Analytical study and application of new chelating polymers for removal of heavy metals from wastewater sample

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Abstract - This study includes the preparation of new Schiff-base derived from (3-amino phenol) and (2-hydroxy benzaldehyde and (2-hydroxy-3-methoxy benzaldehyde), the characterization of this bases is carried out by FT-IR and ^{1}H-NMR The prepared bases were loaded on Urethane foam to prepare chelating polymers which were characterized by FT-IR, TGA and DSC technique. The loading efficiency of these resins were investigated toward several ions Cu^{+2}, Cd^{+2}, Ni^{+2} and pb^{+2} in different time and pH by Batch method. The prepared chelating polymers showed a good efficiency towards the studied ions and it was maximum for (Cu^{+2}) ions, An application to prepared chelating polymers was carried out on a sample of wastewater of Hamdan´s station in Basrah South of Iraq, and the results showed high and accurate level efficiency to remove the heavy elements.

Introduction:

The ongoing release of metal pollutants into the natural environment from waste streams, air pollution, fossil fuel combustion and urban habitat has contributed to environmental knowledge and the development of an analytical method for selective separation of heavy metal ions. The potential of chelating resin for toxic metal separation has been very well established (Jaishakar *et al.*, 2014; Carolina *et al.*, 2017; Mehrandish *et al.*, 2019).

There is an effective coordination between ligands and the Schiff-base when sufficient exist of these functional groups, besides their shapes as fifth or sixth membered chelating ring when react with metal ions (Warad *et al.*, 2020).

There is an important role that Schiff-base plays in the matter of coordination chemistry development, this role taken in consideration when it forms stable complexes with most of transition metals (Chaudhary *et al.*, 2021).

Polyurethane foam (PUF) is one of the polymers with a wide range of applications, primarily used in home decor, vehicles and thermal insulation (Dzhardimalieva and Uflyand, 2017), in the last years many of researchers starting to focus on the conjugating structure chain that the polymers contains with the structural unit (-CH = N), (Oprea *et al.*, 2020), this structure later on known as Polymeric Schiff-base or poly imines.

Modified PUFs were used as sorbents for the preconcentration of a range of metal ions to be separated (Adnan, 2019). In the present work we are interested to present the potential of a modified PUF by a Schiff-base ligands for loading capacity of different ions.

Materials and Methods:

Chemicals used in this research are:

Ethanol (Fluka), 3-amino phenol (Aldrich), 2-hydroxy benzaldehyde (BDH), 2-hydroxy-3-methoxy benzaldehyde (Fluka), Nickel(II) Nitrate (Fluka), Copper(II) Nitrate (Fluka), Lead(II) Nitrate (Fluka), MDI, Polyester polyol, tri ethyl amine (Fluka).

All chemicals were of analytical grade and were used as supplied without any further purification.

Instrumentation:
- Melting point apparatus of Buchi B190K was used to measure the melting point of all prepared compounds.
- By using the Shimadzu, FTIR-8400S (JAPAN) device, the Infrared (FTIR) Spectra were recorded.
- UV-VIS Spectra were recorded by using UV-2100 Spectrophotometer (Japan).
- HNMR Spectra were recorded on an BRUCKER-500MHz.
- By using Perkin-Elmer STA6000 Simultaneous analyzer the polymer thermal stability study has been evaluated, the test is (TGA, DSC) simultaneous thermal, under below conditions should be completed:
  10 mg of Each sample to be heated 30-1000°C the heating rate is 10°C/min in N_2 gas at flow rate 20 ml/min.

Schiff-base L1 and L2 Preparation:

Schiff-base L_1 and L_2 were prepared by dissolving of 0.05 mmole (5.45 g) of 3-amino phenol in 20 ml of hot absolute ethanol, to this an ethanol solution, 0.05 mmole (6.1 g) of Salicylaldehyde and 0.05 mmole (6.1g) of O-Vanillin, respectively, were add drop wise with constant stirring. The solution was aciditied by glacial acetic acid and the mixture was refluxed for five hours, the solid product that formed after cooling was filtered and recrystallize by ethanol and then dried in an oven at 50 °C.

Preparation of polyurethane Foam:

Polyurethane was synthesized by mixing polyester polyol with prepared Schiff-bases and excess of MDI in the presence of triethylamine at room temperature as a catalyst (Table 1). Then appropriate quantity (30% based on polyester polyol), was mixed to get homogenous and leave the mixture at the laboratory temperature, and then placed in an oven at 70°C for two hours to complete Hardening process. The foam removed unreacted compounds handled twice by using hot water. Then filtrated and dried.

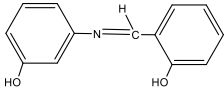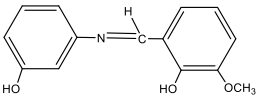Table 1. The reacted materials and their quantities.

Schiff-Bases	Ligand (g)	Poly-ol (g)	MDI (g)
L_1	1.1	2.6	2.75
L_2	1.1	2.6	2.75

Results and Discussion:

Physical measurements:

Table (2) demonstrates the physical characteristics of ligands:

Table 2. Schiff-bases physical characteristics and properties.

