

Research Article

Reusable Ethylenediamine-Grafted Cellulose Fabric for Efficient Cu(II) and Pb(II) Removal from Water

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Abstract

In response to the growing problem of water contamination by heavy metals, this work presents the design of an innovative and promising bioadsorbent: a cellulose fabric functionalized through covalent grafting of ethylenediamine (Cell-EDA). The chemical modification was carried out in three successive steps: alkaline mercerization, tosylation in pyridine medium, and nucleophilic substitution. FTIR spectroscopy, supported by a semi-quantitative analysis of characteristic absorption bands, confirmed the successful introduction of amine groups. The adsorption performance was evaluated for Cu(II) and Pb(II) ions as a function of pH, contact time, and initial concentration. Maximum removal efficiencies reached 90% for Cu(II) at pH 4 and 96% for Pb(II) at pH 8. Kinetic studies followed a pseudo-second-order model, indicating chemisorption. The Freundlich and Temkin isotherms revealed multilayer adsorption on heterogeneous surfaces, while the Langmuir model yielded maximum adsorption capacities of 55.9 mg/g for Cu(II) and 131.6 mg/g for Pb(II), highlighting the strong retention capacity of the material. The Cell-EDA fabric retained over 75% of its adsorption efficiency after five consecutive cycles, demonstrating good stability and excellent reusability. The use of cellulose fabric, which offers greater mechanical strength than powder or paper-based supports, gives Cell-EDA significant potential for sustainable applications in the treatment of heavy metal-contaminated effluents.

Keywords

Functionalized Cellulose, Ethylenediamine, Bioadsorbent, Heavy Metals, Adsorption Isotherms, Water Remediation

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1. Introduction

The contamination of water resources by heavy metals has become a major environmental and public health concern worldwide. Elements such as lead (Pb), copper (Cu), cadmium (Cd), and arsenic (As) are known for their acute toxicity—even at very low concentrations—and their persistence in the environment. These pollutants, mainly derived from industrial, mining, and agricultural activities, can cause serious health effects, including neurological, hepatic, and immune disorders, as well as an increased risk of cancer [1, 2].

To address this issue, the development of efficient and sustainable technologies for the treatment of metal-contaminated wastewater is a priority. Conventional methods such as chemical precipitation, ion exchange, and activated carbon adsorption have shown significant limitations, including pH dependency, high operating costs, poor selectivity, and complex regeneration processes [3]. In this context, bio-based materials—particularly those derived from cellulose—are gaining increasing attention as cost-effective and environmentally friendly alternatives.

Cellulose is an abundant, biodegradable, and non-toxic natural polysaccharide. Its structure is rich in hydroxyl groups that can be chemically modified to introduce active sites capable of selectively binding metal cations [4]. Numerous studies have explored the chemical functionalization of cellulose substrates with amino groups, particularly polyamines, which provide multiple complexation sites for heavy metal ions [5]. Among these, ethylenediamine (EDA) has proven particularly effective for Cu(II) and Pb(II) adsorption, due to the formation of stable complexes with its primary amine functionalities [6, 7]. However, most research has focused on cellulose in powder or paper form, which suffer from drawbacks such as limited mechanical strength and low specific surface area [8]. Using cellulose fabric, a soft yet robust textile material, offers an innovative alternative that enhances mechanical stability, contact surface, and reusability potential of the adsorbent.

In this context, the present study aims to develop a high-performance bioadsorbent based on cellulose fabric grafted with ethylenediamine (Cell-EDA) and to evaluate its efficiency in removing Cu(II) and Pb(II) ions from aqueous media. The approach involves the activation of hydroxyl groups by a chlorinating agent followed by covalent grafting of EDA to obtain a functionalized membrane with high metal-binding capacity. The study also investigates the influence of operational parameters (pH, initial concentration, contact time, reusability) on adsorption performance, with a view to developing regenerable materials suitable for industrial effluent treatment and environmental sensing applications.

2. Materials and Methods

2.1. Materials

All commercial solvents and reagents were used as received from Sigma-Aldrich, Fischer Scientific Ltd., and Alfa Aesar. Primary white cellulose fabric for tufting, with a basis weight of approximately 100 g/m², was used as the cellulosic matrix. FTIR-ATR spectra were recorded on a Bruker Tensor 27 spectrometer. Elemental analyses were performed on a Thermo Fisher Scientific Flash 2000 CHNS organic elemental analyzer.

2.2. Fabric Characteristics



Figure 1. Photograph of the cellulose fabric (Cell).

The substrate used in this study is a nonwoven cellulose fabric, composed mainly of natural cotton fibers (Figure 1). Commonly used as a support in tufting textile applications, this material exhibits interesting physical properties for chemical functionalization. According to the supplier's technical data, the fibers are of cellulose I type, of plant origin, with an average length between 10 and 20 mm. The fabric has a basis weight of 100 g/m² and an average thickness of 0.4 mm. Although the BET specific surface area was not measured in this study, previous research on similar cellulosic fabrics has reported values between 2 and 5 m²/g, depending on the fabric's weave density and porosity [1, 9]. This intrinsically porous fiber structure promotes high accessibility of hydroxyl groups, facilitating chemical modifications such as mercerization or the grafting of functional groups.

