

CHELATING AND METAL IONS UPTAKE PROPERTIES OF POLY (*M*-AMINOPHENOL -FURFURAL)

Mhmoud N. Al-Jibouri

Department of Chemistry, College of Science, Al-Mustansirya University, Baghdad-Iraq.

Abstract

Polymeric chelate of poly(*m*-aminophenol-furfural) with Cr (III), Mn (II), Co (II), Ni (II) & Cu (II) ions have been prepared and characterized by spectral measurements (UV-VIS., IR), magnetic moment, electrical conductivity and element analysis of metal by flame atomic absorption spectroscopy F.A.A.S. Ion-exchange properties of polymeric chelate have also been studied by application of the batch equilibrium method via determination of metal ion before and after adsorption. The stability of polymer chelates were assigned in solution by Ostwald of dilution.

Introduction

Polymers derived from phenols, amines and furfural such as phenolic resins⁽¹⁾, Bis phenol A-furfural⁽²⁾, and resin *m*-aminophenol furfural⁽³⁾ containing-CH-bridges are known for their ion-exchanging properties^(4,5). Recently Patel and Lad^(6,7) have reported the synthesis and characterization of poly (5,5-methylene-bis (8-hydroxy quinone) -7,7-diethylene in which -CH₂- and -CH₂CH₂- groups are attached alternately to 8 HCl units in the polymer chain⁽⁸⁾. The heavy metal ion uptake properties of polystyrene supported chelating polymer resins had been studied by Reddy *et al.*⁽⁹⁾. The work now described deals with the synthesis and characterization of polymeric chelates of MAF with selected metal ions as listed in Table (1). Study of ion-exchanging properties of the chelating polymer with selected metal ions was undertaken with a view for comparing these corresponding metal ions.

Experimental

Poly (*m*-aminophenol-furfural) was prepared according to the paper published in literature survey⁽¹⁰⁾. Its purity was checked by thin layer chromatography (T.L.C.), melting point, solubility and infrared spectroscopy Table (1). All other chemicals used were of analytical grade, CrCl₃.6H₂O, MnCl₂.4H₂O, CoCl₂.H₂O, NiCl₂.6H₂O and CuCl₂.2H₂O solutions were prepared and standardized by conventional methods as described by Vogel⁽¹¹⁾. PH of the metal ions solutions were

maintained using sodium acetate-acetic acid buffer couple.

The batch equilibration^(11,12) was adopted for increasing the chelating ion-exchanging properties of MAF resin. This comprises (a) a study of the effect of pH on adsorption of metal ions by polymer sample (b) estimation of the time required to reach, the state of equilibrium under given experimental conditions and (c) measurement of the distribution ratio of metal ion between the polymer phase and the solution phase over a wide pH-range.

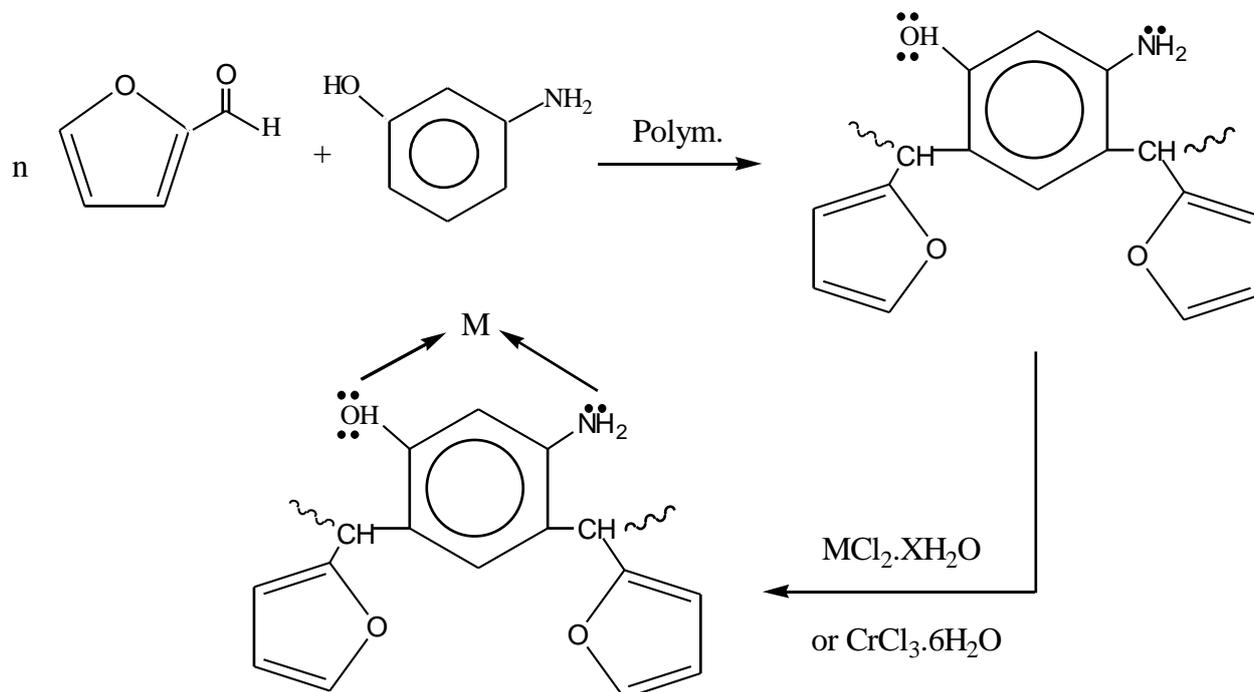
Table (1)
Physical properties of poly
(*m*-aminophenol-furfural)⁽¹⁰⁾.

