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Removal of Heavy Metals From Landfill Leachate Using Electrospun Polyelectrolyte Complex Fiber-Laminated Ultrafiltration Membrane

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REMOVAL OF HEAVY METALS FROM LANDFILL LEACHATE USING ELECTROSPUN POLYELECTROLYTE COMPLEX FIBER-LAMINATED ULTRAFILTRATION MEMBRANE

by

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ABSTRACT

Ultrafiltration (UF) is a low-pressure membrane process that yields higher permeate flux and saves significant operating costs compared to NF/RO. However, UF has not been applied as a primary method for landfill leachate treatment due to its large pore size. This research investigated the removal of heavy metals from landfill leachate using an UF membrane laminated with fiber mats produced from electrospinning of a polyelectrolyte complex. In this research, we modified the surface of the UF membrane with two polyelectrolytes including Polyacrylic Acid (PAA) and Polyallylamine Hydrochloride (PAH). The removal of heavy metals including Pb, Cd, and Cu from water using electrospun (ES) polyelectrolyte (PE) complex fibers of polyacrylic acid (PAA) and polyallylamine hydrochloride (PAH) was investigated. PAA/PAH fiber mats were fabricated under various electrospinning operating conditions to optimize fiber size and stability. The fiber mats exhibited approximately 63%, 42%, and 21% removals of Pb, Cd, and Cu, respectively in synthetic metal solutions at pH 3.4. Furthermore, approximately 70%, 98%, and 92% removals of Pb, Cd, and Cu, respectively were observed at a higher pH (7.4). Moreover, the removal of heavy metals from various synthetic feed solutions and landfill leachate by the PAA/PAH-laminated UF membranes (PAA/PAH-UF) was studied. The PAA/PAH-UF membrane exhibited approximately 38%, 49%, and 85% higher removal of Pb, Cu, and Cd, respectively from laboratory-prepared metal ion solution (DI water) when compared to the unmodified UF membrane (UF). The PAA/PAH-UF membrane exhibited approximately 18% and 15% higher removal of Pb and Cu, respectively in the leachate when compared to DI water. The PAA/PAH-UF membrane

showed around 16% and 72% higher removal of Pb and Cd at the presence of NOM. Moreover, the UF membrane showed approximately 18%, 25%, and 30% more removal of Pb, Cd, and Cu at the presence of NOM, respectively.

This dissertation is dedicated to my parents and my brother for their love, patience, and support throughout my entire education and life.

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LIST OF ABBREVIATIONS

Cd	Cadmium
Cu	Copper
ES	Electrospun
EDS	Energy-Dispersive X-ray Spectroscopy
FAAS	Flame Atomic Absorption Spectroscopy
FT-IR	Fourier Transform Infrared
Pb	Lead
PAA/PAH-UF	PE laminated UF membranes
PAA	Polyacrylic Acid
PAH	Polyallylamine Hydrochloride
PE	Polyelectrolyte
PES	Polyethersulfone
SEM	Scanning Electron Microscopy
UF	Ultrafiltration

CHAPTER 1: INTRODUCTION

Heavy metals possess certain useful physical and chemical properties and hence are used in the manufacturing of various consumer and industrial products. Despite recent efforts of waste minimization and diversion, landfilling is still the primary method for waste disposal in both developed and developing countries. While recent regulations in many countries have dictated the installation of engineered liners and leachate collection systems, historically most landfills were built without engineered liners and leachate collection systems. Further, biosolids generated from wastewater treatment plants contain high concentrations of heavy metals that escape the conventional treatment processes, which are not designed to remove heavy metals from wastewater. The release of heavy metals via landfill leachate (in the case of unlined landfills) or runoff that is not effectively retained by the leachate collection system (failed containment) into the groundwater and eventually to the surface water poses a potential long-term risk to the surrounding environment (Kurniawan et al., 2006).

Conventional biological and physico-chemical treatment of landfill leachate have limitations in removing recalcitrant organics and heavy metals. Membrane processes have been demonstrated as effective barriers to recalcitrant organic and inorganic pollutants (Linde et al., 1995; Renou et al., 2008a), resulting in high effluent quality and reduced sludge volume (Renou et al., 2008a; Ahmed and Lan, 2012), while operating within a smaller footprint when compared to conventional physico-chemical treatments. Nevertheless, high-pressure membrane treatment (nanofiltration (NF), reverse osmosis

(RO)) is energy intensive and is prone to fouling during long-term operation. Ultrafiltration (UF) is a low-pressure (40–1000 kPa) membrane process that yields higher permeate flux and saves significant operating costs compared to NF/RO (Lin et al., 1999); however, UF has not been applied as a primary method for landfill leachate treatment (Tabet et al., 2002a) due to its large pore size (0.001–0.1 μm) (Lin et al., 1999).

This research investigated the application of polyelectrolyte (PE) complexes produced through a cost-effective and scalable electrospinning technology for efficient removal of heavy metals from landfill leachate. PEs have been widely investigated as heavy metal ion removal materials because of high local concentration of functional groups such as carboxylates as well as strong interactions of these functional groups with metal ions. While a major limitation of incorporating PEs in membranes is their solubility in water, recent finding demonstrated that PE nanofiber membranes (NM) produced by electrospinning solutions of PE complexes exhibit excellent stability in aqueous solutions (Chunder et al., 2007; Malhotra et al., 2016b). The electrostatic interactions between partially charged polymeric chains in ES fibers lead to the formation of a polymer hydrogel network without covalent crosslinkers. ES is a low-cost promising technique in generating polymer fibers with diameters in the range of nanometers to micrometers (Chen et al., 2011; Yee et al., 2012; Chen et al., 2013) with a range of applications in various fields.

Objectives

In this study, we fabricated PE fibers from polyacrylic acid (PAA) and polyallylamine hydrochloride (PAH) through ES and UF membranes laminated with PAA/PAH fiber mats to investigate their capability in removing selected heavy metals in landfill leachate. The specific objectives of this study were:

1. To develop methods to fabricate polyelectrolyte complex fibers by electrospinning.
2. To characterize and evaluate the stability of fabricated polyelectrolyte fibers in heavy metal solutions.
3. To determine the removal of heavy metals from landfill leachate using electrospun PE fiber-laminated ultrafiltration (UF) membrane.
4. To determine the effect of water matrix on heavy metal removal by the fibers and fiber-laminated UF membrane using natural organic matters (NOM) as a water matrix component.
5. To acquire mechanistic understanding of metal removal from landfill leachate when using the modified UF membrane.

CHAPTER 2: LITERATURE REVIEW

2.1. Heavy Metal Sources and Usage

The generation of toxic pollutants has a direct relationship to the industrial and agricultural activities globally. The universal environmental pollution is influenced by anthropogenic activities and increased population and urbanization (Hanif et al., 2005; Khan et al., 2009a). Activities such as mining (Li et al., 2014), smelting (Ettler, 2016), agricultural processes (Yang et al., 2018), batteries manufacturing (Horeh et al., 2016), and fossil fuel combustion (Ouellet and Jones, 1983) can result in heavy metals release in the nature. The characteristics of the pollution is related to its source (Bhatnagar et al., 2011). Although different activities result in generating different pollutants, but the common pollutants in wastewater are metal ions in addition to detergents, dyes, pesticides, insecticides, phenols, and a wide range of aromatics (Bhatnagar et al., 2011).

2.2. Occurrence and Fate of Heavy Metals in Landfill Leachates

The global generation of municipal solid waste (MSW) is projected to increase to 2.2 billion tonnes by 2025 (Hoornweg and Bhada-Tat, 2012). Despite recent efforts of waste minimization and diversion, landfilling is still the primary method for waste disposal in both developed and developing countries. A portion of the heavy metals used in the manufacturing of various consumer and industrial products eventually make their ways to the landfill. An estimated 9% of approximately 258 million tons of MSW generated in 2014 in the U.S. consisted of metals[21]. Every year, an estimated 400 tons of mercury,

3000 tons of cadmium, 14,000 tons of nickel, 20,000 tons of copper, and nearly 100,000 tons each of chromium, lead, and zinc are disposed in landfills in the U.S. (Aucott et al., 2006). In addition, due to rapid development of information technology, production of electronic devices has increased. Approximately 70% of the total heavy metals and 40% of total lead in the waste stream that is being sent to landfills can be attributed to E-wastes (Grossman, 2010), only 10% of which is recycled (Li et al., 2009). The E-wastes typically contain lead, cadmium, arsenic, copper, zinc, mercury, and other heavy metals and rare earth metals (Aucott et al., 2006). The increasing production and use of engineered nanoparticles (NP) have triggered research regarding the occurrence and fate of NPs in landfill leachate. A recent study on the behavior of engineered NPs in landfill leachate has reported increased concentrations of Zn, Ti, and Ag when compared to that in background matrix, attributing to the interaction of leachate components with nanoparticle coatings (Bolyard et al., 2013). Biosolids generated from wastewater treatment plants contain high concentrations of heavy metals that escape the conventional treatment processes, which are not designed to remove heavy metals from wastewater. The disposal of biosolids into landfill leads to the generation of leachate that is rich in heavy metals. Sustainable treatment technologies are required to break this vicious cycle either by treating landfill leachate onsite or during co-treatment of leachate and wastewater.

2.3. Adverse Effects Associated with Heavy Metals

In addition to industrial benefits of heavy metals, they are also necessary for normal growth of plants and metabolism functions of microorganisms at certain levels (Rascio and Navari-

Izzo, 2011). On the other hand, the excessive amount of heavy metals are highly toxic (Nies, 1999). Heavy metals such as cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), mercury (Hg), and nickel (Ni) have been considered as the toxic pollutants (Carolin et al., 2017). The accumulation of heavy metals can adversely influence human health (Järup, 2003; Godt et al., 2006; Leung et al., 2008), animals (Pandey and Madhuri, 2014), plants (Nagajyoti et al., 2010), and microorganisms (Nakajima and Sakaguchi, 1986). Habitat destruction because of sedimentation, algal bloom, and death of aquatic lives are observed due to heavy metals contamination (Rai, 2008; Akpor et al., 2014; Paul et al., 2014). In addition, heavy metals exposure can result in reduced growth and development, kidney damage, nervous system damages, endocrine and immunological disorders, cancer, and even death (Khan et al., 2009b; Akpor et al., 2014). Humans exposure to heavy metals can be through ingestion of contaminated drinks and foods or inhalation of contaminated fume or dust (Akpor et al., 2014). These elements can enter the humans and animals' food chains through absorption by plants, and negatively influence their health and functionality (Chary et al., 2008; Jan et al., 2010; Avci and Deveci, 2013; Obiora et al., 2016). The negative effects of heavy metals on human health, and the maximum contamination level (MCL) of each element in drinking water according to the US Environmental Protection Agency is sorted in Table 1 (Babel and Kurniawan, 2005; USEPA, 2009).

Table 1. MCL standards and side effects of heavy metals.

Heavy metal	Negative effects	MCL (mg/L)
Pb	Renal, Cerebral disorders, Circulatory & Nervous disorders	0.015
Cd	Carcinogenic, Renal disorders and damage	0.005
Cu	Liver damage, Insomnia, Wilson's disease	1.3
Zn	Neurological signs, Lethargy, Increased thirst, Depression	5*
Hg	Circulatory & Nervous disorders, Rheumatoid arthritis	0.002
Cr	Carcinogenic, Headache, Diarrhea, Nausea	0.05**
As	Visceral cancer, Skin and vascular diseases	0.01
Ni	Carcinogenic, Chronic Asthma, Dermatitis	0.20**

* reported MCL for zinc is regarding the Secondary Maximum Contaminant Level.
** reported MCL are reported from (Burakov et al., 2018).

Lead, cadmium, and copper - the three heavy metals tested in this research - can be harmful to human health. Lead can cause brain, central nervous system, kidney, liver and reproductive system damages (Naseem and Tahir, 2001). Cadmium can cause skin irritation and serious lung cancer (Mohanty et al., 2005). Although copper plays an important role in the metabolism, excessive amount of copper can cause vomiting, convulsion, cramps, or even death (Paulino et al., 2006). Heavy metals can contaminate both soil (Bååth, 1989; Giller et al., 1998; Nagajyoti et al., 2010; Wuana and Okieimen, 2011) and water (Davies, 1979; Naimo, 1995; Tiwari et al., 2016; Kumar et al., 2019). High levels of ecologically destructive heavy metals have been reported in rivers (Squadrone et al., 2013; Wu et al., 2016). Heavy metals are toxic to living organisms, persistent in the nature, and have low removal rate, high enrichments factor in addition to their bio-accumulative nature (Yilmaz et al., 2010). These enter into water resources via

natural phenomena such as earth erosion and weathering or via anthropogenic activities such industrial and agricultural processes (Yalcin et al., 2007).

2.4. Water Treatment for Heavy Metals (Conventional Technologies for Drinking Water, Wastewater, and Landfill Leachate)

Heavy metals in addition to other contaminants such as humic acid, xenobiotics and chlorinated organic and inorganic salts, ammonia nitrogen, etc., can be found in water, wastewater, and landfill leachate (Pirbazari et al., 1996; Kjeldsen et al., 2002; Baun et al., 2004; Silva et al., 2004; Wiszniowski et al., 2006; Renou et al., 2008a). A variety of on and off-site techniques have been proposed for the treatment of water, wastewater, and landfill leachate (Wiszniowski et al., 2006; Renou et al., 2008a). Some of these technologies are adsorption (De Gisi et al., 2016; Burakov et al., 2018), filtration (Yuan and He, 2015; Yakar et al., 2018; Pronk et al., 2019), coagulation (Verma et al., 2012; Teh et al., 2016), advanced oxidation (Oller et al., 2011; Miklos et al., 2018), solvent extraction (Hu et al., 2005; Kul and Oskay, 2015), electrolysis (Escapa et al., 2016; Lu and Ren, 2016), and aerobic and anaerobic processes (Chan et al., 2009; Kassab et al., 2010). While providing the treatment advantages of each of these processes, there are few limitations. High chemical, operational and maintenance costs, low pollutants removal efficiency, operational difficulties, and generation of toxic pollutants are some of the disadvantages of the available technologies (Qu et al., 2013; Seow et al., 2016).

Conventional methods such as chemical coagulation, adsorption, precipitation, solvent extraction, electrochemical removal, and ion exchanges have been applied for heavy metals

removal from aqueous media. Chemical coagulation technique provides easy operational and maintenance processes. Samrani et al (El Samrani et al., 2008), investigated the effect of ferric chloride solution and a polyaluminium chloride on the coagulation of combined sewer overflow for Pb, Zu, Cr, and Zn removal by jar-testing. The authors reported that the optimum turbidity removal resulted in the heavy metals removal as the result of selective aggregation and interaction of heavy metals and hydrolyzed coagulant species (El Samrani et al., 2008). In another study, Chu investigated the removal of lead by recycled alum sludge at different pH (Chu, 1999) since pH plays an important role in the results of the chemical reactions (Esfahani and Datta, 2018). Different studies have reported other chemicals such as seawater liquid bittern as an inexpensive source of magnesium (Ayoub et al., 2001), calcium oxide (lime) and fly ash (Chen et al., 2009), aluminum sulfate or ferric chloride (Akbal and Camcı, 2010; Lakshmanan et al., 2010), aluminum sulphate (alum), polyaluminum chloride (PACl) and magnesium chloride ($MgCl_2$) (Pang et al., 2009) for heavy metal removal from aqueous solution. It is reported that these and other coagulants have shown acceptable efficiency in heavy metals removal. Adsorption is another economical method which provides flexibility in design and operation (Fu and Wang, 2011). A large number of researchers studied heavy metals removal by different adsorbents such as activated carbon (AC) due to its high surface area because of its high porosity (Jusoh et al., 2007; Kang et al., 2008; Pyrzyńska and Bystrzejewski, 2010; Lo et al., 2012), carbon nanotubes (CNTS) (Abbas et al., 2016; Bhanjana et al., 2017; Hayati et al., 2017), or other low cost adsorbents like chitosan as a biopolymer (Huang et al., 1996; Ngah et al., 2011), zeolites as crystalline aluminosilicates (Shi et al., 2009; Yuna, 2016),

and bioadsorbents like olive pomace (Pagnanelli et al., 2003), raw rice bran (Montanher et al., 2005), wheat bran (Farajzadeh and Monji, 2004), and Rubber wood saw dust (Karthikeyan et al., 2005). Solvent extraction is another simple technique for heavy metals removal. Electrochemical technique for heavy metals removal works based on the anions and cations transportation between the electrodes. This technique makes the heavy metals recovery possible (Rajeshwar et al., 1994). Different kind of electrodes such as carbon aerogel (Rana et al., 2004), mild steel (Golder et al., 2007), stainless steel (Ölmez, 2009), stainless steel and platinum (Casqueira et al., 2006), and stainless steel and aluminum (Arslan-Alaton et al., 2008) have been studied. While all these traditional technologies might be capable of high heavy metals removal, but limitations such as high volume of sludge generation, expensive capital cost, long operational time, and high operation and maintenance requirements for achieving high removal efficiency make the feel of need for new technologies stronger.

