IOSR Journal Of Pharmacywww.iosrphr.org
(e)-ISSN: 2250-3013, (p)-ISSN: 2319-4219
PP. 24-31

Preconcentration of Divalent Metal Ions Using 5-[(4-Hydroxyphenyl)Diazenyl] Quinolin-8-Ol- Formaldehyde

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ABSTRACT: *A novel chelating resin for preconcentration of heavy metals from various environmental samples has been developed by condensing 5-[(4-hydroxyphenyl) diazenyl] Quinoline-8-ol (HPDQ) with formaldehyde (1:2 mole ratio) in the presence of oxalic acid as catalyst. The resin thus obtained was used as a solid sorbent for the separation of divalent metal ions present at trace levels in real samples. The polymeric resin HPDQ-F obtained by condensing the functionalized phenol and formaldehyde was characterized by spectral and thermal studies. The chelating property of the HPDQ-F resin towards divalent metal ions was studied as a function of pH and preconcentration flow rate. The metal uptake properties of the resin were determined by using an Atomic Absorption Spectrophotometer (AAS). The analytical performance of the developed method was validated. Thus, these resins can be widely used as solid sorbents for preconcentration of trace metals at ppm level.*

Keywords : *Preconcentration, Formaldehyde, Functionalized phenol, Trace level, Metal ion*

I. INTRODUTION

The use of metal ions has increased substantially over years due to their importance as valuable intermediates in industries as catalyst, in electric and electronic devices as semiconductors, etc. resulting in contamination of water resources by industrial effluents which have been a serious issue in the recent past [1-3]. As a result, the determination of trace concentrations of metal ions in manmade and natural water resources is of interest in order to have a check on the eco-system [4,5]. Several incidents of metal ion toxicity to humans and aquatic lives were reported [6]. Hence, it requires a time-to-time analysis of these trace metal ions in environmental as well as in bio-fluid samples in order to sustain and preserve the eco-system [7]. But, the determination process is not that simple as the metal ions are surrounded and encapsulated by a variety of complex matrix species which interfered, thus forcing for the need of an extraction technique, which could selectively extract the analytes of interest [8]. This has paved way to the development of solid phase extraction (SPE) technique [9]. Chelating polymeric matrices termed as polychelatogens have been used in SPE technique and have highlighting features such as high degree of selectivity, versatility, durability and a good metal loading capacity, enhanced hydrophilicity, but follow second order kinetics [10-12]. Organic ligand moiety containing active functional groups that can selectively chelate the metal ions of interest are incorporated into a polymeric support via chemical modification [13-15]. Several chelating supports have been used of which the use of functionalized phenol-formaldehyde resins was found to be fruitful. The synthesis of this chelating resin using 8-hydroxyqunioline [16-20], and its characteristic sorption for Cu(II), Cd(II), Co(II), Mn(II), Pb(II) and Zn(II) are the content of the present work. The preconcentrating capability of this chelating resin was ascertained by applying to the analysis of various water samples.

II. EXPERIMENTAL DETAILS

2.1 Synthesis of 5-[(4-hydroxyphenyl)diazenyl]Quinolin-8-ol-Formaldehyde (HPDQ-F) resin

8-hydroxyquinoline (4.35 g, 0.03 M) was dissolved in conc. HCl (20 mL) by heating and the solution formed was cooled down quickly to a temperature below 5°C with vigorous stirring to obtain a solution. To this solution was added sodium nitrite (2.55g, 0.03M) in 20 mL of water. After stirring at 0-5°C for 30 min a yellow solution was obtained.To this, 8-hydroxyquinoline solution was added slowly while stirring. The mixture was then stirred for half an hour and then neutralized with saturated Na_2CO_3 aqueous solution. The product precipitated out from the solution and was collected by filtering (7g, yield80%) of 5-[(4-hydroxyphenyl) diazenyl] Quinolin-8-ol was obtained after recrystallizing the crude product from ethanol (Fig. 1).

