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Senior Thesis
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Functional Polymer Membranes for Heavy Metal Removal

Removal of heavy metals from water is an important and ongoing challenge.¹ Heavy metal removal is vital for drinking water pretreatment. Prolonged exposure to heavy metals in drinking water has been shown to lead to an increased cancer risk.² Heavy metals, especially lead and cadmium, are also known to be neurological and reproductive toxins.^{3,4} In addition to being highly toxic to humans, heavy metals are dangerous to the environment. Metals can be easily released into the environment through industrial wastewater and through contamination from industries such as mining. This means that people in industrial areas or areas with mined metal deposits are at very high risk of disease from metal toxicity.⁵ These substances build up because, as elemental metals, they cannot be degraded in the environment. They build up in the food chain and are likely to poison wildlife, especially carnivores. Because of this, these metals pose a hazard to the stability of many affected ecosystems.⁶ This problem is also of interest to industry because of environmental regulations imposed by the Environmental Protection Agency (EPA). Manufacturers would benefit from simple, cost-effective methods of purifying waste streams so as to meet EPA requirements, and the environment and society would benefit from a lowered exposure to these harmful toxins.

Current heavy metal removal technology takes several forms, including precipitation, ion exchange, distillation, reverse osmosis, and adsorption.⁷ Precipitation involves removing heavy metals through the creation of insoluble salts, often hydroxides, and removing them through sieving as they come out of solution. This works well for streams with very high concentrations

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of metal but may not scale well because of the large amount of waste produced. Ion exchange uses materials that can exchange less dangerous cations while capturing the more dangerous ones. However, these processes are minimally selective, and the resins used can be easily fouled. Although distillation may be practical on a small scale, it is so energy-intensive that it is not feasible for high-throughput applications such as drinking water purification or industrial wastewater treatment. Membrane filtration is increasingly used, but reverse osmosis requires very high pressure, especially for more concentrated solutions, and nanofiltration does not have high enough rejection for safe use.

Several methods have been used to control selectivity by functionalizing membrane pores. One method, described by Nishizawa et al. uses polycarbonate membranes with gold nanotubules.⁸ Using electroless plating, gold nanotubules can be made in the pores of membranes with cylindrical through-pores. The coating thickness, and thus the pore size, can be controlled by changing the plating time. The channels can be charged electrostatically, allowing them to reject ions with the same charge. Because they are metallic, and not inherently charged, the membranes can be either cation or anion selective, depending on the potential applied. These membranes have easily controlled pore sizes and the potential to select for positive or negative charges, but they are difficult to manufacture at scale, have low flux, and have selectivity based on charge only. Another method describes the usage of carbon nanotube pores functionalized with carboxylic acid groups, which mimic biological pore systems.⁹ Carbon-nanotube membranes were shown to exhibit very high rejection of negative ions in a way that suggested a Donnan exclusion-based mechanism. These membranes were highly selective and could be modified to have other types of selectivity, but they have low porosity and low flux.

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An alternative approach to designing polymer membranes that exhibit a high degree of selectivity involves leveraging self-assembly. Although past work has often focused on more complex manufacturing techniques, self-assembly is attractive because it gives ease of processing. For example, phase separation in lyotropic liquid crystal systems has been used to create selective layers.¹⁰ Liquid crystals consisting of self-assembled amphiphiles containing positively charged imidazolium groups showed high rejection of positively charged solutes, including salts.

Self-assembly also occurs in copolymers that contain highly incompatible repeat units, such as two repeat units with very different polarities. Recently, our group has shown that a random copolymer synthesized from the highly hydrophobic, fluorinated monomer trifluoroethyl methacrylate (TFEMA) and the highly hydrophilic monomer and methacrylic acid (MAA) can self-assemble into micelles in organic solvents.¹¹ The micelles have a hydrophilic shell consisting mostly of MAA surrounding a hydrophobic core, consisting mostly of TFEMA.¹¹ MAA is acidic and is deprotonated in aqueous solutions above a pH of ~3-4.¹² TFEMA is known to have a high glass transition temperature (T_G) of ~80°C, so it adds mechanical stability to the micelles. Because the two types of repeat unit are randomly distributed, the shells are thinner than those formed by block copolymers. The micelles were stained with copper (I) acetate, which stains carboxylic acid groups. Stained TEM images showed that the shell was composed mostly of MAA repeat units and that the core was composed mostly of TFEMA repeat units.¹¹ The micelles may aggregate due to hydrogen bonding between the carboxylic acid groups of the MAA and due to single copolymer chains being shared between micelles.

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We have also shown that these micelles can be used to make membrane selective layers with highly tunable properties. To prepare these membranes, the copolymer described above, poly(trifluoroethyl methacrylate-*co*-methacrylic acid) (P(TFEMA-*co*-MAA)), is dissolved in methanol. This micellar solution is coated onto a porous support (e.g. a membrane with large pore size), briefly dried, and then immersed into water to make a thin film composite (TFC) membrane. During the drying process, the micelles pack closely. Upon immersion into water, the copolymer precipitates due to the hydrophobicity of the TFEMA cores. This freezes the selective layer structure, featuring closely packed micelles ~15 nm in diameter. The space between the micelles forms pores which allow controlled solvent and solute transport.¹³ Analysis of images of the membrane surface and cross-section shows that the pores are between 1 and 3 nm (Fig. 1).

