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Electrospinning of Polymeric Solutions Using *Opuntia ficus-indica* Mucilage and Iron Oxide for Nanofiber Membranes for Treating Arsenic Contaminated Water

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Electrospinning of Polymeric Solutions Using *Opuntia ficus-indic*a Mucilage and Iron Oxide for Nanofiber Membranes for Treating Arsenic Contaminated Water

by

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A thesis submitted in partial fulfilment
of the requirements for the degree of
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Atomic fluorescence spectrometry, Life cycle analysis

DEDICATION

This thesis is dedicated to my family and friends who stayed with me in all my endeavours. It's their love and affection that has driven me through my entire work. I am blessed to have a wonderful dad who guided and supported me every time I tried to reach my goals and make me achieve my dreams.

ACKNOWLEDGMENTS

It is a genuine pleasure to express my deep gratitude and sense of thanks to my mentor and major professor Dr. Sylvia Thomas for her help throughout my research work. I may not achieve this without her guidance. I also thank my AMBIR group members who supported me and helped me for this work. I want to thank Dr. Alcantar and her research group member Fei Guo who helped me with providing lab facilities and procedures.

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ABSTRACT

Water is the essential part of every organism and it is also a vital constituent of healthy living and diet. Unfortunately water contamination over the past decade has increased dramatically leading to various diseases. As technology advances, we are detecting many pollutants at smaller levels of concentrations. Arsenic (As) is one of those major pollutants, and Arsenic poisoning is a condition caused due to excess levels of arsenic in the body. The main basis for Arsenic poisoning is from ground water which naturally contains high concentrations of arsenic. A case study from 2007 states that over 137 million people in 70 countries were affected by arsenic poisoning from drinking water [1]. This thesis work is motivated by this study and investigates the fabrication, characterization, and testing of *Opuntia ficus-indica* mucilage nanofiber membranes formed using a mucilage, polystyrene (PS) and iron oxide (Fe_2O_3) solution by an electrospinning process. Cactus mucilage is a jelly-like substance, which is extracted from the cactus pad, and is an inexpensive, biodegradable and biocompatible material. It is also an abundant material available in nature. Polystyrene is a synthetic aromatic polymer prepared from monomer styrene. Polystyrene is further dissolved using D-Limonene as a solvent. D-Limonene is a non-toxic solvent and is a citrus extract of orange peelings. In an effort to enhance adsorption capacity for the mucilage nanofiber membranes, iron oxide nanopowder is incorporated into the polymeric solution. A mucilage and polystyrene-iron oxide solution is mixed in different ratios and electrospun to obtain nanofibers. The fibers will be characterized by certain techniques such as Scanning electron microscopy (SEM), contact angle measurements,

viscosity and Fourier transform infrared spectroscopy (FTIR). The fibers obtained from mucilage and PS-Fe_2O_3 will be further tested under Atomic fluorescence spectrometry (AFS) for testing the removal of arsenic from water. Also, a life cycle analysis (LCA) is conducted to evaluate the environmental impacts of the fabrication of the membranes by using SimaPro® software.

CHAPTER 1: INTRODUCTION

1.1 Thesis Structure

The structure of my entire thesis mainly deals with characterisation and filtration ability of nanofibers obtained using cactus mucilage extracted from *Opuntia ficus indica*. First chapter of thesis is to discuss background, motivation and significance of this project. Material selection and preparation of solutions discussed in chapter 2. Chapter 3 deals with electrospinning process in which I discuss about how nanofibers are made using mucilage with co spinning polymer. Viscosity of solutions and its effect on obtaining nanofibers will be discussed in chapter 4. Contact angle measurements and hydrophobic nature of nanofiber meshes has been discussed in chapter 5. Chapter 6 elaborates complete morphology and fiber thickness, diameter of fibers. Crucial part of my thesis is discussed in chapter 7, where nanofibers ability to filter contaminants from water through atomic fluorescence spectrometry. Chapter 8 deals with Fourier transform infrared spectrometry in which chemical bonds present in solution obtained using cactus mucilage and polymers. Chapter 9 gives life cycle analysis of entire materials used, along with the process parameters in which environmental impacts will be discussed. Finally chapter 10 gives the summary and future scope of this project.

1.2 Background and Motivation

The main goal of the project is to investigate sustainable water filters which are bio degradable by nature and can be economical for all people around the world, especially in rural areas. Arsenic contamination in the world is increasing rapidly, which is affecting millions of

people causing serious health problems. For this project a naturally abundant material, Cactus mucilage, has been chosen, due to the capability of extracting the "gooey" substance from cactus pads which are readily available across the globe. Mucilage has an ability to absorb harmful chemicals present in natural water. It absorbs chemicals like arsenic, bacteria and E.coli etc. [2] There are many filters available in the market, but very few are affordable, fabricated with a sustainable natural material, or utilize inexpensive technology.

In review of arsenic contamination in groundwater, the contamination is found in many places across the globe including the US. Bangladesh is the major nation where arsenic contamination is a serious threat, a study shows that about 28-35 million people exposed to arsenic contamination and the concentration is about 0.05 mg/L. [1] Elimination of arsenic content from water is the goal of this research by using nanofiber membrane formed from mucilage.

There are many nanofiber meshes available in the market but most of them are not bio degradable and are made up of non-organic materials for example SONO filters [25] and also Kanchan filter [26]. Nanofiber filtration has been noted as one of the most efficient processes for water treatment in the removal of contaminated materials.

Therefore, in order to promote a globally sustainable membrane for water filtration through chemical adsorption, this work demonstrates the ability of an *Opuntia ficus-indica* mucilage nanofiber membrane to absorb arsenic from water. Furthermore, this technology is cost effective and non-toxic.

1.3 Significance of the Project

The significance of this work will contribute to several technological areas, such as 1) determining the electrospinning parameter space needed to fabricate a natural plant based

nanofiber membrane; 2) understanding the material composition impacts on fiber formation; and 3) evaluating the ability of a natural plant based membrane to adsorb contaminants from water. Through the successful fabrication of *Opuntia ficus-indica* mucilage nanofiber membranes, researchers will potentially be able to functionalize this natural plant based material for applications in air and gas filtration, tissue engineering, tissue scaffolding, cell culturing, drug delivery etc. This work is mainly focused on whether these plant based nano membranes are able to filter water more effectively than a current industrial filter.

1.4 Research Objectives

The research goals of this work are:

- To fabricate and characterize nanofibers obtained by electrospinning the Gelling extract (GE) of mucilage with a polystyrene(PS) solution which is mixed with an eco-friendly solvent, D-limonene
- To fabricate and characterize nanofibers obtained by electrospinning the GE of mucilage with PS and D-limonene with and without the reactant agent iron oxide.
- To investigate the influence of iron oxide on the nanofiber membranes ability to filter arsenic from water
- To study the environmental impact of fabricating nanofiber membranes from *Opuntia ficus-indica* mucilage.

CHAPTER 2: MATERIAL SELECTION AND PREPARATION

2.1 Cactus Mucilage

2.1.1 Cactus Mucilage Composition

Cactus mucilage [**2**] is a gooey substance secreted from cactus pads. Two types of extractions can be possible due to the presence of two different carbohydrate polymer chains in the mucilage i.e. one extract results in a gelling form containing Ca^{2+} ions and the other is a non-gelling extract. In this document, GE will be used to indicate the gelling extract and NE for non-gelling extract.

Major composition of *Opuntia ficus-indica* known as prickly pear cactus is polysaccharides. Non gelling extract is a heteropolysaccharide mainly consisting of L-arabinose, D-xylose, D-galactose and L-rhamnose and galacturonic acid [2][3].The GE which is also termed as cactus pectin. The main difference between GE and NE is a pectin. Pectins are heteropolysaccharide found primarily in terrestrial plant cell walls. It is mainly composed of a linear α-D-galacturonic acid, which acts as a support in order to neutral sugar residue. Both GE and NE are commonly composed of L-arabinose (67.3%), D-xylose (20.4%), D-galactose (6.3%), L-rhamnose (5.4%) and galacturonic acid [3,4]. Another difference between the two is that GE contains large proportions of galacturonic acid. Figure 1 shows the sugar residue structure in mucilage.

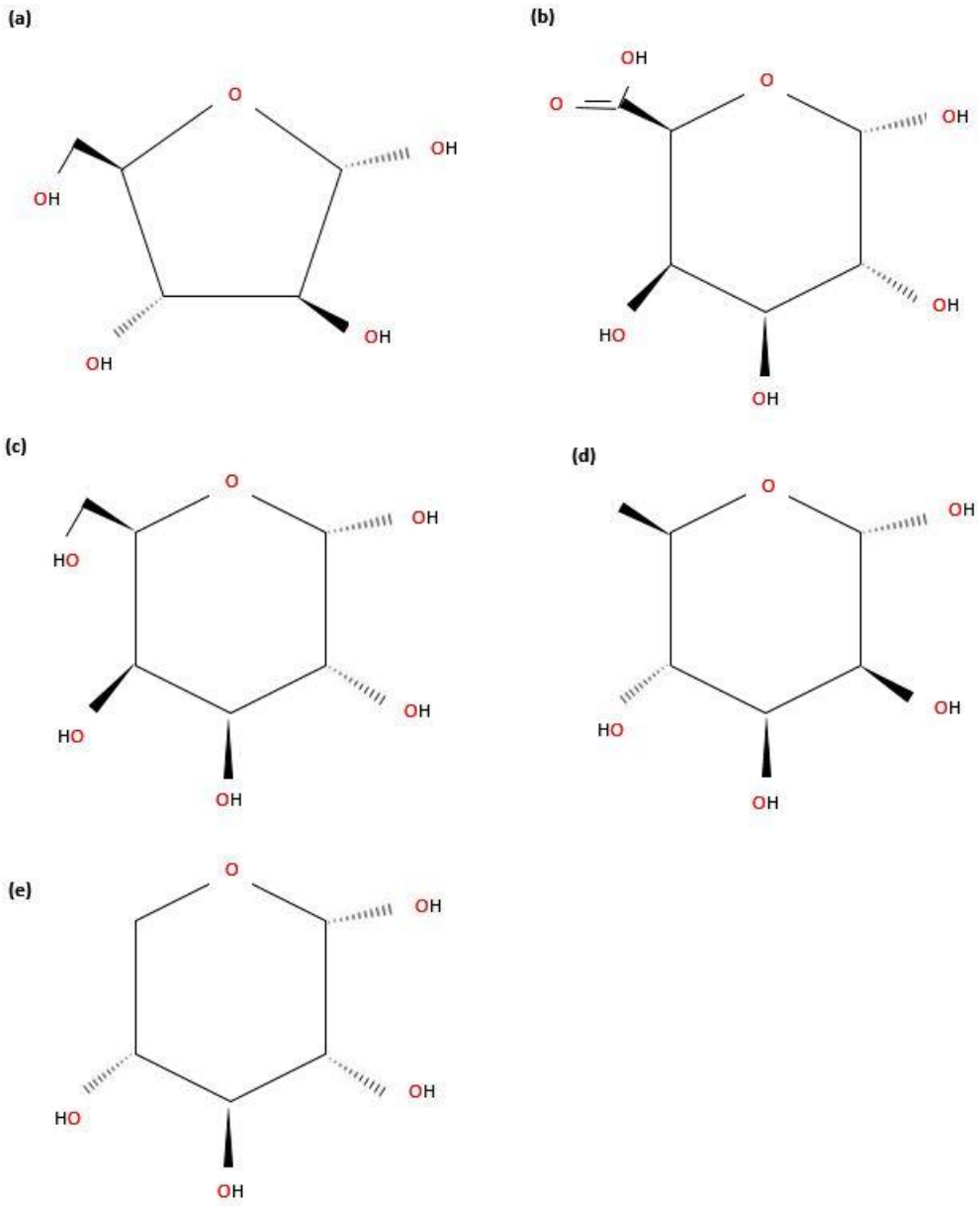


Figure 1 Schematic (a) arabinose (b) galacturonic acid (c) galactose (d) rhamnose (e) xylose

A structure [4] is proposed by for cactus mucilage mostly refer to co-extract of NE and GE. Figure 2 shows the galacturonic acid and rhamnose as backbone with branches of arabinose and xylose.

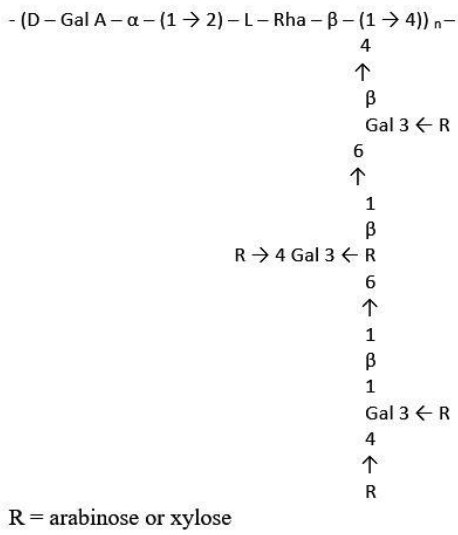


Figure 2 Chemical structure of cactus mucilage showing its composition with sugars

2.1.2 Mucilage Extraction

Mucilage extraction is a patented process by Dr. Norma Alcantar at the University of South Florida, Tampa, USA. Two types of mucilage extractions are possible; gelling extract (GE) and non-gelling extract (NE). Cactus pads should be cleaned, then thorns and brown spots on the pads will be removed. Once pads are cleaned, they are sliced into pieces and then heated at 80-85 ^{0}C in a NaCl solution (1:1 mass to vol ratio) so that enzymes in the pads go to an inactive state. The mixture is now cooled and liquidized. The mixture is separated from solid particles by centrifugation. Solid particles remaining will be used for preparation of gelling mucilage and liquid form is used for the preparation of NE mucilage. Mucilage is a gooey like substance which can retain water in any form of weather conditions. After cleaning, mucilage is added to water. Now dirt particles will settle down. Mucilage has high molecular weight in water so it swells when it come in contact to water. Mucilage is the driving material for this work, and the process of extraction is also important, as it creates a form of the mucilage that can be

functionalized into a membrane that has ability to remove arsenic contamination from water. The presence of arsenic in water for a few minutes can cause serious health issues. This project primarily investigates the electrospinning of the GE mucilage to fabricate nanofiber membranes, which are then tested for the removal of arsenic from contaminated water.

2.1.2.1 Non Gelling (NE) Extraction

In the non-gelling (NE) extraction procedure sodium chloride is added to the mucilage mixture to obtain a 1L solution containing 1M of NaCl concentration. The solution is then filtered by using a Whatman 41 filter or knitted polyester cloth filter [6] depending on the viscosity of the solution. NE will be precipitated by filters using acetone or isopropanol in supernatant to solvent ratio (2:3 ratio). Now resulting mixture will be washed by ethanol-water mixtures to remove any form of impurities. This will be dried at room temperature overnight and will be used for experimental process. In previous studies the NE extraction was used to obtain mucilage membranes with limited results for the removal of arsenic (~18% removal) [8]. This study investigates the GE extraction's potential as a material to form nanofiber membranes and to remove arsenic from water.

2.1.2.2 Gelling (GE) Extraction

The gelling extraction (GE) of mucilage is [7] formed from a solid residue of the mucilage that is mixed with 7.5 g/L $(NaPO_3)_6$ in 50 mM sodium hydroxide (NaOH) in a 1:1 mass to volume ratio. The mixture is stirred and filtered. The pH value of the resulting mixture will be lowered to 2 with hydrochloric acid (HCl) and centrifuged with the required amount of DI water. The pH is adjusted to 8 by adding 1M NaOH. The resulting solution will be filtered using 0.45 µm membrane and is used as the GE extraction in my thesis work.

2.1.3 Preparation of Cactus Mucilage Solution

Mucilage solutions are prepared based on the concentration required for various ratios of polymer to mucilage that were studied for this work. Different weight-to-weight ratios have been prepared and used for this study. Experiments were conducted using 0.5%, 1% and 2% weight-to-weight ratio combinations with distilled water. The GE mucilage in its powder form is mixed with DI water to form a gooey like substance. For example, to make a 10 ml solution with 0.5%, 1% and 2% weight-to-weight with water, GE is weighed on an analytical balance to obtain the accurate ratio. GE mucilage easily mix with water but we observe a non-homogenous mixture.

In previous experiments [8] [9] acetic acid was added to the solution to further break down the carbohydrates, as reported in the investigation of chitosan and cellulose to create fibers [8]. After a more in depth literature review, it was hypothesized that a longer mechanical process (tissue grinding) could be used to obtain a homogenous mixture versus the chemical process of adding acetic acid to the mucilage solution. Therefore, a tissue grinder is used to obtain a homogenous mixture of the solution.

Take a weighing paper and put it on the weighing balance, then close the lid of the glass door and tar it to zero. Based on our calculations and requirements, GE mucilage powder is slowly and gradually added to balance until the required weight is achieved. Once the GE is measured, the amount of water needed for a 0.5%, 1% and 2% ratio is measured in a flask and poured into a tissue grinder. Mucilage powder is then added to the tissue grinder, and pressure is applied to grind the solution until what appears to be a homogenous mixture of the solution is observed. No testing was conducted to quantify homogeniality, but once the solution appeared to be mixed completely, a jelly or gooey like substance was obtained, as seen in the figures 3,4 and 5 showing different w-w mixtures of the GE solution.

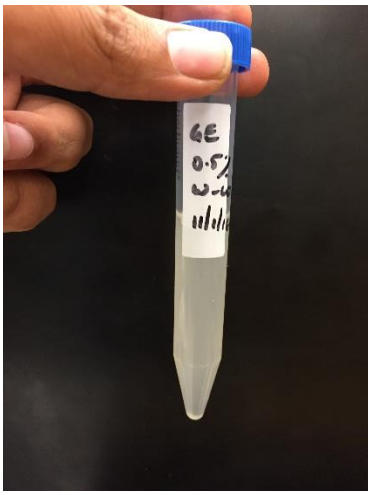


Figure 3 0.5% GE with DI

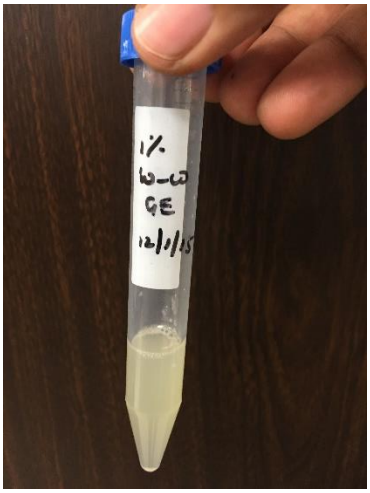


Figure 4 1% GE with DI

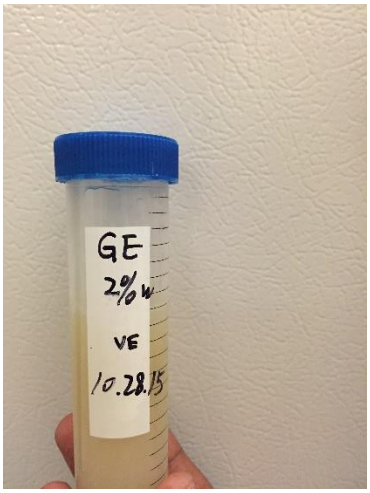


Figure 5 2% GE with DI

As can be observed from the figures 3, 4 and 5, the shades of increased cloudiness of the solution represent an increased concentration of the GE. It is later reported in Chapter 4 that the higher the concentration, the more viscous the solution. To avoid drying of the mucilage solution, it is stored in a refrigerator around 40^0 F. Prior to combining the GE with the polymeric solution for electrospinning the solution is removed and allowed to reach room temperature.

2.1.4 Calculations for Preparation of GE Mucilage Solution

Three concentrations of solutions are prepared for 0.5%, 1%, and 2% GE: DI ratio.

Consider we are preparing 0.5% GE by weight with DI water,

$$\text{GE mucilage} = 0.5/100(\text{GE mucilage} + \text{DI})$$

$$\text{GE mucilage} = 0.005(\text{GE mucilage} + \text{DI})$$

$$\text{GE mucilage} - 0.005(\text{GE mucilage}) = 0.005(\text{DI})$$

$$\text{GE mucilage}\ (1-0.005) = 0.005(\text{DI})$$

$$0.005(\text{DI}) = 0.995\ (\text{GE mucilage})$$

$$\text{GE mucilage} = 0.005 / 0.995(\text{DI})$$

$$\text{GE mucilage} = 0.005025(\text{DI})\ \text{gm}$$

Consider we are preparing 1% GE by weight with DI water,

$$\text{GE mucilage} = 1/100(\text{GE mucilage} + \text{DI})$$

$$\text{GE mucilage} = 0.01(\text{GE mucilage} + \text{DI})$$

$$\text{GE mucilage} - 0.01(\text{GE mucilage}) = 0.01(\text{DI})$$

$$\text{GE mucilage}\ (1-0.01) = 0.01(\text{DI})$$

$$0.01(\text{DI}) = 0.99\ (\text{GE mucilage})$$

$$\text{GE mucilage} = 0.01/\ 0.99\ (\text{DI})$$

$$\text{GE mucilage} = 0.010101\ (\text{DI})\ \text{gm}$$

Consider we are preparing 2% GE by weight with DI water,

$$\text{GE mucilage} = 2/100(\text{GE mucilage} + \text{DI})$$

$$\text{GE mucilage} = 0.02(\text{GE mucilage} + \text{DI})$$

$$\text{GE mucilage} - 0.02(\text{GE mucilage}) = 0.02(\text{DI})$$

$$\text{GE mucilage}\ (1-0.02) = 0.02(\text{DI})$$

$$0.02(\text{DI}) = 0.98\ (\text{GE mucilage})$$

$$\text{GE mucilage} = 0.02 / 0.98(\text{DI})$$

$$\text{GE mucilage} = 0.020408\ (\text{DI})\ \text{gm}$$

We know, weight of water as 1 gram = 1ml.

