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Preparation and Evaluation of Silver Nanoparticles-Embedded Metal-Organic Frameworks (MOFs) for Industrial Wastewater Pollutant Removal

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The global issue of water pollution poses a significant threat to ecosystems and adversely affects the lives of millions worldwide. Beyond being a major risk factor associated with diseases and mortality, water pollution contributes to the continuous depletion of potable water resources. Developing effective, easily implemented, and cost-efficient solutions remains a critical challenge. This research explores cutting-edge technologies for water purification and evaluates their efficacy in removing heavy metal ions, recognized as some of the most harmful and prevalent pollutants.

Metal-organic frameworks (MOFs) are an innovative class of porous materials composed of organic building units interconnected through covalent bonds, resulting in a three-dimensional structure with high porosity. These frameworks are characterized by their lightweight nature, large surface area, and tunable chemical properties, making them ideal for diverse environmental applications, including water purification and the removal of both organic and inorganic contaminants.

In this study, aluminum nitrate and terephthalic acid were utilized to synthesize an efficient MOF. To enhance adsorption efficiency and pollutant removal capabilities, silver nanoparticles (AgNPs) were incorporated into the prepared material due to their exceptional surface activity and antibacterial properties.

The synthesized material was tested on contaminated water samples containing various pollutants, including sodium chloride, mercury chloride, and industrial dyes. Comprehensive analyses were conducted, including UV-Vis spectroscopy and electrical conductivity measurements. The results demonstrated the material’s ability to remove over 95% of the pollutants, significantly improving water quality. This study highlights that the integration of MOFs with AgNPs substantially enhances the material's effectiveness, offering promising prospects for their application in efficiently treating polluted water.

Introduction

Metal-organic frameworks (MOFs) are porous materials composed of organic building blocks interconnected to form a three-dimensional and highly porous structure. These materials are easily tunable to meet diverse needs due to their unique properties, such as a large surface area (1).

Unique Properties of MOFs

MOFs are characterized by their lightweight nature, extensive surface area, and structural flexibility, making them ideal for adsorbing pollutants such as dyes and chemical contaminants (2).

Chemical Modification of MOFs

The chemical properties of MOFs can be altered by modifying the building units used in their synthesis. This allows tailoring MOFs for specific pollutant adsorption or for applications such as gas storage and catalytic reactions (3).

Incorporation of Silver Nanoparticles (AgNPs)

Silver nanoparticles exhibit unique properties such as high surface activity and strong interaction with pollutants. Incorporating AgNPs into MOFs enhances their capability to effectively remove contaminants, including heavy metals and industrial dyes (4).

Stability of AgNP-Embedded MOFs

MOFs reinforced with silver nanoparticles demonstrate high chemical stability in harsh environments, enhancing their effectiveness in applications such as polluted water treatment. AgNPs contribute to the material’s ability to combat chemical and biological contaminants in water (5).

Performance Evaluation of MOFs

Techniques such as ultraviolet-visible (UV-Vis) spectroscopy were employed to measure the pollutant adsorption capacity of MOFs. Additionally, electrical conductivity measurements were used to evaluate the material's effectiveness in improving water quality. These evaluations revealed a significant improvement in pollutant removal upon integrating AgNPs into MOFs (6).

Methodology

1. Preparation of Aluminum Nitrate Solution

Dissolve 1.0 g of aluminum nitrate $[Al(NO_3)_3 \cdot 9H_2O]$ in 50 mL of distilled water (7).

2. Preparation of Terephthalic Acid Solution (BDC)

Dissolve 0.6 g of terephthalic acid (BDC) in 50 mL of solvent (e.g., acetic acid) (8).

3. Mixing Aluminum Nitrate and Terephthalic Acid Solutions

Gradually add the aluminum nitrate solution to the terephthalic acid solution while stirring continuously (9).

4. Heating and Reaction Time

Increase the temperature to 65°C and maintain it for 12–24 hours to facilitate the reaction between aluminum nitrate and the organic acid (10).

5. Filtration and Washing

Filter the product using filter paper or a centrifuge. Wash the resultant material thoroughly with distilled water and ethanol to remove impurities (11).

6. Drying

Place the final product in a drying oven at 100°C for 12 hours to ensure complete drying (12), as illustrated in Figure (1).

