Foam Supported Humic Acid as Chelating Polymer, Synthesis and Analytical Study

Ali T.Al-Samaraie

Chemistry Department , Collage of Science , University of Tikrit , Tikrit , Iraq

(Received 5 / 10 / 2010 , Accepted 13 / 12 /2010)

Abstract

Humic acid is used as a natural chelating polymer, so in this paper a novel method for supporting Humic acid on a rigid polyurethane foam was adopted. The cured polyurethane foam was used as a chelating polymer for the analytical study of Pb^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} and Cu^{2+} ions by batch method.

The new foam showed an outstanding sorption for the studied ions compared to phenol formaldehyde co-polymer of Humic acid, metal ions recovery and foam regeneration was also studied using (3M) HCl as an eluant.

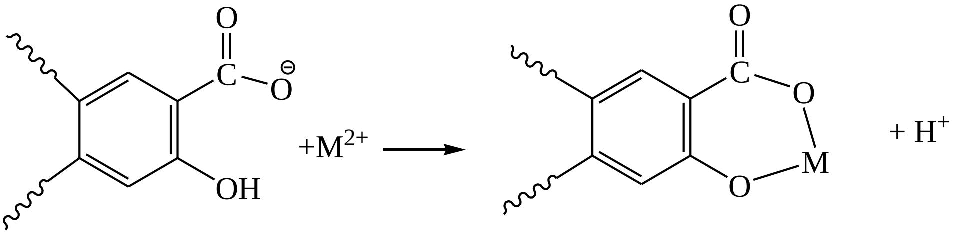
Key words: Humic acid, rigid polyurethane foam, Chelating Polymer, loading capacity, percentage regeneration.

Introduction

Humic acid is one of the three major components of (humus), the organic constituent of soils. Indeed the base soluble but water insoluble part of Humus is usually called Humic acid, a naturally occurring oxygenated polymer mostly as phenolic and carboxylic net work (1,2) Humic acid is used industrially for production of emulsifiers, boiler scale removers and pigment extenders. Humic materials chelate metals and hydrogen bond strongly to proteins and polysaccharides, thus they play an excellent rule as scavenger of metals(3).

The conversion of natural polymers to chelating polymers by chemical modification is used for the production of several modified natural polymer like lignin, chitin, cellulose and humic acid so that to yield chelating resins selective for almost every type of metal(4). Because of the low cost of starting materials, such polymers have been proposed for selective removal of precious metals form sea water, heavy metals removal from weast water and many other applications (5).

Humic acid was used for the chelating of several metal ion i.e. Co^{2+}, Cu^{2+},Ni^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+} and Ca^{2+}, chelating mechanism was proposed to proceed via both phenolic and carboxylic groups of the structure (6,7).



The complex structure of Humic acid shows several heterocyclic nitrogen containing compounds and groups, (Fig1) shows part of this structure(2,8).

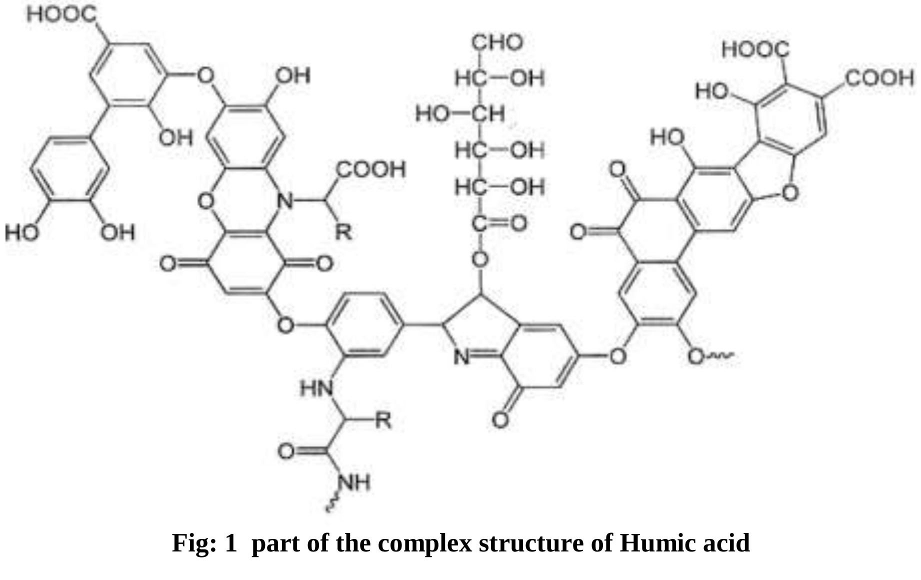
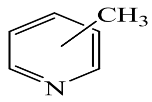
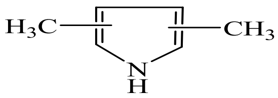
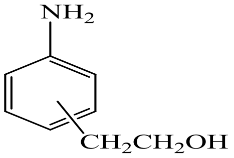


