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Adsorptive dead-end filtration for removal of Cr(VI) using novel amine modified polyacrylonitrile ultrafiltration membranes

Tomi Mantel, ‡^{*a} Sarah Glass, ‡^b Muhammad Usman, ^a
Anastasios Lyberis, ^a Volkan Filiz ^b and Mathias Ernst ^a

The present study investigates the concept of combining the processes of ultrafiltration (UF) and ion exchange into one single filtration step. By this, particulate matter and dissolved toxic hexavalent chromium (Cr(VI)) ions are removed by adsorptive dead-end filtration. For this purpose, we modified a conventional polyacrylonitrile (PAN) UF membrane with two methods to generate weak-base and strong-base anion exchanger functional groups on the membrane surface and in its pore structure. The pristine PAN membranes were chemically modified to generate primary (PAN-NH) and quaternary (PAN-Q) amine groups. Pristine PAN, PAN-NH and PAN-Q membranes were characterized and compared regarding their chemical and mechanical properties. The modified PAN membranes were tested in chromium filtration experiments at pH 5.5, pH 7 and pH 8.5. The fully loaded membranes were regenerated by caustic solution for desorption of the chromium. The effect of the membrane modifications on the pure water permeability, contact angle and BET surface was negligible. However, the charge of the membrane was affected significantly seen by the reversal of zeta potential from negative to positive values after modification. The filtration experiments revealed that the total adsorption capacities of PAN-NH and PAN-Q membranes are 151 mg and 145 mg Cr(VI) per m² membrane surface after complete membrane saturation ($C_{\text{reed}} = C_{\text{permeate}}$), respectively. When compared with pristine PAN and PAN-Q membrane, the PAN-NH membrane has demonstrated high removal rates (>90%) for Cr(VI) in the first ten hours of filtration and thus more relevant for application-orientated membrane water treatment systems. Desorption of previously adsorbed Cr(VI) was achieved by filtering a regeneration solution (1 M NaCl and 0.01 M NaOH) through the loaded membranes. After regeneration, the adsorption capacity was almost completely recovered. The findings of this study verify that low-pressure amine-modified PAN membranes provide an effective and energy-efficient way to process Cr(VI) contaminated water for possible drinking water purposes.

Water impact

The presence of hexavalent chromium in raw water resources poses a major challenge to water suppliers around the world, since highly toxic hexavalent chromium cannot be sufficiently removed by conventional water treatment processes such as aeration, media filtration or coagulation flocculation. With the present work we are investigating the approach of removing Cr(VI) with an novel adsorptive UF membrane.

1. Introduction

The presence of hexavalent chromium in raw water resources poses a major challenge to water suppliers around the world, since highly toxic hexavalent chromium cannot be

^aInstitute for Water Resources and Water Supply, Technische Universität Hamburg, Am Schwarzenberg Campus 3E, 21071 Hamburg, Germany.

E mail: tomi.mantel@tuhh.de

^bInstitute of Membrane Research, Helmholtz Zentrum Hereon, Max Planck Str. 1, 21502 Geesthacht, Germany

‡ These authors contributed equally to this work.

sufficiently removed by conventional water treatment processes such as aeration, media filtration or coagulation-flocculation.¹ Chromium species can be present naturally in groundwater through the erosion of geological formations that promote the release of chromium into groundwater exist on all continents.² In the U.S. alone, the water supplies of millions of people is based on aquifers that exhibit elevated concentrations of chromium.^{3,4} In addition to geological reasons, chromium also enters drinking water resources through pollution from multiple industries (e.g., chrome plating, leather tanning etc.).⁵ In aqueous solutions, chromium is present in the neutral pH range as trivalent

(Cr(III)) or hexavalent form (Cr(VI)).⁶ While Cr(III) compounds in small amounts are essential for metabolic processes in the human body, Cr(VI) compounds are highly problematic as they are carcinogenic.⁷ In the natural environment, Cr(VI) is the most dominant chromium species and it occurs in the oxyanionic form as chromate depending on redox potential and pH conditions.² In drinking water sources, Cr(VI) is typically present as monovalent chromate (HCrO_4^-) at pH-values below 6.5 and divalent chromate (CrO_4^{2-}) at pH conditions above 6.5 most relevant to drinking water supply.^{2,8} In contrast to Cr(III), Cr(VI) cannot be precipitated by shifting the pH to alkaline or acidic values.^{9,10}

To abate toxic effects of chromium on humans, many regulation authorities (e.g., World Health Organization; European Commission) have put in place a maximum contamination limit (MCL) of $50 \mu\text{g L}^{-1}$ for total chromium in drinking water.^{11,12} However, the chromium concentration of groundwater resources in many regions of the world exceed the MCL (e.g. in Greece Cr(VI) concentrations in aquifers reach up to $>100 \mu\text{g L}^{-1}$).⁴

Different water treatment technologies have proved to be effective to minimize the Cr(VI) levels below MCL in natural waters. The most relevant technologies are Cr(VI) adsorption onto activated carbon,^{13,14} rejection by high-pressure membrane processes,¹⁵⁻¹⁷ chemical Fe(II)-reduction of Cr(VI) to Cr(III) combined with precipitation^{9,10} and (strong- or weak-base) anion exchange.¹⁸ However, these technologies are complex to operate and expensive due to high operation costs.⁵ For these reasons, the removal of chromium from drinking water sources is still a problem today in many regions of the world.

In general, membrane processes are regarded as promising methods for the purification of raw waters that are difficult to treat.¹⁹ However, only the dense nanofiltration and reverse osmosis membranes are capable of removing dissolved substances such as Cr(VI) ions. Dense membranes have the disadvantages that they are energy-intensive, require high pressures and have a relatively low recovery rate due to the necessary cross-flow operation.²¹

The aim of this work is to study a new porous membrane process that may remove Cr(VI) by adsorption during a simple and effective dead-end filtration.²⁰ For this purpose, a conventional energy-efficient low-pressure ultrafiltration (UF) membrane was modified with two different anion exchanger groups to generate an adsorption capacity for Cr(VI) oxyanions. Polyacrylonitrile (PAN) was chosen as the membrane material because, unlike other commonly used materials such as PES and PVDF, PAN has the advantage that it can be easily chemically modified.²² This is due to the nitrile group of the PAN monomer, which were reduced to amine groups. The modification of PAN membranes with different anion exchanger groups was reported in a previous publication.²³ In the present study, the PAN membranes were synthesized by reducing the nitrile group to primary (PAN-NH) and quaternary amine (PAN-Q) groups in order to generate weak- and strong-base anion exchanger properties, respectively.

By the combination of the two processes of Cr(VI) adsorption and UF, several treatment tasks might be achieved. On the hand, the dissolved chromium ions should be removed by physical adsorption to the membrane surface. On the other hand, microbiological pathogens such as bacteria and viruses as well as other suspended solids are removed by the UF process.²⁴⁻²⁶ Another advantages of UF membranes with selective adsorptive properties would be the simple operation of low-pressure UF membranes, low footprint/space requirements, relatively low energy demand and therefore low operating costs ($0.8-1.0 \text{ US } \$ \text{ per m}^3$) at moderate capital costs.²⁷

In the last years, several studies reported on the modification of PAN membranes. One work attempted to hydrolyze PAN membranes with NaOH in order to increase the negative surface charge for better Cr(VI) rejection in cross-flow operation.²⁸ Another work modified PAN membranes with quaternary amines *via* electrospinning for protein separation²⁹ and with triethylenetetramine for CO_2 adsorption.³⁰ An additional study reported on the ethanolamine modified-PAN UF membrane with antifouling properties.³¹ An literature overview on Cr(VI) removal approaches with PAN UF membrane is given in Table S1.† To the best knowledge of the authors, no other study has reported the Cr(VI) removal method presented in the present work.

