

JOURNAL OF KUFA-PHYSICS

www.uokufa.edu.iq/journals/index.php/jkp | ISSN: 2077-5830



Synthesis of Polyurethane Based on (Resol Novolac Resin- Polyethylene Glycol) Copolymer and Their Analytical Study

*Maiada Abdulaa Adnan

Chemistry Department, College of Science, University of Missan. *Corresponding Author E-mail: m.alhusain19@yahoo.com

ARTICLE INFO .:

Article history: Received: 8 JUL, 2018 Accepted: 13 NOV, 2018 Available Online: 26 JUL, 2019

Keywords:

Resol novolac resin Copolymer Poluurethane Column Chromatography method and TGA

ABSTRACT:

Resol novolac resin was prepared by condensation of novolac resin with formalin solution in the presence of sodium hydroxide as catalyst, then new copolymer were prepared by reaction of this resin with polyethylene glycol. This new copolymer was supported on polyurethane foam as solid phase and applied to separation a mixture Cr(III) and Cd(II) ions from aqueous solutions prior to the determination by flame atomic absorbtion spectrometry. The optimum conditions of some parameters effect on recovery of the ions such as acidity, eluent condition, shaking time, and eluent flow rate were investigated. At pH 4,5, the maximum recovery (90%) of Cd(II) by stripping with 40 ml of (1N) nitric acid ,while for Cu (11) was 80 % with 50 mL of (2N) nitric acid. On the other hand thermal stability for the prepared polyurethane was evaluated by TGA.

DOI.: http://dx.doi.org/10.31257/2018/JKP/2019/110118

تحضيرودراسة تحليلية للبولى يوريثان المحضر من (راتنج الريسول نوفولاك – بولى اثيلين كلايكول) المشترك ميادة عبد الله عدنان

قسم الكيمياء - كلية العلوم - جامعة ميسان

الكلمات المفتاحبة:

راتنج ريسول نوفولاك كوبوليمر للبولي يوريثان عمود الكروموتوغرافي لتحليل الحراري الوزنى

حضر راتنج (الريسول - نوفولاك) من تفاعل تكثيفي بين النوفولاك والفورمالين باستخدام هيدروكسيد الصوديوم كعامل مساعد ، ثم حضر كوبوليمر جديد من خلال تفاعل الناتج مع البولي اثبلين كلايكول واسناد الكوبوليمر الجديد على الرغوات الاسفنجية الصلدة، واستخدم الكوبوليمر المسند على البولي يوريثان لفصل مزيج من ايونات الكروم والنحاس من محاليلهم المائية باستخدام مطيافية اللهب الذري تم تثبيت الظروف المثلى لعملية استرجاع الايونات والمتمثلة بالحامضية ، نوع وتركيز الشاطف ، زمن الرج ، ومعدل جريان الشاطف . من خلال النتائج لوحظ عند الاس الهيدروجيني ٥٤٠ تكون نسبة استرجاع ايون الكادميوم هي ٩٠% عند تركيز ١ نور مالي من حامض النتريك ، في حين نسبة استرجاع ايون النحاس كانت ٨٠ % وبتريكز ٢ نورمالي من نفس الحامض . من ناحية أخرى تم دراسة الاستقرار الحراري للبولي يوريثان المحضر باستخدام تقنية التحليل الحراري الوزني.

1. INTRODUCTION

Phenolic resins are some of the oldest synthetic polymers. Phenol - formaldehyde resins which are obtained from phenols and formaldehyde depending on the relative amounts of the reactants and the nature of the catalyst , the reaction produce either thermoplastic resins (novolac) in acidic medium or thermosetting resins (resols) in basic medium⁽¹⁾.

Many research works has been carried out on the preparation and characterization of Phenolic copolymers. Copolymer is found useful applications adhesive, as high temperature flame resistant, coating materials, catalysis and chelating polymers ion or exchange resins^(2,3). Chelating resins have been widely used for separating and treating industrial which contains heavy metal ions, Phenol-formaldehyde resin is suitable for preparing ion exchangers or chelating agents because they have hydrophilic groups, so that phenol-formaldehyde resin has good adsorption for metal ions⁽⁴⁻⁷⁾. According to the World Health Organization (WHO), the heavy-metals of most immediate concern are chromium, nickel, cadmium, copper, lead, mercury and zinc. The removal of heavy-metal ions from industrial and human wastewater is attracting many types of polymers increased attention. such as , phenol formaldehyde resin, poly(acrylic acid) grafted cellulose and macro porous poly(glycidyl methacrylate-co-ethylene glycol dimethacrylate) have been reported for the removal of Cu(II), Cd(II) and Cr(III), an example of these polymers have a porous structure and many hydrophilic groups, which can be used for heavy-metal ion removal (8-10). Many research using polyethylene glycol at preparation chelating polymers (11.12). The flame retardancy of toughened phenolic foams was evaluated by limiting oxygen index, and cone calorimeter. Copolymer PEGPs causes an toughness of phenolic Moreover, the thermal stability of PEGPs and

the toughened foams was investigated by TGA analysis (13). Thermal degradation of phenolic /PEG takes place in multiple steps and the thermal degradation, which concurred with the data from the thermal degradation of novolac type phenolic resin/PEG blends by TGA analysis (14,15). Carbon foams are lightweight materials with high mechanical strength, low thermal expansion coefficient, adjustable thermal conductivity and large external surface area, which make them suitable materials for energy storage, catalyst supports filters (16,17). Polyurethane (PU) foams with functionalized colloidal super paramagnetic iron oxide nanoparticles and polytetrafluoroethylene has been reported, which can be used efficiently to separate oil from water (18).