For suppose we need to prepare 10 ml of solution for 0.5% by weight GE: DI, from above equations,

$$\text{GE mucilage} = 0.005025 * 10\ \text{gm}$$

$$\text{GE mucilage} = 0.05025\ \text{gm}$$

Thus we need 0.05025 gm of GE mucilage for 10 ml of DI water to make 0.5% mucilage solution.

For suppose we need to prepare 10 ml of solution for 1% by weight GE: DI, from above equations,

$$\text{GE mucilage} = 0.010101 * 10\ \text{gm}$$

$$\text{GE mucilage} = 0.10101\ \text{gm}$$

Thus we need 0.10101 gm of GE mucilage for 10 ml of DI water to make 0.5% mucilage solution.

For suppose we need to prepare 10 ml of solution for 2% by weight GE: DI, from above equations,

GE mucilage = 0.020408 * 10 ml

GE mucilage = 0.20408 gm

Thus we need 0.20408 gm of GE mucilage for 10 ml of DI water to make 0.5% mucilage solution.

2.2 Polystyrene

Polystyrene is a monomer and a synthetic polymer, it is used as a co-spinning polymer for this work [11] [12]. Usually polystyrene is in a solid form, and typically the natural colour of a polystyrene solution is transparent. It is naturally bio-degradable and abundant in nature. The chemical formula of polystyrene is $(C_8H_8)_n$ and structure is as shown in figure 6, and it contains long chains of hydrocarbons in which carbon centers will be attached to phenyl groups, where n stands for repeating styrene monomer. Due to molecules in the polymer having long chains of hydrocarbons, a strong attractive force is present between the molecules resulting in a solid state of the polymer. In order to break the bonds between molecules and create a polymeric solution, a solvent is needed. D-limonene from sciencelab.com Inc. is used as a solvent for polystyrene. D-limonene is a citrus extract from orange peelings, is selected due to its non-toxic and environmentally friendly properties. [13] D-limonene is a hydrocarbon (structure is as shown in figure 7), is colourless, and has a citrus smell. D-limonene is an oil and is hydrophobic in nature. When the solid form of polystyrene is mixed with a D-limonene solution at a weight-to-weight ratio, D-limonene breaks the bonds between molecules in the polystyrene and a polymeric solution is formed.

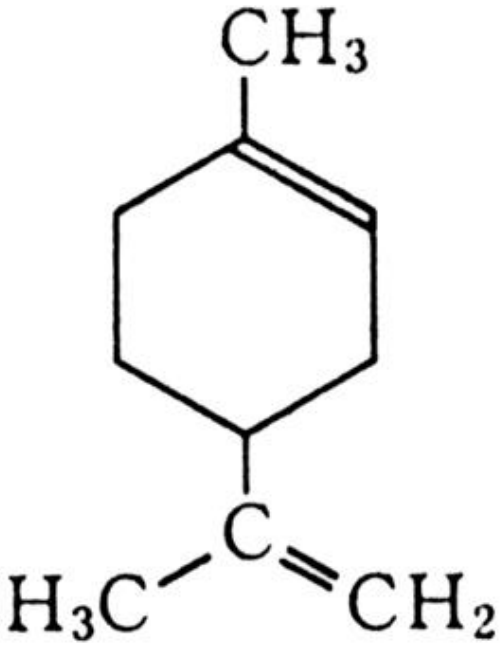


Figure 6 Structure of limonene

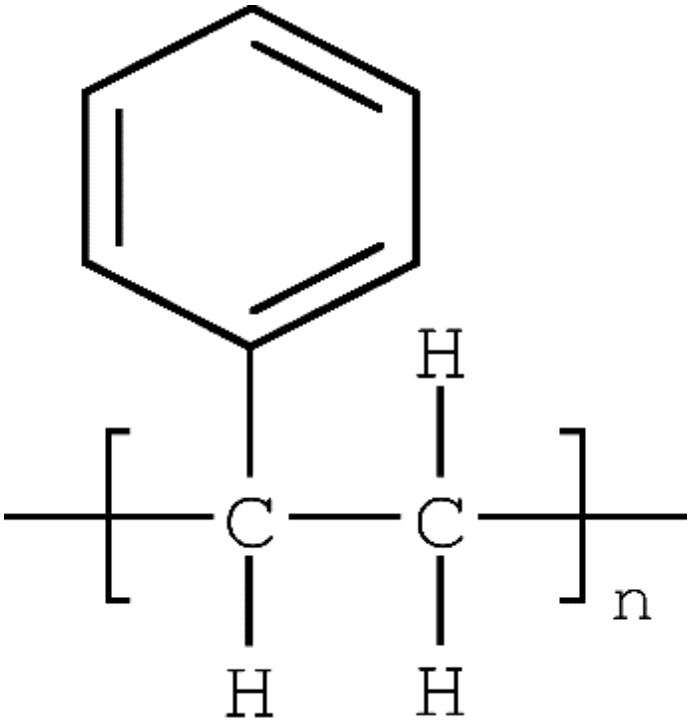


Figure 7 Structure of polystyrene

2.2.1 Preparation of Polystyrene Solution

In preparation of the polystyrene polymeric solution a 20% weight-to-weight was found to provide a homogeneous solution where the solid polystyrene had completely dissolved in the D-limonene solution. A 20% weight-to-weight ratio of polystyrene in D-limonene was used to make the solution. First clean the flask with DI water in which we want to make the solution. Now beaker is cleaned with DI water and blown dry with nitrogen. D-limonene solution in the required quantity based on calculations for 20% w-w is poured into the beaker. The required amount of polystyrene is then weighed using the analytical balance and is then placed into the D-limonene solution. The polystyrene immediately begins to dissolve in the D-limonene.

The mixture is then heated at 90^0 C for 3 hours at 900 rpm using a Corner hot/stir plate. A homogenous mixture of the solution is shown in figure 8.

Figure 8 Polystyrene solution with D-limonene at 20% by weight ratio

2.2.2 Calculations for the Polystyrene Solution

Following are calculations showing the amount of D-limonene needed for a specific amount of polystyrene. Consider polystyrene = PS and D-limonene = D.

In order to have a 20% by weight polystyrene and D-Limonene, the following is considered:

$$PS = 20/100 (PS + D)$$

$$PS = 0.2 (PS + D)$$

$$PS (1-0.2) = 0.2 * D$$

$$PS = 0.2/0.8 (D)$$

$$PS = 0.25 (D)$$

For weight percentages, the weight of D-limonene in its liquid form must be considered. Since the weight of D-limonene = 0.841 g/ml, the above formula for the amount of required PS becomes,

$$PS = 0.25 (D)$$

$$PS = 0.25 * 0.841 \text{ g/ml } (D)$$

$$PS = 0.21 \text{ g/ml} * D$$

Using these calculations, a 20% w-w solution using 20 ml of D-limonene, would call for 4.205 gm of Polystyrene to be added into the 20 ml of D-limonene solution to obtain a homogenous solution.

$$PS = 0.21 * 20$$

$$PS = 4.205 \text{ gm}$$

2.3 Polymeric Solution of Polystyrene and GE Mucilage

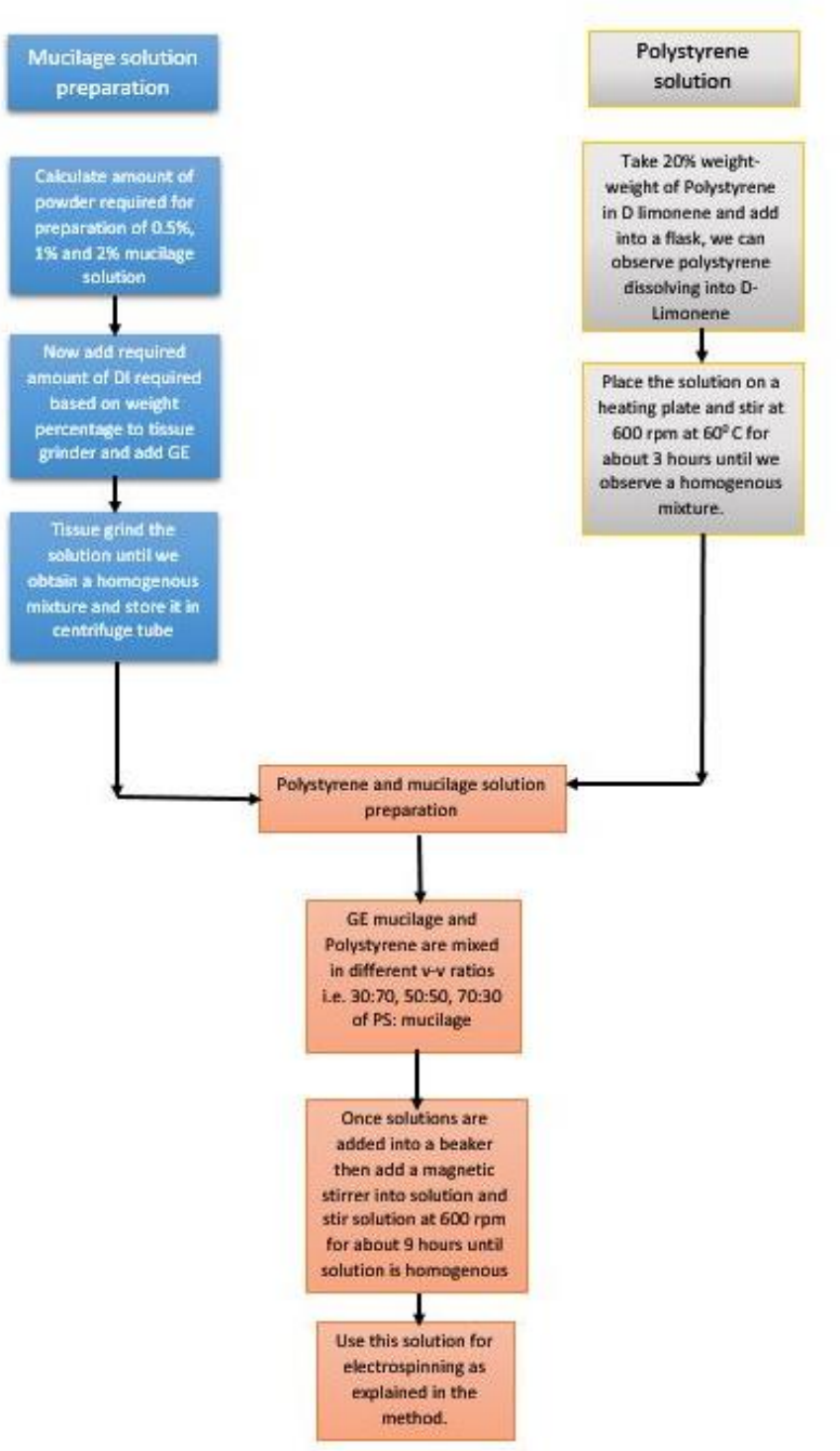


Figure 9 Polystyrene and GE mucilage solution preparation flow diagram

After preparing the individual solutions of GE mucilage and PS: D-limonene, the solutions are combined in different volume-volume ratios of GE to PS: D-limonene. In previous investigations, the ratios of 70:30, 50:50, and 30:70 of non-gelling (NE) to PS: D were found to have favourable results in the electrospinning of mucilage nanofibers. [8] These same ratios were chosen to investigate the electrospinning of GE and PS: D. After mixing solutions based on the calculations and desired ratios, the GE:PS:D solution is stirred for 9 hours at 600 rpm, resulting in a homogeneous solution to be used in the electrospinning system.

2.4 GE Mucilage and PS: D-Limonene with Iron Oxide

Iron oxide, in mineral and powder form, has been reported as having the ability to removal arsenic from water. [14] [15] Based on these results, this work incorporates iron oxide into the GE: PS: D solution in an effort to enhance the mucilage nanofiber membrane removal of arsenic from water [16].

Iron oxide (Fe_2O_3), also known as hematite, was purchased from Sigma Aldrich in a powder form. Fe_2O_3 is an inorganic compound, which is used in several applications, and has been known to act as a catalyst for solutions and boost the reactions of the materials [14]. It is a product which results due to the oxidation of iron. As per the literature review, low concentrations of hematite adsorb arsenic from water. [14] There are different forms of iron oxide which are magnetite, goethite, laterite, and hematite, each one having the ability to adsorb. Hematite has been selected because it only requires 0.5 g per 100 ml of solution for adsorption of arsenic while the other forms need 10 gm per 100 ml. [14] While I used iron oxide to spin the solution, there is continuous formation of fibers leading to get standalone membranes. Iron oxide has good property for adsorption of iron oxide which is crucial part of my thesis work. Our concentration for the experiment is we added 2.7 mg/ml. This is from trial and error

combinations. Initially I tried to electrospin solution with 4 mg/ml of iron oxide concentration but it only results to electro spraying. After several trials, I tried to electrospin solution by reducing concentration of iron oxide to 2.7 mg/ml where I was able to obtain standalone membranes.

2.4.1 Preparation of the GE Mucilage with Polystyrene and Iron Oxide

To prepare 1.5 ml of electrospinning solution containing polystyrene, mucilage and iron oxide powder. Take a beaker and wash it with distilled water. We have to prepare 70:30 volume-volume ratio of polystyrene and mucilage with iron oxide whose concentration is 2.7 mg/ml. Now after making 20% weight-weight polystyrene solution with D-limonene, add measured quantity of polystyrene into beaker. Iron oxide powder is weighed on an analytical balance. First make sure there is no dirt on the balance, then put a weighing paper and tar it to zero. Add iron oxide powder slowly such that it reaches desired quantity. Now measure amount of mucilage needed to be added to the beaker along with iron oxide powder. A magnetic stirrer should be placed in the solution and stir the solution at 600 rpm for about overnight until solution is mixed homogenously. Solution should be mixed overnight because mucilage particles inside the solution need to mixed with iron oxide which is crucial part of our work.

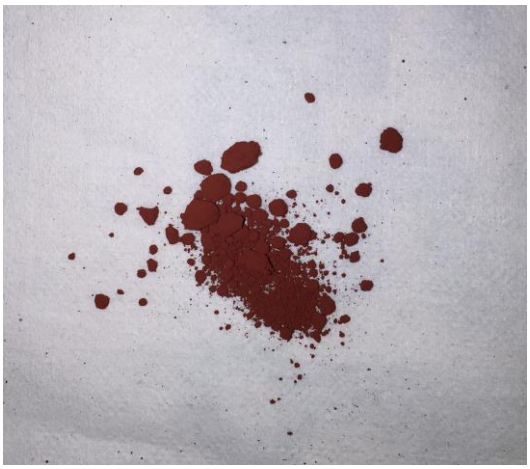


Figure 10 Iron oxide (Fe_2O_3) powder

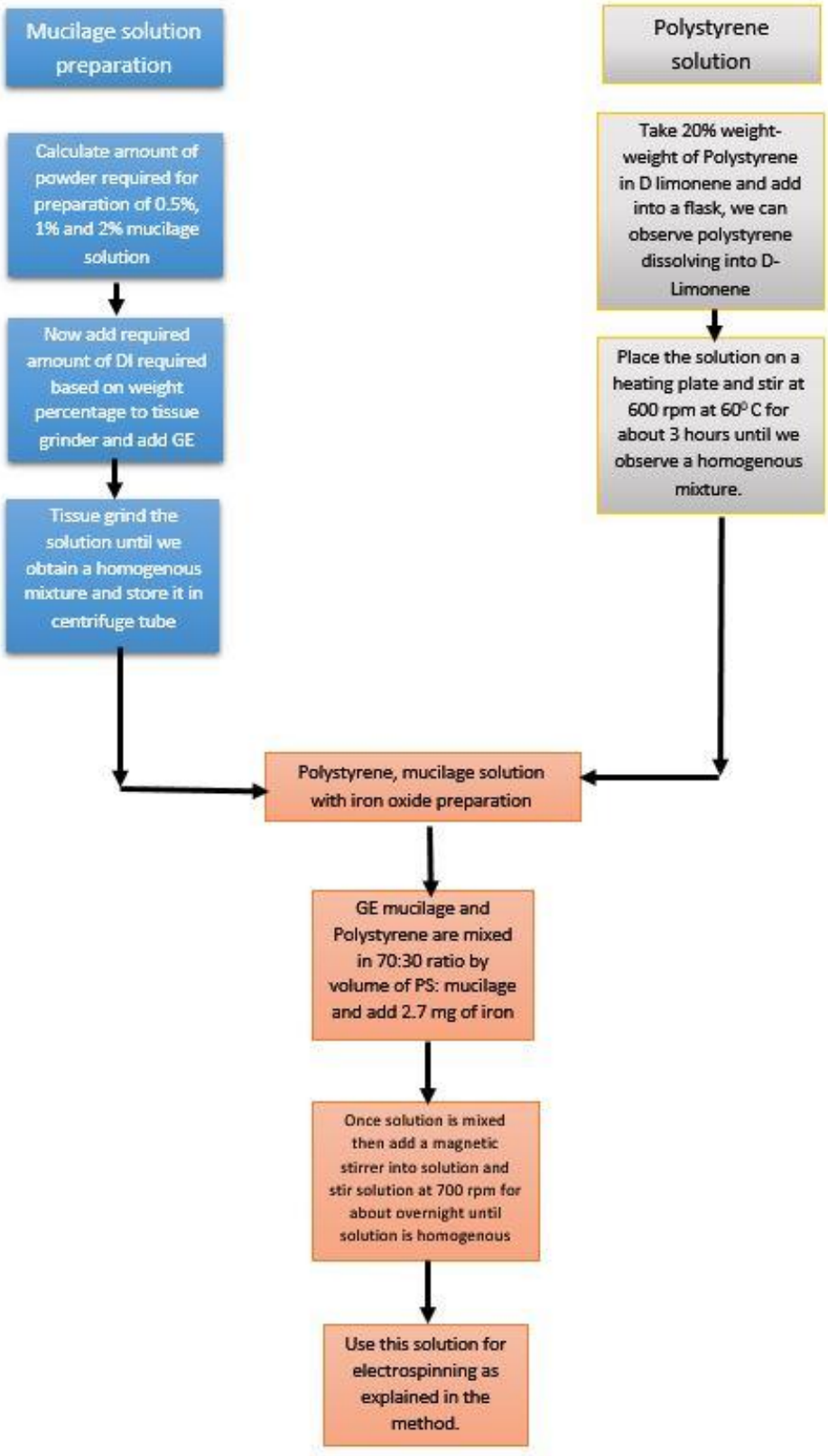


Figure 11 Polystyrene and mucilage solution preparation with iron oxide

2.4.2 Calculations for Preparation of GE with PS and Iron Oxide

Following are the calculations required for preparation of mucilage solution with polystyrene and iron oxide.

To make 1.5 ml of solution for electrospinning, first we need to make 70:30 ratio of polystyrene and mucilage in volume-volume ratio.

Consider polystyrene = PS, Mucilage = GE, Iron oxide = IO

$$PS = 70/100(PS + GE)$$

$$PS = 0.7(PS + GE)$$

$$PS (1-0.7) = 0.7(GE)$$

$$PS (0.3) = 0.7 (GE)$$

$$PS = 0.7/0.3 (GE)$$

$$PS = 2.33 (GE)$$

Thus, for 1 ml of GE, we need to add 2.33 ml of Polystyrene.

In 1.5 ml of PS + GE, we need to add 1.05 ml of polystyrene and 0.45 ml of mucilage. Now in the consideration of a solution containing iron oxide (concentration of 2.7 mg/ml) for a 1.5 ml of solution, there is 4.05 mg of iron oxide needed per the following:

For 1 ml -> 2.7 mg of Iron oxide

For 1.5 ml -> 2.7 * 1.5 = 4.05 mg of Iron oxide.

Hence to make solution, we need to take 1.05 ml of PS, 0.45 ml of GE mucilage and then add 4.05 mg of iron oxide. A magnetic stirrer is then used to mix the solution for 24 hrs at 600 – 700 rpm.

2.5 Summary

Procedures were documented for the preparation of GE mucilage, PS and D-limonene and iron oxide. These solutions will be used to fabricate fiber membranes in the electrospinning process.

