Reuse and Recycle Solutions in Refineries by Ozone-Based Advanced Oxidation Processes: A Statistical Approach

H. Demir-Duz[a], A. S. Aktürk[b], O. Ayyildiz[b], M. G. Álvarez[a*], S. Contreras[a*]

[a]Departamentd'EnginyeriaQuímica, Universitat Rovira i Virgili, AvPaïsosCatalans 26, 43007, Tarragona, Spain
[b]TürkiyePetrolRafinerileri A.Ş. HeadquartersGüneyMah. PetrolCad. No:25 41790, Körfez, Kocaeli, Turkey

Corresponding authors: sandra.contreras@urv.cat; mayra.garcia@urv.cat

Abstract

Fresh water sources are under pressure globally by the increasing population and consequently increasing production, which increases the water demand day by day. Thus, decreasing the industrial fresh water demand and wastewater production became crucial both for the water availability in the future and for its impact to the environment. This study examined the ozone-based treatments as the possible solution to a refinery to treat the effluent already treated by the traditional techniques to reach the final requirements for reuse and recycle purposes. Based on the screening tests performed by fractional factorial design revealed that the significant parameters for the treatment were ozone feed ratio, H_2O_2 amount and processing time while pH was found insignificant for this case. Based on the box-Behnken response surface methodology for effluent collected after biological treatment, the significant parameters were optimized as the ozone ratio of 0.9 g/h, H_2O_2 amount of 47 mg/L and 60 min duration. However, in case of increasing the H_2O_2 amount to 80 mg/L the duration can be minimized to 37.5 min decreasing the energy and reagent consumption costs by a 37%, reaching a final total organic carbon (TOC)under 4 mg/L, that is the target for reuse possibilities.

Keywords: Ozone/H_2O_2; refinery wastewater; sustainability; AOPs; experimental design

1. Introduction

Water scarcity is a worldwide issue even for the countries with significant source of water (Dias et al., 2012). For many industries, economic and environmental impact of the wastewater forms a driving force to find sustainable solutions for its management in terms of the hazard to the environment, especially to the human and animal health (Boczkaj and Fernandes, 2017; Escudero et al., 2017). Petroleum industry is one of those industries that produce significant amount of wastewater, which is sometimes more than the amount of processed crude oil depending on the configuration of the plant and the type of crude oil (El-Naas et al., 2014; Mota et al., 2008).

Petroleum downstream industry composes of a series of separation and treatment steps that process thousands of barrels of crude oil per day into valuable products grouped as light, middle and heavy distillates (i.e. petroleum gas, gasoline, kerosene, fuel oil, asphalt)(Al Zarooni and Elshorbagy, 2006; Srikanth et al., 2018). Due to the complex and large scale continuous processing, high amount of wastes of different nature are generated (Srikanth et al., 2018), wastewater being among the most important one. Although substantial progress has already been made over the last few years to reduce its volume, still now for every 1000 m^3/h of raw water required for refinery processes, 200-600 m^3/h of wastewater are discharged(IFP Energies nouvelles, 2010).Wastewater management is, therefore, essential to decrease the amount of raw water need for the processing and the produced wastewater generated (e.g. production line including vapor condensation, process water and spent caustic in crackers, cooling tower and pump/compressor cooling) (Jafarinejad and Jiang, 2019). The composition of the wastewater may be different depending on the plant configuration. However, in general, it may contain biodegradable or recalcitrant organic and inorganic compounds, which are very toxic, and the treatment efficiencies must be evaluated case by case for each plant and process (Bustillo-Lecompte et al., 2015). Integrated approaches including end-of-pipe treatment and reuse/recycle solutions considering the natural water cycle must be applied for sustainable water management(Jia et al., 2019).

Ozone-based AOPs, including single ozonation and UV/H_2O_2/O_3 combinations, are fast and effective treatments to mineralize a wide number of organic compounds, and especially unsaturated and aromatic hydrocarbons in contaminated water(Mota et al., 2008; Ziabari et al., 2016). Thus, ozone-based treatments for either synthetic refinery wastewater (SRW) or real refinery wastewater (RRW) have been studied several times (Chen et al., 2014; Mota et al., 2008; Rajasekhar Pullabhotla et al., 2008).