Schif-Base	Structure Formula	Molecular Weight	M.P °C	Color	Yield
L1		213 g/mol	128-129	Yellowish Orange	98.6%
L2		243 g/mol	147-148	Red	70%

FTIR spectra of the prepared Ligands:

The L 1 and L 2 ligands shown in Table (3) and Figures (1 and 2) are characteristic for the IR peak which gives a strong new band observed at 1618 cm^{-1} for L_1 and L_2 indicated to carbon nitrogen double bond (HC=N), and the band has been vanished at 1735 cm^{-1} due to carbonyl and 3315 cm^{-1} due to NH2 stretching vibration refers to the absence of starting materials from C=O and NH2 and has been transformed into HC=N (Mandlik and Deshmukh, 2020).
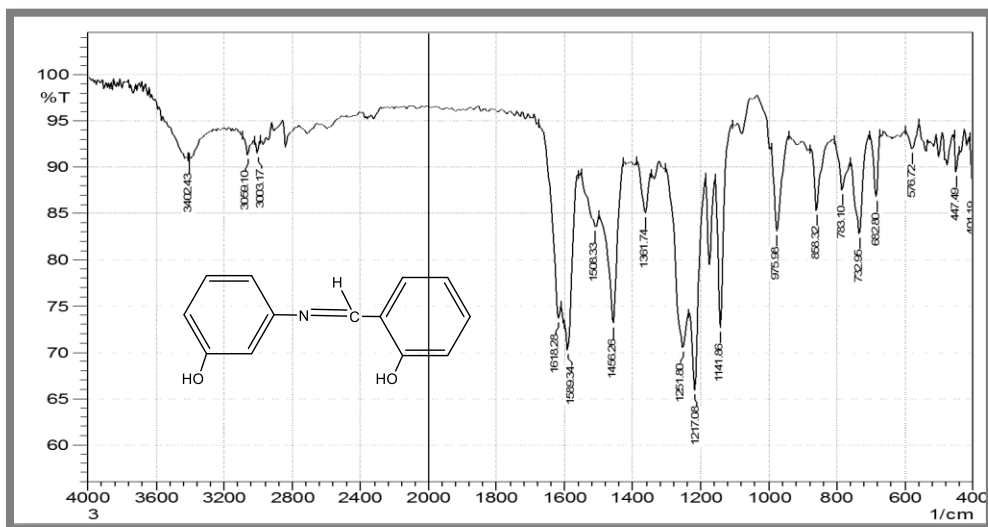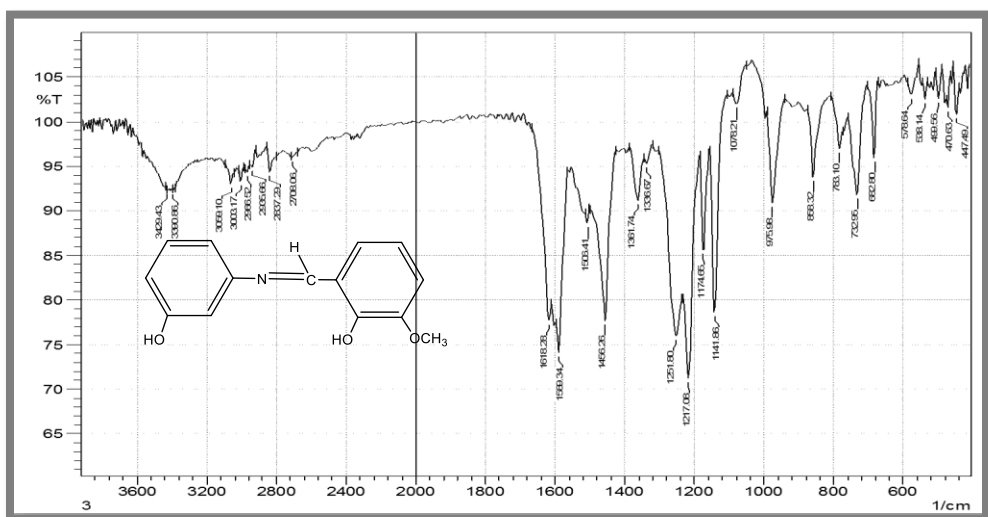
FTIR spectra for polymer based on L_1 and L_2:

The stretching vibration band of the carbonyl group in the region 1700-1720 cm^{-1} related to the urethane connection (-NH-COO) was characterized by the FTIR spectrum of polymer-supported Schiff-bases. Sharp characteristic absorption was seen at 1598 cm^{-1} for the -CH=N group and 1597 cm^{-1} for L1 and L2, respectively (Table 4).

Broad bands 3327 cm^{-1} and 3315 cm^{-1} for L_1 and L_2, respectively, were mainly assented with the remaining water in the product (Gluvchinksy, 1974; Reiss *et al.*, 2015).

The appearance of weak band in the region 2300-2276 cm^{-1} attributed to stretching vibration of N=C=O group indicates the presence of unreacted trace isocyanate, high absorption peak at 2972-2873 cm^{-1} is C-H stretching absorption (Mohammadi *et al.*, 2020). The overall clean spectrum indicates that through efficient formation-CH=N- bond, the polymerization was carried out Figures (3 and 4).

Table 3. IR spectra of the Schiff-Bases of the L1 and L2 ligands.

