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**To cite this Article** Sharma, Rakesh K. and Pant, Parul(2009) 'Solid phase extraction and determination of metal ions in aqueous samples using Quercetin modified Amberlite XAD-16 chelating polymer as metal extractant', International Journal of Environmental Analytical Chemistry, 89: 7, 503 – 514

To link to this Article: DOI: 10.1080/03067310802691680 URL: http://dx.doi.org/10.1080/03067310802691680

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## Solid phase extraction and determination of metal ions in aqueous samples using Quercetin modified Amberlite XAD-16 chelating polymer as metal extractant

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(Received 11 October 2008; final version received 12 December 2008)

A new chelating polymer has been developed using Amberlite XAD-16 anchored with Quercetin. The modified polymer was characterised by Fourier Transform Infra Red (FTIR) spectroscopy, thermogravimetric analysis, surface area analysis and elemental analysis. The Quercetin anchored polymer showed superior binding affinity for Cr(III), Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) with greater than 95% adsorption under optimum conditions. The optimum pH conditions for the quantitative sorption of metal ions were studied. The developed method showed superior extraction qualities with high metal loading capacities of 387, 313, 195, 473, 210 and  $320 \,\mu\text{mol g}^{-1}$  for Cu(II), Co(II), Cr(III), Fe(III), Mn(II) and Ni(II), respectively. The rate of metal ion uptake i.e. kinetics studies performed under optimum levels, showed  $t_{1/2}$  for Co(II), Cu(II), Cr(III), Fe(III), Mn(II) and Ni(II) is 20, 15, 25, 10, 30 and 15 min, respectively. Desorption of metal ions was effective with 10 mL of 2 M HCl prior to analysis using flame atomic absorption spectrophotometer. The chelating polymer was highly ion selective in nature even in the presence of interferent ions, with a high preconcentrating ability for the metal ions of interest. The developed chelating polymer was tested on its utility with synthetic and real samples like river, tap water samples and also with multivitamin tablets. It showed relative standard deviation (R.S.D.) values of/less than 3.0% reflecting on the accuracy and reproducibility of data using the newly developed chelating polymer.

Keywords: chelating polymer; Amberlite XAD-16; preconcentration

## 1. Introduction

Accurate analytical determination of metal ions at trace or subtrace levels requires versatility, specificity, sensitivity and accuracy. In certain cases, direct determination of metal ions using various instrumental methods is not possible due to matrix interferences and their low concentrations in analyte samples. Their recovery is also essential to minimise their discharge into the environment from the point of view of safety and economy. For this purpose various preconcentration techniques like the use of liquid extractants [1,2], co-precipitation methods [3], ion-exchange resins [4], etc. have been

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developed and practised over decades, but these methods were not economical and eco-friendly.

Solvent extraction and ion exchange techniques have been mostly applied to the recovery and separation of metal ions. However, recovery and separation by solvent extraction requires multiuse extraction and back-extraction in order to get successful separation [5]. The process also requires the use of large amounts of environmentally unfriendly and costly chemicals. As an alternative approach, chelating resins have been used for selective separation of metal ions by direct adsorption of the extractant into polymeric supports. Preconcentration of analytes using solid phase extraction not only results in a clean process eliminating matrix interference, clogging effects etc., but also increases analyte sensitivity thereby enhancing the lower limit of metal ion detection (LOD) [6,7]. Solid phase extraction (SPE) technique is thus recognised as the fast and reliable approach for quantitative metal ion extraction and pre-concentration [8–10]. Moreover, modified resins bridge the gap between solvent extraction and ion exchange. They combine not only the advantages of resin ion exchange for processing dilute solutions with specific properties of the extractants, but also a high distribution ratio and selectivity characteristic of the extractants dissolved in a liquid organic phase with the simplicity of equipment and operation characteristics of solid ion-exchange technology [11].

