Produced water treatment by advanced oxidation processes

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HIGHLIGHTS

- An integrated PW treatment is aimed for increasing sustainability of O&G sector.
- PW treatment can include a pretreatment, an AOP and a RO unit.
- Acetic acid is one of the most recalcitrant compounds of PW.
- With photocatalysis a low TOC removal percentage is achieved.
- The highest TOC removal percentages are achieved combining ozone and H_2O_2.

GRAPHICAL ABSTRACT
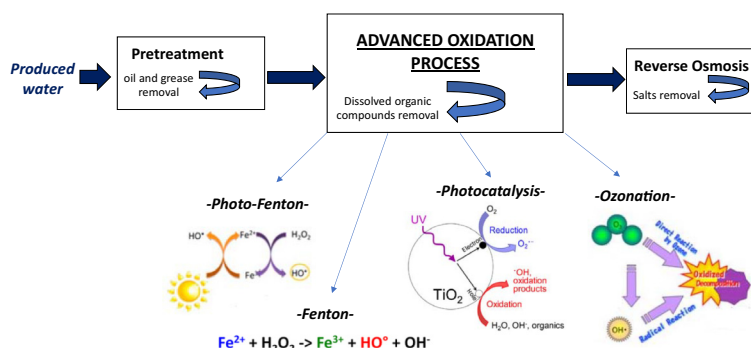
ABSTRACT

Different Advanced Oxidation Processes (AOPs) such as photocatalysis, Fenton-based processes and ozonation were studied to include one of these technologies within an integrated solution for produced water (PW) polishing. Synthetic PW was prepared adding toluene, xylene, naphthalene, phenol, acetic and malonic acids to a seawater matrix. Despite that in all AOPs studied in this work BTEX and naphthalene were removed, the efficiency (in terms of TOC removal) of each treatment varied largely. Among these techniques, photocatalysis was found to be the less effective for the treatment of PW, as TOC removals lower than 20% were obtained for the best scenario after 4 h treatment. In the contrary, best results were obtained by ozonation combined with H_2O_2, where all the organic components were removed, including a high percentage of acetic acid, which was not abated by the rest of the AOPs studied. The optimum conditions for ozonation were 4 g h^{-1} O_3 and 1500 mg L^{-1} H_2O_2 at pH 10, where after 2 h a 74% of TOC removal was achieved and the acetic acid elimination was 78%. This condition enabled that ozonation process accounted for the lowest electric energy consumption per order of target compound destruction regarding total organic carbon (TOC).

1. Introduction

Produced water (PW) is the aqueous effluent that is brought to the surface along with oil or gas in extraction operations. It includes formation water (trapped underground) and injection water that are extracted together with the fossil fuel during oil and gas production (Arthur et al., 2011; Fakhru'l-Razi et al., 2009). The main components of PW are salts, oil and grease (O&G), benzene, toluene, ethylbenzene and xylene (BTEX), polycyclic aromatic hydrocarbons (PAHs), organic acids and phenols (Jiménez et al., 2018a). The chemical composition of PW from an average discharge is summarized in Table 1 (Jiménez et al., 2017; Utvik and Hasle, 2015).

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Table 1
Main components of produced water from oilfields (Jiménez et al., 2017; Utvik and Hasle, 2015).

Compound group	Concentration, mg L^{-1}
Salts	Up to 300,000
O&G	15–200
BTEX	0.7–24
PAHs	0.04–3
Organic acids	7–760
Phenols	0.4–23

Recently, the authors have reported the use of different pretreatments for the O&G removal in PW (Jiménez et al., 2017) obtaining an effluent with an O&G content below the requirements for discharging. However, the treatment efficiency is not enough when the aim is to reuse the treated water, since the rest of the components, mainly the dissolved organic compounds, were not eliminated in that pretreatment. Currently, in the oil and gas industry, the biological treatment is used to further remove some of these compounds, especially in the downstream scenario (Pendashteh et al., 2010; Lu et al., 2009); however, the efficiency of the bioprocess seems to be inadequate when water contains highly toxic recalcitrant compounds (Mota et al., 2008), such as BTEX and phenols. The complexity of PW and its reuse purposes (e.g. for generation of high quality water for steam production, or even for irrigation or aquifer recharge) makes impossible its treatment by a single technology. The solution could be the development of integrated processes, i.e. the combination of individual technologies. These techniques could involve *E*-DAF (enhanced dissolved air flotation) or settling (Jiménez et al., 2017), optionally followed by membrane ultrafiltration (to remove the remaining O&G), an advanced oxidation process (AOP), for dissolved organic matter abatement, and, finally, a reverse osmosis system for salts elimination. With this context, the objective of this work is to essay the suitability of a group of AOP technologies as a stage of the mentioned treatment train.

There are already in the market packaged PW treatment technologies; however, most of these solutions are tailor-made to meet specific treatment needs for each individual exploitation site and usually these solutions do not offer a treatment to remove the different groups of components (Siemens, n.d.; CDM, 2008; Veolia, n.d.; Jiménez et al., 2018b). Therefore, more flexible systems could find a niche in the market.

According to what has been previously stated, this work is therefore the result of an environmental and industrial need, and apart from depolluting a water stream for its potential discharge, it aims to generate water of enough quality to be reused that will increase the overall sustainability of the oil and gas sector. For that reason, the authors have studied the performance of different AOPs such as photocatalysis, Fenton, photo-Fenton, sono-Fenton and ozonation in the removal of dissolved organics from PW, to include one of these processes within the integrated treatment solution for PW polishing.

The choice of AOP technologies is mainly based on the characteristics of the hydroxyl radicals (•OH) generated within, among others, as they are highly reactive and have high oxidation potential. This fact enables these species to oxidize organic compounds completely into carbon dioxide and water, or at least partially into harmless compounds. This is the main advantage of the AOPs in contrast to other processes, which sometimes lead only to the transfer of contaminants from one phase to another, such as active carbon, membrane technologies, etc. (Sinha et al., 2007a).

Most of the AOPs use a combination of strong oxidants such as ozone or hydrogen peroxide (H_2O_2) with either heterogeneous or homogeneous catalysts (usually transition metals and iron), semiconductor solids, radiation or ultrasound to enhance radicals generation.

In the case of Fenton's reagent, it combines H_2O_2 and ferrous ions (Fe^{2+}) in an acid medium, which leads to the formation of •OH radicals through the oxidation of Fe^{2+} to Fe^{3+} (Neyens and Baeyens, 2003). Simultaneously, Fe^{2+} is regenerated by the reaction between Fe^{3+} and H_2O_2 (Duesterberg and Waite, 2006). The photo-Fenton process combines Fenton's reagent with light energy (Pignatello et al., 2006), which accelerates the degradation rate of organic pollutants. Besides, the photolysis of Fe^{3+} enables another path for the regeneration of Fe^{2+} due to its sensitivity to UV–Vis radiation for wavelengths above 300 nm (Pignatello, 1992).

Photocatalytic water treatment using TiO_2 is also a well-known AOP for environmental remediation. Both hydroxyl and superoxide anion (•O_2^-) radicals, produced by the in situ generation of electron-hole pairs on the semiconductor upon irradiation with light, are suggested to be the primary oxidizing species in the photocatalytic oxidation processes (Nath et al., 2012) and mineralize a wide range of organic compounds.

