

## Synthesis, Characterization of New Chelating Amidoxime Resin and Study of its Analytical Properties

Ahmad Dhary. Saleh

Department of Chemistry, College of Education for Pure Sciences, University of Anbar, Iraq

e-mail:dhary\_1973l@yahoo.com

### الخلاصة:

تم تحضير مبادل ايوني كلتي جديد يتألف من (XAD-4) a macroreticular poly [styrene-co-(divinylbenzene)] ويحتوي على ليكاندات 2[[2-(hydroxy) benzylidene] amino] benzamidoxime كمجموعة فعالة. وتم دراسة تطبيقاته في تركيز وفصل كميات نزرّة من ايونات العناصر. اظهر المبادل المحضر ثباتية عالية اتجاه المحاليل الحامضية والقاعدية. وكذلك تم دراسة سعة الامتزاز الكلية لعدد من الايونات مثل [U(VI), V(V), Mo (VI), Pd (II), Zn(II), Cd(II), Hg(II), Ni(II), Cu(II), Fe(III)] كدالة للحامضية (pH) بمدى يتراوح بين (1-7.5). واجريت حركيات الامدصاص للعناصر بطريقة الوجبة. وتم استرداد العناصر الممتزة على المبادل الايوني باستخدام كاربونات الصوديوم (0.5 M) كعامل نزع مناسب لليورانيوم (VI). ثم انتزاع البلاديوم (II) باستخدام حامض الهيدروكلوريك المركز متبوعا بمحلول مخفف حامضي للثايورييا. اما بقية العناصر المدروسة تم استردادها باستخدام حامض الهيدروكلوريك (2 M). واطهر المبادل الايوني خواص مهمه كالاستقرارية الكيميائية الجيدة والانتقائية العالية وسرعة التوازن مع الايونات مما يجعله مفيد للمراكزه السريعة لكميات الضئيلة لايونات العناصر. وكما يمكن استخدام المبادل بطريقة العمود لاكثر من مرة. وتم تقدير تراكيز اغلب العناصر قيد الدراسة بطريقة تقنية الامتصاص الذري اللهبى (AAS)

### Abstract:

A new chelating ion-exchange resin consist of a macroreticular poly [styrene-co-(divinylbenzene)] (XAD-4) copolymer and containing 2[[2-(hydroxy) benzylidene] amino] benzamidoxime ligands as the functional group has been synthesized and its employ for the concentration and separation of metals was studied. It is highly stable in acidic and alkaline solutions. The total adsorption ability of the resin for some metal ions like Fe(III), Cu(II), Ni(II), Hg(II), Cd(II), Zn(II), Pd (II), Mo (VI), V(V) and U(VI) as a function of pH has been determined over pH (1.0 -7.5). Sorption kinetics of metals was achieved by using batch method. These metal ions were quantitatively occupied and resumed by [0.5M] Sodium carbonate as a suitable eluting for uranium (VI); for palladium (II) HCl conc., followed by a dilute acidic solution of thiourea; for the other metal ions, 2M hydrochloric acid]. The resin exhibits the important characteristics that are good chemical stability, high selectivity, and quick equilibration with the metal ion making it useful for fast enrichment of these ions by column and the resin reused repeatedly. The most metal ions concentrations were measured by atomic absorption spectrograph (AAS).

**Keywords:** chelating resin; benzamidoxime; functional group; adsorption capacity

## 1. Introduction

In an ion exchange chromatography, Chelating resins have proved to be constructive in the enrichment and separation metal ions levels. The planned and synthesis of selective ion-exchange resins containing chelating groups is a tedious task. Selection of the chelating ligand is very crucial, where the selectivity of the chelating resin depends upon the functional groups in the ligand. Some of resins containing various functional groups (using ethylenediaminetetra acetic acid,[1] iminodiacetic acid,[2-4] and N-phenylhydroxamic acid[5]) have been reported. Some chelating resins formed with N-substituted hydroxylamine and 8-hydroxyquinoline were used to pre-concentration and separation of some metals [6,7]. Fritz and co-workers prepared resins containing sulfonic, amide and hexylthioglycolate groups.[8-10] Nishizawa *et al.* synthesized and applied polystyrene resin containing bis(2-hydroxyethyl)- amine moiety.[11] Pyrocatechol Violet (PV) and Xylenol Orange (XO), which have a conjugated  $\pi$ -electron system and a sulfonate group, were immobilized on the anion-exchange polystyrene-based resin Dowex-2 and the final products were investigated for the enrichment of Cu(II) and Cd(II) before their determination by (AAS) [12]. Polymeric Schiff bases as an important class of chelating resins. Also, some resins have been prepared and their studied as ion-selective properties. Bayer was first to introduce such polymeric ligands and reported relative stabilities of complexes formed with different metal ions [13,14]. Preferential complexation of nickel (II) over other ions with a polymeric Schiff bases chelating resin have been reported by Kantipuly *et al.* [15]. Samant and Misra [16] were used resorcinol–formaldehyde resin for removal of cesium from nuclear waste. Condensation polymerization of phenol–formaldehyde–piperazine resulted in a resin choose for Cu (II) [17,18]. Also, Bunian *et al* were used Condensation polymerization of 4-hydroxybenzaldehyde–formaldehyde–biuret to give a new resin [19]. Schiff bases by multidentate coordination positions are known to readily for complexes with transition metal ions [20,21]. Series of papers were reported by Vernon [22] and Hodgkin [23] on various methods for the production of chelating ion-exchange resins. The development for such chelating polymers with N,O-donor atoms, as they found to possess very high selectivity for transition metals and show negligible affinity for alkali and alkaline earth metals. Polycondensation reactions have employed to prepare most chelating resins. Though they possess high specificity and capacity, their properties stability are not good [24]. Pathak *et al.* described a method to prepare a resins containing 1-

