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Medicinal Chemistry

Research Article

Synthesis of amberlite XAD-2-ANSA resin for separation, preconcentration and spectrophotometric determination of trace elements in food samples

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ABSTRACT

A new chelating sorbent has been synthesized using Amberlite XAD-2 resin functionalized with 1-amino-2-naphthol-4-sulfonic acid (ANSA) through $-N=N-$ group. This sorbent, characterized by infrared (FTIR) spectra and optimized for sorption-desorption of the studied metal ions then, it was used as packing for the column for separation/ preconcentration of cadmium, cobalt, and nickel prior to their determination spectrophotometrically. Metal ions of Cd, Ni, and Co sorbed in the column were eluted one by one with 0.02 M, 0.10 M, and 0.20 M HCl acid respectively. Under the optimal conditions, the proposed procedure enabled the determination of Cd, Co, and Ni with detection limits of 0.98, 0.30 and 2.10 $\mu\text{g L}^{-1}$ respectively. The developed procedure was evaluated by the analysis of mixed metal ions Cd, Co and Ni solution contained 0.30, 30, and 1.25 μg respectively, and the percentage recovery was 95.5 – 104%. The procedure was applied to the analysis of food samples (grains of Sorghum bicolor), and the results obtained were compared with that of FAAS (before and after separation/preconcentration).

Keywords: Amberlite resin, Synthesis, Analysis, Food.

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Citation | Mohamed MT. 2018. Synthesis of amberlite XAD-2-ANSA resin for separation, preconcentration and spectrophotometric determination of trace elements in food samples. Arch Pharm Sci ASU 2(2): 138-151

DOI: 10.21608/aps.2018.18741

Online ISSN: 2356-8380

Print ISSN: 2356-8399

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1. INTRODUCTION

Different heavy metals of different samples have been determined, after different preconcentration systems, using different analytical instruments. Cadmium has been determined in river water using visible spectrophotometer (Vis-S) after solid phase extraction [1]; Cadmium and Copper have been determined using FAAS after solid phase extraction [2]; Cobalt using Vis-S after solid

phase extraction [3]; Nickel using Vis-S after solid phase extraction [4]; cobalt, copper, and nickel using FAAS after solid phase extraction [5]; lead, Cadmium, Nickel, and Cobalt using ICP-AES and ICP-MS after solid phase extraction [6].

Many studies, after solid phase preconcentration, performed an additional

preconcentration step, this carried out by reducing the volume of eluate, by evaporation, before measuring using FAAS [7, 8]. However, such this additional step is likely to contribute to loss or contamination and to increase in analysis time and chemicals to be used. Some studies have determined heavy metal by flow injection i.e., on-line preconcentration and determination [9–11]. However, such this system maybe complex, if compared with the off-line system, and on-line is not applicable when there are difficulties to perform the separation/preconcentration and the measurement in the same laboratory. In addition, the off-line system gives options to measure with more than one instrument.

Modern instruments such as ICP-MS, ETAAS or ICP-AES, are more sensitive than FAAS. ETAAS is very expensive, needs a separation and preconcentration procedure [12], and the chemical interference effects are often more severe with electrothermal atomization than with flame atomization [13]. ICP-AES does not have sufficiently high sensitivity than FAAS.

The most widely used separation and preconcentration methods are solid-phase extraction [14], liquid-liquid extraction [15], coprecipitation [16], ion exchange [17], electrochemical deposition [18], membrane filtration [19] and cloud point extraction [20].

Solid phase extraction has advantages over the other widely technique used for separation/preconcentration of heavy metals traces. These advantages include simplicity, high enrichment factor, regeneration easiness, and significant reducing the disposal costs and extraction time [21].

The most supporting materials used in the solid phase are Silica gel [22, 23], polyurethane [24], and organic co-polymer resins [25]. Among the solid phase, support materials are Amberlite XAD resins. This type of resins has good

physical properties such as high surface area and uniform pore size distribution [26].

Preconcentration using chelating resins have some advantages such as good selectivity, preconcentration factor, binding energy mechanical stability, and easy regeneration [27]. Chelating resins with amines are preferred [28].

The most important and recently reported chelating matrices using Amberlite XAD supports were different according to the ligands and the ways they loaded by. Some of them are Amberlite XAD-2 modified: by pyrocatechol through $-N=N-$ group [29], by 2-(methylthio) aniline through $-N=N-$ group [30], by 2-aminoacetylthiophenol (AATP) [31]. Amberlite XAD-2 resin has been functionalized with others ligands as 4, 5-dihydroxy-1, 3-benzenedisulfonic acid through $-CH_2$ group [32], o-aminophenol through $-N=N-$ group [33], pyrocatecholviolt through $-N=N-$ group [34].