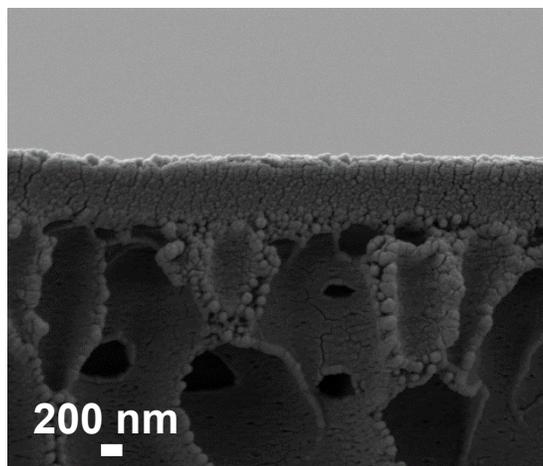


Fig. 1: This figure presents a cross-sectional image of the membrane with the packed micelle selective layer visible on top of the support membrane (reproduced with permission from Sadeghi et al. 2017).¹³

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The surfaces of the pores of these membranes contain primarily MAA. Therefore, all solvents and solutes passing through the channels interact with the negatively-charged carboxylic acid groups lining the surface. Solute interaction with the membrane can be expected to be different depending on charge, which should allow separation based on charge in filtration experiments. To test this, filtration and diffusion tests were performed on these membranes using several positive, negative, and neutral dyes. The diffusion tests found a separation factor of 28.1 between positively-charged basic blue 3 and negatively-charged acid blue 45 as well as a separation factor of 263 between neutral riboflavin and acid blue 45.¹³ Pressure-driven dead-end filtration was performed for a wider selection of dyes ranging in size from 0.8 nm to 1.3 nm. Low rejection (<20%) was observed for all neutral dyes, while high rejection (>80%) was observed for all negative dyes. Rejection of positive dyes ranged between 20% and 40%. This suggests that the mechanism of rejection depends strongly on charge and is largely independent of size. Filtration of several solutes was also conducted at varying ionic strength. Increasing ionic strength decreases solute rejection, which suggests a Donnan exclusion-based mechanism of rejection.¹³ These membranes are very promising for charge-based separations.

Following the success of the charge-based COOH-functional membranes, it is of interest to expand this method to other forms of selective separations. This could be achieved by functionalizing the pore surfaces to introduce other groups that selectively interact with solutes passing through the pores. Because the assembly of the micelles relies on the properties of the MAA's carboxylic acid groups, it is best to add new functionalities after assembly. This can be done by attaching new moieties to the carboxylic acid groups exposed on the channel surfaces. For example, one possibility is to present phenyl groups in the channels of the membranes to

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achieve separation based on aromaticity through interactions between the delocalized π -orbitals. Another is to add functional groups such as thiol with known affinity for certain metals, in order to selectively remove some metals from wastewater. This would potentially enable the removal of specific solutes through an adsorptive mechanism, capturing low concentrations of problematic groups on the membrane while allowing harmless ions such as sodium and calcium to pass through.

When selecting reactions for post-assembly modification, it is important to use reactions that work well with polymer micelles in the solid phase without disrupting the membrane structure. It is also important that the reaction can occur inside the relatively narrow pores without blocking them and reducing membrane performance. Following these constraints, EDC/NHS coupling may be used to functionalize the membranes.¹⁴ This involves activating the carboxylic acid groups on the micelle surfaces with 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) and reacting them with N-hydroxysuccinimide (NHS) to form an NHS ester.¹⁵ This ester can then react with any amine to form an amide linkage, and the NHS can be easily washed off. The high selectivity of this reaction makes it unlikely to have adverse effects on the membrane. Additionally, EDC is considered a zero-length linker because it is able to couple molecules without using a spacer. This is valuable because it will allow the preservation of the original pore size.

Here, the P(TFEMA-*co*-MAA) membranes described by Sadeghi et al. are further investigated to determine their ability to remove heavy metals from water. First, the COOH-functional membranes were tested to investigate the ability of the carboxylic acid groups to remove metal ions through adsorption. The membranes were tested in static adsorption mode and

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in a pressure-driven filtration mode. Then, the membranes were functionalized with thiol using EDC/NHS chemistry. The abilities of the functionalized membranes to remove metal were then tested.

The COOH-functional membranes were found to adsorb metal at rates comparable to, but lower than other similar methods reported in the literature. Washing with acid was proposed as a method to remove metals adsorbed onto the surface of the membrane. It was found that the membranes were stable down to a pH of 3. Furthermore, it was found that after immersion in a pH 3 solution, the membranes regained their starting capacity, suggesting that acid is a viable way to reverse binding and regenerate the membrane. The membranes were successfully functionalized with thiol. The SH-functional membranes were also able to adsorb metal but showed lower absorptive capacities than the COOH-functional ones. However, they did show some selectivity against calcium. This is promising because it could allow these membranes to be used to remove harmful metal ions from the water without losing performance to less harmful ions.

Methods

Synthesis of the random copolymer P(TFEMA-*co*-MAA)

P(TFEMA-*co*-MAA) was synthesized from trifluoroethyl methacrylate (TFEMA) and methacrylic acid (MAA) using free radical polymerization in dimethyl sulfoxide (DMSO) following methods described by Sadeghi et al.¹³ 20 g each of methacrylic acid (MAA) and 2,2,2-trifluoroethyl methacrylate (TFEMA) was dissolved in 100 mL DMOS. 0.02 g AIBN was added as an initiator. Copolymer composition was determined by ¹H-NMR spectroscopy in DMSO-*d*₆.

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The copolymer was found to contain approximately 45% MAA and 55% TFEMA. Molar mass of the copolymer was determined using gel permeation chromatography (GPC) in tetrahydrofuran. The copolymer had a weight-average molar mass of 1064 kg/mol and a dispersity of 1.75, based on polystyrene standards.

