o*-Aminobenzoic acid	Chemical immobilization	Offline	FAAS	CRM of coal and brackish lake water	–	[37]
21	Ni	Amberlite XAD-16	1-(2-Pyridylazo)-2-naphthol	Adsorption	Offline	FAAS	Tap water	–	[38]
22	Co, Ni	Amberlite XAD-16	Sodium diethyldithio carbamate	Adsorption	Offline	GFAAS	–	–	[39]
23	Co, Ni	Amberlite XAD-16	Sodium diethyldithio carbamate	Adsorption	Offline	–	Seawater	–	[40]
24	Co	Amberlite XAD-16	4-(2-Thiazolylazo) resorcinol	Adsorption	Offline	FAAS	Natural water	–	[41]
25	Ni	Amberlite XAD-16	4-(2-Thiazolylazo) resorcinol	Adsorption	Offline	FAAS	–	0.04	[42]
26	Co	Amberlite IR-120	Diethyldithiocarbamate/ acetylacetonate	Adsorption	Online	ETAAS	CRM of natural waters	0.002/0.003	[43]
27	Co, Ni	Styrene–EGDMA	5,7-Dichloroquinoline-8-ol	Embedded	Offline	FAAS	Soil and sediments	2.0, 2.0	Present method

Cobalt is an essential micronutrient for man, animals and plants for a range of metabolic processes [11,12]. On the other hand, nickel is a moderate toxic element as compared to other transition metals. However, it is known that inhalation of nickel and its compounds can lead to serious problems, including respiratory system cancer [13,14]. Moreover, nickel can cause a skin disorder known as nickel eczema, which is a common occupational disease in workers who handle large amounts of these elements [15–17]. Neutron activation analysis (NAA), graphite furnace atomic absorption spectrometry (GFAAS), wavelength dispersive X-ray spectrometry (WDXRF), inductively coupled plasma (ICP) atomic emission spectrometry and ICP-mass spectrometry can be readily adopted for the monitoring of ultratrace amounts of above elements in complex real samples such as sea water, human hair, soils and sediments. However, the analysis of samples by readily available and low cost flame atomic absorption spectrometry (FAAS) demands the use of preconcentration procedures in view of its insufficient sensitivity and matrix interference. Table 1 summarizes various SPE preconcentration procedures reported for cobalt and/or nickel using polymeric sorbents.

This study explores the preparation of chelate embedded macroporous resins by grafting chelating agents via in situ polymerization of styrene–divinyl benzene (DVB)/ethylene glycol dimethacrylate (EGDMA) in the presence of quinoline-8-ol and its dihalo derivatives. The best of the above-synthesized polymer particles in terms of quantitative enrichment via solid phase extraction of admixtures of cobalt and nickel present in dilute aqueous solutions were characterized and tested for various analytical applications (after optimization).

2. Experimental

2.1. Reagents and materials

Quinoline-8-ol, 5,7-dichloroquinoline-8-ol (DCQ), 5,7-dibromoquinoline-8-ol, 5,7-diiodoquinoline-8-ol, 4-vinyl pyridine (VP), divinyl benzene (95%), ethylene glycol dimethacrylate and 2,2′-azobisisobutyronitrile were obtained from Aldrich, USA. Stock solutions (1000 μg ml^{-1}) of cobalt and nickel were prepared by dissolving 0.4039 g and 0.4476 g of $CoCl_2\cdot 6H_2O$ and $NiSO_4\cdot 6H_2O$, respectively, purchased from Aldrich, USA in 100 ml of deionized water. A 5% ammonium acetate (pH 7.0) solution was prepared to maintain the pH of the aqueous phase (7.0 ± 2.0) during solid phase extractive preconcentration experiments.

