Received: 21 March 2021 Revised: 22 June 2021 Accepted article published: 23 June 2021

(wileyonlinelibrary.com) DOI 10.1002/jctb.6836

Experimental study of a reverse osmosis pilot plant for reuse of refinery wastewater

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Abstract

BACKGROUND: The possibility of reusing treated refinery wastewater in the cooling water system (CWS) of the refinery itself is investigated. The contaminant levels in the treated wastewater typically fluctuate around or slightly above the threshold values for recycling to the CWS and this motivates the need for an additional purification unit. To this end, the performance of reverse osmosis (RO) is experimentally investigated through a flat-sheet RO pilot plant installed directly in the refinery (on the treated wastewater streamline).

RESULTS: In the pilot plant, two different RO membranes are tested: seawater (SWM) and brackish water (BWM) membranes. In both cases, the permeate water at the outlet of the RO pilot plant had conductivity below 100 μS cm^{-1}, total hardness (TH) below 8 ppm, chemical oxygen demand (COD) below 45 ppm, Fe below 0.04 ppm, and total ammonia nitrogen (TAN) below 1.1 ppm. The concentration of hydrocarbons (HCs) is a few ppm in the treated wastewater both at the inlet of the RO pilot plant and in the RO permeate. All these data are well below the thresholds for reuse in the CWS. The results were stable and no evidence of degradation was found over the experimentation period (3 days and 6 days, respectively, for the SWMs and the BWMs).

CONCLUSION: The RO permeate water can be reused in the CWS of the refinery. The proposed reuse strategy is expected to make a significant reduction (20–25 t h^{-1}) in refinery primary water withdrawal possible.

Keywords: refinery; reverse osmosis; water reuse; wastewater treatment

NOMENCLATURE

API	American Petroleum Institute
BOD	Biochemical Oxygen Demand
BWM	Brackish Water Membrane
Ca H	Calcic Hardness
COD	Chemical Oxygen Demand
CWS	Cooling Water System
FWN	Fire Water Network
HC	Hydrocarbons
HDC	Hydrocracking
HDS	Hydrodesulfurization
HR	High Rejection
IMO	International Maritime Organization
P50%	Operating condition where permeate flow rate is 50% of the feed flow rate.
P80%	Operating condition where permeate flow rate is 80% of the feed flow rate.
RO	Reverse Osmosis
SWM	Seawater Membrane
TAN	Total Ammonia Nitrogen
TH	Total Hardness
TSS	Total Suspended Solids
UF	Ultrafiltration
VGO	Vacuum Gasoil

INTRODUCTION

Political and social pressure on primary water source management is growing in many parts of the world due to both local and global factors. Therefore, over the years, limitations have been set regarding the rates of withdrawal of primary water and the quality of wastewater discharges,] with the overall goal of decreasing the environmental impact. Besides this, advanced processes are currently under intensive development for water treatment, aiming at producing good quality reclaimed water for reuse.[1-3] In the EU Water Framework Directive,[4] which establishes a framework for EU action in the field of water policy, regulations on minimum requirements for water reuse have recently been issued.[5]

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In refineries, water management is an essential feature of the overall plant. Concawe (Conservation of Clean Air and Water in Europe), which now includes most oil companies operating in Europe, studies environmental aspects relevant to the oil industry. Concawe states that 'Water is a unique resource and its management raises issues. It is also a vital resource for refinery operations, with the volume of water used being comparable to the volume of oil processed'.[6] In 2017, the EU had a refining capacity of 645×10^6 t year^{-1}, representing around 14% of the total global capacities of about 4.6 billion t year^{-1}.[7] A comparable amount of water was used.

In refineries, water is used in different utilities: cooling water system (CWS), process steam production, domestic and sanitation water, tank washing system, flushing equipment, and fire water network (FWN).[8] They are all essential for refinery production and for maintaining proper safety conditions in the plant. Depending on the source, water can be used as-is or it can undergo treatment, mostly filtration, before reaching the utilities. For proper operation, the steam production unit also requires water demineralization. In refineries, the main use of steam is in oil distillation, resulting in a reduction of the oil boiling temperature.[9] In addition, steam is used in stripping operations, in hydrocracking (HDC) and hydrodesulfurization (HDS), in tail gas treatment, and in the vacuum ejector systems. After being used, steam is separated and condensed. This water stream is known as sour water, and, due to its direct and intimate contact with oil, it has a heavy load of pollutants, including NH_3, H_2S, COD (chemical oxygen demand), BOD (biochemical oxygen demand), hydrocarbons (HCs), and heavy metals, that originated from the crude oil and were stripped by the steam in the distillation columns. Sour water also contains complex compounds, emulsified oils, phenols, sulfides, mercaptans, NH_3, cyanides, and other pollutants.[10] Overall, this is the most heavily polluted water stream in refineries. The amount of sour water produced is between 0.2 and 0.5 t per ton of crude oil refined.[8,10] After treatment, sour water takes the name of process water. This stream still contains pollutants (such as sulfates, chlorides, and metals) but it is also rich in HCs. The most commonly detected contaminants in process water are essentially the same as those in sour water, but they appear in a lower concentration.[11] Process water is usually collected in a mixing pit,[12] together with other contaminated water streams coming from other refinery users. The outgoing stream from these tanks is called wastewater and undergoes further treatments[12,13] to comply with the legislative framework for water discharge in the environment, which varies from state to state.

In this work, the focus is on the Iplom refinery (located in Busalla, GE, Italy). This refinery processes up to 1.89×10^6 t year^{-1} of crude oil, consuming an amount of primary water in the order of 1×10^6 t year^{-1}, which, after suitable treatment, is discharged into surface waters. These numbers compare well with literature values of the ratio between wastewater produced and crude oil refined (both in t year^{-1}); this ratio is typically in the range 0.4–1.6,[10] with some authors reporting values as high as 3.5–5.[12,14] Nevertheless, the Iplom refinery aims to reduce primary water withdrawal through water reuse. Water reuse is now widely encouraged, and this is in line with the principles of circular economy, with actions aiming at "closing the loop" of resource lifecycles through greater recycling and reuse, and to extract the maximum value and use from all raw materials, products, and wastes, thereby fostering savings and reducing the environmental impact.[15,16] The Iplom refinery wastewater, after suitable treatment (described in detail in Experimental Procedures section below), has an acceptable quality for discharge into surface waters. Therefore, the possibility of reusing a part of this water stream inside the refinery is investigated in this work. Since the limits for water reuse inside the refinery are even stricter than those for water discharged into surface waters, additional water treatment is necessary. To this end, a membrane unit, i.e., a flat-sheet configuration reverse osmosis (RO) pilot plant, has been installed inside the refinery and experimentally tested.

Overall, membrane processes are currently being widely studied for industrial water treatment in many contexts, such as mining,[17] agriculture, food and beverage industries, textile industry, leachate treatment plants, power plants, refineries, and various types of plants in the oil and gas sectors.[1,18,19] In this context, the literature about membrane processes for oily wastewater treatment is contradictory. On the one hand, several papers have demonstrated that HCs cause membrane fouling[20-24] and, thus, severely reduce performance. For example, in a literature work,[25] commercial spiral-wound forward osmosis membranes made of cellulose triacetate are tested. The reported results underline a good rejection of pollutants, but problems of fouling and deterioration of the membranes were encountered due to the interaction with organic components. In further works,[18,26] membrane applications for refinery wastewater treatment are reviewed, considering microfiltration, ultrafiltration (UF), and RO, and highlighting the huge potential of membrane technologies for water treatment in the petroleum industry.[26] Twelve refineries worldwide are listed, all of which implement water reuse based on membrane processes, mainly RO. Nevertheless, no details about the plant configuration or the membranes used are given. It is underlined that, although the application of membrane technology has important advantages, some unresolved issues undermine the complete success of this technology. Fouling remains the most important problem and it is due to the complex contaminants present. On the other hand, several approaches have recently been proposed to overcome the fouling problem, all of which are based on suitable tailoring of the membrane properties, mainly hydrophilicity. A review carried out on the different approaches[27,28] concludes that excellent antifouling membranes are now available that enable long-term use and good recyclability. A further review work discusses the growing application potential of antifouling membranes in the treatment of oily wastewaters.[28]

This paper reports the results of two experimental campaigns performed with two different types of commercial membranes mounted in an RO pilot plant (installed in the Iplom refinery) on the treated wastewater streamline. For practical reasons, the water obtained from the RO pilot plant is not recycled inside the refinery there, but merely analyzed to ascertain compliance with the thresholds for reuse in the CWS of the refinery. The paper is structured as follows: Experimental section reports a description of the refinery and its water management system. Results and Discussion section presents the details of the experimental RO pilot plant installed inside the refinery and the experimental techniques employed. Conclusions section reports and discusses the RO experimental results obtained. Finally, Conclusions section draws some conclusions.