O_3 has been extensively applied in the degradation of organic contaminants. Depending on the water quality (i.e., type and concentration of organics dissolved and presence of radical scavengers) combinations of ozone with H_2O_2 or/and UV light may also be considered to enhance pollutant removal. These increase the decomposition kinetics of O_3 into radicals (•OH and •O_2), and therefore improve the oxidation of dissolved organic matter.

Although these technologies are very effective, their application highly depends on the type and composition of the wastewater to be treated. Hence, both the determination of the appropriate AOP as well as the operational conditions is an important issue to achieve the maximum removal of recalcitrant compounds at the lowest cost (Gogate and Pandit, 2004a; Gogate and Pandit, 2004b).

To date, most of the reported studies apply AOPs to degrade an individual component contained in a simple matrix. On the contrary, the particularity of this study, focused on the complex system of PW, is the application of the AOPs to degrade different types of components contained together in a salt matrix composed by a high and heterogeneous concentration of salts (Jiménez et al., 2018a). Chemical species such as chloride, carbonate and bicarbonate ions are susceptible to react with the •OH (Andreozzi et al., 1999; Al Jabri and Feroz, 2015), decreasing the efficiency of the chemical process by scavenging. Besides, recalcitrant compounds present in this PW, such as acetic acid, have a low reaction rate with radicals, what makes them refractory and hard to decompose (Park and Lee, 2009). Furthermore, studies treating recalcitrant-to-OH-radicals components, such as acetic acid, in produced water, are scarce and they mainly report low efficiencies of removal (Ogata et al., 1981; Sinha et al., 2007b).

2. Materials and methods

2.1. Synthetic produced water

PW was prepared according to the bibliographic data of oilfields PW, considering the main groups of components usually present in PW (BTEX, PAHs, organic acids and phenols) (Jiménez et al., 2018a), and their concentrations (Table 1). The O&G group was excluded here since it is supposed to be removed in a previous pretreatment (Jiménez et al., 2017); thus, this study entails only the removal of the dissolved organic compounds in the PW.

The synthetic PW was composed by different groups of compounds: toluene (10 mg L^{-1}, Sigma-Aldrich), xylene (10 mg L^{-1}, Sigma-Aldrich) as representatives of the BTEX group, naphthalene (3 mg L^{-1}, Sigma-Aldrich) as representative of the PAHs group, phenol (10 mg L^{-1}, Sigma-Aldrich), and recalcitrant molecules as acetic (150 mg L^{-1}, Panreac), and malonic acids (10 mg L^{-1}, Sigma-Aldrich) dissolved in a real seawater matrix (Mediterranean Sea, Barcelona conductivity ca. 56 mS cm^{-1}).

This synthetic PW had a chemical oxygen demand (COD) and total organic carbon (TOC) of ca. 262 mg L^{-1} and 92 mg L^{-1} respectively, and a pH of 4.95. The value of toxicity EC$_{50}$ (% v/v) of this PW was 10%.

2.2. Photocatalytic experiments

Photocatalytic experiments were performed twice either in a solar simulator (SB), or in an UVAphoto-reactor. In the first case, the equipment was a Solarbox 3000e (Cofomegra, Italy), equipped with a 2500 W Xenon lamp and an outdoor light filter, which allows 290–800 nm wavelength to pass through.

Irradiance was set to 250 W m^{-2}. The irradiation intensity was 6.5×10^{-4} Einstein min^{-1}. In the case of the photo-reactor $4 \times$ 15 W UVA lamps were used (300–400 nm, $\lambda_{max.} = 360$–365 nm). The intensity of the total radiation from the UVA lamps in this case was 1.3×10^{-4} Einstein min^{-1}. The irradiation intensity of the Xe and UVA lamps used in photocatalytic experiments was determined by actinometry using the Parker method, based on the photochemical reduction of the ferrioxalate complex $[Fe(C_2O_4)_3]^{3-}$ to Fe (II) in acidic medium. The reduction takes place with a quantum yield of 1–1.2 mol Einstein^{-1} in the range of wavelengths between 250 and 450 nm (Goldstein and Rabani, 2008). The concentration of Fe (II) over time was followed by UV–VIS spectroscopy with the o-phenanthroline method (Zuo, 1995), based on the formation of a colored complex between Fe (II) in solution and 1,10-phenanthroline in acidic medium acetic acid/acetate at pH 3–4.

Aeroxide® P25 (Acros Organics, Belgium) was used as a commercially available TiO$_2$ photocatalyst. The crystallographic phases were characterized by X-ray diffraction with a Siemens D5000 diffractometer with a Bragg-Brentano-geometry and vertical 2θ goniometer and operated at 80 kV using Cu Kα radiation. Diffractograms were in a 2 theta range from 5° to 70° with an angular step of 0.03° at 5 s per step. The samples were dispersed on a Si (510) low background sample holder. Crystallite size and crystalline phase contents were calculated by means of the program TOPAS working under the programming mode (launch mode) with local routines.

The crystallite sizes estimated for all phases were calculated using the integral breadth method. Using integral breadth instead of FWHM to calculate the crystallite size may reduce the effect of crystallite size distribution on the Scherrer constant K and therefore the crystallite size analysis is more accurate. The composition of P25 was anatase (87.6%) and rutile (12.4%) (Fig. S1 & Table S1, Supplementary information).

2.3. Fenton-based experiments

Fenton related reactions were performed at pH 3 (by acidification with HCl). The reagents used were hydrogen peroxide solution (35 wt %, with stabilizer, from Sigma-Aldrich) and iron (II) sulfate heptahydrate (FeSO$_4 \cdot$7H$_2$O, from Sigma-Aldrich). Fenton experiments were carried out in 1 L topaz bottles, to avoid the light influence, with magnetic stirring. The temperature essayed for these experiments was room temperature (20 °C), 40 °C and 70 °C. Similarly, sono-Fenton reactions were performed at 20 °C under the same experimental conditions than Fenton reactions. Sonication was applied by using a probe-type sonicator with a working frequency of 24 kHz and an acoustic power density of 105 W cm^{-2}.

Photo-Fenton reactions were performed either under UVC radiation (4 × 15 W, $\lambda_{max.} = 254$ nm, 1.3×10^{-4} Einstein min^{-1}) in the photo-reactor, or under the previously described conditions of the SB and the UVA photo-reactor. As in the Fenton experiments, photo-Fenton reactions were performed at pH 3.

2.4. Ozonation

The ozonation of the PW (1 L) was conducted in a jacketed boron-glass semi-batch type reactor (1.5 L). The ozone generated by an ozone generator (ANSEROS COM-AD-02) from pure O$_2$ (50 L h^{-1}) was passed through the solution maintaining a constant production of O$_3$. The O$_3$ flow added was previously determined by iodometry, and

productions between 1.59 and 5.7 g h^{-1} were measured. All experiments were carried out at room temperature (ca. 20 °C) with magnetic stirring (500 rpm) and the injection of the ozone-oxygen mixture took place through a sintered glass diffusor. An O$_3$ trap containing KI solution (20 g L^{-1}) was connected to the reactor outlet.

2.5. Analytical methods

The pH was measured with a PH 25 CRISON pH-meter. COD was determined photometrically using Hach Lange kit LCK 414. H$_2$O$_2$ consumption was semi-quantitatively monitored with QUANTOFIX Peroxide test strips. Residual H$_2$O$_2$ was neutralized at the end of the experiments by the addition of sodium bisulfite (Sigma-Aldrich). TOC analyses were performed with a Shimadzu TOC-L CSN analyzer.