2.5. Heavy Metal Removal using Membrane Technologies

Membrane technologies have presented promising performance in terms of heavy metals removal efficiency. Ease of operation, low space required, and low amount of generated waste are the other advantages of membrane filtration technology (Cleveland, 1999; Strathmann et al., 2011). Among the different types of membrane processes, nanofiltration (NF), forward osmosis (FO), and reverse osmosis (RO) have attracted global attention for both water and wastewater treatment. High reliability and high pollution removal rate have are reported for NF (Hilal et al., 2004; Esfahani et al., 2015b; Mohammad et al., 2015;

Esfahani et al., 2019), FO (Cath et al., 2006; Lutchmiah et al., 2014; Firouzjaei et al., 2019), and RO (Lee et al., 2011; Malaeb and Ayoub, 2011; Shenvi et al., 2015). According to the available extensive literature, these technologies can remove a wide range of pollutants such as micropollutants like viruses and bacteria, salinity, hardness (Van der Bruggen and Vandecasteele, 2003; Pangarkar et al., 2011; Jamaly et al., 2014), dye (Suksaroj et al., 2005; Hassani et al., 2008; Koutahzadeh et al., 2016), natural organic matters (NOM) (Hajibabania et al., 2011; Linares et al., 2011), and pharmaceuticals (Nghiem et al., 2005; Radjenović et al., 2008; Jin et al., 2012; Zaviska et al., 2013). Despite of all the advantages, these processes carry few disadvantages such as membrane fouling, membrane limited lifetime, additional concentrate treatment, and high energy consumption (Van der Bruggen et al., 2008). The major limiting parameters of the usage of high pressure driven membrane technologies are chlorination, precipitation of scaling compounds, fouling, flux reduction, concentration polarization, water matrix characteristics, and high energy and cost demand (Pérez-González et al., 2012; Luo et al., 2014; Akther et al., 2015; Chekli et al., 2016; Paul and Jons, 2016; Esfahani et al., 2019; Esfahani et al., 2020). Therefore, one of the main challenges of this century is in meeting the increasing water treatment demand at low-energy cost.

Extensive literature is available on membrane modification for performance enhancement of polyether sulfone (PES) (Vatanpour et al., 2012; Zinadini et al., 2014), thin film composite (TFC) (Kang et al., 2007; Lau et al., 2012), NF (Ji et al., 2017; Anand et al., 2018) and RO (Kwak et al., 2001; Ni et al., 2014) membranes, etc. In contrast to high-pressure driven membrane systems (NF/RO), the low-pressure driven systems such as

ultrafiltration (UF) has shown high efficiency while being cost-effective (Jermann et al., 2008). The flux decrease due to fouling of the UF membrane is less possible as it runs at low pressure. The advantages of ultrafiltration include simple operation, higher flux and lower fouling potential, lower membrane costs, lower required energy and lower operational costs (Lin et al., 1999). Removal of different contaminants such as natural organic matters (NOM) (Aoustin et al., 2001; Costa and de Pinho, 2002; Costa et al., 2006), humic substances (Yuan and Zydney, 2000; Lowe and Hossain, 2008), dyes (Purkait et al., 2004; Ahmad et al., 2006), microorganisms and particles (Hagen, 1998; Bourgeous et al., 2001; Zodrow et al., 2009), organic and inorganic contaminants (Lee et al., 2005; Esfahani et al., 2015a), nutrients (Baek et al., 2003; Lee et al., 2005), and heavy metals (Trivunac and Stevanovic, 2006; Huang et al., 2017) have been studied by UF membrane. Heavy metals removal by UF process with modified membrane has attracted the attention of the researchers recently. Polymer and polyelectrolyte enhanced UF membrane have been used for heavy metals removal from water (Uludag et al., 1997; Pookrod et al., 2005; Li et al., 2008; Korus and Loska, 2009), wastewater (Molinari et al., 2004; Ennigrou et al., 2009a), leachate (Syzdek and Ahlert, 1984; Calace et al., 2001; Peng, 2017), and industrial wastes (Afonso and Borquez, 2002; Zhang and Xu, 2003; Borbély and Nagy, 2009; Barakat and Schmidt, 2010).

2.6. Polyelectrolytes in Water Treatment

Polyelectrolytes are mostly soluble in aqueous solution and tend to form complexes with different molecules and materials. Different polyelectrolytes such as poly(ammonium

acrylate) (PAC), polyacrylonitrile (PAN), poly(allylamine hydrochloride) (PAH), poly (vinyl alcohol) (PVA), poly(styrenesulfonate) (PSS), polyethylenimine (PEI), polyacrylic acid (PAA), chitosan, etc., have been studied for heavy metal removal (Sasaki et al., 1989; Li et al., 2008; Ennigrou et al., 2009b; Kampalanonwat and Supaphol, 2010; Wu et al., 2010; Mondal et al., 2012; Magnenet et al., 2013; Ennigrou et al., 2014). While polyelectrolytes have high solubility in water, but the fiber mats fabricated through the electrospinning of the polyelectrolyte complexes have shown high stability in aqueous solutions (Chunder et al., 2007; Malhotra et al., 2016b). Hydrophobicity is considered as one of the main membrane characteristics resulting in membrane fouling. Nevertheless, synthetic polymers such as chitosan and polyacrylic acid (PAA) can enhance hydrophilicity of the membranes (Jhaveri and Murthy, 2016).

New studies have reported the layer by layer deposition of polyelectrolytes such as PAA/PAH combination on the membranes for pollutants removal (Magnenet et al., 2013; Jurin et al., 2015; Abtahi et al., 2018). The present study investigates the fabrication of fiber mats from the combination of PAA and PAH. The first objective of this study is to fabricate stable PE fiber (PAA/PAH fiber) mats through electrospinning, determine the efficiency of the fiber mats in removing heavy metals from water, and to test the impact of water matrices on the removal efficiency. The second objective is to modify the surface of the UF membrane by the ES fiber mats and investigate the heavy metals removal from landfill leachate, heavy metals spiked DI water, and heavy metals and NOM spiked DI water.

2.7. Electrospinning of Polyelectrolyte Fibers

A major limitation of applying PEs is their solubility in water. However, recent studies (Chunder et al., 2007; Malhotra et al., 2016b) have reported that PE fibers produced by electrospinning solutions of oppositely charged PEs such as polyacrylic acid (PAA) and polyallylamine hydrochloric acid (PAH) or PAA and chitosan (CS) exhibit excellent stability in aqueous solutions. Ultrathin fibers with diameters in micron and sub-micron ranges can be generated by electrospinning by applying a high electrostatic field to a viscoelastic jet created from a solution of desired polymer(s). Electrospinning has been extensively explored as a scalable approach to manufacturing functional fibers (Persano et al., 2013) offering great control over fiber microstructure and geometry, cost and time, and vast material selection; and is well-suited to scale-up (Homaeigohar and Elbahri, 2014). Due to their high porosity and aspect ratio, large surface area, surface charges, and versatility to immobilize active nanoparticles, the electrospun (ES) fibers have demonstrated great potential in environmental remediations including decoloration of organic dyes (Jadhav et al., 2015), removal of various emerging contaminants (Li et al., 2015; Liu et al., 2015), and treatment of oily wastewater (Obaid et al., 2015a). While few studies (Yari et al., 2015a; Xiao et al., 2016) have focused on metal ion removal using ES fibers in synthetic solutions, there is a lack of studies on the removal of heavy metals using ES fibers produced from PE complexes (Xiao et al., 2010b). Specifically, fiber mats produced via electrospinning of PE complex of PAA and PAH that have excellent stability in aqueous solutions (Chunder et al., 2007) have not been tested for heavy metal removal from waters. Furthermore, determining the effect of water matrix on metal ion removal

using such complex fibers is essential when considering practical water treatment applications.

2.8. References

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CHAPTER 3: MATERIALS AND METHODS

The research tasks included fabricating and characterizing polyelectrolyte (PE) fiber (PAA/PAH fiber) mats PAA/PAH-laminated ultrafiltration membranes (PAA/PAH-UF membrane), evaluating their stability in synthetic DI water and landfill leachate metal ions, procurement of bench-scale membrane filtration units, fittings and accessories, establishing test protocols, and conducting experiments to investigate the efficiency of heavy metal removal from synthetic DI water and landfill leachate using the PAA/PAH fiber mats and PAA/PAH-UF membrane. The following materials and methods were used in this research.

3.1. Materials

Poly (acrylic acid) (PAA, 25 wt % solution in water; approx. M.W. 240,000) was purchased from Acros Organics. Poly (allylamine hydrochloride) (PAH) powder (approx. M.W. 16,000) was purchased from Frontier Scientific. Sodium Hydroxide (Pellets/Certified ACS) and Nitric Acid (Certified ACS Plus) were procured from Fisher Scientific for pH adjustment. Lead, copper, and cadmium standard solutions (1000 µg/mL, Claritas PPT Grade) were obtained from SPEX CertiPrep. The deionized water used in all control and test experiments was collected from a Barnstead Pacific TII Water Purification System, that operated at conductivity of 0.056 µs/cm. The pH was monitored using a multiparameter meter (model PCSTestr 35) that was calibrated with a three-point method at pH 4, 7, and 10. Polyethersulfone (PES) flat-sheet ultrafiltration (UF) membranes with

molecular weight cutoffs (MWCO) of 1 kDa were used as substrates to deposit fiber mats on. The UF membranes (XT) were supplied by Synder Filtration.

3.2. Electrospinning and Crosslinking of PAA/PAH Composite Fiber Mats

A high voltage DC power supply (model EQ50P24) manufactured by Glassman High Voltage Inc. was used for the ES setup. A programmable single syringe pump (model NE-1000) manufactured by the New Era Pump Systems Inc. was used to release the PE solutions using a single needle with 0.0230 mm inner diameter (Sigma-Aldrich) and 3 ml BD Disposable Syringes with Luer-Lok Tips (Fisher Scientific). Figure 1 shows the used ES set up including the power supply, pump, syringe, and the collecting surface.

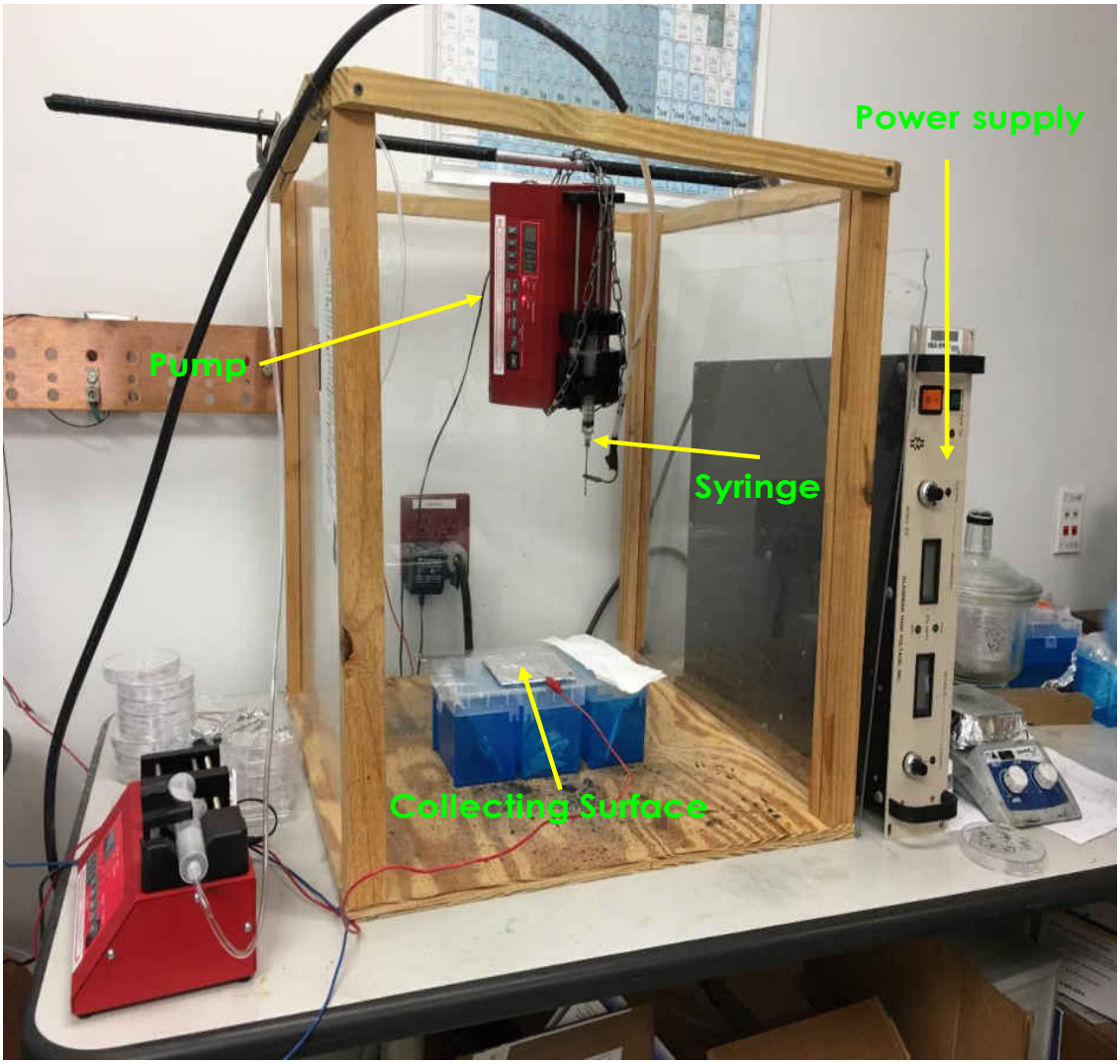

Figure 1. Lab-scale electrospinning setup.

117 mg of PAH and 2,883 mg of PAA were mixed (8:1 molar ratio by repeating unit) using a magnetic stirrer for 10 minutes to reach a homogeneous solution at room temperature. The obtained solution was transferred into a 3 ml plastic syringe attached to the single needle for electrospinning. The feeding pump rate and the applied electrical potential were fixed at 0.6 µL/h and 8.8 ± 0.2 kV, respectively. The working distance between the needle tip and the aluminum foil collector was set at 10.5 cm. A parchment paper was taped onto

the aluminum foil collector for easy collection and removal of the fiber mats. During the thermal crosslinking, the parchment paper would crumble in the oven and allowed the mat to lift a bit from the paper. The generated fiber mats were peeled off from the collector and dried at 140 °C for 6 hr in order to crosslink the polymers. When laminating the UF membranes, the PAA/PAH complex fiber mat was deposited on the PES UF substrate.

3.3. PE Fiber Mats and PAA/PAH-UF Membrane Characterization

The free-standing PE fibers and fiber mats was observed under scanning electron microscopy (SEM) using a Zeiss ULTRA- 55 FEG SEM. All samples were sputter-coated with a 10 nm thin film of gold-palladium before examining under SEM. PAA/PAH ratios of 4:1 and 8:1 were examined to determine the influence of relative polymer concentrations on the morphology of the fiber mats. The morphology of the PAA/PAH-UF membrane too was studied under SEM. The contact angle on the surface of the virgin UF membrane as well as that coated with the PAA/PAH fiber mats was analyzed by an OCA15EC goniometer (DataPhysics Instruments GmbH, Filderstadt, Germany). Flame atomic absorption spectroscopy (FAAS) was conducted to measure metal concentrations in the solution using a PerkinElmer AAnalyst 400 (Figure 2). The adsorbed compounds/metals on the fibers were identified using the Noran system 7 energydispersive X-ray spectroscopy (EDS) equipped with a silicon drift detector x-ray detector. Fourier transform infrared (FT-IR) was employed to identify the chemical bonds, or organic functional groups including amines (proteins), carbohydrates (polysaccharides), and carboxylic acids

(humic substances). FT-IR spectra were obtained using a PerkinElmer spectrum 100 FT-IR and Shimadzu QATR-S spectrometer.

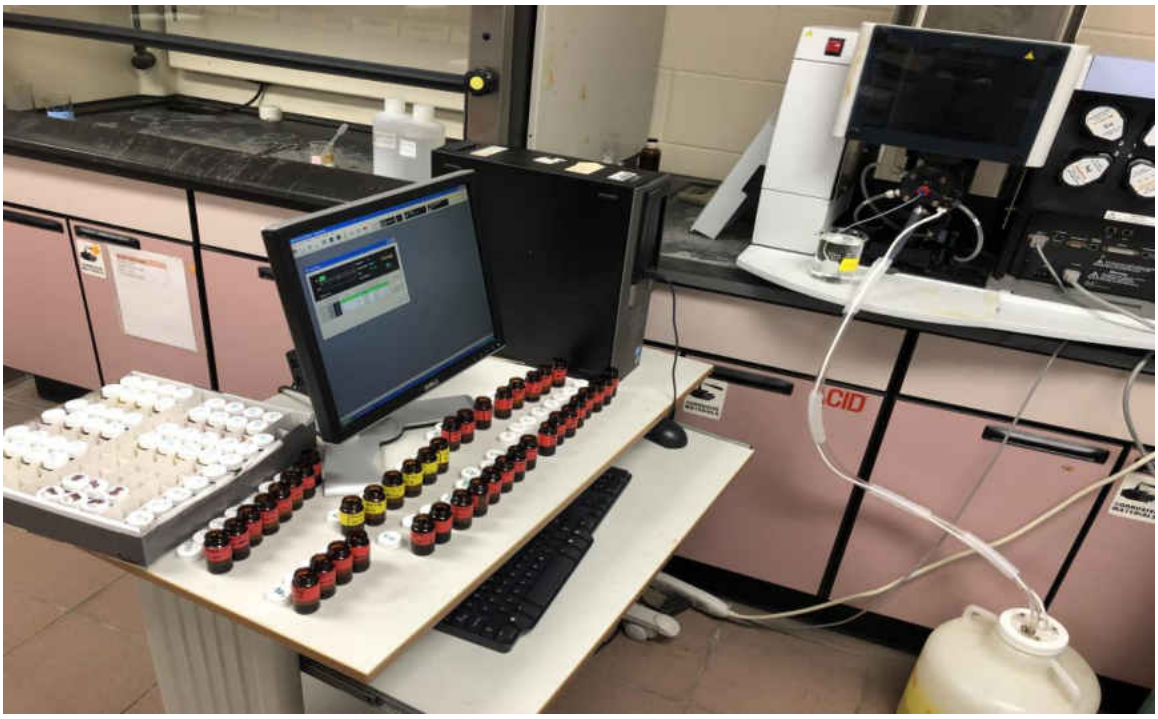

Figure 2. Flame atomic absorption spectroscopy (FAAS) instrument and prepared samples.

