

# Foulant analysis of hollow fine fiber (HFF) membranes in Red Sea SWRO plants using membrane punch autopsy (MPA)

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#### ABSTRACT

Membrane punch autopsy (MPA) is a procedure for quantitative foulant analysis of hollow fine fiber (HFF) permeators. In the past, quantitative autopsies of membranes were restricted to spiral wound. This procedure was developed at SWCC laboratories and tested on permeators of two commercial Red Sea reverse osmosis plants. For membrane autopsies, stainless steel hollow bore picks were penetrated to membrane cores and fibers extracted for foulant analysis. Quantitative analysis of extracted materials contained inorganic and organic foulants including bacteria. Fourier transform infrared spectroscopy analysis confirmed the presence of organic fouling functional groups and scanning electron microscopy with energy dispersive X-ray spectroscopy in the presence of diatoms and silica most likely not from particulate sand. API analysis revealed the presence of *Shewanella* and two *Vibrio* microbial species confirmed by 16S rDNA sequence library. It was observed that fouling content of HFF cellulose triacetate (CTA) membranes were more than 800 times than polyamide spiral wound membranes.

*Keywords:* SWRO; Membrane punch autopsy; SEM/EDX; Hollow fine fiber; Biofilm; Bacteria; Red Sea; Organic foulant; OPEX; CAPEX

#### 1. Introduction

Industrial membranes store records of tangible information reflecting plant operation, environmental disturbances and process failures that can compromise product production. Destructive membrane autopsies are preformed to gain a qualitative and quantitative understanding of feed water effects on permeators. Spiral wound (SW) and hollow fine fiber (HFF) membranes are the prevailing permeators used for seawater reverse osmosis (SWRO). Though much SW– SWRO ex-situ quantitative membrane autopsy information exists, foulant quantification for HFF–SWRO membranes remained challenging. Most HFF membrane foulant analysis methods are qualitative and therefore incapable of providing axial/radial quantitative foulant information over time. A novel attempt to quantitate membrane foulants was introduced by Ishizuka using non-destructive forward cleaning extraction [1]. In a bench-scale experiment, membrane surface foulants were collected and quantified after comparative physical and chemical cleaning methods. Results are promising but the attempt is mostly qualitative relating fouling to membrane resistance.

This paper establishes to new method for foulant quantification of HFF membranes using destructive membrane punch autopsy (MPA). This method is not exclusive and can be used for permeators of different brands or models. Detailed operational parameters and conditions for both plants have been discussed [2,3].

Autopsies were carried out on membranes of two plant locations of similar operational configurations and

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Fig. 1. Typical SWRO plant configuration (Red Sea, Saudi Arabia).

Table 1 Important plant operation parameters

Plant operations	Jeddah SWRO	Al-Birk SWRO
	plant	plant
Capacity (m <sup>3</sup> /day)	5.68E+04	2.27E+03
Feed dosing	2.0	3.75
chlorine, ppm		
Residual chlorine	0.50	0.50
(ICI), ppm		
Anti-scalant, ppm	40	97
SBS (for ICI)	7 h on/1 h off	(7 h on/1 h off),
		6.00 ppm
Flocculent	Ferric chloride	Magnifloc 2.30 ppm
	1.7 ppm	

membrane types with different total product capacities (Fig. 1). Both plants used intermediate chlorination injection (ICI) 7 h on/1 h off. Membranes were cellulose triacetate-hollow fine fiber (CTA-HFF) elements from the same manufacture. Chemical pretreatment consisted of chlorination, acid dossing, ferric chloride flocculation and SBS dosing to manage ICI (Table 1) [3]. Physical pretreatments consist of intake screens, dual media filters (DMF) and cartridge filters. In both plants, pretreated water was pumped to membranes at a feed pressure of 60 bar. After an approximate period of 2.50 × 10<sup>4</sup> h of operation, membranes were extracted, and punch autopsied.

The purpose of MPA is to provide a quantitative method for autopsy of HFF membranes. This is important to understanding fouling impact as a function of plant operation, pretreatment and membrane configurations. Foulant quantification and distributions are important in accessing membrane capital expenditures (MBR CAPEX) and membrane operating expenditures (MBR OPEX). Before this method, HFF membrane autopsies were qualitative. MPA offers a quantitative method for HFF membrane autopsies.

#### 2. Experimental setup

MPA is an invasive method for permeator autopsies of HFF membranes. It allows quantification of biological, chemical and biochemical species associated with permeators. Stainless steel bore picks are penetrated to a membrane core and excised (Fig. 2). Hollow picks contain fibers that are transferred to a 250-mL flask containing sterile filtered ddH<sub>2</sub>O. A dipstick ruler is inserted into membrane shafts to



Fig. 2. Membrane punch autopsy devices.

measure depth of penetration to cores. Foulant concentrations can be determined per unit area.

