**Deanship of Graduate Studies**

**Al-Quds University**

# Synthesize and Characterization of Polyimine and Its Application for Removing Amoxicillin from Polluted Water

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# Synthesize and Characterization of Polyimine and Its Application for Removing Amoxicillin from Polluted Water

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Al Quds University- Palestine

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# Thesis approval

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1446/2025

***On Behalf of my mother's soul***

## Declaration

I certify that this thesis submitted for the degree of Master in Applied and industrial technology is the result of my own research, except where otherwise acknowledged, and that this thesis (or any part of the same) has not be submitted for a higher degree to any other university or institution.

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# Abstract

This study aimed to prepare and characterize crosslinked polyimine polymer and its efficiency in removing pharmaceutical contaminants, specifically amoxicillin and paracetamol, from polluted water. A polyimine was prepared by reacting 1,4-diaminobutane, glutaraldehyde, and tris(2-aminoethyl) amine in a fixed molar ratio of 1:1:0.05. The FTIR and DSC were used to analyze the chemical structure and thermal behavior of the polyimine. Adsorption capacity was determined by HPLC, and the data were examined using both Langmuir and Freundlich isotherms. The impact of pH on adsorption was also studied. Despite the exciting application of polyimine-polymers in molecular filtration, no previous study had examined their efficiency in pharmaceutical removal from contaminated water.

The FTIR results indicated the successful synthesis of polyimine. The DSC results suggested a crosslinked structure and a thermoset-like behavior due to the lack of thermal transitions. In addition, the polyimine's insolubility in organic solvent supported the high degree of crosslinking within its structure. The reattached polyimine grains in aqueous environments indicated a self-healing property. The amoxicillin removal reached 63% at pH 7, while the removal of paracetamol was negligible. Experimental data fitted both to the Langmuir and the Freundlich models, suggesting a partially heterogeneous surface.

The research findings suggested further modifications for polyimine to enhance its adsorption efficiency. Such modifications, which will increase the positively charged species $N^+$, could be applied by increasing the crosslink density or introducing quaternary ammoniums. In addition, the study demanded that toxicological evaluation should be considered before any large-scale environmental application.

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## List of Abbreviations:

FTIR:  Fourier Transform Infrared Spectroscopy.
HPLC:  High-Performance Liquid Chromatography.
DSC: Differential Scanning Calorimetry.
TAEA: Tris(2-aminoethyl) amine
$q_e$: The amount of adsorbate adsorbed per unit mass of adsorbent.
$q_{max}$: The maximum adsorption capacity.
$K_L$: The Langmuir constant.
$C_e$: The equilibrium concentration.
$R_L$: The dimensionless separation factor.
GTA: Thermogravimetric Analysis.
CP: crosslinked polyimine.
P1: Polyimine-1.
Amox: Amoxicillin.
Para: Paracetamol.

# Chapter One:

## Introduction

### 1.1 Pharmaceutical Contaminates in Water

In the past decades, it has been discovered that pharmaceutical products are leaking into drinking water in several countries. Researchers have collected samples across the world to discuss the percentage of pharmaceutical products leakage and explain some of the causes that lead to the leakage (Wilkinson et al., 2022). Also, the World Health Organization published an article in 2012 indicating that pharmaceuticals leakage in the water is increasing and mentioning their risk to the environment and humans' health. (World Health Organization,. 2012)

Paracetamol has been detected in many aquatic environments, including surface water, sewage, and drinking water. Although it is usually detected in small amounts, these amounts are often decomposed by microorganisms in the environment and used as an energy source due to their carbon content. However, the continuous leakage of paracetamol into the environment, through waste from individuals and hospitals, could lead to undesirable environmental effects despite its current low concentrations. Paracetamol, also known as acetaminophen, is one of the most widely used medications worldwide. It works as a painkiller and fever reducer. Its chemical structure consists benzene ring with a hydroxyl group and an amide group, and it is highly soluble in water. Paracetamol works by blocking enzymes involved in inflammation. One of its breakdown products is 4-aminophenol, which is known to be harmful as it can cause kidney damage (Wu et al,. 2012).

Another pharmaceutical waste is amoxicillin, a commonly used antibiotic for humans and animals. It leaks to the environment through the disposal of solid or liquid waste from hospitals and veterinary practices. Amoxicillin plays a significant threat to aquatic ecosystems, affecting the growth and reproduction of aquatic organisms. One of the most serious risks is the development of antibiotic-resistant bacteria. When bacteria are exposed to lethal amounts of antibiotics, they can adapt and develop resistance mechanisms, making it very hard to treat infections caused by these bacteria. Amoxicillin is one of the most widely used medications worldwide due to its effective oral absorption and broad antibacterial activity against both Gram-positive and Gram-negative bacteria. Amoxicillin ($C_{16}H_{19}N_3O_5S$) is soluble in water. It has multiple pKa values due to the presence of carboxylic acid and phenol groups within its structure (Baghapour et al., 2015).

## 1.2 Attempts to Purified Water from Pharmaceuticals

Although pharmaceutical compounds are not currently considered a significant threat to the environment due to their low concentrations, their accumulation over time could become a serious environmental issue. As a result, efforts to remove these substances from the environment have gained significant attention from researchers seeking proactive solutions to prevent the potential effects of pharmaceutical leakage. Multiple strategies are developed in order to effectively eliminate these compounds, including the following:

- Textile-derived sorbents are effective in removing certain types of pharmaceuticals from wastewater. However, its performance is influenced by factors such as pH (Mazure et al., 2024).

- Chitosan-based materials have also proved their effectiveness in removing various pharmaceutical compounds. It is considered environmentally friendly for being derived from natural resources (Papagerogios et al., 2024)

- Advanced oxidation processes (AOPs) includeing ozonation and photocatalysis techniques, have shown a great potential in eliminating pharmaceuticals, achieving up to 99% degradation of certain drugs (Sierers et al., 2011).

- Filtration technologies such as microfiltration, ultrafiltration, and reverse osmosis, together with existing water purification systems, enhance the removal of pharmaceuticals (Eykamp et al., 1995).

- Polymer-based separation technologies, which are the most promising approaches to remove pharmaceuticals from water, gain the prominent attention due to their efficiency, versatility, and low energy consumption. For example, covalent organic polymers, molecularly imprinted polymers, and chitosan derivatives, show promising results (Lalit et al., 2024).

One of the promising polymers is polyimine, which is a polymer contained a repeating C=N (imine) bond (Suematsu et al., 1983). However, no previous studies specifically test polyimine for pharmaceutical removal. Literatures examine polyimine in separating other substances from water and even from the atmosphere (Wang et al., 2013). This study investigates the hypothesis that polyimine can effectively remove pharmaceuticals from water.

## 1.3 Adsorption Isotherm Model

Adsorption is when molecules from a liquid accumulate on the surface of a solid particle. One of the most common methods used to characterize accumulation phenomena is the adsorption isotherm model, which describes the amount of the substance on the solid surface in comparison with its concentration in the solution (Foo et al., 2010).

Adsorption isotherm is critical for designing adsorption systems, as it provides analytical insights about the adsorption mechanism, the adsorption surface, and the strength of the interaction between adsorbate and adsorbent. The most common used isotherm models are the Langmuir and Freundlich models (Foo et al., 2010).

Langmuir isotherm assumes homogeneous surface and a monolayer adsorption. Also, it

assumes that there is no interaction between adsorbate and adsorbent.
The mathematical form of the Langmuir isotherm is shown as

$$q_e = \frac{q_{max}.K_l.C_e}{1 + K_l.C_e}$$

where:

- $q_e$ is the amount of adsorbate adsorbed per unit mass of adsorbent (mg/g).
- $q_{max}$ is the maximum adsorption capacity (mg/g).
- $K_L$ is the Langmuir constant (L/mg).
- $C_e$ is the equilibrium concentration. (mg/g).

Langmuir model is suitable for chemisorption, because it assumes that once a site is occupied, no other adsorption can occur at the same site. $R_L$ is used to indicate the favourability of the adsorption process. An $R_L$ value between 0 and 1 indicates favourable adsorption. It can be measured using the equation:

$$R_L = \frac{1}{1 + K_L + C_e}$$

Where $R_L$ is the dimensionless separation factor (Hall et al ., 1966).
On the other hand, the Freundlich Isotherm model assumes a heterogeneous surface, and it also assumes that the adsorption capacity is related to the concentration of the adsorbate at equilibrium. The equation is:

$$q_e = K_f C_e^{1/n}$$

Where $K_f$ and n are the Freundlich constants.
When 1/n is between 0 and 1, it indicates a favourable adsorption and a surface heterogeneity (Wang et al,. 2020).

## 1.4 Surface Charge and its Correlation to Adsorption:

Surface charge is a physicochemical property that affects the adsorption process, especially in the aquatic environment. When the adsorbate is ionic in the aqueous systems, the surface charge of the adsorbent interacts electrostatically. The charge not only affects the capacity of the adsorption, but also the selectivity toward certain ions.
The surface charge depends on the pH of the medium and the point of zero charge. The point of zero charge (pzc) is the pH where the adsorbent surface carries no net electrical charge. When the pH is below the point of zero charge, the adsorbent surface tends to be positively charged, favouring the adsorption of anions.

