Porous Cellulose Acetate/Block Copolymer Membranes for the Recovery of Polyphenolic Compounds from Aquatic Environments

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ABSTRACT: Polyphenols are natural compounds with strong antioxidant properties synthesized by plants and widely distributed in plant tissues. They compose a broad class of compounds that are commonly employed for multiple applications such as food, pharmaceutical, adhesives, biomedical, agricultural, and industrial purposes. Runoffs from these sources result in the introduction of polyphenols into aquatic environments where they further transform into highly toxic pollutants that can negatively affect aquatic ecosystems and humans. Therefore, the development of extraction and remediation methods for such compounds must be addressed. This study describes the identification and operation of a method to recover polyphenolic compounds from water environments by utilizing membrane-based separation. Composite membranes derived from electrospun cellulose acetate (CA) fibers and diblock copolymer (DiBCP) PEO-b-P4VP were prepared to evaluate the adsorption of polyphenolic compounds from aqueous environments. The highly porous CA fibers were developed using the electrospinning technique, and the fabricated DiBCP/CA membranes were characterized using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), Fourier-transform infrared (FT-IR) spectroscopy, and tensile testing. Finally, the ability of the composite membranes to adsorb the soluble polyphenolic compounds catechol (CAT) and gallic acid (GA), from a wetland environment, was studied via batch adsorption experiments and by solid-phase extraction (SPE). Results revealed a successful recovery of both polyphenols, at concentrations within the parts per million (ppm) range, from the aqueous media. This suggests a novel approach to recover these compounds to prevent their transformation into toxic pollutants upon entrance to water environments.

1. INTRODUCTION

Urban, agricultural, and industrial runoff to streams, reservoirs, and channels is one of the most significant contributors to water quality concerns. Runoffs from different land use areas are a significant source of excess nutrients, heavy metals, and other contaminants. These have multiple adverse effects on ecosystem functions and biodiversity, including eutrophication, health risks, among others. Within the numerous types of water pollutants present in the runoffs, there is a class of organic chemicals with an industrial and chemical value known as polyphenols.

The presence of polyphenols and phenol-based compounds in aquatic environments results from natural, industrial, domestic, and agricultural activities. Their wide applications within the food, agricultural, pharmaceutical, and cosmetic industries have primordially arisen from their biological properties as potent antioxidants, antimicrobial, anti-inflammatory, and neuroprotective agents. Moreover, because of their polymerization properties, they are commonly employed in adhesives, dyes, plastics, sealants, coatings, and biomedical applications, all of which further negatively promote the entrance of these compounds into aquatic environments.

This major concern of environmental pollution has prompted researchers into the recovery of polyphenols from aquatic environments using different water treatment approaches; however, membrane technologies remain an undefeated standard for such purposes. Membrane technology has multiple advantages because it can be tailored to specific contaminants. Frequently, these membranes are made of polymers such as polysulfone, poly(ether sulfone), poly(vinylidene fluoride), polypropylene, and polyamides because of their effectiveness in removing water pollutants, increased thermal stability, and good chemical resistance and...
mechanical properties.\textsuperscript{11,12} Nonetheless, they have certain drawbacks such as being prone to fouling and having low permeate fluxes during filtration processes because of their hydrophobic character.\textsuperscript{13}

By contrast, cellulose acetate (CA) is a nontoxic, hydrophilic, and economic material prepared from natural purified cellulose that has been extensively used in desalination, reverse osmosis, and ultra- and nano-filtration processes. As a material easily processed using spinning and casting techniques, CA electrospun films result in high porosity, biocompatibility, and good performance with high permeate fluxes, thereby making them promising candidates for water treatment processes.\textsuperscript{14,15} However, the heterogeneity in pore size distribution following electrospinning can offer low selectivity and poor retention of target molecules, thus limiting its applications.\textsuperscript{16}

