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Polymeric membranes of PVDF and PS for adsorption of copper ions in water

Membranas poliméricas de PVDF y PS para adsorción de iones de cobre en el agua

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KEYWORDS

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Nanotecnología; fibras; magnetismo; medio ambiente

ABSTRACT: Water pollution caused by heavy metals represents a critical global concern due to its harmful effects on human health and aquatic ecosystems. Ion adsorption membranes have emerged as effective solutions for water decontamination. Accordingly, this study provides a physicochemical evaluation of a magnetic polymeric membrane designed for the adsorption of copper ions (Cu^{2+}), fabricated via electrospinning. The membrane consists of a polyvinylidene fluoride (PVDF) and polystyrene (PS) polymeric matrix embedded with magnetite (Fe_3O_4) nanoparticles (NPs) functionalized using ethylenediaminetetraacetic acid (EDTA). Morphological characterization through scanning electron microscopy (SEM) indicated fiber diameters averaging approximately 3 μm . Fourier-transform infrared spectroscopy (FTIR) confirmed successful functionalization with EDTA as a chelating agent. Adsorption data fitted to the Langmuir isotherm model indicated a maximum adsorption capacity of 25.1 mg g^{-1} for the PVDF/PS@ Fe_3O_4 -EDTA polymeric membrane. Magnetic characterization revealed superparamagnetic and ferromagnetic properties. Overall, the membrane demonstrated proficient adsorption of copper ions due to available functional adsorption sites and the incorporation of magnetic nanoparticles.

RESUMEN: Un problema de interés mundial es la contaminación del agua con metales pesados, porque afecta la salud humana y los ecosistemas acuáticos. Las membranas de adsorción de iones metálicos se



han convertido en una buena alternativa de descontaminación, por tal razón, en este estudio, se presentan resultados de la evaluación fisicoquímica de una membrana polimérica magnética para adsorción de iones de cobre Cu^{2+} , elaborada con la técnica de electrohilado. Esta membrana está constituida por una matriz de polifluoruro de vinilideno (PVDF) y poliestireno (PS) con incorporación de nanopartículas (NPs) de magnetita (Fe_3O_4) funcionalizadas con el ácido etilendiaminotetraacético (EDTA). La membrana polimérica se caracterizó morfológicamente a través del Microscopio Electrónico de Barrido por sus siglas en inglés (SEM: Scanning Electron Microscopy) y se identificaron diámetros de fibras alrededor de las 3 μm , la funcionalización con el agente quelante EDTA se demostró con el análisis espectroscópico por Espectroscopia Infraroja por Transformada de Fourier por sus siglas en inglés (FTIR: Fourier-Transform Infrared Spectroscopy). La isoterma de Langmuir sugiere que la máxima capacidad de adsorción de la membrana polimérica de PVDF/PS@ Fe_3O_4 -EDTA fue de 25.1 mg g^{-1} y el estudio magnético mostró un comportamiento superparamagnético y ferromagnético. El material reveló, capacidad de adsorción de iones de cobre debido a los sitios funcionales y la presencia del material magnético nanoparticulado.

1. Introduction

Mining, metallurgy, and agriculture are the principal anthropogenic sources of copper contamination in aquatic and soil environments. Copper is essential for human health at trace concentrations; however, it becomes hazardous at higher concentrations due to its toxicity and resistance to degradation. Therefore, it is crucial to regulate and reduce copper concentrations in natural waters [1][2].

Several methods exist for removing harmful substances, such as heavy metals, including membrane filtration, photocatalytic degradation, and adsorption. Adsorption has emerged as an efficient and cost-effective technique for removing copper from water, resulting in superior-quality treated water.

This technique, which exploits surface phenomena, is widely used for extracting heavy metal ions from aqueous solutions. The quintessential adsorbent is characterized by a large surface area, hydrophobic properties, affinity toward micropollutants, and efficient adsorbent recoverability. Adsorption is thus recognized as an effective and widely employed method for environmental remediation [3][4][5].

Within the field of materials science, nanotechnology offers promising opportunities to develop innovative adsorbent materials for heavy metal ion sequestration. Electrospinning stands out as a highly adaptable method for producing membranes from diverse polymers, that are characterized by high porosity, large specific surface areas, and ease of recycling. When reinforced with nanoparticles (NPs), electrospun membranes become exceptionally efficient adsorbents [6]. This process can produce non-woven fiber arrays—either aligned or randomly oriented—consisting of three-dimensional intersecting fibers, whose dimensions range from sub-micron to nanometer scales. Electrospinning produces nanofibers by applying uniaxial stretching to a viscoelastic polymeric solution under electrical forces. A high electrostatic voltage disrupts the solution's surface tension, allowing the polymer to elongate and solidify as it proceeds toward the collector [7][8][6].

Reinforcing nanocomposites, such as magnetite (Fe_3O_4), are magnetic substances characterized by strong saturation magnetization, biocompatibility, low toxicity, and cost-effectiveness [3].

Nanoparticulate iron minerals, such as magnetite (Fe_3O_4), when immersed in a polymeric matrix and chemically modified, acquire properties conducive to metal-ion adsorption due to their distinctive



physical and chemical characteristics. These attributes promote the selective binding of metal ions, molecules, and colloidal particles, which provides them with properties conducive to the adsorption of metal ions. Magnetite also exhibits significant magnetic behavior, which is advantageous for adsorbent recovery due to the influence of external magnetic fields [9][10][11]. On the other hand, the formation of complexes using compounds, such as ethylenediaminetetraacetic acid (EDTA), creates an effective binding mechanism with metal ions, offering promising nanoparticles of chelating cations for the adsorption of environmental pollutants [3][12][13]. Some studies have successfully intercalated EDTA into electrospun polymer matrices, facilitating copper ion adsorption through interactions between the metal ion surfaces and EDTA [1][14].

