Experimental evaluation of Fenton and modified Fenton oxidation coupled with membrane distillation for produced water treatment: Benefits, challenges, and effluent toxicity

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ABSTRACT

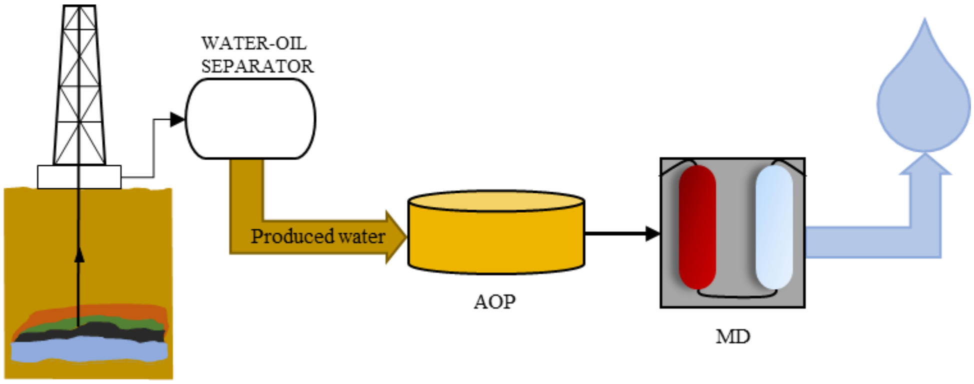
Membrane distillation is a promising technology to desalinate hypersaline produced waters. However, the organic content can foul and wet the membrane, while some fractions may pass into the distillate and impair its quality. In this study, the applicability of the traditional Fenton process was investigated and preliminarily optimized as a pre-treatment of a synthetic hypersaline produced water for the following step of membrane distillation. The Fenton process was also compared to a modified Fenton system, whereby safe iron ligands, i.e., ethylenediamine-N,N'-disuccinate and citrate, were used to overcome practical limitations of the traditional reaction. The oxidation pre-treatments achieved up to 55% removal of the dissolved organic carbon and almost complete degradation of the low molecular weight toxic organic contaminants. The pre-treatment steps did not improve the productivity of the membrane distillation process, but they allowed for obtaining a final effluent with significantly higher quality in terms of organic content and reduced *Vibrio fischeri* inhibition, with EC_{50} values up to 25 times those measured for the raw produced water. The addition of iron ligands during the oxidation step simplified the process, but resulted in an effluent of slightly lower quality in terms of toxicity compared to the use of traditional Fenton.

Keywords: membrane distillation; produced water; advanced oxidation; iron ligands; ecotoxicity

HIGHLIGHTS

- Thermal and modified Fenton degraded target contaminants in produced water.
- The oxidative pre-treatment reduced organics in the membrane distillation effluent.
- Coupled oxidation and membrane distillation reduced the toxicity of the final effluent.
- Traditional Fenton pre-treatment provided the best effluent in terms of toxicity.
- Modified Fenton nearly degraded all target contaminants in hypersaline solutions.

GRAPHICAL ABSTRACT



1. Introduction

Despite the current transition to more sustainable sources of energy, oil and gas extraction still plays a significant role in the energy sector and wastewater treatment is quickly emerging as one of the most significant challenges of this industry. Indeed, the so-called produced water (PW) is the largest waste stream generated in oil and gas extraction activities (Ahmadun et al. 2009). Considering both onshore and offshore sites, the global PW production has increased from around 150 million to around 300 million barrels per day from 1990 to 2015 (Ahmadun et al. 2009; Liu et al. 2021). The average water cut, namely, the amount of water volume produced per oil volume, is roughly 3:1 (McCormack et al. 2001; Ahmadun et al. 2009; Jimenez et al. 2018; Liu et al. 2021). As oilfields age during the current energy transition, the water cut will also increase, together with wastewater treatment difficulties (Igunnu and Chen 2014). PW is a highly complex matrix, rich in organic and inorganic compounds, with widely diverse composition as a function of geological formation, age of the oilfield, and type of hydrocarbon product being produced (Ahmadun et al. 2009; Estrada and Bhamidimarri 2016). However, the major compounds are typically dispersed oils, dissolved organics (e.g., phenols, benzene, toluene, xylenes), dissolved minerals (e.g., sodium chloride, calcium and magnesium salts), and natural organic matter (NOM) (Neff et al. 1992; Ahmadun et al. 2009; Estrada and Bhamidimarri 2016; Jimenez et al. 2018; Al-Ghouti et al. 2019; Kabyl et al. 2020; Coha et al. 2021; Liu et al. 2021).

The oil and gas industry faces increasing pressure to limit its environmental footprint (Mohammad-Pajooh et al. 2018). Expensive treatment trains for a multi-contaminated water, as well as water scarcity and increasing international attention to environmental issues, are the drivers pushing this industry to use water more sustainably, bringing along the concepts of water reuse and safe water discharge. As a result, innovative, environmentally focused, and reliable methods of meeting water treatment demands, capable of operating in this specific application are being developed (Estrada and Bhamidimarri 2016; Mohammad-Pajooh et al. 2018; Liu et al. 2021). These technologies should be versatile to meet the requirements of low cost and compactness, the latter characteristic being especially important in offshore activities (Kabyl et al. 2020; Liu et al. 2021).

One of the target parameters that needs abatement to allow for water reuse or safe discharge is salinity, which presents an average value of 100,000 ppm in PW (Estrada and Bhamidimarri 2016; Coha et al. 2021). Such salt concentration can plug the reinjection well or may be toxic if PW is discharged in the environment without desalination (Kleinitz et al. 2001; Aquiliina 2012; Ariono et al. 2016; Chen et al. 2016; Canedo-Arguelles et al. 2019; Liu et al. 2021). Membrane distillation (MD) is a promising emerging technology, capable to extract high-quality effluents from hypersaline solutions using low-grade energy and with relatively low capital cost, due to the absence of high pressure and high temperature components (Howell 2004; Shaffer et al. 2013; Lin et al. 2014; Chen et al. 2017; Han et al. 2017). In recent studies, MD was successfully tested on hypersaline PW (Han et al. 2017; Ricceri et al. 2019). However, since the MD membranes are highly hydrophobic (PTFE and PVDF membranes are generally used), this process may present important practical limitations in the presence of a large and broad content of organic compounds, such as for typical PW (Estrada and Bhamidimarri 2016; Gonzalez et al. 2017). Organics may either induce wetting phenomena or freely pass through the hydrophobic membrane and end up in the final effluent (Franken et al. 1987; Kargbo et al. 2010; Chen et al. 2017; Wang et al. 2018). Wetting phenomena in MD occur when the transmembrane pressure (ΔP) exceeds the liquid entry pressure (LEP), according to eq. (1), thus allowing the contaminated feed water to pass undisturbed through the porous membrane (Franken et al. 1987; Ricceri et al. 2019; Horseman et al. 2021).

$$\Delta P \geq LEP \quad (1)$$

LEP is defined according to eq. (2):

$$LEP = -\frac{2B\gamma cos\theta}{r} \qquad (2)$$

where γ is the feed water surface tension, θ is the intrinsic contact angle between the feed water and the solid membrane material, r is the equivalent pore radius, and B is a geometric factor accounting for the noncylindrical nature of the membrane pore geometry (B = 1 for perfectly cylindrical pores). A low surface tension γ reduces also cosθ, thus facilitating membrane pore wetting. The degradation of toxic organic compounds in the feed solution both increases its surface tension and thwart their interaction with the hydrophobic membrane, potentially allowing for a more efficient MD process and a more effective management of the PW.

