


Amine-Terminated PAN Membranes as Anion-Adsorber Materials

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Anion-adsorbing membranes provide an interesting possibility to remove toxic arsenate and chromate from drinking water. A promising way to prepare anion-exchange materials is to introduce positively charged amine groups on polymers. In this study, polyacrylonitrile (PAN) ultrafiltration membranes were modified with amine functionalities on the membranes. The success of the modifications was demonstrated using infrared spectroscopy and zeta potential measurements. Additionally, the arsenate adsorption was analyzed. The modified membrane showed arsenate adsorption 5 times higher than the pristine PAN membrane.

Keywords: Amine modification, Anion adsorbing materials, Chromate/arsenate, PAN membranes, Water purification

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1 Introduction

Clean drinking water is a very important resource. Unfortunately, it is not accessible everywhere. Besides microbiological contaminations, pollution by geogenic and industrial chemicals like arsenate (AsO_4^{3-}) and chromate (CrO_4^{2-}) are harmful issues nowadays. Both oxyanions are naturally occurring on earth in minerals and soils. [1, 2] As a result of weather conditions or watercourses, these compounds are released and end up in drinking water. Additional pollutions, especially of chromate, also result from its numerous applications in industries like leather tanning, alloy manufacturing and chrome plating production. [3]

The leaching of chromate and arsenate is highly hazardous for humans (and nearly every other living species), since both are highly genotoxic and cause serious illnesses like cancer and fetal malformation due to oxidative and nonoxidative damage of the DNA [3, 4]. Therefore, it is important to eliminate these contaminants from drinking water completely. An interesting possibility to remove arsenate and chromate without adding chemicals to drinking water are anion-adsorbing materials [5]. Anion-adsorbing membranes are recognized, especially, since they are cost-effective, energy-saving and environmentally friendly. The adsorption is usually achieved by positively charged groups on the surface of the membranes, e.g., (quaternary) amines. [6]

In this study, we report the post-modification of polyacrylonitrile (PAN) membranes with primary, secondary, tertiary, and quaternary amines using different modification reactions. In comparison to other membrane materials PAN is chemically easier to modify, since it is carrying a nitrile group. Several modification reactions of nitrile-carrying

substances like PAN are known. [7, 8] Nevertheless, these modification reactions were usually not applied on PAN ultrafiltration (UF) membranes, which requires heterogeneous reactions in order to preserve the membrane structure.

All four membrane modifications in this study were successful as shown by an increased zeta potential. One of the membranes was applied in adsorption analysis of arsenate. The amine-modified membrane had an increased arsenate adsorption compared to the pristine PAN membranes. Therefore, amine-modified PAN membranes are promising candidates as anion-adsorbing materials for drinking water purification.

2 Experimental

2.1 Materials

Dimethylformamide, ethanol, *iso*-propanol, lithium aluminiumhydride, 1-octylbromide, tetrahydrofuran, ethylene diamine, and poly(ethylene imine) (average molecular

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weight of 600 g mol^{-1}) were purchased by Sigma Aldrich (St. Louis, MO, USA). All chemicals were used without further purification.

2.2 Preparation of PAN UF Membranes

The preparation of the PAN membranes was described elsewhere [7]. PAN is dissolved in DMF and coated on a non-woven support using a doctor blade. Subsequently, the membranes were drop-casted in water. The membranes were washed in water and dried. An overview of all modifications performed in this article is shown in Fig. 1.

2.3 Preparation of Reduced Membranes

The reduced PAN membranes (PAN-NH) were prepared by dissolving 0.4 g LiAlH_4 (LAH) in 40 mL tetrahydrofuran and adding 0.5 g of the PAN membranes (1 eq. LAH per mol of the repeating unit of PAN) under Ar atmosphere. The reaction mixture was shaken at 50 rpm for 24 h. Afterwards, the membranes were taken out of the solution and washed with THF, *iso*-propanol, water, 1 M NaOH and ethanol. Finally, the membranes were dried in an oven at 60°C and 1 mbar overnight.