2.2. Instrumentation

Analyst 100 flame atomic absorption spectrometer (Perkin Elmer, USA) was used during solid phase extraction enrichment studies of cobalt and nickel. LI-120 digital pH meter (ELICO, India) was used for pH measurements. FTIR spectra were recorded in the frequency range 4000–400 cm^{-1} by KBr pellet method using MAGNA FTIR-560 spectrometer (Nicolet, USA). Elemental analysis studies were carried out using Perkin Elmer CHN analyzer (USA). Thermogravimetric analysis (TGA) was carried out using TGA-50H (Shimadzu, Japan). The surface area analysis was carried out by using GEMINI-2735 (micromeritics, USA) surface area analyzer

2.3. Polymerization studies

Quinoline-8-ol (Q) (2 mmol) and its dihalo derivatives (DHQ) (2 mmol), viz. 5,7-dichloroquinoline-8-ol, 5,7-dibromoquinoline-8-ol, 5,7-diiodoquinoline-8-ol embedded polymers were synthesized by bulk polymerization. Q and DHQ in presence of vinyl pyridine (VP) (2 mmol) embedded polymer particles were also prepared in a similar manner. Styrene (10 mmol) and divinyl benzene (10 mmol)/ethylene glycol dimethacrylate (10 mmol) were used as monomer and crosslinking monomers, respectively. The polymerization mixtures were prepared with 2-methoxyethanol (10 ml) as porogen and 2,2′-azobisisobutyronitrile (AIBN) (0.05 g) as initiator, cooled to 0 °C and purged with N_2 for 10 min and sealed. The bulk polymerization was carried out by keeping in an oil bath at 80 °C while stirring for 2–3 h. The polymer materials thus obtained were ground and sieved to get particles in the size range 45–212 μm. These particles were washed thoroughly with water and 10% HCl to remove unembeded chelating agents and reactants.

2.4. Solid phase extractive preconcentration experiments

Batch static preconcentration studies were carried out by taking 1000 ml of sample solution containing 25 μg each of cobalt and nickel and adjusting the pH to around 7.0 after the addition of 0.1 mol l^{-1} ammonium acetate buffer. 0.04 g of polymer (P_1–P_{12}) particles were added to above solution and stirred for 5 min. The enriched metal ions were eluted with 5 ml of 2 mol l^{-1} HCl and subjected to FAAS determination. Control or blank experiments containing no metal ion were also done in a similar manner for each polymer and subjected to FAAS determination. The results obtained are shown in Table 2 from which it is clear that

(i) Quantitative enrichment of cobalt and nickel were obtained in case of DCQ embedded styrene–EGDMA (P_{11}) and styrene–EGDMA–VP (P_{12}) polymers with a preconcentration time of 5 min.
(ii) Quantitative enrichment of cobalt and nickel with P_3, P_7 and P_8 polymers requires 15 min of preconcentration time.
(iii) Nascent styrene–DVB (P_1) and styrene–EGDMA (P_{10}) polymers enrich cobalt and nickel to an extent of <10%. As DCQ embedded styrene–EGDMA polymer (P_{11}) itself gave quantitative enrichment of cobalt and nickel present in admixtures within 5 min, styrene–EGDMA

Table 2
Percent enrichment of cobalt and nickel with the polymers synthesized in Table 1 (pH 7.0 ± 2.0, 0.04 g of polymer preconcentration and elution times = 5 min; eluent = 5 ml of 2 mol l^{-1} HCl, aqueous phase volume = 1000 ml)

Polymer code	Chelating agents	Enrichment (%)			
		Cobalt		Nickel	
		Blank	Sample	Blank	Sample
Monomers (styrene–DVB)					
P_1	–	0.05	5.43	0.03	9.43
P_2	Q	0.15	23.92	0.05	43.12
P_3	DCQ	0.10[a]	>99.95[a]	0.03[a]	>99.95[a]
P_4	DBQ	0.10	64.10	0.03	60.55
P_5	DIQ	0.15	23.07	0.10	33.94
P_6	Q–VP	0.15	43.59	0.05	89.90
P_7	DCQ–VP	0.05	75.56	0.03	91.54
		0.05[a]	<99.95[a]	0.03[a]	>99.95[a]
P_8	DBQ–VP	0.10	71.74	0.03	80.19
		0.15[a]	>99.95[a]	0.03[a]	>99.95[a]
P_9	DIQ–VP	0.15	43.40	0.03	74.50
Monomers (styrene–EGDMA)					
P_{10}	–	0.05	3.26	0.03	7.55
P_{11}	DCQ	0.05	>99.95	0.03	>99.95
P_{12}	DCQ–VP	0.05	>99.95	0.03	>99.95

[a] 15 min preconcentration time.

