

Synthesis, Analytical and Uptake Behavior of Copper, Cadmium and Lead by New Schiff-base Chelating resin

Al-Mosawi Fatima Husham, Al-Abbawy Dunya A. and Abbas Abbas F.*

Department of Ecology, College of Science, University of Basrah, IRAQ

Department of Chemistry, College of Science, University of Basrah, IRAQ

*dunya.hussain@uobasrah.edu.iq

Abstract

The current study aims to improve the quality of wastewater collected from the raw, primary sedimentation tank and secondary sedimentation tank of Hamdan wastewater treatment plant, Basrah, Iraq. Heavy metals contamination is one of the most critical environmental issues. Therefore, appropriate steps need to reduce pollutants in wastewater to acceptable levels before being discharged to the environment. Several treatment methods have been developed recently to adsorb these pollutants. This study reviews the ability of polymer, a new resin (3,3'-(1,4-phenylene) bis(1-(4-(4-hydroxybenzylidene) amino) phenyl) prop-2-en-1-one) to adsorb copper, cadmium and lead from wastewater.

The new Schiff base was prepared on polyurethane foam diagnosed by FT-IR and ¹H-NMR spectroscopic methods. The polymer has excellent sorption capacities due to the large specific surface area, chemical composition and the removal metals efficiency in varying proportions. For Cd²⁺, the efficiency removal was 100% in wastewater and the efficiency of removing Cu²⁺ was 100% in raw wastewater and primary sedimentation tank. The removal efficiency of Pb²⁺ was 86%, 64% and 79% 79% in raw sewage, primary and secondary sedimentation tank respectively.

Keywords: Pollutants, wastewater treatment plant, Schiff base, Polyurethane foam.

Introduction

Wastewater from numerous industries such as paints and pigments, glass production, mining operations, metal plating and battery manufacturing processes contains contaminants such as heavy metals. Heavy metals are present in industrial wastewater, these heavy metals in wastewater are not biodegradable and their existence in receiving lakes and streams causes bioaccumulation in living organisms⁴.

Heavy metals are a group of trace elements that include metals and metalloids and they have a relatively high density of over 5gm/cm³. The metal ions such as Pb, Cd, Cr, Ni, Zn, Cu and Fe contaminate the soil, atmosphere and water systems and are poisonous even in low concentrations¹. There are two main sources of heavy metals in water—natural and anthropogenic. Natural sources comprise volcanic activities, soil erosion, activities of living

organisms and weathering of rocks and minerals. In contrast, anthropogenic sources include landfills, fuel combustion, street run-off, sewage, agricultural activities, mining and industrial pollutants such as textile dyes². Heavy metals are toxic and carcinogenic; they can accumulate in tissues and cause diseases and disorders. Contamination of aquatic systems is a severe environmental issue and therefore, the development of efficient and suitable technology to remove heavy metals from aqueous solutions is necessary.

Several methods have been used to remove heavy metals from contaminated water. They include chemical precipitation^{10,18}, ion exchange^{12,22}, adsorption⁵, membrane filtration^{13,21} reverse osmosis^{19,23} solvent extraction¹⁶ and electrochemical treatment^{9,16}. Many of these methods suffer from high capital and operational costs. Adsorption seems to be one of the best-suited methods due to its high efficiency, low cost and ease of operation. Various adsorbents such as carbon foam¹⁵, activated carbon¹⁷, zeolite²⁰, clay minerals^{6,11}, organic polymers,³ biochar⁸ and many waste materials such as fly ash have been used.

Polyurethane foams are plastic materials in which a proportion of the solid phase is replaced by gas in the form of numerous tiny bubbles (cell)⁷. From the geometrical point of view, if the gas bubbles occupy a volume smaller than 76%, they may be spherical. If they occupy a volume more significant than 76%, they will be distorted into quasispheroidal polyhedral¹⁴. Polyurethane foams have been prepared in soft, flexible and rigid forms using a variety of polyesters and polyether. The two most important reactions in the preparation of urethane foams are those between isocyanate and hydroxyl compounds polyester or polyether polyols) and those between isocyanate and water.