2.3. Methods

2.3.1. Pretreatment of Cellulose Fabric (Cell)

Five pieces of primary white tufting cellulose fabric (approximately 750 mg total) were dispersed in 250 mL of freshly prepared 10% (w/w) aqueous NaOH solution. The mixture was stirred for 24 h on an orbital shaker. The pre-

treated fabric samples were washed six times with 50 mL of ethanol and stored in ethanol until further use.

2.3.2. Preparation of Tosylated Cellulose Fabric (Cell-pTs)

A piece of pretreated cellulose fabric (145 mg, 0.81 mmol) was immersed in pyridine (10 mL) and reacted with p-toluenesulfonyl chloride (464 mg, 2.44 mmol). The reaction mixture was stirred for 20 h at 40 °C on an orbital shaker. The resulting Cell-pTs fabric was washed three times by sonication with 20 mL of DMF and stored in DMF for subsequent functionalization.

2.3.3. Preparation of Ethylenediamine-Grafted Cellulose Fabric (Cell-EDA)

A piece of Cell-pTs material (0.81 mmol of glucose units) was immersed in DMF (10 mL) and reacted with ethylenediamine (1.08 mL, 16.20 mmol). The mixture was stirred for 40 h at 80 °C on an orbital shaker. The resulting Cell-EDA (Figure 2) was washed three times by sonication with 20 mL of acetone, once with CH₂Cl₂, and then dried under vacuum. The degree of substitution (DS) was calculated to be approximately 0.30 based on elemental analysis, suggesting that about three diamine moieties were grafted for every ten glucose units.

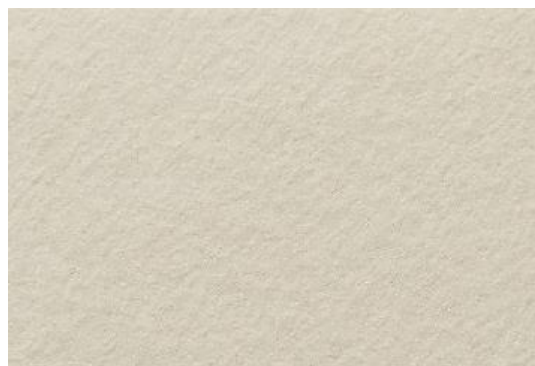


Figure 2. Photo of the membrane, grafted cellulose fabric (Cell-EDA).

2.3.4. General Procedure for Metal Adsorption

Metal solutions were freshly prepared by dissolving the desired amount of metal salt in Milli-Q water in a plastic vial, and a piece of chemically modified cellulose fabric (Cell-EDA) was immersed. The vial was then shaken on an orbital shaker for the required time. The material was subsequently removed from the solution, which was then analyzed by Atomic Absorption Spectroscopy (AAS). If necessary, the sample was diluted to achieve linearity within the calibration curves.

2.3.5. Operating Conditions for Atomic Absorption Spectroscopy (AAS)

Residual concentrations of Cu(II) and Pb(II) ions in the solutions after adsorption were determined by flame atomic absorption spectroscopy (AAS) using a PerkinElmer AAnalyst 400 spectrometer equipped with an air-acetylene burner. The specific wavelengths used for detecting the metal ions were 324.8 nm for Cu(II) and 217.0 nm for Pb(II). Calibration of the instrument was performed with certified standard solutions (Merck), prepared over a concentration range from 0 to 5 mg/L. Linearity of the calibration curves was confirmed with a correlation coefficient (R^2) greater than 0.999, thereby ensuring the reliability of the measurements. Each sample was analyzed in triplicate, and the average of the obtained values was used to calculate the percentage of metal ion retention. When necessary, samples were pre-diluted to ensure that the measurements remained within the linear response range of the instrument.

3. Results and Discussion

3.1. Preparation of Adsorbents: Cell-EDA Membrane Based on Cellulose Fabric

Chemical functionalization of cellulose is a major challenge, particularly due to the dense structure and extensive hydrogen bonding network that stabilizes the polymer chains within the cellulose fabric. These characteristics significantly limit the reactivity of the hydroxyl groups present on the anhydroglucose units [10, 11]. Specifically, classical reactions such as esterification or substitution of hydroxyl functions prove ineffective in cellulose fabrics because of the chemical inertness of primary and secondary alcohols in these materials. To enhance the reactivity of the hydroxyl groups, an alkaline pretreatment known as mercerization was performed. This treatment, widely used in the paper industry, involves immersing the raw fabric in a 10% aqueous NaOH solution for 24 hours. It alters the crystallinity of cellulose, breaks the interchain hydrogen bonds, and thus makes the amorphous regions more accessible to chemical modification [12].