Various solid phases including Chelex 100 [12], silica gel [13–15], Amberlite XAD resins [16–23], polyurethane foam [24] and activated carbon [25] have been used for the solid-phase extraction of traces of heavy metals in environmental samples prior to their instrumental analysis. Many chelating sorbents have been developed, of which the XAD-based chelating resins [26–51] have proved themselves as an efficient preconcentrating and clean-up sorbents.

Advantage of using Amberlite XAD series over other supports lies in the fact that they have good physical properties such as their porosity, uniform pore size distribution, high surface area as chemical homogeneous non-ionic structure and good adsorbent properties for great amounts of uncharged compounds [52–55]. Amberlite XAD-16 has an edge over the most commonly used XAD-2 and XAD-4 resins due to the high surface area in comparison to the XAD-2 and XAD-4 resins [36].

In the present work, Quercetin modified Amberlite XAD-16 was studied for the recovery of transition ions and was found to have superior preconcentration and metal loading ability compared to other chelating polymers reported in literature. The developed resin was selective in preconcentrating analytes from synthetic and real samples, with relative standars deviation (R.S.D.) value of less than 3.0%.

## 2. Experimental

#### 2.1 Instrumentation

Metal ion determinations were performed using AAnalyst 200 model flame atomic absorption spectrophotometer (FAAS). The chelating resin was characterised by a Perkin Elmer Spectrum 2000 FTIR spectrometer. Elemental analysis was performed using Elementar Analysen Systeme GmbH Vario EL-III instrument. Thermal analysis was carried using DTG-60 Shimadzu instrument, equipped with TG units. Equilibration studies were carried using mechanical shaker at 200 rpm. Elico LI 120 pH meter was employed for pH variation. The surface area of the prepared resin was determined by using surface area analyser, Micrometrics ASAP 2010.

## 2.2 Reagents and chemicals

Amberlite XAD-16 (non-ionic divinyl polystyrene, surface area  $800 \text{ m}^2 \text{ g}^{-1}$  was procured from Alfa Aesar, USA. Stock solutions of Cr(III), Co(II), Cu(II), Ni(II), Mn(II) and Fe(III) containing  $1000 \,\mu\text{gmL}^{-1}$  of metal ion (Merck, Germany) were used for preparation of the standards for the calibration curve. All reagents and chemicals used were of AR grade unless otherwise specified.

Acetate buffer solutions were prepared by adding an appropriate amount of acetic acid (0.2 M) (Merck) to sodium acetate (0.2 M) solutions for pH 2–6 and ammonium chloride buffer solutions were prepared by adding an appropriate amount of ammonia to ammonium chloride solutions (0.2 M) for pH 8.

## 2.3 Synthesis of chelating resin

Ten grams of Amberlite XAD-16 was treated with a nitrating mixture, containing 20 mL of concentrated nitric acid and 50 mL of concentrated sulfuric acid for 1 h at 60°C on a water-bath. The nitrated mixture was poured into ice-cold water. It was further filtered, washed repeatedly with distilled water until free from acid. It was then reduced by refluxing with  $SnCl_2$  (40 g), concentrated hydrochloric acid (45 mL) and ethanol (60 mL), for 12 h at 40°C. The amino polymer was filtered off and washed with mixture of HCl–ethanol, water and 2 M NaOH so as to get the free amino polymer. The aminated Amberlite XAD-16 (5 g) was suspended in ice-cold water and treated with a 1 M HCl and 1 M NaNO<sub>2</sub> (added in small aliquots of 2 mL) until the reaction mixture showed permanent dark blue colour with starch iodide paper. The diazotized resin was filtered washed with ice-cold water and treated with Quercetin (5 g in 100 mL of 5% NaOH solution.) at 0–3°C for 24 h. The resulting resin was filtered and washed with distilled water.

## 2.4 Procedures adopted for carrying out different studies

## 2.4.1 Column method

A glass column  $(15 \times 4.5 \text{ cm})$  having a porous disc and stop cock was packed with 50 mg of preconditioned resin beads, by soaking in optimum pH solution for 60 min. After each use, the resin in the column was washed thoroughly with water and related buffer solution and then stored in water for further applications. The optimum experimental parameters for quantitative metal ion sorption and desorption are listed in Table 1.