This behaviour depends on the surface functional group, (e.g. -OH, -COOH, -NH2) which could gain or lose protons depending on the pH value.
$-NH_2 \leftrightarrow NH_2^{\delta-}$ at high pH
$-NH_2 + H^+ \leftrightarrow -NH_3^+$ at low pH

## 1.5 Imine Bond Formation:

Imines, also known as Schiff bases, are organic compounds contain C=N bond, it is formed from a condensation reaction of primary amine and aldehyde or ketone. The reaction, which results in losing water molecule, is widely used in organic synthesis due to its simplicity and versatility. Imine bond plays an important role in designing functional materials, drug delivery system, and sensors because of its dynamic and reversible nature (Zhu et al., 2020).
The mechanism for C=N formation involves nucleophilic attack of the amine on the carbonyl

carbon of the aldehyde, forming a tetrahedral intermediate. A proton then transfers resulting in the dehydration of water molecule from the intermediate in order to form C=N bond (Subasi et al., 2022). The general reaction is:

$R\text{-}CHO + R'\text{-}NH_2 \longrightarrow R\text{-}CH{=}N\text{-}R' + H_2O$

Imine are typically stable, but it can hydrolyse back to the original amine and carbonyl in the presence of water, especially under acidic environments. This reversable behaviour makes the imine bonds suitable for smart materials, such as pH-sensitive drug carriers and dynamic covalent frameworks (Zhu et al., 2020).

Several factors affect the imine formation, such as pH, temperature, and solvent. If the reaction condition is acidic, it activates the carbonyl group and the dehydration of water molecule. But it can also lead to hydrolysis of the imine product (Subasi et al., 2022).

## 1.6 Research Aim and Objective:

To synthesize and characterize a crosslinked polyimine for the adsorption of pharmaceutical pollutants, specifically amoxicillin and paracetamol.

The main objectives of the research are:

- To synthesize a crosslinked polyimine using 1,4-diaminobutane, gluteraldehyde, and tris(2-aminoethyl) amine at a fixed molar ratio.
- To characterize the chemical and thermal properties of the synthesized polyimine using FTIR and DSC analysis.
- To examine the adsorption efficiency of the polymer toward amoxicillin and paracetamol using HPLC, and adsorption isotherm models.

# Chapter Two:

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# Literature review

## 2.1 Introduction

The application of polyimines in molecular filtration attracted considerable interest from researchers, making them focus on polyimines' synthesis and development. This section of the research provides a summary of polyimines' synthesis and characterization. Additionally, it provides an overview of their uses and applications, with a focus on molecular filtration.

## 2.2 Polyimine Synthesis

The polymerization of polyimine is a condensation polymerization. The properties of the final product are primarily determined by the choice of monomers and the reaction conditions. During this process, a dialdehyde reacts with a diamine to form the imine (C=N) bond. (Suematsu et al., 1983; Yang et al., 1992). (As shown in Figure 2.1).

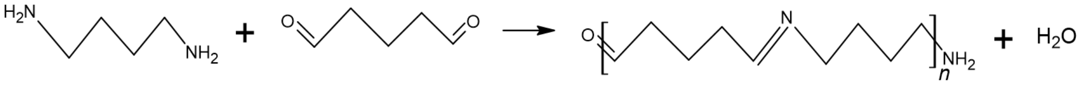

Figure 2.1: Shows the condensation reaction between 1,4diaminobutane and glutaraldehyde.

As a result, this is a spontaneous reaction that does not require catalysts or additional energy to be completed. However, reaction conditions have a direct impact on the quality and type of the final product (Zhu et al.,2017).

Natansohn et al., 1991, synthesized polyimine using terephthalaldehyde and aliphatic diamines containing methylene units (3-10 and 12). A number of polyimines were prepared through a condensation reaction between aldehyde and amine groups, resulting in the formation of the imine (-C=N-) linkage. The reaction was carried out in a solution of hexamethylphosphoramide (HMPA) and dimethylaminocarbonylamide, where the later was used as a catalyst to facilitate the imine bond formation. The resulting product was transferred into a tetrahydrofuran (THF) solution, evaporated, and left to dry at room temperature for 24 hours. The final material was described as a white, semi crystalline precipitate that is insoluble in organic solvents. The synthesized polyimines have a unique melting point and a crystallization behavior. The

researchers mentioned their potential for various applications due to its unique structure and mechanical properties.
$\mathrm{CHO{-}Ar{-}CHO + NH_2{-}R{-}NH_2 \longrightarrow [{-}CH{-}Ar{-}CH{=}NR{-}]_n + H_2O}$

To compare the properties of co-polyimine, polyimines synthesized by different types of diamines, with homo polyimines, polyimines synthesized using one type of diamine, Yang et al., 1993, prepared polymers using a similar method to, Natansohn et al., 1991,. Yang et al., 1993, used diamines containing even numbers of methylene unit (8,10). The authors noted that using two types of diamines significantly altered the polymer's properties. The new product dissolved in chloroform and THF, unlike the homo polyimine, which were completely insoluble. Furthermore, the co-polyimine exhibited less crystallinity and greater structural disorder than the homo polyimine.

$\mathrm{CHO{-}Ar{-}CHO + NH_2{-}(CH_2)_8{-}NH_2 + NH_2{-}(CH_2)_{10}{-}NH_2 \longrightarrow}$
$\mathrm{[{-}(CH_2)_8N{=}CH{-}Ar{-}CH{=}N(CH_2)_{10}{-}]_n}$

In a separate study, Suematsu et al., 1983, synthesized polyimine by polymerization reaction using hexamethylenediamine and terephthalaldehyde in m-cresol as a solvent. The resulting solution contained 10–30% polymer. Methanol was added to the solution to precipitate the polymer, which was then filtered and dried at 80°C for two hours. The final product was a strong, flexible, opaque white fiber with a high degree of crystallinity. Also, they mentioned that the degree of crystallinity increased with longer polymerization time, as the crosslinking ratio increases (as shown in the Figure 2.2). The polymer shows unique mechanical strength and it is soluble in m-cresol but resistant to water and alkaline solutions.

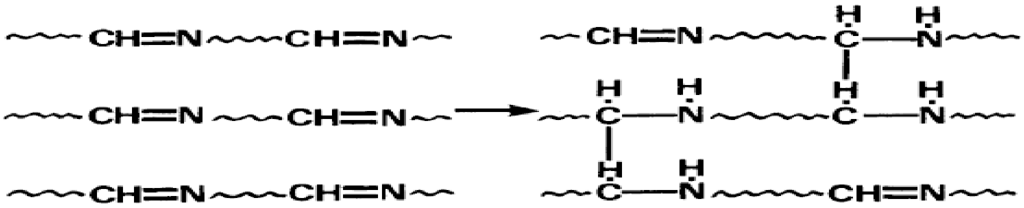

Figure 2.2: created by Suematsu et al,. 1982. It shows the crosslinking occurs within polyimine chains without using crosslinking agents. This is due to the dynamic nature of the C=N bond.

When comparing Suematsu et al,1982, with Natansohn et al., 1991, it is a clear evidence that the reaction medium directly influences the properties of the polymer. The latter observed that the polyimine, synthesized by using hexamethylenediamine, is insoluble in organic solvents and has an initial semi-crystallin form. While the former reported that the polyimine with the same monomers is fibrous and soluble in m-cresol.

In another study, Zue et al,. 2017, developed a polyimines film through step-growth polymerization. They synthesized different polyimines by reacting terephthalaldehyde, TAEA amine, and ethylenediamine with fixed ratios in various solvents. The researchers used the solvents individually, such as dichloromethane, tetrahydrofuran, ethyl acetate, methanol, ethanol, and isopropanol. The final products are yellow-orange films. The resulting polyimines properties were significantly influenced by the choice of solvent. The best performing polymers were characterized to exhibit smooth surface and higher mechanical properties, and were produced by using tetrahydrofuran and methylene chloride as solvents.
$\mathrm{OHC{-}Ar{-}CHO + H_2N(CH2)2NH_2 + N(CH_2CH_2NH_2)_3 \longrightarrow}$ Polyimines

Table (2.1 A) summarizes the scientific articles reviewed, listing the monomers used and the reaction media. It highlights how altering these variables can lead to changes in polyimines' properties, allowing researchers to modify materials to their specific study goals.

| **Monomers** | | **Solvent** | **Additives** | **NOTES** | **Ref** |
|---|---|---|---|---|---|
| **Amine** | **Aldehyde** | | | | |
| Alphatic amines<br>$H_2N(CH_x)NH_2$<br>X=(3-10)&12 | Terephthalaldehyde | N'Ndimethylacetamide | X | Hexamethylphosphoramide (Catalyst) | Natansohn et al. (1991) |
| $H_2N(CH_2)_5NH_2+$<br>$H_2N(CH_2)_{10}NH_2$ | Terephthalaldehyde | N'Ndimethylacetamide | X | Hexamethylphosphoramide (Catalyst) | Yang et al. (1992) |
| $H_2N(CH_2)_3NH_2+$<br>$H_2N(CH_2)_{10}NH_2$ | | | | | |
| $H_2N(CH_2)_7NH_2+$<br>$H_2N(CH_2)_9NH_2$ | Terephthalaldehyde | N'Ndimethylacetamide | X | Hexamethylphosphoramide (Catalyst) | Yang et al. (1992) |
| $H_2N(CH_2)_{10}NH_2$ | Terephthalaldehyde | N'Ndimethylacetamide | X | Hexamethylphosphoramide (Catalyst) | Natansohn et al. (1993) |
| $H_2N(CH_2)_8NH_2+$<br>$H_2N(CH_2)_{10}NH_2$ | Terephthalaldehyde | N'Ndimethylacetamide | X | Hexamethylphosphoramide (Catalyst) | Yang et al. (1993) |
| Polyethyleneimine | Glutaraldehyde | DI Water | GOx & CNT | The Amine was connected to the CNT and GOx through physical charges | Yang et al. (1995) |
| | Terephthalaldehyde | Ethanol | | | |
| Hexamethylenediamine | Terephthalaldehyde | m-Cresol | X | X | Suematsu et al. (1983) |
| Ethylenediamine+<br>TAEA | Terephthalaldehyde | Tetrahydrofuran, CH2Cl2, ethylacetate, isopropanol, MeOH, or EtOH | X | Each of the solvents was used separately | Zhu et al. (2015) |
| Tris(4-aminophenol)benzene | Terephthalaldehyde | 1,4dioxane& mesitylene | X | The interfacial polymerization occurs in between water and the monomer solution | Valentino et al. (2017) |
| Diethylenetriamine | Glutaraldehyde | Isopropylalcohol | Silica nanoparticles | Silica nanoparticles were generated by hydrolyzing (3-aminopropyl) trimethoxysilane within the polymer | Liang et al. (2022) |
| Polyethyleneimene | Terephthalaldehyde | Ethanol | X | X | Jarach et al. (2022) |
| Diethylene+<br>Triethylenetetramine | Terephthalaldehyde | $CH_2Cl_2$+EtOAc+EtOH | X | Thin film product | Taynton et al. (2016) Zhu et al. (2017) |
| | | Ethylacetate EtOAc | X | Powder product | |