CHAPTER 3: PROCESS OF CHOICE

3.1 Introduction and Application

Water filtration has become a huge problem for many decades and there are many studies still being conducted on this for obtaining pure bio-degradable filters. Filters obtained by nanofibers are currently used for studying the use of different materials which have the ability to absorb contaminates in water, such as toxic wastes, bacteria and microorganisms. Several studies have been conducted across the world to find a natural material for making filters and also to make a bio-degradable filter. [18] *Opuntia ficus-indica,* which is also known as prickly pear, is a plant whose origin is from native Mexico [18]. Cactus mucilage is extracted from the plant which is jelly like substance and is also abundant in nature. Cactus mucilage is a completely bio-degradable material and is also non-toxic which makes it a good natural material candidate to be used for water filtration. Rural people from Mexico used this plant to treat many diseases such as diabetes, gastritis, arteriosclerosis etc. [19] but as our research is only focused on water filtration, we consider its ability to absorb arsenic contamination from water. GE mucilage extracted from *Opuntia ficus-indica* cactus will be used to obtain fibers by the electrospinning process. Electrospinning is a cost effective process for fabricating fibers by electrospinning material composites with different copolymers. Fibers electrospun into a membrane will be used in a filtration process to treat contaminated water. Electrospinning is the most reliable technique used to obtain nanofibers ranging from millimetre to nanometre sizes. As per literature review from Rasudha [8] and Dawn Fox [2], it is known that cactus mucilage can be used for water filtration.

Therefore by utilizing the electrospinning process to fabricate fibers that form a nanofiber membrane, cactus mucilage is functionalized into a product/device that can be used for various applications. More specifically for this work, the application of water treatment will be explored.

3.2 Electrospinning Process

Electrospinning is a method used for growing fibers in which an electric field is used to draw charged threads of polymer solutions i.e., polymer solution will be transformed into fibers on the order of nanometres. Electrospinning has been drawing more attention in recent years due to its easier fabrication technique and low cost process, and the process can be observed in many fields of study.

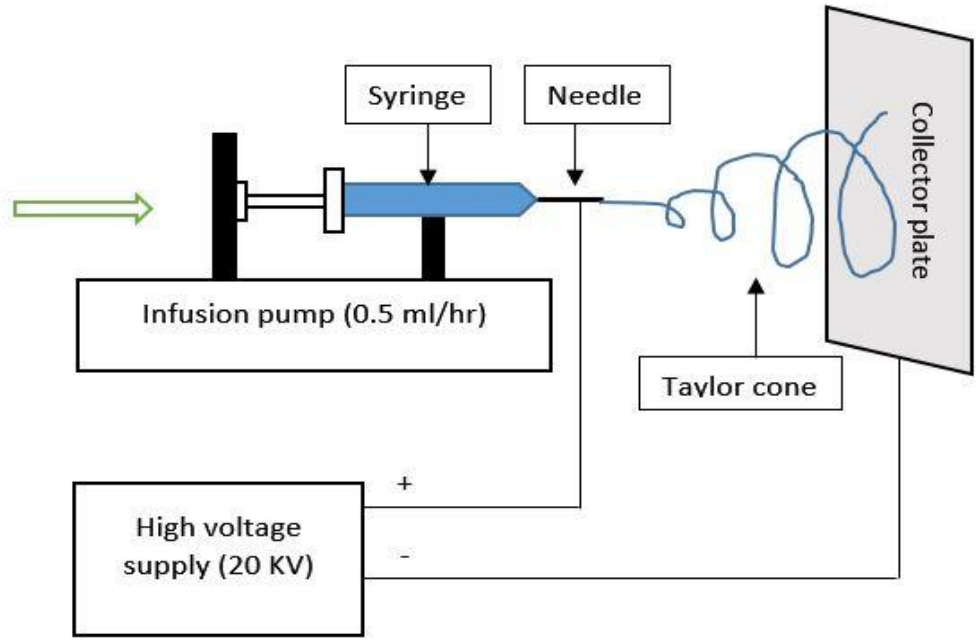


Figure 12 Electrospinning process

In this process (Figure 12), a syringe filled with polymer solution is loaded into a pump from Harvard apparatus. The pump induces the polymer solution into the syringe and a high

voltage is applied to the liquid droplet at the tip of the needle and a low voltage is applied to the collector. [20, 21] At some voltage point (13kV ~ 30kV), the liquid droplet at the tip of the needle forms a Taylor cone and becomes charged. As electrostatic repulsion overcomes surface tension of the liquid, the cone starts stretching and forming long fibers which are collected on the collector plate. If molecular cohesion in the liquid is too low, liquid eruption or Taylor cone formation does not occur and, the solution starts electro spraying. On the other hand, elongation and thinning of the fiber results due to sufficiently high chain entanglement or molecular cohesion in the liquid and is observed in the formation of the Taylor cone leading to the spinning of nanofibers with diameters in the nanometre range. In addition to Taylor cone formation and solvent evaporation, there are other factors which effect the formation of fibers: 1) Distance between collector plate and tip of the needle need to be varied per spin to observe formation and only at certain distances can the formation of fibers be achieved; 2) Needle gauge; 3) Infusion rate of the solution also plays vital role for the growing of fibers; 4) Viscosity of the solution should be less in order to get fibers, as viscosity is inversely proportional to the formation of fibers; 5) Ambient parameters (temperature, humidity and air velocity in the chamber); and 6) Motion and size of collector plate.

For this study the following research parameters were considered,

- Distance between needle and collector plate: 16 ~ 20 cm.
- Needle Gauge
- Infusion rate for polymeric solution: 1 ml/hr ~ 0.5ml/hr.
- Applied voltage: 19 ~ 20 kV
- Viscosity should be around 180 ~ 220 cp
- Ambient Parameters: Room temperature, Ambient air

- Collector Plate: Stationary square plate

These fabrication parameters are studied to prepare fibers using polystyrene (PS) and GE mucilage using different ratios and concentrations. PS is the long chain polymer needed to be present in the solution to help form fibers using GE mucilage. In previous investigations with NE mucilage, the concentration of 70:30 (PS: NE) produced good fiber formation as compared to concentrations of 50:50 or 30:70 [8]. Using this data point as a reference, this work primarily investigates solutions of PS: GE mucilage at a 70:30 ratio by volume with different weight percentages of GE mucilage i.e. 0.5%, 1% and 2% by weight of GE mucilage and water.

3.3 Results

3.3.1 Polystyrene and GE Mucilage

Polystyrene with GE mucilage are used for electrospinning in different ratios for obtaining fibers to form a membrane which can be used for water filtration. After several initial experiments were performed with PS:GE ratios of 30:70, 50:50, and 70:30 by volume, it was discovered that the 30:70 ratio of PS:GE resulted in the electro spraying of the solution and the 50:50 ratio resulted in the inconsistent formation of fibers, possibly due to the low concentration of PS in the solution. Repeatable and continuous fiber formation was obtained using the 70:30 ratio containing PS and GE mucilage, and all the results of this work further characterize and investigate this material composition for membrane formation and functionality.

From the 70:30 PS: GE solution, standalone membranes were generated which will be used for water filtration. With the successful formation of fibers using a fixed volume-volume ratio of PS: GE at 70:30 with GE concentration of 1% and 0.5% by weight with water, it was important to investigate if I started changing the concentration of GE mucilage in the 70:30 volume-volume ratio of PS: GE would impact fiber formation. GE concentrations of 2%, 1%

and 0.5% weight-weight ratio of GE and water were investigated to generate standalone membranes repeatedly. Concentrations containing more than 2% resulted in non-homogenous solutions. Once standalone membranes were generated using 2%, 1%, and 0.5%, different characterization tests were performed as reported in Chapters 4-6 and 8 and the functionality to filter water was measured as reported in Chapter 7.

3.3.2 Polystyrene, GE Mucilage and Iron Oxide

As stated in Chapter 2 Section 4, iron oxide has the ability to absorb arsenic content from water, and PS and GE mucilage are mixed together with iron oxide (concentration 2.7 mg/ml) to be used in the electrospinning process for fiber giving the iron oxide time to react with mucilage and obtain a homogenous solution for effective fiber formation. After 24 hours, solution can be loaded into syringe and start electrospinning with infusion rate set to 0.5 ml/hr keeping the voltage to 20kV, then you can observe formation of fibers (Figure 13).

After conducting several experiments, it was observed that the PS: GE solution with iron oxide formed fibers, partially due to the electrical conductivity nature of iron oxide. Iron oxide is mixed with a 70:30 ratio (by volume) of PS and 1% weight-weight of GE and a 70:30 ratio (by volume) of PS and 0.5% GE. Standalone membranes are observed for both experiments. Membranes using PS and GE (1% and 0.5%) with iron oxide will be tested for characterization and also water filtration. For this experiment, 2% weight-weight of GE mucilage was eliminated, because after conducting different studies of 2% GE, the solution was found to have a very long processing time (> 48 hrs.) to initiate a homogenous solution.

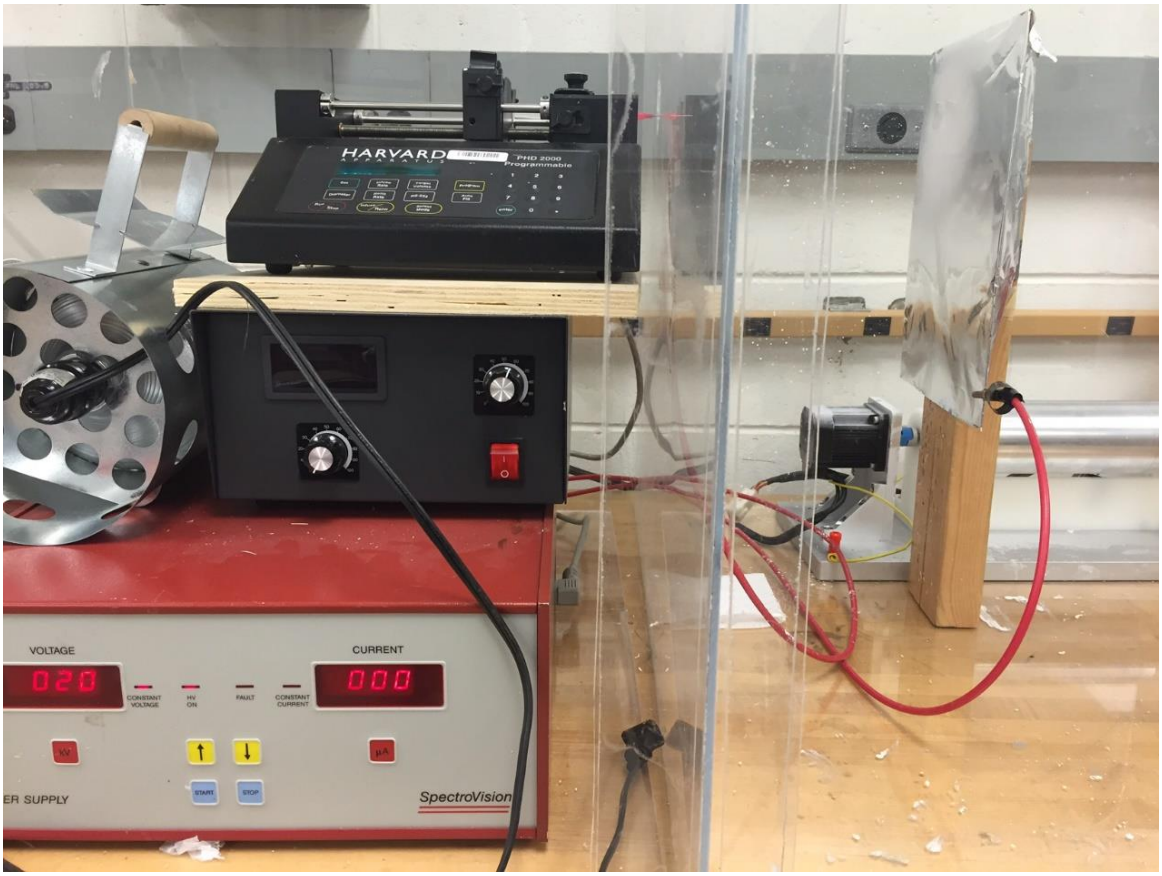


Figure 13 Electrospinning setup with solution loaded into syringe

CHAPTER 4: VISCOSITY

4.1 Introduction

Viscosity of a solution is measured using several instruments. I used Fungilab smart series rotational viscometer to measure viscosity of each solution. There are many factors affect the formation of fibers such as infusion rate of syringe, distance between collector plate and syringe, voltage applied to needle and also viscosity of solution. Viscosity of a solutions is nothing but a solution resistance for deformation by shear stress. [22] Shear stress refers to the stress applied on a fluid in parallel to another layer of fluid. In order to measure viscosity of a fluid, consider a fluid is in between two parallel plates and one plate is attached or fixed and other plate is in horizontal motion at a speed u. When top plate is moving, liquid particles start moving parallel to the plate and reach speed u from zero. Now each layer of particles from top starts moving but due to friction between those molecules try to oppose the moment resulting in less speed than layers at top. As from every layer, an opposing force is developed to keep the particles stable even though plate is moving at constant speed at top. An external force F need to be applied across the plate to keep it moving. The relation between force (F), speed (u), area of plate (A) and separation (y) is given by following formula,

$$F = \eta A \frac{u}{y}$$

The proportional factor η is the viscosity.

Viscosity is also given by, $\eta = \frac{F}{S} = \frac{Shear\ stress}{Shear\ rate}$

Shear rate is calculated by du/dy. Viscosity is an important factor for electrospinning. Bead formation in nanofibers depends on viscosity, as density or solution viscosity increases bead formation increases [23]. As charge density of solution increases, beads become smaller and diameter of fibers also decreases.

4.2 Methodology

A Fungilab smart L series rotational viscometer is used for measuring viscosity of all the solutions which have different concentrations. A spindle needs to be selected depending on the concentration and volume of the solution. For experimental solutions, a TR9 spindle is used to measure viscosity. A solution needs to be loaded into sample container and inserted into circulation jacket at bottom of viscometer. Before attaching spindle, just test the viscometer for calibration on the screen. Now install the spindle which is loaded by a spring attachment, then you can start measuring viscosity by varying rpm (rotations per minute) of spindle. As spindle rotates, solution drags the surface of spindle and viscometer starts measuring viscosity of solution.

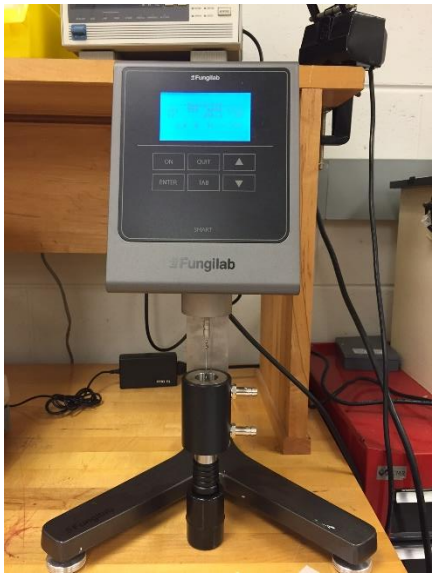


Figure 14 Fungilab smart L series rotational viscometer

Figure 15 Viscometer screen setup

Mucilage solution from cactus plant is used for measuring viscosity. It is mixed in different concentrations of polymer solution (polystyrene) and also by varying concentrations of GE mucilage. In this procedure I tested four solutions in order to measure viscosity. When the concentration of polymer is reduced below 40% of entire solution, no fiber formation was observed and even solution electro spraying was found to be present. This change in concentration of solution of PS: GE has direct impact on viscosity for growing fibers. From earlier studies, it was observed that the concentration of polystyrene has impact (such as size of fibers and beads) on viscosity and fiber formation, which was verified through scanning electron microscopy (SEM) images [8]. Therefore, SEM and viscosity will be used to analyse fiber formation, fiber diameter, and impact of viscosity on formation from the following solutions:

- 70: 30 volume to volume ratio of Polystyrene (with D-Limonene) and 1% w/w GE mucilage with water.
- 70: 30 volume to volume ratio of Polystyrene (with D-Limonene) and 0.5% w/w GE mucilage with water.
- 70: 30 volume to volume ratio of Polystyrene (with D-Limonene) and 1% w/w GE mucilage with water and iron oxide with concentration of 2.7 mg/ml.

- 70: 30 volume to volume ratio of Polystyrene (with D-Limonene) and 0.5% w/w GE mucilage with water and iron oxide with concentration of 2.7 mg/ml.

4.3 Results and Analysis

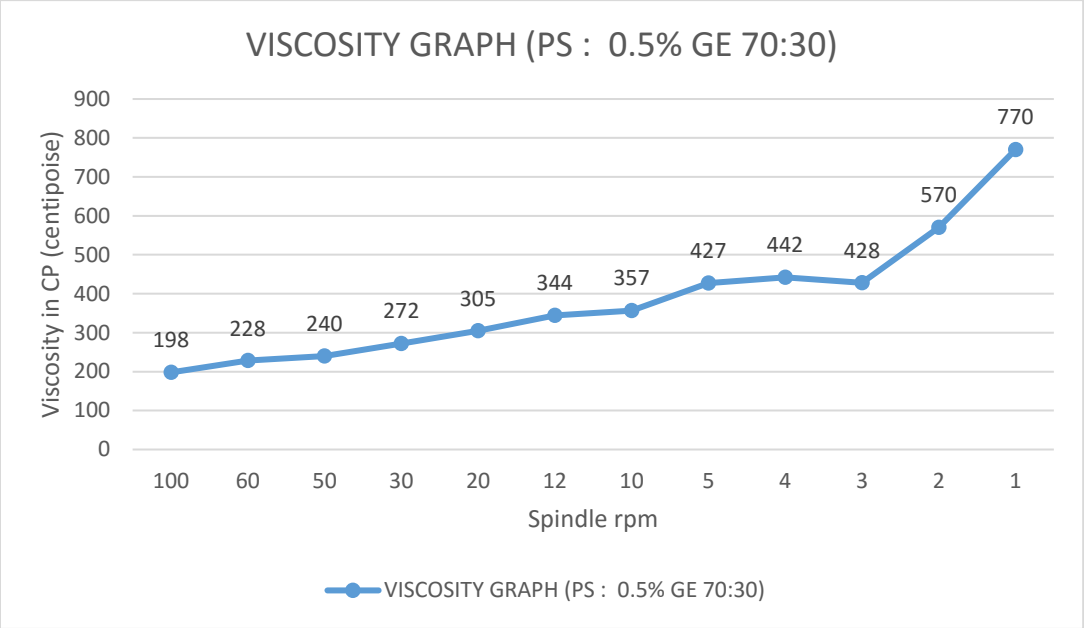


Figure 16 Viscosity plot of polystyrene: 0.5% GE (70: 30 by volume)

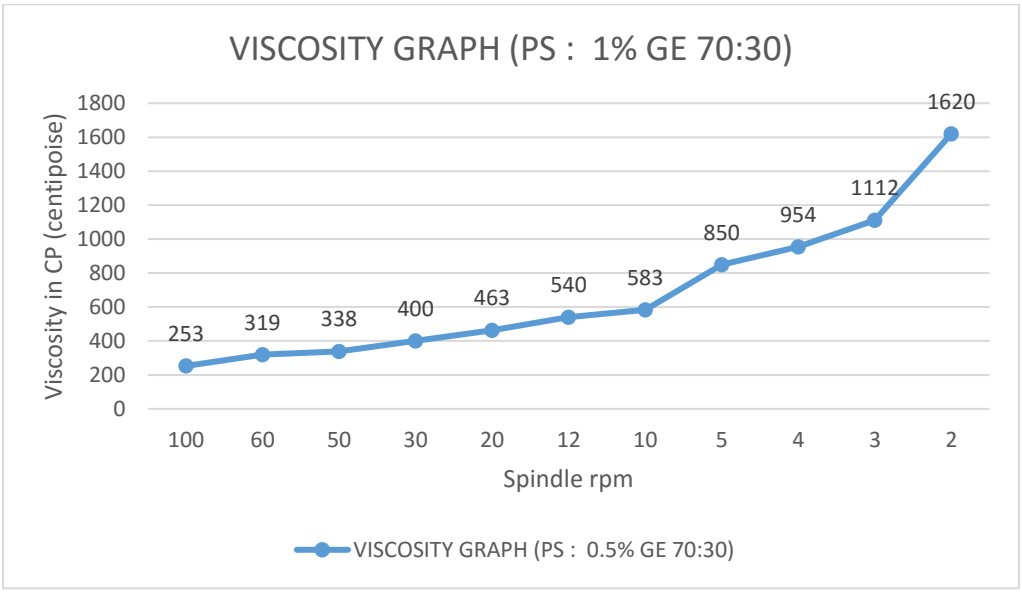


Figure 17 Viscosity plot of polystyrene: 1% GE (70: 30 by volume)

