

Article

Bio-Based Cellulose/Lignin–Tannin Membranes for Sustainable Water Purification

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Abstract

This study reports the development, optimization and mechanistic evaluation of bio-based cellulose/lignin–tannin membrane adsorbents for the removal of representative inorganic and organic water pollutants: Cr(VI), Pb²⁺, difenoconazole (DFC) and bisphenol A (BPA). Waste cellulose fibers (wCF) from cigarette-package paperboard were converted into reactive membrane constituents by amino/ester and epoxy functionalization and subsequently cross-linked with epoxy-modified kraft lignin (EpKL), with or without tannic acid (TA), yielding wCF/EpKL and wCF/EpKL/TA membranes. Response surface methodology was used to optimize formulation parameters, while structural, morphological, and physicochemical analyses supported successful functionalization, cross-linking, and formation of porous, structurally modified surfaces. At 298 K, the Langmuir adsorption capacities of wCF/EpKL/wCF/EpKL/TA reached 85.37/88.78 mg g^{−1} for Cr(VI), 155.6/163.9 mg g^{−1} for Pb²⁺, 51.80/84.49 mg g^{−1} for DFC, and 194.4/195.4 mg g^{−1} for BPA, respectively. Isotherm, kinetic, and thermodynamic analyses indicated favorable, heterogeneous, and spontaneous adsorption involving specific surface interactions and diffusion-related contributions. Spectroscopy-supported mechanistic interpretation suggested that metal species are retained mainly through complexation with amino, phenolic, and oxygen-containing groups, together with electrostatic interactions, whereas DFC and BPA adsorption involves hydrogen bonding, hydrophobic interactions, and π – π interactions with lignin/tannin aromatic domains. Fixed-bed experiments confirmed the applicability of the membranes under continuous-flow conditions, while regeneration, stabilization/degradation, and soil-burial tests supported their potential within a more sustainable water treatment cycle. Overall, the results demonstrate that waste-derived cellulose/lignin–tannin membranes are promising regenerable sorbents for the adsorption of chemically diverse inorganic and organic pollutants.

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1. Introduction

Water pollution by toxic heavy metals and organic micropollutants has become a critical global issue, fueled by industrial discharge and insufficient wastewater treatment [1]. Among heavy metals, lead (Pb(II)) and hexavalent chromium (Cr(VI)) are especially problematic. Lead is a highly toxic metal used extensively (e.g., in batteries, pigments, and ceramics), and its widespread industrial use has led to pervasive environmental contamination [2]. Even low-level lead exposure can cause severe and irreversible health effects—from neurological and developmental disorders in children to cardiovascular and kidney damage in adults [3]. Hexavalent chromium, a common form of chromium in industrial effluents (e.g., from electroplating and tanning), is a known human carcinogen with no safe level of exposure [4]. In contrast to trivalent chromium, which binds to carbohydrates and lipids to control cardiovascular disease and diabetes [5], exposure to hexavalent chromium in humans leads to diarrhea, swelling of the liver, kidneys, respiratory tract problems, and internal bleeding [6]. Like Pb(II) and Cr(VI), various synthetic organic chemicals have emerged as persistent water pollutants. For example, bisphenol A (BPA) is a high-production-volume compound used in polycarbonate plastics and epoxy resins. BPA can leach into water from plastic waste and has potent endocrine-disrupting activity, binding to hormone receptors and causing reproductive and developmental abnormalities [7]. Consequently, BPA is frequently detected in surface waters and even drinking water sources worldwide. Another problematic organic contaminant is difenoconazole (DFC), a widely used triazole fungicide. Due to extensive agricultural application, DFC residues are often found in irrigation runoff, surface waters, and soils [8]. This pesticide is considered highly toxic to aquatic life and has raised serious environmental health concerns; for instance, regulatory assessments have shown DFC contamination levels exceeding safe thresholds for fish and other biota [9]. Given the dangers of such pollutants to ecosystems and human health, efficient strategies for their removal from wastewater are of paramount importance.

Multiple water treatment technologies have been developed to eliminate heavy metals and organic pollutants. Conventional methods include chemical precipitation, coagulation–flocculation, membrane filtration, ion exchange, advanced oxidation, and adsorption, among others [10]. Each approach has merits, yet also limitations in cost, complexity, or efficacy across different contaminants. Among these, adsorption has emerged as one of the most widely favored techniques for the decontamination of both metals and organics [10,11]. This popularity is due to its relative operational simplicity, versatility, and effectiveness. In particular, adsorption processes offer high removal efficiency, are easy to design and operate, and can often be carried out with affordable materials [12]. An added benefit is that many adsorbents can be regenerated and reused, thus reducing costs and waste generation [12,13]. Traditional adsorbents like activated carbon and zeolites achieve a good removal performance, but they can be prohibitively expensive to produce or regenerate at scale [3,10]. Such economic and sustainability drawbacks have driven research toward more cost-effective and eco-friendlier adsorbents.

In recent years, the focus has shifted to developing sorbents from naturally abundant or waste-derived materials (often termed “biosorbents”) as a sustainable alternative [10,14]. The appeal of biosorbents lies in their wide availability, low cost, and minimal environmental footprint, especially when sourced from agricultural or industrial waste streams [1]. Many biosorbents contain functional groups (e.g., hydroxyl, carboxyl,

phenolic groups) that can bind heavy metal ions or organic molecules, though their native adsorption capacity is sometimes limited [15]. To overcome this, researchers often modify or functionalize natural materials to enhance their affinity for target pollutants. For example, chemical modifications (such as oxidation, grafting of new functional groups, or composite formation) can greatly improve the sorption capacity of cellulose, lignin, chitosan, and other bio-polymers [16–18].

Lignocellulosic materials—in particular, cellulose (the most abundant bio-polymer on Earth) and lignin (the second most abundant)—have attracted considerable interest as base materials for adsorbents [19,20]. These polymers are renewable, inexpensive (may be derived from waste biomass), and feature numerous polar functional groups that can participate in binding contaminants. Cellulose fibers, for instance, contain many hydroxyl groups that make them amenable to chemical derivatization. Lignin, a complex aromatic polymer obtained as a byproduct from the pulp and paper industry, contains phenolic, carboxylic, and methoxy groups that can interact with metal cations or aromatic pollutants. Tannins, a class of plant polyphenols (such as tannic acid (TA)), also offer multiple binding sites (galloyl groups) capable of chelating metals or forming hydrogen bonds and π – π interactions with organic molecules. Numerous studies have demonstrated the effectiveness of modified lignocellulosic adsorbents for removing the pollutants of interest here [21–24]. For example, cellulose membranes functionalized with lignin and TA have been shown to capture both cationic and oxyanionic contaminants from water with high efficiency [25]. Similarly, other researchers have reported excellent uptake of Pb(II), Cr(VI), and similar metal ions using cellulose-based or nanocellulose-based biosorbents impregnated with tannins or other natural polyphenols [26,27]. These successes underscore the potential for predominantly bio-based and waste-derived membrane adsorbents in addressing diverse pollutant classes. However, here remains a need to develop adaptable sorbent systems capable of targeting chemically diverse pollutant classes (both heavy metals and organic compounds), while ensuring the materials are easily regenerable and ultimately biodegradable.

In this context, the present study introduces a predominantly bio-based and waste-derived cellulose membrane adsorbent designed for broad-spectrum pollutant removal. We developed two variants of a cellulose-based membrane using renewable building blocks: (1) epoxy-modified kraft lignin (EpKL) (a wood-industry byproduct) and (2) TA, in addition to the cellulose fiber matrix. In practice, the membranes were prepared by chemical grafting or cross-linking the bio-polymers onto cellulose, yielding robust sheets enriched with functional groups from lignin and tannin. The wCF/EpKL membrane incorporated epoxy-activated lignin within the cellulose network to introduce aromatic phenolic sites beneficial for binding metal ions and aromatic pollutants. The wCF/EpKL/TA membrane contained both the lignin derivative and TA, the latter expected to provide additional multi-dentate binding sites and further improve adsorption capacity. By combining waste-derived cellulose with lignin and tannic-acid-derived functional domains, the membranes are designed to increase the renewable content of the adsorbent and to improve end-of-life degradability, although their environmental acceptability after use must be assessed through regeneration, leaching, and degradation tests. A key motivation for using dominantly natural constituents was to ensure the spent membranes would be biodegradable, avoiding secondary pollution at end-of-life. We also anticipated that the combination of lignin and tannin functionalities on a cellulose scaffold would yield an adsorbent with a high affinity across a spectrum of pollutants—from metal species to hydrophobic organic molecules. The proposed preparation strategy incorporates several elements consistent with green chemistry principles, including the use of waste-derived cellulose and renewable or bio-derived building blocks, functional material reuse through regeneration, and consideration of end-of-life management [28].

At the same time, the present laboratory-scale route includes several chemical functionalization steps, and further process intensification, solvent recovery, and reduction in hazardous reagents remain important targets for future scale-up.

The purpose of this work was to evaluate the adsorption performance and interaction mechanisms of two related waste-cellulose/epoxy-kraft-lignin membrane systems, with and without tannic acid, toward four chemically distinct pollutants: Pb(II), Cr(VI), BPA, and DFC. The main novelty lies in the design of a cross-linked cellulose/lignin-based membrane platform in which tannic acid provides an additional phenolic/aromatic functional domain, and in the systematic comparison of its adsorption behaviour toward representative metal species and organic micropollutants under single-solute conditions. The study combines formulation optimization, equilibrium and kinetic analysis, regeneration assessment, spectroscopic characterization, and mechanistic interpretation to establish structure–function relationships within the developed membrane systems. These particular contaminants were chosen as representative high-priority pollutants: Pb(II) and Cr(VI) for toxic heavy metals, and BPA and DFC for persistent organic pollutants of emerging concern. We investigated how operating parameters such as solution pH, contaminant concentration, temperature, and contact time influence the adsorption efficiency of each membrane. Adsorption isotherms and kinetic models were applied to quantify the membranes' capacity and to elucidate the rate-limiting steps of uptake. To gain insight into the adsorption mechanisms, we carried out spectroscopic analyses and theoretical calculations. Fourier-transform infrared (FTIR) and Raman spectroscopy were used to identify the functional groups on the membrane surfaces involved in binding the pollutants (e.g., observing shifts in peaks corresponding to -OH , -COOH , or aromatic groups after adsorption).

Notably, the membranes exhibited high adsorption capacities for Pb(II), Cr(VI), BPA, and DFC, comparable to or exceeding those of many conventional synthetic adsorbents. Equally important, the bio-membranes demonstrated a high degree of regeneration—the pollutants could be desorbed, and the membrane reused over multiple cycles with only minimal loss of performance [17]. Furthermore, because the membranes are constructed from biodegradable components, their end-of-life management must include regeneration, pollutant recovery/stabilization, leaching assessment, and controlled disposal, addressing concerns about solid waste generation. The findings of this study illustrate the potential of integrating natural polymers and green chemistry approaches to create effective adsorbent materials with low environmental impact. The following sections will detail the adsorption results and mechanistic observations, showing how these bio-based membranes can contribute to sustainable water purification.

2. Materials and Methods

2.1. Materials

Detailed information on all reagents (including chemical names, suppliers, and purities) is provided in the Supplementary Materials (SM) Section S2.1.

2.2. Procedure for Preparation of Cellulose wCF Membranes and Their Constituent

Detailed procedures for the preparation of cellulose-based membrane adsorbents and the synthesis of modification agents from bio-renewable precursors are provided in Section S2.2 (Sections S2.2.1–S2.2.5) and Figure S2 [29–43].

2.3. Response Surface Methodology (RSM) for the Optimization of the Preparation Membranes

The optimization procedure for the preparation of adsorbents is given in Section S2.3.

2.4. Synthesis of Lead Chromate (PbCrO_4)

The procedure for the synthesis of lead chromate (PbCrO_4) is given in Supplementary Materials Section S2.4 [44,45].

2.5. Characterization Methods

Information about characterization methods of adsorbents before and after adsorption is given in Section S2.5 [46–54].

2.6. Adsorption, Desorption and Regeneration Experiments

Adsorption methods performed in a batch and bed column system, and desorption and regeneration methods, are described in Supplementary Materials Section S2.6 (Sections S2.6.1–S2.6.4).

2.7. Applied Technologies for Exhausted Membrane Disposal and Pollutant Wastewater Treatment

The procedure for the stabilization of pollutants, including precipitation, the toxicity characteristic leaching procedure (TCLP) and photocatalytic experiments, as well as biodegradability experiments of membranes, are described in Supplementary Materials Section S2.7 [55–61].

3. Results and Discussion

3.1. Physicochemical Characterization of wCF/EpKL and wCF/EpKL/TA

In addition to adsorption capacity, the contents of amino, acid and epoxy groups, expressed through AN, AV and EEW values, together with porosity and pH_{PZC} , are important physicochemical parameters defining the adsorption performance of the obtained membranes (Table 1).

Table 1. Porosity, AV, AN, EEW, and pH_{PZC} of synthesized materials.

Material/ Properties	Porosity ¹	AV, mg KOH/g	AN, mmol g ^{−1}	EEW g eq ^{−1}	pH_{PZC}	
					Initial	After Adsorption
wCF/Am ²	-	126	2.51	-	7.46	
wCF/Ep ³	-		-	296	4.39	
EpKL ⁴	-		-	372	4.85	
wCF/EpKL ⁵	61		1.40	Nd ⁶	6.25 ⁷	5.69 ⁷
wCF/EpKL/TA ⁵	58		1.01	Nd ⁶	6.18 ⁷	5.78 ⁷

¹ Dry-wet weight method was used for membrane porosity determination (Supplementary Materials Section S2.5); ² AN = 2.51 mmol g^{−1}, calculated from N content of 3.51%; AV = 126 mg KOH g^{−1}, corresponding to 2.25 mmol COOH g^{−1}; ³ 3.38 mmol epoxy g^{−1} for wCF/Ep; ⁴ phenol, hydroxyl, and carboxyl group content (mmol g^{−1}) in non-modified kraft lignin (KL) are given in Table S5, 2.69 mmol epoxy g^{−1}; ⁵ specific gravity of membrane: 0.53 and 0.49 g cm^{−3} for wCF/EpKL and wCF/EpKL/TA, respectively; ⁶ not detectable; ⁷ pH_{PZC} before 6.25 and after Pb(II) adsorption 5.69 for wCF/EpKL membrane, and 6.18 before and 5.78 after DFC adsorption wCF/EpKL/TA membrane.

The titration-derived AV, AN and EEW values confirmed the successful introduction of acid, amino and epoxy functionalities into the reactive constituents and final membranes. The high porosity values (Table 1) indicate the formation of open and water-accessible membrane structures suitable for adsorption under batch and flow conditions. The pH_{PZC} values were determined from the dependence of final pH on initial pH (Table 1, Figures S7 and S8). The pH_{PZC} value of wCF/Am was 7.46, which is consistent with the introduction of protonable amino groups onto the cellulose surface. After membrane formation, the pH_{PZC} values decreased to 6.25 for wCF/EpKL and 6.18 for

wCF/EpKL/TA, indicating that part of the amino functionality was involved in cross-linking reactions, and that the surface chemistry of the final membranes was additionally governed by lignin- and tannic acid-derived phenolic, hydroxyl, carbonyl and ether groups. Overall, the titration-derived AV, AN and EEW values, together with FTIR/Raman evidence, support the successful introduction of amino/ester and epoxy functionalities and the formation of cross-linked membrane networks.

3.2. Optimization of Membrane Preparation Using RSM Design

The preparation of cellulose bio-based membrane included a combination of reagents and materials mainly based on bio-renewable sources, optimized synthesis, and functionalization of surface cellulose fibers through several steps (Figure S2). The first step was making cellulose fibers (wCF) from waste cigarette packs using a mixture LiCl/DMSO for controlled swelling.

In order to improve the reactivity of the cellulose membrane surface, in the second step, we performed the functionalization of wCF fibers using previously synthesized modification agents to obtain two amino (wCF/Am) and epoxy (wCF/Ep) membrane constituents (Sections S2.2.2 and S2.2.3). wCF/Am membrane constituent was obtained by ester/amino functionalization cross-linking under optimal reaction conditions and appropriate modification amounts of 4-chloro-4-oxobutanoate (ECB) and Ethyl L-lysinate dihydrochloride (EtLysChl) agents [35]. The modification was performed using ECB agent obtained from renewable sources, starting from fructose to obtain levulinic acid (LA) [30]. Then, we performed the oxidation of LA to succinic acid (SA), and dehydration of SA to succinic anhydride [29,31,32], which produced ECB [33]. The other EtLysChl agent used as a cross-link in modification was synthesized from commercial chemicals by reaction of a mixture of ethanol and thionyl chloride with L-lysine hydrochloride [34]. wCF/Ep membrane constituent was obtained by epoxide functionalization of wCF with epichlorohydrin (ECH), which was synthesized from bio-based glycerol [36,37].

The third step of modification was the synthesis of epoxy kraft lignin (EpKL) using synthesized ECH [35,39].

In the fourth step, ester/amino and epoxy cross-binding of membrane constituents with epoxy kraft lignin (EpKL) (Section S2.2.4.) and tannic acid (TA) was performed to obtain two membranes, wCF/EpKL and wCF/EpKL/TA (Section S2.2.5), with a high performances and porosity, which could be used as adsorbents for the removal of pollutants from water (Figure S2).

Preparation of these membranes was performed as a result of the optimization procedure using RSM design. The optimized reaction conditions were selected by considering the molar ratios of the reactive functional groups in the membrane constituents and the solvent composition used during membrane preparation (Supplementary Materials Section S2.3).

A response surface methodology (RSM) with a D-optimal design was applied as an empirical statistical technique to analyze the simultaneous effects of two sets of factors on adsorption performance.

Figure 1a shows the response surface for DFC adsorption by the wCF/EpKL/TA membrane as a function of X1 (wCF/Ep content) and X2 (TA content). Figure 1b shows the response surface for Pb²⁺ adsorption by the wCF/EpKL membrane as a function of X1 (wCF/Ep content) and X2 (wCF/Am content). The response surfaces indicate that the adsorption capacity strongly depended on the selected formulation factors. For the wCF/EpKL/TA membrane, the highest DFC uptake was obtained in the intermediate X1–X2 region, whereas, for the wCF/EpKL membrane, the highest Pb²⁺ uptake was achieved at intermediate X1 and higher X2 values.

