

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

Hussain Fatima Husham

Al-Abbawy Dunya A.

Abbas Abbas F. *

Department of Ecology, College of Science, University of Basrah
Department of Chemistry, College of Science, University of Basrah.
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 paper 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. While 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 containing contaminants such as heavy metal. 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 deficient 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^{18,10}, ion exchange^{12,22}, adsorption⁵, membrane filtration^{13,21} reverse osmosis^{19,23}, solvent extraction¹⁶ and electrochemical treatment^{16,9}. 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 polymers³, and biochar⁸, and many waste materials, such as fly ash.

Polyurethane foams can be defined as 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.

2. Materials 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 added 0.2 moles of 4-hydroxybenzylidene (dissolved in 15 ml of ethanol) with a little of p-toluene sulphonic acid, the mixture heating for 3 hours stirring by using reflux. After complete reaction residue was obtained after cooling and recrystallization from ethanol gave a black powder with melting point and yield. This reaction mentioned by thin-layer chromatography by eluent toluene:methanol (8:2)

Preparation of polyurethane foam:

The first synthesis of polyurethane terminated isocyanate 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) were added and mixed with 3 drops of trimethylamine get homogenous for about (30 min) to complete polymerization. After this, let in room temperature 24 hours then put it in the oven with 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, and 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 shook at 130 rpm at a room temperature of (25 °C) for 30 min. The suspension is 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.

The percentage of metal ions removed obtained from equation (1):

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

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):

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

Result 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 as shown in (scheme 2) in (84) % yield were obtained. 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 that was attributed to the (NH₂) stretching which appeared at (3300-3400) cm⁻¹. These facts confirmed the correct expected chemical structure of these compounds. 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 which related to (C=N) stretching, a peak at (1213-1224) cm⁻¹ which appeared due to (C-N) stretching and a peak at 1593 cm⁻¹ which occurred due to (C=C stretching of aromatic ring). While the C=C stretching aliphatic showed a peak within the range 1519 cm⁻¹, the C-H stretching aromatic rings showed a peak within the range 3100 cm⁻¹ and the C-H stretching aliphatic showed a peak within the range 2918 cm⁻¹. The C-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 3 were characterized by the presence protons (4) of azo methane group showed singlet signals at 9.00 ppm. The protons of aromatic rings showed singlet signals at 7.91 ppm, which appeared to be protons in position (9). In comparison, the protons in position (6) showed doublet signals within the range (7.65-7.67) ppm because of interaction with protons in position (5). The protons in position (5) showed doublet signal within the range (7.57-7.59) ppm because of interaction with protons in position (6). While the other protons in (3) position showed doublet signals within the range (6.73-6.75) ppm because of interaction with protons in position (2). The protons in position (2) showed doublet signals within the range (6.00-6.60) ppm because of interaction with protons in position (3). The aliphatic protons in position (7) showed doublet signal within the range (5.87-5.90) 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 (5.77-5.80) ppm because of interaction with protons in position (7). While the (OH) protons in position (1) showed singlet signal at 10.50 ppm.

