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# Making of cellulose active surfaces through layer-by-layer technique: MDI-EDTA bilayer

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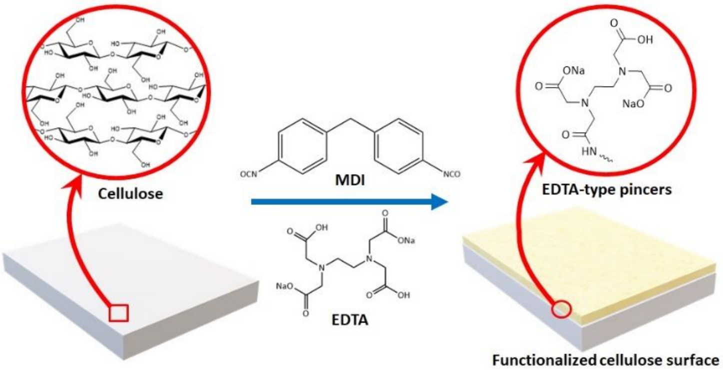
## Graphical Abstract



**Abstract.** The contamination of water resources by metal ions has highlighted the need for efficient technologies and novel materials for the *in situ* retention and monitoring of contaminants, which are both low-cost and environmentally friendly. This study aims to develop surfaces for the retention of metallic contaminants in aqueous media. The approach involves the insertion of EDTA onto microporous cellulose surfaces. The surfaces were formed by functionalizing cellulose with diisocyanates, such as MDI, in the first stage, providing -NCO groups available for EDTA insertion in the second stage through their -COOH groups. The materials were characterized using Fourier Transform Infrared Spectroscopy coupled with Attenuated Total Reflectance (FTIR-ATR), Thermogravimetric Analysis (TGA), and Differential Scanning Calorimetry (DSC). FTIR-ATR spectra results confirmed successful material formation. In the first stage, bands associated with the tension vibration of the free -NCO and carbonyl of the Cellulose-OCONHR' group appeared at 2258 cm$^{-1}$ and 1637 cm$^{-1}$, respectively. In the second stage, the band associated with the vibrations of the C=O showed greater intensity and overlap in the region of 1700 cm$^{-1}$ to 1600 cm$^{-1}$, attributed to the amide bond. Additionally, a band at 1400 cm$^{-1}$ was observed, attributed to the vibration of the -COO- groups of EDTA. TGA and DSC further demonstrated different thermal behaviors, indicating successful functionalization. The results show that the functionalization of the surfaces was successfully achieved using the layer-by-layer technique, resulting in functionalized surfaces with terminal EDTA-type pincers.

**Keywords:** Cellulose, layer-by-layer technique, 4,4'-methylenebis(phenyl isocyanate), ethylenediaminetetraacetic acid, surface functionalization.

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## 1. Introduction

Heavy metals are considered significant pollutants of environmental mediums such as soils and waters. They originate from both anthropogenic activities (industrial production, fertilizers, and pesticides, agriculture, and waste management, among others) and natural sources, thereby affecting the environment and posing a challenge to drinking water quality (Huang et al., 2024; Sankhla et al., 2016). Technologies such as ion exchange and chemical precipitation have been implemented to remove heavy metals from water. However, these methodologies often result in the excessive generation of sludge, which must be removed from water treatment plants, thereby increasing the cost of the process (Kurniawan et al., 2023). To overcome these limitations, biosorption using functional polymeric materials has emerged as a promising alternative, mainly due to its cost and high environmental abundance (Torres, 2020).

Several approaches are available for making functional polymeric materials: (i) synthesis from precursor materials, (ii) polymer mixtures, (iii) physical modification, and (iv) chemical modification of polymer structures, including chemical modification of functional groups, end-chain reactions, degradative reactions, and grafting reactions, among others (Wang et al., 2020). Natural polymers such as cellulose, starch, chitin, and others are potential raw materials for forming functional polymeric materials due to their physical and chemical properties. These properties give them good adaptability, ease of processing, availability, and economic viability (Rao et al., 2014). Additionally, these polymers are considered biocompatible, biodegradable, and nontoxic, promoting the development of green methodologies for removing heavy metals (Marin et al., 2020).

For instance, cellulose is the most abundant biopolymer in nature. It has a linear polysaccharide structure with long chains of β-D-glucopyranose units linked by β-1,4 glycosidic bonds. Structurally, it is formed by glucose units, and consequently, it contains primary and secondary hydroxyl functional groups on its surface. These groups give the material properties like high hydrophilicity and specific reactivity, mainly for the adsorption of dyes and pigments (Kausar, 2023). However, cellulose shows poor properties related to heavy metal ion retention, limiting its applications in this area. Therefore, chemically modifying cellulose to enhance its heavy metal retention properties is challenging. Activating the cellulose surface is necessary to promote the ability to interact selectively at the surface level with specific molecular species, such as heavy metals (Fabbri and Messori, 2017).