2. MATERIALS AND METHODS

2.1. Chemicals and reagents

All chemicals and reagents used were analytical reagent grade and used without previous purification.

2.2. Instruments and equipment

Spectronic 20, Milton Roy Company (USA). UV-Visible Specord 200, Analytik Jena AG (Germany). Vista MPX CCP Simltaneous ICP-AES Instrument, Varian. Atomic absorption spectromerer 6800, Shimadzu, Japan. Microwave digester, Milestone, Microwave Laboratory System, Ethos Touch Control, N. America.

Stopped flasks, 100 mL capacity were used in batch sorption experiments. Glass columns of about 25 cm length and 0.5-0.6 cm internal diameter with stopcock were used in column mode.

2.3. Spectrophotometric (Vis-S) determination of heavy metal ions

Each M^{2+} ion was determined using Vis-S according to the procedure described in the literature [35]. The absorbance of Cd^{2+} was measured (556 nm) at pH 10 using 5-Br-PADAP (0.02% in ethanol) as a reagent. The absorbance of Co^{2+} was measured (586 nm) at pH 7 using 5-Br-PADAP (0.03% in DMF) as a reagent. The absorbance of Ni^{2+} was measured (558 nm) at pH 5.5 using 5-Br-PADAP (0.02% in ethanol) as a reagent.

2.4. Synthesis of the chelating resin

According to literature researches [36-38], 15 g of Amberlite XAD-2 resin were treated with a mixture consisting of 75 mL conc. H_2SO_4 acid and 30 mL of conc. HNO_3 acid. The mixture was placed on a water bath at 60 °C for 1 hr with continuous stirring. Then it was poured into a mixture of ice-cold water. Thereafter the nitro resin was filtered and washed with DDW until become free of acid traces.

Nitro resin was mixed, in a rounded bottom flask, with 60 g $SnCl_2$, 67 mL conc. HCl and 75 mL ethanol. The mixture was refluxed at 90 °C for 12 h, filtered, washed with DDW and then with 2 M NaOH. The amino resin was washed with 2 M HCl, then with DDW. The amino resin was suspended in 200 mL ice-cold water, then treated with portions each of 2 mL 1 M $NaNO_2$ and 2 mL 1M HCl acid until a dark blue color with a starch iodine paper obtained, then it filtered and washed with ice-cold water. Diazotized resin was treated with a solution made up of 5.0 g ligand 1-amino-2-naphthol-4-sulphonic acid (ANSA) in 8% solution of NaOH at 0-5 °C for 36 h. The produced chelating resin was filtered, washed with DDW until washes become colorless and, finally, it washed with methanol and air-dried.

2.5. IR spectra of the prepared new chelating resin (ChR12)

The IR spectra of the prepared new stationary phase and compounds of different preparation stages were recorded using FTIR according to the procedure mentioned in literature [39]. The data obtained and its interpretations will be present in the section of results and discussion.

2.6. Optimization of ChR12 for sorption-desorption of metal ions

2.6.1. Batch mode

In a 100-mL stopped flask, 0.1 g ChR12 was shaken, at room temperature, with 25.0 mL aqueous solution of each tested metal ions. Resin material was separated. The amount of metal ion remained in the aqueous phase was determined using Vis-S. The percentage extraction (% E) was calculated by the equation: $\% E = (C_0 - C / C_0) \times 100$ Where C_0 and C are the concentrations of metal ion before and after extraction, respectively. Effect of pH was studied in batch mode at 10 mg/L of each tested metal ion, which adjusted at different pH values. Effect of shaking time was studied in batch mode at 10 mg/L of each tested metal ion, which adjusted at optimal pH value. Effect of initial metal ion concentration (C_i) was studied in batch mode at varied C_i of each tested metal ion, which adjusted at optimal pH value.

2.6.2. Column mode

In this present study glass column of 25 cm length and 0.5-0.6 cm i.d., with stop cock and a small piece of glass wool, was used.