Good chelating sorbent was synthesized by covalently linking carbon Nano-fiber with ion exchange polyurethane with good sorption properties of platinum (IV) and successfully applied for extraction of platinum (IV)from different samples of ores⁽¹⁹⁾. Polyurethane foam was modified by the addition of halogen atoms and amino groups into the foam matrix in order to increase its polarity for the sorption of ionic species with high accuracy of the procedure was verified by the analysis of food, ground water and pharmaceutical samples ⁽²⁰⁾.

The aim of this study was planning to characterization synthesis and copolymer resin supported on polyurethane foam and study the ability of this foam to up take some metal ions. These foam synthesized through two steps, first copolymer prepared from resol novalac resin with PEG (molecular weight 600 g per mole) and second polyurethane was prepared from the reaction of copolymer resin with methylene diphenyl diisocyanate .The optimum condition of the efficient to up take the ions by this polyurethane resin was determined and also use this polyurethane to separation of mixed ions by column technique.

2. EXPEREMENTAL

2-1- Chemicals

All the standard chemicals used during this work are listed below , where the purity and the suppliers of those chemical are given as well:

Acetone 99% , Formalin solution 37% , phenol 98 % were supply from Sigma – Aldrich.

Polyethylene glycol (PEG- molecular weight 600 g per mole) , Hydrochloric acid 36% were supply from Riedel-de Haen. Sodium Hydroxide pellet 99% and polymeric methylene diphenyl diisocyanat (PMDI) with NCO content 35% were supply from Aldrich Chem.While metals as nitrate form $\text{Cu(NO}_3)_2.5\text{H}_2\text{O}$ and $\text{Cd(NO}_3)_2$ supply from Merck – Germany company.These material used with out further purification .

2.2 FTIR –spectroscopic test:

The FTIR spectra of cured resin prepared in this study were performed in shimadzu, FTIR-8400. (Chem.Dep , College of Sci. University of Basrah) .Each spectrum was record in a frequency rang of 400-4000 cm⁻¹ using potassium bromide (KBr) disc.The KBr was previously oven-dried at 300 C⁰ to reduce the interference of water.

2.3-Thermogravemetric analysis (TGA):

TGA measurement were evaluated on TGAQ50 V20.13 Build 39. (Chem.Dep , College of Sci. University of Basrah) Dynamic scan were measure in temperature range 25-700 C^0 , at heating rate $50C^0$ / min.Under nitrogen atmosphere at flow rate 30ml/min.

2.4-Viscosity mesyrements:

The viscosity of the resins were measured using Brookfield rotary viscometer Type Alpha Series Code V100002 with spindle (Chem.Dep , College of Sci. University of Basrah) at 25 $\rm C^0$.An average value of three replicate measurements was reported.

2.5 Synthesis

2.5.1 Synthesis of Novolac.

Novolac were prepared dy reacting phenol with formaldehyde in the molar ratio (1: 0.7) in the presence of Oxalic acid catalyst in three necked flask fitted with a mechanical stirrer , water condenser and thermometer . The reaction mixture was heated under hot plate and allowed to reflux at about 100 c for 2-3 hours . when the resin separated from aqueous phase the reaction was neutralized with phosphoric acid (10%) , filtered , washed several time with hot distteld water in order to remove unreacted phenol. The resin formed contains 4-6 benzene ring per molecule according to litreture (21).

2.5.2. Synthesis of Resol Novalac Resin (RN)

In three necked flask fitted with a mechanical stirrer water condenser thermometer, (50 mL) of formalin solution was added and heated to about 40-50 C. Then (25 g) of novolac was added gradually mean while sodium hydroxide solution (10%) was added drop wise until the PH was 9.5. After complete the addition of novolac the reaction mixture still in good mixing and the temperature rice to about 65-70 C for 3 hrs., to get viscose material , neutralize with (10%) phosphoric acid in order to separate the product as thick resin, washed several time with hot distelled water inorder to remove unreacted novolac and formalin, then small amount of absolute ethanol was added to solve the resin in order to protect the resin from curing.

2.5.3 Reaction of RN with PEG 600 (RNG)

PEG (10 g) are place in a reaction flask previously with a mechanical stirrer, then (5 g) of uncured RN is added under constant stirring until a homogeneous mixture is obtained subsequently, the temperature is allowed to stay at about 70-80 $\rm C^0$ and the reaction is stirred for (2hrs.). The final mixture is obtained as brown viscous material.