The list of available technologies and processes counts a plethora of options to remove or partially degrade organic compounds (Adewumi et al. 1992; Ahmadun et al. 2009; Estrada and Bhamidimarri 2016; Chang et al. 2019; Chang et al. 2019; Shang et al. 2019; Liu et al. 2021; Tang et al. 2021). Activated carbon adsorption and sand filtration are low-cost treatment processes; however, they produce harmful waste since they do not degrade the toxic organic compounds. Biological treatment is not effective toward biorecalcitrant organic compounds, such as benzene, toluene, xylenes (BTX), and requires large plants with long retention times, hence not available for offshore platforms (Ayed et al. 2017). Electrochemical, photocatalytic, and ozone-based oxidations are growing rapidly, but they are still currently associated with high capital costs and with difficulties in practical implementation (Dalmacija et al. 1996; Bessa et al. 2001; Ma and Wang 2006; Ahmadun et al. 2009; Shokrollahzadeh et al. 2012; Ricceri et al. 2019; Coha et al. 2021). Among advanced oxidation processes (AOPs), the Fenton reaction involves the use of iron sulfate and hydrogen peroxide to generate highly reactive hydroxyl radicals able to oxidize almost all the organic compounds (Haber et al. 1934; Miklos et al. 2018; Coha et al. 2021). The main reaction is as follows:

$$Fe(II) + H_2O_2 \rightarrow Fe(III) + {}^{\bullet}OH + OH^{-} \quad (1)$$

The Fenton process is a promising candidate to treat PW both onshore and offshore since it is versatile, characterized by high kinetics also at room temperature and capable to remove organics from a multi-contaminated matrix. This method has some limitations, mainly the need for acidic pH to avoid iron hydroxide precipitation, and the production of sludge once neutral pH is restored (Diya'uddeen et al. 2012). A modified Fenton process encompassing the addition of an iron ligand helps overcoming these precise challenges (Chahbane et al. 2007; Farinelli et al. 2019; Messele et al. 2019; Farinelli et al. 2020). However, the literature lacks reports about the application of Fenton processes carried out in presence of iron ligands to treat PW.

The first objective of this work is to evaluate a coupled system including Fenton (or modified Fenton) pre-oxidation and MD to desalinate PW and to allow for an easy management of the final effluent. This sequence is applied to treat a synthetic PW that mimics the effluent from primary treatment, which typically includes de-oiling and flotation or sedimentation. A thermal Fenton reaction is first applied as a potential PW oxidation step and as a pre-treatment for MD desalination. The study gives insight into the relationship between the content of organics and the performance of the membrane distillation step by comparing a raw feed stream with the feed subject to Fenton oxidation. Furthermore, the performance of traditional Fenton is compared with that of modified Fenton systems. To this purpose, non-toxic and biodegradable organic ligands, namely, citrate and EDDS, are added in PW at unadjusted pH to assess the ability of iron-ligand complexes to act as effective oxidation catalysts (Van Devivere et al. 2001; Tandy et al. 2006; Chen et al. 2019). The safety of the final desalinated effluent from the coupled system is then fully evaluated through acute toxicity measurements.

2. Materials and Methods

2.1. Chemicals, membrane, and produced water preparation

All the organic contaminants, the iron ligands, i.e., sodium citrate and EDDS, ferrous sulfate ($FeSO_4$), hydrogen peroxide (30% w/w), HCl, and NaOH, were purchased from Sigma-Aldrich (Milan, Italy). Sodium chloride, sodium sulfate, and sodium bicarbonate were acquired from Carlo Erba (Milan, Italy). All the solutions needed for the acute toxicity analysis, namely, the reconstitution, the diluent, and the osmotic solutions were purchased from Modern Water (London, UK). The freeze-dried *Vibrio fischeri* culture was purchased from Ecotox LDS (Cornaredo (MI), Italy). Type I ultrapure water was used for the experiments. A commercially available polytetrafluoroethylene (PTFE) membrane (Aquastill, Sittard, Netherlands) was deployed in MD filtration tests.

The composition of the synthetic PW was based on published values of real wastewaters and is listed in **Table 1**, together with the resulting total organic carbon (TOC) and total dissolved solids (TDS) values (Olsson et al. 2013; Estrada and Bhamidimarri 2016; Coha et al. 2021). Humic acids and a liquid petroleum jelly consisting of paraffins were used as representative compounds for natural dissolved organic matter and oil & grease, respectively (Lester et al. 2015). Xylenes, benzene, toluene, and methyl *tert*-butyl ether (MTBE) were selected as representative volatile organic compounds (VOCs) (Coha et al. 2021). Cyclohexane was added as representative of the $<C_{10}$ hydrocarbon fraction (Lester et al. 2015; Estrada and Bhamidimarri 2016). Phenol was added as representative substance for the common phenols content in PW. The TDS included sodium, calcium, and magnesium

chlorides. All the components were added into water and the matrix was sonicated at room temperature for 1 h to enhance solubilization and mixing.

Table 1 Composition of the synthetic produced water, compared with the reference real streams. The matrix includes representative pollutants to mimic typical TOC and TDS values.

		Synthetic produced water		Real produced water
Parameter	**Component**	**Concentration (ppm)**	**Equivalent TOC (ppm)**	**Concentration (ppm)**
TOC	Paraffins	200	Not dissolved	
	Humic acids	200	60	
	Cyclohexane	2	1.8	
	Phenol	2.5	1.9	
	Xylenes	1	1	
	Benzene	12	11.3	
	Toluene	4	3.4	
	MTBE	260	178	
	TOT	681.5	257.4	Maximum ~500
TDS	Sodium chloride	100,000		Typically, 35,000 – 240,000
	Calcium chloride	2,500		
	Magnesium chloride	4,000		
	TOT	106,500		Average ~100,000
pH	5.5			

2.2. Oxidation conditions

All the oxidation reactions were performed at room temperature under gentle stirring for a total duration of 1 h, using different ratios of hydrogen peroxide and catalyst, intended as iron(II) in the case of the traditional Fenton process and as the complex ligand-iron(II) in the case of modified Fenton. To promote organics oxidation, three additions of hydrogen peroxide (0, 20, 40 min) were carried out, each one of a 1/3 aliquot of the desired total amount. The dosages of iron sulfate and hydrogen peroxide are listed in **Table 2** for the traditional Fenton system; in these cases, the pH of the synthetic PW was adjusted to ~3 (HCl). At the end of the reaction, the pH was increased to ~10 by addition of NaOH and this step caused the precipitation of $Fe(OH)_3$. After the sedimentation of the precipitate at 4 °C overnight, the supernatant was collected and used for analysis and as a feed matrix for the following MD filtration tests.

Table 2 Traditional Fenton dosages in tests operated at different oxidation conditions.

Entry	$FeSO_4$ (mM)	H_2O_2 (mM)
MQ H_2O	-	-
Produced water	-	-
Ox 1	0.5	5
Ox 2	5	50
Ox 3	5	25
Ox 4	1	25
Ox 5	1	50
Ox 6	0.1	5
Ox 7	5	100

To perform the modified Fenton oxidations, the iron-ligand complexes, namely, Fe-EDDS and Fe-citrate were spiked in the synthetic PW from a stock solution of 0.1 M of iron(II) and 0.1 M of individual ligand. The pH was not adjusted and was equivalent to ~4 upon addition of Fe-EDDS and to ~5 upon addition of Fe-citrate. No precipitate formation was observed in these systems. The resulting samples were used for analysis and as feed for the following MD filtration tests without further processing.

2.3. Membrane distillation tests

The MD tests were performed in direct contact configuration using a lab-scale batch system (Ricceri et al. 2019). The feed and distillate streams were circulated counter-currently on their respective sides of the membrane. A constant crossflow rate of 1.66 L/min (0.278 m/s crossflow velocity) was maintained during the tests. The housing cell comprised a 250-mm long, 50-mm wide, and 2-mm deep rectangular channel for a total active membrane area of 125 cm^2. The flux across the membrane was computed by recording the change in weight of the distillate tank in time through a computer-interfaced balance. Initial volumes of ~1.9 L and 1 L were used for the feed and distillate streams, respectively, unless otherwise stated. Water was used in the distillate side, with specific conductivity always below 20 μS/cm. The specific conductivity in the distillate tank was measured continuously during each test by a conductivity meter (COND 7+, XS Instruments, Italy). The temperature of the feed and distillate tanks were maintained constant throughout the experiments, at respective values of 50 ± 2 and 25 ± 1 °C, by means of a thermostatic water bath and a chiller.

2.4. Analytical methods

The TOC of the matrices was measured using a Shimadzu TOC-L analyzer (catalytic oxidation on Pt at 680 °C). The calibration was performed using standards of potassium phthalate, $NaHCO_3$/Na_2CO_3. The headspace, solid phase microextraction technique (HS-SPME) was chosen as extraction method before carrying out the GC-MS analysis. Following each reaction experiment, the vials were left in a thermostatic bath at 50 °C for 10 min to promote the transfer of all the relevant compounds into the gas-phase headspace. Then, a SPME fiber (df 75 μm, fiber assembly carboxen/polydimethylsiloxane, Supelco) was inserted through the septum of the cap and was left in the headspace for 10 min, before withdrawing it for the subsequent GC-MS analysis. Samples were analyzed on an Agilent 6890 GC system coupled with an Agilent 5973 mass selective detector (MSD). For the chromatographic separation, a Zebron-5MS capillary column (30 m·× 0.25 mm·× 0.25 μm) was used. The injection port temperature was 270 °C, and the oven temperature program was set as follows: 35°C for 5 min, followed by an increase to 260 °C at a rate of 15 °C/min (total run time 25.33 min). Helium was used as carrier gas at a constant flow of 1 mL/min, and the injector was held in splitless mode. The interface temperature was 270 °C and the ionization energy was 70 eV. The molecular structures of the by-products were identified by means of mass spectrum library.