3. RESULTS & DISCUSSION

3.1. Characterization of the Synthesized Chelating Resin (ChR12) and M^{2+} -Retaining ChR12

The recorded infrared spectra were used to confirm the introduction of -NH_2 group into the skeleton of the plain (Amberlite XAD-2 copolymer resin) and then coupled with chelating ligand 1-amino-2-naphthol-4-sulfonic acid (ANSA). Infrared spectra were recorded for the plain, nitrated, and reduced nitrated and finally ligand-coupled-resin. The recorded IR spectra of these four types are shown in **Fig. 1**. As seen from this figure, there are three distinct infrared vibration bands. The first one band at (1555- 1485, 1355-1320 cm^{-1}), confirming the introduction of the NO_2 group to the skeleton of the plain because of the nitration processes. The second is the disappearance of some these bands assigned to the -NO_2 group (band at 1555-1485, 1355 - 1320 cm^{-1}), which others were sharply reduced (1480 and 1335 cm^{-1}) showing a high reduction percentage was performed during the reduction processes. On the other hand, the clear formation of a new sharp band due to the reduction of -NO_2 group and characteristic to the -NH_2 group was recorded at 3443 cm^{-1} confirming the previous observation related to the -NO_2 group. The third is the appearance (in the ligand-coupled resin) of azo group peak at ($\approx 1585\text{cm}^{-1}$), C-S peak at ($\approx 684\text{cm}^{-1}$) and -OH group peak at ($\approx 1319 \text{cm}^{-1}$), confirming the diazotization and the coupling with ligands (1-amino-2-naphthol-4-sulphonic acid). Moreover, the interaction of ligands in the new phase leads to a distinct color change (dark brown) which is no longer obtained with the parent phase. There are some similar IR spectral features have been described in the literature [40-44]. IR spectra, from **Table 1**, demonstrate metal

ions retention on ChR12. It is clear that most of the bands of M^{2+} - free ChR12 have undergone changes in their features due to metal retention. There is a similarity between some of these changes and between changes that have been observed and described in many literature types of research [43-46].

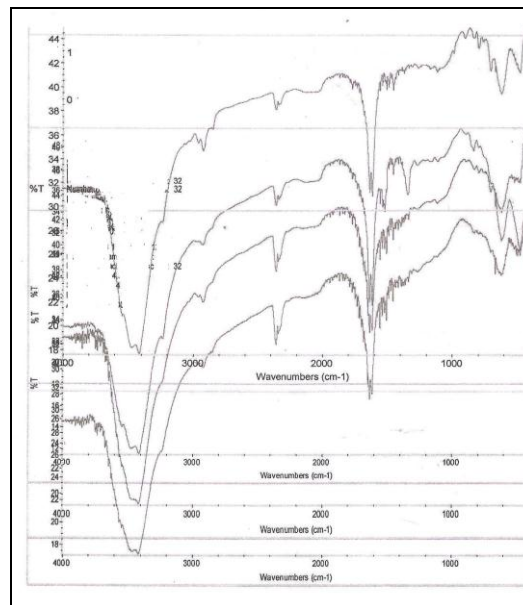


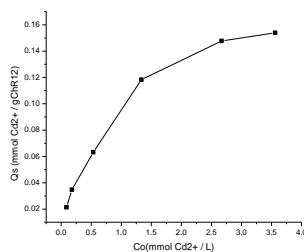
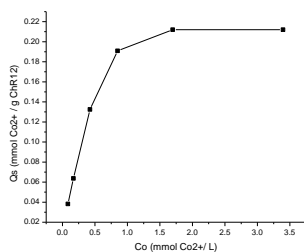
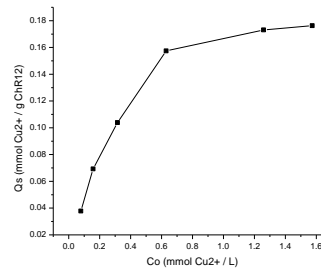
Fig. 1. IR spectra of Amberlite XAD-2 at Different stages of ChR12 synthesis

3.2. Effect of different parameters on extraction efficiency of metal ions

The effect of pH on the extraction of Cd^{2+} , Co^{2+} , and Ni^{2+} ions, by the newly prepared stationary phase ChR12, has been critically investigated. The obtained results are summarized in **Fig. 2a-c**. It is obvious from these curves that the percentage extraction increases with increasing pH value from 3 to 8-9 for all studied metal ions. It has been observed that there is a maximum percentage of extraction at pH 8-9 for all studied metal ions.

Table 1. Spectral data of the observed infrared vibrational frequencies of M^{2+} - free ChR12 and M^{2+} -retaining ChR12

Compound	Phenolic $\nu(\text{O-H})$	Primary amine $\nu(\text{N-H})$	Phenolic $\nu(\text{C-O})$	- N=N-	Primary amine (N-H) bending	Ar-S $\nu(\text{C-S})$	Phenolic (O-H) bending	M-O	M-N	M-N azo
M^{2+} _free ChR12 resin	3614- 3230	3464, 3443	1197	1585	1656	684	1319	-	-	-
Co^{2+} _ChR12 resin	3565- 3230	3454	1202	1574	1645	684	1330	528	492	471
Ni^{2+} _ChR12 resin	3563- 3227	3448	1204	1574	1645	684	1341	551	525	468