For the analysis of components such as the organic acids and phenol, an HPLC system (LC Shimadzu 2010) equipped with a diode array detector (DAD) was used. For the separation of the analytes, a Mediterranean HPLC column (C18, 2.1 × 150 mm, 3.5 μm, Teknokroma, USA) was used at a temperature of 40 °C. Isocratic program was used with a flow rate of 0.8 mL min^{-1} mobile phase (deionized water at pH 2.2). The DAD wavelength was set at 220 nm.

Other components such as BTEX, naphthalene and phenol were analyzed by gas chromatography coupled to a mass spectrometer detector (GC–MS) using a GC–MS 2010 of Shimadzu equipped with a Zebron ZB-5 column, together with a splitless injection mode of 0.5 μL of sample.

Samples with TiO$_2$ or iron were previously filtered through 0.20 μm Phenex Nylon filter membranes before TOC, GC and HPLC analysis.

Ecotoxicological evaluation was performed using *Vibrio fischeri* as test organisms to evaluate acute aquatic toxicity according to the basic test methodology developed for the equipment Microtox 5000. The principle used for the determination of toxicity is the inhibition of luminescence emitted by the bacteria when in contact with the sample. The basic test was performed in duplicate for a control sample and applying four dilutions of the initial concentration of each sample (5, 11, 22 and 45%), except for the samples treated with ozone/H$_2$O$_2$, where the 81.9% basic test was applied. Exposure time was 15 min, and EC$_{50,15min}$ (% v/v) was calculated with the supplier's software. Samples can be classified on four classes depending on their toxicity using EC$_{50}$ values as established by Calleja et al. (Calleja et al., 1986): Class 1, when EC$_{50} \le$ <25% (very toxic); Class 2, when <25% < EC$_{50}$ < 75% (toxic); Class 3, when EC$_{50}$ = 75% (slightly toxic); and Class 4, when EC$_{50}$ > 75% (non-toxic).

3. Results

3.1. Photocatalysis

Firstly, adsorption tests in dark conditions were performed for 2 h after the reagents addition. Once this time had elapsed, a sample was withdrawn, and the remaining solution was irradiated either with UVA or solar light. During the dark test, a TOC removal of about 4–13% was observed due to the adsorption of the organic matter on the P25 surface.

After irradiation, TOC removal was in general poor and minor differences were observed depending on the catalyst loading, as can be seen in Table 2, which shows the results of the experiments, and in Fig. 1-A&B, which represents the evolution with time. When a concentration of 0.1 g L^{-1} of P25 was used, the TOC removal was very low (ca. 8% after 3 h), even with the addition of 1500 mg L^{-1} of H$_2$O$_2$ (10 times more than the amount of acetic acid (w/w), which as it will be shown later, was the most recalcitrant compound). No significant differences were observed in TOC removal when a higher P25 concentration was used (0.5 g L^{-1}) either after 3 h of reaction. 10% of TOC removal, and a maximum of 15% TOC removal was achieved after 6 h when working at free pH (pH = 5). This indicated that degradation occurred with a very low rate. The difference on TOC reduction among the

Table 2
Operational conditions and TOC removal by photocatalysis after 3 h.

P25 loading (mg L^{-1})	Light	pH	TOC removal (%)	Phenol removal (%)	Malonic acid removal (%)	Acetic acid removal (%)
100	UVA	4.8	8	23	–	–
100[a]	UVA	4.8	12	–	–	–
500	UVA	4.8	10	55	–	–
500	UVA	3	8	–	–	–
500	UVA	6.25	5	60	39	0
500	UVA	8	4	51	42	0
100	SB	4.8	3	50	30	0
100[b]	SB	4.8	8	–	–	–
500	SB	4.8	16	≥99	70	0
500[b]	SB	4.8	14	≥99	53	0

[a] Reaction performed with PW synthesized in MilliQ water.
[b] With the addition of 1500 mg L^{-1} of H$_2$O$_2$.

photocatalytic tests performed at different pH (namely 3, 6.25 and 8) was also negligible. This showed that pH had not significant influence on the catalytic performance.

In order to determine if salinity contributed negatively on the poor TOC removal obtained by UVA photocatalysis with TiO$_2$, a new test was performed with a PW synthesized in a milliQ water matrix, instead of seawater; a catalyst concentration of 0.1 g L^{-1} was used. In this case, TOC removal achieved a 12% of mineralization after 3 h, and increased to 20% after 6 h. These values confirmed that salts contained in the seawater hindered TOC removal, probably because the present ions (e.g., chlorides) scavenge the photoinduced radicals from the TiO$_2$ surface. This may limit the destruction of organic molecules by photocatalysis (Kim et al., 2010). However, it must be pointed out that TOC removal, in this case, was also poor, which demonstrated the recalcitrant characteristics under UVA of this type of wastewater.

Photocatalysis experiments were also performed in the SB to test the influence of the wavelength and intensity, and results of a representative experiment are depicted at Fig. 2-C. As previously found with UVA lamps, when 0.1 g L^{-1} of P25 was added, there was hardly any TOC elimination. With this dose, TOC removal was ca. 4%, after 3 h. In this case, a phenol decrease of about 50% was observed; however, both the presence of oxidation by-products and the poor TOC removal indicated that phenol was not completely mineralized. When 0.5 g L^{-1} of P25 was added, TOC removal increased to 16% after 3 h. The theoretical TOC removal corresponding to BTEX and PAHs was about 20%, rather close to the experimental TOC removal obtained in this case. GC–MS analysis confirmed the total abatement of these components (i.e. toluene, xylene and naphthalene) and the decrease of the phenol content (up to 99%); however, the formation of oxidation by-products such as benzaldehyde and hydroquinone was also observed. By HPLC it was observed that malonic acid concentration decreased in some extent (30–70% depending on the experiment), but acetic acid concentration remained unaltered. Therefore, photocatalysis did not result on an effective process for the PW treatment, even when the addition of an oxidant such as H$_2$O$_2$ was used. However, the results obtained in the SB were moderately better than using UVA light, probably due to the higher irradiation intensity of the Xe lamp used (according to the actinometric tests), and the configuration and geometry of the equipment, which allowed taking better profit of the light.

Toxicity values, expressed as EC$_{50}$, for the samples treated by photocatalysis ranged between 13 and 16%, which indicates that the effluent resulted somewhat less toxic than the initial PW (EC$_{50}$ = 10%).

