

IDENTIFICATION OF MEMBRANE FOULANTS IN NATURAL WATERS

WRRI PROJECT REPORT

Prepared by

KHALID MEHBOOB
Department of Civil Engineering
University of New Mexico

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The University of New Mexico

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Khalid Mehboob

B.E., Civil Engineering, Nagpur University, 2000

ABSTRACT

The purpose of this project was to evaluate the effect of dissolved calcium and silica on fouling of membranes. Previous researches have shown that calcium forms a complex with organics and promotes fouling. Four different membranes, cellulose acetate, polyethersulfone, polypropylene and polyvinylidene fluoride, were chosen to be tested. Initially, water samples were collected from the Rio Grande in Albuquerque, New Mexico. The feed water was tested for calcium, silica and organic concentration and permeates were also analyzed for the same. Flux decline for each membrane was monitored and plotted. Further analyses were done with scanning electron microscope and Fourier transform infrared spectroscopy to study the surface deposits on the membranes. The results obtained were not as expected. Dissolved calcium and silica did not show any effect on fouling of membranes. Instead, it was the soil (clay) that caused major fouling and that too, by cake layer formation on the membrane surface.

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1 Introduction

Membranes are one of the many new technologies being used for water treatment. Since the inception of this technology, it has grown to be a multi-billion dollar industry and is still growing. Treatment of water using membranes is a relatively new technology and is still in its infancy. This process is so effective in removing contaminants from water that it can even remove the smallest of viruses and therefore, pathogen-free water can be supplied to consumers. Membrane treatment process for water can replace many stages in a conventional treatment plant as shown in Figure 1.1. Industries that require ultra-pure water for their processes also use membrane treatment.

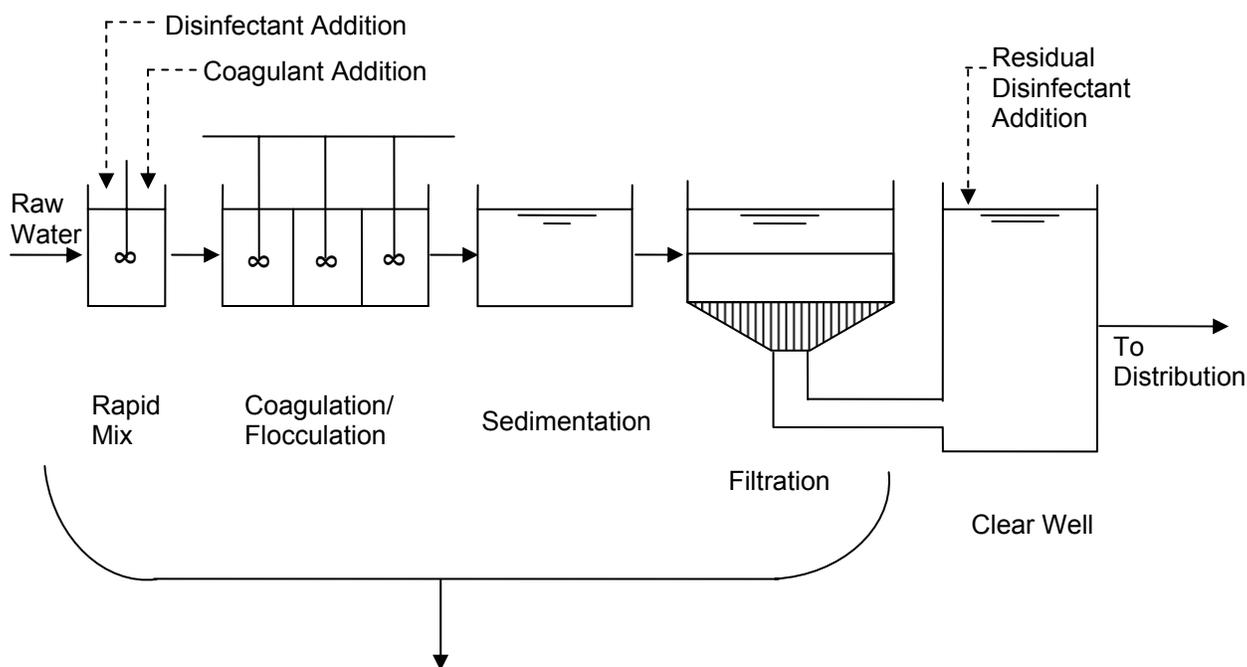


Figure 1.1. Conventional water treatment unit processes replaced by Microfiltration.

(Adapted from Peter E. Odendaal et. al. Water Treatment Membrane Processes)

An efficiently running membrane filtration system must have a reasonable and stable flux and the energy consumption should be as low as possible. To achieve these goals, the process must be optimized with respect to permeate flux, pressure, and temperature. As stated previously, extremely high permeate flux is not a goal in itself, and can lead to unstable operation. A generalized drawing of flux as a function of pressure is shown in Figure 1.2. It is a much-generalized drawing, but nevertheless basically correct. [1].

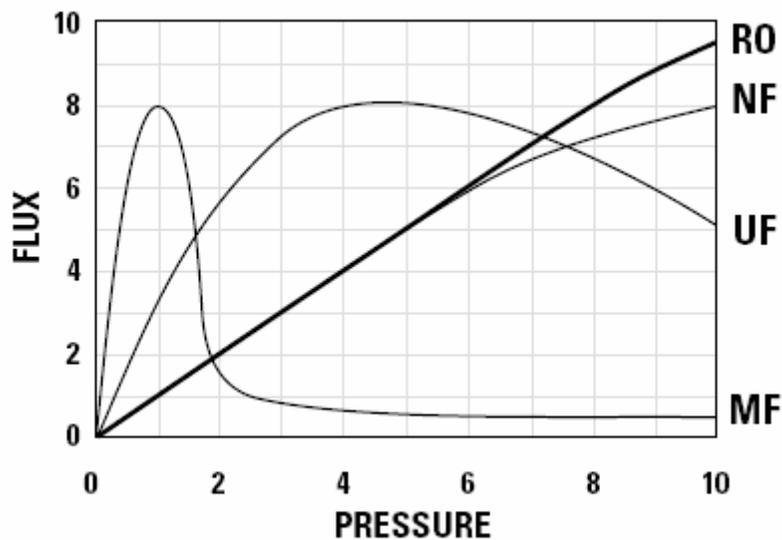


Figure 1.2 Flux as Function of Pressure (Adapted from Membrane Filtration Handbook Practical Tips and Hints).

Membrane treatment processes are categorized based on their pore size and ability to remove contaminants. They are categorized as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). Microfiltration is the oldest of the four pressure driven membrane technologies. Initially, microfiltration was primarily used for laboratory and industrial purposes. It

basically followed the depth filtration phenomenon so particles and microorganisms are entrapped within the internal structure of the membrane. However, it should also be noted that most microfiltration membranes do not use depth filtration. Microfiltration membranes have the largest pores and are generally the least costly option. The thickness of microfiltration membranes can range from 10 – 150 μm with a pore size of 4 – 0.02 μm . As a consequence of its larger pore size, it can be operated under very low pressure conditions.

Objective:

The primary objective of this research will be to investigate the effect of dissolved calcium and silica present in water on the removal of TOC using organic microfiltration membranes and to identify the conditions under which this phenomenon will be of more influence. Specifically, the following questions will be addressed:

1. How will the presence of calcium and silica in raw water affect the removal of TOC? What will be their effect on the rate of fouling of membranes? What will be their effect on the removal of TOC? Do they foul the membranes on their own or aid in fouling when present along with other organic colloids?
2. What is the effect of membrane material chemistry on flux decline, focusing on the common material of polypropylene (PP), polyethersulfone (PES), cellulose acetate (CA) and polyvinylidene fluoride (PVDF)

membranes? Can the fouling of specific membrane products be related to specific material properties of the membrane like Hydrophobicity (determined through previous research)?

3. How will varying feed pressure affect the membrane behavior with respect to flux decline and fouling?

2 Project Approach

The project objectives will be achieved by following the approach given below:

2.1 Samples

Two types of water samples were used in this project. One was deionized water with calcium and silica added in known quantity and the other was settled and prefiltered Rio Grande river water. Prefiltration was done with 1-micrometer glass fiber filter to remove particulate matter. Thus, permeate had only colloidal and dissolved matter. The samples were analyzed for pH, calcium concentration, silica concentration, and TOC concentration. These water samples were stored in a refrigerator at 4°C for future use.

2.2 Filtration Tests

The prefiltered water sample was filtered through four different organic microfiltration membranes in a dead end filtration cell and the flux was continuously monitored. The experiments were performed at two different feed pressures. Flux decline during filtration will indicate whether fouling is taking place. The experimental setup is illustrated below in Figure 2.1. The used membranes and permeates will be collected for analysis.

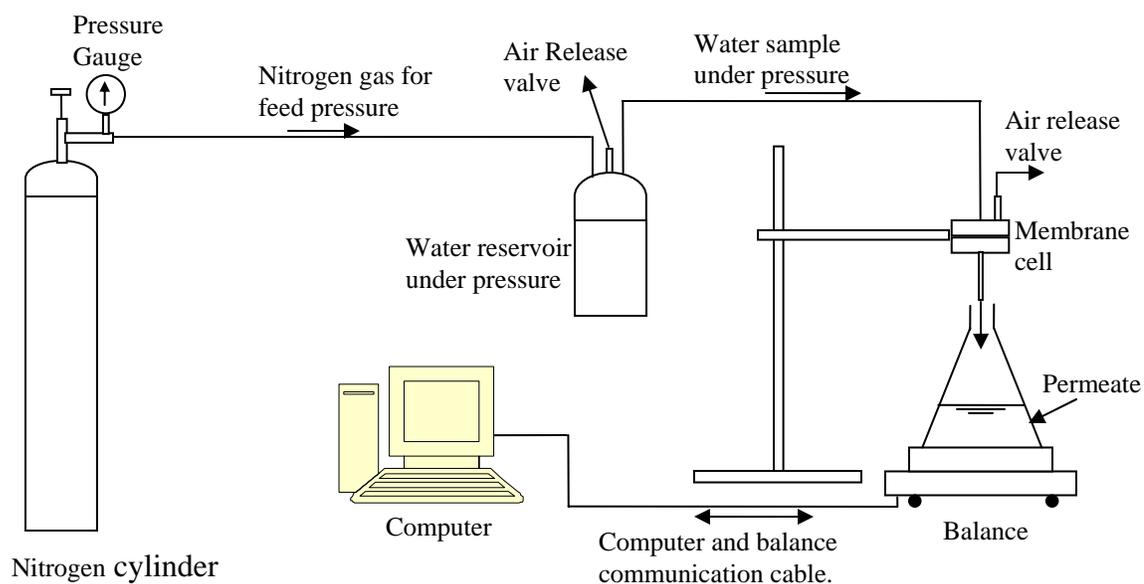


Figure 2.1 Schematic of Experimental Setup.

2.3 Analysis

The membranes will be analyzed with Fourier Transform Infrared Spectrometry (FTIR) and Scanning Electron Microscope (SEM) for adsorbed components on the membrane. Permeates will be analyzed with Tekmar Dohrmann Total Organic Carbon Analyzer, Varian UV/Visible Spectrophotometer and Flame AA or Graphite furnace AA for TOC, dissolved silica and dissolved calcium.

After correlating experimental conditions and analyzing results for feed water, permeate water and the membranes, conclusions can be drawn on how calcium, silica and TOC are affecting membrane fouling. Thus, their role in fouling of membranes can be identified.

3 Literature Review

3.1 Microfiltration Membranes

Microfiltration (MF) ideally removes only suspended solids; however, there is quite a gap between real life and this ideal situation. In spite of many benefits of using membranes, membrane fouling (clogging of membranes by contaminants) is an issue that has not yet been resolved. Though there has been substantial progress in understanding the variables involved in the fouling of membranes, the causes of fouling are still not clear. Many studies have been done on this issue to make membranes more efficient. However, the efficiency depends on the feed quality and other operating parameters.

Microfiltration membranes can be fouled very seriously by natural waters. Fouling can cause these membranes to rapidly lose 90 – 95 % of their permeability. In spite of extensive research attempting to relate membrane fouling with the contaminants present in natural waters, it is still not clear what causes membranes to foul. The factors considered to affect fouling of a membrane are [2]:

1. Membrane Properties:
 - Hydrophilicity.
 - Surface topography.
 - Charge on the membrane.
 - Pore size.

- Surface modification.
2. Solute Properties:
- Proteins
 - Salts
 - pH
 - Lipids, fats and oils.
 - Antifoams.
 - Humic substances.
3. Process Engineering:
- Temperature.
 - Flow rate and turbulence.
 - Pressure.

There are many types of microfiltration membranes available in the market. These membranes can differ in their geometries and their chemical composition. Newer membranes are being developed with new materials that are superior to their predecessors in performance and reliability.

3.2 Membrane Properties

To have an understanding of the behavior, performance and limitations of a particular membrane when used in certain applications, it is important to understand some crucial aspects of membrane chemistry. There are over 130 materials (polymers, composite and inorganic) that have been used to

manufacture membranes; however very few have been used commercially. Of these materials, four of them will be discussed in the following sections:

3.2.1 Cellulose Acetate

Cellulose acetate (CA) is a classic membrane material. It is prepared from cellulose by acetylation that involves reaction with acetic anhydride, acetic acid and sulfuric acid. Cellulose acetate and its derivatives have several advantages for use as membranes materials [2]:

1. Hydrophilicity – makes the membrane less prone to fouling
2. Wide range of pore sizes can be manufactured
3. Relatively easy to manufacture
4. Low cost material

There are many “die hard” membrane users who insist on buying “the same membrane as last time,” and who simply stay with CA because it works for them. However, the membranes made from cellulose acetate or its derivatives like cellulose diacetate or cellulose triacetate have a number of limitations [1, 2]:

1. Capable of operating in a fairly narrow operating temperature range. It is recommended to maintain the temperature below 30°C.
2. It can tolerate a narrow range of pH and the recommendation is from 4-8.
3. CA has poor resistance to chlorine as chlorine oxidizes cellulose acetate and weakens the membrane, thus opening up the pores.

4. CA can have a gradual loss of membrane properties under high pressure, a process called “creep”.
5. An inherent weakness of CA is that it can be eaten by microorganisms.

3.2.2 Polyethersulfone

This material is quite stable because of electronic attraction of resonating electrons of $-\text{SO}_2$ group between adjacent aromatic groups. The oxygen molecules in this group each have two pairs of unshared electrons to donate for strong hydrogen bonding with solute or solvent molecules [3]. Polyethersulfone is widely used these days because of the following favorable characteristics [1, 2]:

1. PES has high temperature stability and up to 75°C can be used routinely. Some manufactures also claim their PES membranes can be used up to 125°C .
2. It has wide pH range tolerance and can be continuously exposed to pHs from 1 to 13 thus making it advantageous for cleaning purposes.
3. It has good chlorine resistance and can be exposed to 50 ppm chlorine used for short-term storage of the membranes. However, prolonged exposure to high chlorine levels can damage the membranes.
4. It is quite to fabricate PES membranes in different configurations and modules.

5. It demonstrates good chemical resistance to aliphatic hydrocarbons, fully halogenated hydrocarbons, alcohols and acids.

Even though, PES membranes have many advantages, they have some disadvantages, too. The short-comings of PES membranes are listed below:

1. The membranes are low pressure type and cannot be operated under high pressures.
2. Its hydrophobicity makes it more prone to fouling as compared to other hydrophilic membranes such as CA.
3. PES does not offer much resistance to aromatic hydrocarbons, ketones, ethers and esters.

3.2.3 Polypropylene

Polypropylene can be made by thermal inversion process or by melt-extruding and stretching. This membrane is hydrophobic, chemically very resistant polymer and can withstand moderately high temperatures. However, it has a tendency to creep [1, 2].

3.2.4 Polyvinylidene Fluoride

This is a traditional membrane material, but not widely used because it is difficult to make membranes with good and consistent separation characteristics. Its main advantage is its high resistance to hydrocarbons and oxidizing environments. It is chemically almost as resistant as Teflon. PVDF

can tolerate high temperatures and is known to operate at 95°C without any problems. It can also tolerate a wide range of pH from 0 to 12. It has better resistance to chlorine than the polysulfone family. This membrane is very hydrophobic although, some membranes have its surface modified to so that it can be wetted.

The first microfilters were of the depth filtration type in which particles and microorganisms were trapped within its internal structure. Depth filtration microfilters have had limited application for primary treatment of drinking water as a result of its life cycle or loss of efficiency. As a distinction to the depth filtration concept, microfiltration provides absolute removal of contaminants based on retention on the membrane surface and can be called as sieving. As microfilters have large pore sizes, from 4 – 0.02 μm , they can be operated under very low pressure conditions to remove particles and microbes. However, research shows that microfiltration does not remove contaminants strictly based on pore size of the membrane in all cases. A cake layer consisting of particles present in the feed can be formed on the membrane surface and provide additional removal capabilities.

Gekas and Hallstrom [4] used a synthetically prepared mixture for feed containing two kinds of components: one was a biopolymer like BSA protein and the other was silica particles ranging in size from 600 nm to 800 nm. They observed during cross-flow microfiltration experiments that the flux decline was higher with the presence of silica and protein as compared to protein in the

absence of silica. They were also able to conclude that the flux recovery in case of silica particles was up to 90% as compared to the case of proteins. So it can be said that the proteins resulted in irreversible fouling mechanism and the opposite was true in case of silica particles. A study done by Persson et. al. [5] also considered model solutions prepared for use as feed water. They used spherical Stober sols, i.e. colloidal silica with a diameter of $500 \text{ nm} \pm 30 \text{ nm}$ and Lacprodan 80 from Denmark Proteins to prepare the feed solution. They did a study on flux versus time for different commercially available membranes with different surface properties with the help of hydrophobic and hydrophilic silica, whey protein and a mixture of silica and protein. They observed a tendency of the hydrophobic particles to build clusters and that flux was lower with hydrophilic particles than with hydrophobic particles. They also observed that with hydrophilic particles, increased feed pressure caused significantly higher flux. They concluded that irreversible protein fouling can be avoided by mixing the protein with hydrophilic particles. As expected, they did not find any silica in permeate because the size of the silica particles were larger than the pore size of the membranes. Therefore, silica resulted only in cake layer build up on the membrane surface.

After studying several different organic and inorganic molecules, Lahoussine–Turcaud et. al. [6] concluded that organic substances like humic and tannic acids have a greater effect on the flux decline than inorganic colloids. Humic substances are complex macromolecular products, which are products of the chemical and biological degradation of plant and animal residues including

lignin, carbohydrates, and proteins [7]. Humic substances can be divided into three broad categories: humic acids, fulvic acids and humin depending on their ability to dissolve in solutions of different pH. Humic acids are heterogeneous mixture of aromatic as well as aliphatic components with carboxylic acids (COOH), phenolic alcohols (OH) and methoxy carbonyls (C=O) as the three main functional groups. Humic acid fouling of membrane increases in the presence of multivalent ions as they have a tendency to bind with them and form a complex [7]. Nystrom et. al. [7] also found out that humic acid fouling increased when the pores were larger or when the membranes were charged so they attributed dramatic flux decline to electrostatic interactions between the negatively charged humic acid and the positively charged inorganic membranes.

Jucker and Clark [8] showed that humic acid adsorption on hydrophobic ultrafiltration membranes was greater at low pH. This was attributed to a reduction in net charge and an increase in hydrophobicity of humic acids caused by neutralization of acid side groups at low pH. They also showed that this phenomenon was enhanced in the presence of Ca^{2+} , possibly due to electrostatic shielding of divalent cation. Schafer et al. [9] also reported significant irreversible fouling during nanofiltration of surface waters with natural organic matter and that the extent of fouling was greatest in the presence of high concentrations of calcium.

Kaiya et. al. [10] tested water samples from a eutrophic lake in a dead end filtration setup. The water sample was directly fed into the treatment system with no pretreatment. They used hollow fiber microfiltration membrane modules made

of hydrophilic polyethylene with an outer diameter of 410 μm and a nominal pore size of 0.1 μm . Filtration was carried out under a constant flow rate and the membranes were scrubbed for 1 minute in every hour of operation. On analyzing the extracts from the membrane surface, they found that TOC and manganese were the major fouling materials. Ca and Si along with other materials also contributed to fouling but in less significant amounts. On further analysis of the extracted fouling materials and the recovery of membrane permeability, Kaiya et al. [10] concluded that irreversible fouling is mainly caused by organic matter. This was in contrast with the findings of Mallevalle et al. [11] where they reported that more than 80% of the constituents of the cake formed on membrane surface comprised of Si, Ca, Al, and Fe.

Lin et al. [12] studied filtration of an Aldrich humic acid solution through a 100kD polysulfone membrane. They observed a significant (up to 50%) and largely irreversible flux decline that was caused by irreversible adsorption of the largest molecular weight species within the membrane pores. More recent studies on humic acid fouling during microfiltration have shown that humic acid fouling plays a critical role in the fouling process [13]. They also showed that the concentration polarization effect on the flux decline was very small. Yuan and Zydney [13] performed some experiments with 100kD prefiltered humic acid solution after storage for 24 hours at either 50°C or 4°C in deionized water or at 4°C in the presence of 1mM Ca^{2+} . They observed that the rate of flux decline for the solutions stored at 50°C and 4°C in the presence of Ca^{2+} was quite dramatic, mostly within the first hour of filtration run. This is due to the physical deposition

of large humic acid aggregates followed by the non-aggregated humic acid macromolecules. They also found that the 100kD prefiltered solution stored at 4°C without Ca²⁺ caused almost no increase in fouling. They concluded that both Ca²⁺ and high temperature increases the rate of fouling during microfiltration of humic acid solution.

Teng et. al. [14] used sea water to conduct their experiments and showed that a significant amount of colloidal silica can be removed with hollow fiber PES ultrafiltration membrane (pore size of 0.01 µm) along with a small percentage (16%) removal of organics. They also performed the same experiments with hollow fiber PVDF microfiltration membrane (pore size of 0.1 µm) and found that a moderate removal of colloidal silica was possible but approximately 40% rejection of organics was achievable. Moreover, membrane surface morphology also plays an important role in membrane fouling; rough surface enhances the deposition of colloids on the membrane surface resulting in severe fouling as compared to a smooth surface membrane [15].

It has been found that one major contributor to fouling are particles that are much smaller than the pore size of the membranes, ranging from about 3 – 20 nm in diameter [16]. Howe and Clark [17] showed that colloids are a major contributor to fouling of membranes. They showed that flux decline is dependent not only on the type of contaminant in water but also on the type of membrane used for filtration. Schafer et. al. [18] conducted experiments on GVHP and GVWP microfiltration membranes with surface water containing colloids and natural organic matter, largely composed of humic substances. They observed

that calcium played different roles in fouling of membranes. In the presence of inorganic colloids, calcium contributed to an increase in flux where as calcium led to a decreased flux in the absence of inorganic colloids.

4 Methods And Materials

4.1 Sample Collection

Water samples were collected from Rio Grande River in Albuquerque, New Mexico. Samples were collected from knee-deep water, facing upstream. Water was collected into 3 Gallon Nalgene containers by submerging the whole container but keeping the opening just below the water surface.

4.2 Membranes Used

Four different types of microfiltration membranes were used in this project. All the membranes were flat sheet type and 47 mm in diameter. The details of the membrane are given below in Table 4.1.

Table 4.1 List of different membranes.

No.	Code	Membrane Type	Manufactured by	Purpose
1	GF	Glass Fiber (1 μm)	Gelman Sciences	Pre-filtration
2	CA	Cellulose acetate	Osmonics Inc.	Filtration
3	PES	Polyethersulfone	Osmonics Inc.	Filtration
4	PP	Polypopylene	Osmonics Inc.	Filtration
5	PVDF	Polyvinylidene Fluoride	Osmonics Inc.	Filtration

4.3 Chemicals Used

Chemicals were used to prepare stock solutions, treat membranes and to adjust the pH of the water sample, as listed in Table 4.2.

Table 4.2 List of Chemicals.

No.	Chemical	Purpose
1	Methanol	Wet membranes to allow water flow.
2	Hydrochloric acid	Lower the pH of water sample.
3	Sodium hydroxide	Increase the pH of water sample.
4	Calcium chloride	Stock solution for calcium (573.24 mg/L).
5	Sodium silicate (meta)	Stock solution for silica (1000 mg/L).

4.4 Equipments and Machines Used

The equipments used for experiments in this project are listed in Table 4.3 and photos are shown in FiguresFigure 4.1 and Figure 4.2.

Table 4.3. List of equipments and Apparatus.

No.	Equipments/Apparatus	Manufacturer
1	pH meter	Orion – Model 720A
2	Pressure vessel for water sample	Amicon (800 mL, 75 psi max.)
3	Steel pressure vessel for DI water	Alloy Products Corp.
4	Weighing scale	Mettler Toledo – PB3002S
5	Gas line low-pressure filter holder	Fisher Scientific (275 psi max.)