Table 1.	Optimum	experimental	parameters fo	r quantitative	metal ion	sorption and	desorption.
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Experimental parameters	Cu(II)	Co(II)	Cr(III)	Fe(III)	Mn(II)	Ni(II)
pH range	5–7	5–6	3–4	5–6	5–6	4–6
Metal sorption capacity $(\mu mol g^{-1})$	387	313	195	473	210	320
Eluent for desorption (HCl)	2 M	2 M	2 M	2 M	2 M	2 M
Lower limit of detection $(ng mL^{-1})$	18.5	20	25	16.6	16.6	12.5
Preconcentration factor	270	250	200	300	300	400

## 2.4.2 Batch experiment

Fifty milligrams of the resin was added to 10 mL of metal ion solution ( $5 \mu \text{g mL}^{-1}$ ) adjusted to the desired pH and the mixture was shaken for 1 h. The mixture was filtered off and the concentration of the solution was determined by FAAS.

#### 3. Results and discussion

## 3.1 Resin characterization

The modification of Amberlite XAD-16 with Quercetin was confirmed by FTIR spectra with stretching frequencies at 1613, 1580 and  $1320 \text{ cm}^{-1}$  corresponding to C=O, N=N and C-OH (bending) frequencies, respectively, were detected which were originally absent in the non-functionalised resin matrix. The new bands at 1457, 1234 and 1092 cm<sup>-1</sup> due to the attachment of Quercetin were also detected in Amberlite XAD-16–Quercetin further supporting the loading of Quercetin onto the Amberlite XAD-16.

The CHNO analysis gave the following results: C, 64.20 (64.93); H, 4.55 (4.80); N, 6.23 (6.06); O, 25.02 (24.02), the values given in brackets are the theoretical values. Correlation of the obtained and the calculated values suggest that the Quercetin moiety has been successfully immobilsed onto the Amberlite support. The thermogravimetric analysis (TGA) of the XAD-16-Quercetin chelating resin shows three-step degradation. In the first step, a mass loss of 4.1% up to 110°C is due to removal of physisorbed water on the resin. In the second step, mass loss is 10.4% from 204 to 354°C corresponding to loss of two -OH moieties and 394–599°C shows 30.5% mass loss corresponding to a further loss of organic groups attached to the resin.

The surface area of AL-XAD-16-Quercetin was found to be  $240.9 \text{ m}^2 \text{ g}^{-1}$  by Brunauer, Emmett, Teller (BET) method. The decrease in surface area of modified polymer (surface area of unmodified resin was  $800 \text{ m}^2 \text{ g}^{-1}$ ), in comparison to unmodified Amberlite XAD-16, further confirms the incorporation of gallic acid to Amberlite XAD-16.

#### 3.2 Effect of pH on enrichment of metal ions

The influence of pH on the retentions of Cr(III), Ni(II) Mn(II), Cu(II), Fe(III) and Co(II) on the XAD-16-Quercetin resin were investigated in the pH range of 2–8 for 1 h. For this purpose, column experiments were performed by using 10 mL of test solutions containing  $5 \mu g m L^{-1}$  of each analyte ion. The pH of the solutions was adjusted by using buffer solutions given in the Experimental Section. The results are depicted in Figure 1. Optimum pH for adsorption of Cu (II), Co(II), Cr(III), Fe(III), Mn(II) and Ni(II) is 5–7, 5–6, 3–4, 5–6, 5–6 and 4–6, respectively.