Membrane fibers suspended in ddH<sub>2</sub>O are vortex and sonicated to dissociate foulants [4]. Suspended foulants are decanted and process repeated until fibers appear unstained. Decant is collected, volume measured, then assayed for biocide tolerance and organic/inorganic biofilm content. Cleaned fibers are air dried and placed in a desiccator pending microscopic evaluation and intrinsic viscosity analysis.

Biofilm associated bacteria are isolated, enumerated, purified and identified with API and 16S rDNA sequence library [5]. Chlorine sensitivity tests are conducted on biofilm extracts and phenotypically diverse colonies enumerated and purified for biochemical identification.

#### 2.1. Biocide tests

Biocide analysis is conducted on biofilm suspensions (containing microbial isolates) after 30 min exposure with and without chlorine (at various pHs in sterile seawater and sterile double distilled water). From decanted biofilm extract, 1 mL is transferred to 9 mL of ddH<sub>2</sub>O and serial diluted. From serial diluted tubes, 1 mL of biofilm/bacteria stock is transferred to tubes containing 9 mL of chlorinated aseptic seawater and ddH<sub>2</sub>O at different pHs. Controls are prepared from non-chlorinated aseptic seawater and ddH<sub>2</sub>O and spiked with serial diluted bacterial stock (from biofilm extract).

Biocides is prepared from a stock solution of sodium hypochlorite and assayed to 0.3 mg/L (pH 6.6) and 0.55 mg/L (pH 5.5) in seawater medium and 0.16 mg/L (pH 6.7) and 0.55 mg/L (pH 6.2) in ddH<sub>2</sub>O medium. After 30 min exposure, test and control vials (containing bacteria without chlorine) are platted on MAA (Difco marine agar 2216 + 5% agar) and incubated for 24 h. Colonies are quantified by colony forming units per mL (CFU/mL) and identified using API and 16S rDNA sequence library [5].

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#### 2.2. Organic chemical analyses

# 2.2.1. CTA-HFF membrane

Organic analysis is conducted by modified methyl tertiary-butyl ether (MTBE) extraction [6–8] substituting liquid chromatography–mass spectrometry injection for base/ acid precipitation. Foulant suspensions used in preparation for the chorine test are thoroughly vortexed and transferred to 100 mL flasks containing 75 mL MTBE. The mixtures are slowly transferred to 250 mL separation funnels. Next, 15 mL of 1 M HCl is slowly added (phase separation observed). Samples are mildly agitated and periodically vapor purged.

Aqueous phase is transferred to 100 mL glass beakers, and above process repeated twice (beginning with addition of 15 mL of 1 M HCl [to pre-extracted organic phase]). For each sample set, aqueous extracts are combined and 10 M of NaOH added dropwise to precipitate organic bases. Precipitations of organic bases are further enhanced by refrigeration. Suspended organics are sieved onto pre-cleaned, dried and pre-weighed 47 mm Whatman GF/C filters. Filtered suspensions are aseptically air dried (in a desiccator) and weighed to record extraction masses.

The remaining organic phases are extracted from solvents by adding 15 mL of 1 M sodium bicarbonate solution NaHCO<sub>3</sub> to pre-extracted organic phases (after the acid extraction). After the third extraction, aqueous phases are combined and precipitated with 10 M HCl (dropwise additions). To the remaining organic phases (containing MTBE), 15 mL of 1 M NaOH (strong base) are dosed with slow mixing and periodic purging. After the third extraction, aqueous phases are collected in sample set beakers and precipitated with 10 M HCl (dropwise additions). Suspended organics

are filtered (on pre-cleaned, dried and pre-weighed 47 mm Whatman GF/C filter papers). Filters with residuals are aseptically air dried (in a desiccator) and weighed to record extracted masses. Organic contents from sample sets are weighed, and the two highest mass categories from organic extracts are subjected to Fourier transform infrared (FTIR) analysis.

## 3. Results

#### 3.1. Biofilm bacteria identification

Four colonies were isolated from the Al-Birk and Jeddah SWRO plants. Of the four isolated colonies, *Shewanella* and two *Vibrio* species were present in both plants' membrane autopsies. The fourth species was unidentifiable and associated with membranes from the Al-Birk SWRO plant. Samples from the Al-Birk plant were subjected to chlorine tolerance tests.