Table (2.1 B) summarizes the scientific articles reviewed, listing the monomers used and the reaction media. It highlights how altering these variables can lead to changes in polyimines’ properties, allowing researchers to modify materials to their specific study goals.

| | | | | | |
|---|---|---|---|---|---|
| p-phenylenediamine+ aniline | Terephthalaldehyde | Gama-aminopropyltriethoxysilane | X | Aniline and launylamine were used as a cap in the termination process | Takeuchi et al. (1983) |
| Hexamethylenediamine+ Launylamine | | | | | |
| Terephthalicdihydrazide | Glutaraldehyde | Dimethyl sufoxide | X | X | Tarannum et al. (2019) |
| P-phenylenediamine | Glutaraldehyde | Dimethylformamide | 1,2-propanesult-one +gama-butyrolactone | X | Tarannum et al. (2010) |
| TAEA + 4,7,10-trioxa-1,13-tridecanediamine | Terephthalaldehyde | Tetrahydrofuran | X | X | Schoustra et al (2021) |
| Diamine+triamine | Furan-based dialdehyde | Tetrahydrofuran | X | Different diamines and triamine are used | Hajj et al. (2020) |
| Diethylenetriamine+ tris(2- aminoethyl)amine | Terephthaldehyde | Ethanol | Cellulose paper | X | Su et al. (2020) |
| Triethylenetetramine+ Ethylenediamine | Terephthaldehyde | Methylene chloride, tetrahydrofuran, ethyl acetate, methanol, ethanol, or isopropanol. | X | Each of the solvents was used separately. | Zhu et al. (2017) |
| M-phenylenediamine | Terephthalaldehyde | Dimethyl sulfoxide | KOH | X | Zhu et al. (2015) |
| Ethylenediamine | Tris(4-formyl phenyl) Benzene | Dimethylbenzene (Xylene) | X | The monomers were mixed to form the oligomers, then the polymerization occur at the interfacial part between xylene solution and water | Tiwari et al. (2020) |

## 2.3 Polyimine Characterization

### 2.3.1 Molecular Structure:

FTIR and NMR spectroscopy are commonly used to analyze the structure of polyimine compounds. In FTIR analysis, the presence of a band near 1650 $cm^{-1}$ indicates the formation of the imine (C=N) bond, confirming the successful synthesis of polyimine. Additionally, the disappearance of bands close to 1720 $cm^{-1}$ shows the completion of the reaction and the absence of any unreacted glutaraldehyde. Further, their disappearance verifies polymer formation. Peaks corresponding to functional groups such as N-H, C=O, O-H, or any groups introduced during the polymerization process are also analyzed to determine the chemical properties of the compound. (Tarannun et al., 2010; Olmo et al.,2019; Yeganeh et al., 2004).

In a study, Tarannun et al,. 2010, used FTIR analysis to identify the peak at 1658 $cm^{-1}$, confirming the formation of the imine (C=N) bond. Additional peaks were observed at 2925–2928 $cm^{-1}$ for the C-H asymmetric stretch, 2800–2858 $cm^{-1}$ for the C-H symmetric stretch, and 1515 $cm^{-1}$ for the aromatic carbon-carbon (ArC-C) stretch. These bands are recognized as fundamental features of the polyimine structure.

### 2.3.2 Thermal Analysis:

The thermal stability of polyimine is significantly influenced by the C=N bond and the structural configuration of the polymer. Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA) are typically employed for the thermal analysis of polymers.

Table (2.2) summarizes the thermal findings reported in the literature, highlighting the variations in thermal stability among different types of polyimines. It focuses on the overall molecular structure of the polyimines, melting temperature (Tm), glass transition temperature (Tg), and degradation points.

Table 2.2: summarize the thermal behavior of different polyimines synthesized in the literature. Where (HomoPolyimine) means that the authors used one type of diamine and one type of aldehyde in the reaction. (Aromatic) means aromatic rings appear in the backbone chain. (Aliphatic) means no appearance of an Aromatic ring in the backbone chain. (Yes) means the presence of a crosslinking agent during the reaction. (Low) means no presence of crosslinking agent, but there is a crosslinking bond along the chains, while (No) means there is no presence of crosslinking agent or crosslinking bond along the chains. (X) means the authors did not mention the value. (Multi) means multiple Polyimines were synthesized in the study, where each polymer has its unique Tg or Tm values

| CoPolyimine or Polyimine | Polyimine backbone structure | Presence of crosslinking agent | Tm (Cº) | Tg (Cº) | Degradation (Cº) | Ref |
|---|---|---|---|---|---|---|
| HomoPolyimine | Aromatic | Yes | X | X | 350 | Valentino et al. (2017) |
| CoPolyimine | Aliphatic | No | >200 | X | 350 | Olmo et al. (2019) |
| HomoPolyimine | Aromatic | Low | >100 | X | <200 | Yang et al. (1992) |
| HomoPolyimine | Aromatic | Yes | X | X | X | Chung et al. (2015) |
| CoPolyimine | Aromatic | No | Multi | Multi | 400 | Yang et al. (1993) |
| HomoPolyimine | Aromatic | Low | 110,150 | X | 300 | Natansohn et al. (1993) |
| CoPolyimine | Aromatic | No | Multi | Multi | X | Yang et al. (1992) |
| HomoPolyimine | Aromatic | Low | Multi | Multi | 300 | Suematsu et al. (1983) |
| HomoPolyimine | Aromatic | Yes | X | X | 300-400 | Tarannum et al. (2019) |
| HomoPolyimine | Aliphatic | Low | X | X | X | Takeuchi et al. (1983) |
| CoPolyimine | Aromatic | No | X | X | X | Zhang et al. (2017) |
| CoPolyimine | Aliphatic | Yes | X | 50-70 | 200-600 | Liang et al. (2022) |
| HomoPolyimine | Aromatic | Yes | X | 298 | 300 | Schoustra et al. (2021) |
| CoPolyimine | Aromatic | No | 164,248 | X | 250 | Taannum et al. (2019) |
| HomoPolyimine | Aromatic | No | 93-113 | X | X | Yang et al. (1992) |
| HomoPolyimine | Aromatic | Yes | X | X | 232-243 | Zhu et al. (2015) |
| HomoPolyimine | Aromatic | Low | 107 | X | >130 | Natansohn et al. (1993) |
| CoPolyimine | Aromatic | Yes | X | 170, 182 | 358-441 | Yeganech et al. (2004) |

### 2.3.3 Molecular Weight Determination:

Suematsu et al., 1983, highlighted that some researchers have successfully determined the molecular weight of polyimine using the end-group analysis method. This approach involves measuring the concentration of end groups in the polymer, calculating the degree of polymerization (DP), and subsequently estimating the molecular weight (Rossbach et al., 1992).

Yang et al., 1992, studied coPolyimine synthesis with two types of diamines, successfully used GPC to determine the molecular weight, as the polymers were soluble in tetrahydrofuran. While Yang et al., 1993, in another study, estimated the degree of polymerization to be greater than 20 for certain homoPolyimines, but GPC could not be applied because these polymers were insoluble in organic solvents.

## 2.4 Using Polyimine in Molecular Filtration

Polyimines gained significant attention from researchers in the field of material separation due to their unique chemical properties. These properties include the ability to form hydrogen bonds with other materials (Su et al., 2020), as well as the capability of polyimines to make electrostatic interactions with anions. The positive charged nitrogen in the polyimine chain contributes to its electrostatic affinity, enabling it to separate negative-charged materials from their environment. (Takeuchi et al., 1983).

Takeuchi et al., 1983, developed a stationary phase in open-tubular microcapillaries using polyimine. The polyimine was synthesized by reacting terephthalaldehyde, phenylenediamine, and aniline. The results revealed an effectiveness of the polymer in retaining negative charged compounds due to electrostatic interactions with the positive charged nitrogen in the polyimine structure. The study highlighted the potential of using polyimine in material separation fields, such as environmental analysis and chemical processing.

Tarannum et al., 2019, synthesized a polyimine by reacting terephthalic dihydrazide (produced through aminolysis of polyethylene terephthalate) with glutaraldehyde in a molar ratio of 1:4. This polyimine was used in water treatment, specifically to eliminate the organophosphate pesticide acephate. The polyimine absorbed 42% of the pollutant from a 100 mL, 1 mg/mL aqueous solution. Although the study indicated the potential use in water treatment, it did not contain any adsorption isotherm data or address any potential side effects on the environment.