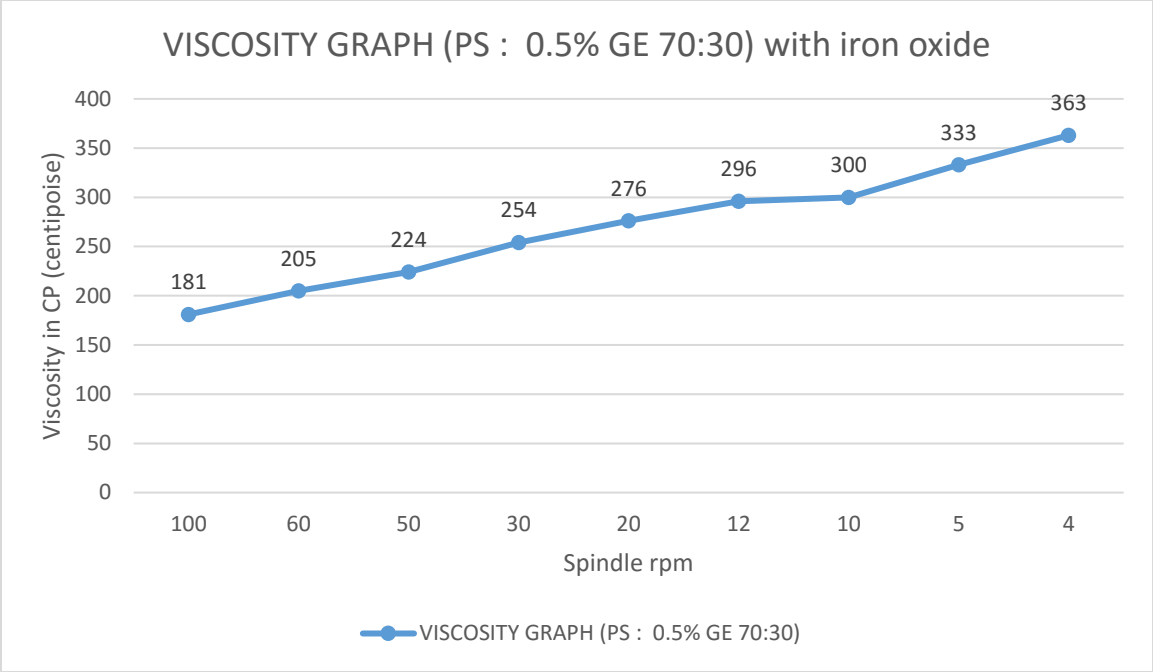


Figure 18 Viscosity plot of polystyrene: 0.5% GE (70: 30 by volume) with iron oxide

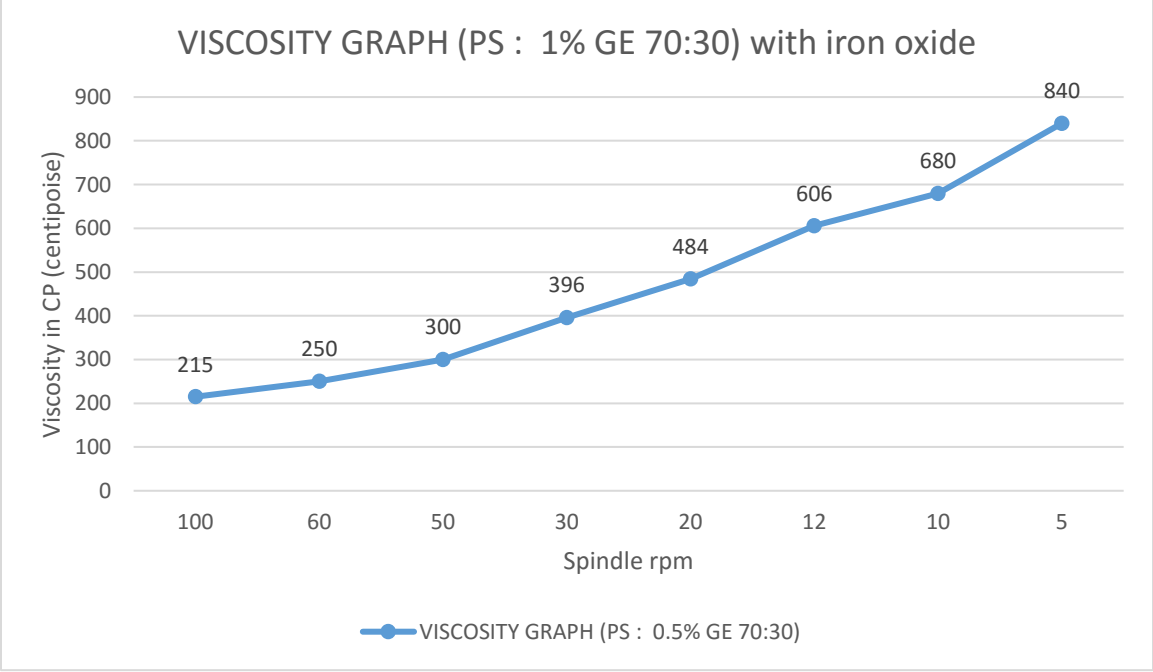


Figure 19 Viscosity plot of polystyrene: 1% GE (70: 30 by volume) with iron oxide

From viscosity measurements as shown above, it is observed that a PS: 0.5% GE (70: 30 v/v) solution has a viscosity of 198 cp at 100 rpm. For a PS: 1% GE (70: 30 v/v) solution, a viscosity of 253 cp at 100 rpm was measured. For PS: 0.5% GE mucilage (70: 30 v/v) with iron oxide has a viscosity of 181 cp at 100 rpm. Finally, a solution of PS: 1% GE mucilage (70: 30 v/v) with iron oxide has a viscosity of 215 cp at 100 rpm.

4.4 Summary

In conclusion, solutions with iron oxide have a lower viscosity (181 and 215 cp) than samples without iron oxide (198 and 253 cp) for PS: 0.5% GE and PS: 1% GE respectively at 100 rpm. I can observe that by adding iron oxide viscosity of solutions is getting reduced. From chapter 6, I can clearly observe that thickness of fibers and beads is getting reduced along with reduction in viscosity. By having thinner fibers and beads, I can get more fibers on nano mesh. For suppose consider a sq.cm area where nanofibers have been spread, if size of fibers is less then you can have large number of fibers bound together which also leads to smaller pore sizes. Hence when a water droplet is passed through fiber mesh, it will have greater contact time with fibers and this leads to better filtration results.

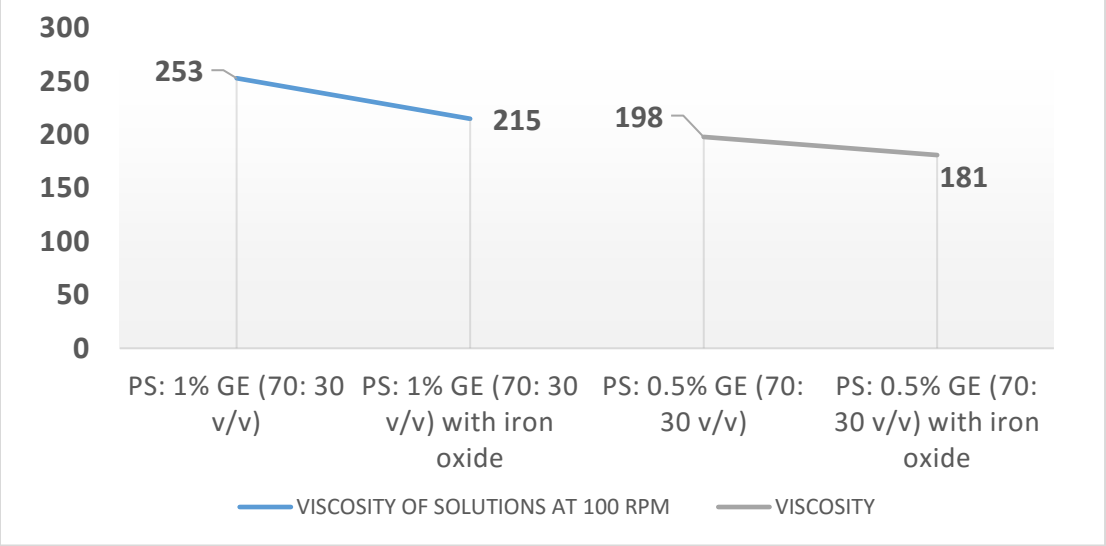


Figure 20 Comparing viscosity of solutions with and without iron oxide

CHAPTER 5: CONTACT ANGLE MEASUREMENTS

5.1 Introduction

Contact angle measurement (CAM) is used to measure contact angle of a water droplet on a surface. KSV instrument CAM 101 which is a computer controlled and user programmable instrument which will have a video output for calibration is used to measure contact angle of cactus mucilage nanofibers. The contact angle for fiber is measured by growing fibers on a glass plate. It is a tangent which is marked and measured at the contact of solid (glass plate) and liquid droplet to the surface of glass plate. Contact angle gives the hydrophilic nature of our fibers. Wetting phenomena gives the material wettability and non-wettability nature. This will be measured by using CAM. There are many factors which affect the contact angle of a solid surface such as surface roughness, shape and size [24]. Only at equilibrium temperatures, we can measure exact contact angle which will be in between advancing contact angle (maximum contact angle) and receding contact angle (minimum contact angle). This contact angle gives the strength of the liquid and solid molecular interaction which ultimately determines the hydrophobicity nature of solid surface.

Contact angle is directly proportional to hydrophobicity. The higher the contact angle, surface will be more hydrophobic in nature. The lesser the contact angle, surface will be more hydrophilic in nature.

5.2 Methodology

A pendant drop technique is used to measure the contact angle of liquid to the surface. Experimental setup will be as shown in the figure 21. One side of the pole contains light source and a syringe (Hamilton microliter syringe) loaded with water and it is a one touch drop dispenser. Light source is LED based. CAM 101 uses a FireWire video camera with a resolution of 64 x 480 pixels and we can measure the contact angle on the KSV contact angle measurement optical contact angle and the pendant drop surface tension software v4.04. Once we load water into syringe, we will place glass plate coated with nanofibers and syringe will be slowly released until we get a water bubble at the end of syringe needle. Now tap the syringe, water drop will be dropped onto the surface of glass plate. Software measures by recording the video image, it will draw a tangent at the edge of droplet where it had a contact with glass plate. The exterior angle b/w glass plate coated with fibers and water droplet is the contact angle. Hydrophobic nature of fibers will be determined based on contact angle. If contact angle is greater than 90^0 then fibers are hydrophobic and if contact angle is less than 90^0 then fibers are hydrophilic in nature.

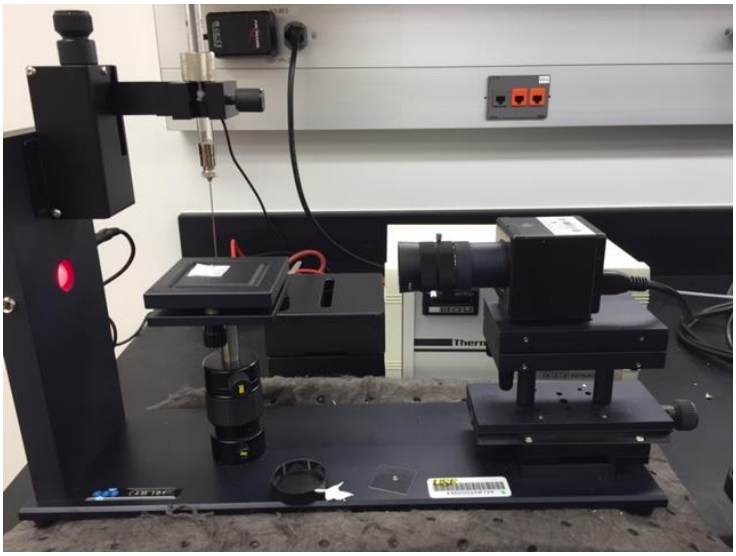


Figure 21 Complete experimental setup for CAM

Following figure shows how nanofiber coated glass slide is placed and how water droplet is dropped. You can observe from figure 22, how droplet is placed on glass plate.

Figure 22 Water droplet placed on glass plate

Once droplet is on the surface, now video camera will start recording and capture an image as shown in figure 23 to measure.

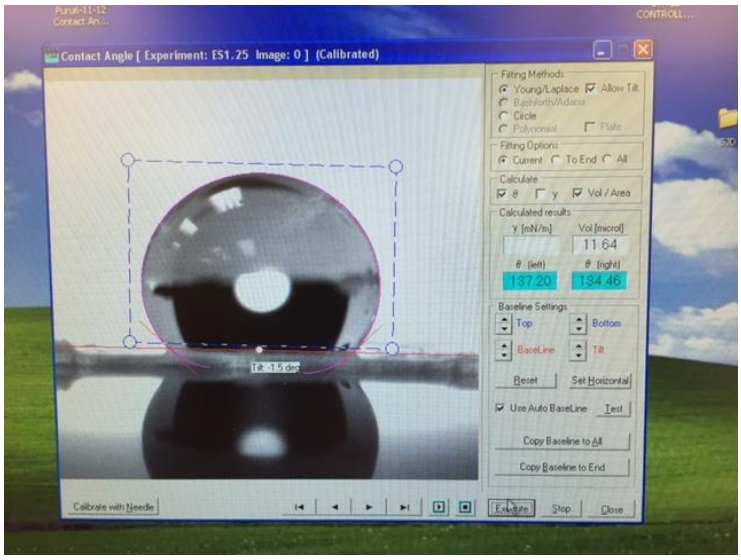


Figure 23 Software measuring contact angle by drawing tangents to water droplet

5.3 Results and Summary

Contact angle is measured for four solutions,

- Polystyrene: 1% GE mucilage (70:30 v/v ratio) without iron oxide
- Polystyrene: 0.5% GE mucilage (70:30 v/v ratio) without iron oxide
- Polystyrene: 1% GE mucilage (70:30 v/v ratio) with iron oxide (2.7 mg/ml)
- Polystyrene: 0.5% GE mucilage (70:30 v/v ratio) without iron oxide (2.7 mg/ml)

Following table gives the contact angle measurements.

Table 1 Contact angles of polymeric solutions

S.No	Solution	Contact angle in degrees
1.	PS: 1% GE (70:30 v/v) without iron oxide	135.83
2.	PS: 0.5% GE (70:30 v/v) without iron oxide	125.36
3.	PS: 1% GE (70:30 v/v) with iron oxide	133.37
4.	PS: 0.5% GE (70:30 v/v) with iron oxide	122.23

The contact angle gives us the result whether nanofibers are hydrophobic or hydrophilic in nature. It also allows us to determine surface tension and wetting phenomena of the nanofibers. Four solutions are hydrophobic in nature as their contact angles are greater than 90^0. If we observe from earlier literature reviews [8], when they used non-gelling extract of mucilage (NE) with polystyrene, solution is hydrophilic in nature. Following images show how water droplet is on the surface of glass plate and we can easily observe hydrophobicity of the nanofibers.

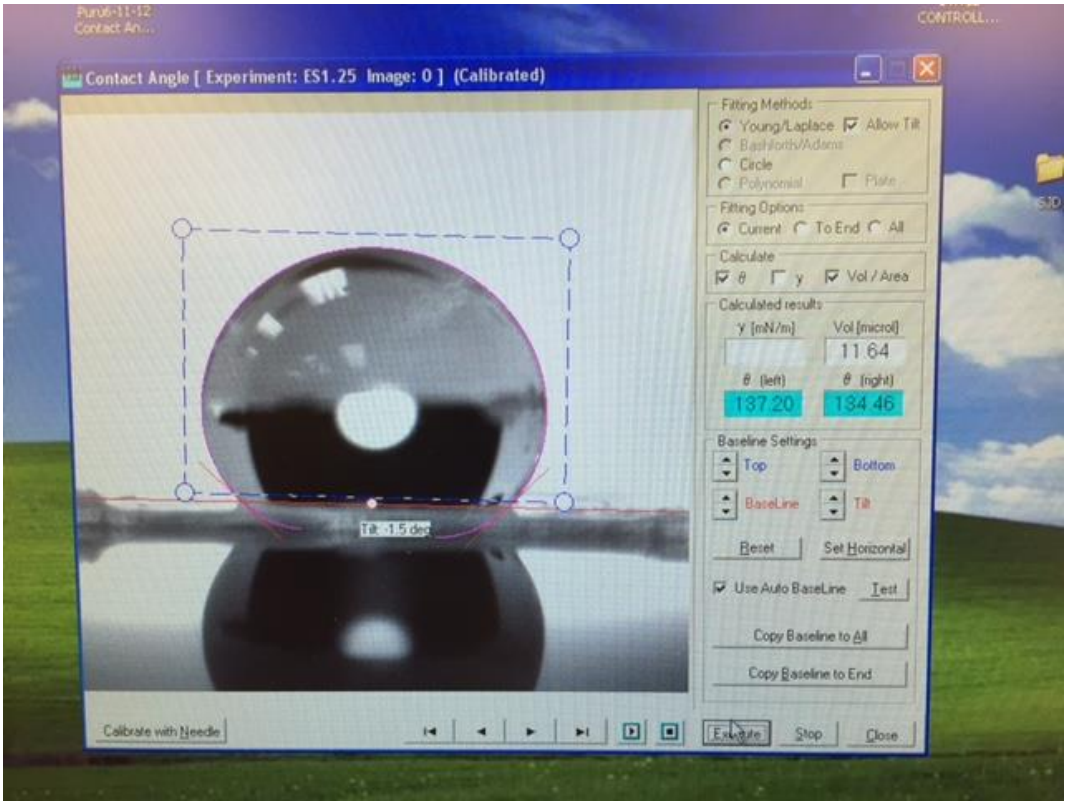


Figure 24 CAM measurement for PS: 1% GE (70:30 v/v) without IO

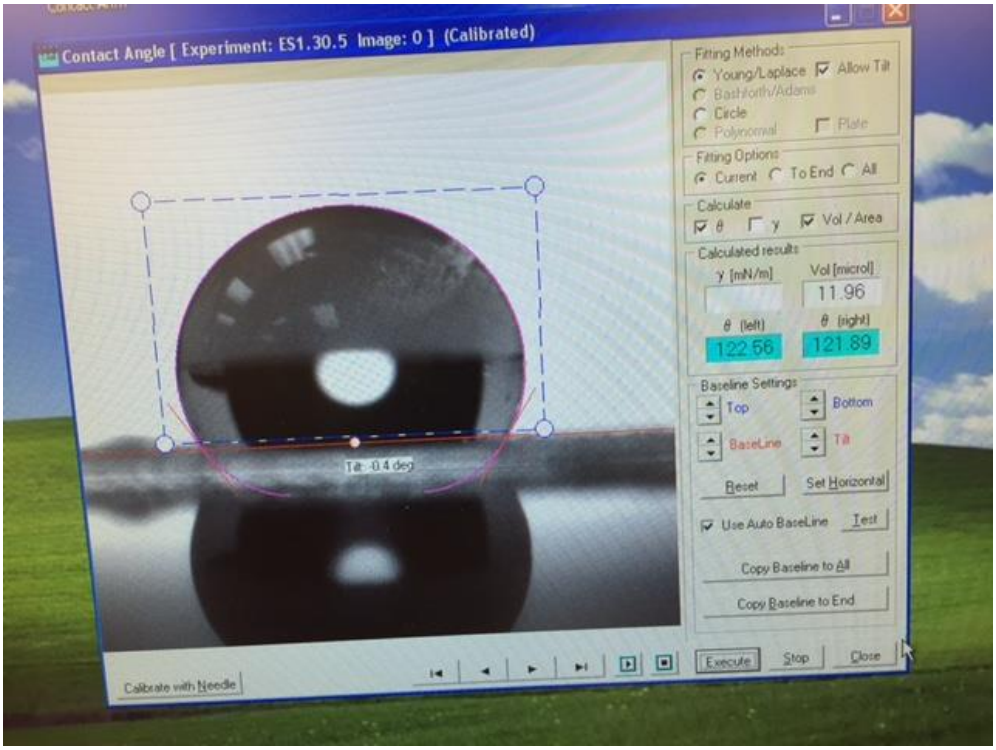


Figure 25 CAM measurement for PS: 0.5% GE (70:30 v/v) with IO

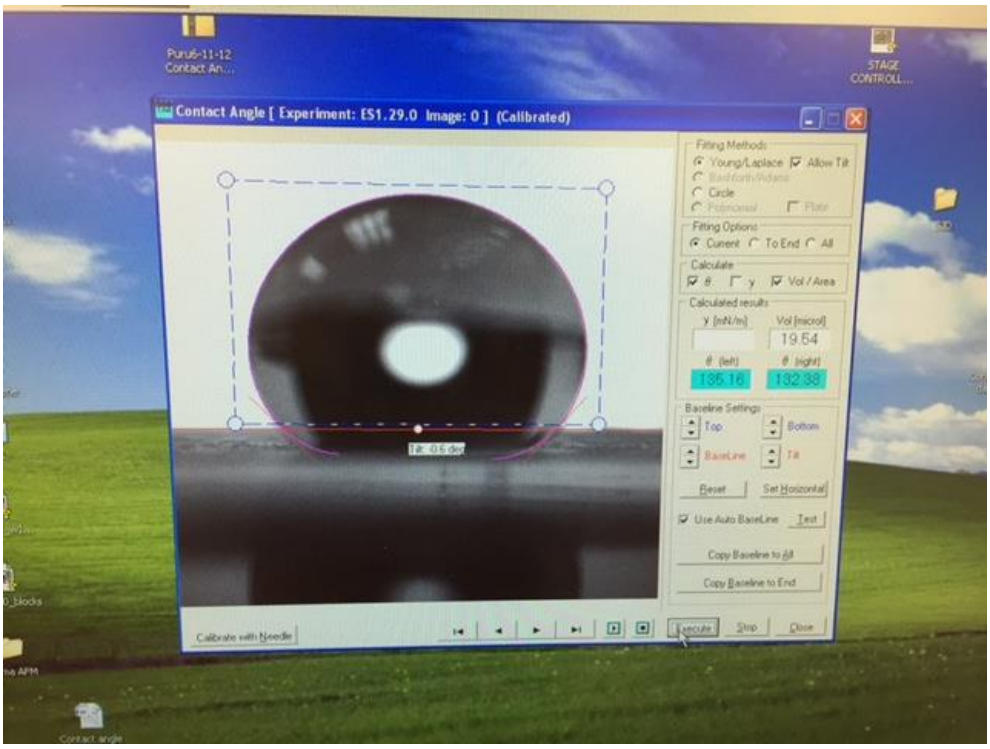


Figure 26 CAM measurement for PS: 1% GE (70:30 v/v) with IO

In conclusion, we can observe from table 1, all solutions are hydrophobic in nature. This really plays a major role for applications like water filtration because I can make repeated number of cycles for filtering contaminated water.