Material and Methods

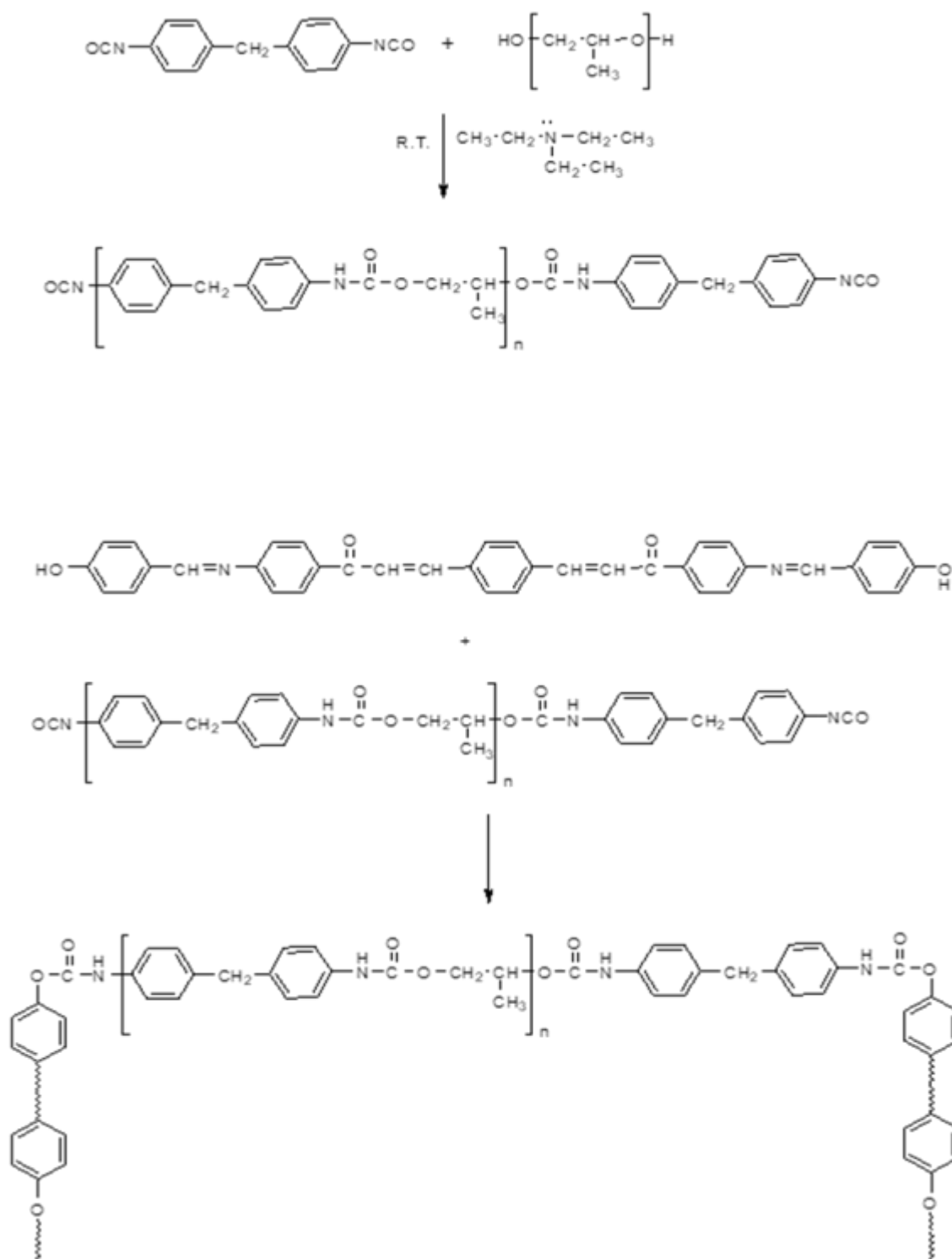
Materials: All the reagents, starting materials and solvents were purchased commercially and used without any further purification.