#### 3.1.1. Chlorine tolerance test

Biofilm samples from autopsied membranes spiked with chlorine appeared to have bacteria concentrations (CFU) more than 93% (Table 2) of controls when seawater was chlorinated to 0.28 ppm (at pH 6.6). Bacteria concentrations were >82% when seawater was chlorinated to 0.55 ppm (at pH 5.5).

Bacteria density (CFUs) was 89% (Table 3) more than the control when distilled water was chlorinated to 0.16 ppm (at pH 6.7) and 82% more when chlorinated to 0.55 ppm (at pH 6.2). As chlorine concentrations increased from 0.16 to 0.55 ppm, CFUs decreased. Concentrations were higher than blanks giving the impression of bacterial proliferation in presence of chlorine. This warrants further investigation. Chlorine

Table 2 CFUs of biofilm bacteria in chlorinated seawater (after 30 min exposure)

Bacterial isolates	Blank seawater pH 6.1 (purified isolates [CFU/mL])	Seawater 0.28 ppm chlorine pH 6.60 (CFU/mL)	Seawater 0.55 ppm chlorine pH 5.50 (CFU/mL)
Colony I	1.81E+06	3.28E+07	6.05E+06
Colony II	1.21E+06	1.83E+07	4.54E+06
Colony VI	2.57E+05	5.21E+06	5.54E+06
Colony VII	1.76E+06	1.64E+07	1.16E+07
Total	5.34E+06	7.27E+07	2.78E+07

Note: Colony I: Schewanella; Colony II: Vibrio P.; Colony VI: Vibrio; and Colony VII: Unknown.

### Table 3

CFUs of biofilm bacteria in chlorinated ddH<sub>2</sub>O (after 30 min exposure)

Bacterial isolates	Blank ddH <sub>2</sub> O pH 6.70	$ddH_2O$ 0.16 ppm chlorine pH 6.74	$ddH_2O$ 0.55 ppm chlorine pH 6.20
	(purified isolates [CFU/mL])	(CFU/mL)	(CFU/mL)
Colony I	9.58E+05	1.36E+07	5.88E+06
Colony II	9.32E+05	9.07E+06	2.35E+06
Colony VI	3.78E+05	4.87E+06	4.70E+06
Colony VII	2.32E+06	1.36E+07	1.23E+07
Total	4.59E+06	4.11E+07	2.52E+07

did not have a collective or colony based biocide impact on biofilm suspensions in seawater or in ddH<sub>2</sub>O. CFU concentrations of chlorine treated bacteria in ddH<sub>2</sub>O are generally less than those in chlorine treated seawater. A 9% reduction in CFUs is observed for chlorinated bacteria in ddH<sub>2</sub>O than in chlorinated seawater at 0.55 ppm. A 14% reduction in CFUs is observed in control samples, which may be attributed to impact of osmotic shock from microbial exposure to hypotonic solution [9].

# 3.2. Membrane analysis

# 3.2.1. Membrane foulant content (SEM/EDX)

SEM EDX analysis was conducted for CTA-HFF foulants in the Al-Birk and Jeddah Red Sea plants. At the Al-Birk plant, large amounts of foulant were observed. Upon SEM/EDX inspection, major elements consist of oxygen (38.0%), carbon (31%), silica (13%) and iron (6%). At the Jeddah plant, pressure vessels contained two membrane elements in series. Average foulant percent compositions in feed elements (first elements) were oxygen (45%), silica (29%), carbon (16%), sodium (6%), barium (5%) and zinc (3%). Silica was abundant in the feed end of the feed element with an abundance of carbon in the brine end of the feed element. In brine elements (second elements) major elemental constituents contained oxygen (33%), carbon (27%), iron (22%) and silica (13%). Silica presence was unexpected (as particulate sand should be captured in first element). However, SEM revealed the presence of diatoms, which may explain the presence of silica peaks.

# 3.2.2. Membranes foulant content (organic extraction at Al-Birk and Jeddah plants)

At Al-Birk, average foulant weight on feed-end orientation of membranes was approximately 63 mg/cm<sup>3</sup> (Table 3)

#### Table 4

Foulant concentrations from punch autopsy of the Al-Birk and Al-Jeddah Plants

Stations	Concentration	Concentration	
	total foulant	organic foulant	
	(mg/cm <sup>3</sup> )	(mg/cm <sup>3</sup> )	
Al-Birk feed-end element	63.44	32.09	
Al-Birk brine-end element	35.76	20.92	
Jeddah feed element	123.46	52.50	
Jeddah brine element	134.68	23.89	

and 36 mg/cm<sup>3</sup> at the brine end. Thus, feed ends of membranes contained 43% more foulant mass than brine ends. In Jeddah plant, average feed element deposits weighted 124 and 134 mg/cm<sup>3</sup> for brine element deposits. Thus, the brine membranes contained 7% more fouling mass than its feed membranes (in series configuration).