The determination of the residual iron in solution was evaluated by a spectrophotometric procedure adapted from previous literature (Harvey et al. 1955; Goncalves et al. 2020). The total iron was determined by reducing the Fe(III) to Fe(II) with ascorbic acid (4×10^{-4} M) and complexing the Fe(II) with o-phenanthroline (4×10^{-3} M) under acidic conditions (buffer pH = 3: H_3PO_4 1 mM, NaH_2PO_4 3 mM). The Fe(II) was determined without performing the reduction step, and Fe(III) was obtained as the difference between total iron and Fe(II). The calibration was obtained using a commercial standard solution of Fe(III) (1000 mg^{Fe}/L, Sigma-Aldrich). The spectrophotometric analyses were performed using a Varian CARY 100 Scan double-beam UV–vis spectrophotometer, using quartz cuvettes with 10 mm path length and working at a wavelength of 510 nm.

2.5. Toxicity analysis

All the toxicity experiments were performed with a Microtox Model 500 analyzer (Milan, Italy). The analysis was performed by evaluating the bioluminescence inhibition assay using the marine bacterium *Vibrio fischeri*. Samples were tested in a medium containing 2% sodium chloride, and the luminescence was recorded after 5, 15, and 30 min of incubation at 15 °C. The luminescence inhibition percentage was determined by comparison with a non-toxic control. The toxicity curves and the values of EC_{50} were obtained from the software (MicrotoxOmni). The pH of all the samples was adjusted in the range 6-8 before the analysis. The method used for the toxicity analysis is the method APAT-IRSA 8030 (APAT 2003). All the samples obtained at the end of the oxidation experiments were quenched with catalase in order to avoid the detrimental effect of the residual hydrogen peroxide on the toxicity measurements; see Figure S1 of the Supplementary Material (SM). Moreover, the samples after the oxidation experiments were quantified for residual iron content and EDDS was added in EDDS:Fe molar ratio of 1:1, to prevent the toxic effect of the residual iron in solution (see Figure S2 in SM).

3. Results and Discussion

3.1. Efficacy of thermal Fenton oxidation on organics removal

Table 3 and **Figure 1a** summarize the results of the Fenton oxidations in terms of TOC removal and surface tension (ST) values, as a function of the relative addition of iron(II) and H_2O_2. The highest TOC removal rates were obtained with Fe/H_2O_2 ratios between 0.02 and 0.2. At low iron dosage (≤ 0.5 mM, Ox1, Ox6), insufficient catalyst was available in solution, while at high reagent concentrations (Ox7), the reaction was possibly self-inhibited. Previous studies highlighted that a Fe/H_2O_2 molar ratio around 0.02 should avoid self-inhibition reactions while providing high efficiency of oxidation (Voelker and Sulzberger 1996; De Laat and Gallard 1999). Oxidation 3 (Ox3) reached the highest percentage of TOC removal, coinciding with the largest dosage of $FeSO_4$ (5 mM) and a Fe/H_2O_2 ratio of 0.2. However, Ox4 also achieved a high percentage of TOC removal, but with a substantially lower amount of iron(II), namely, 1 mM, corresponding to a Fe/H_2O_2 ratio of 0.04. These conditions also allowed reaching the highest value of ST (69 ± 3.1 dyn/cm), close to the ST measured for pure water (72 ± 1.8 dyn/cm) and substantially higher than that of the PW (50.8 ± 2.7 dyn/cm). Ox4 was thus identified as the most promising oxidation and further tests were conducted using the matrix oxidized under this condition.

Table 3 Resulting TOC removal rates, and surface tension values of the oxidized matrix in tests operated at different oxidation conditions.

Entry	TOC removal (%)	Surface tension (dyn/cm)
MQ H_2O	-	72 ± 1.8
Produced water	-	50.8 ± 2.7
Ox 1	47.6 ± 0.5	67.8 ± 1.6
Ox 2	55.3 ± 1.3	63.5 ± 1.8
Ox 3	58.5 ± 2.2	60.1 ± 2.3
Ox 4	52.2 ± 2.4	69.5 ± 3.1
Ox 5	50.9 ± 1.7	54.2 ± 2.1
Ox 6	34.7 ± 2.1	68.6 ± 2.0
Ox 7	33.3 ± 2.3	59.3 ± 1.7

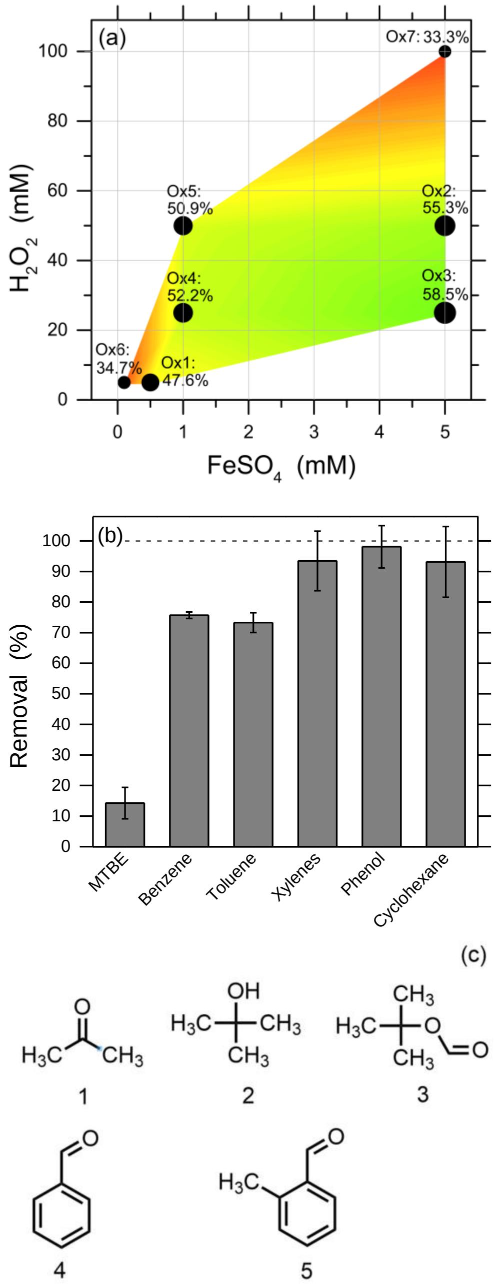


Figure 1. (a) Graphical representation of the relationship between TOC removal and reagent dosage. The green color represents higher values of TOC removal. (b) Percentage of degradation of the parent organic contaminants in the synthetic produced water after Fenton reaction (Ox4, 60 min). The percentage of degradation was obtained by computing the target peaks area detected by GC-MS. (c) Chemical structures of the residual by-products preconcentrated onto the fiber during the SPME extraction and detected by GC-MS at the end of the Fenton reaction (Ox4, 60 min).

The solution obtained after Fenton oxidation Ox4 was further characterized through GC-MS analysis. Figure S3 in the SM presents the chromatograms and the profile of target substance degradation observed after 20, 40, and 60 min of oxidation. **Figure 1b** summarizes the degradation efficiency after 60 min toward various organic contaminants. A near total degradation of phenol, xylenes, and cyclohexane was observed. The oxidation process degraded benzene and toluene with a yield around 75%. However, only a portion of MTBE was degraded, and this result may also explain the residual TOC after Ox4 (see **Table 3**). Indeed, MTBE contributes to a large part of the total TOC of the synthetic PW (see **Table 1**). The major challenge for the high efficacy of the Fenton reaction in a hypersaline PW is arguably the ability of humic acids and chloride to scavenge the hydroxyl radical (Kiwi et al. 2000; Goldstone et al. 2002), although humic acids may also favor the Fe(III)-Fe(II) recycling (Vione et al. 2004). Nevertheless, the observed TOC removal rates and the yield of degradation of target parent substances suggest the high potential of the Fenton reaction to reach suitable levels of decontamination, also in the presence of a significant amount of scavengers.

The GC-MS also allowed detection of the main volatile by-products of the Fenton process (**Figure 1c**). Based on the molecular structure, the compounds labeled as 1, 2 and 3 in Figure S3 reasonably derived from MTBE, while 4 and 5 likely derived from toluene and o-xylene, respectively. Note that the identified by-products were more hydrophilic than the starting contaminants, thus explaining the observed increase in ST. The relatively high percentage of TOC removal together with the formation of more hydrophilic by-products are promising conditions to obtain an improved feed solution of an MD step.