2. Materials and methods

2.1 Materials

Sodium hydroxide, γ -butyrolactone and ethanol were purchased from Merck KGaA (Darmstadt, Germany). PAN powder was obtained from DOLAN (Kelheim, Germany). Sodium chloride, hydrochloric acid, polyethylene glycol, dimethylformamide, ethanol, iso-propanol, lithium aluminiumhydride, 1-octylbromide and tetrahydrofuran were purchased by Sigma Aldrich (St. Louis, MO, USA). All chemicals were used without further purification.

2.2 Membrane preparation and modification

The PAN membranes (Fig. 1) were prepared by non-solvent induced phase separation as described elsewhere.²⁶ In short, PAN powder was dissolved in dimethylformamide and γ -butyrolactone. The solution was coated onto a non-woven support using a doctor blade (gap size = $400 \mu\text{m}$). Afterwards, the polymer solution was drop-casted in water. The membranes were washed in water and dried. The dry membranes had a thickness of approximately $150 \mu\text{m}$ (active and support layer; Fig. S5†).

The amine-modified membranes were prepared in two steps. First, the nitrile group of PAN was reduced (PAN-NH) and subsequently, the newly formed primary amine groups were alkylated (PAN-Q).²³

In detail, PAN-NH membranes were prepared by adding lithium aluminiumhydride equimolar to the pristine PAN membranes (Fig. 1A). Tetrahydrofuran (anhydrous) was added under argon atmosphere. After shaking the reaction

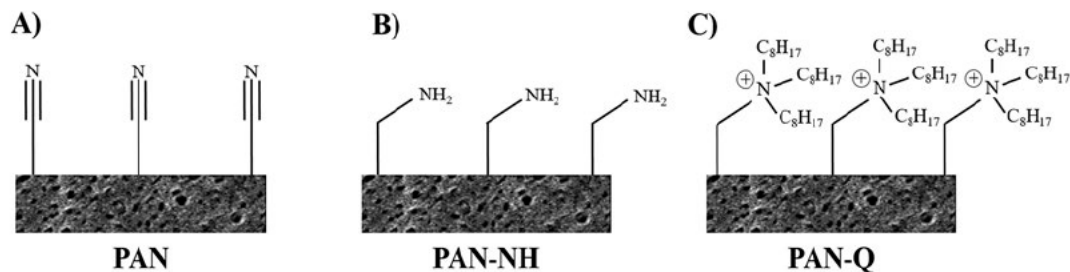


Fig. 1 Modification of PAN membranes, A) pristine PAN with nitrile group, B) reduced PAN with primary amine group, C) quaternized PAN Q with quaternary amine groups.

mixture at 50 rpm for 24 h, the membranes were taken out and washed intensely in tetrahydrofuran, isopropanol, water and 1 M NaOH. Finally, the membranes were dried at 60 °C in vacuum (Fig. 1B).

In a further step, PAN-Q membranes were synthesized. The reduced PAN-NH membranes were placed in absolute ethanol and a 3 molar excess of 1-bromooctane was added. The reaction mixture was heated at 90 °C for 24 h under reflux conditions. Afterwards, the membranes were taken out of the reaction solution and washed in water and ethanol. In the end, the membranes were dried at 60 °C in vacuum (Fig. 1C).

2.3 Membrane characterization

The membranes were characterized using water permeability measurements, water contact angle measurements, molecular weight cut-off and BET measurements.

Water contact angle (WCA) was measured in sessile drop mode using a drop shape analyzer DSA 100 from Krüss (Hamburg, Germany). Here, one drop (2 μl) of water was placed on the membrane. The form of the drop was recorded with a camera. Since the water drop is soaked in the membrane only the initial water contact angle was measured using the first single frame of the movie. The measurement was repeated for at least 3 independent samples and the values were averaged.

Water permeability measurements were performed using a homemade device in dead-end mode. The transmembrane pressure (Δp) was set to 2 bar. Membranes with a diameter of 1.45 cm ($A = 2.3 \text{ cm}^2$) were used. The water permeability was calculated by eqn (1):

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

Ultrapure water was used in the measurement. The permeated volume of water ΔV was measured at room temperature every minute (Δt) to determine the permeance. The measurement was performed for a total time of 5 h.

BET surface was calculated from nitrogen adsorption-desorption experiments. Between 0.30 and 0.65 g of the membranes were cut in small stripes and placed in the measurement cell. The measurements were performed using an ASAP 2000 from Micromeritics (Norcross, GA,

USA). Full adsorption isotherms with subsequent gas desorption were recorded.

The molecular weight cut-off (MWCO) of the membranes was determined by filtering solutions of polyethylene glycols (PEG) with different molecular weight in water in a dead-end cell through the membranes. To avoid concentration polarization, the feed solution was stirred with a stirring speed of 300 rpm. The MWCO was defined as the smallest molecular weight, which was rejected to more than 90%. PEGs with an average molecular weight of 359, 222 and 106 kDa were used (PSS Polymer Standards Service GmbH, Germany). The concentrations of PEG in the feed and the permeate were measured by gel-permeation chromatography.

2.4 Chemical characterization

The success of the chemical modification was analyzed using attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) and zeta potential measurements (using streaming potential method). Additionally, the amine content was analyzed by acid-base titration.

ATR-FTIR spectra were recorded using an ALPHA II from Bruker (Billerica, MA, USA) with a diamond probe head. The spectral range was 400 to 4000 cm^{-1} , the resolution was 4 cm^{-1} .

The zeta potential of the 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). 1 mM NaCl solution was used as electrolyte solution. The pH was adjusted using 0.1 M NaOH and HCl. The zeta potential values were measured between pH 3 and pH 9.

The amine content of the membranes was determined by titration.³² One membrane with a diameter of 7.5 cm (containing 150 mg PAN) was first immersed in 50 ml of water. After 30 min of immersion the pH value of the solution was checked to preclude contamination of the sample. Subsequently, 20 μmol HCl were added and allowed to protonate the amine groups on the membrane for 90 min. Afterwards, the membranes were taken out of the solution and rinsed briefly. The remaining amount of protons was determined by titration with 2 mM NaOH. Methyl red was used as an indicator. The measurements of each modified membrane were repeated for three independent samples and the values were averaged. The total amount of quaternized

was calculated to be the difference between the amine content before and after quaternization, since the quaternized amine group (Fig. 1C) cannot be determined using the titration method. However, the total amount of amine groups had to be the same for both membranes because no amine groups were synthesized or degraded during the quaternization reaction.