Additionally, extensive research has been conducted on the adsorption of various heavy metals using functionalized magnetic nanoparticles encapsulated in polymer-based electrospun membranes [9][15][16][17]. Considering the combined adsorption properties of EDTA and magnetic nanoparticles for copper ions, along with the inherent advantages of electrospun polymeric materials, such as high surface area and porosity, the objective of this research was to synthesize and characterize an electrospun polymeric membrane composed of polyvinylidene fluoride (PVDF) and polystyrene (PS), integrated with EDTA-modified Fe_3O_4 nanoparticles. Figure 1 illustrates the schematic representation of the fabrication process of the PVDF/PS@ Fe_3O_4 -EDTA membrane via electrospinning for the adsorption of Cu^{2+} ions. Both PVDF and PS are inherently hydrophobic, with PS being noted for its lightweight nature and effectiveness in embedding magnetite nanoparticles [4]. PVDF, meanwhile, enhances the mechanical strength of electrospun fibers and is known for its chemical resistance, thermal stability, and widespread use in filtration systems [18][19][20][21]. The proposed PVDF/PS@ Fe_3O_4 -EDTA composite is specifically examined as an adsorbent for Cu^{2+} ions in experimental adsorption isotherm models.

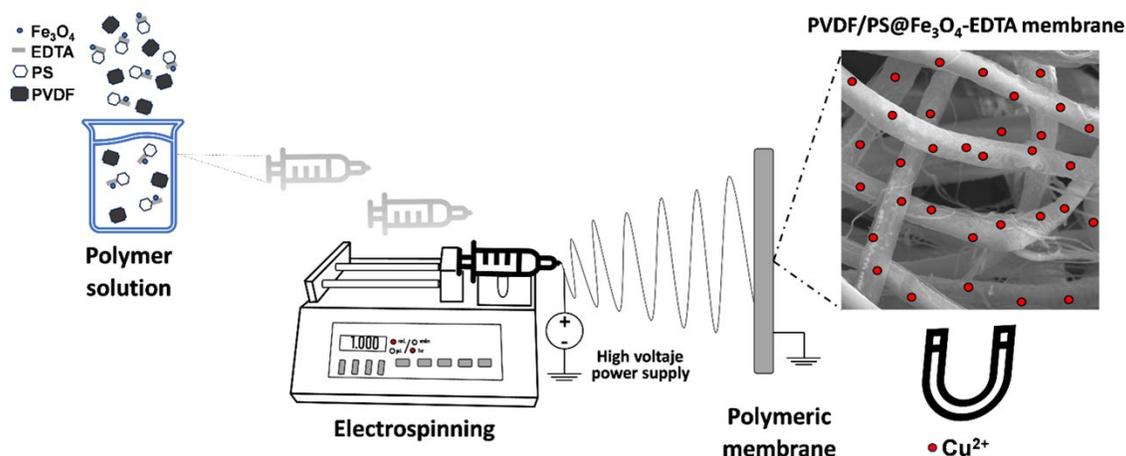


Figure 1. Schematic illustration of PVDF/PS@ Fe_3O_4 -EDTA membrane fabrication by electrospinning through the copper adsorption method.

2. Experimental

2.1. Materials

Magnetite nanoparticles (Fe_3O_4), with diameters ranging from 50 to 100 nm, were purchased from Sigma Aldrich. These nanoparticles were functionalized using ethylenediaminetetraacetic acid (EDTA), a potent chelating agent obtained from J.T. Baker. For membrane synthesis, two polymers were employed: polyvinylidene fluoride (PVDF), with an approximate molecular weight of $534,000 \text{ g mol}^{-1}$, sourced from Alfa Aesar, and polystyrene (PS), with a molecular weight ranging between $100,000$ and $400,000 \text{ g mol}^{-1}$, supplied by Dexton. PVDF was dissolved in a mixture of N-dimethylformamide (DMF, analytical grade 99.8%) and acetone (analytical grade 99.5%), both procured from PanReac Applichem. Polystyrene was dissolved in a solvent mixture consisting of DMF and tetrahydrofuran (THF, analytical grade 99.8%), sourced from Emsure. Adsorption isotherms were obtained using solutions of copper sulphate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 99% purity) prepared in deionized water, also acquired from Sigma Aldrich.

2.2. Functionalization of EDTA with magnetite NPs

In a beaker, EDTA (0.2 mol L^{-1}) was dissolved in 50 mL of distilled water and stirred magnetically for 12 hours at room temperature. Subsequently, 1.51 g of Fe_3O_4 was added to the EDTA solution, and the mixture was subjected to ultrasonic bathing for 30 minutes until a homogeneous dispersion of magnetite NPs was observed. A neodymium magnet (NdFeB) was then placed at the bottom of the beaker, attracting the functionalized NPs and allowing the supernatant to be decanted into another vessel. The Fe_3O_4 -EDTA functionalised NPs were then dried in an oven at $100 \text{ }^\circ\text{C}$ for 72 hours, macerated in an agate mortar for 2 hours, and finally dried again at $100 \text{ }^\circ\text{C}$ for an additional 12 hours [14].

2.3 Preparation of spinning solutions

Polyvinylidene fluoride (PVDF) at a concentration of 17% (w/v) was dissolved in a solvent mixture consisting of N-dimethylformamide (DMF) and acetone at a 7:3 volumetric ratio. This solution underwent continuous magnetic stirring for 18 hours at approximately $55 \text{ }^\circ\text{C}$. Concurrently, polystyrene (PS) at a concentration of 20% (w/v) was dissolved in a mixture of DMF and tetrahydrofuran (THF) at a volumetric ratio of 3:1, and stirred magnetically for 18 hours at room temperature. Subsequently, 5% (w/w) of EDTA-functionalized magnetite NPs (Fe_3O_4 -EDTA) were added to the uniform PS solution, which was then ultrasonically dispersed for 2 hours to ensure homogeneous NP distribution. Finally, the PVDF and PS@ Fe_3O_4 -EDTA polymer solutions were combined in equal proportions and sonicated for 3 minutes to produce a homogeneous physical mixture [4].

2.4 Electrospinning Process

For electrospinning, the needle was aligned vertically at a distance of 15 cm from the collector's plane. An aliquot of $200 \text{ } \mu\text{L}$ of the polymeric solution was dispensed at every 90° interval during a complete clockwise rotation, for a total volume of $1600 \text{ } \mu\text{L}$. The flow rate was precisely controlled at 1 mL/h using an injection pump. Fiber formation was initiated by applying a voltage differential of 12 kV. The electrospinning apparatus consisted of a high-voltage power supply (model EB-40K) with an input voltage of 220 V and an adjustable DC output range of 3–40 kV, alongside an injection pump supplied by New Era.