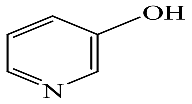
Fig: 1 part of the complex structure of Humic acid

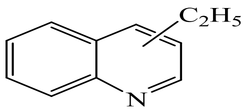
Pyrolysis GC-Mass study of Humic acid and other organic matter isolated agricultural, forests and rivers showed several nitrogen containing compounds some of which are listed below(19,20).

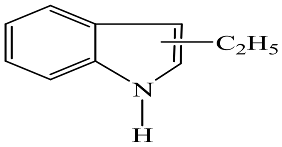


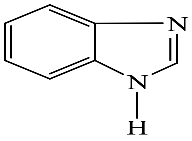


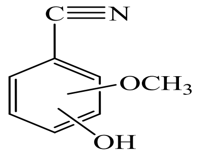


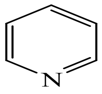


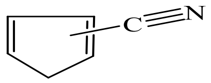












The presence of nitrogen as a heteroatom in the structure of humic acid along with oxygen (phenolic and carboxylic groups) gives a good explaination for the high chelation capacity of humic acid towards several soft ,border line and hard metal ions usually sorbed with chelating polymers incorporating humic acid (5,6,8,11)

The solubility of (humic acid – metal ion) complexes at different pH values was the major limitation for using humic acid as a chelating polymer. Copolymers incorporating humic acid with phenol and formaldehyde solved the solubility problem but with a high decrease in chelation sensitivity (10).

In the present work a novel method for the supporting of humic acid on a regid polyurethane foam is described. The foam support chelating polymer showed a large increase in the chelating capacity for several metal ions compared to other resole based chelating polymers containing humic acid.

Experimental

I) Materials

1. Humic Acid was obtained by extraction from soil adopting previous methods (2,13)

2. Polyester polyol , 4,4-diisocyanate diphenyl methane (MDI) and amine activator was supplied by the Iraqi plastic Co. with the following specifications : Polyester polyol : Average molecular weight 700 , water content 0.1% max , acid number 0.1 and d= 1.094g/cm^3 at 20°C . Amine activator : 33% tetra ethylene diamine and 67% dipropylene glycol , d=0.88g/cm^3 at 20°C and water content less than 1.5%

3. Standard solutions of metal nitrate (1000mg/ml) for Zn^{2+} , Co^{2+} , Pb^{2+} , Cu^{2+} , and Ni^{2+} ions were supplied by Fluka Co. and diluted with deionized water.

II) Instruments

1- Du Pont thermoanalyser model 990 was used for TGA .

2- FT-IR Spectrophotometer model Shimadzu 8400.

3- Shimadzu AA- 630-12 Atomic Absorption Spectrophotometer .

III) Preparation and characterization of foam supported humic acid

Reaction vessel was charged with polyester polyol (5g) , humic acid (0.5g) , amine catalyst (0.1g) and few drops of distilled water as foaming agent . All the components were mixed well using mechanical stirrer with gentle heating to (50°)C , to this mixture 4,4-diisocyanate diphenyl methane – MDI (5g) was added and fast mixing was carried .

