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UF and RO membrane fouling during wastewater desalination in the petrochemical industry

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ABSTRACT

The large consumption of fresh water in petrochemical industry makes wastewater reuse almost mandatory, with UF and RO membrane desalination playing a crucial role. To that aim, frequent and expensive recovery treatments are required, not always sufficient to prevent (ir)reversible fouling of the membranes, as experienced with a major European petrochemical factory. The paper describes the detailed physio-chemical investigation and instrumental analyses carried out to discover the cause(s) of the fouling and the operational measures required to contrast the phenomenon.

Keywords: Membrane fouling; UF; RO; Wastewater desalination; Petrochemical industry

1. Introduction

Oil refining industry consumes huge amount of fresh water (≈1.5 m^3/m^3 of crude oil processed) for crude washing, heat exchange control, steam producing as power source, etc., which in the last three decades made wastewater reuse (WWR) almost mandatory [1]. To that aim, wastewater treatment plants (WWTP) typically include *primary* (physico-chemical) and *secondary* (biological oxidation) steps, followed by a *tertiary* step WWR based on the use of ultrafiltration (UF) and reverse osmosis (RO) semi-porous membranes, producing desalted water for steam feeding the factory power plant. The membranes (especially the UF ones) need to undergo periodically expensive physical (air bubbling backwash) and chemical recovery treatments, called *Cleaning In Place* (CIP), and *Chemically Enhanced Backwash* (CEB), that reduce their technical life to 6–8 years [2,3]. Recent innovative solutions such as adding granular-activated carbon into the biological reactor for direct adsorption of oils and refractory organics tested in Saudi Arabia [4] or the moving bed bioreactor [5,6] introduced at a large refining complex in Taiwan [7] have still to pass the demonstrative stage. Accordingly, successful operation of the above three-step approach to WWR in the oil refining industry is still a minority, as fouling by oil and organics, scaling by metals, etc. yield to rapid and expensive membrane replacements, usually not reported in the literature [8–12].

This was also the case of the Italian petrochemical factory studied, among the largest in the EU. Created in the 1960s on a 2 km^2 area facing the Mediterranean sea with a capacity to treat 6 Mt/year of crude oil (being increased to 11 Mt/year), the factory consumes over 80 Mm^3/year of water, coming prevailingly from the sea (94%, used for heat exchange and fire prevention and discharged to sea) and from the aquifer (5.8%, used mainly to produce the demineralized feed to the

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internal power station and to back-up process requirements) plus 0.2% of drinking water for civil use and consumption. In order to reduce groundwater withdrawal, in 2006, the existing WWTP was implemented with a WWR step based on UF and RO membranes serial treatment to feed the factory power station with demineralized water, so as to achieve the *semi-zero-discharge* goal. To that aim, the 550 m^3/h WWTP secondary effluent was submitted to tertiary treatment to yield 300 m^3/h of demineralized water. 250 m^3/h cumulative blowdown from UF and RO was pressure filtered by granular activation carbon (GAC) and discharged to the sea under the limits in force. After approx. 1 year of operation, however, the performance of the WWR section kept deteriorating, requiring the substitution of one of the four UF lines in 2009 (after only three years of run) and of all the three RO lines in 2011 (five years of run). In spite of the frequent and expensive physico-chemical recovery treatments carried out to ensure their (partial) operation, in 2012 all the UF and RO membrane lines were renovated.

A detailed investigation was carried out to ascertain the cause(s) and possible remedial action(s) of the phenomenon as described in this study.

2. Materials and methods

The WWTP collects and treats all meteoric and process wastewater (main characteristics in Table 1).