2.5 Physicochemical characterization

The morphological, topographical, and compositional properties of the electrospun PVDF, PS@ Fe_3O_4 -EDTA, and PVDF/PS@ Fe_3O_4 -EDTA membranes were analyzed using a Scanning Electron Microscope (SEM), JEOL brand (model JSM-6490LV). This instrument is equipped with



an Energy-Dispersive X-ray Spectroscopy (EDS) detector, allowing the evaluation of chemical constituents present on membrane surfaces. Micrographs were captured at an acceleration voltage of 10 kV. The mean diameter of 50 randomly selected fibers was measured using ImageJ software. Additionally, the porosity percentage (P) was estimated from the SEM images according to Equation 1 [9]:

$$P = \left(1 - \frac{n}{N}\right) \times 100 \quad (1)$$

The porosity percentage (P) was calculated as the ratio of white pixels (representing pores, n) to the total number of pixels (N) in the processed binary image. Fourier Transform Infrared (FT-IR) spectroscopy studies were conducted to elucidate the interactions of functional groups on the surfaces of the electrospun PVDF, PS@Fe₃O₄-EDTA, and PVDF/PS@Fe₃O₄-EDTA membranes. These analyses were carried out using a Shimadzu IRPrestige-21 spectrophotometer employing Attenuated Total Reflectance (ATR). Spectra were recorded within a wavenumber range of 500–4000 cm⁻¹ at a spectral resolution of 4 cm⁻¹, aggregating 30 scans per sample.

2.6 Adsorption studies of copper

The adsorption efficiency of the PVDF/PS@Fe₃O₄-EDTA electrospun membrane was evaluated using aqueous solutions with varying concentrations of copper salt (CuSO₄·5H₂O) at 300, 600, 900, 1200, and 1400 mg L⁻¹, prepared from a stock solution of 2000 mg L⁻¹ in deionized water (Figure 2a) [22][23]. Each experiment was repeated three times, demonstrating good reproducibility.

These evaluations were conducted at ambient temperature with pH values maintained between 4 and 5.5, representing typical conditions of wastewater from the electroplating section of an automobile factory [24]. A constant-flow approach was employed for the copper solutions during the filtration phase, using an injection pump set at a flow rate of 70 mL h⁻¹. The diverse Cu²⁺ solutions were loaded into a syringe and subsequently passed through a Swinnex filter holder positioned at the syringe outlet, as depicted in Figure 2b, with filtrates collected in a beaker (Figure 2c). Post-filtration, Cu²⁺ concentrations in the supernatant were determined using a Shimadzu AA-7000 Flame Atomic Absorption Spectrophotometer (AAS) equipped with an air/acetylene flame atomizer. The spectral analysis for Cu²⁺ was performed at a wavelength of 193.7 nm. Adsorption tests were conducted in duplicate. The resulting adsorption data were analyzed according to the Langmuir linear isotherm model using regression analysis.

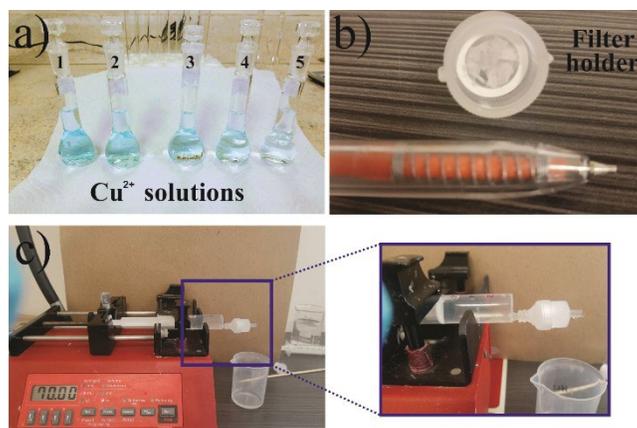


Figure 2. (a) Cu^{2+} solutions used for adsorption tests (1-1400 mg L^{-1} , 2-1200 mg L^{-1} , 3-900 mg L^{-1} , 4-600 mg/L , 5-300 mg/L), (b) Electrospun membrane placed in a Swinnex® filter holder (c) Experimental setup for Cu^{2+} adsorption.

3. Results and discussion

3.1. Physicochemical characterization of the electrospinning membrane.

Scanning Electron Microscopy (SEM) images provided insights into the morphological characteristics of PVDF, PS, and PVDF/PS@ Fe_3O_4 -EDTA membranes, as illustrated in Figure 3. The PVDF microfibers (Figure 3a) are characterized by their uniform cylindrical morphology, with an average diameter of $0.8 \pm 0.301 \mu\text{m}$, without observable defects or bead formation. The PS@ Fe_3O_4 -EDTA membrane (Figure 3b) displayed uniformly distributed fibers, reflecting the optimized viscosity of the polymer solution [7]. These fibers presented a larger average diameter ($3.2 \pm 0.701 \mu\text{m}$) when compared to PVDF fibers, potentially attributable to the incorporation of magnetite [25]. Microscopic analysis confirmed the successful embedding of magnetite NPs within the polymer matrix, as evidenced by the brighter spots on the fiber surface. This homogeneous non-clustered NP distribution increases surface area, thereby enhancing the membrane's adsorption capacity.

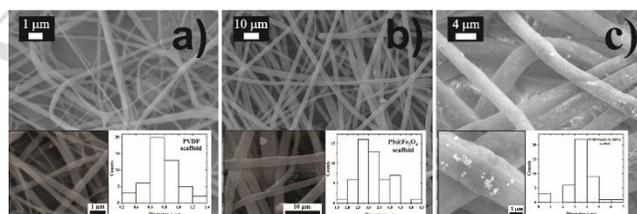


Figure 3. Scanning electron microscopy images of electrospun microfibers: (a) PVDF, (b) PS@ Fe_3O_4 -EDTA, (c) PVDF/PS@ Fe_3O_4 -EDTA.

The composite PVDF/PS@ Fe_3O_4 -EDTA membrane (Figure 3c) exhibited solid, cylindrical fibers with an average diameter of $3.0 \pm 0.556 \mu\text{m}$. The inter-fiber pore size, which is relatively small in relation to the diameter, indicates significant membrane porosity (approximately 60%), calculated using Equation 1. Such porosity may contribute to the improved retention of metal ions, as posited by Jiang et al. [4]. The concentration of the polymer solution plays a pivotal role in imparting the

requisite electrical conductivity and rheological properties essential for successful fiber formation [26], while also facilitating the optimization of electrospinning parameters.