hydrazioptthalazine as functional group [25]. Fenglin *et al.* prepared amidoxime polyacrylonitrile as chelating resin which have selectivity toward  $\text{Fe}^{+3}$ ,  $\text{Cu}^{+2}$  ions [26]. Recently, many studies were reported to synthesis a commercial resins which was used to remove heavy metals from waste-water. [27-30]. It is of interest to synthesize chelating resins showing good selectivity. In the present study, it have prepared a Schiff base of 2-hydroxy benzaldehyde and 2-amino benzonitrile 2[[2-(hydroxy) benzylidene] amino] benzonitrile and conversion it to amidoxime 2[[2-(hydroxy) benzylidene] amino] benzamidoxme which incorporated on the macroporous resin poly [styrene-co-(divinyl benzene)] (XAD-4). The functionalized Polystyrene divinyl benzene is expected to give additional stability while retaining the analytical characteristic of amidoxime ligand. It is a multidentate ligand containing hydroxyl and amine functionalities as binding sites for metal ion. The synthesis resin has been characterized, and the adsorption of some metal ions had investigated.

## **2. Experimental**

### *2.1. Instrumentation*

A Shimadzu A.A.630, 12 flame atomic absorption spectrometer was used for monitoring the enrichment of the metals. (D-82362 digital pH meter, Weiheim, Germany) was used for pH measurements. Infrared spectra were done on a Nicolet DX FTIR spectrophotometer with KBr pellets. A mechanical shaker (SGM 3000100, Gallenkamp, Orbital Shaker) with an incubator, which had a speed of 200 strokes  $\text{min}^{-1}$ , was used for batch equilibration.

### *2.2. Reagents*

All chemicals were of guaranteed purity and deionized water was used to preparation of the solutions. All of stock solutions of metals were done by dissolving the reagent grade nitrate and chloride salts with deionized water and they were standardized by recommended procedures. Poly-[styrene-co-(divinyl benzene)] resin (Amberlite XAD-4) was obtained from Fluka (Buchs, Switzerland). 2-amino benzonitrile and 2-hydroxy benzaldehyde were purchased from E. Merck and were used after distillation. pH of experimental solutions were adjusted using buffers prepared with 0.2M hydrochloric acid, 0.2M sodium acetate, 0.1N NaOH and 0.1N hydrochloric acid.

### 2.3. Preparation of 2[[2-(hydroxyl)benzylidene]amino]benzamidoxme

#### a. Synthesis of Schiff Base

2-amino benzonitrile (0.01 mole) in 20 mL of ethanol was put in a round-bottomed flask and 2-hydroxy benzaldehyde (0.01 mole) in 20 mL of ethanol was added with vigorous stirring. A 0.1 g of p-toluene sulfonic acid was added and the mixture was refluxed for 3 h at 90 °C and then it was cooled in an ice bath. The resulting product was filtered and recrystallized from absolute ethanol to produce a yellowish crystals, 2[[2-(hydroxy) benzylidene] amino] benzonitrile (70 %), (m.p = 80-82 °C) . The compound showed  $\nu_{max}$ : 3270, 3025, 2250, 1630, 1600 , 1150, 830  $\text{cm}^{-1}$ .

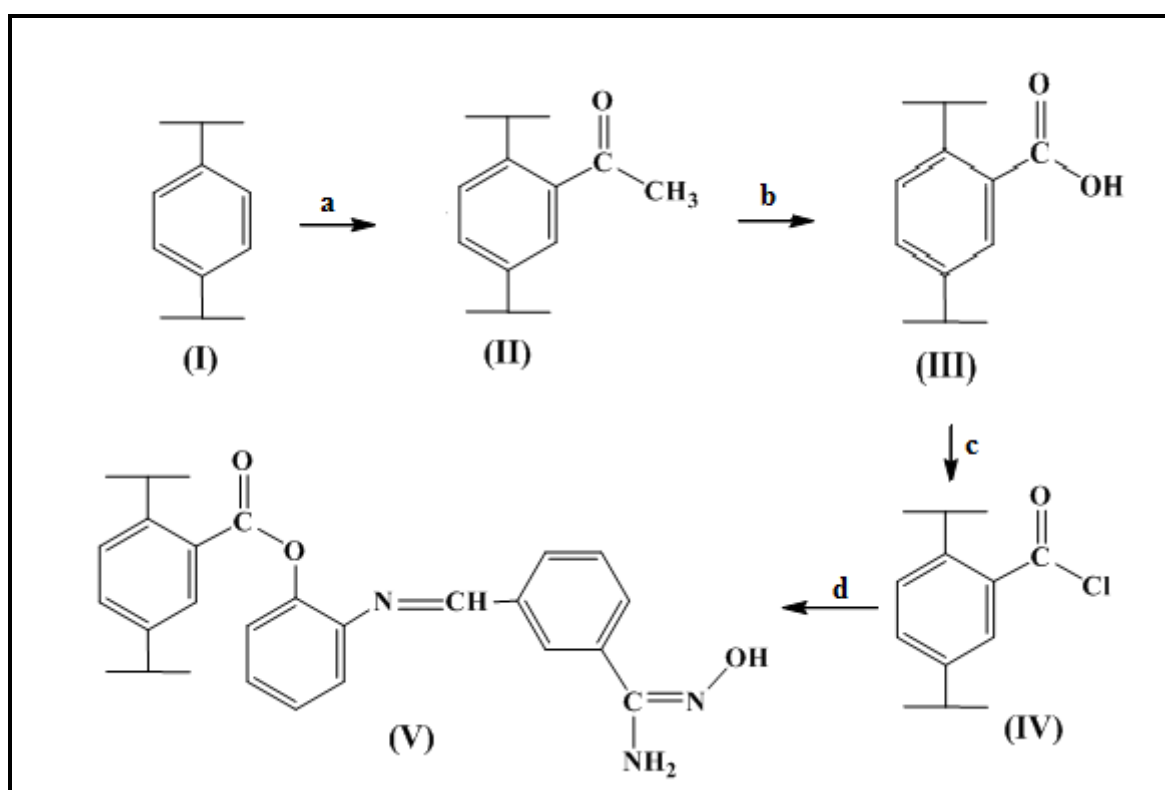
#### b. Conversion A Schiff Base to Amidoxime [31]