3.2. Fenton-based processes

Fenton, photo-Fenton and sono-Fenton processes were applied and compared for PW treatment. Operational parameters and TOC removals are presented in Table 3.
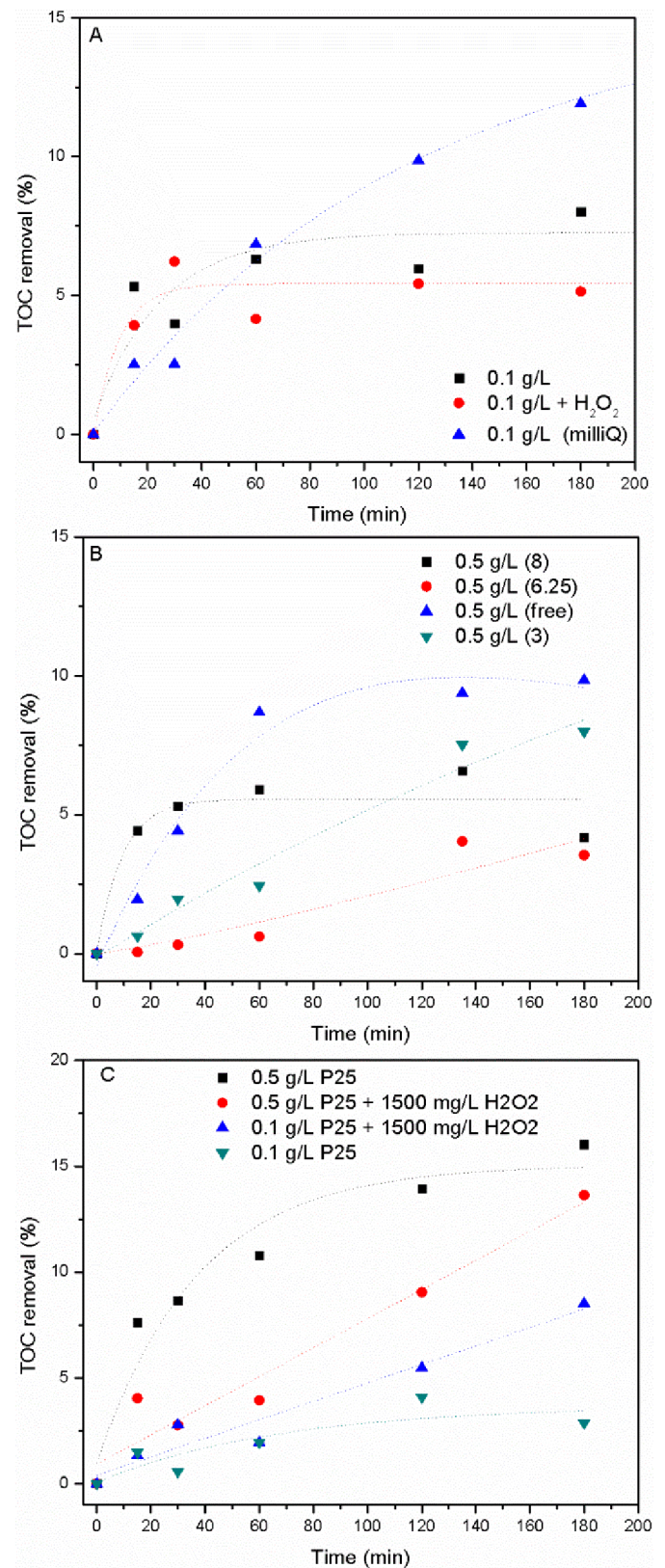

Fig. 1. TOC removal percentages obtained by photocatalysis applying UVA light (A&B) and under solar simulated radiation (C), using 0.1 g L^{-1} and 0.5 g L^{-1} P25.

Fenton experiments were performed with a fixed H$_2$O$_2$/COD ratio (i.e. stoichiometric ratio) and a variable H$_2$O$_2$/Fe ratio at an initial pH 3 and variable temperature (20 °C, 40 °C and 70 °C). Fenton at 20 °C
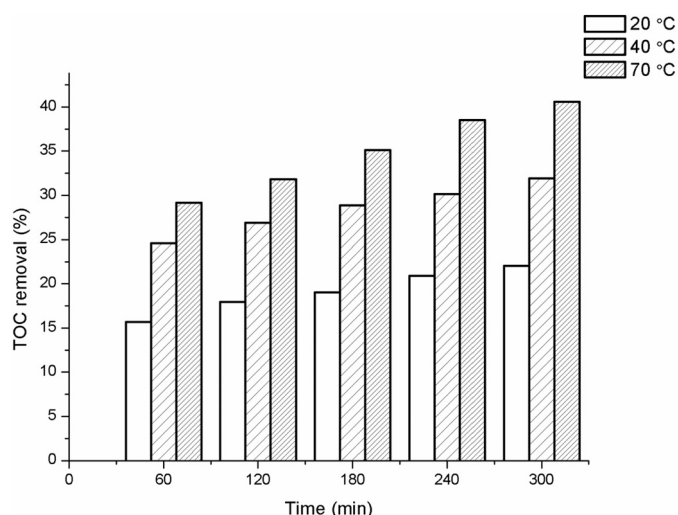
Fig. 2. TOC removal at different times by Fenton's process at different temperatures. Reaction conditions: $H_2O_2/COD = 2.1$ and $H_2O_2/Fe = 0.5$.

resulted in a TOC decrease in a range of 13–18% depending on the Fe^{2+} concentration used; the maximum TOC removal corresponded to the $H_2O_2/Fe = 0.5$ ratio. Increasing the iron concentration above $H_2O_2/Fe = 0.5$ did not enhance the efficiency of the oxidation process and even resulted in a decrease of the TOC removal, probably due to the hydroxyl radical scavenging occurring in the presence of an excess of Fe^{2+} to form Fe^{3+} and OH^- anion. On the other hand, higher H_2O_2 concentrations did not improve the organic matter oxidation (in terms of TOC removal), probably due also to a scavenging effect, in this case related to high H_2O_2 concentrations (Buxton and Greenstock, 1988). Optimal results were therefore obtained when neither H_2O_2 nor Fe^{2+} were overdosed. Furthermore, an optimal ratio between H_2O_2 and Fe^{2+} should be fixed in order to minimize scavenging effect.

Due to the low degrees of mineralization achieved, different strategies were tested. Increasing the temperature resulted in a slight increase of mineralization in those experiments with a H_2O_2/Fe ratio different from 0.5. However, when the H_2O_2/Fe ratio of 0.5 was used, the effect of temperature was more marked, it yielded a 32% of TOC removal at 70 °C, compared to 18% obtained at 20 °C as it can be seen in Fig. 2.

BTEX, naphthalene and phenol were rapidly eliminated in the first minutes of reaction, but only a small amount of acetic acid removal occurred (<10%) and intermediate compounds were also formed; namely, benzaldehyde, p,m-methylbenzaldehyde and phthalic esters were the main by-products found by GC–MS.

To explore the effect of salinity in the Fenton's reaction performance, a new set of experiments was conducted with PW synthesized in a milliQ water matrix, using a $H_2O_2/Fe = 10$ ratio at different temperatures (Table 3, entries 10–12). Notably, when milliQ water was used as matrix, TOC removal was twice higher in all the range of temperatures tested compared to TOC removals obtained for PW synthesized in a seawater matrix, at the same operational conditions. As previously found for photocatalysis, salts contained in seawater resulted detrimental for the organic matter oxidation.

It is assumed that the combination of Fenton's reagent and UV radiation (photo-Fenton process) produces more hydroxyl radicals compared to conventional Fenton's reaction, thus promoting the degradation of organic pollutants. For this reason, photo-Fenton experiments were executed under the same conditions than Fenton experiments for comparison.