The produced foam was post cured at room temperature for (6)hrs then at (100°)C for (2)hrs , the rigid foam containing 5% of its weight humic acid was grinded and characterized by FT-IR using Shimadzu 8400 Spectrophotometer , FTIR spectrum was recorded as KBr disc .

The spectrum of the foam fig(2) exhibits the characteristic carbonyl stretching absorption of the carboxylic groups of the humic acid and the stretching absorption of the carbonyl of the urethane groups of the foam [at 1707cm^{-1} and 1668cm^{-1} respectively] .

The sharp absorption at 1599cm^{-1} can be attributed to the C=N stretching of the C=N groups in the heterocyclic nitrogen containing compounds of the humic acid, other characteristic bands of the IR are shown in table(1).

Table (1) Characteristic IR-spectral bands of the Prepared Polyurethane foam loaded with humic acid

ν cm^{-1}	Assignment
(3330-3390)br	Stretching Vibration of bonded N-H groups of PU overlapped with O-H Stretching Vibration of the free and carboxylic OH groups of humic acid
3037(w)	Stretching Vibration of aromatic C-H
2972,2877(m)	A Symmetrical and Symmetrical Stretching Vibration respectively for (C-H) of the methylene groups
2272(s)	Stretching Vibration of unreacted isocyanate groups
1539(s)	(C=C) Stretching Vibration
1514(s)	(N-H) Bending Vibration
1232(m)	(O-H) Stretching Vibration
1095(s)	(C-O) Stretching Vibration of urethane
817(m)	(C-N) Bending of the aromatic Skeleton of MDI
511(w)	(C-N) Bending of the aromatic Skeleton of MDI