Valentino et al., 2017, developed a polyimine-based covalent organic framework (COF) thin film. COF is a type of porous material with a crystalline structure formed by organic building blocks. These blocks are linked through strong covalent bonds to create a network of interconnected pores. The polyimine was synthesized via interfacial polymerization with terephthalaldehyde and tris(4-aminophenyl) benzene. The outcome for the polymerization integrated with a polyeithersulfone (PES) ultrafiltration membrane. This combination enhanced the solute rejection of organic materials such as rhodamine-WT compared to PES alone and effectively rejected NaCl, supporting its potential use in water treatment.

Various studies also highlighted the potential of polyimine for water treatment applications. It was noted that polyimine exhibits stability in air and resistance to water, alkali solutions, and polar solvents like amides and alcohols. However, polyimine is prone to decomposition in acidic environments, such as HCl and $H_2SO_4$. This stability in various environments, coupled with its resistance to certain materials, enhances its potential for use in applications like water treatment (Zhu et al,. 2017; Suematsu et al., 1983).

# Chapter Three:

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# Materials & Methods

## 3.1 Chemicals

1,4-Diaminobutane 99% ($NH_2(CH_2)_4NH_3$), and Glutaraldehyde 50 wt% ($OHC(CH_2)_3CHO$) were obtained from Sigma-Aldrich, which was used as a monomer for polyimine synthesis. Tris(2-aminoethyl) amine 96% ($(NH_2CH_2CH_2)_3N$) was also achieved from Sigma-Aldrich and used as a crosslinker for polyimine synthesis. Ethanol 99.5% ($CH_3CH_2OH$) was used as a solvent for polyimine synthesis. Paracetamol ($CH_3CONHC_6H_4OH$) and amoxicillin ($C_{16}H_{19}N_3O_5S$) were used as a pharmaceutical model for water treatment with polyimine. Potassium phosphate (KH2PO4) was used in a buffer solution to study the effect of pH on polyimine adsorption. Sodium hydroxide 0.2M (NaOH) was used to adjust the buffer solution to desired pH levels. Hydrochloric acid 2M (HCl) was used to decompose polyimine. Distilled water ($H_2O$) was used as a solvent to study water treatment with polyimine. Chloroform, tetrahydrofuran, isopropanol, dimethylformamide, N'Ndimethylacetamide, and hexamethylphosphoramide were used to test the solubility of polyimines.

## 3.2 Methodology

### 3.2.1 Polyimine-1 Synthesis:

The polyimine synthesis was carried out using 1,4-diaminobutane and glutaraldehyde in a 1:1 molar ratio. This condensation polymerization reaction involves the formation of an imine linkage between the aldehyde groups of glutaraldehyde and the amine groups of 1,4-diaminobutane. The polymerization was performed in a 25 mL round-bottom flask equipped with a magnetic stirrer. The reaction was conducted at room temperature with continuous stirring until a gel-like material formed then the stirring stopped. The reaction was then left for 8 hours to ensure complete polymerization. The polyimine was collected by vacuum filtration and washed several times with ethanol to remove any unwanted monomers or oligomers. Then left to dry at room temperature for three days before being placed in plastic containers. (Liang et al., 2022; Jarach et al., 2022).

### 3.2.2 Crosslinked Polyimine Synthesis:

A crosslinked polyimine (CP) synthesis was applied using a similar method as previously mentioned at polyimine-1 synthesis, with the exception that tris(2-aminoethyl) amine (TAEA) was used as a crosslinking agent at a ratio of 0.05. The first sample was obtained after 8 hours, though the other samples were collected after 24 hours in order to ensure complete crosslinking.

### 3.2.3 FTIR Analysis:

In order to detect the chemical structure of polyimine and identify its functional groups, such as imine, amine, and alkane, Fourier-transform infrared spectroscopy (FTIR) was performed. The samples were prepared by grinding a small amount of dried polyimine grains using a clean mortar and pestle to achieve a fine, homogeneous powder. The powder was then directly placed onto the diamond crystal of the attenuated total reflectance (ATR) accessory of the FTIR spectrometer.

### 3.2.4 DSC Analysis:

Polyimine-1 (P1) and CP were analyzed using Differential Scanning Calorimetry. The DSC was performed at the Nano lab of Al-Quds University using TA instruments. The measurements were carried out in a sealed aluminum pan under a nitrogen atmosphere, with a heating rate of 10 $^{o}$C/min over a temperature range of 25 to 400 $^{o}$C. The samples were collected as follows:

- Samples of P1 were collected after drying for three days.
- CP samples were collected after drying for three days and two weeks.
- One of the two-week-old-CP samples was collected after being heated on a hot plate at 150°C for 10 minutes.

### 3.2.5 Remove Paracetamol and Amoxicillin from Water Using Polyimine:

To quantify the removal efficiency of paracetamol and amoxicillin from water using CP as an adsorbent through high-performance liquid chromatography (HPLC), the following steps were performed:
First: Sample preparation in a 1 L volumetric flask, 0.1 g of paracetamol or 0.2 g of amoxicillin was dissolved in water to prepare solutions with concentrations of 100 ppm and 200 ppm, respectively. The amoxicillin solution was then adjusted by adding more water to obtain concentrations of 25 ppm, 100 ppm, 150 ppm, and 200 ppm.

A 50 mL aliquot of each solution was placed in separate flasks, one for each concentration. To each flask, 0.1 g of CP was crushed using a clean mortar and pestle. The samples were then placed on an orbital shaker with clamps, set to 100 rpm. HPLC samples were taken at 0h, 10 min, 20 min, 1h, and 2h by filtering the solution through HPLC syringe filters.

Second: The HPLC samples were tested at the Pharmaceutical Department at Al-Quds University, using a Water Alliance HPLC system with a Waters photodiode array detector. Separation was performed on an XBridge column ® (4.6 mm x 150 mm, 5µm). The mobile phase consisted of 10% acetonitrile and 90% phosphate buffer (pH 3.5), delivered at 0.8 mL/min.

Third: The HPLC data were analyzed using the following method.
To estimate the remaining concentration, we used the following equations.

$$\text{Removal efficincy } (\%) = \frac{c_i - c_f}{c_i} \times 100\%$$

Ci: initial concentration of the compound before treatment.
Cf: final concentration of the compound after treatment.

In order to estimate the concentration value in ppm, we use a calibration method by the following equation.

$$Y = mx + b$$

Where: Y is the peak area from HPLC analysis, m is the slope of the calibration Curve, x is the concentration of the compound, and b is the y-intercept of the calibration curve.

The m value was obtained using Origin 2024 software (m=11703.9). While the b value was obtained using Excel software by approaching the following equation.

$$b = Y - m.x$$

**Langmuir and Freundlich Isotherm Models.**

The experimental data were collected and analyzed using Microsoft Excel and Origin 2024 software. The equilibrium concentration of the solute (Ce) was measured at various initial concentrations. The amount of solute per unit mass of adsorbent (qe) was measured using the equation:

$$qe = \frac{(C_i - Ce)v}{m}$$

Where Ci is the initial concentration, v is the volume of the solution, which =50ml, and m is the mass of the adsorbent=0.1g.

1/Ce, log(Ce), ln(Ce), qe, 1/qe, and log(qe) were calculated using Excel.

Then the data were applied to the Langmuir and Freundlich isotherm models.

Langmuir isotherm equation $\frac{1}{qe} = \frac{1}{q_{max} K_L} \times \frac{1}{c_e} + \frac{1}{q_{max}}$

Where $K_L$ is the Langmuir constant. And $q_{max}$ is the maximum adsorption capacity.

Freundlich isotherm equation: $\log q_e = \log K_L + \frac{1}{n} \log Ce$

Where $K_f$ is the Freundlich constant and n is the heterogeneity factor. We used Origin 2024 to create a plot of $\frac{1}{qe}$ versus $\frac{1}{Ce}$ for the Langmuir model and log(qe) versus log (Ce) for the Freundlich model; the slope and intercepts of these plots were determined to find the isotherm parameters.

Slope=$\frac{1}{n}$, intercept =log (Kf) and $R^2$ the correlation coefficient for Freundlich model.

$q_{max} = \frac{1}{intercept}$, $K_L = \frac{1}{slope.q_{max}}$ and $R^2$ is the correlation coefficient for the Langmuir model (Alnajrani et al., 2020).

**pH impact on Polyimine adsorption.**

To study the effect of pH on CP adsorption of amoxicillin, a 1000 ppm solution was prepared by adding 1g of amoxicillin to 1L of water in a 1L volumetric flask, with continuous stirring using a magnetic stirrer. In a separate flask, 13g of potassium phosphate was added to 1L of distilled water. Then, in several beakers, we added the potassium phosphate solution and adjusted the pH to the desired values (5, 6, 7, and 8) by adding 0.2M NaOH, using a pH meter to monitor the pH.

In five 50 mL volumetric flasks, 5 mL of the 1000 ppm amoxicillin solution was added, and then added 45 mL of buffer solutions with different pH values to each flask (distilled water with pH = 6.5, buffer solutions with pH = 5, 6, 7, and 8). The solution was then transferred to graduated flasks, and 0.1 g of the synthesized Two-Week-Old CP was added to each. The flasks were placed on an orbital shaker at 100 rpm. HPLC samples were collected at 0, 10, 20, 60, and 120 minutes using HPLC syringe filters. The HPLC was performed by the Pharmaceutical Department at Al-Quds University.