2.4 Preparation of Quaternary Amine Membranes

5 mL 1-Octylbromid were dissolved in 50 mL absolute ethanol. The dried PAN-NH membranes were added to the solution. 3 eq. 1-octylbromid per mol of the repeating unit of PAN were used. The reaction mixture was heated to 90°C under reflux for 24 h. Afterwards, the membranes were taken out of the solution and washed with ethanol and water. Subsequently, the quaternary amine membranes (PAN-Q) were dried in an oven at 60°C and 1 mbar overnight.

2.5 Preparation of Ethylene Diamine Modified Membranes

The preparation of ethylene diamine modified PAN membranes (PAN-EDA) took place through a modified synthesis according to El-Newehy et al. [8]. 0.5 g of the PAN membrane were added to 50 mL ethanol and 10 mL of water. Ethylene diamine was added to the reaction mixture. Subsequently, the reaction mixture was stirred at 70°C for 24 h. Afterwards, the membranes were taken out of the solution and washed with ethanol and water. In the end, the membranes were dried in an oven at 60°C and 1 mbar overnight.

2.6 Preparation of PEI-Modified Membranes

4.2 g of branched poly(ethylene imine) with an average molecular weight of 600 g mol^{-1} (PEI 600) was dissolved in 10 mL deionized water and 50 mL ethanol completely. Subsequently, 0.5 g of the PAN membrane were added. A 10-fold molar excess of PEI 600 was used. The reaction mixture was heated to 90°C under reflux for 24 h. Afterwards, the membranes were washed with ethanol and water. In the end, the PEI-modified membranes (PAN-PEI) were dried in an oven at 60°C and 1 mbar overnight.

2.7 Attenuated Total Reflection – Fourier Transform Infrared Spectroscopy (ATR-FTIR)

IR spectra were recorded using an ALPHA II from Bruker (Billerica, MA, USA). The spectra were recorded from 400 to 4000 cm^{-1} from the average of 32 scans at a resolution of 4 cm^{-1} using a diamond probe head.

2.8 Streaming Potential Measurements

The zeta potential of the modified and non-modified membranes was determined using the streaming potential technique. The measurements were performed at room temperature using a SurPASS Eco 3 from Anton Paar (Graz, Austria). 0.01 M NaCl solution was used as electrolyte solution. The measurements were performed at different pH values between pH 3 and pH 10 using NaOH and HCl for adjusting the pH.

2.9 Water Permeance

Water permeance tests were performed using a homemade testing device in dead-end mode. The transmembrane pressure (Δp) was set to 2 bar. The diameter of the membrane was

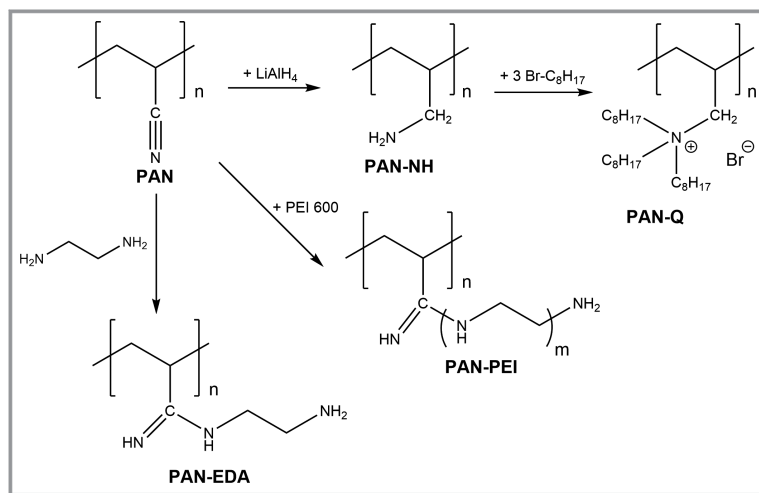


Figure 1. Overview of the reactions used in this article.

1.45 cm ($A = 2.3 \text{ cm}^2$). The water permeance was calculated by the following equation:

$$J = \frac{\Delta V}{\Delta p \Delta t A} \quad (1)$$

Ultrapure water was used for tests. The permeated volume of water ΔV was measured at room temperature after $\Delta t = 3 \text{ h}$.