Ligand	C-H alphatic	C-H aromtic	C=N	C-N	C=C	OH
L_1	--	3055	1618	1340	1449-1539	3313
L_2	2708	3059	1618	1361	1589	3429

Figure 1. FTIR spectra for Schiff-base L₁"

Figure 2. The"FTIR spectra for the schiff-base L₂

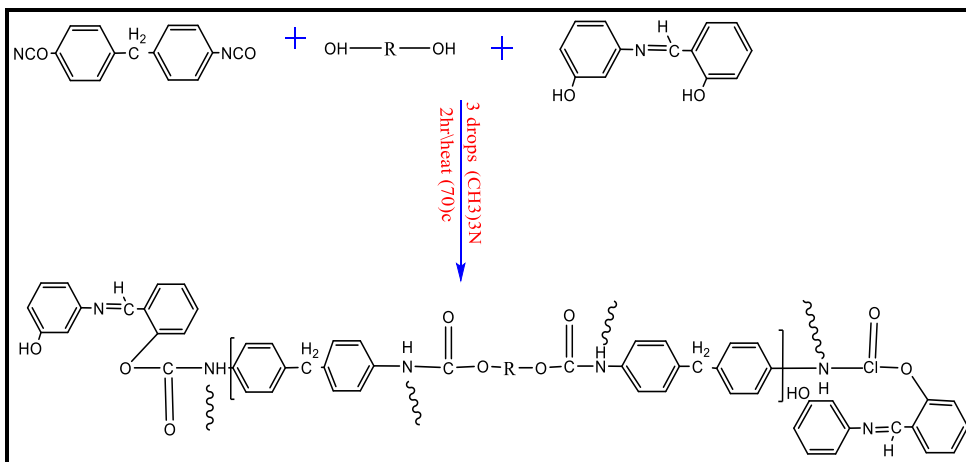Table 4. Spectrum of FT-IR for polymerized L1 and L2.

POLYMERS	-CH=N	NCO	NH-COO	CH aliphatic	OH
R_1	1598	2300	1712	2972	3327
R_2	1597	2276	1720	2873	3315
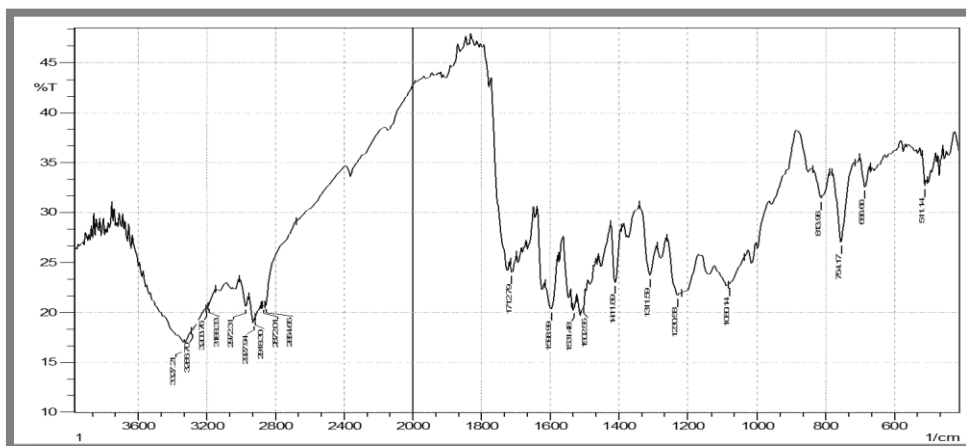
Figure 3. The FTIR spectra for polymer R_1
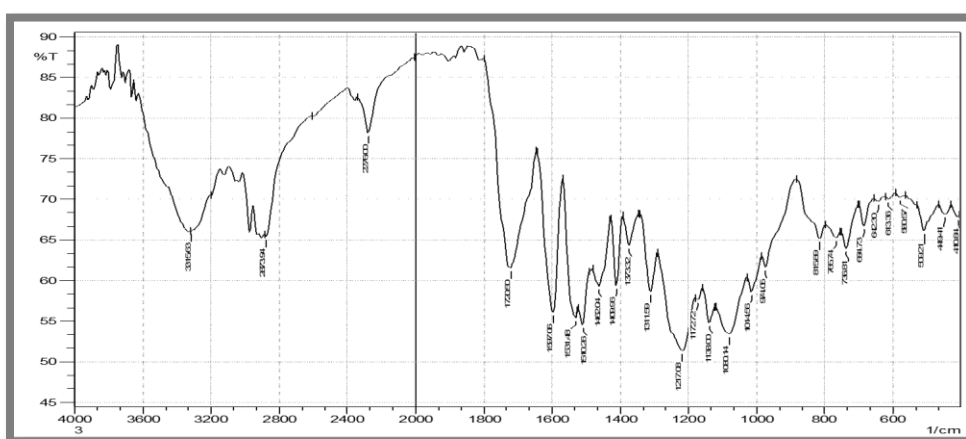
"Figure 4. The FTIR spectra for polymer R_2"
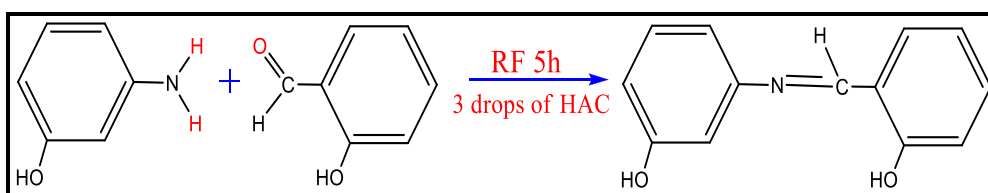
Schem-1. The synthesis of Schiff-base compounds"
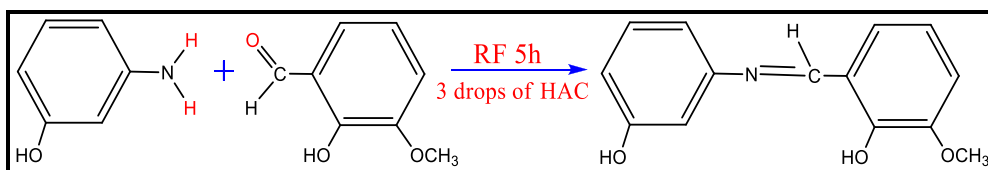
Schem-2. The synthesis of Schiff-base compounds