In Al-Birk, the average organic foulant content was 32 mg/cm<sup>3</sup> in feed ends of elements and 21 mg/cm<sup>3</sup> in brine ends of elements (Table 4) making the feed 34% greater in organic fouling content. In the Jeddah SWRO plant, the average organic content of feed elements was 53 mg/cm<sup>3</sup> as compared with 24 mg/cm<sup>3</sup> in brine elements making feed elements 55% greater in average organic foulant.

The highest density of total organic content was in feed elements of the series configured membranes of Jeddah plant. In this plant, brine membranes had the highest total fouling density with the lowest organic foulant concentrations and consequently the lowest percentages of organic foulants (Fig. 3). These membranes tend to have lower organic fouling and more inorganic foulants. This is consistent with results observed for brine elements in series configurations. Conversely, Al-Birk membranes had the highest percentage of organic foulants and the lowest total foulant and organic foulant concentrations (Fig. 3).

Further analysis of organic components from membranes through MTBE acid/ base extraction were illuminating. In Al-Birk Plant, the highest average concentration of organics were acid extracted foulants (9 mg/cm<sup>3</sup>) followed by residuals remaining in MTBE solvent (8 mg/cm<sup>3</sup>). This was followed by foulants from weak base extracts (6 mg/cm<sup>3</sup>) and strong base extracts (4 mg/cm<sup>3</sup>), respectively (Table 4).





#### Table 5

Organic foulant distributions from punch autopsy from Al-Birk and Jeddah plants

Membrane location	Mass distributions of organics from membrane foulants			
	Foulant density retained	Foulant density	Foulant density from	Foulant density from
	in organic solvent	from aid extraction	weak base extraction	strong base extraction
	(mg/cm <sup>3</sup> )	(mg/cm <sup>3</sup> )	(mg/cm <sup>3</sup> )	(mg/cm <sup>3</sup> )
Al-Birk	7.455	9.26	6.05	3.74
Jeddah feed element	18.81	19.74	7.4	6.55
Jeddah brine element	3.76	1.79	2.84	3.49

In Jeddah feed elements (Table 5), the highest organic concentrations were from acid extractions (20 mg/cm<sup>3</sup>), followed by those remaining in the organic solvent after extractions (19 mg/cm<sup>3</sup>). Next, those of weak base extracts (re-extracted from a weak base [7.4 mg/cm<sup>3</sup>]) then strong base extracts (6.55 mg/cm<sup>3</sup>). Organic densities were more abundant in feed elements than brine elements (in these membranes which are series configured).

3.2.3. *Membrane foulant analysis by FTIR (from acid extractions)* 

3.2.3.1. Al-Birk membranes FTIR analysis for both feed and brine ends of membranes were similar in representation of functional group spectra with regard to organics extracted with acid (Table 6). The lower frequency of the spectra 1,031 cm<sup>-1</sup> is indicative of the silica GF/C standard. Its signal is not strong in comparison with the standard (GF/C filter) because it is masked by a C–N stretch from aliphatic amines. Between the ranges of 1,550–1,700 cm<sup>-1</sup> (Fig. 4), amide and carbonic group exist. At 1,552–1,651 cm<sup>-1</sup>, peaks for proteins and polypeptides are present. At approximately 3,000 cm<sup>-1</sup>, C–H carbohydrate groups are present. Amine groups (from proteins) exist between frequencies 3,100 and 3,600 cm<sup>-1</sup>. Though spectrum for both feed and brine ends of Al-Birk membranes are similar, there is a difference in intensity, which may be attributed to organic presence.

3.2.3.2. Jeddah membranes Jeddah feed elements contain organic peeks. The silica peak 1,003 cm<sup>-1</sup> is slightly masked by the presence of protein amine groups (Fig. 5). Between the ranges of 1,550 and 1,700 cm<sup>-1</sup> amide and carbonic groups exist. At approximately 3,000 cm<sup>-1</sup>, C–H carbohydrate groups are present. There are high amine signals between 3,100 and 3,600 cm<sup>-1</sup> stretch. Feed membrane FTIR results for Jeddah are different from brine membranes. In brine membranes, spectrums are similar to GF/C standards with exception of an apparent amine (3,000 cm<sup>-1</sup>) and C–H carbohydrate peek (3,100–3,600 cm<sup>-1</sup>). Results indicate the possible presence of

Table 6 FTIR results for Al-Birk membranes



Fig. 4. FTIR analysis of foulants from feed and brine ends of membranes at the Al-Birk commercial SWRO Plant.