In recent years, block copolymers (BCP) have been widely studied because of their diverse functionalities, arrangements, and tunable nanoporous structures, properties that have made them attractive assets in membrane technology.\textsuperscript{17−20} Furthermore, scientists have studied the ways in which BCPs can interact to adsorb different contaminants. Recent publications have reported the interaction of the diblock copolymer (DiBCP) poly(ethylene oxide-b-4-vinylpyridine) (PEO-b-P4VP) with different emerging contaminants present in water. It has been established that the PEO-b-P4VP is able to adsorb pharmaceutical compounds through electron donor–acceptor or π-π interactions.\textsuperscript{21,22} Additionally, PEO-b-P4VP can interact with water molecules through hydrogen bonding, thus maintaining a hydrophilic character. Furthermore, the interaction between PEO and polyphenols has been widely studied and hydrogen bonds have been identified as the main mechanism of interaction.\textsuperscript{23,24} Previous reports have proposed that the P4VP monomer on the block copolymer interacts with hydroxyl groups in surfaces, leaving PEO, the hydrophilic monomer, exposed and able to interact with the polyphenol through hydrogen bonding.\textsuperscript{25,26}

Herein, we present the synthesis and characterization of porous cellulose acetate membranes via electrospinning, their subsequent functionalization with PEO-b-P4VP and the evaluation of their polyphenolic adsorption potential for water remediation. The model polyphenolic compounds used throughout this study were catechol (CAT) and gallic acid (GA) because of their low degradability and high toxicity in aquatic environments (Figure S1).\textsuperscript{27,28} The adsorption of CAT and GA onto the functionalized membranes was studied using batch adsorption experiments and solid-phase extraction (SPE). Water samples from the Ciénaga Las Cucharillas wetland (Figure S2) were used as complex matrices for adsorption experiments.

2. RESULTS AND DISCUSSION

Recovering molecules of commercial interest from polluted areas or from wastewater is an important and urgent task from the sustainability and environmental remediation standpoint. As briefly mentioned, phenol-based compounds are an interesting class of compounds because a good number of commodities of daily use are largely based on such compounds, including plastics, adhesives, cosmetics, drugs, and others.\textsuperscript{30,31} Moreover, the design and fabrication of materials that selectively adsorb compounds of interest is an area of increasing attention.\textsuperscript{32} The selectivity of the material is typically dictated by the molecular interactions that occur at the interface of the host material and the adsorbing molecule.\textsuperscript{33}

Before proceeding to test the porous membranes fabricated for the adsorption of polyphenolic compounds, a thorough characterization of the porous membranes was accomplished. First, the CA porous fibers were characterized via scanning electron microscopy (SEM), as observed in Figure 1. As illustrated in the figure, two aspects were evaluated toward the fabrication of the optimal conditions of the fibers: the mixed solvent system ratio and the CA concentration in solution. In terms of the mixed solvent system ratio, an increase in the chloroform: acetone ratio, from 3:1 to 9:1, progressively influenced the outcome of the fiber morphology, leading to a notorious rough surface with a higher pore development. As reported by Tungprapa et al., this is due to the low boiling point of acetone. Subsequently, they tested different concentrations of CA in the solution, observing that the lower concentrations resulted in smoother surfaces whereas the higher concentrations led to the formation of rougher surfaces, a behavior that has been related to the formation of more porous structures.\textsuperscript{25,26}

Figure 1. SEM images of CA electrospun fibers showing an increasing solvent ratio and CA concentration.