2.10 Arsenate Adsorption

Adsorption experiments were performed using a 200 mL Amicon stirred cell from Millipore (Bedford, MA, USA) in dead-end mode. The diameter of the membranes was 63.5 mm (active membrane area = 28.7 cm^2). The standard solution of As(V) was H_3AsO_4 in HNO_3 (0.05 mol L^{-1}) with a concentration of 1 g L^{-1} . It was purchased from Merck chemical GmbH (Darmstadt, Germany). For filtration experiments, arsenate was diluted to $400 \mu\text{g L}^{-1}$ arsenate at pH 4.5. A constant flux of $100 \text{ L h}^{-1} \text{ m}^{-2}$ was adjusted. The arsenate concentration in the permeate solution was measured after 100, 250, 550, 750, and 950 mL of filtration.

The arsenate concentration in the permeate solution was detected using atomic absorption spectroscopy (AAS). For this, a Perkin-Elmer AAS with a Perkin-Elmer Graphite Furnace Tube atomizer was used. In order to measure total arsenic concentration, the pH of the samples was decreased to pH 2 by adding hydrochloric acid. [9] Argon gas was used to atomize the samples. The AAS setup parameters were 0.7 nm slit width, 380 mA lamp current, detection at a wavelength of 193.7 nm, and peak area as measurement mode.

3 Results

3.1 Membrane Modification

The ATR-FTIR spectra of all membranes are displayed in Fig. 2. All spectra showed an absorbance at 2240 cm^{-1} . This band was related to the stretching vibration of the nitrile ($\text{C}\equiv\text{N}$) bond in PAN. [10,11] The intensity of the nitrile band was decreased for all modified PAN membranes compared to the pristine PAN.

The spectra of all amine-modified membranes showed new bands at 3364 cm^{-1} and 1650 cm^{-1} . These bands were assigned to the stretching bands of amines and amidines ($\text{N}=\text{C}-\text{N}$) [12]. The amine and amidine bands increased, while the nitrile bands were decreasing. The presence of the amine and amidine bands and the decrease of the nitrile group of PAN showed the success of the amination reactions. The decrease of the nitrile band is higher for the membranes PAN-NH and PAN-Q compared to the PAN-EDA and PAN-PEI membranes. This indicated a higher conversion of the nitrile group in these reactions.

Additionally, all modified membranes except the PAN-Q membrane showed an N-H vibration band at 1570 cm^{-1} . The absence of the band indicated a successful reaction of the primary amine (PAN-NH) to either a quaternary or a tertiary amine.

Successful modification of the PAN membranes with amines will lead to a change of the charge of the membrane surface. Since surface charge itself cannot be measured, it is usually represented by the zeta potential. The zeta potential curves of the modified and unmodified membranes are displayed in Fig. 3. While PAN – like most polymers – has a negative zeta potential due to adsorption of hydroxyl ions on the surface [13], amine-modified surfaces usually provide a positive surface charge [14].

As expected, the zeta potential of the unmodified membrane was negative (-40 mV to -17 mV) over a broad pH range. The isoelectric point (IEP) was not detectable since it