CHAPTER 6: SCANNING ELECTRON MICROSCOPY

6.1 Introduction

Scanning electron microscopy gives in detail physical structure of nanofibers. It uses electron beam instead of light source to form an image. We can take pictures in nanoscale and observe physical structure of the sample material. GE mucilage is electrospun along with polystyrene as a co-spinning polymer. D-Limonene is used to break molecular bonds in polystyrene and make a solution. After preparing solution, it is used in different ratios by mixing polystyrene and GE mucilage i.e., ratios of 30:70 and 70:30 by volume. And also try along with iron oxide with a concentration of 2.7 mg/ml. Iron oxide has a property of adsorbing arsenic content from water. These solutions will be mixed at room temperature at 600 rpm over night until homogenous mixture of solution is obtained. These samples will be loaded into a syringe and electro spun to obtain nanofibers. Nanofibers will be taken and different tests conducted to know the characteristics of the fibers. Scanning electron microscopy is one among those characterization techniques used for testing nanofibers. Based on SEM images analysis I was able to observe mucilage and iron oxide is placed all over the Nano sheet and wrapped up by fibers.

6.2 Results

6.2.1 SEM Analysis of Polystyrene: 1% GE Mucilage with Iron Oxide

GE mucilage is mixed with polystyrene at 30: 70 (1% GE: PS) and also 2.7 mg/ml concentration of iron oxide is added to the solution and stirred well to obtain a homogenous

solution. This solution is electrospinned and form nano fibers. Figures 27 shows SEM images giving us sizes of fiber mesh and beads obtained for this solution.

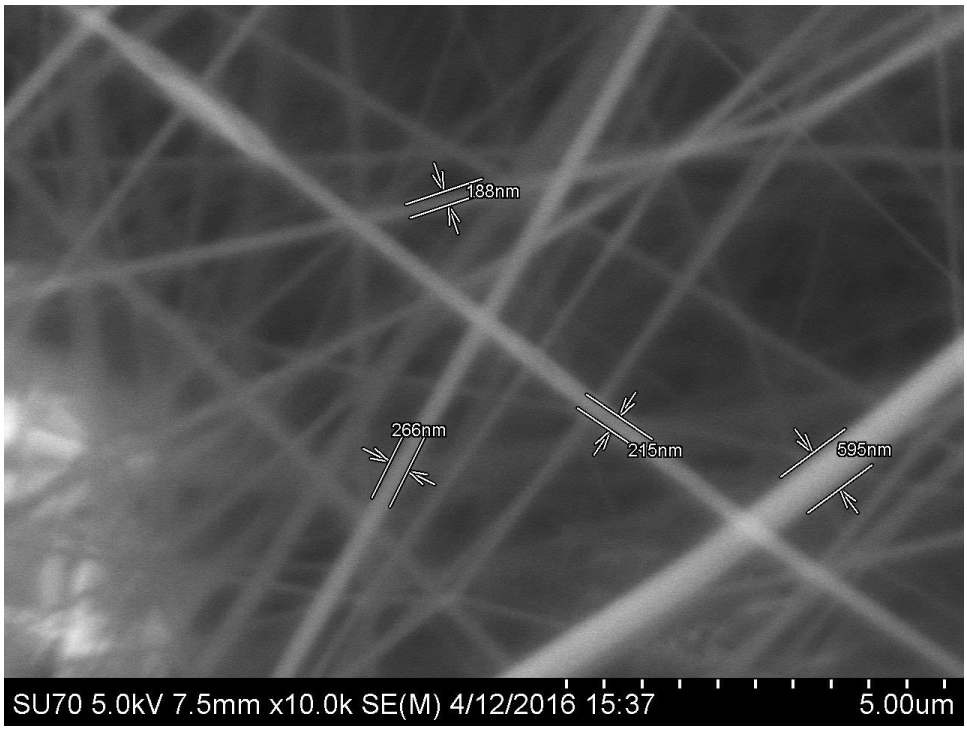


Figure 27 SEM of polystyrene: 1% GE mucilage with iron oxide showing fibers

From above picture (figure 27), I can observe that size of nano fibers is around 233 nm. And size of beads us about 10-15 µm. Obtained beads are definitely not due to polymer but on future studies I can determine to find what particles are wrapped around by fibers. This solution has average viscosity of 215 cp. From earlier works, [8] we know that solution shows less beading by increasing amount of polymer i.e., 70: 30 ratio by volume of Polystyrene and mucilage, hence my thesis is strictly restricted for 70: 30 ratio.

6.2.2 SEM Analysis of Polystyrene: 0.5% GE Mucilage with Iron Oxide

Polystyrene is mixed with 0.5% GE mucilage with iron oxide (2.7 mg/ml concentration) and stirred well to obtain homogenous solution. This solution is electrospinned and nanofibers obtained. Figures 28 and 29 show SEM analysis of the fibers.

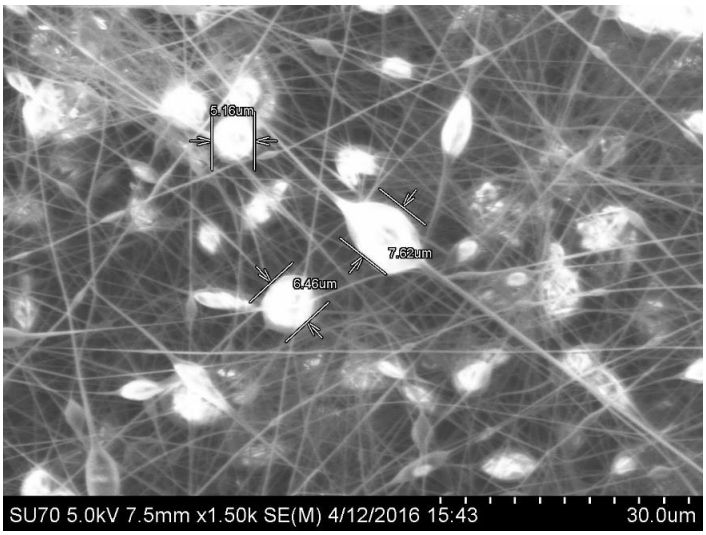


Figure 28 SEM of PS: 0.5% GE mucilage with iron oxide showing beads and fibers

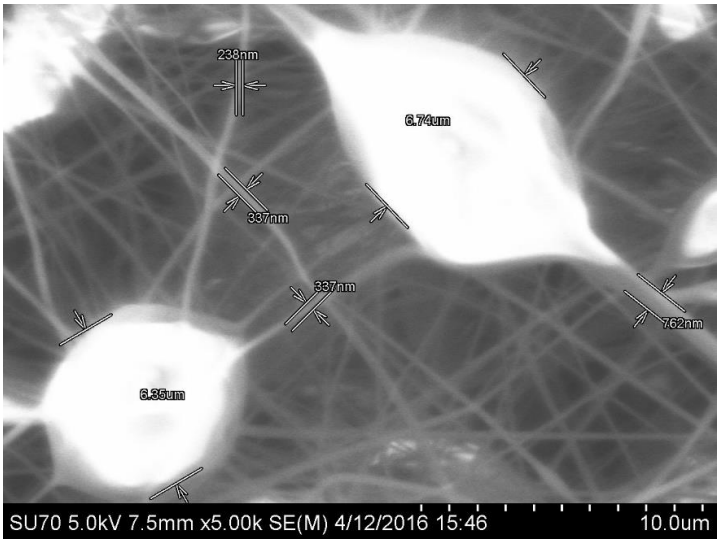


Figure 29 SEM of PS: 0.5% GE mucilage with iron oxide showing fibers and beads

From above pictures (fig 28 & 29), I can observe that average diameter of nano fibers is about 310 nm. Sizes of beads is about 6.2 µm. The viscosity of this solution is 181 cp. I can also

observe from SEM pictures that solution with 0.5 % GE mucilage (viscosity of 181 cp) and iron oxide has smaller beads (about 6.2 µm) than solution with 1% GE mucilage (viscosity of 251 cp) and iron oxide.

6.2.3 SEM Analysis of Polystyrene: 1% GE Mucilage

Polystyrene is mixed with 1% GE mucilage but now without iron oxide in 70: 30 ratio. This solution is mixed well and stirred to obtain homogeneous mixture. After obtaining nano fibers from electrospinning, samples will be taken for SEM analysis. Figures 30 and 31 show SEM pictures of the solution.

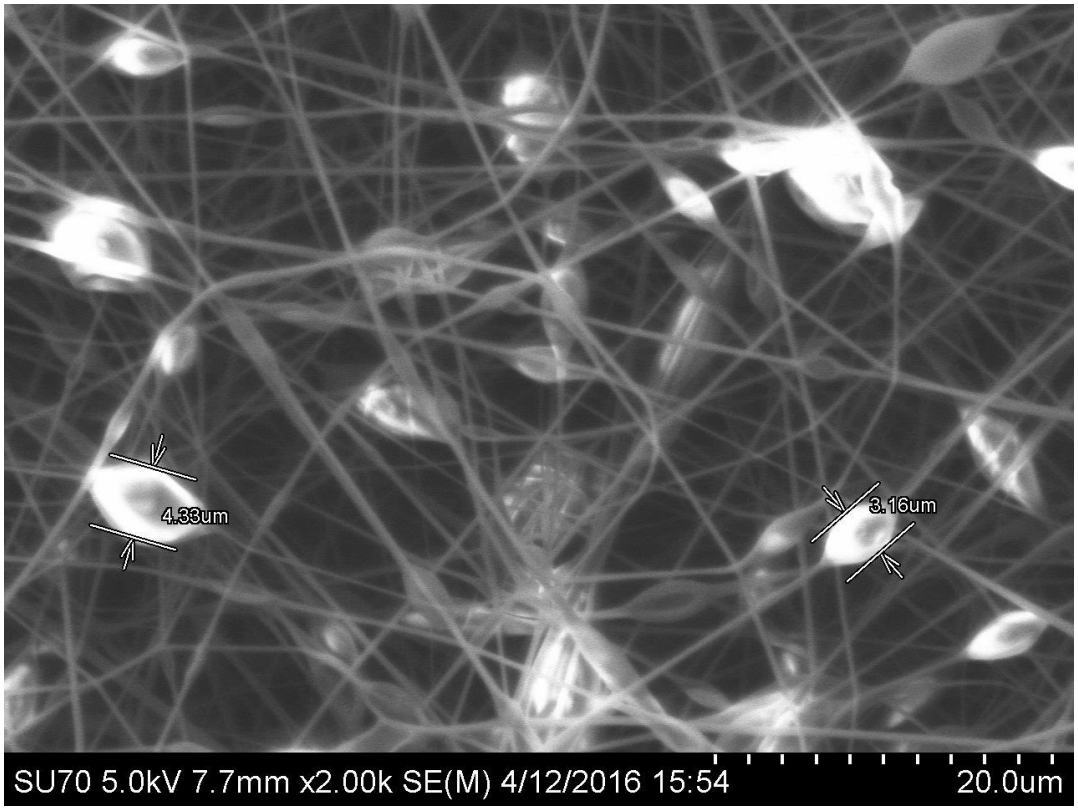


Figure 30 SEM of PS: 1% GE mucilage without iron oxide showing beads and fibers

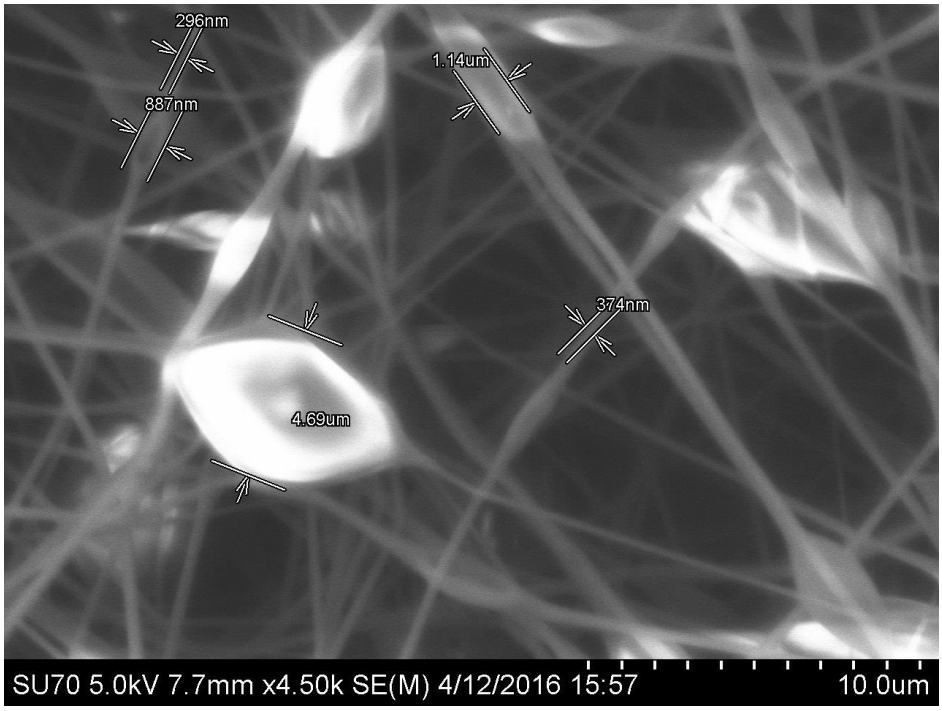


Figure 31 SEM of PS: 1% GE mucilage without iron oxide showing fibers and beads

From analysing above SEM pictures (fig 30 & 31), the average diameter of these nanofibers is about 300 nm. The size of beads is about 4.5 µm. Viscosity of this solution is 253 ps.

6.2.4 SEM Analysis of Polystyrene: 0.5% GE Mucilage

In this solution, polystyrene is mixed with 0.5% GE mucilage without iron oxide. Now this solution will be stirred until a homogenous mixture is obtained and is electro spinned to get nanofibers. These fibers will be again taken for testing SEM. Figures 32 and 33 represent SEM pictures of this sample solution.

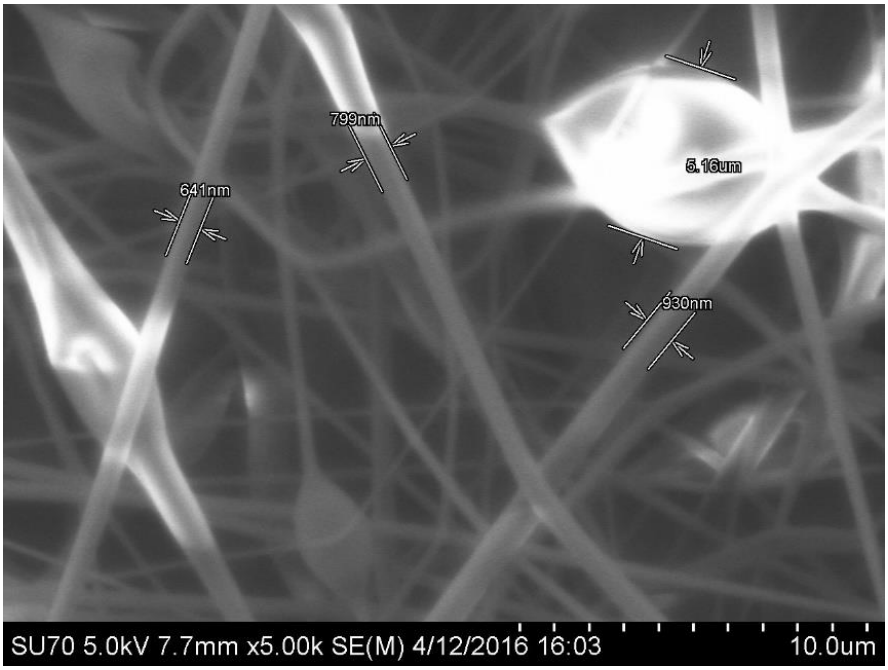


Figure 32 SEM of PS: 0.5% GE mucilage without iron oxide showing beads and fibers

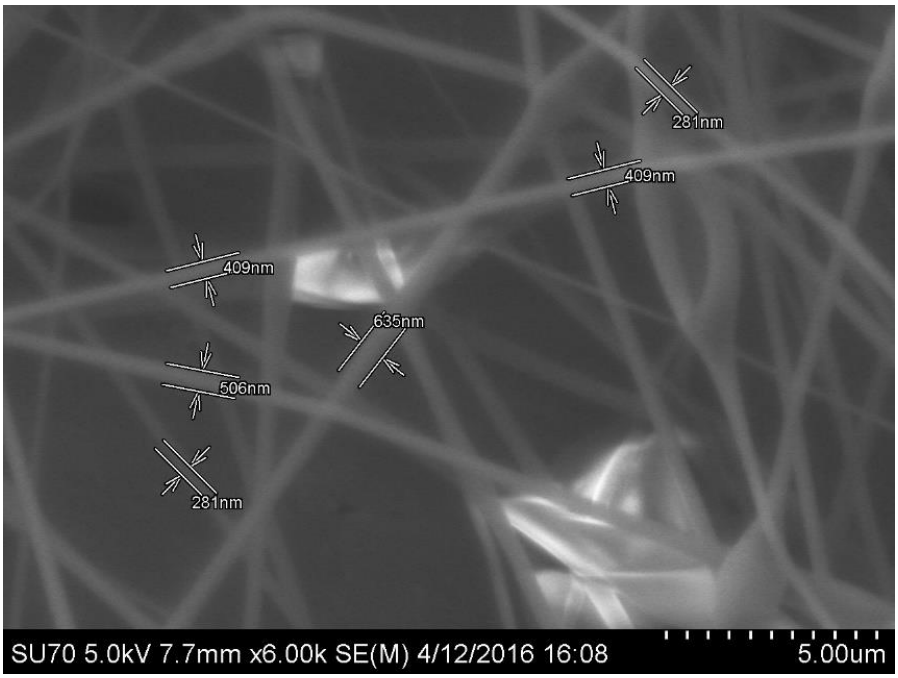


Figure 33 SEM of PS: 0.5% GE mucilage without iron oxide showing fibers and beads

From above SEM analysis (fig 32 & 33), we can state that diameter of nanofibers is about 450 nm. Size of the beads is about 5 µm. Viscosity of this solution is 198 cp.

6.3 Summary

From SEM analysis (Chapter 6) and viscosity measurements (Chapter 4), it was observed that PS: 0.5% GE (70: 30 v/v) with viscosity of 198 cp had produced nanofibers with size of about 500 nm and bead size of about 6 µm. Nanofibers obtained for PS: 1% GE (70: 30 v/v) with viscosity of 253 cp had a size of about 350 nm and bead size is about 4 µm. Nanofibers obtained for PS: 0.5% GE mucilage (70: 30 v/v) with iron oxide had a size of 220 nm and bead size about 6 µm and had a viscosity of 181 cp. Finally nanofibers with PS: 1% GE mucilage (70: 30 v/v) with iron oxide ratio had a size of about 200 nm and bead size of 12 µm and also had a viscosity of 215 cp. It is clearly observed that fiber thickness increases with a decrease in viscosity for concentrations of PS: GE with iron oxide. From chapter 4, I observed that viscosity of solution is getting reduced when I add iron oxide into solution and by having less viscous solution I can obtain nano fibers with less fiber size and bead size which is really great for water filtration. This is because if you have smaller size of fibers, it will result into smaller pore size which leads to better filtration.

CHAPTER 7: ATOMIC FLUORESCENCE SPECTROMETRY

7.1 Introduction

PSA 10.055 Millennium Excalibur (PS Analytical) is used for testing selenium, arsenic, antimony, tellurium, bismuth and other hydride forming elements and analyse the results. In this procedure, initially sample solutions will be acidified with HCl and then treated with sodium borohydride in order to get covalent hydride. This procedure can be shown by equation as follows:

$$NaBH_4 + 3H_2O + HCl \rightarrow H_3BO_3 + NaCl + 8H \rightarrow EHn + H_2 \text{ (excess)}$$

Excess amount of hydrogen and hydrides from above reaction will be passed through generation vessel via an argon stream and it will be converted into a hydrogen diffusion flame. Hydrides coming out of argon stream will be atomized by hydrogen flame. Sample solutions made from filtration will be quantified by making reference to solutions made for calibration.

7.2 Methodology/ Protocol

AFS testing is used for detecting amount of arsenic content that has been removed or filtered by the mucilage nanofibers. Before starting of the experiments, always we need to follow lab safety procedures. Turn on the gases (nitrogen and argon), also check the pressure on the cylinder and pressure needs to be at least 400 psi. Pressure also depends on number of samples you need to run. If you observe the tubing connections always make sure that grey tubing will go into reductant, two green tubes will go into blank in and blank out in the reagent blank respectively as shown in the figures 34 & 35.