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points of the solvents, which causes different evaporation rates in the outer and inner surfaces of the fibers, thereby collapsing them and forming these open structures.34

On the other hand, increasing the concentration of the CA in solution enlarges the pores and reduces their depth. As previously studied by Liu et al., this is accounted to a higher viscosity of the solution being subjected to the electrospinning system, which limits the flowability of the CA solution in the tip of the needle after the phase separation of the solvents.35 Apart from this, bead-free and uniform fibers were electrospun at both CA concentrations. This can be explained by the use of a relatively low electrical field applied to the system, which Deitzel et al. has stated to be strongly correlated to the bead density.36 The average distance of the tip from the collector within the electrospinning system also seemed favorable toward the formation of fibers in a low micrometer range. Based on the images, it was determined that the ideal concentration of CA and the ratio of the binary solvent system were 5% and 9:1, respectively. Continuous electrospinning of fibers with these optimal conditions revealed a nonwoven structure with uniform fibers exhibiting an average fiber diameter of 5.52 μm, as illustrated in the fiber diameter distribution graph of Figure S3.

After SEM, the DiBCP/CA membranes were characterized via energy-dispersive X-ray spectroscopy (EDS) and Fourier-transform infrared (FT-IR) spectroscopy. Elemental analysis via EDS was performed in order to find distinctive atomic footprints after each step of the material preparation (see Figure S4). The presence of PEO-b-P4VP and trimethoxy(2-phenylethyl)silane (TMPES) onto the composite membranes was also studied by FT-IR, as seen in Figure 2a. Bands commonly assigned to the phenyl group stretching of the silane (around 1450 cm⁻¹) and the C−H symmetric and asymmetric stretching (around 3000 cm⁻¹) were not identified in the composite membrane because of the low PEO-b-P4VP and TMPES volumes added to the activated solutions. Also, the characteristic Si−O−Si bond stretching peak of TMPES (between 1000 and 1200 cm⁻¹) was overlapped by the CA’s C−O stretching at 1100 cm⁻¹.37,38 However, DiBCP had characteristic bands corresponding to (1) the hydrogen bending of the pyridine ring at 1595 cm⁻¹ and (2) the C−H out-of-plane bending of the pyridine ring at 818 cm⁻¹.39,40 In addition, the presence of TMPES was confirmed by the band at 697 cm⁻¹ in the fingerprint area that accounts to the Si−CH₂ stretching bonds.41

Additionally, the mechanical properties of the membranes were examined in order to evaluate the good stability in water conferred by the TMPES treatment; the obtained values are summarized in Table S1. Previous research has found that organosilicon compounds can significantly improve the composite mechanical strength by penetrating into pores and developing mechanically interlocked coatings on their surface,
thus preventing ingress of water in an aqueous environment and bond displacements at the fiber interface.42,43 Stress−strain curves for DiBCP and TMPES-treated CA membranes shown in Figure 2b were obtained by applying uniaxial stress membranes at a strain rate of 0.5 mm/s. The values obtained from these curves confirm the strong mechanically interlock coating formed by TMPES within the pores of the membranes, yielding good ductility (elongation of 6.23%) and increased tensile strength (6.46 Mpa) over the resulting DiBCP/CA membranes.

Finally, X-ray photoelectron spectroscopy (XPS) survey results revealed the presence of silicon and nitrogen in the composite membranes treated with TMPES and DiBCP (Table S2). Furthermore, high-resolution deconvolution for carbon was performed to confirm the molecular interactions between CAT and GA (Figure S5) and the DiBCP/CA membrane (Figure S6 for spectra with CA membranes); the spectra, as shown in Figure 2d, reveals the appearance of C=C bonds after adsorption, attributed to the phenolic structures within the polyphenols.