Manufacture and Characterization of COOH-Functional Membranes

Thin film composite (TFC) membranes with the P(TFEMA-*co*-MAA) micelles making up the selective layer were prepared following procedures described in Sadeghi et al.¹³ Briefly, a 5 % wt solution of the copolymer in methanol was prepared. This allowed the polymer to self-assemble into micelles as shown by Sadeghi et al.¹¹ The solutions were filtered through a 1 µm glass fiber syringe filter to remove dust and kept in an oven at 50°C to remove any bubbles before casting. A commercially available polyacrylonitrile ultrafiltration membrane (PAN400, Nanostone) was used as the porous support. The solution was coated onto the support using a doctor blade set to a gate size of 20 µm. The solvent was left to evaporate for approximately 20 seconds, and the membrane was submerged into a water bath. This served to completely precipitate out the micelles and fix them on the membrane surface. If the membranes were not dried for long enough, then they would have high flux and low rejection, which suggests incomplete coverage of the base membrane by the selective layer. If they were dried for too long, however, they would show drastically lowered flux, suggesting that the micelles began to merge into a continuous polymer layer. This is undesirable because it breaks down the pores that form between the micelles. Once sheets of the membrane were cast, swatches were cut from each batch to perform tests on.

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The membrane structure was characterized using several microscopy techniques. First, field emission scanning electron microscopy (FESEM) was performed on the membranes. The membranes were dried, frozen in liquid nitrogen, and cut to reveal their cross sections. These samples were attached to the SEM stage and sputter-coated with gold and palladium in an argon atmosphere. They were then characterized with the SEM at 4 kV with a 10 mm working distance. The samples were also characterized using atomic force microscopy (AFM) in tapping mode on dried membranes.

Manufacture of SH-Functional Membranes by EDC/NHS Functionalization

The membranes were functionalized to introduce thiol groups onto the pore walls using EDC/NHS chemistry. The first step uses 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide (EDC) and N-hydroxysuccinimide (NHS) to form an NHS ester from the exposed carboxylic acid groups. A solution of 10 mM EDC and 20 mM NHS was prepared in a 20x diluted CaCO_3 buffer in a glove bag filled with dehumidified nitrogen in order to prevent side reactions. Membrane swatches with a surface area of 5 cm^2 of previously prepared COOH-functional membranes were soaked in 20 mL of this solution for two hours. A sample was removed and examined with ATR-FTIR as described above to confirm the progress of the reaction. A solution of 10 mM mercaptoethylamine in 100 mM MES buffer was prepared. The activated membranes were removed from the EDC/NHS solution, rinsed with DI water, and immersed in 20 mL each of the mercaptoethylamine solution for 12 hours. Swatches were again taken out and examined with ATR-FTIR to confirm the progress of the reaction. The general scheme of this reaction is

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shown in Figure 2. Filtration and static adsorption tests were performed on the SH-functional membranes.

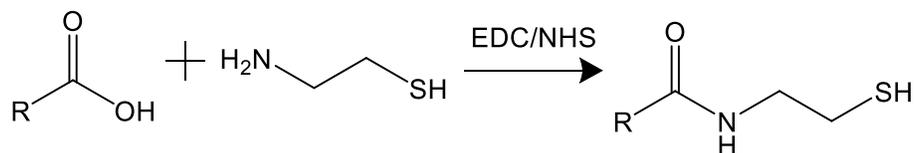


Fig. 2: This shows the general scheme of the functionalization reaction. EDC/NHS functionalization is used to allow a carboxylate group on the micelle surface to react with an amine to form an amide bond with a terminal thiol.

Dead-end Filtration

Dead-end filtration was performed on the membrane samples to determine their permeability to water and their rejection of various heavy metal ions. Many polymers change their structure under pressure. This is especially likely with packed structures such as the selective layer of the membranes being tested. To ensure that the structure and properties of the membranes remained constant, as well as to reflect the operating conditions of filtration, the membranes were compacted for several hours with water flow at 2.75 bar. The flux through the membrane at 2.75 bar was recorded over several hours, and the stable water flux was recorded and used to calculate the permeability.

To test the rejection of metal ions by the membranes, filtration tests were performed with salt solutions as the feed. Circular membrane swatches with surface areas of 5 cm² were cut and fitted into a 50 mL cell. Swatches for tests being compared were taken from the nearby on the same membrane sheet to ensure comparability. The cell was pressurized to 2.75 bar and fed with

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a 50 ppm salt solution containing the metal in question. Chloride salts were used for all salts except for lead (II) and cobalt (II), whose acetates were used. A fraction collector was used to automatically collect new permeate fractions every five minutes. Due to the permeances of the membranes tested and applied pressures used, each fraction was between one and two milliliters. These fractions were analyzed to determine the concentration of desired ions.

Ion concentrations were measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). The ICP-OES was calibrated using standard solutions of the ion of interest diluted to 50 ppm, 10 ppm, 5 ppm, and 1 ppm. Signal strengths at peaks characteristic of various metals were measured and used to calculate the concentrations in each sample. These were used to find the change in metal concentration over the course of filtration.

Static Adsorption

In addition to pressure-driven filtration, static adsorption tests were performed. Swatches of membrane with surface areas of 5 cm^2 were cut and immersed in vessels with 10 mL salt solution and left to allow the membranes to become saturated. The same 50 ppm feed solutions were used here as in filtration. After leaving the membranes for 24 hours to reach their capacity, the concentration of metal in the remaining solution was measured using ICP-OES and used to determine the amount of metal ions taken up by the membrane. The membranes were dried, and their functionalized surfaces were examined with attenuated total response Fourier transform infrared spectroscopy (ATR-FTIR) over the range from 600 cm^{-1} to 4000 cm^{-1} to investigate the coordination environments of the metals. These tests were performed in triplicate.