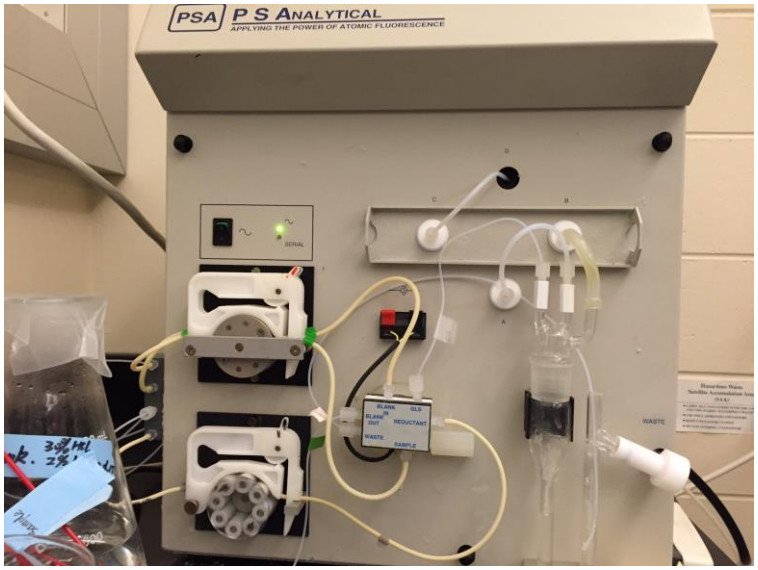


Figure 34 PS Analytical Millennium Excalibur tubing set up

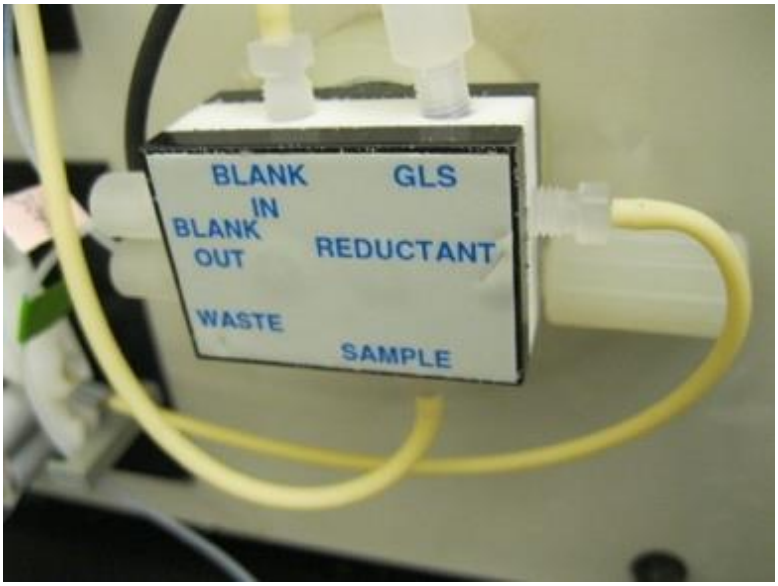


Figure 35 Tubing setup for reductant, blank in and blank out, distilled water connections

Now after connecting tubes into required solutions, pump tubing and cassette head on the pumps need to be correctly attached as shown in figure 36.

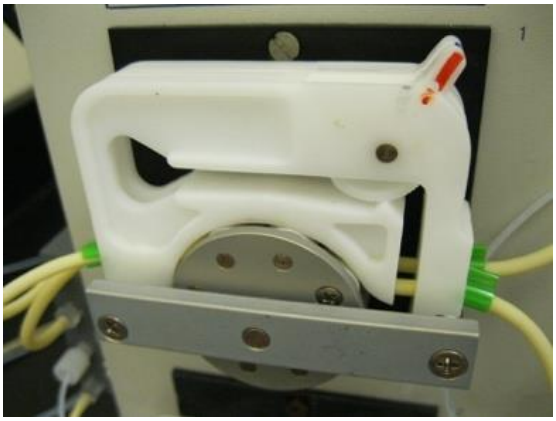


Figure 36 Pump tubing and cassette head on the pumps connection

Turn on the computer and enter details of the user and let the system warm up at least for 30 min. Now open Millennium software in the computer and use default calibration. In the analysis tab you can control the system operation and turn on the instrument.

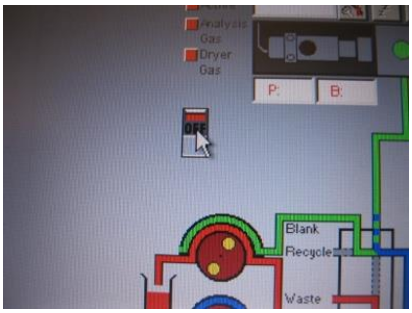


Figure 37 Analysis tab of the millennium software

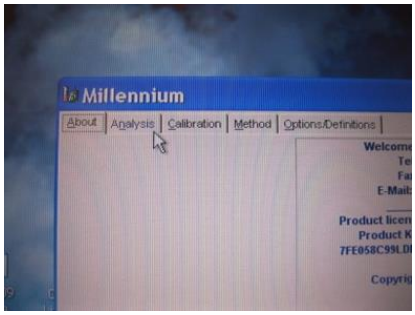


Figure 38 Manual control of instrument

Open the method tab and choose the method. Also apply gain settings as follows.

Table 2 Gain setting and range of As concentration

Gain setting	Range of As concentration
1	0-400 µg L^{-1}
10	0-40 µg L^{-1}
100	0-4 µg L^{-1}
1000	0-0.4 µg L^{-1}

If you open the manual control page, you can check if the gases and pumps are on or off and you can also manually turn it on.

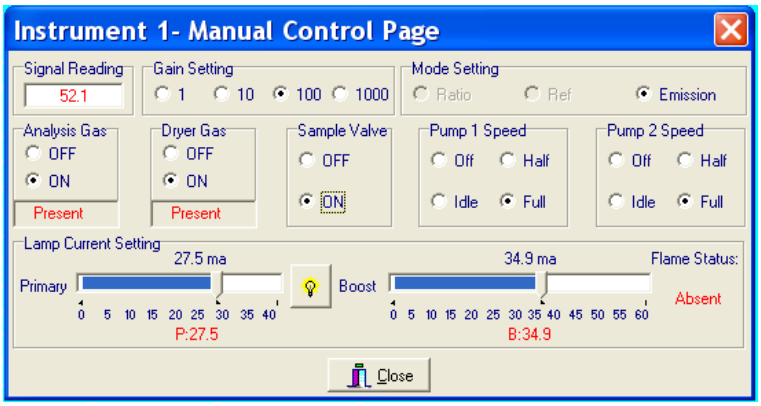


Figure 39 Manual control page of PS analytical instrument

Ignite the flame by using lighter and make sure the conduit is on the top of the flame, you can observe flame status on manual control page. Now organize the sequence as shown in figure 40 for testing the sample solutions.

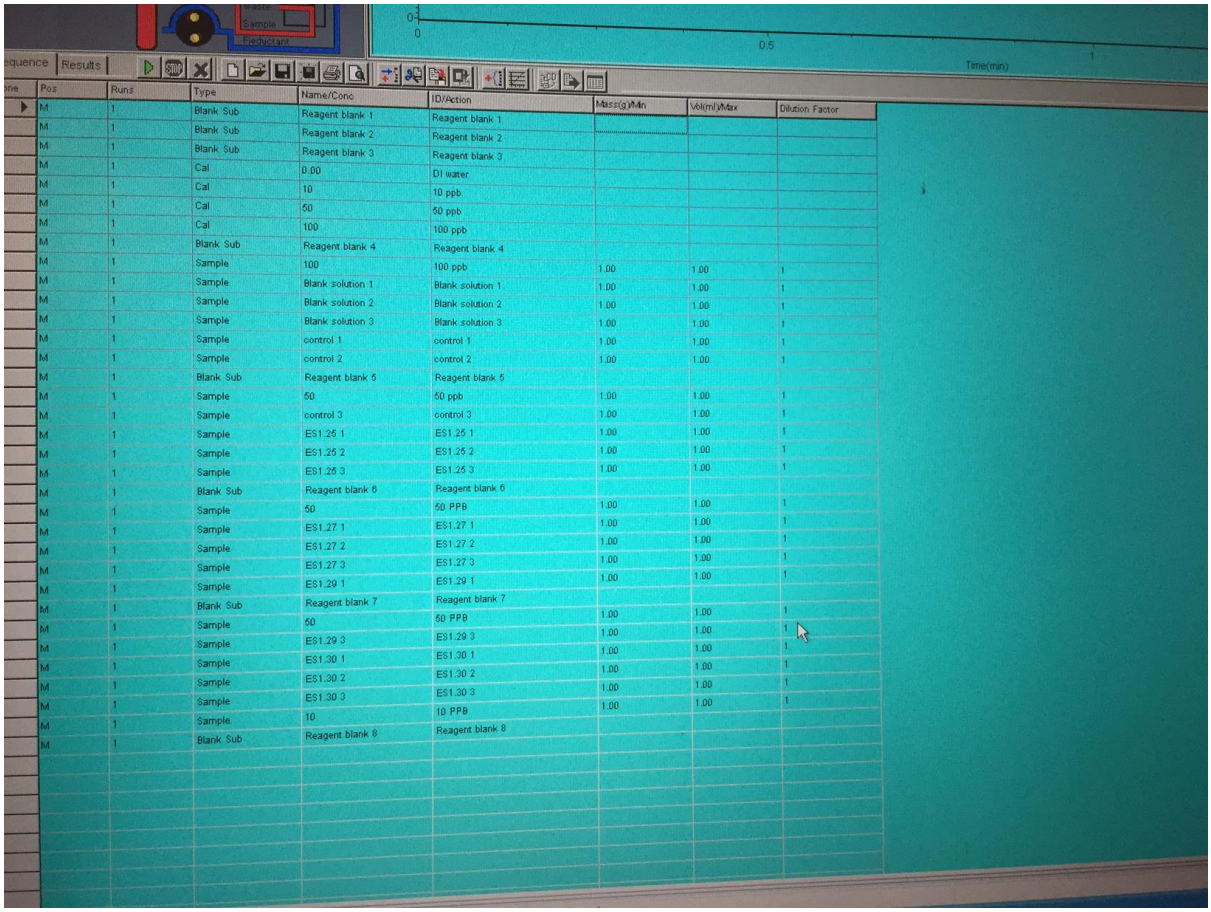


Figure 40 Sequence to test the sample solutions in millennium software

The sequence needs to be done in five steps:

- Reagent blank should be three times
- Add new calibration solutions
- Drift monitor
- Now add five sample solutions
- Drift monitor

After organizing the sequence you can start the procedure, we can export data and save our data in an excel format. After finishing the experiment, run the tubing with distilled water to clean the system and also clean gas/liquid separator.

7.2.1 Preparation of Solutions

AFS testing is used to determine arsenic concentration in the solutions, and for that we need to prepare solutions for running the entire procedure. The solutions for AFS analysis need to be prepared as follows,

- Arsenic stock solution

Concentration of Arsenic (As) stock solution will be as follows,

76.6 µg/L of As_2O_5 = 50 µg/L of Arsenic = 50 ppb of Arsenic

a. In order to prepare 500 mL of 50 ppb As stock solution, first you need to prepare 1L of 0.038 g/L of As_2O_5 solution i.e. add 0.038 g of As_2O_5 into 1L of distilled water.
b. Take out 1 mL of 0.038 g/L As_2O_5 solution and complete the volume to 500 mL with distilled water.

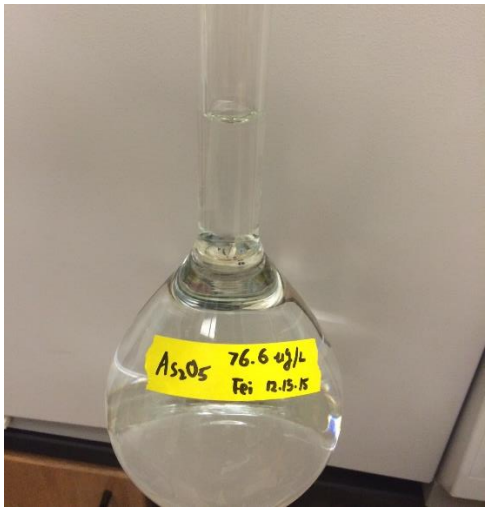


Figure 41 As_2O_5 solution with concentration of 76.6 µg/L of As_2O_5

- Potassium Iodide (KI solution)

In order to make potassium iodide solution, add 5 gm of ascorbic acid and 25 gm of potassium iodide (KI) into 50 mL of distilled water and stir the solution.

- Sample solutions

Sample solutions are the solutions used for testing arsenic concentration from filters, the volume to volume ratio of solutions containing in samples are as follows,

30% v/v HCl + 2% v/v KI solution + sample component

a. Take 25 mL of As stock solution for filtration and filter the solution with each membrane and collect sample solution.
b. Now take 17 ml of solution from each filtered As solution and complete the volume to 25 mL by adding 7.5 mL of HCl (12M) 0.5 mL of KI solution.

These solutions are made for every sample filter we are going to test.

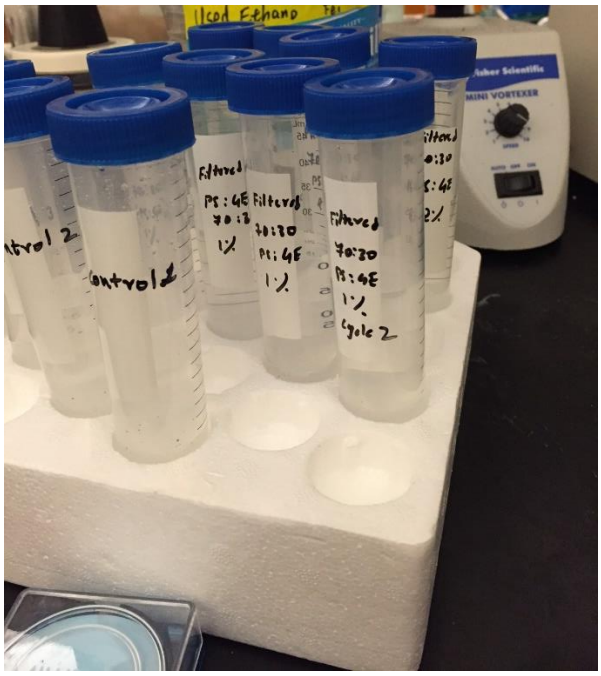


Figure 42 Sample solutions prepared after filtration

- Reductant

The concentration of reductant will be 0.7% m/v H_4BNa in 0.05M NaOH and it is prepared as follows,

a. Add 2 gm of NaOH in 300 mL of distilled water and stir the solution until you see homogenous mixture.

b. Add 7 gm of H_4BNa and complete the volume to 1000 mL with distilled water.

c. Filter the solution through 0.45 or 0.22 µm membrane. This solution needs to be prepared freshly each day and do not store it in a container.

- Reagent blank

The concentration of reagent blank will be 30% v/v HCl + 2% v/v KI solution and it is prepared as follows,

a. Add 300 mL of HCl (conc.) in 200 mL of distilled water.

b. Add 20 mL KI solution and complete the volume to 1000 mL with distilled water.

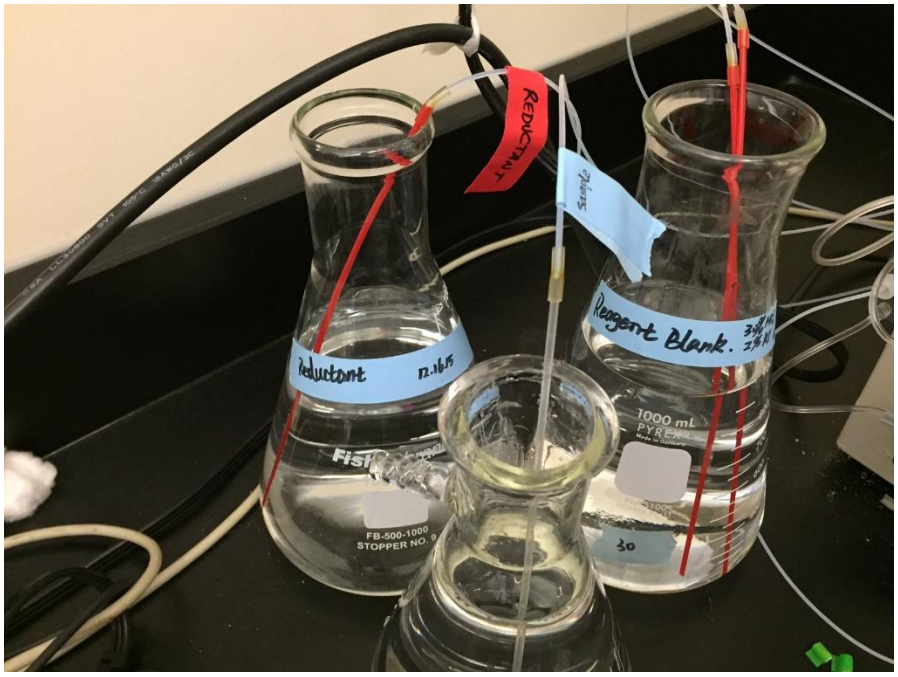


Figure 43 Reagent blank and reductant solutions

- Calibration solutions

The concentration of calibration solution will be 30% v/v HCl + 2% v/v KI solution + As standard solution. The final concentration of the calibration solutions always depends on the

expected concentration range of your samples. Starting from 1000 ppb As solutions, you need to dilute solutions for 100 ppb, 50 ppb and 10 ppb by adding 30% v/v HCl (12M), 2% v/v KI solution.

If the highest As concentration in your sample solutions is 50 ppb, you can prepare calibration solution in 25 mL of 10 ppb, 100 mL of 50 ppb and 25 mL of 100 ppb and use 50 ppb solution as drift monitor.

Table 3 Concentrations and final volumes of calibration solutions

Concentrations (ppb)	**10**	**50**	**100**
Total volume (mL)	25	100	25
Vol of HCl (mL)	7.5	30	7.5
Vol of KI solution (mL)	0.5	2	0.5
Vol of 1000 ppb As (mL)	0.25	5	2.5
Vol of DI water (mL)	16.75	63	14.5

Use 100 mL of 50 ppb As calibration solution as an example. To prepare it:

a. Prepare 10 mL of 1000 ppb As solution with 1000 µg/mL standard As solution. Dilute 10 µL of 1000 µg/mL As standard solution, and complete the volume to 10 mL with distilled water. (10 µL * 1000 µg/mL = 10 mL * 1000 ppb)
b. Now you need 30 mL of HCl (12M), 2 mL of KI solution, 5 mL of 1000 ppb As solution and add 68 mL of distilled water. (5mL * 1000 ppb = 100mL * 50 ppb)

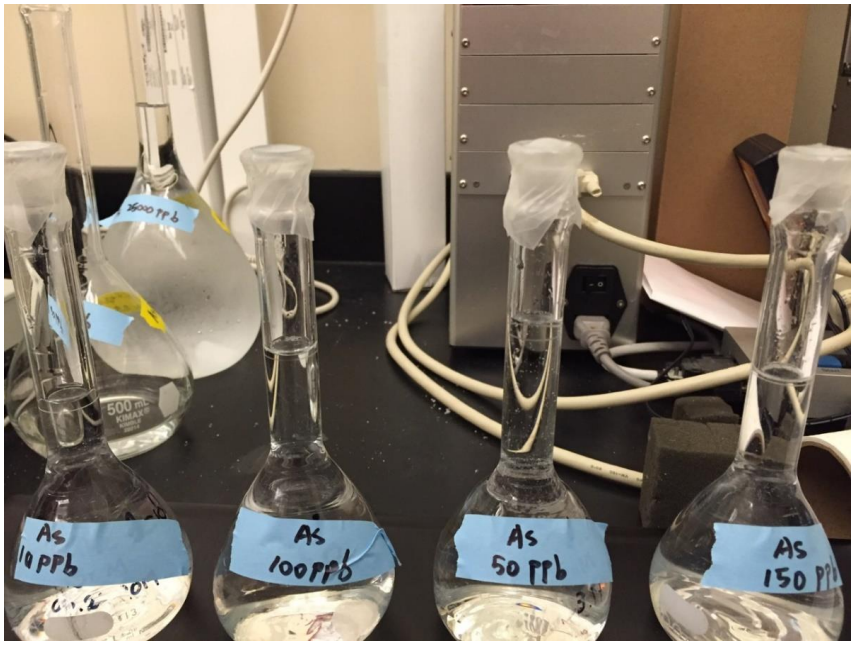


Figure 44 Calibration solutions

7.2.2 Filtration Procedure for Nano Fibers

This test requires Millipore membrane which is GVWP47 Nano filters having pore size of 0.22 µm and a diameter of 47 mm.