Photo-Fenton experiments were performed with three different sources of light: Xe lamp in the SB, and UVC and UVA radiation at 20

°C in the photo-reactor. Experimental conditions and TOC removals after 2 h of reaction are shown in Table 3. Photo-Fenton experiments under simulated solar radiation led to a maximum reduction of TOC of ca. 17% after 2 h of reaction when using 557 mg L^{-1} of H_2O_2 and 55.7 mg L^{-1} of Fe, i.e. $H_2O_2/COD = 2.1$ and $H_2O_2/Fe = 10$ (Table 3, entry 23). These results were similar to that reported by Aljubourya and colleagues (2015) for the photo-Fenton treatment of petroleum wastewater, when using 1000 mg L^{-1} H_2O_2 and 40 mg L^{-1} Fe after 180 min (Aljubourya et al., 2015). Other authors have reported higher TOC removals; however, the composition of those wastewaters was different and excluded refractory compounds such as the acetic acid present in this PW (Coelho et al., 2006). Similar results were obtained in experiments performed with UVA light.

As in the previous experiments with photocatalysis, in the photo-Fenton process the highest TOC reduction rather corresponded to the theoretical reduction of BTEX and PAHs (i.e. naphthalene). In this case, BTEX and naphthalene were removed after 60 min of reaction and most of the phenol was abated in the first minutes of reaction (>90%

Table 3
Operational conditions and TOC removal (after 2 h) for Fenton-based processes.

Fenton				
Entry	H_2O_2/COD (wt.)	H_2O_2/Fe (wt.)	T (°C)	TOC removal (%)
1	2.1	10	20	14
2	2.1	10	40	16
3	2.1	10	70	17
4	2.1	2	20	13
5	2.1	2	40	15
6	2.1	2	70	19
7	2.1	0.5	20	18
8	2.1	0.5	40	27
9	2.1	0.5	70	32
10	2.1[a]	10	20	20
11	2.1[a]	10	40	32
12	2.1[a]	10	70	40
13	2.1	0.25	20	13
14	2.1	0.25	40	15
15	2.1	0.25	70	17
16	10	10	20	21
17	10	10	40	22
18	10	10	70	25
19	10	0.5	20	25
20	10	0.5	40	27
21	10	0.5	70	28

Photofenton				
Entry	H_2O_2/COD (wt.)	H_2O_2/Fe (wt.)	Source of irradiation	TOC removal (%)
22	2.1	0.5	SB	22
23	2.1	2	SB	8
24	2.1	10	SB	17
25	4.5	10	SB	16
26	2.1	10	UV-C	10
27	2.1	2	UV-C	16
28	2.1	0.5	UV-C	19
29	2.1	0.25	UV-C	14
30	2.1	2	UV-A	7
31	2.1	10	UV-A	17
32	4.5	2	UV-A	8
33	4.5	10	UV-A	16

Sonofenton				
Entry	H_2O_2/COD (wt.)	H_2O_2/Fe (wt.)	Frequency (kHz)	TOC removal (%)
34	2.1	10	24	17
35	2.1	2	24	26
36	2.1	0.5	24	26
37	2.1	0.25	24	15

[a] Experiments performed with milliQ water.

after 5 min). However, TOC decrease was lower than expected according to the mineralization of all BTEX, PAHs and phenol (ca. 29%, theoretical), due to the formation of oxidation by-products such as benzaldehyde, phthalates and p,m-methylbenzaldehyde, identified by GC–MS. On the other hand, most of the acetic acid remained in the solution with <10% of acetic removal; whereas malonic acid concentration decreased about 50%. The application of UVC light did not resulted in an increase of TOC removal, and similar results to those found in the SB were obtained.

TOC removals in photo-Fenton were only slightly higher than those observed in conventional Fenton (Fig. 3). Besides, the toxicity of photo-Fenton treated PW was not improved by this treatment.

If Fenton oxidation is used in combination with ultrasonic irradiation, the rate of generation of hydroxyl radicals may be increased due to the extreme conditions of temperature and pressure locally generated due to the cavitation phenomenon. Hence, reaction with organic matter may be improved. Sono-Fenton experiments were performed at a fixed H_2O_2 concentration (stoichiometric $H_2O_2/COD = 2.1$) and variable H_2O_2/Fe ratios at 20 °C with a 24 kHz ultrasound application (Table 3, entries 34–37). Results may be improved if higher frequencies are applied.

The application of ultrasound (US) favored the TOC removal, which increased in all the range of H_2O_2/Fe studied, compared to regular Fenton. Likewise to what was observed in Fenton, in sono-Fenton the best results were obtained for the ratio $H_2O_2/Fe = 0.5$, with a 26% of TOC removal compared to 18% obtained in t is also remarkable that sono-Fenton resulted more efficient than photo-Fenton reaction in all the ranges (H_2O_2/COD and H_2O_2/Fe) studied (Fig. 3). In the case of sonochemical degradation, there was direct exposure to US radiation in the reaction medium by using a horn type sonicator for direct production and interaction of hydroxyl free radicals with the pollutant. In this case, the number of cavitation bubbles produced in the reactor can be higher; and therefore the formation of radicals in the interface boundary layer of the bubbles (Adewuyi, 2001; Yim et al., 2002; Suzuki et al., 1999). This may improve the contact between radicals and organic matter, enhancing the oxidation efficiency. As in previous cases, the most recalcitrant compound was acetic acid, which was removed in ca. 10% in all the Fenton-like processes studied.

These results supported the fact that not only the type of pollutant nor the type of treatment are the parameters to take into account in water remediation, but operating conditions and equipment configuration may also play an important role in the rate of radicals generation and oxidation efficiency.
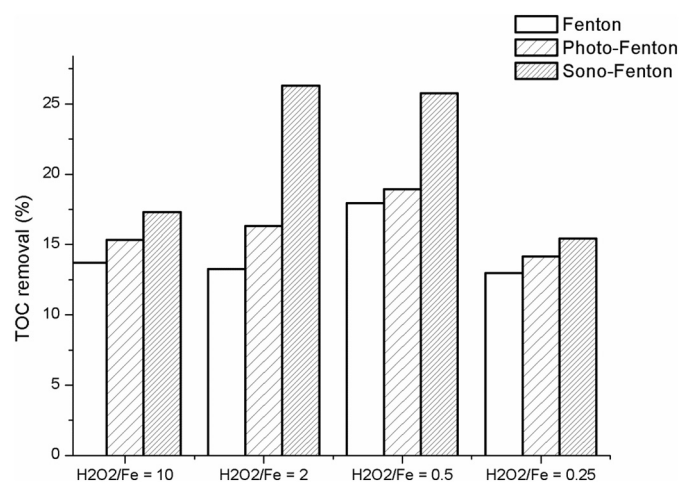

Fig. 3. Comparison of the Fenton-like processes for a fixed concentration of H_2O_2 ($H_2O_2/COD = 2.1$; [H_2O_2] = 557 mg L^{-1}) and variable Fe^{2+} concentration.

3.3. Ozonation

Ozonation experiments were performed in a glass reactor with a residence time of 2 h and O_3 productions ranging between 1.59 and 5.7 gO_3 h^{-1}. TOC removal values in the range 18–24% depending on the O_3 dose were obtained (Table 4).

It was found that BTEX and naphthalene could be eliminated simply by striping with O_2 (or air in a real industrial application), whereas phenol and organic acids remained in solution. However, when O_3 was injected, phenol was removed in the first 15 min of reaction, while the acids remained after 2 h of treatment. This was consistent with the TOC value obtained, which was equivalent to the theoretical removal of BTEX, PAHs and phenol. Oxygenated molecules such as methylacetoin or C5-C7 alcohols were observed by GC–MS as by-products, which increased in concentration with reaction time. Additionally, alkyl halides were also detected.