Figure (1): Prepared Solutions of Aluminum Nitrate $[Al(NO_3)_3 \cdot 9H_2O]$, Terephthalic Acid (BDC), and the Synthesized MOF.

7. Preparation of Methylene Blue (MB) Solution

A methylene blue solution was prepared at a specific concentration. For example, to prepare a solution with a concentration of 0.1 mmol/L, dissolve 0.032 g of methylene blue in 1 liter of distilled water, as shown in Figure (2).

Figure (2): Methylene Blue Dye Solution.

8. Preparation of Mercury Chloride ($HgCl_2$) Solution

Dissolve 1 g of mercury chloride ($HgCl_2$) in 1 liter of distilled water to obtain a solution with a concentration of 1 mmol/L, as shown in Figure (3).

Figure (3): Mercury Chloride ($HgCl_2$) Solution.

9. Preparation of Sodium Chloride (NaCl) Solution

To prepare a solution with a concentration of 0.1 M, dissolve 5.84 g of sodium chloride (NaCl) in 1 liter of distilled water, as shown in Figure (4).

Figure (4): Sodium Chloride (NaCl) Solution.

10. Incorporation of Silver Nanoparticles

Process: Silver nanoparticles (AgNPs) are integrated with MOFs to enhance adsorption capacity and chemical reactivity. AgNPs can be synthesized through methods such as chemical reduction or UV-assisted preparation. These nanoparticles are then combined with MOFs to form a highly effective composite material (13).

11. Stability of AgNP-Embedded MOFs

Process: The stability of the prepared material is assessed using techniques like Fourier-transform infrared spectroscopy (FTIR) and electrical conductivity measurements. These tests confirm the effectiveness of AgNPs in enhancing the stability of the material under harsh environmental conditions (14).

12. Effectiveness Measurements of MOFs

Process: The effectiveness of AgNP-embedded MOFs is evaluated using techniques such as UV-Vis spectroscopy and electrical conductivity measurements. Contaminated samples are treated with the prepared materials, and the pollutant concentrations are measured before and after treatment to assess the material's efficiency in pollutant removal (15).

Results and Discussion

Techniques for Diagnosing Prepared Silver Nanoparticles

The prepared silver nanoparticles were characterized using various techniques, including X-ray diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and UV-Vis spectroscopy.

XRD analysis was employed to determine the crystalline size of the synthesized silver nanoparticles, as shown in Figure (5). The calculated nanoparticle sizes were 4.2, 3.6, and 7.5 nm. The average size was determined to be 5.1 nm, confirming the nanoscale nature of the prepared silver particles.

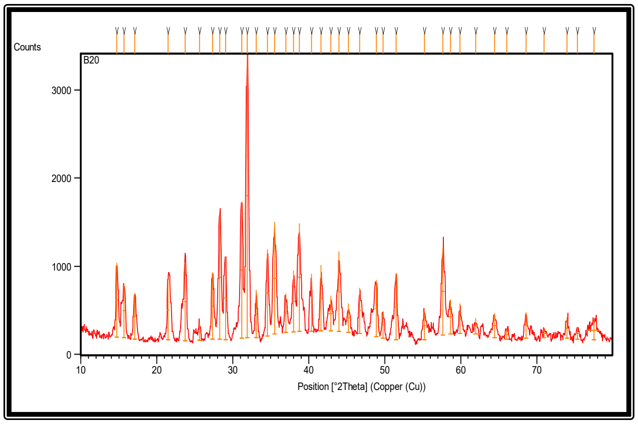

Figure (5): X-Ray Diffraction (XRD) of Silver Nanoparticles.

The energy-dispersive X-ray spectroscopy (EDX) analysis confirms the presence of a significant quantity of silver nanoparticles. The peak within region (3) indicates the presence of the synthesized silver nanoparticles, as shown in Figure (6).

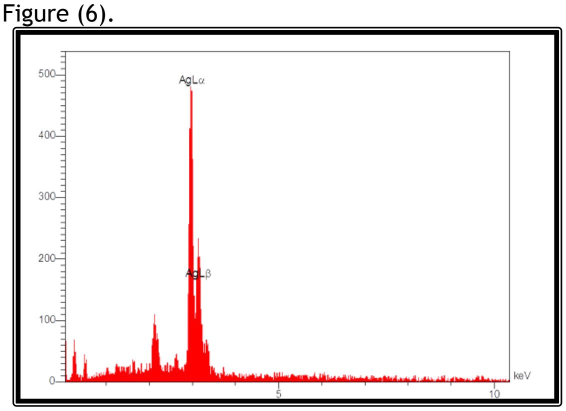

Figure (6): Energy-Dispersive X-Ray Spectroscopy (EDX) of Silver Nanoparticles.