Preparation Methods

Preparation of Schiff base (3,3'-(1,4-phenylene) bis(1-(4-(4-hydroxybenzylidene) amino) phenyl) prop-2-en-1-one): This compound was prepared through dissolved 0.1 mole of chalcone in 35 ml of ethanol and add 0.2 moles of 4-hydroxybenzylidene (dissolved in 15 ml of ethanol) with a little of p-toluene sulphonic acid. The mixture was heated for 3 hours with stirring by using reflux. After complete reaction, residue was obtained after cooling and recrystallization from ethanol gave a black powder.

Preparation of polyurethane foam: The first synthesis of polyurethane terminated isocyanate is by mixing polyester polyol with an excess of MDI in the presence of triethylamine as a catalyst at room temperature for one hour. The Schiff base compound 3,3'-(1,4-phenylene) bis(1-(4-(4-hydroxybenzylidene) amino) phenyl) prop-2-en-1-one) was added and mixed with 3 drops of trimethylamine. After this, keep in room temperature for 24 hours and then put it in the oven at 70°C to complete hardening process as shown in scheme 1.

Adsorption study: Adsorption experiment was done by measuring 200 mL of the wastewater sample 0.2 g of the previously prepared chelating polymer was added to the wastewater in the conical flask. The conical flask containing the adsorbent and the wastewater was placed on a rotary shaker and shaken at 130 rpm at a room temperature of (25 °C) for 30 min. The suspension was separated by a centrifuge. A flame atomic absorption spectrophotometer (FAAS) was used to analyze the concentrations of the different metal ions present in the filtrate.



Scheme 1: Loading the Schiff base on the polyurethane foam

The percentage of metal ions removed was obtained from equation 1:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where (R %) is the ratio of the difference in metal concentration before and after adsorption.

The mass balance equation was used to determine the adsorption capacity (Q_e) from equation 2:

$$Q_e = \frac{C_0 - C_e}{M} \times V \quad (2)$$

Results and Discussion

Treatment of chalcones with 4-hydroxy benzaldehyde in boiling ethanol gave 3,3'-(1,4-phenylene) bis(1-(4-((4-hydroxybenzylidene) amino) phenyl) prop-2-en-1-one). After purification by recrystallization from ethanol, pure compound is shown in scheme 2 to give 84 % yield. The structures of these products were established from their FT-IR and ^1H NMR spectra. The FT-IR spectra of 3,3'-(1,4-phenylene) bis(1-(4-((4-hydroxybenzylidene) amino) phenyl) prop-2-en-1-one) compounds were characterized by the disappearance of the absorption band attributed to the (NH_2) stretching which appeared at ($3300\text{-}3400$) cm^{-1} .

The IR spectra of 3,3'-(1,4-phenylene) bis(1-(4-((4-hydroxybenzylidene) amino) phenyl) prop-2-en-1-one) showed a peak at 1654 cm^{-1} related to ($\text{C}=\text{N}$) stretching peak at $1213\text{-}1224$ cm^{-1} which appeared due to ($\text{C}-\text{N}$) stretching and a peak at 1593 cm^{-1} which occurred due to $\text{C}=\text{C}$ stretching of aromatic ring. The $\text{C}=\text{C}$ stretching aliphatic showed a peak within the range 1519 cm^{-1} , the $\text{C}-\text{H}$ stretching aromatic ring showed a peak within the range 3100 cm^{-1} and the $\text{C}-\text{H}$ stretching aliphatic showed a peak within the range 2918 cm^{-1} . The $\text{C}-\text{O}$ stretching showed a peak within the range 1122 cm^{-1} . Figure 1 shows the FT-IR spectrum of Schiff base.