In this case, toxicity was slightly reduced with EC_{50} values between 12 and 20%.

To improve the mineralization degree achieved by single ozonation, combinations of ozone with H_2O_2 and/or Fe^{2+} were tested. It was observed that the addition of Fe in the ozonation process was not necessary and even detrimental, probably because O_3 was consumed in the oxidation of Fe^{2+} to Fe^{3+} (Fig. 4-A). On the contrary, the performance of the ozonation process was improved in presence of H_2O_2.

Fig. 4-B shows the TOC removal percentages of the ozonation experiments with a fixed ozone production (1.6 gO_3 h^{-1}) and different doses of H_2O_2. A slight improvement in TOC removal was observed from ca. 25% with 557 mg L^{-1} of H_2O_2 to ca. 33%, when the H_2O_2 concentration was increased to 1500 mg L^{-1}.

Fig. 4-C shows the TOC removal percentages, for 1500 mg L^{-1} H_2O_2, with different O_3 production rates, namely 1.6, 2.8, 4 and 4.8 g O_3 h^{-1}. After 2 h of treatment, the TOC eliminations achieved were ca. 33%, 37%, 50%, and 56%, respectively. Under these conditions, all the components in PW were removed and no by-products of oxidation were found by GC–MS. This indicated comprehensive mineralization of BTEX, PAHs and phenol. Moreover, malonic acid was completely removed and the acetic acid (which was only slightly oxidized in the other AOPs tested) was removed in an important extent, up to 70% for a dose of 4.8 gO_3 h^{-1}. In addition, with O_3 productions above 1.6 gO_3 h^{-1}, H_2O_2 was completely consumed during the reaction and no residual H_2O_2 was detected after 2 h.

By increasing O_3 production to 5.7 gO_3 h^{-1} and setting H_2O_2 concentration in 1500 mg L^{-1}, mineralization was not improved, and TOC removal dropped to 40%. This suggested that an optimal ratio between O_3 and H_2O_2 should be considered. By working at 5.7 gO_3 h^{-1} and increasing the H_2O_2 dose up to 3000 mg L^{-1}, an improvement of TOC removal was observed; however, the mineralization degree attained was

Table 4
Operational conditions and TOC removals in the initial ozonation experiments.

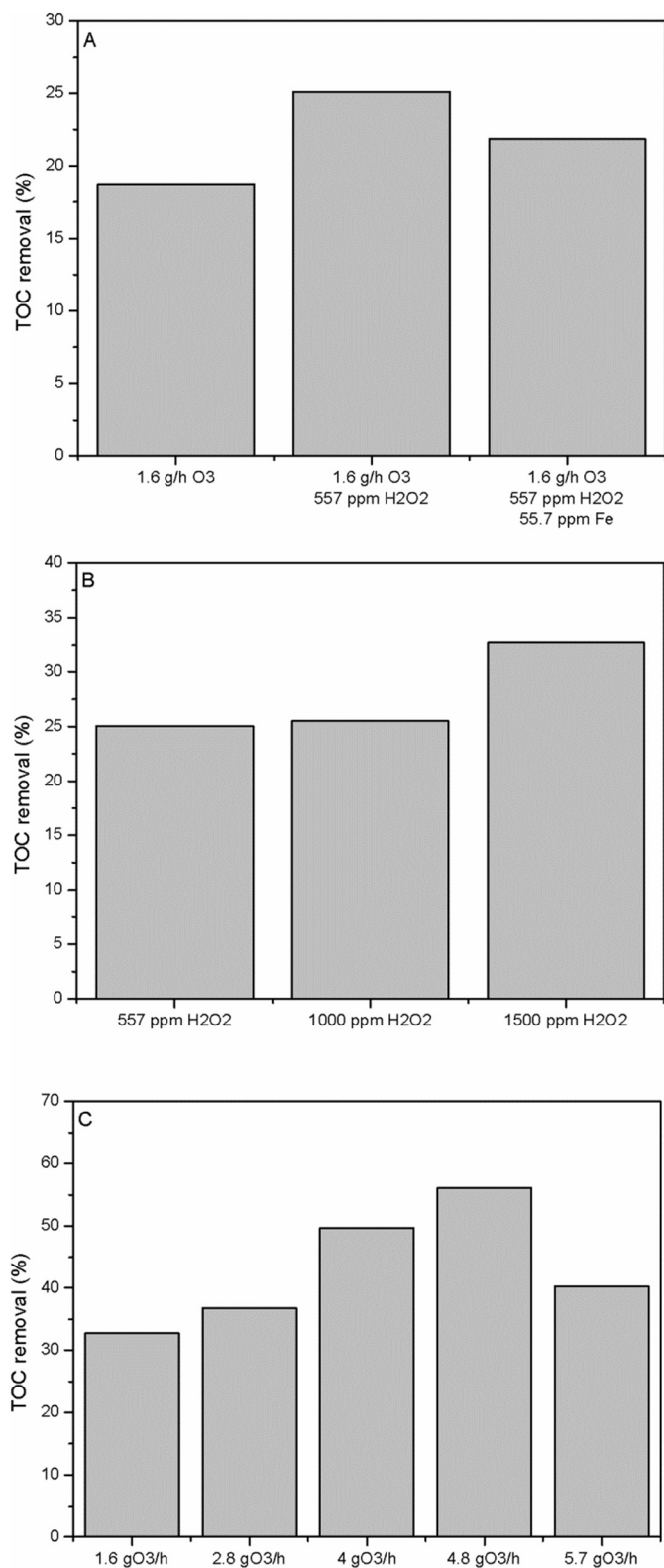| Entry	O_3, g h^{-1}	H_2O_2, mg L^{-1}	Fe^{2+}, mg L^{-1}	TOC removal (%)
1	1.6	–	–	18
2	2.8	–	–	18
3	4.0	–	–	20
4	4.8	–	–	24
5	5.7	–	–	24
9	1.6	557	–	25
10	1.6	1000	–	24
11	1.6	1500	–	33
16	1.6	557	55.7	22
18	1.6	1500	–	33
19	2.8	1500	–	37
20	4.0	1500	–	50
21	4.8	1500	–	56
22	5.7	1500	–	40
23	5.7	3000	–	49

Fig. 4. TOC removal observed upon 120 min of ozonation treatment: A) With a fixed dose of 1.6 g O_3 h^{-1} in presence and absence of Fe and H_2O_2; B) with a fixed dose of 1.6 g O_3 h^{-1} under different H_2O_2 concentration; C) with a fixed dose of 1500 mg L^{-1} H_2O_2 under different production rates of O_3 from 1.6 g h^{-1} to 5.7 g h^{-1}.

rather similar to that obtained previously with O_3 production of 4 gO_3 h^{-1} and 1500 mg L^{-1} H_2O_2.