2.5 Dead-end filtration of hexavalent chromium

Filtration experiments were carried out in a non-stirred dead-end filtration cell (Fig. 2), which has an active membrane area of 28 cm² (Amicon® Model 8200, Merck Millipore, Darmstadt, Germany). The filtration flux was kept constant at 100 L (m² h⁻¹) for 24 h with a fully automated pilot plant (Hydra, Convergence, Enschede, Netherlands). The transmembrane pressure (TMP) was automatically adjusted by the gear pump of the pilot plant with TMP in the range of 0.12–0.25 bar. Permeate samples were collected automatically in intervals of 60 minutes (Fraction Collector, Lambda Laboratory Instruments, Baar, Switzerland) and analyzed for Cr(VI) concentrations. All experiments were carried out in triplicate.

Feed solutions. According to the literature, Cr(VI) concentrations in groundwater can reach up to 100 µg L⁻¹.³³ In order to evaluate the adsorption capacity of the virgin PAN, PAN-NH and PAN-Q, 100 µg L⁻¹ Cr(VI) was dissolved in pure water. Hexavalent chromium was added as K₂Cr₂O₇ which was first dissolved in a stock solution. Additionally, 1 mmol L⁻¹ NaCl was added to the solution to increase the ionic strengths of the feed solution. Afterwards, the pH was adjusted by dosing 0.1 M NaOH or 0.1 M HCl to reach the desired pH values of pH 5.5, pH 7.0 and pH 8.5. At pH 7.0 and pH 8.5, the dominant chromium species was CrO₄²⁻ and at pH 5.5 next to CrO₄²⁻, Cr₂O₇²⁻ and HCrO₄ are present in the feed solution additionally.

2.6 Adsorption isotherms

Dead-end filtration experiments in a closed-loop were carried out in order to record the adsorption isotherms of the

modified PAN-NH and PAN-Q membranes for Cr(VI). The scheme of the laboratory installations for dead-end UF experiments by continuous recirculation of Cr(VI) contaminated water is shown in Fig. 3A. To generate data for the isotherm experiments, six different Cr(VI) start concentrations were filtered at a flowrate of 5 ml min⁻¹ through the PAN-NH and PAN-Q membranes in a closed-loop until the concentration in the feed tank was not changing anymore (adsorption equilibrium was obtained). The volume of the feed tank was 1 L and the start concentrations were 100, 200, 300, 400, 500 and 600 µg L⁻¹ Cr(VI) at pH 7 (Fig. 3A).

For the equilibrium adsorption isotherms of Cr(VI), two types of isotherm models (Langmuir and Freundlich) were applied using eqn (2) and (3) below,

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \quad (2)$$

where C_e is the equilibrium/residual Cr(VI) concentration in the solution; q_{\max} is maximum adsorption value for capacity; b is the Langmuir adsorption constant.

$$q_e = K_F C_e^n \quad (3)$$

where K_F is the Freundlich capacity constant and n is the heterogeneity factor. The values of C_e and q_e were calculated using the experimental isotherm data and all the constants in both equations were determined using non-linear regression analysis.

2.7 Membrane regeneration experiment

After the adsorption capacity was exhausted, the PAN-NH and PAN-Q membranes were regenerated by desorption of the previously adsorbed chromium (Fig. 3B). This was achieved by rinsing the used membrane with the regeneration solution. The regeneration solution contained 1 M NaCl and 0.01 M of NaOH in order to increase the ionic strength and the pH value. The rinsing was achieved by simple dead-end filtration of 1 L of the regeneration solution through the loaded membrane with a flux of 100 L

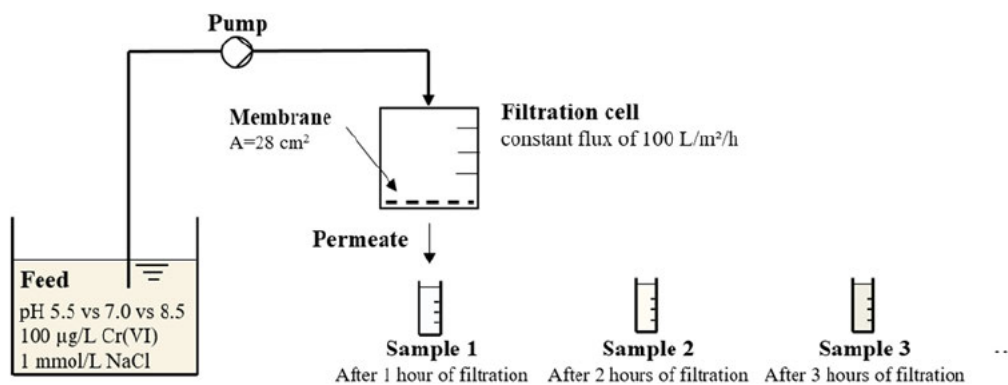
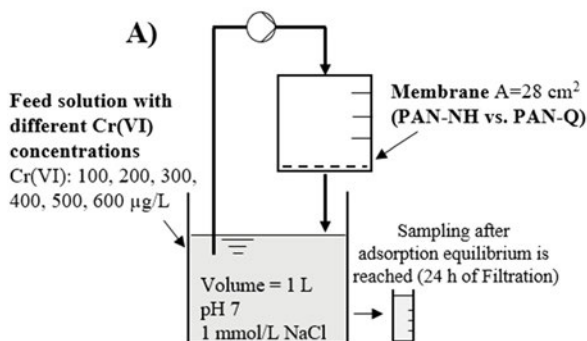


Fig. 2 Dead end filtration with amicon cell, membrane surface 28 cm², constant flux 100 L m⁻² h⁻¹, permeate samples were collected every 60 min and analyzed for hexavalent chromium concentration.

Adsorption isotherms



Regeneration of exhausted membranes

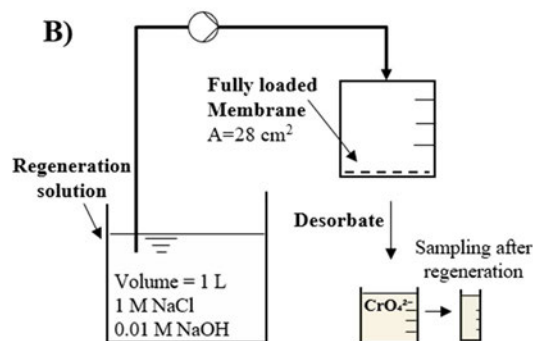


Fig. 3 Experimental set up for A) adsorption isotherm experiments and B) regeneration of exhausted membranes.

$\text{m}^2 \text{h}^{-1}$. The filtration time was 3 hours. Experiments were carried out in duplicate.

2.8 Determination of Cr(vi) concentration

Cr(vi) concentrations in feed and permeate samples were measured photometrically applying the diphenylcarbazide (DPC) method (Spectrophotometer DR5000, Hach Lange, Germany).⁸ For this, 400 μL DPC solution and 400 μL sulfuric acid (2 M) were added to the samples (20 mL) and absorbance at a wavelength of 540 nm was measured.

