



Approaching zero discharge concept in refineries by solar-assisted photo-Fenton and photo-catalysis processes

Hande Demir-Duz^a, Ozgul Ayyildiz^b, Ali Sinan Aktürk^b, Mayra G. Álvarez^a, Sandra Contreras^{a,*}

^a Departament d'Enginyeria Química, Universitat Rovira i Virgili, Av Països Catalans 26, 43007, Tarragona, Spain

^b Türkiye Petrol Rafinerileri A.Ş. Headquarters Güney Mah. Petrol Cad. No: 25, 41790, Körfez, Kocaeli, Turkey

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ABSTRACT

To undertake a better water management in Oil&Gas sector, it is essential to decrease the wastewater generation by increasing the current reused water rates. Focused on this motivation, this study presents the performances of solar-assisted photo-Fenton and heterogeneous photo-catalysis on refinery wastewater treatment for reuse purposes with the aim of zero discharge. While initial tests were made on synthetic refinery wastewater, real case studies were performed with two types of refinery effluent in order to test the feasibility of using AOPs either as a secondary or tertiary treatment. Even though heterogeneous photo-catalysis and a combined process showed promising results for the treatment of the refinery effluents, photo-Fenton treatment revealed a superior effectiveness for application in both secondary and tertiary treatment, considering the improvements on TOC removal, toxicity and biodegradability. Photo-Fenton as secondary treatment resulted as efficient as the biological treatment, reaching final TOC values ca. 20 mg/L and 88% of COD removal presenting values lower than those achieved after the biological treatment. Moreover, a marked increase in the BOD₅/COD ratio from 0.38 to 0.83 was obtained. Furthermore, as a tertiary treatment, photo-Fenton process either with H₂O₂/COD = 10 and H₂O₂/Fe²⁺ = 50 or H₂O₂/COD = 4 and H₂O₂/Fe²⁺ = 10 provided a final TOC value < 4 mg/L. This result reveals the possibility to reuse the effluent in the refinery plant, thus increasing the sustainability.

1. Introduction

Petroleum refinery is one of the industrial activities, which use larger amount of water and consequently produce large amount of wastewater that contains various organic pollutants, from aromatic to aliphatic compounds [1]. Although it has a very important place in the world economy, there are too many concerns for its environmental effects [2,3]. The discharging limits determined by legislations have been decreasing, forcing the industries to develop more effective methods for the removal of these various organic recalcitrant contaminants [4].

On the other hand, depending on the refinery size and process configuration, the amount of produced wastewater is 0.4–1.6 times the amount of processed crude oil [5,6]. Recycling this water for different purposes such as process water, cooling water and fire water after treatment (depending on the quality standards) is a remarkable option to meet the water needs of the plant [7,8]. From this point of view, the treated effluent may play an important role in sustainable management of water resources through decreasing wastewater discharges, which also presents an economical advantage [9].

So far, conventional treatment techniques based on physicochemical, mechanical and biological methods have been used to remove the organic contaminants from wastewater [4]. However, these processes produce concentrated sludge, which requires further operations. Besides, they perform with limited efficiency in case of emulsified oil and small oil droplets [10]. Thus, in recent years, attentions have been directed toward advanced oxidation processes (AOPs), which generate highly reactive oxidants such as hydroxyl radicals, to transform organic compounds by means of oxidation and mineralization into harmless compounds like H₂O, CO₂ and inorganic salts [11,12].

Conventionally, treatment of refinery effluents composes of preliminary, primary and secondary treatments. In the preliminary step, crude solids and substances are removed mechanically. In the primary treatment, API (American Petroleum Institute) oil-water separators and dissolved air flotation (DAF) processes are applied in order to remove free and emulsified oils. As a secondary treatment, biological treatment is applied, which may remove up to 90% of organic materials in the effluent. Although the discharging requirements are reached after secondary treatment, reuse of this treated water can only be possible by removal of some specific compounds [9]. Apart from this, although

* Corresponding author.

E-mail address: sandra.contreras@urv.cat (S. Contreras).

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biological treatment is considered as the most cost-effective technique, the treatment units require large area due to residence time required and the biomass after treatment must be separated by membrane filtration that requires more energy [13,14]. However, this study wants to explore AOPs as an alternative to biological treatment or as an improver to this treatment.

Among the different types of AOPs, photo-Fenton and heterogeneous photo-catalysis processes have been investigated as treatment solutions to petroleum refineries. However, they have been mainly applied to one-component synthetic wastewaters, especially with phenols, and only few of them deal with real refinery wastewaters (RRWs). For photo-Fenton processes, mostly the effects of the Fenton reagent rates, pH and temperature under UV-A/UV-C irradiation sources have been investigated. Mustafa et al. have treated synthetically prepared gas oil contaminated wastewater by photo-Fenton under UV-C irradiation for 150 min. They achieved 72% of COD removal at 30 °C and pH 3 under optimal amounts of H_2O_2 and Fe^{2+} (400 mg/L and 40 mg/L, respectively) [2]. Coelho et al. compared the efficiencies of different AOPs on petroleum refinery sour waters. They observed slightly better DOC removal by Fenton and photo-Fenton processes rather than other AOPs. They achieved 88% of DOC removal by preliminary Fenton (30 min) and photo-Fenton (60 min) with 8 g/L H_2O_2 and 0.8 g/L FeSO_4 [15]. Kavitha et al. also suggested a method to recover the iron used in the treatment in order to use it several times avoiding the production of sludge [16]. However, this kind of multistep recovery processes may be more costly than conventional solid waste management due to some additional processes and energy consumptions. Thus, exploring the advantages of photo-Fenton using the reagents under discharging limits could be worthier than recovery processes. Y.-H. Huang et al. studied the photo-Fenton treatment with low concentration of ferric ions for phenol-contaminated water under UV-A irradiation. A 98% of COD removal was achieved by 120-min photo-Fenton treatment with 5 mg/L Fe^{3+} , revealing that efficient organic removal can also be achieved through the use of few amount of reagents [17].

