

# IMPACT OF FOULING ON PERFORMANCE OF DIFFERENT HFF MEMBRANES OPERATED AT DIFFERENT COASTS<sup>1</sup>

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## ABSTRACT

*Fouling of SWRO membranes and resulting performance decline are major concerns for the desalination industries utilizing SWRO process to produce potable water. In order to prevent fouling in SWRO membranes, pretreatment of the seawater is carried out prior to sending the feed to the SWRO membranes. The pretreatment needs to be efficient, especially when the hollow fine fiber (HFF) type membranes are employed because they require better quality water compared to the spiral wound membranes.*

*An investigation was carried out to find causes of poor performance of two different HFF membranes, one cellulose triacetate (CTA) and the other aromatic polyamide (PA), of which the former was operated on the Red Sea and the latter on the Gulf Sea seawater feed. In both cases, the pretreatment used the same polyelectrolyte for coagulation and for PA membrane, FeCl<sub>3</sub> was also used in addition to the polyelectrolyte. The investigation involved autopsy of membranes and various analyses such as visual inspection, biological, SEM & EDAX of membrane fibers, degree of acetylation and intrinsic viscosity measurement.*

*It was found that in both cases the major foulants are organic in nature, originating from biological sources, such as algae and bacteria. Inorganic fouling that is usually observed with the use of FeCl<sub>3</sub> coagulant alone was absent. In the CTA membrane, the organic fouling resulted in the built up of differential pressure across the membrane ( $\Delta P$ ) leading to the failure of epoxy glue holding the permeate tube, in addition to slight oxidation as well as hydrolysis observed due to suspected chlorine exposure. Moreover, bacteriological analyses revealed presence of heavy and highly pure growth of*

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<sup>1</sup> This paper has been presented at International Desalination Association (IDA) World Congress Conference held at Singapore in 2005. Also published in D&WR Quarterly Vol.14, pp 19-24, 2004.

*bacterium, even though the membrane was exposed to chlorine during operation. In the PA membrane, foulant appeared to be of biological origin and was produced by slime producing bacteria present on the membrane surface. These foulants are loosely bound to the membrane surface and could be easily removed by washing with caustic (NaOH) solution at pH = 11. It is also evident that the foulants adhering to the inner membrane fibers were responsible for high  $\Delta P$  that resulted in frequent chemical cleaning of the PA membrane.*

## **1. INTRODUCTION**

Seawater reverse-osmosis (SWRO) desalination process is gaining popularity throughout the world due to its simplicity and significant reduction in cost, which was possible due to various advancements made in membranes, energy recovery devices, materials, etc. However, one of the major hindrances to popularization of SWRO process is fouling of membrane which affects both product quantity and quality. Membrane fouling is an extremely complex phenomenon that has not been defined precisely but in general the term is used to describe the undesirable formation of deposits on membrane surfaces. This occurs when rejected solids are not transported from the surface of the membrane back to the bulk stream.

Prevention of fouling is one of the major objectives in desalination industries utilizing SWRO process. Fouling can develop due to the presence in feed water of colloidal and particulate matter, dissolved organics, and as a result of biological growth in the RO system. The formation of inorganic scale, sometimes encountered in the tail position elements in brackish systems does not present a problem with the majority of seawater feeds. Precipitation of sparingly soluble salts from SWRO concentrate is less likely to occur due to the relatively low recovery rate.

In order to prevent fouling in SWRO membranes, pretreatment of the seawater is carried out prior to sending the feed to the membranes. The pretreatment needs to be efficient, especially when hollow fine fiber (HFF) type membranes are employed because they require better quality water compared with the spiral-wound membranes. This paper describes about incidence of fouling occurred and the effect of fouling on the membrane performance on two different HFF membranes, one cellulose triacetate

(CTA) and the other aromatic polyamide (PA), of which the former was operated on the Red Sea and the latter on the Gulf Sea seawater feed.

## **2. EXPERIMENTAL METHODS**

### **2.1 *Membrane Details***

In both cases, the feed consisted of pretreated (coagulation – filtration) seawater obtained from open intakes using same type of polyelectrolyte as coagulant. However, in the case of the PA membrane, FeCl<sub>3</sub> was also used in addition to the polyelectrolyte. The plant with the CTA membrane was exhibiting a decline in plant production and recovery ratio as well as a slight increase in salt passage. On inspection of the plant, it was found that some of the membranes were damaged - the permeate tube was protruding out of the membrane after breaking the epoxy glue (see Figure 1) and hence affecting the product quantity and quality. Some of these membranes were removed, and one of them was subjected to autopsy and analyses.