REFINERY DESCRIPTION

Oil treatment

A basic layout of the refinery is shown in Fig. 1. Iplom refines up to 1.89×10^6 t year^{-1} of crude oil from various sources, producing mainly diesel fuel and low sulfur fuel oil. The refinery is specialized in low sulfur fuels, producing, for example, a low sulfur marine fuel oil in line with the 0.5% sulfur cap introduced by the International Maritime Organization (IMO). Therefore, crude oils treated in the refinery are classified according to their sulfur content, such as crude oils with sulfur content lower than 1% (naphthenic or paraffinic) and crude oils with a sulfur content greater than 1%. The crude oils are first stored in tanks, and then, after suitable blending, they are distilled in the topping tower. Top products are virgin naphtha and petroleum gas. The intermediate fraction is gasoil, and the bottom products are the heaviest compounds, which are then further distilled in the vacuum distillation column; this produces vacuum gasoil (VGO) as the top product and vacuum residue as the bottom product, which is used to produce fuel oil or bitumen according to the type of crude processed. To lower the sulfur content to 10 ppm, the gasoil fraction separated by the topping column is treated with hydrogen in an HDS unit, producing diesel fuel. In parallel, the VGO obtained from the vacuum distillation tower is treated with hydrogen in a mild HDC reactor, converting VGO to a low sulfur intermediate fraction (i.e., diesel fuel and low sulfur fuel oil). In both the HDS and the HDC processes, sulfur is removed in the form of hydrogen sulfide, which is then fed to a Claus process, producing elemental sulfur (which is also commercialized).

Water management

The layout of the water management plant is shown in Fig. 2. Overall, Iplom uses primary water with a ratio of 0.5 $\frac{t\ primary\ water}{t\ crude\ oil\ refined}$. The refinery draws primary water from different sources: about 50% from a nearby dam (Busalletta, GE, Italy) and about 50% from two wells that were drilled inside the refinery. The quality of the well water is stable and reproducible over time. The quality of the dam water is like that of the well water, but more subject to fluctuations related to weather conditions. Altogether, dam and well waters are referred to as primary waters, and Table 1 reports the average results of various analyses collected over two years. In addition, an amount of water (not well quantified) contained in the crude oil is purged from the storage tanks and is also treated. The quality of this water is much more subject to fluctuations, depending on the quality of the crude oil. This water is conveyed directly to the wastewater treatment (API tanks, discussed in detail in Wastewater Treatment section) in an intermittent manner. Fig. 2 displays how primary water is employed in the water management plant. The dam water is fed to the CWS. The well water is fed to a storage tank, supplying sprayers and backwashing processes. Furthermore, both dam and well water are fed to a membrane filtration unit upstream of the steam production system, and, when needed, to the firewater network (FWN). Inside the refinery, six main water streamlines can be identified, and they are represented in Fig. 2 and described in more detail in CWS section to Wastewater Treatment section below. Concerning the water output and referring to the totality of the primary water withdrawn, about 5–20 % is lost in vapor losses in the cooling water system (CWS) and about 80–85% is treated in the wastewater treatment plant and discharged into surface water (the nearby river Scrivia, Italy). All the data reported so far are an average of the data obtained over time.

CWS

The CWS is mainly composed of six cooling towers. The scope of the CWS is to reduce the temperature of the liquid water circulating as a cooling fluid in the heat exchangers of the refinery. In the CWS, liquid water is not in a closed-circuit configuration because steam is released from the cooling towers, so water must be reintegrated through freshwater. Furthermore, because of evaporation, salt concentration tends to rise in the liquid water in the CWS. To avoid excessive concentration that may cause corrosion and encrustations, part of the hot water that reaches the cooling towers is purged. It is not represented in Fig. 2, but this purge is conveyed to the wastewater treatment plant (API tanks). This

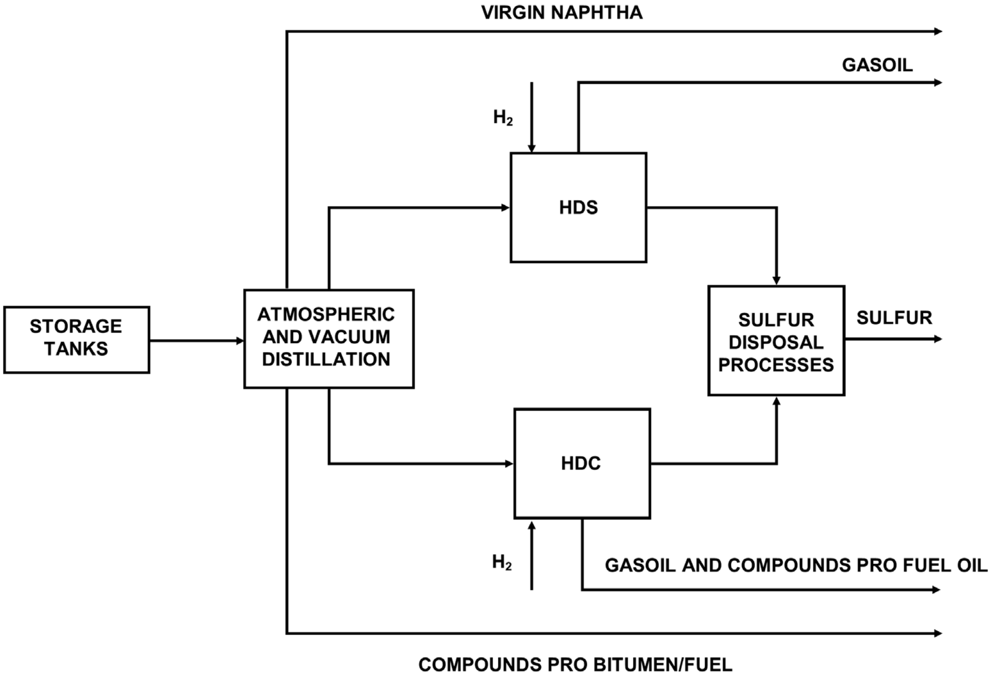

Figure 1. Layout of the Iplom refinery.