3. Results and discussion

3.1 Membrane characterization

Firstly, the membranes were analysed regarding their chemical properties and membrane characteristics before and after modification. The success of the chemical modification of the PAN membranes is shown by zeta potential data (Fig. 4) as well as FTIR measurements (Fig. S2[†]). The zeta potential of the membranes was increased

after the amination of the nitrile groups.²³ While pristine PAN showed zeta potential values between -35 and -22 mV, the modified membranes had zeta potential values between -6 and +21 mV in case of PAN-NH and +8 and +21 mV in case of PAN-Q. The isoelectric point of PAN-NH was at pH 7.5. Pristine PAN and PAN-Q had no isoelectric point, since their zeta potential was completely negative (PAN) or positive (PAN-Q), respectively. Table S1[†] displays the zeta potential of the analysed membranes at pH 5.5, 7.0 and 8.5, which were used in the Cr(vi) adsorption experiments (see section 3.2). At pH 5.5 and 7.0 the modified membranes PAN-NH and PAN-Q had a positive zeta potential while pristine PAN was negatively charged. Since the primary amine-modified PAN-NH was deprotonated and had an isoelectric point at pH 7.5, its zeta potential was negative at pH 8.5. The quaternary amine-modified PAN-Q on the contrary was still positively charged at pH 8.5 because the alkylated amine groups cannot be deprotonated.

Additionally, the formation of the amine groups was confirmed by IR spectroscopy (Fig. S2[†]). The pristine PAN membranes showed a prominent signal at 2244 cm^{-1} . This signal was related to the $\text{C}\equiv\text{N}$ stretching vibration. After modification the signal decreased because of the consumption of the nitrile groups and formation of the amine groups.³⁴⁻³⁶ At 1650 cm^{-1} a signal appeared after modification, which corresponded to the newly formed C-N bond of the amine groups. This signal was present for both membrane modifications. PAN-NH membranes showed an additional signal at 1577 cm^{-1} . The PAN-Q membranes, which contains quaternary amine did not show that signal, because it corresponded to the N-H stretching vibrations, which is only present in the primary amine groups of PAN-NH.

Furthermore, the degree of modification was determined by measurement of the amount of amine groups on the membranes using acid-base-titration. The amount of amine groups with respect to the membrane area is displayed in Fig. 5. Even before modification, a protonation of the PAN membrane was measured, which corresponds to a small amount of amine groups of $0.75 \pm 0.1 \text{ mmol m}^{-2}$. Since PAN is not having amine groups on its surface this protonation

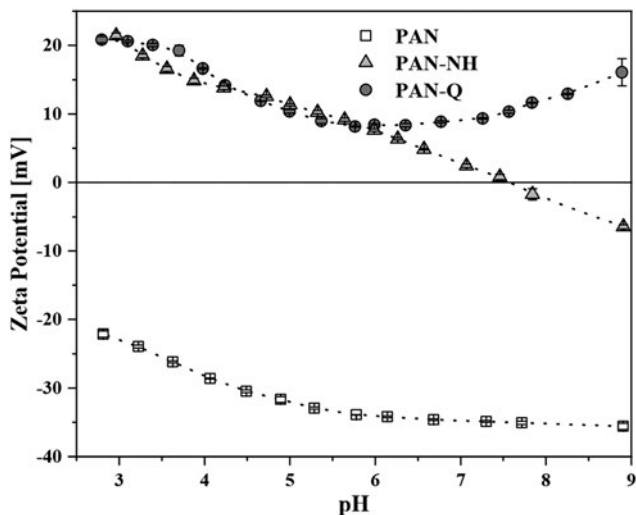


Fig. 4 Zeta potential of PAN Q (circles), PAN NH (triangles) and pristine PAN (squares) membrane.

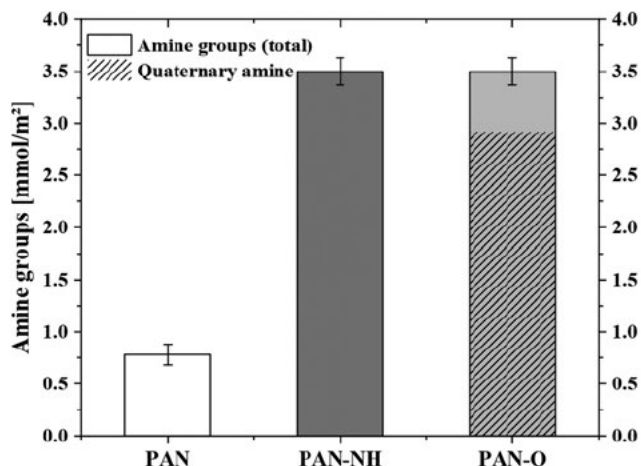


Fig. 5 Determined amount of amine groups per membrane area. Total amount of amine groups (including primary and quaternary amines) on the pristine and modified membranes in grey. Dashed pattern displayed the amount of quaternary amine groups.

was most likely due to an unspecific interaction of the membrane (or the membrane support) and the protons used during the titration. The total amount of amine groups after modification was determined to be $3.5 \pm 0.1 \text{ mmol m}^{-2}$ for both membranes PAN-NH and PAN-Q. The total amount of amine groups was the same for both membranes since PAN-Q was synthesized from PAN-NH by quaternization of the primary amine groups. In PAN-Q membranes the amount of quaternized amines was determined to be $2.9 \pm 0.1 \text{ mmol m}^{-2}$. Therefore, more than 80% of the primary amine groups were completely alkylated in PAN-Q.

In Table 1, membrane properties like water contact angle (WCA), BET surface and molecular weight cut-off (MWCO) of pristine and modified membranes are shown. Neither the BET surface nor the MWCO were affected by the modification significantly. BET surface area of all investigated membranes was found in the range of $13\text{--}14 \text{ m}^2 \text{ g}^{-1}$ (Table S3†), which is in accordance with literature data of UF flat-sheet membranes.³⁷ The MWCO of pristine and modified membranes was measured in the range of 359 kDa (Fig. S1†), which is in the region of conventional UF membranes.

The WCA of pristine PAN membranes was $51.8 \pm 3.3^\circ$. The first modification step - the formation of the primary amine (PAN-NH) - did not change the WCA. However, the quaternization of the amine groups using an octyl residue (PAN-Q) increased the WCA slightly to $65.1 \pm 1.5^\circ$. Therefore, the membranes were marginally more hydrophobic. The increased hydrophobicity may be caused by the relatively long

Table 1 Membrane properties of the pristine (PAN) and modified membranes (PAN NH and PAN Q)

Membrane	BET surface [$\text{m}^2 \text{ g}^{-1}$]	MWCO [kDa]	WCA [$^\circ$]
PAN	13.07 ± 0.18	359	51.8 ± 3.3
PAN NH	14.35 ± 0.09	359	48.9 ± 4.2
PAN Q	13.23 ± 0.03	359	65.1 ± 1.5

and hydrophobic alkyl chain used for quaternization. However, the higher hydrophobicity did not influence the membrane performance regarding permeability (Fig. 6).

The pure water permeability of the pristine PAN membranes was measured as $900 \pm 40 \text{ L m}^{-2} \text{ h}^{-1}$ (Fig. 6 and S3†). The permeability of the PAN-Q membrane was not significantly decreased by the modification. However, a slight decrease of permeability was observed for the PAN-NH membrane for unknown reason. Since the membranes were still open-pored after modification, the water permeability was not influenced substantially.