br=broad , w=week , m=medium , s=strong

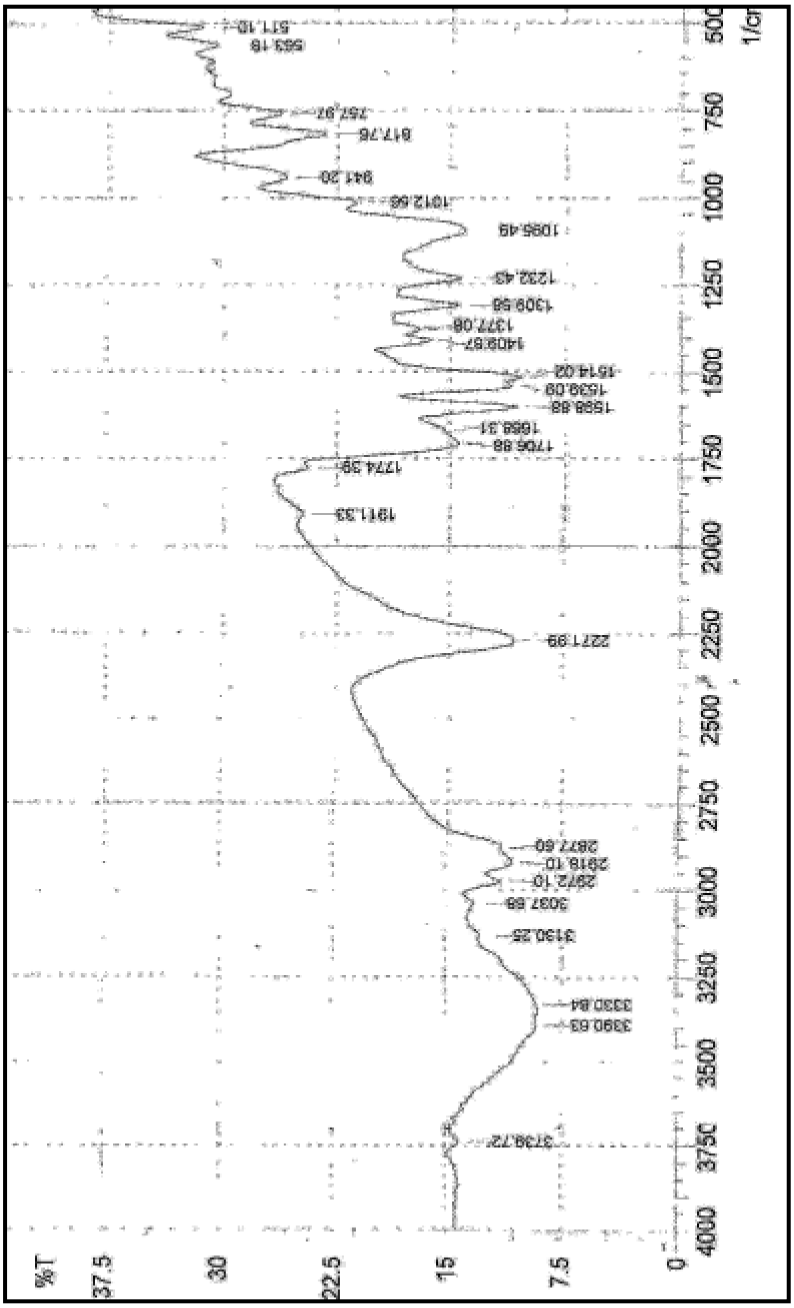


Fig. 2 FTIR- spectrum for the new foam supported humic acid

Then the thermal stability of both Humic acid loaded foam and the unloaded foam was studied by TGA technique. The TGA thermograms are shown in fig.(3) and the data of the thermal analysis in table(2).

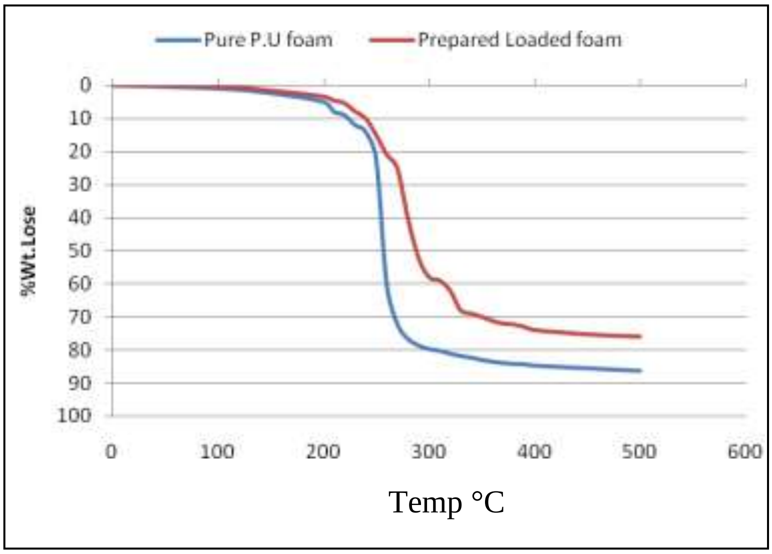


Fig (3): TG curve for the pure and loaded polyurethane foam

Table (2) Some thermal stability characteristics for pure and loaded polyurethane determined from TGA thermograms .

Foam type	Ti (initial decomposition temperature °C) idt	Rate of Decomposition % / min	T50% (Temperature of 50% weight loss) °C	% Char Content	Temperature °C
Unloaded PU foam	225	23.5	257	13.8	500
Loaded PU (The prepared resin)	243	17.6	289	24.0	500

The thermal stability characteristics of humic acid loaded polyurethane foam are increased clearly as shown in both fig(3) and table(2) . Increment in the decomposition temperature and the % char content of humic acid containing foam can be attributed to the aromatic and heterocyclic compounds presented in the complex structure of humic acid, a result much in line with previous studies on the thermal characteristic of loaded polyurethane foam(14 , 15) .