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Characterizing Membrane Stability at low pH

Several tests were performed to determine the membrane stability over a range of pHs. First, membrane swatches were soaked for 24 hours in solutions adjusted to pH 3, 7, and 10 using HCl and NaOH. After soaking, these membranes were examined with ATR-FTIR as described before to ascertain the nature of chemical changes due to the change in pH. Additionally, pressure-driven filtration was conducted as described above using a pH 3 solution of HCl as the feed for 16 hours. Flux was recorded, and this was used to determine if there was any change in permeance over time due to the flow of acid.

Regeneration Studies

Tests were performed to assess the ability of an acid wash to regenerate the membranes. First, static adsorption was conducted as described above. Then, the membrane swatches were removed from the used metal solution and immersed in pH 3 solution with HCl for 24 hours. After this, the swatches were removed from the acid wash, rinsed with DI water, and placed in 10 mL of a fresh solution containing 50 ppm of the same metal each had been used for previously. The membranes were left in these solutions for a further 24 hours, and then they were removed and ICP-OES was used to determine the quantity of metal they were able to remove. This was compared to the quantity removed on the first trial in order to determine the ability of acid to regenerate the membranes.

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Results and Discussion

Preparation of COOH-Functional Membranes

COOH-functional membranes were prepared following the procedures previously described by Sadeghi et al.¹³ Briefly, the copolymer was dissolved in methanol to form micelles. This solution was coated onto a base membrane for mechanical support, then immersed in water to precipitate out the micelles. The membrane structure and performance were found to be comparable to previous samples. The membrane swatches tested had DI water permeances around 3 LMH/bar, comparable to previous reports and to commercial membranes with similar pore size.

Metal Removal with COOH-Functional Membranes

Some rejection of metal salts by COOH-functional membranes has already been observed through a charge-based rejection mechanism.¹³ It is hypothesized that in addition to this mechanism, the membrane will be able to remove metals through an adsorptive mechanism. Carboxylate groups are known to form complexes with many metal ions including calcium, copper, cadmium, iron, and lead.^{16,17} Because of this, we expected to observe some adsorption due to the complexation in addition to some rejection, in accordance with previous work.

To test this hypothesis, static adsorption experiments were performed to measure the adsorption of several of salts onto the membranes, by immersing a known area of membrane into a salt solution and measuring the change in concentration (Fig. 3). As a control experiment, we also performed the same experiment on the support membrane. Many commercial membranes are designed to have mildly negatively charged surfaces to limit fouling, because most major

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contributors to fouling are negatively charged. This may lead to some adsorptive removal of ions by the support membrane through electrostatic interactions. When the contribution of the support layer was subtracted, we found that approximately 0.2 nmol/cm^2 of each metal can be adsorbed by the selective layer of the membrane. Based on the amount of polymer coated onto each membrane sheet, it was determined that the average amount of polymer in the selective layer was 0.050 mg/cm^2 . This was used to find that the membrane selective layer has a capacity of between 5 and 10 nmol/mg . Past work using carboxylate-rich substrates as metal removal agents has shown lower capacities, between 0.2 and $0.8 \text{ } \mu\text{mol/mg}$, so further work will be needed to bring these membranes into competition with what is currently available.^{18,19} It was calculated that the membranes have 0.49 nmol/cm^2 COOH functional groups. This indicates that a very high proportion of the COOH groups are involved with metal uptake.