3.2. Evaluation of thermal Fenton oxidation as a pre-treatment for membrane distillation

Organic compounds in the feed matrix may affect the MD step by fouling and by wetting the membrane, hence lowering the desalination efficiency, or by freely passing through the hydrophobic membrane material (PTFE) (Vesterkvist et al. 2012; Pasternak and Kolwzan 2013). Wetting is theoretically described by eq. 1 and experimentally observed with an increase of conductivity in the distillate stream of the MD step (Donaldson et al. 1969; Rezaei et al. 2017). The water flux values presented in **Figure 2a** suggest that the Fenton pre-treatment did not have an effect on the productivity or on the achievable recovery of the MD step under laboratory filtration conditions: the recovery was roughly 75%, upon which the water flux went to zero due to scaling (namely, the deposition of crystals on the membrane or within its pores) and pore blockage. Note that similar productivity was also observed when synthetic PW matrices containing solely salts or solely organics were used as the feed solutions. In the latter case the flux did not go to zero, due to the absence of salt precipitation, but it steadily decreased during the test possibly due to fouling phenomena. Increased conductivity of the distillate solution was measured beginning roughly at 50% recovery for the various feed streams, except that containing only organic compounds; see Figure S4 of the SM. This result suggests that in our study salt passage and possibly wetting were mostly imputable to high salt concentrations, with organics only associated with fouling mechanisms. Salts can crystallize within the pores of the membrane, enlarging them, hence lowering the LEP.

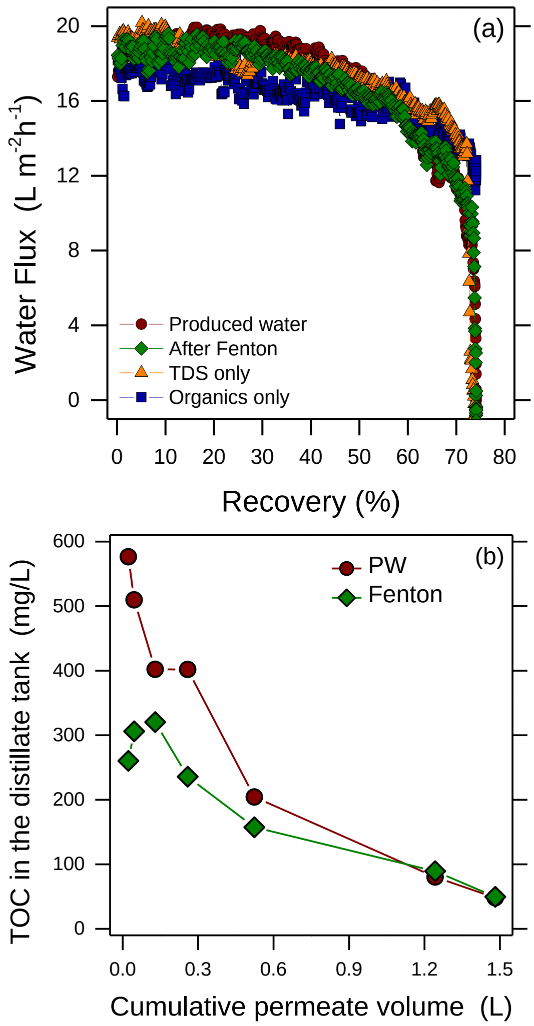


Figure 2 (a) Results of MD filtration tests with different feed solutions: (red circles) synthetic produced water, (blue squares) only the organic content of the synthetic produced water, (orange triangles) only the TDS content of the synthetic produced water, and (green diamonds) the resulting feed after the thermal Fenton oxidation. (b) TOC concentration in the distillate tank (initial volume 1 L) as a function of cumulative permeated volume; the lines connecting the data points are only intended as guides for the eye.

The only organic compounds in the synthetic PW which may induce wetting were humic acids (HA) and the water-miscible compounds (WMC), namely, BTX, MTBE, phenol, and cyclohexane. HA are amphiphilic and may partly act as surfactants; however, not presenting a clear separation between the hydrophobic and hydrophilic portion of the molecule, they can virtually maintain a repulsive behavior for liquid water after the interaction with the hydrophobic membrane, thus resulting in fouling, but not necessarily in wetting (Klavins and Purmalis 2010; Wang et al. 2018; Horseman et al. 2021). On the other hand, WMC may induce wetting by lowering the ST of the solution. However, since no wetting from organic compounds was detected in this study, it is reasonable to assume that the ST threshold needed to observe wetting under the condition of this study was lower than the ST value of the synthetic PW (50.8 ± 2.7 dyn/cm). The fact that organic fouling did not cause wetting may be rationalized with the short duration of the lab experiments, which were run for approximately 8 h before the observed drop in water flux due to scaling. The slow kinetics of fouling phenomena in such a system may require longer filtration times to show wetting effects and should become important at real scale during operation. Note that paraffins form a different phase, hence they cannot lower the ST of the solution or create water bridges within the membrane pores, but only freely pass through the PTFE membrane by virtue of their hydrophobic nature.

While the Fenton pre-treatment did not provide specific advantages in terms of productivity, which was governed by salt concentration and partly affected by fouling, or of prevention of wetting, which was not observed even for the use of untreated PW as feed stream, oxidation had beneficial effect in terms of MD effluent quality and toxicity. The results in **Figure 2b** suggest a clear reduction of the TOC in the distillate when desalinating the feed matrix subject to Fenton reaction; see Figure S5 of the SM for the chromatograms of the final effluent treated only in MD and by the coupled Fenton-MD system. As expected, the MD process did not separate water from volatile WMC or non-aqueous oils. The first data points in **Figure 2b** showed a high TOC passage, justifiable considering an instantaneous passage of a fraction of the organic content, specifically, paraffins and WMC. Subsequently, the TOC in the distillate tank decreased steadily by dilution with the nearly pure water vapor permeating the membrane. The lower amount of TOC measured upon oxidation of the feed stream with Fenton is imputable to both the mineralization of a fraction of toxic compounds (~52% of mineralization, **Table 3**) and the transformation of organic substances to more hydrophilic compounds, which are less prone to pass through the hydrophobic membrane. Fenton oxidation may also provide beneficial effects in terms of MD performance at real scale by thwarting fouling phenomena that would occur at longer time scales, but this effect could not be observed in this study.

3.3. Effect of the coupled system on the toxicity of the final effluent

A general index of the safety of an effluent is its toxicity. Toxicity is also a legislated parameter, allowing or denying the discharge of an effluent in the sewage system. According to the Italian regulations (D.Lgs. 152/2006), the acute toxicity limit to discharge an effluent in the sewage system is 80% of the inhibition of the target microorganism (in this case, *Vibrio fisheri*). The synthetic PW of this study presented an acute toxicity around 100% (Figure S6a of the SM), a value also expected for most of the real PW due to the wide variety and large concentrations of contaminants typically present. Both organics and concentrated salts may present large toxic effects, hence they both require a specific treatment. **Figure 3** presents the residual acute toxicity of the effluent treated with only MD and with the coupled Fenton-MD system expressed in term of dilution factor of the original samples. The EC_{50} value was used as a comparative parameter of the quality of different effluents, and it is defined as the half maximal effective concentration, namely, the concentration required to obtain 50% of microorganism inhibition. This parameter increased significantly (from a dilution factor of 0.094 ± 0.009 to 0.25 ± 0.03) when the effluent was oxidized and then desalinated, compared to a stream that was not pre-treated, i.e., the coupled system gave lower toxicity. However, when tested as is, the residual toxicity of the effluent was still high and over the limit of 80% after 30 min of contact time with the bacteria.