In conclusion, pristine and modified PAN membranes showed the characteristics (permeability, MWCO) of a conventional UF membrane. Using an empirical correlation between MWCO and membrane pore size, the nominal pore size can be estimated to be 35–40 nm.³⁸ It has been described elsewhere that this kind of PAN membranes will show high removal rates for particles and bacteria that are commonly found in raw waters.²⁶ Also SEM investigation of the pristine and modified PAN membrane did not show a visual change of the membrane morphology and pore size (ESI,† Fig. S4 and S6). Nevertheless, the chemical properties of the membranes were changed by the introduction of amine groups into the membranes structure. The modified membranes had a high amount of amine groups on their surface and therefore, an increased zeta potential. The completely positively charged PAN-Q membranes were containing quaternary amine groups, which are well investigated as strong base anion exchange groups. In contrast, the primary amine of the PAN-NH membranes is known as a weak-base anion exchange group.

3.2 Adsorption isotherms

Fig. 7 shows the Freundlich (Fig. 7A) and Langmuir (Fig. 7B) adsorption isotherms and the relevant parameters (Freundlich: K_F , n ; Langmuir: q_{max} , b) at pH 7. Since the actual mass of the aminated and quaternized PAN was not

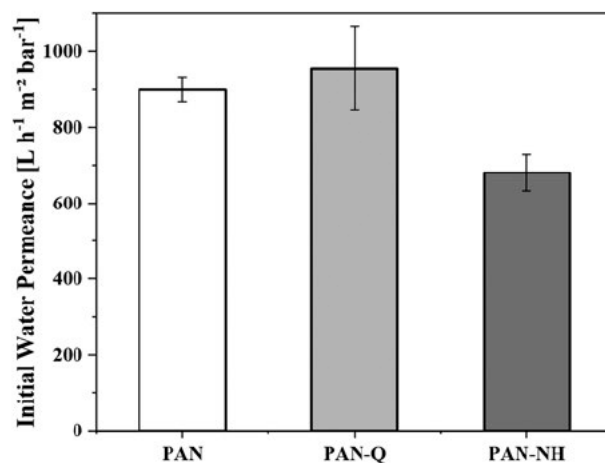


Fig. 6 Pure water permeability of pristine PAN, PAN Q and PAN NH membrane.

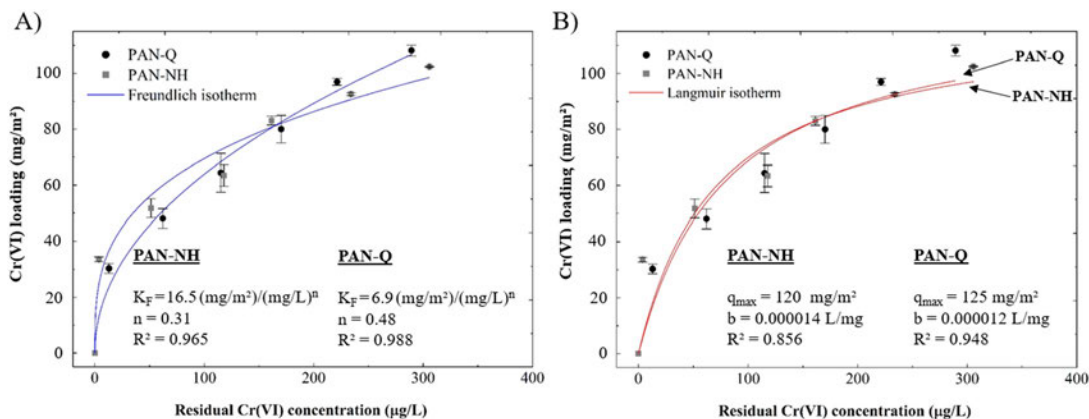


Fig. 7 Adsorption isotherms of Cr(vi) for PAN NH and PAN Q membranes and relevant isotherm parameters A) Freundlich isotherm; B) Langmuir isotherm.

known, the amount of adsorbed Cr(vi) was related to the membrane area (with the unit $\mu\text{g m}^{-2}$). For both modified PAN membranes, the adsorption phenomena was better described by the Freundlich isotherm ($R^2 > 0.96$) than by the Langmuir isotherm.

The isotherm experiments revealed that at starting concentrations below $600 \mu\text{g L}^{-1}$ Cr(vi), the PAN-NH membrane adsorbed more Cr(vi) and at starting concentrations above $600 \mu\text{g L}^{-1}$, the PAN-Q adsorbed more Cr(vi). However, the adsorption capacity parameter of Freundlich isotherm for PAN-NH [$K_F = 16.5 (\text{mg m}^{-2})/(\text{mg L}^{-1})^n$] membrane was higher than that of PAN-Q membrane [$K_F = 6.9 (\text{mg m}^{-2})/(\text{mg L}^{-1})^n$]. Similarly, the value of the constant “n”, which is a parameter describing the “adsorption intensity” of the material, is lower for the PAN-NH ($n = 0.31$) membrane than the PAN-Q membrane ($n = 0.48$). It is relevant to mention that a lower value of n is favourable as it indicates a strong adsorption intensity between Cr(vi) and adsorptive material.³⁹ Due to lower the n-value of the Freundlich isotherm, adsorption kinetics of Cr(vi) onto PAN-NH ($n = 0.31$) is faster than the PAN-Q ($n = 0.48$) membrane. This can also be seen by the shape of the breakthrough curve in Fig. 8 and 9 (chapter 3.3). The

breakthrough curve of the PAN-NH membrane (Fig. 8A) is closer to an ideal S-shaped curve⁴⁰ and thereby, showing higher removal rates up in the beginning of the adsorption process.

Adsorptive materials are generally evaluated according to the adsorption capacity that corresponds to a regulation limit of a specific hazardous pollutant. Accordingly, the index Q_{50} is defined, which represents the adsorption capacity at residual Cr(vi) concentration of $50 \mu\text{g L}^{-1}$. In this work, the value Q_{50} is calculated by setting $C_e = 50 \mu\text{g L}^{-1}$ in the Freundlich isotherm equation ($Q = K_F(C_e)^n$). The calculated Q_{50} values are 55.3 mg m^{-2} and 45.1 mg m^{-2} for the PAN-NH and PAN-NH membranes, respectively.