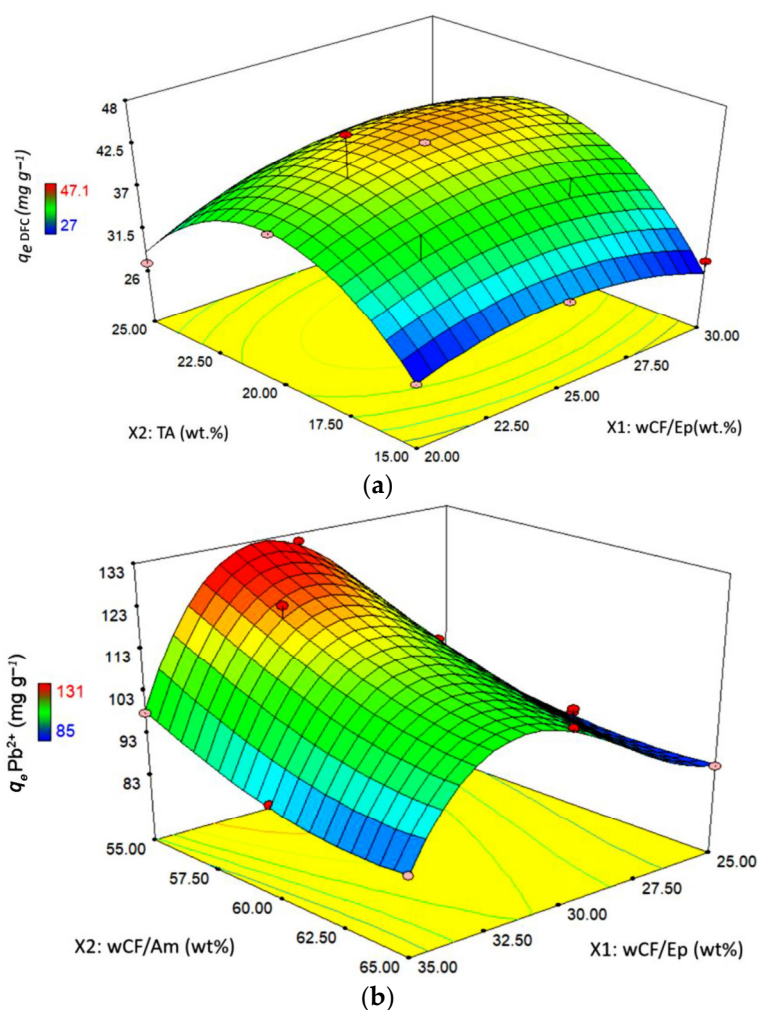


Figure 1. Response surface plots obtained from the D-optimal formulation screening: (a) effect of formulation factors X1 and X2 on the experimentally determined DFC adsorption capacity of the wCF/EpKL/TA membrane; and (b) effect of formulation factors X1 and X2 on the experimentally determined Pb^{2+} adsorption capacity of the wCF/EpKL membrane. Other synthesis and adsorption conditions were kept constant.

The two membrane formulations were optimized independently rather than through a simultaneous multi-response optimization. Preliminary screening indicated that the wCF/EpKL membrane was particularly suitable for removal of inorganic pollutants, and its formulation was therefore optimized using $\text{Pb}(\text{II})$ adsorption capacity as the response. The quadratic model, expressed in coded factors A (wCF/Ep content) and B (wCF/Am content), was

$$q_{e\text{Pb}^{2+}} = +114.35 + 0.92A - 6.81B - 2.05AB - 26.37A^2 + 3.63B^2$$

The model was highly significant ($F = 22.80$, $p < 0.0001$), with B and A^2 identified as significant model terms. Since preliminary experiments showed that incorporation of TA enhanced the adsorption of organic pollutants, the wCF/EpKL/TA formulation was optimized separately using DFC adsorption capacity as the response. For this system, A represented the wCF/Ep content and B represented the TA content, and the resulting model was

$$q_{e\text{DFC}} = +43.31 + 1.21A + 2.27B + 1.67AB - 3.58A^2 - 10.56B^2$$

This quadratic model was also significant ($F = 12.05$, $p = 0.0004$), with B and B2 being significant terms. Accordingly, no mathematical trade-off between Pb(II) and DFC responses was imposed within a single formulation. Rather, one formulation was optimized primarily for an inorganic-pollutant response and the TA-containing formulation for an organic-pollutant response. Both optimized membranes were subsequently tested against both pollutant classes to evaluate their broader applicability. The complete experimental design and ANOVA results are provided in Tables S1–S4.

Through graphical RSM optimization, using only a small number of experiments, we identified the best combination of properties for the adsorbents.

Based on the titration-derived amino and epoxy contents of the reactive constituents, the optimized wCF/EpKL formulation was close to epoxy/amino equivalence. In the wCF/EpKL/TA formulation, a moderate excess of epoxy groups relative to amino groups was used, while, additionally, residual epoxy groups may also react with phenolic hydroxyl groups of TA, forming additional ether-type linkages and contributing to a more chemically heterogeneous cross-linked network. Therefore, TA may act not only as a polyphenolic adsorption domain but also as a secondary multifunctional cross-linking component that contributes to the formation of a denser and more chemically heterogeneous membrane network. In that way, the optimized adsorbents exhibit the high adsorption capacities for Pb(II) ions and difenoconazole (DFC), satisfactory membrane porosity, along with suitable membrane dimensions, and good mechanical stability of the membrane. All of these properties make the material suitable for application in a continuous flow system.

3.3. Structural and Morphological Characterization of wCF/EpKL and wCF/EpKL/TA

3.3.1. FTIR Spectroscopy Analysis

The successful modification of wCF was monitored by ATR-FTIR spectroscopy (Figure 2). The spectra were analyzed depending on the shape, intensity, and frequency of the characteristic peak of the functional group.

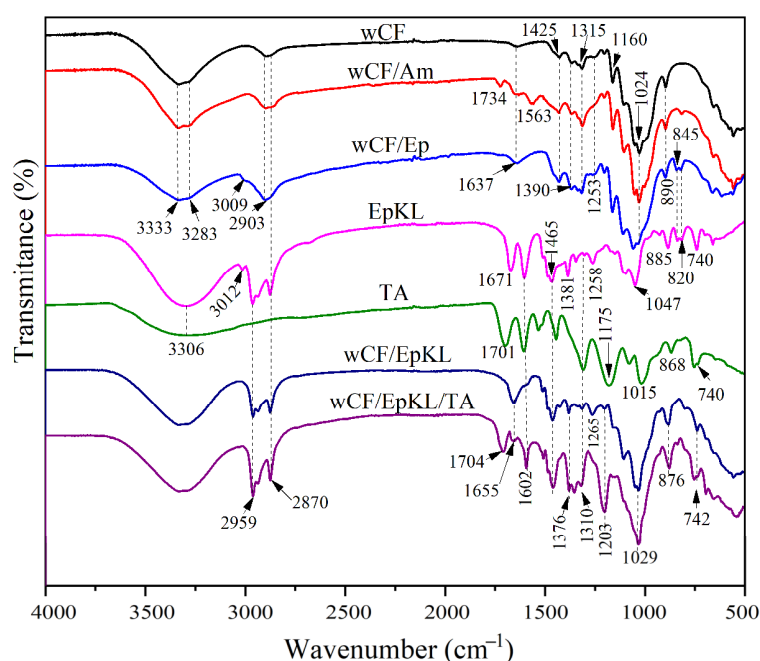


Figure 2. FTIR spectra of membrane constituents and wCF/EpKL and wCF/EpKL/TA membranes.

The broad bands in all spectra at about 3333, 3283, and 3280 cm^{-1} (Figures 2 and S1a) refer to hydroxyl and phenolic groups originating from cellulosic material, lignin, and

tannic acid. These bands are overlapped with the band assigned to N-H stretching vibration of the amino group, resulting from the functionalization of cellulose fibers wCF with wthyl L-lysinate dihydrochloride (EtLysChl). Bands at 2903, and 2870 cm^{-1} in the spectra of wCF show the presence of stretching vibrations of methyl $\nu(-\text{CH}_3)$ and methylene $\nu(-\text{CH}_2)$ groups, while bending vibrations of $\delta(-\text{CH}_3)$ and $\delta(-\text{CH}_2)$ were observed between 1465 and 1315 cm^{-1} . In the spectrum of wCF fibers, the peaks at about 1637 cm^{-1} , 1160–1024 cm^{-1} , and 890 cm^{-1} are attributed to the bending vibrations of O-H groups, stretching asymmetric and symmetric vibration of C-O and C-O-C, glycoside and β -glycosidic linkages in cellulose, respectively [62,63].

The introduction of ester, amino, and epoxy functional groups into the cellulose skeleton, by a cross-linking reaction with modification agents (ECB, EtLysChl, and ECH), causes a change in shape and intensity of the peaks of membrane constituents (wCF/Am and wCF/Ep) in these regions. In the wCF/Am spectrum, three new peaks appeared at 1734, 1563 and 825 cm^{-1} , which can be assigned to ester C=O stretching, amide II vibration and N-H bending, respectively. The amide I band is overlapped with the O-H bending region of cellulose. In the wCF/Ep spectrum, new bands at 1253, 845 and 820 cm^{-1} support the presence of epoxy groups.

Further modification with EpKL and TA during membrane formation caused changes in the intensity and position of characteristic bands originating from EpKL and TA (Figures 2 and S1a), supporting the formation of cross-linked membrane networks. Thus, the spectra of both membranes' disappearance of epoxide group vibrations (Figures 2 and S1a) indicate their cross-linking reaction with functional groups from membrane constituents. Further, the vibrations of stretching aliphatic groups are slightly shifted towards a higher frequency, and new bending bands in these groups from EpKL and TA are observed at 1465, 1381, and 1310 cm^{-1} (Figures 2 and S1a). The main vibrations at 1671 and 1701 cm^{-1} (EpKL and TA spectra, respectively) in the spectra of formed membranes are observed at 1721 and 1704 cm^{-1} and are attributed to the C=O stretching group. In addition, the wavenumbers at 1655 and 1602 cm^{-1} belong to the bending phenolic/C=O stretch vibration mode of conjugated p-substituted aryl ketones in lignin groups, and the C=C aromatic ring, respectively [42]. The area of ether groups at 1172/1175–1047/1015 vibrations was shifted and found at 1203–1029 cm^{-1} , and bands for $=\text{CH}_2$ bending vibrations out-of-plane of aromatic lignin and tannin units were noted at 885–742 cm^{-1} . Based on the appearance of the spectrum in Figure 2, this result indicates the different interaction between carbonyl/carboxyl functional groups of modification agents (EpKL and TA) and the cellulose structure.

3.3.2. Raman Spectroscopy Analysis

Changes in functional groups during the modification process of pre-treated cellulose fibers were monitored by Raman spectroscopy, in addition to FTIR spectroscopy (Figure 3).

Raman bands for cellulose are identified according to the literature [64,65]. The bands at 904, 972, 1005 and doublet at 1100 and 1127 cm^{-1} are assigned to H-C-C and H-C-O bending vibration at C6 atoms of cellulose, stretching C-C and C-O, CH_2 rocking vibration in the plane, and symmetric and asymmetric C-O-C stretching vibration in the plane of the glycosidic ring. Further, the region at 1387–1473 cm^{-1} corresponded to H-C-O, H-O-C bending vibrations, and C-H scissoring vibrations in the plane of the methylene group. After modification, the peaks appeared at 857, 1036, and 1592 cm^{-1} , which were associated with stretching vibrations of C-C, C-C-N structure, C-N of amino, and bending vibrations of N-H Amid I bands, respectively, and the presence of ester groups at 1705 and 1752 cm^{-1} from ECB and EtLysChl in membrane constituents wCF/Am confirmed the successful functionalization. The bands about 1245–1430 cm^{-1} are attributed to C-H bending

vibrations of aliphatic groups. In the Raman spectra of epoxy-modified cellulose fibers, successful modifications followed the appearance of epoxy groups. The bands of this group are observed at 1260 cm^{-1} , belonging to the stretching vibration of the epoxy ring, and $764/967\text{ cm}^{-1}$, for symmetric/asymmetric stretching vibrations of C-O-C groups. In the spectra of membranes wCF/EpKL and wCF/EpKL/TA obtained by cross-linking reaction membrane constituents, EpKL and TA are observed to decrease and shift bands of C-H and C-H-O from cellulose and membrane constituents. Further, aromatic C-H out-of-plane and in-plane vibrations observed at 787 cm^{-1} and 968 cm^{-1} , respectively, in both membranes, originate from epoxy lignin (Figures 3 and S1b) [42,43]. Also, the disappearance of epoxy groups and decrease/increase in amino shift confirm the cross-linking reaction. These results are in accordance with results obtained from analysis of the FTIR spectra. The weak band at 1641 cm^{-1} may result from the shift/overlap of bands at 1620 and 1640 cm^{-1} originating from tannic acid and lignin, respectively, and can be attributed to C=C and C=O stretching vibrations of aromatic rings in TA and EpKL structures [41,45]. Also, in the spectrum of wCF/EpKL/TA membrane, vibration at 1711 cm^{-1} belongs to C=O stretching vibration from TA [66].

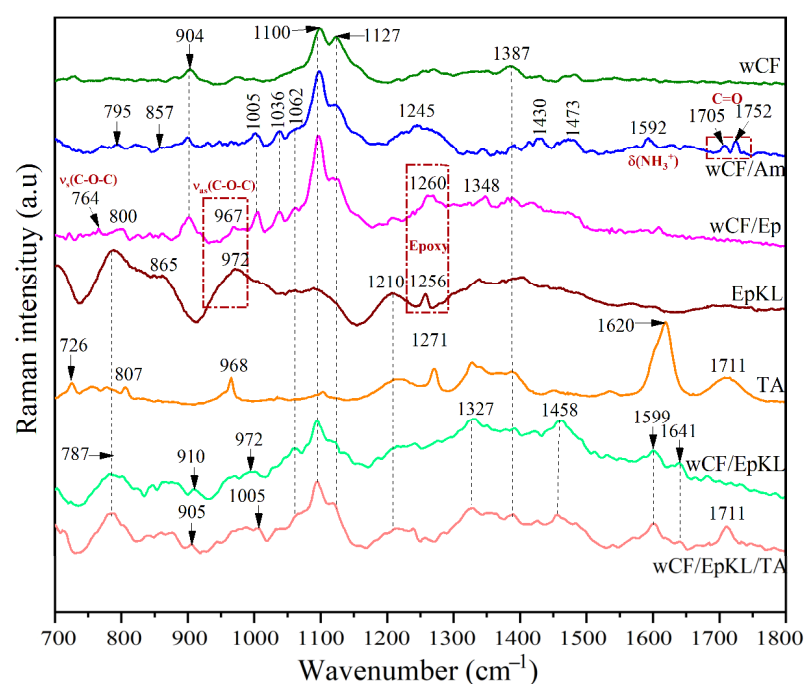


Figure 3. Raman spectra of membrane constituents and wCF/EpKL and wCF/EpKL/TA membranes.

3.3.3. SEM Surface Morphology Analysis

The surface morphology of obtained membranes was studied using Scanning Electron Microscopy, and SEM images are shown in Figure 4. From the images, we noted the change in surface after multistep modification, and the surface of the obtained membranes (Figure 4b,c) gives adsorbents with a highly porous morphology in relation to unmodified cellulose fibers wCF (Figure 4a)

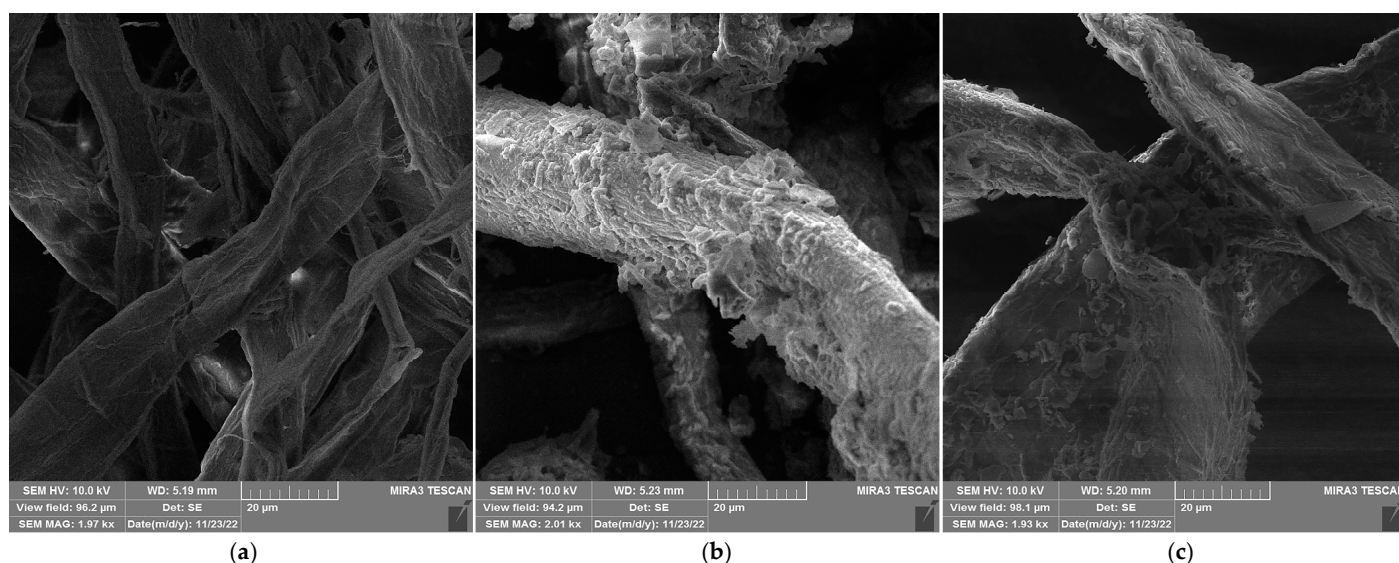


Figure 4. SEM images of (a) unmodified wCF cellulose fibers, (b) wCF/EpKL membrane, and (c) wCF/EpKL/TA membrane.

Unmodified wCF fibers (Figure 4a) are characterized by a relatively smooth surface and a clearly defined fibrillar structure, with the presence of inter-fiber gaps. From the images, it was noted that the change in surface after multistep modification and the surface of obtained membranes (Figure 4b,c) gives adsorbents with a highly porous morphology in relation to unmodified cellulose fibers wCF. Upon the introduction of epoxy-modified kraft lignin (Figure 4b), on the previously amino/esterified functionalized fiber surface, the surface of wCF/EpKL membrane becomes significantly rougher and is covered with irregular deposits, which indicates the successful binding of lignin derivatives and the formation of additional interactions with the hydroxyl groups of cellulose. In wCF/EpKL/TA, which additionally contains tannic acid (Figure 4c), an even more pronounced morphological transformation is observed, with partial fiber deformation, layered structures, and a reduction in inter-fiber spaces, which suggests increased cross-linking and a more compact structure. These results confirm that the combined modification leads to significant changes in the surface and structural organization of the cellulosic material.

3.4. Adsorption Study

3.4.1. Study of pH_{PZC}

The adsorption behavior of the prepared membranes is influenced by both the surface charge of the adsorbent and the pH-dependent speciation of the target pollutants. Therefore, the pH_{PZC} values of the membranes and the ionic speciation of Pb(II) and Cr(VI) were considered when selecting the operating pH for the adsorption experiments. The pH_{PZC} values of wCF/EpKL and wCF/EpKL/TA were 6.25 and 6.18, respectively (Table 1, Figures S7 and S8). Together with Pb(II) and Cr(VI) speciation calculated using MINTEQA 3.0 software (Figure S6) [67], these values were used to select pH 6.5 as a compromise of operating pH that minimizes Pb(II) precipitation and enables a comparison among cationic, oxyanionic and neutral organic pollutants [68]. Estimation of the pK_a values of DFC and BPA was performed theoretically using ADMET Predictor [69] and experimentally [70], giving values of 1.2 and 9.80, respectively. Accordingly, at pH 6.5, $\text{Pb}^{2+}/\text{Pb}(\text{OH})^+$ retention cannot be attributed solely to electrostatic attraction, whereas Cr(VI) removal may involve electrostatic attraction of $\text{HCrO}_4^-/\text{CrO}_4^{2-}$ species to protonated surface sites, together with hydrogen bonding and specific interactions with the polymeric network.

3.4.2. Adsorption Isotherm

Langmuir, Freundlich, Temkin, and Dubinin–Radushkevich (D-R) models (Equations (S11)–(S16)) were used in the processing of adsorption isotherm data fitting. The equilibrium non-linear fitting adsorption data using the isotherms models at temperatures of 298, 308, and 318 K for Cr(VI), Pb(II) ions, difeniconazole (DFC), and bisphenol A (BPA) removal onto wCF/EpKL and wCF/EpKL/TA, respectively, are presented in Tables 2 and S6–S13 [61,68]. Adsorption results using Temkin and Dubinin–Radushkevich models for the removal of pollutants onto adsorbents are shown in Tables S4–S11.