3.4. Experimental Protocol

3.4.1. Batch Experiments

The removal of heavy metals by stable PAA/PAH fiber mats was evaluated by batch experiments (Figure 3). 30 ± 5 mg of fiber mats were submerged in 100 ml solution containing 2 ppm of lead (Pb), cadmium (Cd), and copper (Cu), individually. The solution was left for 120 minutes on the shaker at 120 revolutions per minute (rpm). Samples were

analyzed for heavy metal concentration via AAS, and the fibers were examined by EDS and FT-IR before and after their contact with the metal solutions.

Figure 3. PE fiber (PAA/PAH fiber) mats in metal ion solutions.

3.4.2. Bench-scale Membrane Filtration Apparatus

A bench-scale flat-sheet membrane apparatus (Sterlitech CF042, Sterlitech, Kent, WA), as shown in Figure 4 and Figure 5, was used for metal ion removal experiments when using flatsheet virgin UF membrane and PAA/PAH-UF membrane coupons. The experimental setup consisted of two cross-flow membrane cells, feedwater delivery pump, flow control valves, pressure gauges, flow meters, and a 4.0-gal reservoir. Two types of feedwaters were run (for up to 12 hrs.) through the membrane setup: DI water spiked with 2 ppm of each of

Pb, Cd, and Cu and landfill leachate from Orange County Landfill. The permeate flow rates were continuously measured to monitor flux decline. The filtration units will be run in duplicates to minimize the variability in properties of membrane coupons cut from large sheets and to facilitate analyses of statistical significance of experimental results. The membrane removal performance was evaluated by comparing metal ion concentrations in feed and permeate samples. The removal (R) of metal ions by the PAA/PAH-UF membrane was calculated as:

$$R\,\% = (C_f - C_p)/C_f \times 100\%$$

Where C_p is the metal-ion concentration in the permeate and C_f is the metal-ion concentration in the feed solution. The integrity of the ES PE mats over the duration of filtration were examined using SEM.

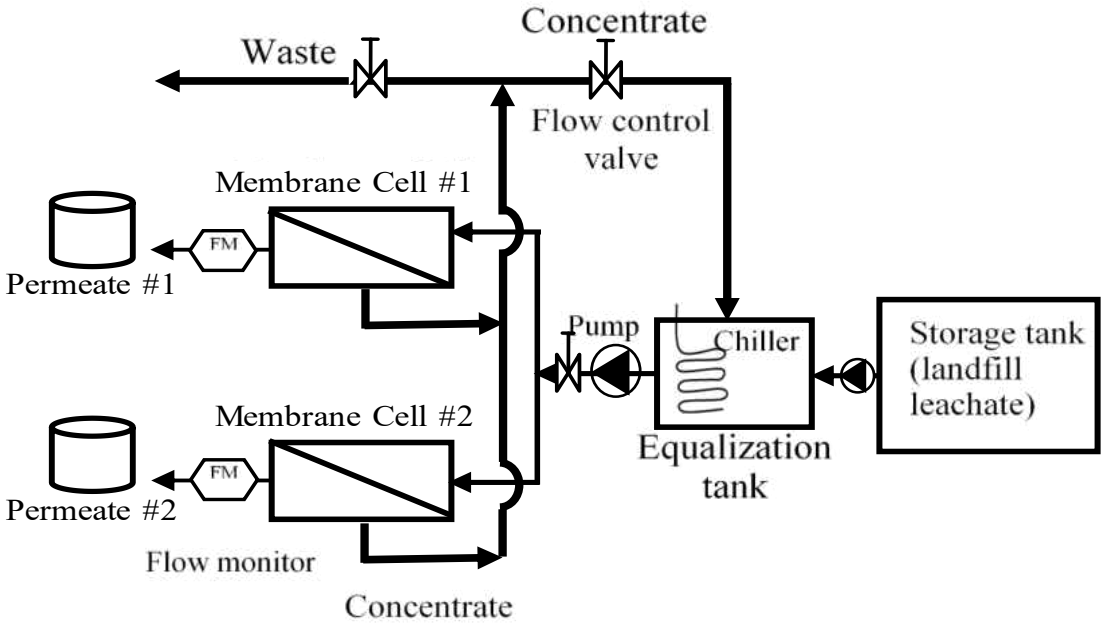

Figure 4. Layout of bench-scale membrane rejection experimental setup.

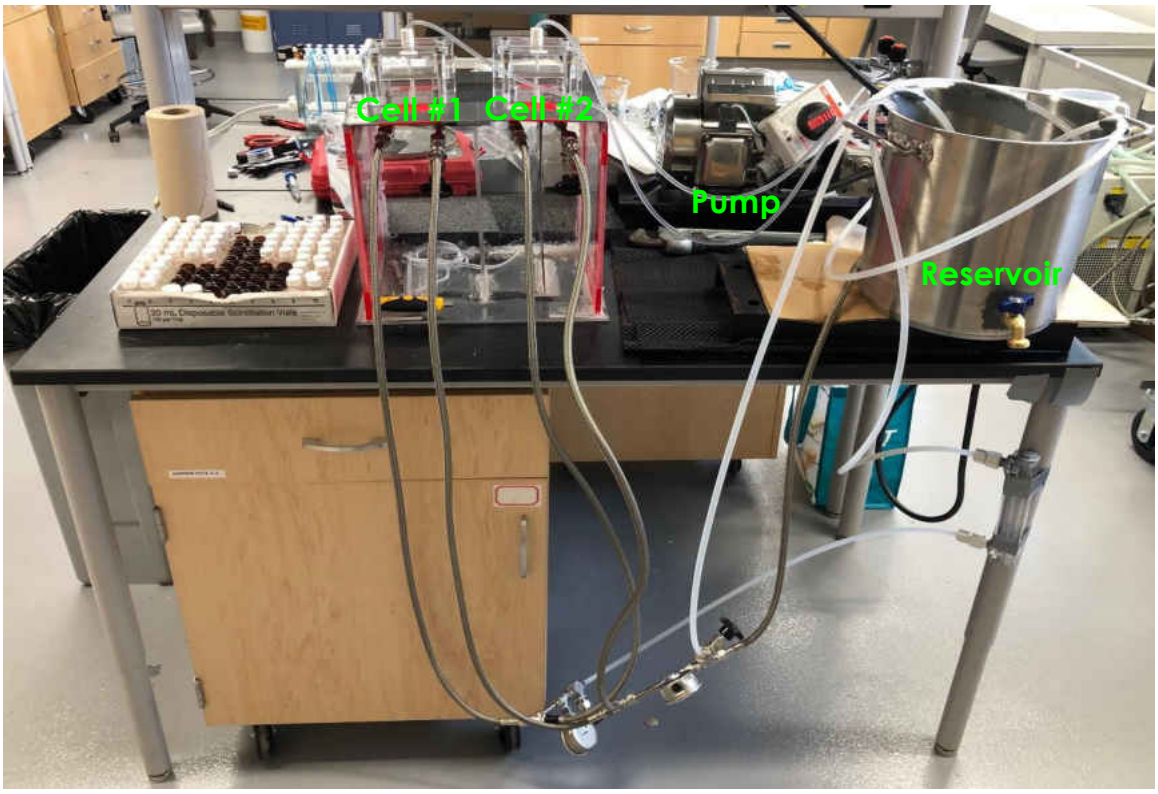

Figure 5. Photograph of the Sterlitech CF042 cross-flow membrane filtration setup.

CHAPTER 4: POLYELECTROLYTE FIBER MATS AND FIBER MAT LAMINATED ULTRAFILTRATION MEMBRANE CHARACTERIZATION

4.1. Introduction

The parameters investigated in the fabrication method as well as the characterization of polyelectrolyte (PE) fibers from polyacrylic acid (PAA) and polyallylamine hydrochloride (PAH) through electrospinning are presented in this chapter. In addition, the characterization of the laminated UF membranes with the PAA/PAH fiber mats was studied. Different factors influencing the ES process like applied voltage, pump rate, and working distance were considered in order to develop the fiber mat fabrication method. In general, SEM and CA were applied for fiber mats characterization. The other tools applied to characterize the fibers will be discussed in the relevant sections in Chapters 5 and 6. The surfaces of both modified and unmodified UF membranes before and after running the bench-scale experiments with spiked DI water and landfill leachate were studied.

4.2. Materials and Methods

A laboratory-scale electrospinning setup as described in Section 3.2 of Chapter 3 was used to fabricate fiber mats from PE complex solutions. In addition to producing free standing fibers, the PAA/PAH complex fiber mats were deposited on the UF membrane to laminate the membrane with the mats. Different combinations of electrospinning parameters including applied voltage, pump rate, and working distance were examined during the

electrospinning process as shown in Table 2. The detailed tested electrospinning parameters are presented in appendix A.

Table 2. Electrospinning parameters for PAA/PAH molar ratios of 4:1 and 8:1.

Parameter	Values
Working Distance (cm)	9.0, 9.5, 10.0, 10.5, 11.0, 11.5, 12.0
Pump Rate (µl/hr)	0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9
Voltage (Kv) (± 0.2)	8.0, 8.2, 8.4, 8.6, 8.8, 9.0, 9.2, 9.4, 9.6, 9.8, 10.0

The PAA/PAH fiber mats and the PAA/PAH-UF membranes were characterized using the tools described in Section 3.3 (Chapter 3).

4.3. Results and Discussion

4.3.1. Polyelectrolyte Fiber Characteristics

Stable PAA/PAH fiber mats were produced from homogeneous polyacrylic acid (PAA)/polyallylamine hydrochloride (PAH) complex solutions by dissolving PAH into 25% PAA aqueous solutions at 4:1 and 8:1 molar ratios of PAA and PAH. The pH of the mixture was maintained at around 2.1 during the electrospinning process. The impacts of electrospinning voltage and the distance between the needle and collecting pad (i.e., the working distance) on fabrication of the PAA/PAH fiber mats were also examined to determine the optimal PAA: PAH ratio and fiber size. The free-standing fibers and fiber mats were examined using SEM. As shown in Figure 6 (a and b), the free-standing fibers appear to remain unchanged at the two different applied voltages of 8 kV and 9 kV. The

fiber diameters, ranging from approximately 600 nm to 1500 nm, appear to remain unchanged at the two electrospinning voltages applied. As shown in Figure 7 (a and b), varying the PAA/PAH ratios did not result in any distinct difference in fiber diameter or shape. The stability of the optimized fiber mats was evaluated by weighing the mass of fabricated fibers before and after mixing in metal ion solutions. It was observed that the fibers were stable in the metal ion solutions and the weight difference before and after soaking the fibers in the metal ion solution was less than 6 %.

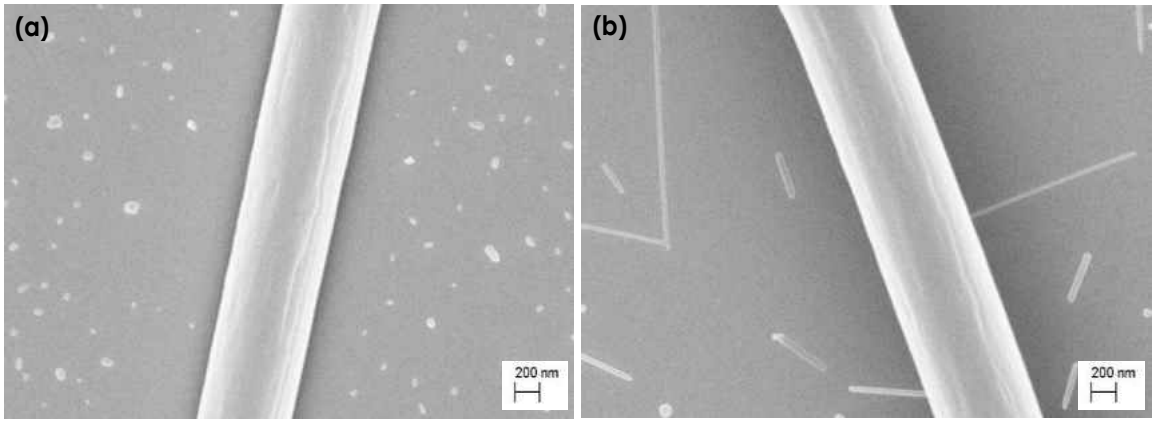

Figure 6. SEM images of PAA/PAH electrospun fibers fabricated at (a) 8 kV and (b) 9 kV.

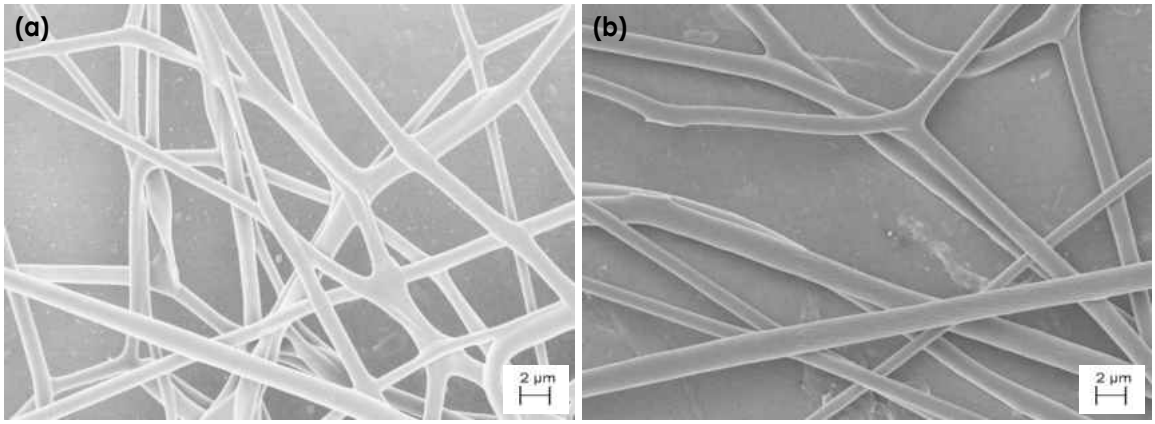

Figure 7. SEM images of fibers produced from PAA/PAH rations of 4.1 (a) and 8:1 (b).

4.3.2. PAA/PAH-UF Membrane Characteristics

4.3.2.1. Virgin PAA/PAH-UF Membrane Characteristics

Figure 8 shows the photographs of the electrospun (ES) fiber mat and the coated PAA/PAH-UF membrane, respectively. Figure 9 presents the SEM images of the PAA/PAH-UF membrane cross-section at electron high tension (EHT) value of 5.00 kV. The surface of the UF membrane was coated with ES PAA/PAH fibers for 15 minutes such that the whole surface was coated uniformly. After the electrospinning application, the PAA/PAH-UF membrane was put into the oven and dried at 140 °C for 6 hours for crosslinking. Figure 9 (a, b, and c) display the UF membrane substrate at the bottom and the coated fiber layer on top. The fiber mat layer is magnified in Figure 9f. Contact angle (CA) measurements of the UF and PAA/PAH-UF membranes were conducted to evaluate the change in surface hydrophobicity of the membrane due to PAA/PAH functionalization. As illustrated in Figure 10, the CA of the PE laminated membrane (10b) was lower when compared to the unmodified membrane (10a), indicating that the PE modification enhanced the hydrophilicity of the membrane. The average CA (measurements at 5 different locations) of the virgin UF membrane was 26.2° while that of the modified membrane was 19.1°. The droplet volume of 8 µL and three dropping rates of 0.2, 2.0, and 5.0 µL/s were considered while obtaining the CA data. As shown in Figure 3c, the surface of the UF membrane was coated with multiple layers of PAA/PAH fibers with the diameter approximately ranging from 600 to 1500 nm.

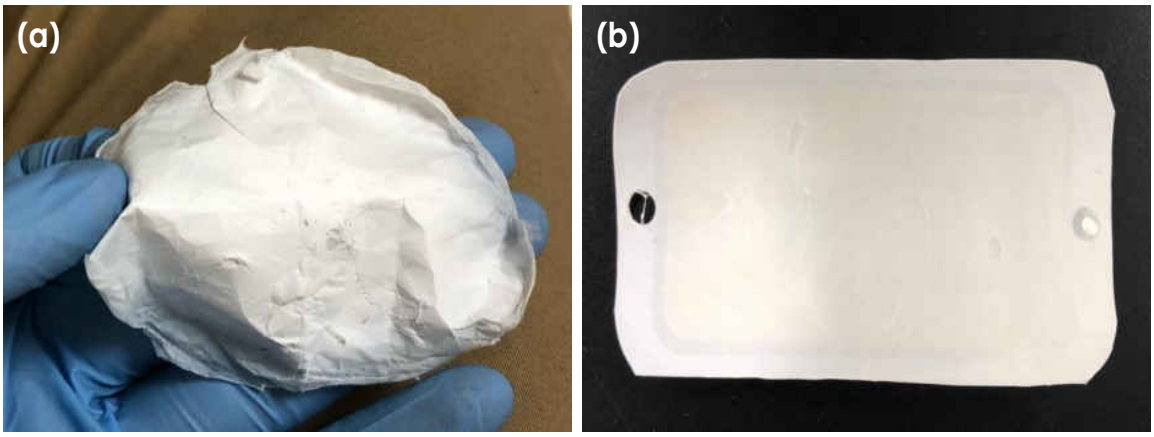

Figure 8. The fabricated ES fiber mat (a) and the coated PAA/PAH-UF membrane (b).

