

Low-cost poly(vinyl formal) for heavy metal removal from water of a polluted river

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ABSTRACT

Heavy metal pollution in drinking water is a serious health risk, particularly in developing countries. Membranes of poly(vinyl formal) (PFA) were synthesized to explore their use for heavy metal removal from water samples from the polluted Mexican river 'Atoyac.' A single incubation step with PFA membranes for 24 h was sufficient to reduce lead, iron, manganese, arsenic, and thallium concentrations to acceptable levels for drinking water, according to the Mexican standards. PFA showed high adsorption capacities (Q_e), even in the presence of multiple metals and low cation concentration. Mass transport phenomena were characterized as a function of the crosslinking degree and pH. To simulate real-life operation conditions, water fluxes across PFA membranes were characterized as a function of their crosslinking degrees and controlled external pressures. PFA membranes allowed fluxes at pressures of up to 2 kg/cm² with no deformation or breaking. Tensile strength, strain stress, elastic deformation, and Young's modulus were assessed. In contrast with previous reports, no further PFA modifications were required to obtain an excellent adsorption performance, which results in lower production costs. The ease of PFA synthesis and handling, and low production cost make it an ideal material to be applied for remediating the polluted urban water.

Key words: adsorption, heavy metals, ionic exchange, polymer, wastewater

HIGHLIGHTS

- PFA membranes can efficiently adsorb hazardous cations from complex water samples.
- Material properties could be easily modulated to obtain a desired adsorption capacity.
- PFA has good mechanical and chemical resistance.
- PFA is easily synthesized and handled, has a very low cost, and is an ideal candidate material for remediating the polluted urban water.

INTRODUCTION

Heavy metal poisoning remains a significant problem for all life forms, especially in developing countries with deficient sanitation control. Heavy metals accumulate in living organisms due to their recalcitrant properties and non-biodegradability (Igiri *et al.* 2018; Haroon *et al.* 2019). Heavy metals are incorporated into the food chain from leaching through the soil to the aquifers used to irrigate crops and as drinking water (Hejna *et al.* 2018; Jiang *et al.* 2021; Peng *et al.* 2021).

In Mexico, groundwater supplies 75% of drinking water. Several studies have shown that Mexican aquifers and adjacent soils contain high concentrations of heavy metals (Armienta & Segovia 2008; Maldonado *et al.* 2008; Pastrana-Corral *et al.* 2017; Navarrete-Rodríguez *et al.* 2020). Heavy metals and other hazardous elements are naturally present in the environment as minerals, but human activities release them into the environment. The primary human sources of heavy metals and other dangerous elements are mining, smelters, oil refineries, brickwork and cement plants, coal combustion, paints, among many others (Romieu *et al.* 1994; Rodríguez-Mercado & Altamirano-Lozano 2013; Diaz-Ruiz *et al.* 2017).

Some of the most hazardous elements found in groundwater are arsenic (As), lead (Pb), thallium (Tl), and copper (Cu). These elements negatively affect human and animal health through different mechanisms. For example, the toxicity of As, Pb, and Tl is due to their structure being similar to those of phosphorous (P), calcium (Ca), and potassium (K), respectively, and their consequent incorporation into metabolism (Bressler & Goldstein 1991; Hughes 2002; Rodríguez-Mercado & Altamirano-Lozano 2013; Paithankar *et al.* 2021).

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Conventional procedures for removing heavy metals from wastewater are flocculation by chemical or natural additives, adsorption (agro-based waste materials, polymers, biopolymers, nanocomposites, etc.), electrochemical adsorption, ionic exchange, electrochemical deposition, precipitation, and membrane separation (such as electrodialysis, nano- and microfiltration, reverse osmosis, and ultrafiltration) (Kurniawan *et al.* 2006; Demirbas 2008; Sherlala *et al.* 2018; Al-Saad *et al.* 2019; Yang *et al.* 2020; El-Gaayda *et al.* 2021).

Heavy metal precipitation is one of the most frequently applied methods for wastewater treatment; however, it is only effective for metal concentrations around 1,000 mg/L. This method has disadvantages such as low precipitation rates and sedimentation, and it produces toxic sludges (Kurniawan *et al.* 2006). To overcome these limitations, it is common to combine two or more purification methods to obtain high-quality water, such as precipitation followed by ion exchange. Ion exchange is based on the adsorption of metallic cations from the polluted water into a negatively charged network. The main advantages of ion exchange are metal recovery, tunable selectivity, and low sludge production (Verbych *et al.* 2005; Renu *et al.* 2017; Nasir *et al.* 2019).

Synthetic polymers are one of the most promising materials for ion exchange matrices. Unlike other materials, synthetic polymers are produced at low cost, and they have tunable physicochemical properties, great absorptive capacity, good mechanical properties, and are stable at rough environmental conditions (Khulbe & Matsuura 2018). Among synthetic polymers, poly(vinyl alcohol) (PVA) has promising characteristics as an ion exchanger, such as biodegradability, safety, hydrophilicity, thermal resistance, stability to different solvents and pH, high antifouling potential, and water permeability. These characteristics make PVA an attractive material to develop membranes for treating wastewaters (Bolto *et al.* 2008). However, PVA is a water-soluble material and must become insoluble by crosslinking to make it useful for water treatment. Chemical and physical methods can be used to crosslink PVA. Physical procedures have the advantages of avoiding toxic reagents for crosslinking PVA. Wang & Wang (2016) synthesized a composite of PVA and carboxymethyl cellulose prepared using a freeze-thaw method. Al-qudah *et al.* (2014) obtained a PVA/acrylic acid copolymer crosslinked using gamma radiation. However, according to Hassan & Peppas (2000), physical crosslinking of PVA resulted in less stable materials than those obtained through chemical procedures. Because of the superior stability, most of the works in the literature of PVA-based polymers for water treatment are crosslinked by chemical methods. For example, Ajitha *et al.* (2017) synthesized a composite of chitosan oligosaccharide-graft-maleic anhydride/polyvinyl alcohol/silk fibroin, which is used for water treatment at moderate concentrations of toxic heavy metals. Recently, Zeng *et al.* (2020) reported a modified copolymer of PVA crosslinked with acrylonitrile. However, these works use expensive reagents and sophisticated methods, which are not economically accessible for their application in developing countries.