Elemental analysis conducted via Energy-Dispersive Spectroscopy (EDS) on the PVDF/PS@Fe₃O₄-EDTA membrane revealed carbon, fluorine, iron, and oxygen as the primary surface elements. Compositional analysis indicated that the membrane surface consisted of 86.60% carbon, 2.44% oxygen, 9.76% fluorine, and 1.20% iron, confirming successful incorporation of Fe₃O₄ NPs into the fiber matrix (Figure 4).

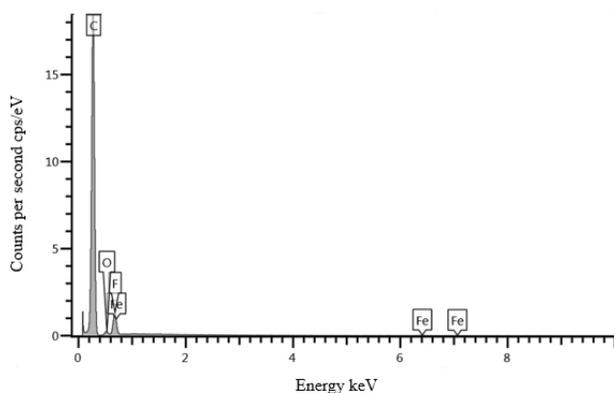


Figure 4. EDS analysis showing the elemental composition of PVDF/PS@Fe₃O₄-EDTA electrospun membranes.

3.2. Spectroscopic analysis of EDTA functionalization and membrane crystalline phases

Figure 5a, elucidates the spectra of pristine EDTA alongside its functionalization with magnetite nanoparticles. In the FTIR spectrum of Fe₃O₄-EDTA, the observed decrease in band intensity at 3026 cm⁻¹, corresponding to O–H stretching vibrations, indicates the involvement of hydroxyl groups in the chemical bonding process during functionalization. Furthermore, the complexation between magnetite and the carboxylate groups of EDTA is evidenced by the shifts and changes in the COO⁻ stretching bands when compared to the spectrum of unmodified EDTA, confirming successful coordination.

The spectrum featured in Figure 5b delineates the electrospun PVDF membrane, with the α crystalline phase distinctly presenting at 757, 697, and 482 cm⁻¹. These bands correspond to vibrational modes, CF₂ bending, and bond oscillations within the CCC structure, respectively. Concurrently, the β crystalline phase is discernible at 839, 795, and 537 cm⁻¹, indicating a combination of CH₂ rocking and asymmetric CF₂ stretching vibrations. This is complemented by additional absorption bands characteristic of asymmetric CF₂ stretching at 1179 cm⁻¹ and C–F stretching vibrations at 1401 cm⁻¹. Furthermore, CH₂ asymmetric stretching vibrations are observable at 3025 cm⁻¹, manifesting as weaker vibrations that imply a diminished change in dipole moment relative to the stronger symmetric vibrations at 2924 cm⁻¹ associated with the CH₂ group.

Figure 5c presents the FT-IR spectra for electrospun PS membrane (20% w/v) and PS@Fe₃O₄ membranes. Characteristic C–H stretching bands of the benzene ring appear between 2920 and 3020 cm⁻¹, while harmonic and combination bands (1940–1650 cm⁻¹) indicate benzene substitution levels. Prominent ring stretching frequencies occur at 1600–1582 and 1490–1450 cm⁻¹, with in-



plane C–H bending bands at 1490–1030 cm^{-1} , and out-of-plane C–H bending bands at 905–842 cm^{-1} . Vibrations at 697 and 756 cm^{-1} correspond respectively to CH_2 vibrations and monosubstituted benzene rings. A pronounced band at 539 cm^{-1} is indicative of the Fe–O structural motif within the magnetic core of the Fe_3O_4 particles [27].

In Figure 5d, the FT-IR spectrum of the PVDF/PS@ Fe_3O_4 -EDTA composite membrane highlights vibrational bands at 877 cm^{-1} (correlated to the C–H bonds from methylene, CH_2 groups), 1174 cm^{-1} (difluoromethyl (CF_2) moiety), and 1400 cm^{-1} (C–F stretching). The CH vibrational bands at 3026 cm^{-1} are characteristic of PS@ Fe_3O_4 functionalization. Furthermore, a notable hydroxyl (O–H) band at 3502 cm^{-1} associated with EDTA emphasizes the membrane's potential for metallic copper ion adsorption through hydrogen bonding [1].