2.5.4 Synthesis of Polyurethane

Polyurethane was prepared from RNG resin and PMDI. In a reaction flask equipped with mechanical stirrer (10g.) of RNG resin was place , then triethylamine (1%) was added with good mixing . Finally was (10g.) of PMDI was added gradually, for about (30min.) .Then the reaction mixture heated with continues stirringfor (1.5 hrs.) at (50 $^{\circ}$ C). The product is then removed from the stirring and placed in an oven at (100 $^{\circ}$ C) for about (3hrs.) to complete polymerization , post cur at (140 $^{\circ}$ C) for 1hrs.

2.5.5- Dry solid content:

The percentage of dry solid content of resin was calculated by the following equation (22):-

$$S \% = S_1 / S_2 \times 100 \dots 1$$

Where S_1 and S_2 the weight of the resin befor and after dried (3 hurs. At 105 C^0) respectively.

2.5.6- Free formaldehyde content:

The free formaldehyde content of the prepared resin (novolac and resol novolac) were determined by the hydroxyl amine hydrochloride method. Accurately weighted about 0.003 -0.005 g of the resin sample was transferred into 250 ml beaker and dissolved in 50 ml methanol .Simultaneously the pH value of the solution was adjusted to 3.5 by adding 1 N hydrochloric acid solution. 25 mL of 10 % hydroxylamine hydrochloride solution was added and stirred for 10 min. Finally the mixture solution was titrated with 0.1 Normal (N) sodium hydroxide solution. Free formaldehyde content was calculated by the following equation:

Where V_1 and V_0 are volumes of sodium hydroxide reguired in the titration for sample and blank respectively. C is the exact normality of sodium hydroxide

solution . m is the weight of sample resin in grams .

3. RESULT AND DISCUSSION

3-1-Reaction Schem:

Novolac are the first synthetic resin to be prepared by acid catalyzed addition – condensation of phenol with formaldehyde⁽²³⁾. and have already been used in practical application.In this research novolac was synthesis using oxalic acid as catalyst and in the ratio of phenol/ formaldehde 1:0.76 .The chemical structure of novolac are listed below with some physical properties.

Schem .1: Chemical structure of novolac resine.

Apperance: slightly yellow.

Melting point: $88-95 \, \text{C}^0$.

Free phenol: less than 1%.

During the curing of novolac hexamethylenetetramine is freguently used as curing agent (24) however the resultant curing products usually tend to contain amine derivatives and the unreacted curing agent as impurites, which often lead to coloration and degradation of the products, also the final product is free of reactive group. Here in this research new methd used to convert novolac to new resin containe methylol group (-CH₂OH) which was undergo self condensation during heating by reacted novolac resin with excess of formaline solution in the presence of sodium hydroxide as catalyst. The reaction pathway was shown in schem 2.

Apperance: very thick bbrowm in color.

Dry solid content : 51 % 3 hurs at $105 \,\mathrm{C}^0$.

Gel time: 21-25 min. Viscosity: 321 mpa.s.

The apperance of this resin are thick viscuse soluble in alcoholic solvents. This resin under heat curing convert to brittle phenolic resin which fusible and not soluble in most organic solvent, so inorder to modified this resin flexeble aliphatic chain well be introduce in the back bone of this polymer. Here new copolymeric material prepared by reaction of this resin with polyethylene glygol (PEG- with molecular weight 600g/mole) in the presence of diluted sulphuric acid as catalyst. The reaction are shown in schem 3.

Schem. 3: synthesis of resol novolac resin-co-polyethylen glygol.

This resin have the following specification:

Viscosity: was 452 m pas.

Apperance: brown viscuse material.

Density: 1.121 g/cm^3 .

Solubility: soluble in most polar organic solvents.

Dry solid content : 55 %. 3hrs at 105 C^0

Gel time : 32-37 min. at 100 C^0 .

Finally this copolymer will be converted to new polyurethane as shown in schem 4, and use its as new material to study the ability to take up some polution elements from aqueouse solution.

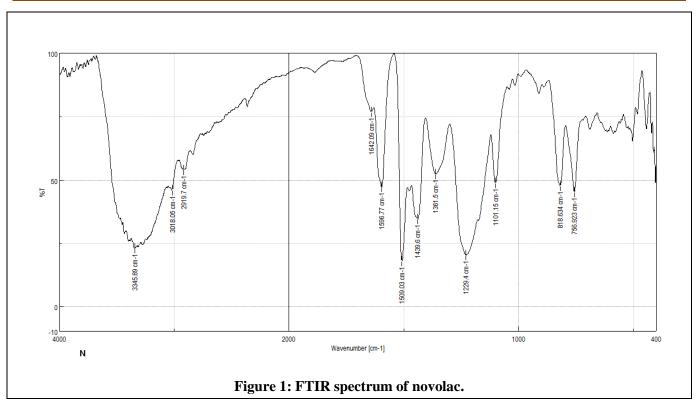
$$\begin{array}{c} H \stackrel{\downarrow}{+} OH_2CH_2C - O \stackrel{\downarrow}{+} \stackrel{\downarrow}{C} \stackrel{\downarrow}{-} OH \\ \\ CH_2 \\ \\ CH_2$$

Schem .4: Proposed structure of polyurethane repeating unit production from copolymer and MDI.