On the other hand, for heterogeneous photo-catalysis process, some researchers have focused on developing new type of catalysts active especially under visible light. Z. Ghasemi et al. immobilized the TiO_2 nanocrystals into the structure of Fe-ZSM-5 zeolite by sol-gel method and achieved 80% of COD removal from a petroleum refinery wastewater collected before DAF. The treatment took place during 240 min at pH 4 [18]. R.-C. Wang et al. also explored the phenol removal with visible-light photo-catalysis and sonolysis using $\text{ZnFe}_2\text{O}_4/\text{TiO}_2$ -immobilized granular activated carbon. Despite the degradation of organics reached a maximum of 84% after 240-min treatment, the reuse of the catalyst decreased the degradation performance [19].

Degussa P25 is a well-known semiconductor, with applications in air purification, solar energy conversion, and wastewater treatment [20], where huge number of studies report its high efficiency as photocatalyst. This may be due to the high surface area and the mixed anatase and rutile crystal structure, and due to these properties, P25 was selected in this study for reclamation of wastewater in refineries.

This study is focused on finding a feasible solution for a refinery located in Turkey to minimize the fresh water requirement by reuse and recycle of treated effluent with solar AOPs avoiding massive use of reagents, limiting energy consumption and favoring its implementation in a present plant with minor changes. For this, our approach entails the use of solar energy in either heterogeneous photo-catalysis or photo-Fenton processes (or a combination of both) as wastewater polishing treatment, using minimum catalyst amounts and reactants below the discharging limits. This limit for iron is 10 mg/L for 2-hour composite sample and 8 mg/L for 24-hour composite sample for hydrocarbon production facilities such as petroleum refineries in Turkey. Moreover, the limit for COD is 300 mg/L and 250 mg/L, and that for hydrocarbons is 15 mg/L and 10 mg/L for 2-hour and 24-hour composite sample, respectively. Composite sample is defined as a method that several samples are collected periodically in the same sample bottle before the

measurement to represent all process during 2 h or 24 h.)

Unlike the studies focused on reduction of the catalyst amounts, this study portrays the initial optimization attempts of solar-assisted processes on a multicomponent synthetic wastewater and then the corresponded real case optimizations for the two different effluent type in the refinery to find the best AOP position to be settled. TOC and COD removal efficiencies, water compositions, BOD and toxicity analyses were performed to establish whether these AOPs are more advantageous as a secondary or tertiary treatment.

Furthermore, this study is focused on the basis of a zero-discharge approach through both reducing the amount of generated wastes, and reducing fresh water consumption through reuse of the treated water in the different refinery operations. For the reuse purposes, it is essential to maintain the TOC content below 15 mg/L and 4 mg/L for firewater and cooling water, respectively. Therefore, TOC removal results were followed closely in this study for the assessment of initial sustainability objective.

2. Experimental

2.1. Materials

Toluene (Sigma-Aldrich, 99.5%), phenol (Sigma-Aldrich, 99–100%), o-cresol (Sigma-Aldrich, 99%), nonane (Sigma-Aldrich, 99%), hexadecane (Sigma-Aldrich, 99%), naphthalene (Acros Organic, 99%) and xylene (Panreac, 98%) were used in the preparation of synthetic refinery wastewater (SRW) as the organic representatives of the real refinery wastewater (RRW). Ammonium chloride, sodium bicarbonate (Sigma-Aldrich, 99.9%) and sodium chloride (Fluka, 99.5%) were used as inorganic representatives of the RRW. Triton™ X-100 (Sigma-Aldrich) were used as a surfactant in order to emulsify nonane, hexadecane and naphthalene, which are almost non-soluble in water. Sulfuric acid and sodium hydroxide solutions were used to adjust pH.

H_2O_2 (Acros Organic, 35 wt%), $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (Panreac, 99%), sodium bisulfite solution (Sigma-Aldrich, 40%) and TiO_2 , Aeroxide® P25 (Acros Organics, nanopowder form, 25 nm average diameter, particle size < 100 µm) were used in Fenton, photo-Fenton, and photocatalysis experiments. Dichloromethane (DCM, Sigma-Aldrich, 99.5%), acetonitrile (ACN, Riedel-de Haën, 99.9%) and phosphoric acid (Sigma-Aldrich, 85%) were used for analytical procedures.

The real wastewaters before and after secondary biological treatment have been supplied from a petroleum refinery which is located in Turkey to examine the performance of the processes on real cases.