In this work, we selected a simple and low-cost procedure to chemically crosslink PVA. Formaldehyde (FA) and hydrochloric acid (HCl) have been previously used to crosslink PVA to obtain poly(vinyl formal) (PFA) membranes (Li *et al.* 2005). PFA has been industrially used as wire enamel, structural adhesive (e.g., Redux), as foam to separate organic solvents from water-organic solvent mixtures, and to adsorb and recover oils (Feldman 2020). PFA synthesis occurs when a pair of electrons of the hydroxyl group of PVA attacks the FA carbocation (favored at a low pH) through a nucleophilic addition to form a hemiacetal. Then, the hemiacetal loses a molecule of water, and a new hydroxyl of the alcohol is added to form an acetal. This mechanism is repeated until the final polymerized product is obtained (Ogata *et al.* 1956). Incomplete polymerization results in free alcohol and aldehyde groups in the matrix, which can act as ion exchangers. Here, we hypothesize that an incomplete polymerization (or a low crosslinking degree) favors ion exchange in PFA membranes. Moreover, mechanical properties, water uptake, and transport phenomena in polymers depend on their crosslinking degrees (or pore size) (Krumova *et al.* 2000). Open matrices show an enhanced water flux and diffusion rate, but poor mechanical properties.

Therefore, this work aims at evaluating the potential of PFA membranes as ion exchangers for heavy metal removal from real-life and complex samples of a polluted Mexican river. To maintain low costs of production, no modifications to the PFA membranes were performed. Instead, operating conditions in simulated rough environmental conditions were extensively characterized, such as crosslinking degrees, temperature, pH, and pressure. This is the first work that solely uses PFA (without any combination with other materials) for heavy metal removal, which significantly lowers costs (Chanas & Roy 2008; Pan *et al.* 2013; Pan *et al.* 2014). The feasibility of using PFA membranes in real-life conditions on a large scale is discussed here.

MATERIALS AND METHODS

PFA membrane synthesis

PVA (Aldrich, 11773 Mowiol® 20-98, Mw 125,000) was dissolved in deionized water at 10% (w/v) in a water bath at 80 °C with magnetic stirring. This solution was mixed with different amounts of FA (Sigma, 252549) and HCl (Sigma, 320331). The

reaction was performed in different containers for each experiment, as indicated below. It was performed in two steps: (1) 36 h at 25 °C and then (2) 6 h at 45 °C, as shown in Figure 1, described by Li *et al.* 2005. At the end of the reaction, remnant reactants were exhaustively washed with double-distilled water.

Heavy metal adsorption

Sampling of the Atoyac River

Samples of 500 mL water from the Atoyac River were collected in the spring of 2017 (19°00'08.5" N 98°15'14.9" W) when the flow is the lowest. Samples were collected in 10 sterile centrifuge tubes (Corning, 430829) and immediately preserved in dry ice and protected from light, as described by Aburto-Medina *et al.* (2017).

Metal quantification in water samples of the Atoyac River

Thin films of PFA were synthesized in Nunc® Petri dishes (Merck, P7741). The adsorption of metals and metalloids in PFA membranes was performed at room temperature (25 °C). A 10 mL aliquot of water samples from the Atoyac River was filtered through nylon membranes with a pore size of 0.45 µm (Sigma, WHA7404004) and was added to the synthesized PFA membranes. After 24 h of interaction, supernatants were collected, acidified with 1% HNO₃ (Sigma, 695025), and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) in a Thermo Scientific iCAP Qc model spectrometer.

Determination of the adsorption capacity and removal efficiency

The adsorption of metals and metalloids in PFA membranes was performed at room temperature (25 °C). A 10 mL aliquot of the metallic salt standard solution (25 mM) was filtered through nylon membranes with a pore size of 0.45 µm (Sigma, WHA7404004) and was added to the PFA membranes synthesized in Nunc® Petri dishes (Merck, P7741) for 24 h. The metallic salts used were as follows: K₂Cr₂O₇ (Sigma, 209244), MnCl₂·4H₂O, (Sigma, M8054), FeCl₃·6H₂O (JT Baker, 1996-01), CuCl₂·2H₂O (Mallinckrodt, UN2802), and ZnCl₂ (Sigma, Z0173). After 24 h of interaction of each metallic salt solution with PFA membranes, supernatants were collected, acidified with 1% HNO₃ (Sigma, 695025), and analyzed by the ICP-MS in a Thermo Scientific iCAP Qc model spectrometer. The instrument was set up before sample analysis with an aqueous certified solution containing 1 µg L⁻¹ of lithium (Li), cobalt (Co), indium (In), barium (Ba), bismuth (Bi), cerium (Ce), and uranium (U) (High Purity Standards, QCS-26). A calibration curve with 16 points (0, 0.1, 0.25, 0.5, 0.75, 1, 2.5, 5, 7.5, 10, 25, 50, 75, 100, 250, and 500 µg L⁻¹) was constructed to quantify metals. Instrumental drift was corrected with an internal standard (10 µg L⁻¹). Limits of detection (LOD) were calculated using the following equation (see calibration data in Supplementary Material 1).

$$LOD = \frac{3(SD \text{ int } BCO)(conc \text{ STD})}{(int \text{ STD} - prom \text{ int } BCO)} \quad (1)$$

where *SD int BCO* is the standard deviation of blank intensity, *conc STD* is the concentration of the standard solution, *int STD* is the intensity of the standard solution, and *prom int BCO* is the average of the blank intensity.

The adsorption capacities of PFA membranes in the equilibrium were calculated using the following equation

$$Q_e = \frac{C_0 - C_e}{m} \times V \quad (2)$$

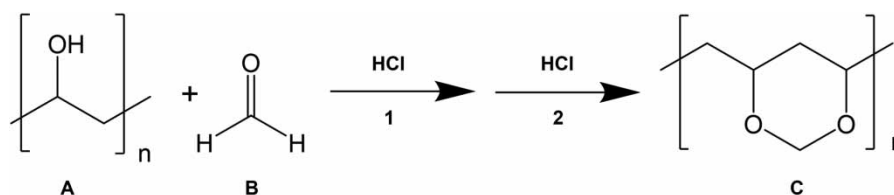


Figure 1 | Polymerization reaction between PVA (molecule A) and FA (molecule B) catalyzed by HCl to form PFA (molecule C). Numbers indicate the reaction step.

where Q_e is the adsorption capacity, C_0 is the initial concentration of the solution (mg/L), C_e is the concentration after sorption (mg/L), V is the volume (L), and m is the mass (mg).

The removal efficiency of metals or metalloids in water from the Atoyac River into PFA membranes (1% HCl and 20% FA) was calculated using the following equation:

$$\% \text{ Removal efficiency} = \frac{M_2}{M_1} \times 100 \quad (3)$$

where M_1 and M_2 correspond to the metal content before and after the PFA treatment.