Chemical modifications of cellulose surfaces are based on the formation or breaking of bonds concerning surface functional groups. These modifications are strong, irreversible, and can be directed toward producing structural changes, hydrophobicity, charge density, stability, and reactivity of the material's surface. As a result, the modified material can acquire new applicability and economic value (Lerma et al., 2020). Various chemical reactions have been employed to chemically functionalize a polymer surface, including hydrolysis, esterification, urethanization, and acetylation (Fabbri and Messori, 2017).

In the case of cellulose, hydroxyl groups allow for various chemical modifications to obtain functional cellulose materials for various applications, such as the removal of soluble organic compounds and the adsorption of metals, among others (Palencia et al., 2021). For instance, cellulose was modified with dibenzo-18-crown-6 to form a composite material that was applied to the removal of Cd(II), Zn(II), Ni(II), Pb(II), and Cu(II), achieving higher metal removal efficiencies (Fakhre et al., 2018). However, the high cost of producing these materials limits their application in large quantities. Another example is the formation of carboxymethyl cellulose, which was cross-linked with epichlorohydrin to retain Cd(II), with a maximum uptake of 150.60 ± 10.47 mg/g (Wei et al., 2015). However, using toxic reagents in producing carboxymethyl cellulose poses challenges for large-scale implementation.

A versatile technique for polymer surface modification is the layer-by-layer (LbL) method, which can be performed using physical and chemical interactions (Yang et al., 2012). In the first case, adsorption processes are controlled to immobilize a first layer, followed by the deposition of subsequent layers. Typically, ionic interactions are utilized, and the formation of each layer is based on the attractive forces between positive and negative charges. For instance, a substrate with a negative surface charge density can adsorb poly(diallyl dimethyl ammonium chloride) (first layer), followed by the adsorption of poly(sodium styrene sulfonate) (second layer), and then another layer of poly(diallyl dimethyl ammonium chloride) (third layer), and so on (Wang and Hauser, 2009). In the second case, LbL based on chemical interactions involves the formation of new bonds between the substrate and a molecule capable of reacting with it while also introducing a new reactive functional group (Atoufi et al., 2022). For example, fumaric acid can be chemically immobilized on a cellulose surface through an esterification reaction between the hydroxyl groups of cellulose and the carboxylic acid group of the organic acid. This results in a first layer formed by units of ethylenedicarboxylic acid anchored to the substrate via ester groups. Subsequently, the end carboxylic groups remain available for further reactions, allowing a second layer to be formed by reacting these carboxylic groups with, for instance, 3-hydroxypentanoic acid.

Various investigations have focused on the functionalization of cellulose. One example involves creating cellulose fibers with a high hydrophobic character by modifying the surface hydroxyls with 4,4'-methylenebis (phenyl isocyanate) (MDI) as a bridging molecule. In this specific case, MDI serves as the first layer, while acetic acid is used to form the second layer (Palencia et al., 2020). Another example is the derivatization of cellulose through the esterification of carboxymethyl cellulose, followed by ammonolysis and carboxymethylation, resulting in groups similar to ethylenediaminetetraacetic acid disodium dihydrate (EDTA) (Hu et al., 2022). These functionalized cellulose materials offer a promising alternative for developing materials to recover pollutant ions from aqueous systems (Otálora et al., 2021).

Given the above, to advance the studies and design of polymeric surfaces for environmental applications, this research focuses on synthesizing a functional multilayer system that can retain metal

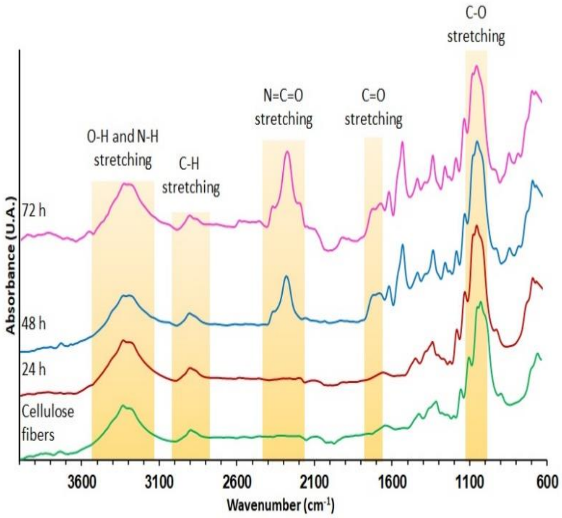

**Figure 1.** FTIR-ATR spectra of cellulose fibers (—), and porous surfaces of functionalized celluloses in the first layer at 40 °C for 24 (—), 48 (—) and 72 h (—).