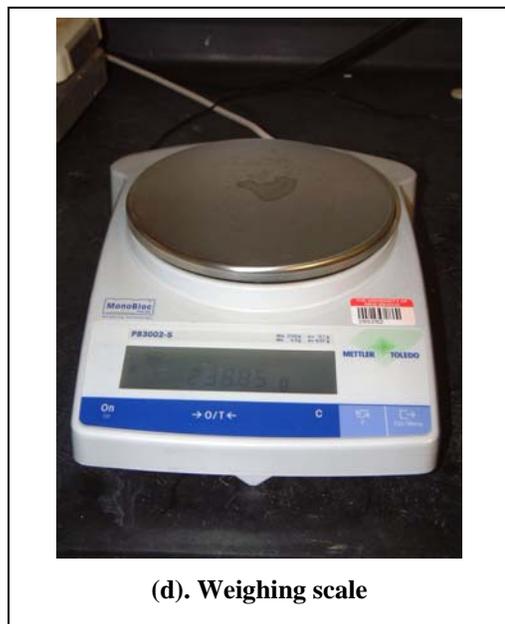
(a). pH meter.



(b). Pressure vessel for sample water.



(c). Steel pressure vessel for DI water.



(d). Weighing scale



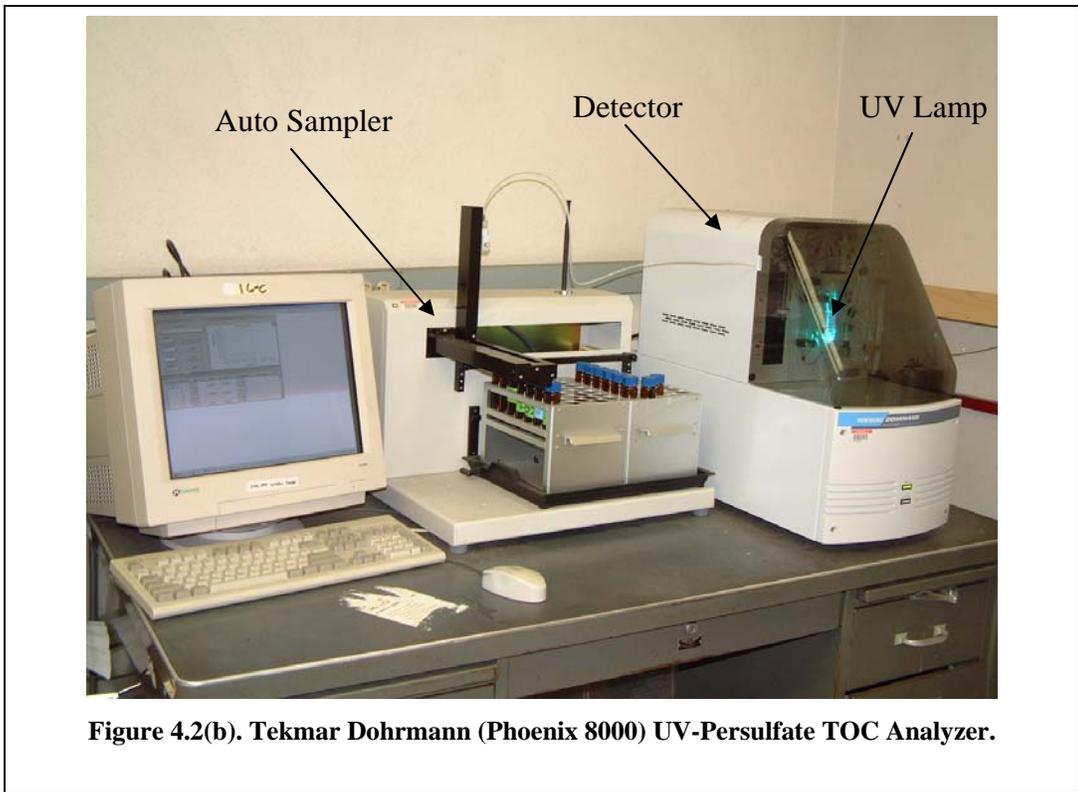
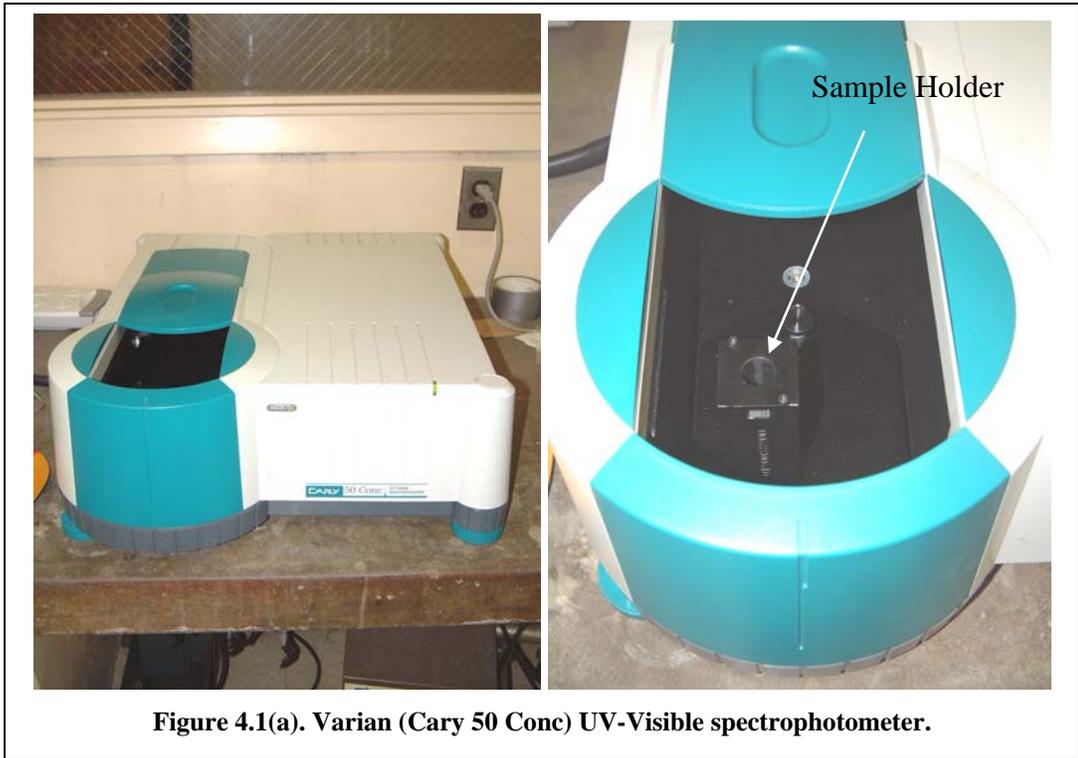
(e). Gas line low-pressure filter holder.

Figure 4.1 Apparatus and equipments.

The machines listed in Table 4.4 were used for analysis in this project. The table also lists the different analysis that the specific machines were used for.

Table 4.4. List of and machines used for analysis.

No.	Machines	Purpose
1	Varian (Cary 50 Conc) UV-Visible spectrophotometer. <i>(Figure 4.2a)</i>	To test for concentration of dissolved silica in water samples.
2	Tekmar Dohrmann (Phoenix 8000) UV-Persulfate TOC Analyzer. <i>(Figure 4.2b)</i>	To test for total organic carbon concentration in water samples.
3	Varian (55B) Atomic Absorption Spectrometer. <i>(Figure 4.2c)</i>	To test for calcium concentration in water samples.
4	Scanning Electron Microscope (JEOL 5800LV SEM) attached with an Oxford Analytical ultra-thin window EDS and an Oxford Isis 300 X-ray analyzer. <i>(Figure 4.2d)</i>	To take pictures of the membrane surface and do X-ray elemental analysis.
5	Bruker Tensor 27 FTIR. <i>(Figure 4.2e)</i>	To analyze the membrane surface for deposited matter.



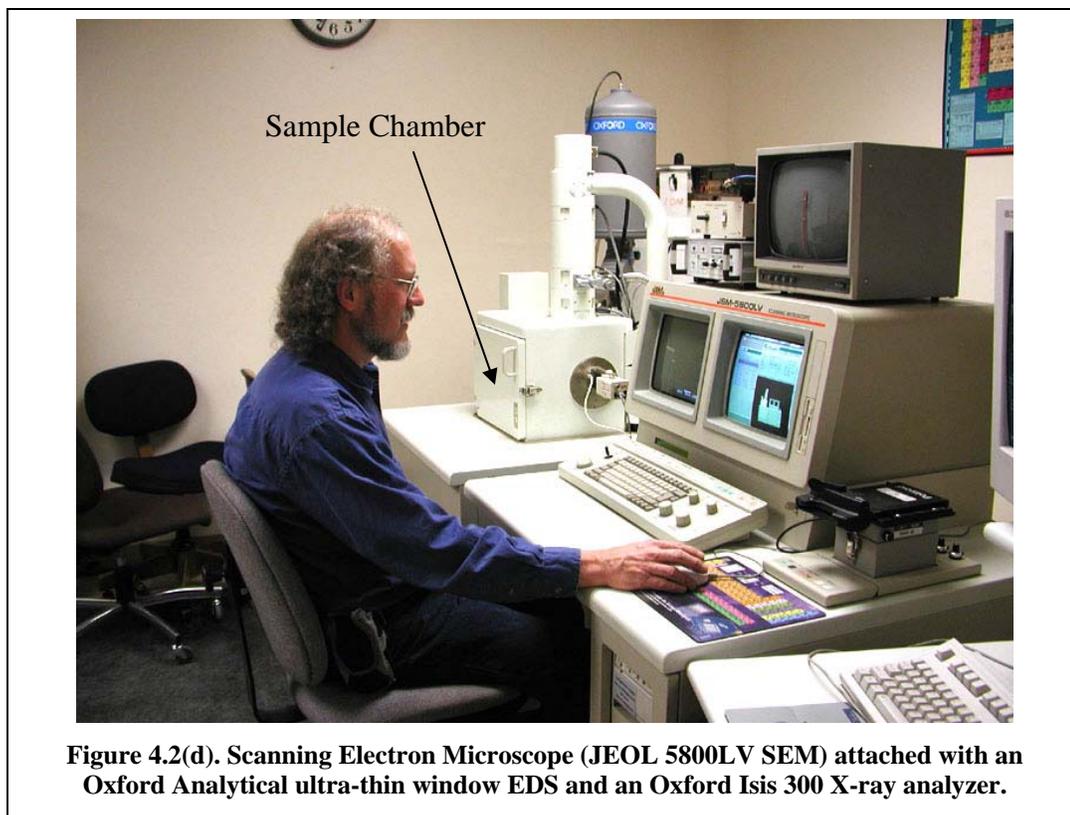
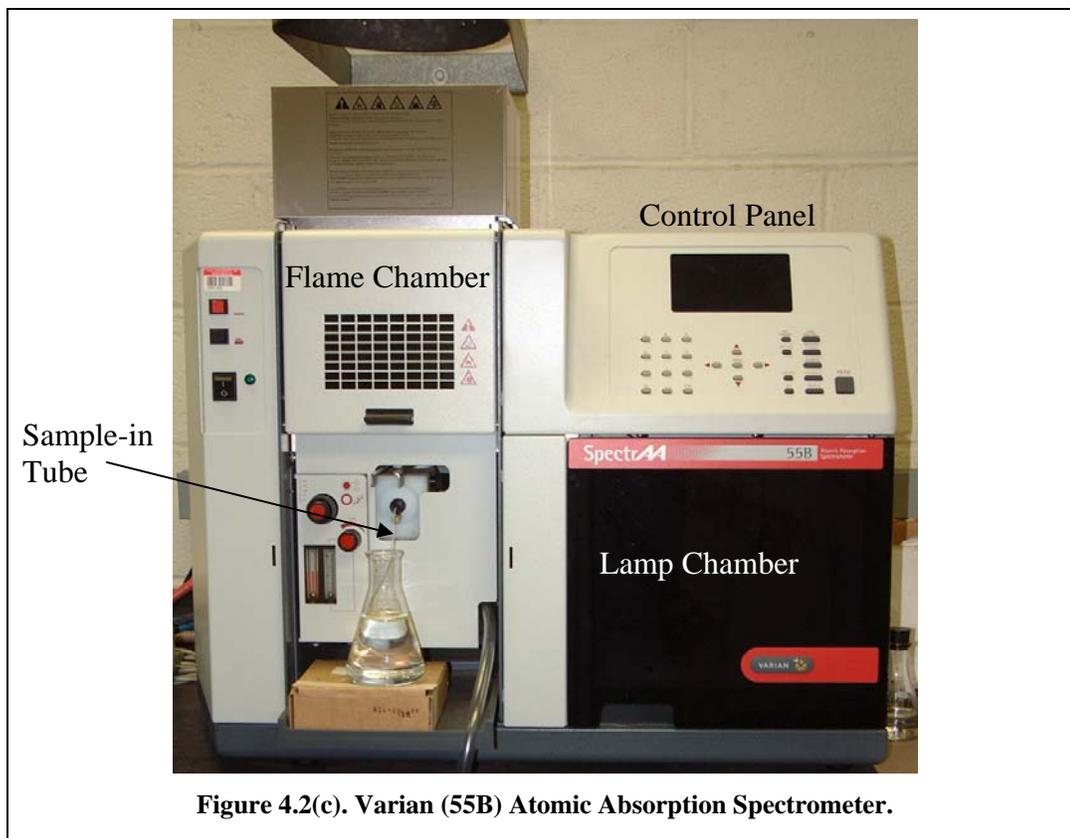




Figure 4.2 Pictures of analytical instruments used in the project.

4.5 Procedure

4.5.1 Sample Preparation

After getting the water to the environmental engineering laboratory, it was put undisturbed in a dark place for 24 hours to allow the suspended particles to settle. After 24 hours, water was passed through 1 μm Gelman Sciences glass fiber filter to remove particulate matter. Before passing the sample water through the GF filter, about 1 liter of DI water was passed through the filter to remove any impurities that might be present in the filter. It was also necessary to avoid overloading the filter so that particles smaller

than 1 μm were not filtered out. To maintain the consistency of the particle size in the GF filtered water, filters were changed after about 400 mL of river water was passed through it. The filtered water was collected in a collapsible jar and stored in the refrigerator at 4°C to prevent organic activity and deterioration of water sample. The jar was kept at room temperature in a dark place for 24 hours before the water was used for filtration experiments.

Three different types of feed water samples were prepared. Two types of feed water were prepared from Rio Grande water after GF prefiltration and one type was from DI water. One of the Rio Grande samples was just GF prefiltered water and the normal pH of the sample was 8.02 ± 0.03 . In the second type of Rio Grande water, 20 mg/L of silica and 11.46 mg/L of calcium was added. This resulted in an increase in pH that was reduced by adding dilute HCl. The pH was adjusted to the normal pH of the Rio Grande water by adding dilute HCl or NaOH solution. The DI water sample was prepared by adding 20 mg/L of silica and 11.46 mg/L calcium. Addition of these cations increased the pH of the sample. The pH was lowered by adding dilute HCl. The pH of the DI sample with cations was adjusted to 8.02 ± 0.05 by adding dilute HCl or NaOH solution.

The membrane feed water quality of the three types of water samples was tested and is tabulated below in Table 4.5.

Table 4.5. Feed water quality.

Water Sample	pH	Silica Conc. (mg/L)	Calcium Conc. (mg/L)	TOC Conc. (mg/L)
DI with cations	8.02 ± 0.05	19.9	11	0.01
RGN	8.02 ± 0.03	20.1	22.5	4.06
IRGN	8.02 ± 0.03	39.5	40	4.07

RGN - Rio Grande water pre-filtered.

IRGN – Rio Grande water pre-filtered with Ca and Si added.

4.5.2 Membrane Preparation

CA and PES membranes were soaked in DI water for at least 4 hours before using them in filtration experiments. PP and PVDF membranes were treated by soaking in methanol for a few seconds and then soaking them in DI water for 24 hours. The DI water was changed three to four times during this period.

4.5.3 Filtration Runs

Sets of experiments were performed to test the fouling behavior of different types of microfiltration membranes. The experiments conducted are listed in Table 4.6. Each type of water sample was filtered through four different membranes at two different feed pressures. The pH of the water sample was kept in the normal range for Rio Grande water. Feed pressure of 10 psi or 20 psi was provided by nitrogen gas.

All the membranes used in the experiments were flat sheet, 0.22 μm pore size and 47 mm in diameter.

Normal pH = 8.02 ± 0.03

Table 4.6. List of experiments conducted.

S. No.	Experiment	Membrane	Water	Remarks
1	RGNCA10	CA	Rio Grande Pre-filtered	pH = Normal. Feed Pres. = 10 psi
2	RGNPE10	PES	Rio Grande Pre-filtered	pH = Normal. Feed Pres. = 10 psi
3	RGNPP10	PP	Rio Grande Pre-filtered	pH = Normal. Feed Pres. = 10 psi
4	RGNPV10	PVDF	Rio Grande Pre-filtered	pH = Normal. Feed Pres. = 10 psi
5	RGNCA20	CA	Rio Grande Pre-filtered	pH = Normal. Feed Pres. = 20 psi
6	RGNPE20	PES	Rio Grande Pre-filtered	pH = Normal. Feed Pres. = 20 psi
7	RGNPP20	PP	Rio Grande Pre-filtered	pH = Normal. Feed Pres. = 20 psi
8	RGNPV20	PVDF	Rio Grande Pre-filtered	pH = Normal. Feed Pres. = 20 psi
9	IRGNCA10	CA	Rio Grande Pre-filtered	pH = Normal. Feed Pres. = 10 psi. Ca and Si added.
10	IRGNPE10	PES	Rio Grande Pre-filtered	pH = Normal. Feed Pres. = 10 psi. Ca and Si added.
11	IRGNPP10	PP	Rio Grande Pre-filtered	pH = Normal. Feed Pres. = 10 psi. Ca and Si added.
12	IRGNPV10	PVDF	Rio Grande Pre-filtered	pH = Normal. Feed Pres. = 10 psi. Ca and Si added.
13	IDINCA10	CA	DI	pH = Normal. Feed Pres. = 10 psi. Ca and Si added.
14	IDINPE10	PES	DI	pH = Normal. Feed Pres. = 10 psi. Ca and Si added.
15	IDINPP10	PP	DI	pH = Normal. Feed Pres. = 10 psi. Ca and Si added.
16	IDINPV10	PVDF	DI	pH = Normal. Feed Pres. = 10 psi. Ca and Si added.
17	IDINCA20	CA	DI	pH = Normal. Feed Pres. = 20 psi. Ca and Si added.
18	IDINPE20	PES	DI	pH = Normal. Feed Pres. = 20 psi. Ca and Si added.
19	IDINPP20	PP	DI	pH = Normal. Feed Pres. = 20 psi. Ca and Si added.
20	IDINPV20	PVDF	DI	pH = Normal. Feed Pres. = 20 psi. Ca and Si added.

Before running the sample water through the membranes, about 2 liters of DI was passed through it to get the normal flux of the membrane. The feed was instantly changed from DI water to sample water to minimize changes in operating parameters. The filtrate from the membranes was collected in a flask on the balance, which was directly connected to a computer.

The computer collected information from the balance at an interval of 1 minute and converted them into flux values. The flux thus obtained was standardized for pressure and temperature according to the formula:

$$J_S = (J_M (1.03)^{(T_S - T_M)}) / \Delta P \quad (4.1)$$

J_S = flux corrected for standard temperature and pressure (L/m².h)

J_M = measured flux (L/m².h)

T_S = standard temperature (20 °C)

T_M = measured temperature (°C)

ΔP = Feed pressure for the membrane (bar)

The standardized flux calculated was normalized with DI flux by using Equation 4.2. DI flux obtained initially was also standardized using Equation 4.1.

$$J_{\text{norm}} = J_S / J_O \quad (4.2)$$

J_{norm} = normalized flux

J_O = standardized DI flux

J_{norm} values thus obtained are plotted against the unit volume of water filtered. Unit volume is calculated by dividing the volume of sample (in liters) by the area of the membrane (in meter square).

$$V_{\text{flux}} = (\text{volume cumulative in mL} / 1000) / (17.3/10^4) \quad (4.3)$$

$$17.3 = \text{area of the membrane surface in cm}^2$$

A schematic of the experimental setup is shown in Figure 4.3 below.

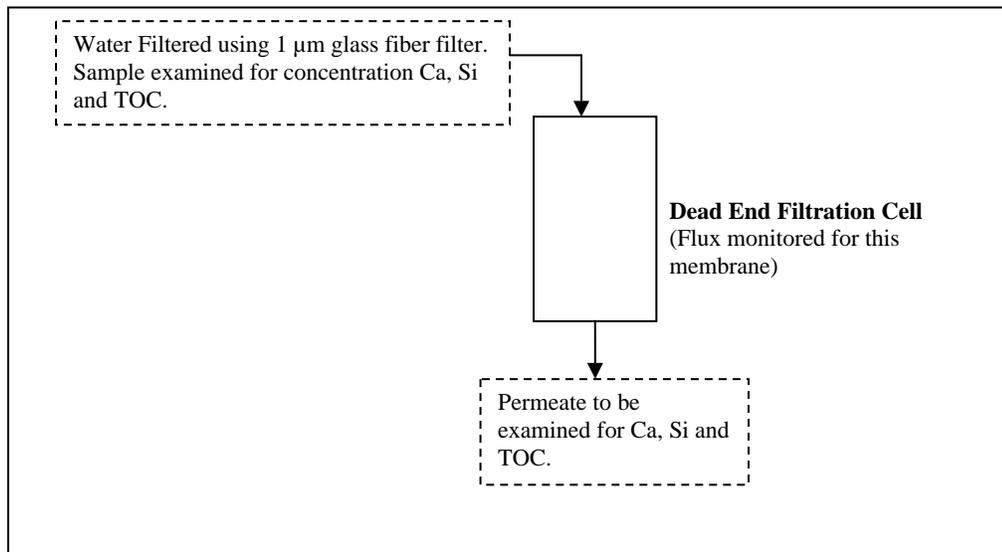


Figure 4.3 Schematic of the filtration experiment setup.

Permeate was collected in nalgene bottles and stored in the refrigerator at 4°C for further analysis. The used membranes were also stored in the refrigerator for further analysis.

4.6 Analysis

Permeates obtained were analyzed for TOC, dissolved calcium and silica. TOC was measured by Tekmar Dohrmann (Phoenix 8000) UV-Persulfate TOC Analyzer. The feed water was also tested for TOC concentration so that permeate and the feed could be compared and TOC removal measured. The feed water and permeates were also tested for silica and calcium concentrations by Varian (Cary 50 Conc) UV-Visible spectrophotometer and Varian (55B) Atomic Absorption Spectrometer respectively. Special care was taken for calcium measurements as the calibration curve for calcium shows that as the concentration increases the absorbance interval decreases. So, feed water and permeate were diluted by a known factor and then calcium concentration was measured. The values thus obtained were multiplied by the factor to get the actual concentration.

The membranes were analyzed by Scanning Electron Microscope (JEOL 5800LV SEM) attached with an Oxford Analytical ultra-thin window EDS and an Oxford Isis 300 X-ray analyzer and Varian FTIR. SEM was used to take pictures of the membrane surface and to do X-ray elemental analysis on the surface get the elemental composition of the deposits on the membrane surface. FTIR analysis was done to find the type of deposits on the membrane surface. FTIR give a series of peaks, which depicts the qualitative values of various constituents on the membrane surface. This technique required that the membrane be completely dry to avoid the interference in peaks presented by water.

The results of the filtration experiments and the analysis of permeate and membranes are presented and discussed in the next chapter.

5 Results And Discussion

This chapter presents the results of the experiments done and the analysis performed on permeates and used membranes. The filtration experiment results are presented in the form of flux data.

5.1 Flux Results

The following graphs present the flux data for four types of membranes used at varying feed pressures and different feed water.

The flux data for DI water with calcium and silica through four different membranes at 10 psi feed pressure is plotted in Figure 5.1. The PP membrane shows the lowest flux followed by PVDF membrane. This is because these two were hydrophobic and were treated with methanol to reduce the hydrophobicity. However, 10 psi of feed was not enough to overcome the hydrophobic characteristics of these two membranes and so there is about 20% difference in the flux through PP and PES or CA membranes. Thus, the difference in flux is not as much due to fouling as it is due to membranes characteristics. This can further be confirmed from Figure 5.2 which shows flux data for 20 psi feed pressure and all the other parameters are the same as in Figure 5.1. In this figure, it can be seen that the flux for PVDF and PP membranes are much closer to the flux for other two membranes. Here, the hydrophobic characteristic of the membranes are being overcome by the feed pressure. Increased feed pressure leads to increased loading rate of the contaminants in the feed water. It can be

seen that the maximum reduction in flux is in PES membrane followed by PP membrane. PVDF membrane exhibits maximum flux and the difference is flux between PVDF and PES at the beginning of the experiment was about 5 percent. This difference increases to about 15 percent at the end of the experiment. So, it can be concluded that PES is getting fouled here along with PP membrane but the fouling rate is very low in other words, it is not significant enough to be considered.