3.3 Filtration experiments for Cr(vi) adsorption

The filtration experiments revealed that both membrane modifications show an increased adsorption capacity for Cr(vi) when compared to pristine PAN (Fig. 8). The total adsorbed Cr(vi) mass was $151 \pm 10 \text{ mg m}^{-2}$ of membrane surface for the PAN-NH membrane and $145 \pm 6 \text{ mg m}^{-2}$ of membrane surface for the PAN-Q membrane. Whereas, the pristine PAN membrane only showed an Cr(vi) adsorption of

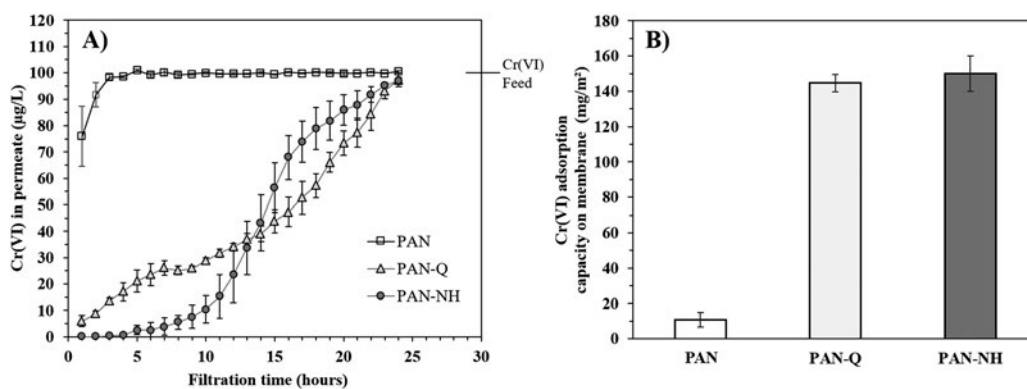


Fig. 8 Cr(vi) adsorption of PAN membranes (A) Cr(vi) concentration of permeate samples at dead end filtration; feed: $100 \mu\text{g L}^{-1}$ Cr(vi), pH 7.0, 1 mmol L^{-1} NaCl, constant flux of $100 \text{ L m}^{-2} \text{ h}^{-1}$; (B) total Cr(vi) adsorption capacity; $n = 3$, error bars represent standard deviation.

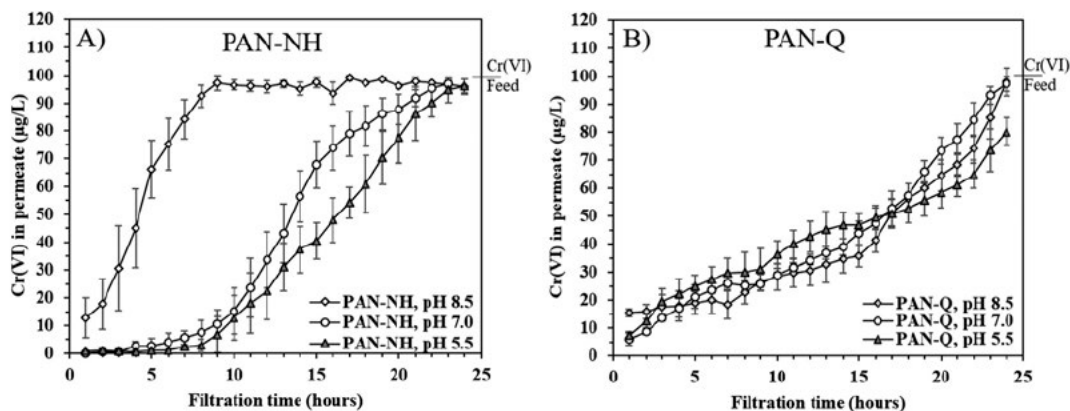


Fig. 9 Impact of the feed solution pH on the Cr(vi) adsorption: (A) filtration with PAN NH; (B) filtration with PAN Q membrane; feed: $100 \mu\text{g L}^{-1}$ Cr(vi), 1 mmol L^{-1} NaCl, pH 5.5, pH 7.0, pH 8.5 filtration at constant flux of $100 \text{ L (m}^{-2} \text{ h}^{-1})$; $n = 3$, error bars represent standard deviation.

$10 \pm 5 \text{ mg m}^{-2}$. The total adsorption capacities (Fig. 8B) correlate with the results from the determination of the amount of the amine groups (Fig. 5), which also indicated that even the pristine PAN membrane should show some adsorption capacity for Cr(vi). In total, the modifications led to an adsorption capacity of 2.9 and $2.8 \text{ mmol Cr(vi) per m}^2$ of membrane surface for the PAN-NH and PAN-Q membranes, respectively.

In general, the PAN-NH membrane showed a faster adsorption kinetic for Cr(vi) with a removal rate higher than 95% in the first 7 hours of dead-end filtration. In contrast, for filtration with the PAN-Q membrane, the Cr(vi) removal rate was less than 95% from the beginning of the filtration experiment. Moreover, for the PAN-Q membranes, the breakthrough curve was less S-shaped and more linear when compared to PAN-NH membranes (Fig. 8A). This led to a more constant increase of Cr(vi) concentration in the permeate during the filtration.

Considering the zeta potential measurements (Fig. 4) and the strong-base functional group, the PAN-Q membrane should actually have a stronger electrostatic attraction, which should lead under similar geometric conditions to a faster adsorption kinetic and higher Cr(vi) adsorption capacity. The lower performance of the PAN-Q membrane might be explained by the fact that not all quarterized amine groups were available for the adsorption process due to a steric hindrance effects.⁴¹ As seen in Fig. 1C, the quarterisation of amine groups leads to the attachment of numerous atoms to the amine group, which may lead to a shortage of space at the anion exchanger group.

Moreover, the permeability of the membranes were not affected by the adsorption of chromate, since the permeability was not significantly decreased during the experiments. Therefore, it can be concluded that the attachment of Cr(vi) ions does not lead to a significant narrowing of the membrane pores.

Effect of solution pH. In general, the pH affects both the Cr(vi) species present in the solution and the surface charge of the membranes. At pH 5.5, the monovalent HCrO_4^- is

predominantly present, at pH 7.0, the monovalent and the divalent CrO_4^{2-} are present simultaneously, and at pH 8.5, CrO_4^{2-} is predominantly present. Accordingly, the pH of the feed solution had a strong impact on the Cr(vi) adsorption capacity of the PAN-NH membrane (Fig. 9A). At pH 5.5, pH 7.0 and pH 8.5 the start of breakthrough began after 11 h, 6 h and 1 h, respectively. Likewise, the total adsorption capacity increased with decreasing pH. At pH 5.5, pH 7.0 and pH 8.5 the adsorption capacity of PAN-NH for Cr(vi) adsorption was calculated with $175 \pm 14 \text{ mg Cr(vi) per m}^2$, $151 \pm 10 \text{ mg Cr(vi) per m}^2$ and $33 \pm 5 \text{ mg Cr(vi) per m}^2$, respectively. This behaviour was not observed with the PAN-Q membrane (Fig. 9B), which showed a similar adsorption kinetic and capacity for all three investigated pH values. This can be explained with the properties of the two different PAN modifications. As seen in Fig. 4 and S2,† the PAN-NH membrane, owned only primary amine groups as anion exchanger functional groups. The charge of the amine groups is sensitive to a change of pH, which can be seen by the isoelectric point at pH 7.5 (Fig. 4 and Table S2†). Therefore, at pH 8.5 the PAN-NH membrane was not positively charged anymore and consequently did not bind the negatively charged chromate ions any longer. On the other side, the PAN-Q membrane was positively charged at all investigated pH values and therefore not affected by the pH change.