ions in aqueous effluents. The use of a reaction between isocyanates and cellulose hydroxyl to produce urethane and between isocyanate and carboxylic acid to produce amides is suggested for making cellulose-MDI-EDTA multilayer systems through the LbL technique. The anchoring of EDTA molecules, a compound widely used as a chelating agent for metal ions, emerges as a promissory alternative for developing active surfaces.

## 2. Methodology

### 2.1. Materials

Quantitative Munktell grade 388 filter paper was used as a model porous cellulose surface obtained from Ahlstrom-Munksjö. Dimethyl sulfoxide (DMSO, 99.5%) and acetone ($C_3H_6O$, 99.8%) were purchased from Merck. Toluene ($C_6H_5CH_3$, 99.9%) was acquired from Sigma-Aldrich. Ethylenediamine tetraacetic acid (EDTA, 99.0%) was purchased from PanReac. Commercial MDI, known as "Polyurethane B," was obtained from Agenquímicos in Cali, Colombia. All reagents were used without pretreatment.

### 2.2. Cellulose surface functionalization

For the modification of porous cellulose, 1.0 cm² pieces of filter paper were used. To create the first layer, the cellulose surfaces were impregnated with MDI by direct immersion, followed by heating the samples to 40°C in an oven. The reaction time was evaluated at three different intervals: 24, 48, and 72 hours. Subsequently, the samples were washed with an excess of acetone to remove any remaining MDI and dried at 40°C for 1 hour.
For the second layer, the samples were immersed in 5.0 mL of DMSO containing an excess of EDTA at 40°C for 16 hours. After this period, they were removed and washed with 10.0 mL of acetone. Finally, they were dried in an oven at 50°C for 1 hour.

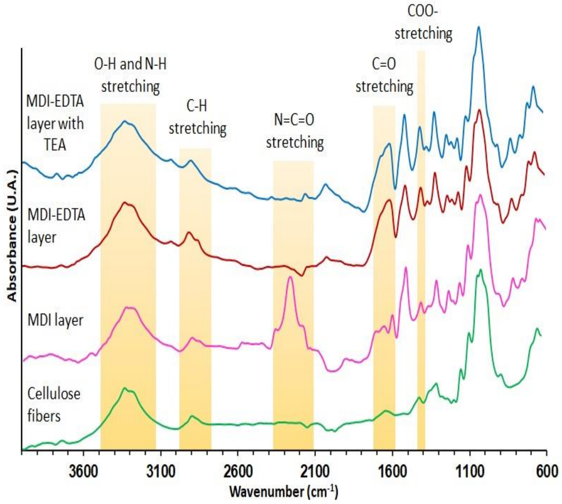

**Figure 2.** FTIR-ATR spectra of cellulose (—), cellulose with MDI layer (—), cellulose with MDI-EDTA layer (—), and porous cellulose surfaces of functionalized celluloses in the second layer (—).

### 2.3. Characterization of cellulose active surfaces

The porous surfaces of cellulose functionalized in the first and second layers were characterized using FTIR-ATR, TGA, and DSC.
*FTIR-ATR Measurements:* These were performed on an IRAffinity-1S spectrophotometer (Shimadzu Co., Kyoto, Japan). The spectra were recorded in the range of 4000 to 600 $cm^{-1}$ with a resolution of 4 $cm^{-1}$, using 16 scans per sample. All samples were analyzed in quintuplicate.
*TGA Analysis:* The TGA analysis was conducted using an SDT-Q600 thermogravimetric analyzer (TA Instruments, New Castle, DE, USA). Approximately 10 mg of each sample was weighed and heated from room temperature to 550 °C under a nitrogen flow of 20 mL/min, with a heating rate of 15 °C/min. The first-order derivative of the weight loss thermogram was obtained to evaluate the materials.
*DSC Analysis*: The thermal properties of the materials were assessed using a DSC2500 (TA Instruments, New Castle, DE, USA). The samples were heated from 0 °C to 450 °C at a rate of 15 °C/min, under a nitrogen flow of 20 mL/min.