The WWTP includes in the order:

(1) Pretreatments: desulphuration of the so-called *sour water*, mixing, equalization, demulsification.
(2) Primary treatments: air mechanical floatation in a four-parallel cell installation (WEDCo, Bermuda) entrapping fines and oil droplets on the bubbles floating upward, followed by pressure filtration through two lines with four parallel sand filters each.
(3) Secondary treatments: simultaneous bioxidation and filtration carried out in four (+1 back-washed in a merry-go-round sequence) BIOPUR® (VaTech Sulzer, CH) upflow cells containing a suspended bed of Si–Al sphere with adhesive biomass through which water and air flow co-currently. Before the build-up of the tertiary section (2006), the secondary effluent joined the huge amount of sea water utilized for heat exchange (≥8,000 m^3/h) into a swallow-tailed decanter to be discharged to the sea.
(4) Tertiary treatments:

2.1. UF plant

After the addition of $FeCl_3$ to help SS flocculation, pH correction with H_2SO_4 and bacteria disinfection by NaOCl, the biological effluent batchwisely feeds the UF plant, which is made of four parallel lines (A–B–C–D) soaked into a 100 m^3 concrete vessel (Fig. 1). Each vessel contains 48 ZeeWeed 500D-48 modules (Zenon-GE, Heverlee, Belgium) of freely flowing (*shell-less*) PVDF hollow-fibre ZW 500D membranes operated in *out*→*in* depressurized mode at 70/700 m bar trans-membrane pressure (TPM_{max} ≤ 830 mbar) for an estimated recovery ratio $\eta \geq 85\%$ (≥0.85 m^3 permeate/m^3 treated).

Table 1
Average characteristics of wastewater treated at the WWTP (dry weather conditions)

		In (≤)	Out (≤)	Discharge limits in force* (Table 3 Annex V Part III Legs. Decree #152/2006)
Flow rate	m^3/h	550		
pH		6–9	6–9	5.5–9.5
TDS (total salinity)	mg/l	22.500	22.500	
COD	mg/l	500	120	160
BOD	mg/l	50	35	40
SST (total suspended solids)	mg/l	315	50	80
Sulphides	mg/l	20		
Phenols	mg/l	3		
NH_3	mg/l	12	7	15
NO_3	mg/l	1		
P	mg/l	0.1		
THC (total hydrocarbons)	mg/l	55		
Oils	mg/l	350		

*plus BTEX ≤ 50 μg/l, MTBE ≤ 55 μg/l and TPH ≤ 100 μg/l.

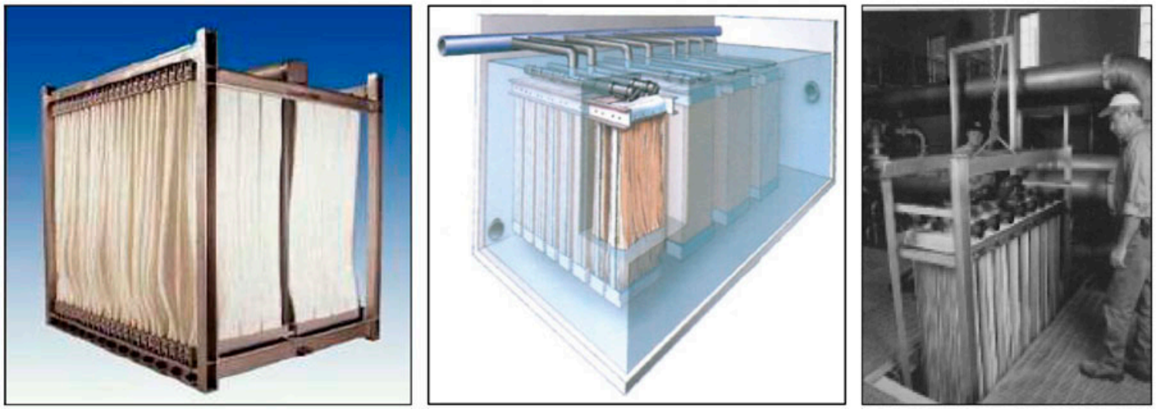

Fig. 1. ZeeWeed 500D-48 module (L), sketch of the vessel (M), typical immersion/extraction procedure (R).

Table 2 and Fig. 2 report the characteristics of the membranes and their modules.