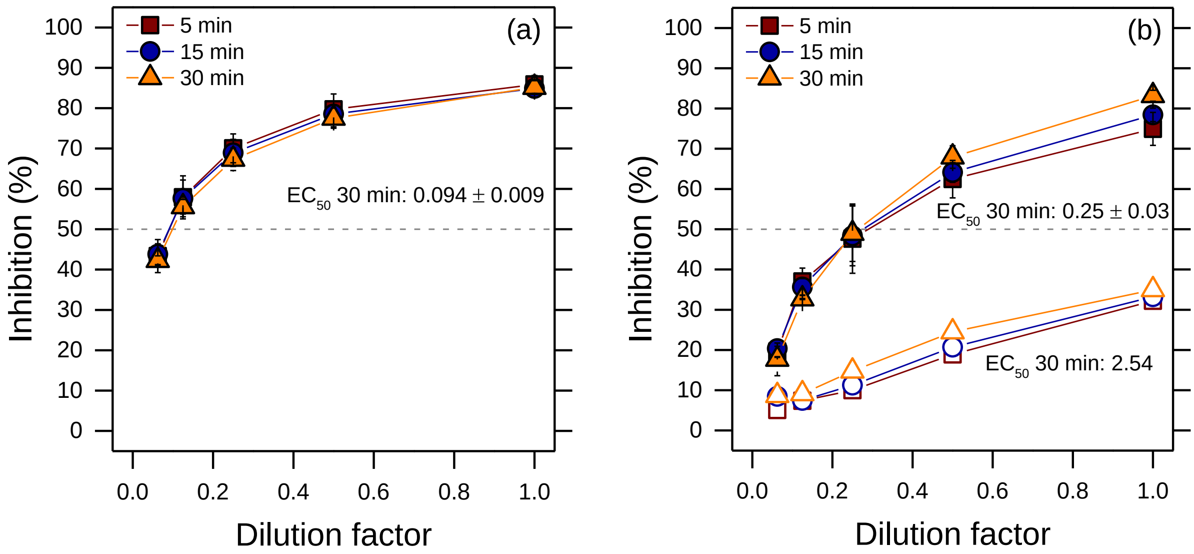


Figure 3. Residual toxicity of the effluent expresses in term of dilution factor of the original sample (a) after MD treatment only, and (b) upon treatment by the coupled Fenton-MD system (solid data points) with and (empty data points) without Fe sequestration. The toxicity was measured after 5, 15, and 30 minutes of contact (in red, blue, and orange, respectively) with the *Vibrio fischeri* culture. The dash line indicates the point where 50% of acute toxicity is reached.

To understand the relative contribution to toxicity of the different contaminants, toxicity experiments were carried out with individual components (Figures S6 and S7 of the SM). Low toxicity was associated with HA and paraffins, while higher toxic effects were related to parent WMC, which however were degraded effectively by the Fenton oxidation. Calcium and magnesium chloride also showed negligible toxicity, while sodium chloride showed some toxicity only at concentrations >50 g/L, that is, far above the concentration measured after the MD desalination. On the other hand, iron (II) sulfate showed a significant toxicity: residual iron may thus be responsible for the toxicity observed for the effluent from Fenton and MD treatments. Indeed, by addition of EDDS in molar ratio 1:1 to the residual iron (0.26 mM), the acute toxicity of iron was shut down (see Figure S2 and S7 in SM for the toxicity of Fe-EDDS and iron, respectively) and that of the effluent markedly decreased (from ~80% to ~40%), accompanied with a substantial increase in EC_{50} (from a dilution factor of 0.25 ± 0.03 to ~2.5). The remaining toxicity after this post-treatment step may be reasonably attributed to the residual WMC and to the by-products of Fenton oxidation. Note that in this study EDDS was added to mask the toxic behavior of the residual iron, which confirms the fact that residual metal concentration causes toxicity in the effluent. However, different strategies to remove the residual iron may be implemented in real plants, for example, its precipitation under basic pH. Cleaner and more novel steps may involve enhanced ion exchange resins and the use of adsorbents, such as magnetic nanoparticles (Khatri et al. 2017).

3.4. Comparison between traditional Fenton and Fenton process in the presence of iron ligands

Iron ligands keep iron in solution without the need for the pH adjustment to 3 and limit the production of sludge, thus potentially allowing for a more streamlined operation compared to the traditional Fenton process. Citrate and EDDS were chosen as non-toxic (Figure S2 of the SM) ligands and the Fe-citrate and Fe-EDDS systems were applied as catalysts (Zhang et al. 2016). The optimized condition in terms of Fe-ligand to H_2O_2 molar ratio corresponded to the dosages relative to Ox7 in **Table 2**; each ligand was dosed equimolarly with iron. The results summarized in **Figure 4a** suggest higher degradation efficiency of the modified Fenton systems toward WMC with respect to the traditional thermal Fenton. Specifically, the modified Fenton processes achieved near complete degradation of all WMC, including MTBE that was instead not removed by the classic Fenton reaction; see also the chromatograms and percentage of substrates removal at different oxidation times in Figures S8, S9, and S10 (SM).

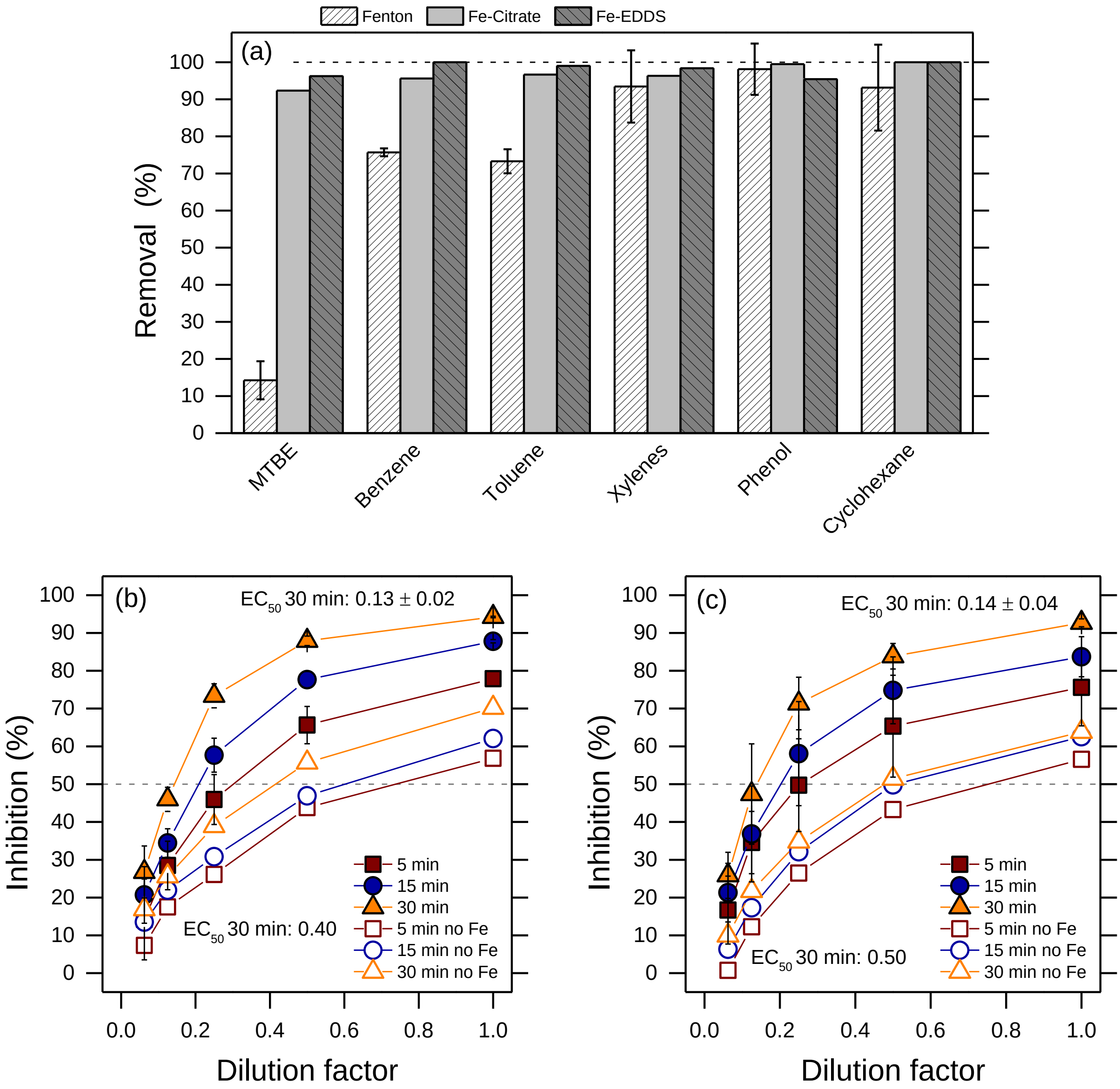


Figure 4 (a) Comparison of the organics removal rate by traditional Fenton and modified Fenton reactions with citrate and EDDS as iron ligands. Residual toxicity of the final effluent treated by the coupled system comprising modified-Fenton and MD using (b) Fe-citrate and (c) Fe-EDDS as catalyst. The open symbols are related to the effluent upon iron sequestration by EDDS. The toxicity was measured after 5, 15, and 30 minutes of contact with the *Vibrio fischeri* culture. The dash horizontal line indicates the point where 50% of acute toxicity is reached; the lines connecting the data points are only intended as guides for the eye.