Solubility	Water (-), acetone (+), ethanol(-)
viscosity	5.2×10^{-2} dl.g ⁻¹
Conversion	78%
Softing point	85-100 °c
Color	Dark red

Preparation of Polymeric Metal Chelates (MQ)

A solution of 0.01 mole, chelating polymer in 25 mL of 2:1 vol. acetone : formic acid mixture was added drop wise to a solution of 0.011 mole of MnCl₂.4H₂O or CoCl₂.H₂O, or 0.021 mole of CrCl₃.6H₂O, NiCl₂.6H₂O and CuCl₂.2H₂O in 25 mL of distilled water at room temperature with good stirring. The

reaction mixture was heated on a water bath for 1hr, colored precipitates were obtained, which were then filtered, washed with excess of ethanol, Scheme (1).



Scheme (1) : Preparation of Polymeric Metal Chelates (MQ).

Measurements

Elemental analysis

Analysis for metal ions in the polymeric chelates was carried out by flame atomic absorption technique via Shimadzo AA-670, moreover the percentages of Cr(III) and Mn(II) were obtained by decomposition of a known amount of the chelate with concentrated mineral acid followed by dilution with distilled water, filtration and estimation of metal ion Ni^{+2} and Cu^{+2} by standard method.⁽¹⁰⁾

I.R spectra of all polymeric chelates were scanned in CSI on F.T.I.R-8300 Shimadzu spectrophotometer. The U.V-visible spectra of the metal polymeric chelates were measured in N,N-dimethyl formamide (D.M.F) of 10^{-3} M concentration using Shimadzu UV-Vis. 160 A, Ultra-Violet visible spectrophotometer in the range 200-800 nm. Magnetic susceptibility (Xg) measurement of polymeric chelates were made at room temperature by the Gouy method, $\text{Hg}\{\text{Co}(\text{NCS})_4\}$ was used for calibration⁽¹⁴⁾. Molecular susceptibilities were

corrected for diamagnetism of component atoms by using Pascals constants⁽¹⁵⁾.

The pH of the solutions was adjusted to about 4.5-8.0 by addition of 3 mL of $\text{CH}_3\text{CO}_2\text{Na} / \text{CH}_3\text{CO}_2\text{H}$ buffer couple. The polymeric chelate which separated out as a suspension was digested for about (3 hrs.) on water bath and was then allowed to settle. The solid was filtered, washed with acetone, water and then with ethanol, and finally with petroleum ether (25 mL). The polymeric chelates were air dried and designed as in Table (2).

Table (2)
Characterization of polymeric metal chelates.