A small depression (TMP 350 mbar) inside the hollow-fibre membrane permits continuous filtration of the feed, while SS, large organic molecules and micro-organisms with $\phi_{pore} > 0.040/0.100$ μm build up progressively at the external membrane surface, causing progressive increase in TMP to keep the permeate flow constant. On a routine schedule (or when TMP exceeds a preset value), the module is automatically shut down and regenerated according to the following ≤1 h working cycle:

(1) *service* (15/45´);
(2) *relaxation* (5´), when a current of air bubbles from the vessel floor shakes the free-flowing membranes vigorously to remove the externally adherent cake;
(3) *backwash* (5´), when treated water flowing *in→out*, eventually added with detergents, flushes the remaining cake.

Every 24th hour (or when oil and SS concentration in the UF reject becomes excessive), the vessel is drained off and filled with fresh feed to start a new working cycle. Once per month (or when necessary), all modules undergo thorough membrane cleaning (*CEB or CIP*) consisting of a series of backwash and soaking cycles with detergents, acidic, basic and oxidant chemicals (Table 3). To that aim, the membranes are soaked into a 500 mg/l NaOCl solution at pH ≤ 9.1 for 24 h, then in a 2,000 mg/l Citric Acid solution at pH ≥ 2.1 for 4 h at ≤40˚C (eventually repeated two or more times). Once per year (or when necessary), the modules receive longer/more energetic cleaning cycles.

The UF reject (approx. 15% of feed with TSS ≥ 300 mg/l) reaches a special high-rate lamella clarifier/thickener (DensaDeg®, Degremont, CH), from where the sludge is sent to the centrifuge treatment and the clarified solution is recycled to the UF section.

2.2. RO plant

After the addition of $NaHSO_3$ to reduce free Cl_2 residue and O_2, H_2SO_4 to correct pH and anti-scalant to prevent $CaSO_4$ precipitation, the UF permeate

Table 2
Characteristics of GE-Zenon membranes (L) and modules (R) utilized

Brand name	ZW 500D	Product name	ZW 500D-48
UF or MF	MF	Process designation	SUB
Polymer	Mod.PVDF, supported	Module (ht × width)(m)	2.54 × 2.11
Hydrophilicity	Moderate	Fibre length (m)	1.9
Pore size (μm)	0.02 (0.2)	Depth (diam) (m)	1.175
Fibre i.d. (mm)	0.8	Membrane area (m^2)	31.6
Fibre o.d. (mm)	1.9	Max TMP (bar)	0.83
Cl_2 resistance	High	Temperature rating (˚C)	40
pH range	2–10	Weight (kg)	1,201

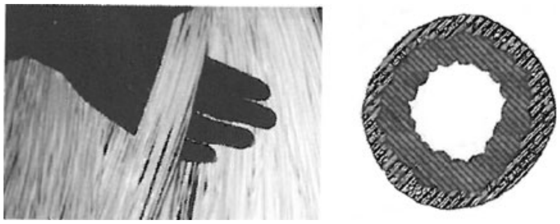

Fig. 2. Picture and internal structure of the hollow fiber ZW 500D membrane.

(TDS ≤ 22.500 mg/l) is desalinated to ≤10 mg/l (99.9% overall salt rejection) by RO before being completely demineralized in the nearby steam power station (Fig. 3).

The RO section uses spiralwound membranes by Filmtech (Dow, USA) with $\phi_{pore} \leq 0.001$ μm, contained into a cylindrical vessel (seven spirals/vessel) arranged in a two-pass two-step configuration to achieve ≥99.9% TDS rejection. The 1st pass–1st step is made of three parallel units (20 vessels each with FilmtechSW30HR320 membranes) at 50 bar; the permeate reaches the 2nd pass, while the reject undergoes a 1st pass–2nd step in 10 more vessels at 75 bar. The joined permeates (≤7,000 mg/l, 48% recovery) are sent to the 2nd pass–1st step made of three parallel units (11 vessels each with Filmtech BW 30–400i membranes) run at 14 bar; the reject undergoes 2nd pass–2nd treatment step in the last four vessels operated at 30 bar. The joined permeates (TDS ≤ 10 mg/l, 88% recovery) are sent to the nearby steam production.