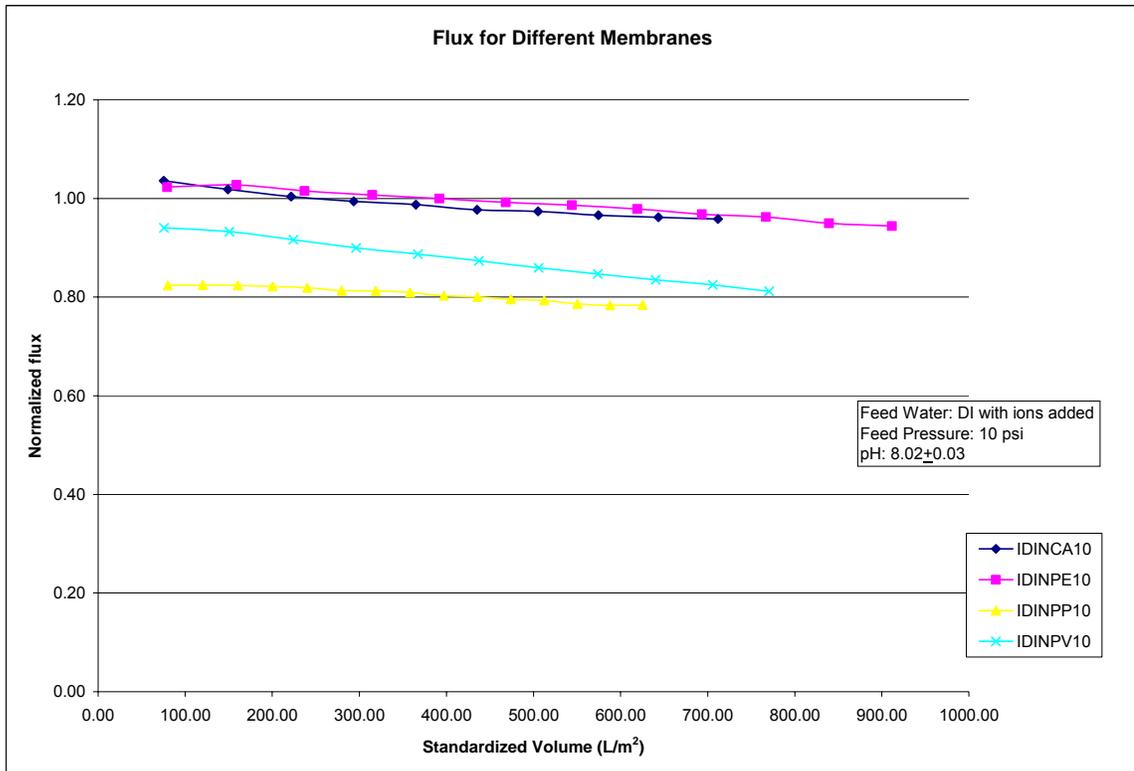


Figure 5.1 Comparison of flux through different membranes at 10 psi feed pressure and normal (8.02±0.03) pH.

(Note: For abbreviations used in legend, refer Table 4.6)

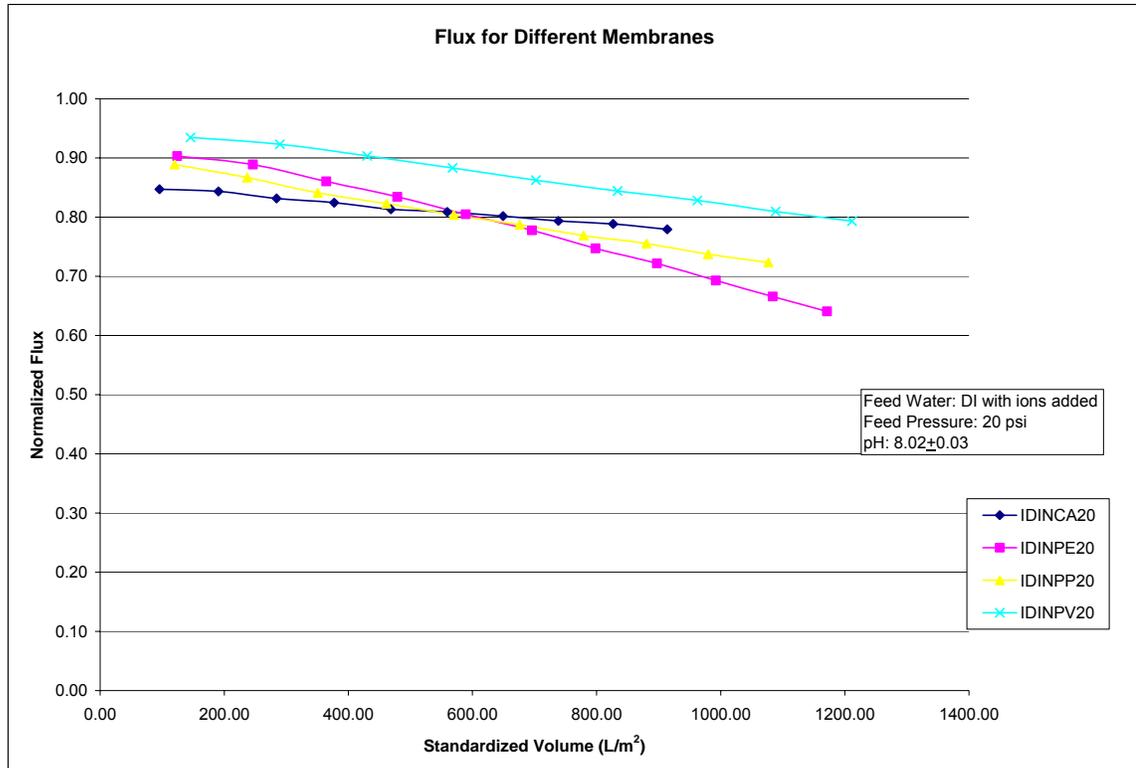
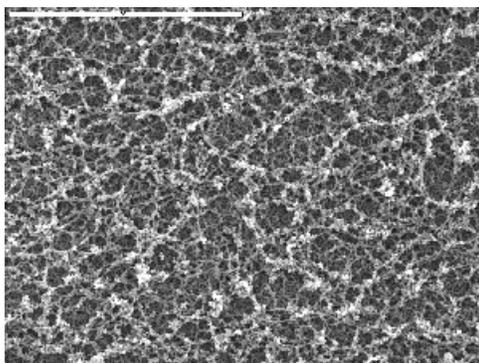


Figure 5.2 Comparison of flux through different membranes at 20 psi feed pressure and normal (8.02±0.03) pH.

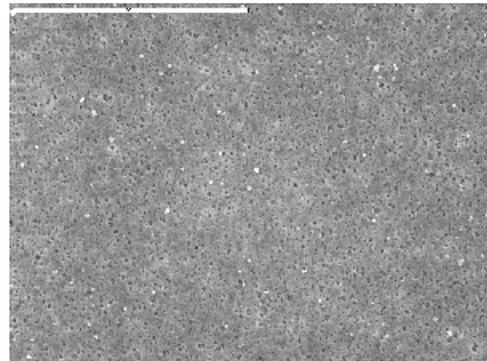
(Note: For abbreviations used in legend, refer Table 4.6)

Figure 5.4 illustrates performance for each membrane separately where the only difference in operating parameters is feed pressure. The flux curves are similar in Figure 5.4 (a) and (b) for CA and PES Membranes respectively. However, the flux for IDINPE20 is steeper than its counterpart. In both the cases, Flux curves for 10 psi and 20 psi feed pressures start at different values with the one 20 psi feed pressure being lower than the other. The flux curves in Figure 5.4 (c) and (d) for PP and PVDF membranes respectively show a different trend with values for 20 psi feed pressure being higher than the values for 10 psi feed pressure. Another thing to note is that the flux for 20 psi feed pressure in case of PP membrane crosses the flux curve for 10 psi feed pressure. This supports that

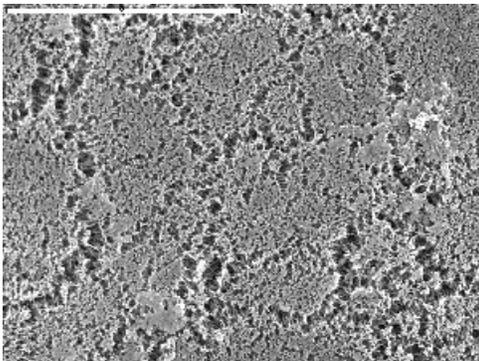
high feed pressure increases the loading rate for membranes thus resulting in more fouling. The behavior of PVDF membrane in Figure 5.4 (d) is quite different from PP membrane. Flux curve for 20 psi feed pressure starts at a higher value than for 10 psi feed pressure. This difference increases towards the end of the experiment. Thus, a PVDF membrane seems to exhibit characteristics very different from the other three membranes. This behavior can be attributed to the chemical composition of the PVDF membrane and the surface of the membrane which is very rough as shown in Figure 5.3 (d). All the other membranes have very smooth surface as compared to the surface of a PVDF membrane. This rough surface characteristic leads to various components of forces that act between the contaminants and the PVDF membrane surface.



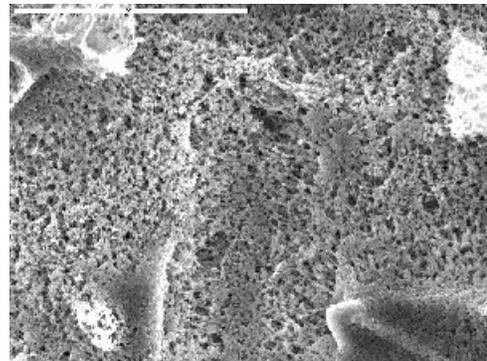
(a) CA Membrane.



(b) PES Membrane.

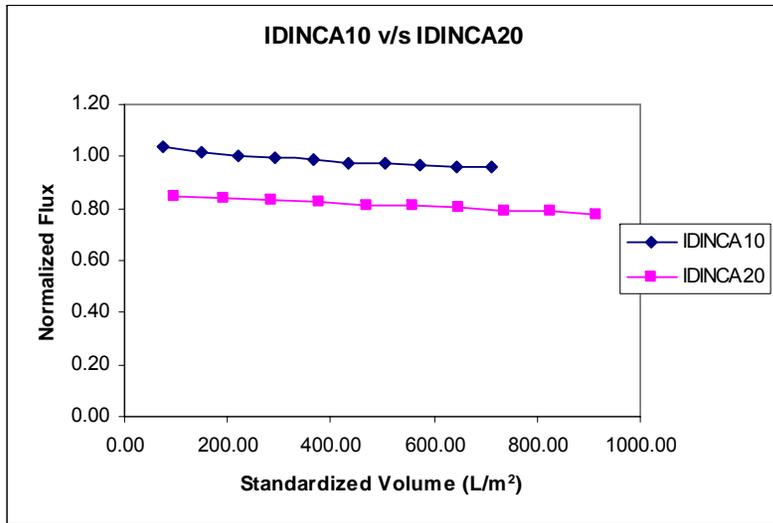


(c) PP Membrane.

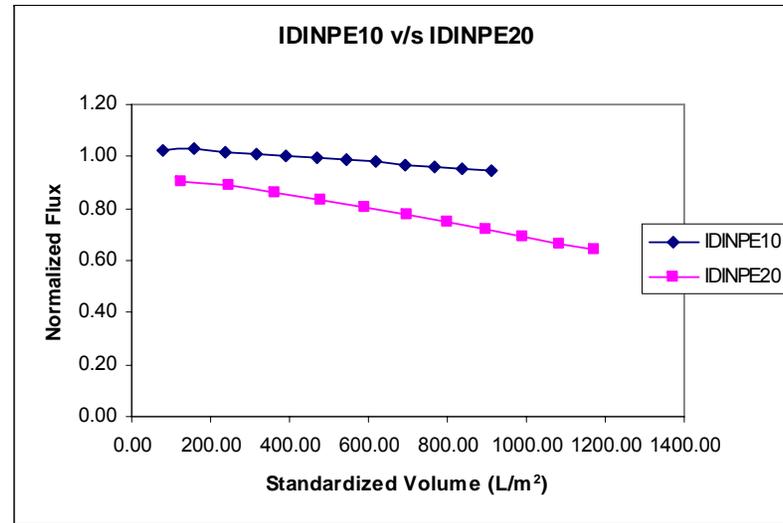


(d) PVDF Membrane.

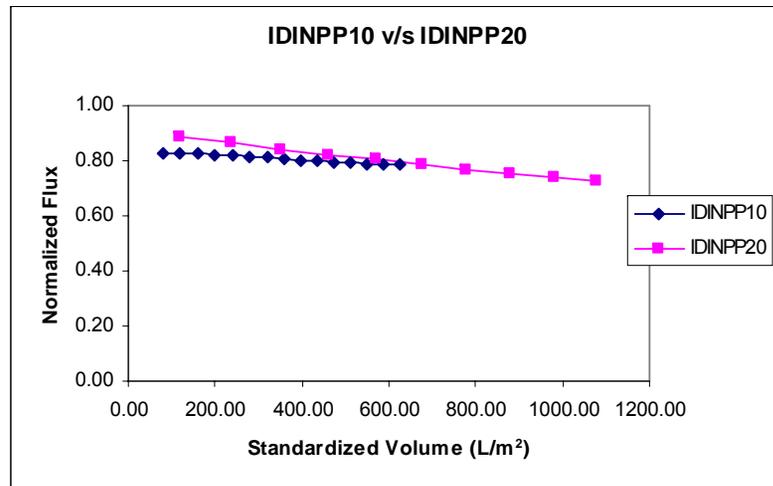
Figure 5.3 SEM images of the four types of membranes showing surface texture.



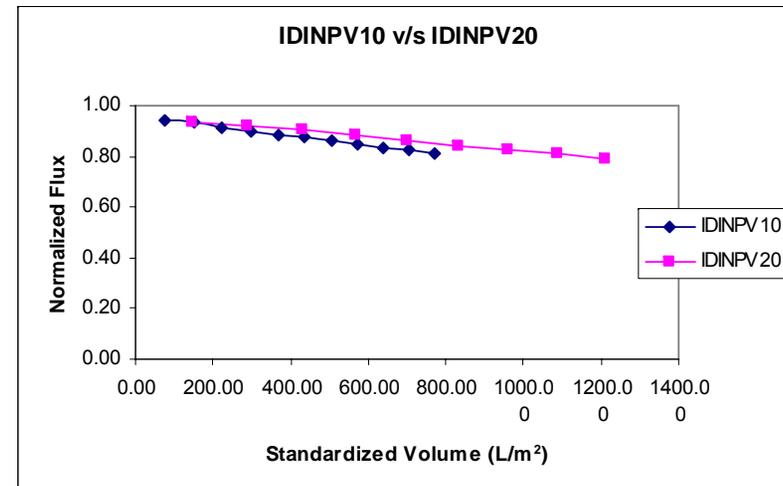
(a) CA Membrane



(b) PES Membrane



(c) PP Membrane



(d) PVDF Membrane

Figure 5.4 Comparison of flux through membranes for DI water with calcium and silica at 10 psi and 20 psi feed pressure.

(Note: For abbreviations used in legend, refer Table 4.6)

The experiments performed with DI as feed water was also done with water from Rio Grande which was filtered through 1 μm GF filter to remove particulate matter that is naturally present in river waters. The details of the experiments are given in Table 4.6. The flux data for the experiments with Rio Grande water is presented as normalized flux curves against standardized volume of water filtered through the membrane. In the first set of experiments with 10 psi feed pressure, all the membranes showed significant amount of fouling and flux reduction as shown in Figure 5.5. It is interesting to note the difference in flux curves for the DI water and the Rio Grande water.

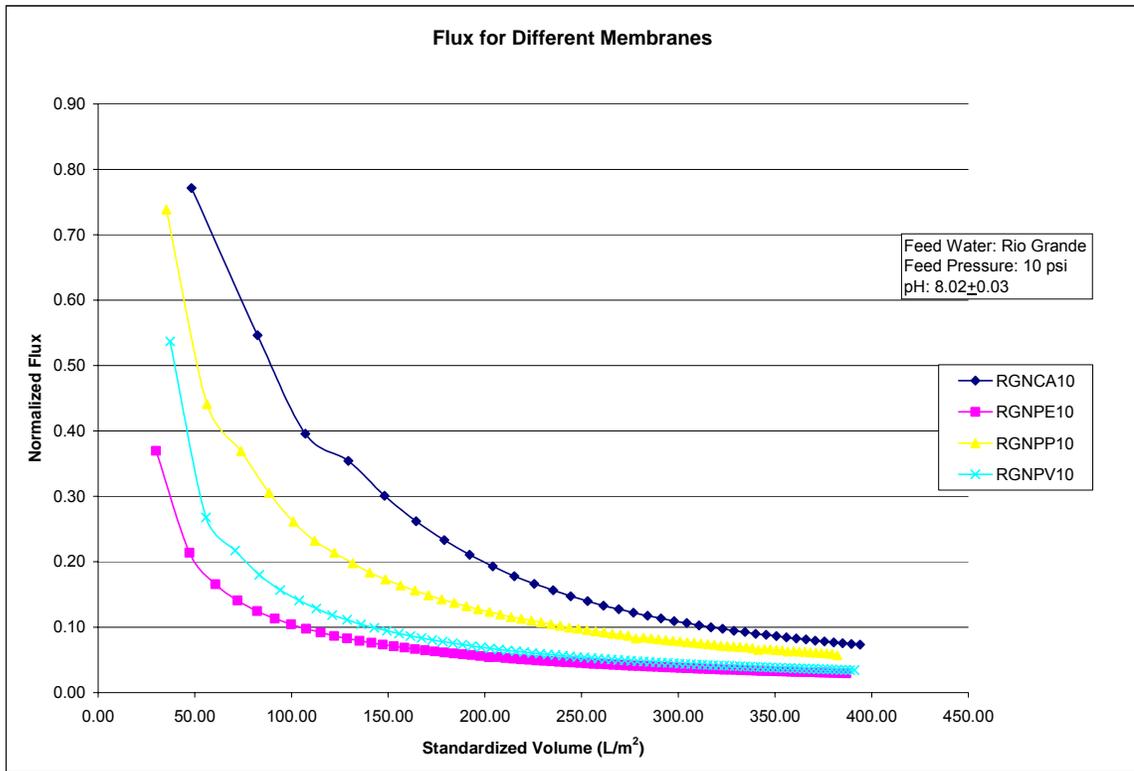


Figure 5.5 Comparison of flux through different membranes for Rio Grande water at 10 psi feed pressure and normal (8.02 ± 0.03) pH.

(Note: For abbreviations used in legend, refer Table 4.6)

It can be easily said that Rio Grande water fouls the membrane very rapidly. This can be attributed to the presence of unaccountable contaminants present in river water in colloidal and dissolved state. In Figure 5.5, fouling of each membrane takes place and at a different rate, PES membrane was the worst affected followed by PVDF, PP and CA membranes. Figure 5.6 shows the curves for experiments when the feed pressure was 20 psi. The sequence of membranes fouling is similar to that shown in Figure 5.5. The only differences are that CA and PP membranes cross each other and the gap between PES and PVDF membrane curves increased. It is difficult to conclude the effect of increased feed pressure from Figure 5.5 and Figure 5.6.

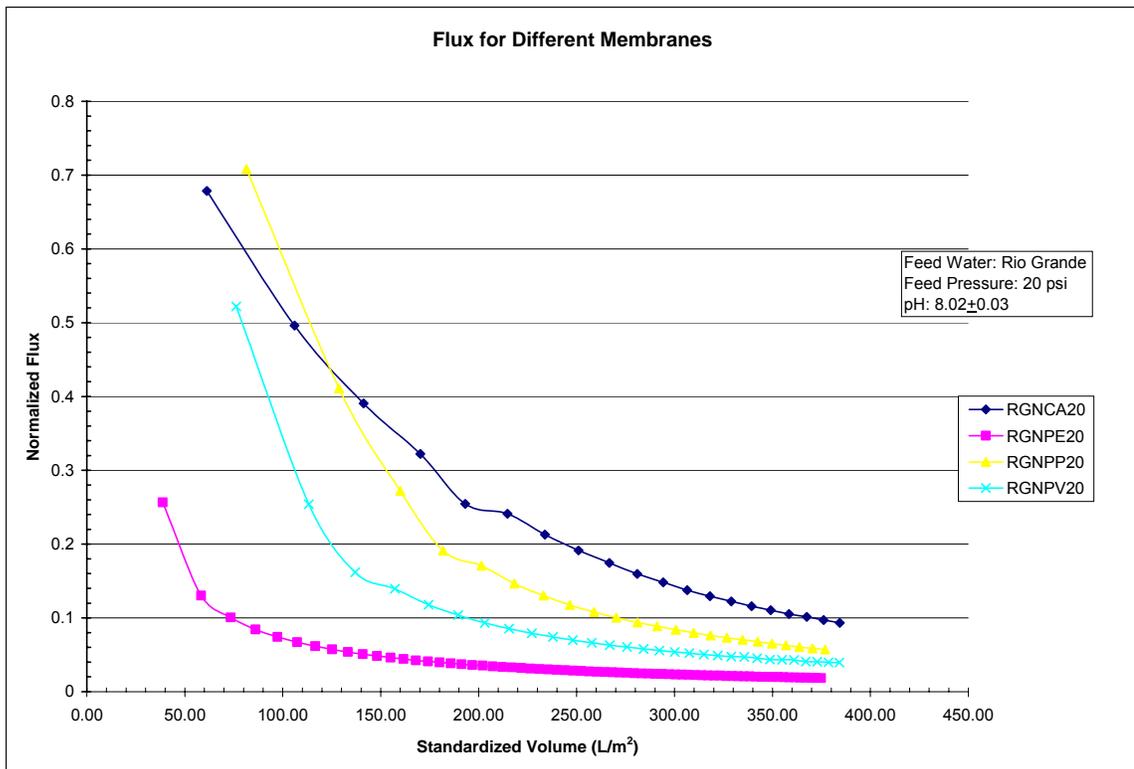
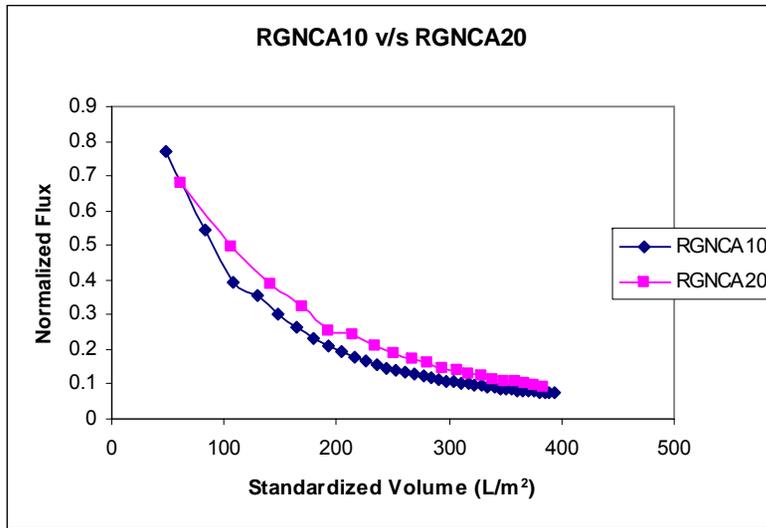


Figure 5.6 Comparison of flux through different membranes for Rio Grande water at 20 psi feed pressure and normal (8.02±0.03) pH.

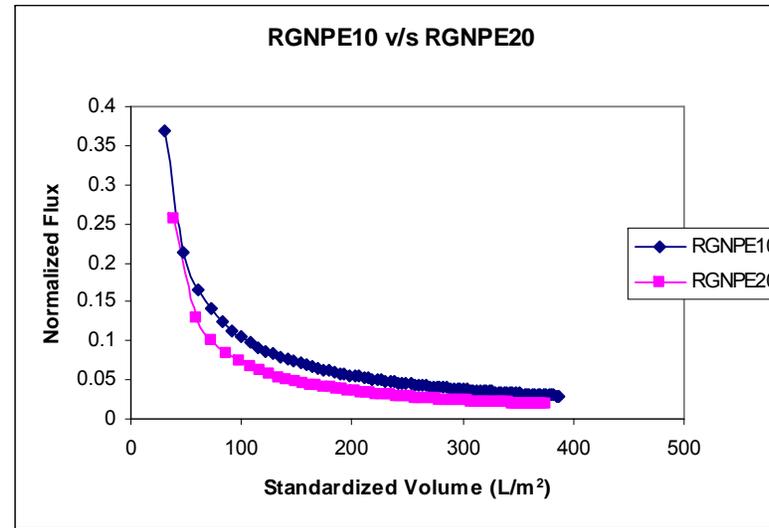
(Note: For abbreviations used in legend, refer Table 4.6)

The effect of different feed pressures has been clearly presented in Figure 5.7 where each graph has two curves – both are for the same membrane with same feed water but at different feed pressure. Figure 5.7 (a), (c) and (d) are similar in the sense that the curves for filtration experiments conducted at 20 psi feed pressure lies above the ones for 10 psi feed pressure. But in Figure 5.7 (b), for PES membrane, the curve for 10 psi feed pressure lies above the curve for 20 psi feed pressure. Although the increased feed pressure should increase loading rate on the membrane and the membrane should foul more rapidly, it is not the case with CA, PP and PVDF membranes. Therefore, it can be said that the performance of PES membrane is quite different from the other three membranes. PES membrane removed some specific contaminants from water that the other membranes did not. The curves for PP and PVDF membranes show noticeable difference. Increased feed pressure did increase the flux through the membranes. However, towards the end of the experiments, flux through all the membranes leveled out i.e. the rate in decline of flux decreased to a very low value.