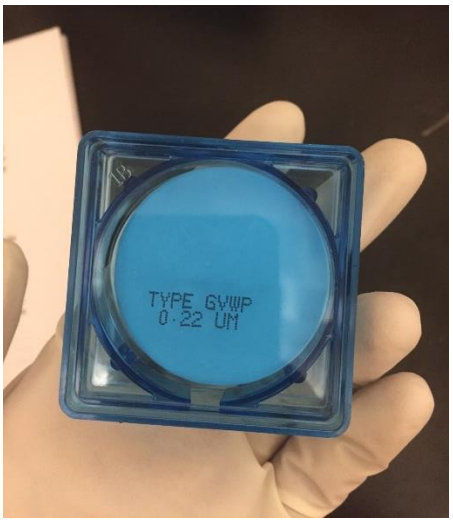


Figure 45 GVWP durapore membrane with pore size 0.22 µm

As from results I was unable to get a complete standalone membrane, so you have to test the fibers by putting fibers into glass pipets. First I filled up glass pipets with control sand. I

made triplets for each sample, in order to observe error graph. If you have 4 samples of fibers to test, then you need to prepare 3 glass pipets for each sample with 0.5 gm of pre-washed sand from Fisher scientific and then put enough fibers on the top of sand as shown in following figure 46.

Figure 46 Glass pipets with control sand and mucilage nanofibers [8]

As explained earlier, I have prepared 500 mL of 50 ppb arsenic solution which needs to be made from arsenic (V) oxide. As shown in fig 46, I have made 3 pipets for each sample and another 3 pipets only with control sand in order for a reference point after filtering arsenic solution using nanofibers. Once the columns are filled with fibers, then I made following set up to filter arsenic contaminated water using nanofibers.

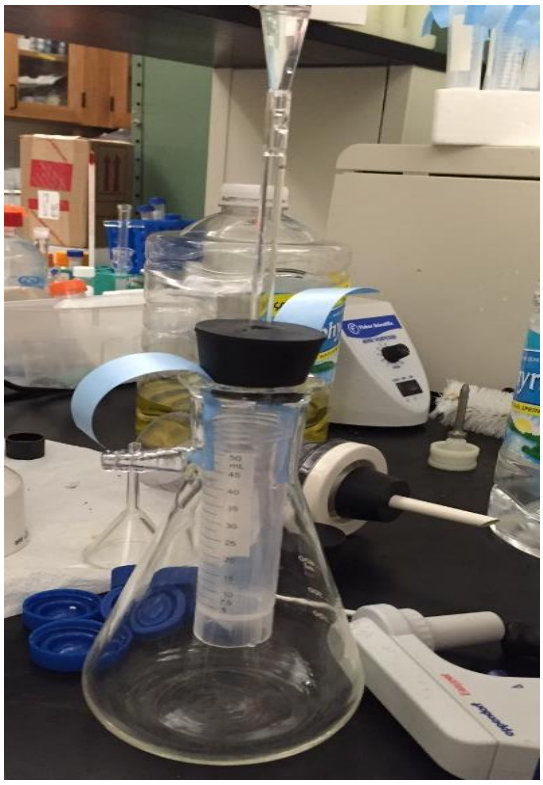


Figure 47 Filtration system setup for testing arsenic contaminated water

After having setup as shown in figure 47, I started flowing arsenic water through glass pipets and collected the sample solution from bottom in a centrifugal tubes. Make sure you install vacuum pump to the glass pipets and seal it with a rubber cork before running down arsenic water. Sample solutions will be collected for each nanofiber. These solutions will be analysed using PSA 10.055 Millennium Excalibur (PS Analytical).

7.3 Results and Summary

I have tested 4 different samples through AFS analysis in order to verify which sample is useful for arsenic filtration. Following are samples tested for AFS analysis

- ES 1.25 – Polystyrene: 1% GE mucilage (70:30 volume-volume ratio) without iron oxide
- ES 1.27 – Polystyrene: 0.5% GE mucilage (70:30 volume-volume ratio) without iron oxide

- ES 1.29 – Polystyrene: 1% GE mucilage (70:30 volume-volume ratio) with iron oxide
- ES 1.30 – Polystyrene: 0.5% GE mucilage (70:30 volume-volume ratio) without iron oxide

Each sample fiber will be loaded into glass pipette as explained earlier and arsenic water is allowed as a filtration layer, after collecting sample solution from filters I analysed the concentration of filtered solution and compared it with sample blank solution. Blank solution sample is nothing but just sample solution without any filtration.

7.3.1 Arsenic Removal from Polystyrene: Mucilage Nanofibers

For each sample we run three cycles, and also we used control sand for filtration and it is also run for 3 cycles.

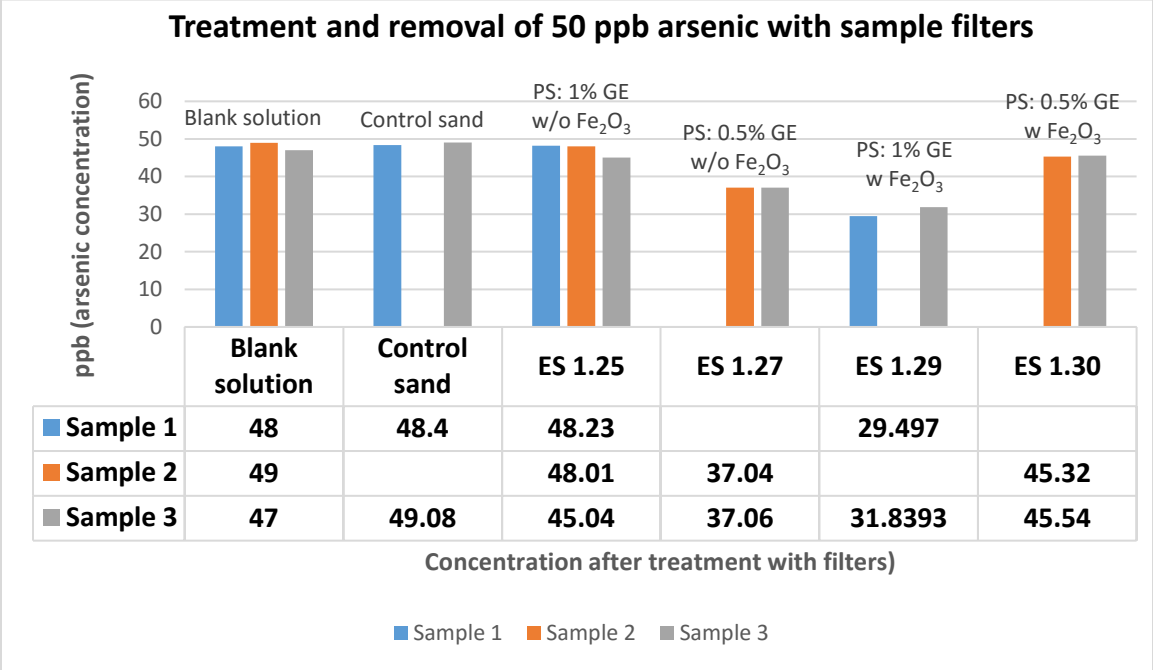
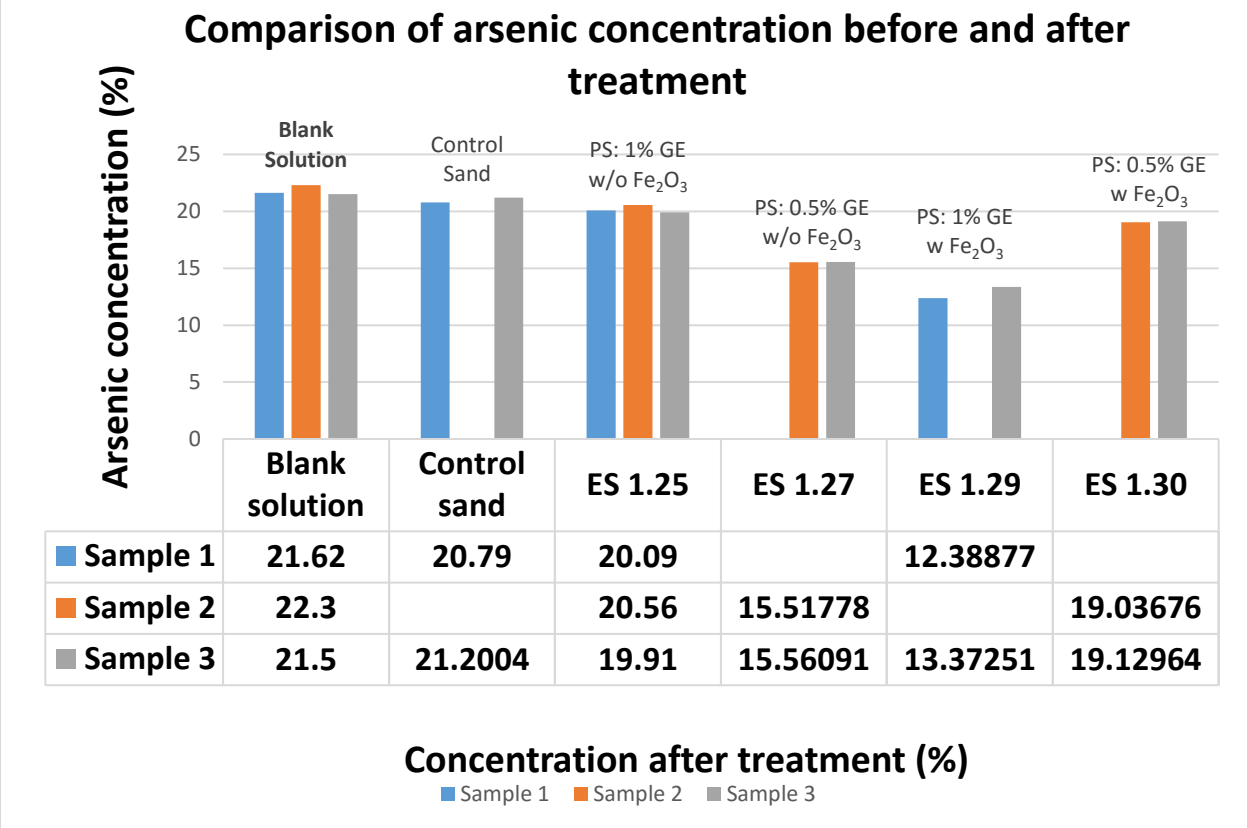


Figure 48 Treatment and removal of 50 ppb arsenic solution with filters

Initial concentration of the arsenic concentrated solution is 50 ppb, when I measure using PS analytical the output concentration of blank solution is about an average of 48 – 48.5 ppb. While doing experiment, I measured and calibrated the entire system before analysing each

sample. After analysing the data, I observed concentration of contaminated water (after filtration) from ES 1.25 is about 48 ppb which shows that polystyrene and 1% GE mixed in ratio of 70: 30 volume to volume ratio doesn't show much effect filtering arsenic contamination. But ES 1.27 sample has shown very good results by filtering 50 ppb arsenic contaminated solution to 37 ppb. And on further evaluations I observed that ES 1.29 has been able to reduce contamination from 50 ppb to average of 30 ppb which is the least amount of concentration so far reduced using nanofibers obtained by GE mucilage. ES 1.29 has iron oxide as a catalyst which increased the adsorption capability of the filters as studied earlier. And ES 1.30 only removed 5 ppb of contamination from 50 ppb. Hence we finally observed that polystyrene: 1% GE mucilage with iron oxide (2.7 mg/ml) had removed highest amount of arsenic contamination from water.



	Blank solution	Control sand	ES 1.25	ES 1.27	ES 1.29	ES 1.30
Sample 1	21.62	20.79	20.09		12.38877	
Sample 2	22.3		20.56	15.51778		19.03676
Sample 3	21.5	21.2004	19.91	15.56091	13.37251	19.12964

Figure 49 Comparison of arsenic concentration before and after treatment with nanofilters

Atomic fluorescence spectrometry (AFS) from PS analytical is used to evaluate nanofibers made from polystyrene and GE mucilage with and without iron oxide. 50 ppb concentrated arsenic contaminated water is used for filtration process. Contaminated water will be treated with all sample filters and I measured concentration of samples using PS analytical system. I observed that all the filters are hydrophobic in nature, hence I can do a second cycle for each individual filter. This will be tested in future. After analysing results from AFS testing, I observed that polystyrene: 1% GE mucilage (70:30 v/v ratio) with iron oxide (2.7 mg/ml) is able to remove 38% of arsenic contamination from water i.e., reduced concentration from 22% to 13%. At the same time, polystyrene: 0.5% GE mucilage (70: 30 v/v ratio) without iron oxide reduced about 28% of concentration.

In conclusion, if I can do more evaluations and obtain fibers with different ratios then I might be able to generate complete natural and biodegradable filters for arsenic treatment. My analysis shows that, in future if I vary concentration of iron oxide (best suggestion is to reduce concentration of iron oxide as observed) and also by varying concentration of GE mucilage I can be able to obtain good standalone membranes that can remove greater percentages of arsenic contamination from water.

CHAPTER 8: FOURIER TRANSFORM INFRARED SPECTROMETRY

8.1 Introduction

FTIR analysis is a tool with analytical mechanism in order to identify inorganic, organic and polymeric materials on the surface of Nano fibers. It uses infrared spectrum of absorption or emission of a liquid, solid and gas. It uses attenuated total reflectance (ATR) for analysing the sample. We use absorption spectroscopy to find functional groups on sample. It is used to determine how much amount of wavelength is being absorbed by sample at each wavelength. FTIR generates absorbance spectra that determines chemical bonds and molecular structure for the sample. Absorption spectra is plotted against frequency in which peaks determine functional groups such as alkanes, C-H bonds, ketones, C=O bonds etc.

8.2 Results and Analysis

The following graphs plotted between absorbance and wavelength represent FTIR results for all solutions. Peaks obtained while plotting wavelength describe functional groups assigned to sample material.

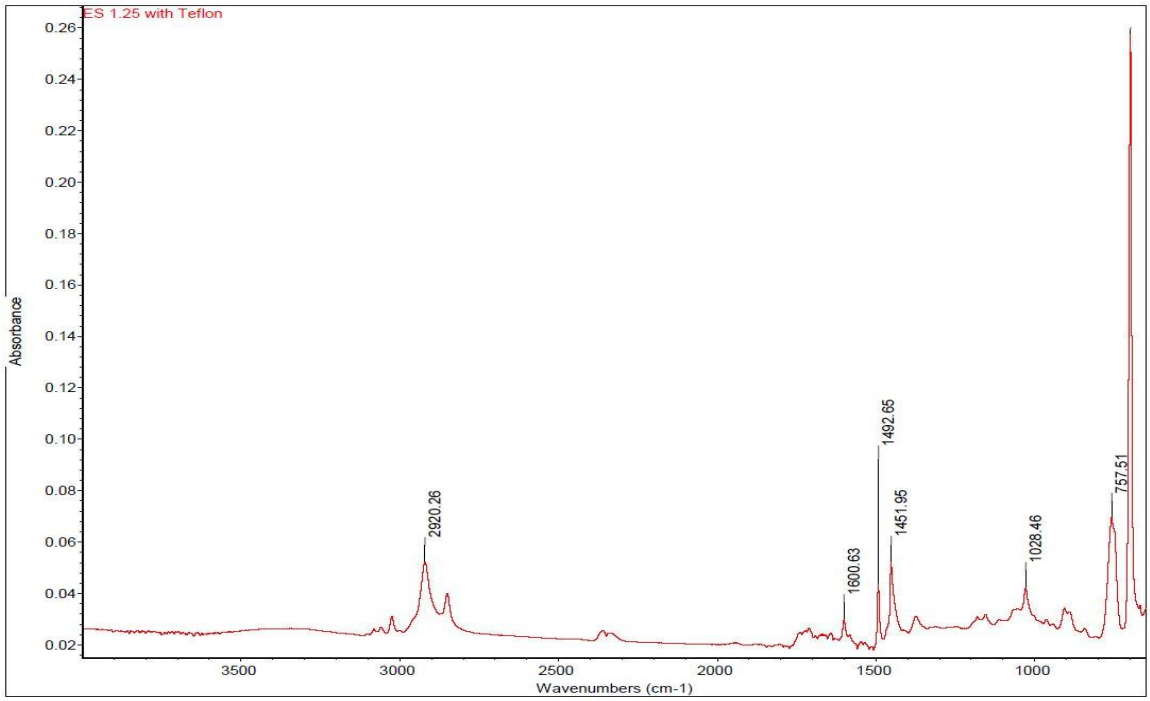


Figure 50 Infrared spectrum of polystyrene: 1% GE (70:30 v/v ratio)

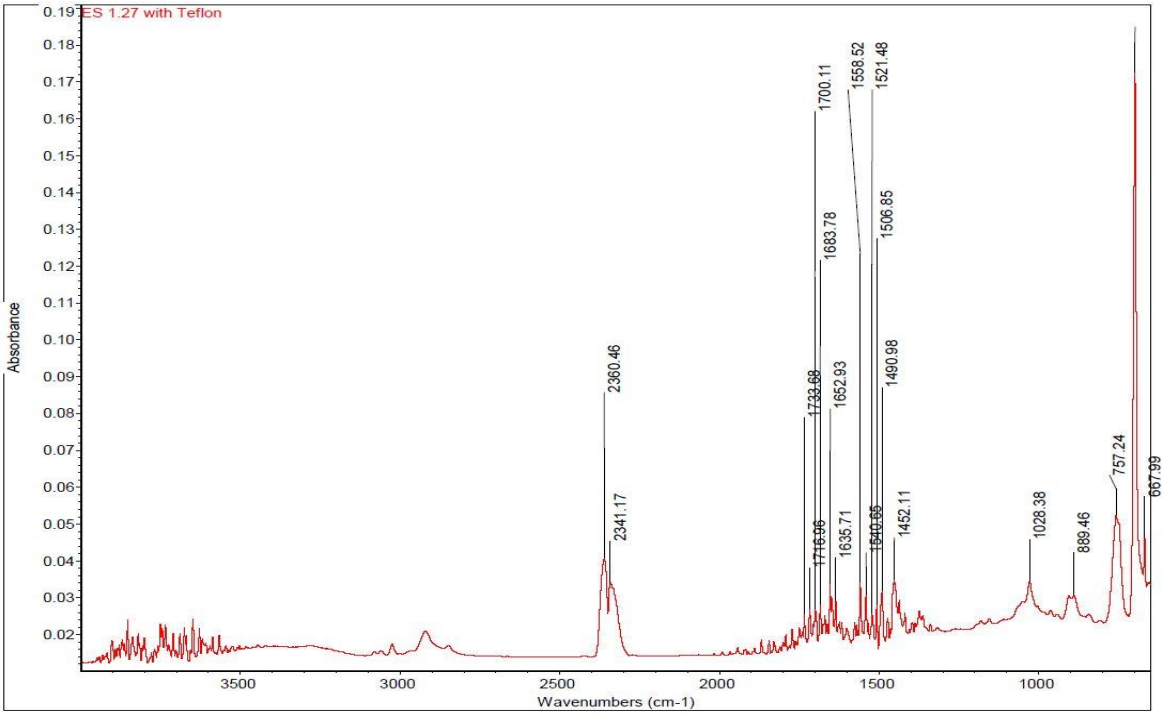


Figure 51 Infrared spectrum of polystyrene: 0.5% GE (70:30 v/v ratio)

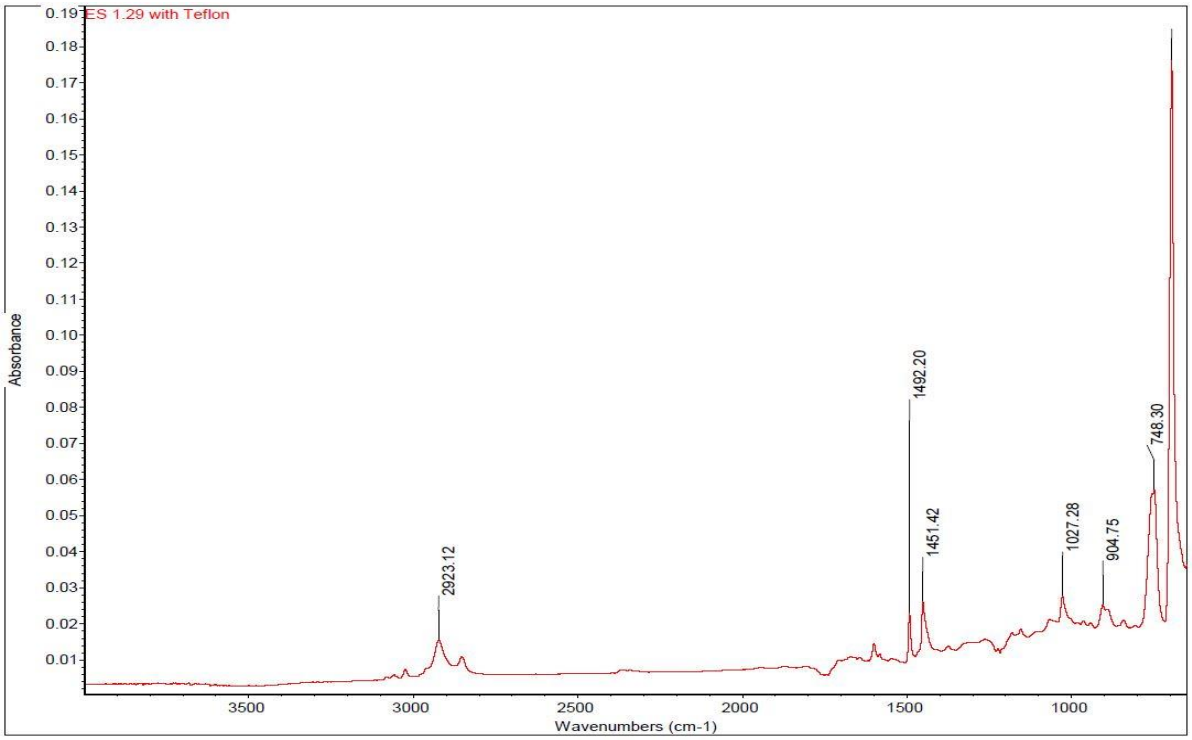


Figure 52 Infrared spectrum of polystyrene: 1% GE with Iron oxide (70:30 v/v ratio)