Table 3
Reactants used in CEB or CIP treatments against membrane fouling

Cleaning agent	Chemical	Typical concentration	Reaction
Base	NaOH	PVDF : pH 10–11 (12) PES (PS): pH 11.5–12.5	Hydrolysis, solubilization
Alkaline chelate	EDTA, Na_3PO_4, Polymeric phosphonates	0.5–1.0%	Chelation
Acid	H_2SO_4	pH (1.7) 2–2.5	Solubilization
	HCl	pH (1.7) 2–2.5	Solubilization
	HNO_3	0.3–05%	Solubilization
Inorganic acid chelate	H_3PO_4	0.3–05%	Solubilization and chelation
Organic acid/acid salt chelate	Citric acid	1–2%	Solubilization and chelation
	Oxalic acid (with ascorbic)	1% (with 0.25% ascorbic)	Solub., chelation, reduction
	Sodium gluconate	0.1% (with SHS or caustic)	Solub., chelation, reduction
Oxidizing agent	NaOCl—CEB	PES : 30(50) ppm active Cl_2 PVDF: 200(500) ppm active Cl_2	Oxidation and disinfection
	NaOCl—CIP	PES : 100(200) ppm active Cl_2 PVDF: 500(900) ppm active Cl_2	Oxidation and disinfection
	H_2O_2	200–1,000 ppm	Oxidation (weak disinfectant)
	CH_3COOOH (with H_2O_2)	0.1–0.5% (with 200 ppm H_2O_2)	Strong oxidant and disinfectant
Reducing agent	Sodium metabisulphite (SBS)	200 ppm	Reduction
	Sodium hydrosulphite (SHS)	0.5 – 2.0% (can be used with SBS)	Strong reducing agent
Surfactant	Anionic, non ionic detergents Enzymatic detergent cleaner with proteases and lipases		Emulsification, dispersion and surface conditioning with catalysed reactions

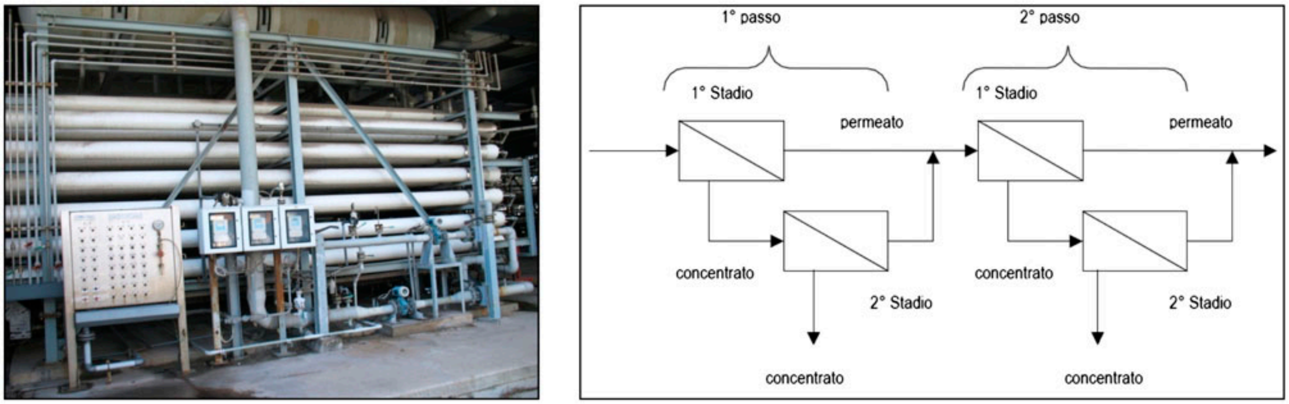

Fig. 3. Typical membrane rack and the two-passes two-steps configuration of the RO section.