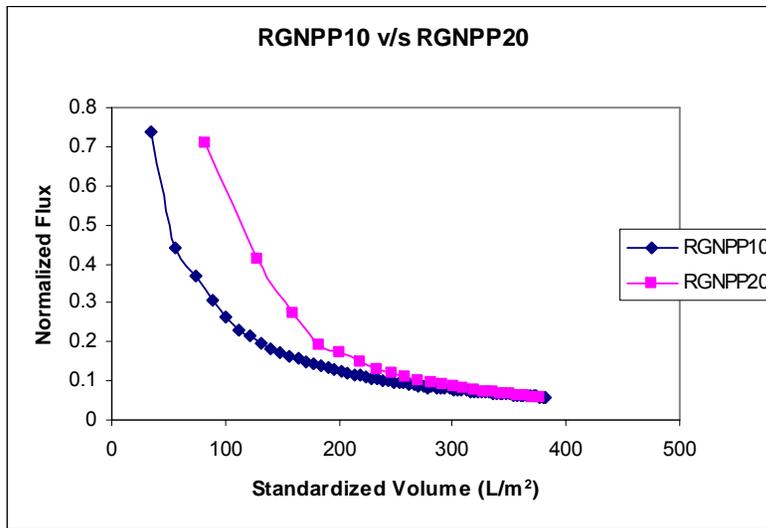
At this point it was difficult to entail the effect of calcium and silica in feed water on fouling of membranes. So, the next set of experiments was done with adding additional calcium and silica in the feed water from Rio Grande and adjusting the pH. The details of the feed water (IRGN) quality are given in Table 4.5. The flux data obtained from the experiments is presented in Figure 5.8.



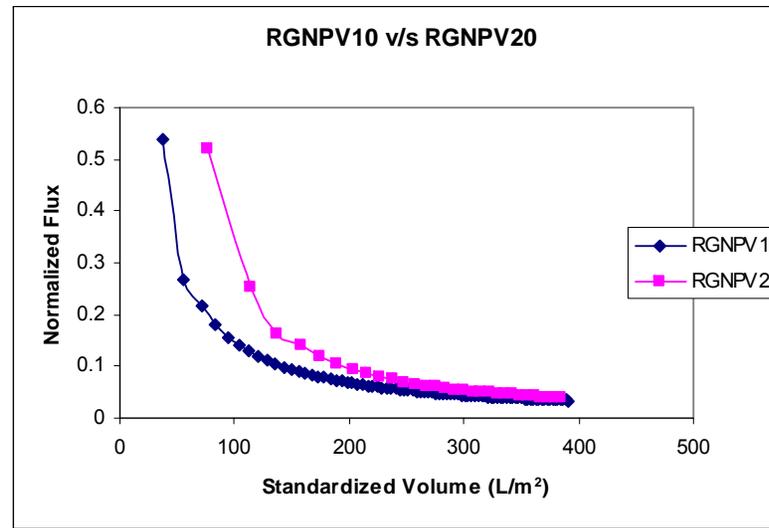
(a) CA Membrane



(b) PES Membrane



(c) PP Membrane



(d) PVDF Membrane

Figure 5.7 Comparison of flux through different membranes for Rio Grande water at 10 psi and 20 psi feed pressure.

(Note: For abbreviations used in legend, refer Table 4.6)

The flux decline curves for different membranes in Figure 5.8 are quite similar to the ones in Figure 5.5. PES membrane showed maximum decline in flux rate followed by PVDF, PP and finally CA membrane with the least decline in flux rate. Therefore, the data from filtration experiments for different types of Rio Grande feed water (RGN and IRGN) at 10 psi feed pressure has been compared in Figure 5.9. The flux curve pattern for PES membrane in Figure 5.9 (b) is as expected. Increase in calcium and silica concentration did lower the flux to a greater extent. The flux curves for other membranes are not as expected where increase in calcium and silica increased the flux through the membranes.

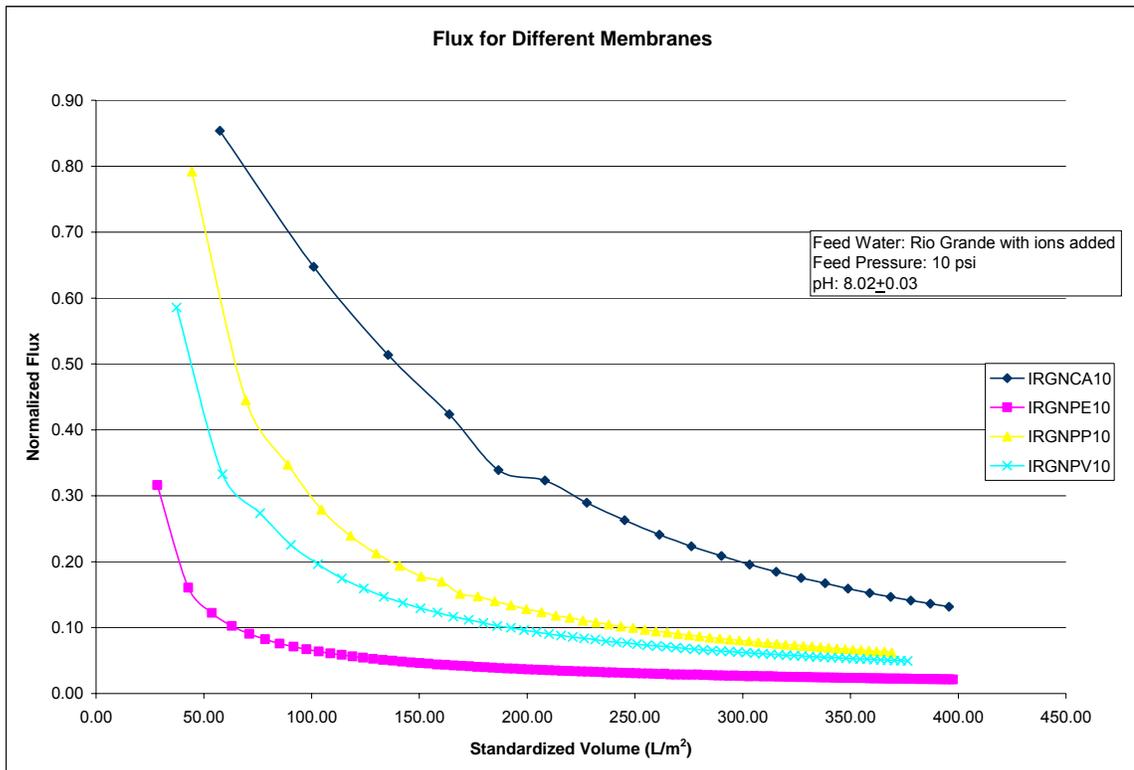
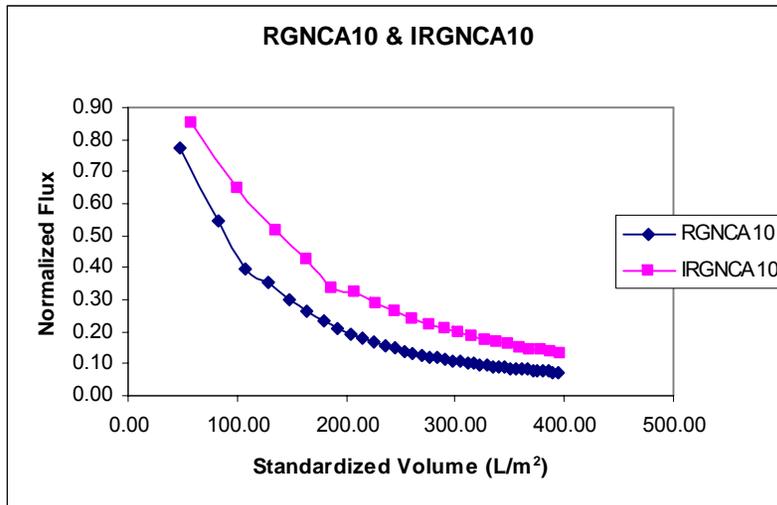
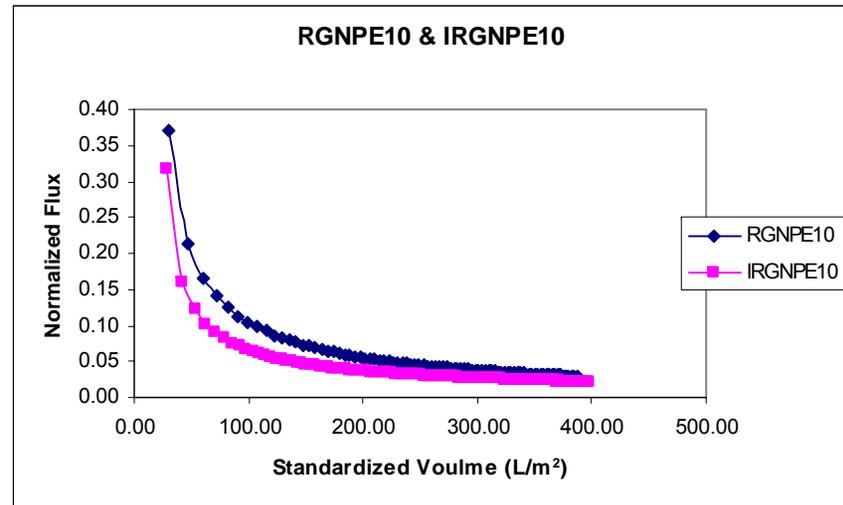


Figure 5.8 Comparison of flux through different membranes for Rio Grande water with calcium and silica added at 20 psi feed pressure and normal (8.02±0.03) pH.

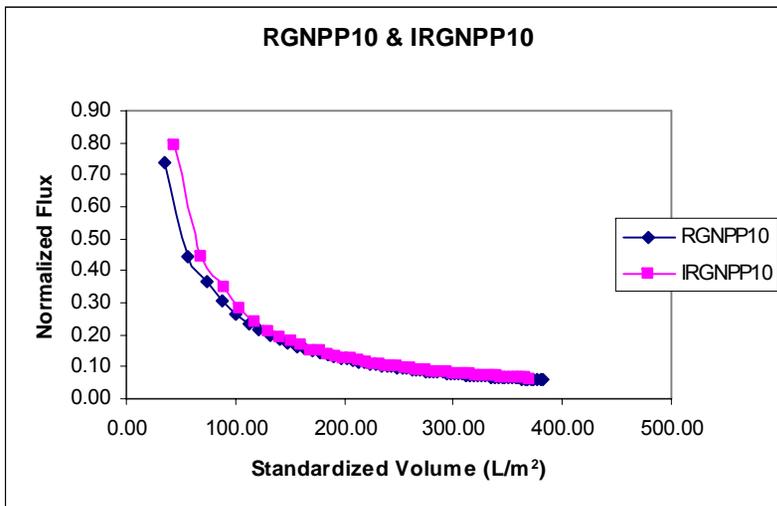
(Note: For abbreviations used in legend, refer Table 4.6)



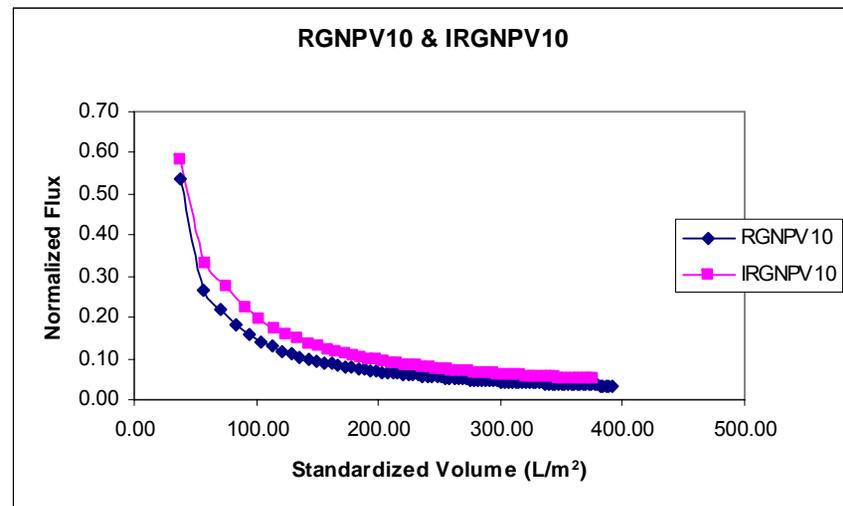
(a) CA Membrane



(b) PES Membrane



(c) PP Membrane



(d) PVDF Membrane

Figure 5.9 Comparison of flux through different membranes for Rio Grande water with and without calcium and silica at 10 psi feed pressure.

(Note: For abbreviations used in legend, refer Table 4.6)

When DI water with calcium and silica added to it was used as feed water for experiments at 10 and 20 psi feed pressure, all the four membranes did not show significant reduction in flux through them. Rio Grande fouled the membranes very rapidly. When flux for different feed pressures was observed, only PES membrane showed different pattern in the sense that increased feed pressure increased the loading rate on the membranes and thus resulted in increased fouling. So, PES membrane fouled at a higher rate when the feed pressure was increased. This was not the case with other three membranes (CA, PP, and PVDF). Flux through the other three membranes increased with the increase in feed pressure. Similarly, when Rio Grande water with additional calcium and silica was used as feed water, the flux curves were similar to the ones for Rio Grande water as feed with no additional calcium and silica (figures Figure 5.7 and Figure 5.9). It will be safe to conclude here that PES membrane is the only that showed increased fouling with the increase in feed pressure and also with the increase in calcium and silica concentration in feed water. The reason for such behavior cannot be explained at this point and additional work will be needed to explain so.

5.2 Total Organic Carbon (TOC) Results

This section presents the results of TOC concentration for the feed water samples and permeates from different membranes under varying feed pressures. The values in Table 5.1 give the TOC concentration of the various feed water and permeates. RGN and IRGN was the feed water used for experiments. As

mentioned earlier, RGN is the Rio Grande water filtered through 1 μm GF filter and calcium and silica was added to the prefiltered feed water to get IRGN. The TOC concentration in permeate from CA membrane in all the experiments was higher than the feed water TOC concentration. Similarly, permeate from PES membranes also had higher TOC concentration than in feed water. Permeates from the other two membranes PP and PVDF had TOC concentration lower than the TOC concentration in the feed water. So, it can be said that PP and PVDF were removing organics during the filtration experiments. In other words, PP and PVDF membranes were getting fouled by organics dissolved in Rio Grande water. The reason for increase in TOC concentration in permeates of CA and PES membranes can be attributed to two cases that could have been taking place during the experiments. First, the membranes could have been contaminated during its handling before the experiments and soaking them in DI water for some time did not yield any cleaning of the membranes. The other reason could be that the membrane material might have disintegrated slightly during the experiments and so a small amount of organic might have been added in permeates. The second explanation seems difficult to comprehend because PES membrane is quite stable to temperature and pH changes of feed water. The most logical reason seems to be the first one – where the membranes must have become contaminated during handling at different stages from the manufacturers to the experimental bench.

Table 5.1 TOC concentration for feed water and permeates.

Membrane Used	Sample	Av. µg Carbon	Av. ppm Carbon
	DI	0.0529	0.0132
(Feed water)	RGN	16.2355	4.0589
CA	RGNCA10	16.4501	4.1125
PES	RGNPE10	16.2876	4.0719
PP	RGNPP10	15.6270	3.9067
PVDF	RGNPV10	16.1752	4.0438
CA	RGNCA20	16.6751	4.1688
PES	RGNPE20	16.3930	4.0982
PP	RGNPP20	15.3926	3.8482
PVDF	RGNPV20	15.9191	3.9798
(Feed water)	IRGN	14.9321	3.7330
CA	IRGNCA10	16.2803	4.0701
PES	IRGNPE10	15.2944	3.8236
PP	IRGNPP10	14.6374	3.6593
PVDF	IRGNPV10	14.7827	3.6957

5.3 Silica and Calcium Concentrations

The objective of this project was to see if dissolved calcium and silica would assist in fouling of membranes. In order to do so, it was important to analyze the raw water and permeates for calcium and silica concentration. The analyses were performed with machines mentioned in Table 4.4. Comparing calcium and silica concentrations for feed water and permeates in Table 5.2 and taking into account some tolerance for error, there was negligible difference in the concentration values except for some cases. To make a sound assessment, any difference in the concentration values for feed water and permeates of more than 1 ppm can be considered to be of some importance. Looking at the

numbers for the DI feed water and permeates obtained from all the four types of membranes, it can be said that neither calcium nor silica acts as foulants on their own.

Table 5.2. Calcium and silica concentrations for feed water and different permeates.

Membrane Used	Sample	Calcium Concentration (mg/L)	Silica Concentration (mg/L)
	Blank		-0.4
	DI		-0.5
(Feed water)	DI with Ca and Si	11	19.9
CA	IDINCA10	11	19.6
PES	IDINPE10	11	19.5
PP	IDINPP10	11	20.0
PVDF	IDINPV10	10	19.9
CA	IDINCA20	10	19.5
PES	IDINPE20	11	19.6
PP	IDINPP20	10	19.6
PVDF	IDINPV20	10	19.4
(Feed water)	RGN	33	22.5
CA	RGNCA10	32	21.9
PES	RGNPE10	34	21.6
PP	RGNPP10	32	21.6
PVDF	RGNPV10	33	21.4
CA	RGNCA20	32	21.4
PES	RGNPE20	32	21.1
PP	RGNPP20	31	21.0
PVDF	RGNPV20	32	21.2
(Feed water)	IRGN	40	39.5
CA	IRGNCA10	40	39.6
PES	IRGNPE10	42	39.4
PP	IRGNPP10	38	39.2
PVDF	IRGNPV10	40	38.1

When RGN was used as feed water, only permeate for PP membrane showed a decline of 2 ppm in calcium concentration. Whereas, noticeable reduction in silica concentration was observed in permeates of PVDF at 10 psi feed pressure and all the four membranes at 20 psi feed pressure.

When IRGN was used a feed water, permeate for PES membrane shows an increase of 2 ppm for calcium concentration which seems to be an error. The calcium concentration for permeate of PP membrane is reduced by 2 ppm. Only permeate for PDVF membrane shows noticeable reduction in silica concentration.

PP membrane removes calcium from the Rio Grande feed water when the feed pressure is increased or when additional calcium is added to the feed water. The reason for this could be that calcium is forming complexes with organics in the water and promoting fouling as the numbers for TOC concentration for both the conditions were also favorable [10, 13]. Other than that it could not be clearly established that either calcium or silica or both are the foulants independently or in combination with other contaminants that are present in river water.

5.4 Scanning Electron Microscopy and Fourier Transform Infra-red Spectroscopy

SEM and FTIR were used to study the surface deposits on the used membranes and compared the same with the clean membranes. Elemental analysis was also done during electron microscopy to find the elemental constituents of the surface deposits on the used membranes. Figure 5.10 shows the SEM image of a clean CA membrane. The nodules in the SEM image that look like some kind of deposits on the membrane is a part of the membrane matrix. FTIR results for clean CA membrane are presented in the Figure 5.11 where a few well defined absorption peaks can be seen. These peaks represent

the membrane material. The two important areas for a preliminary examination of a spectrum are the regions $4000 - 1300$ and $900 - 650 \text{ cm}^{-1}$. The high-frequency portion of the spectrum is called the functional group region with the characteristic stretching frequencies for important functional groups such as OH, NH, and C=O. The lack of strong absorption bands in the $900 - 650 \text{ cm}^{-1}$ region generally indicates a non-aromatic structure. The intermediate portion of the spectrum, $1300 - 900 \text{ cm}^{-1}$, is usually referred to as “fingerprint” region. The absorption pattern in this region is extremely complex with the bands originating in interacting vibrational modes. The peak at around 1700 cm^{-1} in Figure 5.11 represents benzene group and the peaks between 1000 and 1400 mainly represent alkanes, alkenes, and mononuclear aromatics (benzene) [19]

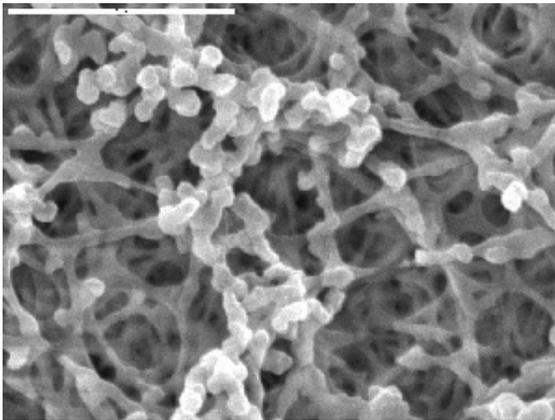


Figure 5.10. SEM image for clean CA membrane.

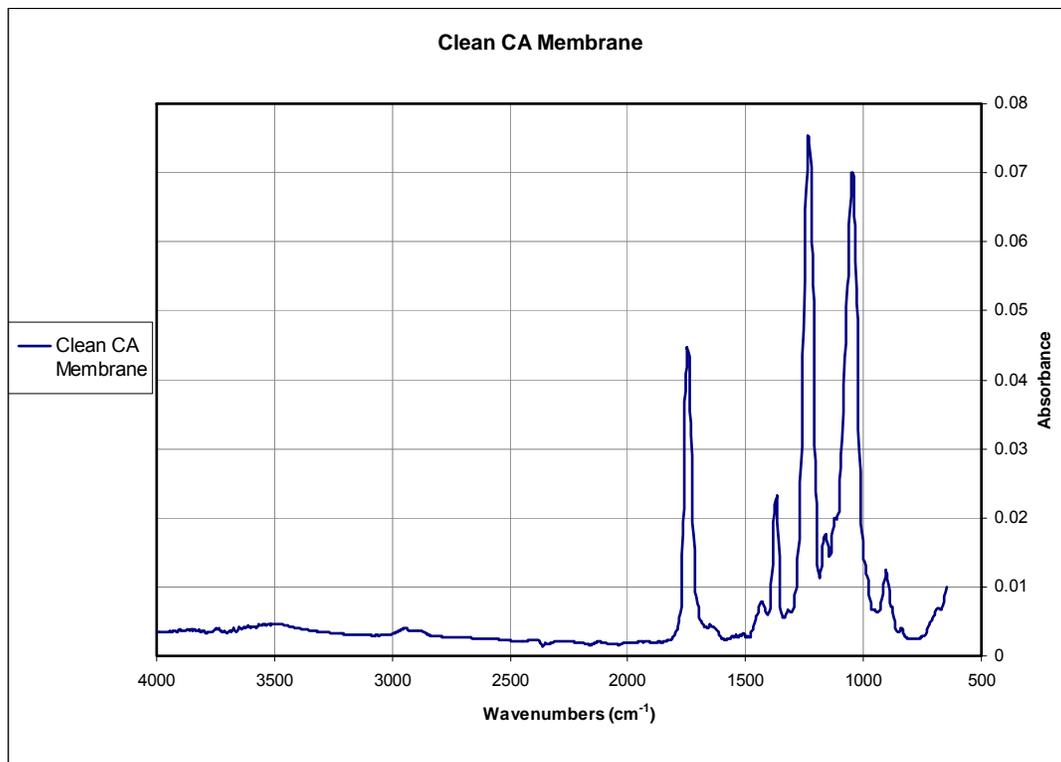


Figure 5.11. FTIR for Clean CA Membrane.

The Figure 5.12 shows a SEM image and elemental analysis for CA membrane used in the experiment IDINCA10 and IDINCA20. For both the experiments, the images were very similar and no difference could be seen. Elemental analysis chart shows Au and Pd deposits on the surface of the membrane because the membrane is sputter coated with gold palladium before observing under the electron microscope. Oxygen and carbon peaks could be because of the presence of organics or the membrane material itself. There is a very small, almost negligible, peak for calcium as well as for silica. This deposit of Ca and Si was not enough to reduce its concentration in permeate by a measurable amount.

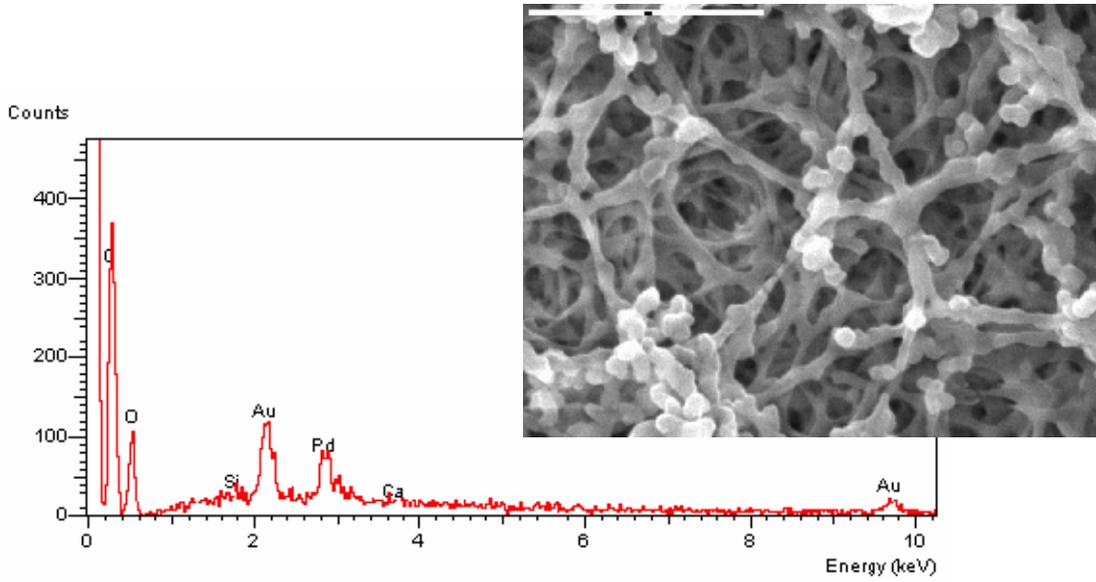


Figure 5.12. SEM image for used CA membrane with elemental analysis. DI water with calcium and silica used as feed water.