3-2-FTIR-analysis:

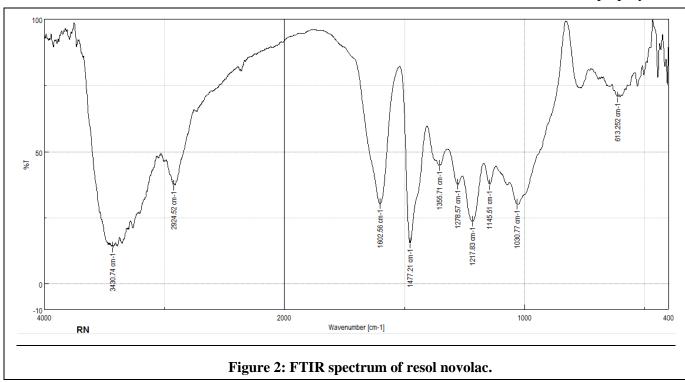
Fourier transformation Infrared spectroscopy is an important and common technique to idetermaind the active group, the chemical structare, chain orientition and compostion of different componds which may be organic, inorganic and polymers (25). This spectroscopy is an important to exaimne the polymers, it allows the analysis of structural features like functional groups (hydroxyl, carbonyl,amines, urethane and aromatics ets), and chain consititution.

FTIR spectra was used by forming KBr film.For novolac resin the Figure (1) show significant peaks at 3345 cm⁻¹ due to –OH strtching vibration , 2919 cm⁻¹ for CH₂ stretching vibration. C-C aromatic double bond in the region 1642 and 1596, absorption beak in the region 1439 due to CH₂ bending while C-C double bond bending vibration at 1361 cm⁻¹ ,while at 818,756 cm⁻¹ was due to asym.stretching of aromatic C-C-OH and CH out of plane.The spectrum was shown in Figur (1).



In the case of resol novolac resin the spectrum was shown in Figure 2. , some absorption bands appear at $3430~\text{cm}^{-1}$ due to the –OH stretching vibration, more intense band at $2924~\text{cm}^{-1}$ was attributed to CH_2 , also band at

1602 cm⁻¹ related to C-C double bond. Anew band appear at 1030 cm⁻¹ due to C-O-C which is not exixt in the spectrum of novolac. Figure 3. Show the FTIR spectra of novolac and resol novolac prepolymers.



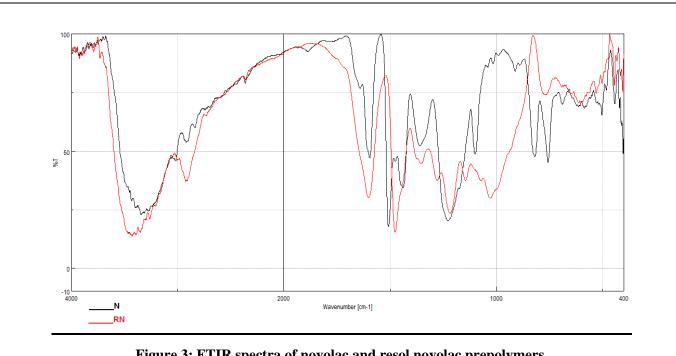
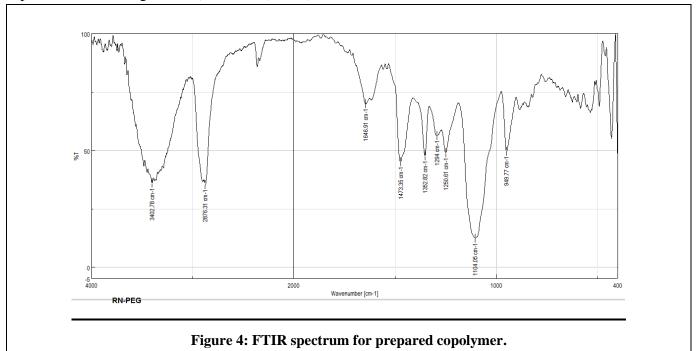
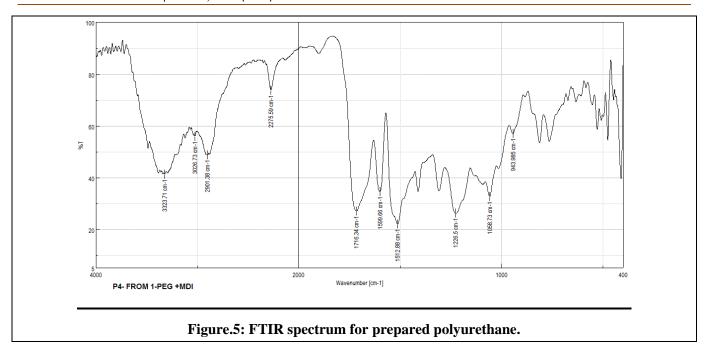