The RO membranes, also subjected to fouling phenomena largely due to mineral scaling (Mg and Ca hydroxides, carbonates, sulphates, silica, etc.), are submitted routinely (1–4 times/year) to extended washing with desalted water and, when needed, to CIP treatment with acid, base, detergents and bactericides.

2.3. GAC filtration

In order to remove excess COD and specific organic contaminants (BTEX, TPH, MTBE, phenol, etc.), the rejected blow-down from 1st and 2nd RO passes (η 30%, ≤160 m^3/h) flows through two parallel lines of three pressurized filters, each containing 18 m^3 of FV2B granular activated carbon (Degremont, CH), before final discharge to the sea.

Membrane-specific permeability H [L/m^2 h bar] was calculated by the Hagen–Poiseuille equation [13]:

$$J = (\varepsilon \cdot r^2 \cdot / \cdot 8 \cdot \eta \cdot \tau \cdot \sigma) \cdot \mathrm{TMP} = H * \mathrm{TMP} \quad (1)$$

where J = membrane flux [L/m^2 h], TMP = trans-membrane pressure [bar], ε = membrane porosity, r = average radius of membrane pores [m], η = water kinematic viscosity [m/s], τ = pores intricacy and σ = membrane thickness [m]. When treating wastewater above a "*critical*" flux value, H decreases with membrane fouling so as, to keep the flux constant, TMP must be proportionally increased until the periodic CEB or CIP membrane treatments. For each membrane type, in the given experimental conditions, a "*sustainable*" flux value exists below which the fouling is considered irreversible. For the UF GE-Zenon PVDF membrane ZeeWeed 500D, in sea water treatment, with TMP = 0.2/1 bar, H usually ranges between 75 and 200 L/m^2 h bar, where the lower value indicates the *sustainable* value.

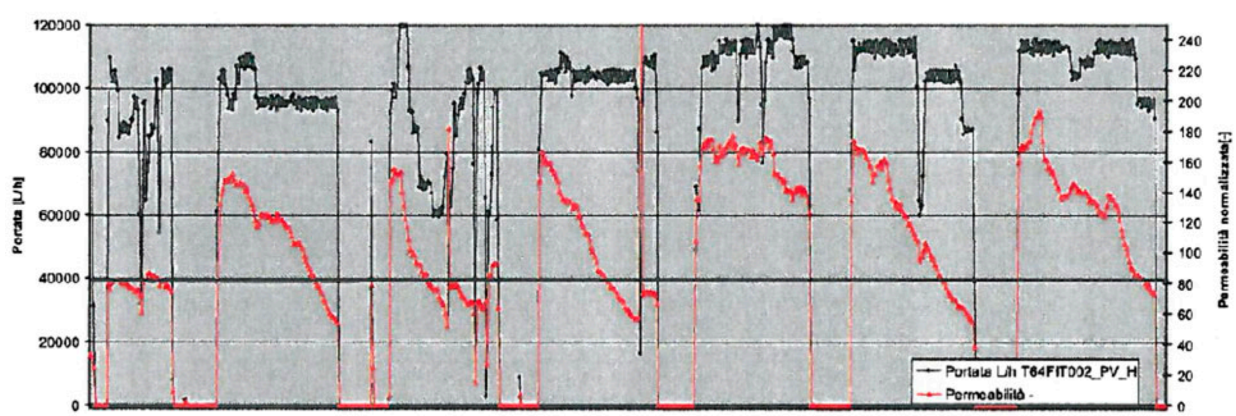

Fig. 4. Frequency of anti-fouling treatments required to keep UF plant at productivity and permeability target values.

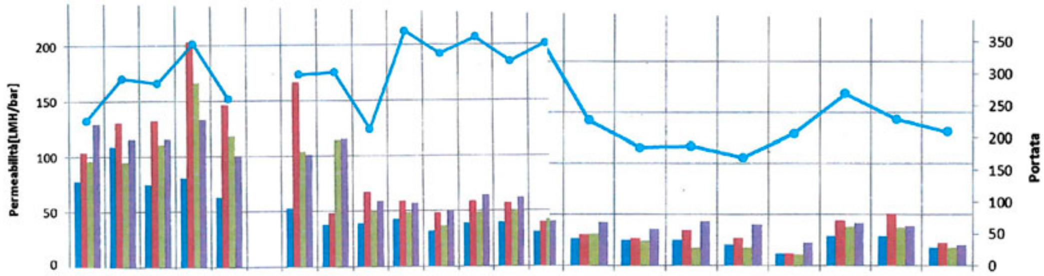

Fig. 5. Performance decay of the UF plant sections (section).

