

AMERICAN UNIVERSITY OF BEIRUT

PREPARATION AND CHARACTERIZATION OF  
TRIETHYLENETETRAMINE MODIFIED ELECTROSPUN  
MEMBRANES (TETA - PVC) AND THEIR ADSORPTION  
BEHAVIOR IN REMOVING LEAD(II) FROM WATER

by  
FATIMA GHALEB YOUNESS

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for the degree of Master of Engineering  
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# AMERICAN UNIVERSITY OF BEIRUT

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# ABSTRACT OF THE THESIS OF

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Title: Preparation and Characterization of Triethylenetetramine Modified Electrospun Membranes (TETA - PVC) and their Adsorption Behavior in Removing Lead(II) from Water

Water pollution is a global environmental concern threatening the entire biosphere and posing a significant risk on aquatic environments, leading to deterioration in the quality of water, thus affecting living organisms and limiting access to clean water. The development of sustainable and affordable water purification methods is crucial, yet remains challenging due to the wide range of pollutants (organic, inorganic, and heavy metals) present in water bodies. Owing to their persistence, toxicity, and bio-accumulative nature, heavy metals gained special attention from researchers investigating efficient approaches for the sequestration of metals from water. Adsorption is one of the most favored water treatment technologies due to its low cost, simplicity in design, and high efficiency. Electrospun polymeric nanofibrous membranes are among the developed adsorbents employed for water treatment due to their high porosity, large surface area, and ease of surface modification.

In this study, functionalized nanofibrous membranes were designed and fabricated to sequester lead(II) selectively from water. PVC membranes were prepared through electrospinning technique and modified with an organic linker, triethylenetetramine (TETA) resulting in TETA-PVC membranes. The membranes were characterized and their adsorption behavior towards the removal of lead was investigated. The incorporation of TETA on the membrane's surface significantly improved the removal efficiency of lead(II), at ambient conditions, up to 99.8% in 30 minutes. The adsorption mechanism was investigated and kinetic data showed the best fit for the pseudo-second-order. Similarly, the equilibrium data best fitted with the Langmuir adsorption isotherm model with a maximum adsorption capacity of 1250 mg/g for lead(II) ions. The membrane also showed high selectivity to lead(II) in a tertiary system containing lead(II), mercury(II), and cadmium(II). The functionalized membrane was regenerated, where desorption of lead(II) was achieved, under mildly acidic conditions. The removal efficiency of the regenerated membrane was maintained at 98% of its removal efficiency after six cycles of adsorption/ desorption. The proposed design offers a simple yet effective, sustainable, and environmentally friendly solution for water treatment.

## **Keywords**

Adsorption, electrospun-nanofibrous membrane, electrospinning, surface modification, heavy metals, metal-organic complexes, sustainability, nano-technology

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# CHAPTER I

## INTRODUCTION

### **A. Water Pollution**

The increased burden on the world's freshwater resources has severely impacted the social and economic well-being of many communities and is likely to be exacerbated in the future due to projected population growths, climate change, urbanization, growth in irrigated agriculture, and economic development.<sup>[1]</sup> Nearly 20% of the world's population currently lives in areas facing physical water scarcity and an additional 1.6 billion people live in areas with economic water scarcity,<sup>[2]</sup> the latter limits access to clean water. Anthropogenic processes, mainly industrial and agricultural activities have been considered as the main contributor to the contamination of the available fresh water by different pollutants worldwide. Over the years, water management has become a major challenge with the rapid increase of population accompanied with industrialization and significant climatic variations.<sup>[3]</sup> The change in land use/land cover as a result of human activities causes severe effects on the ecological, environmental, and hydrological characteristics.<sup>[4]</sup> In fact, urban growth alters the impervious surface area which in turn reduces the infiltration rate and increases runoff. Eventually, toxic contaminants are transferred through runoff to water bodies, deteriorating the quality of available fresh water threatening the aquatic and terrestrial environments.<sup>[5-7]</sup> The transfer of toxic metals within the aquatic environment into human bodies is illustrated in Figure 1.<sup>[8]</sup>

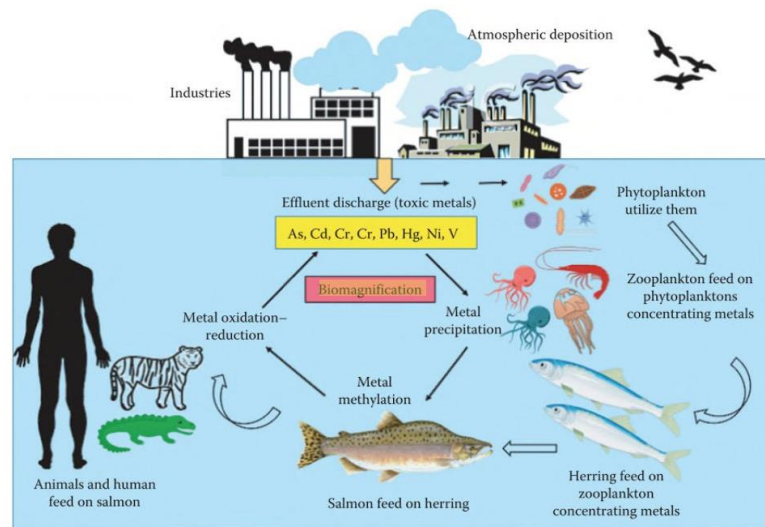


Figure 1: The bioaccumulation of heavy metals and their effect on living organisms [8]

Heavy metals are among the hazardous pollutants, due to their high toxicity at low concentrations, persistence in nature, and potential to bio-accumulation in food chains. [9–11] Heavy metals are naturally occurring elements known for their high atomic weight and high density. [12] Apart from being naturally toxic, studies indicated that these elements also have the tendency to change some organic substances into toxic metal-organic contaminants. [13] These characteristics render heavy metals a major threat for living organisms. Human exposure to heavy metals have increased tremendously due to their excessive use in various sectors such as industrial, agricultural, and technological activities. [14] Utilized heavy metals end up discharged to water bodies from different sources (industries, agricultural lands, domestic houses, etc.) intensifying water pollution. Heavy metals are transferred to human bodies through food or drinking water exposing them to chronic and sub-chronic diseases which may include cancer, diabetes, liver/kidney, heart, and others. [15] Sources and toxic effects of a selection of heavy metals is presented in Table 1.

Table 1: Heavy metals and their toxic effects

Heavy metal	Source	Effect	References
<b>Arsenic (As)</b>	Volcanic eruptions, soil erosion, and anthropogenic activities (mining, fertilizers, medications)	Cardiovascular, skin disorder, renal, neurological, carcinogenic effects	[16,17]
<b>Cadmium (Cd)</b>	Mining, smelting, and manufacturing of pigments and batteries, pesticides	Bone marrow damage, osteoporosis, liver and kidney damages, cancer	[12,16]
<b>Chromium (Cr)</b>	Metal processing, tannery facilities, stainless steel welding	Stomach tumors, respiratory, cardiovascular, gastrointestinal, hematological, hepatic, renal, and neurological effects	[16,17]
<b>Lead (Pb)</b>	Burning, paint, ceramic products, smoking, pesticides	Anemia, central nervous, renal, cardiovascular, gastrointestinal, musculoskeletal, reproductive, neurological, developmental, and immunological effects	[12,15,16]
<b>Mercury (Hg)</b>	Electrical industry (switches, batteries), dental applications, production of caustic soda, pharmaceutical products	Kidney and liver damage, central nervous system,	[12,15,16]

The adverse effects of heavy metals in human body and aquatic organisms necessitates the removal of these contaminants from water. Several techniques have been reported in the literature to eliminate heavy metals from polluted water including chemical precipitation, coagulation-flocculation, ion exchange, reverse osmosis, membrane filtration, and electrodialysis.<sup>[17-21]</sup> However, several factors limit the exploitation of these methods to reduce pollutants such as their complexity in treatment,

high maintenance and operational cost, high energy consumption, low efficiency, and the production of secondary pollution.<sup>[16, 20]</sup>

Recently, sustainable eco-technologies have been designed to treat water containing different classes of contaminants. A sustainable water treatment approaches should aim to be affordable, reliable, easy to operate, eco-friendly, and energy-saver and this is attained through continuous innovation and advancements. Adsorption showed high and relatively better performance over the conventional treatment methods in the removal of contaminants, due to its simple operation, high adsorption capacity, wide applicability, and flexibility in the design.<sup>[15, 19, 21]</sup> Moreover, adsorption is a reversible process, hence, adsorbents could be recycled and reused contributing to waste minimization.<sup>[6,23]</sup> Adsorption is the process by which a solute in a liquid or gas (adsorbate) is attracted to the surface of a solid (adsorbent) when they are in contact, either due to physical forces or by chemical bonds.<sup>[24,25]</sup> Different adsorbents have been investigated, and reported in the literature such as activated carbon,<sup>[26]</sup> zeolites,<sup>[27]</sup> silica,<sup>[28]</sup> activated alumina<sup>[29]</sup> and others for sequestering heavy metals, dyes, and other organic contaminants. The mentioned adsorbents showed have high adsorption capacities, however, the high cost associated with their synthesis and difficulty to be recycled limit their use for water treatment.<sup>[19, 21]</sup> This implies the need to develop sustainable (green, low cost, and highly efficient) adsorbents. Membrane technology is regarded as a promising treatment method due to its high recovery rate of heavy metals from aqueous solutions.<sup>[30]</sup> However, membrane fouling by which the solute block the pores of the membrane reduces its performance and weakens the designed system.<sup>[31]</sup> In order to overcome this problem, altering the membrane's surface to enhance its adsorptive properties has been considered by introducing functional groups (carboxyl,

amino, and thiol) [32–34] on the surface. Among them, amine-functionalized membranes are highly recommended due to their ability to complex with different heavy metals. [30, 31]

Recently, researchers have shifted their interest to polymeric nanofibrous membranes for the removal of heavy metals from water. Nanofibrous membranes are known for their high porosity which makes them good candidates for extracting pollutants from aqueous solutions. [36] Many studies have been performed on the fabricated membranes to assess their potential use in the removal of heavy metals and other pollutants. [37,38] Surface modification strategies of adsorbent materials have been extensively explored to enhance their adsorption capacity by altering the physical or chemical properties of the material to increase the surface area, active sites, kinetics of adsorbent, or improve stability. [39] To date, different fabrication techniques have been employed to produce polymeric nanofibrous membranes; however, electrospinning has been considered the most suitable method for the production of continuous nanofibers. [40] Table (2) presents current studies that reported the modification of electrospun nanofibrous membranes for the removal of heavy metals.

Table 2: Reported electrospun nanofibrous membranes for the uptake of heavy metals from water

<b>Material</b>	<b>Modification</b>	<b>Heavy metal</b>	<b>Adsorption capacity/ Removal efficiency</b>	<b>References</b>
<b>Polyacrylonitrile (PAN)/polyaniline (PANI)-nylon</b>	Diethylenetriamine (DETA)	<b>Pb(II)</b> and <b>Cd (II)</b> ions	960 mg/g for <b>Pb(II)</b> ,	[41]

			911.72 mg/g for Cd (II)	
<b>Polyacrylonitrile/cellulose acetate (PAN/CA)</b>	hydrolysis and amidoximation	Fe(III), Cu(II) and Cd(II) ions	7.47 mmol/g for Fe (III), 4.26 mmol/g for Cu (II), 1.13 mmol/g for Cd (II)	[42]
<b>Chitosan/Polyvinyl alcohol (PVA)/ polyether sulfone (PES)</b>	Fe <sub>3</sub> O <sub>4</sub> nanoparticles	Cr (IV) and <b>Pb(II)</b> ions	509.7 mg/g for Cr (IV), 525.8 mg/g for <b>Pb(II)</b>	[43]
<b>Chitosan/ poly (glycidyl methacrylate) (PGMA)/polyethyleneimine (PEI)</b>	Amino group	Cr (VI), Cu (II) and Co (II) ions	138.96 mg/g for Cr (VI), 69.27 mg/g for Cu (II) and 68.31 mg/g for Co (II)	[44]
<b>Poly methacrylic acid (PMA) / Cellulose acetate</b>	-	<b>Pb(II)</b> ions	146.2 mg/g	[45]
<b>Polyvinyl alcohol (PVA) and polyacrylic acid (PAA)</b>	Thiol-modified silica nanoparticles	Cu (II)	125.47 mg/g	[46]
<b>Polyvinyl chloride (PVC)</b>	thiol-functionalized HMO nanoparticles	Cu (II) and Ni (II) ions	90% Cu (II), 90% Ni (II)	[47]

## B. Lead

Due to its abundance in the earth's crust and its various uses by humans, lead (Pb), being a harmful component, threatens the life of all organisms. It is considered as



the second highly toxic heavy metal due to its persistence and non-biodegradability in nature.<sup>[48]</sup> Lead production had reached 10 million tons worldwide by the year 2012.<sup>[49]</sup> It is widely used in several industrial processes; in the production of batteries, paint, cosmetics, ceramic glazes, toys, plumbing systems and pipes.<sup>[49]</sup> Despite human's awareness of the toxicity of lead exposure long time ago, it is still an issue needed to be addressed to date.

As a heavy metal of different forms, lead can be divalent (II) or tetravalent (IV). However, Pb(II) is more frequently found in the environment forming salts when binding to most anions. On the other hand, Pb(IV), which is a strong oxidizing agent, is rarely found at the Earth's surface.<sup>[49]</sup> Lead is relatively immobile in the environment (in soils and freshwater bodies) compared to other heavy metals. Owing to natural (volcanic eruptions) and anthropogenic (mining, smelting, industrial and agricultural) sources, lead is being accumulated in the atmosphere. The latter has led to an increase in lead mobilization in the environment, contaminating aquatic and terrestrial ecosystems through wet (precipitation) and dry (prevailing wind) deposition of lead particulates present in air.<sup>[49]</sup> Lead is then transported through rivers and lakes and gets deposited in oceans. This will lead to the accumulation of Pb in fish due to its ability to bind to the sulfhydryl group in proteins present in aquatic organisms.<sup>[48]</sup> Thus, lead is expected to enter the humans' body and other living organisms through the food chain (Figure 2).

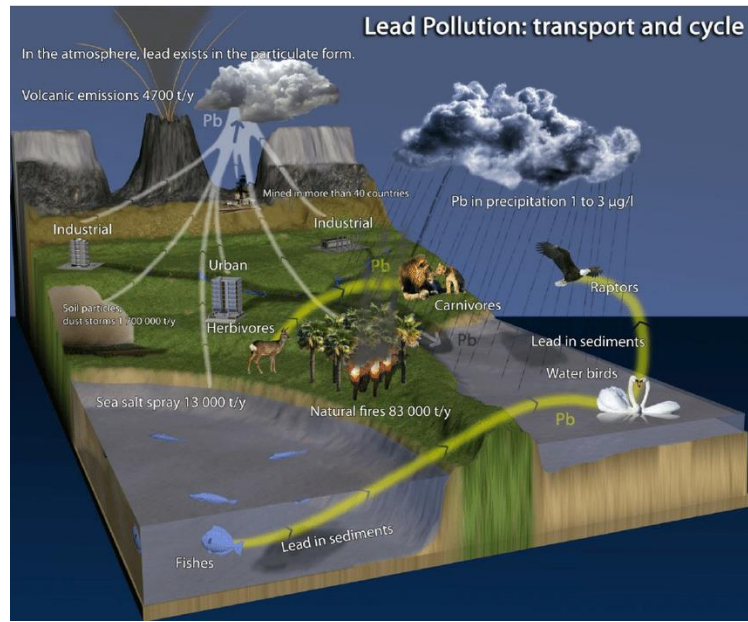


Figure 2: Lead pollution - transport and cycle<sup>[50]</sup>

Lead poisoning causes several health problems ranging from mild symptoms such as headache, vomiting, or dizziness to acute symptoms such as coma, cancer, renal failure, etc. Gastrointestinal disorders, constipation, abdominal pain, and damage of the central nervous system are other reported lead-induced issues. The severity and frequency of the symptoms may vary according to the level of exposure of lead. Lead is known to be a neurotoxin metal mainly affecting the central nervous system (decreased cognitive function, impaired concentration, encephalopathy). It can also affect human organs such as the kidney, liver, the reproductive system, and brain functions.