Once the mercerized fabric (designated Cell) was obtained, we proceeded with its functionalization using a diamine, aiming for covalent grafting of primary amine groups capable of chelating heavy metals. The strategy adopted involved prior conversion of hydroxyl groups into good leaving groups via a tosylation reaction using p-toluenesulfonyl chloride (p-TsCl) in a pyridine medium. This activation step was carried out at 40 °C for 20 hours, with an equimolar amount of p-TsCl relative to available hydroxyl groups, resulting in a tosylated material (named Cell-pTs) (Figure 3) with an estimated degree of substitution (DS) of 0.5 [13]. This means that, statistically, one glucose unit out of two is modified, probably at the C6 position, which is the most accessible and reactive, although residual substitutions at C2 and C3 cannot be com-

pletely excluded [14].

Although the Cell-pTs material can be isolated and dried, it was observed that maintaining it as a suspension in dimethylformamide (DMF), after removal of pyridine and excess reagents by three successive washes, resulted in more efficient grafting during the subsequent reaction with the diamine. Indeed, air drying tends to partially restore the initial hydro-

gen bonding network, reducing the accessibility of tosylated functions to nucleophilic agents such as ethylenediamine [15]. Therefore, to optimize grafting efficiency, the reaction between Cell-pTs and ethylenediamine was systematically performed directly on the material suspended in the organic medium (DMF).

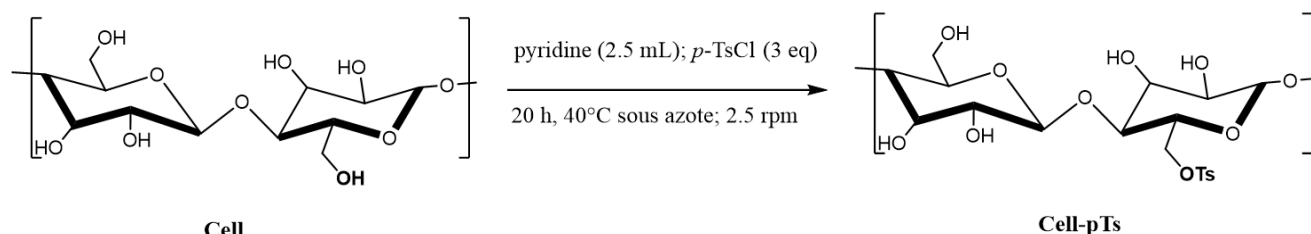


Figure 3. Preparation of Cell-pTs.

The grafting of diamine groups by substitution of the tosyl leaving group was optimized in DMF at 80 °C for 40 hours under agitation using an orbital shaker (Figure 4). It is important to note that the use of a magnetic stirring bar was avoided, as it completely destroyed the material by abrasion.

Ethylenediamine was selected as the chelating agent for covalent anchoring onto the Cell-pTs material, leading to the formation of the Cell-EDA compound. The degree of substitution (DS), determined from elemental analysis results, was 0.3 for Cell-EDA.

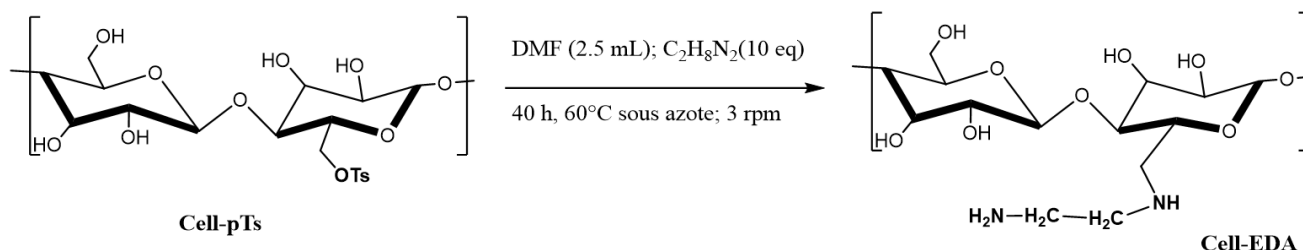


Figure 4. Preparation of Cell-EDA.

3.2. Characterization

The covalent modification of the cellulose fabric was confirmed by Fourier-transform infrared spectroscopy (FT-IR), a preferred technique for monitoring the evolution of functional groups during the functionalization steps [16]. As shown in Figure 5, the spectra of both raw and modified samples display the characteristic bands of the cellulose backbone. The broad bands around 3400 cm^{-1} and 1100 cm^{-1} are attributed to O-H stretching vibrations (hydroxyl groups) and C-O-C vibrations (glycosidic linkages), respectively. The band around 2900 cm^{-1} corresponds to the $\nu(\text{C-H})$ vibrations of the glucosidic units, while a band at 1641 cm^{-1} reflects the bending mode of adsorbed water, commonly observed in hydrophilic cellulose-based materials [17, 18].

The success of the tosylation step is evidenced by the appearance of specific bands at 1596 cm^{-1} ($\nu(\text{C}=\text{C})$) of the aro-

matic ring), 1351 cm^{-1} ($\nu_{\text{as}}(\text{SO}_2)$), 1172 cm^{-1} ($\nu_{\text{s}}(\text{SO}_2)$), and 812 cm^{-1} ($\delta(\text{C-H})$), which are signatures of tosyl groups introduced onto the cellulose [14].