(P_{10}) and DCQ embedded styrene–EGDMA (P_{11}) polymers were chosen for detailed characterization and analytical application studies.

3. Results and discussion

Characterization of styrene–EGDMA and DCQ embedded styrene–EGDMA polymer materials were carried out as described below.

3.1. Elemental analysis

The elemental analysis studies of styrene–EGDMA (P_{10}) and DCQ embedded styrene–EGDMA (P_{11}) polymer materials are shown in Table 3. Table 3 also shows the calculated/theoretical percentages of C, H and N. The agreement between calculated and experimentally found values is quite good. Thus, the close similarity of % N in case of P_{11} between experimental and calculated values indicates that DCQ is indeed embedded in the styrene–EGDMA polymeric matrix.

Table 3
Elemental analysis studies

Polymer	Calculated (%)			Experimentally found (%)		
	C	H	N	C	H	N
P_{10}	71.52	7.28	–	71.20	6.79	–
P_{11}	68.90	6.67	0.8	68.29	6.82	0.80

3.2. Surface area studies

Surface area studies of styrene–EGDMA (P_{10}) and DCQ embedded styrene–EDGMA (P_{11}) were carried out using surface area analyzer. The single point and BET surface areas for P_{10} polymer materials are 85.93 $m^2\ g^{-1}$ and 85.73 $m^2\ g^{-1}$ and for P_{11} polymer materials are 113.66 $m^2\ g^{-1}$ and 118.81 $m^2\ g^{-1}$. It is clear from the above observations that there is increase in surface area on embedding DCQ into styrene–EGDMA polymeric matrix.

3.3. IR spectra

From the IR spectral studies of styrene–EGDMA, DCQ embedded styrene–EGDMA, cobalt-bonded styrene–EGDMA and nickel-bonded styrene–EGDMA, it can be seen that the spectra contain a strong peak at 765 cm^{-1} corresponding to the C–Cl bond indicating the presence of DCQ in all the materials excepting styrene–EGDMA polymer material. The –C=N stretching vibration at 1640 cm^{-1} in the spectrum of DCQ embedded styrene–EGDMA polymer get shifted to 1620 cm^{-1} and 1627 cm^{-1} on bonding with cobalt and nickel, respectively, confirming the involvement of –N of the quinoline ring during the metal binding. Also –O–H stretching vibration at 3072 cm^{-1} in the spectrum of DCQ embedded styrene–EGDMA polymer is shifted to 3065 cm^{-1} on bonding with cobalt or nickel due to metal coordination.

3.4. TGA

The TGA studies of DCQ embedded styrene–EGDMA (A), cobalt-bonded styrene–EGDMA (B) and nickel bonded styrene–EGDMA (C) were carried out. These studies indicate that the thermal stability of the DCQ embedded polymer increases as a result of metal bonding. The thermal decomposition of A starts at 130 °C, due to the decomposition of DCQ in the polymeric matrix, which is having a melting point of 180 °C. In the case of B and C, the metal bound polymers were stable up to 300 °C and 240 °C since the thermal stability of Co–DCQ and Ni–DCQ complex is up to 295 °C and 235 °C, respectively.

3.5. Optimization of experimental parameters for enrichment of cobalt and nickel from dilute aqueous solutions

3.5.1. Effect of pH

A series of solutions containing 0 μg and 25 μg each of cobalt and nickel were taken and the pH of the solutions were adjusted between 2 and 9 and the recommended preconcentration procedure was followed using 0.04 g of P_{11} polymer particles. The enrichment of cobalt and nickel is constant and maximum in the pH range 5–9 (see Fig. 1). Hence, the pH was adjusted to 7 ± 2 in all subsequent studies after the addition of 10 ml of 1 mol l^{-1} ammonium acetate buffer.