2.2. SRW preparation and water properties

Seven representatives of aromatic and aliphatic hydrocarbons that are frequently detected in refinery wastewater were selected as target contaminants to investigate their removal efficiency by photo-assisted AOPs. The composition of SRW was selected according to previous researches conducted with RRWs and is given in Table 1 [6,15,21–24]. The SRW preparation procedure started by the addition of 5 mg Triton-x and the required amounts of salts and non-soluble components into 900 mL distilled water, then followed by the emulsification step with a homogenizer at 7000 rpm during 30 min. Salts were added before emulsification due to their positive effect on decreasing interfacial

Table 1
Composition of SRW.

Component	Conc (mg/L)	Component	Conc (mg/L)
Toluene	10	Naphthalene	10
Nonane	10	Hexadecane	10
Phenol	10	Ammonium Chloride	70
o-Cresol	20	Sodium Chloride	247
Xylene	10	Sodium bicarbonate	160

Table 2
Characterization of wastewaters used in the present study.

Water characteristics used in the experiments							
	TOC (mg C/L)	COD (mg O ₂ /L)	pH	Cl [−] (mg/L)	NH ₄ (mg/L)	HCO ₃ (mg/L)	
SRW	68	236	8.00	196	24	116	
RRW1	130	450	8.78				
RRW2	17	40	6.72				
3 Months average characteristics of RRW							
	Suspended Solid (mg/L)	Oil & Grease (mg/L)	COD (mg O ₂ /L)	TOC (mg C/L)	BOD	Conductivity (μS/cm)	pH
RRW1	25.6	32.1	476.8	111.3	181.2	1804.8	8.5
SD*	8	18.3	142.5	66.1	52.4	934.6	0.5
RRW2	43.3	22.6	108.2	39.3	38.5	3396.7	7.1
SD**	11.1	1.4	22.7	27.2	6.6	1694.7	0.2
	HCO ₃ (mg CaCO ₃ /L)	Zn (μg/L)	Cl [−] (mg/L)	NH ₄ (mg/L)	Mn (μg/L)	SO ₄ (mg/L)	Fe (mg/L)
RRW1	156.8	229	183.7	23.2	105.9	288.9	0.6
SD*	42.6	207.4	100.6	13.5	15.2	104	0.5
RRW2	78.3	228.3	309.2	10	164.1	408.5	0.6
SD**	30.9	134.9	289.5	6.1	74.1	41.9	0.5

SD*: Standard deviations of the analyses performed with RRW1.

SD**: Standard deviations of the analyses performed with RRW2.

tension between oil and surfactant solution [25]. Afterwards, the required amounts of soluble organic components were added into the mixture under continuously stirring at 450 rpm with a magnetic stirrer. Finally, the solution was completed into 1000 mL with distilled water and stirred 30 min more to ensure a stable wastewater before using in the experiments.

RRW1 was collected after primary treatment process before biological treatment and it is composed mostly of phenols and derivatives, as well as BTEX, naphthalene and derivatives and C14–C19 alkanes. On the other hand, RRW2 collected after biological treatment process contained mainly C11–C16 alkanes. The effluents were kept in the fridge at 4 °C before the experiments. A characterization (such as COD, BOD, suspended solid, the concentration of metals and trace elements) of the real wastewaters (3-month average values) was performed and compared to those of SRW in order to explain the possible performance differences (see Table 2).

2.3. Treatment procedures

Solar light was simulated by a solar box equipped with an air-cooled 1500-W Xenon lamp, which allows 300–800 nm wavelengths to pass through (ATLAS, SUNTEST CPS+). Irradiance was set to 250 W/m².

SRW and RRW2 (300 mL) were treated only by photo-Fenton and heterogeneous photo-catalysis while RRW1 was also treated by the combination of these two methods. The mean reaction temperature during the reactions in solar box was 35 °C. All the experiments were performed by duplicate.

Furthermore, Fenton treatment was also applied to confirm the efficiency of the light activity for both SRW and RRW1–2 with the H₂O₂/COD weight ratio (w/w) of 2 and H₂O₂/Fe²⁺ weight ratio (w/w) of 10 at pH 3 and at 35 °C.

2.3.1. Photo-Fenton

Photo-Fenton experiments were carried out during 90 min at pH 3, which was found to be optimum pH for Fenton process [26–28]. The H₂O₂/COD ratio (w/w) ranged from 1 to 10 while the H₂O₂/Fe²⁺ ratio (w/w) was between 5 and 100. Before the experiments, pH of the wastewaters was adjusted around 4 to make the iron species soluble. Then, the required amount of FeSO₄·7H₂O was added. Afterwards, the

reaction has been started by addition of H₂O₂ under continuous stirring and pH was adjusted to 3, immediately. Samples were collected at specific intervals during the reaction for analyses and checked with semi-quantitative H₂O₂ strips to determine its remaining concentration in the samples. In case of containing H₂O₂, sodium bisulfite has been used to quench the reaction in the samples.

For the RRW treatments the duration enlarged up to 180 min depending on the degradation rates and H₂O₂ concentrations of the intermediate samples.

2.3.2. Heterogeneous photo-catalysis

Heterogeneous photo-catalysis experiments have been firstly performed at free pH during 360 min with TiO₂ catalyst concentrations of 100, 250 and 500 mg/L. All experiments have been started with 30-min adsorption step under dark condition. This duration has been decided according to the results of 60-min adsorption tests of the catalyst. In addition, the pH effect between 3 and 8 has been examined with 250 mg/L catalyst.