### 3.2.6 Evaluation of The Synthesized Polyimines Solubility:

In order to evaluate the solubility of the synthesized polyimines, a 0.1 g of polyimine was placed in 10ml each of the following solvents: Chloroform, tetrahydrofuran, isopropanol, dimethylformamide, N’Ndimethylacetamide, and hexamethylphosphoramide.

# Chapter Four:

# Results & Discussion

## 4.1 Polyimine-1 Synthesis:

The synthesis of Polyimine-1 (P1) from 1,4-diaminobutane and glutaraldehyde underwent several transitions during the reaction. Initially, a white fiber formed in the solution within 2 minutes; similar observation was reported by (Natansohn et al,. 1991). Over time, the reaction mixture transitioned into a yellow gel, which progressively darkened. After 8 hours, the material had turned orange. Also, a similar observation was reported by (Liang et al. 2022).

The precipitate was collected using filter paper and a vacuum pump, followed by washing with ethanol to remove any unreacted monomers or oligomers. The material was then left to dry at room temperature for 3 days. During the drying process, the polymer became harder and darker, eventually turning red with a crystalline appearance. None of the discussed studies have reported this phenomenon. (See Picture 1A).

This observation suggests that a reaction may continue even after washing and drying. Which is aligns with some of studies that have noted that reactions continued after collecting the synthesized polymers. Kazumi et al,. 1982, reported that even in the absence of a crosslinking agent, polyimine can form crosslinked bonds, with the degree of crosslinking increasing over time. (As shown in Figure 2.2). In Addition, several articles have mentioned a self-healing process, where the polyimine can repair damages, due to its dynamic covalent bonds (Zhu et al.2017; Schoustra et al,. 2021). Thus, the changes in color and hardness could be related to crosslinking.

## 4.2 Crosslinked Polyimine Synthesis

The Crosslinked Polyimine (CP) was synthesized using 1,4-diaminobutane, tris(2-aminoethyl) amine (TAEA), and glutaraldehyde. In contrast to the synthesis of P1, a red gel-like material formed within 5 minutes. This gel gradually became even darker and thicker over time. During the drying process, the material became darker and harder, eventually exceeding the hardness of P1(Figure 4.1). The increased hardness and darker color are attributed to enhanced crosslinking promoted by the TAEA crosslinker.

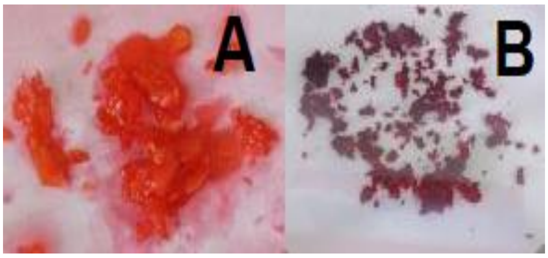


Figure 4.1: (A) Polyimine-1. (B) Crosslinked Polyimine.

## 4.3 FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR), was performed to characterize the chemical structure of polyimines, with a focus on identifying the main functional groups and confirming the formation of imine bonds.

### 4.3.1 Polyimine-1 FTIR Analysis:

The FTIR analysis of P1 was performed as follows: The band at 3322 $cm^{-1}$ represents the N-H stretching, while the bands at 2928 $cm^{-1}$ and 2855 $cm^{-1}$ correspond to the asymmetric and symmetric C-H stretching, respectively. The absorption band at 1648 $cm^{-1}$ is attributed to the C=N stretching, and the absence of a C=O stretching band near 1720 $cm^{-1}$ confirms the successful formation of polyimine and the total consumption of glutaraldehyde. similar reading was observed by (Nazia et al. 2010). Additionally, the band at 1558 $cm^{-1}$ is associated with N-H bending (Stuart et al,. 2005). As shown in Figure (4.2). These bands are recognized in the literature as fundamental features of the polyimine structure.

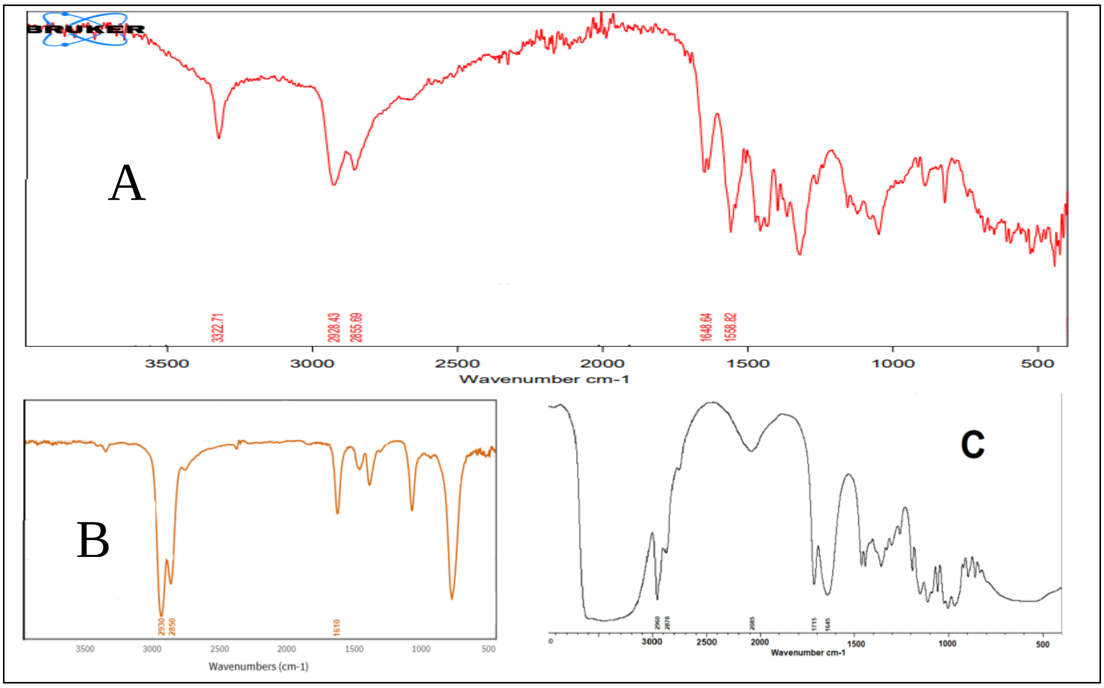


Figure 4.2: FTIR spectra of (A) Polyimine-1, (B) 1,4diaminobutane (C) glutaraldehyde.

## 4.3.2 Crosslinked Polyimine FTIR Analysis:

To evaluate the effect of the crosslinking agent TERN on the synthesized polyimine, FTIR spectra were obtained after eight hours, one day, three days, and two weeks. After eight hours, the spectrum remained nearly identical to that of P1, suggesting minimal crosslinking at this stage. By day 1, a decrease in the N-H stretching and bending band was observed. The N-H stretching band began to overlap with a broad absorption between 3100-3400 cm$^{-1}$, likely due to the hygroscopic nature of the polyimine, which was mentioned by (Stuart et al., 2005). After three days, the N-H bending band disappeared, and the N-H stretching band became weaker (Figure 4.3.A, B). After two weeks, the broad band at 3100-3400cm$^{-1}$, becomes more stronger (Figure 4.3.C). The changes in the spectra indicate an increasing degree of crosslinking due to the corresponding reduction in free -$NH_2$ terminal groups.

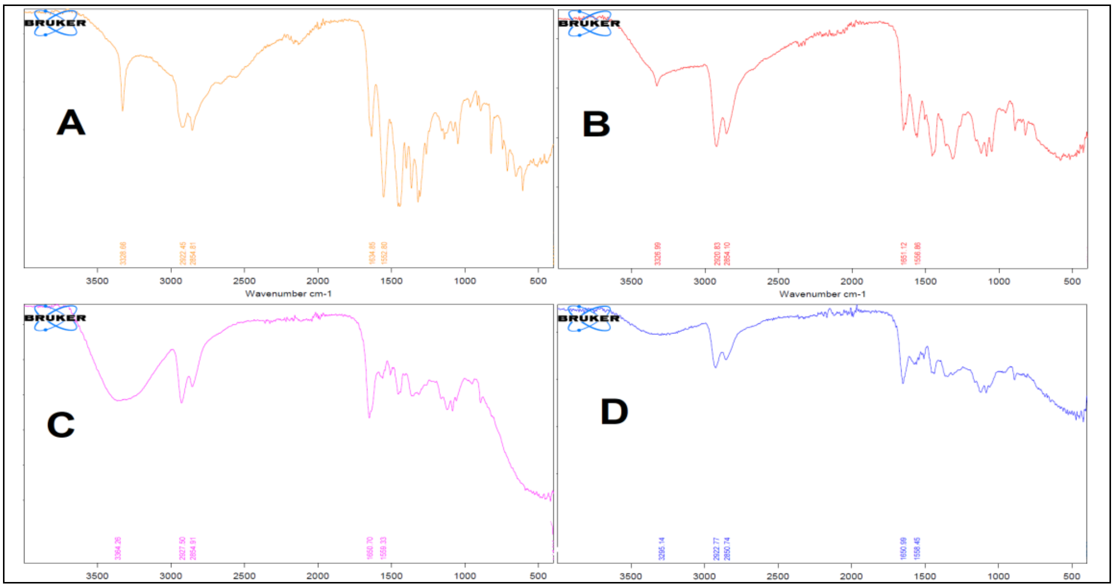


Figure 4.3: FTIR spectra of Crosslinked Polyimine. (A) Sample was collected after 8 h, (B) sample was collected after 1 day, (C) sample was collected after 2 weeks, (D) sample was collected after 3 days.