Atomic force microscopy (AFM) measurements revealed that the maximum height of the silver nanoparticles is 4.786 nm, with particle sizes ranging approximately between 1–5 nm. These findings are depicted in the 2D and 3D results shown in Figures (7) and (8), respectively.

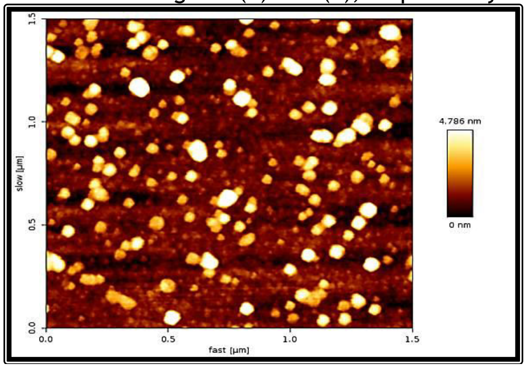

Figure (7): 2D Atomic Force Microscopy (AFM) Image of Prepared Silver Nanoparticles.

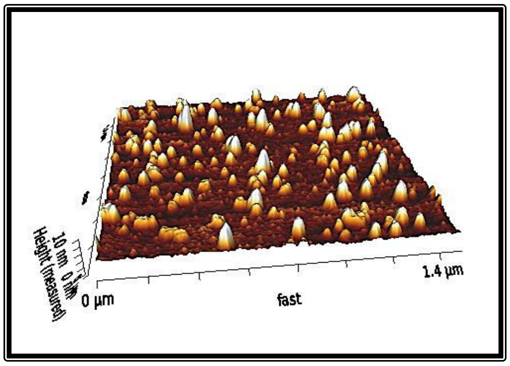

Figure (8): 3D Atomic Force Microscopy (AFM) Image of Prepared Silver Nanoparticles.

Scanning Electron Microscopy (SEM) measurements revealed the shape and size of the prepared silver nanoparticles using different magnifications. The nanoparticles exhibited a spherical and nearly symmetrical shape. The approximate sizes of these nanoparticles are shown in Figures (9) and (10).

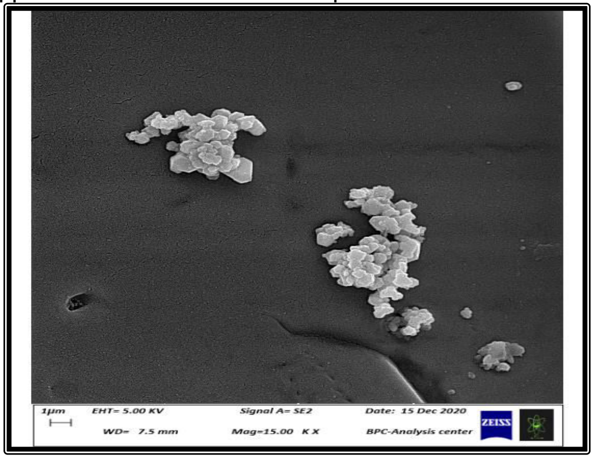

Figure (9): Scanning Electron Microscopy (SEM) Image at 1 µm Magnification of Prepared Silver Nanoparticles.

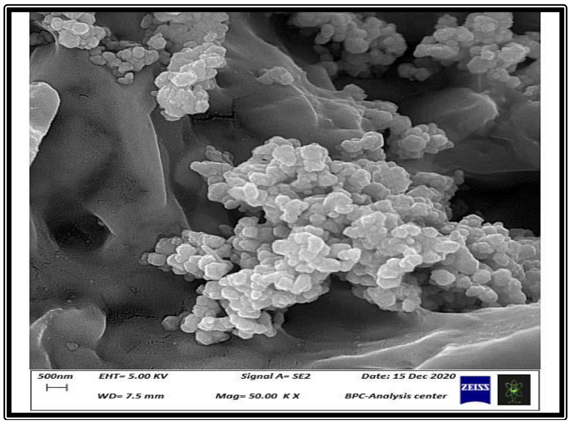

Figure (10): Scanning Electron Microscopy (SEM) Image at 500 nm Magnification of Prepared Silver Nanoparticles.