Membrane integrity was measured with the *Pressure Decay Test* [13], wherein the liquid entering the pores of a semi-permeable membrane is expelled at a pressure equal to:

$$P_{BP} = 4f \cdot \cos\theta \cdot \sigma/\phi \quad (2)$$

where P_{BP} = bubble point pressure [bar], f = pore correction factor (≤1), θ = liquid to membrane contact angle (for hydrophilic membranes $\cos\theta \approx 1$), σ = liquid superficial tension (for water 73×10^{-3} Newton) and ϕ = average pore diameter (for UF membranes 0.04 μm). With the above values, for a brand new ZeeWeed 500D UF membrane, $P_{BP} \approx 0.73$ bar.

3. Results and discussion

As shown in Fig. 4, in order to keep UF membrane permeability and specific productivity constant, CEB and CIP treatments were carried out as frequently as twice per week. Nevertheless, the overall plant flow rate continued to decrease, reaching unacceptable performance in 22 months (Fig. 5), thus suggesting the formation of irreversible membrane fouling.

This was confirmed by laboratory measurement of the membrane-specific permeability *H* (Table 4).

The exceeding H values measured with membrane samples taken from UF sections A–B (300/350 L/m^2 h bar) indicated the presence of holes and

Table 4
Results of laboratory measurements of ZeeWeed 500D PVDF membrane-specific permeability (TMP 0,75 bar)

UF plant section	Flux J ($L/m^2 h$)	Permeability H (L/m^2 h bar)
A1	2,655	354
A2	2,421	323
B1	2,419	323
B2	2,297	306
C1	1,549	207
C2	1,063	142
D1	13.3	18
D2	13.8	18

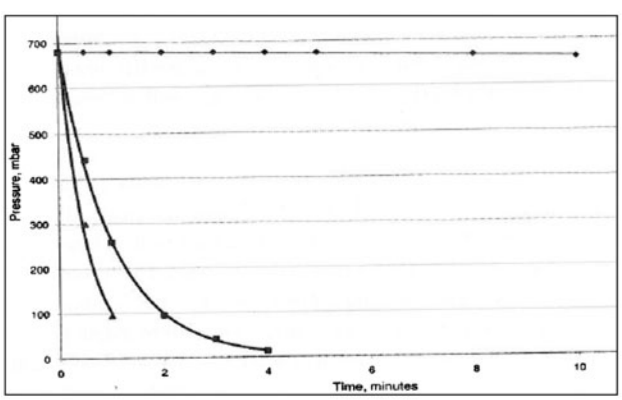

Fig. 6. Integrity test with samples taken from UF sections A (▲) and B (▬) compared with the brand new membrane (◊).

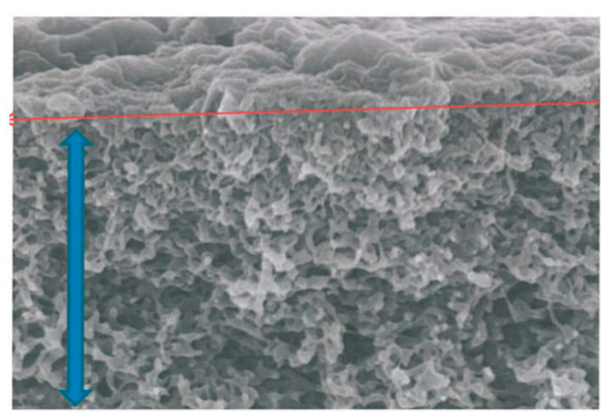

Fig. 7. SEM analysis of a UF membrane section D.