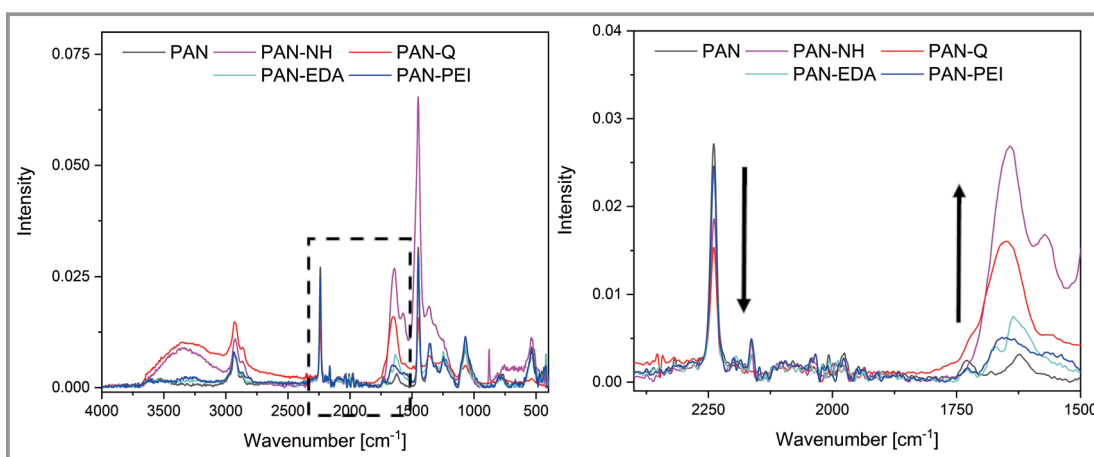


Figure 2. ATR-FTIR spectra of the pristine (black) and modified membranes. Left: complete spectra; right: detailed view on the spectral region of interest.

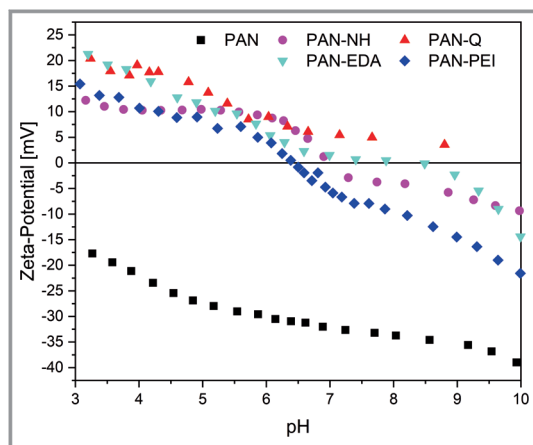


Figure 3. Zeta potential of the pristine membrane (black) and the modified membranes.

was lower than 3. The zeta potential of all modified membranes was higher. The zeta potential of the amine-functionalized PAN changed from positive values (between +12 mV and +22 mV at pH 3) at acidic pH to negative values (−17 mV to −7 mV at pH 10) at alkaline pH for all modified membranes but the quaternized one. The IEPs of these membranes was detected between pH 6.5 and 8.5. Primary, secondary, and tertiary amines as used in these modifications are deprotonated in alkaline milieu. Therefore, the zeta potential of the modified membranes was positive only at low pH values.

The quaternized membranes had a positive zeta potential over the analyzed pH range. Since quaternary amines cannot be deprotonated, the zeta potential of the PAN-Q membranes did not show an IEP. Thus, the success of all presented modifications was confirmed.

3.2 Membrane Performance

The permeance of the modified and unmodified membranes is displayed in Fig. 4. The pristine membranes showed an initial permeance of $1100 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$. The permeance decreased about 15 % (to $950 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$) during the measurement because PAN membranes were swelling slightly in water. The modified membranes showed a similar behavior. The permeance of the PAN-PEI and PAN-EDA membranes decreased slightly compared to the unmodified membranes (initial permeance of $900 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ and $1000 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$, respectively). All other modified membranes had similar or even slightly higher permeance than the unmodified PAN. However, this indicated the pore size of the membranes did not change after the post-modification extensively.

Additionally, the arsenate adsorption of one selected membrane was analyzed. PAN-EDA was chosen for the experiment. The results of the adsorption experiments were displayed in Fig. 5. The PAN-EDA membranes showed a

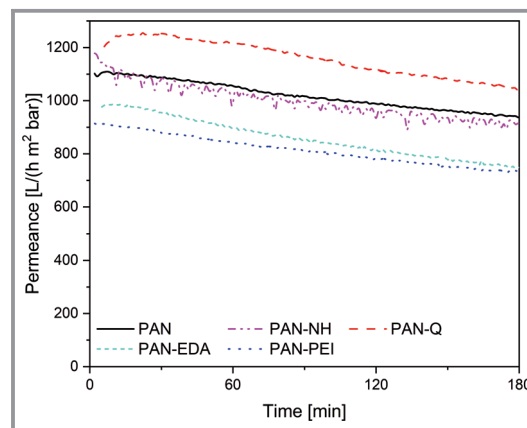


Figure 4. Water permeance of the pristine membrane (black) and the modified membranes.