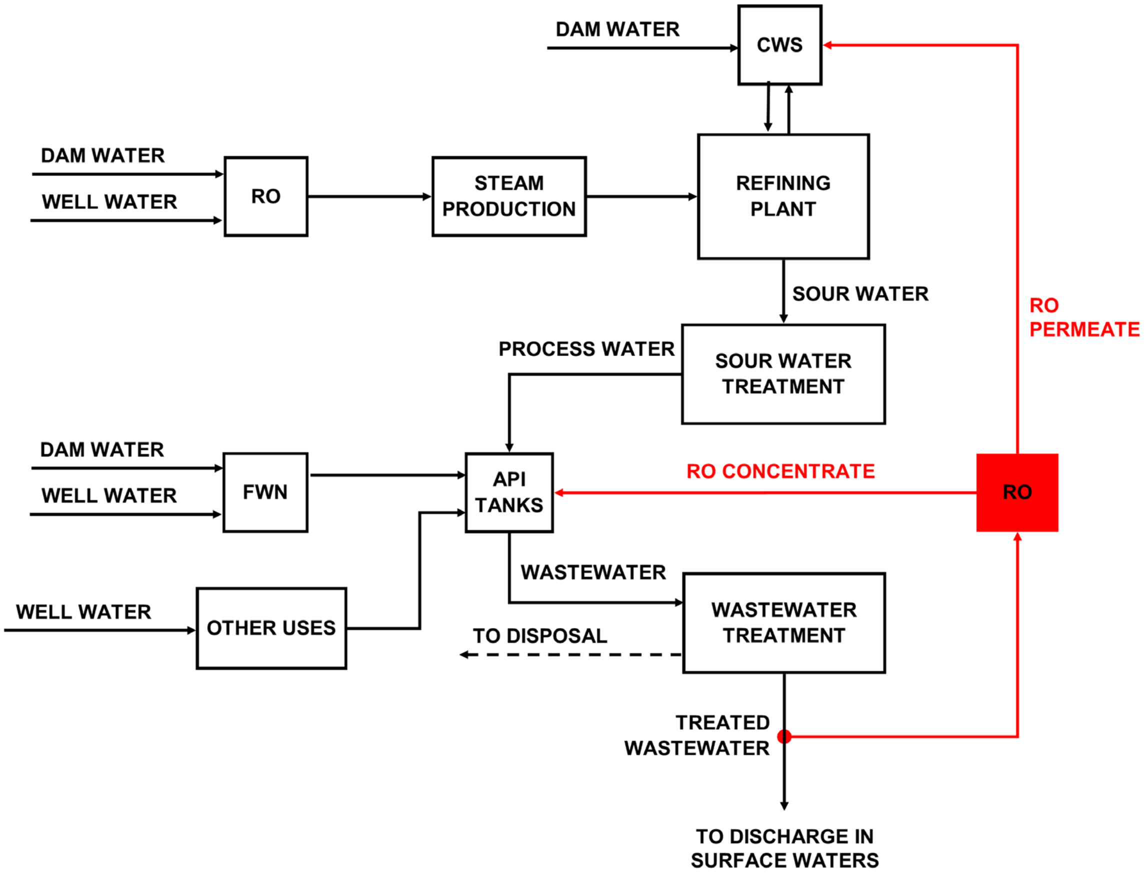

Figure 2. Layout of the water management plant in the Iplom refinery. In black: present configuration. The dashed line represents the water contaminants, separated and discontinuously conveyed to disposal. In red: proposed water re-use technique and additional RO unit.

Table 1. Primary water analysis. Average from measurements collected over two years

	Unit	Value
pH	—	7–8
Conductivity	$\mu S/cm^{-1}$	350–360
Alkalinity	ppm	110–130
Ca H	ppm	110–130
Mg H	ppm	40–50
Total H	ppm	150–180
TSS	ppm	1–1.5
Chlorides	ppm	10-15
Fe	ppm	0.2–0.3
Mn	ppm	0.05–0.1
Phosphates	ppm	1.5–2
Sulfates	ppm	10–15

purge is an additional loss of water that must also be compensated for, through reintegration. The overall primary water stream used for reintegration is about 20–25 t h^{-1}. This water, flows through two sand filters, for the removal of suspended solids, before entering the CWS.

FWN

The FWN consists of a 3000 m^3 storage tank, which is constantly kept at a full level for safety reasons, and a pipeline that reaches all areas of the refinery. To avoid stagnation, water is circulated through the FWN and then discharged in the API tanks.

Tank sprayers and backwashing processes

This stream collects all the water drains and all the water used in the refinery for washing procedures (tanks, etc.). This stream is eventually conveyed to the wastewater treatment plant (API tanks).

Process steam production

Refinery process steam is produced from demineralized water. To obtain this, water is treated with two membrane filtration units in series: UF and a pre-existing RO. UF mainly aims at removing most pollutants and suspended solids, so typical hollow fiber modules are employed. The pre-existing RO unit upstream of the process stream production mainly aims at removing dissolved salts and solids and is based on traditional spiral-wound membranes. The permeate obtained from the RO unit is used in the boiler of a cogeneration system to produce high-pressure steam that drives a steam turbine, producing the electrical power necessary to run the refinery. The low-pressure steam discharged by the turbine is used as a refinery utility. Conversely (not represented in Fig. 2), the concentrate obtained from the RO unit is conveyed in part to the FWN and in part to the API tanks for treatment in the wastewater treatment plant.

Sour water treatment

After being used in the refinery, steam is recovered and condensed, taking the name of sour water; due to its direct and intimate contact with crude oil, sour water has a heavy load of pollutants.[10] Sour water's first treatment is based on stripping, which mainly removes NH_3. After stripping, sour water is treated in two sand filters. Then, it is conveyed to an ozone-based treatment based on a traditional controlled corona discharge process fed with pure oxygen and producing a stream of 6% ozone in oxygen. The ozone stream is brought into contact with the sour water in two contact towers arranged in series. At the outlet of the contact towers, the depleted ozone stream (containing non-reacted ozone) is conveyed to a burner, in which ozone is destroyed. Thanks to the oxidizing effect of ozone, a reduction in concentration of about 95–99% of phenols and 45–55% of the COD is observed in the sour water at the exit of the contact towers. Subsequently, sour water is treated through active carbon filters, and finally, through anionic resins. Once this stream current has undergone these treatments, it is referred to as process water, and it is conveyed to the API tanks for further treatment. This stream is about 15–20% of the total amount of wastewater produced, corresponding to about 0.1 t of sour water per ton of crude oil refined. This value compares well with the literature, which reports an amount of sour water between 0.2 and 0.5 t per ton of crude oil refined.[8,10]

Wastewater treatment

Two API oil-water separators are present.[8] The name derives from the American Petroleum Institute (API), which defined the standards to be followed in the design of these separators. In the Iplom API tanks, one API collects mainly process water and the other collects all the other streams, including the concentrate of the pre-existing RO plant, the washing water, the water coming from the sprayers, the water originally contained in the crude oil, and all minor refinery water streams. In the API tanks, the oily fraction is separated from water for gravimetric decantation. Separation is not complete, and therefore the water streams from the API tanks, after being mixed in an equalization tank acting as a buffer, are treated in a flotation system,[29] providing further oil-water separation. Downstream, an active carbon filtration unit removes residual HCs and phenols. After separation, the contaminants are collected and discontinuously conveyed to disposal, as represented in Fig. 2. Conceptually, this discontinuous stream is a purge stream. A typical analysis of the treated wastewater is shown in Table 2. The results are an average of the results obtained with different types of crude oil treated in the refinery. The treated water stream complies with the site-specific limits for discharge into surface waters (Italian legislative decree 152/2006).

Water reuse strategy

To implement a water reuse strategy, the most suitable water stream to recycle appears to be the wastewater, after treatment but just before discharge into surface waters, since the analysis reported in Table 2 demonstrated a very low level of pollutants. There are several options to substitute this water stream with fresh water in several water streamlines of the water management plant. The reused water quality must satisfy the acceptable limits for water feeding in the selected streamline. This is not a trivial requirement because, in many cases, these limits are even stricter than those for discharge into surface water. Therefore, reuse in the steam production line is not feasible because the pre-existing RO unit, which is based on traditional spiral-wound membranes, is prone to fouling and very sensitive to water impurities (zero tolerance to HCs). Thus, as the first step towards water reuse in the refinery, the idea under study here is to withdraw an amount of treated wastewater before discharge into surface water and to use this for water reintegration to the CWS.

Table 2. Analysis of the main contaminants present in wastewater after treatment, before discharge in surface water (average over the results obtained processing different kinds of crude oils in different seasons)

	Unit	Value
pH	—	7–8
Alkalinity	ppm	100–250
TSS	ppm	0–15
Al	ppm	0.001–0.003
Chlorides	ppm	100–200
COD	ppm	5–105
Cu	ppm	0–0.1
Fe	ppm	0.1–0.4
HC	ppm	0–3
Mn	ppm	0.08–0.1
Phosphates	ppm	0–3
Sulfates	ppm	30–50
TAN	ppm	2–8

Table 3 reports the water purity requirements for the CWS, displaying that they are stricter than those for discharge into surface waters. Overall, the reason for these stricter limits is that, due to the water evaporation in the cooling towers of the CWS, the concentration of contaminants in liquid water tends to rise, causing either encrustation and clogging on one side, or corrosion on the other side. In line with this, Table 3 shows that CWS requirements include pH to be maintained between 7.6 and 8.2: larger values increase the formation of encrustations, whereas lower values increase the probability of corrosion. In other words, the indicated range of 7.6–8.2 offers a trade-off between fouling and corrosion. Analogously, calcic hardness (Ca H) and alkalinity are mainly associated with the presence of Ca compounds, including $CaCO_3$ and $Ca(HCO_3)_2$. The CWS limits reflect the fact that a low Ca level helps to keep the formation of encrustations under control, whereas a high Ca level is protective against corrosion. Once again, the thresholds reported in Table 3 for Ca H and alkalinity correspond to a trade-off between fouling and corrosion. An additional parameter to monitor and the concentration of which must be maintained within the limit values is TAN (total ammonia nitrogen). Here, the increase in concentration can cause bad odors and foaming, with related hydrodynamic problems in the circuit.