Table 2. Non-linear fitting results using Langmuir isotherm model for Cr(VI), Pb(II), DFC and BPA adsorption onto wCF/EpKL and wCF/EpKL/TA (C_i [Cr(VI)] = 10 mg dm^{−3}; C_i [Pb(II)] = 15 mg dm^{−3}; C_i [DFC] = 18 mg dm^{−3}; C_i [BPA] = 44 mg dm^{−3}; m/V = 125–1250 mg dm^{−3}).

Adsorbent		T (K)	q_m (mg g ⁻¹)	K_L (dm ³ mg ⁻¹)	K_L (dm ³ mol ⁻¹)	R^2
wCF/EpKL	Cr(VI)	298	85.37 ± 6.52	0.99301 ± 0.17	51,608.9 ± 2638.2	0.977
		308	87.52 ± 6.29	1.04710 ± 0.17	54,442.9 ± 2629.1	0.980
		318	87.94 ± 6.11	1.14706 ± 0.18	59,649.7 ± 3205.2	0.980
	Pb(II)	298	155.6 ± 12.60	2.42635 ± 0.49	502,524.9 ± 7377.1	0.969
		308	156.3 ± 11.48	2.63319 ± 0.48	545,407.1 ± 7256.1	0.973
		318	157.0 ± 10.51	2.87237 ± 0.49	594,987.0 ± 8125.2	0.977
	DFC	298	51.80 ± 4.35	0.12407 ± 0.024	50,587.3 ± 8117.7	0.983
		308	51.23 ± 3.26	0.14599 ± 0.018	59,529.5 ± 7969.4	0.988
		318	51.93 ± 3.75	0.16750 ± 0.024	68,300.5 ± 8015.1	0.983
	BPA	298	194.4 ± 11.77	0.14657 ± 0.023	33,460.4 ± 3537.9	0.982
		308	203.2 ± 7.82	0.15582 ± 0.018	35,572.2 ± 1894.2	0.993
		318	215.0 ± 7.52	0.15875 ± 0.015	36,241.1 ± 1948.3	0.994
wCF/EpKL/TA	Cr(VI)	298	88.78 ± 8.25	2.92629 ± 0.71	152,137.8 ± 37,068.9	0.957
		308	97.18 ± 10.10	3.19022 ± 0.85	165,859.5 ± 44,206.1	0.954
		318	107.9 ± 13.74	3.61750 ± 0.97	188,073.8 ± 50,366.9	0.944
	Pb(II)	298	163.9 ± 15.29	2.22925 ± 0.50	461,900.6 ± 102,903.8	0.971
		308	169.3 ± 15.16	2.31805 ± 0.49	480,299.9 ± 100,661.9	0.974
		318	167.6 ± 9.81	3.09049 ± 0.43	640,349.5 ± 89,288.1	0.987
	DFC	298	84.49 ± 9.153	0.09948 ± 0.018	40,402.6 ± 7312.7	0.984
		308	79.50 ± 4.268	0.13581 ± 0.013	55,170.1 ± 5281.4	0.994
		318	83.24 ± 5.100	0.14612 ± 0.016	59,354.6 ± 6500.2	0.992
	BPA	298	195.4 ± 14.48	0.10059 ± 0.02	22,963.7 ± 3657.4	0.980
		308	197.3 ± 11.49	0.10505 ± 0.01	23,981.9 ± 1843.3	0.987
		318	198.6 ± 10.38	0.10931 ± 0.01	24,954.4 ± 1703.6	0.989

Based on the results obtained with the help of the Langmuir adsorption isotherm, shown in Table 2 and Figures S9 and S10, it can be concluded that with an increasing temperature, there is an increase in capacity (q_m) in both materials. The Langmuir-derived apparent maximum adsorption capacities (q_m) at 298 K, 85.37 and 88.78 mg g^{−1} for Cr(VI), 155.6 and 163.9 mg g^{−1} for Pb(II), 51.80 and 84.49 mg g^{−1} for DFC, and 194.4 and 195.4 mg g^{−1} for BPA, indicate that the modified wCF/EpKL and wCF/EpKL/TA membranes, respectively, are very efficient when removing pollutants. For all types of pollutants, with both types of materials, at all temperatures, higher values of the Langmuir constant, K_L , were observed. Higher values of the Langmuir constant, K_L , indicate that the adsorbent surface has a higher affinity towards the pollutants. Based on the results presented in Tables S4–S11 and Figures S9 and S10, the Freundlich model generally provided a better description of the equilibrium data than the Langmuir model, indicating adsorption on

heterogeneous membrane surfaces. The temperature-driven change in the Freundlich constant $1/n$ reveals how each membrane's surface chemistry controls adsorption. Although the Langmuir q_m values were used for comparison of maximum adsorption capacities with literature data, the Freundlich model generally provided a better description of the experimental equilibrium data, confirming the heterogeneous nature of the modified membrane surfaces. The $1/n$ values were within the range characteristic of favorable adsorption, while their moderate temperature-dependent variations suggest that temperature affects the accessibility and energetic distribution of adsorption sites in a pollutant-dependent manner.

The temperature-dependent variations in the Freundlich heterogeneity parameter $1/n$ further support the pollutant-dependent nature of adsorption on both membranes. For DFC, $1/n$ decreased with an increasing temperature on both wCF/EpKL and wCF/EpKL/TA, suggesting that heating favors access to more specific high-affinity sites and leads to a more heterogeneous distribution of adsorption energies. In contrast, Cr(VI) showed only minor changes on wcf/epkl, whereas a gradual increase in $1/n$ was observed on wcf/epkl/ta, indicating that tannic acid incorporation may partially homogenize the chromate-binding environment at a higher temperature. For Pb(II) , the $1/n$ values changed only moderately and followed a slight increase–decrease trend, which suggests that temperature affects the accessibility of amino-, hydroxyl- and phenolic binding sites rather than producing a simple monotonic change in surface heterogeneity. bpa also showed only limited variation in $1/n$, indicating that its adsorption remains favorable over the investigated temperature range and is governed by a balance of hydrogen bonding, hydrophobic association and π – π interactions. Overall, these trends indicate that tannic acid modifies the energetic distribution of adsorption sites in a pollutant-specific manner, especially for dfc and Cr(VI) , while the adsorption of Pb(II) and bpa remains comparatively less sensitive to temperature-induced change

Temkin and Dubinin–Radushkevich fits (Tables S4–S11) support this conclusion: as temperature rises, the mean free-adsorption energy (E_a) for Cr(VI) , Pb^{2+} , DFC and BPA climbs from about 8 to 16 kJ mol^{-1} on both membranes, suggesting an increasing contribution of specific, energetically stronger adsorption interactions at elevated temperature. Taken together with the $1/n$ trends, the data indicate that Pb^{2+} and Cr(VI) bind predominantly through temperature-enhanced complexation at amino and phenolic sites, whereas DFC and BPA rely on a mix of hydrogen-bonding and π – π interactions that are increasingly accessed or reorganized with heating. Thus, the two lignin-based surfaces offer energetically stronger and progressively more heterogeneous sites for cationic or hydrophobic guests at higher temperatures, while chromate uptake becomes more uniform as proton-donor complexes form.

3.4.3. Thermodynamic Parameters of Adsorption

Van't Hoff equations (Equations (S17) and (S18)) were used in the analysis of thermodynamic parameters, free Gibbs energy (ΔG), enthalpy (ΔH), and entropy (ΔS) [71]. In Table 3, the calculated values of thermodynamic parameters for wCF/EpKL and wCF/EpKL/TA adsorbents are shown.

Table 3. Calculated Gibbs free energy (ΔG°), enthalpy (ΔH°), and entropy (ΔS°) for Cr(VI) , Pb(II) , DFC, and BPA adsorption onto wCF/EpKL and wCF/EpKL/TA adsorbents.

Adsorbent	Ion/ Pesticide	ΔG° (kJ mol^{-1})			ΔH° (kJ mol^{-1})	ΔS° ($\text{J mol}^{-1} \text{K}^{-1}$)	R^2
		298 K	308 K	318 K			
wCF/EpKL	Cr(VI)	−37.33	−38.69	−40.13	4.37	139.81	0.979
	Pb(II)	−43.07	−44.74	−46.43	7.06	168.13	0.999

wCF/EpKL/TA	DFC	−37.18	−38.73	−40.31	9.46	156.40	0.999
	BPA	−35.74	−37.13	−38.42	4.20	134.02	0.961
	Cr(VI)	−40.19	−41.96	−44.01	16.63	190.43	0.980
	Pb(II)	−42.98	−44.57	−46.48	9.11	174.55	0.925
	DFC	−36.88	−38.56	−40.05	10.29	158.31	0.974
	BPA	−34.91	−36.17	−37.43	2.69	126.10	0.999

The thermodynamic parameters (Table 3) confirm that adsorption on both membranes is spontaneous, endothermic and entropy-driven. All $\Delta G^\ominus$ values are negative and become more negative with rising temperature, showing that higher thermal energy facilitates pollutant binding spontaneity; the most negative $\Delta G^\ominus$ on wCF/EpKL is observed for Pb(II), whereas on wCF/EpKL/TA, the most negative $\Delta G^\ominus$ values were also obtained for Pb(II), while the introduction of TA particularly improved the thermodynamic favorability of DFC adsorption compared with the non-TA membrane. Because the absolute $\Delta G^\ominus$ values are below the commonly used threshold of -80 kJ mol^{-1} , they may indicate a chemisorptive contribution to some extent, but not a predominantly chemisorptive mechanism [72]. The magnitude of $\Delta G^\ominus$ suggests strong and favorable adsorption rather than purely weak physisorption; however, these values alone do not prove a purely chemisorptive mechanism. Therefore, the uptake is more appropriately described as a mixed process involving specific surface interactions, including coordination/electrostatic interactions for ionic species and hydrogen bonding/ π -interactions for organic micropollutants (Figures 5 and S12). Positive $\Delta H^\ominus$ values across all solute–membrane pairs indicate that the process is endothermic; BPA shows the lowest enthalpy on both membranes, suggesting weaker interaction energies than those for the metal ions or DFC. Finally, the positive entropy changes ($\Delta S^\ominus$) imply an overall increase in randomness, consistent with displacement of bound water and counter-ions from the membrane surface during complex formation. These entropy gains corroborate the high affinity of both wCF/EpKL and wCF/EpKL/TA for the target contaminants, with the greatest entropy gain recorded for Pb(II) on wCF/EpKL and for DFC on wCF/EpKL/TA.

Entropy changes ($\Delta S^\ominus$) reflect the balance between the ordering that accompanies formation of surface complexes and the disorder introduced when solvated ions or water molecules are released into bulk solution. For Cr(VI) on wCF/EpKL and for BPA on wCF/EpKL/TA, the $\Delta S^\ominus$ values are comparatively low, indicating that their uptake yields a more ordered interfacial layer—consistent with chromate coordinating in a relatively rigid inner-sphere geometry and BPA anchoring through specific π – π /hydrogen-bond contacts that restrict molecular motion at the adsorbent–solution boundary. In contrast, the larger positive $\Delta S^\ominus$ recorded for Pb(II) and DFC is attributed to the displacement of multiple hydration or counter-ions during complexation, which increases the number of mobile species in solution and therefore the overall disorder of the system [68]. Because a higher positive entropy contribution favors a more negative Gibbs energy, these larger $\Delta S^\ominus$ values translate into more thermodynamically feasible and ultimately more stable pollutant–membrane complexes, in line with the correlation reported by reference [35]. However, these thermodynamic parameters should be interpreted together with spectroscopic and modelling results, rather than used alone as definitive evidence of chemisorption.

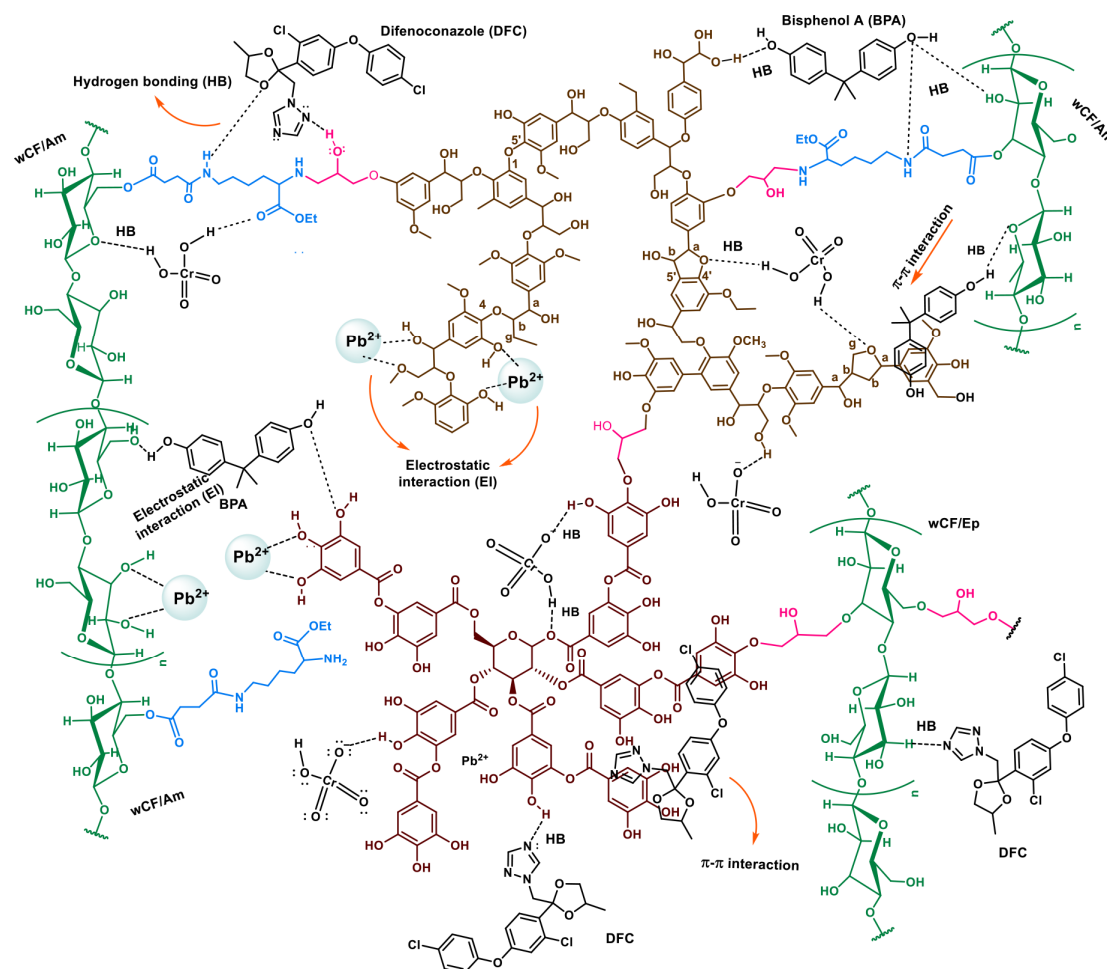


Figure 5. Schematic representation of plausible cooperative interaction pathways involved in Pb(II), Cr(VI), BPA and DFC uptake by the wCF/EpKL/TA membrane. The illustrated arrangements are conceptual and do not represent experimentally resolved atomic-level binding geometries.

3.4.4. Competitive Adsorption

Competitive adsorption was investigated using two experimental sets. In Set 1, the initial concentrations of Cr(VI), Pb(II), DFC, and BPA were 10, 15, 18, and 44 mg L⁻¹, respectively, whereas, in Set 2, all pollutants were present at 20 mg L⁻¹. The obtained results are presented in Tables 4–6 [73,74].

Table 4. Competitive adsorption of Cr(VI), Pb(II), DFC, and BPA onto wCF/EpKL and wCF/EpKL/TA membranes in single-solute and four-component systems at pollutant-specific initial concentrations (298 K, pH 6.5).

Pollutant	Membrane	C _i (mg L ⁻¹)	q _{e,single} (mg g ⁻¹)	q _{e,mix} (mg g ⁻¹)	R _q (%)	Decrease (%)	C _{e,mix} (mg L ⁻¹)	Removal (%)
Cr(VI)	wCF/EpKL	10	14.7	6.1	41.5	58.5	6.19	38.1
Pb(II)	wCF/EpKL	15	22.3	9.6	43.0	57.0	9.00	40.0
DFC	wCF/EpKL	18	11.6	2.0	17.2	82.8	16.75	6.9
BPA	wCF/EpKL	44	52.7	15.4	29.2	70.8	34.38	21.9
Cr(VI)	wCF/EpKL/TA	10	15.8	6.3	39.9	60.1	6.06	39.4
Pb(II)	wCF/EpKL/TA	15	23.6	9.9	41.9	58.1	8.81	41.2
DFC	wCF/EpKL/TA	18	14.6	2.2	15.1	84.9	16.62	7.6
BPA	wCF/EpKL/TA	44	48.2	13.8	28.6	71.4	35.38	19.6

The multicomponent matrix decreased adsorption for all pollutants. Cr(VI) and Pb(II) retained approximately 40–43% of their corresponding single-solute capacities, BPA retained approximately 29%, whereas DFC retained only approximately 15–17%. Thus, the resistance to competitive suppression followed approximately $\text{Pb(II)} \approx \text{Cr(VI)} > \text{BPA} > \text{DFC}$.

Table 5. Competitive adsorption of Cr(VI), Pb(II), DFC, and BPA onto wCF/EpKL and wCF/EpKL/TA membranes in single-solute and equimass four-component systems (20 mg L⁻¹ of each pollutant, 298 K, pH 6.5).

Pollutant	Membrane	$q_{e,\text{single}}$ (mg g ⁻¹)	$q_{e,\text{mix}}$ (mg g ⁻¹)	R _q (%)	Decrease (%)	C _{e,mix} (mg L ⁻¹)	Removal (%)	K _d (L g ⁻¹)
Cr(VI)	wCF/EpKL	28.6	11.2	39.2	60.8	13.00	35.0	0.862
Pb(II)	wCF/EpKL	30.2	12.8	42.4	57.6	12.00	40.0	1.067
DFC	wCF/EpKL	13.1	2.9	22.1	77.9	18.19	9.1	0.159
BPA	wCF/EpKL	27.8	11.1	39.9	60.1	13.06	34.7	0.850
Cr(VI)	wCF/EpKL/TA	29.2	12.1	41.4	58.6	12.44	37.8	0.973
Pb(II)	wCF/EpKL/TA	31.8	13.3	41.8	58.2	11.69	41.6	1.138
DFC	wCF/EpKL/TA	15.5	3.5	22.6	77.4	17.81	10.9	0.196
BPA	wCF/EpKL/TA	24.1	10.4	43.2	56.8	13.50	32.5	0.770

At equal mass concentrations, Cr(VI), Pb(II), and BPA retained approximately 39–43% of their single-solute adsorption capacities, while DFC retained only approximately 22%. The same pattern was observed for both membranes. Based on K_d, preferential uptake under the investigated equimass conditions followed $\text{Pb(II)} > \text{Cr(VI)} \approx \text{BPA} \gg \text{DFC}$ for wCF/EpKL, and $\text{Pb(II)} > \text{Cr(VI)} > \text{BPA} \gg \text{DFC}$ for wCF/EpKL/TA.

Table 6. Distribution coefficients and pairwise preferential adsorption factors for Cr(VI), Pb(II), DFC, and BPA in the equimass four-component system (20 mg L⁻¹ of each pollutant, 298 K, pH 6.5).