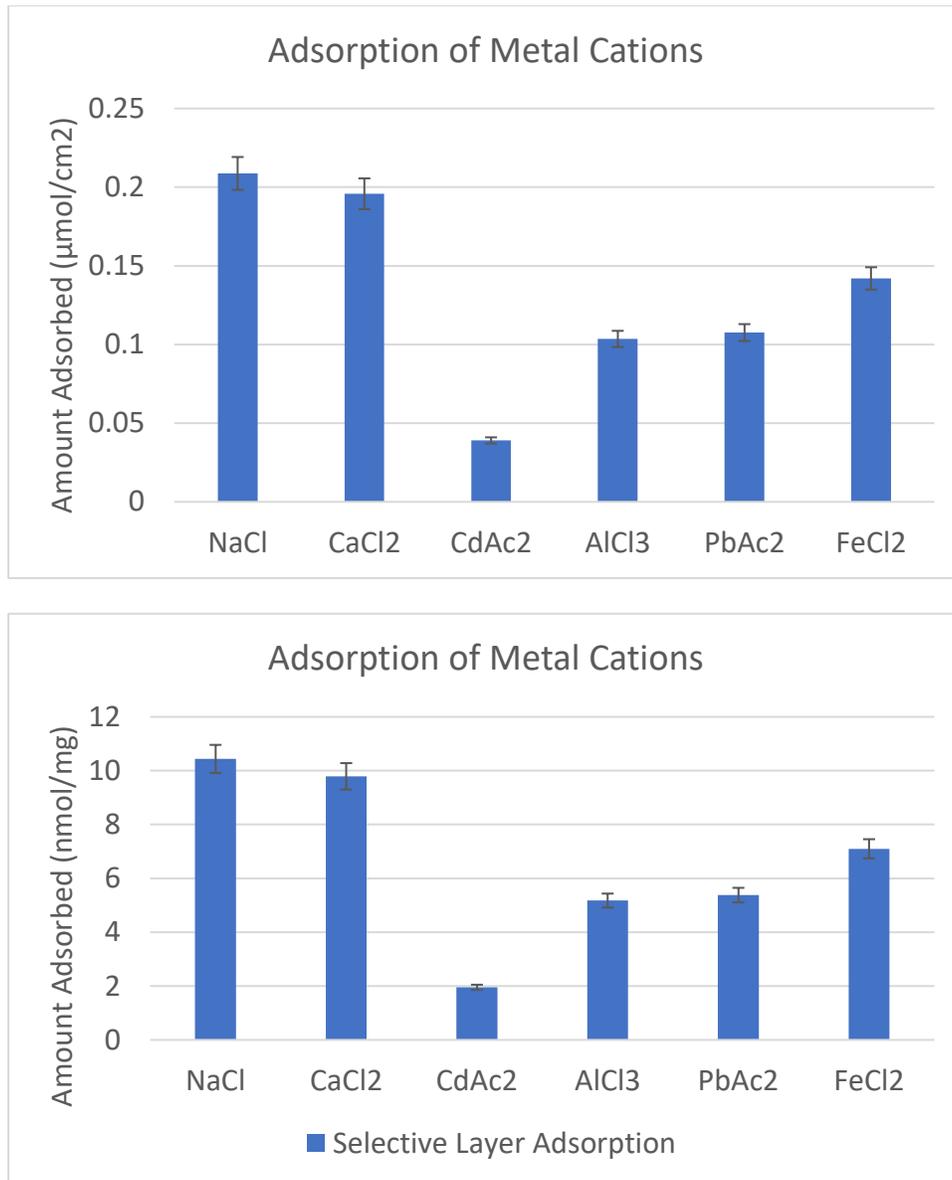


Fig. 3: Adsorption of metal cations by the selective layer for feed concentrations of 50 ppm. This was found by subtracting the total metal adsorbed by the base membrane from the total metal adsorbed by the COOH-functional membrane. The data is shown first normalized by membrane area, and then as a capacity per mass of selective layer.

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This system is not designed to operate in static adsorption mode, however. To test the performance of the membranes in a more realistic setting and to observe the synergistic effects of adsorptive and charge-based removal, we measured the rejection of calcium chloride, iron (II) chloride, and lead (II) acetate versus time in dead-end filtration experiments (Fig. 4).

Breakthrough curves were observed with some residual rejection, likely due to electrostatic effects. The membrane capacities were calculated from the breakthrough curves as the area between the maximum permeate concentration and the measured permeate concentration. They were found to be 11.2 nmol/mg for calcium, 10.6 nmol/mg for iron (II), and 9.6 nmol/mg for lead (II). These agree reasonable well with the values found for capacity using static adsorption, which are 9.8 nmol/mg, 7.1 nmol/mg, and 5.4 nmol/mg respectively. The reason the capacities found through filtration are higher than those found through static adsorption is likely due to transport limitations of the ions in the membrane in the static adsorption mode that were less important in filtration mode, where the metal was being driven through the membrane. The steady state rejections are found to be 18% for calcium, 21% for iron (II), and 23% for lead (II). These are in line with the values found for charge-based rejection of divalent cations, so it is assumed that the residual rejection is due to this effect.¹³

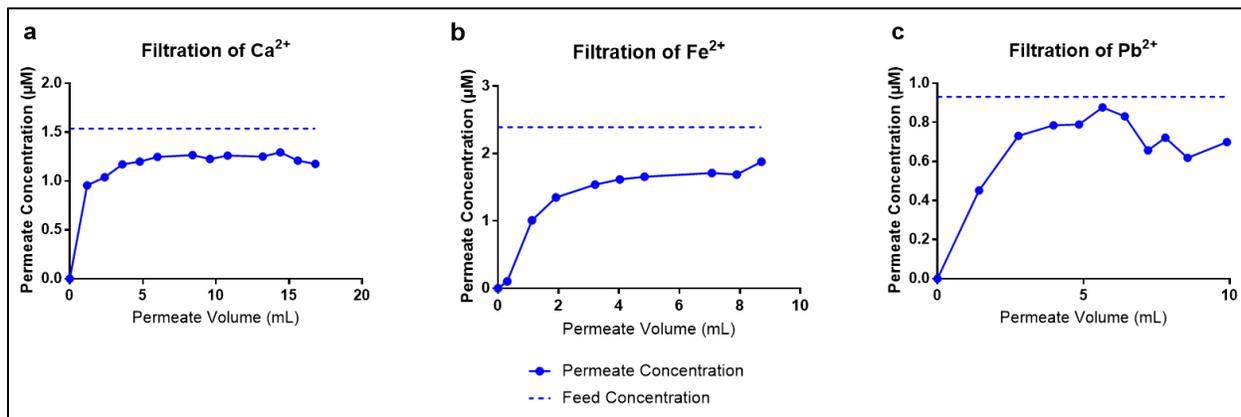


Fig. 4: Filtration of salts by P(FTEMA-co-MAA) membrane. This figure shows the change in permeate concentration for dead-end filtration of CaCl_2 (a), FeCl_2 (b) and $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ (c).

Although these values seem small, they compare favorably to the quantity of metal needing to be removed from polluted water. Polluted water contains between 10 and 100 ppb heavy metal ions.¹⁷ For lead, for example, the upper bound of 100 ppb equates to a concentration of 0.0079 μM . This means that one square meter of this membrane could remove lead from 314 thousand liters of water contaminated at this concentration. A problem arises, however, since all metals compete for the same sites. Harmless metals, such as calcium may be found in the water in much higher concentrations. Hard water may contain around 150 ppm calcium.²⁰ At these concentrations, if the adsorption capacity is roughly constant, the membranes would be saturated after filtering only around 200 liters, which is too low to be viable. As such, it is of interest for the membranes to either be easily regenerable or to find a way to achieve selectivity in the binding.

pH-Based Regeneration of COOH-Functional Membranes

Most COOH-functional materials that remove metal ions through adsorption can be regenerated by protonating the carboxylate groups. This leads to the replacement of metal ions with protons, releasing the metal ions.^{18,21} However, for this procedure to be successful, the membrane has to be stable during exposure to the very acidic conditions required.