The samples collected during the experiments were centrifuged during 10 min at 5000 rpm before the analytical procedures.

2.3.3. Photo-Fenton/photo-catalysis combination

RRW1 was exposed to the combination of these two processes either subsequently or at the same time in order to evaluate the performance of these systems either separately or together. In “one after the other” concept, 360-min photo-catalysis with 500 mg/L TiO₂ has been employed after 180-min photo-Fenton treatment with a H₂O₂/COD ratio (w/w) of 4 and a H₂O₂/Fe²⁺ ratio (w/w) of 100. Before adding the catalyst, pH was increased to 7. In the case of synchronous mode, firstly the pH of the water has been adjusted around 4. Afterwards, 100 mg/L TiO₂ has been added into the water in order to perform adsorption procedure before the addition of Fenton reagents. Subsequent to 30-min adsorption, Fenton reagents have been added to the reaction medium and pH has been adjusted to 3, immediately. Reactions took place during 90 min under solar light.

2.4. Characterization

Total organic carbon (TOC) analyses were performed with a

Shimadzu TOC-L (CSN 638-91109-48) analyzer to evaluate the mineralization degree during experiments.

Chemical oxygen demand (COD) analysis was performed by colorimetric method with AQUALYTIC® Tube Tests COD Vario.

The biological oxygen demand (BOD₅) was measured using respirometric method with a Velp equipment (VELP Scientifica). Polyseed® was used as the microbial culture source.

Microtox® acute toxicity testing was performed with *Vibrio Fischeri* according to the 81.9% basic test protocol with 9 dilutions from Microtox Omni Software during 15 min using a Microtox® Model 500 Analyzer that is a laboratory-based, temperature-controlled, self-calibrating luminometer used for measuring acute toxicity. The results were expressed by EC50 value, which was defined as the effective nominal concentration of treated wastewaters by volume percent that caused reduction in the intensity of light emission by 50%.

Before the BOD₅ and toxicity analyses, the pH of the samples were adjusted into 6–8 range and filtered. For the purpose of better comparison between the treatment methods, all analyses results have been examined and compared for the 90-min-sample of the treatments.

Qualitative and quantitative analyses of the samples were performed by GC–MS and HPLC combined with a diode array detector (DAD). Before GC–MS analysis, samples have been extracted by dichloromethane (DCM). The extraction and analyses procedures are given in the supplementary information.

3. Results & discussion

3.1. SRW (synthetic refinery wastewater)

In photo-Fenton experiments, the TOC removal ranged from 72 to 81%, the best TOC removal being achieved for a H₂O₂/COD ratio of 2 and a H₂O₂/Fe²⁺ ratio of 50. This result may be considered as the first proof of concept approach to the zero-discharge philosophy, since only less than 10 mg/L Fe²⁺ was necessary to reach more than 80% of mineralization in 90 min. Fig. 1a and b show the results with a fixed H₂O₂/COD ratio of 2 and a variable H₂O₂/Fe²⁺ ratio, and a fixed H₂O₂/Fe²⁺ ratio of 50 and varying H₂O₂/COD ratio, respectively. The importance of finding an optimum H₂O₂ and Fe²⁺ ratio has been highlighted, similarly to that found in many studies related to Fenton reactions. Thus, at a fixed H₂O₂/COD = 2, an increase in the iron concentration did not enhance the efficiency of the oxidation reaction, in terms of TOC removal (Fig. 1a). Furthermore, the mineralization of organic matter increased with the decreasing Fe concentration. This is often attributed to the competitive reactions of H₂O₂ with the excessive

Fe²⁺ ions to form Fe³⁺, which leads to lower degradation rates [3,29]. On the other hand, it was found that the optimal H₂O₂ concentration corresponded to a ratio H₂O₂/COD = 2 with a H₂O₂/Fe²⁺ ratio of 50 (Fig. 1b).

According to GC–MS results (Fig. S1), the oxidation of BTEX, phenols and naphthalene has been observed after 90 min of treatment. Whereas, some part of alkanes (nonane and hexadecane) still remained. This result was confirmed by HPLC analysis (Fig. S2), which showed the abatement of the aromatic components and appearance of some acids and other by-products at retention times between 2–5 min. These products may be tentatively small chain organic acids such as formic acid, acetic acid, benzoic acid, maleic acid and oxalic acid [17,30,31], however they could not be defined specifically. On the other hand, although hexadecane and nonane after GC–MS analyses presented almost the totality of the components in the sample (ca. 96% in area basis), traces of xylene, o-cresol and ketones were also detected after photo-Fenton treatment.

The recalcitrant properties of the alkanes are due to the absence of electron pairs in these saturated molecules with no low energy empty π orbitals and no high energy filled n orbitals. The oxidation of the alkanes by hydroxyl radicals takes place by abstraction of a hydrogen atom to form water, presenting k_2 values between 10^6 – 10^8 M⁻¹s⁻¹, while that of aromatic components takes place by the hydroxylation or electrophilic addition with k_2 values between 10^8 – 10^{10} M⁻¹s⁻¹. Hence, oxidation of that saturated molecules need very reactive reagents or very extreme reaction conditions [32,33].

In the case of heterogeneous photo-catalysis, the best result achieved was around 80% of TOC removal after 360-min reaction at pH 8. This result was obtained with 250 mg/L of TiO₂ catalyst, and an increase of catalyst to 500 mg/L did not lead to an increase of TOC removal (81%) (Fig. 1c).