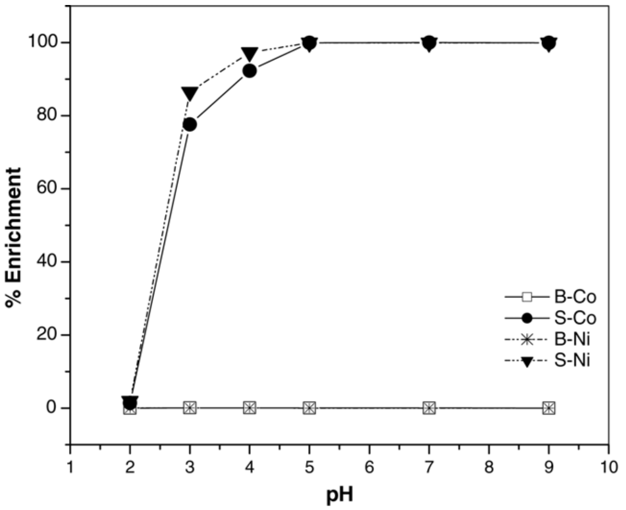

Fig. 1. Effect of pH on the preconcentration of cobalt and nickel ions using DCQ embedded styrene–EGDMA (P_{11}) polymer particles [0 μg (B) and 25 μg (S) each of cobalt and nickel, weight of P_{11} = 0.04 g; preconcentration and elution times = 5 min; eluent (HCl) concentration = 2 mol l^{-1}; eluent volume = 5 ml; aqueous phase volume = 1000 ml].

3.5.2. *Effect of weight of polymer particles*

Fig. 2 shows the percent enrichment of cobalt and nickel with different weights of P_{11} polymer particles. The corresponding blank values were also shown in Fig. 2 for comparison. As low as 0.04 g of P_{11} polymer particles were enough for quantitative enrichment of cobalt and nickel.

Table 4
Influence of various parameters on the percent enrichment of cobalt and nickel with DCQ embedded styrene–EGDMA polymer (0.04 g of P_{11}, pH 7 ± 2)

S. No.	Parameter	Enrichment (%)			
		Cobalt		Nickel	
1	Preconcentration time (min)				
	5	0.05	>99.95	0.05	>99.95
	10	0.05	>99.95	0.03	>99.95
	15	0.05	>99.95	0.03	>99.95
2	Elution time (min)				
	5	0.05	>99.95	0.03	>99.95
	10	0.05	>99.95	0.05	>99.95
	15	0.10	>99.95	0.10	>99.95
3	Eluent concentration (mol l^{-1})				
	1.0	0.05	73.85	0.03	74.59
	2.0	0.05	>99.95	0.03	>99.95
	5.0	0.10	>99.95	0.05	>99.95
4	Eluent volume (ml)				
	5	0.03	>99.95	0.02	>99.95
	10	0.10	>99.95	0.10	>99.95
	15	0.10	>99.95	0.10	>99.95
5	Aqueous phase volume (ml)				
	100	0.05	>99.95	0.03	>99.95
	500	0.05	>99.95	0.03	>99.95
	750	0.05	82.99	0.03	86.49
	1000	0.10	75.53	0.10	80.41

3.5.3. *Effect of other experimental variables*

The percent enrichment of cobalt and nickel as a function of preconcentration time, elution time, eluent concentration, eluent volume and aqueous phase volume were studied with 0 μg and 25 μg each of cobalt and nickel. The results obtained are shown in Table 4 from which it is clear that as low as 5 min each of preconcentration and elution times and 5 ml of 2 mol l^{-1} of HCl as eluent were enough for quantitative recovery of Co and Ni using DCQ embedded styrene–EGDMA. Aqueous phase volume variation study showed that quantitative preconcentration of cobalt and nickel were possible up to a maximum volume of 1000 ml and thus enabling the enrichment factor of 200 for both cobalt and nickel. Table 6 compares the enrichment factors obtained in the present work with those reported so far using several chelate functionalized commercial polymeric styrene–DVB resins.