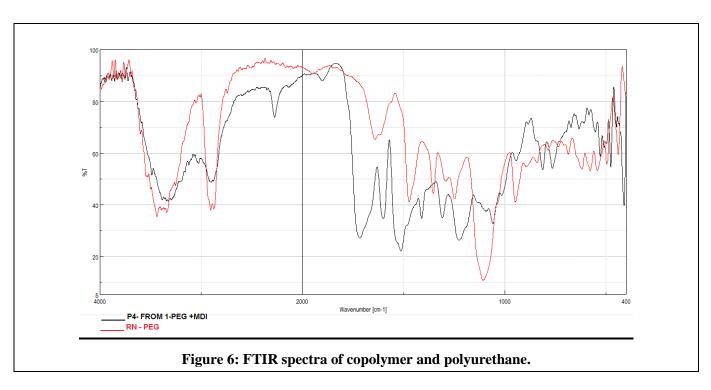
Figure 3: FTIR spectra of novolac and resol novolac prepolymers.

Finally the spectrum of prepared polyurethane foam in this study showed cm⁻¹ absortion peak at (1716)(C=O)stretching of urethane linkage obtained from the reaction of (NCO)groups present in MDI with (OH) groups present in the copolymers, while the absorption peak at 3323 cm⁻¹ due to (N-H) units in the polyurethane chains. The other observed peaks in the FTIR spectrum were assigned as (2901 cm⁻¹) for (C-

H) symmetric stretching of CH₂ groups, also there is absorption peak at (1512 cm⁻¹) is indicative of urethane linkage (C-N-H)⁽²⁶⁾. Finally peak at (1599 cm⁻¹) due C-C aromatic double bond. Absorption band at 2275 cm⁻¹ appeare in this spectrum indicate to unreactive some of isocyanate groups .The spectrum of the copolymer and polyurethane was showing in Figures 4-6.







4-2-Water absorption test.

The gravimetric method using in static immersion test as a standard method (ASTM D 570) used to calculate water absorption of polymer. PU foam immersed in distilled water at 25°C for (24 hrs.). Weight change was calculated by the following equation

where Esw is the water uptake ratio of the PU foam

W_e: weight of the PU foam after immersion in water for 24 hrs.

W₀: dry weight of PU foam before immersion in water

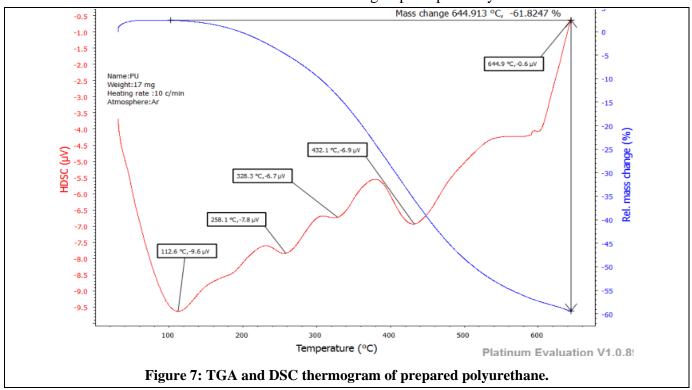
$$E_{sw} = 99.3\%$$
.

5-2-Thermal Analysis TGA/DSC

The important applications of polymers is by the ability to predict product lifetime is valuable because the costs of premature failure in end use can be high⁽²⁷⁾. Thermal analysis (TGA) provides good method for accelerating the lifetime testing of polymers which monitors weight changes in material as temperature changes offers viable alternative to oven aging⁽²⁸⁾. In the TGA method, the material was heating at several different rates through its decomposition region.

From the resultant thermal curves, the tempertuers for aconstant decomposition level are determined .The TGA techninque is particularly usful for the following types of measurements like, Thermal stability, oxidative

stability, decomposition kinenties, filler content of materials, moisture and volatile content. So from the thermograms (TGA and DSC) showed in figuer (7), the TGA result indicate the decomposition temperature of the copolymer was $(294C^0)$ while the char contant at $500C^0$ and 600C⁰ were 51% and 43% respectively. On the other hand the temperture of 50% weight less was $511C^0$. In the case of DSC resultes, there is more exothermic peak indication several reaction between remeaning methylol group or hydroxyl group present in the copolymers to form ether linkage, while the remaining two exothermic peaks at 328C⁰ and 432C⁰ due to the reaction of remaning hydroxyl group and isocyanate group and for the cyclization of remaining unreactive isocyanate groups respectively.