The nucleophilic substitution of tosyl groups by ethylenediamine (EDA) is clearly indicated by the appearance of two new bands at 1654 cm^{-1} and 1650 cm^{-1} , characteristic of the N-H bending modes $\delta(\text{N-H})$ of primary amines [19]. The FT-IR spectrum of the final sample (Cell-EDA) remains stable after 12 hours of vacuum storage, ruling out the presence of adsorbed solvents or residual amines. Furthermore, the disappearance or significant attenuation of the bands associated with tosyl groups at 1351, 1172, and 812 cm^{-1} in the Cell-EDA spectrum suggests an effective replacement of leaving groups by nucleophilic amine functions, thereby confirming the success of the covalent grafting.

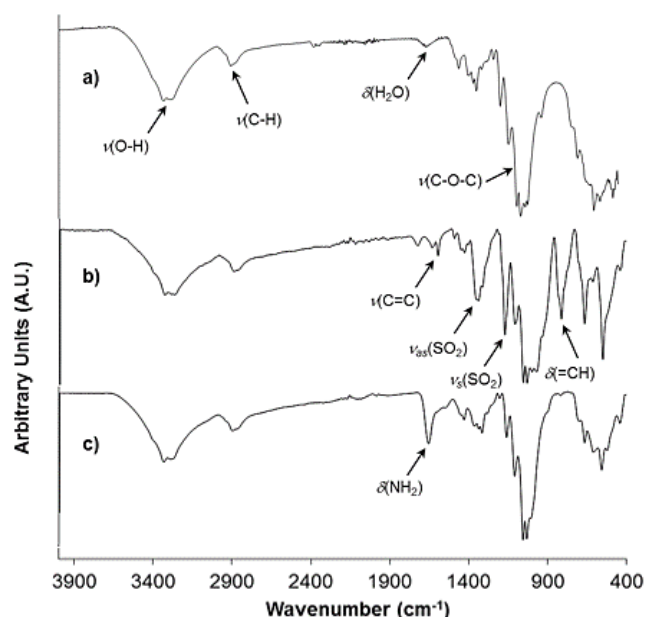


Figure 5. FT-IR spectra of (a) Cell (raw cellulose fabric), (b) Cell-pTs (tosylated fabric), and (c) Cell-EDA (fabric grafted with ethylenediamine).

3.3. Semi-Quantitative Comparative Analysis

A semi-quantitative analysis of the fourier-transform infrared (FT-IR) spectra was conducted to assess the effective-

ness of each step in the chemical functionalization of the cellulose fabric (Table 1). In the spectrum of the Cell-EDA sample, a characteristic band of primary amine groups clearly appears between 1650 and 1654 cm^{-1} . Its relative intensity is approximately 2.5 times higher than that of the band centered at 1596 cm^{-1} , attributed to aromatic C=C bond vibrations, which here serve as residual markers for tosyl groups. This increase in intensity suggests significant introduction of amine groups onto the cellulose matrix.

Furthermore, the specific bands of sulfonate (SO_2) functions, located at 1351 and 1172 cm^{-1} in the spectrum of Cell-pTs, are reduced by more than 70% in the Cell-EDA spectrum. This marked attenuation indicates efficient substitution of the tosyl groups during the grafting reaction with ethylenediamine. The near-complete disappearance of the band at 812 cm^{-1} , also associated with the tosyl moiety, supports this observation.

These spectroscopic results are consistent with the elemental analysis data, which indicate a degree of substitution (DS) of approximately 0.30. They thus confirm the effective incorporation of amine functionalities onto the fabric surface. The observed spectral modifications—including the weakening of tosyl-specific signals and the pronounced emergence of the N-H band—corroborate the successful nucleophilic substitution. This chemical conversion is a key step in imparting selective metal cation adsorption capacity to the material.

Table 1. Relative intensity of characteristic IR bands for Cell, Cell-pTs, and Cell-EDA.

Band Number	Vibrational assignment	Position (cm^{-1})	Cell (a.u.)	Cell-pTs (a.u.)	Cell-EDA (a.u.)
1	$\nu(\text{O-H})$ (stretching)	~3400	0.82	0.74	0.71
2	$\nu(\text{C-H})$ (CH_2)	~2900	0.65	0.63	0.62
3	$\delta(\text{H}_2\text{O})$ (adsorbed)	1641	0.52	0.48	0.47
4	$\nu(\text{C}=\text{C})$ aromatic (tosyl)	1596	—	0.54	0.19
5	$\nu_{\text{as}}(\text{SO}_2)$ (tosylate)	1351	—	0.47	0.11
6	$\nu_{\text{s}}(\text{SO}_2)$ (tosylate)	1172	—	0.50	0.14
7	$\delta(\text{C-H})$ aromatic	812	—	0.38	0.08
8	$\delta(\text{N-H})$ primary amines	1650-1654	—	—	0.58

Note: a.u. = arbitrary units of absorbance measured by ATR-IR.