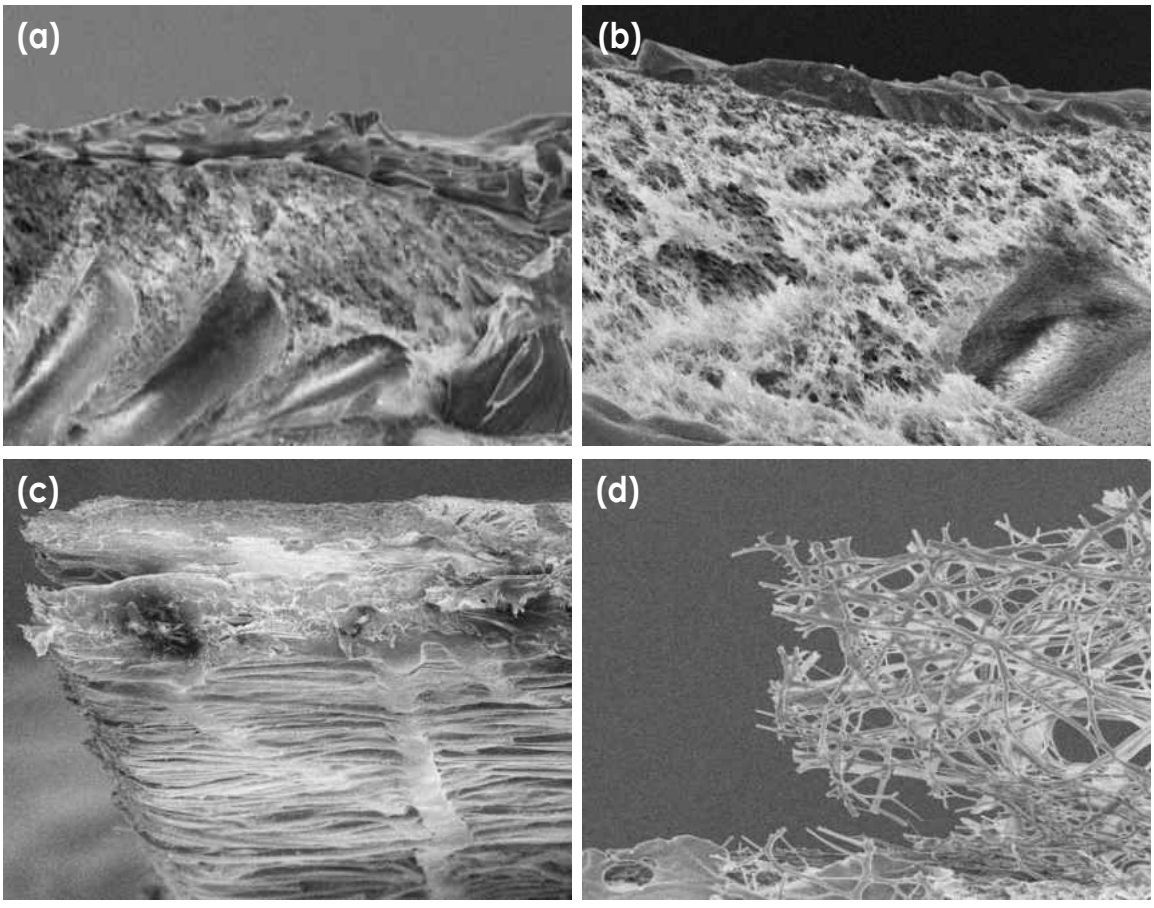

Figure 9. SEM images of the PAA/PAH fiber-laminated UF membrane cross-section at 1.00 K× (a), 2.5 K× (b), and 150× magnifications (c), and the fiber mat at 750× magnification (d).

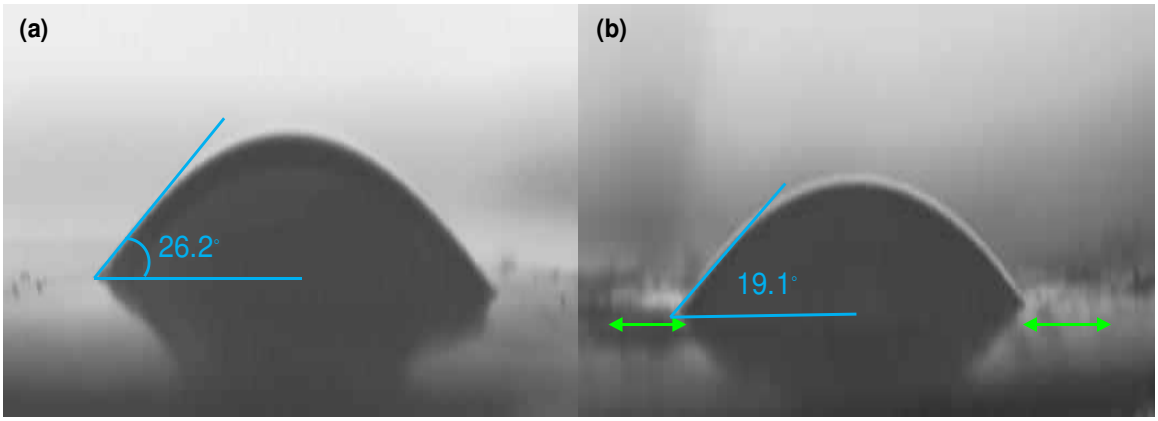

Figure 10. Contact angle of virgin UF membrane (UF) (a) and contact angle of PE laminated UF membrane (PAA/PAH-UF membrane) (b).

4.3.2.2. PAA/PAH-UF Membrane Characteristics

The SEM images of the surface of the unmodified UF membrane (UF) before and after the bench-scale filtration experiments using the synthetic metal solution and landfill leachate samples are shown in Figure 11, depicting the deposition of leachate matrix components on the membrane surface (Figure 11c) in comparison with surface of the membrane filtering the synthetic solution (Figure 11b). The SEM images of the surface of the PAA/PAH-UF membrane before and after the filtration experiments with landfill leachate are shown in Figure 12. While the fiber layer appears to retain its structural integrity with signs of some relaxation (Figure 12b) following pressure-driven filtration, the fiber mat layer is seen to be fouled by the leachate (Figure 12c). This is further demonstrated by the SEM images of the cross-sections of the PAA/PAH-UF membrane filtering the synthetic water (Figure 13a) and that filtering the landfill leachate (Figure 13b).

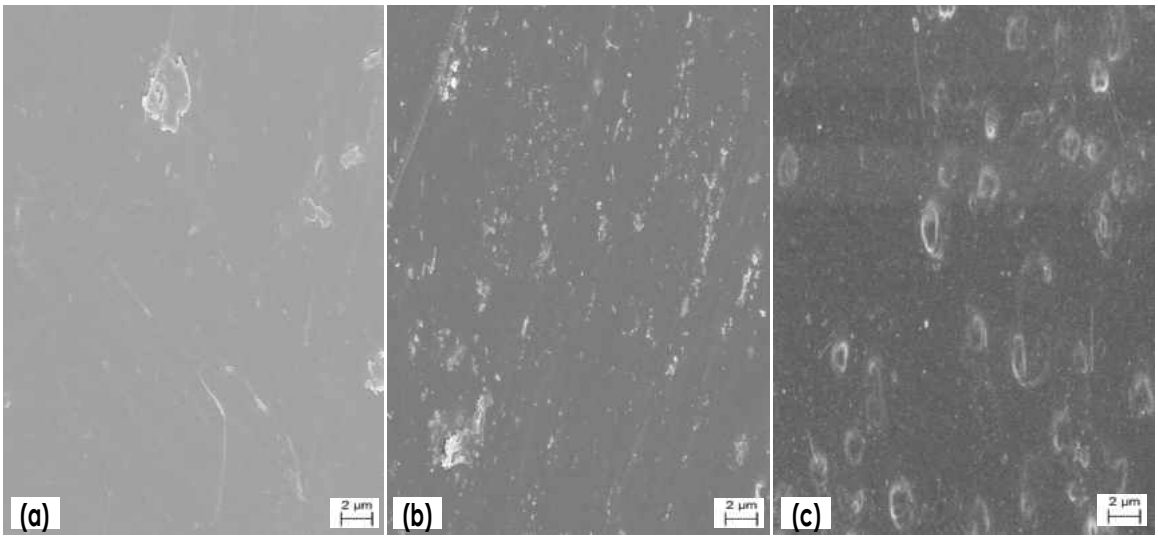

Figure 11. SEM images of the surface of the UF membrane (a), after filtering synthetic metal ion solution (b), and after filtering landfill leachate (c).

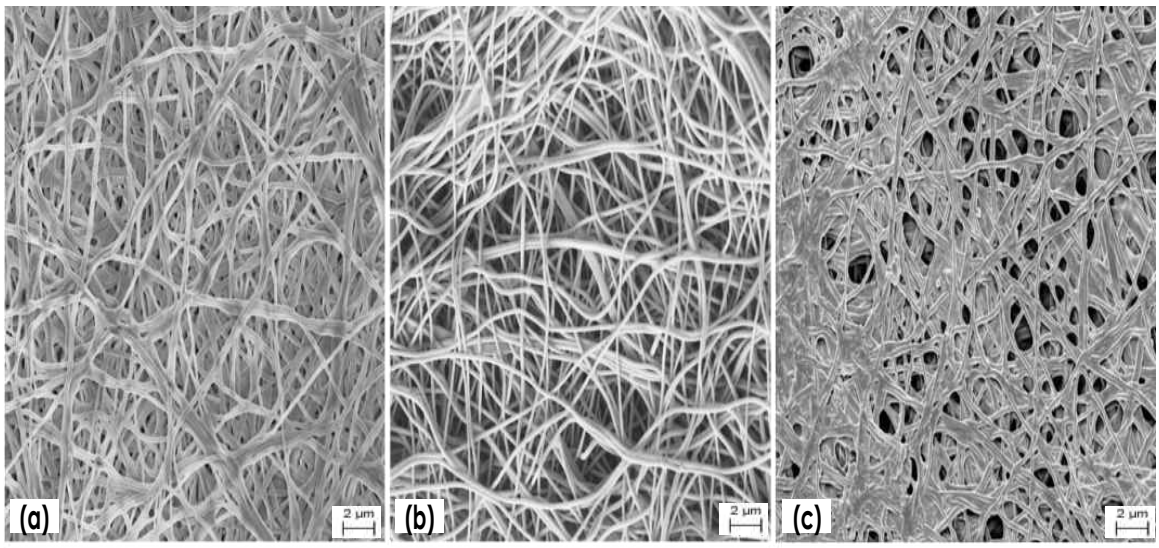

Figure 12. SEM images of the surface of the clean PAA/PAH-UF membrane (a), after filtering synthetic metal ion solution (b), and after filtering landfill leachate (c).

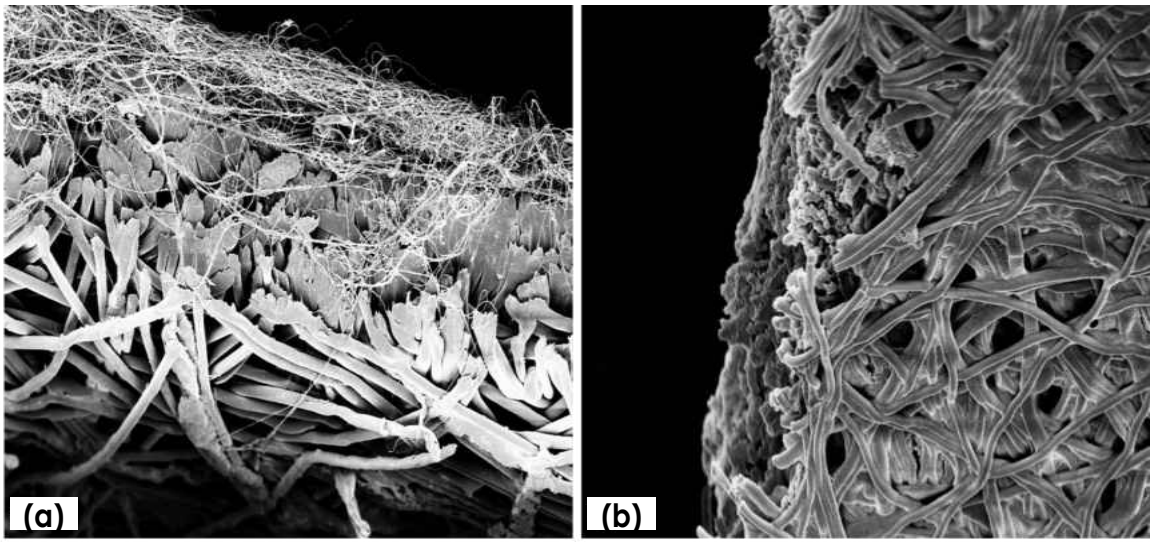

Figure 13. SEM images of the cross-section of the PAA/PAH-UF membrane filtering synthetic metal ion solution (a), and that after filtering landfill leachate (b).

4.4. Conclusion

This study developed a method of fabrication of PE complex fibers to functionalize UF membranes to determine their efficiency in removing heavy metals. Stable PE fiber (PAA/PAH fiber) mats were produced from homogeneous PAA/PAH complex solutions. The PAA/PAH ratio of 8:1 was chosen for fiber fabrication for the rest of this research. Different combinations of applied voltage, pump rate, and working distance were examined as the electrospinning parameters to find the optimized conditions for fabricating the fiber mats. Optimized applied voltage, pump rate, and working distance were determined to be 8.8 ± 0.2 kV, 0.6 μL/h, and 10.5 cm, respectively. Fabricated fiber mats showed high stability in heavy metals solution as around 6% weight loss was observed before and after soaking the fibers. The morphology and integrity of the PAA/PAH-UF membrane were

studied under SEM. The fiber mats retained their structural integrity although signs of some relaxation were observed after the pressure-driven filtration. The hydrophilicity of the surface of the UF membrane increased as the result of the PAA/PAH fibers coating. The average CA of the virgin UF membrane was 26.2° while that of the modified membrane was 19.1°.

CHAPTER 5: REMOVAL OF HEAVY METALS USING POLYELECTROLYTE COMPLEX FIBER MATS

5.1. Introduction

Several technologies including ion exchange, chemical oxidation, chemical precipitation, and electro-dialysis have been investigated to remove heavy metals from aqueous solutions.(Zhang et al., 1998; Bailey et al., 1999; Jüttner et al., 2000; Dąbrowski et al., 2004) These technologies have demonstrated various efficacy of metal removal; however, the drawbacks associated with these technologies include variable efficiencies, high operation costs, and the production of secondary contaminants. Alternatively, 'biosorbents' derived from various industrial byproducts and agricultural wastes(Garg et al., 2004; Zulkali et al., 2006; Garg et al., 2007; Nasir et al., 2007) have shown promising metal removal efficiency with low operation cost, but incurred high biological and chemical oxygen demands.(Gaballah and Kilbertus, 1998) Membrane process can serve as effective barriers to recalcitrant organic and inorganic pollutants; (Linde et al., 1995; Renou et al., 2008b; Sadmani et al., 2014) however, it is energy intensive and prone to fouling during long-term operation.(Esfahani et al., 2018)

Polyelectrolytes (PE), have been widely investigated as heavy metal ion removal media because of their high local concentration of functional groups such as carboxylates as well as strong interactions of these functional groups with metal ions.(Rivas et al., 2005; Matilainen et al., 2010; Fu and Wang, 2011; Kalaiselvi et al., 2013) PEs are macromolecules containing ionizable repeating units (e.g. carboxylate, amine, and

sulfonate). A major limitation of applying PEs is their solubility in water. However, recent studies(Chunder et al., 2007; Malhotra et al., 2016a) have reported that PE fibers produced by electrospinning solutions of oppositely charged PEs such as polyacrylic acid (PAA) and polyallylamine hydrochloric acid (PAH) or PAA and chitosan (CS) exhibit excellent stability in aqueous solutions. Ultrathin fibers with diameters in micron and sub-micron ranges can be generated by electrospinning by applying a high electrostatic field to a viscoelastic jet created from a solution of desired polymer(s). Electrospinning has been extensively explored as a scalable approach to manufacturing functional fibers,(Persano et al., 2013) offering great control over fiber microstructure and geometry, cost and time, and vast material selection; and is well-suited to scale-up.(Homaeigohar and Elbahri, 2014; Burke et al., 2015) Due to their high porosity and aspect ratio, large surface area, surface charges, and versatility to immobilize active nanoparticles, the electrospun (ES) fibers have demonstrated great potential in environmental remediations including decoloration of organic dyes,(Jadhav et al., 2015) removal of various emerging contaminants,(Li et al., 2015; Liu et al., 2015) and treatment of oily wastewater.(Obaid et al., 2015b) While few studies,(Yari et al., 2015b; Xiao et al., 2016) have focused on metal ion removal using ES fibers in synthetic solutions, there is a lack of studies on the removal of heavy metals using ES fibers produced from PE complexes (Xiao et al., 2010a). Specifically, fiber mats produced via electrospinning of PE complex of PAA and PAH that have excellent stability in aqueous solutions(Chunder et al., 2007) have not been tested for heavy metal removal from waters. Furthermore, determining the effect of water matrix on metal ion removal

using such complex fibers is essential when considering practical water treatment applications.

To address the above-mentioned critical knowledge gap, we aimed to determine the heavy metal removal capability of stable fiber mats fabricated through electrospinning of PAA/PAH complex solution in environmentally relevant aqueous solutions. We performed scanning electron microscopy (SEM) to determine the effect of electrospinning operating conditions and PAA:PAH ratios on the physical morphology of PAA/PAH fiber mats. We also evaluated aqueous stability of the fiber mats by exposing them to metal ion solutions. We performed adsorption of three environmentally important heavy metals i.e., lead (Pb), cadmium (Cd), and copper (Cu) by the PAA/PAH fiber mats at different pH conditions. We quantified the heavy metal removal efficiencies of the PAA/PAH fiber mats by determining the metal concentrations remaining in the solution using Flame atomic absorption spectroscopy (FAAS) and also by examining the adsorbed metals on the fiber mats using energy-dispersive x-ray spectroscopy (EDS). The effect of water matrix on heavy metal removal using the PAA/PAH fiber mats was probed by comparing metal removals in the presence and absence of natural organic matter (NOM). Mechanistic understanding of the NOM-metal-fiber interaction was revealed through characterization of NOM and metal adsorbed PAA/PAH fiber mats using Fourier transformed infrared (FT-IR) spectroscopy.