Despite the higher percentage of degradation of the target contaminants, the modified Fenton process did not show further beneficial effect on the MD process in terms of productivity and effluent quality compared to traditional Fenton; see Figure S11 of the SM. With regard to EC_{50}, the quality of the effluent treated with the coupled system including modified Fenton and MD clearly increased compared to the PW treated only with MD, specifically, from a dilution factor of 0.094 ± 0.009 to 0.13 ± 0.02 and to 0.14 ± 0.04 in the case of Fe-citrate and Fe-EDDS, respectively (see **Figure 4b and c**). However, the EC_{50} was lower compared with the residual toxicity observed in the system that included the traditional Fenton oxidation (0.25 ± 0.03), possibly due to the formation of more toxic by-products (Zhang et al. 2016). When the contribution to toxicity of the residual iron (residual iron was 0.27 and 1.30 mM for Fe-citrate and Fe-EDDS, respectively) was prevented by EDDS addition, the acute toxicity of the effluent clearly decreased (from ~90% to ~70% in both cases) and the EC_{50} further increased (to 0.4 and 0.5 for Fe-citrate and Fe-EDDS, respectively). At the end of the process, the effluent treated with the Fe-EDDS-based Fenton system presented a slightly better quality in terms of toxicity than that treated with the Fe-citrate system, consistently with the slightly higher degradation efficiency of the former compared to the latter.

4. Concluding remarks, challenges, and implications

This work evaluated the impact of traditional and modified Fenton oxidations for the abatement of highly toxic organic contaminants and as pre-treatment options for the subsequent desalination of hypersaline produced waters by membrane distillation. Fe-citrate and Fe-EDDS were used as inexpensive, easy to handle, environmentally friendly and biodegradable systems in the modified Fenton processes. All the oxidative processes provided relatively high degradation efficiency toward target contaminants also in presence of typical scavengers of the Fenton reaction, namely, chloride and humic acids. The observable beneficial effects of an oxidative pre-treatment were not evident in terms of MD productivity, fouling, or wetting, but directly translated into lower permeation of organics during distillation and in a significantly lower toxicity of the desalinated effluent. Specifically, the EC_{50} and the acute toxicity (inhibition % of target organisms) were used as indexes for the evaluation of the quality of the final effluent. The target values of acute toxicity should be below the regulated limit of 80%. **Figure 5** offers a final evaluation of the toxicity parameters from the various treatments. The traditional Fenton coupled with the MD desalination was the best in terms of toxicity. However, the modified Fenton-MD coupled systems were able to overcome some of the practical limitations of the traditional Fenton while still providing an effluent with suitable quality for safe discharge as sewage (toxicity <80%). The modified Fenton oxidation may be more advisable for applications whereby easier operational tasks and lower sludge production are important, such as offshore.

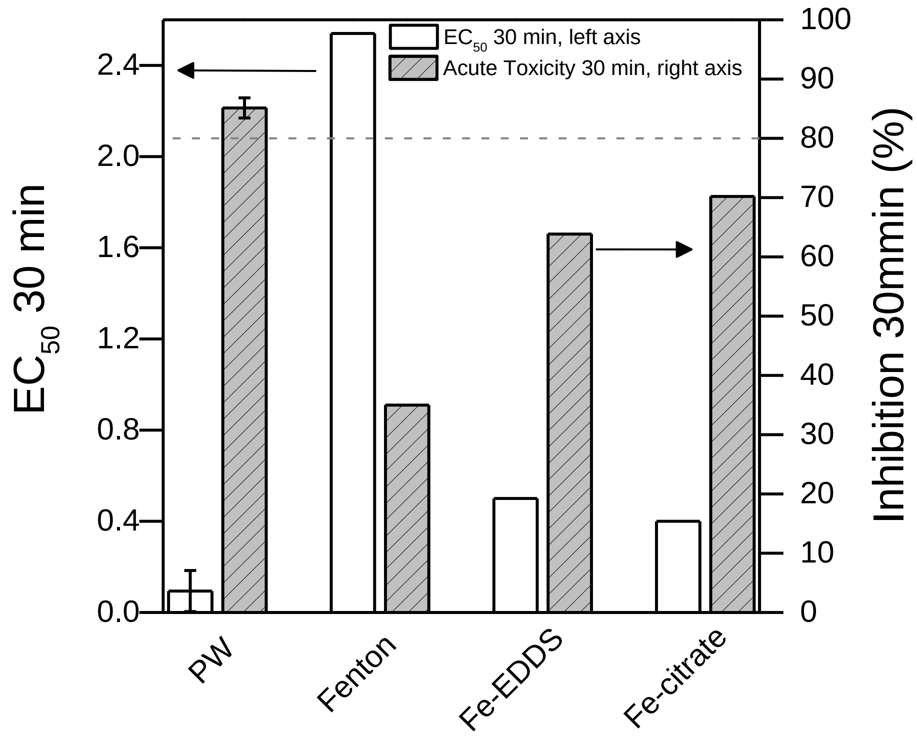


Figure 5 Summary of the residual toxicity and EC_{50} values of the various effluents treated with both MD and oxidation processes after 30 minutes of contact with the *Vibrio fischeri* culture. The dash line is relative to the value of 80% of acute toxicity, namely, the regulated legislative limit for a safe discharge in the sewage system in Italy.

In conclusion, the coupled oxidation-MD systems to treat PW allow a less toxic effluent compared to the initial PW toxicity. All the final effluents obtained in this study may be safely discharged in the sewage system and treated within the civil wastewater treatment trains, according to the Italian legislation. The oxidation processes are promising for PW treatments since they are able to degrade the toxic initial target contaminants almost completely. Moreover, the modified Fenton process is able to effectively treat PW while overcoming the practical limitations of traditional Fenton (sludge production and acidic pH). The Fenton processes add iron in the effluent environment, this metal being associated with intrinsic toxicity; thus, the toxicity associated with the residual iron needs to be properly addressed and managed in real plants. A wide range of options are available to remove iron and the best-fitting one should be selected case-by-case. Moreover, the oxidations struggle in achieving the complete mineralization of all the organics in PW, thus some potentially toxic by-products may be formed. Therefore, an accurate monitoring of the by-products may be necessary, possibly also enforcing some control on the reaction pathway, to evaluate in each case the possibility to safely discharge the final effluent to a civil wastewater treatment plant and in case to specifically target the most troublesome by-products in a tertiary treatment step.

CRediT authorship contribution statement

Giulio Farinelli: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Visualization, Writing - original draft. **Marco Coha**: Data Curation, Formal analysis, Investigation, Methodology, Visualization, Writing - review & editing. **Marco Minella**: Data curation, Validation, Methodology, Writing - review & editing. **Debora Fabbri**: Resources, Supervision, Writing - review & editing. **Marco Pazzi**: Formal analysis, Methodology. **Davide Vione**: Resources, Supervision, Writing - review & editing. **Alberto Tiraferri**: Funding acquisition, Project administration, Resources, Supervision, Visualization, Writing - review & editing.

Declaration of Competing Interest

The authors declare no competing financial interest.

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Appendix A. Supplementary data.

Supplementary material related to this article can be found, in the online version.

References

Adewumi, M. A., Erb, J. E., Watson, R. W. (1992). Initial Design Considerations for a Cost-Effective Treatment of Stripper Oil-Well Produced Water. Produced Water. R. J. P. and E. F. R. Botsom, MA, Springer. **46:** 511-522.

Ahmadun, F. R., Pendashteh, A., Abdullah, L. C., Biak, D. R. A., Madaeni, S. S., Abidin, Z. Z., 2009. Review of technologies for oil and gas produced water treatment. J. Hazard. Mater. 170, 530-551. https://doi.org/10.1016/j.jhazmat.2009.05.044

Al-Ghouti, M. A., Al-Kaabi, M. A., Ashfaq, M. Y., Da'na, D. A., 2019. Produced water characteristics, treatment and reuse: A review. J. Water Process Eng. 28, 222-239. https://doi.org/10.1016/j.jwpe.2019.02.001

APAT, I., CNR (2003). Metodi Ecotossicologici. Manuali e linee guida 29/2003 - Serie 8000.

Aquiliina, P. (2012). Impairment of Gas Well Productivity by Salt Plugging: A Review of Mechanisms, Modeling, Monitoring Methods, and Remediation Techniques. SPE Annual Technical Conference and Exhibition. San Antonio, Texas, USA.