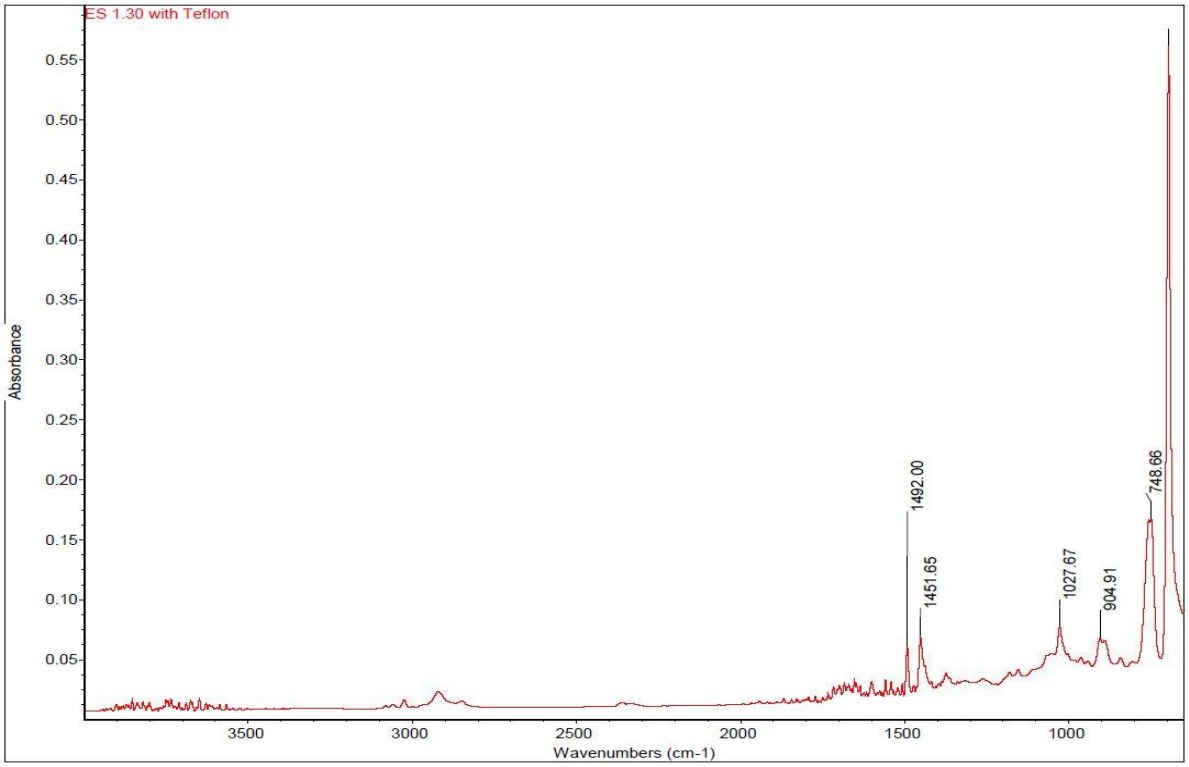


Figure 53 Infrared spectrum of polystyrene: 0.5% GE with Iron oxide (70:30 v/v ratio)

These graphs represent band peaks drawn between absorbance and wavelength representing IR spectra of the samples. There are two methods for performing FTIR i.e., transmittance and observance. I used observance. Wavenumbers will be obtained due to total internal reflection of light. Each wave number gives us a functional group that is present on the material and I figured it out from observance table.

Table 4 Functional groups detected and assigned to bands in Infrared spectra for sample polystyrene: 1% GE (70: 30 v/v ratio)

Functional groups	**Sample material bands**
Conjugated C=C	1600
Aromatic C=C	1492, 1451
Ether C-O	1028
Aromatic C-H (meta-disub. Benzene)	757
Carboxylic acid O-H stretch	2920

Table 5 Functional groups detected and assigned to bands in Infrared spectra for sample polystyrene: 0.5% GE (70: 30 v/v ratio)

Functional groups	**Sample material bands**
Carbonyl C=O	1733, 1716, 1700, 1683
Aromatic C=C	1521,1506, 1452
Ether C-O	1028
Aromatic C-H	889,757,667

Above two tables represent spectrum for samples Polystyrene with 1% GE and 0.5% GE. You can observe almost same functional groups are present on both samples. This is because I used same material but only difference in the weigh percentage of GE mucilage in the solution.

Table 6 Functional groups detected and assigned to bands in Infrared spectra for sample polystyrene: 0.5% GE (70: 30 v/v ratio) with iron oxide

Functional groups	**Sample material bands**
Aromatic C-C	1492, 1451
Ether C-O	1027
Aromatic C-H (meta substituted benzene)	904
Aromatic C-H (mono substituted benzene)	748

Table 7 Functional groups detected and assigned to bands in Infrared spectra for sample polystyrene: 1% GE (70: 30 v/v ratio) with iron oxide

Functional groups	**Sample material bands**
Aromatic C-C	1492, 1451
Ether C-O	1027
Aromatic C-H (meta substituted benzene)	904
Aromatic C-H (mono substituted benzene)	748
Carboxylic acid O-H stretch	2923

Table 6 and 7 represent IR spectrum for sample materials polystyrene with 1% and 0.5% GE mucilage along with iron oxide. These two samples have same spectra as they are made of same sample solutions except weight percentage of GE mucilage.

Functional groups	Gelling extract GE (cm^{-1})	Non-gelling extract NE (cm^{-1})
Hydrogen bonded O-H from alcohol and carboxylic acid groups	3350	3347
CH groups from aliphatic backbone	2937	2929
Carbonyl group from carboxylic acid (C=O)		1727
Carboxyl group from carboxylic acid	1609	1615
	1416 – 1331	1411 - 1317
Ether groups (C-O-C)	1250	1245
	1140	
CHOH of cyclic alcohols		1041

Figure 54 IR spectrum of gelling and non-gelling extract and their functional groups

Fig 54 represents functional groups present on the spectra of Gelling (GE) and non-gelling (NE) extracts [2]. From spectra of functional groups observed from tables 4, 5, 6 and 7, I can validate the presence of GE mucilage all around fibers. In conclusion, FTIR results show us the presence of OH bonds on mucilage nanofibers which helps us to remove arsenic contaminants from water.

CHAPTER 9: LIFE CYCLE ANALYSIS

9.1 Introduction

Life cycle analysis of a product analyse the environmental impact of entire process or a product over the life cycle. Life cycle analysis is carried out by using Life cycle assessment (LCA) tool. In this study, I will evaluate my solutions and the complete procedure to make the samples using LCA and analyse its environmental impacts. *Opuntia ficus indica* – cactus mucilage is used for water filtration systems. My thesis deals with cactus mucilage being mixed with polystyrene (polymer solution) and generating nanofiber meshes that can be used for water treatment. I have analysed four sample solutions, which are made using polystyrene, cactus mucilage and iron oxide. LCA compares polystyrene: 1% GE mucilage (70: 30 v/v), polystyrene: 0.5% GE mucilage (70: 30 v/v), polystyrene: 1% GE mucilage (70: 30 v/v) with iron oxide, polystyrene: 0.5% GE mucilage (70: 30 v/v) with iron oxide. In LCA you analyse about the whole procedure involving preparation of solutions such as power consumption involved in the process, equipment used for process and their power consumptions, materials used for the samples. Simapro7® is used for analysing all four samples. Method used for the process is ReCiPe Endpoint (I) V1.04. Once we entered every detail into the software about the procedure, software analyses global impacts such as climate heating, human toxicity, fresh water ecotoxicity, ozone depletion etc., due to samples.

9.2 Procedure

Life cycle assessment requires every detail of the samples such as materials used, energy consumption etc., in order to analyse environmental impacts. Libraries inside software contain almost every inventory used for the project. In case if you are unable to find a material which is not in the library, you have to create a product stage involving whole process involved for making the material. I created a few product stages for D-Limonene, GE mucilage as I am unable to find these inventory in library list. The functional unit considered for the entire procedure is 2 ml of sample solution used for making nanofiber mesh.

9.3 Results and Summary

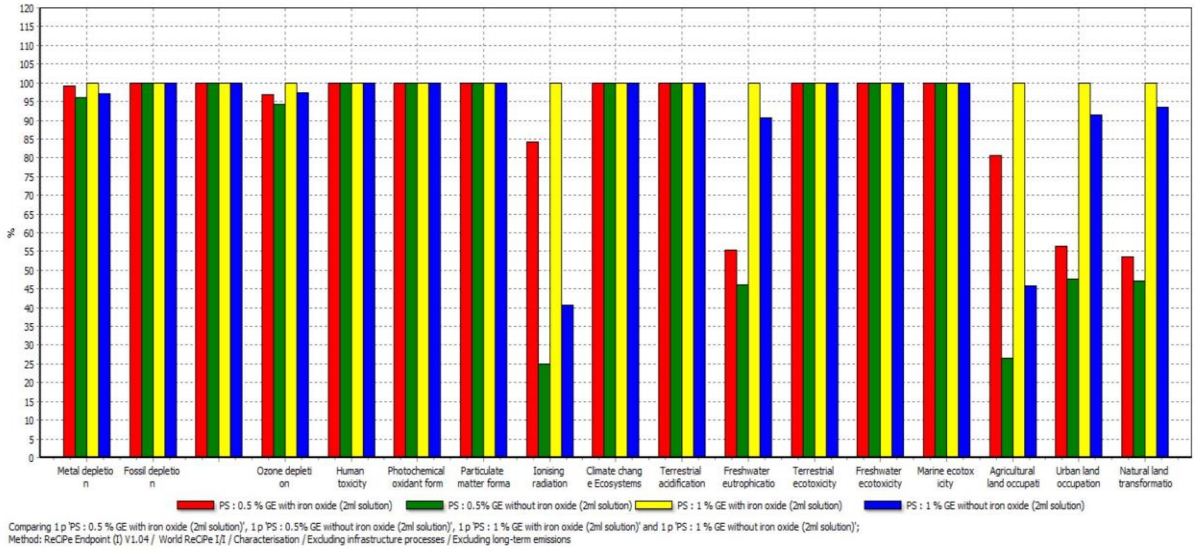


Figure 55 Life cycle analysis of characterization using method ReCiPe Endpoint (I)

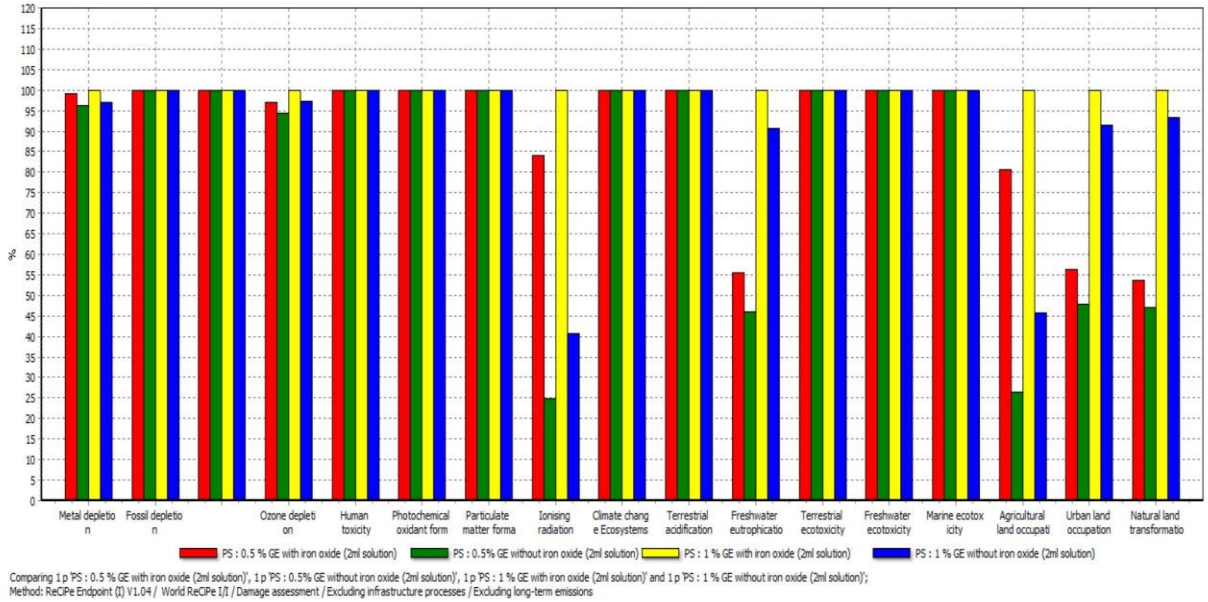


Figure 56 Life cycle analysis of damage assessment using method ReCiPe Endpoint (I)

In this analysis, I considered four samples:

- Polystyrene: 1% GE mucilage (70: 30 v/v) with iron oxide (yellow bar in graph)
- Polystyrene: 0.5% GE mucilage (70: 30 v/v) with iron oxide (red bar in graph)
- Polystyrene: 1% GE mucilage (70: 30 v/v) without iron oxide (blue bar in graph)
- Polystyrene: 0.5% GE mucilage (70: 30 v/v) without iron oxide (green bar in graph)

The characterization is done using method ReCiPe Endpoint (I). Damage assessment is also done using ReCiPe Endpoint (I). By comparing results of natural land transformation, fresh water eutrophication, ionising radiation, ozone depletion from all four samples, polystyrene with 0.5% GE mucilage showed very least impact on environment compared to other samples. But this is expected as it contains very less quantity of GE mucilage, same quantity of polymeric solution as other samples and there is no iron oxide. However solution, polystyrene with 1% GE mucilage and iron oxide had greatest environmental impact than the others but it is the solution which got best results.

CHAPTER 10: CONTRIBUTIONS TO THE TECHNOLOGY

Nanofibers have been generated for effective water filtration using Opuntia ficus-indica cactus mucilage and iron oxide. Polystyrene when mixed with 1% GE mucilage in the ratio 70: 30 by volume and iron oxide, nanofibers able to remove 38% arsenic contamination from water. Nanofibers generated are completely non-toxic and techniques used for generating fibers are cost efficient. Someday GE mucilage, polystyrene and iron oxide nanofibers potentially can be used for treating water contamination in ground water.

10.1 Results and Conclusion

Fibers obtained using polystyrene: 1% GE mucilage (70:30 by volume) with iron oxide has greatest environmental impact when compared to other samples. This is because it is the only solution which has large amount of GE mucilage and iron oxide. Hence this is expected. But I hypothesized that if I do a comparative LCA analysis with filters available right now in market for arsenic treatment, nanofibers obtained using GE mucilage have least impact on environment. For suppose consider SONO and Kanchan filters developed for rural areas in Bangladesh, they use a layer of rusted iron nails for treating arsenic contamination but in this thesis I only use very minute amount of iron oxide in order to increase adsorption capability of filters. And also as I stated earlier, less viscous solution will result into thinner fibers and it leads to effective water filtration has been proved. PS with 1% GE mucilage (70: 30 by volume) and iron oxide had fiber thickness of 233 nm which is the thinnest compared to other samples able to remove highest amount of arsenic contamination (38%) from water.

CHAPTER 11: SUMMARY AND FUTURE WORK

In conclusion and evaluating whole functionality of nanofibers obtained by polystyrene and GE mucilage with and without iron oxide, there is a wide scope involved in future for creating biodegradable nanofilters for water filtration. By conducting atomic fluorescence spectrometry(AFS) using PS analytical, I determined that arsenic contamination in water can be removed by forming nanofiber membranes using polystyrene with 1% and 0.5% GE mucilage (70: 30 v/v ratio). I also observed that by adding iron oxide to the fibers, it clearly improved adsorption capacity of fibers. When I used 50 ppb concentrated arsenic contaminated water for treatment using filters.

Results show that PS: 1% GE mucilage (70: 30 v/v) with iron oxide on performing AFS analysis, it removed about 38% of arsenic contamination from water. And also PS: 0.5% GE mucilage (70: 30 v/v) able to remove 28% of arsenic contamination. These fibers are natural and biodegradable. The technique and procedure used for fabricating these fibers is really cheap by comparing to several filters in the industry. If I can evaluate this work further, I can really make a nanofiber mesh which can completely remove arsenic contamination from water. But for this analysis, I need more literature work and also I need to perform different characterizations. By changing concentration ratios, I can also be able to get much thicker membranes for filtration. However from my thesis, I finally concluded that *Opuntia ficus-indica* can be used for arsenic treatment. This natural ability of the plant can be enhanced by adding catalysts, so that adsorption capacity of the nanofiber meshes can be increased. But still there has to be more

testing phenomena where I can study how really mucilage is getting involved or interacts with arsenic. I can also test these filters' efficiency by observing some industrial filters.

Fourier transform infrared spectrometry gives us functional groups present on the fibers. Results will be analysed based on wavelengths. This test helps us to find bonds present on the mucilage nanofibers. I observed various bonds present on the fibers which show us combination of several sugars. O-H bonds present on the solution helps in adsorption of arsenic contamination from water. And also presence of iron oxide also improved adsorption capacity of nanofibers. SEM images show us that mucilage and iron oxide traces around nanofiber mesh. Contact angle measurements show that polystyrene when mixed with GE mucilage, nanofibers are completely hydrophobic in nature both with and without iron oxide. I also analysed environmental impacts of the solution where we can conclude that D-Limonene, polystyrene and GE mucilage is less harmful to environment.

Future work mainly deals with how I can be able to generate fiber meshes of high thickness and less beads. By varying concentration of GE mucilage and also varying concentration of iron oxide in solution, I can generate fibers to eliminate arsenic contamination from water and it can also be used to treat other contaminants in water. I also need to work in order to improve the efficiency and longevity of nanofibers, so that nano meshes can treat arsenic contamination in several cycles. Thus I can generate nanofibers using GE mucilage and also be able to improve arsenic adsorption capacity of nanofibers by adding iron oxide. PS: 1% GE mucilage with iron oxide able to reduce arsenic concentration to 0.029 mg/L (29 ppb) but further work needs to be done in order to achieve WHO limit which is 0.01 mg/L (10 ppb). And from SEM analysis, I hypothesize that GE mucilage and iron oxide particles have been wrapped

together by fibers (fig 57, 56) but there is no proper evaluation done. Hence a microscopic analysis is needed in order to evaluate what materials are present within beads of nanofibers.

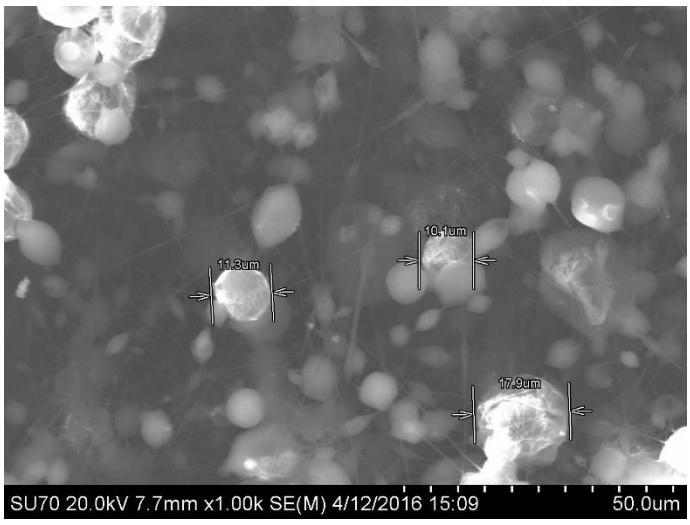


Figure 57 Nano mesh showing beads at 1K magnification

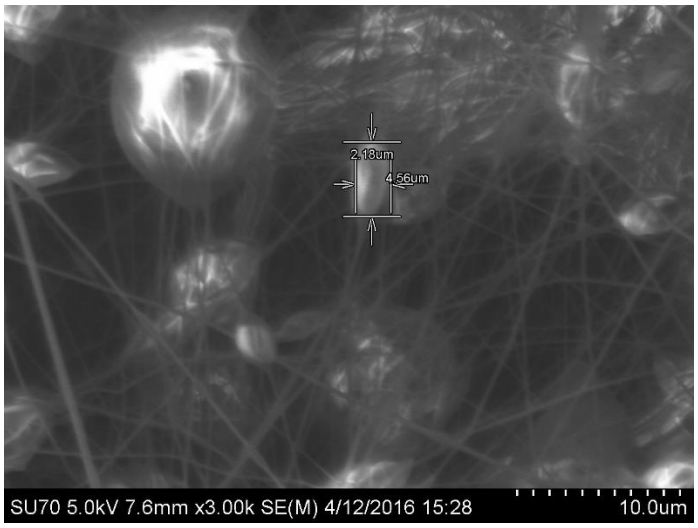


Figure 58 Nano mesh showing beads at 3K magnification

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