## 4.4 DSC Analysis

To evaluate the impact of crosslinking on the thermal stability of the polyimine, Differential Scanning Calorimetry (DSC) was performed on various samples of the synthesized polyimines, focusing on the key thermal transitions.

### 4.4.1 Polyimine DSC Analysis:

Differential Scanning Calorimetry (DSC) of both P1 and early collected CP samples ( 8 hours, 1 day, and 3 days) showed an endothermic peak below 80°C. This peak is related to liquid evaporation, most likely ethanol used during the synthesis process. However, P1 showed an exothermic peak between 250 and 350°C which could be related to degradation or that P1 experiences crystallization at high temperature. Farther analysis (such as TGA) is required to confirm which one accurate. (Figure 4.4).

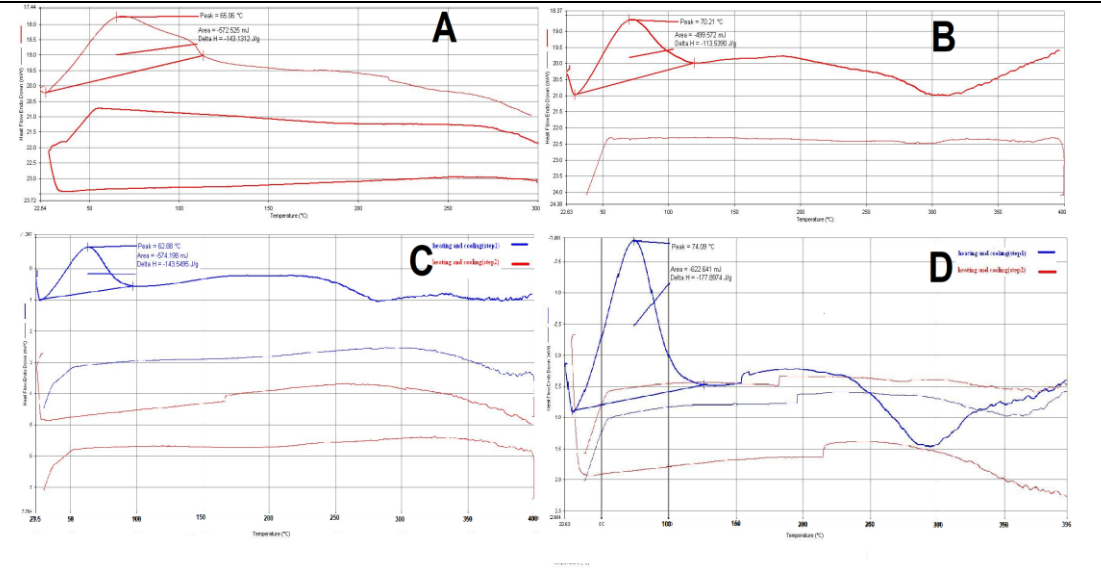


Figure 4.4: DSC thermograms of early collected Polyimines. (A) Eight-hour-old Crosslinked Polyimine. (B) One-day-old Crosslinked Polyimine. (C) Three-day-old Crosslinked Polyimine. (D) Polyimine-1.

### 4.4.2 Crosslinked Polyimine DSC Analysis:

For the two-week-old CP samples, the DSC thermogram showed an interesting observation. The only notable feature was an evaporation peak near 70 °C , meanwhile, no other significant major thermal transitions were observed. This likely suggests a high degree of crosslinking, which makes the polyimine rigid and prevents the formation of any ordered crystalline structures. Amorphous nature of the polyimine. As a result, the polyimine demonstrates a mainly amorphous structure (see Figure 4.5A).

To confirm these results and rule out the possibility of degradation below 100 °C, a sample was heated to 150 °C for 10 minutes. No change in color, shape, or weight were observed. Next, the sample was analyzed using DSC. The scan shows no significant changes, except for an endothermic peak at 107 °C, which was attributed to water evaporation. It’s likely that the polyimine absorbed moisture from the atmosphere during the sample transfer process. This presence of water further supports the earlier observation of polyimine’s hygroscopic nature as seen in the FTIR analysis (see Figure 4.5B).

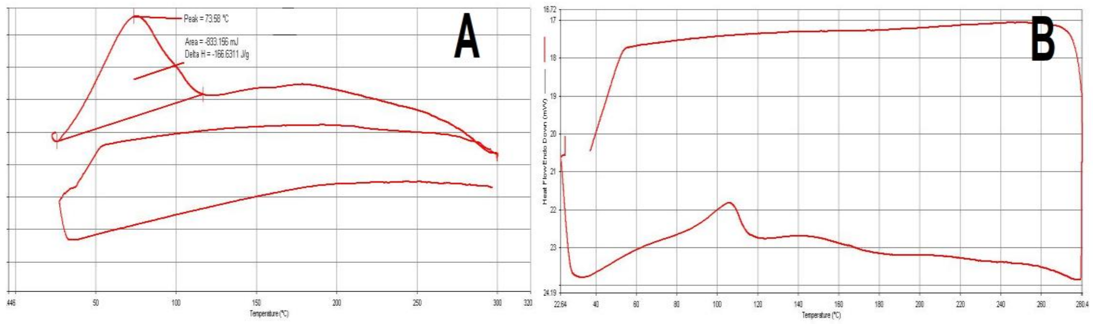


Figure 4.5: Thermograms of two-week-old CP. (A) Before heating to 150C°. (B) After heating to 150C°.

This thermal behavior of polyimine, the absence of clear Tg or melting peaks, has not been reported for any other polyimines discussed in the literature. However, it aligns with our analysis of the literature review section. The thermal properties of polyimine reported in the literature revealed that polyimines containing aromatic rings and synthesized without the usage of crosslinking agents exhibit higher crystallinity compared to those lacking aromatic rings or synthesized with the usage of crosslinking agents, as shown in Table (2.2). Also, polyimines with aromatic rings and without crosslinking agents show a clear melting temperature (Tm). In addition, polyimines prepared with shorter monomers exhibit shorter and broader Tm peaks, as was noticed in DSC thermograph in a study done by Natansohn, et al,. 1991. However, no correlation between the number of methylene units of the monomers and the thermal properties of the polyimine was established in the literature. But another study observed that reaction time impacts the thermal properties. Suematsu et al,. 1982, noted that longer reaction time, shorter and broader Tm peaks were, and explained that by an increase in the crosslinking ratio in the polyimine. The comparison between these two studies suggests that the shorter monomer lengths lead to higher crosslinking percentages, even in the absence of crosslinking agents.

Also, Table (2.2) shows that the glass transition temperature (Tg) of polyimines can be affected by the crosslinking ratio and the presence of aromatic rings. Thus, coPolyimines synthesized without crosslinking agents show a weak Tg. However, in coPolyimines lacking aromatic rings, Tg was not reported in the studies investigating the thermal properties of polyimine. In conclusion, a highly crosslinked or fully amorphous polyimines often lacks a detectable Tg and Tm (Menczel et al,. 2009).

To elucidate the structure properties of the polyimine, attention should be given to imine bond formation. When a primary amine reacts with a primary aldehyde, two possible stereochemical configurations can form: the *E configuration* and the *Z configuration*. If the *E configuration* occurs, the resulting polyimine chain is more likely to be linear, with a minimal number of branches. However, if *Z configuration* is formed, less linear or more irregular. In the case where aromatic rings are a part of the polyimine structure, it is less likely to form the *Z stereo configuration* due to increased steric hindrances and steric interaction than the polyimine, compared to polyimine with only an aliphatic backbone (Khan et al, 2019). (Figure 4.6)

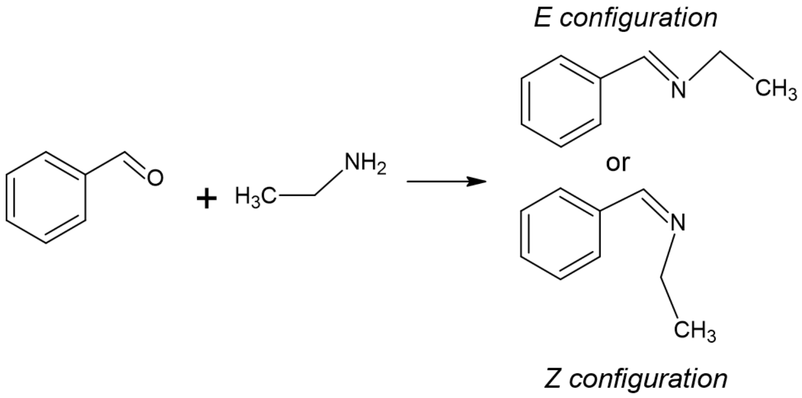


Figure 4.6: shows the imine bond formation with two possible stereo configurations.

By comparing the results from the DSC thermograms and the literature review (Table 2.2) with the possible stereochemical configurations resulting from the imine bond formation, it can be concluded that the synthesized polyimines exhibit a highly amorphous structure and a high degree of crosslinking.

## 4.5 Removing of Paracetamol and Amoxicillin from Water Using Polyimine

Many studies have suggested that polyimine polymers could be used for water treatment, including of removing pharmaceutical wastes, as it was mentioned before in the literature review section. in this study the synthesized polyimine was used to remove paracetamol and amoxicillin from water.

### 4.5.1 Paracetamol Removal by Polyimine:

For paracetamol removal, HPLC was used to analyze and calculate the removal percentage. No significant adsorption values were obtained when pH impact was studied. So, it can be concluded that the polyimine is not efficient at removing paracetamol from water and other methods may be more efficient (Table 4.1) and (Figure 4.7).