Ariono, D., Purwasasmita, M., Wenten, I. G., 2016. Brine Effluents: Characteristics, Environmental Impacts, and Their Handling. J. Eng. Technol. Sci. 48, 367-387. https://doi.org/10.5614/j.eng.technol.sci.2016.48.4.1

Ayed, L., Asses, N., Chammem, N., Ben Othman, N., Hamdi, M., 2017. Advanced oxidation process and biological treatments for table olive processing wastewaters: constraints and a novel approach to integrated recycling process: a review. Biodegradation. 28, 125-138. https://doi.org/10.1007/s10532-017-9782-0

Bessa, E., Sant Anna, G. L., Dezotti, M., 2001. Photocatalytic/H2O2 treatment of oil field produced waters. Appl. Catal. B-Environ. 29, 125-134. https://doi.org/10.1016/S0926-3373(00)00199-5

Canedo-Arguelles, M., Kefford, B., Schafer, R., 2019. Salt in freshwaters: causes, effects and prospects - introduction to the theme issue. Philos. T. R. Soc. B. 374, https://doi.org/10.1098/Rstb.2018.0002

Chahbane, N., Popescu, D. L., Mitchell, D. A., Chanda, A., Lenoir, D., Ryabov, A. D., Schramm, K. W., Collins, T. J., 2007. Fe-III-TAML-catalyzed green oxidative degradation of the azo dye Orange II by H2O2 and organic peroxides: products, toxicity, kinetics, and mechanisms. Green Chem. 9, 49-57. https://doi.org/10.1039/b604990g

Chang, H. Q., Li, T., Liu, B. C., Vidic, R. D., Elimelech, M., Crittenden, J. C., 2019. Potential and implemented membrane-based technologies for the treatment and reuse of flowback and produced water from shale gas and oil plays: A review. Desalination. 455, 34-57. https://doi.org/10.1016/j.desal.2019.01.001

Chang, H. Q., Liu, B. C., Wang, H. Z., Zhang, S. Y., Chen, S., Tiraferri, A., Tang, Y. Q., 2019. Evaluating the performance of gravity-driven membrane filtration as desalination pretreatment of shale gas flowback and produced water. J. Membr. Sci. 587, https://doi.org/10.1016/J.Memsci.2019.117187

Chen, L., Wang, D., Long, C., Cui, Z. X., 2019. Effect of biodegradable chelators on induced phytoextraction of uranium- and cadmium-contaminated soil by Zebrina pendula Schnizl. Sci. Rep. 9, https://doi.org/10.1038/S41598-019-56262-9

Chen, W., Zhang, F. F., Hong, J. L., Shi, W. X., Feng, S. T., Tan, X. F., Geng, Y., 2016. Life cycle toxicity assessment on deep-brine well drilling. J. Clean. Prod. 112, 326-332. https://doi.org/10.1016/j.jclepro.2015.07.062

Chen, Y. M. L., Wang, Z. X., Jennings, G. K., Lin, S. H., 2017. Probing Pore Wetting in Membrane Distillation Using Impedance: Early Detection and Mechanism of Surfactant-Induced Wetting. Environ. Sci. Tech. Let. 4, 505-510. https://doi.org/10.1021/acs.estlett.7b00372

Coha, M., Farinelli, G., Tiraferri, A., Minella, M., Vione, D., 2021. Advanced oxidation processes in the removal of organic substances from produced water: Potential, configurations, and research needs. Chem. Eng. J. 414, https://doi.org/10.1016/j.cej.2021.128668

Dalmacija, B., Karlovic, E., Tamas, Z., Miskovic, D., 1996. Purification of high-salinity wastewater by activated sludge process. Water Res. 30, 295-298. https://doi.org/10.1016/0043-1354(95)00170-0

De Laat, J., Gallard, H., 1999. Catalytic decomposition of hydrogen peroxide by Fe(III) in homogeneous aqueous solution: Mechanism and kinetic modeling. Environ. Sci. Technol. 33, 2726-2732. https://doi.org/10.1021/Es981171v

Diya'uddeen, B. H., Aziz, A. R. A., Daud, W. M. A. W., 2012. On the Limitation of Fenton Oxidation Operational Parameters: A Review. Int. J. Chem. React. Eng. 10, https://doi.org/10.1515/1542-6580.R2

Donaldson, E. C., Thomas, R. D., Lorenz, P. B., 1969. Wettability Determination and Its Effect on Recovery Efficiency. Soc. Pet. Eng. J. 9, 13-20. https://doi.org/10.2118/2338-PA

Estrada, J. M., Bhamidimarri, R., 2016. A review of the issues and treatment options for wastewater from shale gas extraction by hydraulic fracturing. Fuel. 182, 292-303. https://doi.org/10.1016/j.fuel.2016.05.051

Farinelli, G., Minella, M., Pazzi, M., Giannakis, S., Pulgarin, C., Vione, D., Tiraferri, A., 2020. Natural iron ligands promote a metal-based oxidation mechanism for the Fenton reaction in water environments. J. Hazard. Mater. 393, https://doi.org/10.1016/j.jhazmat.2020.122413

Farinelli, G., Minella, M., Sordello, F., Vione, D., Tiraferri, A., 2019. Metabisulfite as an Unconventional Reagent for Green Oxidation of Emerging Contaminants Using an Iron-Based Catalyst. ACS Omega. 4, 20732-20741. https://doi.org/10.1021/acsomega.9b03088

Franken, A. C. M., Nolten, J. A. M., Mulder, M. H. V., Bargeman, D., Smolders, C. A., 1987. Wetting Criteria for the Applicability of Membrane Distillation. J. Membr. Sci. 33, 315-328. https://doi.org/10.1016/S0376-7388(00)80288-4

Goldstone, J. V., Pullin, M. J., Bertilsson, S., Voelker, B. M., 2002. Reactions of hydroxyl radical with humic substances: Bleaching, mineralization, and production of bioavailable carbon substrates. Environ. Sci. Technol. 36, 364-372. https://doi.org/10.1021/es0109646

Goncalves, N. P. F., Minella, M., Fabbri, D., Calza, P., Malitesta, C., Mazzotta, E., Prevot, A. B., 2020. Humic acid coated magnetic particles as highly efficient heterogeneous photo-Fenton materials for wastewater treatments. Chem. Eng. J. 390, https://doi.org/10.1016/J.Cej.2020.124619

Gonzalez, D., Amigo, J., Suarez, F., 2017. Membrane distillation: Perspectives for sustainable and improved desalination. Renew. Sust. Energ. Rev. 80, 238-259. https://doi.org/10.1016/j.rser.2017.05.078

Haber, F., Weiss, J., Pope, W. J., 1934. The catalytic decomposition of hydrogen peroxide by iron salts. Proc. R. Soc. Lond. A - Math. Phys. Sci. 147, 332-351. https://doi.org/10.1098/rspa.1934.0221

Han, L., Tan, Y. Z., Netke, T., Fane, A. G., Chew, J. W., 2017. Understanding oily wastewater treatment via membrane distillation. J. Membr. Sci. 539, 284-294. https://doi.org/10.1016/j.memsci.2017.06.012

Harvey, A. E., Smart, J. A., Amis, E. S., 1955. Simultaneous Spectrophotometric Determination of Iron(II) and Total Iron with 1,10-Phenanthroline. Anal. Chem. 27, 26-29. https://doi.org/10.1021/ac60097a009

Horseman, T., Yin, Y., Christie, K. S., Wang, Z., Tong, T., Lin, S., 2021. Wetting, Scaling, and Fouling in Membrane Distillation: State-of-the-Art Insights on Fundamental Mechanisms and Mitigation Strategies. ACS ES&T Eng. 1, 117-140. https://doi.org/10.1021/acsestengg.0c00025

Howell, J. A., 2004. Future of membranes and membrane reactors in green technologies and for water reuse. Desalination. 162, 1-11. https://doi.org/10.1016/S0011-9164(04)00021-9

Igunnu, E. T., Chen, G. Z., 2014. Produced water treatment technologies. Int. J. Low-Carbon Technol. 9, 157-177. https://doi.org/10.1093/ijlct/cts049

Jimenez, S., Mico, M. M., Arnaldos, M., Medina, F., Contreras, S., 2018. State of the art of produced water treatment. Chemosphere. 192, 186-208. https://doi.org/10.1016/j.chemosphere.2017.10.139

Kabyl, A., Yang, M., Abbassi, R., Li, S. H., 2020. A risk -based approach to produced water management in offshore oil and gas operations. Process Saf. Environ. 139, 341-361. https://doi.org/10.1016/j.psep.2020.04.021

Kargbo, D. M., Wilhelm, R. G., Campbell, D. J., 2010. Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities. Environ. Sci. Technol. 44, 5679-5684. https://doi.org/10.1021/es903811p

Khatri, N., Tyagi, S., Rawtani, D., 2017. Recent strategies for the removal of iron from water: A review. J. Water. Process Eng. 19, 291-304. https://doi.org/10.1016/j.jwpe.2017.08.015

Kiwi, J., Lopez, A., Nadtochenko, V., 2000. Mechanism and kinetics of the OH-radical intervention during fenton oxidation in the presence of a significant amount of radical scavenger (Cl-). Environ. Sci. Technol. 34, 2162-2168. https://doi.org/10.1021/Es991406i

Klavins, M., Purmalis, O., 2010. Humic substances as surfactants. Environ. Chem. Lett. 8, 349-354. https://doi.org/10.1007/s10311-009-0232-z

Kleinitz, W., Koehler, M., Dietzsch, G. (2001). The Precipitation of Salt in Gas Producing Wells. SPE European Formation Damage Conference. The Hague, Netherlands.