5.2. Materials and Methods

PAA (25 wt % solution in water; approx. M.W. 240,000) was procured from Acros Organics. PAH powder (approx. M.W. 16,000) was procured from Frontier Scientific. Sodium hydroxide (pellets/certified ACS) and nitric acid (certified ACS Plus) were procured from Fisher Scientific for pH adjustment. Lead, copper, and cadmium standard solutions (1000 µg/mL, Claritas PPT Grade) were obtained from SPEX CertiPrep. Suwannee River natural organic matter (NOM) was procured from the International Humic Substances Society (IHSS). The deionized (DI) water used in all control and NOM-spiked experiments was collected from a Barnstead Pacific TII Water Purification System. pH was measured using a multiparameter meter (model PCSTestr 35).

The adsorbents on the fibers were identified using the Noran system 7 energy-dispersive X-ray spectroscopy (EDS) equipped with a silicon drift x-ray detector. Fourier transform infrared (FT-IR) spectroscopy was employed to identify the chemical bonds, or organic functional groups including amines (proteins), carbohydrates (polysaccharides), and carboxylic acids (humic substances) (Amy 2008, Chan and Chen 2004). FT-IR spectra were obtained using a Shimadzu QATR-S single reflection ATR accessory with a diamond crystal.

The fiber mats were fabricated through electrospinning process as discussed in section 4.2. The removal of heavy metals by stable PAA/PAH fiber mats was evaluated by batch experiments. 30 ± 2 mg of fiber mats were submerged in to 100 mL DI water containing 2 ppm of lead (Pb), cadmium (Cd), and copper (Cu), individually. The solutions were left on

a shaker (120 revolutions per min [rpm]) for 120 min and then metal concentrations in the solutions were measured using FAAS. The effect of NOM on metal removal by the fiber mats was investigated using DI water spiked with Suwannee River NOM at 10 ppm and 20 ppm concentrations.

5.3. Results and Discussion

5.3.1. Heavy Metal Removal

Batch experiments were conducted following the protocol discussed in the Materials and Methods section 3.4.1 to determine the adsorptive removal of selected heavy metals (Pb, Cd, and Cu) from DI water by the PAA/PAH complex fiber mats with PAA to PAH ratio of 8:1. The experiments were carried out at two different pH values (3.4 and 7.4) to probe the impact of pH on metal adsorption by the fibers. At pH 3.4, the stabilized adsorptive removals of Pb, Cd, and Cu by the fiber mats were approximately 63%, 42%, and 21%, respectively, after 120 min of contact time (Figure 14a). While the adsorptive removal of Cu equilibrates after around 10 min, that for Pb takes about 30 min. The adsorption of Cd, however, appears to continue beyond the experimental duration (120 min). The adsorptive removals and capacity at equilibrium for all three metals increased at the higher pH (7.4) (Figure 14b). At pH 7.4, the maximum adsorptive removals of Pb, Cd, and Cu by the fiber mats reached to approximately 70%, 98%, and 92%, respectively. The equilibrium was reached in between 80 to 100 min (after 80 min for Cu and Cd and after 100 min for Pb). It is interesting to note that the initial adsorption of Pb was lower at pH 7.4 (compared to pH 3.4) until around 75 min, but the adsorptive removal at equilibrium was approximately

7 % higher at a higher pH (Figure 14b). The Cu ion removal efficiency is comparable to that in a study conducted by Xiao et al (Xiao et al., 2010a). who reported 91% stabilized removal of Cu when using composite PAA/polyvinyl alcohol (PVA) nanofibers; however, the influence of NOM or any other water matrix components on Cu removal was not verified in that study. In the current study, the influence of water matrix on heavy metal removal using the PAA/PAH complex fiber mats was determined by comparing metal removals in the presence and absence of NOM, as discussed in the following section.

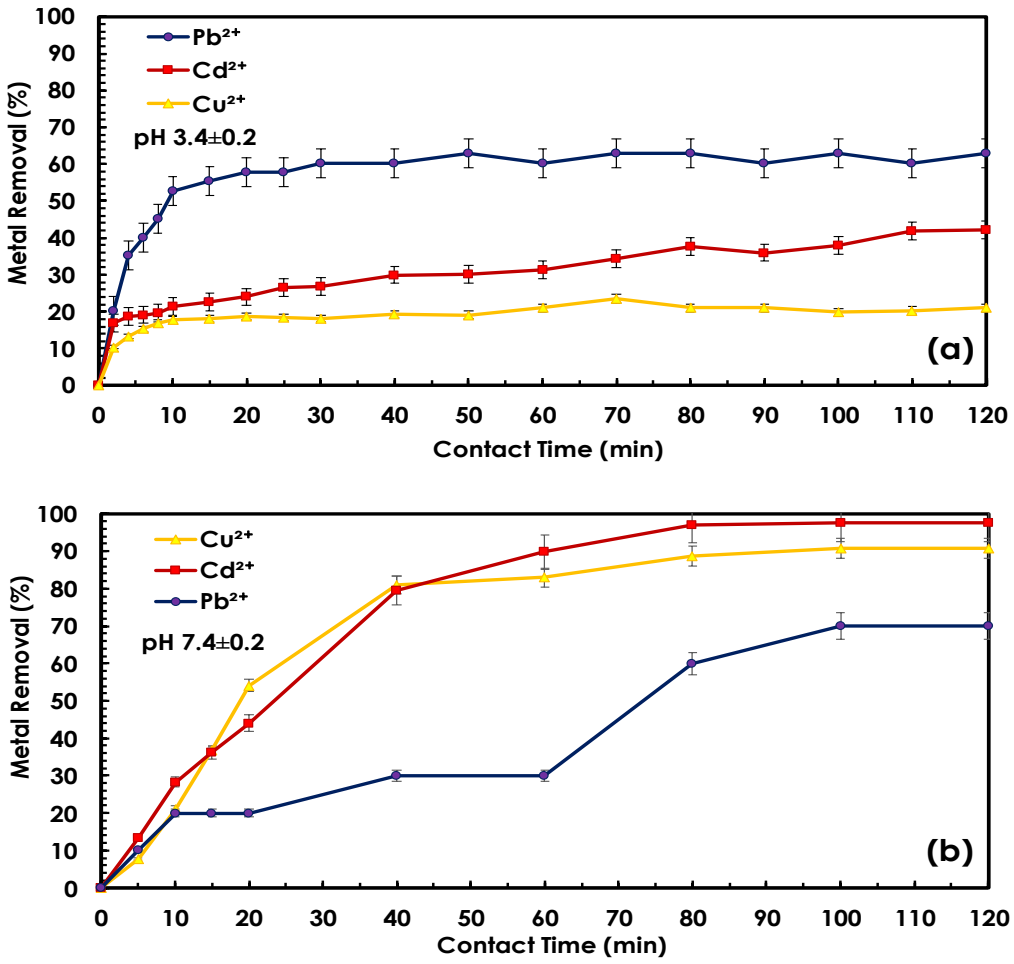

Figure 14. Adsorptive removal of heavy metals as a function of time at (a) pH 3.4 and (b) pH 7.4.

EDS analysis was conducted to confirm the presence of metals on the fiber mats. Fiber mats were prepared for EDS analysis by first placing them into individually spiked metal solutions of 100 ppm of Pb, Cu, or Cd for 2 h and then drying at room temperature for 24 h. The EDS spectra (Figure 15) show the presence of carbon, oxygen, nitrogen, and sodium, which signify the composition of the polymers that constitute the fiber mats. Figure 15 b, c, and d show the presence of Pb, Cd, and Cu, respectively, on the fiber mats that were in contact with the respective metal solutions. It should be noted that there were locations on the fibers where peaks were not observed, indicating that metal adsorption on to the fibers was not probably uniform. Hence, the local concentrations and availabilities of functional groups such as carboxylates may have influenced the metal-fiber interactions and metal removal from water. The disappearance of or decrease in Na peaks for the fibers exposed to metal solutions, when compared to the control fibers (Figure 15a), could be due to that fact that the metal ions had replaced Na^+ of the Na salt of PAA when in solution.

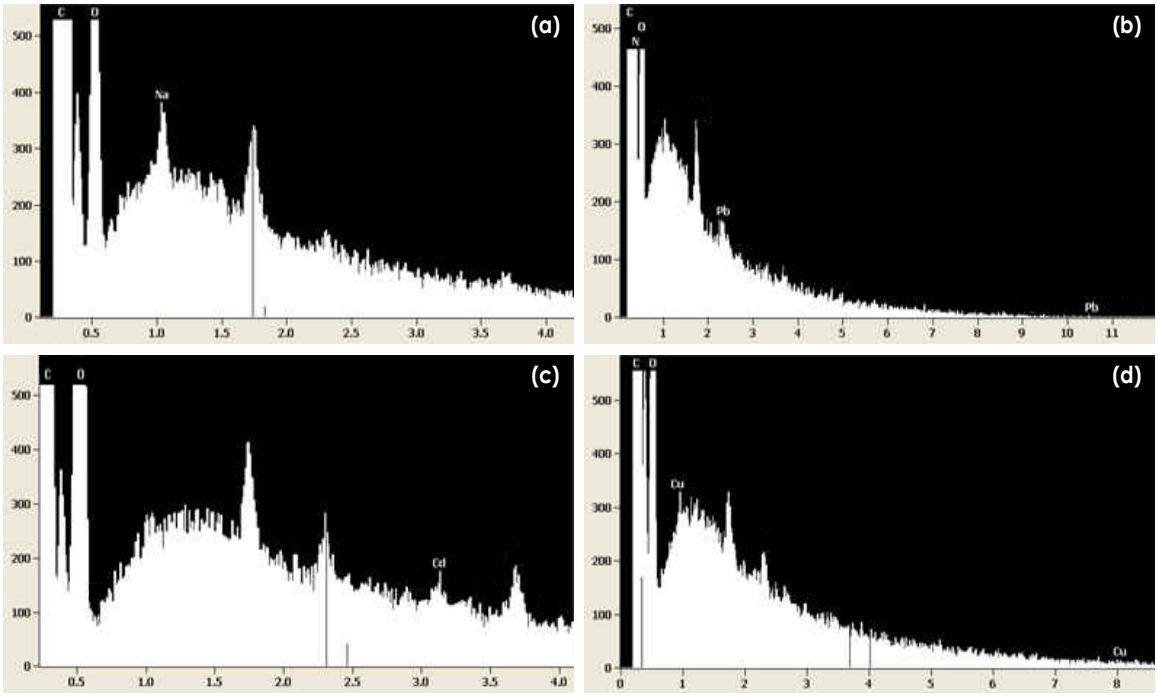

Figure 15. EDS spectra of PAA/PAH fiber mats in DI water with no metals spiked (control) (a), in Pb solution (b), in Cd solution (c), and in Cu solution (d).

5.3.2. Effect of NOM on Heavy Metal Removal by PE Fiber Mats

The effect of NOM on the removal of heavy metals by the ES stable PAA/PAH complex fiber mats was evaluated at concentrations of 10 ppm and 20 ppm at pH 7.4. While the adsorptive removal of Cd and Cu was already very high (98% and 92%, respectively) in DI water, the presence of NOM resulted in almost complete removal of all of the three metals at both the NOM concentration levels tested (Figure 16). The removal of Pb was approximately 30% higher in the NOM-spiked water when compared to the DI water. The enhanced removal of metal ions, in the presence of NOM, can be attributed to the additional complexation due to functional groups from NOM (He et al., 2017).

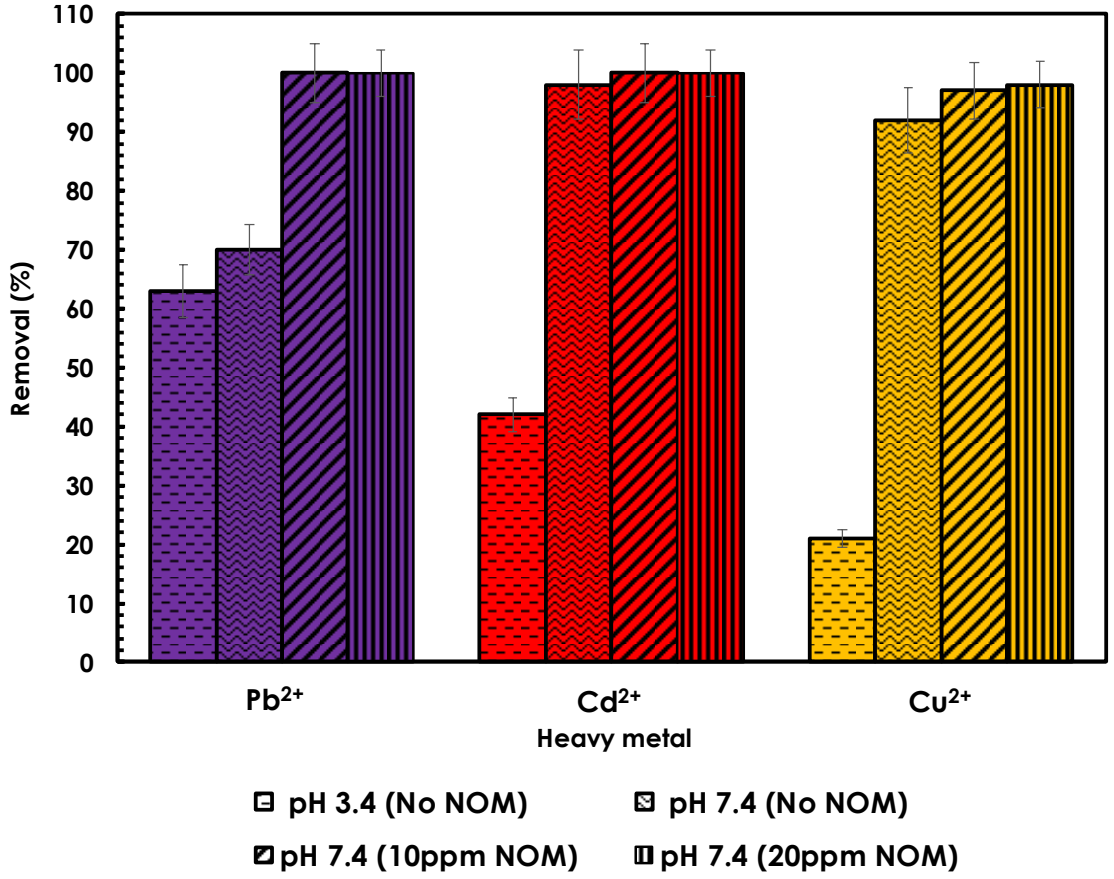

Figure 16. Heavy metal removal by PAA/PAH fiber mats in the presence of NOM (after 120 min).

The fiber mats were examined using FT-IR to identify the functional groups and possible bonds with NOM and metal ions. When the fibers are exposed to IR radiation, corresponding vibrational energy of atomic bonds are absorbed, and the FT-IR spectra show absorbance intensity against the wavenumbers (or IR bands) corresponding to the characteristic frequencies at which certain functional groups/chemical bonds in the sample absorb IR. This results in absorption spectra that are a unique fingerprint of a compound

(Howe et al., 2002). Figure 17 shows the FT-IR spectra of the stable fiber mat ('control') and fibers collected from the batch experiments that were conducted using only NOM-spiked or both NOM and metal-spiked solutions. The FT-IR spectra in the ranges of 1720-1706 cm^{-1} and 1250-1020 cm^{-1} correspond to carboxylic acid (–COOH) and amine (C-N stretching) groups, respectively (Sigma-Aldrich, 2019). Peaks at around 1400 cm^{-1} and 1600 cm^{-1} indicate carboxylate ion ($–COO^-$) and those at around 1650 cm^{-1} and 1550 cm^{-1} indicate amides (Howe et al., 2002). The amide peaks (1553 and at 1551 cm^{-1}) confirm PAA/PAH crosslinking via carboxylate groups of PAA and ammonium groups of PAH (Harris et al., 1999).

While the –COOH and $–COO^-$ peaks for all of the samples were observed at 1706 cm^{-1} and 1405 cm^{-1}, respectively, the fiber mats from the NOM solutions showed higher intensities (Figure 17), indicating higher availability of –COOH and $–COO^-$ in the presence of NOM. Hence, the removal of the tested metals by the fiber mats may be attributed to the metal ions' association with $–COO^-$ (Kirwan et al., 2003). Accordingly, the enhanced metal removal in the presence of NOM is likely due to the higher availability of $–COO^-$. Interestingly, the PAA/PAH functional groups as well as the NOM functional groups were so dominant in this case that the shifts in peaks that one might expect due to new complexations were not distinctly identified in Figure 17.