Hydroxyl amine hydrochloride (0.70 g, 0.01 mole) in 5 mL of distilled water was added with stirring to the solution of 2[[2-(hydroxy) benzylidene] amino] benzonitrile (0.01 mole) in 35 mL of distilled ethanol and then it left to stir for 30 min. The solution of sodium ethoxide which prepared of dissolving of Sodium metal (0.23 g, 0.01 mole) in 20 mL of ethanol was added gradually and then it was refluxed with stirring for 96 h at steadily temperature (80-90 °C). Subsequently, it was passing through a filter to eliminate sodium chloride. Then the filtrate was put in an ice bath for 24 h and the yield was filtered, then washed with 10 ml acetone and recrystallized by ethanol to yield 2[[2-(hydroxy)benzylidene]amino] benzamidoxime, as a yellowish crystals ( 72 %), ( m.p = 257-259 °C) . The compound showed  $\nu_{max}$ : 3325, 3225, 3062, 1650, 1637, 1587, 1165, 1100, 975, 750  $\text{cm}^{-1}$ .

### 2.4. Synthesis of XAD-4 Amidoxime Ligand Resin

The starting material, Styrene divinyl benzene copolymer (XAD-4) was functionalized via esterification. The polystyrene resins (10.0 g) were refluxed with acetic anhydride (20 mL) and anhydrous aluminium trichloride (1.0 g) in petroleum ether (60-80 °C) at 70 °C for 30 h.

The crude was filtered, washed in excess of hexane and then it was dried under high pressure for 24 h. The intermediate result (II, Scheme 1) was put in 500 mL water containing 8.5 g  $\text{KMnO}_4$  and 10 g  $\text{NaOH}$  and then it stirred for 1 h at 40 °C. The product was filtered off, washed with water and then treated with  $\text{HCl}$  (1:1). It was then refluxed with 50 mL thionyl chloride at 60 °C for 30 min. The intermediate resin (IV) was refluxed with amidoxime ligand (2.5 g) and sodium ethoxide ( $11.3 \text{ mmol l}^{-1}$ ) in toluene at 100 °C for 8 h. A light yellow resin was obtained.



a)  $(\text{CH}_3\text{CO})_2\text{O}$ ,  $\text{Al}(\text{Cl})_3$ , petroleum, 30 h reflux, 70 °C

b)  $\text{H}_2\text{O}$ ,  $\text{KMnO}_4$ ,  $\text{NaOH}$ , 1 h stirring at 40 °C

c)  $\text{SOCl}_2$ , 30 min reflux, 60°C

d)  $\text{C}_2\text{H}_5\text{ONa}$ , amidoxime, toluene, 8 h reflux, 100 °C

### Scheme 1. Synthesis of the resin

A total of (18.0 g) resin (V) was washed with deionized water. Later it was air-dried and powdered in a mortar and particles of 200-250 mesh size (ASTM) were used for metal

sorption studies. IR spectra for intermediates were (for **III**  $\nu_{max}$ : 3200, 1735, 1580, 1165, 750  $\text{cm}^{-1}$ , and for **IV**  $\nu_{max}$ : 1740, 1575, 870, 750, 675  $\text{cm}^{-1}$ ). While the resin showed  $\nu_{max}$ : 3325, 3062, 1745, 1670, 1630, 1587, 1165, 1080, 930,  $\text{cm}^{-1}$ .

### 2.5. Determination of Water Regain

Weighed amounts of the final product (**V**) were kept soaked in deionized water for 24 h. The resin was then filtered by suction and dried by pressing between filter paper folds. Weighed of the swollen resin was dried at 90°C for 72 h and reweighed. The water taken up (in g) by 1g of the dry resin was calculated.

$$\text{Water regain (\%w/w)} = \frac{\text{Weight of water absorbed}}{\text{weight of dry resin}} \times 100$$

### 2.6. Effect of pH on Total Sorption Capacity

The influence of the pH on total sorption capacity (millimoles of metal ion taken up by 1 g of dry resin) was studied by a batch method. Solutions of ions (50 mL, 100  $\mu\text{g mL}^{-1}$ ) were shaken with 0.1 g of resin for 2 h. The pH of solution was adjusted prior to equilibration over the range (1.0-7.5) with buffers prepared with 0.2M hydrochloric acid and 0.2M sodium acetate. After the equilibration, the metal sorbed was calculated from the differentiation between the original and residual concentrations in mobile phase. The metal ion concentration was also determined in the eluent after desorbing the metal ion by a suitable reagent [0.5M Sodium carbonate for uranium(VI); for palladium (II) HCl con. followed by a dilute acidic solution of thiourea; for the other metal ions, 2M hydrochloric acid]. The eluted metal ions, except uranium, were determined by atomic-absorption spectrometry. The uranium was determined spectrophotometrically by using 4-(2-pyridylazo)-resorcinol (PAR) as a reagent [32]. Sorption tests were achieved in duplicate each time. In all cases capacities and related parameters are expressed of dry weight of the resin.

### 2.7. ( Sorption Kinetics) Equilibrium Time

For studying the kinetic of metal sorption under investigation, a batch method was used (50 mL; 10  $\mu\text{g mL}^{-1}$ ) of each metal ion, at optimum pH (the value where maximum sorption

capacity was observed), was sampled in six stoppered conical flasks. The first flask was uptake from the shaker after 10 min and the remaining flasks at intervals of 15 min. The last flask was removed after 4 h. The amount of the metal ion was done by AAS. The kinetics of sorption for all the metal ions were determined in a similar manner. The duplicate values agreed to within a precision of  $\pm 2\%$ .