Structural characterization of PFA

Fourier-transform infrared

Thin films of PFA were synthesized in 24-flat-well plates (Costar[®], 2548) with a final reaction volume of 200 μ L and different proportions of FA (Sigma, 252549) and HCl (Sigma, 320331) at the reaction conditions mentioned before. Films were dried in a desiccator in the presence of MgSO_4 (Merck, 106067) for 7 days or until the dry weight remained constant. Fourier-transform infrared (FTIR) spectra were obtained in a range of 400–4,000 cm^{-1} using a Perkin-Elmer Spectrum GX spectrometer in the attenuated total reflectance (ATR) mode.

Scanning electron microscopy

PFA dried films were coated with carbon and visualized by scanning electron microscopy (SEM). Micrographs were obtained using a JSM 5600-LV microscope operated at 200 kV.

Mechanical properties of PFA membranes

PFA samples to characterize the polymer's mechanical properties were synthesized in 50-mL centrifuge tubes (Corning, 430829) varying the amounts of FA or HCl as previously described. PFA samples were removed from the tubes and cut into cylindrical-shaped samples of 10 cm in length and 2.5 cm in diameter. Tensile strength, Young's modulus, strain stress, and elastic deformation were determined by uniaxial compression of the hydrated PFA network at 24 $^{\circ}\text{C}$ and 65% relative humidity using a mechanical testing machine (MTS, model Sintech 1/S, USA). A cylindrical flat tip (25 mm diameter) at a constant velocity of 100 mm/min with a cell nominal load of 500 N (353.45 N of effective charge) was used.

Tensile strength was calculated according to the maximum strength in graphs of strength versus time. Young's modulus was calculated from the slopes of the strain (σ) versus deformation (ϵ) graphs, as follows (Equations (4) and (5)):

$$\text{Young's modulus} = \frac{\Delta\sigma}{\Delta\epsilon} \quad (4)$$

$$\Delta\epsilon = \frac{\Delta l}{l_0} \quad (5)$$

where $\Delta\epsilon$ is the ratio between the change of length (Δl) over the initial length, l_0 .

Strain stress was calculated from the maximum strain in graphs of strain versus deformation. Elastic deformation was the deformation at the maximum strain stress.

Characterization of mass transport phenomena in PFA membranes

Absorption

Absorption experiments were performed using PFA membranes synthesized in 96-well plates (Corning Costar, 3591), varying the amounts of FA or HCl, as previously described. Absorption was characterized by determining the water content and swelling degree of PFA films as follows.

Water content. Fully dried PFA films were weighed and placed in deionized water until the weight of the hydrated polymer remained constant. Water content at equilibrium was calculated using the following equation.

$$\text{Water content (\%)} = \left(\frac{W_d}{W_h} \right) \times 100 \quad (6)$$

where W_h and W_d are the weights of hydrated and dehydrated polymers, respectively.

Swelling degree. Completely dried and pre-weighed PFA disc-shaped films were placed in 5 mL of deionized water. Polymer disks were removed from the water and weighed at different times after blotting with a filter paper to remove unabsorbed liquid. Swelling degrees (D_s) (%) were calculated using the following equation (Boruah *et al.* 2015):

$$D_s (\%) = \left(\frac{W_h - W_d}{W_d} \right) \times 100 \quad (7)$$

where W_h and W_d are the weights of hydrated and dehydrated polymers, respectively.

Permeation

Molecular diffusion. Thin films of PFA were synthesized in Nunc[®] Petri dishes (Merck, P7741) with a final reaction volume of 15 mL and different proportions of FA and HCl, as mentioned before. PFA membranes of 1.0 mm thick were cut to size and placed in a stirred ultrafiltration cell (Amicon Millipore, Cat. 5121, Model 8010) filled with 10 mL of deionized water. The applied pressure was controlled with a manometer (Silverline, DC-A2020R). Water flux was determined by measuring the volume of eluted water over time as a function of the applied pressure.

Statistical analysis

All measurements are expressed as the average \pm standard deviation of at least three independent experiments. Statistical significances were calculated using a two-way analysis of variance (ANOVA) followed by Tukey's test.

RESULTS AND DISCUSSION

Synthesis and structural characterization of PFA membranes

The synthesized PFA membranes were white, soft, elastic rubbers, as shown in Figure 2(a). The cost of the materials used for the synthesis was low, 0.017 USD cm⁻³, considering the cost of laboratory-grade reagents (no energy costs, labor, maintenance, and depreciation of machinery are considered in this estimation). At a large scale, it can be assumed that the polymer cost will be lower, as wholesale reagents will be used. Moreover, a high demand and a competitive business environment would also decrease the price further.

To characterize the microscopic structure of PFA at various HCl contents, SEM analysis was performed (Figure 2(b)–(d)). SEM cross-sectional views showed a microporous polymer. The PFA network was more entangled as HCl content increased due to the higher crosslink degrees (Antonietti *et al.* 1999).

Reactants and polymerization products were analyzed by the FTIR according to the vibrational modes previously reported (Gaffney *et al.* 2012). FTIR spectra are shown in Figure 2(e)–(g), where the principal peaks are highlighted. In Figure 2(e), the spectrum of PVA had a wide band of 3,350–3,200 cm⁻¹ representing the stretching vibration of the intramolecular and intermolecular hydroxyl groups (–OH), a peak at 2,840–3,000 cm⁻¹ corresponds to the stretching vibration of PVA alkyl groups (–CH), a peak at 1,461–1,417 cm⁻¹ corresponds to the bending vibration of PVA methylene groups (–CH₂), and a peak at 1,141 cm⁻¹ corresponds to –C–O bonds, an indicator of PVA crystallinity (Mansur *et al.* 2008). Figure 2(f) shows the spectrum of FA, where the band at 3,350–3,200 cm⁻¹ represents the stretching vibration of the intramolecular and intermolecular hydroxyl groups (–OH) due to water, a doublet at 2,830–2,695 cm⁻¹ corresponds to the stretching vibration of alkyl groups from aldehydes (–CH), a peak at 1,750–1,735 cm⁻¹ corresponds to the stretching vibration of carbonyl groups, and a peak at 1,740–1,645 cm⁻¹ corresponds to the stretching vibration of carbonyl groups from aldehydes. Finally, in Figure 2(g), the spectrum of the polymerization product showed a wide band of 3,350–3,200 cm⁻¹ representing the stretching vibration of the intramolecular and intermolecular hydroxyl groups (–OH), due to remnant water and/or remnant –OH groups from PVA, a peak at 2,830–3,000 cm⁻¹ corresponds to the stretching vibration of –CH groups from remnant aldehyde, a peak at 1,740–1,720 cm⁻¹ corresponds to the stretching vibration of –C=O groups from saturated aliphatic aldehydes, and a peak at 1,150–1,085 cm⁻¹ corresponds to the stretching vibration of acetal bonds (–C–O–C). Here, the peak from the –C–O–C– groups shifted to higher frequencies in the spectrum, indicating the formation of –C–O–C– acetal and ether bonds (Gaffney *et al.* 2012). The obtained spectrum was similar to the reference spectrum reported by Pan *et al.* (2014) for PFA, indicating that synthesis was successful.