### **2.2 *Biological Analyses***

Samples of fibers were aseptically collected from two spots from CTA membranes: one dark region closer to the feed tube and one yellowish brown region in midsection. Fibers from each region were incubated each in a commercial sulfate reducing bacteria (SRB) medium. Following incubation for 7 – 14 days at 30°C, media were observed for presence of SRB. Fibers were also fixed on the surface of brain heart in fusion agar plates containing 2% salt. Following incubation at 30°C for 2 days, restreaking was carried out to obtain pure bacterial isolates. Bacteria were identified using standard growth tests and commercial test systems. Samples of fibers were aseptically collected from various portions of PA membranes, in a similar way to the CTA membranes, and were analyzed for both bacteria and fungi according to standard protocol [1]. A test was also performed to verify the presence of sulfur-reducing bacteria on the membrane surface. Additionally, concentrations of proteins and sugars on the surface of membrane fibers were also determined.

### **2.3 SEM and EDX Analyses**

Fiber samples as well as reemay (spacer web) samples were collected from both the membranes and dried thoroughly before analyzing the deposits on the membrane fiber surfaces using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) Analyses.

### **2.4 Degree of Acetylation**

The degree of acetylation of CTA membrane fibers, which is normally expressed as a percentage of the acetyl group in the polymer, was determined using the same procedure as described elsewhere with a slight modification [2]. The modification involved replacement of the solvent methanol with dimethyl sulfoxide (DMSO).

### **2.5 Intrinsic Viscosity**

Intrinsic viscosity measurements were carried out after cleaning the CTA membrane fibers overnight using distilled water and rinsing PA membrane fibers using caustic (NaOH) solution at pH = 11 followed by washing the membrane fibers overnight using flowing distilled water to remove any deposits adhered to the fibers and drying the samples at 105°C in an oven for 6 hours. The intrinsic viscosity [ $\eta$ ], which is related to the polymer molecular weight, was determined following the procedure described elsewhere [2]. An Ubbelohde type capillary viscometer was used at a constant temperature of  $30 \pm 0.05^\circ\text{C}$ , however, DMSO was used as solvent instead of methylene chloride/methanol mixture for both the membranes.

## **3. RESULTS AND DISCUSSION**

### **3.1 Visual Inspection**

Figure 1 shows that the permeate tube of CTA membrane is protruding out from the membrane module after breaking the epoxy seal. Also, the membrane has been subjected to compressive force as can be seen from the folds developed on the membrane as shown in Figures 2.

Thus, it is clearly evident that there had been leak of feed seawater through this broken portion of epoxy, which made the feed to leak out through this broken path and mix with brine resulting in very little feed water actually getting through the membrane. This naturally increased recovery for this particular membrane, which forced the membrane to produce a permeate of poor quality as well as quantity. It was also found that (Figure 3) the outer membrane fibers were very clean with pure white color indicating possible bleaching due to chlorine.

However, the inner fibers, i.e., the fibers closer to membrane feed tube are found to be yellowish brown in color, which was intense for the fibers closer to the feed tube, indicating some sort of foulant adhesion on these fibers. The color diminishes gradually towards the outer fibers. This is a typical situation of HFF membrane fouled by foulants of colloidal and/or biological in nature. Moreover, a black stain was visible (Figure 4) closer to the feed tube, which is suspected to be biologically active.

During visual inspection of the PA membrane bundle (Figure 5), the outer membrane fibers appeared to be very clean, retaining the original bright golden brown color of virgin membrane fibers, indicating absence of any foulants on these fibers. However, the inner fibers, i.e., the fibers close to membrane feed tube, were found to be dark brown in color, which was very intense for the fibers nearer to the feed tube. These fibers were also found to be bound together, indicating possible foulant deposits on these fibers close to the feed tube.