successful adsorption especially considering the high arsenate concentration. While the unmodified PAN adsorbed only $0.77 \mu\text{g}$ arsenate per cm^2 membrane ($22 \mu\text{g}$ total adsorption capacity), the modified PAN-EDA membranes showed a five-time higher adsorption of arsenate ($96 \mu\text{g}$ total adsorption capacity). $3.33 \mu\text{g}$ arsenate were adsorbed per cm^2 membrane. The modified PAN-EDA membranes showed a high adsorption of arsenate in the beginning, but after 550 mL the arsenate concentration in the permeate solution reached the level of the feed solution.

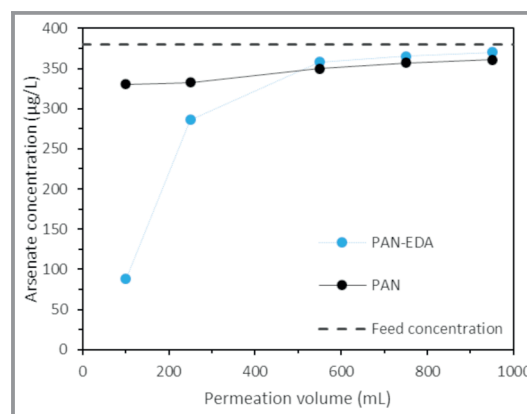


Figure 5. Arsenate adsorption at pH = 4.5 of the PAN-EDA membrane compared to the pristine PAN membrane.

Considering the fact that the arsenate concentrations in drinking water is usually between 50 and $100 \mu\text{g L}^{-1}$ the adsorption of the PAN-EDA membranes was very promising [15]. The results presented here indicated that the modified membranes adsorb arsenate even if the feed concentrations are higher.

4 Discussion

In this study, PAN membranes were presented as interesting materials for post-modification with amine groups. In total four different successful modifications were displayed. The membranes were modified using primary amines (PAN-NH), secondary and tertiary amines (PAN-EDA and PAN-PEI), as well as quaternary amines (PAN-Q). The success of the modifications was demonstrated using IR spectroscopy and zeta potential measurements. The zeta potential of the membranes increased after modification. All membranes except the one modified with the quaternary amine showed an IEP between pH 6.5 and 8.5. The membrane PAN-Q had a positive zeta potential in the total analyzed pH range and had, therefore, no IEP.

The water permeation of the modified membranes did not change significantly compared to the unmodified PAN. This indicated the structure of the membranes were not changing after the modification procedure. For one selected membrane, the arsenate adsorption was analyzed additionally. The membrane PAN-EDA showed an arsenate adsorption five-times higher than the unmodified membrane. Considering the high concentration of the arsenate feed solution, these results were very promising for drinking water applications. In the future, further studies of these materials will be performed. The adsorption of other toxic anions like chromate will be analyzed as well as the performance of the membranes in real water (containing natural organic matter or other anions).

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Symbols used

A	[cm]	Area of the membrane
J	[L m ⁻² h ⁻¹ bar ⁻¹]	Membrane permeance
Δp	[bar]	Transmembrane pressure
t	[min]	Time
ΔV	[mL, L]	Filtrated volume

Abbreviations

ATR-FTIR Attenuated total reflection – Fourier transform infrared spectroscopy

IEP	Isoelectric point
PAN	Unmodified polyacrylonitrile
PAN-EDA	Polyacrylonitrile modified with ethylene diamine
PAN-NH	Modified polyacrylonitrile carrying a primary amine group
PAN-PEI	Polyacrylonitrile modified with poly(ethylene imine)
PAN-Q	Modified polyacrylonitrile carrying a quaternary amine group
UF	Ultrafiltration

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Research Article: In this study, polyacrylonitrile (PAN) membranes were modified to create positively charged amine groups on the surface. The success of the modifications was demonstrated by an increased zeta potential of the membranes. Additionally, the arsenate adsorption was analyzed to be 5 times higher compared to the pristine membrane.