In order to evaluate the polyphenolic recovery potential of the DiBCP/CA membranes for water remediation, batch adsorption experiments in function of concentration and time of each polyphenolic compound were performed. The experimental values of absorbances, obtained from these experiments, were later used to determine the equilibrium adsorption amount of each polyphenol throughout concentration and time. Figure 3a,b elucidates the results of the adsorption capacity of DiBCP as a function of the equilibrium concentration of the polyphenols. As seen in the experimental values of these figures, the tendency of target molecule’s recovery by the DiBCP/CA membranes was higher for GA than that for CAT. As previously studied by many researchers, this can be explained by the quantity of available sites of each molecule for hydrogen bonding, through hydroxyl groups, with the ether group of the PEO block of the DiBCP.44−47 Additionally, it has been stated that PEO-b-P4VP assembles in such a way that the P4VP monomer, which is more hydrophobic than PEO, interacts with the available hydroxyl groups on the surface of the CA electrospun membranes, leaving the hydrophilic PEO monomer exposed to the water molecules (Figure S6a). On the other hand, CAT and GA have strong affinity for hydrophilic surfaces in an aqueous environment regardless of a large excess of competing water molecules.48 Therefore, if we analyze the quantity of available sites of each molecule for hydrogen bonding, we can determine...
that GA has (4) possible sites of interaction (three phenolic hydroxyl groups and the hydroxyl group of carboxylic acid) and CAT has (2) possible sites of interaction (two phenolic hydroxyl groups). However, following previous literature, other mechanisms could be allowing the interaction between the phenolic compounds and the modified membranes. These

Table 1. Thermodynamic Parameters Obtained by Fitting Data to Langmuir and Freundlich Equations for CAT and GA

| polyphenol | $q_m$ (mg/g) | $K_d$ (mg/L) | $R^2$ | $n$ | $K_F$ (mg/g) | $R^2$ |
|------------|--------------|--------------|-------|-----|---------------|-------|
| CAT        | 67.431 ± 62.36 | 0.001 ± 0.001 | 0.991 | | 1.089 ± 0.059 | 0.993 |
| GA         | 25.532 ± 2.763 | 0.021 ± 0.005 | 0.982 | | 1.882 ± 0.312 | 0.947 |

Table 2. Kinetic Parameters Obtained by Fitting Data to the Pseudo-First Order and Pseudo-Second Order Equations for CAT and GA

| polyphenol | $q_e$ (mg/g) | $k_1$ (g/mg min) | $R^2$ | $q_e$ (mg/g) | $k_2$ (g/mg min) | $R^2$ |
|------------|--------------|------------------|-------|--------------|------------------|-------|
| CAT        | 3.534 ± 0.260 | 0.094 ± 0.099 | 0.840 | 3.597 ± 0.302 | 0.090 ± 0.189 | 0.845 |
| GA         | 17.398 ± 0.691 | 0.050 ± 0.006 | 0.954 | 18.074 ± 0.639 | 0.003 ± 0.001 | 0.972 |

Figure 4. (a) Adsorption capacity of DiBCP and TMPES-treated CA membranes and untreated CA membranes using 50 ppm CAT and 50 ppm GA laboratory-controlled samples. Adsorption of polyphenols in the complex matrices of Ciénaga Las Cucharillas: (b) equilibrium adsorption amount (mg) of CAT and GA adsorbed by the gram of DiBCP/CA membranes in matrix spike batch experiments, (c) response signals of GC–MS analysis to different concentrations of CAT, and (d) response signals of GC–MS analysis from the standard solution of CAT and SPE-treated samples using CA and DiBCP/CA membranes.
mechanisms include (1) hydrophobic interactions between polyphenols and cellulose; 49 (2) ionic interactions that lead to the formation of GA-(4-VP) complexes within the polar environment of water; 50 and (3) the formation of electron donor–acceptor complexes between the benzene rings of GA and CAT with the pyrimidine rings of PEO-b-P4VP. 51