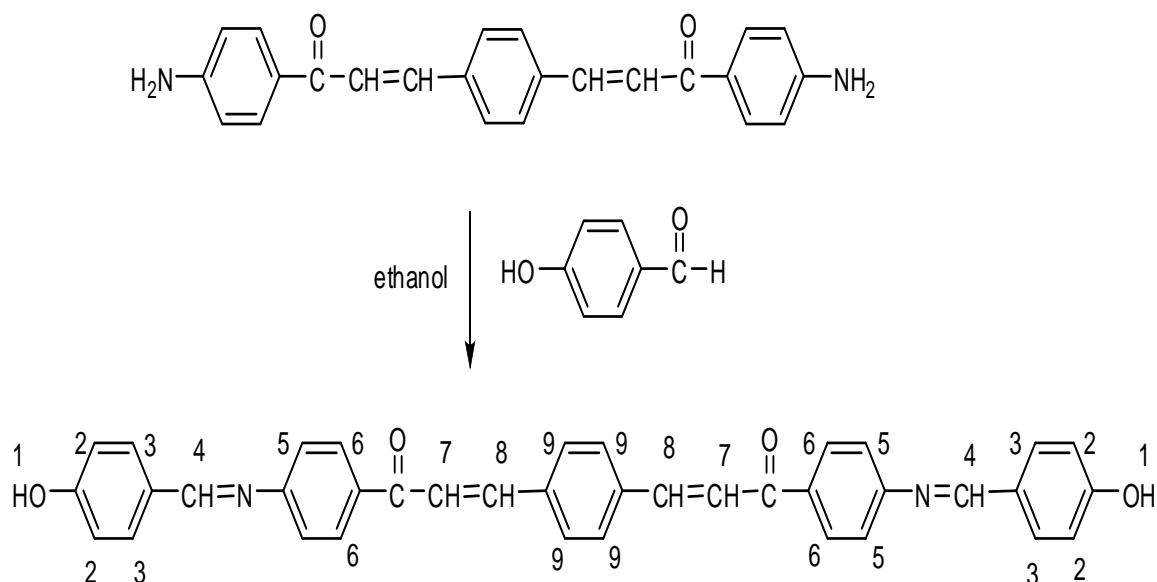
The ^1H -NMR spectra of 3,3'-(1,4-phenylene) bis(1-(4-((4-hydroxybenzylidene) amino) phenyl) prop-2-en-1-one) in scheme 2 and figure 2 were characterized by the presence of protons of azo methane group showing singlet signals at 9.00 ppm. The protons of aromatic rings showed singlet signals at 7.91 ppm. In comparison, the protons in position (6) showed doublet signals within the range $7.65\text{-}7.67$ ppm because of interaction with protons in position (5). The protons in position (5) showed doublet signal within the range $7.57\text{-}7.59$ ppm because of interaction with protons in position (6). The other protons in (3) position showed doublet signals within the range $6.73\text{-}6.75$ ppm because of interaction with protons in position (2).

The protons in position (2) showed doublet signals within the range $6.00\text{-}6.60$ ppm because of interaction with protons in position (3). The aliphatic protons in position (7) showed doublet signal within the range $5.87\text{-}5.90$ ppm because of interaction with protons in position (8).

At the same time, the other protons in positions (8) showed doublet signals within the range $5.77\text{-}5.80$ ppm because of interaction with protons in position (7). The (OH) protons in position (1) showed singlet signal at 10.50 ppm.

Reduction of heavy metals and removal efficiency after using chelating polymer:

The results in tables 1 to 3 indicate that the Cd^{2+} ion removal rate was 100% in the three sites of the station. Cu^{2+} ion removal percentage reached 100% when using the resin in the external collection basin and the primary treatment basin. The removal percentage in the secondary treatment basin was 50%. The results indicate that the Pb^{2+} lead ion removal rates reached 86%, 64%, 79% in the external collection pool, the primary treatment pool and the secondary treatment pool respectively as shown in figure 3 of Hamdan sewage water treatment plant.