Fig. 5. FTIR analysis of foulants from feed and brine ends of membranes (in series) at the Jeddah commercial SWRO plant.

proteins or sugars, which are typical components of a biofilm matrix. Low intensity may be due to low concentrations.

#### 4. Discussion

Four bacterial isolates were identified as part of the fouling milieu. They are *Shewanella*, two *Vibrio* species and one unknown. The three known species were isolated in plants studied while the unidentified species was found in the Al-Birk plant.

Chlorine tolerance studies of bacteria (from biofilm suspensions) reveal marine agar growth higher in CFU concentrations than standards. This result was unexpected but considering that samples are not from sessile bacteria but homogenized biofilm in suspension, several plausible explanations that can be suggested. One suggestion is that chlorine may be acting on biofilm digesting micronutrients and liberating bacteria. An increase in bacterial populations resulting from chlorine may not be an indication of growth but liberation of sessile bacteria into the bulk media. Another possibility is that chlorine is being consumed in the reaction with biofilm liberating bacteria (from the matrix) and increasing micronutrients in solution. This may promote growth. Lastly, it may be possible that chlorine is not an effective biocide with regard to biofilm bacteria, which may have metabolic pathways to survive its effect. In some microbes, chlorine may induce a cascade of biochemical effects resulting in the production of organic acids, ligands and lipids that they excrete as protection against external environments [10–12].

Analysis of SWRO membrane biofilms on Al-Birk and Jeddah permeators reveal inorganic and organic foulants. In Jeddah SWRO permeators, inorganics are the main foulants in series configured membranes. Over 57% and 82% of feed and brine element foulants, respectively, are inorganics. The amount of inorganic foulants in brine membranes are 36% more than in feed membranes. This is understandable in series configured permeators that concentrate brine around fibers during desalting and source concentrated brine as feed to the next membrane. The presence of iron, which comprised nearly one-fourth of the inorganic foulants, in the Jeddah plant, was odd. This can be an indication of channeling in DMF and/or overdosing.

Inorganic content of the Al-Birk plant was 47% of the total foulant mass, which is less than that observed in Jeddah membranes. Distributions of inorganic and organic foulants throughout permeators differ by 7%. Feed ends and brine ends of membranes contain 49% and 42% of organic foulants and 51% and 58% organic foulants, respectively. Al Birk plant differs from Jeddah in that most of its fouling content is organic rather than inorganic. The organic fouling content of Jeddah membranes is less than its inorganic fouling content. Though both plants are located on the Red sea, there is a difference in intake depth. The Jeddah plant has a deep intake, and the intake of Al Birk is shallow. Intakes that are deep tend to have better water quality due intakes gravitational filtration and the negligible impact of benthic disturbance from storms or tides on water quality parameters.

The use of MPA provides a quantitative understanding of membrane fouling of CTA–HFF membranes. Used in conjunction with known analytical techniques, MPA is a powerful tool for obtaining a quantifiable biological, organic and inorganic profile of membrane fouling for single elements or membranes in series. Though further investigation of its application and use and optimization are required, results obtained are promising. MPA allows for a direct shift from qualitative to quantitative membrane autopsy exploration for HFF membranes.

# 5. Conclusions

Analysis of SWRO membrane biofilm of the Red Sea reveals the presence of organic and inorganic foulants. Quantitatively, inorganic constituents appeared to be the main fouling component of Jeddah SWRO membranes whereas organic foulants were most abundant in Al-Birk membrane autopsies. At both sites, SEM/EDX analysis revealed abundant percent compositions of carbon and oxygen and silica. Carbon and oxygen are the backbone structures of sugars, proteins and fats that may be indicative of biofilm. The presence of silica is not odd due to the shallow intakes of Al-Birk and frequent sandstorms and sand drifts of the region (for deeper intakes such as Jeddah). However, in Jeddah plant, high silica levels in brine membranes are unusual because of their series configuration. Instead of sand, high levels could be from the presence of orthosilic acid from the digestion or breakdown of shelled creatures, which may contribute to the presence and proliferation of diatoms on membranes (as confirmed by SEM/EDX).

The use of MPA provides a qualitative and quantitative look into the cause for HFF membrane fouling. This is essential for exploring the root causes of fouling problems so that relevant remedies can be suggested, studied and implemented. MPA in conjunction with chemical, biological and molecular techniques provides a platform for membrane evaluation with the aim of improving its performance. MPA can provide insight into plant operations, corrosion issues and possible anthropogenic problems that impact membrane performance and longevity.

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