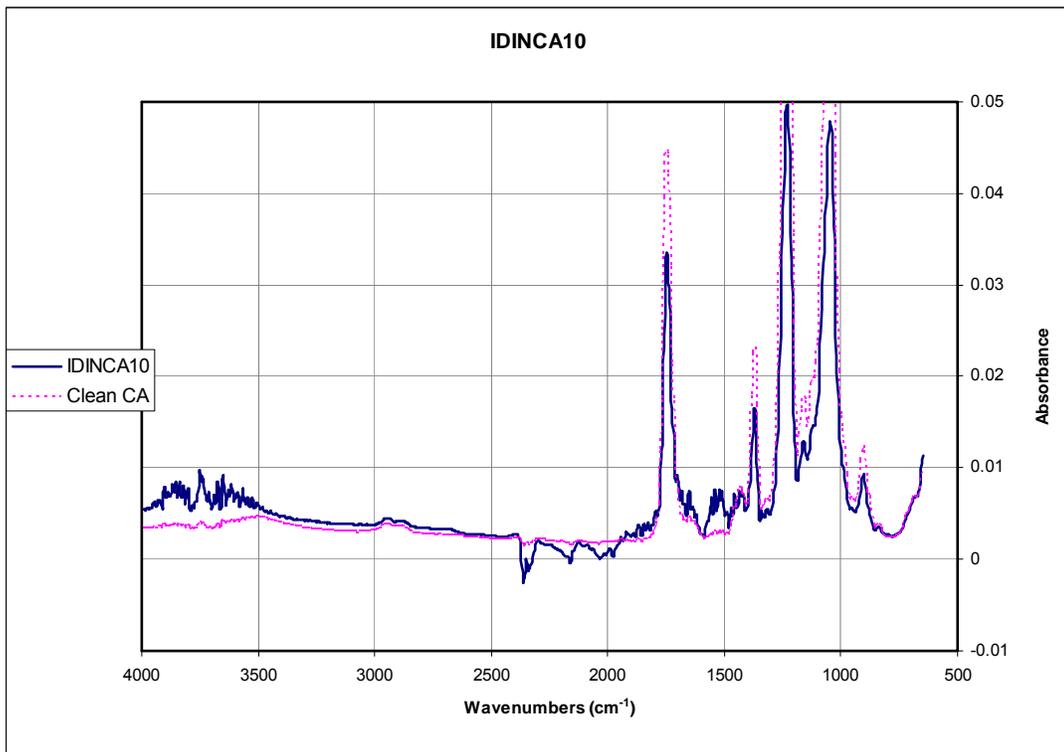


Figure 5.13. FTIR for used CA membrane, feed water was DI with calcium and silica at 10 psi feed pressure.

The peaks in the Figures Figure 5.13 and Figure 5.14 are much weaker than the one for clean CA membrane. The reason for this is that the membrane surface has coating of gold palladium which reduced the absorption of infra-red by the membrane material. There is a dip in the peak readings at about 2350 cm^{-1} . This dip is because of the water molecules.

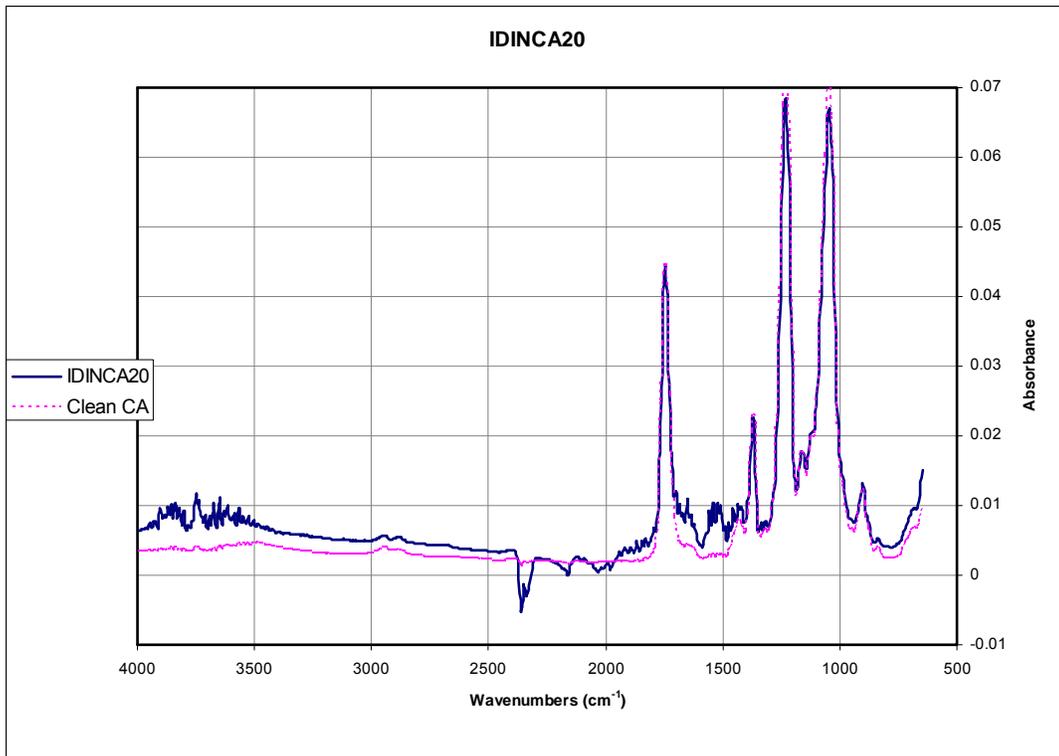


Figure 5.14. FTIR for used CA membrane, feed water was DI with calcium and silica at 20 psi feed pressure.

The SEM image in Figure 5.15 clearly shows that the membrane surface is covered with a layer of deposit. The elemental analysis shows that the deposits mainly consists of silica and aluminum and small amounts of Ca, Fe, Mg and K. Dominance of Si and Al in the deposits can be inferred as clay. Although, the river water was filtered through 1 μm GF filter to remove particulate matter,

some of the colloidal soil and other contaminants could have passed through the GF filter. These particles got deposited on the membrane surface in the form of cake layer and reduced the flux through the membrane. Even the FTIR in Figure 5.16 shows that a peak for silica at 1000 cm^{-1} . The peaks between $1300 - 1700\text{ cm}^{-1}$ represents benzene group, ketones, amine salts, alkynes and alkanes. These could be the organics in the soil that is forming a cake layer on the fouled membrane.

Similarly, all the other types of membranes fouled with Rio Grande water also produced the same peaks for the deposits on the membranes. Looking at all the images and plots from figures 5.15 to 5.53, it can be concluded that the flux decline in these experiments was mainly due to clay matter in soil and some organics which could be identified according to their characteristic group absorption FTIR spectroscopy. In figures 5.50 and 5.52, pores can be seen even after the membrane got fouled with the cake layer that formed on the PVDF membrane surface. This can be attributed to the rough surface of the membrane and characteristic leads to various components of forces that act between the contaminants and the membrane surface. These forces will result in uneven distribution of the deposits on the membrane surface thus, exposing some pores.

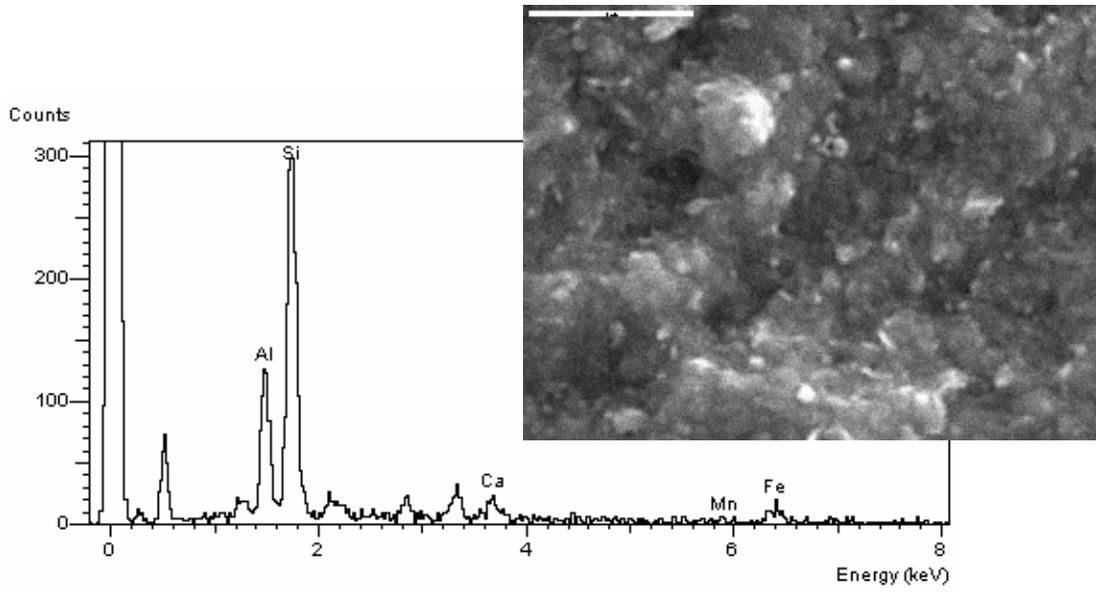


Figure 5.15. SEM image for used CA membrane with elemental analysis. Rio Grande water used as feed water and the feed pressure was 10 psi.

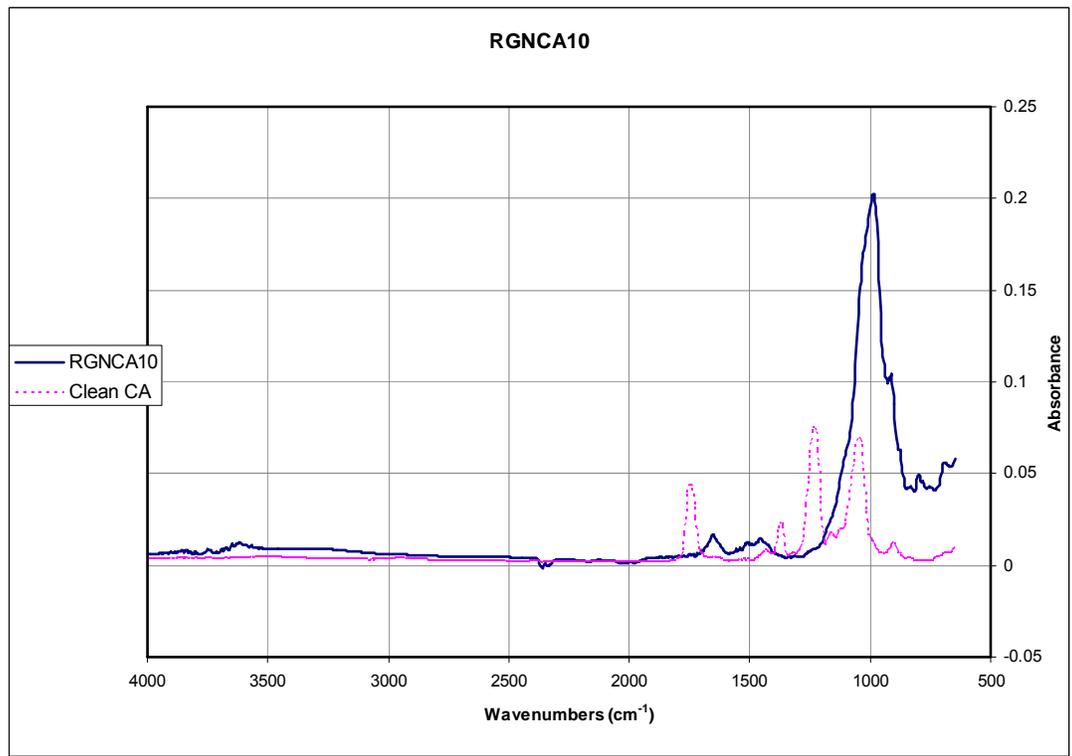


Figure 5.16. FTIR for used CA membrane, feed water from Rio Grande at 10 psi feed pressure.

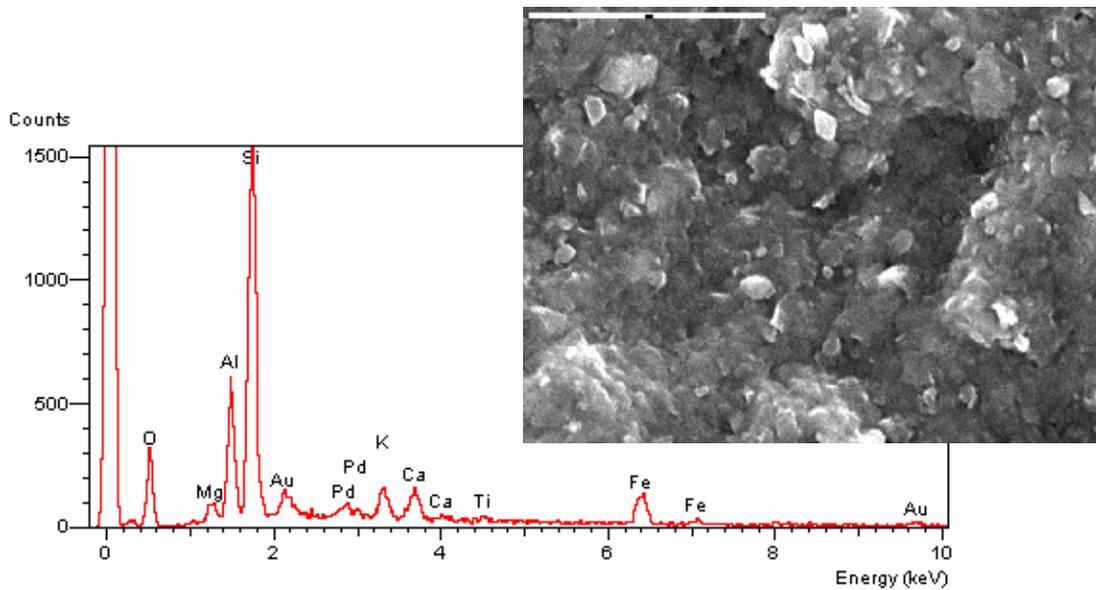


Figure 5.17. SEM image for used CA membrane with elemental analysis. Rio Grande water used as feed water and the feed pressure was 20 psi.

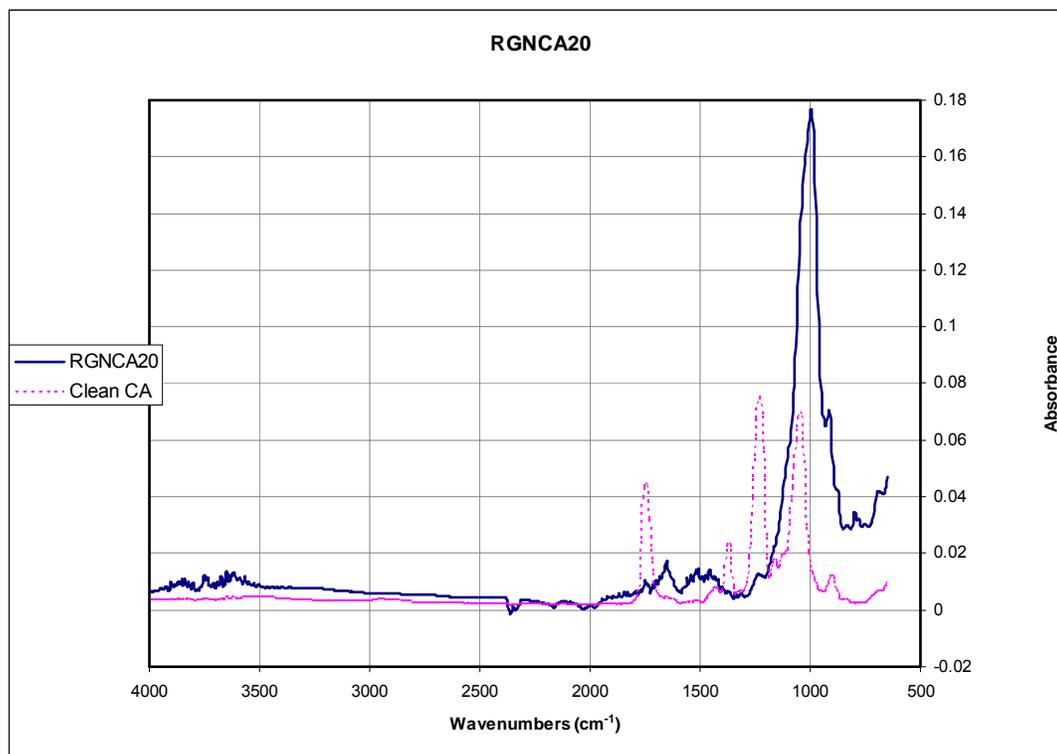


Figure 5.18. FTIR for used CA membrane, feed water from Rio Grande at 20 psi feed pressure.

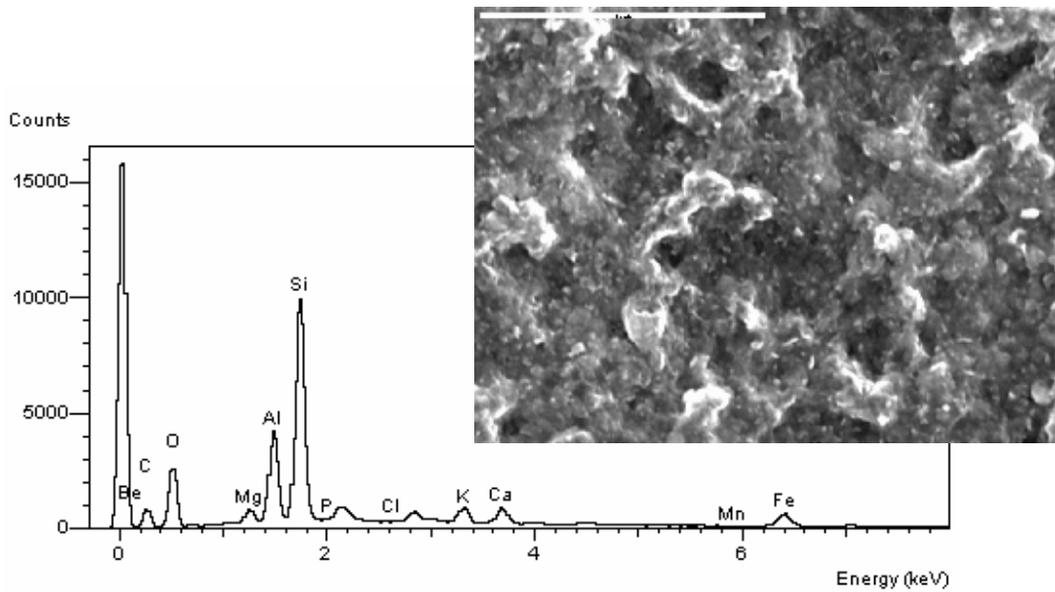


Figure 5.19.. SEM image for used CA membrane with elemental analysis. Rio Grande water with calcium and silica added, used as feed water and the feed pressure was 10 psi.

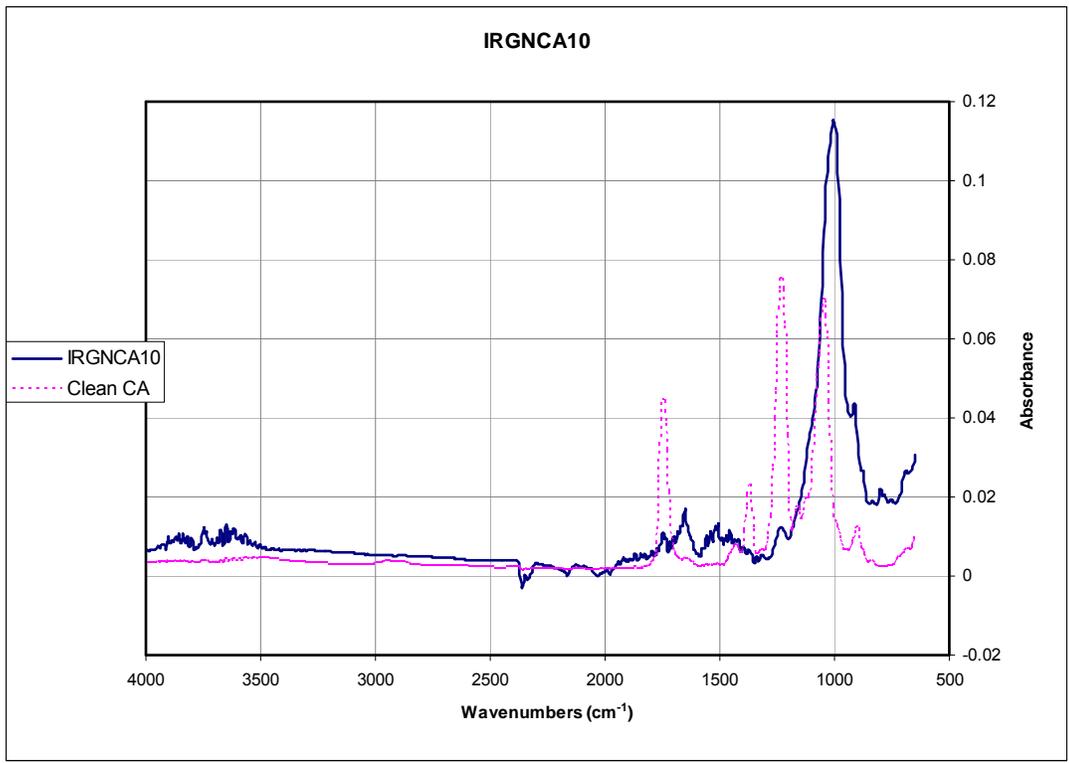


Figure 5.20. FTIR for used CA membrane, feed water from Rio Grande with calcium and silica added, at 10 psi feed pressure.

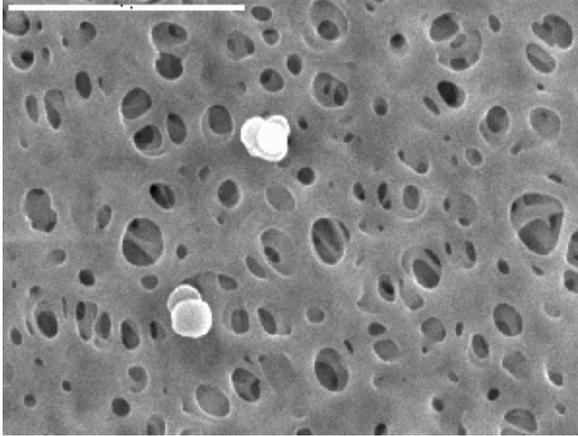


Figure 5.21. SEM image for clean PES membrane.

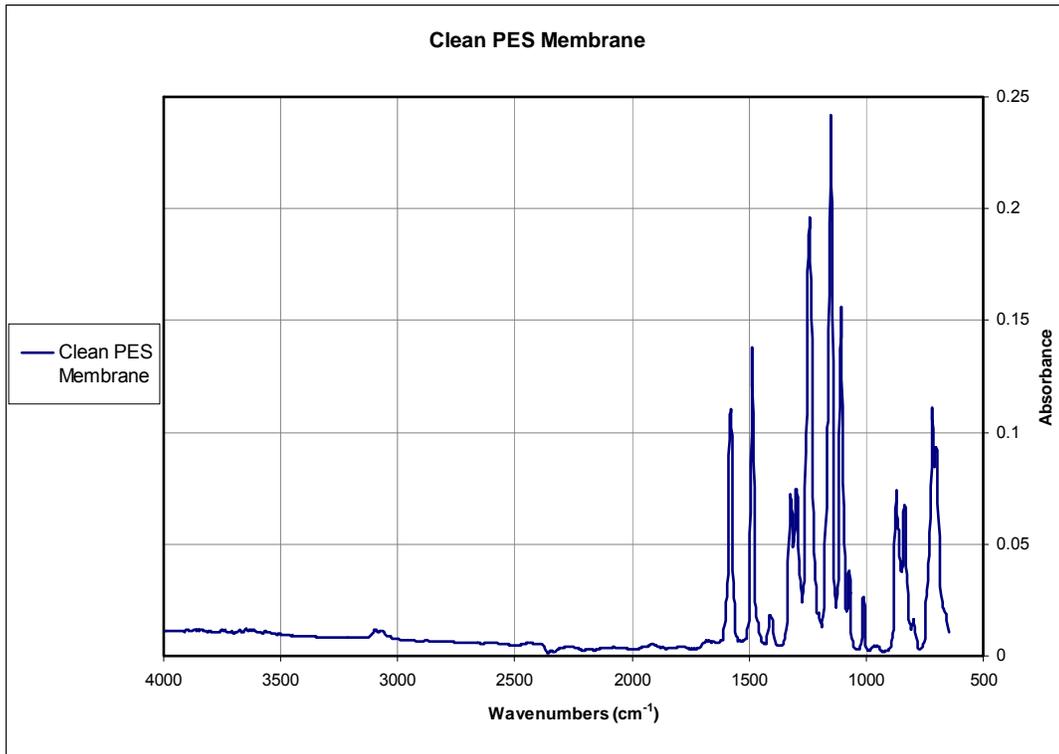


Figure 5.22. FTIR for Clean PES Membrane.