**Fig. 2a.** Effect of pH on extraction of Cd^{2+} ion**Fig. 2b.** Effect of pH on extraction of Co^{2+} ion**Fig. 2c.** Effect of pH on extraction of Ni^{2+} ion

3.3. Effect of extraction time and sorption kinetics.

The loading rate of Cd^{2+} , Co^{2+} , and Ni^{2+} ions on ChR12 resin was studied in batch mode at optimal pH value and shaking for different periods (10-120 min) at about 25 °C. The sorption kinetics of the metal ions is shown in **Table 2**. It was observed that the shaking time

required to reach equilibrium state were 60-120 min for 73-80% E of Cd^{2+} , 20-30 min for 99 - 100% E of Co^{2+} and 60-120 min for 86-98% E of Ni^{2+} . However, all of the studied metal ions were of very good sorption rates. The good rates of extraction of the studied metal ions with ChR12 resin may indicate good accessibility of metal ions to one or more chelating sites (OH, -N=N- or NH_2).

The loading half time $t_{1/2}$ which is defined as the time required for reaching 50% of the total uptake, was estimated. The Lagregren first-order rate equation is the simplest rate equation for the sorption in liquid/solid system based on solid capacity [47], $dq/t = k_1 (q_e - qt)$ where k_1 is the equilibrium rate constant of first-order (1/min), q_e ($\mu\text{g/g}$) is the amount (μg) of metal ions sorbed, with one gram of sorbent (ChR12), at equilibrium, and qt ($\mu\text{g/g}$) is the amount (μg) of metal ions sorbed, with one gram of sorbent (ChR12), at any time t . Integrating this Equation, for the boundary conditions $t = 0$ to t and $qt = 0$ to qt , yields $\log (q_e - qt) = \log (q_e) - (k_1/2.303) t$. Plotting $\log (q_e - qt)$ versus t gives a straight line and, therefore, slope = $- k_1/2.303$, and $t_{1/2} = 0.693/k_1$. Lagregren plot for Cd^{2+} , Co^{2+} and Ni^{2+} are shown in figure 3.8.a-c. The values for k_1 and $t_{1/2}$ are found in **Table 3**.

Table 2. Effect of shaking time on extraction efficiency

Cd^{2+}		Co^{2+}		Ni^{2+}	
Shaking Time (min)	% E	Shaking Time (min)	% E	Shaking Time (min)	% E
10	46.7	10	81.5	10	48.3
20	60.0	20	98.8	25	67.5
30	66.7	30	100	35	78.3
60	73.0	40	100	55	85.8
120	80.0	60	100	120	97.5
-	-	-	-	180	93.3

Table 3. kinetic data from Lagregren plot with Ch R12 at 25 °C

No.	M^{2+}	$\text{K}_1(\text{min}^{-1})$	$t_{1/2}(\text{min})$
1	Cd^{2+}	0.03	23.1
2	Co^{2+}	0.069	10.0
4	Ni^{2+}	0.03	23.1

3.4. Effect of initial concentration (C_i) on Static Sorption capacity (Q_s) of ChR12

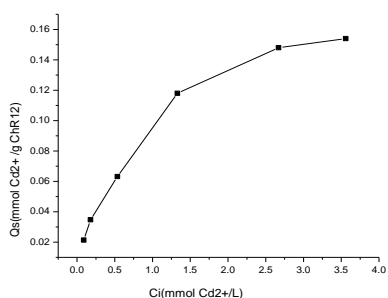
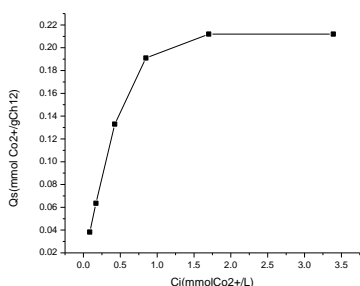
The sorption capacity of metal ions was studied by batch mode at different initial concentration C_i (mmol/L) solution at optimal pH and shaking time. The total sorption capacity Q_s (mmol/g ChR12) was calculated using the equation:

$$Q_s (\text{mmol/g ChR12}) = C_i/m = [(\% E * C_0 * V)/\text{mol wt.}] / m$$

Where C_0 is the initial concentration (mg/L), V is the sample volume (L) of the metal concentration C_0 , mol wt. is the weight of mole atoms of the metal, and m is the weight of ChR12 (g). **Fig. 3a-c**, show the effect of the initial concentration (C_i) on static sorption of ChR12 for Cd^{2+} , Co^{2+} and Ni^{2+} respectively. The calculated total static capacity (Q_s) at a higher initial concentration (C_i) are summarized in **Table 4**. These results show that ChR12 has sufficient high Q_s for the studied metal ions. Co^{2+} and Ni^{2+} ions appeared to have higher affinity than Cd^{2+} to be sorbed with ChR12 and their approximate capacity is 0.20 whereas of Cd^{2+} ion is 0.15 mmol/g ChR12.