3.4. Adsorption Studies

3.4.1. Effect of pH

The adsorption efficiency of Cu(II) and Pb(II) metal ions by the functionalized membrane Cell-EDA was evaluated as a function of the pH of the aqueous solution. pH is a critical

parameter influencing adsorption behavior, as it determines both the speciation of metal ions and the surface charge of the adsorbent. Indeed, the efficiency of the process relies on the balance between the chemical form of the metal species in solution and the protonation state of the active sites on the adsorbent [20, 21].

In this study, experiments were conducted within a pH range of 3 to 9. Defined amounts of Cell-EDA (5 g/L) were

immersed in solutions containing 100 mg/L of Cu(II) or Pb(II) at room temperature (25 °C). After 90 minutes of agitation using an orbital shaker, the membranes were separated, and the residual metal concentration was measured by atomic absorption spectroscopy (AAS).

For Cu(II) adsorption, the results (Figure 6a) show maximum efficiency at pH 4, with a high retention rate maintained in the pH range of 4 to 5. Under these conditions, copper is predominantly present as free Cu^{2+} ions, favoring interaction with the amine groups on Cell-EDA [22, 23]. As the pH increases beyond 5, the formation of hydrolyzed species such as $[\text{Cu}_2(\text{OH})_2]^{2+}$ (pH 6-7) and $\text{Cu}(\text{OH})_2$ (pH ≥ 8) becomes significant, leading to a decrease in adsorption due to precipitation or reduced mobility in solution [19, 24]. At pH < 4, the high concentration of H^+ ions causes excessive protonation of the amine groups, resulting in electrostatic repulsion with

metal cations and thus reduced adsorption efficiency. In contrast, the adsorption profile of Pb(II) differs significantly (Figure 6b). Maximum adsorption is observed at pH 8, where lead is primarily present as $\text{Pb}(\text{OH})^+$, a species more reactive with the amine functions of Cell-EDA [25, 26]. At acidic pH (< 5), the dominance of free Pb^{2+} ions and protonation of the adsorption sites significantly reduce interactions with lead, explaining the low retention observed.

For comparison, raw cellulose fabric (Cell) was subjected to the same experimental conditions. Results show that the unmodified cellulose exhibits very low adsorption capacity (<10%) for both metal cations, regardless of pH. This stark contrast clearly demonstrates the impact of chemical functionalization on enhancing the chelating properties of the cellulose matrix [27].

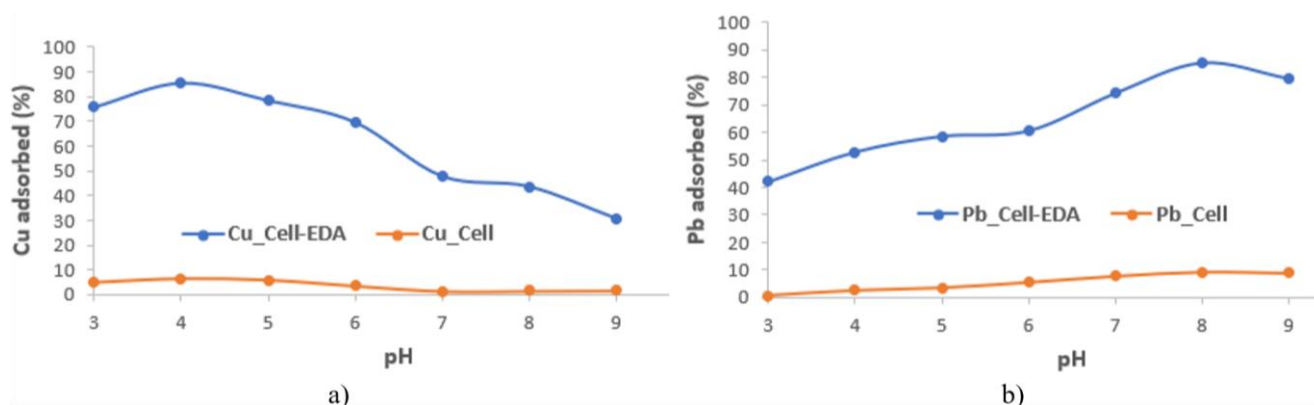


Figure 6. Effect of pH on the adsorption of (a) Cu(II) and (b) Pb(II) by Cell and Cell-EDA (metal ion concentration = 100 ppm; contact time = 90 min; adsorbent dose = 5 g/L).