In order to further describe the adsorption mechanism, the obtained results were fitted to the nonlinear forms of the Langmuir and Freundlich isotherms. Following Gile’s classification, a linear plot type-C was obtained by both models in regard to CAT adsorption (see Figure 3a), proposing that the adsorption capacity of the DiBCP/CA membrane is proportional to the CAT concentration up until the maximum possible adsorption, which is not reached within the studied experimental conditions. As shown in Table 1, both models demonstrate correlation coefficients over 0.99 and suggest that both, homogeneous and heterogeneous surfaces, existed within the experimental conditions, a case previously discussed by Hamdaoui. 52 On the other hand, based on Gile’s classification, an L-type (subgroup 1) curve is seen in the two fittings with respect to GA adsorption (see Figure 3b), describing progressive saturation of the DiBCP/CA membranes with available adsorption sites that have not been fully occupied using the studied experimental concentrations. 53 With regard to GA adsorption, a better fit was achieved with the Langmuir model ($R^2 > 0.98$), suggesting a uniform monolayer coverage of GA onto the DiBCP/CA membranes. That said, when comparing the Freundlich model fittings between the polyphenols, the values of $K_F$ (the indicator of adsorption capacity) indicate that the adsorption capacity for GA is higher than that for CAT, which is accounted to the available sites for hydrogen bonding of each polyphenol. The maximum adsorption amount ($q_m$) for GA and CAT calculated from the Langmuir model was 25.5318 and 67.4314 mg/g, respectively, similar to the $q_m$ value reported by Song et al. using diatomite as the absorbent and CAT as the absorbate. 54 Moreover, the values of $n$ between the range of 1–2, using the nonlinearized models, reveal a moderate adsorption capacity of the DiBCP/CA membranes over the studied polyphenols. 55

Furthermore, data were fitted to the pseudo-first and pseudo-second orders to evaluate the performance of the adsorbents for adsorbates. As seen in Figure 3c,d, the modified membranes reached a saturation adsorption capacity of CAT after 30 min and GA after 200 min. It has been previously stated that adsorption systems of natural chemical components onto adsorbents that reach equilibrium in several minutes to hours happen via intermolecular forces, supporting the molecular interactions previously mentioned. 56 A better correlation fit was seen in GA rather than CAT, as demonstrated in Table 2, further suggesting that this adsorption system in specific is controlled by chemisorption mechanisms. 57,58

Following this analysis, Figure 4a further evidences the selectivity of the DiBCP over the polyphenolic compounds; the figures show the equilibrium adsorption amount (mg) of CAT and GA adsorbed by the gram of PEO-b-P4VP-treated CA membranes, TMPES-treated CA membranes, and untreated CA membranes after 24 h under 50 ppm CAT and GA solutions. As it can be seen, the addition of the DiBCP, PEO-b-P4VP, plays a notable role in the adsorption of GA and CAT granted mainly to the hydrogen bonding interactions of the PEO monomers with phenolic hydroxyl groups of the polyphenols.

Finally, matrix spike batch adsorption experiments and solid-phase extraction procedures were performed to study the polyphenolic recovery by the membranes in complex matrices collected from Ciénaga Las Cucharillas, an urban coastal palustrine/estuarine wetland located in the western side of the San Juan Bay in the northern metropolitan area of Puerto Rico. Currently, this wetland is surrounded by highly urbanized and industrialized areas, where discharges from septic tanks, gray waters, illegal industrial intermittent flows, clandestine landfills, and atmospheric emissions from power-generating plants nearby are the main sources of organic and inorganic inputs into the system. 59,60

The matrix spike batch adsorption experiments demonstrated a different behavior, in comparison to the laboratory-controlled samples, between CAT and GA recovery after being incorporated into the wetland samples. As seen in Figure 4b, the adsorption of both polyphenolic molecules was significantly reduced, specifically for GA; this is primarily accounted to the diversity of naturally occurring chemical species of polyphenolic compounds present in the marsh samples that could be interacting with the DiBCP/CA membrane. Also, the sole quantities of CAT and GA molecules could overcome transformation because of their antioxidant nature in donating electrons with other chemical species present in the samples, 61 as it is clearly evidenced in Figure S7 with the flattening of the curve in the GA matrix spike batch samples subjected to ultraviolet–visible (UV–vis) spectroscopy. 62