Coelho et al. compared different AOPs treatments including ozonation for petroleum refinery sour water with initial dissolved organic carbon (DOC) of 300-440 mg/L. The authors compared H_2O_2,H_2O_2/UV, UV, photocatalysis, ozonation, Fenton and photo-Fenton. The most efficient treatment was photo-Fenton yielding up to 83% DOC removal. In contrast, single ozonation removed only 35% of DOC(Coelho et al., 2006).Souza et al. studied several homogeneous AOPs for industrial reuse purposes in a Brazilian refinery. The wastewater treated in this study (initial TOC = 12-19 mg C/L) was collected after biological treatment to enhance the quality of the effluent by AOPs before the reverse osmosis application. They found that around 90% of TOC removal can be achieved through UV/O_3 combination, while the single UV or O_3treatments led to a maximum removal of 10% and 20%, respectively (depending on the UV power and O_3 concentration)(Souza et al., 2016).

The presence of H_2O_2 during the ozone treatment has been found to improve organics degradation (Boczkaj and Fernandes, 2017) via a O_3 decomposition to produce HO• (Mota et al., 2008). However, this fact may change by the composition of the wastewater, which varies by the stage where the water is collected (before or after the pretreatment of secondary treatment). Boczkaj et al. studied the treatment of wastewaters from petroleum bitumen by O_3 and O_3/H_2O_2 methods at basic pH, the latter being the most effective method to reduce COD (up to 43%), which make this system valid as a pretreatment method (Boczkaj et al., 2017).

Besides finding the most efficient treatment for a case, identification and optimization of the significant operational parameters is fundamental. Experimental design may give a complete picture of the system response to the changes of the different variables with less amount of experiments, and consequently, less resources and time (Narenderan et al., 2019). Depending on the purpose, the applications may vary as either screening designs (factorial designs) or optimization designs (response surface designs)(Sahu et al., 2018).

This study explores the efficiency of ozone-based advanced oxidation processes (AOPs) as treatment method for reusing and recycling purposes in a refinery in Turkey, for which we presented the efficiencies of solar light-based AOPs in a previous study (Demir-Duz et al., 2019).Here, it is aimed the study of the O_3/H_2O_2 system to achieve great values of mineralization in refinery wastewaters collected after secondary treatment to fulfill with the water standards for reusing and, hence, reduce the refinery water demand. With this motivation, a final TOC value lower than 4 mg C/L was established as the target to reach for water reuse in cooling towers in the plant (cooling/boiling water) or as firewater. The study composed of preliminary screening on SRW to determine the working boundaries for experimental design and optimization studies on RRW. SRW was used to ensure the stable experimental conditions reducing RRW consumption. Thus, experimental design for screening was performed on SRW only to understand the role of parameters on the removal efficiency. Based on the well-established parameter effects, experimental design for optimization was done specifically for RRW collected in two different stages of the refinery treatment system to decide the placement of AOPs that may achieve the reuse aims.

2. Experimental

2.1 Materials

Synthetic refinery wastewater (SRW) was prepared from the mixture of toluene (Sigma-Aldrich, 99.5%), xylene (Panreac, 98%), phenol (Sigma-Aldrich, 99-100%), o-cresol (Sigma-Aldrich, 99%), naphthalene (Acros Organic, 99%), nonane (Sigma-Aldrich, 99%), hexadecane (Sigma-Aldrich, 99%), ammonium chloride, sodium bicarbonate (Sigma-Aldrich, 99.9%) and sodium chloride (Fluka, 99.5%). Sulfuric acid and sodium hydroxide solutions were used to adjust pH. H_2O_2 (Acros Organic, 35wt%) was used in peroxone experiments while potassium iodide (Sigma-Aldrich, KI) was used for trapping remaining ozone. Dichloromethane (DCM, Sigma-Aldrich, 99.5%), acetonitrile (ACN, Riedel-de Haën, 99.9%) and phosphoric acid (Sigma-Aldrich, 85%) were used for analytical procedures.

Preparation procedure and characteristic properties of the SRW are given in our previous study (Demir-Duz et al., 2019). The detailed composition can be found in supplementary information (SI), ***Table S1***.