By comparing Table 2 to Table 3, it is found that COD, Fe, and TAN in treated wastewater may be near or above the limits for recycling to the CWS. It is important to remember that the values in Table 2 are average values and that temporary fluctuations may occur due to variations in the crude oil treated in the refinery, or variations in the dam water due to weather conditions. Thus, to avoid the risk of exceeding the limits on water quality for feeding to the CWS, an additional water treatment unit must be added. As mentioned above, the idea proposed in this work is to add an RO pilot plant along the treated water streamline, after the carbon filters and before discharge into surface waters. An innovative

Table 3. Comparison between limits for site-specific discharge into surface waters (Italian legislative decree 152/2006), and for input to the refinery CWS. CWS input limits vary depending on the actual operative conditions of the plant; the numbers reported in the table are average values

	Unit	Limit for discharge into surface water (Italian legislative decree 152/2006)	Limit for input to the CWS
pH	—	5.5–9.5	7.6–8.2
Alkalinity	ppm	—	>150
Ca H	ppm	—	≤480
TSS	ppm	≤80	≤4
Al	ppm	≤1	≤0.2
Chlorides	ppm	≤1200	≤400
COD	ppm	≤160	≤120
Cu	ppm	≤0.1	≤0.008
Fe	ppm	≤2	≤0.4
HC	ppm	≤5	≤5
Mn	ppm	≤2	Fe+Mn +Al<1
Sulfates	ppm	≤1000	≤400
TAN	ppm	≤15	≤2

flat-sheet RO configuration is considered. A scheme of the water management plant, modified to implement the water reuse strategy described above, is reported in Fig. 2. It must be noted that the additional RO unit produces a purified permeate stream that is recycled to the CWS. The contaminants would be mostly conveyed to a concentrate stream that would be forwarded to the API tanks. Consequently, the operating conditions in the Wastewater Treatment section may change to cope with the slightly higher load of contaminants.

It needs to be clarified that, when the RO is set in operation, there is no risk that the recycle will trigger a transient behavior of the plant, i.e., a situation where the stream entering the RO would be of lower and lower quality with time because the system recirculates a contaminated concentrate that, in turn, lowers the quality of the wastewater to be treated. This would not happen thanks to the presence of a purge in the Wastewater Treatment section (dashed streamline in Fig. 2). As is well known in chemical plants,[9] the presence of a purge guarantees that, when the RO is put in place, a (new) steady-state will be reached. In this new steady-state, the Wastewater Treatment section will perform a slightly more intense purification. For example, the active carbons in the filtration units may need more frequent regeneration. This will make it possible to obtain a treated wastewater quality that will still comply with the site-specific limits for discharge into surface waters.

According to the numbers reported above for the refinery water streams, the proposed reuse strategy will reduce the withdrawal of primary water by about 20–25 t h^{-1}, which is a significant portion of the overall primary water withdrawal. In this work, to test the proposed idea, an additional flat-sheet RO pilot plant is installed along the treated water streamline (after the carbon filters and before discharge into surface waters), and the quality of the permeate water is tested to check whether the water obtained is compliant with the requirements for reuse in the CWS. The RO geometrical arrangement used for the pilot plant (flat-sheet) is the same as envisaged for the final plant so that the experimental data obtained from the pilot plant are relevant for scale-up.

EXPERIMENTAL

RO pilot plant

The RO pilot plant is manufactured by EXXRO (Genova, Italy). The RO plant includes a two-stage quartzite filter (Pevasa, Barcelona, Spain) to separate any suspended solids possibly present in the water stream. Between the quartzite filter and the RO unit, a high-pressure piston pump (Cat Pumps, Minneapolis, Minnesota, US) is present. Focusing now on the RO unit, it is formed by a single-stage embedding four RO modules in parallel. A sketch of a single module is shown in Fig. 3(a). The geometry is a typical flat-sheet (also called plate and frame)[30] configuration consisting of a series of annular membranes, each of which is supported by a channeled polysulfone disk. The feed is pumped into the module at high pressure, from the bottom, into a vertical manifold located at the outer rim of the disks. Then, the feed flows upwards, and at the top of the module, it finds an orifice through which it enters the disk located at the top of the stack. The feed flows above the membrane from the center to the outer rim, where it finds another orifice that makes a U-turn of the water stream. Afterward, the water stream flows from the outer rim to the center, staying in contact with the lower side of the membrane. Thus, on each disk, water is in contact with the membrane from above and from below, and the filtration area is calculated considering both sides. Indeed, the membrane is formed by two sheets superimposed and coupled together, with the outer rims joined together by ultrasonic welding (Fig. 3(b)). A spacer sheet is inserted between the two membrane sheets, keeping them separated from each other and making it possible for the permeate to flow from the outer rim towards the center, where six small holes are present. Subsequently, the permeate flows down through six small channels present between the disks and the central tightness rod. This is then repeated for the membrane below until the water stream reaches the bottom of the module, where it is discharged (concentrate). The bottom of the module is made of a stainless-steel plate with three holes: feed input, permeate output, concentrate output. Concerning the operating conditions for the RO pilot plant, the maximum water flow rate is 1 m^3 h^{-1}.

The membrane sheets are thin-film composite RO membranes of the series FILMTEC® FT30 and were supplied by The Dow Chemical Company (Midland, Michigan, US). The membrane sheet consists of three layers: a polyester nonwoven support web, a microporous polysulfone interlayer, and an ultrathin barrier coating on the top surface. The polyester nonwoven web provides the major structural support. Since the polyester web is too irregular and porous to provide a proper substrate for the salt barrier layer, a microporous layer of polysulfone interlayer is cast onto the surface of the web. The polysulfone coating has surface pores controlled to a diameter of approximately 150 Å. The superimposed ultrathin barrier layer, which is about 2000 Å thick, can withstand high pressures because of the support provided by the polysulfone layer. These membrane sheets can operate over a pH range of 2 to 11 (optimal water pH = 6.4–6.5), are resistant to compaction, and are suitable for temperatures up to 45 °C. Membrane sheets are cut, the spacer sheet is inserted between them, and the membrane outer rims are welded together in-house using ultrasonic welding.

Mainly due to the flat geometry associated with the presence of the spacer sheet, the flat-sheet configuration is less prone to fouling than the more common spiral wound geometry.

Two experimental campaigns are performed separately, with the RO pilot plant equipped with two different membranes of the FILMTEC® FT30 series. To investigate the two different

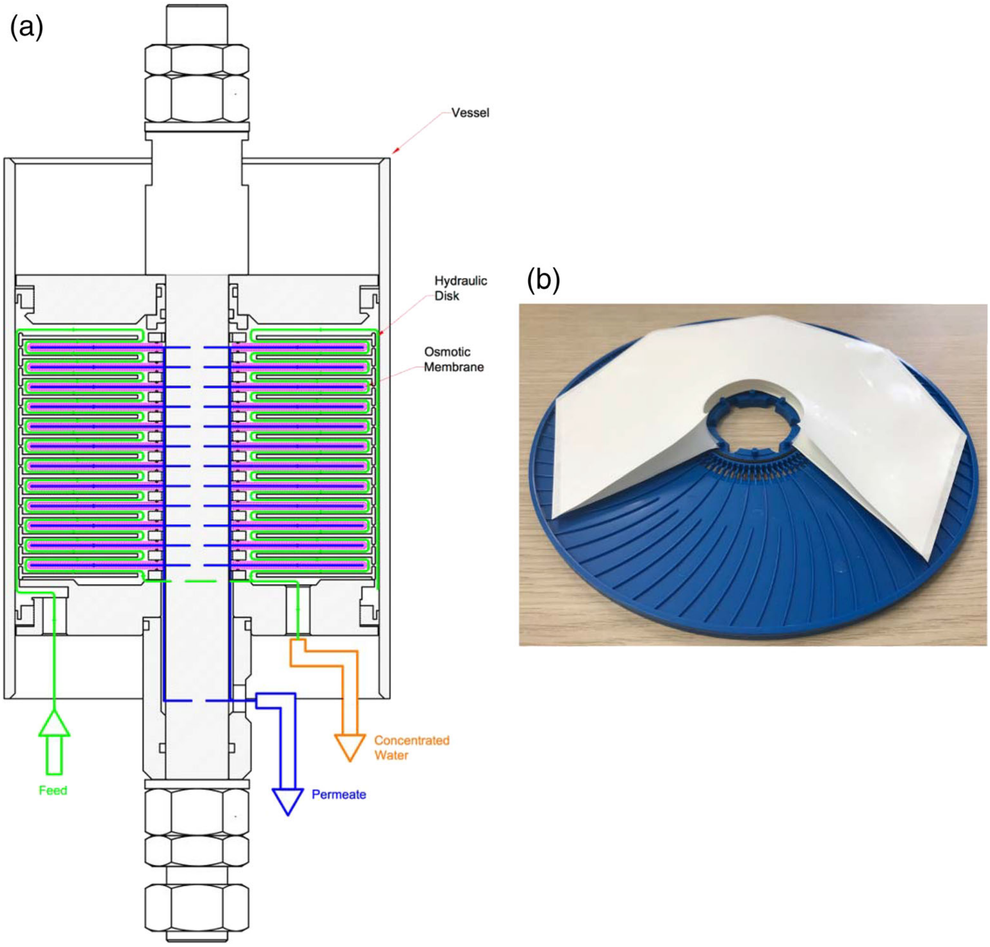

Figure 3. (a) Scheme of an RO module; and (b) channeled polysulfone disk with the two osmotic membranes and the spacer sheet in between (EXXRO).