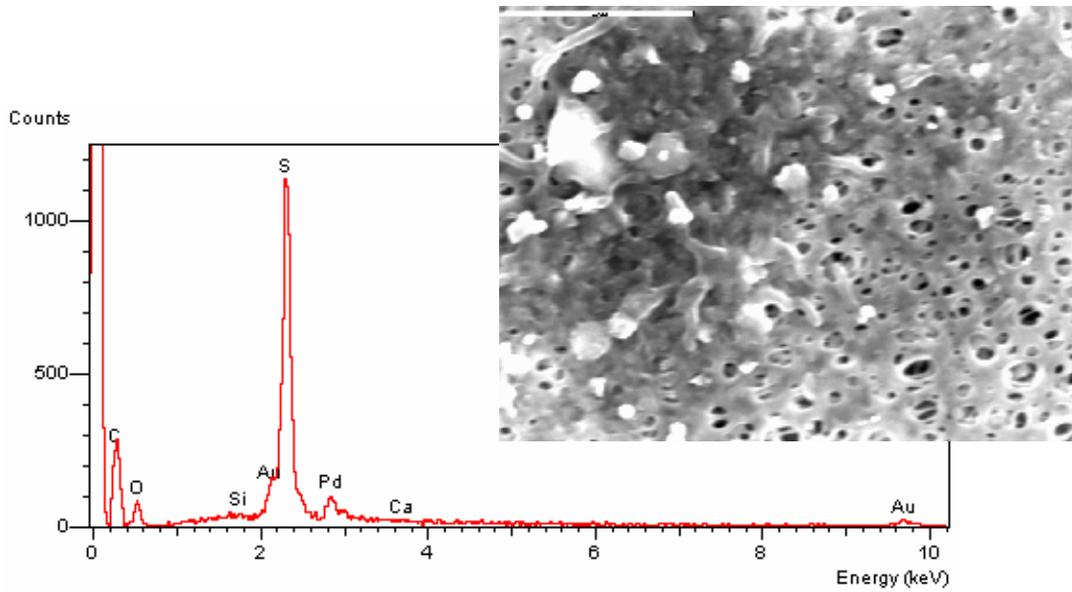


Figure 5.23. SEM image for used PES membrane with elemental analysis. DI water with calcium and silica used as feed water.

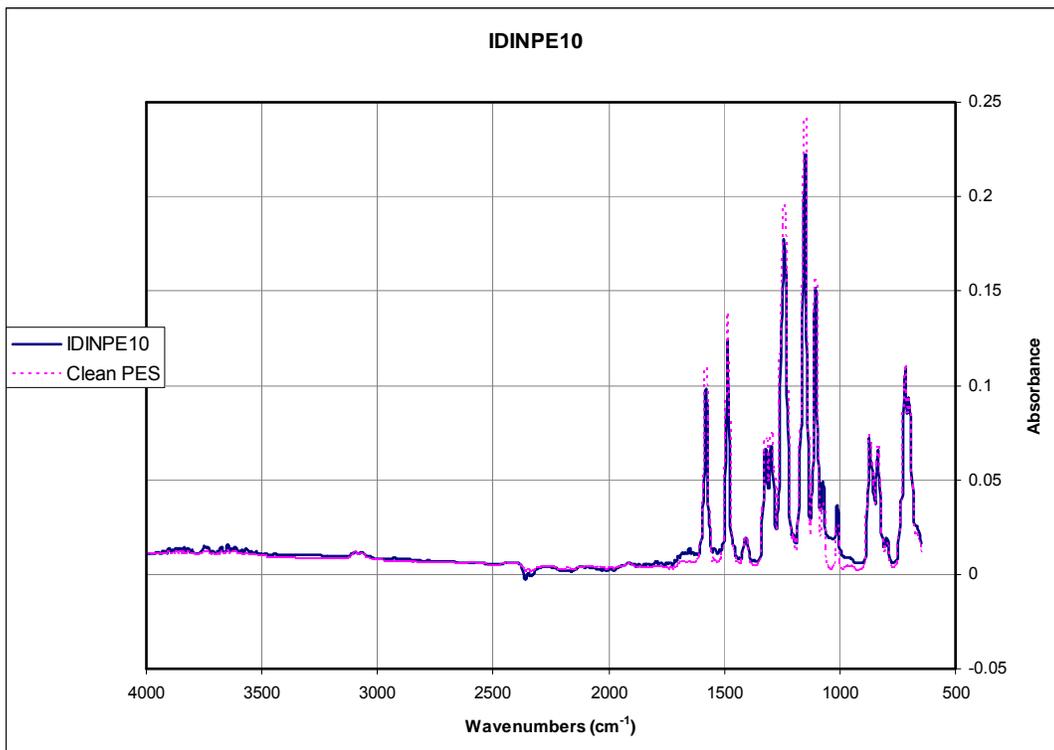


Figure 5.24. FTIR for used PES membrane, feed water was DI with calcium and silica at 10 psi feed pressure.

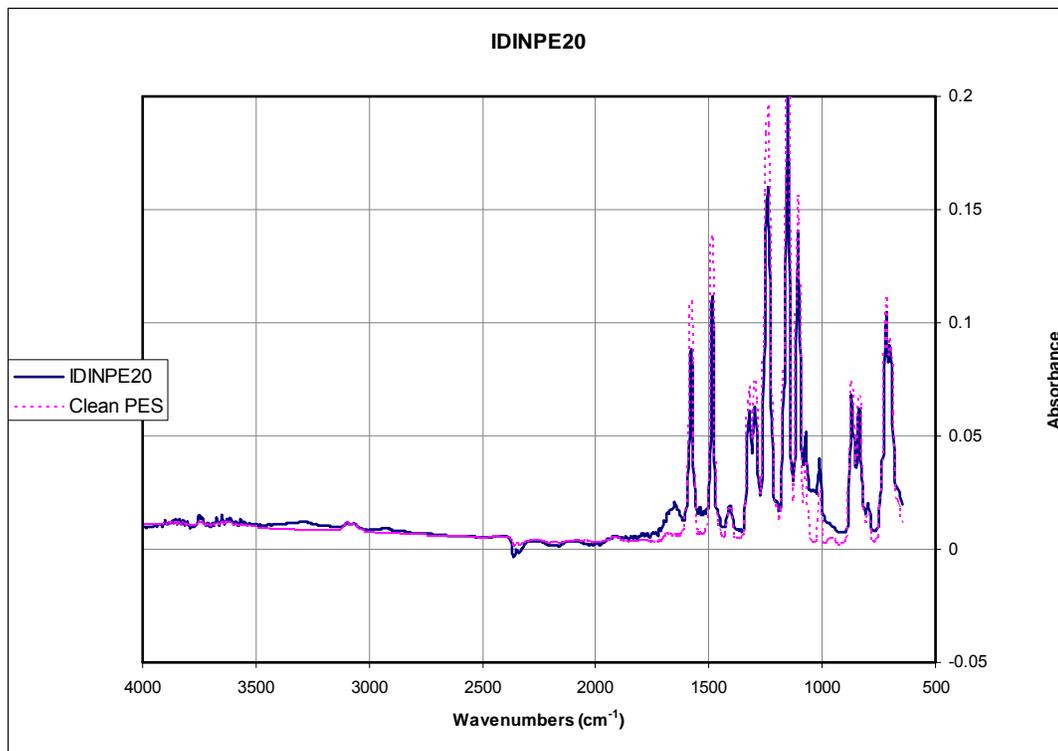


Figure 5.25. FTIR for used PES membrane, feed water was DI with calcium and silica at 20 psi feed pressure.

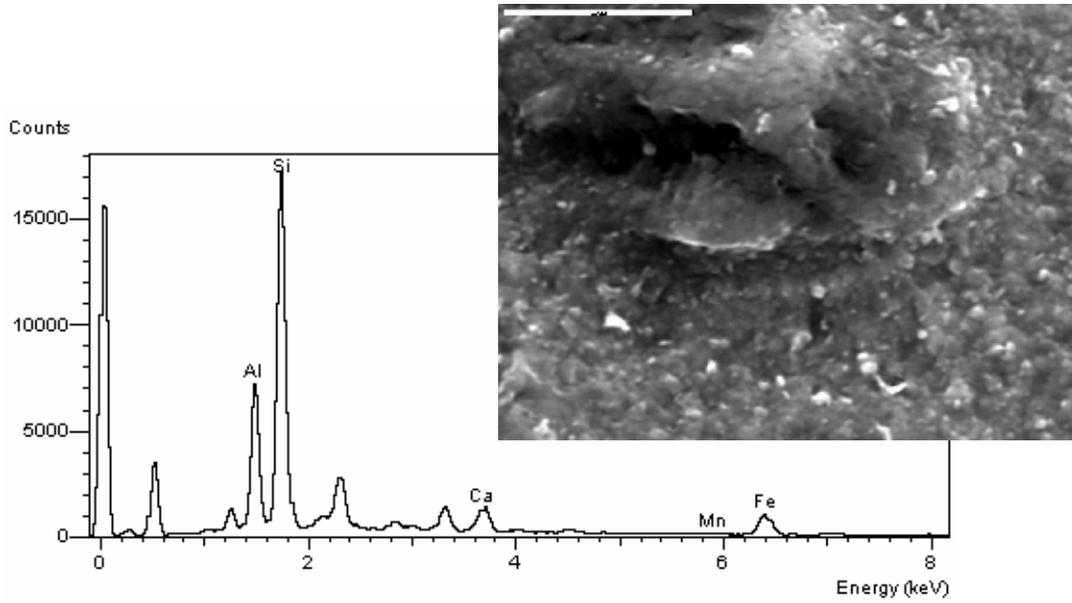


Figure 5.26. SEM image for used PES membrane with elemental analysis. Rio Grande water used as feed water and the feed pressure was 10 psi.

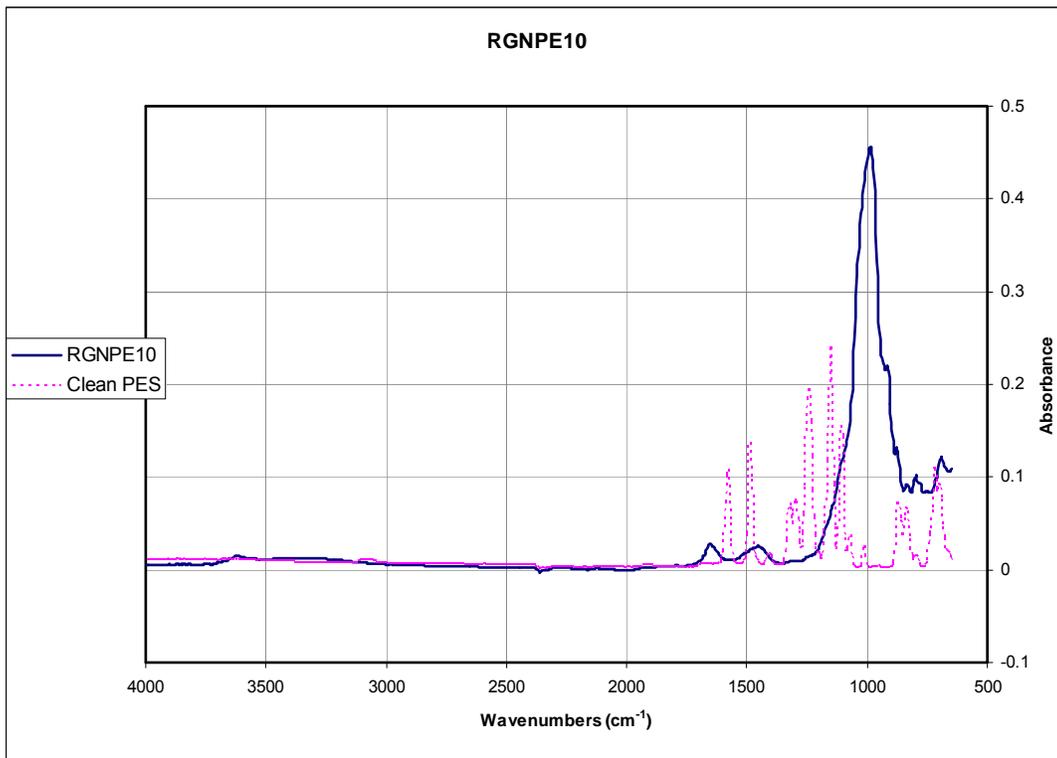


Figure 5.27. FTIR for used PES membrane, feed water from Rio Grande at 10 psi feed pressure.

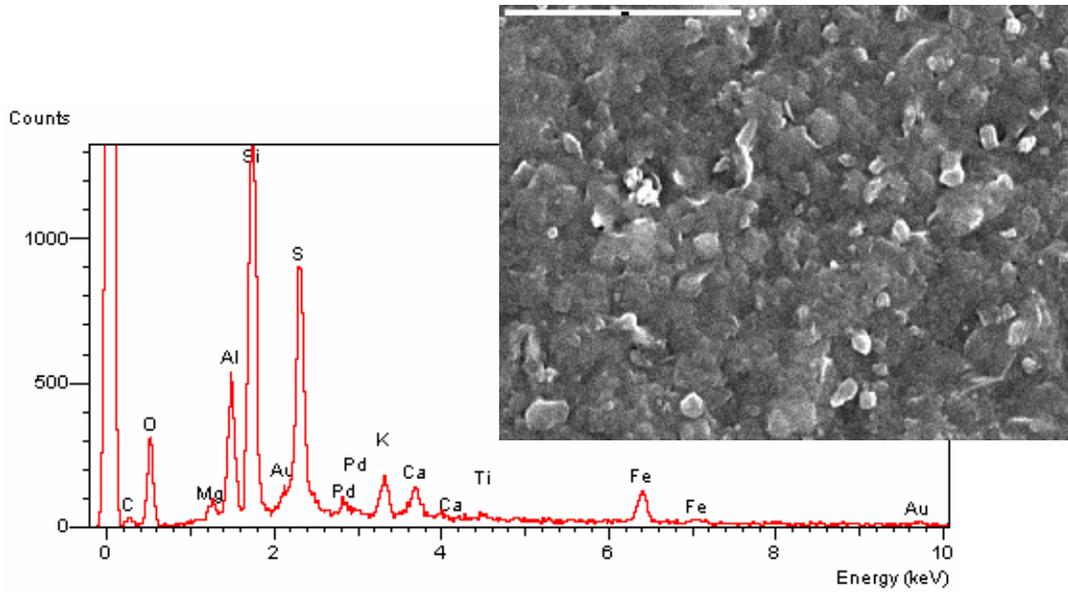


Figure 5.28. SEM image for used PES membrane with elemental analysis. Rio Grande water used as feed water and the feed pressure was 20 psi.

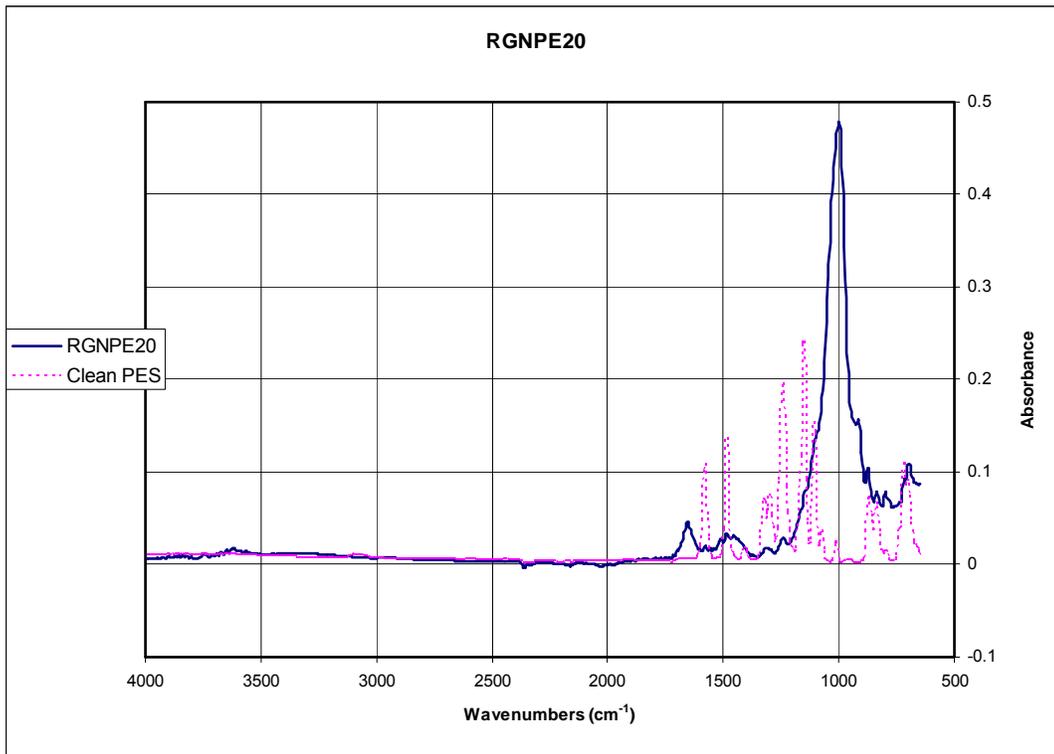


Figure 5.29. FTIR for used PES membrane, feed water from Rio Grande at 20 psi feed pressure.

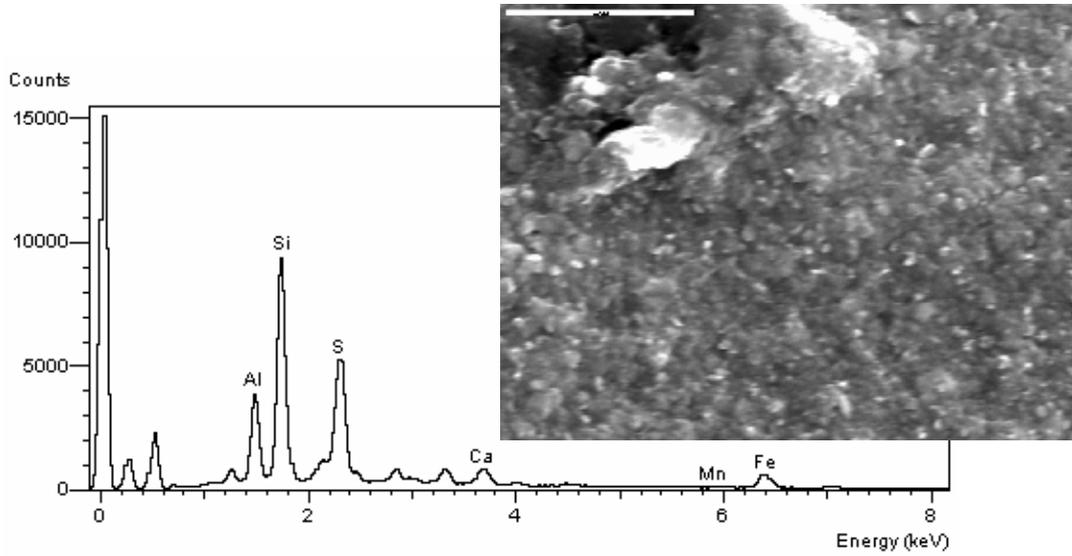


Figure 5.30. SEM image for used PES membrane with elemental analysis. Rio Grande water with calcium and silica added, used as feed water and the feed pressure was 10 psi.

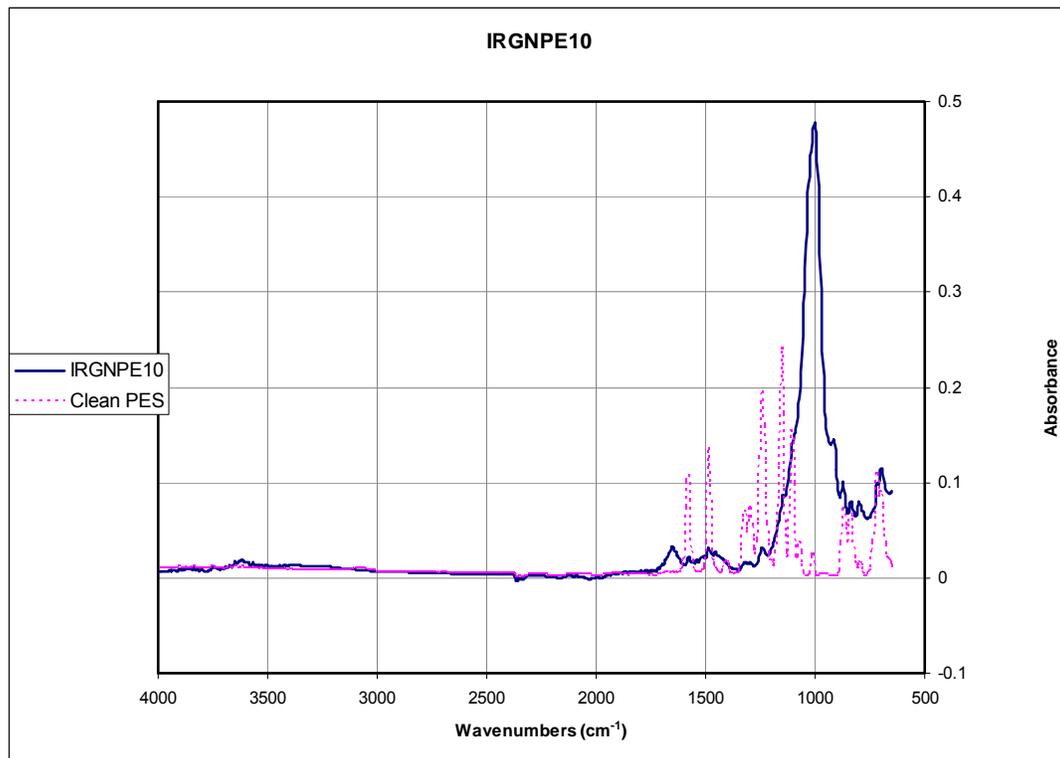


Figure 5.31. FTIR for used PES membrane, feed water from Rio Grande with calcium and silica added, at 10 psi feed pressure.

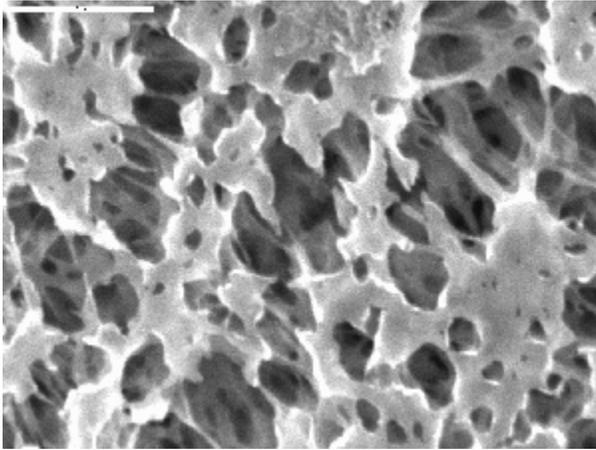


Figure 5.32. SEM image for clean PP membrane.

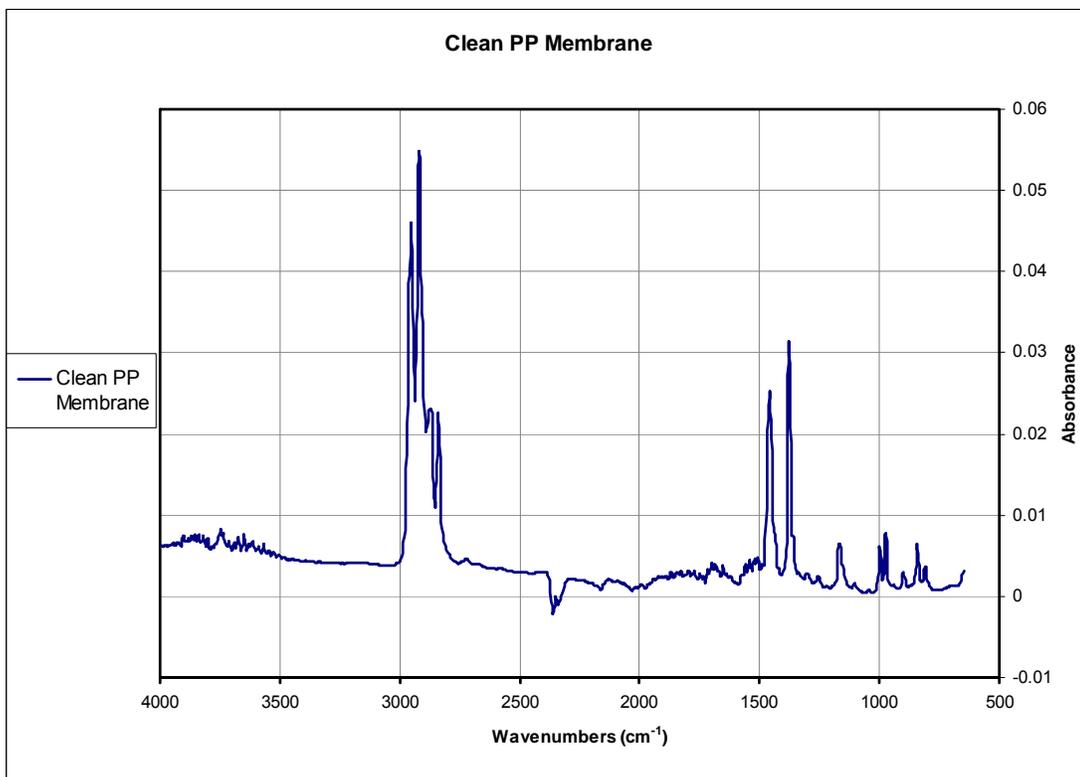


Figure 5.33. FTIR for Clean PP Membrane.