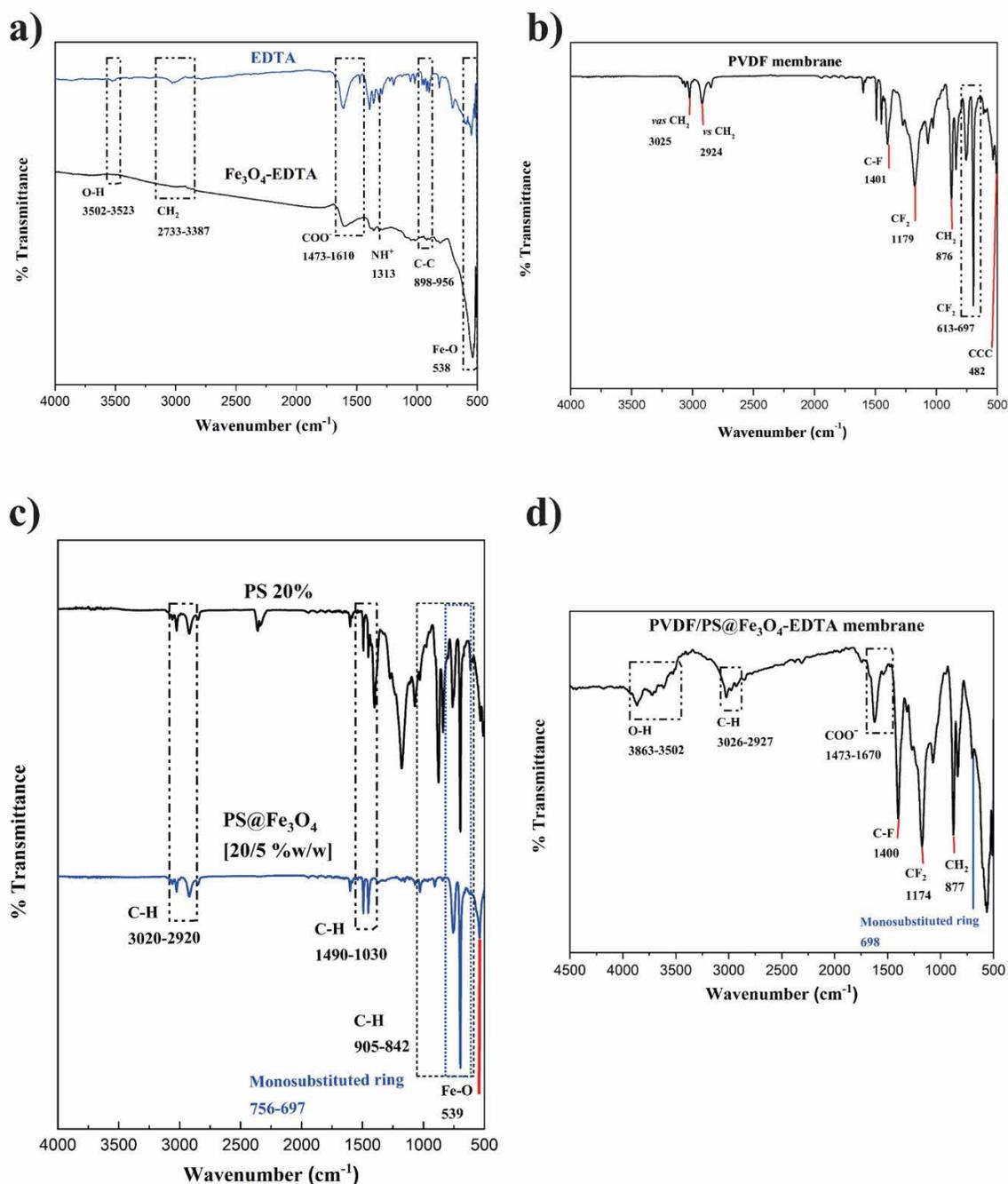


Figure 5. FTIR spectra of (a) EDTA, Fe_3O_4 -EDTA and electrospun membranes of (b) PVDF, (c) $\text{PS}@ \text{Fe}_3\text{O}_4$, (d) PVDF/ $\text{PS}@ \text{Fe}_3\text{O}_4$ -EDTA.

The electrospinning process effectively integrated structural elements into the composite PVDF/ $\text{PS}@ \text{Fe}_3\text{O}_4$ -EDTA membrane, incorporating functional groups and vibrational bands that provide adsorption sites conducive to efficient copper ion sequestration.

3.3. Magnetic characterization of the PVDF/PS@Fe₃O₄-EDTA

Figure 6 illustrates the magnetization characteristics of the PVDF/PS@Fe₃O₄-EDTA membrane, depicting the curve of magnetization versus applied magnetic field (M–H curve). The membrane demonstrates a near-zero hysteresis loop, indicative of the superparamagnetic behavior typical of materials embedded with magnetic NPs [25]. The magnetization of the electrospun membrane, augmented with magnetite NPs and EDTA, is approximately 1.5 emu g⁻¹. This figure is notably lower than the magnetization observed in pure magnetite, typically around 90 emu g⁻¹ [28]. Nonetheless, this degree of magnetization is sufficient to facilitate magnetic recovery after adsorption without the need for a strong external magnetic field. Additionally, the diminutive size of the NPs significantly increases the membrane's surface area, enhancing its adsorption capacity for heavy copper ions [11].

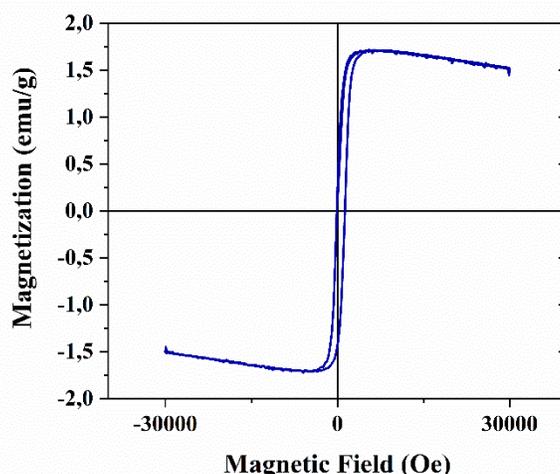


Figure 6. Room-temperature magnetization hysteresis (M-H) curve of the PVDF/PS@Fe₃O₄-EDTA membrane, measured at 300 K. Magnetization values are expressed in emu g⁻¹.

The parameters of magnetic saturation (M_s), remanent magnetization (M_r), and coercivity (H_c) are quantified in Table 1. The attenuation in saturation magnetization may be ascribed to the likely interaction between the polymer matrix and the surface of the functionalized magnetite NPs, as well as to the disturbance in the collinearity of spin structures, stemming from the immobilization of surface spins by the polymer matrix at the magnetite interface [29][25].

Table 1. Results for saturation magnetization, remanent magnetization and coercivity

Sample	Saturation Magnetization, M _s (emu g ⁻¹)	Remanent Magnetization, M _r (emu g ⁻¹)	Coercivity, H _c (kOe)
PVDF/PS@Fe ₃ O ₄ -EDTA [17:20:5]	□ 1.50	□ 0.50	□ 1.20

Despite the inherent ferromagnetic properties of magnetite at ambient conditions, a subdued magnetic hysteresis loop was observed in the magnetization curve at 300 K. Consequently, the



membrane can be classified as superparamagnetic, an advantageous characteristic for recovery following adsorption processes. The application of an external magnetic field facilitates easy separation of the adsorbent membrane from aqueous solutions contaminated with the heavy metal ion Cu^{2+} (findings not included in this manuscript).

The low magnetization values also indicate that the NPs exhibit magnetic responsiveness and redispersibility, supporting their potential application as magnetic adsorbents, as described by Liu et al. [30].

