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Bioinspired tannic acid-copper complexes as selective coating for nanofiltration membranes

Tina Chakrabarty, Liliana Pérez-Manríquez, Pradeep Neelakanda, and Klaus-Viktor Peinemann*

Advanced Membrane and Porous Materials Center, King Abdullah University of Science and Technology (KAUST), 23955-6900, Thuwal, Saudi Arabia

E-mail: klausviktor.peinemann@kaust.edu.sa

ABSTRACT

Bio-polyphenols that are present in tea, date fruits, chocolate and many other plants have been recognized as scaffold material for the manufacture of composite filtration membranes. These phenolic biomolecules possess abundant gallol (1,2,3-trihydroxyphenyl) and catechol (1,2-dihydroxyphenyl) functional groups, which allow the spontaneous formation of a thin polymerized layer at the right pH conditions. Here, we report a facile and cost-effective method to coat porous membranes via the complexation of tannic acid (TA) and cupric acetate (mono hydrate) through co-deposition. The modified membranes were investigated by XPS, ATR/FTIR, water contact angle, SEM and water permeance for a structural and morphological analysis. The obtained results reveal that the modified membranes with TA and cupric acetate (CuII) developed a thin skin layer, which showed excellent hydrophilicity with good water permeance. These membranes were tested with different molecular weight polyethylene glycols (PEG) in aqueous solution; the MWCO was around 600 Daltons.

Keywords: Polyphenols, tannic acid-copper complex, membrane surface modification, nanofiltration.

1. Introduction

Nanofiltration (NF) is a pressure driven membrane process which has properties between ultrafiltration (UF) and reverse osmosis (RO) [1]. NF membranes are widely used in the food industry, for water softening and treatment, and in the textile and pharmaceutical industries [2,3]. A recent review describes the common methods for NF membrane manufacturing [4]. NF membranes can be integrally skinned asymmetric membranes made by immersion precipitation [5,6] or they are thin-film composite membranes made by interfacial polymerisation [7,8, 9, 10]. Composite membranes are also made by solution coating [11], plasma polymerization [12] and surface grafting [13] over a substrate.. Following a pioneering article of Lee et al.[14] bio-inspired coatings using natural compounds have been introduced recently for NF membrane fabrication [15,16]. Recently Cheng et.al. reported a NF membrane modification for antibiotics removal by a phenolic derived dopamine coating [17].

Polyphenols derived from plants are attractive coating materials due to their broad chemical versatility, their metal chelating and antimicrobial properties [18]. Tannic acid (TA) which is a plant derived polyphenol are abundantly found in nature materials like tea leaves, fruits, nettle, oak wood etc. [19]. The presence of catechol or gallol groups in TA provides good binding with organic/inorganic/metallic surfaces by covalent and/or non-covalent bond interactions [20,21].

For the first time Ejima et.al reported a simple and one step coating method on a range of substrates by mixing TA and FeIII to develop films and particles [22]. Membranes for water filtration application was reported by TA-FeIII coating over a ultrafiltration membrane support by Kim et.al [23].

Here we report a bio-polyphenolic coating from TA and CuII metal ions to prepare NF membranes with a thin skin layer over an ultra-filtration polyacrylonitrile (PAN) membrane

support. This is a one step process where the coordination reaction between the phenolic groups of TA and CuII forms a surprisingly stable film..

2. Experimental

2.1. Materials

Tannic acid (TA), polyethylene glycol (PEG) of average molecular weight (400, 600, 800 and 1000 Daltons) and Protoporphyrin IX disodium salt were purchased from Sigma-Aldrich. Methyl Orange and Brilliant blue dyes were acquired from Acros Organics and Fisher Scientific. Cupric acetate (monohydrate) was purchased from Loba Chemie and ethanol solvent was obtained from VWR Chemicals. All the chemicals were used as received without any additional purification. Polyester backed polyacrylonitrile (PAN) support material was purchased from GMT Membrantechnik GmbH (Germany).

2.2. Preparation of TA/CuII Membranes

PAN ultrafiltration membrane was used as support membrane for all experiments. The procedure of surface coating is shown in Fig. 1.

Fig. 1. Schematic illustration of membrane coating procedure by one-step coordination assembly of Tannic acid (TA) and Cu II on PAN support.