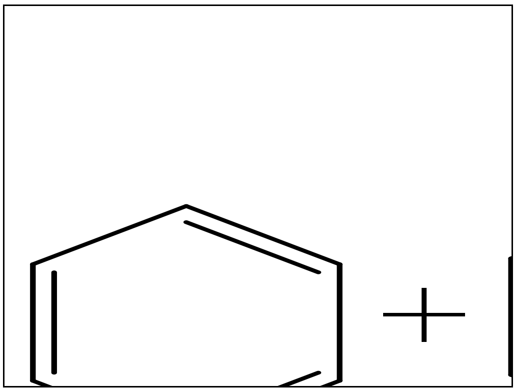


Figure 1. Synthesis of HPDQ-F resin and its metal chelate

A mixture of 1:2, 5-[(4-hydroxyphenyl) diazenyl] Quinolin-8-ol and 37% formalin solution, and 3% (W/W) of oxalic acid were taken in a round-bottomed flask, sealed and kept in an oil bath at 100°C for 24 h. The flask was then cooled to room temperature, desealed and water was decanted. The solid remaining in the flask was dissolved in N,N-dimethylformamide and the resulting solution was added drop wise to large excess of 10% aqueous sodium chloride solution with constant stirring and the red compound was filtered, washed several times with distilled water until free of chloride ion and dried at 60°C in vacuum. The yield obtained was 83%.

2.2 Preconcentration of Cu(II), Cd(II), Co(II), Mn(II), Pb(II) and Zn(II) using HPDQ-F resin using batch method

2.2.1 Metal ion sorption as a function of solution pH

Each metal ion solution (50 mL, 10 mg/L) was shaken with 100 mg of the resin in the pH ranging from 2 to 10 for a period of 60 min. The resin samples were filtered through Whatman No.1 filter paper and the filtrates were collected. The sorbed metal ions were stripped with different concentrations of hydrochloric acid. The concentration of metal ions of interest present in both the filtrate samples and the stripped samples were analyzed by FAAS.

2.2.2 Kinetic studies on the metal ion sorption

The time duration required for the complete sorption of the metal ion of interest was studied using 100 mg resin, with metal ion solution (50 ml, 9 mg/L) in the case of Mn(II), Pb(II) and Zn(II) and (50 ml, 8 mg/L) for Cu(II), Cd(II) and (50 ml, 6 mg/L) for Co(II) under optimum pH conditions for various intervals of time.

2.2.3 Loading capacity of the functionalized chelating resin

The maximum loading capacity of the resin were studied by saturating 100 mg of the resin with an excess metal ion solution (50 ml, 100 mg/L) in the case of Pb(II), Mn(II) and (50 ml, 60 mg/L) for Cu(II), Cd(II), Zn(II), Co(II) under optimum pH conditions for a duration of 6 h. The amount loaded was estimated using FAAS.

2.2.4 Tolerence limits of electrolytes

Effect of diverse ions on the recovery of metal ions was tested by batch equilibration method using 50 mg resin equilibrated with metal ion solution (40 mL, 1.25 µg/mL) in the presence of various concentrations of electrolyte species up to which 0% loss in the analytical signal was observed.

2.2.5 Limit of metal ion detection (LOD)

LOD for various metal ions were studied by equilibrating metal ion solution (125 mL, 0.01-0.1mg/L) with 100 mg resin under optimum conditions for 10 min and then determining their concentration by FAAS.

2.2.6 Resin reusability test

To test the resin reusability, 100 mg of the resin was shaken with (50 ml, 100 mg/L) of the metal ions 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 plenty of water till neutral pH.

2.3 Preconcentration of Cu(II), Cd(II), Co(II), Mn(II), Pb(II) and Zn(II) using HPDQ-F resin using column method

The chelating polymeric resin were preconditioned (1g) by soaking in buffer solution for 2 h and packed in a glass column (0.635 cm) by slurry method. A suitable aliquot of the solution containing the analyte of interest in the concentration range (0.01-0.20 mg/L) was passed through the packed column. The flow rate was optimized using a Mariotte type apparatus. The sorbed metal ions were eluted with 10 mL of eluting agent at a flow rate of 1 mL/min and the metal ion concentrations were determined by FAAS. In order to ensure quantitative sorption of the metal ion from large volumes of sample solutions, breakthrough volume studies were performed using sample volumes ranging from 500 to 5000 mL containing 100 µg of the metal ion of interest under optimum flow rate through a preconditioned column. After desorption the resin bed was subjected to water wash till neutral pH and subsequently reused.

2.4 Application of the method to synthetic sea water

The interference of diverse ions was then studied using synthetic mixture of sea water. The results were further confirmed by spiking with trace amount of analyte of interest (0.03 µg/mL). The concentration of metal ion in the solid phase in each case was determined by FAAS.