3.4 Adsorptive efficacy of the PVDF/PS@Fe₃O₄-EDTA membrane for copper ion removal

The PVDF/PS@Fe₃O₄-EDTA membrane demonstrated significant adsorptive capacity, achieving a maximum copper ion removal efficiency of 70.8%, surpassing results previously reported by Xu et al. [6]. The percentage removal of Cu^{2+} was calculated using Equation 2:

$$\%R = \left(1 - \frac{C_e}{C_0}\right) \times 100 \quad (2)$$

Where, $\%R$ represents the efficiency percentage of removal, and C_e and C_0 represent the equilibrium and initial concentrations, respectively. This notable efficiency is likely due to the membrane's expansive surface area, which facilitates the near-complete utilization of available chelation sites, coupled with the absence of internal diffusion barriers [31]. Analysis of adsorption data demonstrated good agreement with the linear representation of the Langmuir isotherm model, evidenced by a regression coefficient of 0.90. The Langmuir model can be expressed as in Equation 3:

$$\frac{C_e}{q} = \frac{C_e}{b} + \frac{1}{kb} \quad (3)$$

Where C_e is the equilibrium copper ion concentration in solution (mg L^{-1}), b is the maximum adsorption capacity (mg g^{-1}), k is the Langmuir adsorption constant (L mg^{-1}) and q is the equilibrium adsorption capacity of copper ions on the adsorbent (mg g^{-1}), calculated by Equation 4:

$$q = \frac{(C_0 - C_e)V}{m} \quad (4)$$

Where V is the volume of the solution in L and m is the mass of the adsorbent.

The Langmuir isotherm model (Figure 7) indicated a maximum adsorption capacity of 25.1 mg g^{-1} , indicative of a monolayer adsorption process wherein the adsorbed molecules do not interact, and the adsorption energy remains consistent across the adsorbent's surface. This adsorption value is compared with those reported by Wang et al. [23] and Liu et al. [13], where the adsorption capacity is shown to be favorable for the removal of Cu^{2+} .



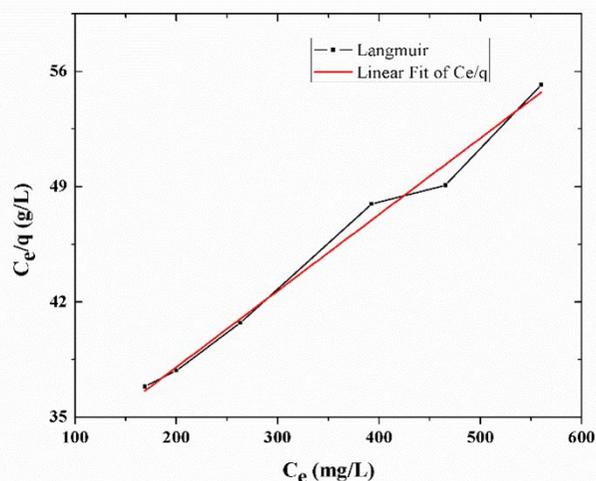


Figure 7. Langmuir isotherm for the PVDF/PS@Fe₃O₄-EDTA membrane (pH: 4-5.5, room temperature).

The results indicate that incorporating EDTA as a chelating agent enhances ion adsorption by providing additional vacant active sites on the membrane surface. Experimental data suggest that the adsorption efficiency of the PVDF/PS@Fe₃O₄-EDTA membrane remains unaffected by variations in initial concentrations, implying consistently available active adsorption sites across a broad spectrum of initial copper ion concentrations. The high specific surface area and the ability to form complexes with the metal ions of the nanomaterial make magnetite a potential magnetic adsorbent, consistent with recent studies conducted by Akbarpour et al. [32][33][34][11].

Several studies have demonstrated that functionalizing magnetite nanoparticles with EDTA enhances adsorption capacity by forming stable surface complexes with divalent metal ions, even in the presence of other coexisting ionic species [35][36]. Additionally, it has been noted by Shan et al. [37] and Santos et al. [38] that saturation magnetization decreases upon functionalizing magnetite with chelating agents or catalysts.

4. Conclusions

The successful fabrication of a PVDF/PS@Fe₃O₄-EDTA polymeric membrane via electrospinning was achieved, and evidenced the uniform dispersion and effective integration of magnetite NPs within the polymer matrix. The membrane fibers exhibited an average diameter of 3 μ m, highlighting the material's suitability for adsorption due to its favorable morphological and intrinsic magnetic properties. Notably, the membrane exhibited 60% porosity, significantly increasing the available surface area for Cu²⁺ ion adsorption and demonstrating a removal rate of up to 70.8%. This enhanced adsorption capability primarily arises from the saturation of EDTA's active hydroxyl sites via hydrogen bonding.

Adsorption dynamics of this membrane were most accurately delineated by the Langmuir isotherm model, demonstrated by a high regression coefficient of 0.90. These findings indicate that adsorption transpires as a monolayer across the membrane surface without intermolecular interactions between adsorbate entities. Furthermore, the membrane exhibited superparamagnetic properties, a trait that is advantageous not only for enhancing adsorption efficiency but also for facilitating the subsequent recovery of materials contaminated with heavy metals.

5. Declaration of competing interest

We declare that we have no significant competing interests including financial or non-financial, professional, or personal interests interfering with the full and objective presentation of the work described in this manuscript.

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8. Author contributions

L. A. Montes-Malagón: Experimental development and performed the analysis. Y. Pineda-Triana: Contributed data or analysis tools. E. Gómez-Pachón: Methodological design of the research. A. Sánchez-Cepeda: Experimental development and performed the analysis.

9. Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article [and/or] its supplementary materials.