#### 3.3 Adsorption kinetics

The adsorption kinetics was determined according to the following procedure: 100 mL of metal ion solution  $(0.5 \,\mu\text{g m L}^{-1})$  was shaken with 0.1 g of the resin at room temperature for 1 h. At predetermined intervals, aliquots of 1 mL solution were withdrawn for analysis and the concentration of metal ion was determined by FAAS. The loading half time  $t_{1/2}$ , i.e. the time required to reach 50% of the resin total loading capacity was estimated from the resulting isotherm. As can be seen from Figure 2,  $t_{1/2}$  for Co(II), Cu(II),



Figure 1. Effect of pH on sorption of Cr(III), Mn(II), Ni(II), Cu(II), Co(II) and Fe(III) onto Quercetin modified Amberlite XAD-16.



Figure 2. Rate of metal sorption for Cr(III), Mn(II), Ni(II), Cu(II), Co(II) and Fe(III) ions onto Quercetin modified Amberlite XAD-16.

Cr(III), Fe(III), Mn(II) and Ni(II) is 20, 15, 25, 10, 30 and 15 min, respectively. Reasonable adsorption (>95%) was achieved in 45 min for all studied metal ions except Cr(III) where the time required for the same is 50 min.

## 3.4 Volume of elution solution

The effects of different volumes of HCl on the recoveries of Fe(III), Cu(II), Co(II), Ni(II), Mn(II) and Cr(III) retained on AL-XAD-16-Quercetin column were investigated.

Metal ion	Breakthrough volume (mL)	$\begin{array}{c} \text{Concentration} \\ (\text{ng}\text{mL}^{-1}) \end{array}$	Final volume (mL)	Percentage recovery	Preconcentration factor
Cr(III)	2000	25.0	10	95.4	200
Mn(II)	3000	16.6	10	97.3	300
Ni(II)	4000	12.5	10	98.7	400
Co(II)	2500	20.0	10	97.2	250
Cu(II)	2700	18.5	10	99.5	270
Fe(III)	3000	16.6	10	96.2	300

Table 2. Enrichment factors and enrichment limits of metal ions (AL-XAD-16-Quercetin).

Fe(III), Cu(II), Co(II), Ni(II), Mn(II) and Cr(III) retained on AL-XAD-16-Quercetin column could be completely eluted with  $2 \mod L^{-1}$  of HCl. Quantitative recovery values for analytes were obtained with 10 mL of  $2 \mod L^{-1}$  of HCl.

## 3.5 Reuse of the chelating resin

The stability and regeneration of the XAD-16-Quercetin polymer were examined. To test the resin reusability, 50 mg of the resin was shaken with  $(10 \text{ mL}, 5 \mu \text{gmL}^{-1})$  of the Cu solution and their concentrations in both aqueous and sorbent phase were determined. Thereafter, the sorption and desorption of metal ions were repeated on the same resin beads after washing them with water till neutral pH. The resin was found to be stable up to 25 runs.

## 3.6 Breakthrough volume and preconcentration factor

When dealing with real samples containing very low concentrations of element ions, the maximum applicable sample volume must be determined. The maximum applicable volume of aqueous sample (containing metal ion in low concentrations) for which the concentration of metal ion can be determined is known as breakthrough volume. For this, same amount of individual metal ions of  $50 \,\mu g$ , were spiked to samples of varying volumes (2000–4000 mL) and was passed through the XAD-16-Quercetin column, and the breakthrough volumes are listed in terms of preconcentration factor as indicated in Table 2.

The results indicate the superior chelating properties of the resin matrix in targeting trace analytes from large sample volumes. The data confirms the high kinetic properties, selectivity and sensitivity of the polymeric matrix. The elution of metal ions prior to determination was carried out with 10 mL of eluent as preconcentrating agent. The maximum preconcentration value of 400 is achieved for Ni(II) where the breakthrough volume of solution is 4000 mL.

## 3.7 Effect of sample flow rate

The rate of metal ion equilibration with variation of flow rate was studied for the column in order to find the effect of flow rate on adsorption. The flow rate of  $2 \text{ mL min}^{-1}$  was found to be suitable for optimum loading of the metal ions. At higher flow rates,



Figure 3. The matrix ions and the recovery of the metal ions (sample volume: 100 mL).

there was a reduction in the percentage adsorption of metal ions. This could be probably due to the insufficient contact time between the sample solution and the AL-XAD-16-Quercetin resin column. A flow rate of  $2 \text{ mL min}^{-1}$  was maintained for the elution of the metal ions.