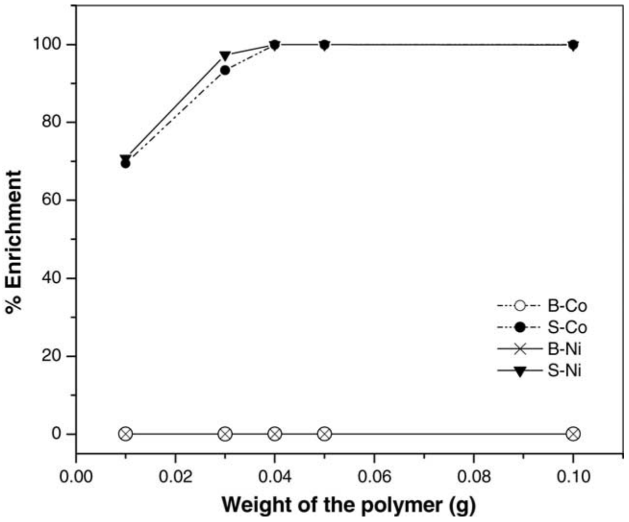

Fig. 2. Effect of weight of DCQ embedded styrene–EGDMA (P_{11}) polymer particles on the preconcentration of 0 μg (B) and 25 μg (S) each of cobalt and nickel ions (conditions are same as in Fig. 1, pH 7 ± 2).

3.6. *Retention capacity studies*

This experiment was carried out by taking 1 mg of cobalt or nickel and 0.05 g of P_3, P_7, P_{11} and P_{12} polymer particles after adjusting the pH to 7 ± 2 with 5 ml of 1.0 mol l^{-1} ammonium acetate buffer and then diluting to 25 ml. These solutions were stirred for 20 min on a magnetic stirrer and filtered through a filter paper. The amount of cobalt or nickel enriched onto polymer particles were determined by FAAS technique. The retention capacities of DCQ embedded styrene–DVB and styrene–EGDMA polymers were calculated to be 12.35 and 11.45 (for cobalt) and 7.23 and 7.05 (for nickel), respectively. Table 5 compares the retention/sorption capacities obtained in the present work with those reported so far using chelate functionalized commercial styrene–DVB polymer supports for cobalt and nickel. Barring two cases in the case of nickel, the retention capacities obtained by the DCQ embedded polymers are higher com-

Table 5
Comparison of retention/sorption capacities and enrichment factors

S. No.	Support	Immobilized ligand	Retention/sorption capacity (mg of M^{2+} per g of support)		Enrichment factor		References
			Co	Ni	Co	Ni	
1	Amberlite XAD-4	*o*-Amino benzoic acid	5.36	7.10	150	200	[37]
2	Amberlite XAD-7	Xylenol orange	2.60	2.60	100	100	[44]
3	Amberlite XAD-2	Pyrocatechol	1.36	3.12	200	200	[25]
4	Amberlite XAD-2	Pyrocatechol violet	–	0.62	–	18	[28]
5	Amberlite XAD-2	Alizarin red S	–	0.14	–	40	[45]
6	Amberlite XAD-2	Chromotropic acid	3.84	3.24	150	200	[20]
7	Amberlite XAD-2	Tiron	6.49	12.60	56	150	[22]
8	Amberlite XAD-2	*o*-Aminophenol	3.29	3.24	100	65	[21]
9	Amberlite XAD-2	Pyrogallol	6.71	4.11	65	120	[24]
10	Amberlite XAD-2	Thiosalicylic acid	6.30	18.20	180	200	[23]
11	Amberlite XAD-2	1-(2-Pyridylazo)-2-naphthol	–	0.11	–	50	[26]
12	Silica gel	Salicyldoxime	3.54	2.34	40	40	[46]
13	Silica gel	Acid red	0.89	0.66	–	–	[47]
14	Silica gel	3-Hydroxy-2-methyl-1,4-naphthoquinone	–	–	10	–	[48]
15	Silica gel	Didecylaminoethyl-β-tridecyl-ammonium iodide	7.07	–	49	–	[49]
16	Silica gel	3-Methyl-1-phenyl-4-stearoyl-5-pyrazolone	2.65	2.88	40	40	[50]
17	Styrene–DVB	5,7-Dichloroquinoline-8-ol	12.35	7.23	200	200	Present work
18	Styrene–EGDMA	5,7-Dichloroquinoline-8-ol	11.46	7.05	200	200	Present work