Furthermore, studies showed that children are particularly at risk to lead exposure who were exposed to lead experience a permanent cognitive impairment. The U.S. Centers for Disease Control and Prevention (CDC) defined lead poisoning as “one of the most common and preventable pediatric health problems”. Young children are the most affected by lead exposure due to their frequent hand-to-mouth behavior where lead could be easily ingested and absorbed into the blood stream. CDC set a threshold

for blood lead concentration of 100  $\mu\text{g/L}$  for children, where it was labeled as the “level of concern”. They reported that reduction of lead exposure should be taken into consideration at this level. Moreover, Schwartz studied the effect of very low blood lead concentration and found out that a threshold below which there is no effect on the nervous system does not exist. Other studies have been done to validate whether there is an acceptable level for lead in the blood, all of which agreed that even at very low concentrations, lead produces adverse effects on children’s brain development that might remain into their early adolescence. A study was conducted at the American University of Beirut Medical Center (AUBMC), in Beirut, Lebanon to measure the blood lead concentration in children between 1-3 years old.<sup>[51]</sup> Figure 3 shows the distribution of blood lead concentration among the children. The results indicated that around 14% of the children were identified to have a blood level concentration higher than 100  $\mu\text{g/L}$ . The latter stresses on the need to perform some actions for the reduction of lead in the environment.

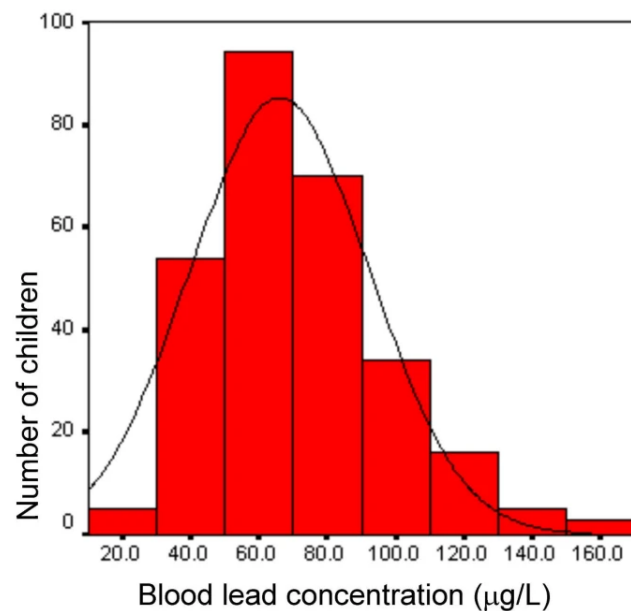


Figure 3: Distribution of blood lead concentration among 1–3-year-old children in Lebanon <sup>[51]</sup>

On the other hand, the EPA indicated that the maximum allowable level of lead in drinkable water is 15 ppb ( $\mu\text{g/L}$ ).<sup>[52]</sup> Unfortunately, lead is still found at levels much higher than that in water bodies such as surface waters and groundwater. Therefore, efficient removal of lead from aqueous solution is highly demanded for the protection of human health and the environment.

### C. Triethylenetetramine (TETA)

Triethylenetetramine (**TETA**), with the formula  $[\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2]_2$ , is an organic polyamine molecule that has been extensively used as a copper chelating agent to treat people diagnosed with Wilson's disease (accumulation of copper in human organs including liver, brain, or eye) for many years.<sup>[53]</sup> **TETA** therapy showed effective results other types of diseases such as diabetes, cancer (chemotherapy), cardiac and Alzheimer's disease.<sup>[54]</sup> Its amine structure (N-C-C-N) was found to chelate metal ions such as copper, zinc, iron, and nickel. Due to its four equally spaced nitrogen atoms (Figure 4), a stable metal-organic complex is formed between copper(II) ions and **TETA** in a planar ring.<sup>[55]</sup>

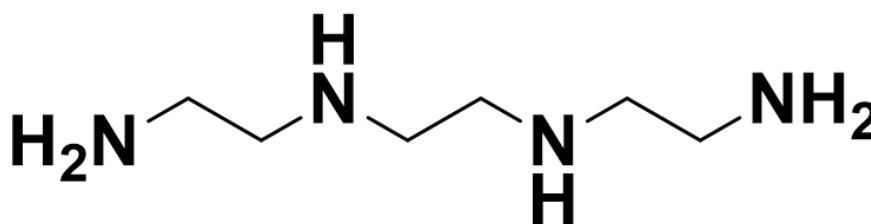


Figure 4: Molecular structure of triethylenetetramine<sup>[55]</sup>

Nurchi et al. (2013) reported that **TETA** forms a complex with copper and zinc with a ratio of 1:1 with high stability in water.<sup>[54]</sup> Another study was conducted by Lachowicz and her coworkers (2020) to investigate the copper and zinc complexation with functionalized mesoporous silica nanoparticles with **TETA** (**SBA-TETA**).<sup>[56]</sup> Different metal: ligand stoichiometric ratios were assessed, and it was found out that the complex was formed with a 1:1 metal: ligand ratio. The modified nanomaterial was characterized using the solid state nuclear magnetic resonance (SSNMR), EPR spectroscopy, and UV-VIS spectroscopy and the results obtained confirm the formation of the metal-ligand complex between Cu (II) and Zn (II) with **TETA** (Figure 5). A complex between **Pb(II)** and **TETA** has been recently studied for the recovery of lead from solid waste upon the addition of **TETA** to the leachate and then an attempt to precipitate the complex was performed.<sup>[55, 56]</sup> We are not aware of any published work where **TETA** has been used to modify electrospun **PVC** membranes for the uptake of lead(II) in water, which is investigated in this study.

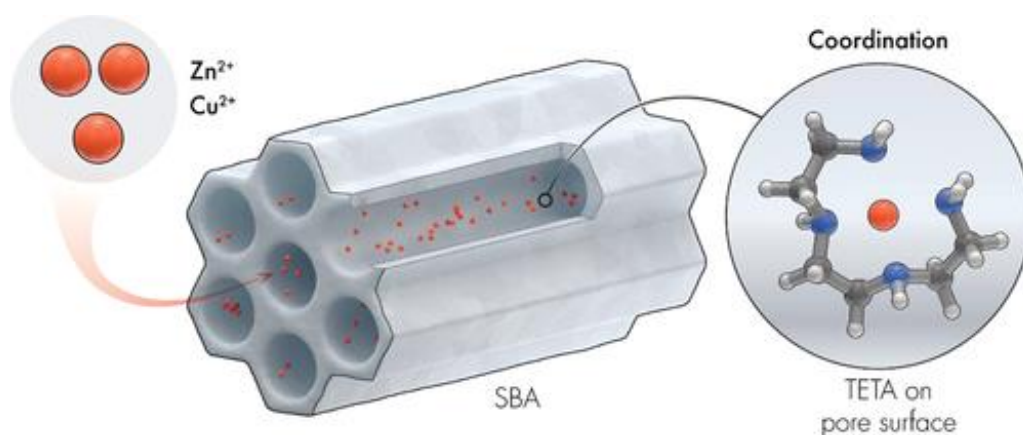


Figure 5: Schematic representation of SBA-TETA material and metal coordination process by **TETA** ligand<sup>[56]</sup>

## CHAPTER II

### RESEARCH OBJECTIVE

Water scarcity and poor quality are major environmental challenges threatening human health and social well-being. The degradation of water quality is a result of the transfer of pollutants to water resources limiting the access to clean and safe water. Heavy metal pollution, in particular, demonstrated hazardous effects on the environment and public health owing to their toxicity and persistence in nature, making them among the most studied pollutants. Intensive research is invested in sustainable water treatment approaches for the elimination of heavy metals from water bodies. Adsorption is relatively the most efficient water purification method used due to its simplicity, effectiveness, and reasonable cost. The main target is to develop low-cost materials possessing high adsorption capacity and ability to be recovered and reused while minimizing the production of secondary hazardous wastes. Adsorptive materials such as electrospun polymeric membranes represent a class of emerging adsorbents for water treatment and is proven to be suitable candidates for the effective removal of pollutants from water.

The aim of this study is to implement a sustainable approach for the removal of heavy metals from water. This project focuses on the development of a modified electrospun membrane and assessing its applicability and potential to capture heavy metals, mainly lead(II), from water. Polyvinyl chloride (**PVC**) is employed in this study for the fabrication of the membrane and is modified with triethylenetetramine (**TETA**). **TETA** is an organic ligand that binds with metal ions to form a metal-ligand complex. It has been shown that **TETA** is able to bind several metal ions including; copper, zinc,

iron, and nickel. In this study, the formation of a metal-organic complex between **TETA** and lead(II) metal ion in water is investigated before suspending **TETA** on the membrane to be used as an adsorbent for lead. The proposed mechanism of the metal chelation is represented in the figure below.

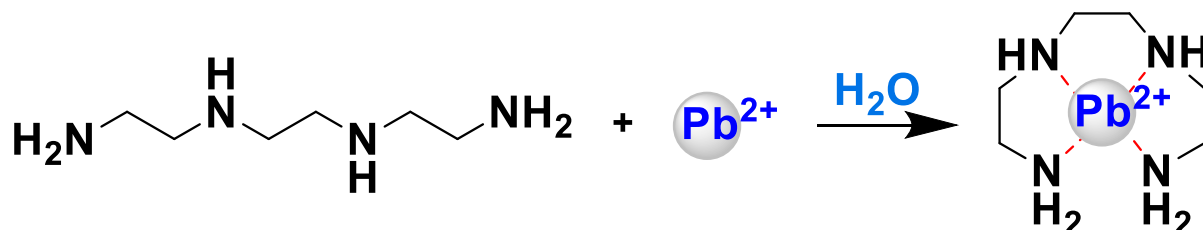


Figure 6: Proposed mechanism of the binding process between lead(II) and **TETA**

The project was conducted in five main steps: (I) *detection and characterization* of the metal-organic complex (lead(II) ions and triethylenetetramine (**TETA**)) in solution, (II) *fabrication of polyvinyl chloride (PVC) membrane* through electrospinning, (III) *suspension* of the organic ligand (**TETA**) on a solid support (electrospun **PVC** membrane), (VI) *investigate the removal* of lead(II) ions from water using the modified membrane and *test its selectivity in a tertiary system of heavy metals*, and (V) *regeneration of membrane and examining its removal efficiency* of lead(II) after several cycles.

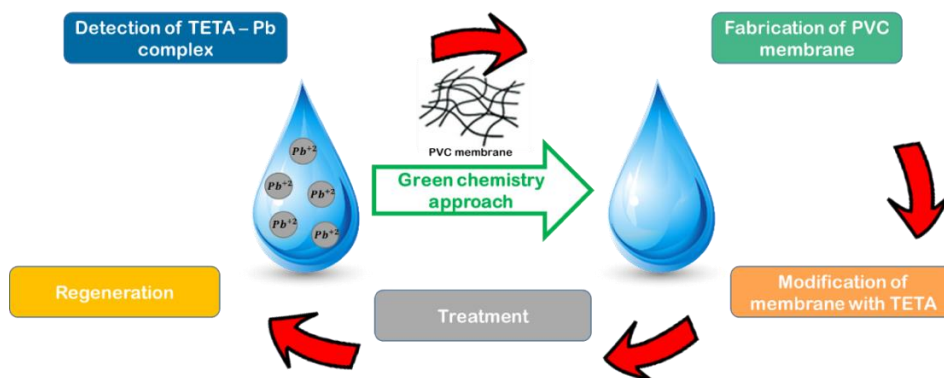


Figure 7: Research objectives

## CHAPTER III

### METHODOLOGY

The study conducted is divided into five major categories. The first step is to detect a complex between **TETA** and **Pb(II)** ions in water. This was achieved using UV-Visible spectrophotometer. The next step is to suspend **TETA** on the solid support for the removal of lead in water; hence, a membrane was fabricated using an electrospinning machine and then modified by **TETA** to enhance its removal efficiency. In order to confirm our modification process, several analyses were performed on the membrane before and after functionalization (FTIR, TGA, SEM and EDX). The membrane was then used to treat contaminated water rich in lead(II) ions and the water was tested on the atomic absorption spectroscopy (AAS) to determine the decrease in lead(II) metal ion concentration in solution. Adsorption experiments were performed to calculate the maximum adsorption capacity, investigate the effect of contact time between lead(II) and the adsorbent, determine the selectivity of the membranes (modified and unmodified) for lead(II) in a tertiary system containing mercury(II) and cadmium(II) as potential interfering metal ions, and confirm the reusability of the membrane.

#### A. Materials

Polyvinyl chloride (**PVC**) with a molecular weight of 80,000 g/mol and a density of 1.4 g/mL, dimethylformamide (DMF) with  $\geq 99.8\%$  purity, tetrahydrofuran (THF) with  $\geq 99.9\%$  purity, triethylenetetramine (**TETA**) with a molecular weight of 146.23 g/mol and a density of 0.982 g/mL, and lead(II) acetate trihydrate



( $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3(\text{H}_2\text{O})$ ) with a molecular weight of 379.33 g/mol were all purchased from Sigma. Commercial nylon screen fabric with an average pore size diameter of 350  $\mu\text{m}$  and thickness of  $215 \pm 2 \mu\text{m}$  was used as a support for the electrospun membranes.

## B. UV-Visible Spectrophotometer

Agilent 8453 UV-Visible spectrophotometer using a 1 cm path length was used to detect the absorption spectra of the samples with a wavelength that ranges from 190 up to 1100 nm. The samples were placed in a standard quartz cuvette and the transparent cuvette was placed in the instrument for analysis. An absorption measurement as a function of wavelength is generated according to amount of light absorbed by the sample. A schematic diagram of the spectrophotometer is represented in the figure below.

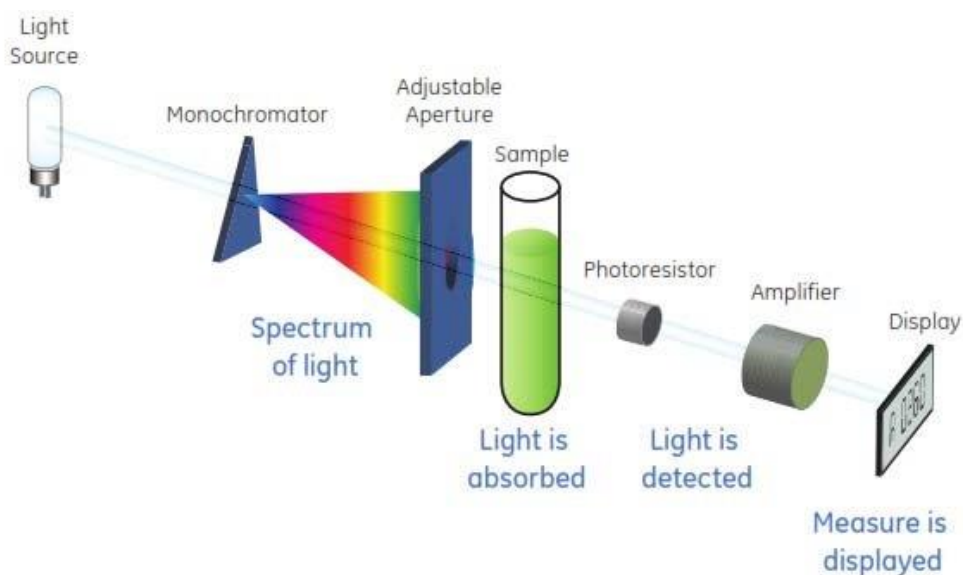


Figure 8: Schematic diagram of UV-Visible spectrophotometer

A solution rich in lead(II) ions (lead(II) acetate trihydrate) was prepared to represent contaminated water. **TETA** solution was also prepared and added to the lead solution to validate the sequestration of **Pb(II)** ions by **TETA**. The hypothesis was tested using the UV-Visible spectrophotometer to verify the presence of a coordination between lead(II) ions and the ligand. The experiment was done at room temperature with no waiting time to detect the formation of the metal-organic complex. Additionally, a potentiometric titration was carried out to determine the binding constant and stoichiometry between the metal and organic ligand, where different concentrations of the ligand were added separately to a solution rich in lead of constant concentration ( $1.71 \times 10^{-4}$  M). The titration was done in 15 mL conical tubes and the solution was then placed in the cuvette for testing, under same ambient conditions, but with different concentrations of **TETA** added.