Schem-1. Polymer (R1) synthesis route (polyurethane based on Schiff-base L₁)
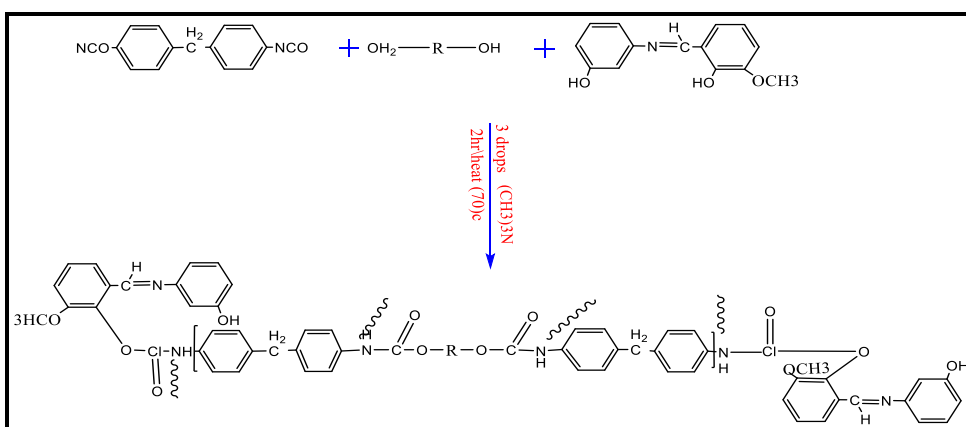
Schem-2. Polymer (R2) synthesis route (polyurethane based on Schiff-base L2).

¹HNMR Spectrum:

    Satisfactory spectral data were provided by the Schiff- base ligand and the molecular structure was assigned to the 1HNMR chemical Schiff-base, ¹HNMR spectra were calculated as an internal reference in a CD 3 OD solution with tetra methyl saline, the spectra of these ligands showed a clear signal. (8.7 ppm) for CH=N azomethane relation, also peaks for alkyl-OH around 3.31 ppm. Several signals at 6.2-7.2 ppm allocated to phenyl ring aromatic protons (Table 5). Figures (5 and 6) display the distribution of HNMR for L1 and L2.

Table 5. Spectra of the HNMR for the Schiff-base.

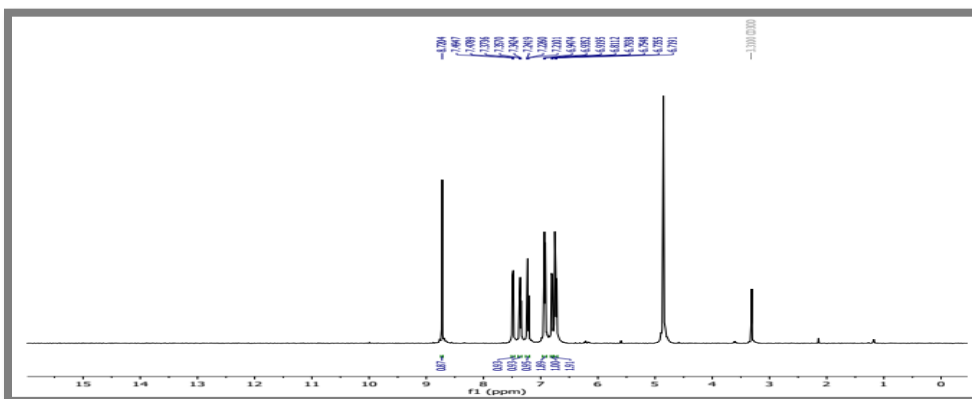| Schiff-Base	-CH=N	OH	CH Aromatic	CH Aliphatic
L₁	8.72	3.31	6.2-7.2	--
L₂	8.7	3.31	6.2-7.2	3.87