## 3.8 Effect of diverse metal ions on adsorption capacities

The effect of the presence of various interfering ions on the adsorption of the target metal ions was investigated. It is worth mentioning that quantitative recoveries for the analyte ions is desirable as the these interfering matrix ions tend to form complexes with the analyte ion of interest. Moreover, the matrix ions studied are commonly present in natural waters, so the study also gives the effectiveness of resin in preconcentration and determination of heavy metals at trace levels in natural waters. The procedure has been performed with 100 mL solution containing 50  $\mu$ g of each metal ion. The concentration of matrix ions was varied from 0.001 to 0.5 mol L<sup>-1</sup>.

The criterion for interference was lowering of recovery by more than 5%. The concentration of electrolytes above which the recovery was lowered by more than 5% is given in Figure 3. As can be seen from the results that the synthesised resin posses reasonably high-tolerance limits for the salts, which are commonly found in saline water and natural water bodies, so AL-XAD-16-Quercetin can be successfully applied for extraction of metal ions from such systems.

Another set of experiments were carried out to study the effect of metal ions on the recovery of Cr(III), Mn(II), Ni(II), Co(II), Cu(II) and Fe(III). A set of solutions having same concentration  $(5 \,\mu g \, m L^{-1})$  of analyte metal ion (metal ion of interest) were taken and mixed with other metal ions. The mixture was passed through a solution containing 0.05 g of modified resin after adjusting its pH to optimum level. The adsorbed metal ions in the solution were eluted with the help of 10 mL of 2 M HCl and determined by FAAS. As can be seen from Table 3, the effectiveness of resin to extract the metal ion of interest was also found out to be very good. The modified resin was able to effectively preconcentrate the target metal ions in the presence of other metal ions except in the case of Cr(III) in presence of Fe(III), Cu(II) and for Co(II) in the presence of Fe(III) and Mn(II) ions where the adsorption of target metal ion decreased to below 90%. The results further reflect the superior chelating ability of the prepared resin.

Test metal ion	Cr(III)	Fe(III)	Mn(II)	Ni(II)	Co(II)	Cu(II)
Cr(III)	_	67.5	95.2	97.1	93.4	83.2
Fe(III)	98.2	_	95.3	95.6	94.5	96.1
Mn(II)	92.3	93.1	_	93.4	92.6	92.7
Ni(II)	90.2	93.5	94.4	_	92.3	92.4
Co(II)	94.7	76.3	88.1	96.8	_	91.0
Cu(II)	94.4	95.2	96.6	94.1	97.2	_

Table 3. Recovery of metal ions in presence of other cations.

## 3.9 Sorption capacity measurement

The resin (0.1 g) was saturated with Cr(III), Mn(II), Ni(II), Cu(II), Co(II) and Fe(III) solution (50 mL of  $100 \,\mu g \,m L^{-1}$ ) by equilibration on a shaker for 1 h after adjusting to the desired pH at 25°C. The mixture was filtered off and the concentration of the solution was determined by FAAS. The adsorption capacities were calculated according to the following equation:

$$S = \frac{(C_0 - C)V}{W}$$

where S is the adsorption amount  $(\mu mol g^{-1})$ ;  $C_0$  and C are the initial concentration and the concentration of metal ion in solution when the adsorbent is separated  $(\mu mol mL^{-1})$ ; V is the volume (mL); W is the dry weight of resin (g). The sorption capacities were found out to be 195, 210, 320, 313, 387 and 473  $\mu$ mol g<sup>-1</sup> for Cr(III), Mn(II), Ni(II), Co(II), Cu(II) and Fe(III), respectively.