### **C. Electrospinning machine**

Electrospinning is an emerging technique based on the fabrication of a porous polymeric nanofibrous membrane. The membrane possesses a high volume to surface area ratio and is known for its flexibility to be modified. These properties render the membrane to be a great candidate for the capture of different types of pollutants. Electrospinning process is based on creating an electric field by applying a high voltage to the polymeric solution. As a result, the solution is ejected from the tip of the needle in the form of a “taylor cone” as shown in Figure 9. The fibers produced are collected on the grounded collector forming the nanofibrous membrane. The morphology of the fibers is affected by different factors such as ambient conditions (humidity, temperature), operating conditions (voltage, tip-to-collector distance, flow rate,

collector rotation speed) and polymeric solution prepared (polymer concentration, viscosity, volatility, and conductivity).

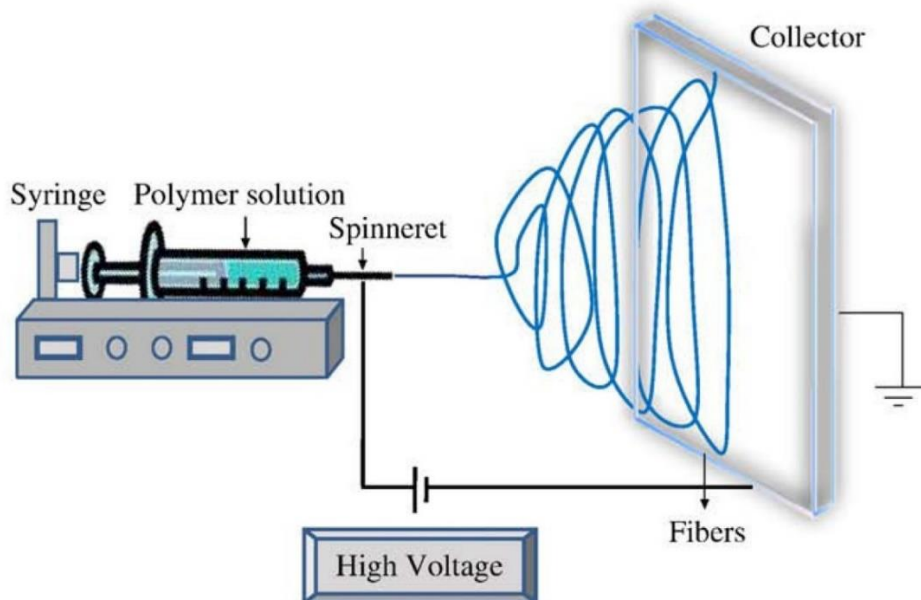


Figure 9: Schematic diagram of the electrospinning machine

An electrospun polymer membrane was fabricated to serve as a solid support for the organic ligand in order to capture lead(II) ions from water. Polyvinylchloride (**PVC**) is the 3<sup>rd</sup> most widely used polymer characterized by its chemical stability and ability to be modified, hence, it was used in this study in the fabrication of the polymeric membrane. For the preparation of the polymeric solution, using THF alone as the solvent showed undesirable results where a wrinkly surface structure was formed due to the high volatility of the solvent. In order to avoid this problem, DMF, which is a less volatile solvent, was mixed with THF to reduce the evaporation time while the solution is being ejected. The fibers produced by mixing both solvents showed a better morphology and high mechanical strength. A solvent ratio of 62.5:37.5 DMF: THF was reported to produce the optimal morphology of the fiber (*Badran, 2019*). The solvent was prepared by mixing 7 mL of DMF with 4 mL of THF. The optimal **PVC** polymer

concentration was 16% by weight (Badran, 2019) resulting the highest fiber diameter, hence, 1.936 g of **PVC** was added to the solvent. The solution was left on a stirrer at a speed of 700 rpm at room temperature. The electrospinning machine was used to fabricate the **PVC** membrane using the polymeric solution prepared under a fixed electric field of 18 kV. After that, the electrospun **PVC** membrane was placed into a solution of **TETA** and ethanol of different ratios for surface modification. The reaction was set at 65°C for 5 hours (Figure 10). The membrane was then washed with ethanol and distilled water and left to dry at room temperature.



Figure 10: Modification setup of the **PVC** membrane in an oil bath

## D. Membrane Characterization

### 1. *Fourier-transform infrared spectroscopy*

Fourier-transform infrared spectroscopy (FTIR) spectroscopy was used to characterize the chemical composition of the nanofibrous membranes and to validate the modification process of the **PVC** membrane. This is done by detecting the presence of the amine bond formed between **TETA** and the membrane. ATR-FTIR spectra (4 scans, 4 cm<sup>-1</sup> resolution, wave number range (4000 – 6500 cm<sup>-1</sup>) were obtained using a Perkin

Elmer FTIR Spectrum 2000 Spectrophotometer with a diamond/ZnSe crystal window. All spectra of the modified and unmodified membranes were recorded under ambient conditions. SPECTRUM software (Perkin Elmer) was used for data collection. The IR bands are reported in wavenumbers ( $\text{cm}^{-1}$ ).

## **2. Thermogravimetric Analyzer**

Thermal stabilities of the electrospun modified and unmodified membranes were measured using thermogravimetric analyzer (TGA), which was performed using a Netzsch TG 209 F1 Libra apparatus. Samples were heated from 30 to 800 °C at a heating rate of 10 K  $\text{min}^{-1}$  under dynamic nitrogen flow.

## **3. Pore size, membrane thickness, and water contact angle**

The average pore size was measured using a capillary flow porometer CFP-1100- from Porous Material Inc. (PMI), USA. In order to measure the average pore size, a membrane sample was horizontally sandwiched in the sample chamber, saturated with a wetting liquid, Galwik, and then, properly sealed. Afterward, air is passed into the chamber at an increasing differential pressure. When the pressure reaches an adequate level to overcome the capillary action of the fluid in the largest pore, the fluid is displaced in that pore. The corresponding pressure is the bubble point. The pressure is increased further until the liquid in all pores is displaced and the sample is considered dry. Meanwhile, the flow rate and gas pressure are monitored in order to generate the pore size distribution and mean pore size diameter.

The contact angle is a quantitative measure of the wettability of a surface or material (wetting of a solid by a liquid). A water droplet with a contact angle over 90

degrees indicates a hydrophobic surface and less than 90 degrees indicates a hydrophilic surface.<sup>[59]</sup> The water contact angle (WCA) was measured using an optical tensiometer (OCA 15EC, DataPhysics, Germany) with a water droplet volume of 5  $\mu\text{m}$ . A sample of the modified (**TETA - PVC**) and unmodified (**PVC**) electrospun membrane was placed on the sample holder and then a droplet of water from a syringe provided in the tensiometer was carefully dropped on the membrane (Figure 11). The software measures the contact angle and a picture of the result was taken. The measurements were repeated five times for each sample and the contact angle was averaged.

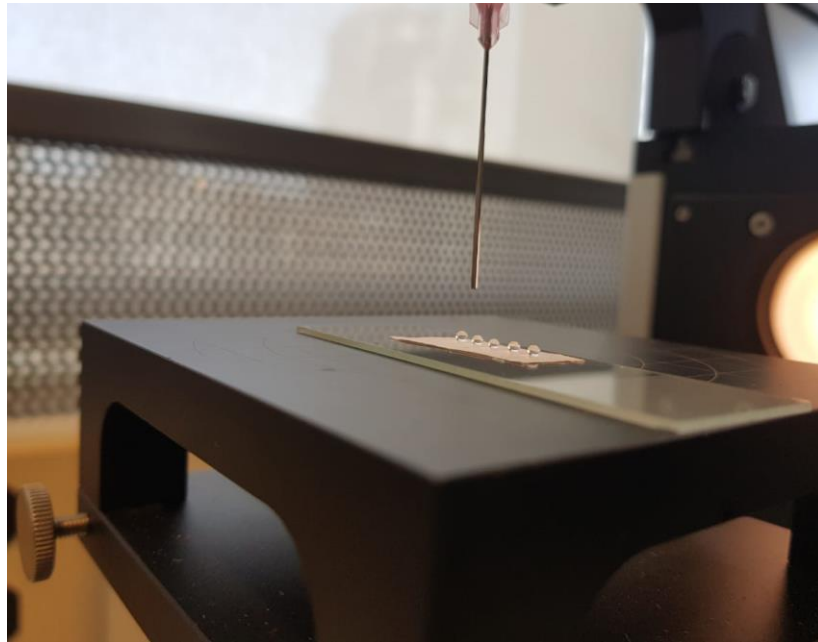


Figure 11: Water contact angle measurements

#### ***4. Scanning Electron Microscopy***

Scanning Electron Microscopy (SEM) was used to study the surface characteristics of the **PVC** membrane before and after modification. SEM images would provide a clear vision whether modification of the membrane has occurred or not according to the difference between the size, porosity, and distribution of the fibers of

both membranes. TESCAN, VEGA 3 LMU, Scanning Electron Microscope was used. Samples were coated with 20 nm of platinum for 10 minutes using the spin coater, then they were placed inside the SEM where the voltage was set to 5 kV, the working directory was set to 15 mm, and different magnification levels were investigated (5  $\mu\text{m}$ , 10  $\mu\text{m}$ , 20  $\mu\text{m}$ , 50  $\mu\text{m}$ , 100  $\mu\text{m}$ ).

### **5. *Energy Dispersive X-ray***

Energy Dispersive X-ray (EDX) analysis was performed on the membrane to identify the elemental composition of the membrane and to provide a quantitative analysis of the elements detected in the sample. EDX analysis is performed while using the Scanning Electron Microscope (SEM), on a specific point or surface area chosen to estimate the chemical composition of that region. The EDX generates a spectrum showing peaks that correspond to the different elements found in the sample. It is noteworthy that EDX results may not necessarily be representative of the chemical composition of the whole sample.

### **E. Atomic Absorption Spectroscopy**

Atomic absorption spectroscopy (AAS) is an instrumental technique used to trace metal concentration in aqueous solutions. It provides a quantitative analysis of the metal present in the sample based on the absorption of light at a specific wavelength of the element. AAS derives a relation between samples of known concentrations referred as “standards” and the measured absorbance, consequently, it generates a calibration

curve to measure the concentration of the metal in the samples. Figure 12 is a schematic representation of the components of the instrument.

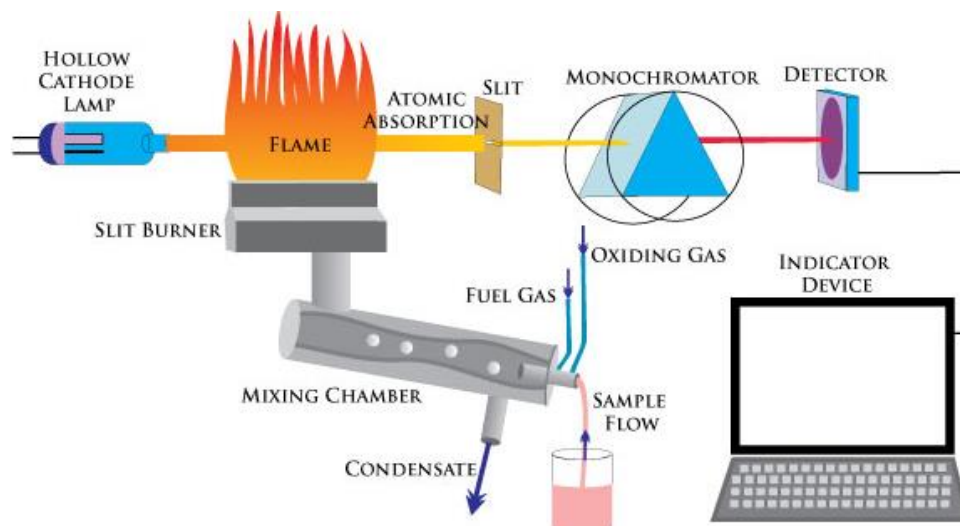


Figure 12: Schematic diagram of the atomic adsorption spectroscopy

An iCE 3000 series atomic absorption spectroscopy was used to determine the percentage removal of lead(II) ions in water after immersing the modified **PVC** membrane. The air/acetylene flame was used to carry out the study and detect the concentration of the metal in ppm. A 150-ppm lead(II) stock solution was prepared and used for the analysis. AAS has an upper detection limit of 17.5 ppm for lead, therefore, dilution of the samples was required. Seven standards of known concentrations were prepared to generate the calibration curve on the AAS (2.5, 5, 7.5, 10, 12.5, 15, 17.5 ppm). Next, four different **PVC** membranes (unmodified, modified with a ratio of 1:1, modified with a ratio of 1:2, modified with a ratio of 1:3) were immersed in a 15 mL conical tubes and an equivalent volume was taken from the 150-ppm stock solution of ratio 1:1 **PVC** (mg): **Pb(II)** solution (mL) and added to the tubes. The samples were left in a shaker at a speed of 100 rpm at room temperature and then 0.665 mL aliquots from



the samples were taken after 0.5, 1, 2, and 24 hours. The samples were filtered using a 100  $\mu\text{m}$  membrane filter, and distilled water was added so that the final volume reaches 10 ml. The diluted samples were then tested to detect the concentration of lead(II) ions using the AAS.

## CHAPTER IV

### RESULTS AND DISCUSSION

Surface modification of adsorbents is an effective approach to achieve an outstanding performance and a high removability of pollutants in water.<sup>[35,39]</sup> Suspension of an organic ligand (**TETA**) on the surface of electrospun **PVC** membranes is reported in this study, where the effect of the modification on the physicochemical properties of the membrane (hydrophilicity, porosity, thermal and chemical stability), and its potential in enhancing its removal efficiency of lead from water was investigated. Prior to suspending the organic ligand on the polymeric membrane, the interaction of **TETA** and lead was evaluated in solution. The stoichiometry and binding association of the metal-organic complex (**TETA** - **Pb(II)**) were evaluated after detecting the complex formation using UV-spectroscopy.

#### **A. Formation of TETA-Lead complex**

##### *1. Detection of TETA - Lead complex using UV-visible spectroscopy*

The UV-Vis spectrophotometer was used to detect the formation of the **TETA** - **Pb(II)** complex in water as a result of the chelation of **Pb(II)** metal ions to triethylenetetramine (**TETA**) ligand. Prior to investigating the metal-organic complex, detection of the metal and organic ligand by UV-Vis in water was optimized separately. A solution rich in lead(II) ions (lead(II) acetate trihydrate) was prepared (representing contaminated water). **TETA** solution was also prepared and added to the lead induced water to validate the complexation of **Pb(II)** ions with **TETA**. Absorption spectra of

**TETA, Pb(II), and TETA - Pb(II)** complex spectra are presented in Figure 13. The concentrations tested were within the acceptable range of absorbance ( $0.5 < \text{Abs} < 2.7$ ). A maximum absorption peak for **Pb(II)** ions is detected at 208 nm; whereas the maximum absorption band for the ligand was observed at a wavelength of 190 nm.