Figure 6 shows difference in color of fibers removed from outer, middle and inner portion of the membrane bundle. It can be seen that dark brown color gradually becomes more intense towards the inner fibers. This is typical situation of an HFF membrane fouled by colloidal and/or biological matters. However, the lack of foul odor in the membrane points towards absence of any severe biofouling on that membrane.

The feed distribution tube was found to be relatively clean (Figure 7) with only a small amount of particles deposited on the reemay (spacer web) close to the feed tube, which might have escaped through the defects in cartridge filter, a common situation [3]. Moreover, no part of the membrane bundle was found to be damaged.

### 3.2 *Biological Analyses*

Sulfate-reducing bacteria (SRB) were isolated from the black region of the CTA membrane (Figure 4) but not from the brown one. The brown region revealed a heavy and highly pure growth of bacterium. The isolate was a gram negative rod which was positive for the following reactions: Motility, Oxidase, Catalase, Arginine, Citrate, Glycogen, Acetic acid, Citric acid, Formic acid, Lactic and Propionic acid. The isolate grew in a pH range of 5 – 10, salinity of 0.5 – 90 ppt and a temperature range of 10 – 40 °C. It grew in media containing 250 ppm but not in 500 ppm formaldehyde. Growth was also positive following 15 min. exposure to 1 mg/L chlorine and 2 – h exposure to 0.5 mg/L chlorine. The isolate belongs to the genus *Pseudomonas* in the cluster *Pseudomonas mendocina-alkaligenes-pseudoalkaligenes – stutzeri – balearica* and is phenotypically most related to the species *Pseudomonas Mendocina*. It can be summarized that formaldehyde preservative would be insufficient below a concentration of 500 ppm. Also, the bacterium was found to adapt well to chlorination and thus chlorine-tolerant membranes are equally susceptible to biofouling as their chlorine – sensitive counterparts.

Bacteriological analyses data of the PA membrane are given in Table 1, which show that the fibers collected from the outer and middle portion of the membrane contain only negligible amounts of bacteria, whereas the inner fibers contain about  $3.15 \times 10^5$  CFU/g dry weight. Moreover, it was found that the foulants were loosely attached to the membrane and most of it could be detached by hand shaking in sterile saline solutions.

The remaining attached biofilm was dominated by a bacterial isolate of a large mucoid (slime producing) colony. The amount of sugars as well as proteins indicate that the foulants are of biological origin and found to be in great numbers in the inner fibers than in the outer fibers where they were present in negligible quantity. One of the sugar components, extracellular polysaccharides (EPS), the substance responsible for the slimy nature of the biofilms and a product of the micro-organisms themselves, are usually produced to a greater or lesser extent by a variety of bacteria species. Also high amount of EPS were found where chlorination / dechlorination is used in the system [4]. As shown in Table 1, the reemay was found to contain very less amount of bacteria

attached to it ( $4.59 \times 10^2$  CFU/cm<sup>2</sup>). It was interesting to see the presence of sulfur reducing bacteria in the inner fibers and not in the outer fibers. This situation indicates presence of anaerobic condition in the inner fibers, probably due to the presence of decomposing biofilm in the inner fiber surface.

### 3.3 *SEM and EDX Analyses*

The amount of foulant adhering to the CTA membrane fibers was very small and could not be removed from the fibers' surface for the wet chemical analyses to be done. Hence, SEM and EDX were utilized to identify the foulants adhering to the inner membrane fibers. SEM and EDX analyses were in conformity with visual inspection results as they showed that the inner fibers had much higher foulants on their surface, the outer fibers had the least and the middle fibers had foulants in between that of inner and outer (Figures 8 – 10). The EDX spectrum showed that the foulant mainly constitutes Al, Si, Fe, Cr, and Cu in addition to the inorganic component typically found in seawater such as Ca, Mg, Na, S and Cl.

Presence of C and O could be from membrane itself or due to organic foulant present on the membrane or from carbonates. Occurrence of Si along with Al indicates presence of aluminum silicate. Aluminium silicate is a common foulant and much of it found on membrane deposits is present as silt, clay and other commonly found compounds such as diatomaceous earth formed from algal skeletons [5]. The algae present in the seawater could have been broken into smaller fragments during chlorination and escaped through the media and cartridge filters before reaching the membrane surface. Also presence of Fe along with Cr indicates presence of corrosion products from stainless steel piping. The middle fibers (Figure 9) also contain foulant similar in composition that found on inner fibers. The outer fiber (Figure 10) was found to be very clean and only peaks due to C and O could be seen in the EDX spectra, which of course corresponds to the membrane material and Au peak seen on all the EDX is from the gold coating applied on the sample during the analysis.

