

## Octa-O-Methoxy Resorcin [4] Arene Amberlite XAD-4 Polymeric Chelating Resin for Solid Phase Extraction, Preconcentration, Separation and Trace Determination of Ni(II), Cu(II), Zn(II) and Cd(II) Ions

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## ABSTRACT

Synthetic resin, Amberlite XAD-4 was linked covalently with the third generation supramolecule, octa-*O*-methoxy resorcin [4] arene through -N=N- group to form chelating resin, which has been characterized and effectively used for the separation and preconcentration of metal ions such as Ni(II), Cu(II), Zn(II) and Cd(II). Critical parameters such as pH, flow rate, sorption capacity, breakthrough studies, distribution coefficient, preconcentration factor, concentration of eluting agents responsible for quantitative extraction of metal ions were optimized. The synthesized resin showed good binding affinity towards Ni(II), Cu(II), Zn(II) and Cd(II) under selective pH conditions. Good breakthrough capacity and fast exchange kinetics of the resin lead to effective separation of metal ions from their binary and ternary mixture by column method on the basis of pH and eluting agents. The resin could be reused for about 8 - 10 cycles. The proposed method having the analytical data with the relative standard deviation (RSD) < 2% and with recoveries of analytes higher than 98%, reflects upon the reproducibility and reliability of the method which has been successfully applied in the separation and determination of Ni(II), Cu(II), Zn(II) and Cd(II) ions in synthetic, natural and ground water samples.

Keywords: Separation; Preconcentration; Amberlite XAD-4; Octa-O-Methoxy Resorcin [4] Arene; Solid Phase Extraction

## **1. Introduction**

It is well recognized that several trace elements are essential constituents of enzymes and play a vital role in human metabolism and primarily supplied through diet and drinking water. However, beyond the essential range, deficiency and toxic effects are observed [1]. Considering biological research, the role of some trace and ultratrace elements in the body is very important and has diverse functions. Some of the trace elements are essential to life while others are toxic even at low concentrations [2-6]. Many metals listed as environmental hazards are essential dietary trace elements required for normal growth and development of animals and human beings. These metals are essential to human life within permissible limits. Toxicity of metal ions such as nickel, copper, zinc and cadmium in human beings is as follows: **Nickel:** Nickel plays important roles in the biology of microorganisms and plants [7-12]. Nickel sulfide fume as well as dust is believed to be carcinogenic, various other nickel compounds may be as well [7-12].

**Copper:** Copper is an economically important element which is found only in trace quantities in the earth's crust. It is required as a trace nutrient for both plants and animals, but excessive amounts are toxic [13].

**Zinc:** Men and many animals exhibit considerable tolerance to high zinc intakes. This tolerance is dependent on the nature of diet, and its Ca, Cu, Fe and Cd contents with which zinc interacts in the process of adsorption and utilization. Symptoms of zinc toxicity in humans include vomiting, electrolyte imbalance, dehydration, abdominal pain, nausea, dizziness etc. [7-12].

**Cadmium:** Cadmium is non-essential and toxic to human and animal systems [14]. Small quantities of cadmium cause adverse changes in the arteries of human

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kidneys and liver [15]. Teratogenic properties have been shown [16] whereas carcinogenic properties are suspected [17-19].

In this regard, evaluation of trace metals in the environmental samples including natural water has been continuously performed to designate the level of pollution which creates health problems [20,21]. Several analytical techniques have been used for the determination of heavy metal ions in the real samples which include Inductively coupled plasma-atomic emission spectrophotometer (ICP-AES) [22], flame atomic absorption spectrometry (FAAS) [23] etc. These techniques are both widely and routinely used for the determination of trace amounts of heavy metal ions. However, the direct determination of heavy metal ions at trace levels is limited not only due to insufficient sensitivity, but also by matrix interference [24,25].

In order to overcome these difficulties, preliminary separation and preconcentration of trace elements from the matrix are frequently used techniques to improve the detection limit and the selectivity [26]. Separation technique, in general, deal with the separation of components of mixtures to enhance the purity of substances while in preconcentration technique, one of the analytes or species have been selectively retained on a solid phase and then eluted with an appropriate eluent, and detected and quantified by an appropriate detection technique [27].

Different separation and preconcentration techniques using solid phase extraction (SPE) [28], co-precipitation [29] solvent extraction [30], membrane filtration [31], cloud point extraction [32,33], flotation [34], electrochemical decomposition [35] ion exchange etc. have been developed for the trace metal ion determination. Among these solid-phase extraction technique have been widely used because of its various advantages over other methods, such as higher preconcentration factor, lesser waste generation, lower matrix effect, use of less toxic solvents, saving of time and cost, easy regenerability of a solid phase and thereby more reusability [36-39].