Scheme 2: Schiff base ^1H -NMR spectrum

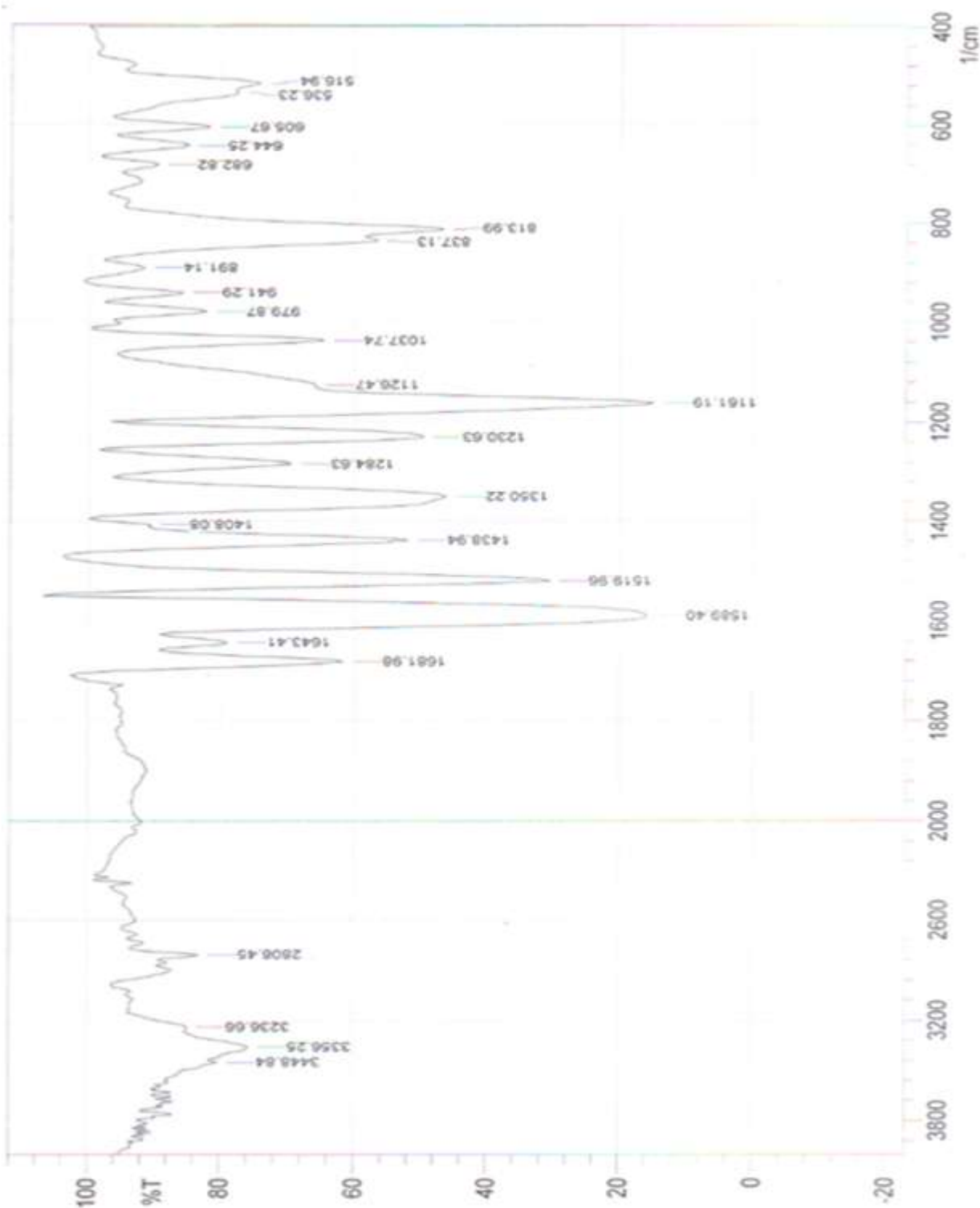


Figure 1: FT-IR spectra for Schiff-base

Table 1
Reduction efficiency to remove heavy metals in Raw wastewater:

| Ions | C ₀ mg/L | C _e mg/L | L.C. mg ions/g resin | Removal% |
|------------------|------------------------|------------------------|-------------------------|----------|
| Cu ⁺² | 0.0141 | 0 | 0.00141 | 100 |
| Cd ⁺² | 0.001033 | 0 | 0.0001033 | 100 |
| Pb ⁺² | 0.0619 | 0.008647 | 0.0053253 | 86.03069 |