IV) Adsorption Experiments

The adsorption of divalent metal ions at different pH values (2-8) and different time intervals required for the chelation equilibrium were developed by batch method in which (0.1g) of the dry resin (mesh size 80) and 25ml of metal ion solution (150mg/ml) at different pH range of (2-8)were placed in a 100ml glass stopper flask. Shaking time ranged from 15min. to 24hrs. in a thermostated orbital shaker at room temperature and a speed of 150rpm.

Samples were filtered and the remaining concentration of metal ions were determined in the filtrate by atomic absorption spectroscopy using air-acetylene flame at the optimum working conditions for each ion(16). The adsorped cation quantity (weight capacity) at certain pH and time was calculated from the following relation(17) .

$$\text{Ads} \cdot \text{M} = (C_i - C_f) \cdot K \cdot V$$

Where Ads · M is the adsorped cation concentration (mg ion / g resin), C_i and C_f are initial and final concentrations of the studied ion in solution (mg/ml) respectively. K is a factor for the conversion of the foam weight used in the experiment into 1g and V is the volume of metal ion solution (L).

V) Foam regeneration

Loaded foams with the highest treatment time and metal ion concentration were treated with 3M HCl as eluent at different time intervals for the study of the regeneration of the foam. The percentage recovery of each ion was determined using Atomic Absorption Spectrophotometery.

Results and Discussion

A – Sorption efficiency

The loading capacity(L.C.) of the new polyurethane supported humic acid was determined towards different divalent metal ions (Cu^{2+} , Zn^{2+} , Co^{2+} , Ni^{2+} and Pb^{2+}) in mg ion / g resin. Two factors affecting L. C were examined namely sorption time and pH while other factors were selected according to previous studies(14-17) .

Figures (4) to (8) shows the effect of sorption time and pH on the total loading capacity of the new foam .

The new foam supported humic acid showed an outstanding loading capacity toward all the studied ions compared with a copolymer of humic acid with phenol and formaldehyde prepared and studied previously by Mahdi(10).

The equilibrium time (after which the increase in the loading capacity increased with time becomes very low) for all studied ions was between 1 to 3 hours. This time decreases with increasing the pH of the studied metal ion solution. The large increase in the loading capacity for our foam supported humic acid can be attributed to the high surface area, good sorption characteristics and favorable hydrodynamic and aerodynamic properties of the cellular system of the foam(15) used as a support for humic acid. Table (3) shows the total loading capacities of the prepared new foam (with 5% humic acid) and the previously prepared phenol formaldehyde copolymer containing 30% of its weight of humic acid.

Table(3) Total loading capacity of the foam supported and the phenol formaldehyde co-polymer of Humic acid

Metal ion	Total loading capacity mg ion / g resin	
	Foam 5% humic acid	Phenol formaldehyde co-polymer 30% humic acid
Cu^{2+}	25.6	9.0
Zn^{2+}	22.2	14.0
Co^{2+}	12.9	5.0
Ni^{2+}	14.4	12.0
Pb^{2+}	31.9	16.0

The results of table (3) clearly revels the advantages of the new foam supporting method not only by the substantial rise of loading capacity but also by the possibility of decreasing the amount of the expensive analytically active reagents, with increasing the sorption characteristics at the same time.