Various SPE materials which have been used for the preconcentration of trace metal ions as their chelates include, activated silica gel [40,41], carbon [42-45], polyurethane foam [46] microcrystalline naphthalene [47], C<sub>18</sub> cartridges [48], Chelex-100 [49], Alumina [50], functionalized polyurethane foam [51], modified silica [52, 53], sulfur powder [54] and Amberlite XAD resins [55-61]. Amberlite XAD (styrene-divinyl benzene copolymer) resins, as the copolymer backbone for the immobilization of chelating ligands, have some physical superiority, such as porosity, uniform pore size distribution, high surface area, and chemical stability toward acids, bases, and oxidizing agents, as compared to other resins [62-65] Either the adsorption of chelating ligands onto these supports or the covalent coupling of chelating moiety has been used to design polymeric chelating resins, which are

versatile, durable, have good loading capacity towards metals, exhibit enhanced hydrophilicity and flexible working conditions. That is why the reaction of Amberlite XAD resin with suitable chelating agents is very popular for separation and preconcentration [66-71].

Calix [4] resorcinarenes possess good capability to form a variety of complexes with organic/inorganic ions, neutral molecules, transition metal complexes and organometallics [72] for the simple reason that they can be functionalized at the upper rim or at C-methyl position or at hydroxyl groups at extra-annular position, enabling them to be used as multifunctional receptors [73]. Literature reveals only few reports on the extraction of metal ions using calyx [4] resorcinarene and its derivatives [74-80]. As far as work on polymer supported calyx [4] resorcinarenes is concerned, Merdivan *et al.* [31,81, 82] have reported the use of calyx [4] resorcinarene impregnated on Amberlite XAD for separation and preconcentration of rare earths.

Here, the use octa-O-methoxy resorcin [4] arene Amberlite XAD-4 chelating resin for extraction, preconcentration and sequential separation of metal ions such as Ni(II), Cu(II), Zn(II) and Cd(II) in a column prior to their determination by Spectrophotometry/FAAS/ICP-AES is described. Different factors influencing the separation and preconcentration of these metal ions, such as pH, concentration of eluting agents, flow rate, total sorption capacity, exchange kinetics, preconcentration factor, distribution coefficient, breakthrough capacity, resin stability, effect of electrolytes, and associated metal ions have been investigated. The newly developed method has also been applied for the determination of Ni(II), Cu(II), Zn(II) and Cd(II) metal ions from industrial affluent, natural river and ground water samples of Ahmedabad (Gujarat) City.

## 2. Experimental

#### 2.1. Reagents

All the chemicals used in this work were of analytical grade purchased from Sigma-Aldrich and Merck. Amberlite XAD-4 with surface area 750 m<sup>2</sup>·g<sup>-1</sup>, pore diameter 50 Å and bead size 20 - 50 mesh was procured from Fluka. All aqueous solutions were prepared with quartz distilled deionized water. Glassware were soaked in 5% HNO<sub>3</sub> overnight and cleaned with double distilled deionized water before use. The pH was adjusted with the following buffer solutions:  $PO_4^{-3}/HPO_4^{-2}$  buffer for pH 2.0 and 3.0;  $CH_3COO^{-1}/CH_3COOH$  buffer for pH 4.0 to 6.0;  $HPO_4^{-2}/H_2PO_4^{-1}$  buffers for pH 7.0 and 7.5;  $NH_3/NH_4^+$  buffers of pH 8 to10.

Standard stock solutions (1000  $\mu$ g·mL<sup>-1</sup>) of Ni(II), Cu(II), Zn(II), and Cd(II) were prepared by dissolving 0.4045 gm NiCl<sub>2</sub>·6H<sub>2</sub>O; 0.384 gm Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O; 0.4541 gm Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O; 0.2744 gm Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O in 1 mL concentrated HNO<sub>3</sub> and dilute upto 100 mL with water in volumetric flask.

#### 2.2. Instruments

Spectral measurements were carried out using JASCO 570 UV-vis spectrophotometer using 10 mm quartz cells. The metal content determinations were carried out using (FAAS) NOVAA 400 p model with hollow cathode lamps, equipped with an air-acetylene flame without background correction and the operating conditions adjusted were carried out according to the standard guide-lines of the manufacturers. When metal ion concentration was too law for its direct determination, inductively coupled plasma-atomic absorption spectrometer (ICP-AES) JY 2000-2 was used. The flow of the liquid through the column was controlled by Miclins Peristaltic pump PP-10 EX. Elico digital pH-meter, model L1 614 equipped with a combined pH electrode was employed for measuring pH.