### 2.8. Effect of Alkali and Alkaline Earth Metal Ions

To find out the interference of  $\text{Na}^+$ ,  $\text{K}^+$ , Potassium,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  as alkali and alkaline earth metal ions on the recovery of various metal ions from solutions was studied. For this purpose, standard solutions of 50 mL of  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Mo}^{6+}$ ,  $\text{V}^{5+}$  and  $\text{U}^{6+}$ . ( $50 \mu\text{g ml}^{-1}$  each) and it was containing the strange ions as interferences were analysed.

### 2.9. Preparation of Synthetic seawater

The process used to prepare synthetic seawater suggested by Muroi and Hamaguzhi [33]. The composition synthetic seawater used in this work is given below.

Salt	Concentration ( $\text{g l}^{-1}$ )
NaCl	23.476
MgCl <sub>2</sub>	4.981
Na <sub>2</sub> SO <sub>4</sub>	3.917
CaCl <sub>2</sub>	1.102
KCl	0.066
NaHCO <sub>3</sub>	0.192
KBr	0.096
H <sub>3</sub> B0 <sub>3</sub>	0.026
SrCl <sub>2</sub>	0.024
NaF	0.003

Deionized water was used to dissolve the salts and diluted to 1 litre. The seawater thus prepared was soaked with aliquots of standard uranyl nitrate solution in order to get an

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appropriate concentration of U (VI).

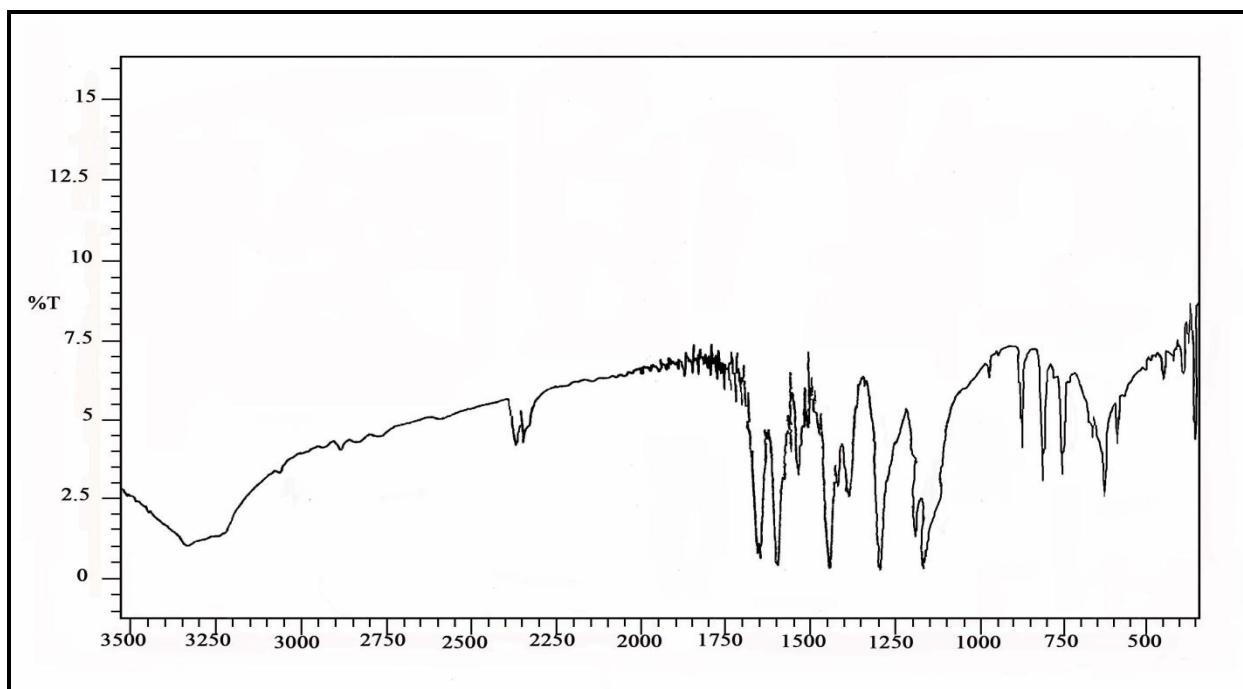
#### *2.10. Separation and concentration of Metal Ions*

A batch equilibration method was used to concentrate the trace metal ions. Sample solutions (250-1000 mL) containing  $0.1 \mu\text{g mL}^{-1}$  metal ion were adjusted to the best pH of adsorption with buffer solution. The above solutions were shaken with 100  $\mu\text{g}$  of resin for about 10 min. Seized metal ions were uptake with a suitable reagent (10 mL) as describe above and the amount of metal ion in the eluent was determined. Based on the adsorption of ions on the XAD-4 amidoxime ligand resin at various pH values and separation of studied metals in the binary mixtures were performed. A 50 mL solution containing Nickel ( $5 \mu\text{g mL}^{-1}$ ) and another metal ion was shaken with 100 mg of resin at pH 6.6. Nickel seized was desorbed with 2M hydrochloric acid (10 mL). Palladium and Vanadium were determined in the effluent and Nickel in the eluent. Similarly copper was separated from Palladium and Vanadium at pH 5.8. Also, Palladium was extracted from Iron, Zinc, Nickel, Copper and Molybdenum at pH 1.2. The resin selectively takes up Palladium at previous pH from the solution containing other metals. Separation of ions was also carried out by a column method. A column with a length of 6 cm and an id of 0.5 cm was used for separation purposes. The dry resin (0.5 g) was loaded into the glass column, soaked in the buffer solution and the metal ion solution was undergoing during the column at of  $0.5 \text{ mL min}^{-1}$  as a flow rate. The adsorbed ion was desorbed by using a suitable reagent as mention above. Pre-concentration of U (VI) from synthetic seawater using XAD-4 amidoxime ligand resin was also carried out by column method. Pre-concentration done at pH=6.5 of (sodium acetate and hydrochloric acid) with flow-rate  $0.5 \text{ mL/min}$ . The selectively sorbed uranium (VI) was eluted with various bed-volumes of 0.5 M Sodium carbonate at  $1 \text{ mL/min}$  flow-rate.