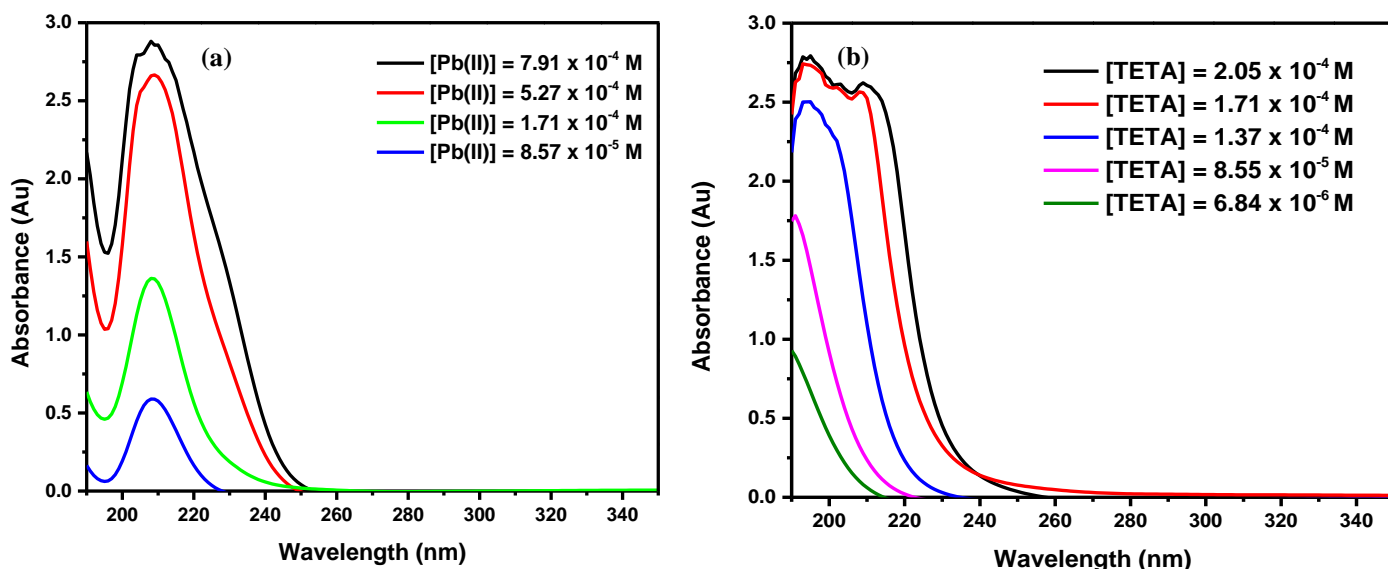


Figure 13: Absorption spectrum of Pb(II) and TETA in aqueous solutions: (a), lead(II) acetate trihydrate within the UV-visible region (b) triethylenetetramine within the UV-visible region

After several trials of mixing different stoichiometric ratios of **TETA** with lead, a 1:1 ratio of  $1.71 \times 10^{-4} \text{ M}$  was found to be the optimum concentration for the detection of metal, ligand and complex formation, based on Beer Lambert's law. The absorption spectra of the **TETA, Pb(II)**, and their mixture in solution are shown in Figure 14. A shift in the absorption peak to a wavelength of 194 nm is displayed in the mixture spectrum, in addition to the emergence of a new broad peak at 250 nm relative to the lead spectra. The change in the absorption pattern (absorption spectrum) of the complex relative to that of the ligand and metal confirms the formation of a new product.

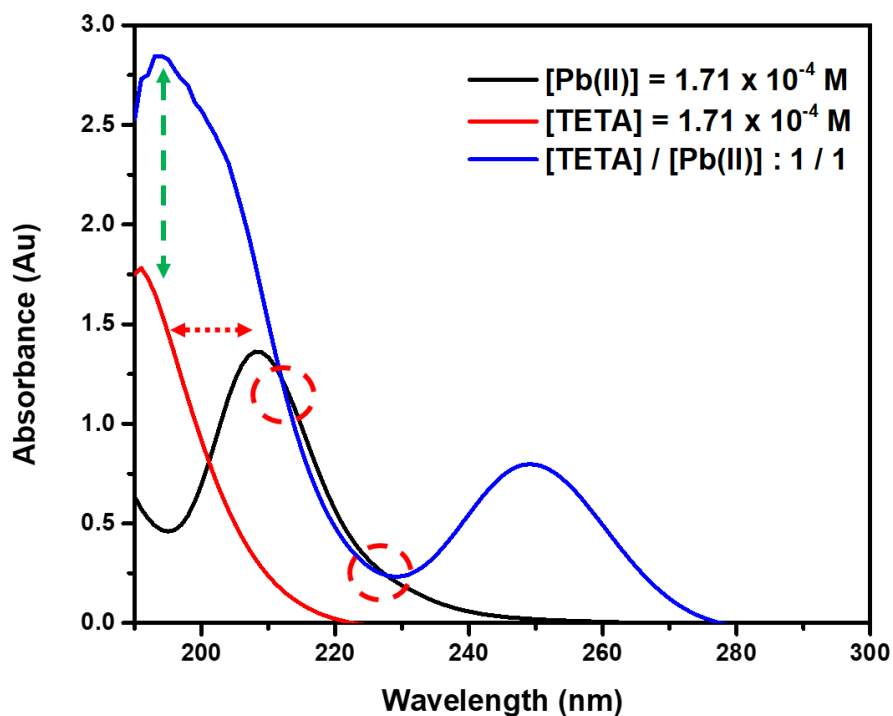


Figure 14: Absorption spectra of lead(II) acetate trihydrate, **TETA**, and their **[TETA / Pb(II)]** complex within the UV-visible region

A hypsochromic shift of the sharp peak of **TETA - Pb(II)** spectrum from 208 to 194 nm along with a hyperchromic shift; an enhancement of the peak's absorbance at 194 nm, were observed relative to the uncomplexed **Pb(II)** spectrum. The change in position and intensity of the absorption band indicates that lead(II) ions have complexed to the ligand, hence, a metal-ligand complex has been formed.<sup>[60]</sup> The changes in the spectrum caused the formation of two well defined isosbestic points at wavelengths 210 nm and 230 nm as shown in Figure 14. The presence of the isosbestic points also implies the complexation mode of the ligand with **Pb(II)** ions in solution.

## 2. Binding mechanism of lead(II) ion and triethylenetetramine

A titration experiment of **Pb(II)** metal ion with **TETA** was carried out to investigate the strength and stoichiometry of the resulting metal-organic complex in aqueous solution. UV-visible absorption spectra of a solution of  $\text{Pb}(\text{OAc})_2$  in  $\text{H}_2\text{O}$  titrated with, increasing concentrations of triethylenetetramine were compared to the uncomplexed metal spectrum shown in Figure 15. Upon the addition of **TETA** to lead solution, a maximum absorption peak was observed at a wavelength of 250 nm. Moreover, a decrease in the metal's absorbance peak until its fading indicates the disappearance of uncomplexed **Pb(II)** ions from the solution (Figure 15).

Furthermore, a clear isosbestic point appears at wavelength of 218 nm, which shows that both species were at equilibrium at this wavelength, and hence, indicating the formation of a metal-organic complex in solution. It is noteworthy that the titration experiment was conducted several times and the results were reproducible.

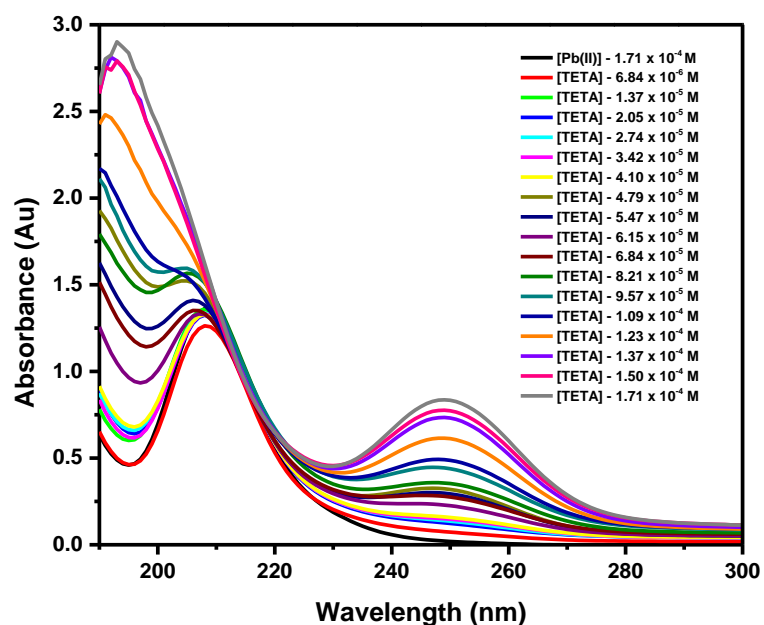


Figure 15: UV-visible absorption spectra of  $1.71 \times 10^{-4} \text{ M}$  solution of  $\text{Pb}(\text{OAc})_2$  in  $\text{H}_2\text{O}$  titrated with, increasing concentrations, of triethylenetetramine

The titration of increased concentrations of **TETA** ( $1.71 \times 10^{-4} \text{ M} < [\text{TETA}] < 3.42 \times 10^{-4} \text{ M}$ ) to a solution of fixed lead concentration ( $1.71 \times 10^{-4} \text{ M}$ ) was analyzed using the UV-vis spectrophotometer (Figure 16). The stoichiometry (ratio of ligand: metal) and the binding constant were calculated by fitting the experimental data, (obtained by the titration experiment) to different stoichiometric equations.

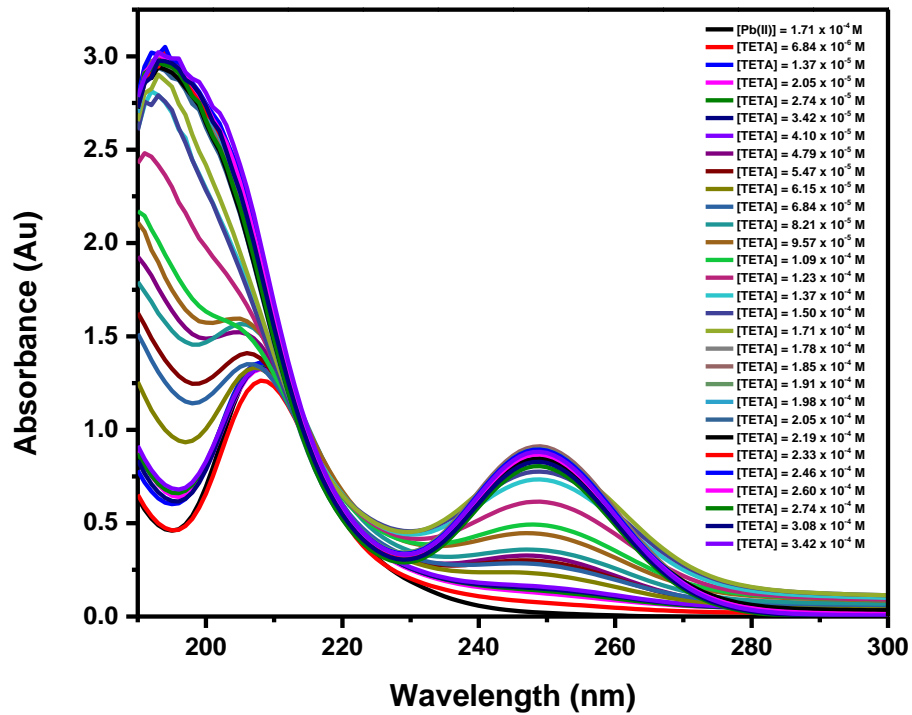


Figure 16: UV-visible absorption spectra of  $1.4 \times 10^{-4} \text{ M}$  solution of  $\text{Pb}(\text{OAc})_2$  in  $\text{H}_2\text{O}$  titrated with, increasing concentrations of triethylenetetramine

The increase in UV-absorbance at 250 nm as the concentration of **TETA** increased in solution was plotted (Figure 17). The experimental data was then fitted using EQN 1, representing a 1:1 binding mode.

$$y = Y_0 + D_Y \times \frac{((K_a \times (P+x)+1) - (((K_a \times (P+x)+1)^2 - 4 \times K_a^2 \times P \times x)^2))}{(2 \times K_a \times P)} \quad (1)$$

Where  $Y$  is the absorbance of the complex,  $Y_0$  is the initial absorbance,  $P$  is the concentration of the metal,  $D_Y$  is the change in absorbance, and  $K_a$  is the binding association/ constant.

Fitting the experimental data with the 1:1 binding model was in good agreement (R-squared of 0.998). The binding constant ( $K_a$ ) was found to be  $1.15 \pm 0.6 \times 10^6 \text{ M}^{-1}$  (Figure 17), which indicates the formation of a very strong and stable complex in water.<sup>[61-64]</sup>

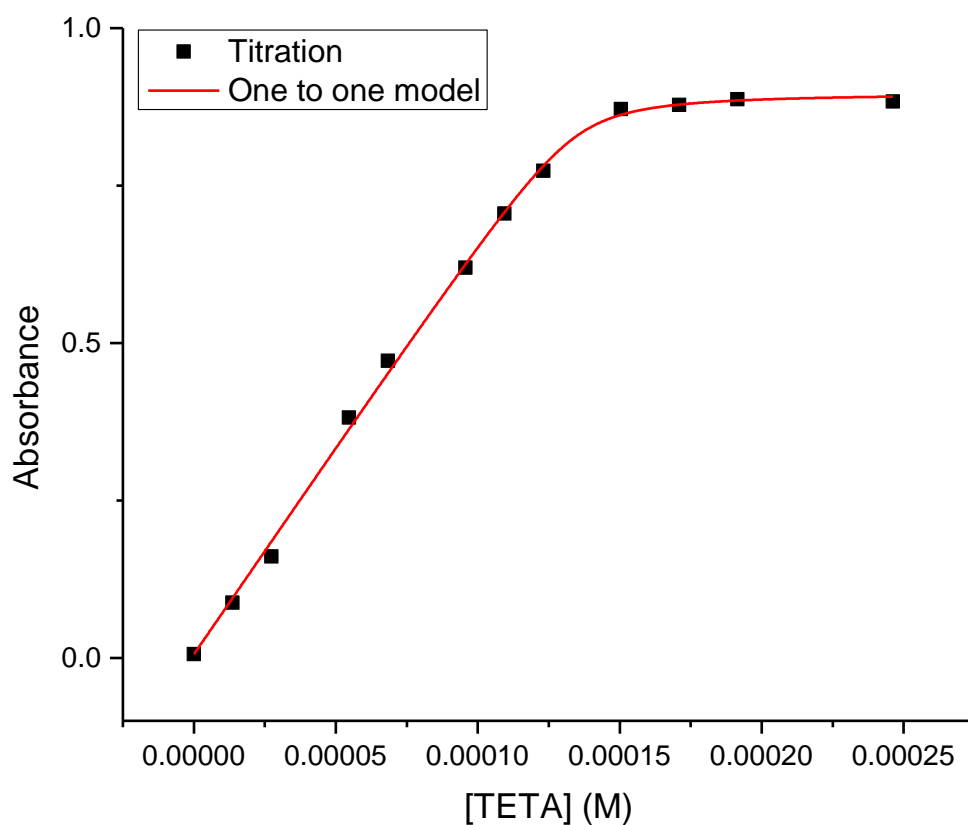


Figure 17: Binding isotherm of the complex formation of **TETA – Pb(II)** in water.