The water samples from Sabarmati River, ground water from the University area and Vatva industrial zone of Ahmedabad city were collected.

#### 2.3. Synthesis

Octa-O-methoxy resorcin [4] arene, the third generation supramolecule was synthesized by the acid catalyzed

condensation reaction of 1,3 dimethoxy benzene and p-hydroxy benzaldehyde as reported earlier [83]. Octa-*O*-methoxy resorcin [4] arene covalently linked with Amberlite XAD-4 through azo (-N=N-) linkage as per **Scheme 1**.

#### Synthesis of Amberlite XAD-4-Octa-O-Methoxy Resorcin [4] Arene

The nitration of Amberlite XAD-4 beads, the reduction of the nitrated resin and the subsequent diazotization of the amino resin was carried out by the procedure reported earlier for Amberlite XAD-2 [84]. The resulting diazotized resin was allowed to react with octa-*O*-methoxy resorcin [4] arene (1.0 g dissolved in 50 mL of 10% NaOH) at 0°C - 5°C for 48 h. The dark brown coloured beads were filtered, successively washed with double distilled water and finally dried for further studies.

#### 2.4. General Batch Method

Octa-*O*-methoxy resorcin [4] arene Amberlite XAD-4 polymeric chelating resin (1.0 gm) was added into a glass stoppered bottle containing 100 mL of each Ni(II)/Cu(II)/Zn(II)/Cd(II) solutions atan optimum pH conditions and the bottle was shaken for about 30 minutes. The resin was filtered and washed with double distilled water. The amount of metal ions extracted by resin was determined by using suitable eluting agents like HCl or HNO<sub>3</sub> by



Scheme 1. Synthesis of octa-O-methoxy resorcin [4] arene supported Amberlite XAD-4 polymeric chelating resin.

spectrophotometry/FAAS/ICP-AES.

#### 2.5. Generalcolumn Method

1.0 gm of octa-*O*-methoxy resorcin [4] arene Amberlite XAD-4 polymeric chelating resin was added to the mixture of CH<sub>3</sub>OH:H<sub>2</sub>O (1:1) and poured onto the (10 cm long, 1 cm inner diameter) glass column equipped with a stopcock and a porous disk. The resin was then washed with deionized water and conditioned with 15 - 20 mL buffer solution of desired pH prior to the passage of suitable aliquot of the sample solution containing metal ions (Ni(II), Cu(II), Zn(II) and Cd(II)) at an optimum flow rate. The amount bound metal ions stripped with suitable eluting agents was determined by spectrophotometry/FAAS/ICP-AES.

## 3. Results and Discussion

## 3.1. Spectral Interpretation of Synthesized Octa-O-Methoxy Resorcine [4] Arene Amberlite XAD-4 Polymeric Chelating Resin

The octa-O-methoxy resorcin [4] arene Amberlite XAD-4 polymeric cheltaing resin was characterized by elemental analysis, FT-IR and mass difference. The nitrogen content in Amino-XAD-4 was found to be 2.73% higher than Nitro-XAD-4, confirms the successful reduction of Nitro-XAD-4 resin. The FT-IR spectra of NO<sub>2</sub>-XAD-4, NH<sub>2</sub>-XAD-4 and octa-O-methoxy resorcin [4] arene Amberlite XAD-4 chelating resin, are given in Figure 1. Asymm (N-O) and symm (N-O) stretching bands of the NO<sub>2</sub>-XAD-4 were observed at 1540 and 1325  $\text{cm}^{-1}$ , respectively. The N-H stretching vibrations of NH<sub>2</sub>-XAD-4 were identified with the bands at 3400 and 1625. The conspicuous band of -N=N- at 1470 cm<sup>-1</sup> confirms the successful formation of octa-O-methoxy resorcin [4] arene Amberlite XAD-4 chelating resin through -N=Nlinkage. Apart from this, the loading of octa-O-methoxy resorcin [4] arene (0.61 mmole  $g^{-1}$ ) on synthetic XAD-4 resin was calculated by mass difference of dried resin, which also confirms nitration, reduction and coupling of diazotized Amberlite XAD-4 resin with octa-O-methoxy resorcin [4] arene.