## 3.10 Applications of the method

## 3.10.1 Determination of metal ions in river water and tap water samples

AL-XAD-16-Quercetin was used to preconcentrate Co(II), Cu(II), Cr(III), Mn(II), Ni(II) and Fe(III) ions in water samples collected from the Ganges (Haridwar). The estimation of the six metal ions in case of water from Ganges was made with and without (referred as direct determination) standard addition (S.A.). For carrying out the studies, 1000 mL of water samples were passed through a Whatmann 41 filter paper prior to column passage to remove particulate matter and then through the column packed with 1.0 g of matrix after adjusting the pH to an optimum value. The water samples were preconcentrated for metal ion extraction without any dilution. The sorbed metal ions were eluted with 2 M HCl and their concentrations were determined by FAAS. Then a known amount of individual metal ions (5 mg) (S.A.) was spiked to the water samples and the data were confirmed by low R.S.D values of less than 3.0%, as indicated. The results are given in Table 4. The water samples were preconcentrated for metal ion extraction without any dilution. The sorbed metal ions were eluted and their concentrations were determined by FAAS as indicated in Table 4.

Determination of Cu(II) in certified multi-vitamin/multimineral tablet Riconia Ginseng obtained from Ranbaxy, India were used for analysis. One tablet was dissolved and decomposed with aqua regia thrice. The residue was dissolved in minimum volumes of dilute HCl and the pH of the solution was adjusted to 6, filtered and the filtrate was

Origin of	Metal ion $(\mu g m L^{-1})$						
sample	Method	Cu (R.S.D)	Co (R.S.D)	Cr (R.S.D)	Fe (R.S.D)	Mn (R.S.D)	Ni (R.S.D)
Ganges river, Haridwar Tap water, Delhi	Direct S.A. Direct S.A.	0.021 (2.1) 5.022 (2.9) 0.034 (1.5) 5.050 (2.7)	0.011 (1.5) 5.010 (2.7) 0.018 (2.5) 5.020 (1.9)	0.002 (2.6) 5.003 (1.2) 0.001 (2.1) 5.002 (2.9)	0.068 (0.6) 5.165 (1.7) 0.190 (0.4) 5.211 (1.4)	0.008 (1.6) 5.008 (2.1) 0.010 (2.3) 5.009 (1.9)	0.008 (0.6) 5.009 (0.3) 0.009 (2.8) 5.010 (1.2)

Table 4. Determination of metal ions in river water and tap water samples.

Table 5. Comparison of sorption capacities ( $\mu$ mol g<sup>-1</sup>).

Support: immobilised ligand	Со	Cu	Cr	Mn	Ni	Fe
Amberlite XAD-2						
Thiosalicylic acid [55]	106	214			310	60
Chromotropic acid [56]	65	134			103	58
Pyrocatechol [57]	23	93			53	74
o-Aminophenol [58]	58	53			55	
Tiron [59]	110	220		182	215	100
Pyrogallol [60]	70	71		82	70	83
Quinalizarin [61]	28	50		17		28
5-Palmitoyl-8-hydroxyquinoline [62]	27	28	21		24	22
Amberlite XAD-4						
Ammonium pyrrolidine dithiocarbamate [63]		174		157	123	
2,6-Diacetylpyridine [64]	255	264			290	
Amberlite XAD-7						
Xylenol orange [65]	44	25			45	29
Amberlite XAD-16						
Quercetin (present work)	313	387	195	210	320	473
2-{[1-(3,4-Dihydroxyphenyl)	221	468		178	269	515
methylidene]amino}benzoic acid [66]						
1,3-Dimethyl-3-aminopropan-1-ol [67]	270	460		210	550	
1-(2-Pyridylazo)2-napthol [68]	79	78	96			
Silica gel						
Resacetophenone [69]	365	186			254	272
8-Hydroxyquinoline [70]	178	400			220	348
3-Hydroxy-2-methyl-1,4-napthoquinone [71]	10	10				10

adjusted to optimum pH and then passed through the preconditioned resin bed. The metal ion concentration were found to be  $86.31 \,\mu g$  of Cu per gram (Concentration of Cu present originally in tablet was  $86.7 \,\mu g$  of Cu per gram of tablet) with R.S.D value of less than 3% for triplicate.