### 3. Results and discussion

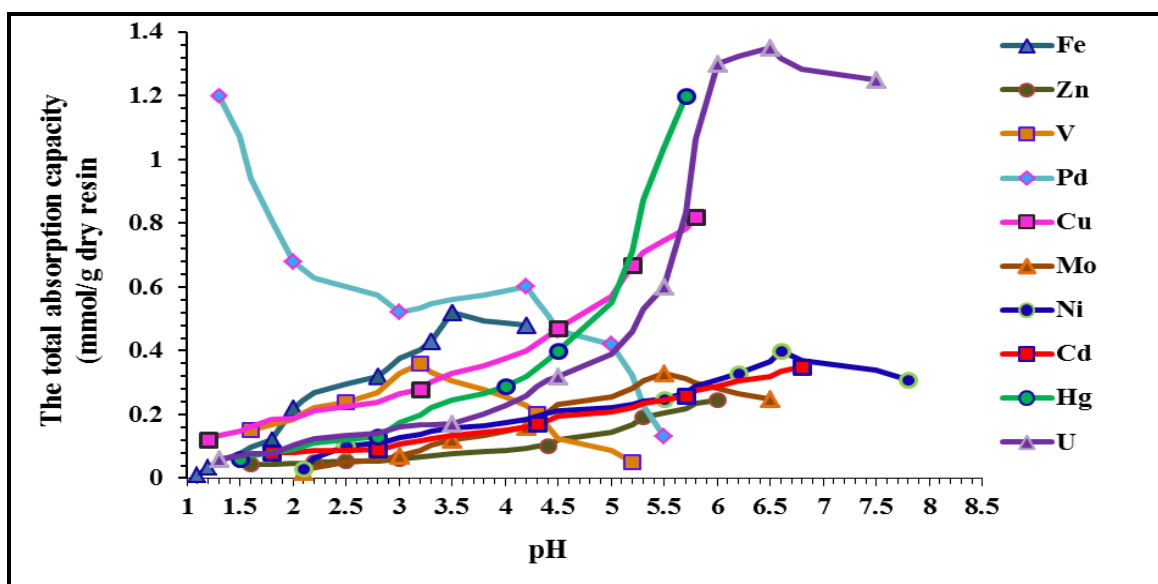
The resin was synthesized according to Scheme 1 and was characterized by IR spectra. In the IR chart of intermediate resin **IV** [Scheme 1] an adsorption band corresponding to  $\nu$  C-Cl appears at  $670\text{ cm}^{-1}$ , which disappears among IR bands of resin **V**. It is further indicated by a shift in the absorption band corresponding to a carbonyl group ( $1740\text{-}1765\text{ cm}^{-1}$ ) in the chart of resin **IV** probably resulting from Fermi-resonance between the C=O band and the overtone of a longer wavelength band near  $870\text{ cm}^{-1}$  [34]. This band reveals in the chart of intermediate resin **IV** and disappears in final resin **V** [Scheme 1, Figure 1]. A band appears at  $1630\text{ cm}^{-1}$  because of the tautomeric amidoxime group. Other major absorption bands of pure amidoxime ligand are also appearing for the final resin **V** with reduced intensities. This confirms the incorporation of amidoxime ligand which works as a multidentate ligand, coordinating with ion through hydroxyl group oxygens and amino group [23]. The water-regain was 0.43.



**Figure 1.** Infrared spectrum of new chelating amidoxime resin

The resin had to be very stable on successive treatment with 2M HCl and 2M NaOH solutions. The stability was checked by alter of the hydrogen-metal exchange capacity and IR spectrum which indicated that there was no change in the bands of the prepared resin pre-treatment by acid and base solutions. The capacity of sorption for the resin is an important to determine and is the quantity of resin required to eliminate quantitatively a selective metal ion from the solution.

The behaviour of capacity of adsorption for several metal ions on XAD-4 amidoxime ligand resin as a function of pH has been tested by a batch method. While most of the ions are precipitated at higher pH, studies were limited to pH 7.5. The findings are plotted in (Figure2).



**Figure 2.** The total absorption capacity (mmol/g dry resin) as a function of pH

Adsorption of the metals generally increases with high pH, reaching a limiting value in each pattern except adsorption of Pd (II). More increase in pH produces an extremely decrease in sorption capacity. A special feature of these curves is the maximum sorption of Mo (VI), Hg (II), Cu (II), Zn (II), U (VI), Ni (II) and Cd (II) at pH values (5.5 - 6.8). While the high sorption of Pd (II), V (V) and Fe (III) ions on pH values (1.2 - 3.5). In the case of U (VI) the capacity of adsorption is increase with pH and reaches a maximum of 1.3 mmol g<sup>-1</sup> /dry resin at pH (6.0-6.5). Cu (II) also shows maximum sorption at pH (5.2-5.8). The capacity

for Zn (II) at pH 6.0 is 0.25 mmol g<sup>-1</sup> dry resin. Also, the resin has a capacity of 0.35 mmol g<sup>-1</sup> /dry resin at pH 6.6 for Ni (II) and 0.4 mmol g<sup>-1</sup>dry resin for Cd (II) at pH 6.8. For Pd (II), V (V) , Fe (III), Mo (VI) and Hg (II) the pH values of maximum sorption are (1.3, 3.2, 3.5, 5.5, and 5.7) with sorption capacities of 1.2, 0.2, 0.52, 0.33 and 1.2 mmol g<sup>-1</sup>/dry resin respectively. The variation of the sorption capacities for investigated ions at lower and higher pH values. This enables the partition of (i.e., Nickel, Copper and Palladium from the binary mixture containing other metal ions.