We did not observe any fouling of the used membranes. However in the present work, we only investigated Cr(vi) adsorption without the interfering of other ions and substances that normally can be found in raw waters. For a real-world application of the positively charged PAN membranes, several other factors must be considered. On the one hand, the positive charge could lead to increased organic fouling of the modified membranes, since most organic foulants carry negative surface charge and could be attracted to the membrane surface.⁴² The organic fouling could possibly be countered by periodic backwashing of the membrane. In this case, the foulants should be removed together with adsorbed Cr(vi). On the other hand, the adsorption capacity for Cr(vi) will probably be decreased

when other anions such as chloride, sulphate, bicarbonate, phosphate and natural organic matter (NOM) are present in the feed solution due to sorption competition.⁴³

3.4 Desorption and regeneration of PAN membranes

Previously adsorbed Cr(VI) was desorbed when the fully loaded PAN-NH and PAN-Q membranes were rinsed (by filtering) with the regeneration solution (Fig. 10A and B). After desorption, the membrane was again loaded with Cr(VI) ions by filtration. This process was repeated with the same membrane for at least three times. The regeneration solution contained 1 M NaCl and 0.01 M NaOH. By filtering this solution through the membrane, an ion exchange process shall be induced where CrO_4^{2-} ions were exchanged with Cl or OH ions. Moreover, the increase of the pH decreased the positive charge of the PAN-NH membrane (Fig. 4 and Table 1), which could have also contributed to the desorption of chromate ions.⁴⁴ After the regeneration procedure, no significant change in permeability was observed. Therefore, it can be assumed that the PAN membranes are not damaged by the high pH and ionic strengths, which was also reported before.²⁶

The experiments showed that after three regeneration steps the breakthrough curve of the PAN-NH membrane was

almost the same as before (Fig. 10C) with a recovery of $93 \pm 4\%$ of the initial Cr(VI) adsorption capacity. However, regeneration of PAN-Q membrane (Fig. 10D) only led to a recovery of $83 \pm 4\%$ of the initial Cr(VI) adsorption capacity. The different types of modification might explain this unique behaviour. The primary amine groups of the PAN-NH membrane acted as weak-base anion exchanger, which are, in general, easier to regenerate compared to the quaternary amines of the PAN-Q membrane, which served as strong-base anion exchanger groups.^{44,45} In addition, the determined amount of amine groups per membrane area for both modifications (PAN-NH: 3.5 mmol amine groups per m^2 ; PAN-Q: 3.5 mmol amine groups per m^2 ; Fig. 5) was slightly higher than the adsorbed amount of Cr(VI) per membrane surface (PAN-NH: 2.9 mmol Cr(VI) per m^2 , PAN-Q: 2.8 mmol Cr(VI) per m^2 ; Fig. 7 and 8). This observation could be explained by the fact that not all amine groups were available for the adsorption process due to steric hindrance effects.⁴¹

The mechanism for Cr(VI) removal of both modified membranes seems to be ion exchange due to electrostatic attraction between negatively charged Cr(VI) ions and positively charged functional groups on the membrane surface.⁴⁶ The characterisation of the membrane did not indicate, that the porosity of the membrane was elevated by the chemical modification, which could have possibly led to

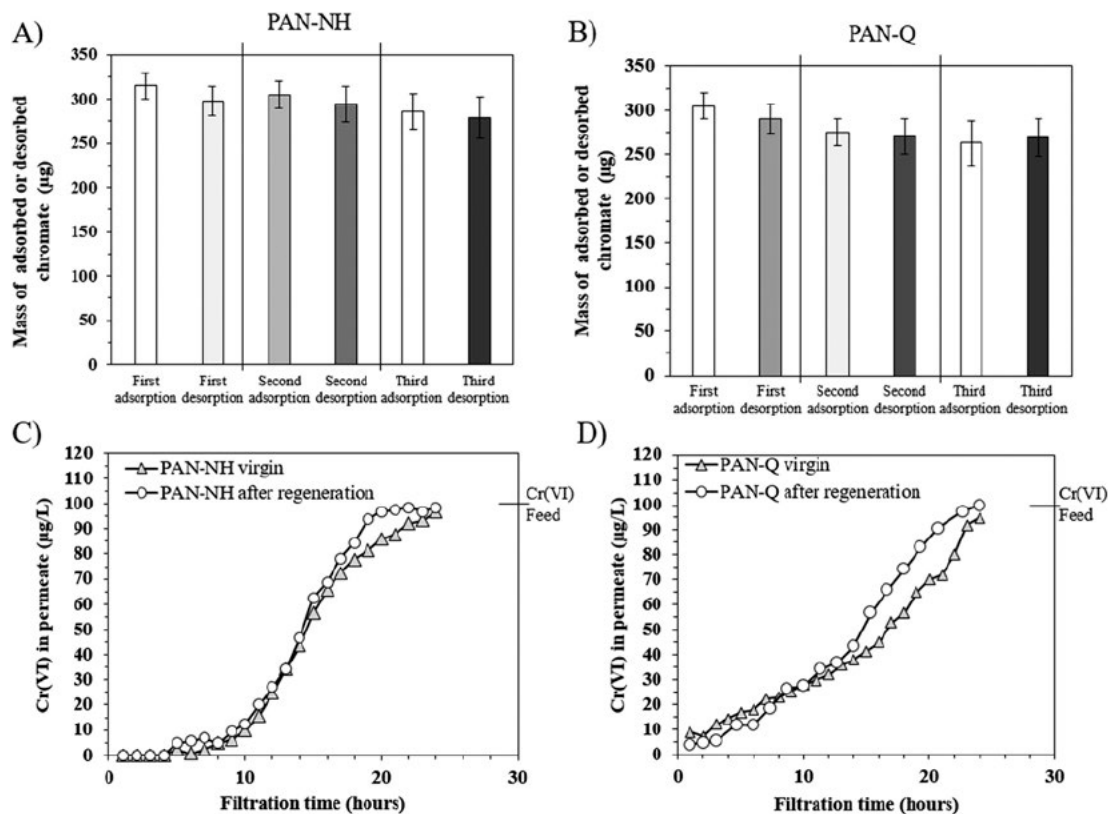


Fig. 10 Adsorbed and desorbed Cr(VI) from PAN NH membrane (A) and PAN Q membrane (B) as well as Cr(VI) breakthrough during filtration with virgin and regenerated PAN NH membrane (C) and virgin and regenerated PAN Q membrane (D); regeneration by filtering 1000 mL of 1 M NaCl and 0.01 M NaOH solution through membranes; feed: $100 \mu\text{g L}^{-1}$ Cr(VI), pH 7.0, 1 mmol L^{-1} NaCl, constant flux of $100 \text{ L m}^{-2} \text{ h}^{-1}$, membrane surface area 28 cm^2 .

pore adsorption of Cr(VI). Moreover, the measurements of zeta potential, amount of amine groups and FTIR showed that the charge properties of the membrane were shifted from negative to positive surface charge. Furthermore, the previous adsorbed Cr(VI) were desorbed by the rinsing of the membrane with high salt concentration at high pH values, which indicates an reversible ion exchange process.