Membrane	Factor	Value
wCF/EpKL	$\alpha \text{ Pb(II)/DFC}$	6.69
wCF/EpKL	$\alpha \text{ Cr(VI)/DFC}$	5.40
wCF/EpKL	$\alpha \text{ BPA/DFC}$	5.33
wCF/EpKL	$\alpha \text{ Pb(II)/Cr(VI)}$	1.24
wCF/EpKL	$\alpha \text{ Pb(II)/BPA}$	1.26
wCF/EpKL	$\alpha \text{ Cr(VI)/BPA}$	1.01
wCF/EpKL/TA	$\alpha \text{ Pb(II)/DFC}$	5.79
wCF/EpKL/TA	$\alpha \text{ Cr(VI)/DFC}$	4.95
wCF/EpKL/TA	$\alpha \text{ BPA/DFC}$	3.92
wCF/EpKL/TA	$\alpha \text{ Pb(II)/Cr(VI)}$	1.17
wCF/EpKL/TA	$\alpha \text{ Pb(II)/BPA}$	1.48
wCF/EpKL/TA	$\alpha \text{ Cr(VI)/BPA}$	1.26

The strongest contrast is observed relative to DFC. For example, $\alpha \text{ Pb/DFC}$ is 6.69 for wCF/EpKL and 5.79 for wCF/EpKL/TA. These values indicate preferential Pb(II) uptake relative to DFC under the tested 20 mg L⁻¹-per component conditions. Because the mixture is equimass rather than equimolar, these factors should be described as conditional preferential adsorption/separation factors, not as intrinsic selectivity constants.

The adsorption experiments discussed above were performed using single-solute systems and therefore describe the adsorption behavior of the prepared membranes toward individual pollutants. To assess the influence of coexisting contaminants,

wCF/EpKL and wCF/EpKL/TA were additionally evaluated in four-component systems containing Cr(VI), Pb(II), DFC, and BPA. Two concentration sets were investigated. In the first, the initial concentrations corresponded to those used in the pollutant-specific batch experiments (10, 15, 18, and 44 mg L⁻¹ for Cr(VI), Pb(II), DFC, and BPA, respectively). In the second, all four pollutants were present at 20 mg L⁻¹, providing an equimass multi-component system for direct comparison of preferential uptake.

In the first concentration set, the presence of the other three pollutants decreased adsorption of all investigated contaminants. The relative adsorption capacity, R_q , was approximately 40–43% for Cr(VI) and Pb(II), approximately 29% for BPA, and only 15–17% for DFC. Importantly, both membranes exhibited nearly the same trend, indicating that DFC adsorption was the most strongly suppressed by the multicomponent matrix. The equimass 20 mg L⁻¹ system further supported this trend independently of the unequal initial mass concentrations used in the first set. Cr(VI), Pb(II), and BPA retained approximately 39–43% of their corresponding single-solute capacities, whereas DFC retained approximately 22% on both membranes. Distribution coefficients calculated for the multi-component system further showed preferential uptake of Pb(II), Cr(VI), and BPA relative to DFC. The Pb(II)/DFC preferential adsorption factor was 6.69 for wCF/EpKL and 5.79 for wCF/EpKL/TA.

The pronounced suppression of DFC suggests stronger competition or lower competitive affinity for the available adsorption domains in the presence of the other contaminants. In contrast, the comparatively higher retention of Cr(VI) and Pb(II) adsorption is consistent with their ability to interact with polar and ionizable functional groups of the membranes, while BPA can additionally interact with aromatic lignin/tannin domains. Because several interaction mechanisms may operate simultaneously, the present multi-component data are interpreted as evidence of competitive and preferential adsorption rather than proof of a unique binding mechanism.

3.4.5. Kinetics of Adsorption

Adsorption kinetics were evaluated with six rate expressions: the pseudo-first-order (PFO, Equation (S19)), pseudo-second-order (PSO, Equation (S20)), general second-order (SO, Equation (S21)), Weber–Morris intraparticle-diffusion (W–M, Equation (S22)), Dunwald–Wagner (D–W, Equation (S23)) and homogeneous solid-diffusion (HSDM, Equation (S24)) models [75]. Model constants were obtained by combined linear and non-linear least-squares regression; the non-linear fits for PFO, PSO and SO are summarized in Table 7 [76,77], while diffusion-based fits are given in the Table 8 [76,78,79]. Activation energies (E_a) were derived from Arrhenius plots of the PSO rate constant at 25, 35 and 45 °C and are also reported in Table 7.

Table 7. PFO, PSO and SO model parameters for the adsorption of Cr(VI), Pb(II), DFC and BPA onto wCF/EpKL and wCF/EpKL/TA adsorbents ($C_i[\text{Cr(VI)}] = 10 \text{ mg dm}^{-3}$; $C_i[\text{Pb(II)}] = 15 \text{ mg dm}^{-3}$; $C_i[\text{DFC}] = 18 \text{ mg dm}^{-3}$; $C_i[\text{BPA}] = 44 \text{ mg dm}^{-3}$; $m/V = 125 \text{ mg dm}^{-3}$, $T = 298 \text{ K}$).

Pollutant	Eq. Parameter	wCF/EpKL			$E_a \text{ (KJ mol}^{-1}\text{)}$
		PFO	PSO	SO	
Cr(VI)	q_e	64.62 ± 3.24	75.18 ± 3.24	$-^1$	12.06
	$k (k_1, k_2)$	0.0772 ± 0.017	0.0012 ± 0.0001	0.002 ± 0.0001	
	R^2	0.822	0.995	0.928	
Pb(II)	q_e	127.1 ± 2.81	135.6 ± 1.23	$-^1$	7.31
	$k (k_1, k_2)$	0.227 ± 0.029	$(2.95 \pm 0.23) \times 10^{-3}$	0.023	
	R^2	0.829	0.983	0.787	
DFC	q_e	41.94 ± 1.88	48.08 ± 2.52	$-^1$	13.00

BPA	$k (k_1, k_2)$	0.0835 ± 0.013	$(2.2 \pm 0.53) \times 10^{-3}$	0.018	4.82
	R^2	0.928	0.947	0.578	
	q_e	184.6 ± 3.96	209.9 ± 7.84	- ¹	
	$k (k_1, k_2)$	0.0960 ± 0.007	$(5.90 \pm 1.07) \times 10^{-4}$	0.0054	
	R^2	0.980	0.986	0.481	
Pollutant	Eq. Parameter	wCF/EpKL/TA			E_a (KJ mol ⁻¹)
		PFO	PSO	SO	
Cr(VI)	q_e	53.91 ± 2.42	85.43 ± 3.62	- ¹	7.34
	$k (k_1, k_2)$	0.0175 ± 0.008	$(1.1 \pm 0.079) \times 10^{-3}$	$(3.5 \pm 0.08) \times 10^{-3}$	
	R^2	0.992	0.994	0.991	
Pb(II)	q_e	37.87 ± 5.96	139.0 ± 4.60	- ¹	2.05
	$k (k_1, k_2)$	0.0422 ± 0.009	$(2.83 \pm 0.08) \times 10^{-3}$	$(7.39 \pm 0.2) \times 10^{-4}$	
	R^2	0.871	0.999	0.865	
DFC	q_e	55.22 ± 1.17	62.37 ± 2.12	- ¹	9.06
	$k (k_1, k_2)$	0.103 ± 0.008	$(2.18 \pm 0.37) \times 10^{-3}$	0.022	
	R^2	0.978	0.989	0.569	
BPA	q_e	180.1 ± 3.08	200.8 ± 7.85	- ¹	5.16
	$k (k_1, k_2)$	0.119 ± 0.008	$(8.26 \pm 1.73) \times 10^{-4}$	0.0076	
	R^2	0.928	0.948	0.478	

¹ Not applicable; q_e is not an independently fitted parameter of the concentration-based SO model.

Among the tested kinetic models, the PSO model generally provided the best or one of the best descriptions of the experimental uptake data, although the quality of fit varied depending on the pollutant and membrane. This indicates that the adsorption rate is strongly influenced by the availability of active sites and by specific adsorbent–adsorbate interactions. However, PSO fitting alone should not be considered definitive proof of chemisorption, and the kinetic results should therefore be interpreted together with equilibrium, thermodynamic and spectroscopic evidence [68,80]. The apparent PSO rate constants and adsorption activation energies indicate a mixed-control adsorption process. The calculated activation energies, ranging from 2.05 to 13.00 kJ mol⁻¹, are relatively low to moderate and are consistent with adsorption controlled by a combination of surface interactions and diffusion-related contributions, rather than by a single purely chemical-bond-forming step [68].

The equilibrium capacities, q_e , obtained from kinetic fitting follow the same general order as the adsorption-capacity trends discussed in the isotherm section. On both membranes, BPA showed the highest uptake, followed by Pb(II), Cr(VI) and DFC. The incorporation of tannic acid increased the kinetic q_e value for DFC and slightly improved Pb(II) uptake, while Cr(VI) remained comparable and BPA changed only marginally. This behavior supports the role of tannic-acid-derived galloyl groups in providing additional phenolic and π -electron-rich domains, which are particularly favorable for aromatic organic pollutants and can also contribute to Pb(II) binding through oxygen-containing coordination sites.

The activation-energy values should be regarded as apparent kinetic parameters that describe the overall energy barrier for uptake under the applied experimental conditions. Lower E_a values for Pb(II) and BPA suggest easier access to favorable binding environments, most likely involving coordination/electrostatic contributions for Pb(II) and hydrophobic/ π - π interactions for BPA. The somewhat higher E_a values obtained for Cr(VI) and DFC indicate that these species require more pronounced diffusional or configurational adjustment before stable retention occurs. In the case of DFC, the decrease in E_a after TA incorporation supports the formation of more accessible aromatic and hydrogen-bonding adsorption domains. For Cr(VI), the slight increase in E_a on the TA-containing membrane

may reflect a more complex balance between electrostatic attraction, hydrogen bonding and diffusion through the modified polymer network. Overall, the kinetic data support a mixed adsorption mechanism governed by active-site availability, pollutant-specific interactions and intraparticle diffusion, rather than by a single rate-controlling process [68,80].

Table 8. Kinetic parameters of the W-M, D-W and HSDM models for the adsorption of Cr(VI), Pb(II), DFC and BPA onto wCF/EpKL and wCF/EpKL/TA adsorbents ($C_i[\text{Cr(VI)}] = 10 \text{ mg dm}^{-3}$; $C_i[\text{Pb(II)}] = 15 \text{ mg dm}^{-3}$; $C_i[\text{DFC}] = 18 \text{ mg dm}^{-3}$; $C_i[\text{BPA}] = 44 \text{ mg dm}^{-3}$; $m/V = 125 \text{ mg dm}^{-3}$, $T = 298 \text{ K}$).

Intra-Particle	Constants	wCF/EpKL			
		Cr(VI)	Pb(II)	DFC	BPA
W-M (Step 1)	$k_{p1} (\text{mg g}^{-1} \text{ min}^{-0.5})$	6.635 ± 0.25	15.404 ± 30	5.497 ± 1.28	32.089 ± 7.25
	$C (\text{mg g}^{-1})$	15.83	57.80	5.80	7.73
	R^2	0.998	0.996	0.999	0.998
W-M (Step 2)	$k_{p2} (\text{mg g}^{-1} \text{ min}^{-0.5})$	0.574 ± 1.28	0.439 ± 0.51	0.638 ± 1.06	1.98 ± 2.30
	$C (\text{mg g}^{-1})$	61.55	127.8	36.58	167.6
	R^2	0.999	0.998	0.999	0.994
D-W	K	$0.0181 \pm 7 \times 10^{-3}$	$0.0334 \pm 7 \times 10^{-3}$	$0.0195 \pm 5 \times 10^{-4}$	$0.021 \pm 1 \times 10^{-3}$
	R^2	0.944	0.786	0.863	0.830
HSDM	D_s	$(2.17 \pm 0.02) \times 10^{-11}$	$(3.62 \pm 0.1) \times 10^{-11}$	$(2.15 \pm 0.5) \times 10^{-11}$	$(2.66 \pm 0.01) \times 10^{-11}$
	45	229.1 ± 4.93		2.236 ± 0.12	0.998
Intra-Particle	Constants	wCF/EpKL/TA			
		Cr(VI)	Pb(II)	DFC	BPA
W-M (Step 1)	$k_{p1} (\text{mg g}^{-1} \text{ min}^{-0.5})$	6.663 ± 2.80	16.109 ± 4.10	9.730 ± 3.82	35.501 ± 8.32
	$C (\text{mg g}^{-1})$	23.03	55.85	3.20	7.44
	R^2	0.999	0.996	0.999	0.999
W-M (Step 2)	$k_{p2} (\text{mg g}^{-1} \text{ min}^{-0.5})$	4.130 ± 1.52	1.974 ± 1.37	0.657 ± 0.23	1.966 ± 1.03
	$C (\text{mg g}^{-1})$	37.68	118.0	49.74	163.3
	R^2	0.992	0.900	0.999	0.996
D-W	K	$0.0192 \pm 1 \times 10^{-3}$	$0.0330 \pm 5 \times 10^{-3}$	$0.022 \pm 1 \times 10^{-4}$	$0.0236 \pm 7 \times 10^{-4}$
	R^2	0.985	0.854	0.837	0.793
HSDM	D_s	2.26×10^{-11} $\pm 8 \times 10^{-15}$	3.59×10^{-11} $\pm 78 \times 10^{-14}$	2.73×10^{-11} $\pm 18 \times 10^{-15}$	2.89×10^{-11} $\pm 8 \times 10^{-14}$
	45	0.990	0.842	0.790	0.745

The intraparticle-diffusion analysis confirms a two-stage uptake process for both membranes. In the initial Weber–Morris step, the introduction of TA markedly increased k_{p1} for DFC and slightly increased k_{p1} for BPA, while the changes for Cr(VI) and Pb(II) were minor. This indicates that the additional galloyl phenols expose more accessible, π -rich external adsorption sites that facilitate the initial capture of aromatic molecules, whereas the early-stage uptake of charged species remains only slightly affected. Once the solutes enter the fiber matrix, the second Weber–Morris step becomes slower than the initial uptake stage for all pollutants, confirming that intraparticle diffusion contributes to the overall mass-transfer resistance. In this second stage, TA incorporation markedly increased k_{p2} for Cr(VI) and Pb(II), whereas the k_{p2} values for DFC and BPA changed only slightly. Therefore, the effect of TA on mass transfer should be interpreted as pollutant-dependent rather than as a uniform acceleration of diffusion for all species. Consistently, the homogeneous solid-diffusion coefficients, D_s , changed only moderately after TA

incorporation: they slightly increased for Cr(VI), DFC and BPA, while remaining almost unchanged for Pb(II). These trends suggest that TA modifies the accessibility and internal transport pathways of the membrane network, most likely through the introduction of additional phenolic/aromatic domains and local changes in pore accessibility, rather than simply increasing diffusion in a non-selective manner. Dunwald–Wagner constants remained in the same general range for both membranes, with Pb(II) showing the highest values, further supporting the conclusion that diffusion behavior is governed by both pollutant structure and membrane composition. Collectively, these results show that TA grafting improves the accessibility of aromatic binding domains for organic micropollutants and modifies internal transport for ionic species, while the overall uptake remains controlled by a combination of surface interactions and intraparticle diffusion. The statistical validation of the selected adsorption models is presented in Tables S14 and S15.

3.4.6. Adsorption Mechanism

The adsorption behavior of the wCF/EpKL and wCF/EpKL/TA membranes can be rationalized by a cooperative, pollutant-dependent combination of plausible interaction pathways rather than by a single dominant mechanism (Figures 5 and S11). The modified cellulose/lignin-based network contains several chemically distinct adsorption domains, including hydroxyl-rich cellulose chains, amino/ester-functionalized cellulose sites, epoxy-derived ether linkages, phenolic and aromatic kraft-lignin domains and, in the case of wCF/EpKL/TA, additional tannic acid-derived galloyl units. This structural heterogeneity provides both polar/ion-binding sites and π -electron-rich aromatic domains, enabling the simultaneous retention of inorganic ionic species and neutral organic micropollutants. This interpretation is consistent with previously reported cellulose/lignin/tannic-acid bio-membranes and lignin-based adsorbents used for cation, oxyanion and organic pollutant removal [30,35]. It is also supported by mechanistic precedent from our previous studies on chemically related cellulose- and lignin-based adsorbents, in which semi-empirical quantum-chemical calculations and, in selected systems, post-adsorption XPS supported analogous coordination, electrostatic, hydrogen-bonding and aromatic interactions [81]. This interpretation is with the known structural features of lignin and tannin-based networks [39,42]

For Pb(II), adsorption is proposed to involve oxygen- and nitrogen-containing functional groups. Amino groups, phenolic hydroxyls, deprotonated hydroxyl/carboxyl-type sites, ether oxygen atoms and carbonyl groups may contribute through electrostatic attraction, surface complexation and partial ion-exchange-type interactions. The high density of neighboring phenolic groups in tannic acid can further contribute to Pb(II) coordination, while lignin-derived aromatic structures may provide additional stabilization of the adsorbed metal species. Therefore, Pb(II) uptake should be interpreted as a combined electrostatic/coordination process involving several oxygen- and nitrogen-rich binding environments [30,35].

The removal of Cr(VI), present mainly as oxyanionic chromate species under the applied experimental conditions, is expected to proceed through interactions with protonated or strongly hydrogen bond-donating surface groups. Electrostatic attraction between $\text{HCrO}_4^-/\text{CrO}_4^{2-}$ species and locally protonated sites, together with hydrogen bonding involving surface $-\text{OH}$, $-\text{NH}$ and phenolic groups, can promote chromate retention within the membrane network. Additional Cr-speciation measurements showed that dissolved Cr(III) remained below $10 \mu\text{g L}^{-1}$ throughout the 90 min adsorption experiment, indicating no measurable accumulation of Cr(III) in solution (Supplementary Materials Section S2.5.14.) [82–84]. Therefore, Cr(VI) reduction is not considered a demonstrated or dominant pathway in the present system. A possible redox contribution involving lignin-

or tannin-derived phenolic groups cannot be completely excluded, particularly for surface-bound species, but is considered only a hypothetical secondary pathway [35].

For BPA, which is largely present in neutral molecular form under mildly acidic to neutral conditions, electrostatic attraction is not expected to be the main driving force. BPA adsorption may instead involve hydrogen bonding between its phenolic hydroxyl groups and the oxygen-containing groups of cellulose, lignin and tannic acid. In parallel, the two aromatic rings of BPA may interact with lignin and tannic-acid aromatic domains through π - π interactions, while its hydrophobic backbone promotes partitioning into less polar regions of the composite network. Such behavior is consistent with adsorption processes on nanocellulose/lignocellulosic surfaces, where hydrogen bonding, hydrophobic association and surface heterogeneity can jointly control adsorption affinity [30,71].

DFC adsorption is also consistent with a non-covalent mechanism involving hydrogen bonding, π - π interactions, dipole-dipole interactions and hydrophobic association. Its triazole nitrogen atoms, ether oxygen atoms and chlorinated aromatic rings can interact with hydroxyl, carbonyl, amino and aromatic domains of the adsorbent. The stronger improvement of DFC uptake after tannic acid incorporation supports the role of additional galloyl phenolic sites and π -electron-rich domains in stabilizing aromatic micropollutants [30,35].

The FTIR spectra recorded after adsorption provide supportive evidence for these interactions (Figure S12). Changes in the intensity and position of bands associated with -OH/-NH stretching, C=O, C-O/C-O-C and aromatic vibrations indicate the involvement of hydroxyl, amino, carbonyl/ether and phenolic/aromatic groups in pollutant binding. After Pb(II) and Cr(VI) adsorption, changes in the C-O/C-O-C and hydroxyl-related regions support the participation of oxygen-containing sites in metal/oxyanion retention. In the spectra recorded after DFC and BPA adsorption, the appearance or intensification of bands characteristic of aromatic C-H and ring vibrations, together with comparison with the spectra of pure DFC and BPA (Figure S13), confirms the successful adsorption of organic micropollutants and is consistent with the possible contribution of hydrogen bonding and aromatic interactions.