Prior coating the PAN support was wetted with ethanol for 5 minutes followed by rinsing with DI water to remove any excess solvents. Subsequently, the wet membrane was mounted between a Teflon plate and frame (with active PAN polymer surface facing up) clamped with metal clips on their sides. A silicon gasket was used in between the PAN support and Teflon frame to avoid any solution leakage [24]. About 5 ml of 10 mM ethanolic solution of $\text{Cu}(\text{CH}_3\text{COO})_2$ was filled into the Teflon frame followed 5 ml of 10 mM ethanolic TA solution after 10 seconds. The reaction setup was maintained at room temperature and was not disturbed for a duration of 10 minutes. The coated membrane was rinsed thoroughly with ethanol to remove any excess particles on its surface and dried at room temperature overnight.

2.3. Membrane Filtration Test

Nanofiltration experiments were performed using a stirred dead end filtration cell (HP 4750 Sterlitech Corporation, USA) with an effective membrane area of 12.6 cm² at 5 bar. Permeates were collected after reaching a steady state and the permeance (J) was calculated using equation (1).

$$J = \Delta V / (A \times t \times \Delta p) \quad (1)$$

where V is the volume of the permeate (L), A is the effective membrane area (m²), t is the time (h) for permeate collection and Δp is the trans-membrane pressure (bar). Rejection of tested solutes (R) was determined using Eq. (2), where C_P and C_R are the concentration of permeate and retantate respectively.

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

2.4. Molecular weight cut-off measurement

Aqueous solutions of PEGs of different molecular weights were used to determine the molecular weight cut-off of the TA/CuII modified PAN membrane. Rejection studies were carried out using a feed solution of 1g/L PEG in DI water. PEG concentrations were measured by GPC (Agilent Technologies) with an RI detector.

2.5. Intrumentation and Characterization Techniques

Surface morphology and cross-section of the membranes were analyzed by scanning electron microscope (SEM) by using a field emission SEM (FEI Magellan) instrument. An Agilent 5400 SPM/AFM microscope (Agilent Technologies) was used for AFM measurement to analyze the

surface morphology over an area of $5 \times 5 \mu\text{m}^2$. Surface composition of the membranes was determined by XPS in a Kratos Axis Ultra DLD spectrometer equipped with a monochromatic Al K α x-ray source ($h\nu=1486.6 \text{ eV}$) operating at 150 W, a multichannel plate and delay line detector under a vacuum of $1 \sim 10^{-9} \text{ mbar}$. Survey spectra was collected followed by high resolution scan of C1s, O1s, S2p, and Cu2p regions. Contact angle measurement for the developed membranes was carried out by using an EasyDrop Contact angle measurement instrument (Kruess GmbH). A UV-VIS (Perkin Elmer Lambda 1050) spectrophotometer was used to analyse dye concentrations at their characteristic wavelengths. To determine the molecular weight cutoff of the membranes Gel Permeation Chromatography (GPC) of Agilent Technology was used. Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra of membranes were recorded on a Thermo Scientific Spectrometer (Nicolet iS10 model) covering a wide range from 3750 to 500 cm^{-1} so the full spectra was recorded up to 16 scans. Conductivity of various salts concentration was determined by using an Oakton's pH/CON 510 conductivity meter.

3. Result and discussion

3.1. Surface composition analysis

The formation of TA/Cu II complex thin layer on top of the membrane surface was confirmed by X-ray photoelectron microscopy (XPS) analysis (Table S1 and Fig. 2a,b).

Fig. 2. Survey X-ray photoelectron spectra (a) for the range 0-1050 eV and (b) narrow scan X-ray photoelectron spectra for Cu 2p region for neat PAN and TA/CuII 10PAN membrane

The appearance of a new peak at around 970 eV confirms the presence of Cu II on the modified membrane. The intensity of the O1s peak at 520 eV increases for the coated membranes. The appearance of this peak is a clear indication for successful coating of TA/CuII complexes on PAN. The elemental analysis of the membrane surface is shown in Table S1. Sequential decrease of N1s and C1s peaks and an increase in O1s peak indicates the deposition of TA/CuII on the PAN membrane surface. The O/C ratio for TA/CuII -coated surface was calculated to be 0.16, which agrees with the theoretical O/C ratio for TA. An XPS narrow scan for cu 2p region also supports the formation of TA/ CuII complex [25]. The peak intensity at 286.3 eV (C - O) was significantly increased after TA deposition, which is due to presence of abundant amount of ester and ether groups present in TA.

Cu 2p peaks are only found in the TA/CuII coated membrane, which indicates the incorporation of CuII on the membrane surface as one of the complex components. It is evident that an increased concentration of $\text{Cu}(\text{CH}_3\text{COO})_2$ increases the O/C ratio (Table S1) which in turn helps to bind more TA on the membranes surface leading to thicker coatings.

ATR-FTIR analysis further confirms the presence of tannic acid in the TA/Cu II coating (Fig.S1). Changes in peak intensity for different TA/CuII coated membranes were found for 10 min and 30 min coating.