The results of SEM and EDX analyses carried out to identify the foulants adhering to the PA membrane fibers conformed with visual inspection results which showed that

the inner fibers had much higher foulants on their surface, the outer fibers had the least and the middle fibers had foulants in between that of inner and outer fibers (Figures 11 – 13).

The outer fiber (Figure 11) was found to be very clean and only peaks due to carbon (C) and oxygen (O), could be seen in the EDX spectra, which, of course, corresponds to the membrane material, and the gold (Au) peak seen on all the EDX spectrum is from the gold coating applied on the sample during the analysis. The magnesium (Mg) and sodium (Na) peaks present in the middle fibers could have originated from the seawater itself and the fibers appear to be relatively clean (Figure 12). The inner membrane fibers (Figure 13) found to contain thick foulant deposit on its surface and the EDX spectrum showed that the foulant mainly constitutes C and O that could be from the organic foulant present on the membrane. This clearly indicates that the foulant is biological in nature as confirmed from the presence of sugars and proteins. It is also quite evident from SEM and EDX analyses that no inorganic fouling has taken place on the membrane, and even the iron (Fe), which was used as coagulant ( $\text{FeCl}_3$ ), was not present in any of the membrane fiber surfaces.

As an additional experiment, a small amount of inner membrane fibers were immersed in NaOH solution at pH = 11 for 2 hours followed by rinsing with distilled water, and it was found that most of the foulants adhering to the membrane surface were removed, as can be seen from the SEM micrographs (compare Figures 14 and 13). This indicated that the biofilms formed on the membrane fibers are not of a stubborn type and are easily removable by high pH cleaning.

The reemay showed (Figure 15) presence of small particles trapped on it, which mainly consists of silicon (Si), aluminium (Al), Mg and potassium (K) and could originate from silt.

### **3.4 Degree of Acetylation**

The results of the degree of acetylation measurements for the CTA membrane are shown in Table 2. The value for outer, middle and inner fibers did not differ much and was in the range of 58.4 – 58.8%.

However, this value is below the value reported for the same type of virgin membrane, which was in the range of 59.9 – 60.7% [2] indicating possible hydrolysis of the membrane fibers regardless of the position of it in the membrane element. The probable cause could be exposure of the membrane to higher amount of chlorine in the presence of heavy metals.

### **3.5 *Intrinsic Viscosity***

The intrinsic viscosity results for the CTA membrane are shown in Table 2. They were in the range 1.25 - 1.29 dl/g. However, these values are below the intrinsic viscosity for the virgin membrane [2], which was in the range of 1.31 – 1.41 dl/g, indicating possible oxidation due to exposure to chlorine which confirms the visual inspection results of outer membrane which were found to be bleached. Intrinsic viscosity results for the PA membrane fibers are given Table 1. It was found that the values were almost the same ( $\approx 0.84$  dl/g) for all the membrane fibers regardless of position of sampling such as outer, middle or inner. As the foulants were present in the inner fibers, to a lesser extent in the middle fibers and least in the outer fibers, the intrinsic viscosity values could have been different for each of them if any sort of oxidation had taken place. Thus it can be inferred that the membrane was not exposed to any oxidative conditions.

## **4. CONCLUSION**

The study revealed that organic fouling resulting from biological activity was the major cause of the poor performance of both the membranes. Organic fouling of the CTA membrane increased differential pressure built up across the membrane ( $\Delta P$ ) and lead to the failure of the epoxy glue holding the permeate tube: This damage allowed only part of the feed flow to reach the membrane thus forcing the membrane to operate at high recovery, which resulted in lower production as well as poor permeate quality. In addition that, it was also found that the membrane did undergo slight oxidative degradation (as indicated by intrinsic viscosity) as well as hydrolysis (as indicated by loss in degree of acetylation), which also increased the salt passage. It is likely that the membrane was exposed to a higher concentration of chlorine than the recommended dose rate.