## 3. Results and discussion

The functionalization of cellulose was performed using commercial MDI as a "bridge" for anchoring EDTA units. **Figure 1** shows the first layer's FTIR-ATR spectra of the functionalized cellulose surfaces. Three characteristic regions can be differentiated in the cellulose spectra, corresponding to the biopolymer's bands: i) 3600-3000 $cm^{-1}$ region: This region features the band associated with the hydroxyl groups (O–H) stretching in cellulose. ii) 3000-2800 $cm^{-1}$ region: The band in this range is attributed to the symmetric stretching of the methylene ($CH_2$) groups in the glucose units. iii) 1100-1000 $cm^{-1}$ region: An intense band appears in this region due

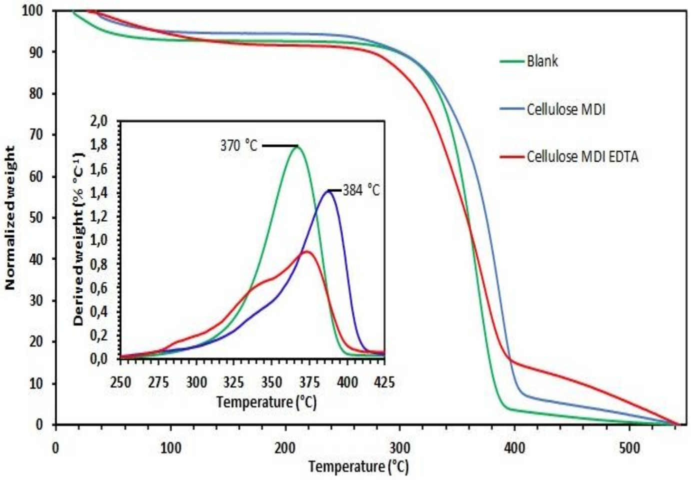

**Figure 3.** Thermogravimetric curve of cellulose (—, blank), cellulose MDI (—), and cellulose MDI EDTA (—). Inside, the derived weight curves of porous cellulose surfaces before and after modifications are observed.

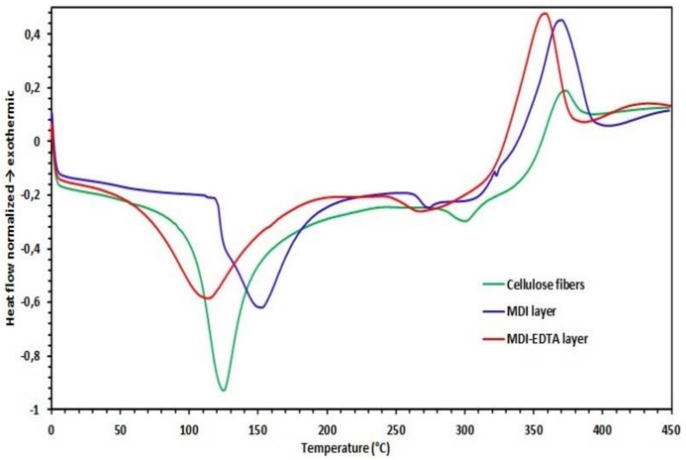

**Figure 4.** DSC curves of cellulose (—), cellulose MDI (—), and cellulose MDI EDTA (—).

to the C–O stretching vibration (C–O–C) of the β-1,4-glycosidic bonds (Yang et al., 2017). No significant differences were observed when comparing the FTIR-ATR spectra of cellulose with the porous surfaces of functionalized celluloses at 24 hours of reaction time. However, for materials formed with 48 hours and 72 hours of reaction time, two intense bands not present in the cellulose FTIR-ATR spectra were observed: at 2258 cm$^{-1}$, assigned to the stretching vibration of the free isocyanate, and at 1637 cm$^{-1}$, attributed to the stretching vibration of the carbonyl groups of the urethane group formed between the hydroxyl groups of the cellulose and the MDI (Cellulose-OCONHR') (Palencia et al., 2020). These bands were only observed after 48 hours, and their intensity increased with longer reaction times. Therefore, it was determined that the functionalization of cellulose surfaces using MDI was effectively carried out, providing -NCO groups available for anchoring a second layer using EDTA. **Figure 2** shows the FTIR-ATR spectra of the product after the cellulose functionalization by the reaction between the free -NCO groups and EDTA molecules using DMSO as solvent.