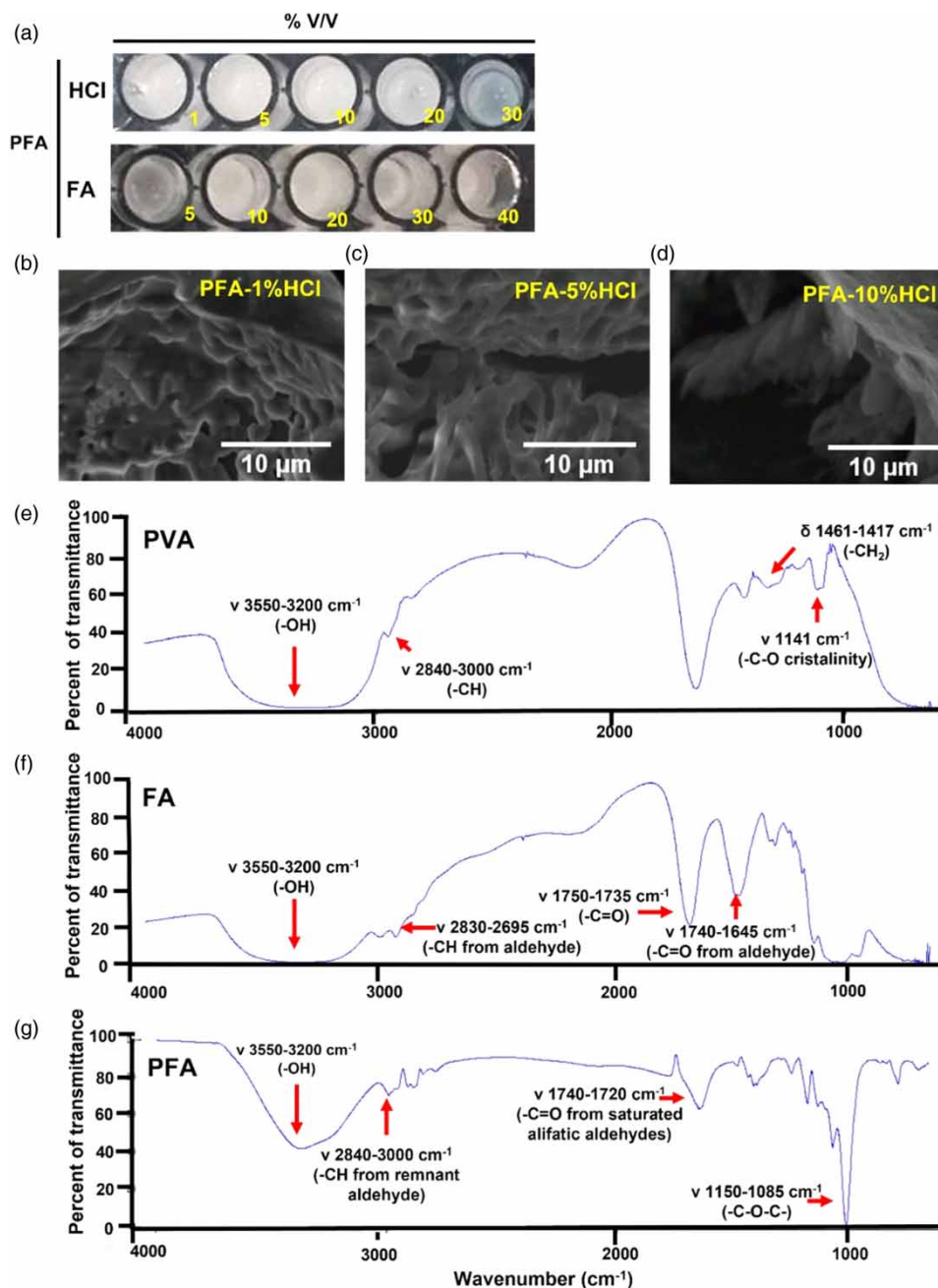


Figure 2 | Synthesis and characterization of PFA membranes. (a) PFA membranes synthesized in 96-well plates at different HCl or FA contents, indicated in yellow, at constant FA (20%) or HCl (1%) contents. (b–d) Cross-sectional SEM images of dehydrated PFA membranes with different crosslinking degrees. Crosslinking was modulated by varying the HCl content: (b) 1%, (c) 5%, and (d) 10% at constant FA content (20%). (e–g) The FTIR spectra of reactants and products of the PFA polymerization reactions: (e) PVA, (f) FA, and (g) PFA (20% FA and 1% HCl). Principal peaks are highlighted by red arrows. Vibration types are indicated in the figure as follows: ν , stretching; δ , bending. Please refer to the online version of this paper to see this figure in color: <http://dx.doi.org/10.2166/wrd.2022.077>.

Metal adsorption into PFA

Other works have reported the use of PVA crosslinked with aldehydes for desalination or heavy metal removal; however, most of them use sophisticated synthesis methods, incorporate expensive additives, or perform further chemical modifications that make the final product more expensive (Kim *et al.* 2019; Tlili & Alkanhal 2019; Yilman *et al.* 2019; Isawi 2020). In this work, PFA adsorptive properties were analyzed with no further modifications to maintain low costs of

production. Most of the studies in the literature for heavy metal adsorption analyze the adsorption of each element individually, but in real-life conditions, metals are mixed and compete according to their affinity to the adsorbent. As the first approach to evaluate the capability of PFA membranes to adsorb metallic cations, membranes were exposed to a mix of metallic salts at a similar concentration each, at room temperature and the pH value of 1 to avoid metal precipitation, and it is recommended for ICP-MS analysis (Rao *et al.* 2017; Wilschefski & Baxter 2019). Figure 3(a) shows that simultaneous adsorption of chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), copper (Cu), and zinc (Zn) occurred after 24 h of interaction with PFA at an amount inversely proportional to the PFA crosslinking degree. Adsorption of heavy metals into PFA was 50% for Cr, 57% for Mn, 39% for Fe, 55% for Co, 60% for Cu, and 70% for Zn. These results are relevant because it has been demonstrated that absorption efficiencies of heavy metals in polymeric membranes decrease when they are added simultaneously (Li *et al.* 2011); nonetheless, PFA showed high removal of six cations interacting at the same time.