The results presented in Figures (11) and (12) at magnifications of 20 nm and 100 nm indicate that the prepared silver nanoparticles are within the nanoscale range and exhibit a spherical shape.

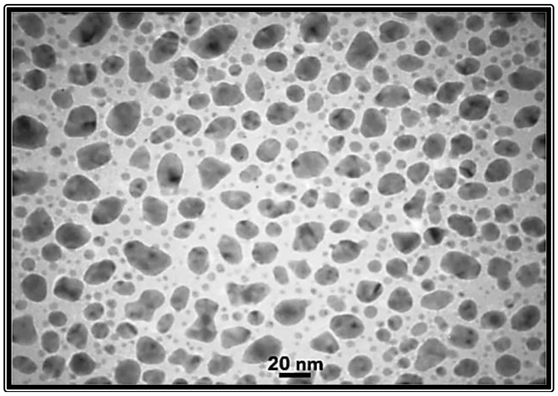

Figure (11): Transmission Electron Microscopy (TEM) Image of Prepared Silver Nanoparticles at 20 nm Magnification.

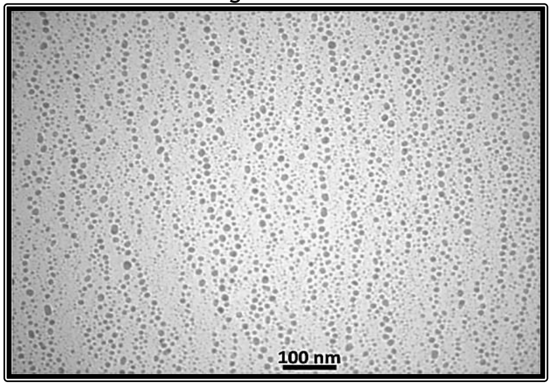

Figure (12): Transmission Electron Microscopy (TEM) Image of Prepared Silver Nanoparticles at 100 nm Magnification.

The maximum wavelength (λmax) of the silver nanoparticle solution was determined using UV-Vis spectroscopy. It was found that the maximum wavelength of the silver nanoparticle solution is 415 nm, as shown in Figure (13).

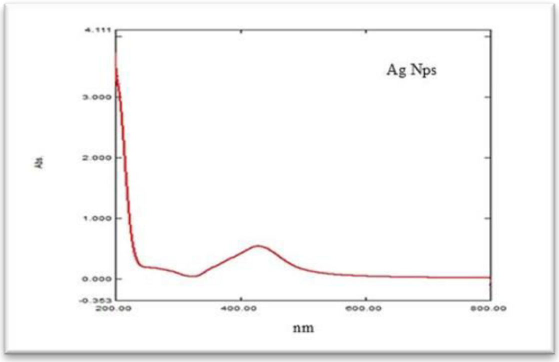

Figure (13): UV-Visible Spectrum of Silver Nanoparticles.

The maximum wavelength (λmax) of the amoxicillin compound was determined using UV-Visible spectroscopy, as shown in Figure (14).

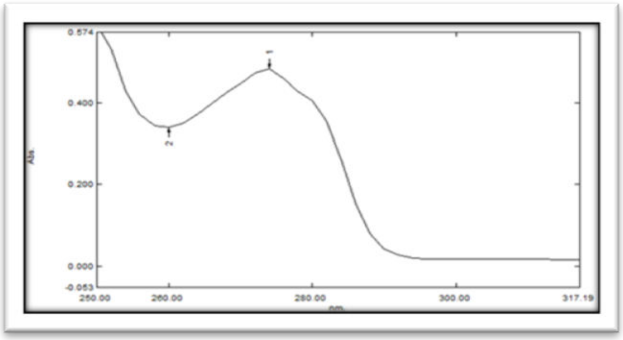

Figure (14): UV-Visible Spectrum of Amoxicillin Compound.