FTIR spectra of TA, PAN support membrane and TA- copper acetate complex composite membranes are given in Fig. S1. Apart from the typical neat PAN bands of the substrate, TA and CuII membranes possessed an additional peak at 1750 cm^{-1} , which can be correlated to ester groups. Also, a shift related to the carbonyl groups ($\text{C}=\text{O}$) and the hydroxyl groups (OH) at the 1716 cm^{-1} and 3519 cm^{-1} peaks respectively was found in the FT-IR spectrum of the TA/CuII coated membrane, confirming once again the presence of the TA-metal complex. After complex

formation two –OH stretching bands, which are usually present in free TA [26] at 3599 cm^{-1} and 3502 cm^{-1} merged completely. The main reason is that most of the free –OH groups are involved in the complex formation. In addition, there was an increment in the C=O vibration in TA, which was changed from 1713 cm^{-1} (free TA) to 1739 cm^{-1} (TA in complex) [27], which indicates an interaction between the C=O of the Cu (CH₃COO)₂ and the O-H groups of TA, as a hydrogen donors. These two types of chemical energy shifts shown in FT-IR were similar to previous reported studies [23, 28], which confirms that both the C=O and –OH found in TA are key elements for the complex formation.

3.2.1. Surface morphology

In order to check the morphological changes in the membranes after coating, the surface morphology of the membranes was characterized by using scanning electron microscopy (SEM) and atomic force microscopy (AFM). Fig. 3a shows that after the TA/CuII deposition, the surface became less porous. The cross sectional image of the TA/Cu II coated membrane (Fig. 3c) shows clearly that a thin dense skin layer of approximate 30 nm is present.

Sample	R_a (nm)	R_{rms} (nm)	Contact angle (deg)
Bare PAN	2.33 ± 1.5	2.12 ± 2.5	68.0 ± 1.2
TA/ CuII 10modified PAN	2.62 ± 1.4	2.69 ± 0.8	54.5 ± 1.0

T

Table 1. Surface properties (roughness, hydrophilicity) of the bare and modified membranes.

In addition, to analyze the roughness and surface morphology of the neat PAN membranes and coated PAN membranes, AFM (Agilent Technologies) was used. AFM images of neat PAN and

coated PAN membranes are presented in Fig. 4. Fig. 4b shows the surface changes after TA/CuII coating. Average roughness (Ra) and root-mean-square roughness ($Rrms$) values increased after coating (Table 1).

Fig. 3. SEM images of the membrane (a) surfaces of neat PAN (b) TA/Cu II coated PAN and (c) TA/CuII 10 PAN membrane cross-sections

Fig. 4. 2D and 3D AFM images of (a) neat PAN and (b) TA/Cu II 10 membrane surface.

3.3. Water permeability and stability

The long term stability of the developed membranes was tested. Filtration performance was tested continuously for 20 days (Fig. 5) and the water permeance almost remained constant (46 L/m²h bar) through out the experiments, which indicates that the TA/CuII coating on PAN membranes is sufficiently stable whereas an slight decrease of water permeance for neat PAN was observed.

Fig. 5. Long term continuous water permeance tests for neat PAN and TA/CuII 10 membrane.

After TA/CuII coating the pure water permeance decreased from 170 L/m²h bar to 52 L/m²h bar. With the increase of Cu(CH₃COO)₂ concentration up to 16 mM the pure water permeance value decreased continuously; above this value a steady state was reached (Fig. 6a). A more concentrated Cu(CH₃COO)₂ solution can bind more TA on the membrane leading to

Fig. 6. (a) Variation in water permeance in coated membrane with different concentration of CuII
(b) Variation in water permeance with coating time (min)

thicker coatings [30]. Film growth is completed when all free CuII is consumed. We also analyzed the influence of coating time on membrane coating formation and membrane performance. When the coating time increased from 5 to 15 min a decreased water permeance was noticed with time but after 15 min no further decrease occurred (Fig. 6b).

3.4. Contact angle and hydrophilicity

The contact angle of neat PAN and TA/CuII 10, 20 and 30 minutes coated membranes were measured with Easy Drop, Kruess GmbH. The contact angle of neat PAN membrane was $68 \pm 1^\circ$, after coating it was decreased to $54 \pm 1^\circ$, $53 \pm 1^\circ$ and $52 \pm 1^\circ$ respectively for 10, 20, 30 minutes TA/CuII coated membranes. The contact angle of coated membranes decreased with the increase in coating time. Fig. 7a shows that the membranes became hydrophilic after coating with TA/CuII when compared with neat the PAN membrane. The time dependent contact angle reveals the

effect of TA/CuII coating on improving hydrophilicity (Fig.7b). Contact angle value for TA/CuII10 membrane slowly decreases from 54° to 45° after 4 minute and then the contact angle value gets almost stable with time.