Lester, Y., Ferrer, I., Thurman, E. M., Sitterley, K. A., Korak, J. A., Aiken, G., Linden, K. G., 2015. Characterization of hydraulic fracturing flowback water in Colorado: Implications for water treatment. Sci. Total Environ. 512, 637-644. https://doi.org/10.1016/j.scitotenv.2015.01.043

Lin, S. H., Nejati, S., Boo, C., Hu, Y. X., Osuji, C. O., Ehmelech, M., 2014. Omniphobic Membrane for Robust Membrane Distillation. Environ. Sci. Tech. Let. 1, 443-447. https://doi.org/10.1021/ez500267p

Liu, Y., Lu, H., Li, Y., Xu, H., Pan, Z., Dai, P., Wang, H., Yang, Q., 2021. A review of treatment technologies for produced water in offshore oil and gas fields. Sci. Total Environ. 775, https://doi.org/10.1016/j.scitotenv.2021.145485

Ma, H. Z., Wang, B., 2006. Electrochemical pilot-scale plant for oil field produced wastewater by M/C/Fe electrodes for injection. J. Hazard. Mater. 132, 237-243. https://doi.org/10.1016/j.jhazmat.2005.09.043

McCormack, P., Jones, P., Hetheridge, M. J., Rowland, S. J., 2001. Analysis of oilfield produced waters and production chemicals by electrospray ionisation multi-stage mass spectrometry (ESI-MSn). Water Res. 35, 3567-3578. https://doi.org/10.1016/S0043-1354(01)00070-7

Messele, S. A., Bengoa, C., Stuber, F. E., Giralt, J., Fortuny, A., Fabregat, A., Font, J., 2019. Enhanced Degradation of Phenol by a Fenton-Like System (Fe/EDTA/H2O2) at Circumneutral pH. Catalysts. 9, https://doi.org/10.3390/Catal9050474

Miklos, D. B., Remy, C., Jekel, M., Linden, K. G., Drewes, J. E., Hubner, U., 2018. Evaluation of advanced oxidation processes for water and wastewater treatment - A critical review. Water Res. 139, 118-131. https://doi.org/10.1016/j.watres.2018.03.042

Mohammad-Pajooh, E., Weichgrebe, D., Cuff, G., Tosarkani, B. M., Rosenwinkel, K. H., 2018. On-site treatment of flowback and produced water from shale gas hydraulic fracturing: A review and economic evaluation. Chemosphere. 212, 898-914. https://doi.org/10.1016/j.chemosphere.2018.08.145

Neff, J. M., Sauer, T. C., Maciolek, N. (1992). Composition, Fate and Effects of Produced Water Discharges to Nearshore Marine Waters. Produced Water. R. J. P. and E. F. R. Boston, MA, Springer. **46:** 371-385.

Olsson, O., Weichgrebe, D., Rosenwinkel, K. H., 2013. Hydraulic fracturing wastewater in Germany: composition, treatment, concerns. Environ. Earth Sci. 70, 3895-3906. https://doi.org/10.1007/s12665-013-2535-4

Pasternak, G., Kolwzan, B., 2013. Surface tension and toxicity changes during biodegradation of carbazole by newly isolated methylotrophic strain Methylobacterium sp GPE1. Int. Biodeter. Biodegr. 84, 143-149. https://doi.org/10.1016/j.ibiod.2012.07.021

Rezaei, M., Warsinger, D. M., Lienhard, V. J. H., Samhaber, W. M., 2017. Wetting prevention in membrane distillation through superhydrophobicity and recharging an air layer on the membrane surface. J. Membr. Sci. 530, 42-52. https://doi.org/10.1016/j.memsci.2017.02.013

Ricceri, F., Giagnorio, M., Farinelli, G., Blandini, G., Minella, M., Vione, D., Tiraferri, A., 2019. Desalination of Produced Water by Membrane Distillation: Effect of the Feed Components and of a Pre-treatment by Fenton Oxidation. Sci. Rep. 9, 14964. https://doi.org/10.1038/s41598-019-51167-z

Shaffer, D. L., Chavez, L. H. A., Ben-Sasson, M., Castrillon, S. R. V., Yip, N. Y., Elimelech, M., 2013. Desalination and Reuse of High-Salinity Shale Gas Produced Water: Drivers, Technologies, and Future Directions. Environ. Sci. Technol. 47, 9569-9583. https://doi.org/10.1021/es401966e

Shang, W., Tiraferri, A., He, Q. P., Li, N. W., Chang, H. Q., Liu, C., Liu, B. C., 2019. Reuse of shale gas flowback and produced water: Effects of coagulation and adsorption on ultrafiltration, reverse osmosis combined process. Sci. Total Environ. 689, 47-56. https://doi.org/10.1016/j.scitotenv.2019.06.365

Shokrollahzadeh, S., Golmohammad, F., Naseri, N., Shokouhi, H., Arman-mehr, M., 2012. Chemical oxidation for removal of hydrocarbons from gas-field produced water. Procedia Engineer. 42, 942-947. https://doi.org/10.1016/j.proeng.2012.07.487

Tandy, S., Ammann, A., Schulin, R., Nowack, B., 2006. Biodegradation and speciation of residual SS-ethylenediaminedisuccinic acid (EDDS) in soil solution left after soil washing. Environ. Pollut. 142, 191-199. https://doi.org/10.1016/j.envpol.2005.10.013

Tang, P., Li, J. L., Li, T., Tian, L., Sun, Y., Xie, W. C., He, Q. P., Chang, H. Q., Tiraferri, A., Liu, B. C., 2021. Efficient integrated module of gravity driven membrane filtration, solar aeration and GAC adsorption for pretreatment of shale gas wastewater. J. Hazard. Mater. 405, https://doi.org/10.1016/j.jhazmat.2020.124166

Van Devivere, P. C., Saveyn, H., Verstraete, W., Feijtel, T. C. J., Schowanek, D. R., 2001. Biodegradation of metal-[S,S]-EDDS complexes. Environ. Sci. Technol. 35, 1765-1770. https://doi.org/10.1021/es0001153

Vesterkvist, P. S. M., Misiorek, J. O., Spoof, L. E. M., Toivola, D. M., Meriluoto, J. A. O., 2012. Comparative Cellular Toxicity of Hydrophilic and Hydrophobic Microcystins on Caco-2 Cells. Toxins. 4, 1008-1023. https://doi.org/10.3390/toxins4111008

Vione, D., Merlo, F., Maurino, V., Minero, C., 2004. Effect of humic acids on the Fenton degradation of phenol. Environ. Chem. Lett. 2, 129-133. https://doi.org/10.1007/s10311-004-0086-3

Voelker, B. M., Sulzberger, B., 1996. Effects of fulvic acid on Fe(II) oxidation by hydrogen peroxide. Environ. Sci. Technol. 30, 1106-1114. https://doi.org/10.1021/Es9502132

Wang, Z. X., Chen, Y. M. L., Sun, X. M., Duddu, R., Lin, S. H., 2018. Mechanism of pore wetting in membrane distillation with alcohol vs. surfactant. J Membrane Sci. 559, 183-195. https://doi.org/10.1016/j.memsci.2018.04.045

Zhang, Y., Klamerth, N., Chelme-Ayala, P., Gamal El-Din, M., 2016. Comparison of Nitrilotriacetic Acid and [S,S]-Ethylenediamine-N,N′-disuccinic Acid in UV–Fenton for the Treatment of Oil Sands Process-Affected Water at Natural pH. Environ. Sci. Technol. 50, 10535-10544. https://doi.org/10.1021/acs.est.6b03050