The pH effect was also examined with 250 mg/L of catalyst. The results (Fig. 1d) highlight the influence of the pH of the reaction medium on the degradation rates. At pH 3, the degradation decreased remarkably compared to pH 5, where a 91% of TOC removal could be achieved. Increasing pH to 8 also led to a decrease in the degradation efficiency of P25, which indicates that the overall degradation is favored at pH near to the zero charge point of TiO₂ (at pH 6.25). The composition of the waters treated in this study is complex, containing both polar and apolar compounds that can interact in different forms with the catalyst surface. Therefore, 60-min adsorption tests with SRW at pH 3, 5 and 8 using 250 mg/L TiO₂ revealed a higher adsorption at acidic pH (slightly higher at pH 5) than at basic pH. The adsorption capacities were 26%, 29% and 10% for the pH 3, 5 and 8, respectively.

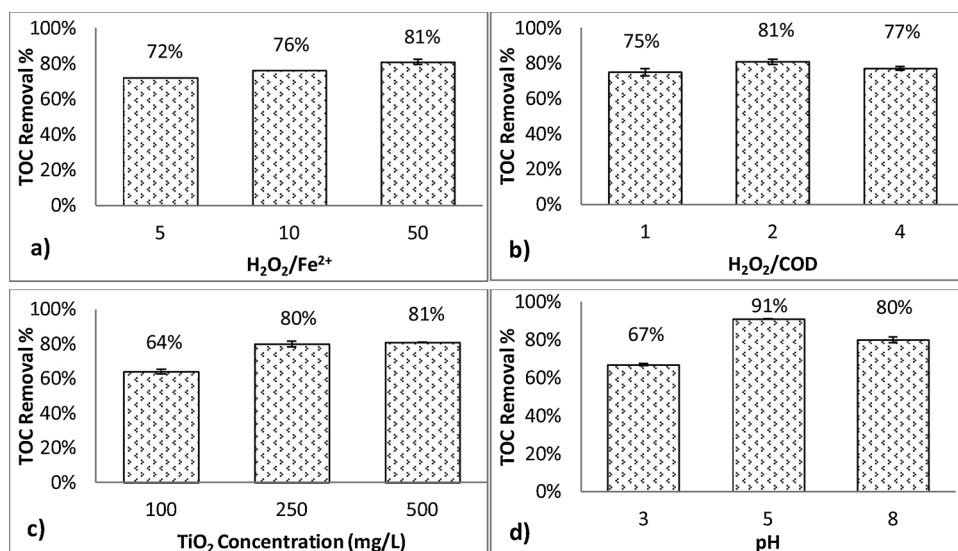


Fig. 1. TOC removals after 90-min Photo-Fenton experiments at pH 3 a) at a constant H₂O₂/COD ratio of 2 with different amounts of Fe²⁺, b) at a constant H₂O₂/Fe²⁺ ratio of 50 with different amounts of H₂O₂; TOC removals by photo-catalysis with TiO₂ after 360 min: c) effect of catalyst amount; d) effect of pH for treatment by 250 mg/L catalyst.

The protonated surface of the TiO_2 at acidic pH (pH 3 and 5) favor the adsorption of phenolic compounds and substituted aromatics. Thus, it seems reasonable that a better adsorption can lead to a better photo-catalytic performance. Oturan et al. also underlined the crucial role of the pH on the efficiency of photo-catalysis that has to be optimized primarily [28]. However, other factors such as the presence of anions in solution or the number of hydroxyl groups and defects on the catalyst surface may also play a role on the degradation performance, and their influence is still under debate. Additionally, the positive effect of UV light exposure of TiO_2 nanoparticles in acidic medium can be the other reason of this enhancement. In acidic medium, when the electrons and holes are generated, the electrons react with oxygen molecules, which produce superoxide radical anions. Instead, the holes react with water producing hydroxyl radicals. Thus, two different reactive species can decompose the organic contaminants improving the treatment efficiency [34].

GC–MS analysis (Fig. S3) showed that, even if some oxidation by-products are produced after 90-min treatment (eg. phenolic compounds from phenol and o-cresol, naphthalene, C9 to C16 alkanes, aldehydes, ketones and BTEX), these compounds were mostly removed after 360 min. A 91% of TOC removal was achieved after treatment, and the remained 9% is formed by C14–16 alkanes, alcohols and ketones (as identified by GC–MS) and carboxylic acids (detected by HPLC, Fig. S4). In addition, nonane was not detected after treatment by heterogeneous photo-catalysis in contrast to photo-Fenton treatments.

Toxicity analyses of the initial sample gave an EC_{50} value of 3%. After photo-catalysis treatment (90 min) with 250 mg/L TiO_2 at pH 3, 5 and 8, the EC_{50} values obtained were 7%, 17% and 10%, respectively. Therefore, toxicity was only slightly decreased by photo-catalysis. However, for 90-min photo-Fenton experiments, samples have been mostly found to be non-toxic, and the highest effect on bioluminescence observed was 9%, 15% and 39% for the $\text{H}_2\text{O}_2/\text{COD}$ ratio of 2, 1 and 4, respectively. Thus, photo-Fenton process showed to be more efficient than heterogeneous photo-catalysis in decreasing the initial toxicity of the SRW after 90-min treatments. This may be due to the presence of residual toxic intermediates after 90-min photo-catalytic treatment, such as phenol and phenolic derivatives [35], which were only able to be decomposed after longer period of treatment by photo-catalysis with TiO_2 .