Fig. 7 (a). Static contact angle for neat PAN membrane and the modified membranes (TA/CuII 10, TA/CuII 20 and TA/CuII 30) (b) Water contact angle of the modified membrane (TA/CuII 10) at varied time interval

3.5. Cu analysis

According to the XPS measurements, the amount of Cu^{2+} in the TA/CuII 10 membrane is 0.41 wt%. This copper content present in the membrane coating increased from 0.41% to 0.43 % and 0.48%, when the coating time was increased from 10 to 20 and 30 min. (Table S1).

3.6. Rejection behavior and molecular weight cutoff

The steady state water permeance of the neat PAN membrane was 170 $\text{L/m}^2\text{h bar}$, whereas the pure water permeance of the TA/CuII 10 coated PAN membrane was 52 $\text{L/m}^2\text{h bar}$. This flux was maintained during the 20 days measurement time as shown on Fig. 5. This is also a proof of good

mechanical stability of the membrane showing that the adhesion behavior between the PAN support and the selective complex thin layer is excellent.

The membrane's rejection was checked with a stirred dead end filtration cell at 5 bar pressure with different molecular weight PEG in aqueous solution. It is important to mention that pore size, membrane thickness, hydrophilic/hydrophobic properties as well as the degree of polymer swelling influence the rejection properties and the MWCO of the membrane [29,30].

Different aqueous solutions of polyethylene glycols (PEGs) between 400 and 1000 Da with a concentration of 1000 ppm were used as feed at 5 bar. The molecular weight cut-off of the membranes was estimated from the rejection vs. molecular weight graph (Fig.8). Furthermore, the rejection of PEG 600 confirms that the MWCO is about 600 Da.

Fig. 8. Determination of molecular weight cut off with PEG's

The rejection performance of the TA/CuII coated PAN membranes was also studied with various dyes (Protoporphyrin IX, Methyl orange and Brilliant blue) at a concentration of 0.001% (w/w) in DI water. The rejection for Protoporphyrin IX disodium salt (MW 606.24) was 97%.

Fig. 9. Rejection (%) of TA/CuII 10 PAN membrane with different molecular weight dyes.

The higher molecular weight dye Brilliant blue (MW 825.97) had a rejection 99%, and Methyl orange with a lower molecular weight (MW 327.32) was rejected to 65% (Fig.9) confirming once more that the MWCO is around 600 Da .

3.6.1. Separation of Salts

Rejection for inorganic salts such as MgSO_4 , Na_2SO_4 and NaCl was studied for the TA/ CuII coated PAN membranes. Salt rejection was checked with TA/ CuII 10, TA/ CuII 20 and TA/ CuII 30 PAN membranes and the salt concentrations were measured via conductivity. The salt rejection of the TA/ CuII coated PAN membrane is shown in Fig.10. The feed salt concentration was 0.01 mol/L. The rejection data were recorded after reaching steady state of water flux and permeate solute concentration. The inorganic salt rejection for the coated membranes followed the order $\text{Na}_2\text{SO}_4 > \text{MgSO}_4 > \text{NaCl}$. The salt rejection of NF membranes is depends usually on size and charge.. Rejection increased with coating time, which can be explained by the thicker coating layer.

Fig.10. Rejection behavior of TA/ CuII 10, TA/ CuII 20 and TA/ CuII 30 PAN membrane with different inorganic salts.

As a result, the prepared NF membranes show very high flux [31,32] with low salt rejection.

This makes the membrane attractive for the separation of organic solutes with a molecular weight of more than 600 from salts.

4. Conclusion

We prepared a high-flux nanofiltration membrane by simple co-deposition of tannic acid and copper acetate on a polyacrylonitrile ultrafiltration membrane. The adhesion of the catechol and gallol rich TA/CuII coating on top of the PAN membrane support is excellent. The membrane shows a molecular weight cut-off of around 600 Da and it exhibits a low sodium chloride rejection of around 5%. This makes the membrane attractive for many applications where organic solutes have to be desalted. The hydrophilic membrane showed no decline in water permeance over a period of 20 days.

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Supporting Information

Supporting information is available from Elsevier online library or from authors.

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Research highlights:

- Nanofiltration membranes were prepared from tannic acid/copper complexes.
- The tannic acid/ copper coating showed excellent adhesion on a PAN-support.
- The composite membranes showed a MWCO around 600 Da with low salt rejection.
- The membranes showed no flux decline over a period of 20 days.

Graphical abstract