4. METAL ION UPTAKE OF POLYURETHANE FOAM STUDY 4-1- Batch method:

Batch method used to determind the ability of uptake ions percentage and disterbution coefficiente (Kd) of Cu(II) and Cd (II) ions of polyurethane. Figure (10) show the result of this study. Weight (0.1 g) of unloaded polyurethane

foam puted in glass conical flasks with (10 mL) of 50ppm metal ion solution was shaken for 6hrs. in michanical shaker at room tempreture. Metal ion solution at different pH values which was adjusted by adding HCl (0.1M) or NaOH (0.1M) using pH meter. After equilibrium, two phases were separated by filtration and an aliquot of filtration was determined ions concentertion by atomic absorbtion model (AI-

1200) (F.A.A). The calibration curves for metal ions were plotted by analyzing aseris of standard solutions of metal ions as showing in Figures 8 and 9. The unknown concentration was was culculasted from using equations 4:

Uptake ions = $(C_a - C_b) V / W \times 100$ 4

where C_b , C_a are intial and final concentration respectively, v refer to volume of solution while W was weight of polymer. Values of uptake ions percentage show in Figure. (8).

 K_d = (concentration of metal ion in organic phase)/(concentration of metal ion in aqueous phase)......5

The results disteribution coneffiticent (K_d) are illustrated in Table (1).

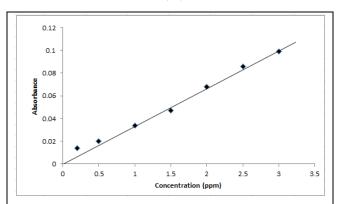


Figure 8: Stander calibration curve for Cd^{+2} at wavelength(228.8nm) and correlation coefficient R^2 0.9979

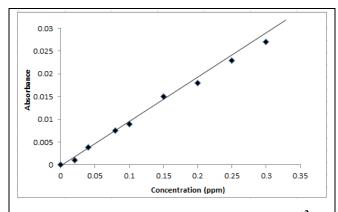


Figure 9: Stander calibration curve for Cu⁺² at wavelength (324.7 nm) and correlation coefficient R² 0.9993.

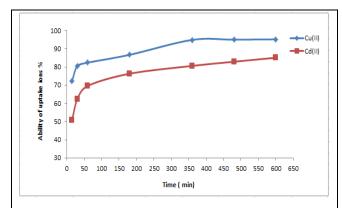


Figure 10: Percentage of uptake ions as a function of time at PH 4.5.

From the Figure (8) show the high ability uptake ions from solution ions by the PU foam and reached the steady state at six hours when the acid medium was (pH 4.5).

Table 1: Distribution coefficients of ions on the PU foam resin at pH 4.5.

Ions	Concentration of HNO ₃ (N)	Distribution coefficient K_d
	1	219
Cu(II)	2	90
	1	82
Cd(II)	2	35

4-2- Column method

The polyuerthan resin was grounded, submerge in a deionised water. The unlouded PU resin was packed into a glass column (12 x 0.4 cm) diameter. The aqueous solution containing mixtuer ions (Cu⁺², Cd⁺²) at equal concetertion (50 ppm) was passed through the column at limmted flow rate, using HNO₃ as elution at optimum concentertion, then collected equal quantity of eluent to determined ions in AAS. All solution were prepaered freshly by dilution of stock solution with deionised water. Serial standed solution were prepaerd at different conceteration to draw calibration carve for each metal.

Recovery of ions (%) = $(C_{recoverd} / C_{removed})$ x 100.....6

C _{recoverd}: concentration of ions recoverd from the resin column(ppm) .

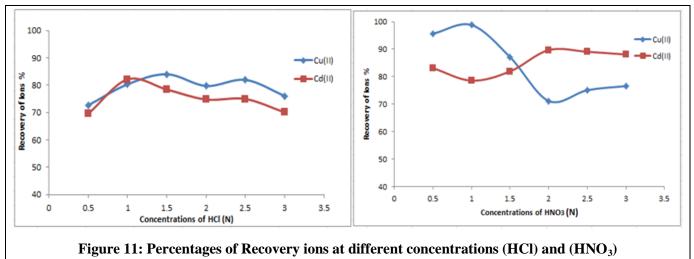
C_{removed}: concentration of ion removed from solustion ions(ppm

4.3- Analytical Study of column separation

4-3-1 Effect of Concentration and Type of Eluent

Different concentrations of the two eluents (HCl and HNO₃) were used to retained the ions on PU foam resin. From figure (11) obtained that percentages of recovery ions were less when using HCl eluent than HNO₃

under pH(4.5) .When HCl eluent highest percentages of recovery ions (84% at 1.5 N HCl) and (82% at 1N HCl) for Cu(II) and Cd(II) ions respectively. Thus, HNO3 had a better elution performance due to its oxidative action and stronger dissolution ability than HCl. Also the highest percentages of recovery ions were (98% at 1N HNO3) and (89% at 2N HNO3) for Cu(II) and Cd(II) ions respectively. So that HNO3 used with two concentrations (1N and 2N) to separation mixture of Cu(II) and Cd(II) ions.



4-3-2-Effect of Eluent Flow Rate

The flow rate of (1N HNO₃) elution was a significant effect on percentages of recovery ions . From results as shown in figure. (12) observed that the percentages of recovery ions increases between 1 and 2 mL/min., and then decrease with increasing flow rate of eluent. The maximum percentages of recovery ions were 90% and 79% for Cu(II) and Cd(II) ions respectively at 2mL/min., flow rate. Thus, the optimum flow rate was selected for elution in other experimental test runs.