After these promising degradation results obtained with the SRW, these processes have been applied to RRWs to make comparisons and improvements for real samples. The possible application of AOPs as either a secondary treatment or a tertiary treatment has been considered. The optimum conditions obtained with SRW has been taken as the reference for the starting points of RWW treatments.

3.2. RRW1 (Real Refinery Wastewater after DAF treatment)

An initial photo-Fenton test with the $\text{H}_2\text{O}_2/\text{COD}$ ratio of 2 and the $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio of 50 resulted in a 58% of TOC removal after 90-min treatment. Total consumption of H_2O_2 has been observed at the end of 90-min treatment. When a new addition of H_2O_2 was done after this time, the degradation of organics increased to 74% after 90 min more treatment. This result showed that the treatment of RRW1 needed more H_2O_2 reagent than that of SRW. This could be because of the composition of the water, which includes transition metals such as manganese (Mn) that acts as H_2O_2 scavenger [36,37].

After these initial observations, new experiments were conducted for 180 min to ensure a total H_2O_2 consumption without quenching with sodium bisulfite. As it is shown in Fig. 2, when the $\text{H}_2\text{O}_2/\text{COD}$ ratio was kept at 4, TOC removal increased from 68% to 74% after 180 min of treatment with the increasing $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio from 10 to 100. In that case the required amount of Fe^{2+} significantly decreased from 180 mg/L to 18 mg/L. Besides that, with excessive amounts of H_2O_2 as in the case of $\text{H}_2\text{O}_2/\text{COD}$ ratio of 10 and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio of 50, where the required amount of Fe^{2+} was 90 mg/L, the degradation

completed at 90 min with the result of 75% TOC removal and with 150–300 mg/L residual H_2O_2 content. After the completion of 180 min, the degradation percentage did not change even though the remained H_2O_2 was consumed completely. Hence, it can be concluded that it is possible to remove the same amount of TOC either by 90-min photo-Fenton treatment with high amounts of reagents or by 180-min treatment with very less amounts of reagents. Aljuboury et al. also evaluated the performance of solar-photo-Fenton treatment on a real petroleum refinery effluent with initial TOC value of 220–265 and, they achieved max. 59.3% of TOC removal with 60 mg/L Fe^{2+} and 850 mg/L H_2O_2 after 127 min of reaction time, which were the optimum conditions determined by an experimental design [38].

For the heterogeneous photo-catalysis experiments, 26%, 27% and 30% of TOC removals have been achieved with the 100, 250 and 500 mg/L TiO_2 , respectively. In comparison to SRW results, the mineralization by heterogeneous photo-catalysis was rather lower. This behavior difference may be explained by the high turbidity presented in RRW1 which blocks the light transmission [39]. On the other hand, since the maximum TOC removal achieved by photo-Fenton was 75%, a 360-min photo-catalysis experiment was performed with 500 mg/L TiO_2 subsequent to 180-min photo-Fenton with the $\text{H}_2\text{O}_2/\text{COD}$ ratio of 4 and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio of 100. Total TOC removal after 180-min photo-Fenton/360-min photo-catalysis resulted in 90%. Although 74% of mineralization has been achieved during photo-Fenton step, photo-catalysis step mineralized the 63% of remained part, which also confirmed the turbidity effect. A decrease in the turbidity during photo-Fenton step might have increased the efficiency of the TiO_2 -photo-catalysis step, which resulted in 63% rather than 30% achieved by only heterogeneous photo-catalysis. In addition, the difference between initial compositions before and after photo-Fenton may be another reason for the improvement of photo-catalysis with TiO_2 .

As photo-Fenton decreased the turbidity and heterogeneous photo-catalysis resulted in an efficient method in waters with low turbidity, the possible synergetic effect of the synchronized combination of both treatments was examined to shorten the reaction time. When $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio were kept at 100, 71%, 79% and 84% of TOC removal was achieved with the $\text{H}_2\text{O}_2/\text{COD}$ ratio of 2, 4 and 10, respectively after 90 min treatment in the presence of 100 mg/L of TiO_2 , which improved the degradation rate achieved by only photo-Fenton (75%). COD removal rates resulted in 85% and 88% for the $\text{H}_2\text{O}_2/\text{COD}$ ratio of 4 and 10, respectively ($\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio were 100 and TiO_2 concentration was 100 mg/L.). The synergetic effect of the combined procedure has also studied by Aljuboury et al, on a real petroleum effluent with an initial TOC value of 243 mg/L. They achieved max. 62% of TOC removal with 660 mg/L TiO_2 , 500 mg/L H_2O_2 and 10 mg/L Fe^{2+} [40].

Furthermore, GC–MS and HPLC results (Figs. S5 and S6), also confirmed the removal of the main products, mostly composed of phenolic components, BTEX and C11–19 alkanes, and formation of some by-products (presumable short chain organic acids) after 90-min combined treatment. In addition, small amount of C12–C16 alkanes, some alcohols and organosulfur compounds have been detected after treatment. Again, alkanes have presented resistance to these oxidation processes. Even though the molecule sizes of the alkanes got smaller by breaking the chains, they were found not to be completely degradable.