## 3.2 Parameters Optimized for Separation and Preconcentration of Ni(II), Cu(II), Zn(II) and Cd(II)

#### **3.2.1.** Effect of pH on Quantitative Absorption

The pH of the solutions plays an important role on ex-

traction of metal ions. The influence of pH of the aqueous solution containing 5  $\mu$ g·mL<sup>-1</sup> of each Ni(II), Cu(II), Zn(II), and Cd(II) on 1.0 gm of octa-*O*-methoxy resorcin [4] arene Amberlite XAD-4 polymeric chelating resin was investigated using the batch method. A 100 mL aqueous solution of each metal ion with buffer solution of desired pH was placed in glass stoppered bottles and stirred slowly for 1 hour. The pH for maximum sorption of Ni(II), Cu(II), Zn(II), and Cd(II) was found to be 3.5, 5.5, 5.0 and 8.0, respectively (**Table 1, Figure 2**).

#### 3.2.2. Effect of Flow Rate on Metal Sorption

The metal ion sorption on 1.0 gm resin was evaluated at different flow rates (0.5, 1.0, 1.5, 2.0, 2.5 etc., mL·min<sup>-1</sup>), maintained by a peristaltic pump. The rate of flow of the effluent at which 98% sorption took place is consider as the optimum flow rate for the sorption of metal ions. For Ni(II), Cu(II), Zn(II), and Cd(II), the optimum flow rate was found to be 2.5, 2.0, 1.5 and 1.0 ml·min<sup>-1</sup>, respectively (**Table 1**, **Figure 3**). The obtained flow rates for maximum sorption were employed for the subsequent analysis.

# 3.2.3. Effect of Type and Concentration of Elutent on Recovery

The choice of a suitable eluent is another important factor to obtain efficient and selective recovery of analytes. In this study, a series of experiments were performed to obtain a reasonable eluent to elute Ni(II), Cu(II), Zn(II), and Cd(II) ions from metal bound resin. The bound metal ions were desorbed with different concentration of eluting agents, (HCl/HNO<sub>3</sub>) and were determined by FAAS/ICP-AES. Quantitative elution was found possible with 1.5 N HCl for Ni(II), 1.0 N HNO<sub>3</sub> for Cu(II), 1.0 N HCl for Zn(II) and 0.5 N HNO<sub>3</sub> for Cd(II) (**Tables 1** and **2**).

**3.2.4. Sorption Capacity and Distribution Coefficients** The batch method was used for the calculation of the sorption capacity of resin for metal ions. 1.0 gm of resin was added to 100 mL of solution containing excess of metal ions (100 mL, 1000  $\mu$ g·mL<sup>-1</sup>) at their respective pH by shaking for 1 h. The amount of metal ions extracted by resin was calculated from the difference in the metal ion concentration before and after sorption (**Table 1**). The capacity of resin for Ni(II), Cu(II), Zn(II), and Cd(II) was found to be 26,000, 49,650, 40,499 and 52,310  $\mu$ g·gm<sup>-1</sup>, respectively.

Exchange equilibria arearticulated in terms of the distribution coefficient  $K_d$ , which is given by the ratio of the

<i>v</i> –	Amount of the metal ion taken up by the resin	Volume of the solution
$\mathbf{n}_d$ –	Amount of the metal ion remaining in the solution	Amount of resin taken



Figure 1. IR of I) NO<sub>2</sub>-XAD-4 resin II NH<sub>2</sub>-XAD-4 resin III octa-*O*-methoxy resorcin [4] arene Amberlite XAD-4 chelat-ing resin.



Figure 2. Effect of pH on the sorption of Ni(II), Cu(II), Zn(II) and Cd(II) on resin; Experimental conditions: Amount of resin in column: 1.0 gm; Amount of metal ions; Ni(II) pH: 3.5; Cu(II) pH: 5.5; Zn(II) pH: 5.0; Cd(II) pH: 8.0.



Figure 3. Effect of flow rate on the sorption of Ni(II), Cu(II), Zn(II) and Cd(II) on resin; Experimental conditions: Amount of resin: 1.0 gm; Amount of metal ions: 5 µg·mL<sup>-1</sup>; Ni(II) pH: 3.5; Cu(II) pH: 5.5; Zn(II) pH: 5.0; Cd(II) pH: 8.0.

equilibrium concentrations of the same metal ion in the resin phase and in the solution.