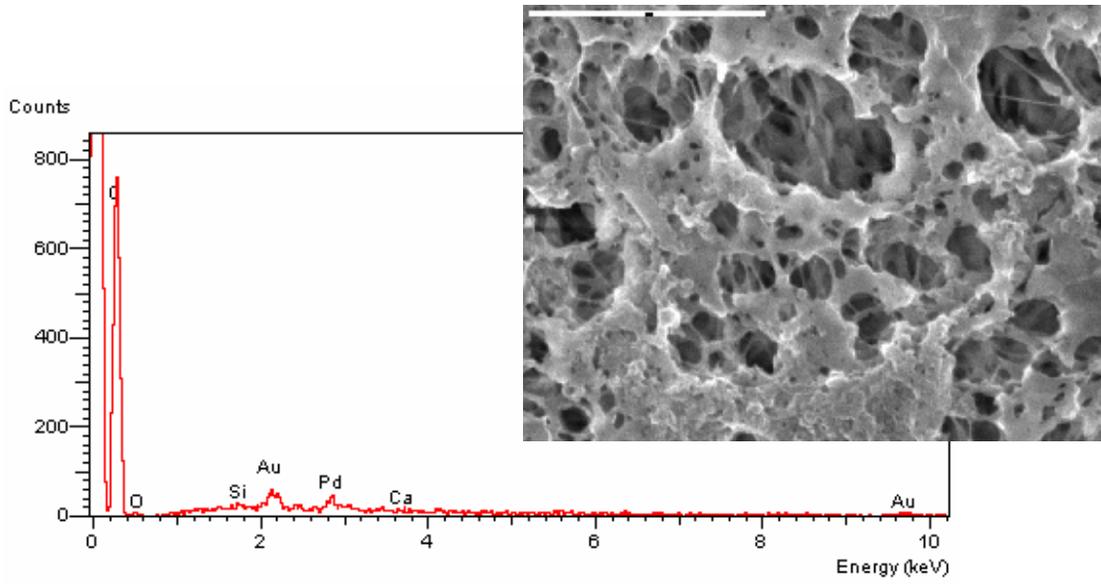


Figure 5.34. SEM image for used PP membrane with elemental analysis. DI water with calcium and silica used as feed water.

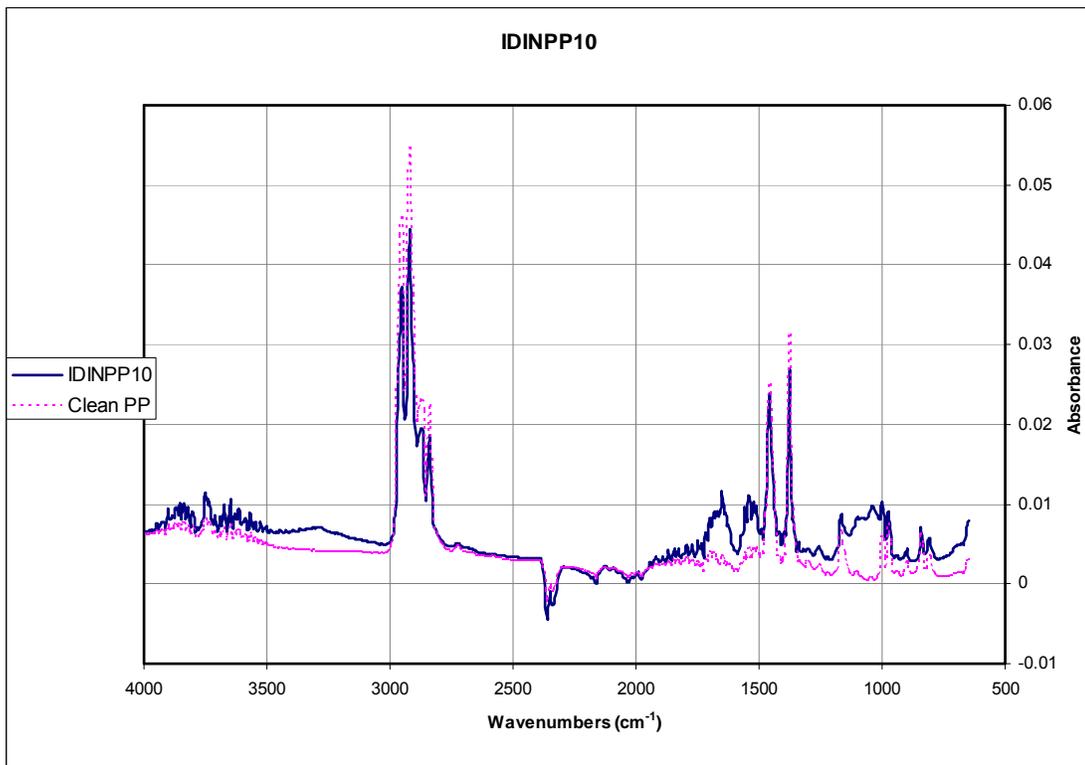


Figure 5.35. FTIR for used PP membrane, feed water was DI with calcium and silica at 10 psi feed pressure.

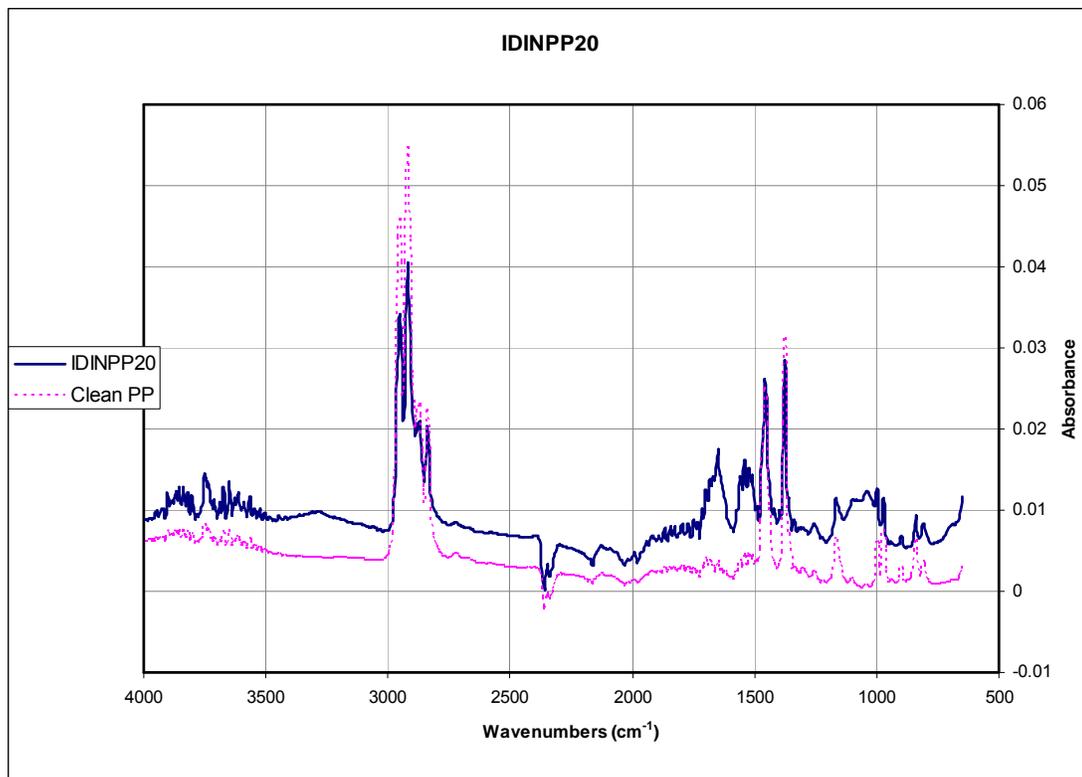


Figure 5.36. FTIR for used PP membrane, feed water was DI with calcium and silica at 20 psi feed pressure.

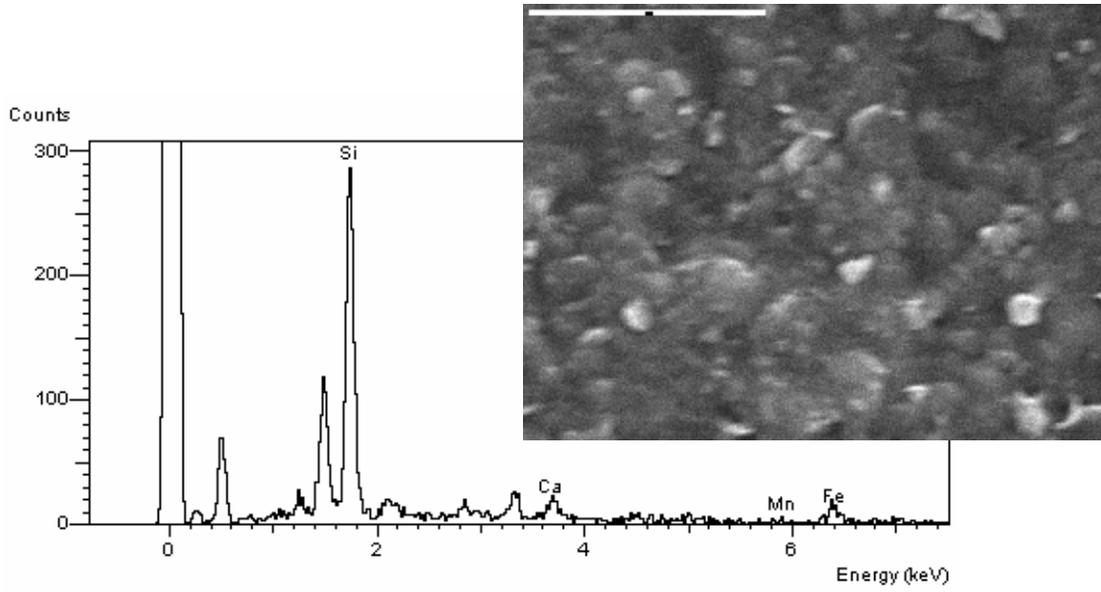


Figure 5.37. SEM image for used PP membrane with elemental analysis. Rio Grande water used as feed water and the feed pressure was 10 psi.

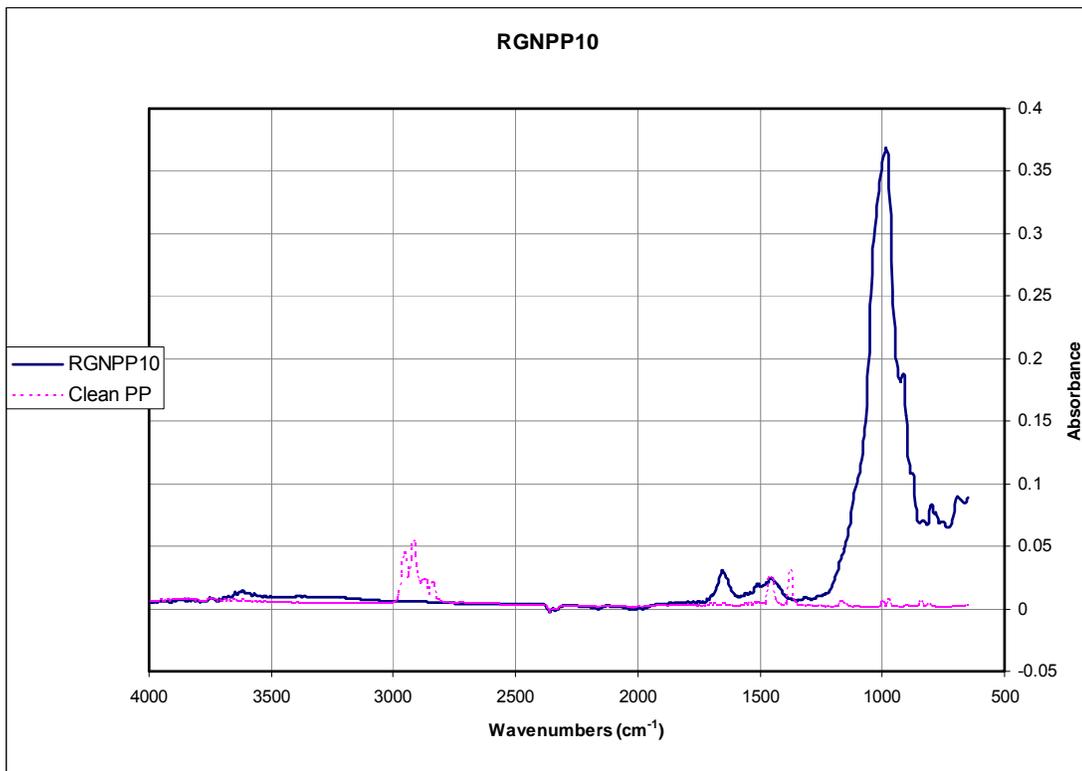


Figure 5.38. FTIR for used PP membrane, feed water from Rio Grande at 10 psi feed pressure.

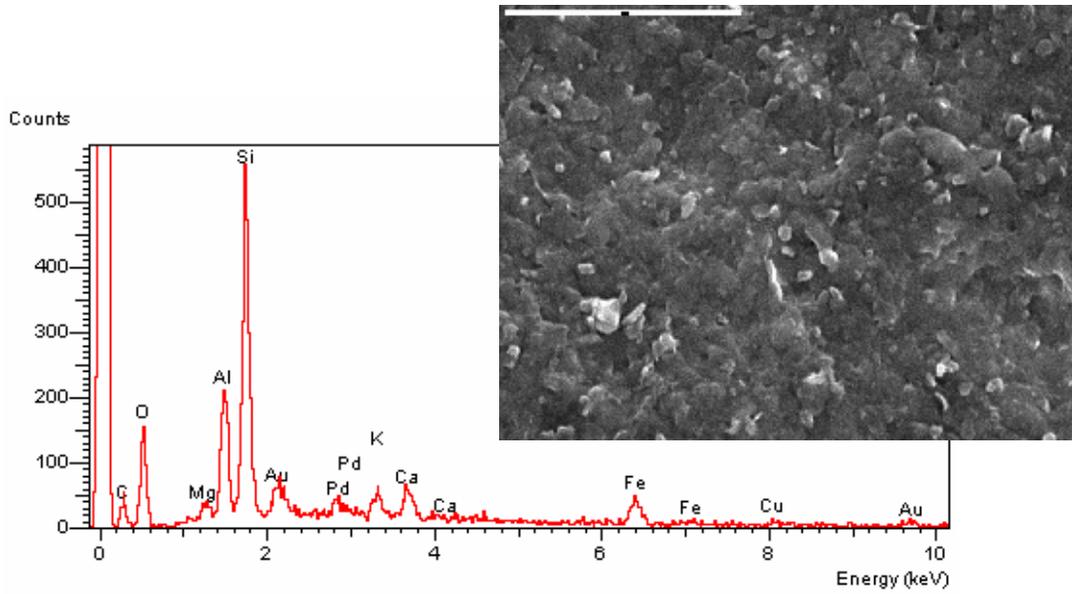


Figure 5.39. SEM image for used PP membrane with elemental analysis. Rio Grande water used as feed water and the feed pressure was 20 psi.

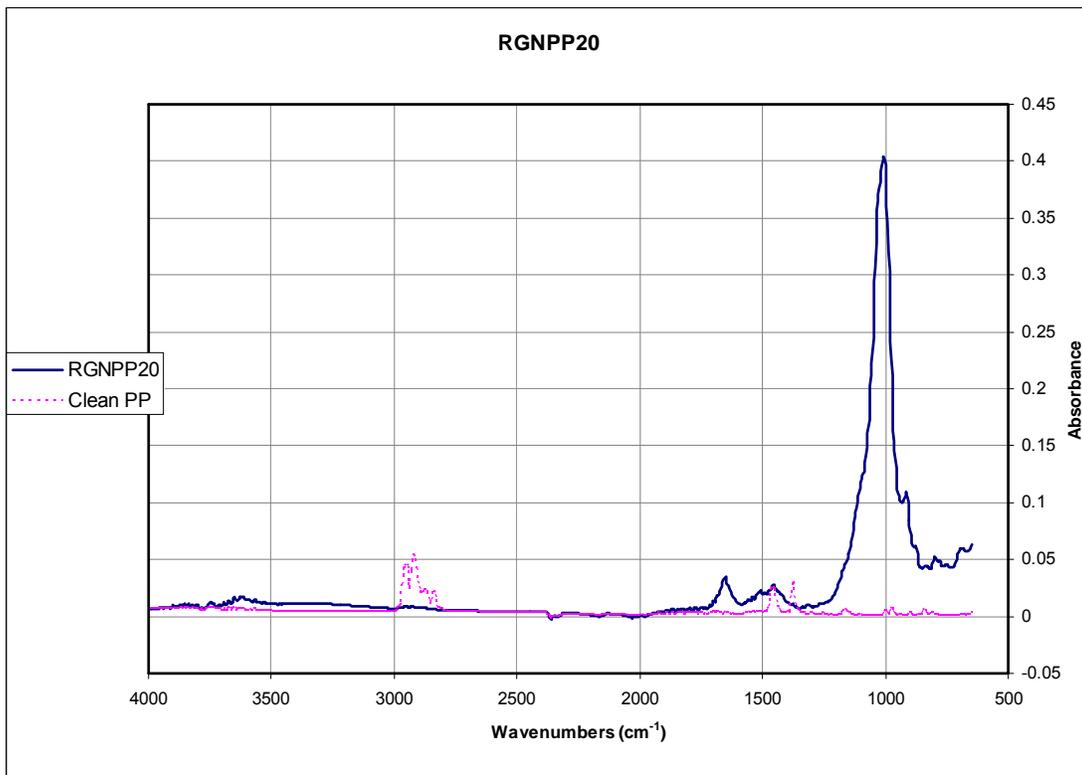


Figure 5.40. FTIR for used PP membrane, feed water from Rio Grande at 20 psi feed pressure.

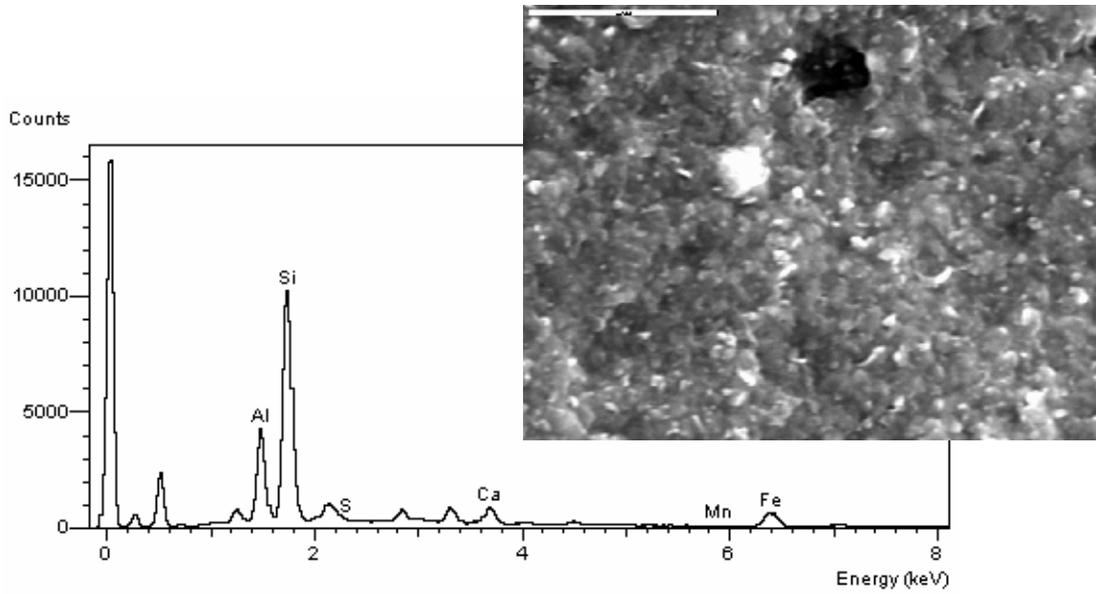


Figure 5.41. SEM image for used PP membrane with elemental analysis. Rio Grande water with calcium and silica added, used as feed water and the feed pressure was 10 psi.

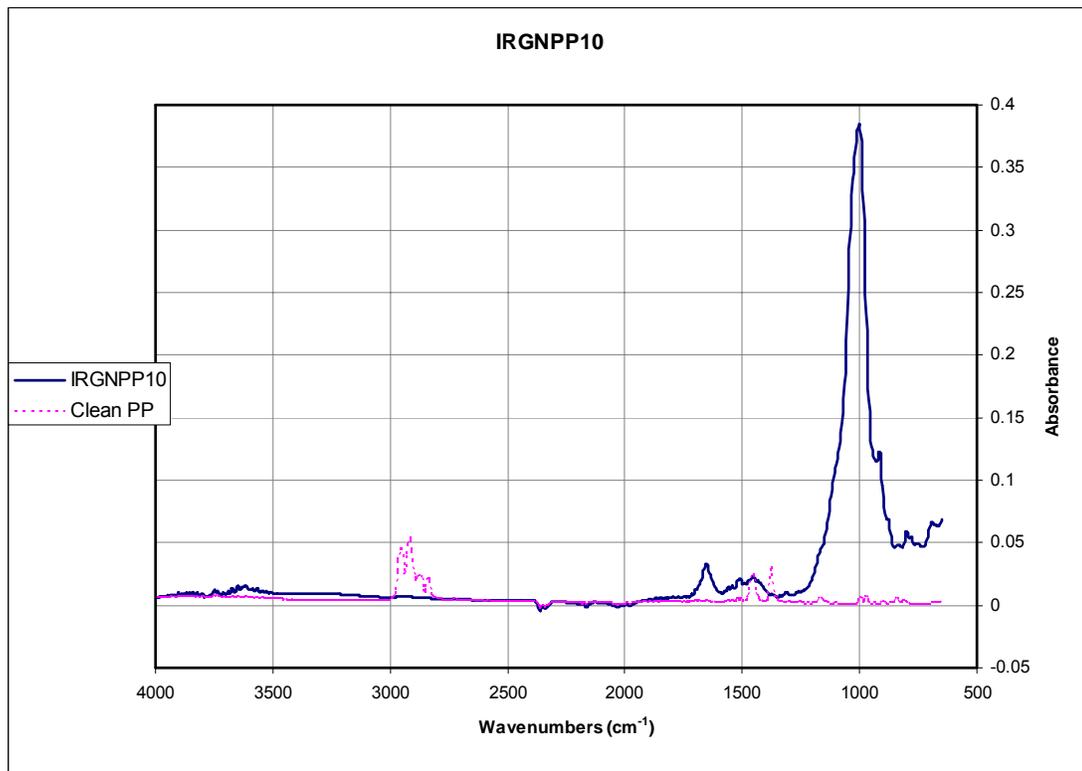


Figure 5.42. FTIR for used PP membrane, feed water from Rio Grande with calcium and silica added, at 10 psi feed pressure.

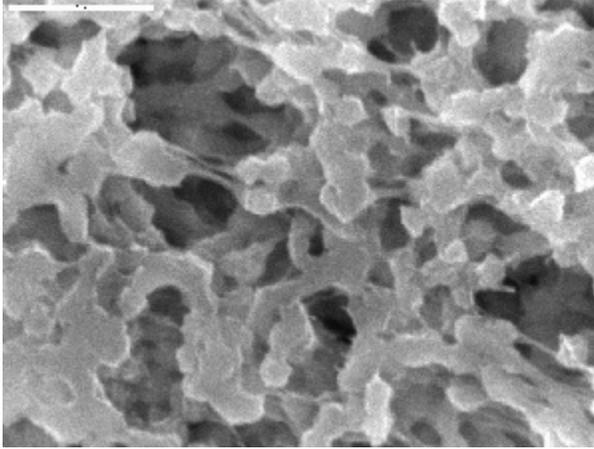


Figure 5.43. SEM image for clean PVDF membrane.

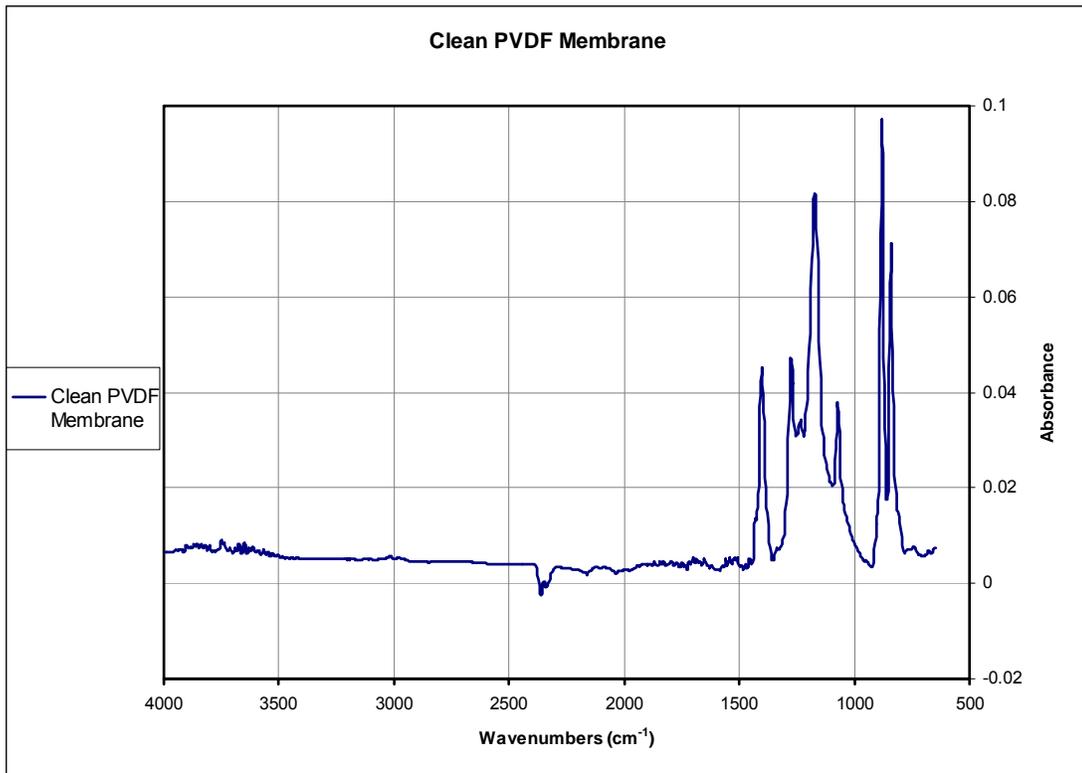


Figure 5.44. FTIR for Clean PVDF Membrane.