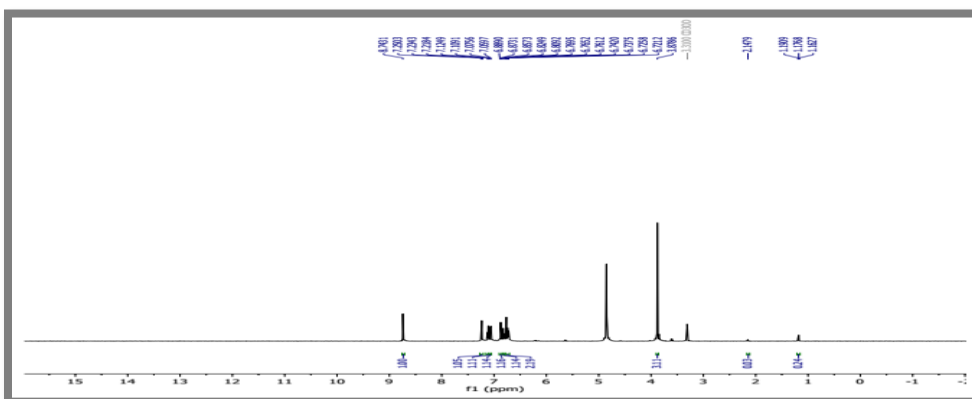Figure 5. Spectra of the HNMR for the Schiff-base L_1

Figure 6. spectra of the HNMR for the Schiff-base L_2

Analytical Studies of Polymerized Ligand:

1-Effect of contact time on the Loading capacity:

Figures (7) and (8) show the effect of treatment time on the loading capacity for R_1 and R_2 toward pb^{+2}, Cd^{+2}, Ni^{+2} and Cu^{+2} ions, these figures showed that the loading capacity increased with time of shaking special for each ions after that there is no effect of increasing of time on the loading capacity.

2-Effect of PH on the loading capacity:

The total loading capacity for polymers of pb^{+2}, Cd^{+2}, Ni^{+2} and Cu^{+2} ions at different pH values was studied. Figures (9 and 10) show the variation in the L.C. of the polymers towards the studied ion as a function of pH.

3-Regeneration of Loading Resins:

desorbing the metal ions from loaded resins R_1 & R_2 was carried out using 1N HCL solution as an eluent. Figures (11 and 12) show the percentage desorption as a function of time more than 75% of the amount of each ion was recovered within 2 hrs. for R_1 and 3 hrs. for R_2, the studied ions from the resins R_1 and R_2 were in the following order: $Ni^{+2}> pb^{+2} > Cd^{+2} > Cu^{+2}$
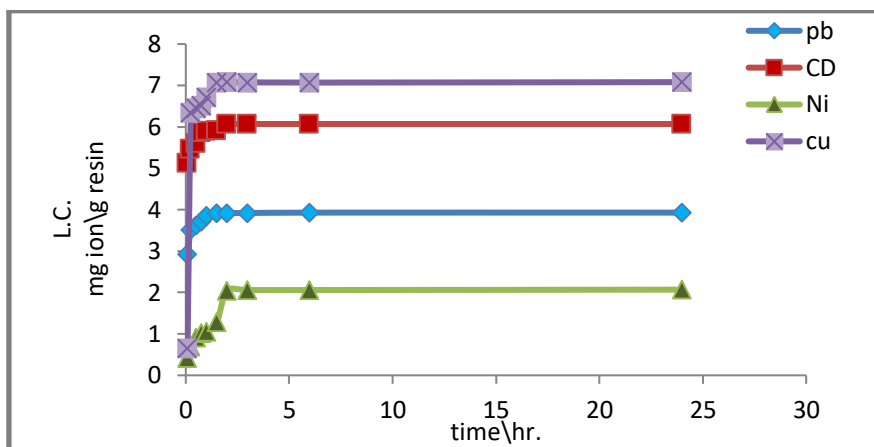
Figure 7. Loading capacity with time for each ion of R_1.
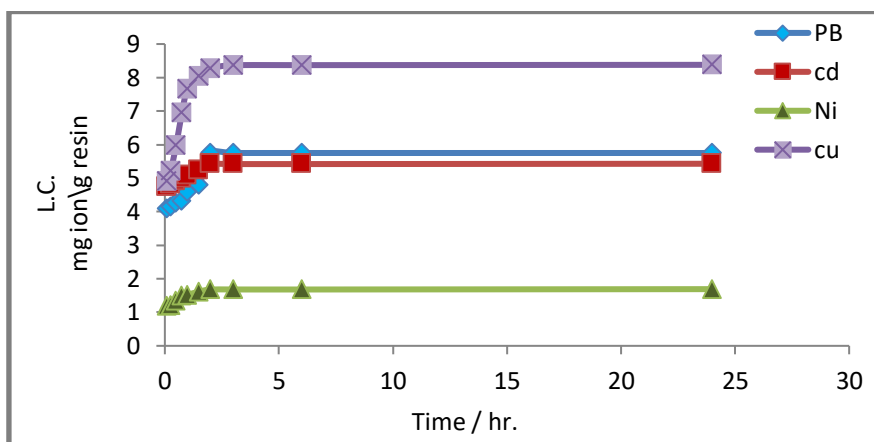
Figure 8. Loading capacity with time for each ion of R_2.
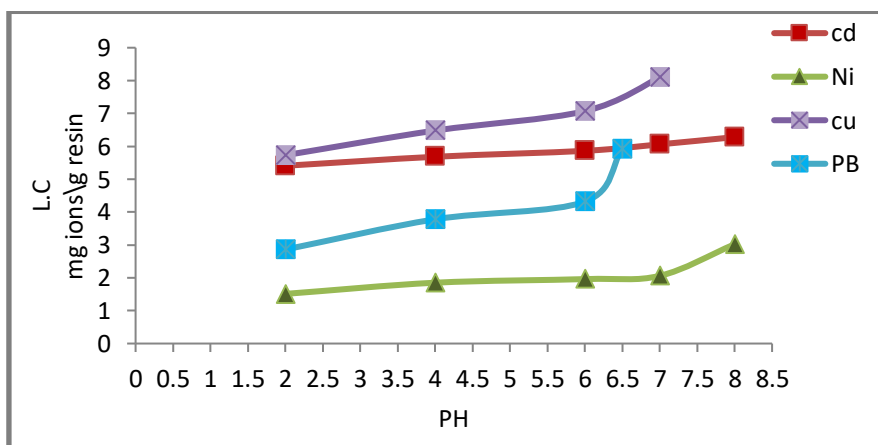
Figure 9. Loading capacity with different pH for each ion of R_1.
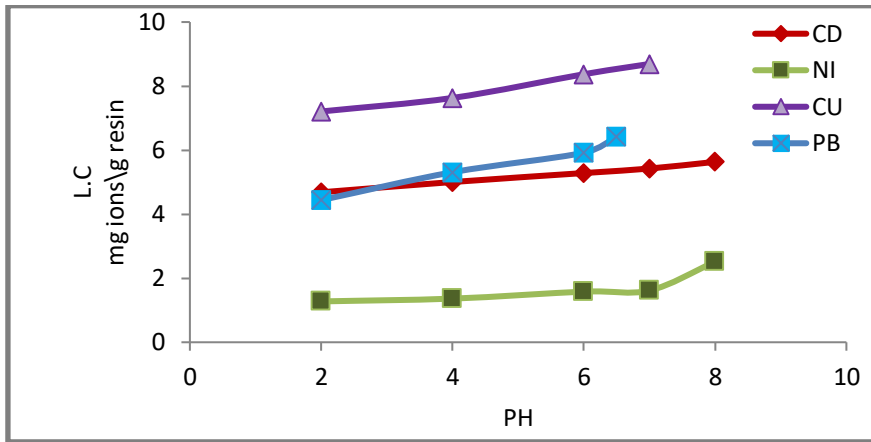
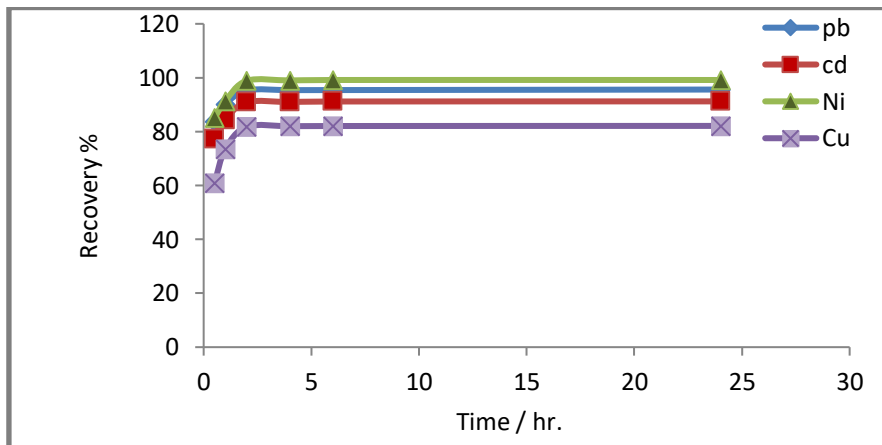Figure 10. Loading capacity with different pH for each ion of R$_2$.

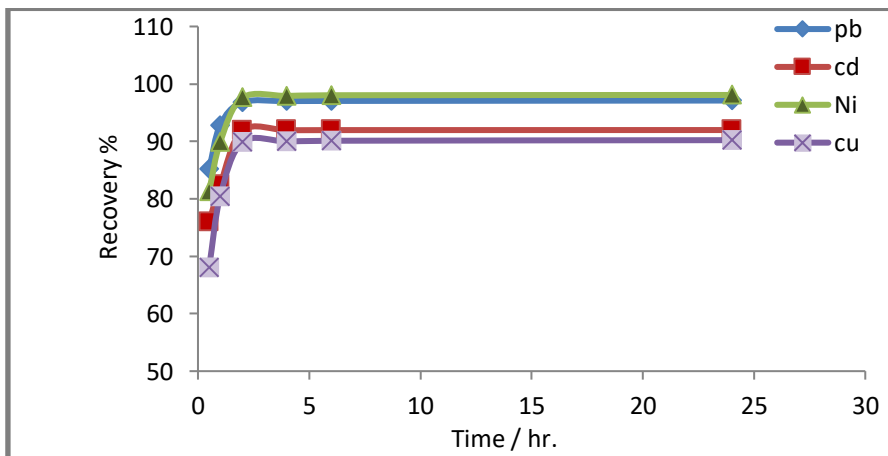Figure 11. Regeneration loading capacity with time for each ion of R$_1$.