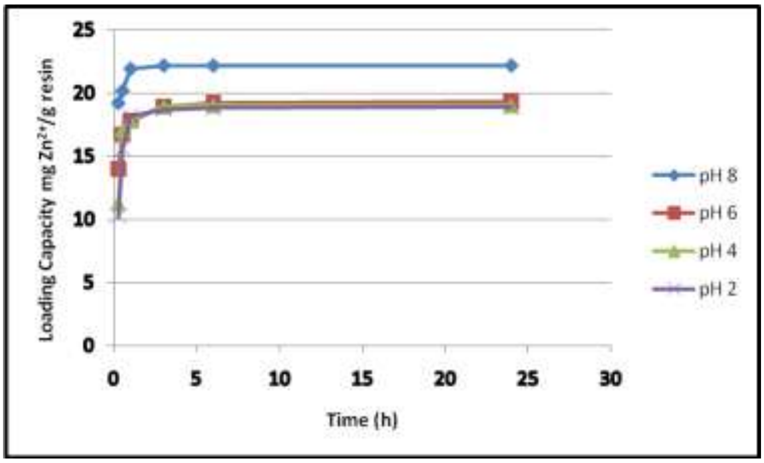


Fig (4) : effect of treatment time and different pH on the loading capacity of the new foam for the (Zn^{2+}) ions

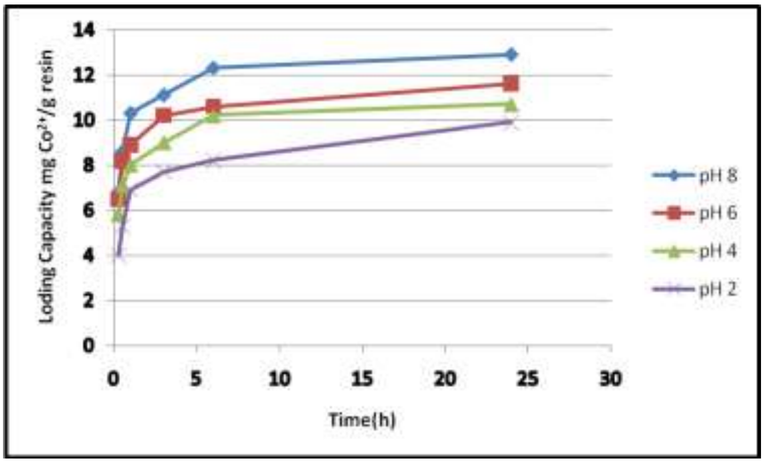


Fig (5) : effect of treatment time and different pH on the loading capacity of the new foam for the (Co^{2+}) ions

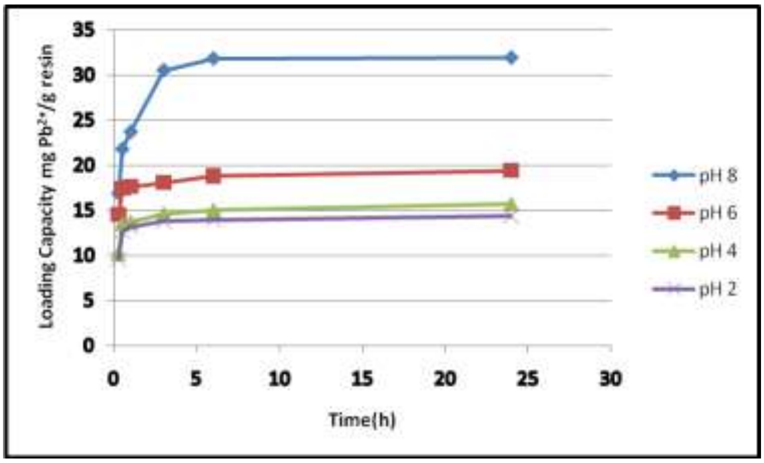


Fig (6) : effect of treatment time and different pH on the loading capacity of the new foam for the (Pb^{2+}) ions