Table 4. Total static capacities of ChR12 for different metal ions

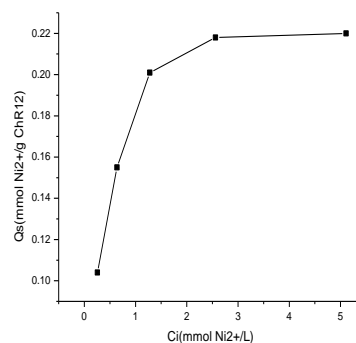
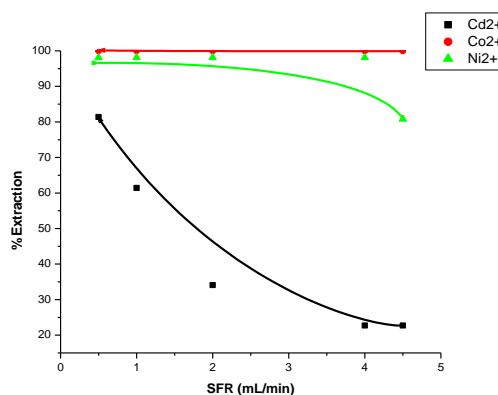
No.	Metal ions	C_i mmol/L	Q_s mmol/g ChR12 resin
1	Cd^{2+}	3.599	0.154
2	Co^{2+}	3.393	0.212
4	Ni^{2+}	5.110	0.220

**Fig. 3a.** The static capacity of ChR12 at different C_i of Cd^{2+} ions.**Fig. 3b.** The static capacity of ChR12 at different C_i of Co^{2+} ions

3.5. Effect of sample flow rate on sorption of metal ions with ChR12

The influence of sample flow rate on the sorption of each metal ion with ChR12 was studied by percolating, at 0.5–4.5 mL min⁻¹ flow rate, 25 mL 10 mg/L metal ion solution at optimal pH value and, finally, measuring the

remains in the effluents by Vis-S. The retention profiles of the elements to the ChR12 at different sample flow rates are depicted in **Fig. 4.**

**Fig. 3c.** The static capacity of ChR12 at different C_i of Ni^{2+} ions.**Fig. 4.** Effect of Solution Flow rate on Sorption of metal ions with ChR12

The obtained results indicated that the optimum flow rate for quantitative metal ions retention is about 2 mL min⁻¹ or less for Co^{2+} and Ni^{2+} , and about 0.6 mL min⁻¹ for Cd^{2+} . The later one metal ion exhibited its need for a long contact time to reach adequate equilibration

3.6. Breakthrough curve and dynamic capacity (Q_d)

A break-through curve is obtained by plotting column effluent concentration versus

volume treated or time of treatment. Breakthrough point is defined as the time when the cation of the feed first appears in the effluent [48]. Furthermore, the volume of solution percolated from the breakthrough point to the point of leveling of the loading curve for a given solution flow rate also depends upon the kinetics of exchange [49]. The breakthrough curve of each M^{2+} ion was carried out by percolating, up ChR12 saturation, a suitable volume of metal ions at optimal condition and, finally, measuring the remains concentration in the effluents. **Fig. 5.** depict breakthrough curves of Cd^{2+} , Co^{2+} , and Ni^{2+} ions. Breakthrough capacity ($mmol\ g^{-1}\ ChR12$) was calculated according to the equation [50]:

$$\text{dynamic capacity} = (V50\% * C_o)/m$$

and dividing by 1000, the equation becomes:

$$\text{dynamic capacity} = [(V50\% * C_o)/m]/1000$$

where V50% is the effluent volume (mL) at 50% breakthrough, C_o is the concentration of the influent solution ($\mu mol\ mL^{-1}$), and m is the mass (g) of ChR12. Breakthrough and dynamic capacities ($mmol\ g^{-1}$) for the studied metal ions are listed in **Table 5.** Breakthrough capacities for all of the studied metal ions are lower than their dynamic capacities. This is normal as the breakthrough capacity is calculated at throughput volume i.e., at first detection of metal ions in the effluent, whereas dynamic capacity is calculated at 50% breakthrough. Dynamic Capacities for all of the studied metal ions are lower than their Static (batch) Capacities. This is also usual and it relies on several parameters such as the column bed height, sample flow rate, temperature of the solution, particle size, and concentration of the feeding solution [49]. High linear velocity may result in premature breakthrough [51]. In addition, the difference between static and

dynamic capacities of a particular metal ion depends on the required time for binding with the chelating sites. From **Table 4,** and **Table 5,** it is seen that there is no large difference between the static and dynamic capacity for Co^{2+} and Ni^{2+} whereas this difference is too large for Cd^{2+} , this maybe because that Cd^{2+} ion needs longer contact time for binding in the chelating sites.