Figure 12. Regeneration loading capacity with time for each ion of R2.

Thermal Stability:

Polymer thermal stability is known as the thermal or thermal-chemical resistance of polymers (Tomić, 2020). It can be expressed as thermal stability of any substance either as temperature functions or as a temperature-time limit. This analysis (TGA and DSC) techniques have been used to determine thermal stability of polymers prepared (Majid *et al.*, 2020). DSC and TGA thermograms megrin in Figures (13 and 14), were analysed and thermal parameters were described and displayed on Table (6) in TGA analyses measuring changes in sample weight of the programmed heating rate based on temperature.

The D.T. where optimal decomposition temperature is a 50 percent weight loss that the temperature at which the decomposition energy activation of the sample which loses half of its total weight, which defines the Arrhenius equation is E Via in random chain scission and radical chain mechanisms thermal degredation took place ,which result that the polymer R2 has less decomposition temperature and activation energy than polymer R_1, which means that polymer R_2 has less stablilty than polymer R_1.
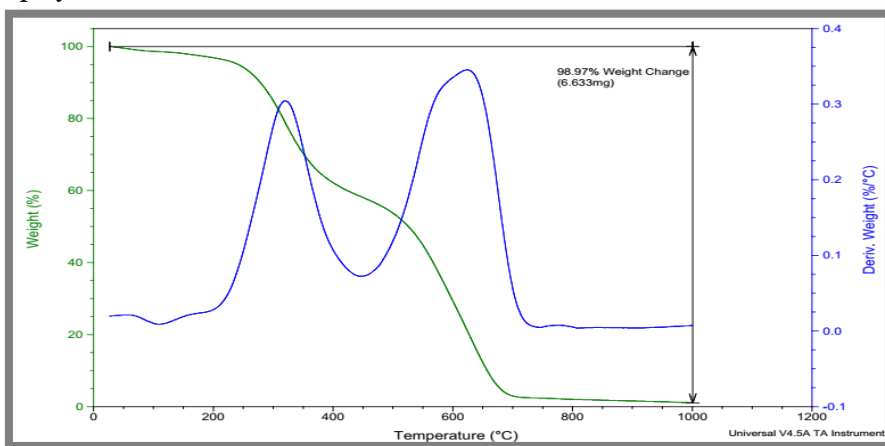

Figure 13. TGA curve of R_1.
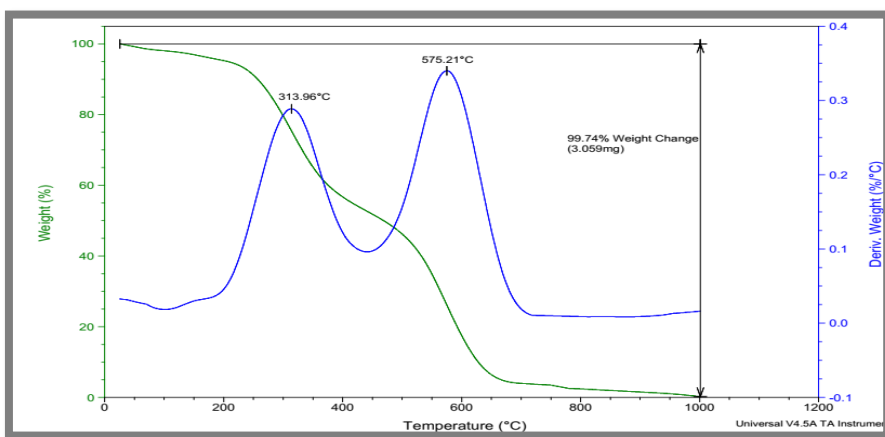
Figure 14. TGA curve of R_2.

Table 6. The most important thermal functions of the prepared polymers.

Polymer	Decomp. Temp. °C				Temp. of 50% Wt loss	Rate of Decomp. % Wt./min	Char cont. % at 600°C	Char cont. % at 1000°C	ΔE (Kj /mol)
	T_i	T_{OP1}	T_{op2}	T_F					
R_1	177	313	600	750	520	3.01	34	1.15	46.32
R_2	168	313	575	780	470	2.103	18	0.3	37.84