III. RESULTS AND DISCUSSION

3.1 Characterization of the functionalized polymeric resin matrix

3.1.1 IR spectral analysis

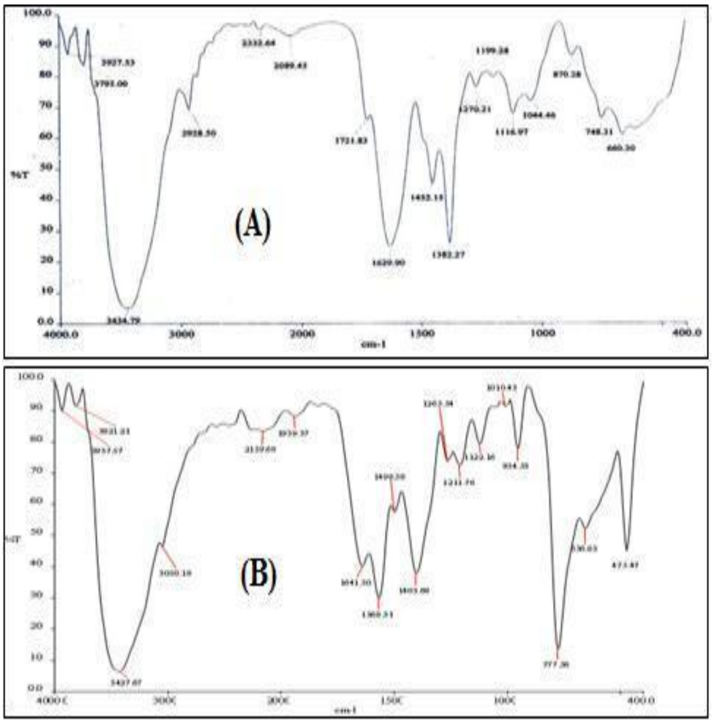
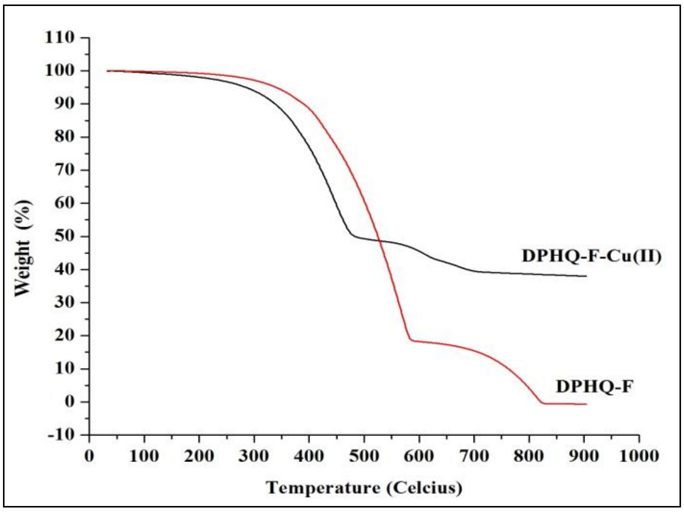


Figure 2. FT-IR spectrum of **(A)** HPDQ-F resin and **(B)** HPDQ-F-Cu(II)

The IR spectra for the vacuum dried functionalized resin showed bands in the region 3400 cm^{-1} corresponding to –OH stretching frequencies. The band at 1629 cm^{-1} correspond to the –N=N- stretching frequency. Further, additional bands at 1452 and 1382 cm^{-1} originating due to C-N stretching frequency confirmed the presence of the chelating ligand moiety attached to the polymeric backbone (Fig. 2A). IR studies of the metal ions Cu(II), Cd(II), Co(II), Mn(II), Pb(II) and Zn(II) chelated resin showed the formation of a band in the region of 475 cm^{-1} indicating the metal chelation with the active sites present in the polymer matrix (Fig. 2B).

3.1.2 Thermal analysis



In the Thermo Gravimetric Analysis (TGA) curve of DPHQ-F resin and its metal chelate (Fig. 3), complete weight loss due to decomposition occurs at a temperature around 800°C whereas the metal chelates were found to be stable and this indicated higher thermal stability of the metal chelates compared with the parent polymer (Table 1). The difference in transition may be ascribed to the crystallinity of the polymer-metal complexes. Further the initial weight loss of the metal chelate was found to be more than that of the resin indicating the presence of water molecules in the pores of the polymeric matrix thereby ensuring a better hydrophilic character to the resin.