Bacteriological analyses of the CTA membrane revealed the presence of a heavy and highly pure growth of bacterium, which was found to grow between pH 5 and 10, as well as in formaldehyde of less than 500 ppm. Also the bacterium was found to be resistant to 1 ppm of chlorine for 15 minutes and 0.5 ppm of chlorine for 2 hours. Moreover, sulfur-reducing bacteria were also found in a small black spot near the feed tube. However, the major foulants on the CTA membrane were found to originate from algal skeletons, which escaped the filters and reached the membrane.

The membrane foulant, which was mainly found only on the inner portion of the PA membrane, was of biological origin and was produced by slime-producing bacteria present in the membrane surface and these foulants were responsible for high  $\Delta P$ , which resulted in frequent chemical cleaning of the membrane. It was found that these biofilms were loosely bound to the membrane surface and were easily removed by washing with caustic (NaOH) solution at pH = 11. The intrinsic viscosity study revealed that the PA membrane was not exposed to any kind of oxidative conditions and, moreover, the membrane was found to be free from any mechanical defects.

## 5. REFERENCES

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**Table 1. Results of Various Analyses Performed on PA Membrane Fibers**

Analyses		Inner Fibers	Middle Fibers	Outer Fibers	Reemay
Biological Analyses	Bacteria (CFU/g)	$3.15 \times 10^5$	Negligible	Negligible	-
	Bacteria (CFU/cm <sup>2</sup> )	-	-	-	$4.59 \times 10^2$
	Sulfur reducing bacteria	Positive	-	Negative	-
Proteins (mg/g)		1.6	-	0.42	-
Sugars (mg/g)		3.18	-	0.11	-
Intrinsic Viscosity (dl/g)		0.83	0.84	0.84	-

**Table 2. Results of Various Analyses Performed on CTA Membrane Fibers**

Analyses	Outer	Middle	Inner
Degree of Acetylation (%)	58.8	58.6	58.4
Intrinsic Viscosity (dL/g)	1.26	1.29	1.25



**Figure 1. View of permeate tube protrusion of CTA membrane**



**Figure 2. View of folds developed on the CTA membrane**



**Figure 3. View of autopsied CTA membrane showing the color difference among the fibers**



**Figure 4. View of autopsied CTA membrane showing a black colored stain near the feed tube**



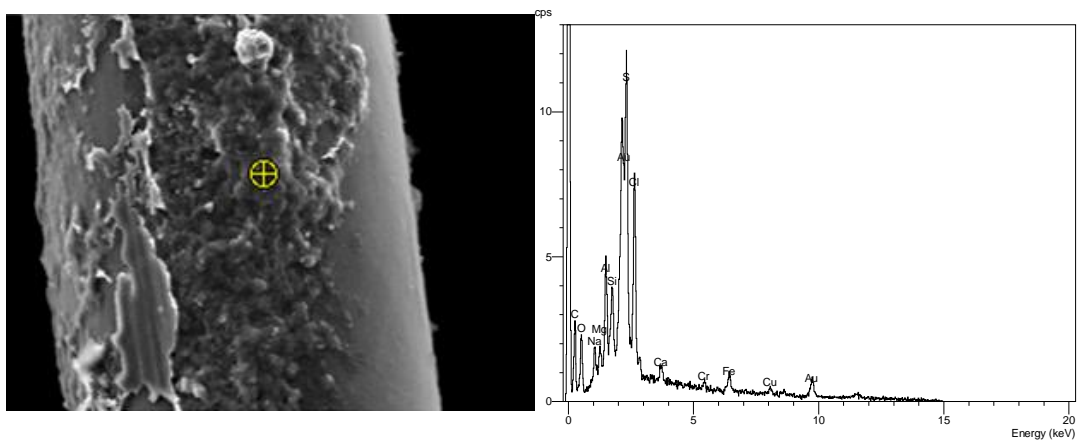
**Figure 5. View of autopsied PA membrane showing the color difference among the fibers**