References

- [1] H. Chen *et al.*, “Preparation of MgAl-EDTA-LDH based electrospun nanofiber membrane and its adsorption properties of copper(II) from wastewater,” *J. Hazard. Mater.*, vol. 345, pp. 1–9, 2018, doi: 10.1016/j.jhazmat.2017.11.002.
- [2] E. Lopez *et al.*, “Removal of Mo(VI), Pb(II), and Cu(II) from wastewater using electrospun cellulose acetate/chitosan biopolymer fibers,” *Int. J. Biol. Macromol.*, vol. 269, no. February, 2024, doi: 10.1016/j.ijbiomac.2024.132160.
- [3] H. Yang *et al.*, “Synergistically active Fe₃O₄ magnetic and EDTA modified cellulose cotton fabric using chemical method and their effective pollutants removal ability from wastewater,” *Int. J. Biol. Macromol.*, vol. 274, p. 132996, 2024, doi: <https://doi.org/10.1016/j.ijbiomac.2024.132996>.
- [4] Z. Jiang *et al.*, “Removal of oil from water using magnetic bicomponent composite nanofibers fabricated by electrospinning,” *Compos. Part B Eng.*, vol. 77, pp. 311–318, 2015, doi: <https://doi.org/10.1016/j.compositesb.2015.03.067>.
- [5] A. Thakur, A. Kumar, and A. Singh, “Adsorptive removal of heavy metals, dyes, and pharmaceuticals: Carbon-based nanomaterials in focus,” *Carbon N. Y.*, vol. 217, no. October 2023, p. 118621, 2024, doi: 10.1016/j.carbon.2023.118621.
- [6] X. Xu, M. Zhang, H. Lv, Y. Zhou, Y. Yang, and D. G. Yu, “Electrospun polyacrylonitrile-based lace nanostructures and their Cu(II) adsorption,” *Sep. Purif. Technol.*, vol. 288, no. February, 2022, doi: 10.1016/j.seppur.2022.120643.



- [7] W. E. Teo and S. Ramakrishna, "A review on electrospinning design and nanofibre assemblies," *Nanotechnology*, vol. 17, no. 14, 2006, doi: 10.1088/0957-4484/17/14/R01.
- [8] V. Mohanapriya, R. Sakthivel, N. D. K. Pham, C. K. Cheng, H. S. Le, and T. M. H. Dong, "Nanotechnology- A ray of hope for heavy metals removal," *Chemosphere*, vol. 311, no. P1, p. 136989, 2023, doi: 10.1016/j.chemosphere.2022.136989.
- [9] O. Hakami, Y. Zhang, and C. J. Banks, "Thiol-functionalised mesoporous silica-coated magnetite nanoparticles for high efficiency removal and recovery of Hg from water," *Water Res.*, vol. 46, no. 12, pp. 3913–3922, 2012, doi: 10.1016/j.watres.2012.04.032.
- [10] M. Shahrashoub and S. Bakhtiari, "The efficiency of activated carbon/magnetite nanoparticles composites in copper removal: Industrial waste recovery, green synthesis, characterization, and adsorption-desorption studies," *Microporous Mesoporous Mater.*, vol. 311, no. August 2020, p. 110692, 2021, doi: 10.1016/j.micromeso.2020.110692.
- [11] S. L. Iconaru, R. Guégan, C. L. Popa, M. Motelica-Heino, C. S. Ciobanu, and D. Predoi, "Magnetite (Fe₃O₄) nanoparticles as adsorbents for As and Cu removal," *Appl. Clay Sci.*, vol. 134, pp. 128–135, 2016, doi: 10.1016/j.clay.2016.08.019.
- [12] S. Chen and F. Xie, "Selective adsorption of Copper (II) ions in mixed solution by Fe₃O₄-MnO₂-EDTA magnetic nanoparticles," *Appl. Surf. Sci.*, vol. 507, p. 145090, 2020, doi: <https://doi.org/10.1016/j.apsusc.2019.145090>.
- [13] Y. Liu, R. Fu, Y. Sun, X. Zhou, S. A. Baig, and X. Xu, "Multifunctional nanocomposites Fe₃O₄@SiO₂-EDTA for Pb(II) and Cu(II) removal from aqueous solutions," *Appl. Surf. Sci.*, vol. 369, pp. 267–276, 2016, doi: <https://doi.org/10.1016/j.apsusc.2016.02.043>.
- [14] A. G. Magdalena, I. M. B. Silva, R. F. C. Marques, A. R. F. Pipi, P. N. Lisboa-Filho, and M. Jafellicci, "EDTA-functionalized Fe₃O₄ nanoparticles," *J. Phys. Chem. Solids*, vol. 113, no. September 2017, pp. 5–10, 2018, doi: 10.1016/j.jpcs.2017.10.002.
- [15] M. Eleonora, B. Pineda, and B. M. Ciencias Biológicas, "Metales pesados (Cd, Cr y Hg): su impacto en el ambiente y posibles estrategias biotecnológicas para su remediación Heavy metals (Cd, Cr and Hg): impact on environment and possible biotechnological strategies for remediation ALIDA MARCELA GÓMEZ RODRIGUEZ," no. 2, pp. 82–113, 2015.
- [16] Y. G. Wibowo *et al.*, "Functionalized magnetite-biochar with live and dead bacteria for adsorption-biosorption of highly toxic metals: Cd, Hg, and Pb," *Next Mater.*, vol. 6, p. 100487, 2025, doi: <https://doi.org/10.1016/j.nxmater.2025.100487>.
- [17] L. Y. Ng, A. W. Mohammad, C. P. Leo, and N. Hilal, "Polymeric membranes incorporated with metal/metal oxide nanoparticles: A comprehensive review," *Desalination*, vol. 308, pp. 15–33, 2013, doi: <https://doi.org/10.1016/j.desal.2010.11.033>.
- [18] A. P. Venugopal, O. Cespedes, and S. J. Russell, "Controlling dielectric and magnetic properties of PVdF/magnetite nanocomposite fibre webs," *Int. J. Polym. Sci.*, vol. 2014, 2014, doi: 10.1155/2014/102946.
- [19] J. A. González Sánchez, "Study of Nanofibers Formed by Magnetic Field Assisted Electrospinning Using Solutions containing PVDF, DMF, Acetone and Fe₃O₄ Nanoparticles," 2015.
- [20] M. T. Rahul *et al.*, "Al₃Fe₅O₁₂ nanoparticles loaded electrospun PVDF fibres: An inorganic-organic material with multifunctional traits," *Mater. Chem. Phys.*, vol. 282, no. February, p. 125977, 2022, doi: 10.1016/j.matchemphys.2022.125977.
- [21] F. Mokhtari *et al.*, "Recent progress in electrospun polyvinylidene fluoride (PVDF)-based nanofibers for sustainable energy and environmental applications," *Prog. Mater. Sci.*, vol. 148, p. 101376, 2025, doi: <https://doi.org/10.1016/j.pmatsci.2024.101376>.