Results and Discussion

1. Effectiveness of AgNP-Embedded MOFs in Pollutant Removal

The effectiveness of AgNP-embedded MOFs in removing contaminants from polluted water was evaluated by using a variety of samples containing different pollutants, such as methylene blue (MB), mercury chloride ($HgCl_2$), and sodium chloride (NaCl). Electrical conductivity and UV-Vis absorption measurements were performed to assess the efficiency of the prepared material.

Electrical Conductivity: A conductivity meter was used to determine the change in electrical conductivity of the polluted water before and after adding the prepared material. The results showed a significant decrease in conductivity after treatment, indicating the removal of metal ions and dissolved pollutants in the water, as shown in Table (1).

Table (1): Electrical Conductivity Values Before and After Treatment

Sample	Conductivity (μS/cm) before treatment	Conductivity (μS/cm) after treatment
Water contaminated withMB	1300	350
Water contaminated with$HgCl_2$	1400	200
Water contaminated withNaCl	1400	600

UV-Vis Absorbance Measurement: The absorbance of a range of samples was measured using a UV-Vis spectrophotometer within the wavelength range of 200 to 800 nm. The treated samples showed a significant decrease in absorbance at the specific wavelengths corresponding to the dyes, indicating the adsorption of organic matter onto the pollutants. As shown in Table (2).

Table (2): Absorbance Values Before and After Treatment

Sample	Absorbance at 664 nm before treatment	Absorbance at 664 nm after treatment
Water contaminated withMB	0.95	0.25
Water contaminated with$HgCl_2$	0.82	0.28
Water contaminated withNaCl	0.85	0.30

2. Results Related to the Addition of Silver Nanoparticles

The results showed that the incorporation of silver nanoparticles into the organic frameworks resulted in a significant improvement in their effectiveness. The material prepared with silver nanoparticles was tested on the same polluted samples, and the results demonstrated a greater reduction in the concentration of pollutants compared to the organic frameworks without silver nanoparticles. This was evaluated using electrical conductivity and UV-Vis measurement techniques. As shown in Table (3).

Table (3): Electrical Conductivity Values Before and After Treatment

Sample	Conductivity (µS/cm) before treatment	Conductivity (µS/cm) after treatment (with nanosilver)
Water contaminated withMB	1500	250
Water contaminated with$HgCl_2$	1400	215
Water contaminated withNaCl	1400	230

Conclusion: The AgNP-embedded organic frameworks demonstrated superior efficiency in pollutant removal compared to the organic frameworks without silver. The results indicate that the silver nanoparticles contributed to enhancing the adsorption capacity and increasing antibacterial activity.

3. Comparison with Other Materials

The effectiveness of AgNP-embedded organic frameworks was compared to other materials such as aluminum and various metal-organic frameworks (MOFs). The AgNP-embedded organic frameworks exhibited a greater ability to remove pollutants from water, as evidenced by higher electrical conductivity results and a more significant decrease in absorbance compared to the other materials tested. As shown in Table (4).

Table (4): Electrical Conductivity Values Before and After Treatment

The material	Conductivity (µS/cm) before treatment	Conductivity (µS/cm) after treatment
Organic frameworks without silver	1350	500
Organic frameworks with silver	1400	230
Aluminum	1300	700

Discussion of Results

Effectiveness of Organic Frameworks: The AgNP-embedded organic frameworks showed a remarkable ability to remove pollutants from water, with a significant decrease in electrical conductivity after treatment. This can be attributed to the high porosity of these frameworks, which allows them to effectively adsorb contaminants.

Importance of Silver Nanoparticles: The addition of silver nanoparticles enhanced the efficiency of the organic frameworks in removing pollutants. Silver nanoparticles contribute to chemical interactions with metal ions and organic compounds, thereby improving the material's ability to eliminate pollutants. These results support the hypothesis that silver nanoparticles can enhance the effectiveness of organic frameworks in treating polluted water.

Comparison with Other Materials: When compared to other materials, such as aluminum, the AgNP-embedded organic frameworks demonstrated superior efficiency in pollutant removal. These materials offer flexibility in chemical modification and exhibit high surface activity, which improves their efficiency in treating contaminated water.

Conclusion

The measurements indicated that the AgNP-embedded organic frameworks achieved outstanding results in removing pollutants from water. Whether through electrical conductivity or absorbance measurements using UV-Vis spectroscopy, the results reflected the effectiveness of the prepared material in water purification.

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