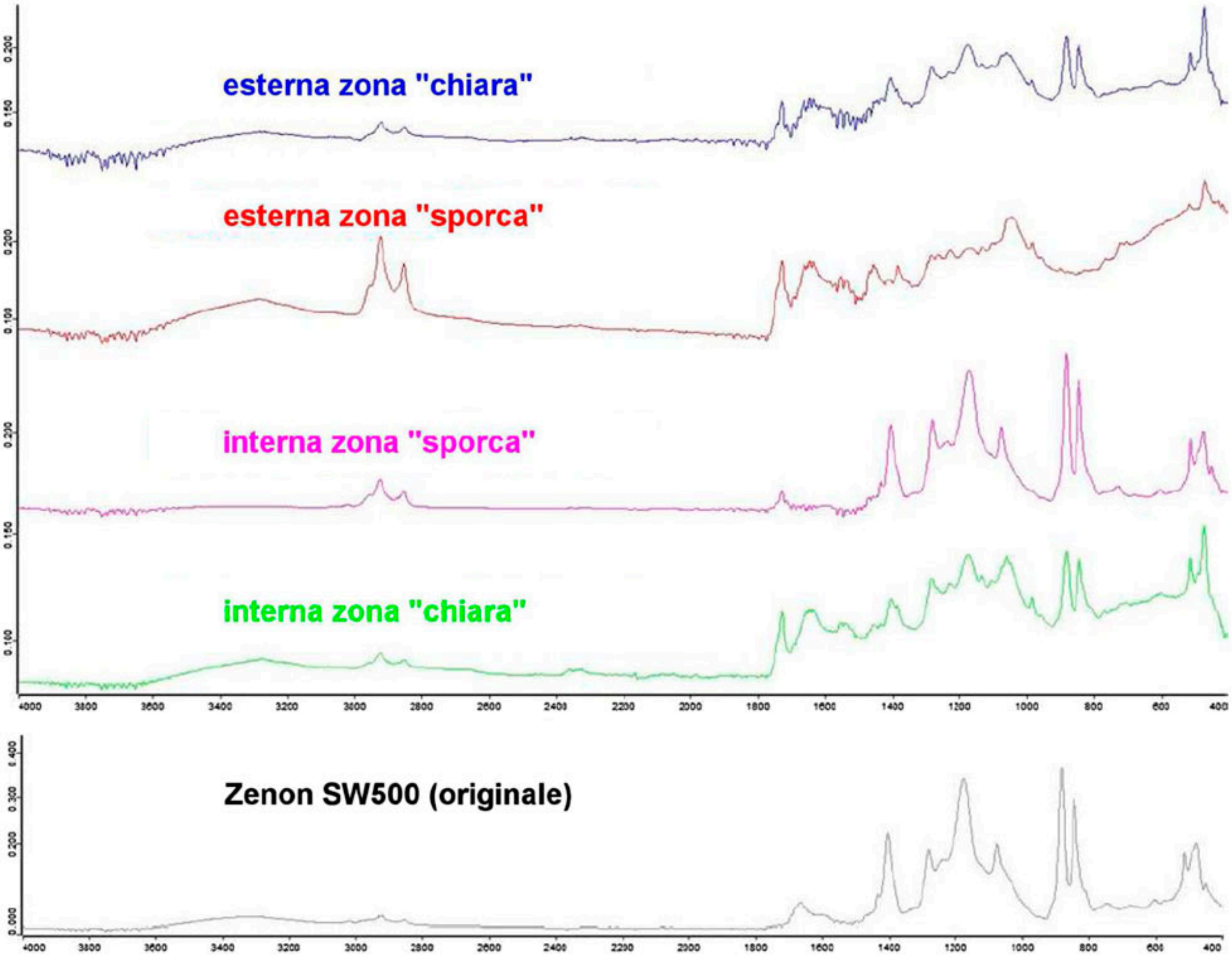

Fig. 8. FT-IR spectra of various parts of UF membrane from section D compared with the same membrane brand new.