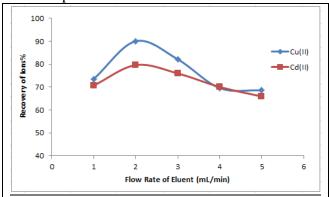


Figure 12: Percentages of Recovery ions at different flow rate (HNO₃) eluent.

4-3-3-Effect of pH

The pH is an important factor in the study of recovery metal ions in analytical because of the competitive reactions between ions and [H⁺] ions in solutions (23). The function pH was adjusted at (2.5, 4.5, 6.5, 8.5 and 10.5) for 50 ppm mixture solution Cu(II) and Cd(II) ions. The resulting shown in Figure (13) show that the optimum pH for percentages of recovery (>90%) of metal ions was 4.5,. When pH value lower than 4.5 the percentage of recovery ions were decreased too, due to the competition between [H⁺] ions for active sites on the PU resin and the metal ions. While the increase in the value of pH occurs precipitation of metals ions so that percentages of recovery ions will be decrease.

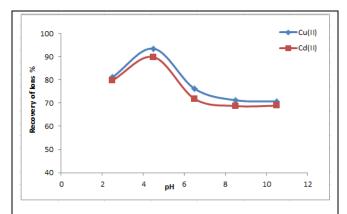


Figure 13: Percentages of Recovery ions at different pH metal ions.

5. SEPARATION OF MIXED IONS BY COLUMN

From the results shown in the Table (1), the PU foam resin can be used to separation mixture of copper and cadmium ions with high efficiency at optimum pH.

The synthesis PU foam resin (10 g) was putted in the colum used to separate a mixture of bivalent $\ metal\ ions\ based\ on\ the\ K_d\ values$ shown in table (1) .Then adjusting the appropriate conditions for the separation (i.e flow rate, type of eluent and pH value). Mixture (20 mL) of both Cu(II) and Cd(II) ions (10 mL ,50 ppm of each metal ion solution) at pH 4.5 passed through the column at a flow rate of 2 ml/min. The Percentages of Recovery ions was carried out with HNO₃ solution. Firstly the cadmium was eluted by 40 mL,1N HNO₃ elution, and then copper eluted by 50 mL, 2N HNO₃. The plot of the percentages of recovery ions eluted of metal ions vs. elution volume is shown in Fig (14). Good curve achieved at 90% for Cd(II) and 80 % for Cu(II) respectively.

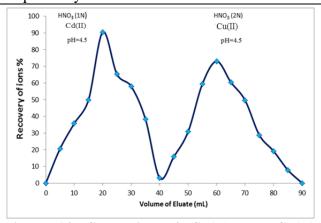


Figure 14: Separation of Cu(II) and Cd(II) mixture ions by PU foam resin.

6. CONCLUSIONS

The novolac resin prepared in this study can be converted to heat cure prepolymer (resol novolac resin) by reacted with formaldehyde in basic medium, and then the resol novolac react with polyethylene glycol through condensation polymerization in acid medium and finally react with MDI to produce new polyurethane foam. These resin were characterized by FTIR which indicate the proposed structure of the repeating units of these polymers and also some physical properties will be determined. Thermal behavior of the polyurethane foame can be evaluated by TGA/DSC technique and from the result show the foam resin have more than decomposition temperature. On the other hand The synthesized PU foam resin obtained percentages of recovery ions. The present investigation shows that chelating PU foam resin can be employed for recovery ions and separation of mixed ions. Batch and column methodsused for separation of metal ions from synthetic bivalent mixture of Cu(II) and Cd(II) ions 90% for Cd(II) and 80 % for Cu(II) respectively .These polymer gives separation efficiency, good regeneration and simplicity; therefor ,this resin can be used in other samples mixtures.

7. REFERENCES

- [1] A. Knop and L. A. Pilato, Phenolic Resins, Springer, Berlin, 1985
- [2] Szabadka O, Varga E, Nagy L: Determination of protonation and metal complex stability constant for chelating monomer and its immobilized in polymer resin). Talanta, 59, 1081-1088, 2003.
- [3] Katkamwar SS. Zade AB, Gurnule WB.: Rahangdale, Terpolymer resin –III-Synthesis and characterization of 8hydroxyl diethiooximamide auinoloneformaldehyde resin), J Appl Polym Sci, 113, 3330-3335, 2009.