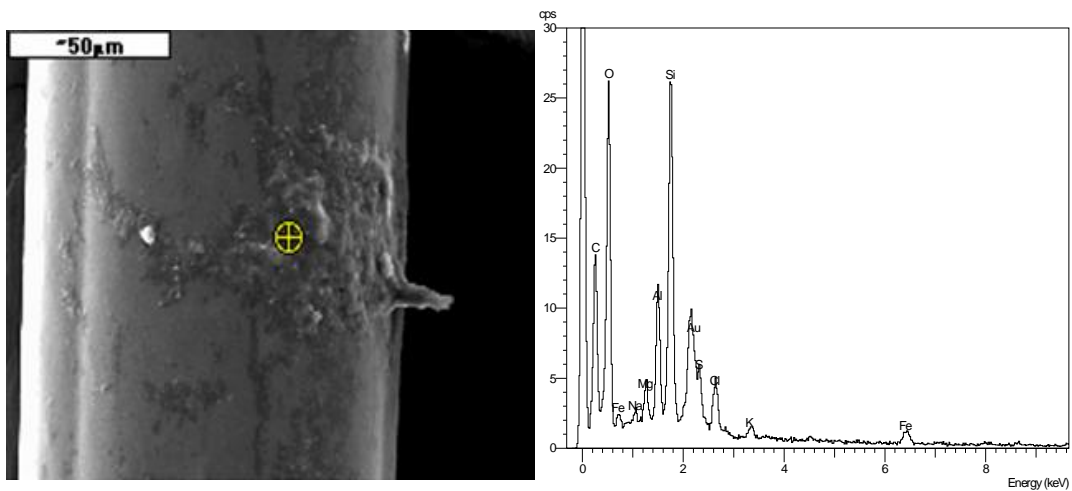
**Figure 6. View of PA membrane fibers showing the color difference among the fibers**



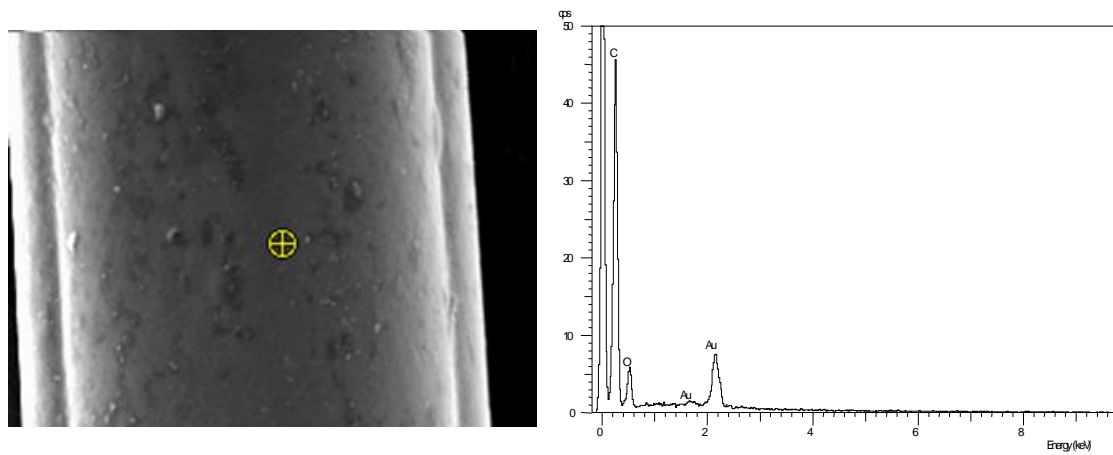
**Figure 7. View of feed distribution tube of autopsied PA membrane**



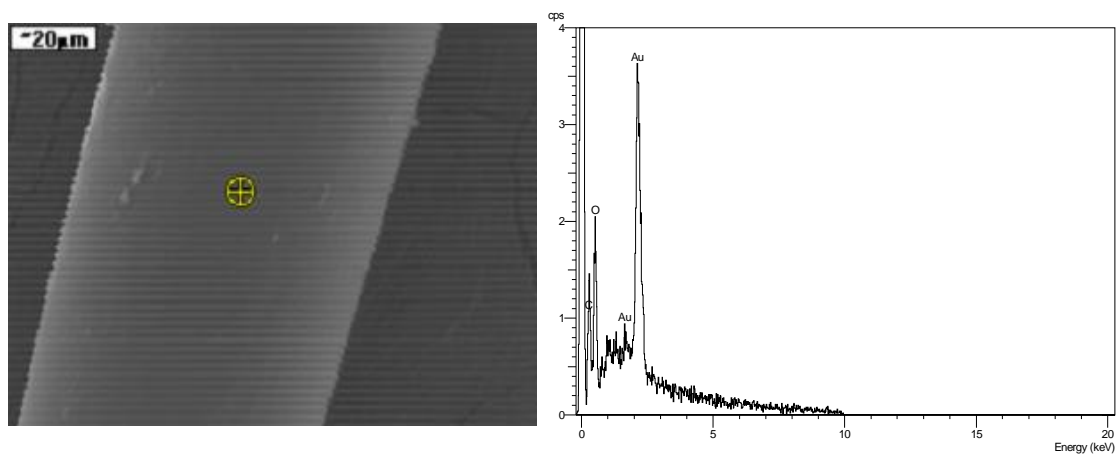
**Figure 8. SEM Micrograph and EDX Spectrum of an Inner CTA Membrane Fiber**