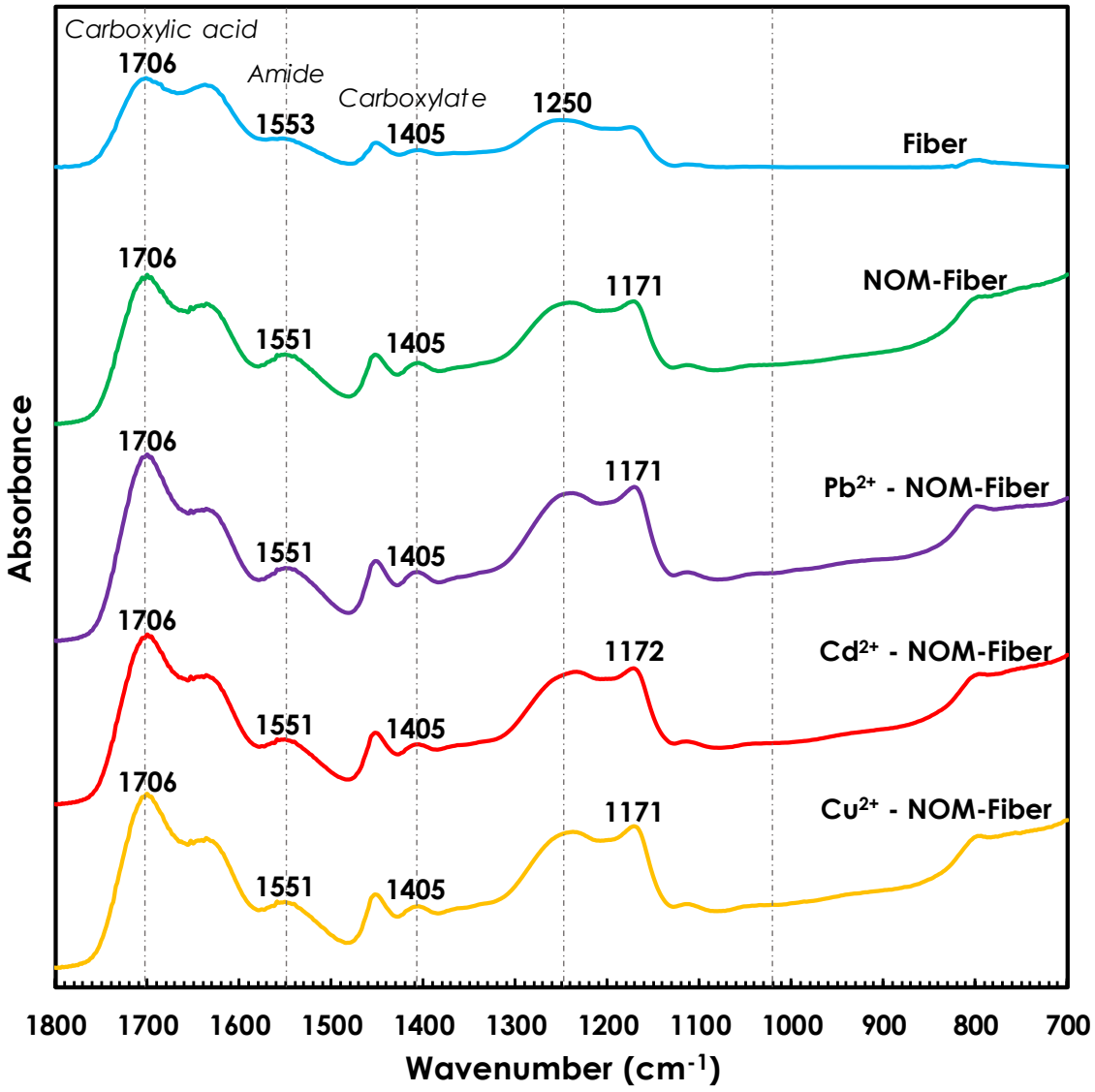

Figure 17. FT-IR spectra of PAA/PAH fibers and metal adsorbing fibers in the presence of NOM.

5.4. Conclusions

In this study, stable PAA/PAH fiber mats were produced through electrospinning of PAA and PAH complex solutions. While the fiber mats exhibited up to approximately 63%

removal of the tested heavy metals (Pb, Cd, and Cu) at pH 3.4, up to approximately 98% removal was observed at pH 7.4 from synthetic metal solutions, confirming that higher pH facilitates more effective removal of Pb, Cd, and Cu. The presence of NOM resulted in almost complete removal of all of the three metals at the higher pH (7.4). The removal of metal ions may be attributed to the dominance of carboxylate ions ($–COO^-$) from the fiber mats leading to metal-COO^- complexation. The enhanced metal removal in the presence of NOM is likely due to the higher availability of $–COO^-$ from NOM.

The PAA/PAH complex fiber mats tested in this study can be applied in heavy metal removal during drinking water production or wastewater treatment as pretreatment media, as a component of hybrid membrane processes, or may serve as nanoreactors where various nanoparticles can be immobilized (Xiao et al., 2010a). The PAA/PAH complex fiber mat has been applied as a commercial membrane modifier to improve the membrane's heavy metal removal efficiency in laboratory-prepared solutions and landfill leachate (Chapter 6).

CHAPTER 6: REMOVAL OF HEAVY METALS USING POLYELECTROLYTE COMPLEX FIBER MAT LAMINATED-ULTRAFILTRATION MEMBRANE

6.1. Introduction

Conventional biological and physico-chemical treatment of landfill leachate have limitations in removing recalcitrant organics and heavy metals. Membrane processes have been demonstrated as effective barriers to recalcitrant organic and inorganic pollutants (Linde et al., 1995; Renou et al., 2008b), resulting in high effluent quality and reduced sludge volume (Renou et al., 2008b; Ahmed and Lan, 2012), while operating within a smaller footprint when compared to conventional physico-chemical treatments. Nevertheless, high-pressure membrane treatment (nanofiltration (NF), reverse osmosis (RO)) is energy intensive and is prone to fouling during long-term operation. Ultrafiltration (UF) is a low-pressure (40–1000 kPa) membrane process that yields higher permeate flux and saves significant operating costs compared to NF/RO (Lin et al., 1999); however, UF has not been applied as a primary method for landfill leachate treatment (Tabet et al., 2002b) due to its large pore size (0.001–0.1 μm) (Lin et al., 1999).

One approach to improve the efficiency of UF is to hybridize it with polyelectrolytes (PE), which have been widely investigated as heavy metal ion removal media because of high local concentration of functional groups such as carboxylates as well as strong interactions of these functional groups with metal ions (Rivas et al., 2005; Matilainen et al., 2010; Fu and Wang, 2011; Kalaiselvi et al., 2013). In Chapter 5, it was demonstrated by batch

experiments that PAA/PAH complex fibers had excellent stability in aqueous solutions and removed heavy metals very efficiently. The hypothesis of this chapter is that the UF membranes will attain improved heavy metal removal efficiency if modified by the PAA/PAH fiber mats. Accordingly, this Chapter investigates the heavy metal removal efficiency of PAA/PAH-UF membranes and compares the removals with those by the unmodified UF membrane.

6.2. Materials and Methods

Polyethersulfone (PES) flat-sheet UF membranes were used as substrates to deposit fiber mats on. The electrospinning and crosslinking of PAA/PAH composite mats were applied as explained in section 4.2 and the lamination of UF membranes was performed following the protocol discussed in Section 4.3.2.1.

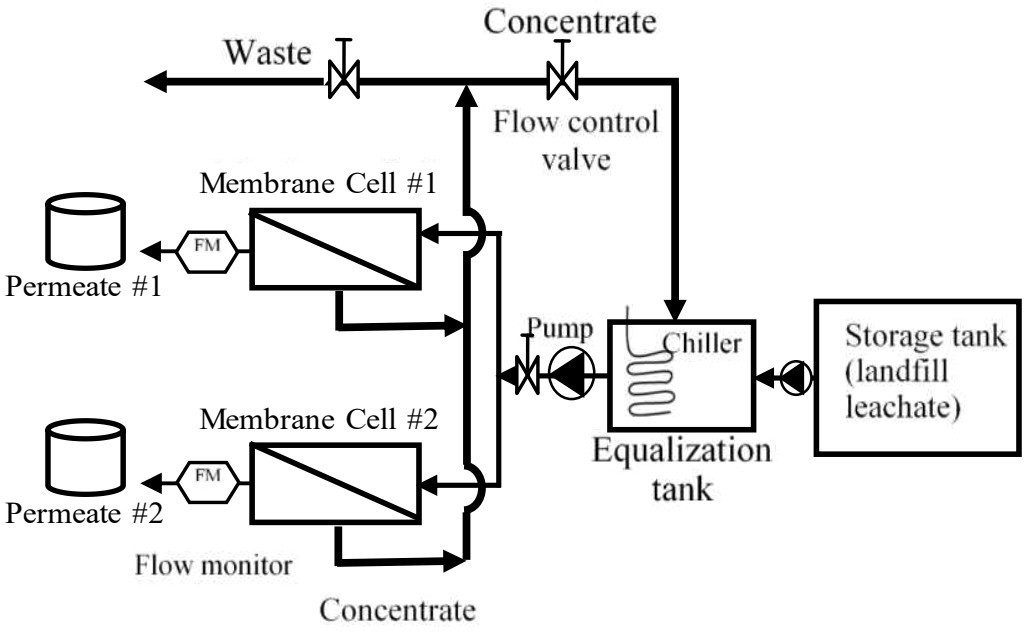

Figure 18. Layout of bench-scale membrane rejection experimental.

A bench-scale flat-sheet membrane apparatus (Sterlitech CF042, Sterlitech, Kent, WA), as shown in Figure 18, was used for metal ion removal experiments when using flatsheet virgin UF membrane (UF) and PE fiber-laminated UF membrane (PAA/PAH-UF membrane) coupons. The experimental setup consisted of two cross-flow membrane cells, feedwater delivery pump, flow control valves, pressure gauges, flow meters, and a 4.0-gal reservoir. The bench-scale flat-sheet membrane apparatus and the cross-flow membrane cells with the membranes are shown in Figures 19 and 20, respectively. Three types of feedwaters were run at 70±5 psi for up to 10 hrs. through the membrane setup: DI water spiked with 2 ppm of each of Pb, Cd, and Cu, spiked DI water with 2 ppm of each heavy metals in addition to 10, 50, and 100 ppm NOM, and real landfill leachate sample spiked with 2 ppm of each heavy metals. The landfill leachate samples were collected from the Orange County Landfill, Orlando Florida (Figure 21).

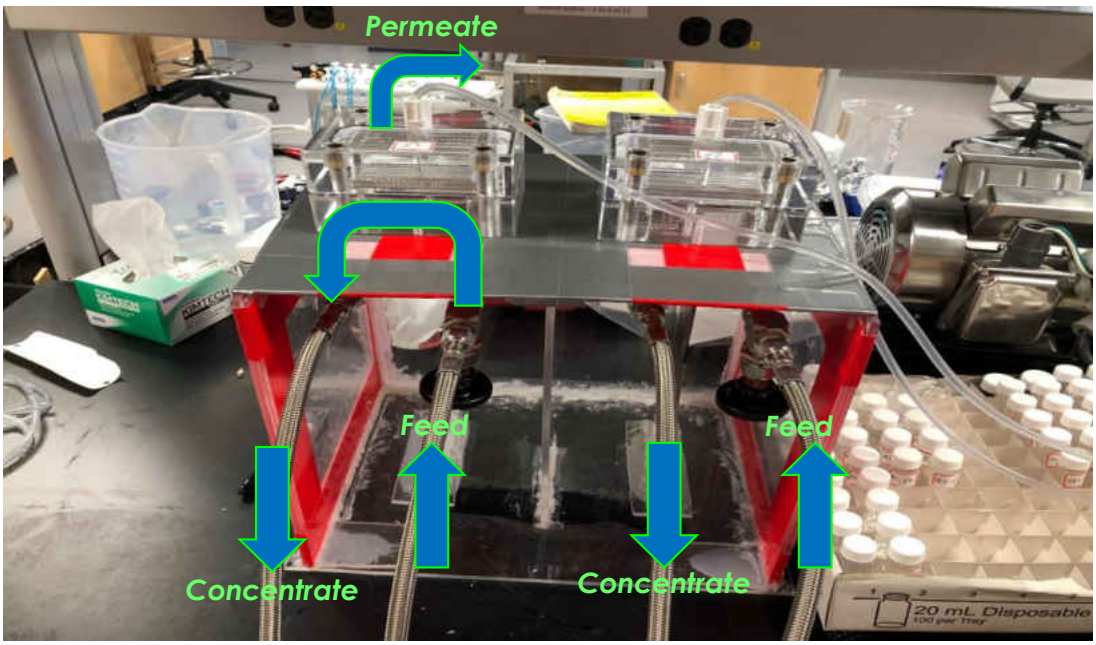

Figure 19. CF042 cross-flow membrane filtration setup.

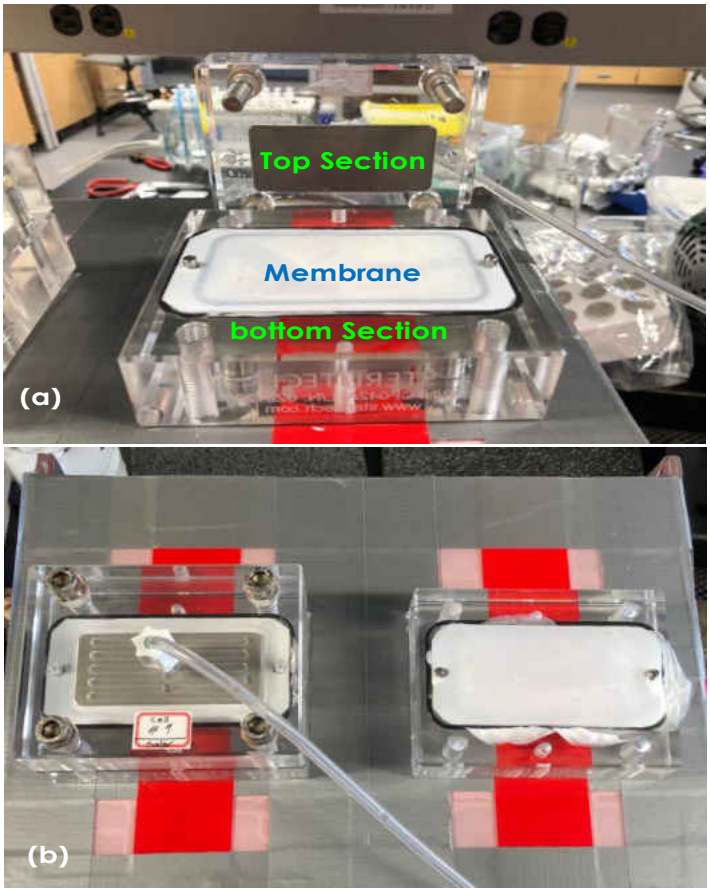

Figure 20. CF042A cross-flow membrane cell (a) section and (b) top view.

Figure 21. Orange County Landfill, Orlando FL, USA 2018.

The filtration units were run in duplicates to minimize the variability in properties of membrane coupons cut from large sheets and to facilitate analyses of statistical significance of experimental results. The membrane removal performance was evaluated by comparing metal ion concentrations in feed and permeate samples. The removal (*R*) of metal ions by UF and PAA/PAH-UF membranes was calculated as:

$$R\ \% = (Cf - Cp)/ Cf \times 100\%$$

Where C_p is the metal-ion concentration in the permeate and C_f is the metal-ion concentration in the feed solution.

6.3. Results and Discussion

6.3.1. Heavy Metal Removal

6.3.1.1. Removal of Heavy Metals from laboratory Prepared Water by PAA/PAH-UF Membrane

The removal experiments were conducted first using DI water spiked with 2 ppm of each of Pb, Cu, and Cd at pH 7.4 ± 0.2 (~ pH of the leachate sample collected from the Orange County Landfill). Membrane filtration was performed for up to 10 hrs to ensure that the metal adsorption on the fiber mats reaches equilibrium. Metal removal from DI water by the UF membrane was observed to be up to only about 31% (for Cu), with the lowest removal (~ 5%) observed for Pb (Figure 22). Metal removal by the PAA/PAH-UF membrane, on the other hand, ranged from 43% to almost complete removal after 4 hrs of

filtration of DI water. The PAA/PAH functionalized UF membrane exhibited approximately 38%, 49%, and 85% higher removal of Pb, Cu, and Cd, respectively when compared to the unmodified membrane (Figure 22). While the UF substrate contributes to metal removal to certain extent, the markedly higher metal retention by the modified membrane may be attributed to the adsorptive interactions of metal ions with the rich functional groups of the fiber mats. As explained in Chapter 5, the enhanced removal of the tested metals by the PAA/PAH-UF membrane compared to the unmodified membrane may be attributed to complexation of the metal ions with the carboxylate ions ($–COO^-$) from the PAA/PAH fiber mats (Kirwan et al., 2003).

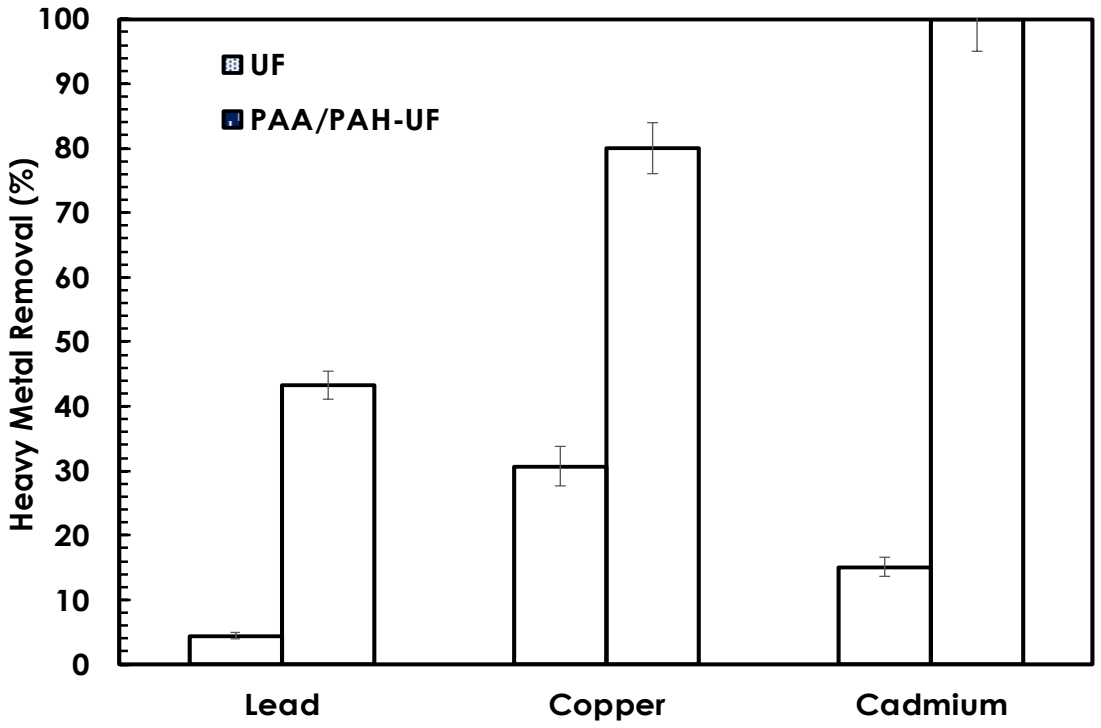

Figure 22. Removal of heavy metals by UF and PAA/PAH-UF membranes from heavy metal spiked DI water. (error bars represent the standard deviation of two or three samples).