| Parameters | | Value |
|------------|------------------------|--|
| 1 | Data File Name | BPC-ANALYSIS CENTER |
| 2 | Title | ¹ H- ¹ H |
| 3 | Comment | ¹ H Gradient map for the probe: ID: Magname : ID_N_2021-03-05 |
| 4 | Origin | Varian |
| 5 | Owner | |
| 6 | Site | |
| 7 | Spectrometer | inova |
| 8 | Author | |
| 9 | Solvent | dmsd |
| 10 | Temperature | 25.0 |
| 11 | Pulse Sequence | zgpg30 |
| 12 | Number of Scans | 16 |
| 13 | Receiver Gain | 22 |
| 14 | Relaxation Delay | 5.0000 |
| 15 | Pulse Width | 0.0000 |
| 16 | Acquisition Time | 2.0494 |
| 17 | Acquisition Date | 2021-04-12T14:41:04 |
| 18 | Modification Date | 2021-04-12T14:41:26 |
| 19 | Spectrometer Frequency | 499.67 |
| 20 | Spectral Width | 7994.4 |
| 21 | Lowest Frequency | -999.2 |
| 22 | Nucleus | ¹ H |
| 23 | Acquired Size | 16394 |
| 24 | Spectral Size | 32768 |

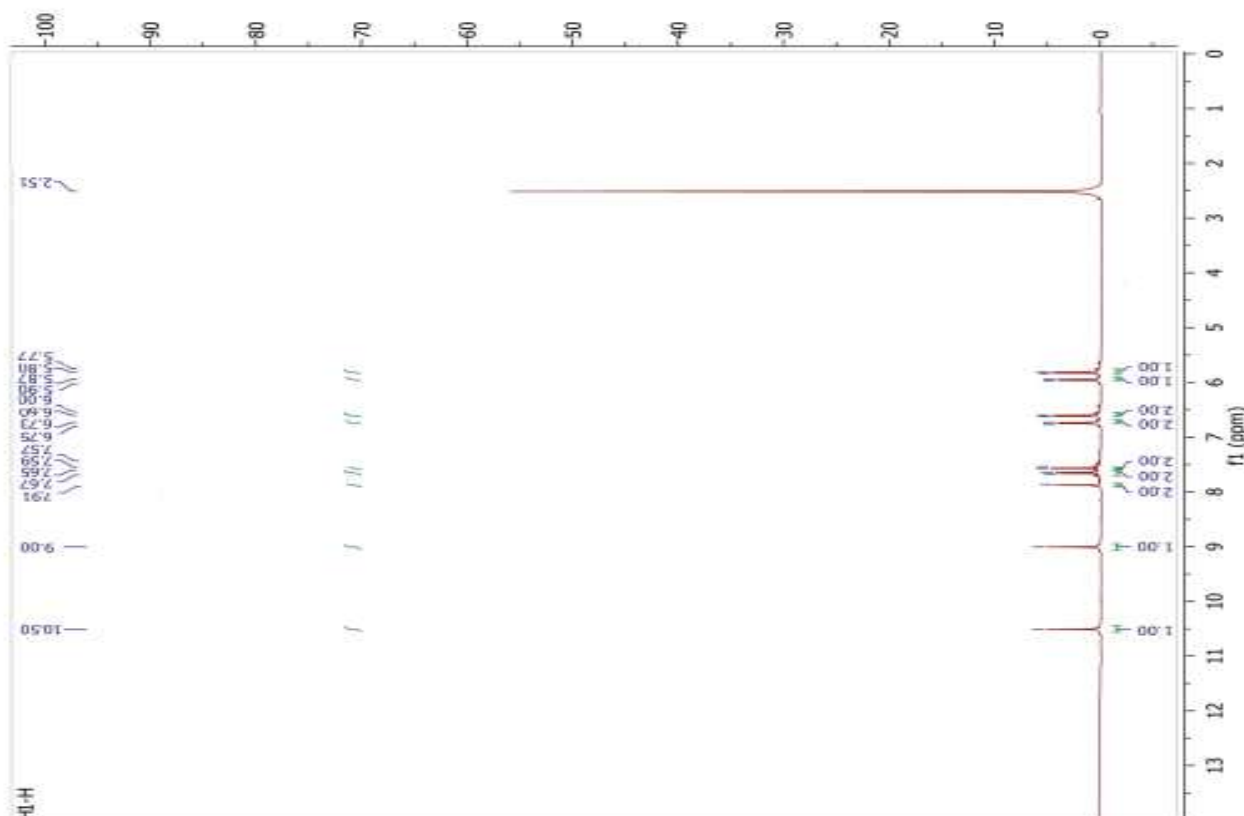


Figure 2: ¹H- NMR Spectrum for Schiff base

Table 2
Reduction efficiency to remove heavy metals in Primary sedimentation tank:

| Ions | C ₀ mg/L | C _e mg/L | L.C. mg ions/g resin | Removal% |