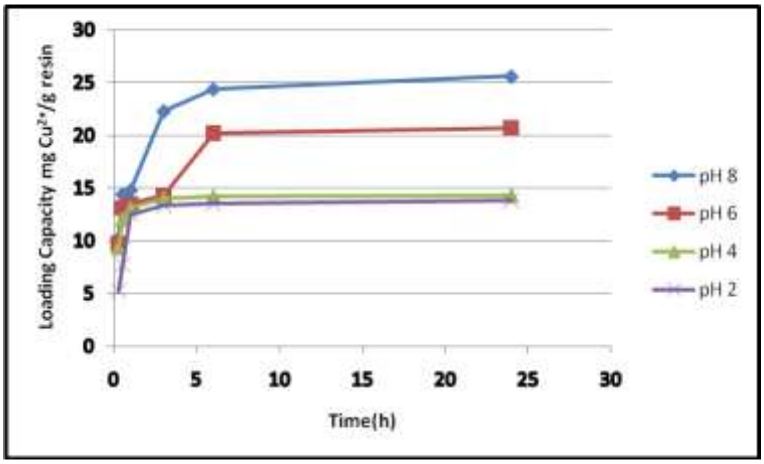


Fig (7) : effect of treatment time and different pH on the loading capacity of the new foam for the (Cu^{2+}) ions

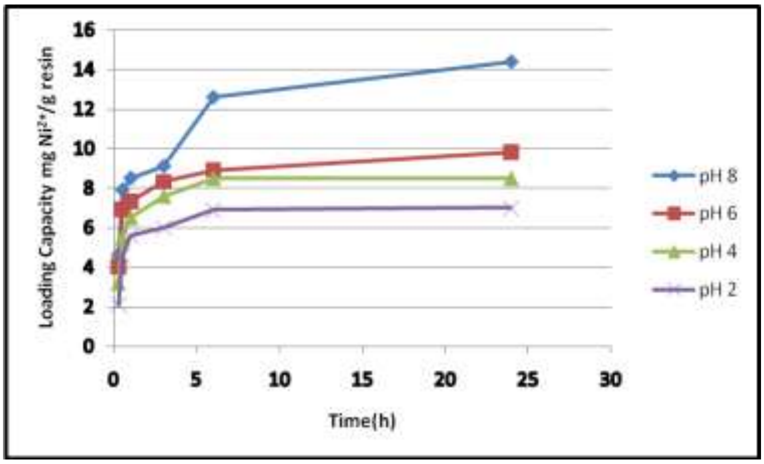


Fig (8) : effect of treatment time and different pH on the loading capacity of the new foam for the (Ni^{2+}) ions

B- Metal ions recovery

The recovery of metal ions from loaded foam was in the following order

Zn^{2+} , Ni^{2+} > Pb^{2+} > Cu^{2+} > Co^{2+}

In which complete recovery for Zn^{2+} and Ni^{2+} ions and more than 70% of every ion was recovered after 6h of treatment time with 3M HCl as shown in fig(9) . These results enhances the application of such loaded foams for preconcentration and recovery of different metal ions from their diluted solutions.