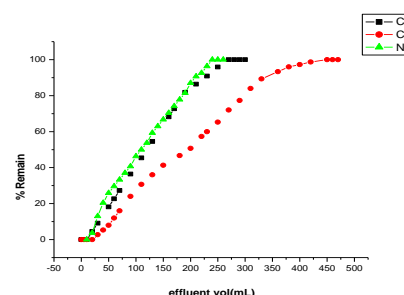


Fig. 5. Breakthrough curves of studied metal ions.

Table 5. Breakthrough and dynamic capacities

M^{2+}	pH	Flow rate mL/min.	Q.b $mmol\ g^{-1}$	Q.d $mmol\ g^{-1}$	C_o $\mu mol/mL$
Cd^{2+}	5.5	0.6	0.00468	0.0281	0.08897
Co^{2+}	9	2	0.0303	0.192	0.424
Ni^{2+}	8.5	1	0.0269	0.148	0.511

3.7. Effect of the eluting agent on elution of metal ions

Elution step is one of important solid phase extraction steps and, here, in this present study, elution gains additional importance and interest since this study, in it's the main part, aimed for determining toxic heavy metals using analytical instruments of good availability as Vis-S and FAAS. So, wide varieties of eluting agents

types, concentration and flow rate were examined for each metal ion. The important results we got for a particular eluting agent, are depicted in one figure for comparison purpose. From **Fig. 6a**, it is obvious that the eluting agent 0.5 M HCl acid can elute all of the studied metal ions. From **Fig. 6b**, it is clear that 0.5 M HCl acid in acetone can elute Cd^{2+} and Co^{2+} , but cannot elute Ni^{2+} . From **Fig. 6c**, 1 M HNO_3 acid can elute Cd^{2+} , Ni^{2+} quantitatively, and Co^{2+} partially. From **Fig. 6d** and **e**, 0.2 M Tartaric acid at $\text{pH}=3$ and 0.3 M Tartaric at $\text{pH}=5$ acetate can elute Cd^{2+} quantitatively, and Co^{2+} and Ni^{2+} partially. From **Fig. 6f**, 3.12 g and 3.12. h, 0.02, 0.03 and 0.05 M HCl acid can elute Cd^{2+} but cannot elute Ni^{2+} and Co^{2+} . From **Fig. 6i**, 0.1 M HCl acid can elute Cd^{2+} and Ni^{2+} but cannot elute Co^{2+} . From **Fig. 6j**, 0.2 M HCl acid can elute Cd^{2+} , Ni^{2+} and Co^{2+} . From the above observations, Cd^{2+} can be eluted an alone firstly with 0.02 M HCl. Ni^{2+} can be eluted an alone secondly with 0.1 M HCl. Co^{2+} can be eluted an alone thirdly with 0.2 M HCl.

3.8. Evaluation and application of the Developed Separation/preconcentration Procedure

Validation must always be carried out for newly developed or modified procedures. This can take place either by comparison of the results of the analyses with those of a validated or an independent analytical procedure or by analysis of reference materials or of control samples prepared in the laboratory itself [52]. The procedure TTEST (one tail, two tails) can be used for two results comparison [151].

In this present study, the developed separation-preconcentration method has been

evaluated and validated by analysis of metals mixture solution and analysis of food samples (grains of sorghum bicolor) and results in comparison with results of another instrument as follows:

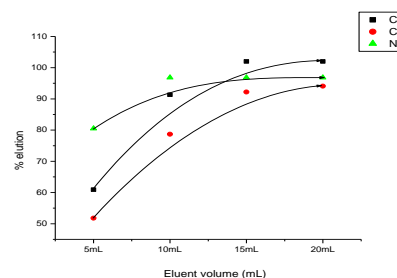


Fig. 6a. Effect of 0.5M HCl acid on elution of metal ions

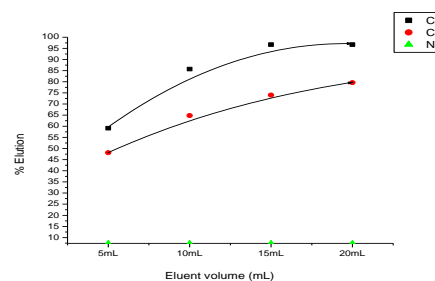


Fig. 6b. Effect of 0.5M HCl acid in acetone on elution of metal ions

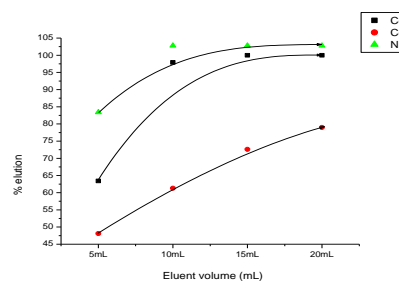


Fig. 6c. Effect of 1M HNO_3 acid on elution of metal ions

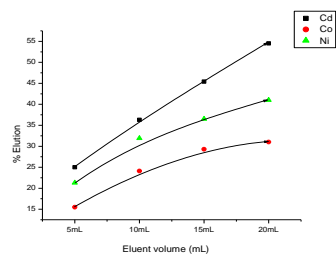


Fig. 6d. Effect of 0.2M Tartaric acid pH= 3 Acetate on elution of metal ions

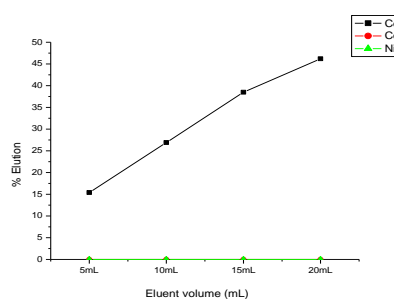


Fig. 6h. Effect of 0.05M HCl acid on elution of metal ions

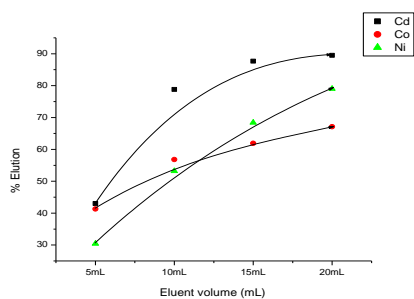


Fig. 6e. Effect of 0.3M Tartaric acid pH= 5 Acetate on elution of metal ions

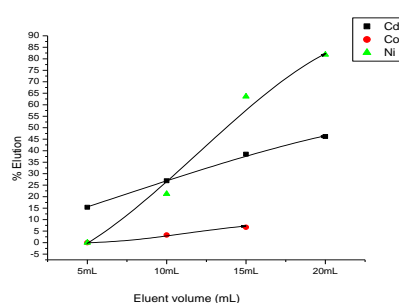


Fig. 6i. Effect of 0.1M HCl acid on elution of metal ions

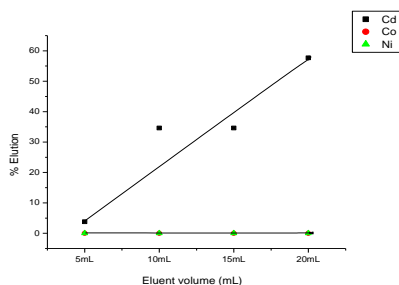


Fig. 6f. Effect 0.02M HCl acid on elution of metal ions

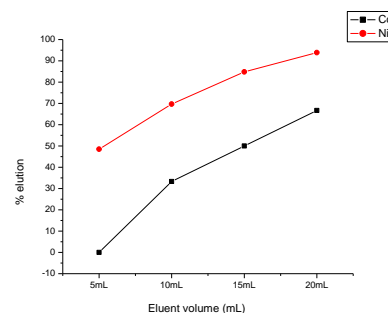


Fig. 6j. Effect of 0.2M HCl acid on elution of metal ions

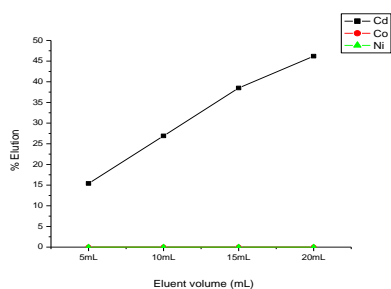


Fig. 6g. Effect of 0.03M HCl acid on elution of metal ions

3.8.1. Separation of mixture metal ions solution

In order to separate Cd²⁺, Co²⁺ and Ni²⁺ ions from a mixture using the ChR12 resin packed in column, the solution containing all metal ions was adjusted to pH 8.5 using buffer solution and suitable masking agents, then the solution was percolated through the column packed with ChR12 resin at flow rate 0.6-0.2 mL/min, analyses of three replicates were carried out. the

tested ions were eluted from the column by the suitable eluting agent and, then, determined by Vis-S. The obtained results are summarized in **Table 6**.

Table 6. Statistical data of the studied metal ions in their mixture solution

M ²⁺	µg added	%R mean	RSD	Replicate
Cd ²⁺	0.3	104	3.9	3
Co ²⁺	0.3	95.5	0.7	2
Ni ²⁺	1.25	97	7.2	3

From **Table 6**, it is very clear that the Proposed separation, a method is valid (accurate and precise) for all tested metal ions. Since the %R average means were excellent, 104, 95.5

and 97, and the RSD were also very good, 3.9, 0.7 and 7.2 for cadmium, cobalt, and nickel respectively.