Taking as optimum concentrations 1500 mg L^{-1} H_2O_2 and 4 g h^{-1} O_3 (since the improvement with higher O_3 and H_2O_2 is not significant), the

effect of initial pH was tested by performing experiments at pH 8 and pH 10. As observed in Fig. 5, there is hardly any difference between doing the ozonation at pH 4.95 and 8, but at pH 10, removals are significantly higher. This may be because when pH is close to pKa value for the H_2O_2 (11.6), the equilibrium is more displaced towards the formation of the hydroperoxide anion (HO_2^-). Moreover, at pH 10, there are more OH^- present in the medium than at free pH and pH 8. Both anions, HO_2^- and OH^-, react rapidly with the O_3 to form hydroxyl and superoxide radicals (Beltrán, 2004). In addition, the O_3 decomposition kinetics, and therefore oxidation, is dependent on pH, and is higher at pHs between 8.5 and 11, while at neutral and slightly acidic pH, the O_3 decomposition kinetics is slower.

The highest elimination was achieved at pH 10 with 1500 mg L^{-1} H_2O_2 and 4 g h^{-1} O_3 after 2 h. Fig. 5 also compares it with single ozonation at initial pH 10, by passing only 4 g h^{-1} O_3 without adding H_2O_2 (where the maximum TOC removal was 42.6% and acetic acid removal of 77.8%), adding 3000 mg L^{-1} H_2O_2 (with a TOC removal of 58.6% and acetic acid removal of 61.1%)) and adding 1000 mg L^{-1} H_2O_2 (with a TOC removal of 56.3% and acetic acid removal of 76.7%). However, the optimal conditions were still 4 g h^{-1} O_3 and 1500 mg L^{-1} H_2O_2, where the TOC removal was 74% and the acetic acid removal was 77.8% (remaining 33.3 mg L^{-1}). In these ozonation experiments the rest of the PW components added were eliminated. Intermediates were not found by GC analysis. Nevertheless, by HPLC, intermediate acids compounds were found but were difficult to identify since they appear in the same peak that salts containing the synthetic PW.

Under these optimum operating conditions, the H_2O_2 was consumed after 1 h and the final pH after 2 h of process was 8.4.

Toxicity ranges expressed as EC_{50} for the samples treated with ozone and H_2O_2 were between 40 and 57% (so they resulted less toxic than with the other AOPs).

According to these results, the best option for the treatment of PW is the ozonation combined with H_2O_2 at pH 10, where 74% of TOC removal was achieved with 1500 mg L^{-1} H_2O_2 and 4 g h^{-1} O_3 after 2 h. The only component that was not totally eliminated was the acetic acid, although its concentration decreased in a 77.8%, in contrast to the other AOPs tested, where no removal occurred. In addition, as H_2O_2 is consumed, treated PW would not contain any residual substance that has to be removed in a later treatment, as the iron sludge obtained after Fenton and photo-Fenton processes or the TiO_2 catalyst in photocatalysis. After O_3 treatment with H_2O_2, no halogenated organic compounds were detected by GC–MS; however, more detailed studies should be performed. Besides, the final pH that is obtained is within the established limits for discharge and reutilization of water.

The only component that was not totally eliminated was the acetic acid. This compound is biodegradable, therefore does not raise a significant concern since subsequent halo-tolerant biological reactor could be suggested if needed. Furthermore, if a reverse osmosis step is added after the ozonation treatment to eliminate the seawater salts contained in the PW, this membrane treatment could also reject an additional 50% of the remaining acetic acid (Aquatechnology, n. d.), which would reduce the organic content to limits suitable for water reutilization and beneficial reuse (i.e. irrigation, conventional plant operations…).

3.4. Comparison of the different AOP tested

Comparing the different AOPs tested with regard to the percentage of TOC removal, it is worthy to compare the technology efficiency on the basis of the energy consumed for a certain contaminant removal. Electrical energy per order of target compound destruction (EEO) is defined as the electrical energy in kWh required for degradation of a contaminant C by one order of magnitude in a unit
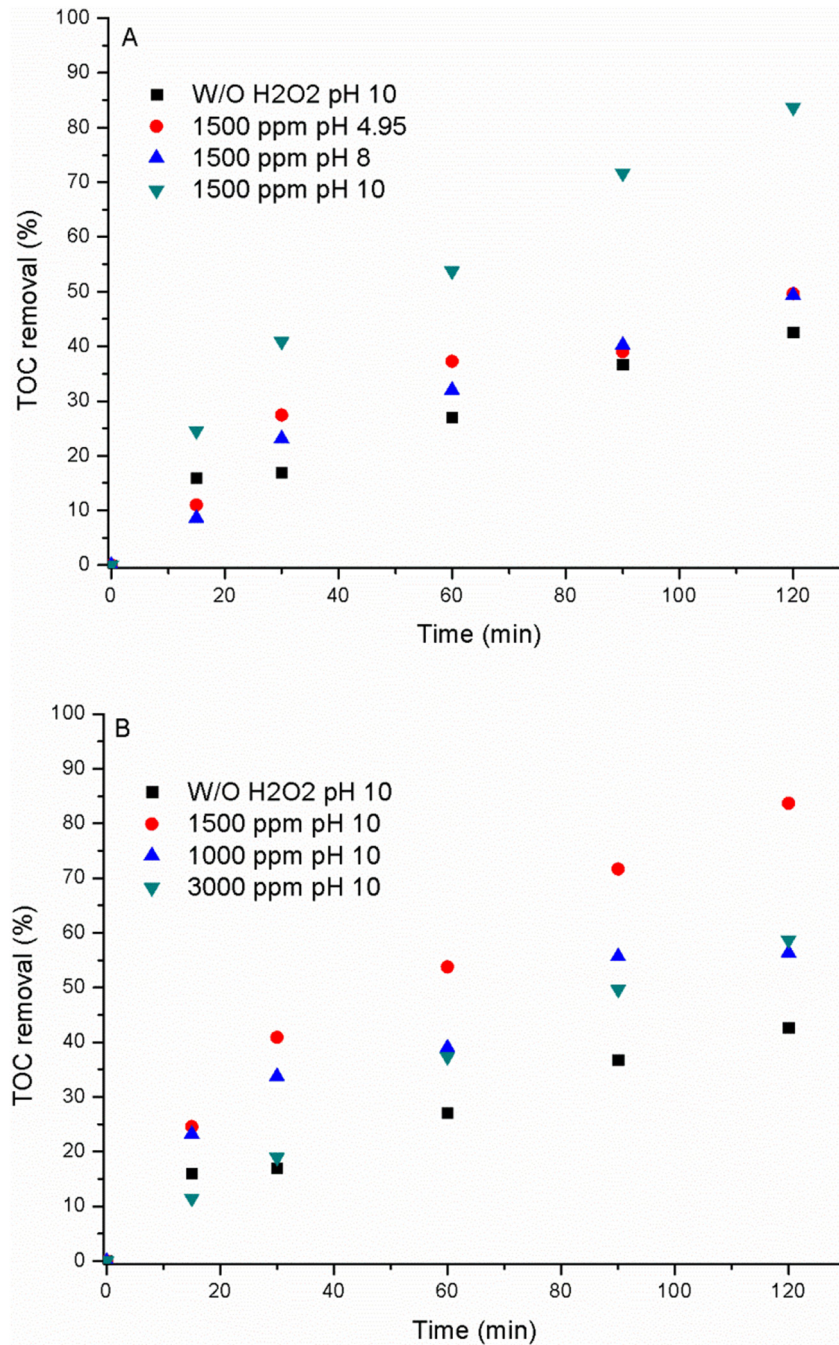
Fig. 5. TOC removal percentage with time during ozonation experiments performed with a production of 4 g h^{-1} O$_3$ at different pH (A) and H$_2$O$_2$ initial concentrations and fixed pH (B).

volume (Bolton et al., 1996). It can be calculated according to [Eq. (1)].

$$\text{EEO} = \frac{P(kW) \cdot t(h) \cdot 1000}{V(L) \cdot \log\left(\frac{C_i}{C_f}\right)} \quad (1)$$

where P is the rated power (kW), V is the volume (L) of water treated in time t (h), and C_i and C_f the initial and final concentration of the target compound (mol·L^{-1}).