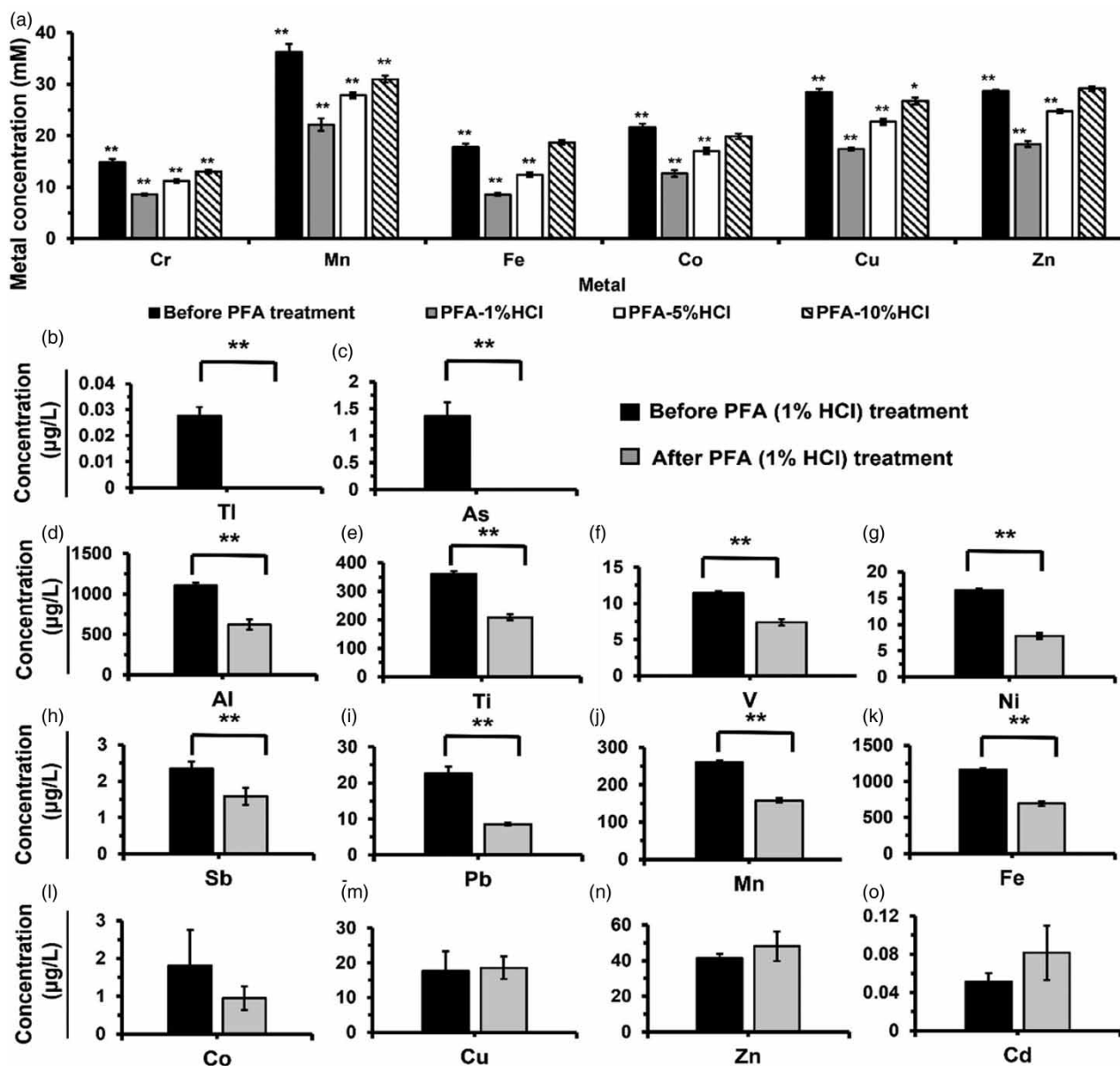


Figure 3 | Metal adsorption into PFA membranes. (a) Metal adsorption in PFA membranes obtained at different HCl contents. Incubations were performed at 25 °C, pH 1 for 24 h. (b–o) Metal content in water samples from the Atoyac River before and after exposure to PFA membranes (20% FA and 1% HCl) ($n = 3$). Error bars represent standard deviations; * $p < 0.05$; ** $p < 0.01$.

Adsorption capacities of PFA membranes at equilibrium (Q_e) (after 24 h of interaction) for Cr, Mn, Fe, Co, Cu, and Zn at different crosslinking degrees are listed in Table 1. The highest metallic adsorption was observed at PFA 1% HCl, followed by 5% HCl and 10% HCl. Note that Q_e is affected by pH, the oxidation state of elements, temperature, contact time, ionic strength, and competitive interactions between metals, among others, so it is impossible to compare our results with other reports.

Most of the materials for heavy metal removal are studied at ideal conditions, where interferences that can affect polymer performance are commonly ignored. Here, the PFA (1% HCl and 20% FA) capability for heavy metal removal was evaluated in the presence of real-life samples from the Atoyac River, containing organic matter, molecules with a neutral, positive, and negative charge, and other metallic cations not considered in the reference solution.

The Atoyac River is located in the Mexican metropolitan area between Puebla and Tlaxcala states. It is considered one of the most polluted rivers in Mexico. The Atoyac River receives multiple discharges of wastewater from urban, agricultural, and industrial sources. The danger to human health and the ecotoxicological impact on aquatic and terrestrial organisms have been widely documented in local communication media (Shruti *et al.* 2019; Mora *et al.* 2021).

The concentrations of aluminum (Al), titanium (Ti), vanadium (V), nickel (Ni), antimony (Sb), lead (Pb), manganese (Mn), iron (Fe), thallium (Tl), and arsenic (As) in samples of the Atoyac River were determined by ICP-MS before and after exposing the water samples for 24 h to PFA membranes at room temperature (Figure 3(b)–(o)).

Our data showed a significant decrease in the levels of Al, Ti, V, Ni, Sb, Pb, Mn, Fe, Tl, and As. Pb, Fe, and Mn concentrations decreased to acceptable levels for drinking water according to the Mexican standards (0.025, 0.030, and 0.015 mg/L, respectively). Moreover, As and Tl levels were reduced below the LOD of the equipment, 0.659 and 0.0185 $\mu\text{g L}^{-1}$, respectively. Mexican regulation allows up to 0.05 mg/L of these metals in drinking water.