membranes separately, in each campaign, all the modules of the pilot plant embed the same type of membrane. The two types of membranes adopted have different performance in terms of rejection *R*, defined as follows:

$$R = \left(1 - \frac{C_p}{C_f}\right) \cdot 100\%$$

where C_f is the concentration of the solute under analysis in the feed stream, and C_p is the concentration in the permeate stream.

The membranes employed in the experimental tests are:

- SWM-test: RO modules equipped with 219 DOW FILMTEC SW30HR-380 membranes, i.e., seawater (SW) high rejection (HR) membranes. Filtration area 9.74 m^2 per module, overall pilot plant filtration area 38.98 m^2.
- BWM-test: RO modules equipped with 170 DOW FILMTEC BW30FR-365 membranes, i.e., brackish water (BW) fouling resistant (FR) membranes. Filtration area 7.56 m^2 per module, overall pilot plant filtration area 30.26 m^2.

As a general comment, SWM membranes are designed to treat lower flow rates with a smaller amount of suspended solids and aggressive chemicals. In these conditions, they display high rejection. BWM membranes are more resistant to fouling and chemicals, but with a lower rejection performance. In multistage RO plants, BWMs are usually employed as a pretreatment, with subsequent treatment with SWMs.

The RO pilot plant is equipped with measurement instrumentation consisting of a pressure gage (model 233.30, 0-100 bar, D100, Wika, Klingenberg am Main, Germany) and a pressure transducer (model A-10, 0-100 bar, 4-20 mA, Wika) installed at the inlet of the RO modules. In the permeate water at the exit of the RO modules, flow rate, temperature, and conductivity are measured again through instrumentation installed on the pilot plant itself. Flow rate is measured through flowmeters (model 807R25D7211415516000, Gemü, Criesbach, Ingelfingen, Germany), coupled to a transmitter (model 1272000z2501, Gemü). Temperature and conductivity are measured simultaneously through a meter (model LF4213-C 0.5-0; Pt1000, Val.co Nerviano, Milano, Italy), coupled to a transmitter UNICON-LF, signal 4-20 mA (GHM, Barsbüttel, Germany). Finally, an external portable multimeter (Multi 3620 IDS, WTW, Weilheim in Oberbayern, Germany) measures conductivity, temperature, and pH of the permeate water at the outlet of the pilot plant. In particular, the pH sensor is SenTix 940 (WTW) with a plastic shaft, gel electrolyte, and fiber diaphragm.

The RO pilot plant embeds a control system that makes it possible to maintain the overall inlet water flow rate (i.e., the feed flow rate) at the desired value. In addition, the control system makes it possible to perform the experiments at a fixed permeation rate. For example, P80% means that the permeate flow rate is 80% of the feed flow rate, and the concentrate flow rate is 20% of the feed flow rate. This is obtained through suitable regulation of the pressure of the feed water at the inlet of the RO unit. In RO, it is well known that an increase in upstream pressure increases the water flux through the membrane, and thus, the permeate flow rate.[31]

Regarding the power consumption of flat-sheet RO plants, it is about 6 kWh m^{-3} (referring to m^3 of feed wastewater). The operating costs are in the order of 5 € m^{-3}, including the cost of energy and all the other costs related to the plant management (i.e., maintenance, consumables, spare parts, and person-hours of work).

Experimental procedures

Concerning the RO pilot plant installed in the Iplom refinery, the feeding water was taken at the outlet of the carbon filters of the wastewater treatment, upstream of the drain into surface waters. In all the experiments, the water flow rate fed to the RO pilot plant was kept at 1 m^3 h^{-1}. The measured average pH of the inlet water was around 7.5, which is higher than the optimal operating value for the RO plant. Nevertheless, no pH correction was applied, nor was antiscalant added, because this would not be done in the full-size plant. The idea is to avoid pre-treatments in the RO plant and, when needed, make any adjustments just before the inlet into the CWS.

Two experimental campaigns were performed. The first experimental campaign (SWM-test) was carried out over a period of 3 days, at a temperature of 12 °C ± 1 °C (winter). Overall, five tests were performed. On the first day, Test 1 was carried out in the morning and Test 2 in the afternoon, about 4 hours from each other. Test 3 and Test 4 were carried out on the second day, with the same timing. Finally, Test 5 was carried out on the last day of operation. For each test, the pilot plant was switched on before collecting the samples. After switching on, a steady-state operation was reached quickly, but the pilot plant was operated continuously for about 1 h before sampling to let the system equilibrate completely. After collecting the water samples, the RO pilot plant was switched off. After a rinse with the permeate, the water contained in the RO modules was drained.

The second experimental campaign (BWM-test) was performed at a water temperature of 20 C ± 1 °C. The RO pilot plant was kept in operation continuously from 9 a.m. to about 1 p.m., and then the plant was switched off and is put back in operation at 2 p.m. until about 4 p.m. The same cycle was repeated for six subsequent days. Again, samples were collected 1 h after switching on the plant. Additional tests were run in different parts of the day to collect permeability measurements in the temperature range of 18–27 °C. At the end of each day, the RO plant was switched off. After a rinse with the permeate, the water contained in the RO modules was drained and the pilot plant remained off all night until the following morning.

Water analysis techniques

Liquid phase chromatograph Thermo Scientific Dionex ICS-5000$^+$ Dual Pumps (Thermo Fisher Scientific, Waltham, Massachusetts, US), performing Ion Chromatography (IC), was used to measure the concentration of individual ions and conductivity. The analysis was done to determine the cation concentration and (in particular) that of ammonium, which was one of the main pollutants in process water.

TH is the total content of calcium and magnesium ions (Ca^{2+} and Mg^{2+}, respectively) in ppm. The detection of TH (total hardness) was carried out through titration with a hydrometric liquor. Standard methodologies[32] were followed to measure COD, HCs, phenols, sulfide, and Fe.

For the spectrometric and colorimetric analyses required by the methods above, the following instrumentation was used: PerkinElmer FT-IR spectrometer Spectrum Two (PerkinElmer, Waltham, Massachusetts, US), Perkin Elmer UV/Vis Spectrometer LAMBDA 25 (PerkinElmer, Waltham, Massachusetts, US), colorimeter NOVA 60 Spectroquant (Merck, Darmstadt, Germany). For the detection of metals, the sample was nebulized and then analyzed through a Spectrometer ICP (Inductively Coupled Plasma) Optima 2100 DV (PerkinElmer, Waltham, Massachusetts, US). Finally, the evaluation of total suspended solids (TSS) was carried out by weighing the residue obtained on a filter after vacuum filtration.

Overall, the error on the experimental results is within 3–5%.

For COD, the sensitivity threshold of the measurement method is 15 ppm. Thus, in all the results, values aligned at 15 ppm are below the sensitivity threshold and they must be interpreted as ≤15 ppm. For TAN and Fe, the sensitivity thresholds of the measurement methods are 1 ppm and 0.005 ppm, respectively. In all the result figures, values aligned at 1 ppm and 0.005 ppm must be interpreted as ≤1 ppm and ≤0.005 ppm, respectively.