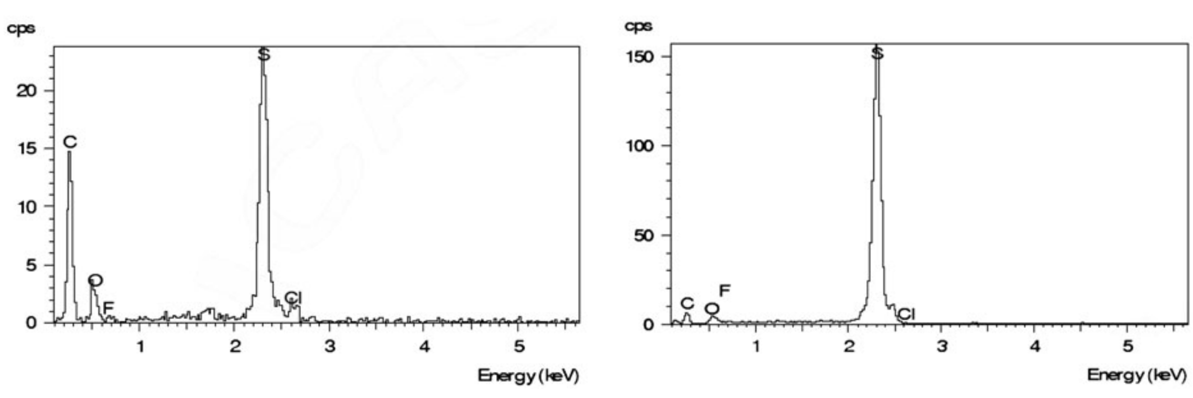

Fig. 9. EDS spectra of the fouling deposit on dirty (L) and clean (R) surfaces of UF membrane samples from section D.

tears, as confirmed by visual inspections and quantified by the results of membrane integrity tests (Fig. 6).

The very low H values with membrane samples from UF section D, on the contrary, confirmed the suspects of irreversible membrane fouling. SEM analysis carried out on samples from section D showed the presence of consistent deposit on membrane surface (i.e., above the red line in Fig. 7).

In order to assess its physico-chemical nature and origin, the deposit underwent a so-called *autopsy*. To that aim, different parts (external/internal, clean/dirty) of membrane samples taken from the UF section D were submitted to FT-IR spectroscopy. As shown in Fig. 8, the spectra exhibit several peaks absent in the corresponding brand new membrane.

Finally, the EDS spectra of the same samples reported in Fig. 9 show the prevailing occurrence of S.

On the basis of the achievement of membrane autopsy, it resulted that the membrane fouling was due prevailingly (≥50%) to build-up of elementary Sulphur (the absence of Ca ion excludes the precipitation of $CaSO_4$), with appreciable occurrence of natural plastics (poly-hydroxy-butyrate), both recalcitrant to CEB and CIP membrane cleaning treatments. Minor amounts of Fe, Al, P, silico-aluminates, carbohydrates and microorganisms were also present.

Proper modification and improvement of the desulphuration of the so-called "sour water" of the WWTP proved successful to solve the problem.

4. Conclusions

The PVDF membranes used in the UF treatment for the wastewater reuse plant of the petrochemical factory examined were affected by serious fouling problems, persistent to the frequent (expensive) usual recovery attempts such as CEB and CIP treatments. Detailed control and investigation, including membrane autopsy, showed a generalized deterioration and almost irreversible fouling of the membranes, due prevailingly to the progressive build-up of elementary Sulphur deposit on their surfaces. Inefficient to overcome the fouling origin, the physico-chemical treatments caused severe stress of membranes, yielding to their very short operation life. In particular, the primary and secondary steps did not achieve full removal of bio-resistant organic molecules, oil, fines, etc. and this causes (ir)reversible fouling of the UF and RO membranes. Due modification and improvement of the desulphuration of the so-called "sour water" of the WWTP ensured prolonged operation life and satisfying performance to the brand new UF/OI membranes.

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