Overall, pollutant uptake by the prepared membranes is proposed to involve complementary contributions from surface complexation, electrostatic attraction, hydrogen bonding, hydrophobic association, aromatic/ π - π interactions and diffusion-controlled transport within the porous fibrous network. The incorporation of tannic acid does not fundamentally change the principal inorganic-pollutant uptake pathway, but increases the density of phenolic and π -electron-rich sites, which is particularly beneficial for the adsorption of aromatic organic pollutants such as DFC and BPA [85].

3.4.7. Bed Column Experiments

In order to apply the adsorption process in industrial processes, the Bohart-Adams (B-A, Equation (S25)), Thomas [86] (Equation (S26)), and Yoon-Nelson [87] (Y-N, Equation (S27)) models were used. With the help of these models, the possibilities of removing pollutants with the help of wCF/EpKL and wCF/EpKL/TA membranes by the adsorption process were examined. Clark's mathematical model (Equations (S28)-(S31)) was used to investigate aspects of mass transfer during dynamic removal of pollutants.

A fixed-bed column was used to evaluate the effectiveness of wCF/EpKL and wCF/EpKL/TA adsorbents for real-world applications in water treatment. Based on the results obtained in Tables 9, 10, S16 and S17, it can be concluded that there is a good agreement with the experimental results for all the studied process parameters and that the wCF/EpKL and wCF/EpKL/TA membranes can be successfully applied, even when the water flow rate entering the system is high.

Table 9. Bohart–Adams and Yoon–Nelson Clark model fitting for Cr(VI), Pb(II), DFC and BPA adsorption by wCF/EpKL ($C_i[\text{Cr(VI)}] = 5 \text{ mg dm}^{-3}$; $C_i[\text{Pb(II)}] = 7.5 \text{ mg dm}^{-3}$; $C_i[\text{DFC}] = 5.0 \text{ mg dm}^{-3}$; $C_i[\text{BPA}] = 5.5 \text{ mg dm}^{-3}$; $m_{\text{ads}} = 502.5 \text{ mg}$; $t = 25 \text{ }^{\circ}\text{C}$; $\text{BV} = 0.75 \text{ cm}^3$).

Model and Parameters			Q (cm ³ min ^{−1})		
			0.5	1.0	1.5
B-A	$K_{\text{BA}} (\text{dm}^3 \text{ mg}^{-1} \text{ min}^{-1})$	Cr(VI)	0.067 ± 0.0015	0.126 ± 0.0018	0.194 ± 0.0036
	$q_0 (\text{mg g}^{-1})$		66.044 ± 0.29	57.80 ± 0.25	48.99 ± 0.31
	R^2		0.999	0.999	0.998
	$K_{\text{BA}} (\text{dm}^3 \text{ mg}^{-1} \text{ min}^{-1})$	Pb(II)	0.041 ± 0.0011	0.080 ± 0.0019	0.122 ± 0.0029
	$q_0 (\text{mg g}^{-1})$		120.93 ± 0.71	108.40 ± 0.66	93.61 ± 0.592
	R^2		0.996	0.997	0.998
	$K_{\text{BA}} (\text{dm}^3 \text{ mg}^{-1} \text{ min}^{-1})$	DFC	0.170 ± 0.0019	0.350 ± 0.0025	0.640 ± 0.0049
	$q_0 (\text{mg g}^{-1})$		34.01 ± 0.072	31.016 ± 0.015	27.78 ± 0.041
	R^2		0.999	0.999	0.999
	$K_{\text{BA}} (\text{dm}^3 \text{ mg}^{-1} \text{ min}^{-1})$	BPA	0.265 ± 0.0070	0.258 ± 0.0051	0.308 ± 0.0060
	$q_0 (\text{mg g}^{-1})$		72.778 ± 0.099	62.907 ± 0.15	55.860 ± 0.19
	R^2		0.995	0.995	0.995
Y-N	$K_{\text{YN}} (\text{min}^{-1})$	Cr(VI)	0.67 ± 0.011	0.63 ± 0.009	0.65 ± 0.012
	$\theta (\text{min})$		6.44 ± 0.029	5.81 ± 0.025	4.92 ± 0.031
	R^2		0.999	0.999	0.998
	$K_{\text{YN}} (\text{min}^{-1})$	Pb(II)	0.609 ± 0.016	0.603 ± 0.014	0.644 ± 0.015
	$\theta (\text{min})$		8.06 ± 0.047	7.22 ± 0.044	6.24 ± 0.039
	R^2		0.996	0.997	0.998
	$K_{\text{YN}} (\text{min}^{-1})$	DFC	1.707 ± 0.019	1.777 ± 0.012	2.139 ± 0.012
	$\theta (\text{min})$		3.39 ± 0.0072	3.06 ± 0.0045	2.77 ± 0.0028
	R^2		0.999	0.999	0.999
	$K_{\text{YN}} (\text{min}^{-1})$	BPA	2.906 ± 0.076	1.413 ± 0.028	1.125 ± 0.021
	$\theta (\text{min})$		6.64 ± 0.010	5.74 ± 0.015	5.10 ± 0.019
	R^2		0.996	0.996	0.995

The fixed-bed data confirm that the flow rate governs column performance and that tannic acid grafting chiefly benefits the uptake of aromatic solutes. For both membranes, the Bohart–Adams, Yoon–Nelson, Thomas and Clark fits (Tables 9, 10, S16 and S17) display excellent correlation coefficients ($R^2 \geq 0.95$), indicating that bed utilization and breakthrough can be described reliably by these models. As flow increases from 0.5 to 1.5 cm³ min^{−1}, the characteristic capacities (q_0 or θ) fall systematically (e.g., Cr(VI) on wCF/EpKL drops from 66.04 to 48.99 mg g^{−1} (Table 9 and Figure S14))—because the shortened residence time limits intraparticle diffusion and contact with high-energy sites. A similar decline is observed for Pb²⁺, DFC and BPA, and for both membranes, in line with the kinetic evidence that internal diffusion becomes rate-limiting as linear velocity rises.

Comparing the two adsorbents at identical flow rates reveals the role of TA inside the wCF/EpKL/TA adsorbent (Table 10 and Figure S15). For Cr(VI) and Pb²⁺, q_0 values are almost unchanged ($\leq 5\%$ difference), whereas for DFC, and especially BPA, the TA-modified bed affords 15–30% higher capacities (for BPA, 98 vs. 79 mg g^{−1} at 0.5 cm³ min^{−1}). These gains echo the batch results and stem from the additional galloyl π -sites that favor hydrophobic and π – π interactions without substantially altering the electrostatic landscape for metal uptake. The q_0 values show that TA incorporation consistently improves the column capacity for BPA and DFC, whereas the changes in k_{BA} are flow-dependent and should not be interpreted as a uniform acceleration of the breakthrough kinetics. This is consistent with earlier observations that TA modestly enlarges pore accessibility for organics but does not accelerate metal transport.

Table 10. Bohart–Adams and Yoon–Nelson model fitting for Cr(VI), Pb(II), DFC and BPA adsorption by wCF/EpKL/TA (Ci[Cr(VI)] = 5 mg dm^{−3}; Ci[Pb(II)] = 7.5 mg dm^{−3}; Ci[DFC] = 5.0 mg dm^{−3}; Ci[BPA] = 5.5 mg dm^{−3}; m_{ads} = 558.6 mg; t = 25 °C; BV = 0.75 cm³).

Model and Parameters		Pollutants	Q (cm ³ min ^{−1})		
			0.5	1.0	1.5
B-A	K_{BA} (dm ³ mg ^{−1} min ^{−1})	Cr(VI)	0.0433 ± 0.001	0.0888 ± 0.0015	0.149 ± 0.0018
	q_0 (mg g ^{−1})		83.36 ± 0.54	77.86 ± 0.42	63.24 ± 0.25
	R^2		0.998	0.999	0.999
	K_{BA} (dm ³ mg ^{−1} min ^{−1})	Pb(II)	0.048 ± 0.0018	0.086 ± 0.0034	0.128 ± 0.0038
	q_0 (mg g ^{−1})		124.7 ± 0.75	111.8 ± 0.92	94.46 ± 0.70
	R^2		0.994	0.992	0.996
	K_{BA} (dm ³ mg ^{−1} min ^{−1})	DFC	0.410 ± 0.0050	0.402 ± 0.007	0.579 ± 0.014
	q_0 (mg g ^{−1})		47.97 ± 0.060	46.31 ± 0.090	44.07 ± 0.13
	R^2		0.999	0.997	0.996
	K_{BA} (dm ³ mg ^{−1} min ^{−1})	BPA	0.366 ± 0.010	0.231 ± 0.0082	0.307 ± 0.0089
	q_0 (mg g ^{−1})		97.85 ± 0.080	89.667 ± 0.29	79.215 ± 0.28
	R^2		0.993	0.977	0.987
Y-N	K_{YN} (min ^{−1})	Cr(VI)	0.433 ± 0.010	0.444 ± 0.0082	0.498 ± 0.0062
	θ (min)		9.32 ± 0.060	8.70 ± 0.045	7.07 ± 0.028
	R^2		0.998	0.999	0.999
	K_{YN} (min ^{−1})	Pb(II)	0.735 ± 0.027	0.643 ± 0.025	0.639 ± 0.027
	θ (min)		9.28 ± 0.056	8.32 ± 0.069	7.03 ± 0.056
	R^2		0.994	0.992	0.996
	K_{YN} (min ^{−1})	DFC	2.056 ± 0.025	2.016 ± 0.036	1.937 ± 0.046
	θ (min)		5.34 ± 0.0060	5.16 ± 0.010	4.91 ± 0.014
	R^2		0.998	0.998	0.996
	K_{YN} (min ^{−1})	BPA	4.011 ± 0.11	1.263 ± 0.045	1.12 ± 0.032
	θ (min)		9.987 ± 0.0082	9.152 ± 0.030	8.00 ± 0.029
	R^2		0.993	0.977	0.987

The Yoon–Nelson parameter θ , which marks 50% breakthrough, decreases with faster flow on both beds but remains longer for BPA and DFC than for the metal ions, reflecting their slower intraparticle diffusion, confirmed by k_{p2} and D_s in the kinetic analysis. Notably, θ (BPA) on the TA bed is ~50% longer than on the parent bed at each flow rate, translating the higher capacity into an extended service time in a continuous system. Clark constants (Tables S16 and S17) echo these findings: the dimensionless adsorption capacity A jumps from 37 to 45 min for DFC and from 48 to 98 min for BPA when TA is present, whereas Cr(VI) shows only a modest rise.

Overall, the column studies reinforce the mechanistic picture drawn from batch kinetics and thermodynamics. TA grafting leaves metal-ion behavior largely unchanged but creates a phenol-rich, π -donor surface that both raises the equilibrium capacity and lowers the kinetic barrier for aromatic pollutants, benefits that persist across practical flow rates. Consequently, wCF/EpKL/TA is the membrane of choice for simultaneous removal of Pb(II) and organic micro-pollutants, while wCF/EpKL already performs optimally for Cr(VI) in systems where the hydrodynamic residence time is the limiting factor.

3.5. Desorption and Regeneration

The desorption process was carried out in order to test the possibility of reusing wCF/EpKL and wCF/EpKL/TA membranes. The reuse of membranes is directly related to the sorption potential of the material. Regeneration of wCF/EpKL and wCF/EpKL/TA membranes would prevent pollution of the environment with pollutants, such as, e.g.,

pesticides containing biomass. Based on the efficiency of the regenerated mass and the degree of pollutant desorption, the reuse potential of wCF/EpKL and wCF/EpKL/TA membranes can be evaluated. Table S16 show the results for the adsorption capacity, the amount of desorbed material, and the concentration of the polluting substance after the five cycles of adsorption/desorption. The regeneration tests (Table S18) confirm that both lignin membranes can be reused at least five times with minimal capacity loss and desorption efficiencies consistently above 94%. For each pollutant, the adsorbed/desorbed ratios remain almost parallel, indicating that the chemisorption complexes identified earlier—amine/phenolate coordination for Pb(II) and Cr(VI), π - π + H-bonding for DFC and BPA—are strong enough for uptake yet readily disrupted by the alkaline eluent. The tannic acid modification lifts the absolute uptake of Cr(VI) and DFC by $\approx 26\%$ and 41% , respectively, without compromising desorbability; indeed, Δq_{tot} after five cycles is only 10.3 mg g^{-1} for Cr(VI) and 4.1 mg g^{-1} for DFC on wCF/EpKL/TA, values comparable to or slightly higher than those on the parent membrane.

For BPA, the TA-containing membrane showed a higher initial adsorption capacity in the regeneration experiment (97.9 mg g^{-1}) than wCF/EpKL (72.8 mg g^{-1}), while both systems maintained high desorption efficiencies throughout five cycles. The cumulative irreversible retention was 9.5 mg g^{-1} for wCF/EpKL and 12.2 mg g^{-1} for wCF/EpKL/TA, indicating slightly higher absolute retention on the TA-containing membrane but comparable desorption efficiency. For Pb^{2+} , both adsorbents showed similar regeneration behavior, with desorption efficiencies remaining $\geq 94\%$ over five cycles, although the adsorption capacities decreased by about 19–20% from the first to the fifth cycle.

Overall, the combination of high reversible uptake and small Δq values corroborates the thermodynamic picture of endothermic yet moderately strong complexation, and it positions wCF/EpKL/TA as the more versatile membrane, delivering superior capacities for chromate and DFC and comparable multi-cycle stability for Pb(II) and BPA while maintaining the $>95\%$ desorption efficiency required for sustainable column operation.

3.6. Stabilization/Solidification and Leaching Assessment of Desorbed Inorganic Pollutants

3.6.1. Precipitation of Chromate and Lead from the Desorption Solution

After completion of the adsorption–desorption cycles, the metal-containing desorption solutions were subjected to an additional stabilization step in order to reduce the mobility of the released inorganic pollutants. Lead and chromate species were converted into a sparingly soluble PbCrO_4 -containing solid phase by precipitation. This route was selected because it enables the simultaneous immobilization of Pb(II) and chromate species into a low-solubility inorganic phase, which can subsequently be stabilized within a cementitious matrix.

The formation of the PbCrO_4 -containing precipitate was supported by FTIR spectroscopy, where bands in the $893\text{--}744 \text{ cm}^{-1}$ region were assigned to Cr–O stretching and chromate-group deformation vibrations. Additional AAS analysis indicated an approximately 64 wt.% Pb content in the precipitated solid, which is consistent with the expected composition of a lead chromate-rich phase.

This stabilization/solidification approach follows the principles previously applied for cement-based immobilization of hazardous inorganic residues with their reduced mobility in the environment [44]. The leaching behavior of the solidified PbCrO_4 -containing samples is summarized in Table S19 [68], which confirmed the successful stabilization of highly stable lead salts (Supplementary Material Section S3.6.1), while the compressive-strength results confirm the formation of mechanically coherent cementitious matrices.

The obtained PbCrO_4 -containing solid was further treated by stabilization/solidification in a cementitious matrix, as described in the Supplementary Material. The resulting solidified specimens showed compressive strength values of 20.7, 23.0 and 22.8 MPa,

confirming the formation of mechanically coherent materials. However, since PbCrO_4 is still a hazardous inorganic phase despite its low solubility, the environmental acceptability of the stabilized product should be assessed primarily through leaching behavior rather than mechanical strength alone. Accordingly, this step should be regarded as a mobility-reduction and waste-stabilization approach within the integrated regeneration/disposal strategy, rather than as complete detoxification of the inorganic pollutants.

3.6.2. Photodegradation of BPA and DFC

With the help of UV radiation, photodegradation of BPA and DFC was carried out, where ZnO was used as a photocatalyst. In addition to TiO_2 , photocatalysts based on ZnO are one of a series of widely studied material classes. Compared to other semiconductors, ZnO possesses high efficiency during the degradation process due to higher photosensitivity, electron mobility, a longer lifetime and photocatalytic capacity [88]. Photocorrosion is the biggest drawback of this class of material [89]. The initial pollutant concentration, pH value and catalyst concentration are the parameters that have the greatest influence on the efficiency of photocatalytic degradation. Figure 6 shows the influence of the initial concentration of the catalyst on the reaction rate photodegradation.

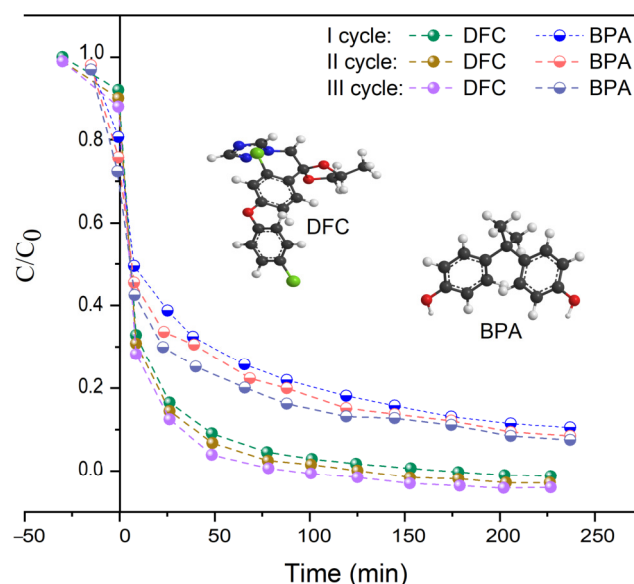
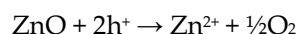


Figure 6. Photocatalytic degradation of DFC and BPA under optimal conditions.

As can be seen in Figure 6, with the help of ZnO after 20 min of irradiation, 82% of DFC degradation and 62% of BPA degradation were achieved, respectively, while 99% of DFC and 82% of BPA were degraded after 210 min. Based on the literature results [56], the degradation of these pollutants is much faster in the presence of a catalyst, compared to UV radiation in the absence of the same. Compared to TiO_2 in the case of BPA, based on previous research [56], better photocatalytic degradation was achieved with the help of ZnO. The higher efficiency of ZnO compared to TiO_2 is due to its hexagonal structure. In photocatalytic reactions, an important role is played by the polar planes of ZnO, which are suitable for creating vacancies for O_2 [90], while the number of vacancies in the case of the tetragonal TiO_2 structure is limited [91,92]. ZnO has a higher adsorption power in the UV spectrum from 320 to 385 nm and from 200 to 400 nm and, therefore, a higher efficiency for generating electron–hole pairs, compared to TiO_2 , which absorbs no longer than 387.5 nm [91,93]. Based on the presented results and by comparing these two catalysts, it was established that ZnO is in this case a much more suitable catalyst for the photodegradation of DFC and BPA. ZnO photocorrosion is a recognized limitation of ZnO-based

photocatalysis in aqueous media. Photogenerated holes can participate in oxidative decomposition of the ZnO lattice, ultimately leading to Zn(II) release; the overall process is commonly represented as [94]



Because ZnO dissolution depends strongly on irradiation conditions, pH, surface structure, and the composition of the aqueous medium [94,95], dissolved-Zn determination under the actual photocatalytic conditions provides a direct assessment of catalyst stability.

The dissolved-Zn concentrations after DFC and BPA photodegradation were 0.042 and 0.036 mg L⁻¹, respectively, compared with 0.040 mg L⁻¹ in the pollutant-free irradiated ZnO control and 0.033 mg L⁻¹ in the dark ZnO control (Table 11). Thus, the DFC system was only 5.0% above the irradiated control, whereas the BPA system was 10.0% below it. The irradiated pollutant-free control was numerically 21.2% higher than the dark control. These small differences, considered together with the narrow overall range of dissolved Zn (0.033–0.042 mg L⁻¹), show that neither DFC nor BPA produced an appreciable increase in Zn release relative to irradiation of ZnO alone. In the absence of a statistical comparison of the Zn measurements, the difference between the irradiated and dark controls is interpreted only as a small numerical increase and not as evidence of a statistically significant irradiation effect.