Fig. 3. TGA curves of HPDQ-F resin and its metal chelate

Table 1. Weight loss (%) of HPDQ-F resin and its Cu(II) chelate at various temperature

Sample	Weight loss (%) at					
	300°C	400°C	500°C	600°C	700°C	800°C
DPHQ-F	2.9	11.5	39.4	81.8	84.6	95.8
DPHQ-F -Cu(II)	6.1	23.1	50.7	54.4	60.5	61.4

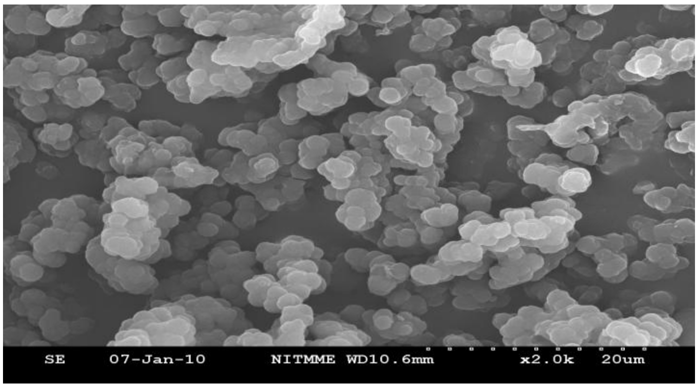


Figure 4. SEM image of DPHQ-F resin

3.1.3 Surface analysis

The SEM images show that the resin shapes into regular spherical particles of uniform size (Fig. 4). The roundness of the particles is not very perfect since the resin is obtained by precipitation polymerization [21].

3.2 Optimized experimental parameters using batch method for the metal extraction

The influence of solution pH on the sorption of metal ions by batch equilibration technique is shown in Fig. 5A. The results depict that the sorption process to be more favourable in near neutral conditions, which is also reflected on the relatively low acidity of the chelating matrix. The rate of metal ion sorption under optimum pH conditions can be seen from Fig. 5B. The preconcentration time was in the range of 2.5-3.3 min for all the metal ions. The preconcentration efficiency of the resin was shown in Table 2. The difference in preconcentration efficiency for different metal ions under study was attributed due to variation in the stability constants of the metal chelates formed by the active sites with the metal ions under study.

Table 2. Analytical performance of the preconcentration method using HPDQ-F resin

Experimental parameters	**Cu(II)**	**Cd(II)**	**Co(II)**	**Mn(II)**	**Pb(II)**	**Zn(II)**
pH	6.5 – 7.5	7.5 – 8.5	7 – 7.5	6 – 7.5	6 – 7	6.5 – 7
Time (min)	3.0	3.3	2.9	3.0	2.8	2.7
Metal sorption capacity (mmol/g)	0.46	0.21	0.27	0.62	0.23	0.25
Concentration of HCl	6	4	4	4	4	4
Optimum flow rate (mL/min)	5 – 6	4 – 5	5 – 6	3 – 4	4 – 5	4 – 5
Average recovery (%)	98.2	99.6	98.6	99.9	100.2	99.1
Lower limit of detection (LOD) (ng/mL)	25	10	25	40	20	40

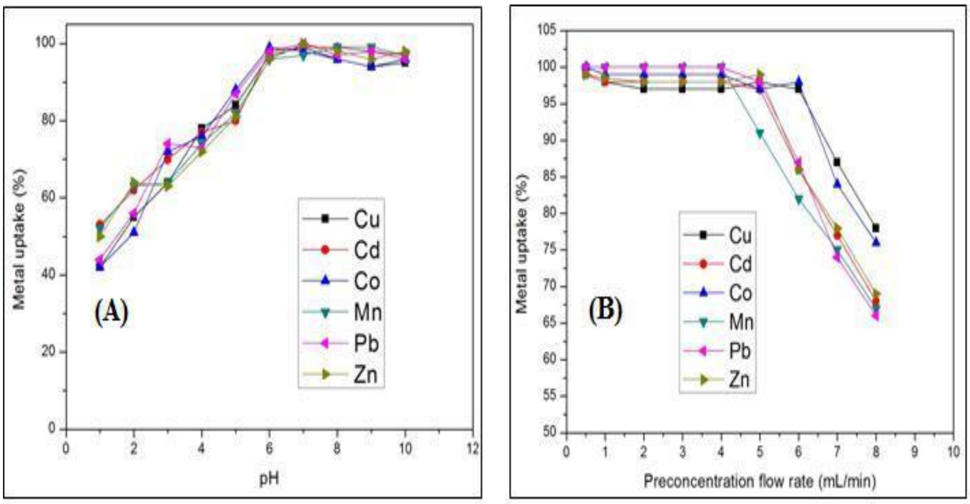


Figure 5. Effect of **(A)** pH and **(B)** Preconcentration on metal uptake

The preconcentration studies were repeated by column method and the results obtained were in good agreement with batch equilibration method. The concentrations of the diverse ions were increased up to which 0% loss in analytical signal was observed is shown in Table 3. The experimental results show a high degree of tolerance towards alkali and alkaline earth metal ion species, in targeting analytes of interest. The above observation was also confirmed by using synthetic sea water mixture in column studies. The results also show nearly 100% recovery of the analyte ion of interest.