0.5 gm resin was added to 100 mL solution containing 130, 248, 202, 261  $\mu$ g·mL<sup>-1</sup> of Ni(II), Cu(II), Zn(II) and Cd(II) at room temperature. The solution was filtered and

No	Davamatars	Resin						
	rarameters	Ni(II)	Cu(II)	Zn(II)	Cd(II)			
1	pH range	3.5	5.5	5.0	8.0			
2	Flow rate (mL·Min <sup>-1</sup> )	2.5	2.0	1.5	1.0			
3	Concentration of acid for desorption	1.5 N HCl	1.0 N HNO <sub>3</sub>	1.0 N HCl	0.5 N HNO <sub>3</sub>			
4	Total sorption capacity (μg·gm <sup>-1</sup> of resin)	26,000	49,650	40,499	52,310			
5	Distribution coefficient ( <i>K<sub>d</sub></i> )	4333	7085	6733	8700			
6	Preconcentration factor (PF)	105	108	95	112			
7	Breakthrough capacity (μg·gm <sup>-1</sup> of resin)	7540	12,909	10,529	14,123			
8	Average recovery (%)	97	95 - 96	96	97 - 98			
9	t <sub>1/2</sub> for exchange (minutes)	7.0	4.0	5.0	10.0			
10	<b>Relative standard</b> deviation (%) <sup>*</sup>	1.5	1.7	1.8	1.6			

\*Average of 10 determination.

the filtrate was subjected to FAAS/ICP-AES for determination of the metal content (**Table 1**).  $K_d$  was found to be 4333, 7085, 6733, 8700 for Ni(II), Cu(II), Zn(II) and Cd(II) respectively.

#### 3.2.5. Exchange Kinetics

To determine rate of loading of metal ions Ni(II), Cu(II), Zn(II) and Cd(II) on resin, the kinetics of sorption was studied by batch method in which 1.0 gm resin was stirred with 100 mL of solution containing 260, 496, 404 and 523  $\mu$ g·mL<sup>-1</sup> of Ni(II), Cu(II), Zn(II) and Cd(II) respectively. An aliquot of 1.0 mL was withdrawn each time at apredetermined interval and analysed using FAAS. The time taken (t<sub>1/2</sub>) for the 50% sorption of Ni(II), Cu(II), Zn(II) and Cd(II) on resin, was found to be 7.0, 4.0, 5.0 and 10.0 minutes (**Table 1**, **Figure 4**) respectively, which indicates comparatively good accessibility of Ni(II), Cu(II), Zn(II) and Cd(II) towards chelating sites.

#### 3.2.6. Breakthrough Studies

The capacity of the Moment when analyte starts appearing in the effluent with increased concentration is defined as the breakthrough capacity or actual working capacity. It is more significant than total sorption capacity. Breakthrough studies with 1.0 gm of rein in the column containing 100  $\mu$ g·mL<sup>-1</sup> of metal ions [Ni(II), Cu(II), Zn(II), and Cd(II)] at their optimum pH and flow rates was carried out. For the metal content determination, 20 mL aliquot was collected each time and analyzed by FAAS/

Resin										
		Н	CI		HNO <sub>3</sub>					
Conc. (N)	Ni(II) (%)	Cu(II) (%)	Zn(II) (%)	Cd(II) (%)	Ni(II) (%)	Cu(II) (%)	Zn(II) (%)	Cd(II) (%)		
0.01	4.1	2.1	5.8	3.5	5.5	9.6	3.2	28.6		
0.05	20.1	3.9	25.4	9.0	25.7	38.8	21.3	66.3		
0.1	30.5	8.9	60.5	12.8	41.5	47.7	55.8	83.5		
0.5	50.2	10.5	75.3	18.5	60.2	72.5	70.2	98.7		
0.7	65.7	12.4	90.1	21.3	75.2	90.8	85.5	98.8		
1	85.5	15.1	98.5	33.5	88.9	98.5	95.5	98.8		
1.5	98.9	25.9	98.5	67.2	95.5	98.6	97.5	98.9		
2	98.9	40.6	98.9	79.8	98.7	98.9	97.8	98.9		

Table 2. Effect of concentration of eluting agents for desorption of Ni(II), Cu(II), Zn(II) and Cd(II) from resin. [Experimental conditions: resin 1.0 gm; volume of solution passed: 100 mL; metal ions:  $5 \ \mu g \cdot mL^{-1}$  Ni(II): 3.5 pH; Cu(II): pH 5.5; Zn(II): pH 5.0; Cd(II): pH 8.0].



Figure 4. Exchange kinetics of Ni(II), Cu(II), Zn(II) and Cd(II) on theresin; Experimental conditions: Amount of resin: 1.0 gm; volume of the feed solution: 100 mL; Ni(II): 260 µg·mL<sup>-1</sup>, pH: 3.5; Cu(II): 496 µg·mL<sup>-1</sup>, pH: 5.5; Zn(II): 404 µg·mL<sup>-1</sup>, pH: 5.0; Cd(II): 523 µg·mL<sup>-1</sup>, pH: 8.0.