Table 11. Dissolved-Zn concentrations measured under photocatalytic and control conditions.

Condition	Dissolved Zn (mg L ⁻¹)	Relative to Matched Control
DFC + ZnO, irradiated	0.042	+5.0% vs. irradiated ZnO control
BPA + ZnO, irradiated	0.036	−10.0% vs. irradiated ZnO control
ZnO, irradiated; no pollutant	0.040	+21.2% vs. dark ZnO control
ZnO, dark; no pollutant	0.033	Reference

The observed behavior is consistent with literature reports showing that ZnO dissolution and photocorrosion are highly condition-dependent. Lee et al. identify photocorrosion as an important limitation of ZnO photocatalysts in water treatment [94], while Dworschak et al. demonstrated by time-resolved ICP-MS that Zn dissolution is affected by UV irradiation, pH, and the ZnO surface structure [95]. These findings support the use of matched irradiated and dark controls rather than an external absolute concentration threshold when evaluating ZnO stability under a specific photocatalytic protocol.

A useful quantitative context is provided by Bellanger et al. [96], who directly measured Zn leakage from approximately 4 nm surface-functionalized ZnO quantum dots. Conversion of their reported final Zn concentrations gives approximately 0.49–1.70 mg L⁻¹ dissolved Zn, with reported Zn leakage of about 9–21%, depending on surface functionalization, illumination, and the presence of bacteria. The dissolved-Zn concentrations measured here (0.033–0.042 mg L⁻¹) are therefore approximately 12–47 times lower. This comparison is intended only to place the present results in a literature context, not as a direct performance ranking, because Bellanger et al. investigated freely dispersed ultrasmall functionalized ZnO quantum dots under substantially different experimental conditions. Recent mechanistic work further indicates that ZnO photocorrosion can involve both surface degradation and partial regeneration during UV exposure [97], further emphasizing the importance of assessing stability under the actual operating conditions.

Overall, the results demonstrate limited but measurable Zn release under the applied conditions. Most importantly, DFC and BPA did not appreciably enhance Zn release

relative to the pollutant-free irradiated control, indicating that photocatalytic treatment of these pollutants did not promote additional destabilization of ZnO.

3.6.3. Biodegradation of Membranes

The soil-burial behavior of the prepared membranes was evaluated gravimetrically by monitoring mass loss over 112 days. Overall, both membranes exhibited substantial mass loss and disintegration under the applied soil-burial conditions (Figure 7), confirming the preliminary soil-burial biodegradation/disintegration assessment of the cellulose/lignin-based network. The wCF/EpKL membrane exhibited a mass loss of 82%, whereas the wCF/EpKL/TA membrane showed an even higher mass loss of 93%. This difference indicates that the membrane composition and incorporation of tannic acid not only contribute to adsorption performance but also facilitate the environmental disintegration of the membrane after use [98,99].

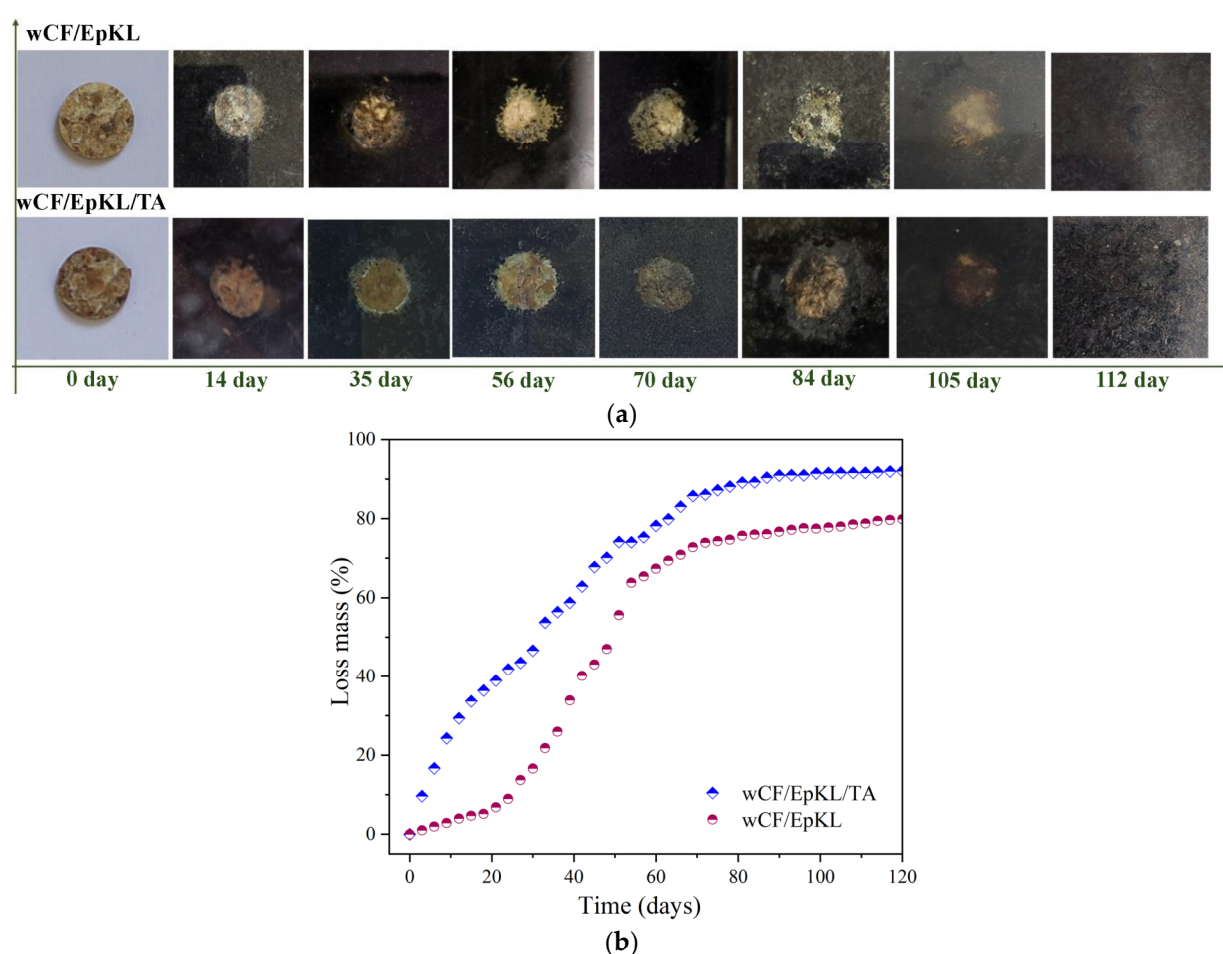


Figure 7. Degradation of wCF/EpKL and wCF/EpKL/TA membranes over time: (a) photographic documentation of the disintegration of the membranes at different degradation times (0–112 days); (b) mass loss (%) of the membranes as a function of degradation time and the change is highlighted in green in the manuscript

The higher degradation degree of wCF/EpKL/TA can be attributed to the chemical structure of tannic acid and its influence on the polymer network. Tannic acid is a hydrolysable polyphenol containing multiple galloyl units connected through ester linkages, which are susceptible to hydrolytic cleavage under moist soil conditions. Hydrolysis of these ester bonds can progressively weaken the cross-linked structure, increase the accessibility of water and microorganisms, and promote fragmentation of the membrane. In addition, the high density of phenolic hydroxyl groups in tannic acid increases the

hydrophilicity of the material, facilitating water uptake and microbial colonization. Consequently, the TA-containing membrane is expected to undergo faster hydrolytic and biological degradation than the lignin-only membrane.

In contrast, the wCF/EpKL membrane showed slightly lower, although still substantial, mass loss. This can be related to the more recalcitrant aromatic structure of kraft lignin, which generally slows down microbial degradation compared with polysaccharide-rich or hydrolysable ester-containing structures. Nevertheless, the high mass loss observed for wCF/EpKL demonstrates that the cellulose-based matrix remains accessible to microbial and hydrolytic degradation. Overall, the results show that both membranes are highly degradable under soil-burial conditions, while the presence of tannic acid enhances degradation due to the combined effects of hydrolysable ester bonds, increased hydrophilicity and improved accessibility of the polymer network.

Therefore, the incorporation of TA provides a dual function: it increases the density of adsorption-active phenolic sites and, at the same time, improves the post-use degradability of the membrane.

3.7. Literature Review

To evaluate the relevance of the obtained adsorption capacities, the performance of wCF/EpKL and wCF/EpKL/TA membranes was compared with previously reported lignocellulose-, lignin- and tannin-based adsorbents for Pb(II), Cr(VI), BPA and DFC removal. The capacity of lignocellulosic adsorbents used for Pb(II) ion removal varies depending on the selected starting material and the type of modification used. Adsorption material based on aminated epoxy lignin reached the maximum adsorption capacity of 55.35 mg g⁻¹ [100], while much higher values were obtained using carboxymethylated lignin, reaching 150.33 mg g⁻¹ [101]. The maximum adsorption capacities of Pb(II) ions on adsorbents based on tannin and epoxy lignin are 23.75 mg g⁻¹ [102,103] and 99.9 mg g⁻¹ [35] at room temperature. In the case of cellulose, which was modified with succinic acid, a significantly higher adsorption capacity was recorded, 207.90 mg g⁻¹ [58]. In the case of a composite adsorbent, based on α -cellulose and chitosan, where the cellulose was modified with HCl and H₂SO₄, the capacity for Pb(II) was 91 mg g⁻¹ [104]. By comparing the capacities of both membranes, with literature data, it can be concluded that the Pb(II) removal is higher, except in the case when the cellulose is modified with succinic acid.

During the removal of Cr(VI) ions, where epoxy cellulose modified with D-glucose (Cell-g-GMA-D-Glu) was used as an adsorbent, the maximum adsorption capacity was 54.59 mg g⁻¹ [105], while in the case of Cell-g-GMA-D-GluN⁺, it was 61.05 mg g⁻¹ [106], which is lower than the capacity values of both membranes presented in this work, wCF/EpKL and wCF/EpKL/TA. The adsorption capacity for the bio-material in which the cellulose is modified with polyvinylimidazole is 134 mg g⁻¹ at a temperature of 25 °C.

By using cetyltrimethylammonium bromide (CTAB) cellulose as a biosorbent, 95% of BPA was removed, at pH = 5.5 [107]. Adsorption capacities in the removal of BPA by hydrophobic [108] and persulfuro-alkoxyranose cellulose fibers are 4.86 $\pm$ 0.3 mg g⁻¹ and 50.37 mg g⁻¹, respectively [109]. Cellulose membranes, Cell-X and Cell-D, modified with 2,6-pyridine dicarbonyl dichloride and 2-furan carbonyl chloride [110], respectively, show a significantly lower $q_{\max}$, when removing DFC, compared to wCF/EpKL and wCF/EpKL/TA. Unlike Pb(II), Cr(VI), and BPA, DFC is not always sufficiently investigated in the literature, and its removal with the help of modified lignocellulosic materials has not been carried out. The comparison with reported lignocellulosic adsorbents confirms that the prepared membranes exhibit competitive or higher adsorption capacities, particularly considering their combined performance toward metal ions and organic micropollutants. Although Langmuir q_m values were used for comparison of maximum adsorption capacities with literature data, the equilibrium data were generally better

described by the Freundlich model, confirming the heterogeneous nature of the modified membrane surfaces. The kinetic data were best represented by the pseudo-second-order model.

Overall, the comparison with literature data confirms that the prepared membranes exhibit competitive adsorption capacities, particularly considering their combined performance toward both metal ions and organic micropollutants. In addition, the pseudo-second-order model provided the best fit to the kinetic data.

4. Conclusions

This work demonstrates that waste-derived cellulose fibers can be successfully transformed into functional bio-based membrane adsorbents through a multistep modification strategy involving amino/ester and epoxy functionalization, followed by cross-linking with epoxy-modified kraft lignin and tannic acid. The obtained wCF/EpKL and wCF/EpKL/TA membranes combine a porous fibrous morphology with chemically active nitrogen- and oxygen-containing groups and aromatic lignin/tannin domains, providing multiple binding sites for both inorganic and organic pollutants. The combined FTIR, Raman, SEM and physicochemical analyses confirmed that the modification strategy produced structurally altered and chemically enriched membrane surfaces suitable for adsorption applications.

Both membranes showed efficient removal of the selected model pollutants, Cr(VI), Pb²⁺, DFC and BPA, confirming their versatility toward diverse contaminant classes. The presence of tannic acid further improved the functionality of the membrane, particularly toward aromatic micropollutants, by introducing additional phenolic groups and π -electron-rich domains. The adsorption behavior was not governed by a single mechanism, but rather by the combined contribution of surface complexation, electrostatic interactions, hydrogen bonding, hydrophobic effects, π - π interactions and diffusion-controlled transport within the porous membrane network.

The mechanistic interpretation suggests that Pb²⁺ and Cr(VI) are mainly retained through interactions with amino, hydroxyl, phenolic and carboxyl-containing groups, with the contribution of electrostatic attraction depending on solution pH and pollutant speciation. In contrast, DFC and BPA adsorption is primarily associated with hydrogen bonding and aromatic interactions with lignin- and tannin-derived domains. The thermodynamic and kinetic analyses support favorable and spontaneous adsorption, while also indicating that active site availability and intraparticle diffusion contribute to the overall uptake process.

Importantly, the membranes were effective not only in batch systems but also under fixed-bed continuous-flow conditions, demonstrating their practical relevance for water treatment applications. Their ability to undergo repeated adsorption–desorption cycles with preserved performance further supports their potential for reuse. In addition, the integration of pollutant stabilization/degradation steps and preliminary soil-burial mass-loss/disintegration assessment provides a broader sustainability perspective for the proposed system.

Overall, cellulose/lignin–tannin membranes represent a promising platform for regenerable and environmentally oriented water purification materials. Future research should focus on testing real wastewater matrices, evaluating long-term hydraulic and mechanical stability, optimizing membrane scale-up and performing more detailed life-cycle and ecotoxicological assessments.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/suschem7040063/s1>, Figure S1: (a) FTIR and (b) Raman spectra of kraft lignin (KL) and epoxy-modified kraft lignin (EpKL); Figure S2: Schematic presentation

route of wCF/EpKL and wCF/EpKL/TA preparation; Table S1: Design matrix and the results of the three-level and two-factor D-optimal design for wCF/EpKL production; Table S2. ANOVA for the quadratic response surface model for Pb(II) adsorption; Table S3: Design matrix and the results of the three-level and two-factor D-optimal design for wCF/EpKL/TA production; Table S4. ANOVA for the quadratic response surface model for DFC adsorption; Figure S3: FTIR spectra of lead chromate; Figure S4: Water flux versus pressure for wCF/EpKL and wCF/EpKL/TA; Figure S5: Two- and three-dimensional structures of DFC and BPA pollutants; Table S5 Phenol, hydroxyl, and carboxyl group contents (mmol g^{-1}) in non-modified kraft lignin (KL); Figure S6: Speciation of (a) Pb^{2+} and (b) Cr(VI) obtained using MINTEQA 3.0 software ($C_i = 1 \text{ mg dm}^{-3}$ for Pb^{2+} and Cr(VI) , $t = 25^\circ\text{C}$); Figure S7: The final pH(pH_f) versus initial pH(pH_i) changes for (a) wCF/EpKL and (b) wCF/EpKL/TA before adsorption; Figure S8: The final pH(pH_f) versus initial pH(pH_i) changes for wCF/EpKL and wCF/EpKL/TA after adsorption; Table S6: Non-linear Freundlich, Temkin and Dubinin–Radushkevich isotherm parameters for Cr(VI) adsorption on wCF/EpKL; Table S7: Non-linear Freundlich, Temkin and Dubinin–Radushkevich isotherm parameters for Pb^{2+} adsorption on wCF/EpKL; Table S8: Non-linear Freundlich, Temkin and Dubinin–Radushkevich isotherm parameters for DFC adsorption on wCF/EpKL; Table S9: Non-linear Freundlich, Temkin and Dubinin–Radushkevich isotherm parameters for BPA adsorption on wCF/EpKL; Table S10: Non-linear Freundlich, Temkin and Dubinin–Radushkevich isotherm parameters for Cr(VI) adsorption on wCF/EpKL/TA; Table S11: Non-linear Freundlich, Temkin and Dubinin–Radushkevich isotherm parameters for Pb^{2+} adsorption on wCF/EpKL/TA; Table S12: Non-linear Freundlich, Temkin and Dubinin–Radushkevich isotherm parameters for DFC adsorption on wCF/EpKL/TA; Table S13: Non-linear Freundlich, Temkin and Dubinin–Radushkevich isotherm parameters for BPA adsorption on wCF/EpKL/TA; Figure S9: Langmuir and Freundlich isotherms of datasets for (a) Cr(VI) , (b) Pb^{2+} ion, (c) DFC, and (d) BPA removal onto wCF/EpKL; Figure S10: Langmuir and Freundlich isotherms of datasets for (a) Cr(VI) , (b) Pb^{2+} ion, (c) DFC, and (d) BPA removal onto wCF/EpKL/TA; Table S14: Analysis of variance and statistical significance for the best adsorption models for the removal of pollutants onto wCF/EpKL adsorbent; Table S15: Analysis of variance and statistical significance for the best adsorption models for the removal of pollutants onto wCF/EpKL/TA adsorbent; Figure S11: Proposed cooperative adsorption mechanism of Pb^{2+} , Cr(VI) , BPA and DFC removal by the wCF/EpKL membrane; Figure S12: FTIR spectra of (a) wCF/EpKL and (b) wCF/EpKL/TA membranes before and after pollutants' adsorption; Figure S13: FTIR spectra of DFC and BPA; Table S16: Clark and Thomas model fitting for Cr(VI) , Pb^{2+} , DFC and BPA adsorption by wCF/EpKL ($C_i[\text{Cr(VI)}] = 5 \text{ mg dm}^{-3}$; $C_i[\text{Pb}^{2+}] = 7.5 \text{ mg dm}^{-3}$; $C_i[\text{DFC}] = 5.0 \text{ mg dm}^{-3}$; $C_i[\text{BPA}] = 5.5 \text{ mg dm}^{-3}$; $m_{\text{ads}} = 502.5 \text{ mg}$; $t = 25^\circ\text{C}$; $\text{BV} = 0.75 \text{ cm}^3$); Table S17: Clark and Thomas model fitting for Cr(VI) , Pb^{2+} , DFC and BPA adsorption by wCF/EpKL/TA ($C_i[\text{Cr(VI)}] = 5 \text{ mg dm}^{-3}$; $C_i[\text{Pb}^{2+}] = 7.5 \text{ mg dm}^{-3}$; $C_i[\text{DFC}] = 5.014 \text{ mg dm}^{-3}$; $C_i[\text{BPA}] = 5.473 \text{ mg dm}^{-3}$; $m_{\text{ads}} = 558.6 \text{ mg}$; $t = 25^\circ\text{C}$; $\text{BV} = 0.75 \text{ cm}^3$); Figure S14: Bohart–Adams breakthrough curves for adsorption of (a) Cr(VI) , (b) Pb^{2+} ion, (c) DFC, and (d) BPA removal onto wCF/EpKL; Figure S15: Bohart–Adams breakthrough curves for adsorption of (a) Cr(VI) , (b) Pb^{2+} ion, (c) DFC, and (d) BPA removal onto wCF/EpKL/TA; Table S18: The results of selected cycles I, III and V from five consecutive adsorption–desorption cycles of Cr(VI) , Pb^{2+} , DFC and BPA removal using wCF/EpKL and wCF/EpKL/TA system ($Q_{\text{desorption}} = 1.0 \text{ mL min}^{-1}$; $V_{\text{desorption}} = 50 \text{ mL}$, $m_{\text{ads}}(\text{wCF/EpKL}) \sim 503 \text{ mg}$, $m_{\text{ads}}(\text{wCF/EpKL/TA}) = 559 \text{ mg}$); Table S19: Results of TCLP testing of the PbCrO_4 -containing cementitious stabilized sample. References [111–114] are cited in the Supplementary Materials.