Real refinery wastewater (RRW) was collected from a petroleum refinery located in Turkey at two different stages after biological treatment denominated as RRW1 and RRW2.

The organic composition of the effluents determined by GC-MS analyses contained mainly long chain alkanes after the traditional treatments applied in the refinery supported by the characteristic analyses results obtained during the collection month as presented in ***Table 1***, where SD* and SD** presents the standard deviation of the measurements. Initial characterization is also given in ***Table 1*** for all kinds of wastewater (synthetic or real effluents) treated in this study.

Table 1 Characterization of wastewaters

Characteristics of the water treated in the experiments							
			TOC (mg C/L)	COD (mg O_2/L)	pH		
		SRW	68	236	8		
		RRW1	15.3	40	8.2		
		RRW2	27	80	7.5		
Average characteristics of RRW							
	Suspended Solid (mg/L)	Oil & Grease (mg/L)	COD (mg O_2/L)	TOC (mg C/L)	pH	C5-C10 TPH (mg/L)	C10-C40 TPH (mg/L)
RRW1	43.3	22.6	108.2	39.3	7.1	11	0.05
SD*	11.1	1.4	22.7	27.2	0.2	0.67	0.02
RRW2		<10	40	13.7	6.5	12.1	0.08
SD**			20.4	6	0.3	1.16	0.01

2.2 Treatment procedure

Peroxone experiments were performed in a laboratory-scale semi-batch setup as illustrated in ***Figure S1***. Ozone was produced from pure oxygen by using Anseros ozone generator (COM-AD-02 or COM-AD-04 depending on the required O_3 amount) and fed into the reactor with a volume of 1Lcontaining300 mL of effluent by an inert, porous diffuser. Residual ozone concentration of the outlet gas stream was measured by Anseros ozone analyzer (GM-6000-RTI). For the treatment of SRW and RRW1, required amount of H_2O_2 was added at once just before starting the O_3 feed, while discontinuous addition of H_2O_2 was also considered for RRW2 beside the former method. For the discontinuous addition, required amount of H_2O_2 was added equally at four times each 15 min from 0 to 45 min. The first addition was done before O_3 feed.

Preliminary experiments were conducted with SRW to determine a working range of parameters initially. Two levels of O_3 concentration were considered as minimum and maximum (1.16 g/h and 4.14 g/h, respectively). The effect of H_2O_2 and O_3dosage, time and pH were roughly examined. Experiments were conducted during 90 min. Single ozone studies were also conducted in order to examine the effect of H_2O_2presence in the reaction medium.

Detailed, statistical analysis of the independent variables was carried out by fractional factorial design as the screening test for the SRW with the boundaries determined according to the preliminary experiments. The optimization was assessed by Box-Behnken design-based response surface methodology for RRW1 according to the initial screening experiment results conducted with SRW.

The treatment conditions of RRW2 were determined according to the optimization boundaries of RRW1 with the expectations of similar consumption behavior since the water specifications were similar although RRW2 contained rather higher initial TOC and COD. Thus, the suitability of the model obtained for RRW1 for other effluents was evaluated, which results highly interesting in case of changes of the wastewater characteristics depending on the processing of the plant in general.

For the experiments conducted with RRW, ozone consumption was studied in detail to enlighten the questions related to minimum required O_3 amount that should be fed into the reactor. To do so, firstly blank studies were performed by passing O_3directly through the measurer and the produced $O_3$was recorded every minute by the ozone detector. Later, during the reactions, ozone content of the reactor outlet was recorded every minute. Applied O_3dose was calculated roughly based on the mass balance (***Equation 1***).

$$O_3 \text{ (reacted + dissolved)} = O_3 \text{ (inlet)} - O_3 \text{ (outlet)} \qquad \textbf{(1)}$$

2.3 Analytical methods

Total organic carbon (TOC) was chosen as the response of the experimental design to estimate the mineralization degree during experiments. TOC analyses were carried out with a Shimadzu TOC-L (CSN 638-91109-48) analyzer.

Ozone consumption was monitored by Anseros ozone analyzer in order to observe the required amount of O_3 that must be fed to the reactor.