Figure 5. Breakthrough curve for Ni(II), Cu(II), Zn(II) and Cd(II) on the resin; Experimental conditions: Amount of resin: 1.0 gm; concentration of the metal ion solution passed: 100 µg·mL<sup>-1</sup>; Ni(II): 3.5 pH; Cu(II): 5.5 pH; Zn(II): 5.0 pH; Cd(II): 8.0 pH.

ICP-AES (**Figure 5**). Breakthrough capacities were found to be 7540, 12,909, 10,529 and 14,123  $\mu$ g·gm<sup>-1</sup> for Ni(II), Cu(II), Zn(II), and Cd(II), respectively (**Table 1**).

# 3.2.7. Preconcentration of Ni(II), Cu(II), Zn(II), and Cd(II)

The purpose of preconcentration study is to transfer metal ions from the large volume of sample solution to the relatively small volume. Preconcentration of trace metal ions have been widely used in order to increase the sensitivity of the analytical methods. To study the preconcentration factor, 1000 mL solutions containing 8  $\mu g \cdot L^{-1}$  of each Ni(II), Cu(II), Zn(II) and Cd(II) at pH 3.5, 5.5, 5.0, 8.0 respectively, were passed through the column containing 1.0 gm resin. Metal content in the striped solution were determined by ICP-AES.

$$PF = \frac{Concentration of metal in stripping solution}{Initial concentration of metal in feed solution}$$

The preconcentrating ability of resin was evaluated from the elution profile of metal ions by plotting the concentration of effluents as a function of the volume of stripping solutions: 9.5 mL, 1.5 N HCl for Ni(II); 9.2 mL, 1.0 N HNO<sub>3</sub> for Cu(II); 10.5 mL, 1.0 N HCl for Zn(II) and 9.0 mL, 0.5 N HNO<sub>3</sub> for Cd(II). Under the optimum experimental conditions, the preconcentration factors were found to be 105, 95, 108 and 112 for Ni(II), Cu(II), Zn(II) and Cd(II) with more than 96% recovery (**Tables 1** and **3**, **Figure 6**).

## 3.2.8. Stability and Reusability of the Resin

The reusability and applicability of the synthesized resin was examined after several loading and elution cycles. It

Table 3. Preconcentration factors for the sorption of Ni(II), Cu(II), Zn(II) and Cd(II) on resin. [Experimental conditions: resin: 1.0 gm; Ni(II): pH 3.5; elution by 1.5 N HCl; Cu(II): pH 5.5; elution by 1.0 N HNO<sub>3</sub>; Zn(II): pH 5; elution by 1.0 N HCl; Cd(II): pH 8; elution by 0.5 N HNO<sub>3</sub>].

Metal ions	Volume of solution passed (mL)	Concentration of feed solution (μg·L <sup>-1</sup> )	Volume of eluted solution (mL)	Recovery (%)	Preconcentration Factor (PF)						
Resin											
Ni(II)	1000	8	9.5	97 - 98	105						
Cu(II)	1000	8	9.2	97	108						
Zn(II)	1000	8	10.5	97	95						
Cd(II)	1000	8	9.0	98	112						



Figure 6. Evaluation of the stability of the resin for Ni(II), Cu(II), Zn(II) and Cd(II) by sorption and elution; Experimental condition: Amount of resin: 0.5 gm; volume of the feed solution: 100 mL; concentration of feed solution: 300  $\mu$ g·mL<sup>-1</sup>; Ni(II): pH 3.5, elution by: 1.5 N HCl; Cu(II): pH 5.5, elution by: 1.0 N HNO<sub>3</sub>; Zn(II): pH 5.0, elution by: 1.0 N HCl; Cd(II): pH 8; elution by: 0.5 N HNO<sub>3</sub>.

was found that the maximum change in the sorption and desorption agreed within 3% - 4 % error upto 8 - 10 cycles for all the matal ions that shows the efficiency of the system resin (**Figure 7**).

#### **3.2.9. Effect of Electrolytes**

To evaluate the selectivity of the synthesized resin, the possible interference of electrolytes on the recovery of Ni(II), Cu(II), Zn(II) and Cd(II) was investigated and the results are summarized in **Table 4**. An error of 2% - 3% was considered to be within the range of experimental error. It was observed that except Na<sub>3</sub>PO<sub>4</sub> and NaF, all others electrolytes did not interfere between 1.5 to 4.0 M concentrations (ranges), which further expand the potential application of resin for the analysis of real samples.