Even when the real-life sample contained multiple molecules of diverse size, nature, and proportions, which can affect the membrane performance, PFA had high heavy metal/metalloid adsorption efficiencies, as shown in Table 2. Best removal efficiencies were obtained for As, Tl (to undetectable levels), and Pb (62%), three of the most hazardous pollutants in drinking water, after a single-step treatment. In summary, these results show that PFA membranes obtained at 1% HCl, 20% FA exhibited interesting properties for heavy metal removal, even in real-life samples with possible interfering molecules. A single incubation step of polluted water with PFA membranes was sufficient to significantly reduce the concentration of metals and metalloids.

Mass transport phenomena

Polymer crosslinking degrees affect mass transport phenomena (Krumova *et al.* 2000). Their understanding is fundamental for applications like desalination, drug delivery, and heavy metal removal, among others. Mass transport through polymer membranes is described as a ‘solution-diffusion’ mechanism. It consists of the following steps: (a) *absorption* of small molecules into the membrane, (b) *permeation (or molecular diffusion)* in or through the polymer, and (c) *desorption* of the diffused molecules (Flory 1985). In this work, absorption and permeation into PFA membranes were characterized as a function of their crosslinking degree.

Absorption: water content and swelling dynamics

The PFA capacity for absorbing small molecules was evaluated using water as a model molecule. Experiments were performed at room temperature and pH 7. Results of water content in PFA membranes at different crosslinking degrees are shown in Figure 4. PFA membranes with 1–20% HCl reached a water content of 75–70%, and membranes with 30–40%

Table 1 | Q_e values calculated for metals simultaneously adsorbed into PFA membranes at different HCl (%v/v) contents at 25 °C, pH 1, and 24 h of incubation (when the equilibrium was reached) ($n = 3$)

%HCl	Cr (mg/g)	Mn (mg/g)	Fe (mg/g)	Co (mg/g)	Cu (mg/g)	Zn (mg/g)
1	79.7 ± 2.8	181 ± 15.5	118 ± 3.5	115 ± 8.2	142 ± 3.6	132 ± 7.0
5	45.8 ± 1.7	107 ± 4.5	68.8 ± 2.4	58.8 ± 5.7	74.6 ± 4.5	50.0 ± 2.3
10	23.8 ± 4.6	73.6 ± 9.4	ND	23.5 ± 6.9	23.9 ± 9.0	ND

Intervals represent standard deviations.

ND, not determined.

Table 2 | Removal efficiency of metals or metalloids in water from the Atoyac River into PFA membranes (1% HCl and 20% FA) at 25 °C ($n = 3$)

Element	Removal efficiency (%)
Al	43.7 ± 5.9
Ti	42.2 ± 3.0
V	35.5 ± 3.8
Ni	35.5 ± 2.9
Sb	32.7 ± 10.2
Pb	62.3 ± 1.5
Mn	39.3 ± 2.2
Fe	40.5 ± 2.9
Tl	100 ^a
As	100 ^a
Cu	ND
Zn	ND

Intervals represent standard deviations. The equipment detection limits for these elements are 0.659 and 0.0185 $\mu\text{g L}^{-1}$, respectively.

ND, not determined.

^aNo residual Tl or As was detected.

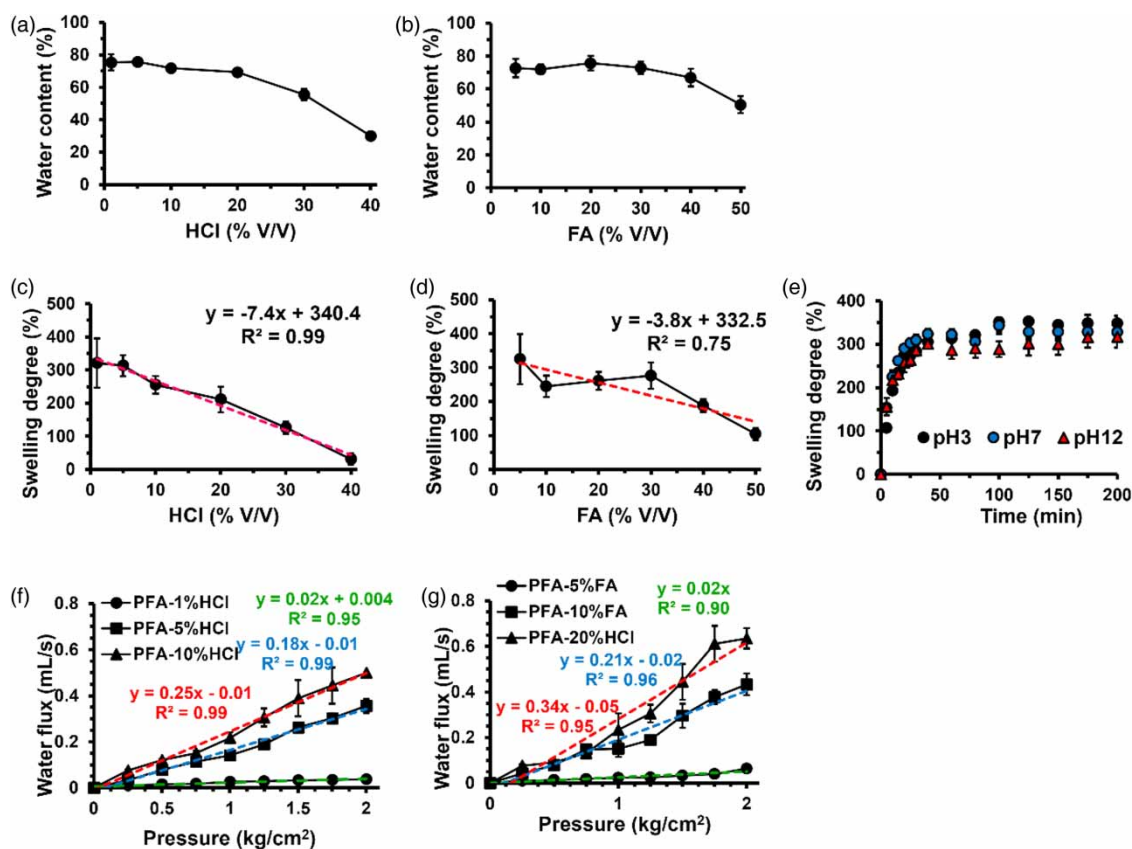


Figure 4 | Characterization of mass transport phenomena in PFA membranes at different crosslinking degrees, obtained by changing HCl or FA contents in polymerization reactions. (a and b) Water content in PFA membranes. Crosslinking was modulated by varying either (a) HCl or (b) FA content. (c–e) Swelling dynamics of PFA membranes synthesized with various contents of (c) HCl or (d) FA. Linear fit (lines), the first-order equation, and Pearson's correlation coefficients (R^2) are shown. (e) Swelling dynamics of PFA (1% HCl and 20% FA) at different pH values. (f) and (g) Water flux through PFA membranes as a function of pressure and crosslinking degree. The crosslinking degree was modulated by varying the amount of (f) %HCl (v/v) keeping constant the FA content at 20% or (g) %FA (v/v) at constant HCl content (1%). Linear fit, first-order equations, and Pearson's correlation coefficients (R^2) are shown ($n = 4$). Error bars represent standard deviations. Some bars were smaller than the symbols shown.