RESULTS AND DISCUSSION

SWM-test

Table 4 reports the results of water analysis performed for one of the tests (Test 3). The water feed, i.e., treated wastewater and the permeates obtained at P50% and P80%, are all analyzed. Theoretically, the pH of pure water at a temperature of 12 °C is 7.2. Thus, the permeate water should have pH = 7.2 immediately after the RO process. Instead, Table 4 shows that pH = 7.0 for the P50% permeate, whereas pH = 6.7 was measured for the P80% permeate. This deviation is explained by the fact that, in water, the equilibria below are established, involving CO_2 dissolved from the atmosphere:

$$H_2O + CO_2 \leftrightarrows H_2CO_3 \tag{1}$$

$$H_2CO_3 \leftrightarrows H^+ + HCO_3^- \tag{2}$$

$$HCO_3^- \leftrightarrows H^+ + CO_3^{--} \tag{3}$$

Considering the equilibria above, theoretically, pure water exposed to atmospheric air with a nominal CO_2 content of 350–380 ppm should have an acidic pH in the range 5–5.5.[33] Nevertheless, the presence of carbonate salts in solution interferes with the equilibrium above because the ionic dissociation leads to the formation of additional carbonate and bicarbonate ions, and this shifts to the left-hand side the equilibria (2) and (3), thus increasing pH. Even tiny amounts of carbonate salts cause this effect. In the case of water in equilibrium with atmospheric CO_2 and saturated with calcium carbonate, pH is in the range 8–8.5. In conclusion, the intermediate value of pH reported in Table 4 (i.e., pH = 7.0 for the P50% permeate and pH = 6.7 for the P80%) is explained, on the one hand, by the presence of the dissolved CO_2, and on the other hand, by the small amounts of residual carbonate salts and/or other ionic species present.

Considering the data above, the effect of RO on the water to be recycled to the CWS seems harmful, since the pH of the RO permeate is less compliant with the requirements of the CWS (pH = 7.6–8.2) than that of the treated wastewater fed to the RO unit. However, it should be noted that there are several options to regulate pH in the CWS, including suitable modulation of the

Table 4. SWM-test, Test 3. Water analysis for the feed and the permeates obtained at P50% and P80%. P50% means that the feed flow rate is divided equally between permeate and concentrate. P80% means that the permeate flow rate is 80% and the concentrate flow rate is 20% of the feed flow rate

	Unit	Feed	P50%	P80%
pH	—	7.4	7	6.7
Conductivity	$\mu S\ cm^{-1}$	860	81	62
Alkalinity	ppm	180	1	1
Ca H	ppm	160	1	2
Total H	ppm	200	2	3
Turbidity	FAU	1	0	0
Al	ppm	0.05	N.A.	N.A.
Cl	ppm	N.D.	N.D.	N.D.
COD	ppm	35	≤15	≤15
Cu	ppm	N.D.	N.D.	N.D.
Fe	ppm	0.15	≤0.005	≤0.005
HC	ppm	1.8	0.6	0.2
Mn	ppm	N.D.	N.D.	N.D.
TAN	ppm	5	≤1	≤1

N.D., not detected; N.A., not available.

purge (CWS section), which impacts the salt concentration in the CWS and eventually regulates the pH at the desired value. Taking this into account, the pH of the RO permeate water is not considered problematic for RO permeate reuse in the CWS.

Table 4 shows that the removal of all contaminants by the RO is very thorough. Rejection, calculated based on the data in Table 4, is above 99% for alkalinity, hardness, turbidity, and Fe. This is the typical rejection obtained with RO applied to ionic species in water, due to a strongly bonded solvation shell surrounding the ions that is able to resist, intact, the impact with the membrane.[34] In some cases, this very thorough removal is not completely beneficial because the alkalinity of the RO permeate is far too low compared to the lower limit threshold reported in Table 3, indicating that calcium carbonate and bicarbonate reintegration is necessary before feeding to the CWS.

Based on the data in Table 4, it is possible to evaluate a rejection associated with conductivity. The rejection calculated for conductivity (91–93%) is slightly lower than that reported above. Regarding conductivity, it is interesting to notice that it decreases passing from P50% to P80%. To explain this, first it must be recalled that the inlet water stream fed into the RO pilot plant is 1 $m^3\ h^{-1}$ in all the experiments. Passing from P50% to P80%, the permeate flow rate increases from 0.5 to 0.8 $m^3\ h^{-1}$. As stated in RO Pilot Plant section, this increase of permeate flow rate is obtained by increasing the pressure of the feed water at the inlet of the RO unit. By doing this, the solvent (water) flux through the membrane (directly proportional to the permeate flow rate) increases, whereas, according to the classical solution-diffusion model,[31] the solute flux through the membrane remains constant. Thus, by increasing the permeate flow rate from P50% to P80%, the salt concentration in the permeate decreases. Therefore, conductivity also decreases.

A further reduced value of rejection is calculated for HCs in the range 66–89%. This is consistent with literature results reporting that organic molecules with a molar weight lower than 100 g mol^{-1} are not well retained by reverse osmosis.[34] Nevertheless, it is remarked that HCs are already well below the CWS thresholds in the treated wastewater fed to the RO pilot plant.

For TAN and COD, due to the sensitivity thresholds of the measurement methods, rejection can be estimated as ≥80% and ≥57%, respectively. For ammonia, it is recalled here that the equilibrium below is established in water solutions:

$$NH_3 + H^+ \leftrightarrows NH_4{}^+ \tag{4}$$

The equilibrium strongly depends on temperature and pH. It is calculated that, at 12 °C and pH = 7.4, 0.5% of TAN is in the form of free ammonia and 99.5% is in the form of ammonium ion.[35,36] Based on this, a rejection as high as 99.5% is expected. Even if the experimental data do not provide a precise value, it is underlined that concentrations of TAN, as well as COD, in the RO permeate are below the CWS thresholds.

A complete overview of the results obtained from Tests 1 to 5 is shown in Fig. 4, which also displays the acceptable thresholds for re-use in the CWS. Regarding pH, the considerations above still hold. The high level of abatement is confirmed for conductivity, hardness, and Fe. Fe is particularly important since, in Tests 4 and 5, the level in the water fed to the RO pilot plant is as high as the threshold for input to the CWS. For Fe, the RO pilot plant confirms a strong abatement with an average rejection ≥96%. The abatement of COD appears to be satisfactory, especially since COD concentrations in the treated wastewater fed to the RO pilot plant are already well below the CWS threshold. Similarly, HCs in the treated wastewater fed to the RO pilot plant are also well below the CWS threshold. The results in Fig. 4 confirm that HCs are not well retained by the RO membranes. The results of HC flux with the permeate during Test 1 (data not reported in the figures) are in the range 15.4–20.5 mg m^{-2} h, practically independent of the applied pressure. During Test 3, the HC flux drops to 4.1–7.7 mg m^{-2} h, whereas during Tests 4 and 5, the HC flux increases to 21.8–35.9 mg m^{-2} h. The HC flux with the permeate does not show a clear correlation with the HC concentration in feeding water, nor with the applied pressure. Moreover, it must be noted that the results of Tests 1 and 5 report a higher HC concentration in the P50% permeate than in the water feed. This suggests that the HC detected in the permeate originates not only from the HCs present in the water feed but also from the dissolution of