## **B. Characterization of modified PVC membrane**

To achieve an efficient large-scale water treatment technology for the recovery of lead(II) metal ions, nanocomposite membranes have been considered for exhibiting high and unique performance for water purification. [32] Thus, the suspension of TETA ligand on an electrospun PVC membrane was implemented, by which chlorine atoms of the polyvinyl chloride (PVC) were subjected to a nucleophilic attack by the amino group present on the organic ligand. This chemical reaction was completed under ambient conditions based on increasing concentrations of TETA to PVC membrane (PVC (mg): TETA ( $\mu\text{L}$ )) 1:1, 1:2, 1:3) in an ethanol solution. Adsorption experiments indicated that the a ratio of 1:3 resulted the highest removal efficiency for lead(II) ions in water. It is noteworthy that a 1:5 PVC to TETA ratio was further tested and the results showed a lower removal efficiency compared to 1:3 ratio.

The modification of the membrane with TETA was characterized in the solid state to validate the modification process of the membrane. Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis were performed to confirm the modification of the PVC membrane with TETA ligand and to characterize the thermal stability of the membrane. The fiber distribution and morphology of the membrane were analyzed using scanning electron microscope (SEM). All samples were coated with a 20 nm layer of platinum before SEM imaging. EDX analysis was also performed to detect the nitrogen on the surface of the membrane. Moreover, the pore size, thickness, and contact angle were measured to characterize the membranes. The contact angle was measured across the membrane at room temperature to determine the hydrophilicity of the membrane before and after modification.



### ***1. Structural characterization and thermal properties***

Functionalization of **PVC** membrane with **TETA** was confirmed using FTIR, where the appearance of N-H functional groups on the surface of the modified **PVC** membrane is expected. As shown in Figure 18, new bands at 1500–1750  $\text{cm}^{-1}$  and 3250–3500  $\text{cm}^{-1}$  corresponding to primary and secondary amines stretching vibrations, respectively, were detected after modification of the membrane. <sup>[60, 61]</sup>

Thermogravimetric measurements of **PVC** and **TETA - PVC** nanofibers were also performed and presented in Figure 19. The fibers of the nonfunctionalized membrane decompose in the range of 220 - 240°C. Many studies examined the thermal stability of electrospun **PVC** membranes and our observations are consistent with other examples in the literature.<sup>[67]</sup> The addition of **TETA** ligand resulted in lowering the thermal stability of the membrane fibers, where the thermal decomposition starts at a 180°C. The resulted change is due to the substitution of chlorine atoms by an amine group.<sup>[68]</sup> These analyses significantly confirm the successful modification of the **PVC** membrane with **TETA** ligand.

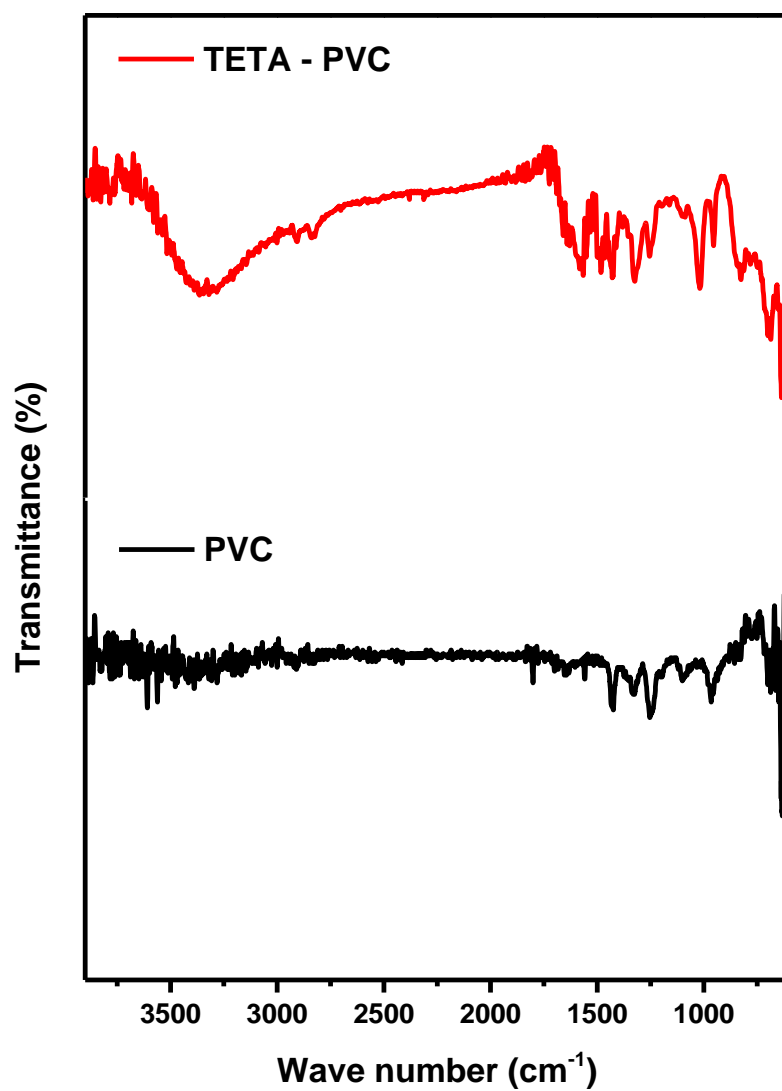


Figure 18: FT-IR spectra of **PVC** and **TETA - PVC** membranes

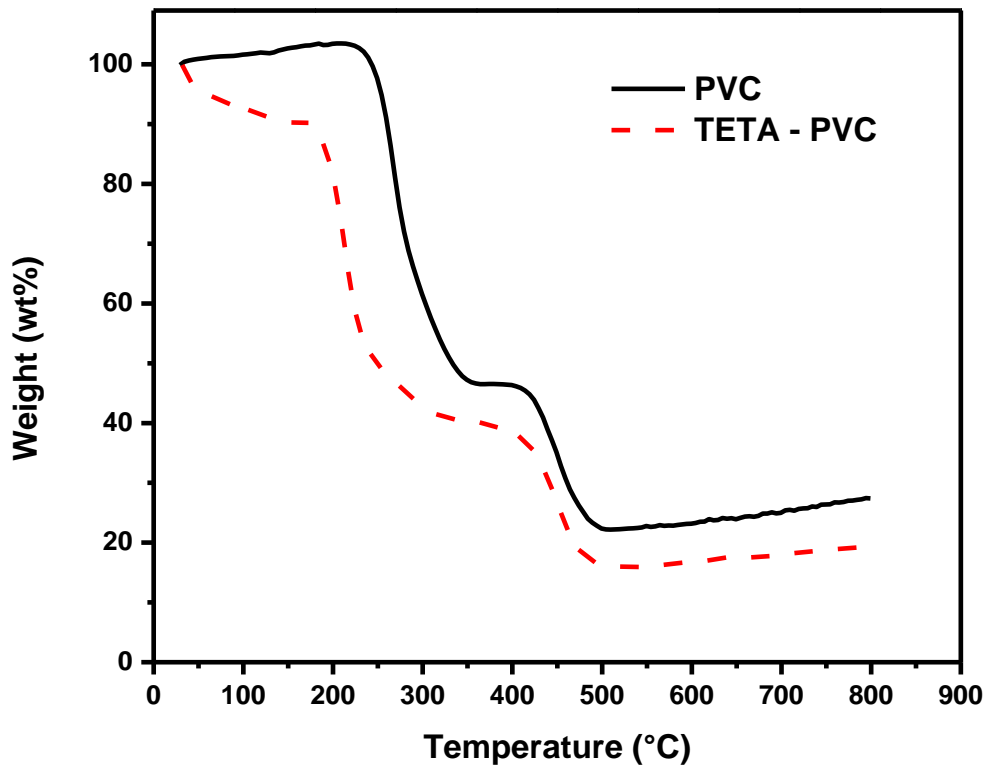


Figure 19: TGA measurements for **PVC** and **TETA - PVC** membranes

## 2. Microscopic analysis; SEM and EDX

The electrospun membranes were analyzed using scanning electron microscope (SEM) and energy dispersive x-ray (EDX). It was observed that the fibers' morphology has changed after immersing the membrane in the three different **TETA** solutions. A comparison between the unmodified and the three modified membranes, with increasing **TETA** incorporation, is demonstrated in Figure 20.

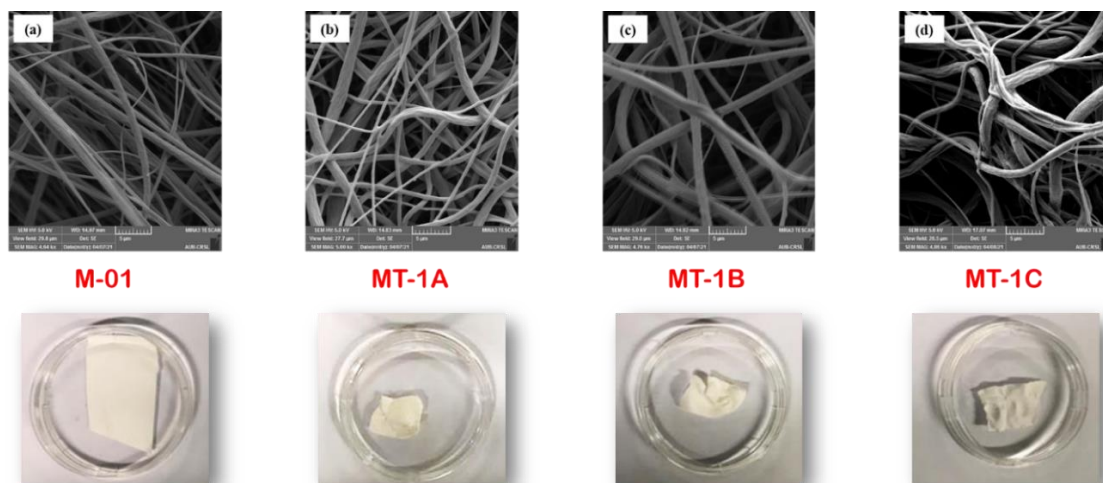


Figure 20: The SEM images (1  $\mu\text{m}$  magnification) of electrospun **PVC** fibers obtained from different **PVC** (g): **TETA** (ml) ratios (a) non-modified **PVC** membrane; (b) 1:1, (c) 1:2, and (d) 1:3 ratios.

Fibers of the **PVC** membrane were observed to be uniformly distributed with almost identical thickness as indicated by the SEM image (Figure 21a). After modification, the spacing between the fibers was reduced as well as the entanglement of the fibers was intensified as shown in Figures 21b-d. Moreover, the presence of nitrogen, from the amine groups of the ligand, was detected on the membrane's surface, by EDX spectra (Figure 21f). The latter is a convenient validation of the modification of the membrane.

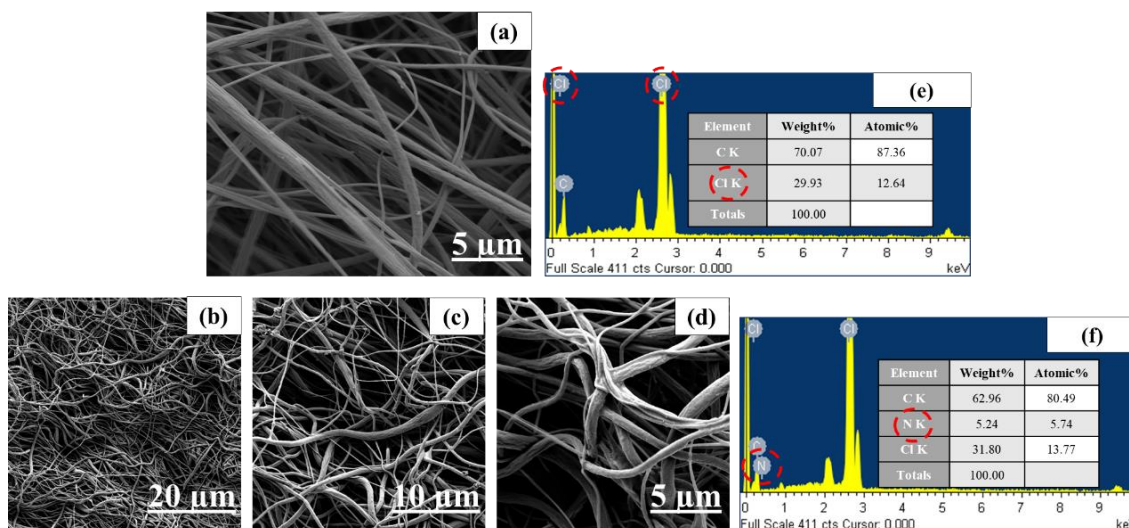


Figure 21: SEM images of polyvinyl chloride (**PVC**) and modified **PVC** nanofiber membranes with different magnifications: unmodified **PVC** (a) 5  $\mu\text{m}$ , modified **PVC** with **TETA** (1:3 ratio): (b) 20  $\mu\text{m}$ ; (c) 10  $\mu\text{m}$ ; (d) 5  $\mu\text{m}$ . EDX analysis of: (e) **PVC** membrane; (f) **TETA - PVC** membrane

### 3. Pore size, membrane thickness, and water contact angle measurements

The microstructure of the unmodified and modified membranes was investigated by analysing the pore diameter of each membrane according to the histogram in Figure 22. The average pore diameter of the pure **PVC** adsorbent was found to be 3.575  $\mu\text{m}$ , which was slightly higher than the mean pore diameter of the functionalized membrane. **TETA – PVC** membrane exhibited a mean pore diameter of 3.201  $\mu\text{m}$ , this decrease in the pore size could lead to a higher solute retention, hence, higher adsorption capacity;<sup>[69]</sup> however, the size distribution broadened slightly in the modified membrane, as shown in Figure 22. It has been reported in previous studies that the thicker an electrospun nanofibrous membrane is, the smaller the pore size.<sup>[70]</sup> This was confirmed in our results where the thickness of the modified membrane was measured to be greater than the unmodified one (144 nm  $\text{TETA-PVC}$  > 105 nm **PVC**) (Table 3).

Table 3: Surface parameters—thickness and pore size distribution

Membrane	Mean flow pore diameter ( $\mu\text{m}$ )	Average thickness (nm)
PVC	3.575	105 $\pm$ 11
TETA - PVC	3.201	144 $\pm$ 24

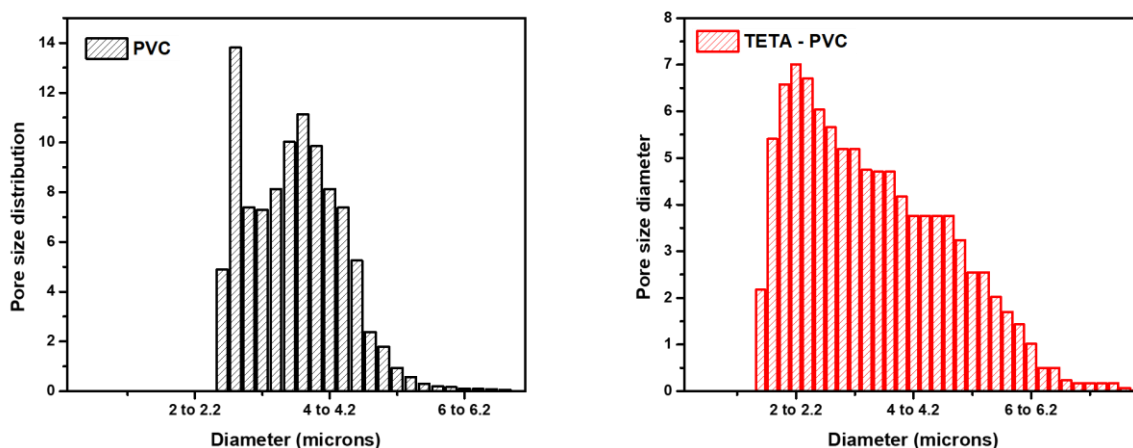


Figure 22: Pore size distribution of **PVC** and **TETA - PVC** membranes

In order to investigate the effect of membrane functionalization on the hydrophilicity of the membrane, the water contact angle was measured for the **PVC** and **TETA - PVC** membranes. As per the literature, pure **PVC** membrane is relatively hydrophobic;<sup>[59]</sup> however, upon introducing **TETA** linker to its surface, the wettability is expected to increase due to the presence of polar amine groups in the organic ligand.<sup>[71]</sup> This was verified by water contact angle measurements by which it decreased from 135° for the unmodified **PVC** membrane to ~80.9° for **TETA - PVC** membrane (Figure 23). The addition of **TETA**, a water-soluble precursor,<sup>[55,72]</sup> to the surface of the **PVC** fibers decreased the contact angle to less than 90°. The improvement of surface hydrophilicity reduces the repulsive forces between the surface and adsorbate in

solution;<sup>[73]</sup> thus, enhancing the adsorption capacity for the removal of **Pb(II)** ions from water.