- [4] Jain, V.K., Sait, S.S., Shrivastav, P. and Agrawal, Y.K.: Synthesis of amberlite resine XAD-2-o-vaniline thiosemecarbazone to the separation and preconcentration of copper, zinc, lead., Talanta, 1997, 45:397.
- [5] Gorshkov V.I , Lvanone I.V ,Stain I.V .: Selectivity of phenolformaldehyde resin and separation of rare alkali metals , Reactive and Functional Polymers Vol. 38, Issue 2-3.157-176 1998.
- [6] Andres F.C, Milton G, Jose H.C, polyphenolic resin synthesis, optimizing plantain peel biomass as heavy metal absorbent, Polimeros Vol. 25, No.4 2015
- [7] Shu-Feng Li , Xin- Lin Yang and Wen- Qian Hung , Preparation of monodisperese crosslink polymer microsphere having chloromethylgroup ,Chinese Journal of Polymer Science Vol.23, No. 2, 197-202, 2005 .
- [8] Yifng Huang , Dihu Wu ...etl , removal of heavy metals from water using polyvinyl amine , Separation and Purification Technology 158 (28) 124-136 2016.
- [9] K. Hussian Reddy, A .Ravikumar Reddy, Removal of heavy metal ions using the chelating polymers , J of Applied Polymer Scin. 88 (2) 2003.
- [10] Syed Ashraf, Angel Cluley, Ckarlos Mercado, Anja Muller, .Imprinted polymers for the removal of heavy metal ions from water: Water .Sci.Technol. 64(6), 1325-1332 2011.
- [11] Qunwei Tang , Xiaoming Sun, Qinghua Li , Jihuai Wu and Jianming Lin , Synthesis of polyacrylate- polyethylene glygol IPNs gel and its sorption of heavy

- metals., Scince and technology of advance material 100 (5) 2011.
- [12] F. Quintanilla-Guerrero , M.A. Duarte-Vázquez b ,Polyethylene glygol improve phenol removal by immobilized turnip peroxidase Bioresource Technology 99 (2008) 8605–8611.
- [13] Xiaoyu Sui, Zhengzhou Wang , Flame retardant and mechanical properties of phenolic foam toughned with polyethylene glygol phosphate ,: Polymer Advance Technology 24 (6) 593-599 , 2013.
- [14] Francisco Cardona , Alan Laukin , Jessica Fedrigo ,, Novel phenolic resin with improved mechanical and toughness properties, J .Applied. Polym.Scin. 123(4) 2131-2139 , 2012.
- [15] Qunwei Tang, Xiaoming Sun, Qinghua Li, JihuaiWu and Jianming Lin "Synthesis of polyacrylate –PEG IPN s hydrogel and its sorption of heavy metal ions., Sci. Technol. Adv. Mater. 10 (2009) 015002.
- [16] Tsyntsarski B, Petrova B, Budinova T, et al. Porosity development during steam activation of carbon foams from, chemically modified pitch,.

 Microporous and Mesoporous Materials, , 154:56-61, 2012.
- [17] Inagaki M, Morishita T, Kuno A, et al. Sorption and recovery of heavy oils using carbonized fibers and recycling, Carbon, 2004, 42: 497-502.
- [18] Calcagnile P, Fragouli D, Bayer I S, et al. Magnetically driven floating foams for the removal of oil contaminants from water ,. Acs Nano, 2012, 6: 5413-5419

- [19] Elhossian Ali Maowed , I.Ishaq , Ali Abdul Ruhman, Mohamed Fatty El-Shahat,, Synthesis , characterization of carbon PU powder and its used application for separation and determination of Pt-in pharmaceutical ore sample ,. Talanta 121) 113-121. 2014 .
- [20] Jong Yuh Cherng , Ting Yi Hou , Mei Fe Shin , Wim E. Hennink , Polyurethane – based drug delivery system ,, International Journal of Pharmacetics 450 (1) 2013.
- [21] M.O.Edoga and A.S.Kovo ,, Development and characterization of phenol – formaldehyde molding power., Leonardo Electronic Journal of Practics and Technology , Issue 8 , 41-48 2006.
- [22] Dev K, Rao GN .Preparation and analytical properties of a chelating resin containing bicine groups. Talanta ,(1995), 42:591
- [23] Zhang L, Chang X, Hu Z, Zhang L, Shi J, Gao R,, Selective solid phase extraction and preconcentration of mercury II from environmental.,, Microchim Acta, 168:79–85. 2010.
- [24] Riya Srivastava and Deepak Studies On The Srivastava Synthesis And Curing Thermosetting Novolac Resin Using Renewable Resource Material International Journal of ChemTech Research Vol.5, No.5, pp 2575-2581, 2013.
- [25] Chalmes J.M , Everall N.J , Schaeberle M.D , Levin I.W , Lewis E.N , Kidder L.H , Wilson J. , Crombe R. , FTIR imaging of polymers , Vib.Spectrosc. 30 , 43-49 2002 .
- [26] Chrles Yang, Chemical analysis of polymeric material using infrared

- spectroscopy, University of Zagreb, Croatia 2011.,
- [27] Herrra M, Matuschek G, Kettrup A., Thermal degradation of thermoplastic polyurethane elastomers, Polymer Degradation and Stability, 78 (2): 323-331 2002.
- [28] Sichina WJ, Characterization of polymers using TGA: Boston (MA), Perkin Elmire 2001 Aplication Notes: PETech-78.