On the other hand, the SPE method was employed to study the extraction of CAT from a complex matrix using the membranes as stationary phases. Direct-immersion solid-phase microextraction (DI-SPME), an efficient sample preparation method for the analysis of compounds at low concentrations in complex matrices, was used to measure the concentration of CAT from aqueous samples before and after the SPE process. 62 Different concentrations of CAT (16.6, 25, and 33.3 ppm) were identified using gas chromatography–mass spectrometry (GC–MS), with a retention time around 9.1626 min, as seen in Figure 4c. In Figure 4d, a shift in the retention time of the 16.6 ppm standard used for the SPE can be observed, from 9.1626 to 9.2256 min, which can be attributed to matrix effects. In complex matrices, components within the matrix can affect the interaction between the analyte and the active sites of the column. 63 With continuous testing, this effect can be exacerbated because of the formation of new active sites by the accumulation of low-volatile matrix components. 64 After the SPE procedure, CAT was not identified in any of the samples, as evidenced in Figure 4d. If trace amounts of CAT were present on the flowthrough from the SPE, the concentration of these samples is very low and outside of the limit of detection of the instrument. Contrary to the adsorption experiments shown in Figure 4a, the CA and DiBCP/CA membranes showed similar recovery efficiency toward CAT. The stationary phase of the SPE contains multiple layers of the CA and DiBCP/CA membranes within the pellet, which increases the surface area of the membranes and consequently, the functional groups available to interact with CAT, along with the likelihood of being adsorbed. As previously mentioned, possible interactions involved in the adsorption of CAT include hydrogen bonding, electron donor–acceptor complexes, ionic interactions with the DiBCP, and hydrophobic interactions with CA. These results suggest that both CA and DiBCP membranes are suitable for
the removal and identification of CAT from complex matrices using the SPE method.

In summary, we present a model for the remediation of polyphenolic compounds from water environments by means of a membrane-based separation method that employs the use of highly porous electrospun DiBCP/CA membranes. Chemical and physical characterization of the fabricated membranes confirmed the incorporation of the diblock copolymer, PEO-b-P4VP, and TMPES onto the electrospun CA membrane, thus providing high selectivity over CAT and GA and a good stability within the aqueous environment. Batch adsorption experiments revealed higher adsorption capacity of DiBCP/CA membranes for polyphenols with greater quantity of sites for hydrogen bonding and electron-withdrawing and donor groups. Additionally, the fittings of adsorption isotherms and kinetics models to our obtained results further suggested the proposed chemisorption mechanisms of interaction between the DiBCP and the polyphenols studied. Furthermore, DiBCP/CA and CA pellets used for the SPE method proved to be suitable in recovering CAT from complex matrices collected from a wetland environment, as revealed via GC−MS analysis. Further studies will address the reusability of the fabricated materials and their thermal stability, target CAT and GA byproducts, and consider ways to enhance the adhesive properties of our materials to provide a sustainable alternative for the recovery and reusability of polyphenols in industrial applications.

3. MATERIALS AND METHODS

3.1. Materials. Analytical-grade CA (Mw 30,000), chloroform, acetone, glacial acetic acid, TMPES (98%), CAT (≥99%), and GA were purchased from Sigma Aldrich, USA. PEO-b-P4VP (Mw 5000 PEO−20,000 P4VP) was purchased from Polymer Source, Inc., Canada. 190 Proof ethyl alcohol was purchased from Ultra-Pure, LLC, USA. Visiprep SPE vacuum manifold DL, Supelclean ENV1-8 SPE Tube bed wt. 500 mg 6 mL, Whatman qualitative filter paper, ethyl acetate ACS reagent (>99.5%), HCl, acetonitrile, and 6 mL glass reaction tubes with Teflon were all purchased from Sigma Aldrich. QuEChERS SpinFiltr dSPE microcentrifuge tubes (MgSO4, PSA, C18, Cholofiltr) were purchased from UCT, Inc, USA. Agilent Technologies GC System 7890A coupled with mass spectrometer inert XL MSD 5975C was used for the analysis of SPE and SPME samples. SPME experiments were performed using SPME fiber assembly 50/30 μm DVB/CAR/PDMS Stableflex 24 ga from Supelco in a standard holder. Nanopure water (NPH2O) from Milli-Q Direct 16 and Aries FilterWorks Gemini Water Purification Systems (18.2 Ω-cm) was used at all times.