Polymeric chelate ^(a)	M% Calc. (found) ^(b)	I.R (v cm ⁻¹) $\nu_{\text{NH}_2\text{OH}}$, ν_{CO} , $\nu_{\text{M-L}}$	λ_{max} nm (ϵ_{max})	μ_{eff} (B.M)	Λ_m $\mu\text{S.mol}^{-1}$	Suggested structure
L		3500-3400(m), 1100,1600	250,315	-	-	-
[Cr(L)Cl ₂]	14.066 (13.9)	3200(br.), 400-500(M-N)	270,370	3.91	40	Tetrahedral
[Mn(L)Cl ₂]	9.31 (8.77)	3180,400, 245(Mn-Cl)	215,550,700	5.10	30	Tetrahedral
[Co(L)Cl ₂]	8.801 (7.66)	3200(br.), 400- 500,390(w) (Co-Cl)	270,390,415	3.5	19	Tetrahedral
[Ni(L)Cl ₂]	8.9 (8.0)	3200,1190, 470,390 (w) (Ni-Cl)	290,385	0	23	Square planar
[Cu(L) ₂ Cl ₂]	4.91 (3.97)	3200(br),1130, 400-490(Cu-N, Cu-O,Cu-Cl)	260,390,520	2.5	25	Octahedral

Where

a = molecular weight of the repeating unite = Mol.wt of Q-liganed + atomic weight of concerned metal .

b = M% was calculated by flame atomic absorption technique via standard addition method.

c = Λ_m conductivity of chelate solutions were recorded in DMSO solvent.

Table(3)
Comparison of the rates of metal ion up take :percentages attainment of equilibrium state.

Time (hr)	Cr (III)	Mn (II)	Co(II)	Ni(II)	Cu(II)
0.5	40	35	40	50	20
1	60	65	60	70	35
3	70	75	78	85	40
5	90	95	95	97	65

* $\text{MCl}_2 \cdot x\text{H}_2\text{O}$ or $\text{CrCl}_3 \cdot 6\text{H}_2\text{O} = 0.01\text{mol.lit}^{-1}$,
 volume = 5mL,
 pH = 4.5-8.0,
 temperature = 25 °C^o, Wt of polymer = 30 mg.

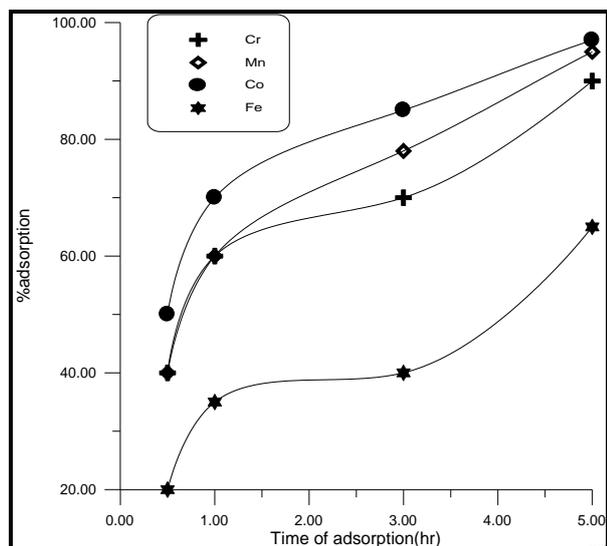


Fig. (1) : The relationships between time of adsorption with %M attainment at equilibrium state.

Results and discussion

Characterization of polymeric chelates

All the polymeric chelates listed in Table (1) are insoluble in common organic solvents and are decomposed by mineral acids affording the original polymeric ligand. The results of metal analyses suggest that the metal:ligand ratio is 1:1 for all complexes except for Cu (II), which was 2:1 ligand : metal, the results were also supported by determination of metal content in the polymeric chelates

The I.R spectra of the polymeric chelates were similar in general shapes and relative intensity of the bands. comparison of the absorption of polymeric ligand⁽¹⁵⁾ and that of each polymeric chelates reveals differences. The medium absorption in the region 3200-3500 cm^{-1} indicates the stretching of (OH) and (NH₂) groups, which were broad in the prepared complex, this indicates the formation of six-membered ring which is kinetically and thermodynamically stable⁽¹⁶⁾.

The band in the I.R spectrum of polymeric chelates due to $\nu_{\text{C=C}}$ and $\nu_{\text{C-O}}$ stretching at 1600 and 1100 cm^{-1} is attributed to $\nu_{\text{C=C}}$ of the furfural ring and C-O-M respectively⁽¹⁷⁾. Moreover the appearance of bands in the region 600-200 cm^{-1} in the metal polymeric chelates supports the complexation and indicates the coordinated bands M-N and M-O⁽¹⁸⁾ of $\nu_{\text{M-N}}$ and $\nu_{\text{M-O}}$.