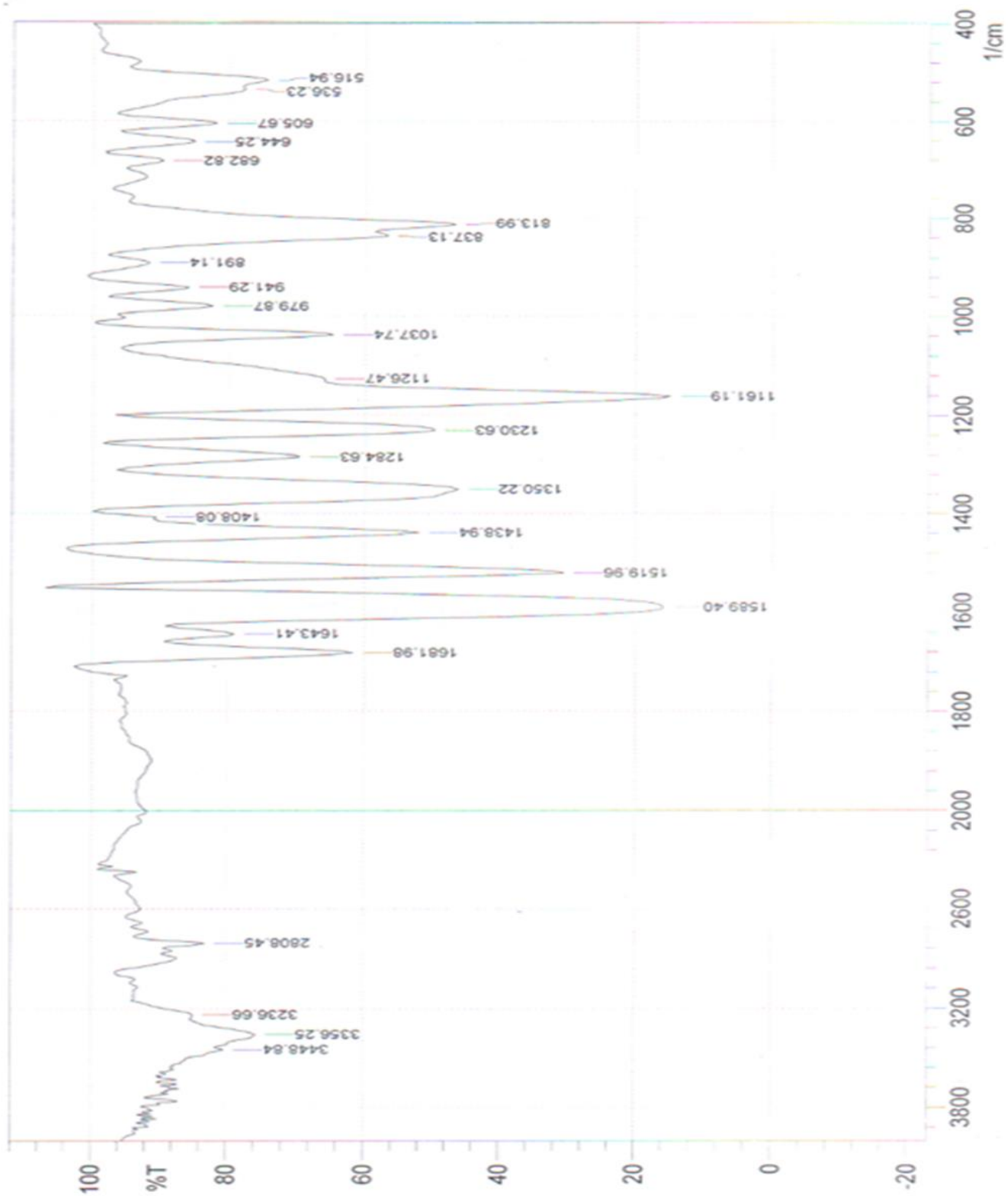
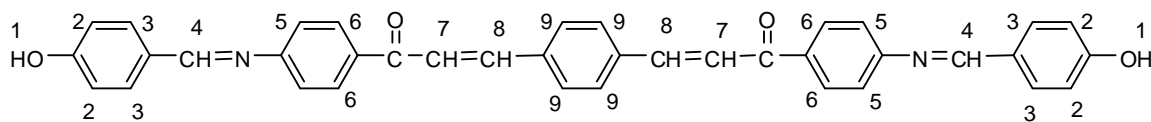
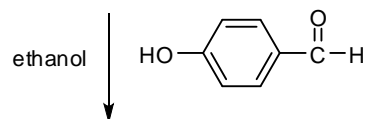
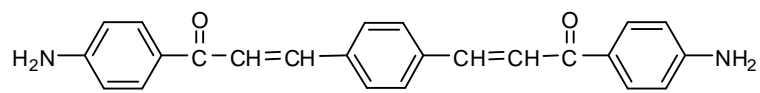


Figure 1: FT-IR spectra for Schiff-base



Scheme (2) Schiff base 1H-NMR spectrum

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

The results in Tables 2, 3, and 4 indicate that the Cd^{2+} ion removal rate was 100% in the three sites of the station. While the results suggest that the 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 4 of Hamdan sewage water treatment plant.

Table 2:
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

Table 3:
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 4:
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

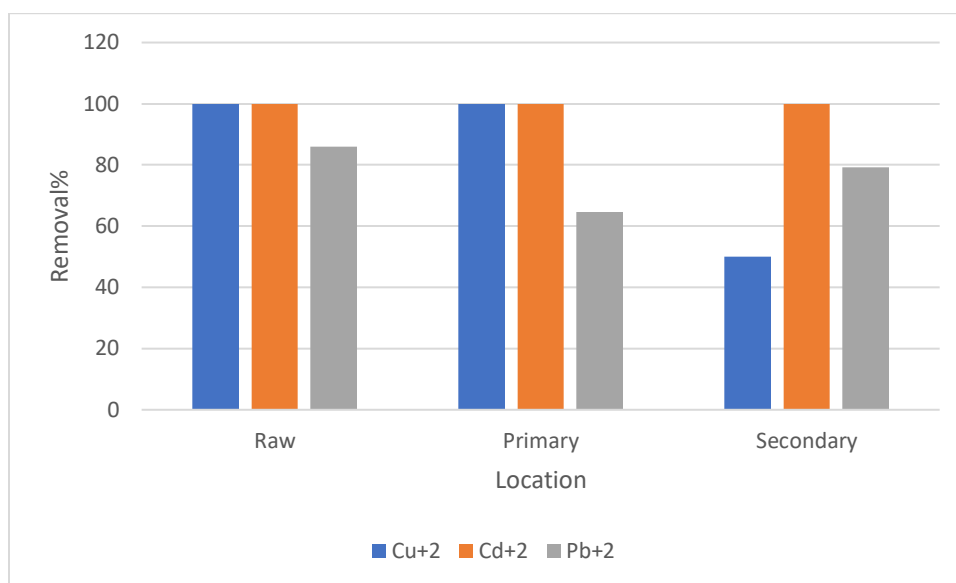


Figure 4: Efficiency of resins R1 and R2 in the removal of heavy metal ions in Hamdan sewage plant

Conclusion

The new Schiff-base compound was prepared from Aromatic aldehyde derivatives. These compounds were characterized using different technique like FTIR, analysis, and ^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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