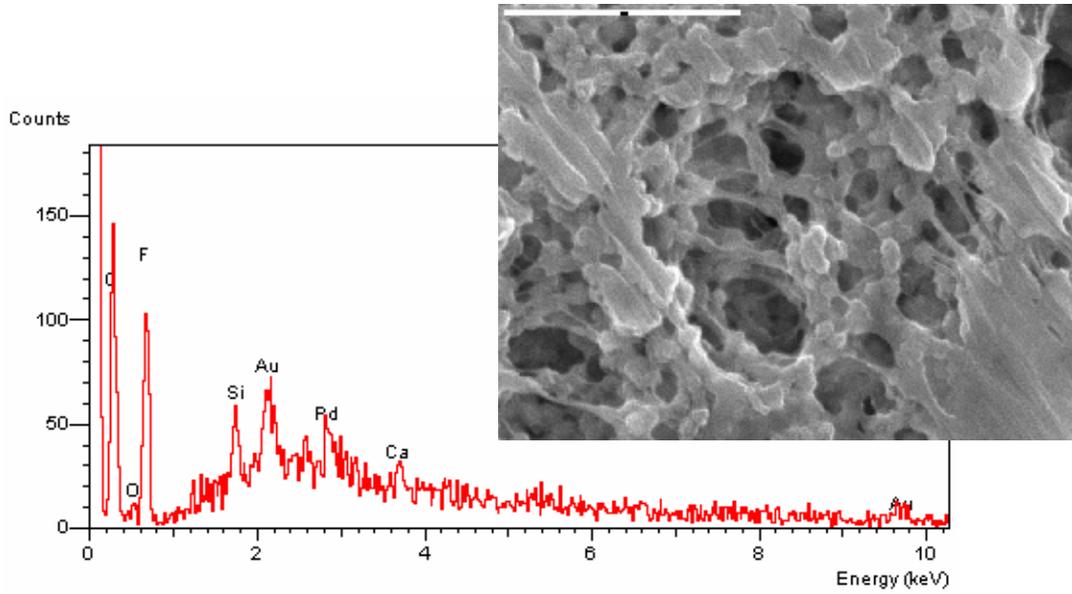


Figure 5.45. SEM image for used PVDF membrane with elemental analysis. DI water with calcium and silica used as feed water.

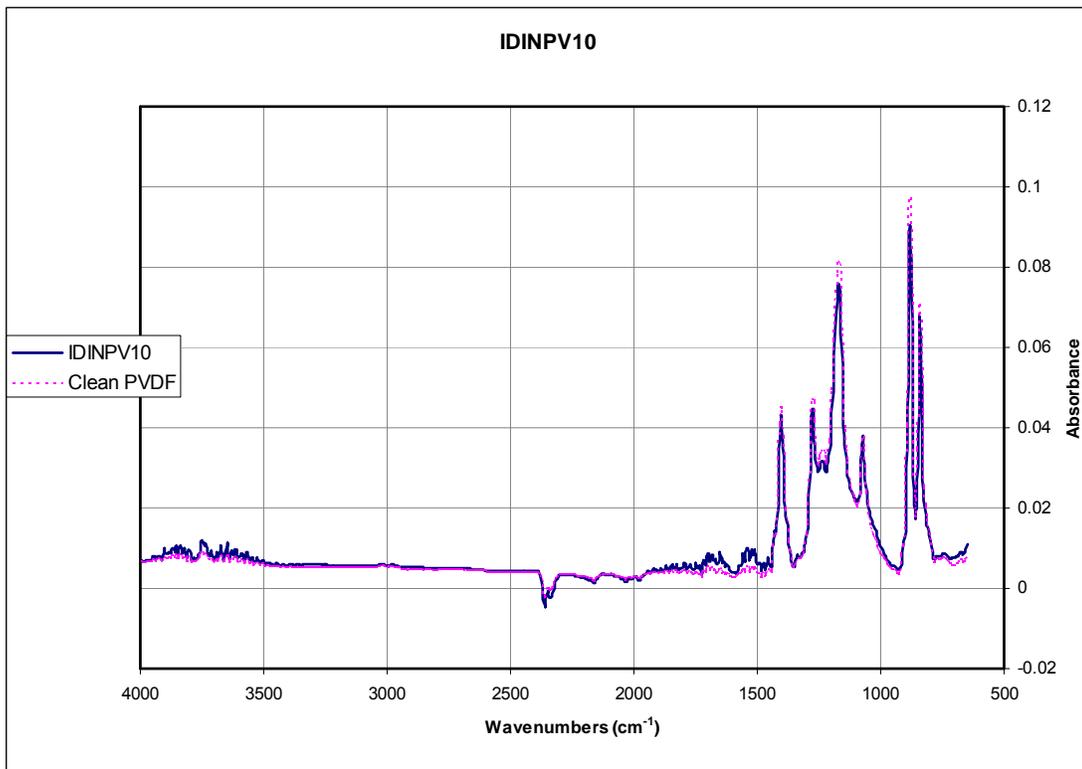


Figure 5.46. FTIR for used PVDF membrane, feed water was DI with calcium and silica at 10 psi feed pressure.

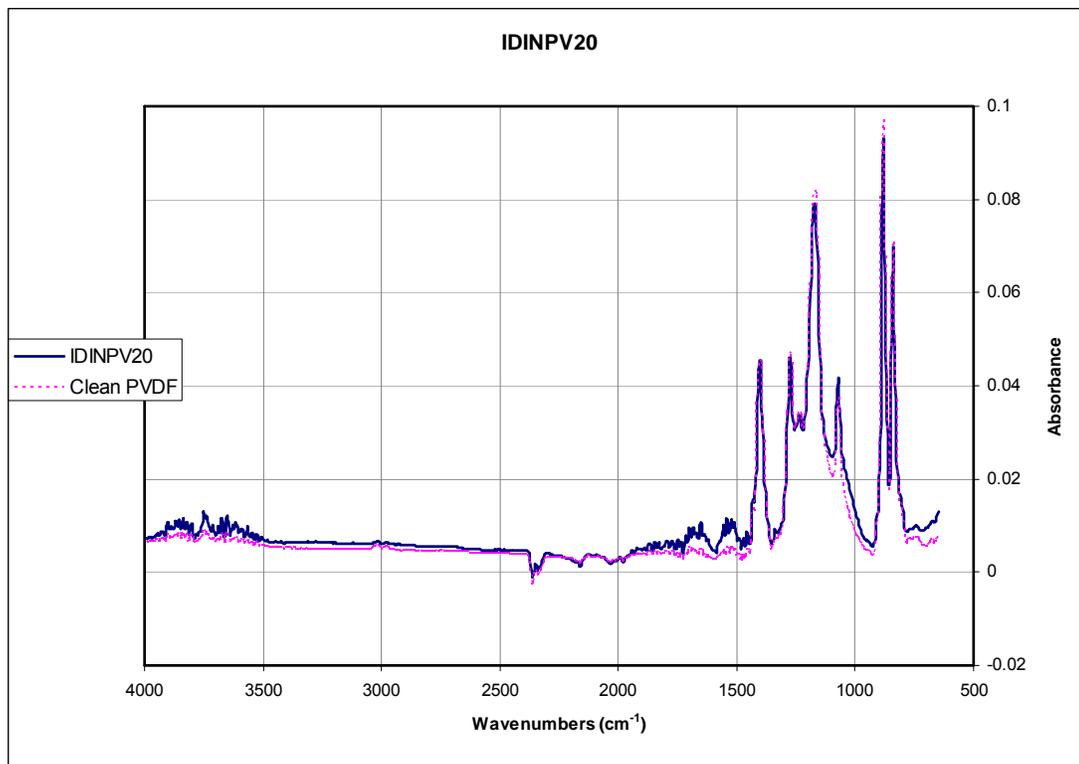


Figure 5.47. FTIR for used PVDF membrane, feed water was DI with calcium and silica at 20 psi feed pressure.

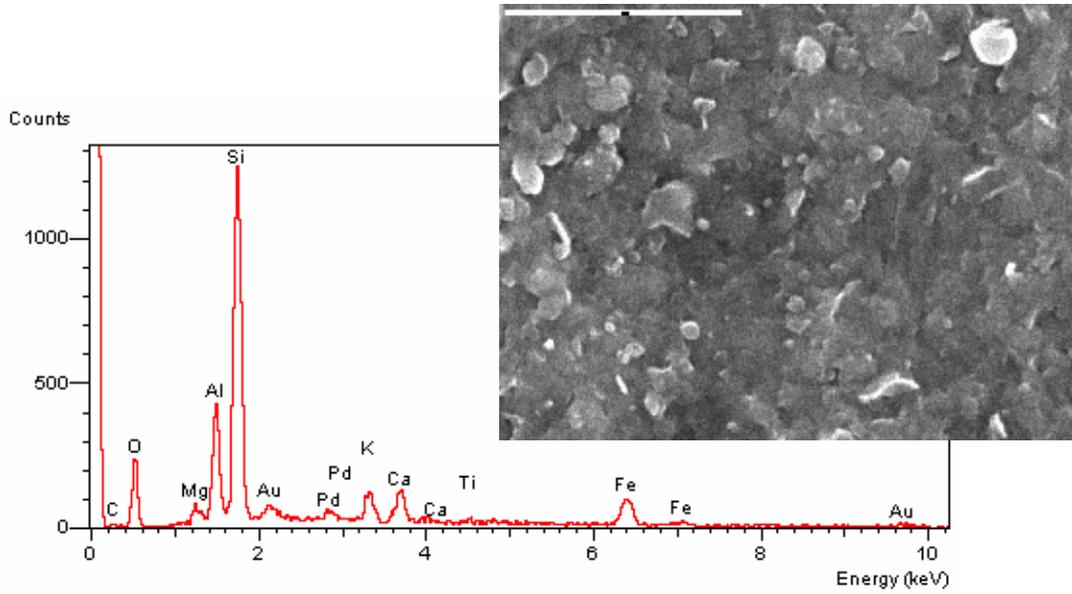


Figure 5.48. SEM image for used PVDF membrane with elemental analysis. Rio Grande water used as feed water and the feed pressure was 10 psi.

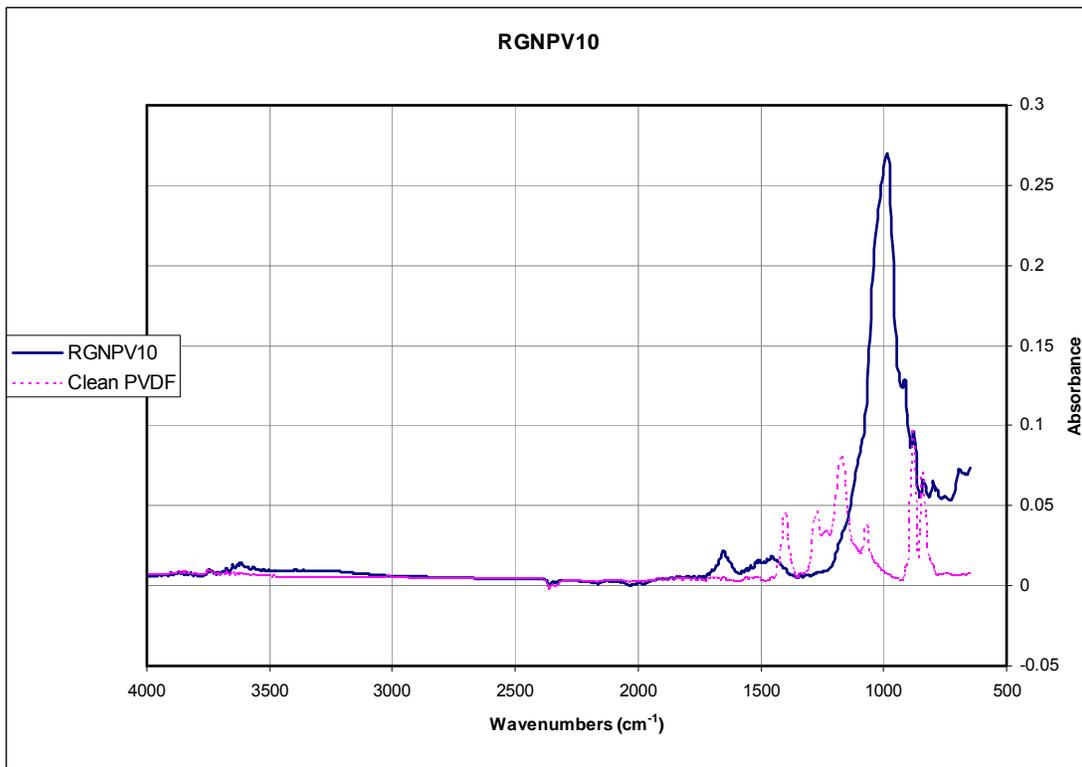


Figure 5.49. FTIR for used PVDF membrane, feed water from Rio Grande at 10 psi feed pressure.

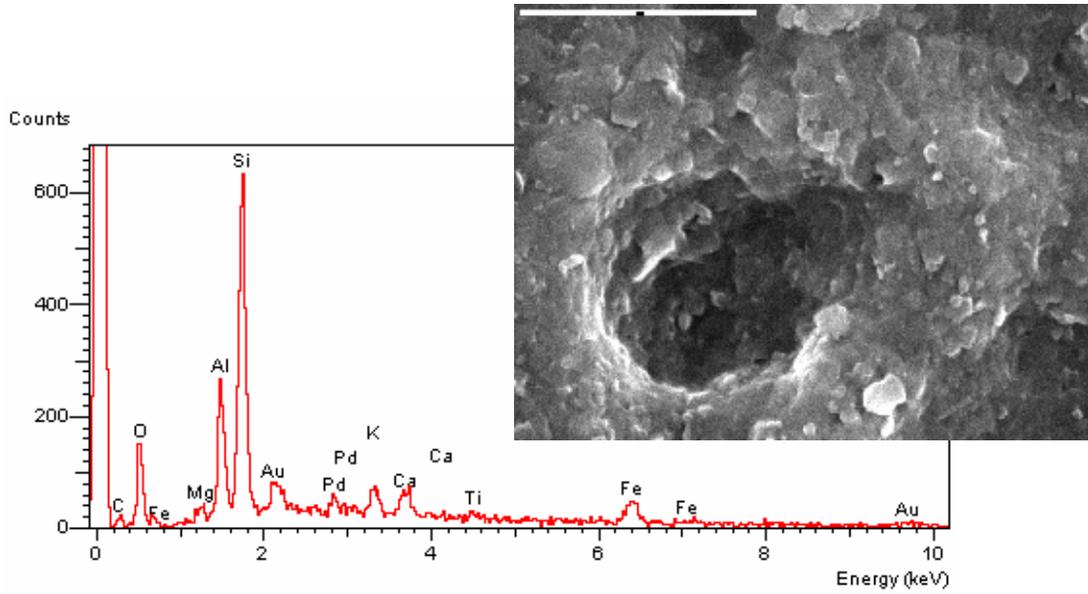


Figure 5.50. SEM image for used PVDF membrane with elemental analysis. Rio Grande water used as feed water and the feed pressure was 20 psi.

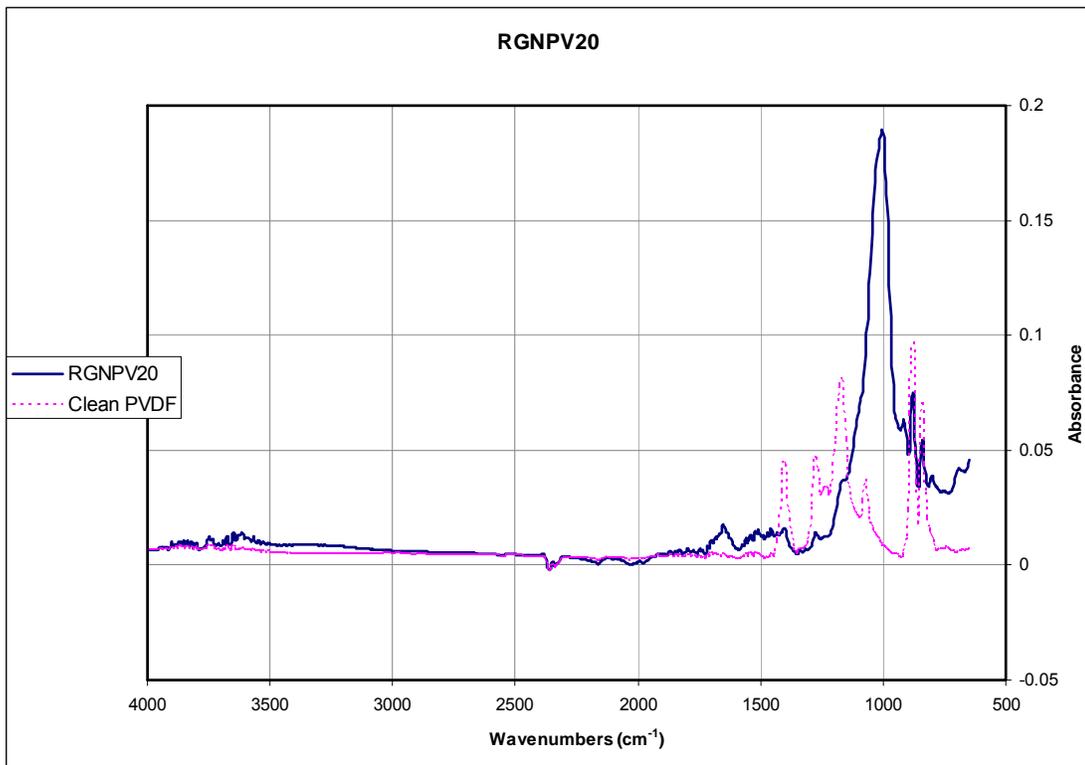


Figure 5.51. FTIR for used PVDF membrane, feed water from Rio Grande at 20 psi feed pressure.

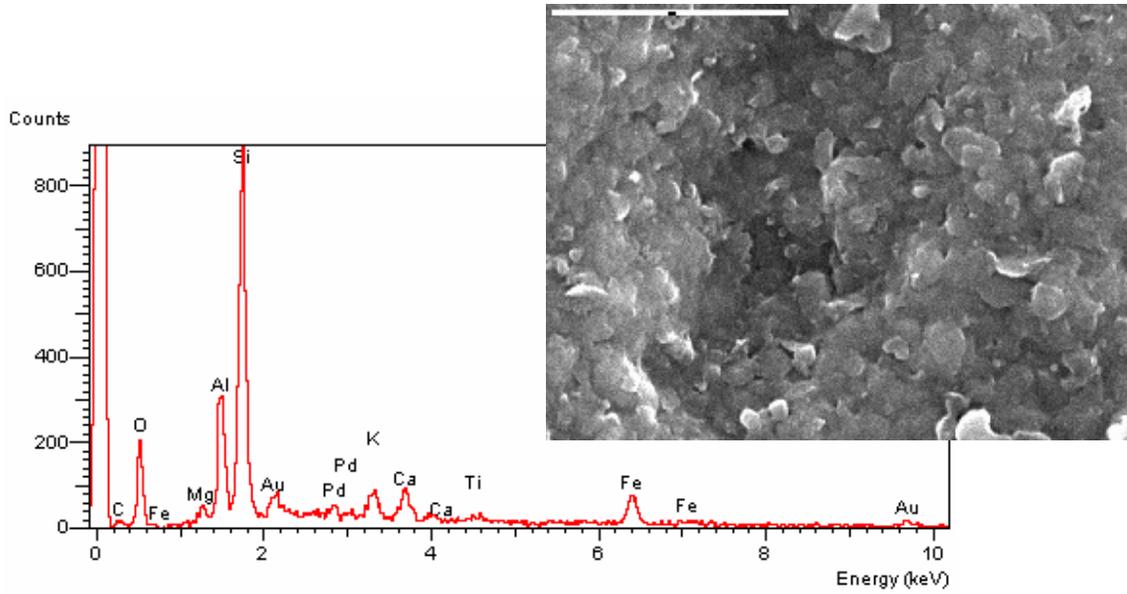


Figure 5.52. SEM image for used PVDF membrane with elemental analysis. Rio Grande water with calcium and silica added, used as feed water and the feed pressure was 10 psi.

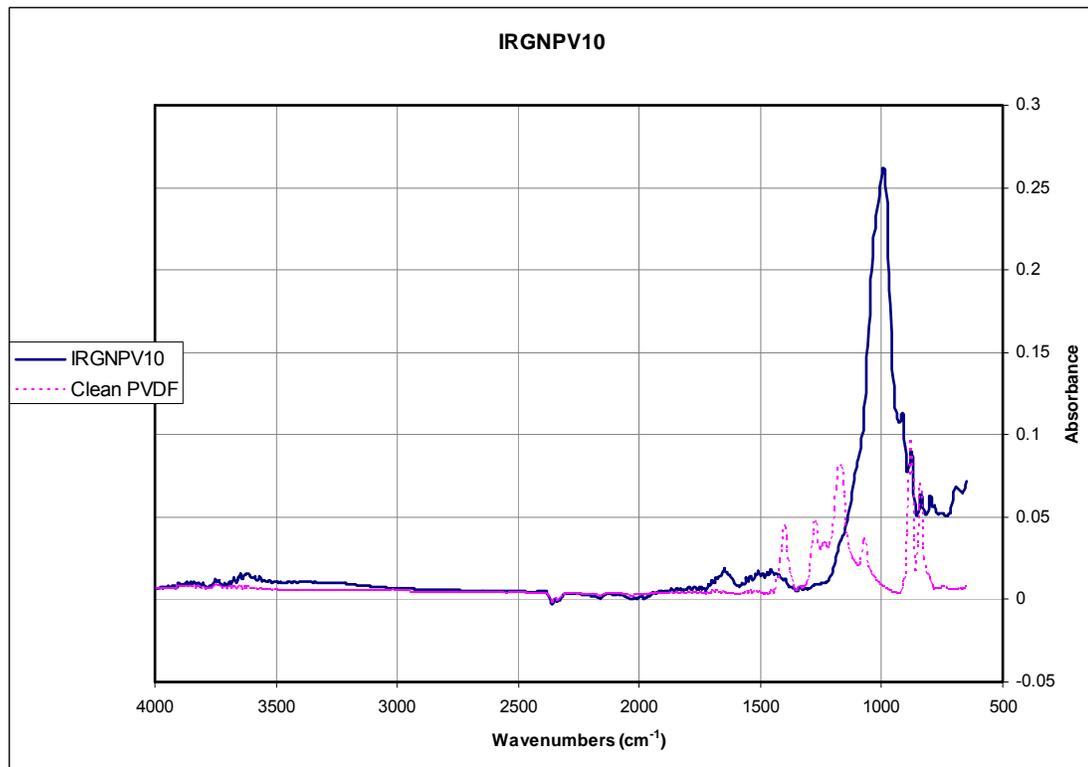


Figure 5.53. FTIR for used PVDF membrane, feed water from Rio Grande with calcium and silica added, at 10 psi feed pressure.

6 Conclusion

The results obtained in this project were not as expected. Earlier researches showed that the calcium along with organics increased fouling of membranes. Silica was also expected to foul the membranes. But the analysis of permeates obtained showed that calcium and silica had negligible or no role in fouling of these four different types of membranes. Instead, colloidal clay was the main cause of reduction in flux through the membranes. This was because the previous researches mostly used synthetically prepared feed water with particles larger than the pore size. Some researchers used surface water but from lakes and not from a river. Others used membranes that were not flat sheet or they did not use a dead end filtration system. To better classify the organic foulants, high-tech equipments like HPSEC and XAD chromatography are needed.

It will be better to use a low flux membrane to get better results by prolonging the time the experiments will run and also requiring less amount of feed water. The membranes used in this project had high flux and it was difficult to run the experiments for a longer duration of time.

All the membranes behaved differently in the filtration experiments. Feed pressure is an important parameter that controls fouling along with the composition of a membrane material. However, the most important parameter is the feed water quality. All the membranes performed differently with the same feed water. So, proper selection of the type of membrane is very important to get good results and for the membranes to perform as required.

There is a lot of potential for further research in this area with the right resources readily available and the correct feed water.

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