The dynamic of ions sorption become favourable for the efficient separation on an ion-exchange column only when the metal ion diffuses fast into the sorption medium and chelation occurs rapidly. If the formation of chelating complex is not rapid for required metals, their amount on a column is hardly owing to the long contact time between the resin and the solution. For such cases a batch method is used, taking a big amount of resin and shaking it with metal solution for a longer period. However, for applying the prepared resin in column chromatography, the kinetics of the resin-metal interaction should be rapid. Kinetic processes were achieved at optimum pH of adsorption for ions and the final results are plotted in (Figure 3).

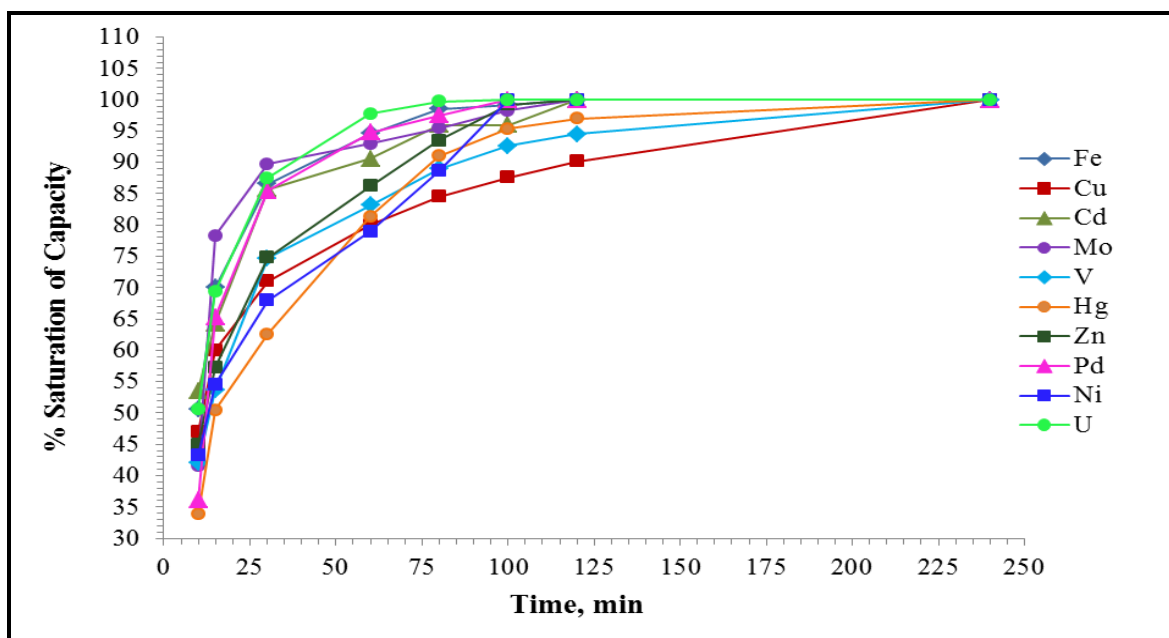


Figure 3. Saturation of capacity for metal ions as a function of time

In all the cases of the studied ions namely, Fe(III), Cu(II), Ni(II), Hg(II), Cd(II), Zn(II), Pd(II), Mo(VI), V(V) and U(VI). The sorption was fast and saturation of capacity reached within 2 h. In fact, the half-saturation time in often cases was less than 15> t 0.5>10 minutes (Table 1). These points to evidence that XAD-4 amidoxime ligand resin is suitable for the ion chromatographic separation of the ions studied.

To estimate the interference of Na<sup>+</sup>, K<sup>+</sup>, and Mg<sup>+2</sup>, Ca<sup>+2</sup>, Sr<sup>+2</sup> on the adsorption behavior of the resin, it was treated with metal ions containing 50 µg/mL of investigation ions, and 40 µg/mL of Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>+2</sup>, Ca<sup>+2</sup>, and Sr<sup>+2</sup> (SO<sub>4</sub><sup>-2</sup> as common anion) for 24 h at the natural pH of the solution. The existence of alkali and alkaline earth ions do no significantly affect on the regaining of metal ion from the solution.

**Table 1.** Time for half saturation for different metal ions on XAD-4 amidoxime ligand resin

Metal ions	Optimum pH	t <sub>0.5</sub> Sat.(min.)
Fe (III)	3.5	10
Cu (II)	5.2	10
Mo (VI)	5.5	15> t <sub>0.5</sub> >10
V (V)	3.2	15> t <sub>0.5</sub> >10
Cd (II)	6.8	10
Hg (II)	5.7	15> t <sub>0.5</sub> >10
Zn (II)	6.0	15> t <sub>0.5</sub> >10
Pd (II)	1.2	15> t <sub>0.5</sub> >10
Ni (II)	6.6	15> t <sub>0.5</sub> >10
U (VI)	6.5	10

The results in Table 2 show the recovery rates in the presence of excess of these foreign ions. This suggests, the resin could be used for trace concentration from natural samples that have a high concentration of alkali and alkaline earth metals, e.g., sea-water, pond water, etc. The resin capacity is also enough for use in the simultaneous concentration and extraction of several metals. The resin has a high characteristic strength and no significant change in the hydrogen-metal exchange capacity was observed on using the resin after recycling. Preconcentration of ions carried out on the resin and the findings are listed in (Table 3). Metal ions could be concentrated up to 100 runs by XAD-4 amidoxime ligand resin. The separation of f Nickel, Copper and Palladium with presence of diverse metal ions was performed both by

batch and column methods.