To test if these membranes can be regenerated, we first aimed to ensure the protonation of the carboxylate groups at pH 3. This was selected because it is known to be well below the pK_a of carboxylic acid, so it would be reasonable to expect that they would be completely protonated at that pH.¹² We also wanted to confirm the membrane remained stable at this pH. For this purpose, we immersed a membrane swatch into solutions at different pH values, and characterized their chemistry using ATR-FTIR (Fig. 5).

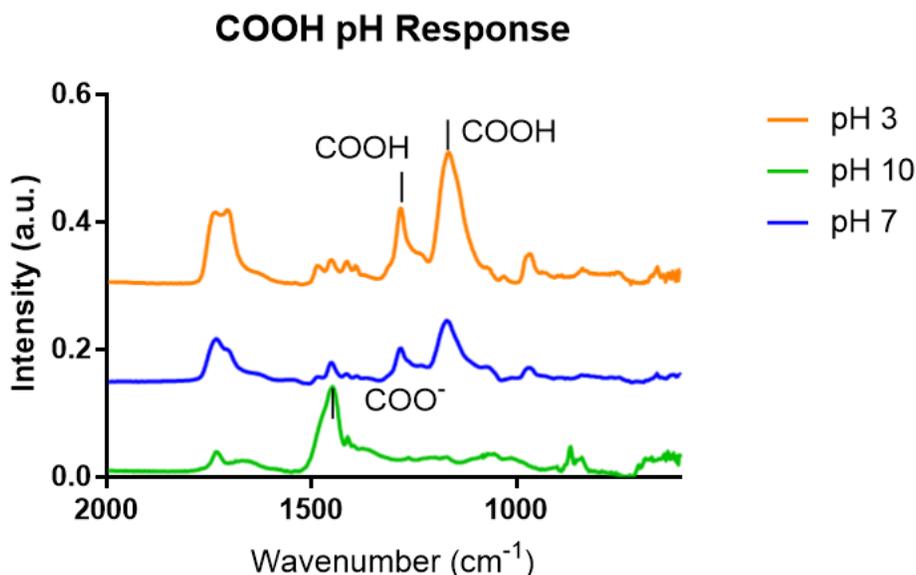


Fig. 5: The FTIR spectra of the membrane after being soaked in an acidic solution of pH 3 HCl, a neutral solution of pH 7, and a basic solution of pH 10 NaOH.

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The peak in the FTIR spectra around 1450 cm^{-1} corresponds to the deprotonated COO^- group. The peak at 1730 corresponds to the $\text{C}=\text{O}$ stretching in the carboxylic acid and the peak at 1700 cm^{-1} corresponds to the protonated COOH . The two peaks at 1165 and 1280 cm^{-1} also correspond to the protonated COOH . From this, it can be seen that the carboxylic acids are almost completely protonated at pH 3 and almost completely deprotonated at pH 10. Additionally, the fact that the only changes in peaks are relatable to the protonation of the carboxylic acid indicates that there is no chemical breakdown of the polymers at either end of the pH scale.

If pH response is to be used to regenerate the membranes, it is vital that the membranes be able to withstand acidic conditions without deterioration. A pH 3 solution of hydrochloric acid was filtered through a membrane for 16 hours and the flux was measured. This was normalized by pressure and membrane area to find the permeance (Fig. 6). The permeance stabilized around 3 LMH/bar , which is consistent with the pure water permeances that were observed. After being exposed to a low pH, when the membrane is again exposed to a neutral pH, the permeance remains constant. This indicates that even in low pH environments, the micelles themselves are stable, as is the selective layer.

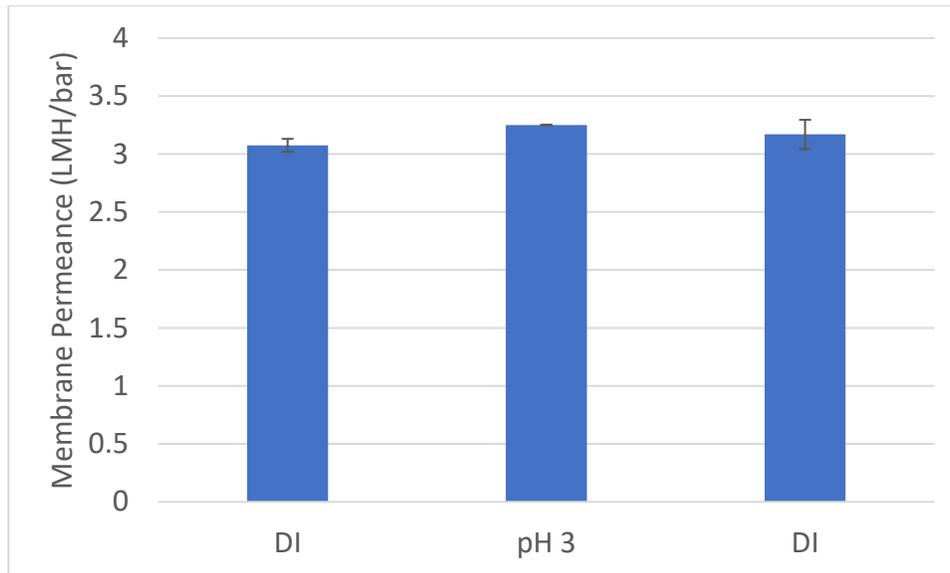


Fig. 6: This figure shows the membrane permeance for pure water, for a pH 3 solution, and for pure water after the pH 3 solution. The permeance remains approximately the same, indicating that the membrane is stable.