HCl had a water content of 50–30% of absorbed water, as shown in Figure 4(a). PFA membranes with 5–40% of FA reached a water content of 70%, and PFA with 50% of HCl had a water content of 50% (Figure 4(b)). Taken together, these results showed that the water content of PFA can be tuned by varying the crosslinker or catalyst amount.

The crosslinking degree influences many of the polymer network properties, including swelling (Gohil *et al.* 2006). Hence, the influence of HCl and FA content in the maximum swelling of PFA membranes was studied. Figure 4(c) shows that the swelling degree decreased linearly with higher HCl contents ($R^2 = 0.99$). The maximum swelling at 1% of HCl was three-fold higher than that at 40% of HCl. In contrast, PFA swelling decreased at higher FA contents in a non-linear way ($R^2 = 0.75$). The maximum swelling at 5% of FA was two-fold higher than that at 50% of FA (Figure 4(d)).

The high swelling found in PFA membranes was attributed to hydrophilic groups, such as hydroxyls or aldehydes, formed from an incomplete polymerization, which are available to form weak intramolecular hydrogen bridges. Hydrophilic groups facilitate water uptake into the PFA network. Also, vice versa, at a higher content of catalyst or crosslinker, the hydrophobic acetals increased, the intramolecular hydrogen bridges decreased, and consequently, swelling also decreased.

pH is not constant in wastewater and can affect the polymer performance. Therefore, swelling of PFA (1% HCl and 20% FA) membranes at different pH values was studied (Figure 4(e)). No differences were found between pH 3, pH 7, and pH 12. Similar results were obtained for other PFA crosslinking degrees (data not shown). These results were surprising. An effect of pH was expected, as polymeric structures with hydrophilic groups are susceptible to be protonated or deprotonated, depending on the pH of the surrounding media, which would result in movement of the polymer network due to the attraction or repulsion between polymeric chains, affecting the network swelling dynamics. PFA contains multiple hydroxyl groups (primary alcohols have a pK_a of approximately 17) that can suffer protonation–deprotonation in acid or alkaline conditions, respectively (Wade & Simek 2017). An explanation of the behavior observed is that chemical crosslinking, and the consequent cyclic acetal formation, increased the rigidity of the polymer and restricted its movement, reducing the effect of pH.

The independence of swelling dynamics to pH of the PFA membranes is an advantage, as the performance of the membrane can be expected to be similar at changing wastewater pH. For example, acid rain has a value of pH between 2.1 and 5.0, whereas the occurrence of $\text{Ca}(\text{OH})_2$ and $\text{Mg}(\text{OH})_2$ deposits has been associated with hyperalkaline groundwater (Likens & Bormann 1974; Neal & Stanger 1984). Then, it is necessary that polymers used for water remediation have chemical stability, keeping a consistent mass transport independent of pH.

In summary, the swelling degree of PFA membranes can be easily manipulated by HCl or FA content. From 1 to 40% of HCl, swelling decreased linearly. Together, our results demonstrate that PFA membranes have a consistent swelling at various pH values, making them materials with good performance at the changing extreme environmental conditions typical of polluted water treatment systems.

Permeation

In real-life ion exchange processes, polymers must have good permeability and resistance to an applied pressure to allow an adequate water workflow. To evaluate the molecular diffusion across PFA membranes, permeation of a water flux was studied as a function of their crosslinking degree and pressure. The results are shown in Figure 4(f) and (g). Contrary to our intuition, at higher HCl or FA content, PFA membranes showed a linear increase in permeability (Figure 4(f) and (g), respectively). These results have three possible explanations not mutually exclusive. First, the compression created by the applied pressure deforms the PFA membrane, which decreases the effective size of the pathways available for water to permeate across the PFA membrane. Second, structural heterogeneities can be formed during the polymerization (Matuzawa & Ogasawara 1972; Tokita & Tanaka 1991a, 1991b). Polymer heterogeneities cause both relaxed and dense domains with higher or lower permeability, respectively (Tanaka *et al.* 1973). In our conditions (1–10% of HCl and 5–20% of FA), PVA is the reagent in excess, FA is the limiting reagent, and HCl is the catalyst that accelerates the reaction. Therefore, more mobile PVA coils exist at lower HCl or FA contents. According to Grattoni *et al.* (2001), such free polymer coils preferentially fill the relaxed domains in the matrix, reducing the spaces for water flow and consequently decreasing the polymer permeability. And third, according to Chen *et al.* 1973, PFA membranes show low water adsorption and permeability when synthesized at 200 °C for 10 min. Here, milder conditions of synthesis were used (36 h at room temperature and 6 h at 45 °C), according to Li *et al.* (2005), and the obtained polymer had excellent swelling, water absorption, and permeation properties needed for an effective ionic exchange. The lower synthesis temperature used here can reduce the semi-crystalline regions, increasing the permeation capacity, swelling degree, and water content (Harland & Peppas 1989; Wypych 2015). In summary, our results showed that PFA permeation was proportional to the crosslinking degree and the applied pressure.

Mechanical properties

Mechanical properties are important parameters to determine the application of polymers for specific purposes. These properties depend on the polymer structure, such as crosslinking density and the type of crosslinking. A material suitable for wastewater treatment should resist high pressures and the consequent high-water fluxes through the membrane. A rational design of materials for wastewater treatment should consider the tensile strength, which indicates the maximum force that the polymer can resist before breaking, and strain stress, defined as the pressure needed to provoke a permanent damage or deformation of the material. Elasticity and the Young's modulus are also important parameters that determine the flexibility of the bulk PFA.

The mechanical properties of PFA at different crosslinking degrees modulated by the HCl content were studied because, unlike FA, HCl influenced the PFA desorption properties (Figure 5).