Toxicity analyses performed with RRW1 confirmed the trend observed with SRW, and photo-Fenton process showed to be more efficient in reducing the associated toxicity. After 90-min photo-Fenton treatment with a $\text{H}_2\text{O}_2/\text{COD}$ ratio of 2 and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ ratio of 100, the effluent produced presented an EC_{50} value of 70% in contrast to the initial value of 1%. However, the effluent produced by photo-catalysis at pH 5 with 250 mg/L TiO_2 showed high toxicity, whose EC_{50} value was 1%. This was because of the poor oxidation efficiency of TiO_2 -photo-catalysis on RRW1. In case of the combined treatment, the synergy observed with respect to the TOC removal was also noticed with regards to toxicity. In the effluent obtained after 90-min combined treatment with the $\text{H}_2\text{O}_2/\text{COD}$ ratio of 2, and the $\text{H}_2\text{O}_2/\text{Fe}$ ratio of 100

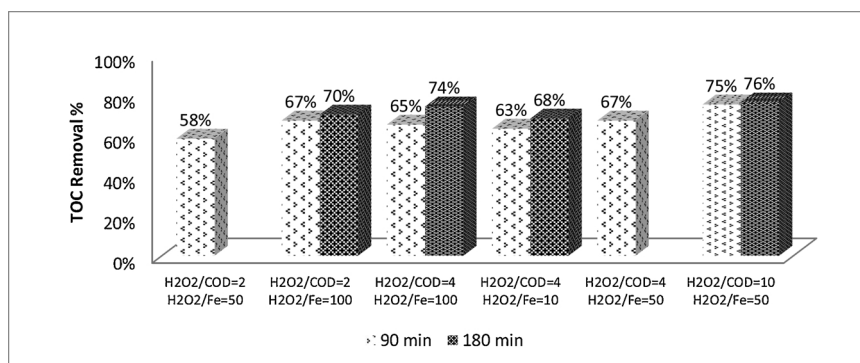


Fig. 2. TOC removal rates in RRW1 by photo-Fenton depending on the reagent ratios and time.

in the presence of 100 mg/L TiO₂, the EC50 value was increased to 82%, while that of H₂O₂/COD = 4 (other parameters were kept constant) presented only highest effect of 39% on bioluminescence (maximum reduction in the intensity of light emission, which did not reach to 50%).

Therefore, photo-Fenton could be applied to the real refinery wastewater after primary treatment as an alternative to a biological process, as similar final TOC values are achieved. In the case of photo-Fenton (using only 9 mg/L Fe²⁺) the final TOC reached up to 24 mg/L, while the TOC after biological treatment was 17 mg/L. Furthermore, the advantages would be a lower COD content of the effluent compared to the one after biological treatment and the non-toxic properties after the treatment, thanks especially to the removal of the aromatic fractions, which are much more toxic than the aliphatic compounds.

Photo-assisted processes can also be applied after the primary treatment to improve the biodegradability, in case that a subsequent biological process is applied. To monitor this property, BOD₅/COD ratios were measured after the different operating conditions tested, revealing that the photo-Fenton process with a H₂O₂/COD ratio of 2 and a H₂O₂/Fe²⁺ ratio of 50 improved greatly the BOD₅/COD ratio, reaching a value of 0.83 after 90 min of treatment, which was 0.38 initially. Generally, BOD₅/COD ≥ 0.4 is considered as highly biodegradable [41].

3.3. RRW2 (Real Refinery Wastewater after biological treatment)

With the idea of having good quality effluents to reuse in the plant, the application of AOPs as tertiary treatment was also considered. From this point of view, despite the low initial TOC concentration of RRW2 (17 mg/L), this concentration was decreased to less than 4 mg/L and 1 mg/L by photo-Fenton and heterogeneous photo-catalysis, respectively. This represents values far below the limit of discharge and makes the process especially attractive for water reuse purposes.

A 78% of mineralization was achieved after 180-min photo-Fenton

treatment either with H₂O₂/COD = 10 and H₂O₂/Fe = 50 or H₂O₂/COD = 4 and H₂O₂/Fe = 10 (Fig. 3), which resulted in less than 4 mg/L of TOC value. In the former case, the concentration of ferrous ion used was 8 mg/L, while the concentration in the second case was 16 mg/L.

Under dark conditions, Fenton experiments conducted with H₂O₂/COD = 2 and H₂O₂/Fe = 10 at pH 3 at 35 °C led to a 19% of TOC removal, while removal at room temperature was only 3%. Here, the positive effect of the light assisted Fenton process might be emphasized. Moreover, although the removal efficiency of the Fenton process over the photo-Fenton was a significantly lower, within the Fenton treatment, increasing temperature led to an increase in the reaction efficiency. This effect may be attributed to the higher generation of hydroxyl radicals due to the increase in the concentration of Fe(OH)²⁺ by elevated temperature [42]. However, the different activation energy between the organics and the hydroxyl radicals may demonstrate different behavior, which results in efficiency or inefficiency of the temperature on the treatment system [43].

Photo-catalysis experiments conducted during 360 min with 100, 250 and 500 mg/L TiO₂ at pH free (pH 6.72) resulted in 33%, 70% and 73% of mineralization, respectively. However, here the positive effect of acidic pH has been emphasized again, which was explained previously. The same treatment with 500 mg/L at pH 5 resulted in 92% TOC removal, where the final TOC value was less than 1 mg/L and the COD value was below the detection limit.