**Table 2.** Effect of diverse ions

Ion interfe reing <sup>a</sup>	Recovery %									
	V(II)	Fe(III)	Cu(II)	Cd(II)	Ni(II)	Hg(II)	Zn(II)	Pd(II)	Mo(VI)	U(VI)
Ca	98.5	98.6	98.9	99.2	99.4	99.8	99.1	98.5	97.6	98.5
Mg	98.6	101.0	99.4	98.4	100.4	100.2	99.5	98.6	99.4	97.8
K	97.6	103.1	98.3	98.6	100.2	98.7	97.6	99.4	103.1	99.4
Na	98.4	99.6	98.7	96.8	99.5	100.6	97.2	98.2	100.2	98.2
Sr	97.8	98.7	97.5	98.2	99.7	98.5	96.9	97.8	99.1	97.4

*a* = 40 µg mL

**Table 3.** Preconcentration of metal ions

Metal ion	Sample volume/ mL	Metal found* /µg mL <sup>-1</sup>
Cd II	250	2,46
	500	4.90
	1000	9.91
Hg II	250	2.47
	500	4.95
	1000	10.01
Cu II	250	2.47
	500	5.02
	1000	9.96
Ni II	250	2.48
	500	4.98
	1000	9.92
Zn II	250	2.51
	500	4.89
	1000	9.98
Fe(III)	250	2.42
	500	4.94
	1000	10.02
U(VI)	250	2.45
	500	4.92
	1000	10.01

Amount of metal ion taken 0.1 µg mL<sup>-1</sup>)

Nickel is extractable from Palladium and Vanadium as they are not seized on the resin at pH 6.6 (Tables 4 and 5). Similarly copper is extractable from Palladium and Vanadium at pH

5.8 (Tables 6 and 7), as only copper is seized at this pH. Also, Palladium is separable from Iron, Zinc, Nickel, Copper and Molybdenum at pH 1.2 ( Tables 8 and 9).The batch method was preferred over the column method for the XAD-4 amidoxime ligand resin as it was depend to be less time consuming, although elution is easier and complete with the column method. prepared sea water spiked to different concentration of U (VI) was used i.e., 0.02, 0.2 and 1  $\mu\text{g mL}^{-1}$  and 100 mL of the spiked test solutions of pH 6.5 were separately via the column conditioned as described above with a flow rate of 0.5 mL min<sup>-1</sup> .

**Table 4.** Extraction of Ni (II) from other metal ions performed at pH 6.6 [amount of Ni (II) taken, 5  $\mu\text{g mL}^{-1}$ ]

Metal ion	Amount of metal added/ $\mu\text{g mL}^{-1}$	Amount of Ni(II) recovered*/ $\mu\text{g mL}^{-1}$	Metal ion recovered* $\mu\text{g mL}^{-1}$
Pd (II)	5.0	5.02	4.86
	10.0	4.94	9.86
	20.0	4.87	20.01
V(V)	5.0	4.92	4.90
	10.0	4.96	9.82
	20.0	4.85	19.86

\* Batch method

**Table 5.** Extraction of Ni (II) from other metal ions performed at pH 6.6 [amount of Ni (II) taken, 5  $\mu\text{g mL}^{-1}$ ]

Metal ion	Amount of metal added/ $\mu\text{g mL}^{-1}$	Amount of Ni (II) recovered*/ $\mu\text{g mL}^{-1}$	Metal ion recovered* $\mu\text{g mL}^{-1}$
Pd (II)	20	4.78	19.76
V(V)	20	4.85	19.82

\* Column method

**Table 6.** Extraction of Cu (II) from other metal ions performed at pH 5.8 [amount of Cu (II) taken, 5  $\mu\text{g ml}^{-1}$ ]

Metal ion	Amount of metal added/ $\mu\text{g ml}^{-1}$	Amount of Cu(II) recovered*/ $\mu\text{g ml}^{-1}$	Metal ion recovered* $\mu\text{g ml}^{-1}$
Pd (II)	5.0	4.95	4.92
	10.0	4.98	10.02
	20.0	4.86	20.02
V(V)	5.0	5.01	4.97
	10.0	4.98	9.92
	20.0	4.87	19.85

\* Batch method

**Table 7.** Extraction of Cu (II) from other metal ions performed at pH 5.8 [amount of Cu (II) taken, 5  $\mu\text{g ml}^{-1}$ ]

Metal ion	Amount of metal added/ $\mu\text{g ml}^{-1}$	Amount of Cu (II) recovered*/ $\mu\text{g ml}^{-1}$	Metal ion recovered* $\mu\text{g ml}^{-1}$
Pd (II)	20	4.90	20.01
V(V)	20	4.82	19.86

\* Column method

**Table 8.** Separation of Pd (II) from other metal ions performed at pH 1.2 [amount of Pd (II) taken, 5  $\mu\text{g mL}^{-1}$ ]

Metal ion	Amount of metal added/ $\mu\text{g mL}^{-1}$	Amount of Pd (II) recovered*/ $\mu\text{g mL}^{-1}$	Metal ion recovered* $\mu\text{g mL}^{-1}$
Fe (II)	5.0	5.01	4.87
	10.0	4.93	9.82
Zn (II)	5.0	4.98	4.91
	10.0	4.92	9.86
Ni (II)	5.0	4.94	4.96
	10.0	4.88	10.02
Cu(II)	5.0	4.92	4.90
	10.0	5.02	9.91
Mo (VI)	5.0	4.96	5.01
	10.0	4.90	9.80

\* Batch method

**Table 9.** Separation of Pd (II) from other metal ions performed at pH 1.2 [amount of Pd (II) taken, 5  $\mu\text{g mL}^{-1}$ ]

Metal ion	Amount of metal added/ $\text{Mg mL}^{-1}$	Amount of Pd (II) recovered*/ $\text{Mg mL}^{-1}$	Metal ion recovered* $\text{Mg mL}^{-1}$
Fe (II)	10.0	4.91	9.82
Zn (II)	10.0	4.85	9.75
Ni (II)	10.0	4.78	9.76
Cu(II)	10.0	4.92	9.80
Mo (VI)	10.0	4.88	9.85