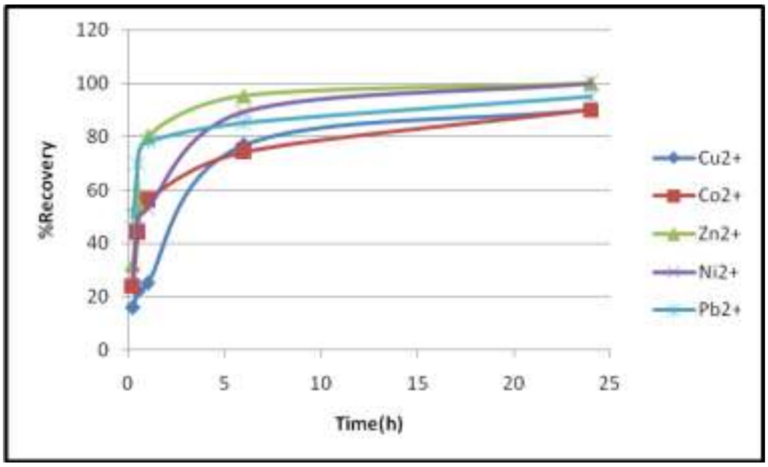


Fig (9): Metal ions recovery from loaded foam after treatment with 3M HCl

References

1. M. Schnitzer and S. U. Khan, Humic Substances in the Environment, Marcel Dekker, New York, (1972) .
2. F. J. Stevenson, Humus Chemistry: Genesis, Composition, Reactions, Wiley – Interscience, New York, (1994) .
3. M. P. Stevens, Polymer Chemistry, Oxford University Press, Inc., New York, (1999) .
4. H. Baker and H. M. Abdel-Halim, Asian J. of Chem., 19(1), 233-245 (2007) .
5. S. K. Lister and M. A. Line, Bioresour. Tech., 79, 35 (2001).
6. M. Pesavento , A. Profuma, G. Albert and F. Conti, Anal. Chim. Acta., 480, 171 (2003) .
7. I. H. Suffet and P. MacCarthy , Aquatic Humic Substances , Amer. Chem. Soc. Washington , (1989) .
8. Y. S. Ho, W. T. Chiu, C. S. Hsu and C. T. Huang, Hydrometallurgy, 73, 55 (2004) .
9. H. Baker and F. Khalili, Anal. Chim. Acta., 542, 240 (2005) .
10. S. A. Mahdi, M. Sc. Thesis, University of Basrah, (1989) .
11. N. Senesi, in “ Biogeochemistry of Trace Metals”, D. C. Adriano (ed.) , Lewis Publishers, U. S. A., (1992).
21.
12. R. Baigorri, M. Fuentes, G. Gonzalez – Gaifano, JM. Garcia – Mina, G. Almendros and F. J. Gonzalez – Vila, J. Agric. Food Chem. 57(8) , 3266-3272 (2009) .
13. S.M. Griffith and M. Schnitzer , Soil Sci. Soc. Amer. Proc., 39, 862 (1975) .
14. I. S. Ahamed , A. K. Ghonaim , A. A. Abdel Hakim M. M. Moustafa and A. H. Kamal El-Din, J. Appl. Sci. Res. , 4(12) , 1946-1958 (2008) .
15. A. T. AL-Samaraee and G. A. Adam , National Jor. of Chem. , 1 , 158-171 (2001) .
16. D. Mahanty and S. Samal, Eur. Journal of Chemistry , 6(4) , 1035-1046 (2009) .
17. E. Taboada, G. Cabrera and G. Cardenas, J. Chil. Chem. Soc. 48(1) (2003) .
18. F. Martin , J. C. del Rio, F. J. Gonzalez – Vila and T. Verdejo , J. Anal. Appl. Pyrolysis 31, 75-83 (1995)
19. K. L. Steelman , M. W. Rowe , T. W. Boutton , J. R. Southon, C. L. Merrell and R. D. Hill, J. Archaeol. Sci., 29, 1189-1198 (2002) .
20. X. Z. Song and S. O. Farwell, J. Anal. appl. Pyrolysis 71, 901-915 (2004).

حامض الهيوميك المسند على الرغوة اليورثانية كراتنج كلابي ، تحضير ودراسه تحليلية

علي طه علي السامرائي

قسم الكيمياء ، كلية العلوم ، جامعة تكريت ، تكريت ، العراق

(تاريخ الاستلام: ٥/ ١٠ / ٢٠١٠ ، تاريخ القبول: ١٣ / ١٢ / ٢٠١٠)

الملخص

يعتبر حامض الهيوميك بوليمر كلابي طبيعي لذا تم في هذه الدراسة استخدام طريقة جديدة لاسناد حامض الهيوميك على رغوة بولي يورثاينية صلدة حيث جرى استخدام الرغوة تامة التقسية كراتنج كلابي للدراسة التحليلية لايونات Pb^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+}, Cu^{2+} بطريقة الوجبة.

إن الرغوة المحملة الجديدة أظهرت قابلية فائقة على امدصاص هذه الايونات من محاليلها المائية مقارنة بكوبوليمرات الفينول فورمالديهايد الحاوية على حامض الهيوميك.

شمل البحث أيضا دراسة استرجاع الايونات وإعادة تنشيط الرغوة المحضرة باستخدام حامض الهيدركلوريك بتركيز 3M كعامل شاطف.