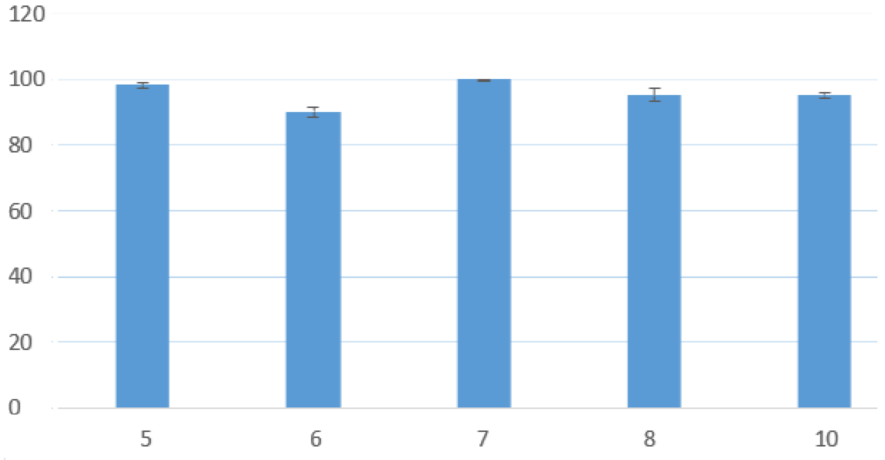


Figure 4.7: shows the pH impact on Polyimine adsorption for paracetamol. X-axis represent pH values. Y-axis represent the remaining paracetamol amount in ppm. Original solution concentration was 100ppm.

Table 4.1: shows the pH impact on polyimine adsorption for paracetamol.

| pH | Remaining Para con (ppm) |
|---|---|
| 5 | 98.2 |
| 6 | 90.3 |
| 7 | 100.0 |
| 8 | 95.4 |
| 10 (not buffered) | 95.2 |

### 4.5.2 Amoxicillin Removal by Polyimine:

#### 4.5.2.1 Langmuir and Freundlich Isotherm Models:

Langmuir and Freundlich isotherm models were applied to describe the adsorption behavior and efficiency of polyimine in removing amoxicillin. These models were as follows:

Table 4.2: Langmuir and Freundlich isotherm variables.

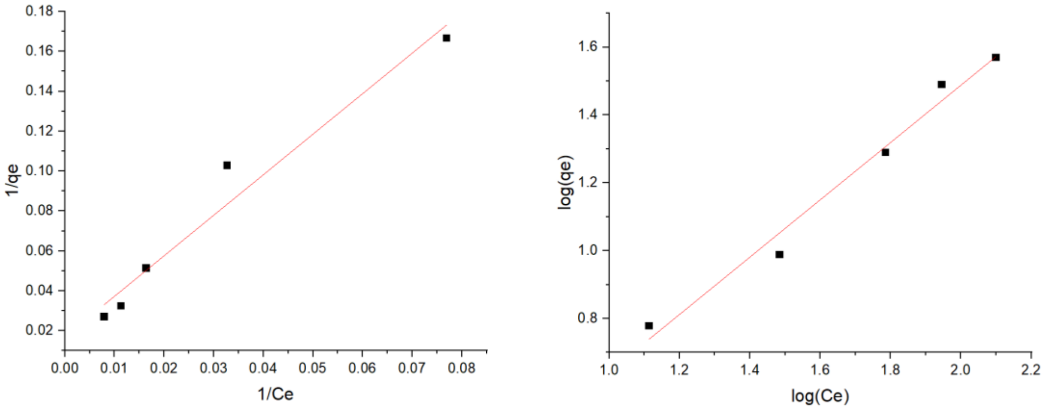
| Exp No. | $R_L$ | $C_i$(ppm) | $C_e$(ppm) | $1/C_e$ | $\log(C_e)$ | $\ln(C_e)$ | $q_e$(mg/g) | $1/q_e$ | $\log(q_e)$ |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.83 | 25.00 | 12.99 ± 0.41 | 0.08 | 1.11 | 2.56 | 6.00 | 0.17 | 0.78 |
| 2 | 0.71 | 50.00 | 30.55 ± 1.06 | 0.03 | 1.49 | 3.42 | 9.72 | 0.10 | 0.99 |
| 3 | 0.54 | 100.00 | 61.05 ± 2.51 | 0.02 | 1.79 | 4.11 | 19.47 | 0.05 | 1.29 |
| 4 | 0.44 | 150.00 | 88.25 ± 0.40 | 0.01 | 1.95 | 4.48 | 30.88 | 0.03 | 1.49 |
| 5 | 0.37 | 200.00 | 125.87 ± 2.37 | 0.01 | 2.10 | 4.84 | 37.07 | 0.03 | 1.57 |

Table: 4.3: Langmuir model parameters

| $R^2$ | $K_L$ | $q_{max}$(mg/g) | Slope | Intercept |
|---|---|---|---|---|
| 0.95014 | 0.008 | 58.893 | 2.03126 | 0.01698 |

Table 4.4: Freundlich model parameters

| $R^2$ | $K_f$ | 1/n | Slope | Intercept |
|---|---|---|---|---|
| 0.97517 | 0.629 | 0.8446 | 0.84464 | -0.20124 |



**A**

**B**

Figure 4.8: (A) Langmuir isotherm model. (B) Freundlich isotherm model.

Both isotherm models fit the experimental data well based on the correlation coefficient ($R^2$). The Freundlich isotherm suggests the presence of heterogeneous adsorption sites, while the Langmuir model implies monolayer adsorption on a uniform surface. This indicates that the synthesized polyimine exhibits a heterogeneous surface with some degree of site uniformity. The Freundlich constant $K_f$ =0.629 and Langmuir maximum adsorption capacity $q_{max}$ = 58.893 suggests a moderate adsorption capacity. The value of 1/n= 0.8446 indicates slightly favorable adsorption, while the Langmuir constant $K_L$ =0.008 reflects a relatively low affinity between the adsorbate and the adsorbent. (Alnajrai et al,. 2020)

### 4.5.2.2 pH Impact on Amoxicillin Absorption:

The Two-Week-Old-Polyimine removed up to 63% of the drug at pH 7, and 60% without using any buffer. However, when the pH was adjusted to 5, 6, and 8, the removal percentages were: 44%, 49%, and 29%, respectively. As it shown in (Tables 4.5, 4.6) and (Figures 4.9, 4.10).

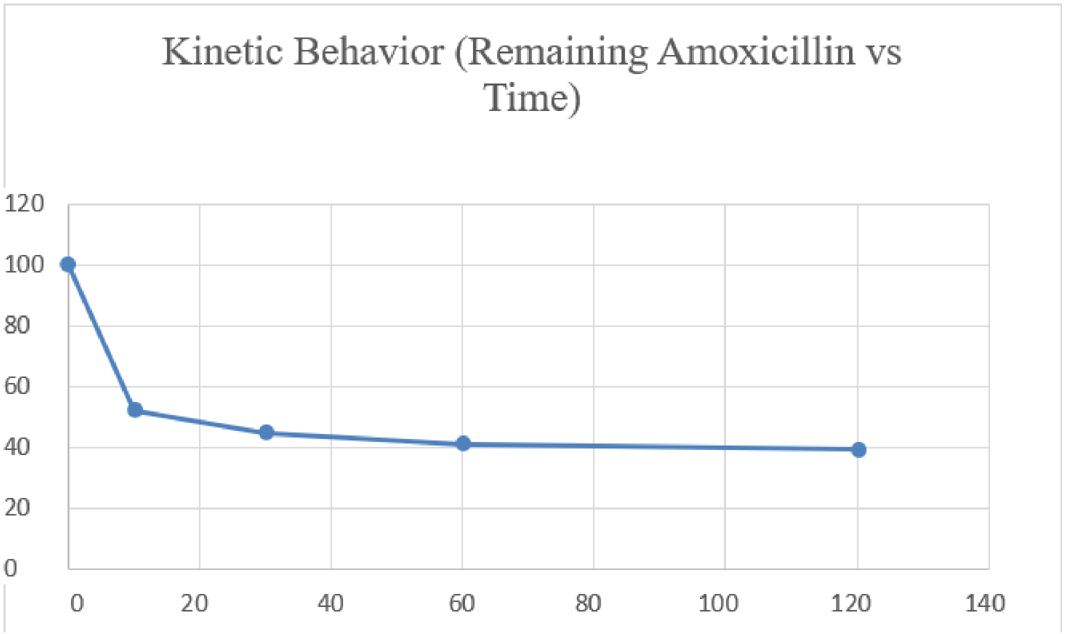


Figure 4.9: a diagram that shows the remaining amoxicillin concentration after treating the solution with polyimine. The X-axis represents the time in minutes, while the Y-axis represents the remaining amoxicillin concentration in ppm.  The initial concentration of the solution was 100 ppm.