pared to other chelate functionalized commercially available styrene–DVB resins.

3.7. Statistical and calibration parameters

Under the optimum conditions described in Section 2, the calibration curves were found to be linear over the concentration range of 0–500 μg of cobalt or nickel in 1 l of solution. The linear equation with regression is as follows:

$$A_{\mathrm{Co}} = 0.0026C_{\mathrm{Co}} + 0.0032$$

$$A_{\mathrm{Ni}} = 0.0033C_{\mathrm{Ni}} + 0.0152$$

where A is the absorbance and C the amount of cobalt or nickel in $\mu\mathrm{g\,l^{-1}}$ of aqueous solution. The correlation coefficients were 0.99917 and 0.99967 for cobalt and nickel, respectively.

Five replicate determinations of 25 μg of cobalt or nickel present in 1 l of solution gave mean absorbances of 0.057 and 0.068 with a relative standard deviations of 2.52% and 2.25%. The detection limits corresponding to three times the deviation of the blank was found to be $2\,\mu\mathrm{g\,l^{-1}}$ of cobalt or nickel.

3.8. Effect of neutral electrolytes and coexisting metal ions

Various neutral electrolytes, viz. NaCl, $NaNO_3$, Na_2SO_4, KCl, $CaCl_2$ and $MgCl_2$ at $0.1\,\mathrm{mol\,l^{-1}}$ level and 100 μg of coexisting metal ions, viz. Fe, Cu, Zn and Mn do not have any deleterious effect on the enrichment of 5 μg each of cobalt and nickel present in 1 l of aqueous solution during enrichment with 0.04 g of P_{11} polymer particles.

3.9. Recovery of cobalt and nickel from synthetic sea water solutions

Table 6 shows the results obtained on the analysis of synthetic seawater solutions of open sea, deep sea and Great Salt Lake water compositions [51,52] with 5 μg each of cobalt and nickel. From the recoveries, it is clear that the developed procedure is suitable for selective enrichment of cobalt and nickel from a variety of seawater samples in addition to dilute aqueous solutions.

3.10. Analysis of certified reference materials

The accuracy of the developed preconcentration procedure was tested by analyzing certified reference materials of soil (IAEA soil-7, supplied by International Atomic Energy Agency, IAEA, Vienna) and marine sediment (MESS-3, supplied by National Research Council, Canada). The soil and sediment samples were brought into solution by treating 0.5 g of sample with 5 ml of HF and 1 ml of Conc. H_2SO_4 at 150 °C. The process was repeated thrice. The residue was cooled and fused with 2 g of $KHSO_4$ at 800 °C in an electric oven for 30 min. Then the melt was cooled, dissolved in 50 ml of water and diluted to 100 ml.

Preconcentration, elution and determination were carried out by following the procedure described in Section 2. The results obtained are shown in Table 7 from which it is clear that the amounts of cobalt and nickel present in IAEA soil-7 and MESS-3 agree well with certified values. Furthermore, the recoveries of cobalt and nickel added to CRMs prior to dissolution, preconcentration, elution and determination were found to be good indicating the suitability of the developed preconcentration/enrichment procedure for the determination of cobalt and nickel in soil and sediment samples.