6.3.1.2. Removal of Heavy Metals from Landfill Leachate by PE Laminated UF Membrane

Bench-scale filtration experiments were conducted to evaluate the efficiency of heavy metal removal by the PAA/PAH-UF membrane from landfill leachate. The landfill leachate samples, collected from the Orange County Landfill, contained 0.04 mg/L, 0.16 mg/L, and 0.6 mg/L of Pb, Cd, and Cu, respectively (Table 3).

Table 3. Landfill leachate characteristics.

Parameter	Concentration (mg/L)
Lead (Pb)	0.043
Cadmium (Cd)	0.158
Copper (Cu)	0.6
Total Suspended Solids (TSS)	630
Total Dissolved Solids (TDS)	25960
Biochemical Oxygen Demand (BOD)	15480
Temperature	20 ˚C
pH	7.4

Figure 23 compares the metal removal performance of the PAA/PAH-UF membrane in DI water vs. landfill leachate. While the membrane removal in DI water ranged from 43% to almost complete removal, that in the landfill leachate ranged from approximately 61% to almost complete removal. The PAA/PAH-UF membrane exhibited approximately 18% and 15% higher removal of Pb and Cu, respectively in the leachate when compared to laboratory-prepared metal ion solution (Figure 23). An almost complete removal of Cd was observed in both the synthetic solution and the landfill leachate. The higher removal of

metals in landfill leachate could be attributed to the fouling of PAA/PAH fiber mat and the UF membrane substrate and metal-organic complexation. Samples of raw leachate, leachate treated with the UF membrane, and that treated with the PAA/PAH-UF membrane are shown in Figure 24.

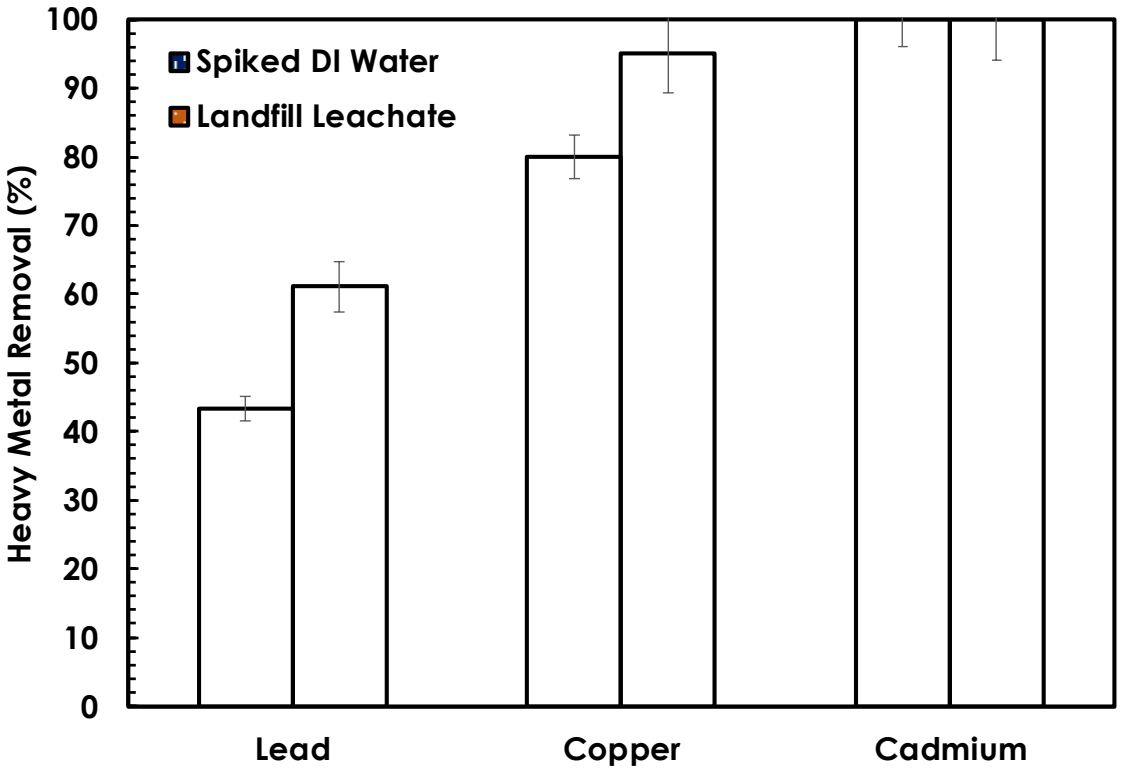

Figure 23. Removal of heavy metals by UF and PAA/PAH-UF membranes from heavy metal spiked DI water and landfill leachate. (error bars represent the standard deviation of two or three samples).

Figure 25 illustrates the membrane samples of heavy metal removal from landfill leachate. While lead and cadmium solutions are colorless, the absorbance of the copper is clearly indicated as the blue light color on the PE-Fiber mats.

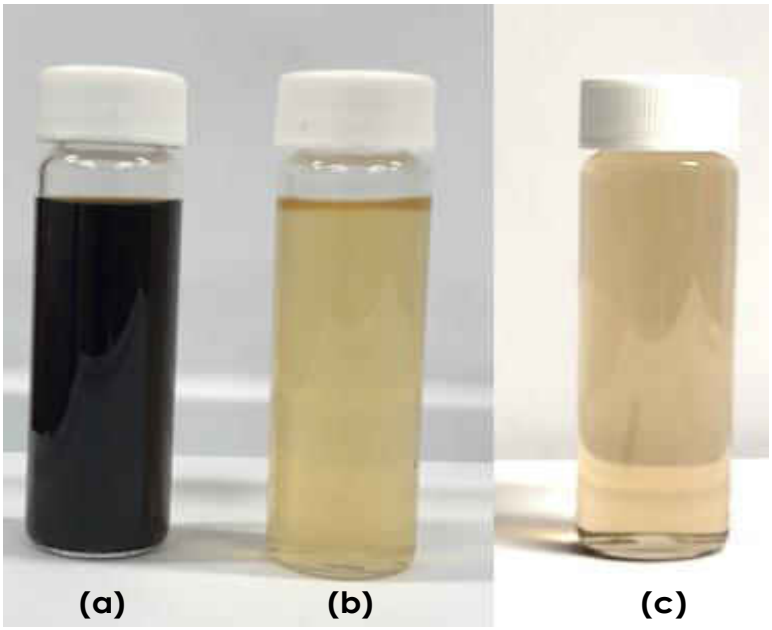

Figure 24. Landfill leachate samples: (a) raw leachate, (b) treated with UF, and (c) treated with PAA/PAH-UF membrane.

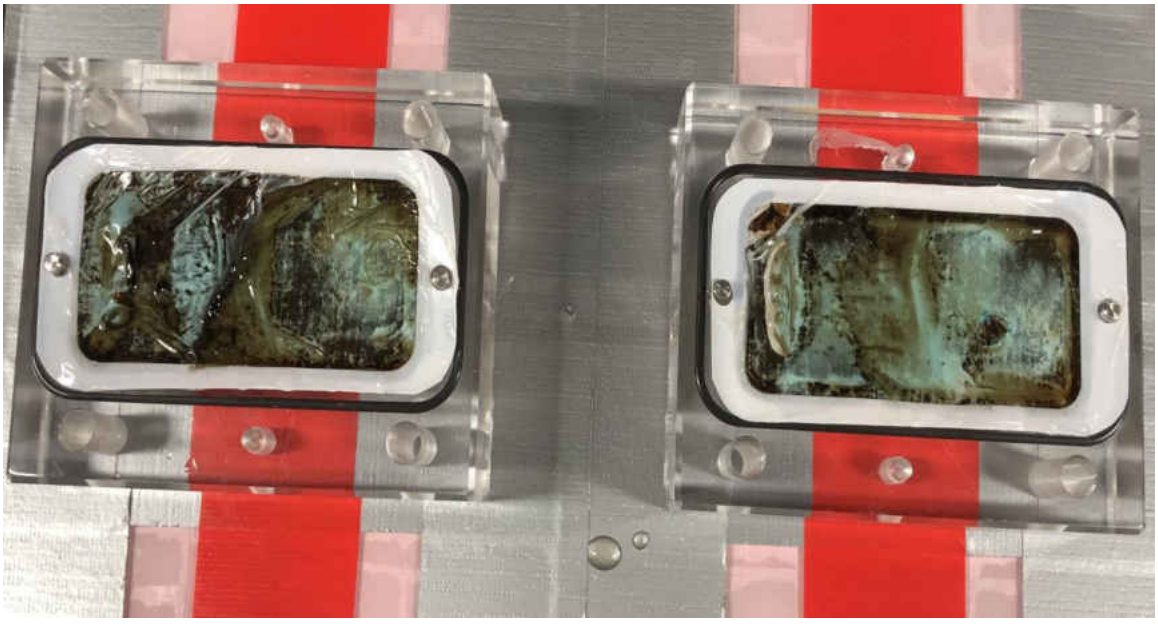

Figure 25. PAA/PAH-UF membrane samples of heavy metal removal from landfill leachate water.

Figure 26 (a, b, c, d, e, and f) shows the EDS spectra of the UF membrane and PAA/PAH-UF membranes that filtered DI water spiked with 2 ppm of each of Pb, Cd, and Cu individually. The retention of Pb, Cu, and Cd on the surface of the PAA/PAH-UF membrane (Figure 26 a, c, and e) and the surface of the virgin membrane (Figure 26 b, d, and f) is shown, respectively, when treating DI water spiked with heavy metals. Also, the EDS spectra of the UF membrane and PAA/PAH-UF membranes used for the treatment of landfill leachate demonstrate the retention of the metals tested in this study on the modified UF membrane (Figure 26g and 26h).

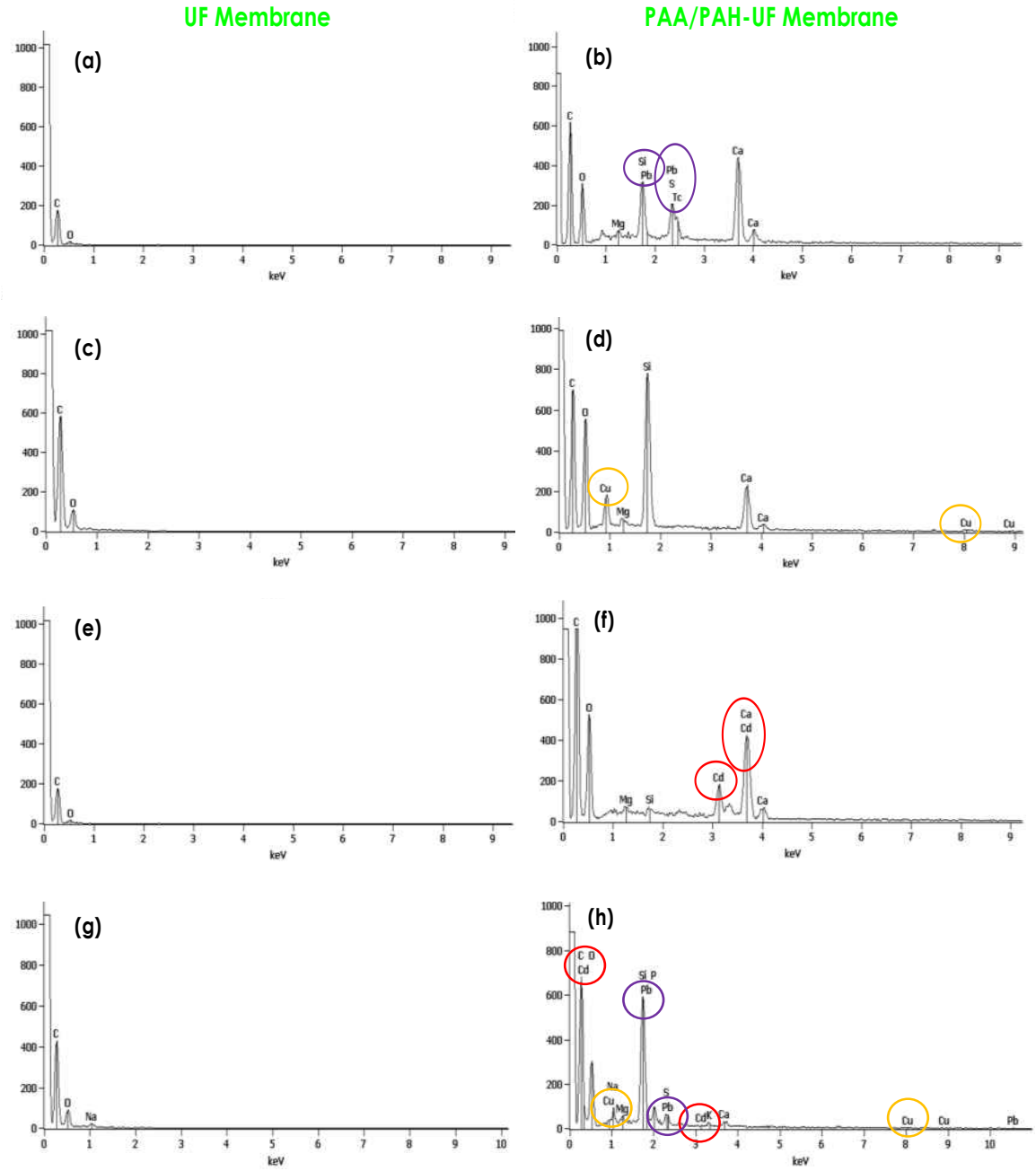

Figure 26. EDS spectra of UF membrane (a, c, e) and PAA/PAH-UF membrane (b, d, f) treating heavy metal spiked DI water spiked, and UF membrane (g) and PAA/PAH-UF membrane (h) treating landfill leachate, respectively.

6.3.1.3. Effect of NOM on Heavy Metal Removal by PE Laminated UF Membrane

The effect of NOM on the removal of heavy metals by the UF membrane and PAA/PAH-UF membrane was evaluated at NOM concentrations of 10 ppm, 50 ppm, and 100 ppm at pH 7.4 ± 0.2. Membrane filtration was performed at 70 psi for up to 10 hrs. to ensure that the fiber metal adsorption equilibrium was achieved. In general, NOM resulted in higher removal of heavy metals. The removal of Pb, Cd, and Cu by PAA/PAH-UF membrane was approximately 18%, 25%, and 30% higher, respectively at higher NOM concentrations. The removal of Pb and Cd by the unmodified UF membrane was 16% and 72% higher at higher concentrations of NOM, respectively. The removal of Cd by PAA/PAH-UF membrane was already very high in the absence of NOM (Figure 22). The presence of NOM resulted in about 20% higher removal of Pb and almost complete removal of Cu (Figure 27) compared to the DI water. The higher concentration of NOM generally resulted in higher removal of all three metals when using the PAA/PAH-UF membranes. The influence of NOM was the most pronounced in the case of Cu, followed by Pb and Cd. A similar trend was observed by a study that investigated the binding of these metal ions with humic acid and fulvic acid (Ghosh and Banerjee, 1997; Gondar et al., 2006). The enhanced removal of metal ions, in the presence of NOM, can be attributed to the additional complexation due to functional groups from NOM (Weng et al., 2002; Hankins et al., 2006; He et al., 2006). The available carboxyl content of NOM (Sahu and Banerjee, 1996; Baker and Khalili, 2005; Rakshit et al., 2009; Uchimiya et al., 2010) in addition to the existing carboxyl content provided by PAA/PAH fiber mats increased the removal of the heavy metals.

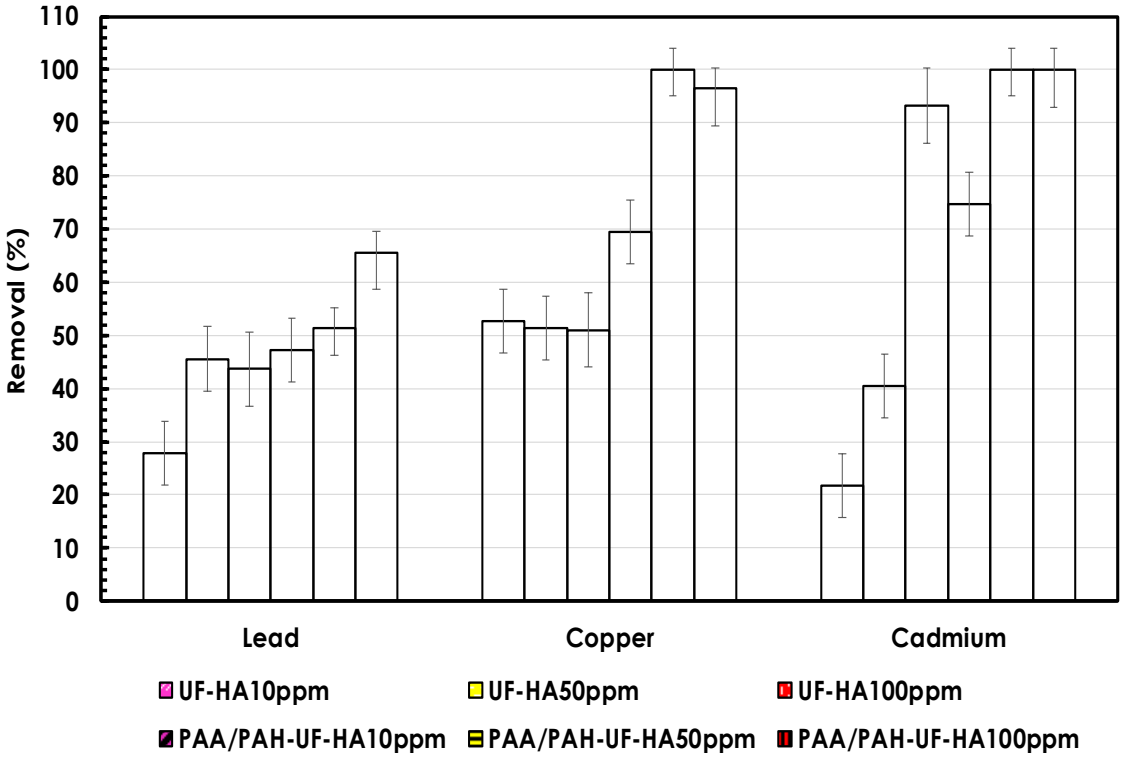

Figure 27. Heavy metal removal by UF and PAA/PAH-UF membranes in the presence and absence of NOM (after 10 hrs). (error bars represent the standard deviation of two or three samples).