The disappearance of the band associated with the vibration of the -NCO group at 2258 cm$^{-1}$ is visualized. At the same time, there is an increase in the intensity and overlapping of the bands associated with the C=O bonds in the region of 1700 to 1600 cm$^{-1}$ due to the Cellulose-OCONHR' and amide bond (R-NHCOR'). Additionally, the FTIR-ATR spectra show an increase in the intensity and overlapping of the bands associated with the C=O bonds in the 1700 to 1600 cm$^{-1}$ region due to the amide bond and structural segments of EDTA molecules. The amide links result from the reaction between the free -NCO and the acid groups of EDTA. Among the coupled bands, the band near 1620 cm$^{-1}$ is associated with the tensile vibrations of the C=C bonds of the aromatic rings of MDI. Moreover, the change in the intensity of the band at 1400 cm$^{-1}$ is attributed to the vibration caused by the carboxylate groups of EDTA. The change in the thickness of the broad band around 3300 cm$^{-1}$ is a product of the N-H vibrations of the R-NHCOR' groups, influenced by the possible hydrogen bonds formed in the reaction (Mattia and Painter, 2007). Based on the above, it is estimated that the covalent anchoring of the EDTA units in the cellulose material was achieved. The evaluation of the spectra resulting from the EDTA anchoring does not show a significant difference, so it is assumed that the use of triethylamine (TEA) as a catalyst for the reaction between the free -NCO and any of the -COOH groups of EDTA was effective. To thermally characterize the materials formed, TGA and DSC analyses were performed. **Figure 3** shows the TGA curves for the cellulose and the two functionalized cellulose surfaces (first and second layers).

In the thermograms, three weight loss regions were observed. The first region, between 25 °C and 120 °C, showed a weight loss of approximately 10 % for all the materials, which is attributed to the evaporation of water. The second region, between 275 °C and 400 °C, showed different maximum degradation temperatures for the materials, as indicated by the derived weight curves.

For the non-functionalized cellulose, the maximum degradation temperature occurs at around 370 °C due to its homogeneous, unbranched, and crystalline structure (Yang et al., 2006). In contrast, the initial degradation temperature of the surfaces functionalized with the first and second layers is lower than that of unmodified cellulose. In the case of cellulose-MDI, mass loss, and a shoulder were observed at 388 °C and 340 °C, respectively, attributed to the increase in surface crystallinity associated with the urethane group and the resistance due to aromatic groups (Jiang et al., 2017). Finally, three thermal degradation peaks were present in this region at 290, 340, and 375 °C for the cellulose-MDI-EDTA. The first peak at 290 °C is attributed to the decomposition of EDTA into $Na_2CO_3$ (Huang and Keller, 2015).

On the other hand, **Figure 4** shows the DSC curves for both functionalized and non-functionalized cellulose surfaces. The endothermic peaks in the 50 to 200 °C region correspond to the melting temperature of the cellulose surfaces, indicating the loss of their crystalline structure. The sharpest peak is observed for the non-functionalized cellulose, reflecting its more uniform structure due to the lack of variety in functional groups. In the region from 250 to 320 °C, small endothermic peaks are attributed to the possible generation of cross-linked material before the degradation process (Jandura et al., 2000). Meanwhile, exothermic peaks in the region from 320 to 400 °C correspond to the degradation of the glycosidic bonds of the amorphous cellulose chains, with levoglucose produced as a degradation product (Ball et al., 2004). Additionally, there is a trend in the degradation of the surfaces, with thermal stability decreasing as more functionalization layers are added. The peak for the Cellulose-MDI-EDTA layer shows the lowest degradation temperature and coincides with the broad degradation region shown in the TGA derived weight curves (see **Figure 4**). This indicates that inserting terminal EDTA groups creates greater disorder on the surface, leading to lower thermal resistance.

## 4. Conclusions

In this research, we successfully developed a functionalized surface for a cellulose-based porous material using diisocyanate, specifically MDI, and a known polydentate chelating agent, EDTA. This was achieved by generating urethane and amide linkages via the layer-by-layer (LbL) technique. FTIR-ATR spectra of the functionalized surfaces confirmed this functionalization's effectiveness, which showed bands related to the presence of free -NCO and various -C=O functional groups, including EDTA pincer-type bonds. These results demonstrate the effective functionalization of cellulose using a simple methodology that avoids solvents in the first stage (MDI functionalization) and catalysts during synthesis. Additionally, TGA and DSC analyses of the functionalized surfaces exhibited the expected thermal behavior with a higher degradation temperature range. This can be attributed to the sensitivity acquired by the surface groups, which impacts the material's structure. Thus, the functionalization of cellulose presented in this work shows great potential for applications in retaining heavy metals in aqueous effluents. Future studies should focus on conducting retention assays to evaluate the material's metal retention capacity and determine the maximum retention capacity using adsorption isotherm models.

**Conflict interest.** The authors declare that there is no conflict of interest.

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