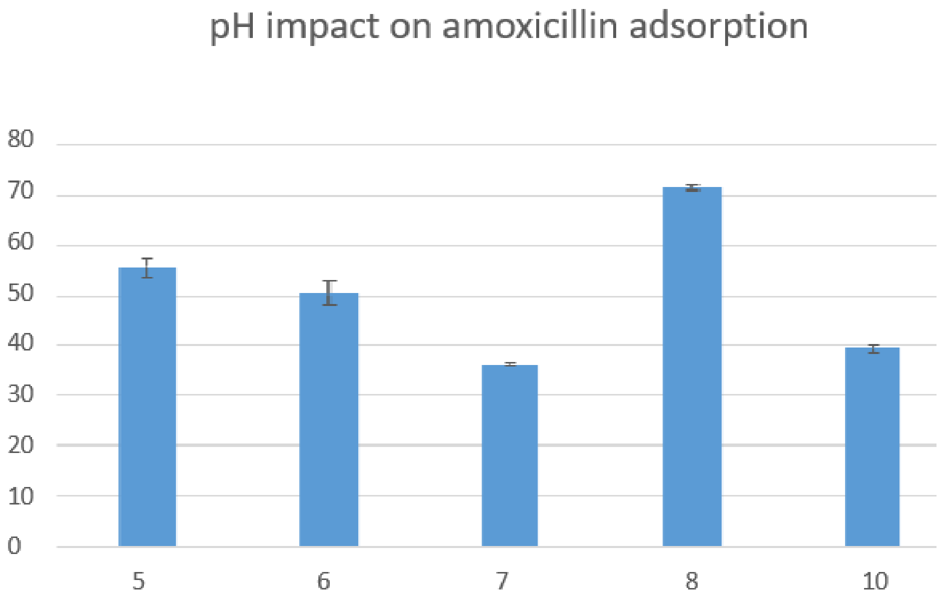


Figure 4.10: shows the pH impact on polyimine adsorption for amoxicillin. The X-axis represents pH values, while the Y-axis represents the remaining paracetamol amount in ppm. The original solution concentration was 100ppm.

Table 4.5: The pH impact on polyimine adsorption for Amoxicillin.

| Remaining Amox con(ppm) | pH |
|---|---|
| 55.50 ± 2.04 | 5 |
| 50.40 ± 2.42 | 6 |
| 36.10 ± 0.36 | 7 |
| 71.50 ± 0.53 | 8 |
| 39.56 ± 0.75 | 10.4 (not buffered) |

Table 4.6: The remaining amoxicillin after treating the solutions with polyimine.

| Remaining Amox con(ppm) | Time(min) |
|---|---|
| 100 | 0 |
| 51.90 ± 0.33 | 10 |
| 44.64 ± 0.11 | 30 |
| 40.76 ± 0.81 | 60 |
| 39.18 ± 1.31 | 120 |

On the other hand, the polyimine is highly sensitive to pH. The material could not withstand low pH values and decomposed. As it shown (Table 4.7).

Table 4.7: shows the recovery percentage of the polyimine at different pH levels.

| pH value | pH value after adding Polyimine | Recovery percentage |
|---|---|---|
| 5 | 6.73 | 25% |
| 6 | 6.9 | 51% |
| 7 | 7.5 | 60% |
| 8 | 8.81 | 100% |
| Not buffered | 10.41 | 100% |

Additionally, polyimine has an impact on the pH of its environment. It was observed that polyimine exhibits an alkaline nature due to the presence of amine groups within its structure. Also, it decomposes at low pH values. While this could be considered a limitation because it cannot withstand the extreme environment of low pH, it may also be considered advantageous, as it enhances its biodegradability and facilitates environmental removal. In addition, because it decomposes at low pH, the adsorbed materials could be recovered.

Another advantage of synthesized polyimine is its selectivity. As mentioned earlier, CP shows a preference for adsorbing amoxicillin over paracetamol. The main reason for this selectivity lies in the structure of the polyimine. As it was described in the FTIR analysis and DSC analysis sections, the two-week-old CP has a much higher crosslinking density compared to the newer CPs and P1. This higher crosslinking density provides more binding sites for the drug.

Both the selectivity and the adsorption capacity of polyimine are related to the presence of stable $N^+$ groups within its structure. As the degree of crosslinking increases, the adsorption capacity is expected to increase. The $N^+$ can easily form electrostatic attractions with negatively charged ions; this feature was mentioned by (Takeuchi et al., 1983). This indicates that the polyimine may be effective at adsorbing acidic drugs, where a greater ionization degree of the drug could lead to higher adsorption. So, because paracetamol has a greater pKa (9.5) than amoxicillin (2.67, 7.11, and 9.55), it makes it less ionizable. So, the Crosslinked Polyimine favors the adsorption of amoxicillin over paracetamol. Further studies on ionized and nonionized drugs are required.

## 4.6 Molecular Weight Determination and Solubility Test

Gel permeation chromatography (GPC) is a widely used method to determine the molecular weight of coPolyimines. However, determining the molecular weight of homoPolyimine is difficult, primarily due to the complexity of its polymer structure. Most homopolyimines exhibit a high degree of crosslinking, making them difficult to dissolve in organic solvents. Since GPC requires soluble samples, this method is often unsuitable for such polymers.

The synthesized polyimine solubility was studied using different solvents, such as (chloroform, tetrahydrofuran, isopropanol, dimethylformamide, N'Ndimethylacetamide, and hexamethylphosphoramide), but none of them were able to dissolve it. This supports the assumption about the high degree of crosslinking within its structure (for both P1 and CP). The reduced crosslinking degree at coPolyimine structure might be attributed to the increased distance between C=N bonds, which enables molecular weight determination, as reported in the literature. (Figure 4.11). Therefore, the synthesized polyimine could not be analyzed using GPC because of its insolubility in solvents.

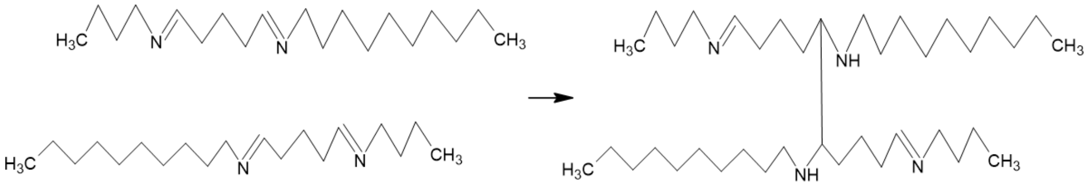


Figure 4.11: Shows how the difference between diamine methylene length can affect the crosslinking degree of coPolyimine.

## 4.7 Polyimine Self-Healing

It was noticed that crushed polyimine, which was used in water treatment, rejoined and formed a bigger grain. Especially at low pH (Figure 4.12). This observation suggests that the synthesized polyimine may exhibit self-healing properties. This behavior is known for the polyimine polymers, which was mentioned several times in the literature due to the dynamic C=N bond.

Figure 4.12: Rejoined grains.

# Chapter Five:

## Conclusion:

The synthesized Polyimine exhibits a unique chemical behavior, such as self-healing, high crosslinking density, and an electrostatic affinity to negatively charged ions. In addition to its unique thermal behavior (it acts like thermoset polymers). The investigated polyimines were analyzed by FTIR and DSC. However, it may not be the best adsorbent for amoxicillin or paracetamol. It could be modified to make it more suitable by increasing the crosslinking density, or alkylating its tertiary amine to introduce quaternary ammonium, which will increase the N+ density (Bruice et al., 2004). Also, its significant increase in pH while treating the solutions is concerning, so a toxicity study should be applied before any environmental treatment. Overall, the synthesized polyimine represents a promising material due to its unique chemical, mechanical, and thermal behaviors.

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## توليف وتشخيص بولي إيمين وتطبيقاته على إزالة الأموكسيسيلين من المياه الملوثة

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**الملخص:**

تهدف هذه الدراسة إلى تحضير وتشخيص شبكة بوليمر بولي إيمين وتقييم كفاءته في إزالة الملوثات الدوائية، وتحديدًا الأموكسيسيلين والباراسيتامول، من المياه الملوثة. تم تحضير بولي إيمين من خلال تفاعل 1,4–ثنائي أمينو البيوتان، والجلوتارالدهيد، وتريس (2–أثيل أمينو) أمين بنسبة مولارية ثابتة مقدارها 1:1:0.05. تم استخدام تقنيتي FTIR و DSC لتحليل التركيب الكيميائي والسلوك الحراري للبوليمر. كما تم تحديد سعة الامتصاص الكيميائي باستخدام جهاز HPLC ، وتم تحليل البيانات باستخدام نماذج لانغموير وفريندلخ. بالإضافة إلى ذلك، تم دراسة تأثير الرقم الهيدروجيني (pH) على عملية الامتصاص الكيميائي. على الرغم من التطبيقات المثيرة لبوليمرات البولي إيمين في الترشيح الجزيئي، لم تُجرَ دراسات سابقة حول كفاءتها في إزالة الملوثات الدوائية من المياه الملوثة.

تشير نتائج FTIR إلى نجاح تحضير بولي إيمين، بينما توضح نتائج DSC أن للبوليمر بنية متشابكة وسلوكًا شبيهًا بالبوليمرات الثرموسيتية، وذلك بسبب غياب الانتقالات الحرارية. كما أن عدم ذوبانية البولي إيمين في المذيبات العضوية يدعم وجود درجة عالية من التشابك في بنيته. وتشير إعادة التحام حبيبات البولي إيمين في الأوساط المائية إلى امتلاكه خاصية الالتئام الذاتي. بلغت نسبة إزالة الأموكسيسيلين 63% عند الرقم الهيدروجيني 7، في حين كانت إزالة الباراسيتامول ضئيلة. وقد تطابقت البيانات التجريبية مع نموذجي لانغموير وفريندلخ، مما يشير إلى وجود سطح غير متجانس جزئيًا.

تشير نتائج البحث إلى إمكانية تحسين كفاءة الامتزاز للبوليمر من خلال زيادة كثافة التشابك أو إدخال مجموعات الأمونيوم الرباعية، مما يزيد من تركيز الأنواع المشحونة إيجابيًا .($N^+$) كما يتطلب تطبيق الطريقة على نطاق واسع تقييم السمية قبل اعتمادها في الاستخدامات البيئية.