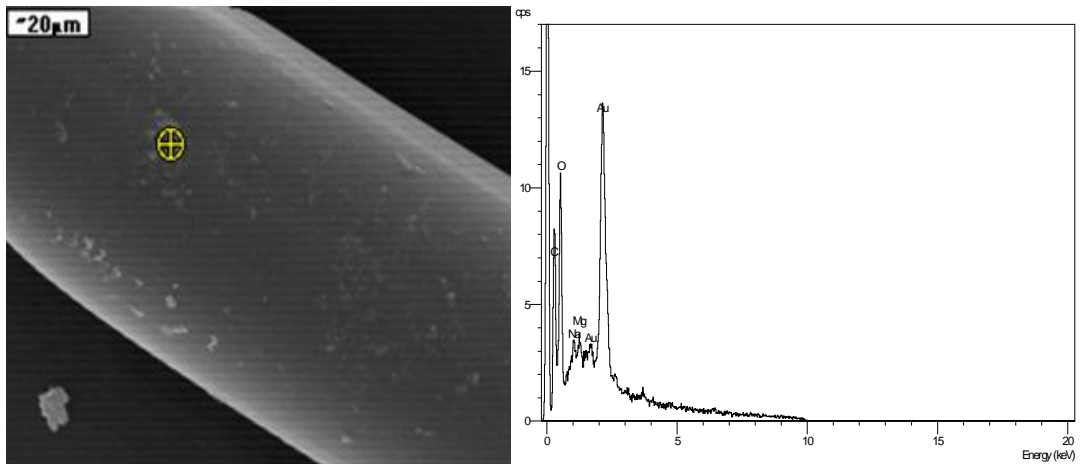
**Figure 9. SEM Micrograph and EDX Spectrum of a Middle CTA Membrane Fiber**



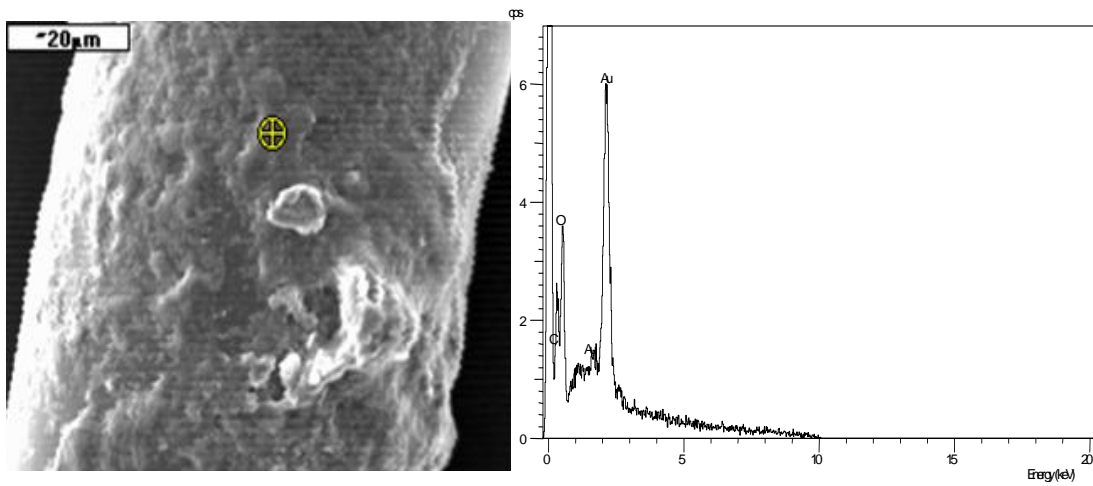
**Figure 10. SEM Micrograph and EDX Spectrum of an Outer CTA Membrane Fiber**