## 4. Chromatographic Separations

As observed from experimental practice synthesized resinposses very good sorption capacity, distribution coefficient and exchange kinetics, therefore it was further used for the separation of Cu(II), Zn(II) and Cd(II) from their binary and ternary mixtures by column method.

The mixtures of metal ions can be effectively separated by selective adjustment of the pH and eluting agents. Hence, the following mixtures (each 100  $\mu$ g in 25 mL buffer solution) were passed through the column at the pH of maximum sorption and optimum flow rate. The column effluents were analyzed for the metal ions by spectrophotometry/FAAS/ICP-AES.

#### 4.1. Separation of a Binary Mixture

100 µg each of both Zn(II) and Cd(II) in 25 mL of buffer solution of pH 5.0 at a flow rate of 1.0 mL $\cdot$ min<sup>-1</sup> were passed through the column. At this pH, Cd(II) was not sorbed on resin and it came out with the effluent while Zn(II) was retained in the column. Zn(II) was eluted with 24.5 mL, 1.0 N HCl. Quantitative separation was achieved in binary mixture as shown in their separation pattern in **Figure 8(a)**.

#### 4.2. Separation of a Ternary Mixture

100 µg each of Cu(II), Zn(II) and Cd(II) in 25 mL of buffer solution of pH 5.0 at a flow rate of 1.0 mL·min<sup>-1</sup> were passed through the column. At this pH, Cd(II) was not sorbed on resin and it came out with the effluent, while Cu(II) and Zn(II) were retained in the column. Cu(II) and Zn(II) were separated on the basis of selective eluting agents. Zn(II) was eluted first with 25 mL, 1.0 N HCl followed by Cu(II) with 22.5 mL, 1.0 N HNO<sub>3</sub>. Quantitative separation was achieved in the ternary mixture as shown in their separation patterns in **Figure 8(b)**.

#### 5. Limit of Quantification and Application

Selectivity and sensitivity are two important factors in the extraction and the separation process. To check the capability of the resin to detect trace amounts of metal ions, studies were performed by passing 1000 mL of sample solutions containing metal ions in the range of 5 -10  $\mu$ g through the optimized column. The quantification limit for Ni(II), Cu(II), Zn(II) and Cd(II) for resin were

Metal ions		Concentrations of electrolytes (mol·L <sup>-1</sup> )								
2.5 ( $\mu g \cdot mL^{-1}$ )	NaF	NaCl	NaBr	NaNO <sub>2</sub>	Na <sub>2</sub> SO <sub>4</sub>	Na <sub>3</sub> PO <sub>4</sub>	CH <sub>3</sub> COONa			
Resin										
Ni(II)	0.7	2.4	1.9	2.5	2.1	1.3	2.2			
Cu(II)	0.8	2.7	2.0	3.1	2.2	1.2	2.1			
Zn(II)	1.0	3.0	1.6	2.9	1.9	1.1	1.9			
Cd(II)	0.6	2.0	1.3	2.8	1.6	1.0	2.0			

Table 4. Tolerance limits of electrolytes on the sorption of Ni(II), Cu(II), Zn(II) and Cd(II) on resin. [Experimental Conditions: resin: 1.0 gm; volume of solution passed: 100 mL; Ni(II): pH 3.5; Cu(II): pH 5.5; Zn(II): pH 5.0; Cd(II): pH 8.0].



Figure 7. The elution profile of Ni(II), Cu(II), Zn(II) and Cd(II) on theresin; Experimental conditions: Amount of resin: 1.0 gm; concentration of the solution passed: 1000 mL, 8  $\mu$ g·L<sup>-1</sup>; Ni(II): pH: 3.5; elution by 1.5 N HCl; Cu(II): pH: 5.5; elution by 1.0 N HNO<sub>3</sub>; Zn(II): pH: 5.0; elution by 1.0 N HCl; Cd(II): pH:8.0; elution by 0.5 N HNO<sub>3</sub>.

found to be 6.4, 5.4, 5.0 and 9.0  $\mu$ g·L<sup>-1</sup>, respectively, indicating the resin's capability to extract the trace metal ions of interest from the real samples. To check the applicability and validity of the proposed method, synthesized resin was subjected to various water sample analyses and the results are compared by the standard procedure. The data is given in **Table 5**.

#### 6. Comparison with Other Solid Phase Extraction Methods

Comparison of sorption capacity and preconcentration factor of different adsorbents are summarized in **Table 6**.