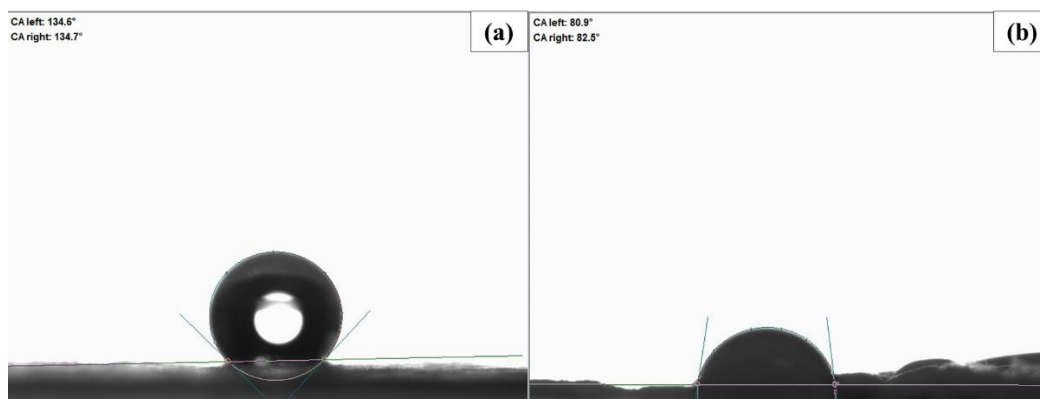


Figure 23: Water contact angle values of (a) **PVC** fibers and (b) modified **PVC** fibers with **TETA** (1:3)

### C. Removal efficiency of lead(II) ions from water

**PVC** and **TETA - PVC** electrospun membranes were tested for the removal of lead from water at ambient conditions (neutral pH and room temperature). Atomic absorption spectroscopy (AAS) was used to monitor the change in the concentration of **Pb(II)** ions in water before and after treatment with both membranes. A 150-ppm stock solution of lead salt (Lead(II) acetate trihydrate) in water was prepared and used for treatment. A calibration curve was generated based on prepared standard solutions of known concentrations to determine the **Pb(II)** ions concentration in the examined samples (Figure 24). Seven standards were prepared upon diluting the stock solution of concentrations 2.5, 5, 7.5, 10, 12.5, 15, and 17.5 ppm in 50 mL conical tubes. The standards were analyzed by AAS building up the calibration curve with a correlation coefficient ( $R^2$ ) of 0.9993.

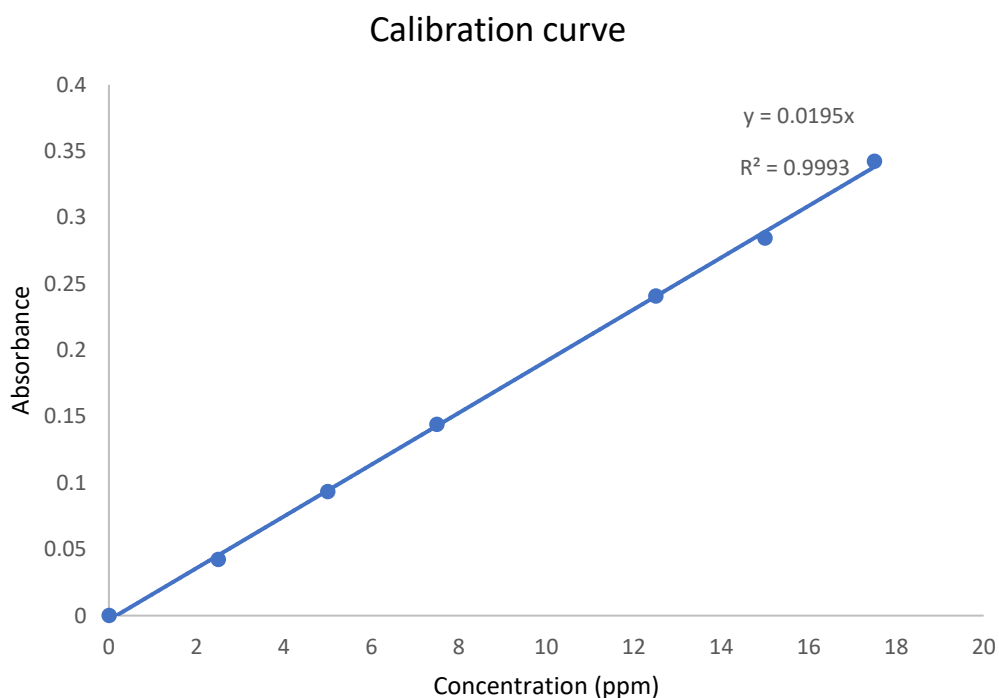


Figure 24: Calibration curve for lead standard solution

Four different **PVC** membranes were immersed in 150 ppm aqueous lead solution samples to investigate their capability if removing **Pb(II)** metal ions. Sample 1 was treated with the unmodified **PVC** membrane, sample 2 was treated with the modified **PVC** membrane with 1:1 ratio of **PVC** (g) and **TETA** (mL), sample 3 was treated with the modified **PVC** membrane with 1:2 ratio of **PVC** (g) and **TETA** (mL), and sample 4 was treated with the modified **PVC** membrane with 1:3 ratio of **PVC** (g) and **TETA** (mL). The samples were subjected to the same conditions, where they were left in the shaker at a speed of 100 rpm and at room temperature. Aliquots were taken from the four samples after being in contact with the **Pb(II)** solution for 0.5, 1, 2, and 24 hours, diluted and then analyzed with AAS. The percentage removal was calculated according to the following equation:

$$\text{Removal (\%)} = \frac{(C_i - C_e)}{C_i} \times 100 \quad (2)$$



Where:  $C_i$  is the initial concentration (mg/L) of metal ions in solution and  $C_e$  is the equilibrium concentration (mg/L) of metal ions in solution.

Unmodified **PVC** membrane and the three different **TETA - PVC** membranes were examined based on increasing **PVC: TETA** ratio and the results are presented in Table 4. The results showed that the modified membranes of ratio 1:1, 1:2, and 1:3 remove lead at a contact time of 30 minutes (31.71%, 73.26%, 88.61% in 150 mg/L Pb concentration, respectively) compared to the unmodified membrane (6.76% in 150 mg/L Pb concentration). This is due to the incorporation of **TETA** ligand into the fibers of the membrane which interacts with lead in solution.

Table 4: Percentage removal of [Pb(II)]=150 mg/L from water at room temperature within 24 hrs, using **PVC** (M-01), **TETA - PVC** 1:1 (MT-1a), **TETA - PVC** 1:2 (MT-1b), **TETA - PVC** 1:3 (MT-1c) membranes

Membrane	PVC (g): TETA (ml)	% Removal of Pb(II) at different time(hr)			
		0.5 hr	1 hr	2 hr	24 hr
<b>M-01</b>	1:0	6.76	18.41	23.70	43.49
<b>MT-1a</b>	1:1	31.71	33.35	36.39	48.73
<b>MT-1b</b>	1:2	73.26	77.26	80.17	81.68
<b>MT-1c</b>	1:3	88.61	89.63	87.90	81.80

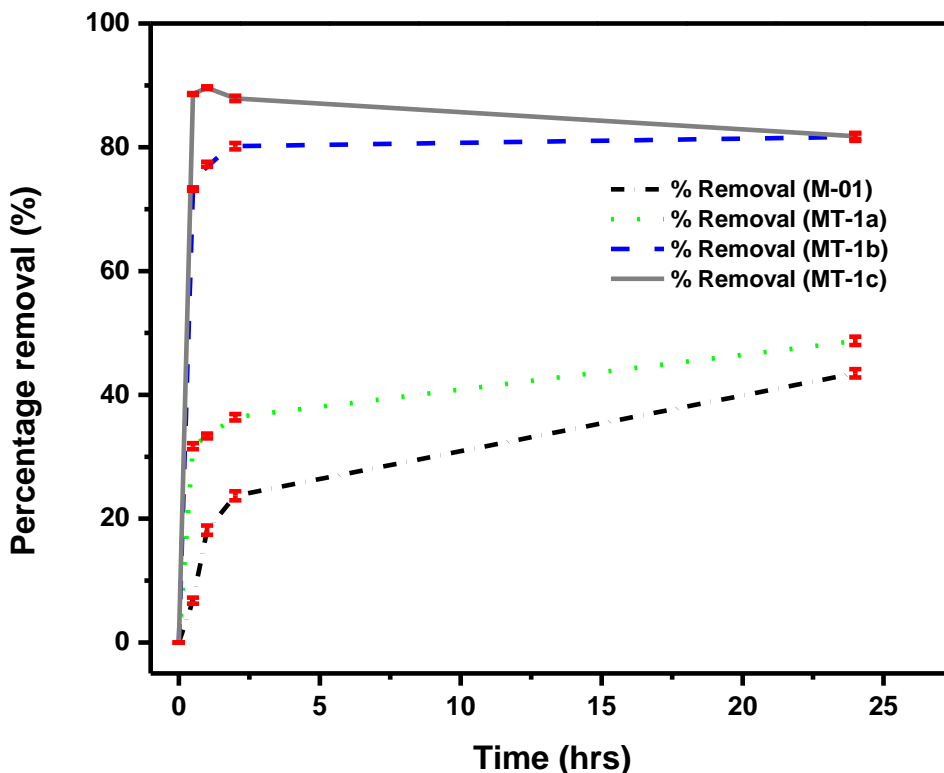


Figure 25: Percentage removal of  $[\text{Pb(II)}]=150 \text{ mg/L}$  from water at room temperature within 24 hrs, using **PVC** (M-01), **TETA - PVC 1:1** (MT-1a), **TETA - PVC 1:2** (MT-1b), **TETA - PVC 1:3** (MT-1c) membranes

Obtained results confirmed the importance of modifying the membrane with **TETA** as the removal of lead was proportional to the degree of membrane functionalization of the membrane. **TETA - PVC** membrane of ratio 1:3 showed the highest percentage removal of **Pb(II)** ions from water, indicating that the optimum ratio of **PVC** (g) to **TETA** (mL) is 1:3. The percentage removal of lead remained almost constant within a contact time of 24 hours as shown in Figure 25. After the removal of **Pb(II)**, membranes were washed with distilled water several times, before they were analyzed with SEM. As presented in Figure 26, the modified membranes exhibit hexagon-shaped structures on the nanofibers compared to the unmodified membrane after

treatment. This confirms the formation of a metal-organic complex between lead(II) and **TETA**. In order to validate our results, the experiment was repeated again with a newly fabricated membrane and the results were reproducible. Moreover, EDX analysis validated the presence of nitrogen and lead elements after adsorption. Accordingly, the adsorption behavior of the 1:3 PVC to TETA membrane was studied.

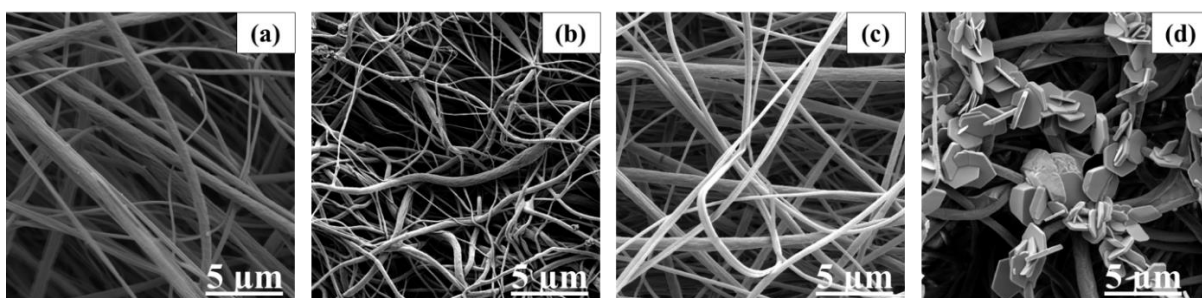


Figure 26: SEM images of (a): **PVC**; (b): **TETA - PVC**, (c): **PVC-Pb**, and (d): **TETA - PVC - Pb** membrane

#### D. Adsorption Kinetics

The kinetic mechanism controlling the adsorption process of lead(II) by **TETA - PVC** was investigated. Kinetic experiments were carried out at different contact times with **Pb(II)** aqueous solution; starting with 10 to 1440 min with initial **Pb(II)** concentrations of 150 mg/L. Other variables were set to the optimum values at room temperature and pH value of 7. Experimental data was analyzed with two kinetic models, pseudo-first order and pseudo-second order. Parameters in these kinetic models are described in Table 5. <sup>[36]</sup> The pseudo-second-order equation plot show high correlation coefficients ( $R^2=0.99$ ) and a good compliance with the proposed pseudo-second-order equation. Whereas, the correlation coefficient ( $R^2 = 0.22$ ) obtained by applying the pseudo-first-order equation to the experimental data was very low.