3.5 Adsorption mechanisms

Fig. 11 describes the adsorption and desorption mechanisms for the PAN-NH and PAN-Q membranes derived from the experimental results of this study. The amine groups of the PAN-NH membrane are protonated at pH 7 (see. Fig. 4) and therefore carry a positive charge (Fig. 11A) and act as anion exchangers as well as the quaternized groups of the PAN-Q membrane (Fig. 11B).⁴⁷ Cr(VI) desorption from the PAN-NH and PAN-Q membranes can be attributed to two different processes. The PAN-NH membrane likely desorbs Cr(VI) ions

due to deprotonation of amine groups at high pH, leading to a decrease in the attraction between Cr(VI) ions and amine groups.⁴⁸ Whereas, the PAN-Q membrane probably is more likely to desorb Cr(VI) ions due to ion exchange of Cr(VI) with chloride ions.⁴⁹

The results of this work suggest that the mechanism for Cr(VI) removal is based on adsorption caused by ion exchange, which is usually not selective for solely one specific ion. However, several previous studies showed that anion exchangers exhibited high affinity for adsorption of Cr(VI) ions even in presence of the typical drinking water anions.⁵³⁻⁵⁵ This is also reported for the common case where the concentrations of the competing ions (*e.g.*, chloride, sulphate, bicarbonate) are considerably higher than the Cr(VI) concentration.⁵⁶ To evaluate the applicability of amine modified polyacrylonitrile ultrafiltration membranes for practical water treatment, further studies should clarify how selective the adsorption of Cr(VI) is in different water matrices.

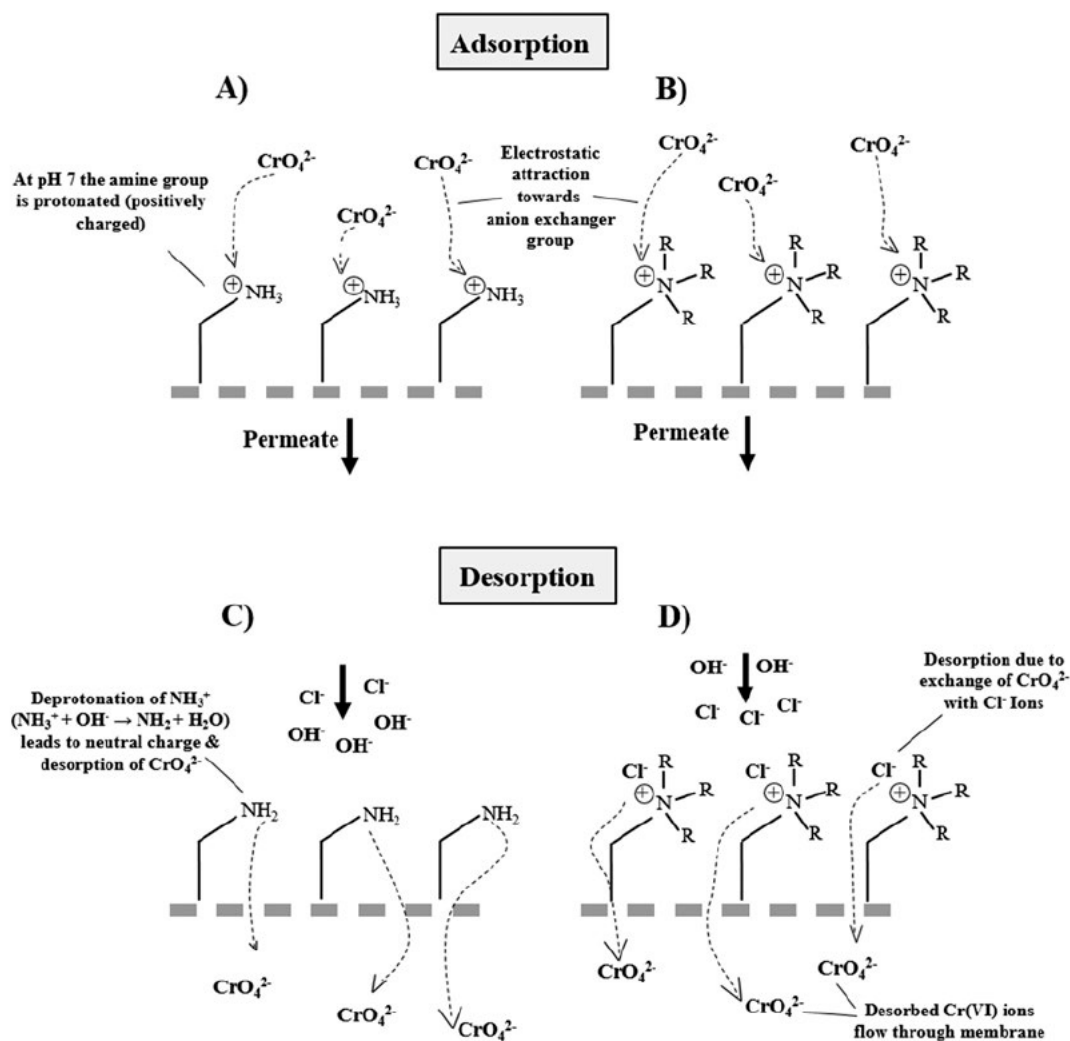


Fig. 11 Scheme of adsorption of Cr(VI) during filtration onto PAN NH (A) and PAN Q (B) at pH 7. Rinsing of the membrane with regeneration solution (0.01 M NaOH & 1 M NaCl) leads to desorption of Cr(VI) form PAN NH membrane (C) and PAN Q membrane (D).

4. Conclusions

The goal of this work was to present a proof-of-concept for the combination of UF and ion-exchange processes in an one-stage filtration step for the removal of Cr(VI) out of drinking water sources. For this, two different PAN modifications were prepared. The chemical modification by reduction (PAN-NH) and quarternisation (PAN-Q) of the pristine PAN membrane did not alter the membrane structure itself significantly since the MWCO, WCA, BET surface area and the permeability did not change intensely. However, the membrane charge was affected by the modification essentially as seen by the reversal of zeta potential from negative to positive values and the increased amount of primary and quaternary amine groups on the membrane surfaces.

In general, the PAN-NH showed slightly higher adsorption capacity for Cr(VI) than the PAN-Q membrane. In addition, the adsorption kinetics of the PAN-NH membranes were faster and thus more beneficial for a water filtration process, as almost no Cr(VI) passed through the membrane during the first six hours of filtration. Whereas, at the filtration with the PAN-Q membrane, little concentration of Cr(VI) passed through the membrane from the beginning of the filtration experiment. Moreover, the desorption rate for Cr(VI) was higher for the PAN-NH (93%) compared to the PAN-Q (83%) membranes.

Viewed in a broader perspective, the practical application of positively charged membranes is not limited to the field of ion-adsorbing membranes.⁵⁰ With decreased pore diameter, PAN-NH and PAN-Q membranes could be facilitated as nanofiltration membranes that reject anions and – due to the Donnan effect – also reject cations.⁵¹ In addition, positively charged tight UF membranes could be used for recovery of valuable substances in industrial processes.⁵²

In conclusion, we report the two novel amine-modified PAN UF membranes, which carry positive surface charges and are capable of adsorbing oxyanions such as Cr(VI). Moreover, desorption experiments revealed that the Cr(VI) adsorption was reversible and therefore might be utilized for long-term water purification processes.

Author contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript. Tomi Mantel: conceptualization, methodology, investigation, writing – original draft, visualization, formal analysis. Sarah Glass: conceptualization, investigation, visualization, formal analysis, writing – original draft. Muhammad Usman: investigation, visualization, writing – review & editing. Anastasios Lyberis: investigation, writing – review & editing. Volkan Filiz: resources, writing – review & editing, supervision, project administration, funding acquisition. Mathias Ernst: resources, writing – review & editing, supervision, project administration, funding acquisition.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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