3.2. Methods. 3.2.1. CA Electrospun Film Development via Electrospinning. Different CA concentrations (5 and 7.5%, wt %) were dissolved in various ratios (3:1, 5:1, 7:1, and 9:1 v/v) of a chloroform:acetone binary solvent system and left under magnetic stirring for 24 h. It has been reported that the use of a binary volatile solvent system within the process of electrospinning can highly affect fiber surface structures because of the different phase separation rates of the solvents as they disperse from the fibers, thereby generating highly porous fibers. The electrospinning process was held under a closed Plexiglass box ranging in temperature from 21 to 23 °C and an average relative humidity of 80–86%. A voltage source (Gamma High Voltage Research UC25-.75P/M257A HV Power Supply, Florida, USA) of 7 kilovolts was used to generate an electrostatic repulsion in the protruding drop of the needle (ID = 0.41 mm) containing the polymer solution. A flow ratio of 3 mL per hour was held to accomplish the desirable highly porous morphology. For the sample preparation, 5 mL of the previously prepared solution was added to the syringe that was placed in a syringe pump (NE-300 Just Infusion) at 10 cm from the collector. The collector gathering the electrospun fibers was covered with an aluminum foil prior to the starting of the process to facilitate the removal of fibers after electrospinning. In addition, the collector was set at 1,000 rpm. After the electrospinning process, the membranes were immersed in water for 2 h to efficiently separate the fibers from the aluminum foil and obtain the CA electrospun membranes. Figure 5 summarizes the solution.
accumulation during SEM imaging. Chemical characterization of samples was initially gold-sputtered to prevent charge buildup and imaging artifacts. SEM was performed using a JEOL 5800LV scanning microscope with an electron beam energy of 20 kV; the XPS analysis was conducted using a Physical Electronics 5600 scanning ESCA system with monochromatic Al-Kα X-ray source at a high vacuum to minimize electron escape effects.

Characterization of DiBCP/CA Membranes. In order to increase the CA membrane stability and mechanical resistance of the membranes, strips ranging from 17 to 20 mm in length, 8.5 to 9.5 mm in width, and 0.3 to 0.5 mm in thickness were loaded to failure at a strain rate of 0.5 mm/s in a tensile testing machine (Instron 5569, CA, USA), and stress curves were plotted using OriginPro 2015.

Dynamic Batch Adsorption Experiments Using Laboratory-Control Samples. The dynamic batch adsorption experiments, summarized in Figure 6, were performed by submerging 3 cm × 1.5 cm DiBCP/CA membranes, weighting from 0.01 to 0.015 g, under 30 mL solutions with different concentrations [0, 10, 20, 30, 50, and 100 (ppm)] of each polyphenol studied (CAT and GA). These solutions were prepared by simply dissolving 0.1 g of each polyphenol in 1 L of NPH2O to generate 100 ppm solutions of each polyphenol to then perform specific dilutions for each concentration. The solutions, held in falcon tubes, were then placed in a Brunswick shaker incubator (Series 2000) for 4 h at a speed of 150 rpm with a temperature of 25 °C and an angle of 45°. After 4 h, the films were removed from solution and allowed to dry at room temperature (RT). Later, the solutions were subjected to UV–vis spectroscopy, using a Shimadzu UV Spectrophotometer UV-1800, where absorbance was measured at the wavelengths (nm) of 266 and 275, where GA and CAT absorb, respectively. It is worth noting that throughout each experiment of 4 h, a falcon tube was designated as blank, where a film was immersed in NPH2O to later measure the absorbance of any other possible compound arising at the same wavelength. Also, another falcon tube, containing 30 mL solutions of specific concentration in ppm, remained with no film and was used as control during the UV–vis analysis. The following equation was used to measure the equilibrium adsorption amount of the films:

\[ q_e = \frac{(C_0 - C_e)V}{w} \]  

where \( q_e \) is the equilibrium adsorption amount (mg/g), \( C_0 \) is the initial concentration of GA or CAT (mg/L), \( C_e \) is the equilibrium concentration of GA or CAT after adsorption (mg/L), \( V \) is the volume (L) of GA or CAT solution, and \( w \) is the mass (g) of the DiBCP/CA membrane. To further assess the adsorption phenomenon of the polyphenols, Langmuir (eq 2) and Freundlich (eq 3) nonlinear isotherm models were employed, fitting the obtained absorbance values into the following equations:

\[ q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \]  

\[ q_e = K_p C_e^{1/n} \]  

where \( q_e \) (mg/g) and \( C_e \) (mg/L) are the equilibrium adsorption amount and concentration of GA or CAT, respectively. \( q_m \) (mg/g) shows the maximum amount of GA or CAT per unit mass of the adsorbent to form a complete monolayer, \( K_a \) is the Langmuir constant, and \( n \) is the Freundlich constant.
monolayer on the surface, and \( K_d \) (mg/L) defines a constant related to the affinity of the binding sites. Finally, \( n \) and \( K_f \) are the Freundlich constant and Freundlich exponent, which indicate the favorableness (\( n > 1 \)) of the adsorption process and the adsorption capacity of the adsorbent, respectively. The slope, \( 1/n \), allows to understand the adsorption process. Experiments were performed in triplicate at 25 °C.

3.2.4.2. Kinetic Studies Using Laboratory-Control Samples. Kinetic batch adsorption experiments were performed using the same procedure as that exposed in 2.2.4.1 but using a constant concentration of 50 ppm in the samples, and adding new time periods, including (in min): 30, 60, 480, and 1440. After each time period, solutions were also subjected to UV–vis spectroscopy, measuring absorbance at the wavelengths (nm) of 266 and 275 where GA and CAT absorb, respectively. The equilibrium adsorption amount of the films was measured using eq 1 previously mentioned. In order to further evaluate the optimum conditions and the mechanism of the sorption of the DiBCP/CA membranes, the obtained results were fitted into the nonlinear forms of the pseudo-first and pseudo-second order kinetic models, using the following eqs 4 and 5:

\[
q_t = q_e (1 - e^{-k_ft})
\]  

\[
q_t = \frac{k_d q_e^2 t}{1 + k_d q_e t}
\]

where \( q_e \) is the calculated equilibrium capacity from the model (mg/g), \( q_t \) is the amount of the solute adsorbed on the adsorbent (mg/g) at time \( t \), and \( k_1 \) and \( k_2 \) define the rate constant of the pseudo-first and pseudo-second order models, respectively.

3.2.4.3. Matrix Spike Batch Adsorption Experiments. Wetland water samples of 2 L were collected at the phreatic level from the P1 well of the Natural Reserve of Ciénaga Las Cucharrillas (Figure S2). Using these water samples, several solutions were prepared by adding a variable volume (mL) of 50 ppm standard of each polyphenol [0, 2, 4, 6, 8, and 10] to a fixed volume of 20 mL of the field samples. Each solution was diluted to a fixed volume of 30 mL using NPH2O. Finally, DiBCP/CA membranes, of the same measurements used in the LCS experiments, were submerged under the 30 mL solutions and placed in the orbital shaker for 24 h at a speed of 150 rpm with a temperature of 25 °C and an angle of 45°. These solutions were subjected to UV–vis spectroscopy after 24 h, where absorbance was measured at the respective wavelengths mentioned earlier in 2.2.4.1. The equilibrium adsorption amount of the films was measured using eq 1.
Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. J.L.R. and X.S.M. equally contributed to this work.

Notes

The authors declare no competing financial interest.

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