The basic assumption of pseudo second-order model is that the adsorption process is major in chemical adsorption. This means that the **Pb(II)** ions form a chemical bond, likely coordination bond, with the potential amine functional groups of the modified **PVC** membrane. These potential binding sites are the amines of **TETA**. [68, 69]

Table 5: The value of parameters in the kinetic models ( $K_1$ : rate constant;  $q_e$ : quantity adsorbed at equilibrium;  $R^2$ : coefficient of determination) (**Pb(II)** concentration = 150 mg/L, amount of adsorbent (**PVC-TETA** = 0.01 g, solution pH = 7, time = 10 to 1440 min, volume = 10 mL and temperature = 25°C)

Model	Parameters	[Pb(II)] mg/L
Pseudo-first order	$K_1$ ( $\text{min}^{-1}$ ) $q_e$ (cal) (mg/g) $R^2$	$8 \times 10^{-5}$ $8.302 \times 10^{-3}$ 0.2246
Pseudo-second order	$K_2$ ( $\text{min}^{-1}$ ) $q_e$ (cal) (mg/g) $R^2$	$1.02 \times 10^{-2}$ 120.48 0.9999

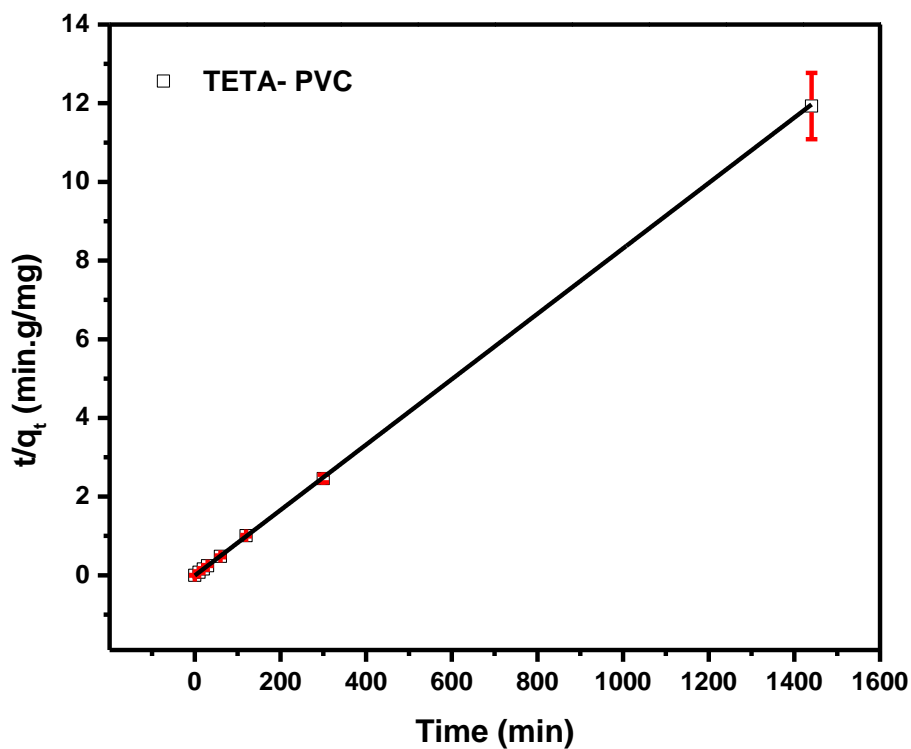


Figure 27: Pseudo-second order kinetic plot for the adsorption of ([Pb(II)] = 150 mg/L) on TETA - PVC

### E. Adsorption isotherm

Adsorption equilibrium experiments were carried out with different initial concentrations of lead(II) ions as 600, 700, 900, 1000, and 1,200 mg/L to assess the interaction between the adsorbate (Pb(II) ions) and the adsorbent (TETA - PVC). 10 mg of the TETA - PVC membrane was immersed in each of the prepared Pb(II) aqueous solutions and left in the shaker at a speed of 100 rpm at room temperature for 30 minutes. Aliquots were taken from the solutions, filtered separately through a 0.45  $\mu\text{m}$  filter syringe and analyzed by AAS. The amount of adsorbed metal ion at equilibrium,  $q_e$  (mg/g) was calculated by EQN 3 [76]:

$$q_e = \frac{(C_i - C_e)v}{w} \quad (3)$$

Where  $C_i$  and  $C_e$  (mg/L) are the initial and equilibrium concentrations of metal ion, respectively. Volume of the solution  $V$  (L), and  $W$  is the mass of TETA - PVC adsorbent used (g). The experimental data were fitted into two adsorption isotherm models, which are mathematical models that give a description about the distribution of the adsorbate and adsorbent in aqueous solution according to the heterogeneity/homogeneity of the adsorbent, coverage type and interaction between the adsorbate species. Langmuir and Freundlich isotherm models [77-79] were used to fit the results of the adsorption experiment conducted.

The Langmuir equation verifies a monolayer interaction between the adsorbate molecules on to the surface of the adsorbent. The linear form of this isotherm is represented by the expression (Langmuir 1916):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \quad (4)$$

Where  $q_e$  (mg/g) and  $C_e$  (mg/L) are the amount of adsorbed metal ions per unit weight of adsorbent and concentration of metal ions in solution at equilibrium, respectively. The constant  $K_L$  (L/g) is the Langmuir equilibrium constant related to the energy of adsorption and  $q_{max}$  is maximum adsorption capacity (mg/g). The essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless constant called separation factor ( $R_L$ , also called equilibrium parameter) which is defined by the following equation:

$$R_L = \frac{1}{1+K_L C_0} \quad (5)$$

Where  $C_0$  (mg/L) is the initial adsorbate concentration. The value of  $R_L$  indicates the shape of the isotherms to be either unfavorable ( $R_L > 1$ ), linear ( $R_L = 1$ ), favorable ( $0 < R_L < 1$ ) or irreversible ( $R_L = 0$ ).

On other hand, the Freundlich model is the most important multisite adsorption isotherm for heterogeneous surfaces and the linear form of this isotherm is expressed as (Freundlich 1906):

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad (6)$$

Where  $q_e$  is the metal uptake (mg/g) at equilibrium,  $K_F$  is the measure of the sorption capacity,  $1/n$  is the sorption intensity, and  $C_e$  is the final ion concentration in solution, or equilibrium concentration (mg/L). The Freundlich isotherm constants  $K_F$  and  $1/n$  are evaluated from the intercept and the slope, respectively of the linear plot of  $\log q_e$  versus  $\log C_e$ . The value of  $n$  reflects the type of isotherm to be favorable ( $0 < 1/n < 1$ ), irreversible ( $1/n = 0$ ) or unfavorable ( $1/n > 1$ ).<sup>[80]</sup>

The calculated parameters as well as the linear plots of both isotherm models are presented in Table 6 and Figure 28, respectively.

Table 6: Adsorption isotherm model parameters

**Langmuir and Freundlich model parameters for adsorption of Pb(II) ions on TETA - PVC**

Langmuir model		Freundlich model	
$R^2$	0.992	$R^2$	0.895
$K_L$ (L/mg)	0.409	$K_F$ (mg/g)	0.422
$R_L$	0.002-0.004	$1/n$	0.256

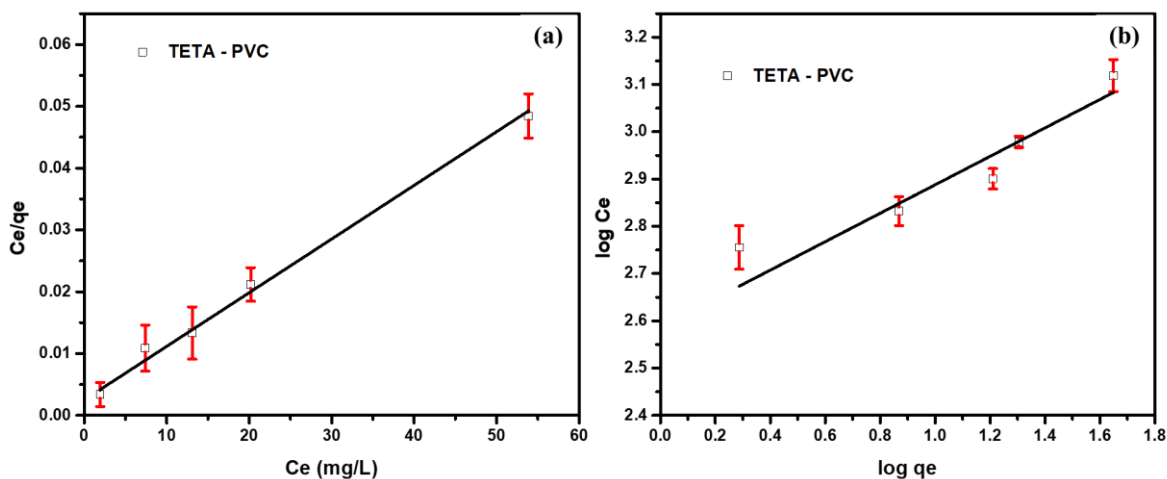


Figure 28: (a) Langmuir and (b) Freundlich isotherm plot for the adsorption of **Pb(II)** onto **TETA - PVC** membrane

Adsorption behaviour followed the Langmuir model with a correlation coefficient of  $R^2 > 0.99$ , whereas the Freundlich model showed a lower correlation factor  $R^2$  of 0.89.

This indicates that the sorption of **Pb(II)** ions on the **TETA - PVC** membrane is a monolayer chemical sorption process.<sup>[81]</sup> The maximum adsorption capacity ( $q_{\max}$ ) and Langmuir constant ( $K_L$ ) were determined from the slope and intercept of the linear plot of  $C_e/q_e$  to  $C_e$  (Figure 28a), and were found to be 1250 mg/L and 0.409 L/mg, respectively. **TETA - PVC** membrane has a higher uptake capacity to **Pb(II)** relative to other recently reported adsorbents in the literature (refer to Table 2). Additionally, the separation factor ( $R_L$ ) was calculated (EQN 5) to be between 0 and 1, hence the adsorption mechanism of lead ions into the **PVC** membrane is favorable (Table 6).<sup>[82]</sup> However, it can be noted that the correlation coefficient of Freundlich is relatively acceptable showing that the adsorption process could be described by both Langmuir and Freundlich models. This elucidates that a chemical interaction between the surface of the membrane and the metal could have occurred.<sup>[83]</sup>

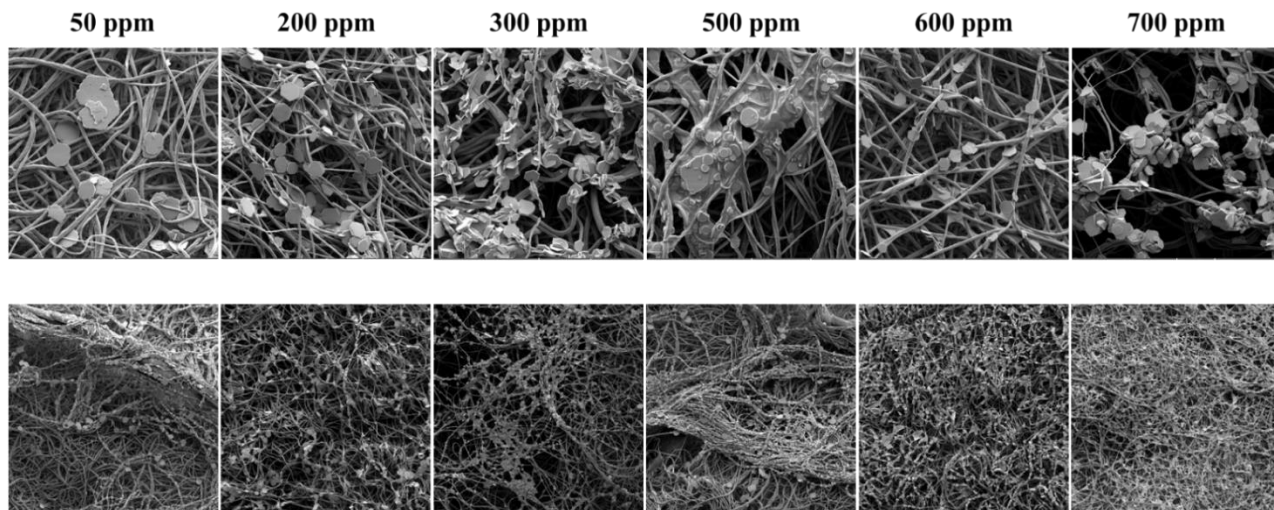


Figure 29: SEM images of **TETA - PVC** membrane used to treat different concentrations of lead(II) solution

#### **F. Characterization of TETA - PVC after removal of lead(II) ions from water**

The formation of hexagon-shaped structures on the surface of the **TETA - PVC** membrane when used to treat contaminated water with lead were observed in SEM



images (Figure 30). The images were compared to the unmodified membrane which did not form any structures within the fibers of the membrane (Figure 30). This could confirm that lead(II) ions have complexed with **TETA** incorporated on the nanofibers forming three dimensional structures resulting in purified water. Moreover, EDX spectrum illustrated that the peaks are attributed to lead on the newly formed shapes, supporting the adsorption of **Pb(II)** onto the modified membrane through the formation of a complex with the ligand (Figure 31). Thermogravimetric analysis was performed on the membrane after adsorption. As presented in Figure 32, the fibers of the membrane used for treatment decompose at a higher temperature compared to the modified membrane before treatment. This indicates that the presence of the **TETA - Pb(II)** complex enhances the strength and stability of the membrane.