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Abbreviations

The following abbreviations are used in this manuscript:

wCF	Waste cellulose fiber
EpKL	Epoxy-modified kraft lignin
TA	Tannic acid
BPA	Bisphenol A
DFC	Difenoconazole
AN	Amino number
AV	Acid value
EEW	Epoxy equivalent weight
DMSO	Dimethyl sulfoxide
wCF/Am	Amino modified waste cellulose fiber
wCF/Ep	Epoxy modified waste cellulose fiber
ECB	4-chloro-4-oxobutanoate
EtLysChl	Ethyl L-lysinate dihydrochloride
LA	Levulinic acid
SA	Succinic acid
ECH	Epichlorohydrin
RSM	Response surface methodology
FTIR	Fourier-transform infrared spectroscopy

References

1. Knežević, N.; Milanović, J.; Veličković, Z.; Milošević, M.; Vuksanović, M.M.; Onjia, A.; Marinković, A. A Closed Cycle of Sustainable Development: Effective Removal and Desorption of Lead and Dyes Using an Oxidized Cellulose Membrane. *J. Ind. Eng. Chem.* **2023**, *126*, 520–536. <https://doi.org/10.1016/j.jiec.2023.06.041>.
2. Ali, S.; Naseer, S.; Rehman, M.; Wei, Z. Recent Trends and Sources of Lead Toxicity: A Review of State-of-the-Art Nano-Remediation Strategies. *J. Nanoparticle Res.* **2024**, *26*, 168.
3. Milošević, D.L.; Tomić, N.Z.; Đokić, V.R.; Vidović, M.M.; Veličković, Z.S.; Jančić-Heinemann, R.; Marinković, A.D. Structural and Surface Modification of Highly Ordered Alumina for Enhanced Removal of Pb²⁺, Cd²⁺ and Ni²⁺ from Aqueous Solution. *Desalin. Water Treat.* **2020**, *178*, 220–239. <https://doi.org/10.5004/dwt.2020.24982>.
4. Dong, X.; Yu, N.; Li, Y.; Lou, J. P16 Hypermethylation Is a Potential Cause of Oxidative Stress Due to Long-Term Exposure to Hexavalent Chromium. *Environ. Toxicol. Chem.* **2025**, *44*, 2198–2205.
5. Bachmann, S.A.L.; Dávila, I.V.J.; Calvete, T.; Feris, L.A. Adsorption of Cr (VI) on Lignocellulosic Wastes Adsorbents: An Overview and Further Perspective. *Int. J. Environ. Sci. Technol.* **2022**, *19*, 12727–12748.
6. DesMarias, T.L.; Costa, M. Mechanisms of Chromium-Induced Toxicity. *Curr. Opin. Toxicol.* **2019**, *14*, 1–7.
7. Ye, T.; Yang, R.; He, S.; Li, J.; Liu, Y.; Li, C.; Luo, H. Synergistic Endocrine Disruption and Cellular Toxicity of Polyethylene Microplastics and Bisphenol A in MLTC-1 Cells and Zebrafish. *Sci. Rep.* **2025**, *15*, 10752.
8. Veloso, A.; Silva, V.; Osman, R.; Simões, M.P.; do Carmo Horta, M.; Geissen, V. Dynamics of Pesticide Residues in Soils during the Growing Season: A Case Study in Peach Orchards, East-Central Portugal. *Environ. Monit. Assess.* **2025**, *197*, 285.

9. Omran, K.M.B.; Shwika, S.I.; Vuksanović, M.M.; Marinković, A.D.; Jovanović, A.; Prlainović, N.; Vasilski, D. Circular Economy Implementation in the Development of Fire-Retardant Materials Used in Construction, Industry, and General-Purpose Products. *Metall. Mater. Eng.* **2022**, *28*, 369–379.
10. Antanasković, A.; Lopičić, Z.; Šošćarić, T.; Adamović, V.; Cvetković, S.; Perendija, J.; Milivojević, M. Toxic Dye Removal by Thermally Modified Lignocellulosic Waste in a Three-Phase Air-Lift Reactor: Kinetic Insights. *Hem. Ind.* **2024**, *78*, 241–252.
11. Lopičić, Z.; Šošćarić, T.; Milojković, J.; Antanasković, A.; Milić, J.; Spasić, S.; Avdalović, J. Efficient Removal of Water Soluble Fraction of Diesel Oil by Biochar Sorption Supported by Microbiological Degradation. *Processes* **2024**, *12*, 964.
12. Dotti, A.; Guagliano, M.; Ferretti di Castelferretto, V.; Scotti, R.; Pedrazzi, S.; Puglia, M.; Orrù, R.V.A.; Cristiani, C.; Finocchio, E.; Basso Peressut, A. Self-Standing Adsorbent Composites of Waste-Derived Biochar and Reduced Graphene Oxide for Water Decontamination. *Molecules* **2025**, *30*, 1997.
13. Savić, A.; Vuksanović, M.M.; Savić, M.; Knežević, N.; Šaponjić, A.; Ilić, S.; Egelja, A. Modified Silica Particles Coated with Cu-Al Layered Double Hydroxide for Phosphate and Arsenate Removal in Water Treatment. *Molecules* **2025**, *30*, 2138.
14. Perendija, J.; Veličković, Z.S.; Dražević, L.; Stojiljković, I.; Milčić, M.; Milosavljević, M.M.; Marinković, A.D.; Pavlović, V. Evaluation of Adsorption Performance and Quantum Chemical Modeling of Pesticides Removal Using Cell-MG Hybrid Adsorbent. *Sci. Sinter.* **2021**, *53*, 355–378.
15. Ljubic, V.; Perendija, J.; Cvetkovic, S.; Rogan, J.; Trivunac, K.; Stojanovic, M.; Popovic, M. Removal of Ni²⁺ Ions from Contaminated Water by New Exopolysaccharide Extracted from *K. Oxytoca* J7 as Biosorbent. *J. Polym. Environ.* **2024**, *32*, 1105–1121.
16. Mohanrasu, K.; Manivannan, A.C.; Rengarajan, H.J.R.; Kandaiah, R.; Ravindran, A.; Panneerselvan, L.; Palanisami, T.; Sathish, C.I. Eco-Friendly Biopolymers and Composites: A Sustainable Development of Adsorbents for the Removal of Pollutants from Wastewater. *npj Mater. Sustain.* **2025**, *3*, 13.
17. Zaimee, M.Z.A.; Sarjadi, M.S.; Rahman, M.L. Heavy Metals Removal from Water by Efficient Adsorbents. *Water* **2021**, *13*, 2659.
18. Tirtom, V.N.; Dinçer, A.; Becerik, S.; Aydemir, T.; Çelik, A. Comparative Adsorption of Ni(II) and Cd(II) Ions on Epichlorohydrin Crosslinked Chitosan-Clay Composite Beads in Aqueous Solution. *Chem. Eng. J.* **2012**, *197*, 379–386. <https://doi.org/10.1016/j.cej.2012.05.059>.
19. Manyatshe, A.; Sibali, L.L. A Review on the Recovery of Cellulose, Lignin, and Hemicellulose Biopolymers from the Same Source of Lignocellulosic Biomass—Methodology, Characterization and Applications. *J. Water Process Eng.* **2025**, *70*, 107037.
20. Mateo, S.; Fabbri, G.; Moya, A.J. Lignin from Plant-Based Agro-Industrial Biowastes: From Extraction to Sustainable Applications. *Polymers* **2025**, *17*, 952.
21. Meena, H.M.; Kukreti, S.; Jassal, P.S. Synthesis of Novel Chitosan-Tannic Acid Adsorbent for Removal of Aluminum (III) from Wastewater: Characterisation, Kinetics, Equilibrium Isotherms and Thermodynamic Studies. *Adsorption* **2025**, *31*, 46.
22. Yang, Q.; Wang, L.; Li, Y.; Zhang, X.; Sun, S.; Niu, K.; Ma, W.; Wang, J.; Liu, Q.; Li, Z. Synthesis of Tannic Acid Based Composite for Efficient Congo Red Removal: Isotherm, Kinetics, and Thermodynamic Studies. *Sep. Purif. Technol.* **2025**, *360*, 131008.
23. Popovic, A.L.; Velickovic, Z.; Radovanovic, Z.; Djolic, M.; Pavlovic, V.; Marinkovic, A.D.; Grzetic, J.D. Hybrid Amino-Terminated Lignin Microspheres Loaded with Magnetite and Manganese Oxide Nanoparticles: An Effective Hazardous Oxyanions Adsorbent. *J. Environ. Chem. Eng.* **2022**, *10*, 108009.
24. Xu, X.; Wen, Y.; Zhao, Y.; Wang, B.; Fan, M.; Chen, Z.; Guo, S.; Huang, W. High-Efficient Removal of Dye across a Wide PH Range over Alkali Lignin-Based Adsorbent: Batch Experiments and DFT Mechanistic Analysis. *Sep. Purif. Technol.* **2025**, *363*, 132322.
25. Liu, Q.; Liu, Q.; Liu, B.; Hu, T.; Liu, W.; Yao, J. Green Synthesis of Tannin-Hexamethylenediamine Based Adsorbents for Efficient Removal of Cr (VI). *J. Hazard. Mater.* **2018**, *352*, 27–35.
26. Akhter, F.; Pinjaro, M.A.; Ahmed, J.; Ahmed, M.; Arain, H.J.; Ahsan, M.J.; Sanjrani, I.A. Recent Advances and Synthesis Approaches for Enhanced Heavy Metal Adsorption from Wastewater by Silica-Based and Nanocellulose-Based 3D Structured Aerogels: A State of the Art Review with Adsorption Mechanisms and Prospects. *Biomass Convers. Biorefin.* **2025**, *15*, 6585–6614.
27. Castellanos, H.G.; Aryanfar, Y.; Mohtaram, S.; Keçebaş, A.; Karaca-Dolgun, G.; Ahmad, S.; Asiri, A.N.M.; Islam, S. The Efficacy of Nano-cellulose-based Composites in Heavy Metal Removal from Wastewater: A Comprehensive Review. *J. Chem. Technol. Biotechnol.* **2025**, *100*, 291–312.
28. Senila, M. Advancing Green Analytical Chemistry Principles for Trace Metal Analysis Using Atomic Spectrometry Techniques—An Overview. *Sustain. Chem.* **2026**, *7*, 28. <https://doi.org/10.3390/suschem7030028>.
29. Abduarahman, M.A.; Vuksanović, M.M.; Milošević, M.; Egelja, A.; Savić, A.; Veličković, Z.; Marinković, A. Mn-Fe Layered Double Hydroxide Modified Cellulose-Based Membrane for Sustainable Anionic Pollutant Removal. *J. Polym. Environ.* **2024**, *32*, 3776–3794. <https://doi.org/10.1007/s10924-024-03192-x>.

30. Salih, R.; Veličković, Z.; Milošević, M.; Pavlović, V.P.; Cvijetić, I.; Sofrenić, I.V.; Gržetić, J.D.; Marinković, A. Lignin Based Microspheres for Effective Dyes Removal: Design, Synthesis and Adsorption Mechanism Supported with Theoretical Study. *J. Environ. Manag.* **2023**, *326*, 116838.
31. Carnevali, D.; Rigamonti, M.G.; Tabanelli, T.; Patience, G.S.; Cavani, F. Levulinic Acid Upgrade to Succinic Acid with Hydrogen Peroxide. *Appl. Catal. A Gen.* **2018**, *563*, 98–104.
32. Fieser, L.F.; Martin, E.L.; Shriner, R.L.; Struck, H.C. Acid Upgrade to Succinic. *Org. Synth.* **1932**, *12*, 66. <https://doi.org/10.15227/orgsyn.012.0066>.
33. Liu, S.; Yu, C.; Tian, H.; Hu, T.; He, Y.; Li, Z.; Tan, W.; Zhang, L.; Duan, L. A Novel Bikinin Analogue for Arabidopsis and Rice with Superior Plant Growth-Promoting Activity. *J. Plant Growth Regul.* **2018**, *37*, 166–173.
34. Tao, Y.; Chen, X.; Jia, F.; Wang, S.; Xiao, C.; Cui, F.; Li, Y.; Bian, Z.; Chen, X.; Wang, X. New Chemosynthetic Route to Linear ϵ -Poly-Lysine. *Chem. Sci.* **2015**, *6*, 6385–6391.
35. Perendija, J.; Veličković, Z.S.; Cvijetić, I.; Lević, S.; Marinković, A.D.; Milošević, M.; Onjia, A. Bio-Membrane Based on Modified Cellulose, Lignin, and Tannic Acid for Cation and Oxyanion Removal: Experimental and Theoretical Study. *Process Saf. Environ. Prot.* **2021**, *147*, 609–625.
36. Pembere, A.M.; Yang, M.; Luo, Z. Small Gold Clusters Catalyzing the Conversion of Glycerol to Epichlorohydrin. *Phys. Chem. Chem. Phys.* **2017**, *19*, 25840–25845. <https://doi.org/10.1039/c7cp05324j>.
37. Lu, Y.; Wang, R.; Zhang, J.; Jin, Q.; Luo, G. Evaluation of an Improved Epichlorohydrin Synthesis from Dichloropropanol Using a Microchemical System. *Chin. J. Chem. Eng.* **2015**, *23*, 1123–1130. <https://doi.org/10.1016/j.cjche.2014.10.021>.
38. Zhang, S.; Zhu, Q.; Wang, T.; Wang, X.; Sun, X.; Wei, Y.; Luo, L. Contact Electrification Property Controlled by Amino Modification of Cellulose Fibers. *Cellulose* **2022**, *29*, 3195–3208. <https://doi.org/10.1007/s10570-022-04500-1>.
39. Gavrilović Grmuša, I.; Rančić, M.; Tešić, T.; Stupar, S.; Milošević, M.; Gržetić, J. Bio-Epoxy Resins Based on Lignin and Tannic Acids as Wood Adhesives-Characterization and Bonding Properties. *Polymers* **2024**, *16*, 2602. <https://doi.org/10.3390/polym16182602>.
40. Bykov, D.L.; Peleshko, V.A. Constitutive Relations for Strain and Failure of Filled Polymer Materials in Dominant Axial Tension Processes under Various Barothermal Conditions. *Mech. Solids* **2008**, *43*, 870–891. <https://doi.org/10.3103/S0025654408060058>.
41. Bykov, I. Characterization of Natural and Technical Lignins Using FTIR Spectroscopy. Master's Thesis, Lulea University of Technology, Lulea, Sweden, 2008.
42. Melro, E.; Filipe, A.; Sousa, D.; Medronho, B.; Romano, A. Revisiting Lignin: A Tour through Its Structural Features, Characterization Methods and Applications. *New J. Chem.* **2021**, *45*, 6986–7013. <https://doi.org/10.1039/d0nj06234k>.
43. Heitner, C.; Dimmel, D.; Schmidt, J. Vibrational Spectroscopy. In *Lignin and Lignans: Advances in Chemistry*; CRC Press: Boca Raton, FL, USA, 2010; pp. 104–136.
44. Mao, C.J.; Wu, X.C.; Zhu, J.J. Shape-Controlled Synthesis of PbCrO₄ Micro/Nanostructures and Their Luminescent Properties. *J. Nanosci. Nanotechnol.* **2010**, *10*, 4906–4913. <https://doi.org/10.1166/jnn.2010.2214>.
45. Aniceto, J.P.S.; Cardoso, S.P.; Silva, C.M. General Optimization Strategy of Simulated Moving Bed Units through Design of Experiments and Response Surface Methodologies. *Comput. Chem. Eng.* **2016**, *90*, 161–170. <https://doi.org/10.1016/j.compchemeng.2016.04.028>.
46. Jablonskis, A.; Arshanitsa, A.; Arnautov, A.; Telysheva, G.; Evtuguin, D. Evaluation of Ligno Boost™ Softwood Kraft Lignin Epoxidation as an Approach for Its Application in Cured Epoxy Resins. *Ind. Crops Prod.* **2018**, *112*, 225–235. <https://doi.org/10.1016/j.indcrop.2017.12.003>.
47. Gosselink, R.J.A.; Abächerli, A.; Semke, H.; Malherbe, R.; Käuper, P.; Nadif, A.; Van Dam, J.E.G. Analytical Protocols for Characterisation of Sulphur-Free Lignin. *Ind. Crops Prod.* **2004**, *19*, 271–281. <https://doi.org/10.1016/j.indcrop.2003.10.008>.
48. Serrano, L.; Esakkimuthu, E.S.; Marlin, N.; Brochier-Salon, M.C.; Mortha, G.; Bertaud, F. Fast, Easy, and Economical Quantification of Lignin Phenolic Hydroxyl Groups: Comparison with Classical Techniques. *Energy Fuels* **2018**, *32*, 5969–5977. <https://doi.org/10.1021/acs.energyfuels.8b00383>.
49. Norgren, M.; Lindström, B. Dissociation of Phenolic Groups in Kraft Lignin at Elevated. *Holzforschung* **2000**, *54*, 519–527. <https://doi.org/10.1515/HF.2000.088>.
50. ASTM D3644; Test Method for Acid Number of Styrene-Maleic Anhydride Resins. ASTM: West Conshohocken, PA, USA, 2022.
51. Kyriakidis, N.B.; Katsiloulis, T. Calculation of Iodine Value from Measurements of Fatty Acid Methyl Esters of Some Oils: Comparison with the Relevant American Oil Chemists Society Method. *J. Am. Oil Chem. Soc.* **2000**, *77*, 1235–1238. <https://doi.org/10.1007/s11746-000-0193-3>.
52. ASTM D1652; Test Method for Epoxy Content of Epoxy Resins. ASTM: West Conshohocken, PA, USA, 2019.