|------------------|------------------------|------------------------|-------------------------|----------|
| Cu ⁺² | 0.01315 | 0 | 0.001315 | 100 |
| Cd ⁺² | 0.000861 | 0 | 0.0000861 | 100 |
| Pb ⁺² | 0.1564 | 0.055164 | 0.0101236 | 64.7289 |

Table 3
Reduction efficiency to remove heavy metals in Secondary sedimentation tank:

| Ions | C ₀ mg/L | C _e mg/L | L.C. mg ions/g resin | Removal% |
|------------------|------------------------|------------------------|-------------------------|----------|
| Cu ⁺² | 0.012516 | 0.006258 | 0.0006258 | 50 |
| Cd ⁺² | 0.000775 | 0 | 0.0000775 | 100 |
| Pb ⁺² | 0.072516 | 0.015054 | 0.0057462 | 79.24044 |

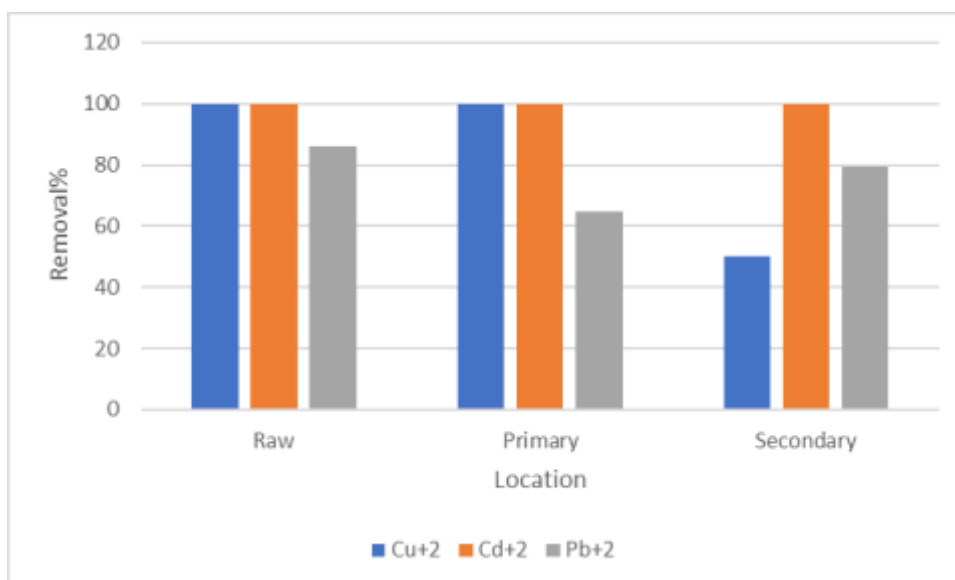


Figure 3: Efficiency of resins R1 and R2 in the removal of heavy metal ions in Hamdan sewage plant

Conclusion

The new Schiff-base compound was prepared from aromatic aldehyde derivatives. These compounds were characterized using different techniques like FTIR. ¹H NMR complexation of this ligand was carried out with some metal's ions (Cu⁺, Cd⁺ and Pb⁺). Finally, a polyurethane copolymer was prepared from this ligand.

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