Membrane fouling due to filtering NOM-spiked DI water by UF membrane and PAA/PAH-UF membrane for all three metals can be compared from the normalized flux plots in Figure 28. The unmodified membrane showed up to approximately 8% flux decline at NOM concentrations of 50 ppm and 100 ppm. On the other hand, the PAA/PAH membrane exhibited only up to 11% flux decline (only ~ 3% more compared to the unmodified membrane) in the presence of NOM. This demonstrates that coating the UF membrane with PAA/PAH complex fiber mats does not cause a significant flux decline. This could be the result of the enhanced hydrophilicity of the membrane due to PAA/PAH

coating as discussed in section 4.3.2.1. The trivial flux decline compared to the commercially available UF membrane may be outweighed by the marked improvement in heavy metal removal when functionalizing the membrane by PAA/PAH complex fiber mats. Figure 29 shows the photographs of the PAA/PAH-UF membrane filtering feedwaters containing different concentrations of NOM.

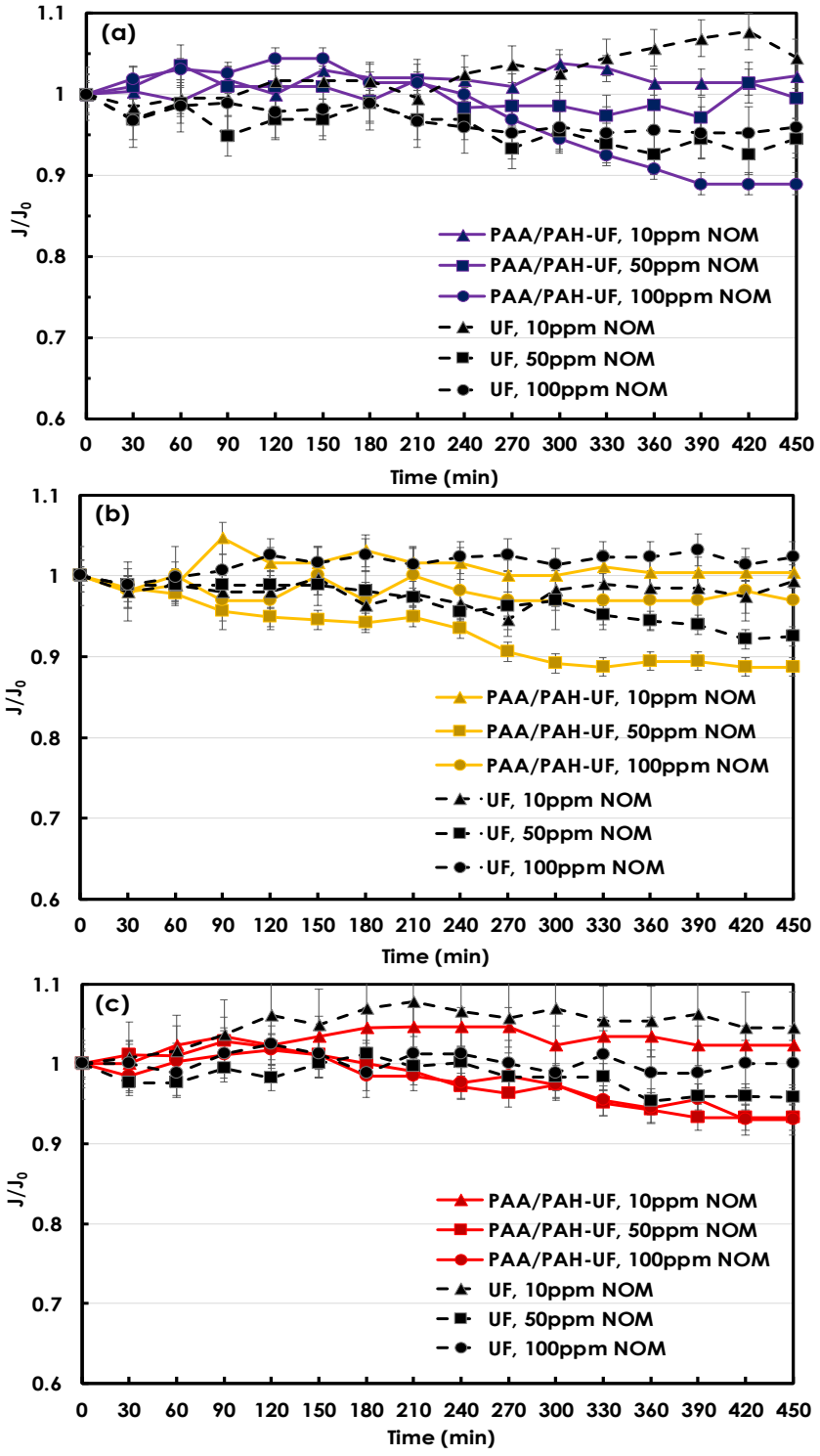

Figure 28. NOM influence on membrane flux of (a) Pb, (b) Cu, and (c) Cd as a function of time in DI water. (represented data are for 8 hrs. as there was no change until 10 hrs.). (error bars represent the standard deviation of two or three samples).

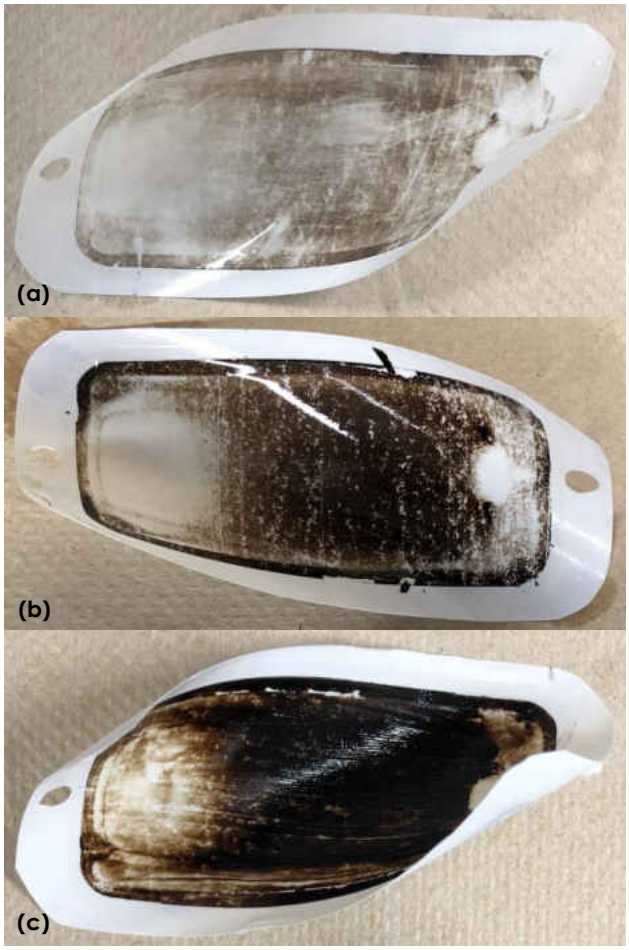

Figure 29. The surface of the UF membranes at the presence of 10 ppm, 50 ppm, and 100 ppm NOM concentrations.

6.4. Conclusions

The PAA/PAH functionalized UF membrane exhibited approximately up to approximately 85% higher removal of heavy metals when compared to the unmodified membrane. While the UF substrate contributes to metal removal to certain extent, the markedly higher metal retention by the modified membrane may be attributed to the adsorptive interactions of metal ions with the rich functional groups of the fiber mats. The enhanced removal of the

tested metals by the PAA/PAH-UF membrane compared to the unmodified membrane may be attributed to complexation of the metal ions with the carboxylate ions ($–COO^-$) from the PAA/PAH fiber mats.

The PAA/PAH-UF membrane exhibited approximately 18% and 15% higher removal of Pb and Cu, respectively in the leachate when compared to laboratory-prepared metal ion solution. For Cd, an almost complete removal was observed in both the synthetic solution and the landfill leachate. The higher removal of metals in landfill leachate could be attributed to the fouling of PAA/PAH fiber mat and the UF membrane substrate and metal-organic matter complexation. NOM-spiked controlled experiments revealed that higher concentration of NOM generally resulted in higher removal of all three metals when using the PAA/PAH-UF membranes. The enhanced removal of metal ions, in the presence of NOM, can be attributed to the additional complexation due to functional groups from NOM. The available carboxyl content of NOM in addition to the existing carboxyl content from PAA/PAH fiber mats may have increased the removal of the tested heavy metals.

While the unmodified membrane showed up to approximately 8% flux decline at NOM concentrations of 50 ppm and 100 ppm, the PAA/PAH membrane exhibited only up to 11% flux decline (only ~ 3% more compared to the unmodified membrane) in the presence of NOM. This could be due to the enhanced hydrophilicity of the membrane resulting from PAA/PAH fiber mat coating. The trivial flux decline compared to the commercially available UF membrane may be outweighed by the marked improvement in heavy metal removal when functionalizing the membrane by PAA/PAH complex fiber mats.

CHAPTER 7: SUMMARY

In this study, stable PE fiber (PAA/PAH fiber) mats were produced through electrospinning of PAA and PAH complex solutions. While the fiber mats exhibited up to approximately 63% removal of the tested heavy metals (Pb, Cd, and Cu) at pH 3.4, up to approximately 98% removal was observed at pH 7.4 from synthetic metal solutions, confirming that higher pH facilitates more effective removal of Pb, Cd, and Cu. The presence of NOM resulted in almost complete removal of all of the three metals at the higher pH (7.4). The removal of metal ions may be attributed to the dominance of carboxylate ions ($–COO^-$) from the fiber mats leading to metal-COO^- complexation. The enhanced metal removal in the presence of NOM is likely due to the higher availability of $–COO^-$ from NOM.

Moreover, this study developed a method of fabrication of polyelectrolyte (PE) complex fibers to functionalize ultrafiltration (UF) membranes, and investigated the removal of Pb, Cd, and Cu from synthetic feed solutions and landfill leachate by the PE laminated UF membranes. In addition, the influence of NOM on the metal removal efficiency of the of PAA/PAH-UF membranes was studied. The PAA/PAH-UF membrane exhibited approximately 38%, 49%, and 85% higher removal of Pb, Cu, and Cd, respectively when compared to the UF membrane. While the UF substrate contributes to metal removal to certain extent, the markedly higher metal retention by the modified membrane may be attributed to the adsorptive interactions of metal ions with the rich functional groups on the fiber mats. The PAA/PAH-UF membrane exhibited approximately 18% and 15% higher removal of Pb and Cu, respectively in the leachate when compared to laboratory-prepared

metal ion solution. The higher removal of metals in landfill leachate could result from the fouling of PAA/PAH fiber mat and the UF membrane substrate and metals complexation with leachate organic matter. Despite the lamination of the PAA/PAH fiber mat, supposedly acting as an additional barrier, on the UF membrane, the flux decline was approximately 10% less in both DI water and landfill leachate after 10 hrs. of filtration, likely due to the enhanced hydrophilicity of membrane imparted by the PE complex. The competitions among the metals for membrane adsorption sites may impact the metal adsorption capacity by the fibers. The retention of the metals tested in this study on the modified UF membrane was confirmed by the comparison of EDS spectra of the unmodified UF membrane and PAA/PAH-UF membranes used for the treatment of landfill leachate. The PAA/PAH-UF membrane exhibited approximately 16% and 72% higher removal of Pb and Cd at the presence of NOM. Moreover, the UF membrane showed approximately 18%, 25%, and 30% more removal of Pb, Cd, and Cu at the presence of NOM, respectively. While the adsorptive removal of Cd by PAA/PAH-UF membrane was already very high in the absence of NOM but the presence of NOM resulted in about 20% higher removal of Pb and almost complete removal of Cu. The enhanced metal removal in the presence of NOM is likely due to the higher availability of $–COO^-$ from NOM. The higher removal of metal ions, in the presence of NOM, can be attributed to the additional complexation due to functional groups from NOM. The addition of carboxyl content of NOM and the available carboxyl content of PAA/PAH increased the removal of heavy metals by UF and PAA/PAH-UF membranes. The presence of NOM increased the metal removal ability of both UF membrane and PAA/PAH-UF membrane while keeping the

membrane flux efficiency acceptable. No significant flux difference was observed between UF and PAA/PAH-UF membranes as the Flux was declined approximately 8% and 11% for UF and PAA/PAH-UF membranes respectively. The low flux decline of coated UF membrane (PAA/PAH-UF) and their high metals removal ability make them an applicable choice compared to the uncounted UF membranes.

CHAPTER 8: ENGINEERING SIGNIFICANCE AND RECOMMENDATIONS FOR FUTUR RESEARCH

Membrane processes have shown high efficiency in pollutants removal from different water matrices, but different factors such as membrane fouling, flux reduction, and high maintenance, energy, operation costs associated with high-pressure membranes have driven researchers to investigate novel approaches to modify membranes. Ultrafiltration (UF) is a low-pressure membrane, but it exhibits lower efficiency in removing heavy metals when compared to the high-pressure membranes. As investigated in this research, one approach to improve the efficiency of low-pressure membranes (such as UF) is to hybridize them with polyelectrolytes (PE), which have been widely investigated as heavy metal ion removal media because of high local concentration of functional groups such as carboxylates as well as strong interactions of these functional groups with metal ions.

In this study, PAA and PAH were considered as the two polyelectrolytes to produce stable fibers mats and functionalize UF membranes. The combination of these two polyelectrolytes showed appreciable performance in terms of heavy metals removal and stability. Future work should investigate other PE complexes for this purpose.

In addition to electrospinning, other modification techniques such as layer-by-layer (LBL) assembly, dip coating, etc., could be applied on the UF membrane and its performance be analyzed for removal of heavy metals and other contaminants. Future work should focus on evaluating the application of the fiber mats as commercial membrane modifiers aimed at improving the membranes' efficiency in removing a range of contaminants from various

water matrices. Furthermore, future research should focus on distinguishing the impact of co-occurrence of metal metals in the feed solutions. Per- and polyfluoroalkyl substances (PFAS) are current threats to human and environmental health and pose a risk to the safety of groundwater, surface water, and drinking water. PFAS such as perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are highly toxic and bioaccumulate in the environment due to low degradability. In the future study, the removal of other contaminants such as PFAS and pharmaceuticals and personal care products (PPCPs) using polyelectrolyte complex fiber mats laminated-ultrafiltration (PAA/PAH-UF) membrane can be investigated.

APPENDIX: ELECTROSPINNING PARAMETERS FOR PAA/PAH MOLAR RATIOS OF 4:1 AND 8:1.

Table 4. Best pattern of electrospinning parameters for PAA/PAH complex.

Steps	Working Distance (cm)	Pump Rate (μl/hr)	Voltage (Kv) (± 0.2)	Time (min)
1	10.5	0.6	8.6	10
2	10.5	0.6	8.6	10
3	10.5	0.6	8.8	20
4	10.5	0.6	8.8	20
5	10.5	0.6	8.8	20
6	10.5	0.6	8.8	20
7	10.5	0.6	8.8	20

Table 5. Other tested patterns of electrospinning parameters for PAA/PAH complex at working distance of 9.0 cm.

Steps	Working Distance (cm)	Pump Rate (μl/hr)	Voltage (Kv) (± 0.2)	Time (min)
1	9.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	10
2	9.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	10
3	9.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20
4	9.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20
5	9.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20
6	9.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20
7	9.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20

Table 6. Other tested patterns of electrospinning parameters for PAA/PAH complex at working distance of 9.5 cm.

Steps	Working Distance (cm)	Pump Rate (μl/hr)	Voltage (Kv) (± 0.2)	Time (min)
1	9.5	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	10
2	9.5	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	10
3	9.5	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20
4	9.5	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20
5	9.5	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20
6	9.5	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20
7	9.5	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20

Table 7. Other tested patterns of electrospinning parameters for PAA/PAH complex at working distance of 10.0 cm.

Steps	Working Distance (cm)	Pump Rate (μl/hr)	Voltage (Kv) (± 0.2)	Time (min)
1	10.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	10
2	10.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	10
3	10.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20
4	10.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20
5	10.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20
6	10.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20
7	10.0	0.3, 0.4, or 0.5	8.0, 8.2, 8.4, or 8.6	20

Table 8. Other tested patterns of electrospinning parameters for PAA/PAH complex at working distance of 11.0 cm.

Steps	Working Distance (cm)	Pump Rate (μl/hr)	Voltage (Kv) (± 0.2)	Time (min)
1	11.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	10
2	11.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	10
3	11.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20
4	11.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20
5	11.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20
6	11.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20
7	11.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20

Table 9. Other tested patterns of electrospinning parameters for PAA/PAH complex at working distance of 11.5 cm.

Steps	Working Distance (cm)	Pump Rate (μl/hr)	Voltage (Kv) (± 0.2)	Time (min)
1	11.5	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	10
2	11.5	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	10
3	11.5	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20
4	11.5	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20
5	11.5	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20
6	11.5	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20
7	11.5	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20

Table 10.Other tested patterns of electrospinning parameters for PAA/PAH complex at working distance of 12.0 cm.

Steps	Working Distance (cm)	Pump Rate (µl/hr)	Voltage (Kv) (± 0.2)	Time (min)
1	12.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	10
2	12.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	10
3	12.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20
4	12.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20
5	12.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20
6	12.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20
7	12.0	0.7, 0.8, or 0.9	9.0, 9.2, 9.4, 9.6, 9.8, or 10.0	20

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