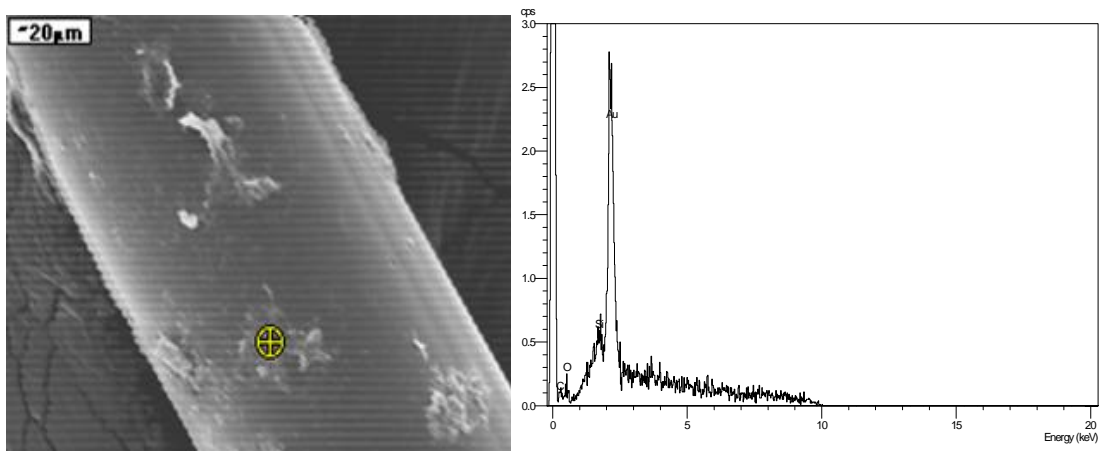
**Figure 11. SEM Micrograph and EDX Spectrum of an Outer PA Membrane Fiber**



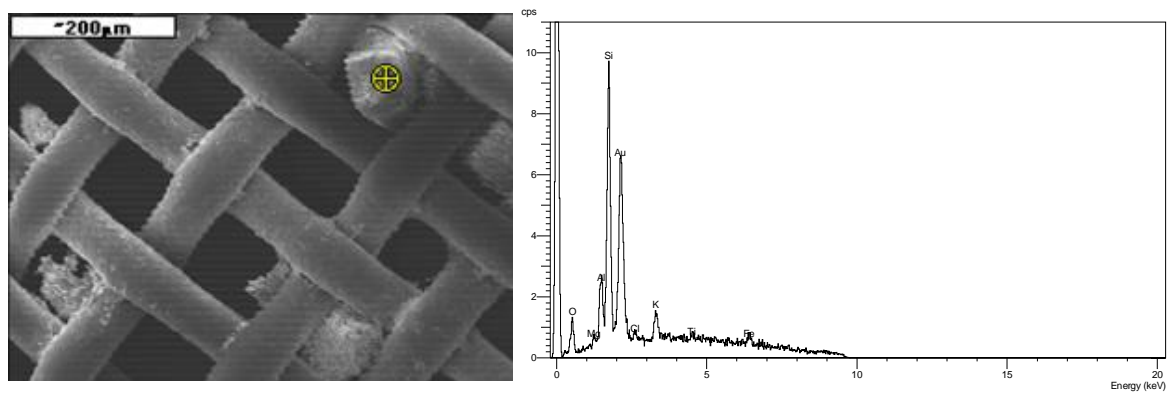
**Figure 12. SEM Micrograph and EDX Spectrum of a Middle PA Membrane Fiber**



**Figure 13. SEM Micrograph and EDX Spectrum of an Inner PA Membrane Fiber**



**Figure 14 . SEM Micrograph and EDX Spectrum of an Inner PA Membrane Fiber Cleaned using Caustic (NaOH) Solution at pH = 11**



**Figure 15 . SEM Micrograph and EDX Spectrum of a Reemay of PA Membrane**