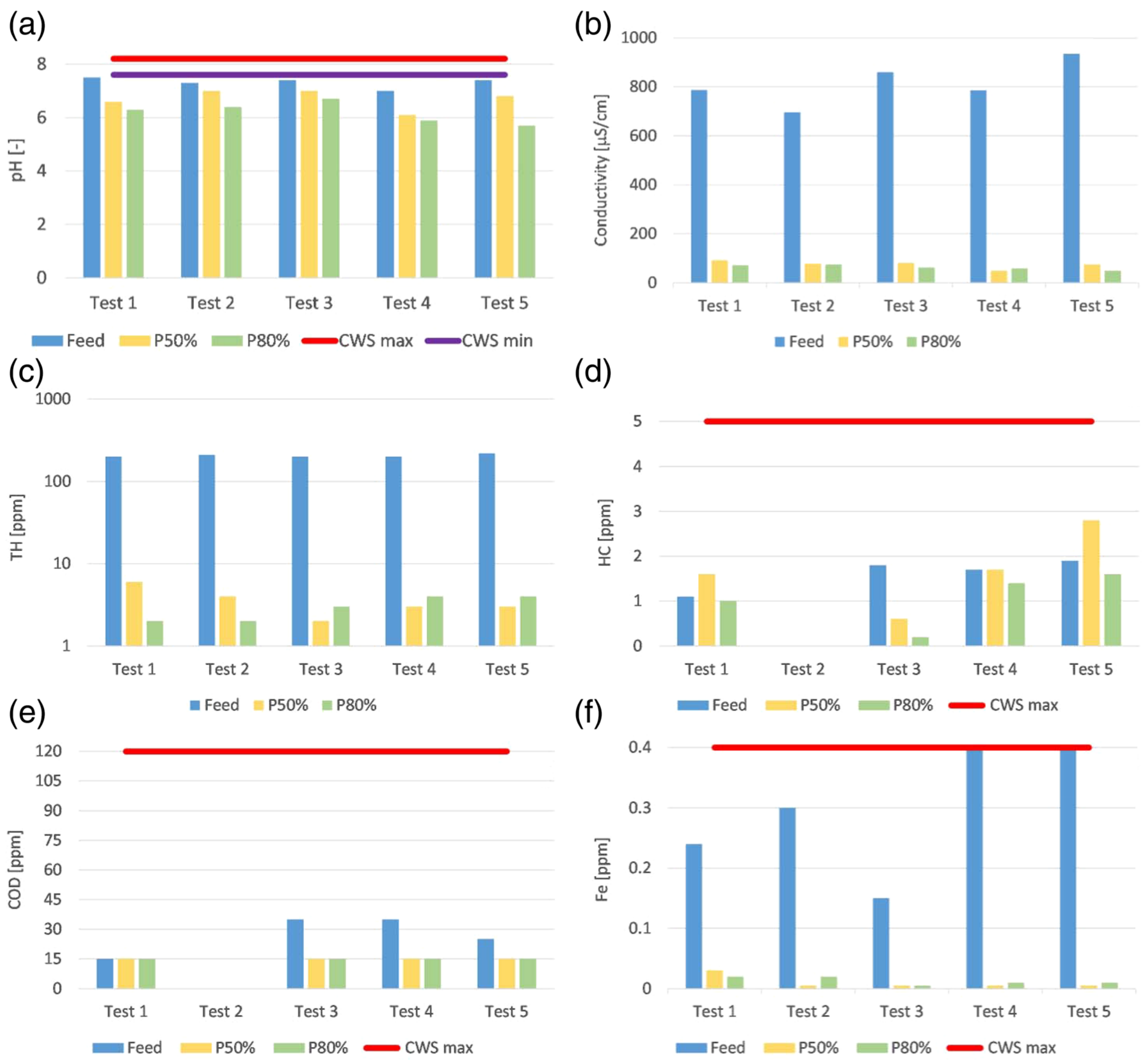

Figure 4. Results of the SWM-test. HC and COD concentrations [respectively, panels (d) and (e)] are not measured during Test 2. Minimum and maximum thresholds for water reuse in the CWS are reported. For COD, values aligned at 15 ppm must be interpreted as ≤15 ppm.

some accumulated organic compounds from the membrane itself.

For a more detailed quantitative analysis of the RO process, Fig. 5(a) shows water (solvent) flux through the membrane in the permeate stream. Fig. 5(a) displays that the results of the first two tests (Test 1 and Test 2) are not perfectly in line with the other results, and this is possibly due to non-complete membrane equilibration at the beginning of the experimental campaign. The results of the subsequent tests (Test 3 to Test 5) lay on a straight line for pressures below 20 bar and are in agreement with the solution-diffusion model.[31] For pressures below 20 bar, the solution-diffusion model is applied to fit the experimental data of water flux as a function of pressure through the following equation:[31]

$$J_w = \overline{P}_{H_2O}(\Delta p - \Delta\pi)$$

Where J_w [L m^{-2} h^1] is the water flux through the membrane, $\overline{P}_{H_2O}$ [L m^{-2} h^1 bar^1] is the permeability of water across the membrane, Δp [bar] is the pressure gradient across the membrane, and $\Delta\pi$ [bar] is the osmotic pressure. Straight-line fitting of the experimental data reported in Fig. 5(a) gives an average water permeability of 1.24 L m^{-2} h bar, which is in line with previous results reported in the literature for other RO membranes.[37,38] In Fig. 5(a), the straight-line fitting of the experimental data intercepts the x-coordinate at a pressure of 2.2 bar, which is the osmotic pressure. For pressures higher than 20 bar, the experimental data do not follow the straight-line behavior any more. Here, the water flux through the membrane approaches asymptotically its maximum value, corresponding to the inlet water flow rate of 1 m^3 h^{-1}.[31]

Regarding the Fe flux through the membrane, values are below 1.1 mg m^{-2} h. According to the solution-diffusion model, the solute (Fe) flux N_s [g m^{-2} h] follows the relationship below:

$$N_S = \overline{P}_S(C_f - C_p)$$

Where $\overline{P}_S$ [L m^{-2} h] is the solute permeability across the membrane. According to the solution-diffusion model, $\overline{P}_S$ should be a constant value that does not depend on the applied pressure nor on the solute concentration in the feeding water. Figure 5(b) reports the results obtained for the Fe permeability across the membrane. Again, in this case, the results obtained from Tests 1 and 2 are not completely consistent with the results obtained from the

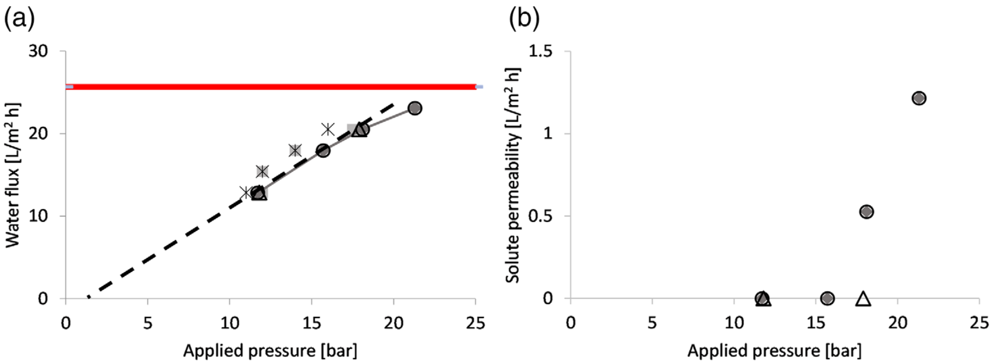

Figure 5. SWM-test. Symbols: experimental data (■ Test 1, ⚹ Test 2, △ Test 3, ○ Test 4, ◆ Test 5). (a) Water flux as a function of applied pressure; ▬ maximum water flux, corresponding to the feeding flow rate 1 m^3 h^{-1}; - - - - linear fit of experimental data of water flux (only from Test 3 to 5) in the pressure range 10–20 bar; (b) Fe permeability through the RO membranes: results from Tests 3 to 5.