Table 3. Effect of interfering ions on the recovery of Cu(II), Cd(II), Co(II), Mn(II), Pb(II) and Zn(II)

Analytes	**Tolerance limit (mol/L) up to 0% loss in analytical signal**			
	Na^+	**K^+**	**Ca^{2+}**	**Mg^{2+}**
Cu	0.34	0.25	0.38	0.63
Cd	0.34	0.71	0.01	0.02
Co	0.20	0.05	0.06	0.10
Mn	0.21	0.12	0.31	0.52
Pb	0.71	0.54	0.51	0.82
Zn	0.13	0.14	0.20	0.31

The sensitivity of the developed method was reflected by the LOD studies, defined as the lowest concentration of metal ion of interest below which quantitative sorption of the metal ion by the chelating matrix is not perceptibly seen. LOD for various metal ions were studied under optimum conditions and the values are indicated in Table 2 ensuring a high degree of selectivity and preconcentrating ability for the developed method.

Durability and reusability of the chelating matrix was tested with metal ion solutions by batch equilibration method, by determining the metal ion concentrations. Thereafter, the sorption and desorption of metal ions were repeated on the same resin. The capacity of the resin was found to be practically constant for more than 30 cycles showing the feasibility of multiple use of the chelating polymeric resin without any loss in its physical and chemical properties.

3.3 Column studies for the preconcentration of metal ions

The optimum flow rates for various metal ions under study were found to be in the range 3-6 mL/min (as shown in Table 2), which, however, can further be improved by using a micro column.

3.4 Application of the method to water samples

Three litres of sea water, well water and tap water were collected from different zones of east coastal region of Tamil Nadu, India, after filtration through 0.45 mm membrane filter was passed through the resin bed preconditioned earlier and the water samples were pH optimized for metal ion sorption and the recovered metal ions were determined by FAAS. The validity of the results was tested by standard addition method, by spiking a known amount (10 µg) of individual metal ions except for Pb(II) wherein 60 µg of the metal ion, was spiked to the water sample. The results pertaining to the analysis of trace amount of metal ion of interest from sea water are shown in Table 4, confirms the satisfactory recovery of the analytes.

Table 4. Analysis of water samples

Analyte		**Concentration (µg/L)**		
		Sea water	**Tap water**	**Well water**
Cu(II)	Present	18.1	27.8	16.8
	Added	2.0	2.0	2.0
	Found	19.9	29.3	18.5
	Recovery (%)	**99.0**	**98.3**	**98.4**
Cd(II)	Present	1.79	2.41	0.91
	Added	0.20	0.20	0.20
	Found	1.95	2.56	1.07
	Recovery (%)	**97.9**	**98.0**	**96.4**
Co(II)	Present	2.81	3.71	4.91
	Added	0.30	0.30	0.30
	Found	3.08	3.97	5.16
	Recovery (%)	**99.0**	**99.0**	**99.0**
Mn(II)	Present	5.0	15.6	17.6
	Added	1.5	1.5	1.5
	Found	6.3	16.9	18.8
	Recovery (%)	**96.9**	**98.8**	**98.4**
Pb(II)	Present	20.6	27.6	24.1
	Added	2.0	2.0	2.0
	Found	22.2	29.1	25.8
	Recovery (%)	**98.2**	**98.3**	**98.8**
Zn(II)	Present	116.1	140.1	80.2
	Added	10.0	10.0	10.0
	Found	125.7	149.5	89.4
	Recovery (%)	**99.6**	**99.6**	**99.1**

IV. CONCLUSION

The chelating resin 5-[(4-hydroxyphenyl) diazenyl] Quinolin-8-ol-formaldehyde (HPDQ-F) was found to have a superior resin loading capacity and a high preconcentration factor for the metal ions Cu(II), Cd(II), Co(II), Mn(II), Pb(II) and Zn(II) when compared with other chelating matrices reported in literature. Furthermore, the preconcentration time of this chelating resin was also very short and the kinetic studies ensured faster exchange kinetics in the process of metal ion uptake. On using a micro column, the time of analysis can be still decreased substantially. High selectivity for metal ions was ensured under saline conditions and the reusability of the resin was greater than 30 cycles without any loss in its sorption behavior. The system was also successful in preconcentrating metal ions from large sample volume. The column and batch methods were in good agreement with low relative standard deviation values reflecting the validity and accuracy of the method when applied to various water samples.

ACKNOWLEDGEMENTS

We thank NIIST (CSIR), Thiruvananthapuram for providing instrumental facilities. We are also grateful to CSIR (MHRD), Government of India, for providing financial support throughout this research.

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