Finally, we tested if the metal ion adsorption capacity of the membranes could be regenerated by immersion into pH 3. To test this, first, fresh swatches were left to take up metal in a static adsorption experiment as described above. Then, these swatches were immersed in an HCl solution adjusted to pH 3 for 24 hours. Then the same swatches were rinsed in DI water and again immersed in 10 mL of a fresh solution of the same metal. Metal ion uptake after regeneration was measured. All tests were performed using 50 ppm stock solutions. The apparent capacity of the membranes did not decrease appreciably after being washed by acid (Fig. 7). The amount absorbed remained approximately equal between tests for all metal ions tested, with the possible exception of Na^+ . This suggests that when the membranes have reached their capacities, they can be easily washed in acid to regenerate them.

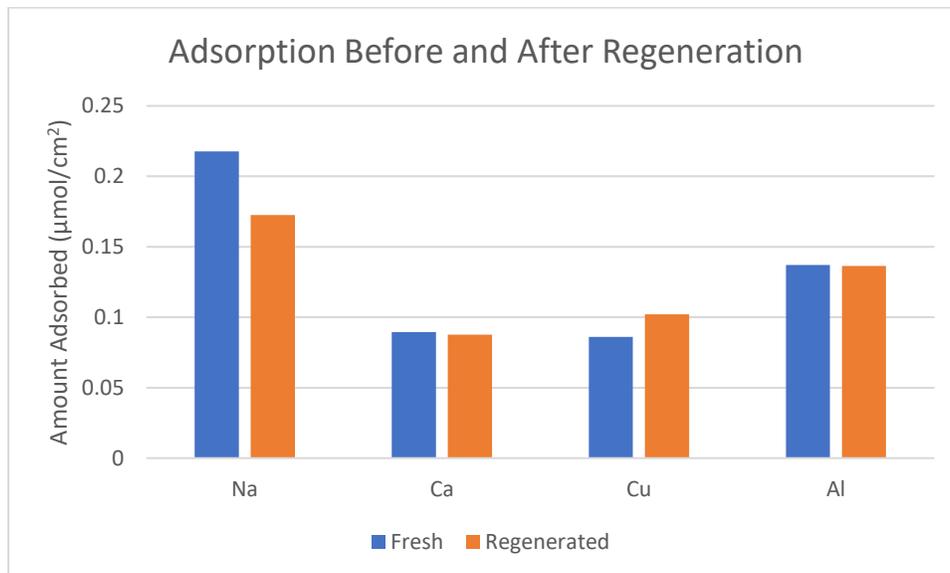


Fig. 7: The quantity adsorbed by membrane swatches before and after washing with acid is compared.

Functionalization

The membranes were functionalized with thiol using EDC/NHS chemistry (see Figure 2 for a general reaction scheme). After completing the functionalization reactions, we aimed to confirm the changes in chemical structure using ATR-FTIR analysis (Fig. 8). The FTIR spectra confirm the successful functionalization of the membrane pores with thiol groups. In the first stage of functionalization, the membrane was activated with the EDC/NHS complex. After this step, a small peak at 1800 cm^{-1} appears, corresponding to the NHS-ester intermediate.¹⁴ This peak is not present on the COOH-functional membrane, becomes visible on the activated sample, but disappears once the functionalization reaction is complete. A peak around 1550 cm^{-1} corresponds to the N-H bond in the amide.¹⁴ This peak is visible in the activated sample and

again visible shifted slightly lower in the SH-functional sample. This shift is due to the change in environment of the amide once the functionalization is complete. Large carboxylic acid peaks are still visible around 1160 and 1280 cm^{-1} , but this is to be expected. Since the reaction was performed after the polymer had been cast into a membrane, not all of the COOH groups were available for the reaction. Due to mass transport limitations, only COOH groups at or near the micelle surface were functionalized. This should not negatively impact the membrane performance, however, as it is those groups which solvents and solutes will interact with. Overall, FTIR confirms that functionalization can be successfully performed after the membranes have been cast.

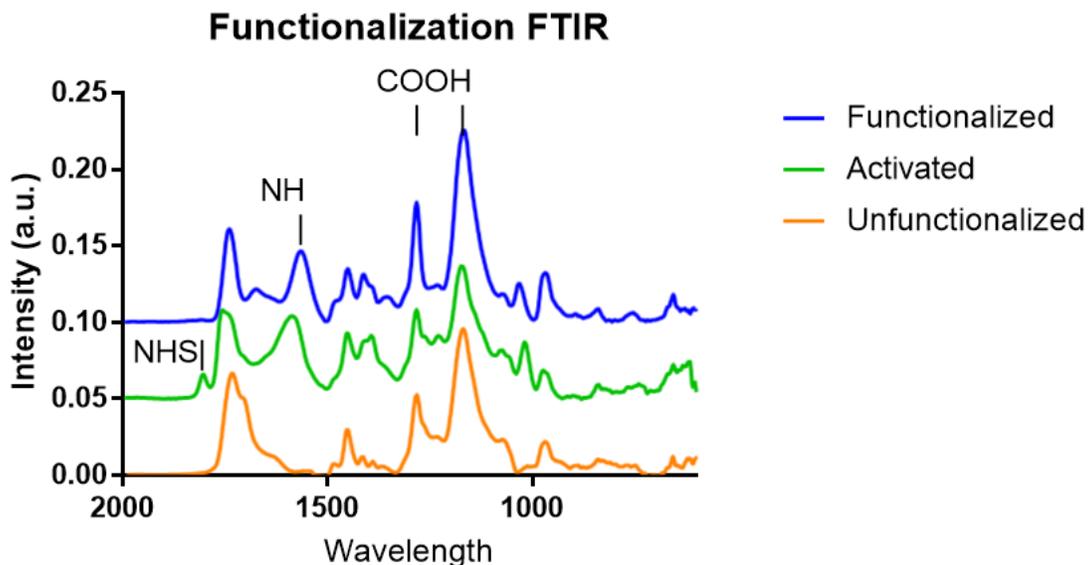


Fig. 8: FTIR spectra over the course of the EDC-NHS functionalization reaction showing characteristic peaks for notable moieties.