53. U.S. Environmental Protection Agency Method 1311: Toxicity Characteristic Leaching Procedure. In *Test Methods for Evaluating Solid Waste: Physical/Chemical Methods (SW-846)*; U.S. Environmental Protection Agency: Washington, DC, USA, 1992; pp. 1–35.
54. U.S. Environmental Protection Agency. *Solidification/Stabilization Resource Guide*; U.S. Environmental Protection Agency: Washington, DC, USA, 1999.
55. SRPS EN 12457-2:2008; Characterisation of Waste—Leaching—Compliance Test for Leaching of Granular Waste Materials and Sludges—Part 2: One Stage Batch Test at a Liquid to Solid Ratio of 10 L/kg for Materials with Particle Size below 4 mm (without or with Size Reduction). Institute for Standardization of Serbia (ISS): Belgrade, Serbia, 2008.
56. An, S.N.; Choi, N.C.; Choi, J.W.; Lee, S. Photodegradation of Bisphenol A with ZnO and TiO₂: Influence of Metal Ions and Fenton Process. *Water Air Soil Pollut.* **2018**, *229*, 43. <https://doi.org/10.1007/s11270-018-3701-9>.
57. Zhao, B.; Zhang, K.; Huang, Y.; Wang, Q.; Xu, H.; Wang, Y.; Li, J.; Song, T.; Xia, W.; Liu, J. A Novel Visible Light-Driven TiO₂ Photocatalytic Reduction for Hexavalent Chromium Wastewater and Mechanism. *Water Sci. Technol.* **2021**, *83*, 2135–2145. <https://doi.org/10.2166/wst.2021.116>.
58. Caligiuri, V.; Tedeschi, G.; Palei, M.; Miscuglio, M.; Martin-Garcia, B.; Guzman-Puyol, S.; Hedayati, M.K.; Kristensen, A.; Athanassiou, A.; Cingolani, R.; et al. Biodegradable and Insoluble Cellulose Photonic Crystals and Metasurfaces. *ACS Nano* **2020**, *14*, 9502–9511. <https://doi.org/10.1021/acsnano.0c03224>.
59. Park, C.H.; Kang, Y.K.; Im, S.S. Biodegradability of Cellulose Fabrics. *J. Appl. Polym. Sci.* **2004**, *94*, 248–253. <https://doi.org/10.1002/app.20879>.
60. Xu, D.; Tan, X.L.; Chen, C.L.; Wang, X.K. Adsorption of Pb(II) from Aqueous Solution to MX-80 Bentonite: Effect of PH, Ionic Strength, Foreign Ions and Temperature. *Appl. Clay Sci.* **2008**, *41*, 37–46. <https://doi.org/10.1016/j.clay.2007.09.004>.
61. Qureshi, U.A.; Hameed, B.H.; Ahmed, M.J. Adsorption of Endocrine Disrupting Compounds and Other Emerging Contaminants Using Lignocellulosic Biomass-Derived Porous Carbons: A Review. *J. Water Process Eng.* **2020**, *38*, 101380. <https://doi.org/10.1016/j.jwpe.2020.101380>.
62. Chung, C.; Lee, M.; Choe, E.K. Characterization of Cotton Fabric Scouring by FT-IR ATR Spectroscopy. *Carbohydr. Polym.* **2004**, *58*, 417–420. <https://doi.org/10.1016/j.carbpol.2004.08.005>.
63. Poletto, M.; Ornaghi Júnior, H.L.; Zattera, A.J. Native Cellulose: Structure, Characterization and Thermal Properties. *Materials* **2014**, *7*, 6105–6119. <https://doi.org/10.3390/ma7096105>.
64. Lupoi, J.S.; Gjersing, E.; Davis, M.F. Evaluating Lignocellulosic Biomass, Its Derivatives, and Downstream Products with Raman Spectroscopy. *Front. Bioeng. Biotechnol.* **2015**, *3*, 50. <https://doi.org/10.3389/fbioe.2015.00050>.
65. Agarwal, U.P.; Ralph, S.A.; Baez, C.; Reiner, R.S. Detection and Quantitation of Cellulose II by Raman Spectroscopy. *Cellulose* **2021**, *28*, 9069–9079. <https://doi.org/10.1007/s10570-021-04124-x>.
66. Brehm, S.; Kraus, J.; Himcinschi, C.; Kortus, J. A Raman Spectroscopic Study of the Pyrolysis of Lactose and Tannins. *J. Raman Spectrosc.* **2022**, *53*, 1361–1370. <https://doi.org/10.1002/jrs.6376>.
67. Gustafsson, J. P. Visual MINTEQ. Version 3.1, Swedish University of Agricultural Sciences, 2011, <https://vminteq.com> (accessed on 25 September 2024).
68. Karanac, M.; Đolić, M.; Veljović, Đ.; Rajaković-Ognjanović, V.; Veličković, Z.; Pavićević, V.; Marinković, A. The Removal of Zn²⁺, Pb²⁺, and As(V) Ions by Lime Activated Fly Ash and Valorization of the Exhausted Adsorbent. *Waste Manag.* **2018**, *78*, 366–378. <https://doi.org/10.1016/j.wasman.2018.05.052>.
69. Simulations Plus; Inc. ADMET Predictor 2016, <https://www.simulations-plus.com/software/admetpredictor/> (accessed on 26 September 2024).
70. Guthrie, J.P. Hydrolysis of Esters of Oxy Acids: PKa Values for Strong Acids; Brønsted Relationship for Attack of Water at Methyl; Free Energies of Hydrolysis of Esters of Oxy Acids; and a Linear Relationship between Free Energy of Hydrolysis and PKa Holding over a Range of 20 PK Units. *Can. J. Chem.* **1978**, *56*, 2342–2354.
71. Lombardo, S.; Thielemans, W. Thermodynamics of Adsorption on Nanocellulose Surfaces. *Cellulose* **2019**, *26*, 249–279.
72. Vuković, G.D.; Marinković, A.D.; Čolić, M.; Ristić, M.D.; Aleksić, R.; Perić-Grujić, A.A.; Uskoković, P.S. Removal of Cadmium from Aqueous Solutions by Oxidized and Ethylenediamine-Functionalized Multi-Walled Carbon Nanotubes. *Chem. Eng. J.* **2010**, *157*, 238–248. <https://doi.org/10.1016/j.cej.2009.11.026>.
73. Petanovska-ilievska, B.; S. Jankulovska, M.; Velkoska-markovska, L.; Spasovska, J. Determination of Bisphenol a in Beverages by Rp-Hplc. *J. Agriculture For.* **2019**, *65*, 243–255. <https://doi.org/10.17707/AgricultForest.65.1.24>.
74. Lazić, S.; Šunjka, D. Determination of Azoxystrobin and Difenoconazole in Pesticide Products. *Commun. Agric. Appl. Biol. Sci.* **2015**, *80*, 375–380.

75. Du, M.; Li, Q.; Wang, L. Adsorption Removal of Pb²⁺ and Cd²⁺ on Lignocellulose-g-Acrylic Acid/Montmorillonite Nanocomposite from Aqueous Solutions. *Desalin. Water Treat.* **2016**, *57*, 3261–3269. <https://doi.org/10.1080/19443994.2014.984338>.
76. Qiu, H.; Lv, L.; Pan, B.; Zhang, Q.; Zhang, W.; Zhang, Q. Critical Review in Adsorption Kinetic Models. *J. Zhejiang Univ.-Sci. A* **2009**, *10*, 716–724. <https://doi.org/10.1631/jzus.A0820524>.
77. Moussout, H.; Ahlafi, H.; Aazza, M.; Maghat, H. Critical of Linear and Nonlinear Equations of Pseudo-First Order and Pseudo-Second Order Kinetic Models. *Karbala Int. J. Mod. Sci.* **2018**, *4*, 244–254. <https://doi.org/10.1016/j.kijoms.2018.04.001>.
78. Soldatkina, L.; Zavrichko, M. Equilibrium, Kinetic, and Thermodynamic Studies of Anionic Dyes Adsorption on Corn Stalks Modified by Cetylpyridinium Bromide. *Colloids Interfaces* **2018**, *3*, 4. <https://doi.org/10.3390/colloids3010004>.
79. Viegas, R.M.C.; Campinas, M.; Costa, H.; Rosa, M.J. How Do the HSDM and Boyd's Model Compare for Estimating Intraparticle Diffusion Coefficients in Adsorption Processes. *Adsorption* **2014**, *20*, 737–746. <https://doi.org/10.1007/s10450-014-9617-9>.
80. Perendija, J.; Milošević, D.; Popović, M.; Dželetović, Ž.; Kovač, S.; Novaković, J.G.; Cvetković, S. Valorisation of Energy Plant *Arundo Donax* Cultivated in Serbia for Biosorption of Cobalt Ions from an Aqueous Solution: Kinetic Aspect. *Hem. Ind.* **2024**, *78*, 253–264. <https://doi.org/10.2298/HEMIND240713017P>.
81. Knežević, N.; Vuksanović, M.M.; Banjanac, K.; Pantić, K.; Veličković, Z.; Cvijetić, I.; Marinković, A.; Milošević, M. Cationic Waste Hemp Fibers-Based Membrane: Case Study of Anionic Pollutants Removal through Environmentally Friendly Processes. *J. Environ. Manag.* **2024**, *371*, 123174. <https://doi.org/10.1016/j.jenvman.2024.123174>.
82. Wiryawan, A.; Retnowati, R.; Burhan, P.; Syekhfani, S. Method of Analysis for Determination of the Chromium (Cr) Species in Water Samples by Spectrophotometry with Diphenylcarbazide. *J. Environmental Eng. Sustain. Technol.* **2018**, *5*, 37. <https://doi.org/10.21776/ub.jeest.2018.005.01.6>.
83. Uzunboy, S.; Karakaş, Ö.; Demirci-Çekiç, S.; Apak, R. Sulfate Radical Formation by Cr(III) Activation of Peroxydisulfate—Diphenylcarbazide Spectrophotometric Determination of Sulfate Radical and Its Scavenging Activity. *Spectrochim. Acta A Mol. Biomol. Spectrosc.* **2021**, *260*, 119941. <https://doi.org/10.1016/j.saa.2021.119941>.
84. Dikobe, J.; Melato, F.A.; Adlem, C.J.L.; Netshiongolwe, K. Determination of Chromium Species in Water Using Diphenylcarbazide with a Sequential Spectrophotometric Discrete Robotic Analyser. *Heliyon* **2024**, *10*, e34670. <https://doi.org/10.1016/j.heliyon.2024.e34670>.
85. Porras, J.D.; Arteta, S.M.; Pérez, L.D. Development of an Adsorbent for Bisphenol A Based on a Polymer Grafted from Microcrystalline Cellulose. *Water Air Soil Pollut.* **2020**, *231*, 499. <https://doi.org/10.1007/s11270-020-04861-y>.
86. Thomas, H.C. Heterogeneous Ion Exchange in a Flowing System. *J. Am. Chem. Soc.* **1944**, *66*, 1664–1666. <https://doi.org/10.1021/ja01238a017>.
87. Yoon, Y.H.; Nelson, J.H. Application of Gas Adsorption Kinetics—II. A Theoretical Model for Respirator Cartridge Service Life and Its Practical Applications. *Am. Ind. Hyg. Assoc. J.* **1984**, *45*, 517–524. <https://doi.org/10.1080/15298668491400205>.
88. Abo, R.; Kummer, N.A.; Merkel, B.J. Optimized Photodegradation of Bisphenol A in Water Using ZnO, TiO₂ and SnO₂ Photocatalysts under UV Radiation as a Decontamination Procedure. *Drink. Water Eng. Sci.* **2016**, *9*, 27–35. <https://doi.org/10.5194/dwes-9-27-2016>.
89. Reddy, P.V.L.; Kim, K.H.; Kavitha, B.; Kumar, V.; Raza, N.; Kalagara, S. Photocatalytic Degradation of Bisphenol A in Aqueous Media: A Review. *J. Environ. Manag.* **2018**, *213*, 189–205.
90. Li, G.R.; Hu, T.; Pan, G.L.; Yan, T.Y.; Gao, X.P.; Zhu, H.Y. Morphology-Function Relationship of ZnO: Polar Planes, Oxygen Vacancies, and Activity. *J. Phys. Chem. C* **2008**, *112*, 11859–11864. <https://doi.org/10.1021/jp8038626>.
91. Han, J.; Liu, Y.; Singhal, N.; Wang, L.; Gao, W. Comparative Photocatalytic Degradation of Estrone in Water by ZnO and TiO₂ under Artificial UVA and Solar Irradiation. *Chem. Eng. J.* **2012**, *213*, 150–162. <https://doi.org/10.1016/j.cej.2012.09.066>.
92. Patil, A.B.; Patil, K.R.; Pardeshi, S.K. Enhancement of Oxygen Vacancies and Solar Photocatalytic Activity of Zinc Oxide by Incorporation of Nonmetal. *J. Solid State Chem.* **2011**, *184*, 3273–3279. <https://doi.org/10.1016/j.jssc.2011.10.016>.
93. Wang, C.; Zhu, L.; Wei, M.; Chen, P.; Shan, G. Photolytic Reaction Mechanism and Impacts of Coexisting Substances on Photodegradation of Bisphenol A by Bi₂WO₆ Inwater. *Water Res.* **2012**, *46*, 845–853. <https://doi.org/10.1016/j.watres.2011.11.057>.
94. Lee, K.M.; Lai, C.W.; Ngai, K.S.; Juan, J.C. Recent Developments of Zinc Oxide Based Photocatalyst in Water Treatment Technology: A Review. *Water Res.* **2016**, *88*, 428–448. <https://doi.org/10.1016/j.watres.2015.09.045>.
95. Dworschak, D.; Brunnhofer, C.; Valtiner, M. Photocorrosion of ZnO Single Crystals during Electrochemical Water Splitting. *ACS Appl. Mater. Interfaces* **2020**, *12*, 51530–51536. <https://doi.org/10.1021/acsami.0c15508>.
96. Bellanger, X.; Schneider, R.; Dezanet, C.; Arroua, B.; Balan, L.; Billard, P.; Merlin, C. Zn²⁺ Leakage and Photo-Induced Reactive Oxidative Species Do Not Explain the Full Toxicity of ZnO Core Quantum Dots. *J. Hazard. Mater.* **2020**, *396*, 122616. <https://doi.org/10.1016/j.jhazmat.2020.122616>.

97. Dimitropoulos, M.; Aggelopoulos, C.A.; Sygellou, L.; Tsantis, S.T.; Koutsoukos, P.G.; Yannopoulos, S.N. Unveiling the Photo-corrosion Mechanism of Zinc Oxide Photocatalyst: Interplay between Surface Corrosion and Regeneration. *J. Environ. Chem. Eng.* **2024**, *12*, 112102. <https://doi.org/10.1016/j.jece.2024.112102>.
98. Erdal, N.B.; Hakkarainen, M. Degradation of Cellulose Derivatives in Laboratory, Man-Made, and Natural Environments. *Biomacromolecules* **2022**, *23*, 2713–2729.
99. Kwon, S.; Zambrano, M.C.; Pawlak, J.J.; Venditti, R.A. Effect of Lignocellulosic Fiber Composition on the Aquatic Biodegradation of Wood Pulps and the Isolated Cellulose, Hemicellulose and Lignin Components: Kinetic Modelling of the Biodegradation Process. *Cellulose* **2021**, *28*, 2863–2877. <https://doi.org/10.1007/s10570-021-03680-6>.
100. Liu, X.; Zhu, H.; Qin, C.; Zhou, J.; Zhao, J.R.; Wang, S. Adsorption of Heavy Metal Ion from Aqueous Single Metal Solution by Aminated Epoxy-Lignin. *Bioresources* **2013**, *8*, 2257–2269. <https://doi.org/10.15376/biores.8.2.2257-2269>.
101. Zhang, Y.; Ni, S.; Wang, X.; Zhang, W.; Lagerquist, L.; Qin, M.; Willför, S.; Xu, C.; Fatehi, P. Ultrafast Adsorption of Heavy Metal Ions onto Functionalized Lignin-Based Hybrid Magnetic Nanoparticles. *Chem. Eng. J.* **2019**, *372*, 82–91. <https://doi.org/10.1016/j.cej.2019.04.111>.
102. Pei, Y.; Xu, G.; Wu, X.; Tang, K.; Wang, G. Removing Pb(II) Ions from Aqueous Solution by a Promising Absorbent of Tannin-Immobilized Cellulose Microspheres. *Polymers* **2019**, *11*, 548. <https://doi.org/10.3390/polym11030548>.
103. Huang, Y.; Tian, X.; Wang, W.; Geng, S.; Ma, Y.; Dai, J.; Pan, J. Bacterial Cellulose/Tannic Acid Molecularly Imprinted Aerogel Microspheres via Metal Coordination and Covalent Sequential Crosslinking for Selective Adsorption of Cordycepin. *Sep. Purif. Technol.* **2026**, *390*, 136901. <https://doi.org/10.1016/j.seppur.2026.136901>.
104. Rahaman, M.H.; Islam, M.A.; Islam, M.M.; Rahman, M.A.; Alam, S.M.N. Biodegradable Composite Adsorbent of Modified Cellulose and Chitosan to Remove Heavy Metal Ions from Aqueous Solution. *Curr. Res. Green Sustain. Chem.* **2021**, *4*, 100119. <https://doi.org/10.1016/j.crgsc.2021.100119>.
105. Qin, X.; Zhou, J.; Huang, A.; Guan, J.; Zhang, Q.; Huang, Z.; Hu, H.; Zhang, Y.; Yang, M.; Wu, J.; et al. A Green Technology for the Synthesis of Cellulose Succinate for Efficient Adsorption of Cd(II) and Pb(II) Ions. *RSC Adv.* **2016**, *6*, 26817–26825. <https://doi.org/10.1039/c5ra27280g>.
106. Zhou, Y.; Jin, Q.; Zhu, T.; Akama, Y. Adsorption of Chromium (VI) from Aqueous Solutions by Cellulose Modified with β -CD and Quaternary Ammonium Groups. *J. Hazard. Mater.* **2011**, *187*, 303–310. <https://doi.org/10.1016/j.jhazmat.2011.01.025>.
107. Meneses, I.P.; Novaes, S.D.; Dezotti, R.S.; Oliveira, P.V.; Petri, D.F.S. CTAB-Modified Carboxymethyl Cellulose/Bagasse Cryogels for the Efficient Removal of Bisphenol A, Methylene Blue and Cr(VI) Ions: Batch and Column Adsorption Studies. *J. Hazard. Mater.* **2022**, *421*, 126804. <https://doi.org/10.1016/j.jhazmat.2021.126804>.
108. Tursi, A.; Chatzisyneon, E.; Chidichimo, F.; Beneduci, A.; Chidichimo, G. Removal of Endocrine Disrupting Chemicals from Water: Adsorption of Bisphenol-a by Biobased Hydrophobic Functionalized Cellulose. *Int. J. Environ. Res. Public Health* **2018**, *15*, 2419. <https://doi.org/10.3390/ijerph15112419>.
109. Lv, Y.; Ma, J.; Liu, K.; Jiang, Y.; Yang, G.; Liu, Y.; Lin, C.; Ye, X.; Shi, Y.; Liu, M.; et al. Rapid Elimination of Trace Bisphenol Pollutants with Porous β -Cyclodextrin Modified Cellulose Nanofibrous Membrane in Water: Adsorption Behavior and Mechanism. *J. Hazard. Mater.* **2021**, *403*, 123666. <https://doi.org/10.1016/j.jhazmat.2020.123666>.
110. Khalaf, B.; Hamed, O.; Jodeh, S.; Bol, R.; Hanbali, G.; Safi, Z.; Dagdag, O.; Berisha, A.; Samhan, S. Cellulose-Based Hectocycle Nanopolymers: Synthesis, Molecular Docking and Adsorption of Difenconazole from Aqueous Medium. *Int. J. Mol. Sci.* **2021**, *22*, 6090. <https://doi.org/10.3390/ijms22116090>.
111. Dohnalová, Ž.; Luxová, J.; Antušková, V.; Šefců, R.; Šulcová, P.; Turková, I.; Kotrlý, M. The Synthesis and Quality Comparison of Nineteenth-Century Chromate Pigments: Strontium, Barium, Zinc and Cadmium Chrome Yellow. *J. Mater. Sci.* **2025**, *60*, 16002–16014. <https://doi.org/10.1007/s10853-025-11351-1>.
112. Liu, S.; Zeng, J.; Tao, D.; Zhang, L. Microfiltration Performance of Regenerated Cellulose Membrane Prepared at Low Temperature for Wastewater Treatment. *Cellulose* **2010**, *17*, 1159–1169. <https://doi.org/10.1007/s10570-010-9450-6>.
113. Perendija, J.; Veličković, Z.S.; Cvijetić, I.; Rusmirović, J.D.; Ugrinović, V.; Marinković, A.D.; Onjia, A. Batch and Column Adsorption of Cations, Oxyanions and Dyes on a Magnetite Modified Cellulose-Based Membrane. *Cellulose* **2020**, *27*, 8215–8235. <https://doi.org/10.1007/s10570-020-03352-x>.
114. Ren, Z.; Zhang, G.; Paul Chen, J. Adsorptive Removal of Arsenic from Water by an Iron-Zirconium Binary Oxide Adsorbent. *J. Colloid Interface Sci.* **2011**, *358*, 230–237. <https://doi.org/10.1016/j.jcis.2011.01.013>.

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