- [22] M. I. Martín, F. A. López, and F. J. Alguacil, “Estudio cinético de la eliminación de Cu (II) de soluciones acuosas mediante cascarilla de laminación,” *Revista de Metalurgia*, vol. 41, no. 4. pp. 292–297, 2005, doi: 10.3989/revmetalm.2005.v41.i4.217.
- [23] Y. Wang, X. Wang, Y. Ding, Z. Zhou, C. Hao, and S. Zhou, “Novel sodium lignosulphonate assisted synthesis of well dispersed Fe₃O₄ microspheres for efficient adsorption of copper (II),” *Powder Technol.*, vol. 325, pp. 597–605, 2018, doi: <https://doi.org/10.1016/j.powtec.2017.11.055>.
- [24] H. Moridi, M. Talebi, B. Jafarnejhad, S. E. Mousavi, and S. Abbasizadeh, “The role of chitosan grafted copolymer/zeolite Schiff base nanofiber in adsorption of copper and zinc cations from aqueous media,” *Int. J. Biol. Macromol.*, vol. 278, p. 135003, 2024, doi: <https://doi.org/10.1016/j.ijbiomac.2024.135003>.
- [25] S. Wang *et al.*, “Magnetic composite nanofibers fabricated by electrospinning of Fe₃O₄/gelatin aqueous solutions,” *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, vol. 190, pp. 126–132, 2014, doi: 10.1016/j.mseb.2014.10.001.
- [26] H. Yang, H. Li, W. H. Shih, Y. Yamashita, and F. Ko, “Multifunctional nanoparticles reinforced nanofibers by electrospinning,” *ICCM Int. Conf. Compos. Mater.*, 2007.
- [27] T. Nitanan, P. Opanasopit, P. Akkaramongkolporn, T. Rojanarata, T. Ngawhirunpat, and P. Supaphol, “Effects of processing parameters on morphology of electrospun polystyrene nanofibers,” *Korean J. Chem. Eng.*, vol. 29, no. 2, pp. 173–181, 2012, doi: 10.1007/s11814-011-0167-5.
- [28] M. Bayat, H. Yang, and F. Ko, “Electromagnetic properties of electrospun Fe₃O₄/carbon composite nanofibers,” *Polymer (Guildf.)*, vol. 52, no. 7, pp. 1645–1653, 2011, doi: 10.1016/j.polymer.2011.01.057.
- [29] S. Si, C. Li, X. Wang, D. Yu, Q. Peng, and Y. Li, “Magnetic monodisperse Fe₃O₄ nanoparticles,” *Cryst. Growth Des.*, vol. 5, no. 2, pp. 391–393, 2005, doi: 10.1021/cg0497905.
- [30] Y. Liu, M. Chen, and H. Yongmei, “Study on the adsorption of Cu(II) by EDTA functionalized Fe₃O₄ magnetic nano-particles,” *Chem. Eng. J.*, vol. 218, pp. 46–54, 2013, doi: <https://doi.org/10.1016/j.cej.2012.12.027>.
- [31] M. Hezarjaribi, G. Bakeri, M. Sillanpää, M. J. Chaichi, and S. Akbari, “Novel adsorptive membrane through embedding thiol-functionalized hydrous manganese oxide into PVC electrospun nanofiber for dynamic removal of Cu(II) and Ni(II) ions from aqueous solution,” *J. Water Process Eng.*, vol. 37, no. July, p. 101401, 2020, doi: 10.1016/j.jwpe.2020.101401.
- [32] T. Akbarpour, A. Khazaei, M. Mohammadi, and N. Sarmasti, “Fe₃O₄ Nanoparticles Decorated with a Modified Carbon Quantum Dot Shell: Synthesis, Characterization and Its Evaluation as an Efficient Adsorbent for Cu(ii) and Zn(ii) Ions Adsorption,” *Polycycl. Aromat. Compd.*, 2025, doi: <https://doi.org/10.1080/10406638.2025.2453527>.
- [33] S. Sulaiman *et al.*, “Structural, morphological, magnetic and adsorption properties of Fe₃O₄ for copper removal from aqueous solution,” *Desalin. Water Treat.*, vol. 215, pp. 136–146, 2021, doi: <https://doi.org/10.5004/dwt.2021.26769>.
- [34] M. Bae, H. Lee, K. Yoo, and S. Kim, “Copper(I) selective chemisorption on magnetite (Fe₃O₄) over gold(I) ions in chloride solution with cyanide,” *Hydrometallurgy*, vol. 201, p. 105560, 2021, doi: <https://doi.org/10.1016/j.hydromet.2021.105560>.
- [35] S. Chander and A. Gupta, “Fabrication of mango-leaf biowaste mediated green magnetite (Fe₃O₄@MBE NPs) and modified EDTA/Fe₃O₄@MBE NCs for enhanced heavy metals sequestration: Characterisation, simulation modelling, mechanism, cost-effectiveness and



- electroplating wastewater performance,” *Sep. Purif. Technol.*, vol. 358, p. 130246, 2025, doi: <https://doi.org/10.1016/j.seppur.2024.130246>.
- [36] L. Mavaddatiyan and B. Zeynizadeh, “A new strategy for immobilization of copper on the Fe₃O₄@EDTA nanocomposite and its efficient catalytic applications in reduction and one-pot reductive acetylation of nitroarenes and also N-acetylation of arylamines,” *Heliyon*, vol. 10, no. 15, p. e35062, 2024, doi: <https://doi.org/10.1016/j.heliyon.2024.e35062>.
- [37] Z. Shan *et al.*, “Kinetics and mechanism of enhanced norfloxacin degradation by Fe₃O₄@La-BiFeO₃ based on weak magnetization and efficient charge separation,” *Chem. Eng. J.*, vol. 466, p. 143229, 2023, doi: <https://doi.org/10.1016/j.cej.2023.143229>.
- [38] G. T. A. D. Santos *et al.*, “Hybrid nanocomposites of Fe₃O₄/SiO₂-EDTA: Holistic comparison of one-step and two-step modification methods,” *Powder Technol.*, vol. 444, p. 120046, 2024, doi: <https://doi.org/10.1016/j.powtec.2024.120046>.