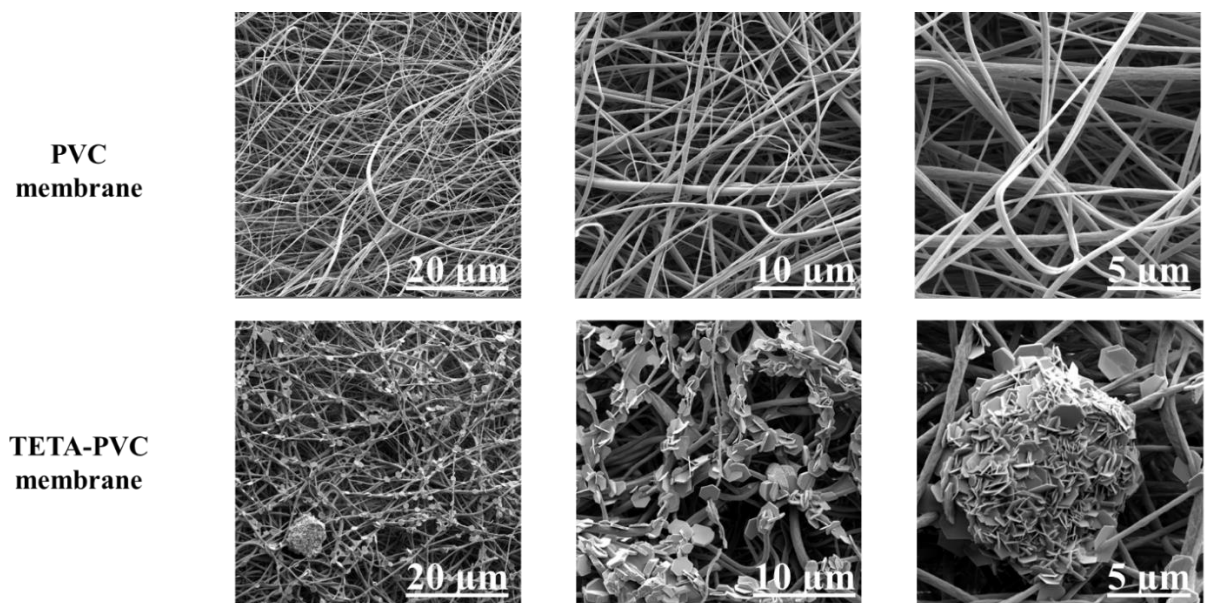


Figure 30: SEM images of **PVC** and **TETA - PVC** membranes after adsorption

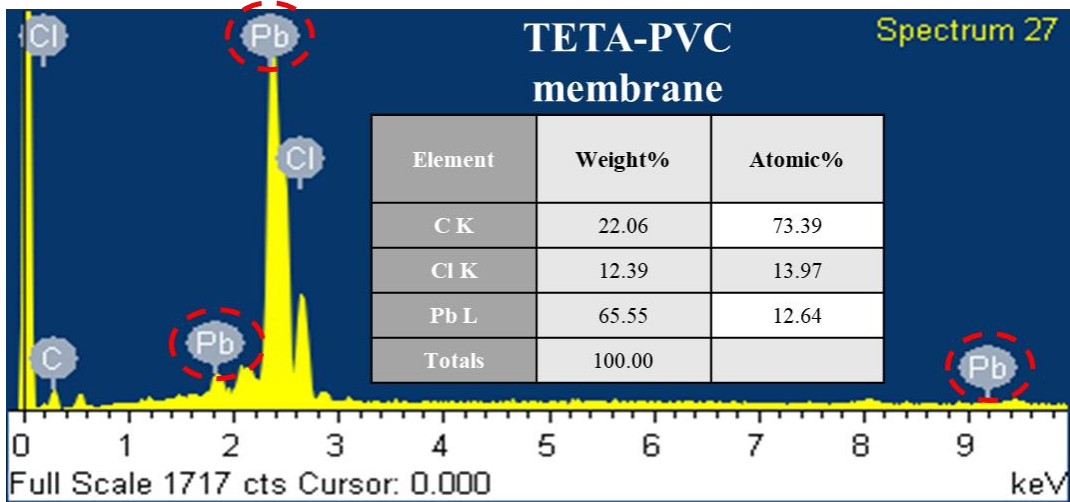


Figure 31: EDX analysis of **TETA - PVC** membrane after adsorption

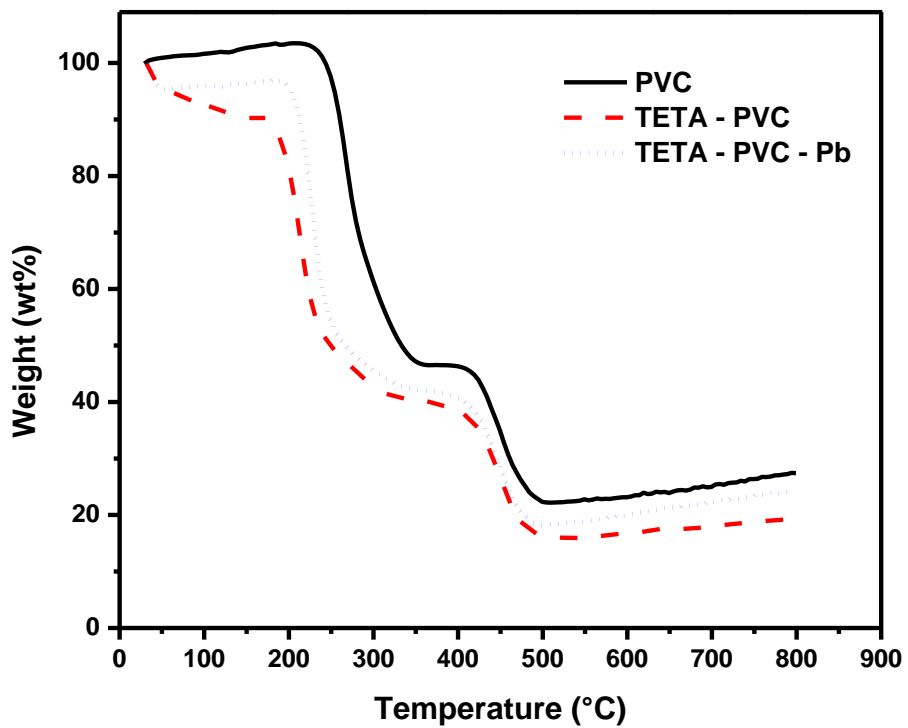


Figure 32: TGA measurements for **PVC**, **TETA - PVC**, and **TETA - PVC - Pb**

### G. Effect of competing metal ions

The synthesized membrane showed promising results for **Pb(II)** ions adsorption from water; however, industrial wastewater includes different metal cations that could affect the uptake of lead by the **TETA - PVC** membrane.<sup>[84]</sup> Therefore, it is of crucial to study the effect of co-existing cations in solution on the removal efficiency of the membrane. In order to evaluate the selectivity of **PVC** and **TETA - PVC** membranes, **Hg(II)** and **Cd(II)** were selected as competing metal ions in the adsorptive removal of **Pb(II)** in water. The experiment was conducted through immersing **TETA - PVC** membrane in a solution containing equal concentration (150 mg/L) of **Hg(II)**, **Cd(II)**, and **Pb(II)** ions. The study was left at ambient conditions for 30 minutes. The interference effect of the foreign ions on the removal efficiency was investigated compared to the single component solution. The effect of **Hg(II)** and **Cd(II)** on **Pb(II)** removal efficiency by **PVC** and **TETA - PVC** membranes is illustrated in Figure 33.

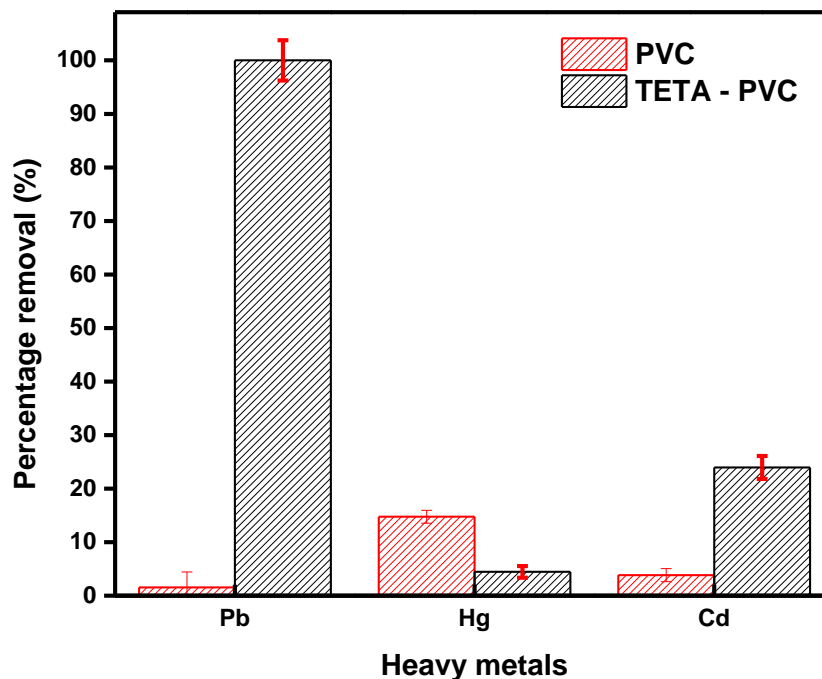


Figure 33: Removal efficiency of 10 mg of **PVC** and **TETA - PVC** membranes in a tertiary system of **Pb(II)**, **Hg(II)**, and **Cd(II)** ( $[M] = 150 \text{ mg/L}$  each)

As can be observed, in the tertiary solution of metal ions, the removal capacity of the unmodified nanofiber membrane towards all three metals is relatively low (less than 20%), with the highest removal capacity towards **Hg(II)** ions (16.5%). Whereas in the presence of the three different cations, the removal of lead(II) by **TETA - PVC** membrane was enhanced relative to the removal of lead in a mono-ionic system. The selectivity of metal ions for **PVC** membrane was in the order of **Hg(II) > Cd(II) > Pb(II)**, as for the **TETA - PVC** membrane was in the order of **Pb(II) > Cd(II) > Hg(II)**. This confirms the strong chelating ability of lead to organic linker on the membrane's surface. It could be attributed to the fact that lead has a smaller hydrated radius (0.401 nm) relative to the other metals (0.422 nm for **Hg(II)** and 0.426 nm for **Cd(II)**). A smaller hydrated radius compared to cations with same charge has a greater electrostatic

interaction between the metal and adsorbent; hence, it will be more effectively sequestered from solution.<sup>[78, 79]</sup> Moreover, electronegativity of heavy metals affects the selectivity adsorption behavior of the adsorbent. Studies showed that heavy metal cations with high electronegativity can easily replace cations with lower electronegativity.<sup>[85]</sup> As such, results show that **Pb(II)** is adsorbed by the functional group on the electrospun membrane by replacing Cd(II) and Hg(II), due to its high electronegativity compared to both cations. Thus, the **TETA - PVC** membrane showed high selectivity towards **Pb(II)** ions.

#### **H. Regeneration**

The reproducibility and reusability of the modified membrane was assessed to reflect on the sustainability of the developed adsorbent. As such, six successive adsorption-desorption cycles were performed at the initial metal ion concentration of 700 mg/L. At the end of each adsorption experiment, the saturated membrane was regenerated in an acidic medium, using 0.1 M *p*-toluene sulfonic acid (pH=5.5), where the acidic media is expected to weaken the coordination bond between **TETA - PVC** and **Pb(II)** ions.<sup>[87]</sup> The obtained results revealed that the amine functional group of the adsorbent (i.e.  $-\text{NH}_2$ ) in the acidic medium became protonated and the adsorbed metal ions on these groups were replaced by  $\text{H}^+$  ions releasing **Pb(II)** in solution.<sup>[81, 82]</sup> The performance of the regenerated **TETA - PVC** nanofiber membrane in each cycle is presented in Figure 34.

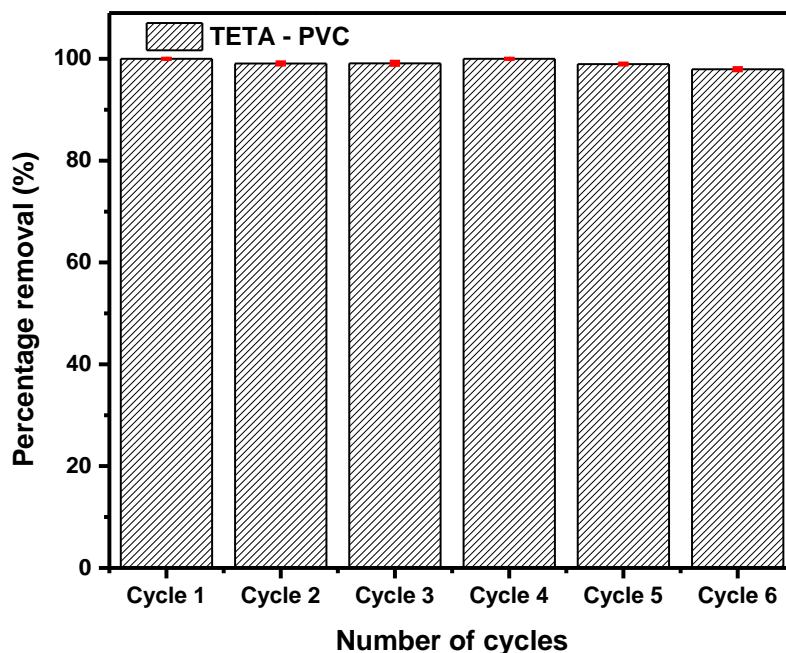


Figure 34: Reusability of **TETA - PVC** for the adsorbed amount of **Pb(II)** ( $[\text{Pb(II)}]=700$  ppm)

The removal efficiency of **Pb(II)** by **TETA - PVC** membrane remained almost constant at around 100% up to 4 cycles. Past the 4<sup>th</sup> cycle, a slight decrease (2%) was observed at a contact time of 30 minutes. SEM images of the **TETA - PVC** adsorbent show that after desorption of **Pb(II)** the hexagon-shaped structures, of the metal-organic complex, disappeared from the surface of the nanofibers of the membrane (Figure 35). Additionally, lead was not detected by EDX (Figure 36).

After six cycles, the membrane maintained a 98% removal efficiency revealing its great potential as a reusable environmentally friendly adsorbent. It is important to note that the above experiment was performed on a wet membrane; however, it was also tested on a membrane that was dried after each cycle and the results obtained were the same for both membranes (wet and dry ones).

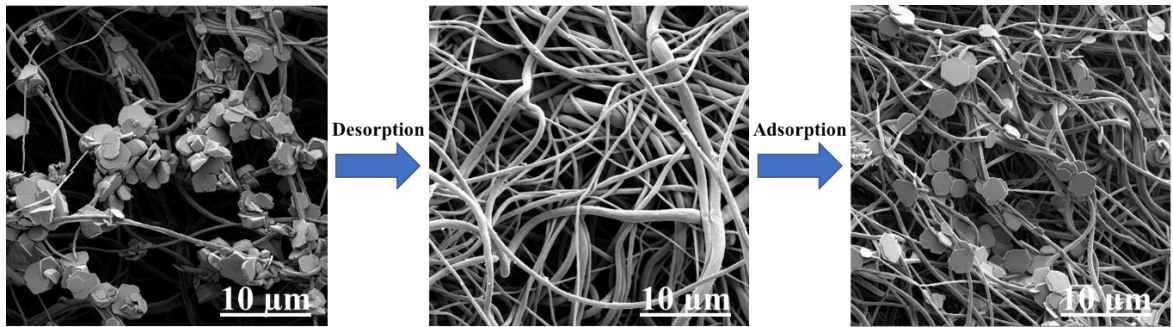


Figure 35: SEM images of the **TETA - PVC** before and after the adsorption of **[Pb(II)] = 700 mg/L** , and after the regeneration

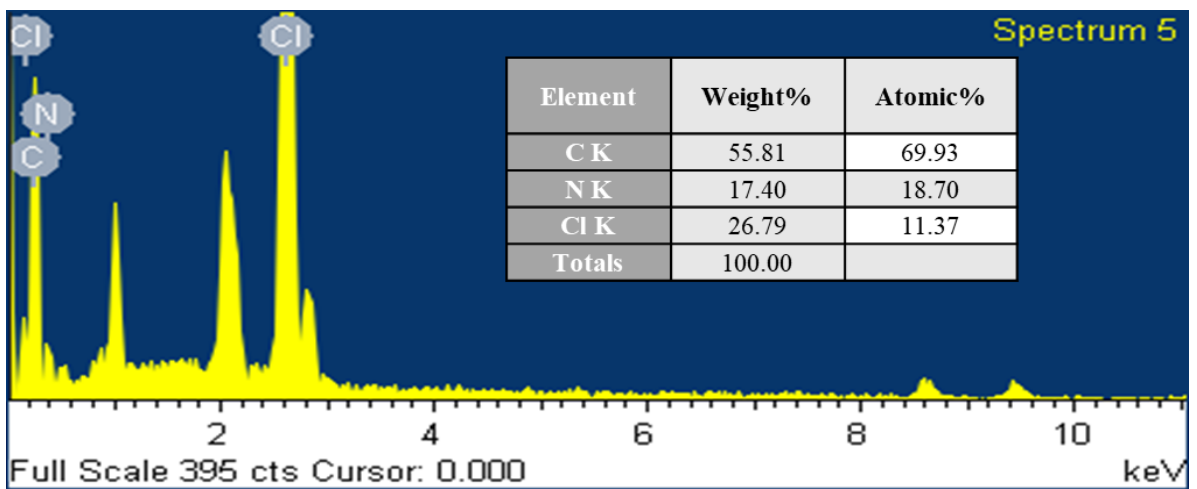


Figure 36: EDX analysis of **TETA - PVC** membrane after desorption

## CHAPTER V

### CONCLUSION AND RECOMMENDATION

Various water treatment technologies have emerged for the removal of contaminants, such as heavy metals, from effluents. Heavy metals could be released in water bodies from different sources affecting the health of living organism. Adsorption was found to be an effective method for water treatment due to its high capacity, nontoxicity, and wide applications. Additionally, adsorbents' main advantage over other techniques is their selectivity property for metal ions depending on the functional group present on the surface.<sup>[90]</sup> Nanomaterials have gained great attention in the recent days as promising adsorbents with high capacity due to their high surface to mass ratio and high porosity such as nanofibers.<sup>[90]</sup>

The development of polymeric electrospun nanofibers as an adsorbent for the removal of lead metal ions in water under ambient conditions has been investigated in this study. Polyvinyl chloride (PVC) membrane was fabricated through electrospinning technique and then modified by introducing an amine functional group (TETA) onto its surface, to enhance its adsorptive capacity. Structural and chemical analyses were performed on the membranes to indicate that the grafting of TETA on PVC membrane has been successfully accomplished. A comparison between the unmodified and modified membrane with TETA was studied and results showed that lead recovery was enhanced from 30% to 99% in 30 minutes. The effect of contact time, initial concentration of the metal ion, and presence of different ions in solution on the adsorption properties of the membranes was reported. The results showed that adsorption followed the Langmuir isotherm model with a maximum adsorption capacity



of 1250 mg/L as well as pseudo second order kinetic model. TETA – PVC membrane also showed high selectivity to Pb(II) in a tertiary system including Hg(II) and Cd(II) ions. Moreover, the performance of the membrane persisted even after six cycles maintaining a high removal efficiency.

In conclusion, the presented work offers several advancements in nanotechnology for the effective removal of heavy metals from water. Surface modification of the membrane offered a robust method to overcome low removal efficiency problem. It is suggested to test its efficiency at a larger scale industrial wastewater. For future work, the incorporation of other functional groups (thiol, carboxyl ...) into the PVC electrospun membrane should be investigated and test its removal efficiency of lead(II) in water. Moreover, increasing the pool of competing metal cations such as copper, nickel, iron, and zinc should be examined. Additionally, the effect of pH on the removal capacity of the designed membrane must be studied upon the addition of salts in water to simulate the real situation. Further work should also investigate and address the economic aspects so that their potentials for commercial scale can be realized.

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