3.8.2. Comparison between results of sorghum grains analysis for metal ions content using Vis-S and FAAS

It is clear from **Table 7**, that the Cadmium analysis result using FAAS (before separation) was less precise as its RSD was somehow high (15.7), n= 1 whereas those of both Vis-S and FAAS (after separation) were more precise as their RSD were somehow lower (4.1), n= 2 for FAAS, and (8.2), n= 3 for Vis-S. In addition, these of Vis-S and FAAS (after separation) are not significantly (p, 2-tails= 0.21) different. Nickel analysis results of Vis-S and FAAS (before and after separation) are not significantly (p, 2-tails= 0.10) different.

Table 7. Comparison between metal analysis results of sorghum grains using Vis-S, FAAS

M	Spectrophotometer (after separation)			FAAS (after separation)			FAAS (before separation)		
	C(µgg ⁻¹)	RSD	n	C(µgg ⁻¹)	RSD	n	C(µgg ⁻¹)	RSD	n
Cd	0.2640	8.2	3	0.2880	4.1	2	0.425	15.7	1
Co	0.5293	11.2	3	-	-	-	-	-	-
Ni	2.474	2.6	3	2.850	8.2	3	3.208	3.4	2

3.9. Advantages of the newly Developed solid phase Procedure

From **Table 8**, it can be concluded that there are similarities in the accuracy (%R), precision

(RSD) and the metal amounts added to be recovered, between the present developed solid phase Procedure and most of the other preconcentration systems. The advantage of our developed separation/preconcentration

procedure is that it enables analysis of three important toxic heavy metals (Cd^{2+} , Co^{2+} , and Ni^{2+}) using one simple column in a single run, reasonable volumes of gradient low

concentration one eluting agent type, and measuring using more than one available and inexpensive Analytical instruments.

Table 8. Comparison between the newly developed solid phase with other preconcentration systems

Preconcentration system	Studied metals	pH	%R	RSD	μg in a sample of evaluation	Anal. Inst.	Sample of Application	Ref.
XAD-2/ 4,5- dihydroxy-1,3-benzenedisulfonic acid	Ni	7.1	94-110	8.2-2.6 for 0.01-0.2	2-4 Shrimp	Vis-S	Food (shrimp)	101
C18/2-(2-quinol la zo)-5-diethylamin oaniline	Co	5.5	94.5	2.6	2.2 Tea leaf	Vis-S	river, Lake & Tap water	39
XAD-2010/4-Hydroxy benzaldehyde -4-bromophenyl hydrazone	Ni	4±0.2	98-99	0.15	0.3 DDW	Vis-S	river, Tap water, alloys	40
AmberliteXAD-16/ gallic acid,	Ni, Cu, Co	6 -7	97.5, 97, 99.4	3.6, 2.9, 2.3	250 river water	FAAS	River water	53
1- benzylpiperazine dithiocarbamate complex	Cd	4-5	97.6	3.6	10.0 Deionized water	FAAS	waters & alloys	54
SDS coated alumina /indane-1,2,3-trione 1,2-dioxime	Cu, Ni Co	9	98.7 96.2 95.0	1.8, 1.5, 1.7	10 model soln.	FAAS	water samples	55
XAD-2/1-amino-2-naphthol-4-sulphonic acid	Cd, Co, Ni	8.5	104, 95.5, 97	3.9, 0.7, 7.2	0.3, 0.3, 1.25 metal mixture soln.	Vis-S and FAAS	food (sorghum grains)	Present study

4. CONCLUSION

Based on this work, the following conclusions can be illustrated:

The synthesized chelating resin12 (ChR12) is a solid phase capable efficiently to preconcentrate traces of Cd^{2+} , Co^{2+} and Ni^{2+}

ions from a reasonable volume of sample solution using applicable one simple column.

The developed procedure is suitable for determination of Cd^{2+} , Co^{2+} and Ni^{2+} ions using low sensitive and inexpensive analytical instruments.

Analyses results of our developed separation/preconcentration method using Vis-S were comparable to that of high sensitivity analytical instruments.

The developed procedure has advantages since it involves working on three important toxic metals, using one column simultaneous extraction and separative elution, reasonable volumes of gradient low concentration one eluent type, and measuring using available analytical instruments as Vis-S, FAAS; these advantages are not together involved in another separation/preconcentration method according to our good knowldgement.

Separation and/or preconcentration is important in trace determination of cadmium and lead regardless of the sensitivity of the instrument to be used.

Conflict of interest

The author declares that there are no conflicts of interest.

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