According to the GC–MS analysis, the main components detected in the raw wastewater were C11–C16 alkanes. This composition is also similar to the RRW1 after treatment that is presented in the section 3.3. Although the concentrations of alkanes were decreased after the treatment of RRW2, some small amount of C11–C16 alkanes, such as pentadecane and hexadecane were detected.

Toxicity analyses were performed in that sample treated by TiO₂-photo-catalysis at pH 5, which was found to be the optimum pH in this study. The results showed that EC50 value was 42% for the treatment with 100 mg/L catalyst. On the other hand, for the catalysts amounts of

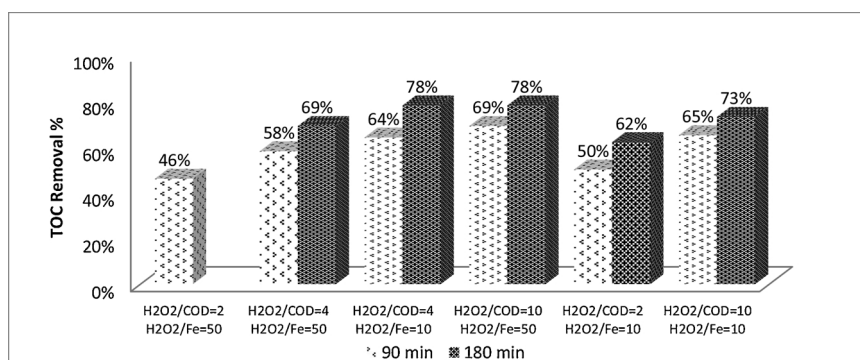


Fig. 3. TOC removal rates in RRW2 by photo-Fenton depending on the reagent ratios and time.

250 mg/L and 500 mg/L, the samples after treatment was mostly non-toxic and the maximum effect of these samples was found to be 24% and 42% for the amounts of 250 mg/L and 500 mg/L, respectively. However, initial RRW2 was already non-toxic with a maximum effect of 28%. Here, the non-toxic properties of the water were maintained while the quality of the effluent was increased for reuse purposes.

3.4. Impact of the tested technologies

As mentioned in section 1, the amount of produced wastewater is 0.4–1.6 times the amount of processed crude oil. 40–45% of this water requirement used in cooling towers and steam generation units. The other part is mostly used for other purposes such as processing units or firewater [44]. However, in a typical refinery, fresh water is used for different purposes such as process water, boiler and cooling water, firewater, tap water and utility water systems [8].

Even though every application within the refinery presents different water requirements, for the main applications needed, it is essential to maintain the TOC content below 15 mg/L and 4 mg/L for firewater and cooling water, respectively. Besides that, pH and conductivity values, oil, total suspended solid (TSS) and chloride contents are other criterions that must be controlled for firewater, while the hardness and alkalinity are additional criterions for cooling water.

According to the obtained results of this study, AOPs as the tertiary treatment (on RRW2) may allow to obtain water of the requested quality to be reused as fire water or cooling water either after 360-min photo-catalysis with 250 mg/L and 500 mg/L TiO_2 that reduced the TOC value under 4 and 1 mg/L, respectively, or after 180-min photo-Fenton with 8 mg/L ferrous ion, which resulted in a TOC value of 3 mg/L. Here, in the case of cooling water reuse, precipitated ferrous ion has to be managed since it is higher than the requirements for cooling water, although it is lower than the discharging limits. Besides that, although AOPs as secondary treatment (on RRW1) was not sufficient to reach reuse aims by itself, it may be useful to reduce reaction time and waste production compared to biological treatment, achieving similar final TOC values and enhanced biodegradability.

4. Conclusions

In this work, high efficiencies of solar-light assisted photo-Fenton and photo-catalysis treatments on SRW have been revealed. However, when considering real effluents with different characteristics and, economic and environmental limitations, photo-Fenton process under solar light presented the best performance either as pre-treatment or post-treatment.

In case of the photo-Fenton application as pre-treatment to a biological treatment, improved biodegradability and toxicity has been highlighted. As a matter of fact, it could be an alternative to a biological treatment with a very similar final TOC value and lower COD content compared to the effluent obtained after biological treatment.

On the other hand, considering photo-Fenton as a post-treatment after a biological treatment, especially the final TOC and COD values achieved meet the water requirements to be reused in the refinery. In case of providing other water properties such as conductivity and hardness, these effluents can be a good candidate to compensate the cooling water and firewater requirements of the refinery. However, although the final iron content is not a problem for reuse issues as firewater, it is an obstacle to handle previously in case of reusing as cooling water. In that case, detailed economic and environmental analysis should be performed to evaluate the possible problems and their solutions such as the management of 8 mg/L iron as a solid waste and the possibility of recovering this iron for reuse purposes.

Depending on the water consumption and required properties of the process units, reducing discharges significantly by reusing and recycling the effluents produced could be possible by a photo-Fenton treatment while reducing the required energy by means of the solar light.

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This Special Issue is dedicated to honor the retirement of Prof. César Pulgarin at the Swiss Federal Institute of Technology (EPFL, Switzerland), a key figure in the area of Catalytic Advanced Oxidation Processes.

Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.apcatb.2019.02.026>.

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