The values of magnetic moment for Cr(III), Mn(II), Co(II) and Cu(II) complexes agree with the suggested structures, however, the diamagnetic property of Ni(II) reveals the square planer geometry.

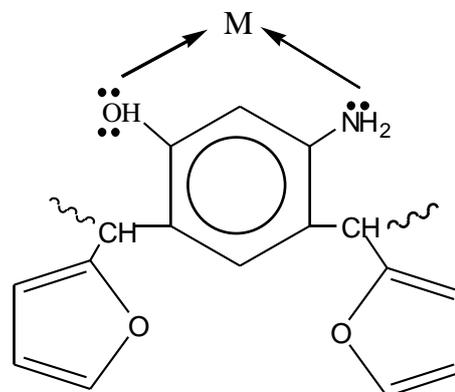


Fig. (2): Suggested of AMF with the metal ion.

Electronic spectra

Bands of maximum absorption related to the chelating polymer and its complexes in the U.V-Visible regions are shown in Figs.(1, 2). The chelating polymer exhibited a high intensity band in the U.V-region is splitted into two components with maximum absorption at wave lengths 250 nm and 315 nm . This band may be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of aromatic and furan system⁽²⁰⁾. For distorted ($T_{2g}^4 \rightarrow A_{2g}^4$, $T_{1g}^4 \rightarrow A_{2g}^4$)⁽²²⁻²³⁾ which supported of the prepared metal complexes. The diffuse electronic spectrum of Cr(III) poly chelates shows high intensity peak at 370 nm, this may be due to $T^4 \rightarrow A^4$ which overlapped with charge transfer of $\text{Cl}^- \rightarrow \text{Cr}^{+3}$ of pure tetrahedral complexes⁽²⁴⁾. The value of magnetic moment $\mu_{\text{eff}} = 3.91$ B.M is comparable with the suggested structure of d^3 high spin as well as Mn(II) and Co(II) complexes showed charge transfer $\text{Cl}^- \rightarrow \text{M}(\text{II})$ which supporte the tetrahedral symmetry. However Ni(II) complex showed a high intensity band of $dxy \rightarrow \pi$ ⁽²⁵⁾ of square planer complexes at 385 nm.

The visible spectrum of Cu(II) poly chelate shows two broad band around 520 nm and 340 nm. The first band may be due to ${}^2T_{2g} \rightarrow {}^2E_g$ transitions, and the second to charge transfer. The first band shows structure suggesting distorted octahedral structure for the Cu(II)

poly chelate. The higher value of $\mu_{\text{eff}}=2.5$ B.M⁽²³⁾ of the Cu⁺² poly chelate supports this view.

Effect of pH and time on uptake of metal ion

The effect of pH on metal ion uptake was studied by stirring 3 mL of 10^{-2} M metal chloride solution, 7 mL buffer solution (pH = 2-9) and resin 1 g in a 100 mL beaker for 2hr. The effect of times was studied by repeating the above procedure at pH 8 at different time internals (0.5,2,2.5,3,4,5 hrs) Table (3). The maximum uptake capacities of polymer resin was determined by reacting 50,100,250 and 400 ppm of metal solutions with polymeric resin under suitable pH conditions for about 2hrs., at lower pH values (< pH 7) protonation of chelating groups (OH & NH₂) takes place, completion with available ligands is reduced, and hence the percentage uptake decreases. At higher pH values (> pH) deprotonation takes place and hence the percentage uptake increases through the formation of stable polymer-metal complexes. The uptake of Cu(II) and Co(II) increases with increase in pH, and reaches a plateau value at (pH =10). In case of Cr(III), Mn(II) and Ni(II), the plateau is observed at (pH = 6.5). The selectivity patterns of the metal ions by the resin are as follows :

pH = 6:Cr(III)>Ni(II)>Mn(II)>Co(II)>Cu(II).
 pH = 8:Co(II)>Cu(II)>Ni(II)>Mn(II)>Cr(III).
 pH= 10:Cu(II)>Co(II)>Ni(II)>Mn(II)>Cr(III).