\* Column method



**Table 10.** Pre-concentration of U(VI) from synthetic seawater using XAD-4 amidoxime ligand resin

Concentration of U(VI) in sea water ( $\mu\text{g mL}^{-1}$ )	Amount of U (VI) loaded ( $\mu\text{g}$ ) *	Eluent volume (mL) **	Amount recovered ( $\mu\text{g}$ )	Percentage recovery
1.00	100	30	98.1	98.1
0.200	20	30	19.5	97.5
0.020	2.0	20	1.92	96.0

\* 100 ml of seawater passed through the column

\*\* Mean of three values

The sorbed U (VI) on the column was eluted with 0.5 M Sodium carbonate. At lower concentrations, the recovery became less quantitative because relatively high losses maybe because the adsorption on the glass surface [35]. Table (10) gives the results of pre-concentration of U (VI) with quantitative recovery. Satisfactory recovery was gained by using 0.5 M Sodium carbonate as eluent.

#### 4. Conclusions

XAD-4 amidoxime ligand resin was useful for enrichment of trace metals and their separation from solutions at a certain pH value. Repaid equilibration of ion made it applicable for the conventional column method as well. The low affinity of the resin towards alkali and alkaline earth metals indicates its use for heavy metals and environmental samples. It is able to seize amounts of elements as of simulated seawater.

## References

- [1] Moyers EM, Fritz JS. [1977]. *Anal. Chem.* 49, p 418-423.
- [2] Marhol M, Cheng KL. [1974]. *Talanta.* 21, p 751-762.
- [3] Tomoshige S, Hirai M, Ueshima H.[ 1980]. *Anal. Chim. Acta.* 115, p 285-292.
- [4] Figura P, McDuffie B. [1977]. *Anal. Chem.*; 49(13), p 1950-1953.
- [5] Mendez R, Pillai VNS. [1990]. *Analyst*, 115, p 213-216.
- [6] Vernon F, Eccles H. [1975]. *Anal. Chim. Acta*, 77, p 145-152.
- [7] Vernon F, Eccles H. [1973]. *Anal. Chim. Acta.* 63(2), p 403-414.
- [8] Arguello MD, Fritz JZ. [1977]. *Anal. Chem.* 49, p 1595-1598.
- [9] Orf GM, Fritz JS. [1978].*Anal. Chem.* 50(9), p 1328-1330.
- [10] Moyers EM, Fritz JS. [1976].*Anal. Chem.* 48(8), p 1117-1120.
- [11] Nishizawa M, Yokoyama T, Kimura T, Suzuki TM. [1983]. *Chem. Lett.* 12(9): p 1413-1414.
- [12] Singh KA, Dhingra KS. [1992]. *Analyst.* 117, p 889-891.
- [13] Zlatkis A, Bruening W, Bayer E. [1971]. *Anal. Chim. Acta.* 56(3), p 399-405.
- [14] Bayer E. [1957]. *Chem. Ber.* 90, p 2325.
- [15] Kantipuly C, Katragadda S, Chow A, Gesser HD. [1990].*Talanta.* 37(5), p 491-517.
- [16] Samanta SK, Misra BM. [1995]. *Solv. Exter. & Ion Exch.* 13(3), p 575-589.
- [17] Sakaguchi T, Nakajima A. [1986]. *Sep. Sci. Technol.* 21, p 519-534.
- [18] Hodgklyn JH, Eilb R. [1985]. *Ion Exch. Sorbents.* 3(2). P 83-162.
- [19] Bunian A., Ibahim F., Kariem K. [2013]. *Oriental Journal of chemistry.* 29(4), p 1391-1397.
- [20] Ueno K, Martell AE. [1956]. *J. Phys. Chem.*, 60(9), p 1270-1275.
- [21] Okawa H, Honda A, Nakamura M, Kida S. [1985]. *J. Chem. Soc. Dalton Trans.* (1). p 59-64.
- [22] Vernon F. [1977]. *Chem. Ind.*.p 634-637.
- [23] Hodgkin JH. [1979]. *Chem. Ind.* p 153-156.
- [24] Wöhrle D. [1983]. *Adv. Polym. Sci.* 50, p 45.
- [25] R. Pathak, G. N. Rao. [1997]. *Talanta.* 44, p 1447-1453.
- [26] Fenglin H., Yunfei X., Shiqin L., Dewei Y., You-Lo H., Qufu W. [2013]. *Materials.* 6, 969-980.

- [27] Lee LH, Kuan YC, Chern JM. [2006]. *J. Hazard. Mater.* 168, p 549-559.
- [28] Silva RMP, Manso JPH, Rodrigues JRC, Lagoa RJL. [2008]. *J. Environ. Sci. Health.* 43, p 311-317.
- [29] Lin LC, Li JK, Juang RS. [2008]. *Desalination.* 225, p 249-259.
- [30] Nizam M. El-Ashgar, Issa M. El-Nahhal, Mohamed M. [2009]. *Intern. J. Environ. Anal. Chem.* 89 (14), p 1057-1069.
- [31] Bicak N, Atay T. [1998]. *Turk J. Chem.* 22, p 261-266.
- [32] Florence TM, Farrar Y. [1963]. *Anal. Chem.* 35(11), p 1613-1616.
- [33] Murio N, Imai S, Hamaguchi A. [1985]. *Analyst.* 110, p 1083-1086.
- [34] Silverstein RM, Bassler GC, Merrill TC. [1991]: *Spectrometric Identification of Organic Compounds.* 5<sup>th</sup> Ed. John Wiley, New York.
- [35] Thiers RE. [1957]. *Contamination in trace element analysis and its control, in methods of biochemical analysis,* Glick D. Edt. Interscience, New York.