Table 6
Analysis of synthetic seawater solutions (Co and Ni = 5.0 μg each, 0.04 g of P_{11}, pH 7.0)

S. No.	Composition of the synthetic sample (%)	Aliquot taken (ml)	Recovery (%)	
			Cobalt	Nickel
1	None	500	>99	>99
2	Seawater			
	Na (1.05), K (0.04)	100	>99	>99
	Mg (0.13), Ca (0.04), Cl (1.89)	500	>99	>99
3	Deep seawater			
	Na (3.2), K (0.64)	100	>99	>99
	Mg (3.67), Ca (1.30), Cl (17.0)	500	>99	>99
4	Great Salt Lake water			
	Na (6.7), K (0.34)	100	>99	>99
	Mg (0.56), Ca (0.03), Cl (11.2)	500	>99	>99

Table 7
Analysis of certified reference materials

S. No.	CRM	Metal added ($\mu g\,g^{-1}$)		Metal found ($\mu g\,g^{-1}$)				Recovery (%)	
				Present method		Certified value			
		Co	Ni	Co	Ni	Co	Ni	Co	Ni
1	IAEA soil-7	–	–	8.8	25.9	8.9	26.0	–	–
		10.0	25.0	18.8	51.0	–	–	100	100.4
		20.0	50.0	28.7	75.7	–	–	99.5	99.6
2	MESS-3	–	–	14.5	46.8	14.4	46.9	–	–
		15.0	50.0	29.5	96.6	–	–	100	99.6
		30.0	100.0	44.2	146.5	–	–	99.0	99.7

Table 8
Analysis of soil and sediment samples

S. No.	Description of sample	Metal added ($\mu g\,g^{-1}$)		Metal found ($\mu g\,g^{-1}$)		Recovery (%)	
1	House soil, Trivandrum	–	–	8.5	11.0	–	–
		10.0	10.0	18.5	21.0	100	100
		20.0	20.0	28.4	31.0	99.5	100
2	Karamana River sediment, Trivandrum	–	–	21.1	23.9	–	–
		20.0	20.0	41.1	43.8	100	99.5
		40.0	40.0	61.0	63.9	99.8	100
3	Arabian Sea sediment, Trivandrum	–	–	14.1	25.4	–	–
		10.0	25.0	24.1	50.0	100	98.4
		20.0	50.0	33.7	75.2	98.0	99.6

3.11. Analysis of soil, river and marine sediments

Soil sample collected from Trivandrum and sediments of Karamana River, Trivandrum and Arabian Sea, Trivandrum were brought into solution as per the procedure described for CRMs. These samples were subjected to preconcentration, elution and determination as per the procedure described in Section 2. The results obtained are shown in Table 8 from which it is clear that the developed preconcentration procedure in conjunction with flame AAS is suitable for rapid and routine monitoring of cobalt and nickel in soils and sediments.

4. Conclusions

The DCQ embedded styrene–EGDMA and styrene–DVB polymers either in presence or absence of 4-vinyl pyridine offer quantitative enrichment of cobalt and nickel from 1.0 l of aqueous solutions with enrichment factors of ∼200. Furthermore, the retention capacities of DCQ embedded styrene–EGDMA and styrene–DVB polymers were found to be 11.46 $mg\,g^{-1}$ and 12.35 $mg\,g^{-1}$ (for Co) and 7.25 $mg\,g^{-1}$ and 7.23 $mg\,g^{-1}$ (for Ni) which are higher compared to hitherto developed chelate functionalized commercial styrene–DVB resins and silica gel. Again, the DCQ embedded styrene–EGDMA polymers gave quantitative enrichment of cobalt and nickel within 5 min of preconcentration time compared to 15 min required for DCQ embedded styrene–DVB polymers. Hence, the characterization studies were restricted to styrene–EGDMA and DCQ embedded styrene–EGDMA polymers only. In addition to testing the accuracy of the developed preconcentration procedure by analyzing soil and marine sediment certified reference materials, the feasibility of the present method in analyzing real soil and sediment samples was successfully demonstrated.

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