3.4.2. Adsorption Kinetics

Following the pH optimization for effective adsorption of Cu(II) and Pb(II) cations by the Cell-EDA membrane, adsorption kinetics were investigated to determine the time required to reach adsorption equilibrium. Kinetics play a crucial role in the design of water treatment systems, as they directly influence the operational efficiency of the adsorbent [28, 29]. The time-dependent adsorption profiles are shown in Figure 5 for both metals, revealing that Cell-EDA rapidly adsorbs Cu(II) and Pb(II) during the initial phase of the process. For Cu(II) at pH 4, approximately 55% of the metal is captured within the first 30 minutes, and saturation is reached after 120 minutes, with a removal rate of about 90% (Figure 7a). This rapid initial uptake is attributed to the high availability of free active sites on the functionalized surface of Cell-EDA [30]. A similar trend is observed for Pb(II) at pH 8

(Figure 7b), where adsorption is also rapid at the beginning and reaches a plateau at 120 minutes, with a maximum efficiency of approximately 96%. This strong affinity can be attributed to the formation of stable complexes between the amine groups of the Cell-EDA membrane and hydrolyzed Pb(II) species such as $\text{Pb}(\text{OH})^+$, which dominate in solution at this pH [31]. Both kinetic profiles generally follow a pseudo-second-order model, suggesting that the adsorption process is governed by chemical interactions involving electron exchange between the functional groups of the adsorbent and the metal ions [2]. The similarity in adsorption behavior observed for Cu(II) and Pb(II) highlights the versatility of the Cell-EDA material as a platform for heavy metal remediation. These promising results pave the way for deeper investigation into the molecular-scale interaction mechanisms, particularly through advanced spectroscopic techniques and molecular dynamics modeling.

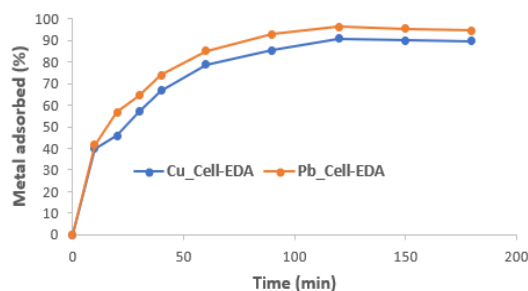


Figure 7. Effet du temps de contact sur l'adsorption du Cu(II) à pH 4 et du Pb(II) à pH 8 par Cell-EDA (concentration d'ions métalliques = 100 ppm, dose d'adsorbant = 5 g/L).

3.4.3. Adsorption Isotherms

Adsorption isotherm analysis is essential for understanding equilibrium interactions between an adsorbent and target species. It also provides insights into the thermodynamic and structural aspects of the process, as well as the material's performance under varying conditions [32]. In this study, three classical models Langmuir, Freundlich, and Temkin were applied to describe the adsorption of Cu(II) and Pb(II) ions onto the Cell-EDA membrane, with the goal of identifying the predominant adsorption mechanism and the nature of interactions between the metal ions and the functional sites of the material. The Langmuir model, based on the assumption of monolayer adsorption on homogeneous and independent sites, is represented by the following equation:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{b q_m} \quad (1)$$

C_e (mg/L) is the metal concentration in solution at equilibrium, q_e (mg/g) is the amount of metal adsorbed at equilibrium, q_m (mg/g) is the maximum adsorption capacity corresponding to the maximal adsorption surface, and b (L/mg) is the Langmuir constant.

The Freundlich model is suitable for heterogeneous surfaces and describes multilayer adsorption. It is expressed as:

$$\ln \ln q_e = \ln \ln K_f + \ln \frac{1}{n} \ln C_e \quad (2)$$

where C_e (mg/L) is the metal concentration in solution at equilibrium, q_e (mg/g) is the amount of metal adsorbed at equilibrium, and K_f and $1/n$ are Freundlich constants describing the adsorption capacity and intensity, respectively [33].

The Temkin model accounts for adsorbent-adsorbate interactions and assumes that the heat of adsorption decreases linearly with surface coverage. The corresponding equation is:

$$q_e = \left(\frac{RT}{b_T}\right) \ln(A_T) + \left(\frac{RT}{b_T}\right) \ln(C_e) \quad (3)$$

where C_e (mg/L) is the metal concentration in solution at equilibrium, q_e (mg/g) is the amount adsorbed at equilibrium, A_T (L/g) is the Temkin isotherm equilibrium constant, b_T (J/mol) is a constant related to adsorption heat, R (8,314 J/mol/K) is the universal gas constant, and T (K) is the absolute temperature [34].

The experimental data were fitted to these three models, and the regression curves are presented in Figure 8. The determination coefficients R^2 were used to compare the fit of each model to the experimental data. The Langmuir model showed a moderate correlation, with an R^2 of 0.92 for Cu(II), but only 0.86 for Pb(II), indicating adsorption imperfectly described by a homogeneous monolayer. This limitation can be attributed to the porous structure of the cellulose fabric and the multifunctional nature of the grafted diamine groups, which may accommodate multiple metal ions on the same chelation site.