Instead of the concentration of a target compound, the different processes will be compared with respect to TOC removal and EEO will be calculated for the best operating conditions of each AOP tested.

The energy consumption at lab scale has been calculated according to the energy consumed by lamps (photochemical processes), stirring, heating (Fenton process) and ozone production (ozonation processes). It has to be taken into account that additional energy demand for the production of catalysts or chemicals is not included in this calculation. Furthermore, it has to be pointed out though that these values may differ significantly from values obtained at industrial scale, since at larger scale e.g. more efficient ozone generator and injection system is used.

Energy consumption for photocatalysis, expressed as KW h, corresponded in this case to the 2 W agitation plate and the 250 W m^{-2} Solarbox Xenon lamp irradiance that was used during 3 h. It has also been taken into account for the energy consumption of the lamp, that 2 experiments can be performed at the same time in the Solarbox. So, for 1 L of PW, the energy consumption corresponding to

the agitation was 0.002 KW × 3 h = 0.006 KW h, and for the lamp: 0.250 KW m^{-2} × 0.086 m^2 × 3 h/ 2 experiments = 0.0323 KW h. The total energy consumption was 0.0383 KW h.

$$EEO\ photocatalysis = \frac{0.0383\ (kW\ h) \cdot 1000}{1(L) \cdot \log\left(\frac{96.16}{80.74}\right)} = 504.57\ KW\ h\ m^{-3}$$

Energy consumption for the photo-Fenton process, expressed as KW h, corresponds to the agitation (0.003 KW h) and the Xenon lamp for 2 experiments that were used during 1.5 h (0.0161 KW h), resulting a 16.4% of TOC removal.

$$EEO\ photo\text{-}Fenton = \frac{0.0191\ (kW\ h) \cdot 1000}{1(L) \cdot \log\left(\frac{92.00}{76.89}\right)} = 245.13\ KW\ h\ m^{-3}$$

For the Fenton reaction at 70 °C the energy corresponds to the plate that consumes 2 W for the agitation (0.004 KW h) and 60 W for heating during 2 h (0.12 KW h).

$$EEO\ Fenton\ 70\ °C = \frac{0.124\ (kW\ h) \cdot 1000}{1(L) \cdot \log\left(\frac{93.68}{75.61}\right)} = 1633.6\ KW\ h\ m^{-3}$$

For the sonoFenton process, the energy corresponds to the agitation (2 W) and the sonicator (45 W) used during 2 h.

$$EEO\ sonoFenton = \frac{0.094\ (kW\ h) \cdot 1000}{1(L) \cdot \log\left(\frac{85}{63}\right)} = 722.64\ KW\ h\ m^{-3}$$

Finally, for the ozonation, 0.004 KW h for the stirring was needed. The generation of 4 g h^{-1} O$_3$ was produced from 50 L h^{-1} O$_2$ (0.143 kg O$_2$ required for 2 h process) and electricity by the ozone generator consumed around 10 kW/Kg O$_3$ according to its manufacturer. Therefore, 10 kW/Kg O$_3$ × 0.004 Kg O$_3$ × 2 h = 0.08 KW h was consumed by the ozone generator. Energy consumption was 0.084 KW h.

$$EEO\ ozonation = \frac{0.084\ (kW\ h) \cdot 1000}{1(L) \cdot \log\left(\frac{88.60}{31.67}\right)} = 188.01$$

As it can be seen, the ozonation with H$_2$O$_2$ at pH 10, besides achieving the highest TOC removal, requires less electrical energy to degrade the TOC compared to other tested AOPs. This is in agreement with findings of Miklos et al. (Miklos et al., 2018), where ozone-based processes were determined to present the lowest energy consumption, and those based on ultrasound and UV-based photocatalysis were considered as not (yet) energy efficient AOPs. In general, obtained values in the present study are high, however it has to be taken into account the scale, and the influence of the water quality, as waters containing higher concentration of radical scavengers will result in higher EEO values. As stated by these authors (Miklos et al., 2018), EEO values should only be calculated when the main operating variables (oxidant demand, reactor geometry, and other process-specific parameters) have been optimized, and if possible estimated based on a full-scale process, as up-scaling enhances energy efficiency.

4. Conclusions

Here, an exploratory study on the treatment of PW using different AOPs such as photocatalysis, Fenton, photo-Fenton, sono-Fenton and ozonation is presented. It had the objective of including one of these processes within an integrated treatment solution for PW polishing.

Despite the fact that in all the AOPs studied in this work BTEX and naphthalene were removed, the efficiency in terms of TOC removal of each treatment varied largely. Among these techniques, photocatalysis was found to be the less effective for the treatment of PW, TOC removals lower than 20% was obtained for the best of the scenarios after 4 h. Besides, several oxidation by-products were detected, and no degradation of acetic acid was produced.

Fenton-based processes resulted slightly more efficient for TOC removal and oxidation of the individual components of the PW. Thus, BTEX, naphthalene and phenol were rapidly eliminated in the first minutes of reaction, but only slight acetic acid removal occurred (<10%) and intermediate compounds were also detected. At 20 °C sono-Fenton resulted more efficient in TOC removal than both photo-Fenton and conventional Fenton; however, the percentage of acetic acid removal was similar in all the cases. Better results were obtained when Fenton was performed at 70 °C in absence of salts, where TOC removals of 40% were observed for ratios H$_2$O$_2$/COD =2.1 and H$_2$O$_2$/Fe = 10. This stated the negative influence of salinity on the tested AOP performance. Despite the fact that these were promising results, optimization should continue, since both the high amount of iron (that will produce significant amounts of sludge, which would have to be subsequently treated) and the temperature needed, would hamper the scale-up of this process.

The highest eliminations were obtained by ozonation combined with H$_2$O$_2$. The optimum result was obtained with 4 g h^{-1} O$_3$ and 1500 mg L^{-1} H$_2$O$_2$ at initial pH 10, where 74% of TOC removal was achieved after 2 h and the acetic acid elimination was 77.8%. For these conditions, all the components in PW were eliminated, including a 70% of the acetic acid content. Besides, H$_2$O$_2$ was consumed during reaction and the final pH of the treated PW was around 8.4 (within the established limits of discharge). Despite the presence of remaining acetic acid after ozonation, this treatment revealed promising results due to the great degree of mineralization achieved. In addition, toxicity was lower for the samples treated with ozone than with the other AOPs. Also, EEO (TOC) for these ozonation conditions was the least value obtained among the AOPs tested. However, ozone and H$_2$O$_2$ doses could still be optimized for larger scale operation. This is the focus of a future study at pilot scale. Besides, if a process of reverse osmosis would be added following ozonation to remove the salts contained in the PW, an additional removal of acetic acid (50%) (Coelho et al., 2006) would be produced, which would reduce the organic content to limits for water reutilization and beneficial reuse (i.e. irrigation, conventional plant operations, etc.).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2019.02.128.

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