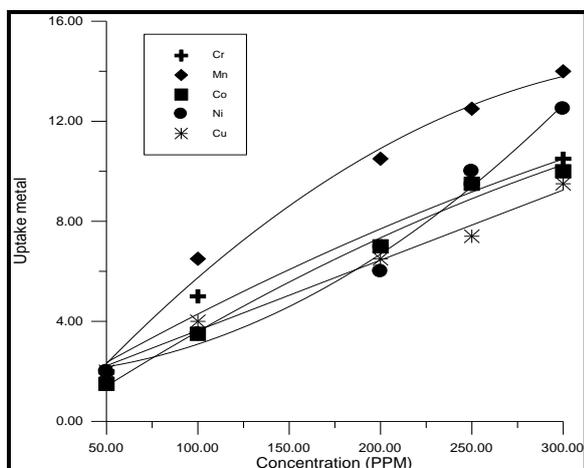


Fig. (3) : Variation of uptake of metal with concentration.

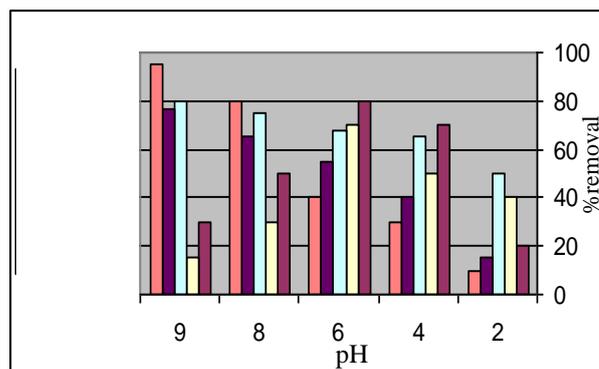


Fig.(4) : Effect of pH on % removal of metal ion.

Effect of initial concentration of metal ions on its uptake by chelating polymer

Effect of initial concentration of transition elements is an important variable, which determine the maximum uptake capacity of the polymer, Fig.(3), shows the uptake capacities of MAf resin for the single metal aqueous solution under study. From the plots obtained for each metal ion, the metal capacities of the present resin are quite comparable to those of resins employed earlier⁽²⁶⁻²⁸⁾.

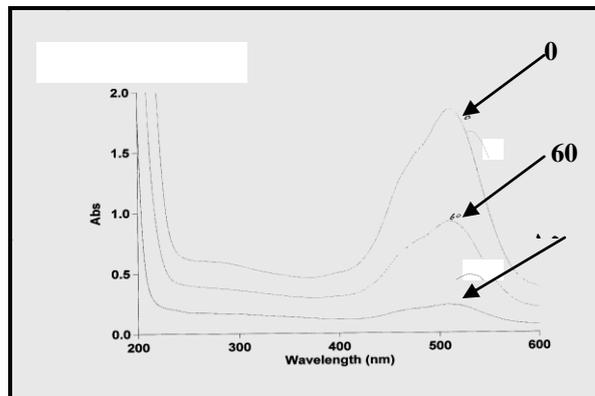


Fig. (5): Variation of Cu²⁺ ions absorbance with time of adsorption (in minutes).

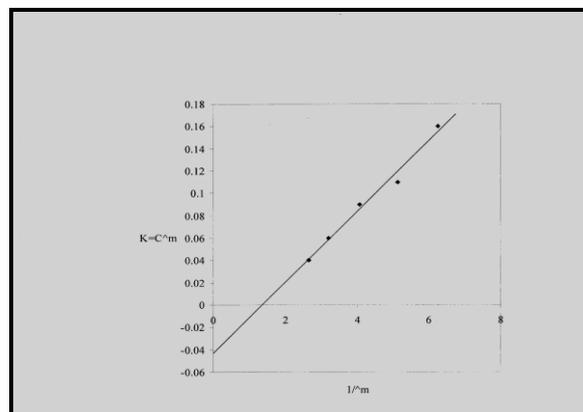


Fig. (6): Calculation of K_f stability constant of Cu(II) chelate.