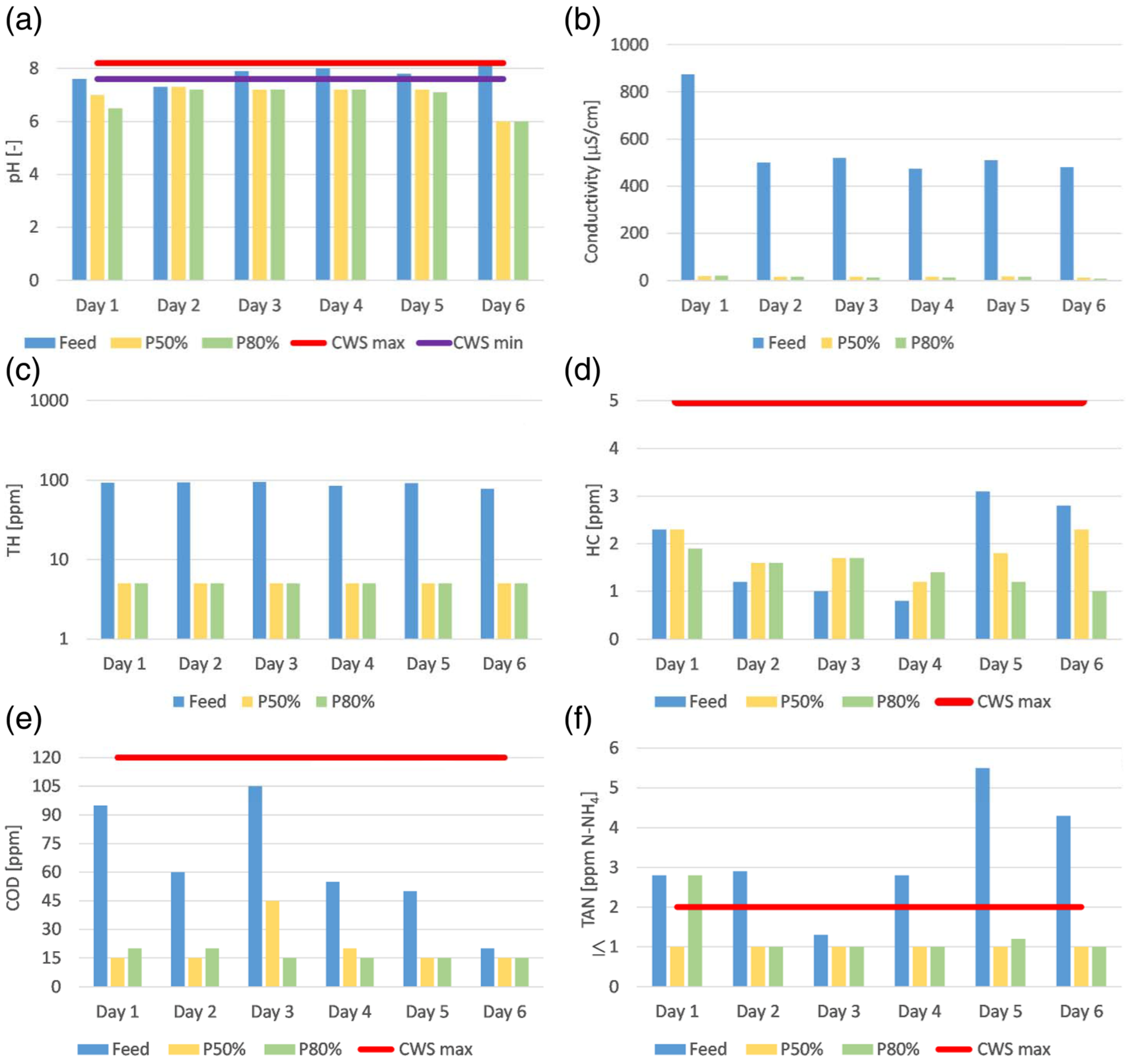

Figure 6. Results of the BWM-test. Minimum and maximum thresholds for water reuse in the CWS are reported. For COD, values aligned at 15 ppm must be interpreted as ≤15 ppm. For TAN, values aligned at 1 ppm must be interpreted as ≤1 ppm.

subsequent tests, and they are not reported in Fig. 5(b). Nevertheless, the results from Tests 3 to 5 are very consistent with each other, displaying an increase of Fe permeability with increasing pressure. Fe permeability is below 0.1 L m^{-2} h for applied pressures below 17 bar, and then, for pressures higher than 17 bar, it increases linearly with pressure, reaching 1.2 L m^{-2} h at 23.1 bar.

Both the behavior and the values in Fig. 5 are in full agreement with those reported in the literature for RO of ammonium sulfate solutions.[37] In particular, the findings reported here confirm that the solution-diffusion model is well followed by the solvent, with values of permeability independent of pressure for water fluxes at least 20% below the maximum value. On the other hand, the solution-diffusion model is not well followed by the solute, which displays a permeability that increases with the applied pressure. This confirms the findings previously reported in the literature for ammonium sulfate:[37] that the solute tends to be transported convectively along with the solvent.

Overall, the results shown in Table 4 and Figs 4 and 5 display that the RO module is very efficient in removing ions, whereas it is less efficient in removing HCs. Results of solvent (water) flux through the membrane, displayed in detail in Fig. 5, are identical during Tests 3 to 5. An Increasing hindrance to water permeation over time, an effect usually associated with the problem of fouling, is not detected in the short time scale.

BWM-test

The BWM-test has the objective of testing a different RO membrane that is more robust (from the mechanical point of view) and more resistant to fouling, but, on the other hand, has a lower expected rejection and permeability. Another objective is to validate the RO results on a longer time scale. The quality of the treated wastewater fed to the pilot RO plant is different from that of the SWM-test because of the different crude oil blends processed in the refinery during the test. For the same reason, the quality of the treated wastewater varies, even during the experimentation period, as is clearly visible in Fig. 6. Here, attention is focused on the same relevant chemical compounds analyzed in detail in the SWM-test. Fe is analyzed only in a couple of tests, displaying a rejection in the order of 74–79%; this is lower than of the SWM-test membranes, but largely sufficient to keep the Fe content below the CWS threshold (0.4 ppm, Table 3). For conductivity and COD, results are reported in Fig. 6. Rejections are 96.5–98.3% and 70–88%, respectively (except for COD on Day 6, when COD is very low in the feeding water and below the limit of detection in the permeates). Thus, rejection is lower than with the SWM-test membranes (as expected), but it is sufficient to keep the contaminant level well below the CWS threshold. This is of particular importance for COD, the values of which (in the treated wastewater fed to the RO pilot plant) are very close to the limit acceptable for reuse in the CWS. A similar situation also holds for TAN (Fig. 6(f)). In the treated wastewater fed to the RO pilot plant in the BWM-test, TAN is often above the limit acceptable for reuse in the CWS. To add more detail, Fig. 6(f) shows that, for all test days (except for Day 3), TAN in the treated wastewater fed to the RO pilot plant is above the threshold value of 2 ppm N-NH_4. Regarding TAN, the average rejection is above 62.6% at P50%, and above 51.3% at P80%. Also in this case, the rejection is lower than that with the SWM-test membranes, but (again) sufficient to keep the contaminant level below the CWS threshold.

HCs are reported in Fig. 6(d). Again here, the behavior is very similar to that reported in Fig. 4(d), with a low HC abatement. Moreover, in some experiments (Day 2–4), the HC concentration is slightly higher in the permeate than in the feeding water. This tends to disappear on Days 5 and 6, supporting the hypothesis of the dissolution of some accumulated organic compounds from the RO membrane into the permeate water occurring in the first days of testing. All results reported in Fig. 6 are stable during the 6 days of experimentation.

Finally, for the BWM membranes, water permeability is evaluated in the range 1.0–1.5 L m^{-2} h bar for temperatures in the range of 18–27 °C.

CONCLUSIONS

The treated wastewater streams produced by refineries typically contain contaminants that must be below the thresholds dictated by governmental regulations for discharge into the environment. Recirculation and reuse of this water inside the refinery itself is not straightforward because the threshold of such contaminants for recycling into some streamlines of the refinery water system (for example, the process steam production) are stricter than those for discharge into the environment. In this work, the possibility of purifying the treated wastewater to use for water reintegration to the refinery CWS is analyzed. At the refinery scale, this would make it possible to significantly reduce the withdrawal of primary water by an amount that can be quantified approximately as 20–25 t h^{-1}. An RO pilot plant with advanced innovative flat-sheet configuration is installed downstream of the wastewater treatment and tested for the abatement of contaminants. The flat-sheet configuration is less prone to fouling than the more common spiral wound geometry. The RO plant is tested employing two different types of RO membranes: high rejection membranes designed for seawater (SWMs), and high fouling resistance membranes designed for brackish water (BWMs). The experimental results show that, with both membranes, the abatement of COD, Fe, and TAN — the values of which, in the treated wastewater, are very close to or higher than the thresholds for recirculation to the CWS (120 ppm, 0.4 ppm, and 2 ppm, respectively) — is very efficient. The results concerning HCs indicate that the HC abatement is not very effective; nevertheless, this is not an issue since the HC level in the treated wastewater is already well below the CWS threshold (5 ppm). For the SWM membranes, water permeability is evaluated as 1.24 L m^{-2} h bar at 12 °C, which is in line with previous results reported in the literature. For the BWM membranes, water permeability is evaluated in the range 1.0–1.5 L m^{-2} h bar for temperatures in the range of 18–27 °C.

In conclusion, the permeate water obtained at the exit of the RO pilot plant during the experimental tests fulfills the requirements for reuse in the CWS of the refinery. During the experimentation period, there was no growing hindrance to the permeation of water over time that is usually associated with fouling. Indeed, the results are stable with both membranes tested during a BWM-test held for 6 days, with 36 hours of discontinuous operation.

The power consumption of flat-sheet RO plants is about 6 kWh m^{-3} (referring to m^3 of feed wastewater). The operating costs are in the order of 5 € m^{-3}, including the cost of energy and all the other costs related to the plant management (i.e., maintenance, consumables, spare parts, and person-hours of work).

ACKNOWLEDGEMENTS

Many thanks to the Analysis Laboratory of Iplom for performing the experimental analyses of the water samples.

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