GC-MS and HPLC were used for qualitative and quantitative analyses of the samples. Before GC-MS analysis, compounds were extracted from either the raw or treated water according to the method developed and explained elsewhere(Demir-Duz et al., 2019).

2.4 Design of experiments

There are many factors affecting the impact of the treatment. Thus, design of experiments is getting crucial to know the most important variables that must be controlled during the treatment to reach a cost-effective treatment. This information can be obtained easily by means of the statistical analysis of a set of experiments in a short time with less resources than the classical experimental plan based on keeping the variables constant in turn.

Statistical analysis of the treatment responses was performed by Minitab 17 Statistical Software. Preliminary statistical assessments of the degradation efficiency depending on the chosen factors and their possible interactions were carried out by 2 level fractional factorial design for screening experiments, which is a widely used method to identify the factors having larger effects on the response (Montgomery, 2017). Further optimization has been then performed by Box-Behnken design with only those significant factors obtained by the former design. Box-Behnken is a three-level fractional factorial design that is efficient in the number of required experiments (Jamshidnezhad, 2015). The independent variables and their levels are presented in ***Table 2***. Experiments were randomized to take the unexplained variability of the response into account(Rodríguez-Chueca et al., 2016).

Table 2 Independent variables of the experimental design

	Level of Value	A: H_2O_2 (mg/L)	B: O_3 (g/h)	C: Time	D: pH
Fractional	-	23.65	0.9	15	6
Factorial	+	473.8	2.7	90	11
Box-	-	4	0.9	15	*N/A*
Behnken	+	80	2.7	60	*N/A*

3. Results & discussion

3.1 Preliminary experiments on SRW

Preliminary ozone and peroxone experiments were conducted with SRW at pH 10 since alkaline pH has been reported in several researches as favorable for ozone-based treatments (Boczkaj and Fernandes, 2017; Jiménez et al., 2019; Ribeiro et al., 2015).According to TOC analyses, higher ozone dosage led to higher TOC removal. Thus, 57% and 63% of TOC removal was achieved by 90-min single ozonation with the O_3 concentration of 1.16 g/h and 4.14 g/h, respectively. Although ozone itself presented relatively good effectiveness on the oxidation of components, ozone/H_2O_2process was much more effective to treat this kind of wastewater. In this case, TOC removal values ranging between 74% and 91% were observed after 90-min treatment with an O_3 concentration of 1.16 g/h and 4.14 g/h, respectively, and variable concentrations of H_2O_2 (H_2O_2/COD ratio (w/w) of 1, 2 and 5). The effect of H_2O_2 and O_3 concentrations on the treatments conducted at pH 10 during 90 min is presented in ***Figure 1-a*** in detail. Blue symbols represent the means of first factor (H_2O_2/COD) at each level of the second factor (O_3 dose), while red symbols represent the means of each level of the second factor. Notably, the H_2O_2addition to the system increased the TOC removal efficiency; however, an increase in the H_2O_2dose did not produce changes in the TOC removal at all, indicating that presence of $H_2O_2$is necessary to improve the oxidation rate; meanwhile its concentration appears to be insignificant for this system. Thus, further studies were made at lower H_2O_2concentrations and variable pH with a constant O_3 concentration of 4.14 g/h, and results are presented in ***Figure 1-b***.