## 7. Conclusion

Octa-*O*-methoxy resorcin [4] arene Amberlite XAD-4, a newly synthesized polymeric chelating resin was successfully applied for the selective separation, preconcentration and determination of metal ions such as Ni(II), Cu(II), Zn(II) and Cd(II) from real samples. The advantages found in the synthesized resin are its faster exchange rates, better sorption capacity and high preconcentration factors. The resin was found to be highly selective in



Figure 8. (a) Separation of Zn(II) and Cd(II) on theresin. Experimental conditions: Amount of resin: 1.0 gm; column maintained at pH 5.0; Zn(II): 100 µg in 25 mL buffer: elution by 1.0N HCl; Cd(II): 100 µg in 25 mL buffer: elution by 0.5N HNO<sub>3</sub>; (b) Separation of Cu(II), Zn(II) and Cd(II) on theresin; Experimental conditions: Amount of resin: 1.0 gm; column maintained at pH 5.0;Cu(II): 100 µg in 25 mL buffer: elution by 1.0N HNO<sub>3</sub>; Zn(II): 100 µg in 25 mL buffer: elution by 0.5N HNO<sub>3</sub>.

extracting the analyses in the presence of various electrolytes. The reusability of resin was about 8 to 10 cycles without any significant loss in its sorption behavior. Separations of binary/ternary mixtures of metal ions are possible by control of pH or gradient elution. Sorption capacity of Ni(II), Cu(II), Zn(II) and Cd(II), attained by resin was found to be reasonably better than some al-

		Ni(II)		Cu(II)		Zn(II)		Cd(II)	
Sample	Method	Amount (μg·L <sup>-1</sup> )	R.S.D. (%)	Amount (μg·L <sup>-1</sup> )	R.S.D. (%)	Amount $(\mu g \cdot L^{-1})$	R.S.D. (%)	Amount (μg·L <sup>-1</sup> )	R.S.D. (%)
Sabarmati river, near thermal	Present method	12	1.25	41	1.15	14	1.15	13	1.15
power station, Ahmedabad	Standard addition	13	1.2	44	1.0	16	1.0	15	1.4
Ground water,	Present method	11	1.65	11	1.2	12	1.15	13	1.35
Ahmedabad	Standard addition	13	1.25	15	1.3	15	1.25	14.5	1.15
Ground water, Vatva Industrial	Present method	26	1.6	56	1.3	29	1.3	41	1.1
Zone, Ahmedabad	Standard addition	28	1.2	59	1.4	31	1.25	43	1.15

# Table 5. Determination of Ni(II) Cu(II), Zn(II) and Cd(II) in natural water samples on resin. [Experimental conditions: resin: 1.0 gm; sample volume: 1000 mL].

Table 6. Comparable methods for preconcentration and determination of Ni(II), Cu(II), Zn(II) and Cd(II).

No	Adsorbent	Sorption capacity(µg/gm)				Preconcentration factor				
		Ni(II)	Cu(II)	Zn(II)	Cd(II)	Ni(II)	Cu(II)	Zn(II)	Cd(II)	
1	Polystyrene divinylbenzene resin functionalized by 1-(2-pyridylazo) 2-naphtol (XAD-16-PAN)				7500					[85]
2	1,6-Bis(2-carboxy aldehyde phenoxy)butane-XAD-16		5380		4436		100		100	[86]
3	Polyethyleneiminemethylene phosphonic acid		85,690							[87]
4	Alumina-(N-{4-[4-{1-[4- (dimethylamino)phenyl]methylidene}- 5-(4-H)oxazolone]phenyle}acetamide		8000		14,000		400		160	[88]
5	MWCNTs-(D2EHPA-TOPO)		4900	4789						[89]
6	8-Hydroxyquinoline Amberlite IR-120		24,814				>166			[1]
7	Dowex optipore SD-2	11,500	12,000							
8	Gallic acid-modified silica gel		15,380		6090		200		100	[90]
9	Dowex optipore SD-2	11,500	12,000							[91]
10	<i>p-tert</i> -butylcalix [4] arene-1,2-crown- 4- <b>anchored</b> chloromethylated polymeric resin		13,652	9744	23,042		208	119	199	[92]
11	Octa- <i>O</i> -methoxy resorcin [4] arene Amberrlite XAD-4 resin	26,000	49,650	40,499	52,310	105	108	95	112	

ready reported solid phase extractants indicating the resin's potential capability to extract the metal ions at trace level in the natural and ground water samples.

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