Reference

- [1] A.Gandini, *adv.polym.sci.*, 25,47(1977) .
- [2] A.A.Al-Saddi, *M.Sc. Thesis, Babylon University* (2002).
- [3] S. Samal, R. K. Dey, S. Acharya and M.K.Mohapatra, "Metal Ion-Adsorption Studies of Chelating Resins Derived from Furfural Condensed with Schiff base of 2,6-diamino-pyridine and immobilized on silica Gel.", *in International Symposium of Polymers beyond A D 2000*, 12-15 Jan Proceedings Indian Insitute of Technology , Delhi.
- [4] R. C. De Geiso, L. G. Donaruma and E.A Tomic, *J. Appl. Polym. Chem.*, 9, 411 (1971).
- [5] B. S. Patel and S. R. Patel, *Makromok. Chem.*, 180, 887, 897, 1159 (1979).
- [6] M. J. Lad and S. R. Patel, *Eur. Polym. J.*, 20, 181 (1984).
- [7] M. J. Lad, H. S. Patel and S. R. Patel, *Eur.Polym.J.*, 22, 207 (1986).
- [8] C.I.Simionescu, M.Grigora, I.Cianga and N.Olaru, *Eur. Polym.J.*, 13y, 7, 891 (1998).
- [9] H. Reddy and R. Avakumar, *Proc. Indian Acad. Sci.*, 155, 155 (2003).
- [10] A.J.Mejili . *M.sc. Thesis, Al-Mustansirya Univerisity*, (2004).
- [11] A.I.Vogel, "A text book of quantitative inorganic analyses", (ELBS Longmans, London) 447, 462, 489 (1978).
- [12] G.E.Ashby, *J.Polym.Sci.*, 50, 99 (1961).
- [13] Y. Kato, D. J. Carlsson and D.M.J.Wiles, *Appl.Polym. Sci.*, 13, 1447 (1969).
- [14] R. Chandra, B. Psingh and S. P. Handa, *J.Polym.Sci.*, 22, 523 (1981).
- [15] R. H. Datta and A. Symal, "Elements of magneto chemistry", 2nd Ed. (West East Press New Dalhi), 101(1993).
- [16] D. T. Turner, *J. Polym. Sci., Polym. Chem. Ed.*, 2, 1699 (1964).
- [17] Ö. Birer, S. Süzer, *Polym.*, 42, 1833(2001).
- [18] E. Owen, "Degradation and Stabilization of P.V.C", *London : Elsevier*, (1989).
- [19] D. Braaum and E. Bezdadea, "Theory of Degradation and Stabilization". *In Encyclopedia of P.V.C*. 2nd Ed, New York : Marcel Dekker, (1989).
- [20] M.M.Patel, M.R.Patel and M.N.Patel , *Indian J. Chem.*, 20A, 623 (1981).
- [21] A.B.Pleaver, "Electronic spectra of some transition metal complexes", *J.of Chem.Edn.*, 45,711(1986).
- [22] R. K. Agarwal and G. Singh, *Asian J. Chem.*, 1, 409 (1989).
- [23] R. K. Agarwal and R. K. Sarin, *Polyhedron* ,12, No. 19, 2411 (1993).
- [24] P.Fantucci and V.Velenti, *J. Am. Chem. Soc.*, 98, 3832 (1976).
- [25] B. N. Figgis, "Introduction to Ligand Fields", (Wiley, Eastern, New Delhi) , 223 (1976).
- [26] M. Kimiaki and A. Masahiro, *Chem. Abstr.*, 109, 134491 (1998).
- [27] A. Denzili, E. Buyuktirel, Gence and E. Piskin, *Anal. Lett.*, 31, 2791 (1998).
- [28] P.Chattopadhyay, C.Sinha and Pd D.K., *J.Anal.Chem.*, 357, 368 (1997).

الخلاصة

تم تحضير خمسة معقدات كلتيية لايونات Cu^{+2} و النحاس Ni^{+2} , Mn^{+2} , Cr^{+3} , Co^{+2} مع بوليمر كلاي مشتق من البلمرة التكتيفية لميتا امينوفينول مع الفورفرال بالوسط القاعدي . تم تشخيص البوليمر مع معقداته الفلزية بواسطة الطرق الطيفية المعروفة IR, UV- فضلاً عن قياس النسبة المئوية للفلز بواسطة طيف الامتصاص الذري اللهبى F.A.A.S وقياس التوصيلية المولارية والحساسية المغناطيسية . تم دراسة قدرة هذا البوليمر على استخلاص الفلزات المسببة لتلوث المياه بواسطة طريقة الوجودات حيث تم قياس تركيز ايون الفلز قبل و بعد الاستخلاص بواسطة قياس %M بالامتصاص الذري اللهبى اضافة الى قياس امتصاصية محلول الايون الفلزي قبل وبعد التعقيد كما تم دراسة استقرارية المعقدات في المحاليل بطريقة اوستوالد للتخفيف.