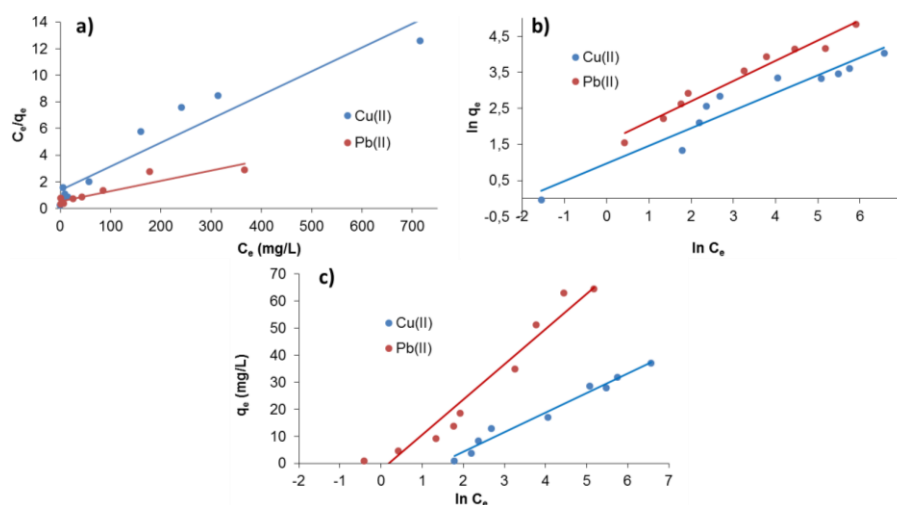


Figure 8. (a) Langmuir, (b) Freundlich, and (c) Temkin isotherms for the adsorption of Cu(II) (blue curves) and Pb(II) (red curves) on the Cell-EDA membrane (pH = 4 for Cu(II) / 8 for Pb(II), contact time = 120 min, adsorbent dose = 5 g/L).

In contrast, the Freundlich and Temkin models proved more relevant, with correlation coefficients ranging from 0.92 to 0.98. These results confirm the heterogeneous character of the Cell-EDA surface as well as the existence of energetically variable interactions between the material and the metal ions [35]. The satisfactory fit to the Temkin model also suggests chemical adsorption involving strong interactions between the nitrogen atoms of the grafted structure and the metal ions. Thus, the Freundlich and Temkin isotherms provide a more accurate description of the adsorption behavior of Cell-EDA, highlighting its potential as an effective bioadsorbent for heavy metal remediation.

Although the Langmuir model is not perfectly representative for describing the adsorption of metal ions on the Cell-EDA membrane due to the heterogeneous and porous nature of the cellulose support, it still provides a useful approximation of the maximum adsorption capacities q_m for Cu(II) and Pb(II). According to the curves shown in Figure 6a, the q_m values are 55.9 mg/g for Cu(II) and 131.6 mg/g for Pb(II) (Table 1), highlighting the material's notable performance towards heavy metals.

The adsorbent's efficiency is further supported by the dimensionless separation factor R_L from the Langmuir model, which serves as a predictive indicator of the adsorption favorability. This factor is calculated as:

$$R_L = \frac{1}{1 + bC_0} \quad (4)$$

where b is the Langmuir constant and C_0 is the initial metal concentration. Depending on the value of R_L , the adsorption process can be classified as irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), or unfavorable ($R_L > 1$) [36]. In our case, R_L values range from 0.07 to 0.94 for Cu(II) and from 0.06 to 0.93 for Pb(II), clearly indicating favorable adsorption across the tested concentration range.

These observations are consistent with the Freundlich model parameters. The constant K_f , reflecting adsorption capacity, and the parameter n indicating adsorption intensity, confirm the strong affinity between the metal ions and the Cell-EDA membrane. A process is considered favorable when n lies between 1 and 10 [32]. The obtained values, $n = 2.05$ for Cu(II) and $n = 1.78$ for Pb(II), confirm the spontaneous and physicochemical nature of the adsorption under the applied experimental conditions. Therefore, despite its conceptual limitations for heterogeneous surfaces, the Langmuir model provides coherent parameters which, when combined with the Freundlich model predictions, validate the strong performance of the Cell-EDA membrane as an adsorbent material

for treating heavy-metal contaminated effluents.

Table 2. Isotherm parameters and regression coefficients (R^2) for Cu(II) and Pb(II) adsorption on Cell-EDA.

Isotherme	Parametre	Cu(II)	Pb(II)
Langmuir	q_m (mg/g)	55.9	131.6
	b (L/mg)	0.013	0.014
	R_L	0.07-0.94	0.06-0.93
	R^2	0.92	0.86
Freundlich	K_f	2.66	4.86
	n	2.05	1.78
	R^2	0.92	0.96
	B_T	7.24	13.02
Temkin	b_T	313.7	174.4
	A_T	0.24	0.83
	R^2	0.98	0.95

3.5. Comparison of Adsorption Capacities of Similar Amine-Modified Materials

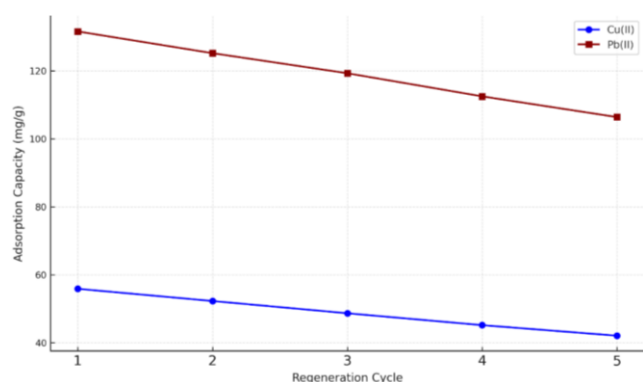
To evaluate the performance of the material developed in this study, the maximum adsorption capacities of the Cell-EDA membrane were compared to those of other amine-functionalized cellulose-based materials reported in the literature (Table 3). The results show that the Cell-EDA membrane exhibits particularly high adsorption capacity, especially for lead, reaching a value of 131.6 mg/g. This performance surpasses that of many analogous materials, such as EDA-functionalized cellulose (98.5 mg/g) or cotton fibers modified with polyethylene glycol-bis-EDA (105.2 mg/g;) [25, 26].