At 5 and 20% HCl contents, PFA had significantly increased tensile strength (Figure 5(a)), strain stress (Figure 5(b)), and Young's modulus (Figure 5(c)) ($p < 0.01$) than at 1% of the HCl content. No difference was detected between 5 and 20% HCl. Elastic deformation decreased at higher HCl content (Figure 5(d)). These results are due to the induced crosslinking by HCl, which restricts the motion of the PFA chains, increasing the stiffness of the polymer. An interesting comparison can be performed with the product of PVA crosslinked with glutaraldehyde to obtain poly(vinyl alcohol co-vinyl acetate) (PACVA). Villanueva-Flores *et al.* (2019) showed that tensile strength, strain stress, and Young's modulus decreased as the content of GA increased. PACVA reached a maximum tensile strength of 120 N, whereas the maximum tensile stress of PFA was three-fold higher. PACVA reached a maximum strain stress of 70 kPa, and PFA was 12-fold higher. PACVA reached a maximum Young's modulus of 160 kPa, and PFA was four-fold higher. The different mechanical behaviors of PACVA and PFA are due to different separation between cyclic acetals (responsible for the stiffness) by three methylene groups on PACVA versus

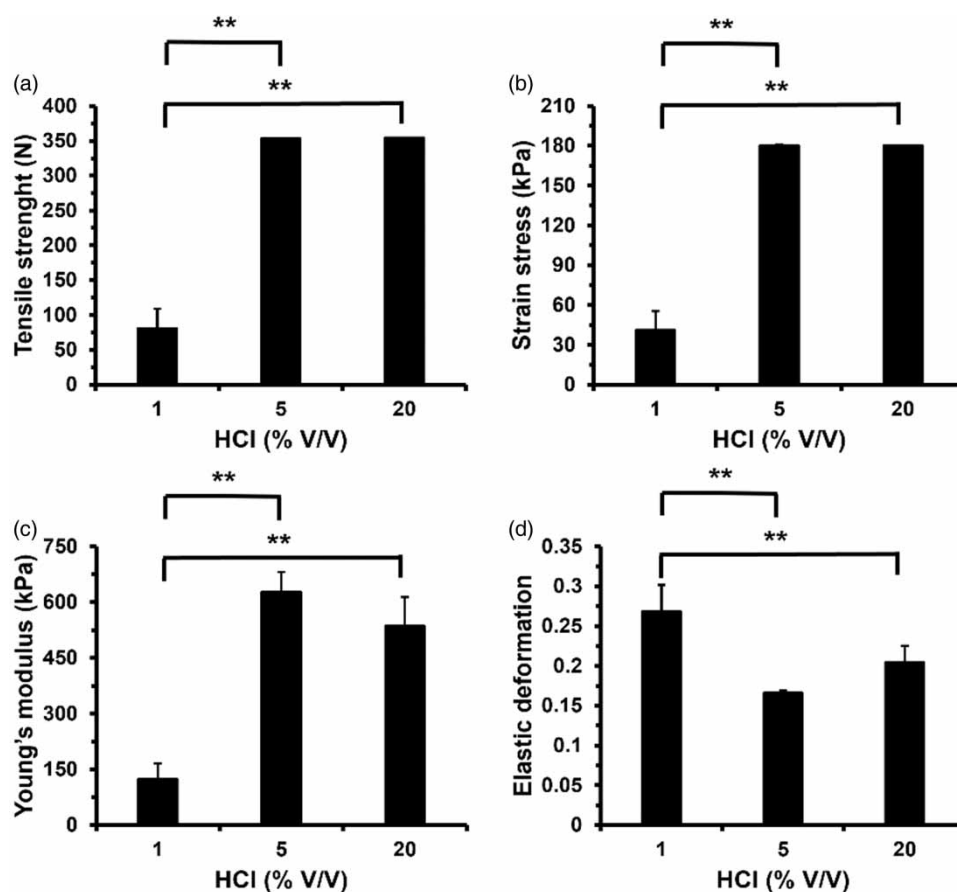


Figure 5 | Mechanical properties of PFA membranes as a function of the crosslinking degree. The crosslinking degree was modulated by varying the amount of HCl during synthesis: (a) tensile strength, (b) strain stress, (c) Young's modulus, and (d) elastic deformation ($n = 3$). Error bars represent standard deviations; ** $p < 0.01$.

one methylene group in PFA. A larger distance between cyclic acetal chains reduces inter-catenary hydrogen bridges and increases the conformational freedom of movement in PAcVA, which PFA lacks. This structural difference also explains why PAcVA is transparent and soft and PFA is opaque and hard, making the second material suitable for applications as the ones described here. In this first approach, it was shown that the mechanical properties of PFA can be modulated by varying HCl content from 1 to 5% to obtain the desired material properties for a specific application.

Taken together, our results show that the efficiency for heavy metal removal is inversely proportional to the HCl concentration used as crosslinker. As the crosslinking increased, negatively charged groups, such as hydroxyls and aldehydes, decreased, reducing the capability of PFA membranes to adsorb metallic cations. Lower crosslinking resulted in a more permeable membrane, which facilitates the ion exchange across the PFA network.

CONCLUSIONS

In this work, we synthesized and characterized PFA membranes at different crosslinking degrees by modulating the FA or HCl content. We found that PFA membranes are easily synthesized, have a low cost of materials, and resist a wide range of pH and showed adequate mechanical resistance, which makes them excellent materials for resisting extreme environmental conditions. The obtained polymer had a significant capacity for heavy metal removal in real-life water samples from a polluted Mexican river, reducing lead, iron, manganese, arsenic, and thallium concentrations to acceptable levels for drinking water according to the Mexican standards. It is worth highlighting that, contrary to other works, no additional PFA modifications were required to obtain a good performance material capable of efficient heavy metal removal with mechanical and chemical resistance. It was possible to select the properties of synthesized PFA by modifying its crosslinking degree simply by changing the HCl content during the polymerization reaction, with low production costs. Further research should be conducted to evaluate PFA membranes under real-life water fluxes to simulate operating conditions of on-site treatment and to recover the adsorbed metals to the reusability of the membranes. We hope that this technology can be applied in home water filters or at the large scale in polymer-assisted ultrafiltration processes, especially in developing countries that still suffer from severe health problems by drinking polluted water.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

AUTHOR CONTRIBUTIONS

F.V.-F. conceptualized the study, prepared the methodology, validated the study, did the formal analysis, carried out the investigation, wrote the original draft, and visualized the study. L.A.P. conceptualized the study, validated the study, did the formal analysis, collected the resources, edited the original draft, supervised the study, and acquired funds for the study.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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