## 3.10.2 Comparison of sorption capacities and preconcentration factors

Comparison of sorption capacities (Table 5) and preconcentration factors (Table 6) of functionalised XAD resins with different ligands showed that Amberlite XAD-16 modified

Table 6. Comparison of preconcentration factors.

Support: immobilised ligand	Со	Cu	Cr	Mn	Ni	Fe
Amberlite XAD-2						
Thiosalicylic acid [55]	180	200			200	400
Chromotropic acid [56]	150	100			200	120
Pyrocatechol [57]	200	100			200	80
o-Aminophenol [58]	100	50			65	
Tiron [59]	56	200		64	150	80
Pyrogallol [60]	65	65		120	120	140
Quinalizarin [61]	40	100		65		
5-Palmitoyl-8-hydroxyquinoline [62]	50	50	50		50	50
Amberlite XAD-4						
Ammonium pyrrolidine dithiocarbamate [63]		230		55	59	
2,6-Diacetylpyridine [64]	_	_	_	_	_	_
Amberlite XAD-7						
Xylenol orange [65]	100	50			100	100
Amberlite XAD-16						
Quercetin (present work)	250	270	200	300	400	300
2-{[1-(3,4-Dihydroxyphenyl)	167	300		250	100	450
methylidene]amino}benzoic acid [66]						
1,3-Dimethyl-3-aminopropan-1-ol [67]	300	400			300	
1-(2-Pyridylazo)2-napthol [68]	200	200	200			
Silica gel						
Resacetophenone [69]	300	240			300	272
8-Hydroxyquinoline [70]	250	300			200	300
3-Hydroxy-2-methyl-1,4-napthoquinone [71]	_	_				_

Quercetin has higher capacity values and greater preconcentration factor values for Cu(II), Co(II), Cr(III), Fe(III), Mn(II) and Ni(II).

The Quercetin modified Amberlite XAD-16 resin when compared with functionalised XAD-2, XAD-4, XAD-7 resins with different ligands like thiosalicylic acid [56], chromotropic acid [57], pyrocatechol [58], *o*-aminophenol [59], tiron [60], pyrogallol [61], Quinalizarin [62], 5-palmitoyl-8-hydroxyquinoline [63], ammonium pyrrolidine dithiocarbamate [64], 2,6-diacetylpyridine [65] had higher sorption capacities and preconcentration factors for the analyte ions. The performance of the synthesised resin is superior or comparable to the Amberlite XAD-16 modified matrices like 2-1-(3,4-dihydroxyphenyl)-methylideneaminobenzoic acid [67], 1,3-dimethyl-3-aminopropan-1-ol [68], 1-(2-pyridy-lazo)2-napthol [69]. As can be seen from Tables 4 and 5, AL-XAD-16-Quercetin has higher capacity values and greater preconcentration factor values for Cu(II), Co(II), Cr(III), Fe(III), Mn(II) and Ni(II) than the resins prepared by modification of silica gel.

#### 4. Conclusion

It can be concluded that Quercetin modified Amberlite XAD-16 is an effective sorbent for trace amounts of Cr(III), Fe(III), Mn(II), Co(II), Ni(II) and Cu(II) ions that can be used for their preconcentration or removal from their dilute aqueous solutions. Under optimal

conditions quantitative sorption is achieved for the analyte ions on functionalised resin and these metals can be desorbed with 2 M HCl. These studies show that the synthesised resin has a good rate of equilibration with higher sorption capacity for the studied metal ions. The synthesised resin has minimum matrix interference with common ions and high sorption capacity and preconcentration factor values for the studied metal ions. Moreover, the matrix effects are low for the present resin as shown by the low R.S.D values obtained for river water and tap water samples. Facility of multiple times usage of resin for the preconcentration of metal ions adds to the above said advantages.

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