On the other side, the DSC thermograms shown in Figures (15 and 16) indicated that R_1 and R_2 had an exothermic peak which curing reactions of the remaining functional group, polymer chains reacting together under heating at degrees 628.70°C and 575.21°C.
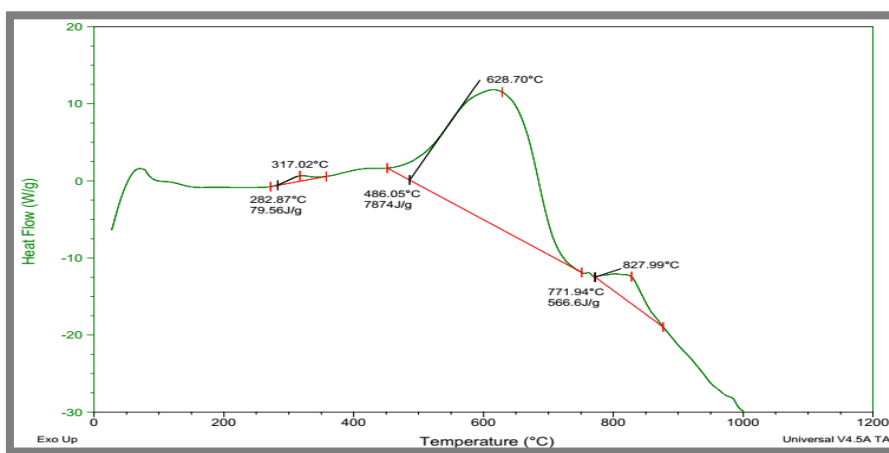
Figure 15. DSC curve of R1.
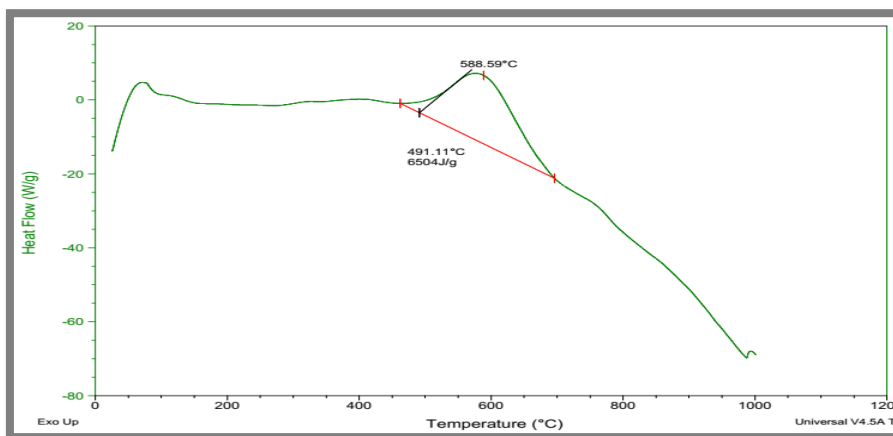
Figure 16. DSC curve of R2.

Application of the Method:

In order to check the applicability of the method, optimum conditions were applied on the real environmental samples for the instance waste water of Hamdan´s station in Basrah South of Iraq. The results indicate high affinity (100%) removal of Cd^{+2}, Cu^{+2} and Pb^{+2} except for Ni^{+2} ion the percentage of removal of R1 by the studied chelated polymers was 33% while that of R2 was 48%. Table (7) shows the (%) removal of ions.

Table 7. Percentage removal of ions.

Resin	Ions	Equilibrium Time (hrs.)	pH	C_o (mg/l)	C_e (mg/l)	L.C. (mg ions/g) Resin	Removal (%)
R$_1$	Cu^{+2}	1.5		0.155	0.0	0.155	100
	pb^{+2}	1.5		1.437	0.0	1.437	100
	Cd^{+2}	2		0.090	00.	0. 09	100
	Ni^{+2}	2	7.7	0.604	2030.	0. 40	33
R$_2$	Cu^{+2}	3		0.155	0.0	0.155	100
	pb^{+2}	2		1.437	0.0	1.437	100
	Cd^{+2}	2		0.090	00.	0.09	100
	Ni^{+2}	1.5		0.604	2910.	0. 31	48

Conclusion:

Two kinds of prepared azomethine compounds were characterized by using FTIR and HNMR technique, Polyurethane polymers were prepared from these ligands also FTIR was characterized and thermal stability was evaluated by using TGA and DSC techniques. Analytical study of these polymers were evaluated toward several ions (Ni^{+2}, pb^{+2}, Cd^{+2} and Cu^{+2}) thus the loading capacities of polymers increased with time and pH increasing thermal study showed that the polymers were thermally stable.

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دراسة تحليلية وتطبيق بوليمرات كلابية جديدة لازالة العناصر الثقيلة من عينة مياه الصرف الصحي

رنا طارق شبلي[1] و طارق زباري جاسم[2]

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المستخلص – يتضمن هذا البحث تحضير نوعين من قواعد شف مشتقة من تكاثف (2-hydroxy benzaldehyde), (2-hydroxy,3-methoxybenzaldehyde) مع (3-amino phenol). شخصت قواعد شف المحضرة بمطيافية الأشعة تحت الحمراء (FT-IR) وطيف الرنين النووي المغناطيسي (HNMR$_1$)، ثم حملت قواعد شف المحضرة على الرغوة اليوريثانية للحصول على البوليمرالكلابي (R1,R2)، وأيضا شخص الراتنج المحضر بمطيافية الأشعة تحت الحمراء (FT-IR) وتقنية التحليل

الحراري (TGA,DS C). درست كفاءة تحميل هذا الراتنج تجاه أيونات (Cd+2,Cu+2,Ni+2,Pb+2) بإتباع طريقة الوجبة (Batch Method) إذ أظهر الراتنج الكلابي المحضر أعلى كفاءة تحميل لأيون النحاس الثنائي، وطبق عمليا البوليمر الكلابي المحضر (R1,R2) على عينة من مياه الصرف الصحي لمحطة حمدان في محافظة البصرة جنوب العراق. أوضحت النتائج كفاءة عالية للسطح المحضر لإزالة أيونات العناصر الثقيلة من العينة.