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Metal Removal with SH-Functional Membranes

Finally, we aimed to determine if this functionalization reaction led to improved metal ion removal selectivity. Based on other work investigating the ability of thiol to remove metals, we believed that these membranes would show some selectivity against calcium. The capacities of the SH-functional membranes were measured using static adsorption as described previously (Fig. 9). All of the capacities were lower than the COOH-functional membranes. This is likely due to a decrease in the effective pore size of the membrane upon functionalization, leading to fewer accessible groups. Furthermore, not all carboxylate groups will be functionalized and converted to thiol groups. Notably, however, the capacity for calcium diminished significantly while that for iron and lead ions showed only minor decline. This implies that while total adsorption capacity decreased, adsorption selectivity increased significantly. This indicates that thiol has some selectivity against calcium when compared with COOH-functional membranes. Theoretical selectivities may be calculated as the ratio of the amount of iron or lead adsorbed to the amount of calcium. COOH-functional membranes show calcium selectivities of 1.5 and 0.5 with respect to iron and lead respectively. The Fe/Ca selectivity is very low, and the Pb/Ca selectivity is below one, indicating that the COOH-functional membranes even preferentially bind to calcium as opposed to lead. However, the SH-functional membranes show selectivities of 9.7 and 4.5 with respect to iron and lead respectively, which indicates far greater selective ability.

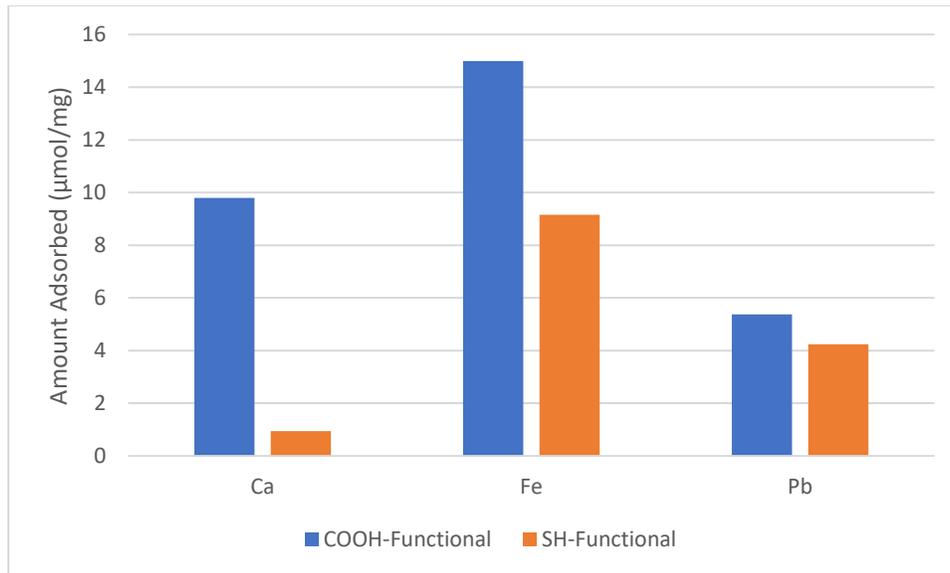


Fig. 9: Comparison of the adsorption capacities of COOH-functional and SH-functional membranes.

Conclusions and Future Directions

The ability of COOH-functional polymer membranes previously described by Sadeghi et al. to remove metals from water was investigated. Through static adsorption tests, it was found that these membranes have functional layers with capacities comparable to other previously described adsorptive materials, but lower. Pressure-driven filtration tests were performed, which showed breakthrough curves with some residual rejection. The capacities calculated with the breakthrough curves reasonably matched those found by static adsorption and the steady-state rejections shown matched those of previously reported charge-based rejection modes. The ability of acid to regenerate these membranes was also investigated. It was found that the membranes

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were stable at pH 3 and that soaking in acid was sufficient to remove the metal ions bound to the membranes, allowing the membranes to be reused.

Some properties of SH-functional membranes were also investigated. First, they were prepared using EDC/NHS coupling to attach SH-terminal groups to the free carboxylic acid groups on the membrane pore surface. Then, the ability of these new membranes to remove metals was investigated in static adsorption. It was found that although the SH-functional membranes did not adsorb as much metal as the COOH-functional ones, they showed a selectivity against calcium, which is useful for applications involving removal of heavy metal contaminants from hard water.

Several aspects of this study remain open for future work. It is of interest to determine the exact coordination structures of the metals being removed, both in coordination with COOH and with SH. Further testing of the SH-functional membranes will also be performed with a wider variety of ions and in pressure-driven dead-end filtration in addition to static adsorption. In order for the thiol membranes to be practical, it is also of interest to find a way to regenerate them, similar to the acid wash method used for the COOH-functional membranes. Both types of membrane exhibited show promise for the ability to remove potentially hazardous heavy metal ions from water.

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