For Cu(II), the Cell-EDA membrane achieves an adsorption capacity of 55.9 mg/g, which lies in the upper range among bio-based materials, when compared with triethylenetetramine-grafted cellulose paper (41.2 mg/g) or modified microcrystalline cellulose (33.7 mg/g) [37, 38]. These results highlight the effectiveness of ethylenediamine grafting onto textile supports, providing a robust architecture rich in active sites, and well-suited for practical shaping in the treatment of metal-contaminated water.

Table 3. Amine-functionalized cellulose-based adsorbent materials reported in the literature.

Adsorbent Material	Main Modifier	Target metal	Adsorption capacity (mg/g)	Reference
Polyamine-grafted cellulose paper	Triethylenetetramine	Cu(II)	41.2	[37]
EDA-functionalized cellulose	Ethylenediamine	Pb(II)	98.5	[25]
EDA-grafted cellulose fabric (Cell-EDA)	Ethylenediamine	Pb(II)	131.6	This study
EDA-grafted cellulose fabric (Cell-EDA)	Ethylenediamine	Cu(II)	55.9	This study
Modified microcrystalline cellulose	Polyethyleneglycol diamine	Cu(II)	33.7	[38]
Functionalized cotton fibers	Polyethylene glycol-bis-EDA	Pb(II)	105.2	[26]
Modified nanocellulose	Aminopropylsilane	Cu(II)	60.8	[28]
Cellulose-based biochar grafted with EDA	Ethylenediamine	Pb(II)	124.3	[13]

3.6. Evolution of the Adsorption Capacity of Cell-EDA After Five Reuse Cycles

**Figure 9.** Recyclability curve of the adsorption capacity after 5 cycles.

The durability of the adsorbent material was evaluated through a series of five consecutive adsorption/desorption cycles, aiming to assess its chemical stability and reusability. Each cycle consisted of an adsorption phase followed by desorption using a 0.1 M NaOH solution. Between each cycle, the Cell-EDA membrane was thoroughly rinsed, neutralized, and reused under the same operating conditions. The results, presented in Figure 9, show a progressive but moderate decline in adsorption capacity over successive cycles. For Cu(II), the capacity decreased from 55.9 mg/g in the first cycle to 42.1 mg/g by the fifth cycle, representing a loss of approximately 24.7%. For Pb(II), the capacity declined from 131.6 mg/g to 106.4 mg/g, corresponding to a loss of 19.2%. Despite this slight reduction in efficiency, the membrane retained significant performance after multiple uses, indicating good structural and functional stability of the material. These

findings highlight the potential of the Cell-EDA fabric as a reusable bioadsorbent suitable for long-term application in the treatment of industrial or domestic wastewater contaminated with heavy metals.

4. Conclusion

This study led to the development of a novel bioadsorbent based on cellulose fabric grafted with ethylenediamine (Cell-EDA) for the removal of Cu(II) and Pb(II) ions from aqueous solution. The process involved three key steps: mercerization, tosylation, and grafting in an organic medium. Spectroscopic characterization (FT-IR) confirmed successful functionalization, as evidenced by the appearance of characteristic amine bands and the significant decrease in tosylate-associated bands, further supported by a semi-quantitative analysis of spectral intensities. The Cell-EDA membrane exhibited excellent adsorption performance for Cu(II) and Pb(II) ions, achieving removal rates above 90% at optimal pH values (pH 4 for Cu(II), pH 8 for Pb(II)) within 120 minutes.

Adsorption studies revealed strong affinity of the material for both metal cations, with maximum capacities of 55.9 mg/g for Cu(II) and 131.6 mg/g for Pb(II), outperforming similar cellulose-based supports reported in the literature. The kinetics followed a pseudo-second-order model, and Langmuir isotherms indicated well-organized monolayer adsorption. Furthermore, the material demonstrated good stability over five consecutive regeneration cycles, with only a moderate efficiency loss of approximately 24%, confirming its potential for repeated applications in water treatment processes.

In summary, the Cell-EDA fabric appears to be an efficient, renewable, and reusable bioadsorbent, suitable for aqueous pollution remediation processes. Future studies will focus on column applications, selectivity in the presence of competing metals, and pilot-scale modeling.

Abbreviations

Cell	Cellulose Fabric
Cell-pTs	Tosylated Cellulose Fabric
Cell-EDA	Ethylenediamine-Grafted Cellulose Fabric
FT-IR	Fourier-Transform Infrared
AAS	Atomic Absorption Spectroscopy

Conflicts of Interest

The authors declare no conflicts of interest.

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