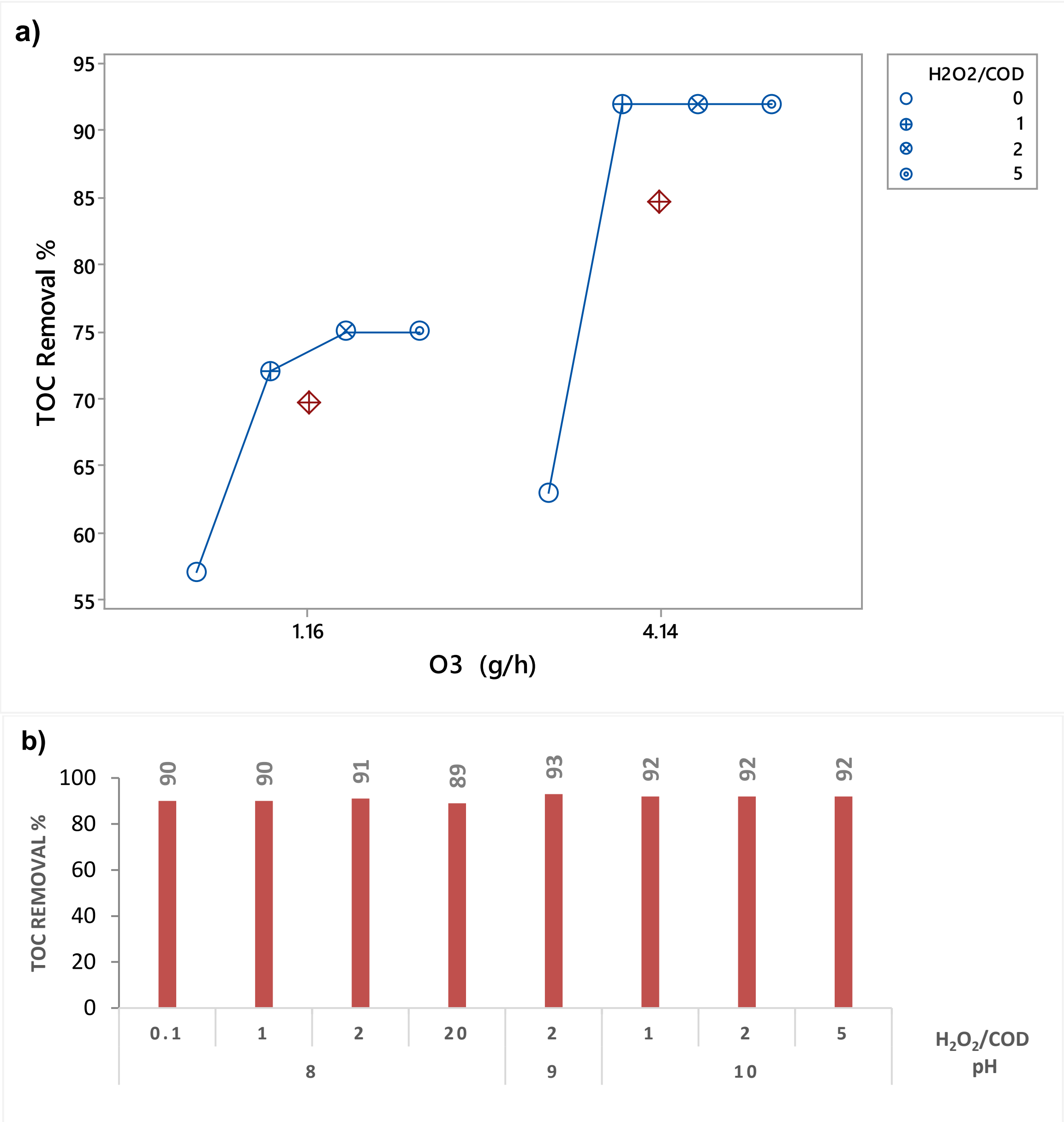

Figure 1a) The effect of variable H_2O_2 and O_3 concentrations on treatment efficiency of SRW at a constant pH 10; b) The effect of variable H_2O_2 concentration and pH on treatment efficiency of SRW at a constant O_3 concentration of 4.14 g/h.

As previously seen, for the treatment of SRW by the ozone/H_2O_2 process, the amount of H_2O_2did not change the TOC removal rate significantly, especially for the high O_3 dose applications. The same behavior was found with varying the pH of the medium. These results may be assigned to the reaction of ozone with hydroxyl and hydroperoxide ions, which initiates the ozone decomposition reaction in water to yield superoxide ion that might make the amount of H_2O_2 insignificant(Beltran, 2004).This fact has been confirmed by very few amount of H_2O_2 addition (for H_2O_2/COD (w/w)=0.1, which used 23.6 mg/L H_2O_2), which again achieved 90% of removal by 4.14 g/h O_3 dosing while that of single ozonation reached only to 63%. Thus, detailed statistical analysis was performed in order to determine the significant factors and their interaction for peroxone treatment in a complex matrix, which may not be achieved by the method that consists of the variation of one variable while keeping the others constant (Deligiorgis et al., 2008). As the amount of $H_2O_2$was insignificant when the O_3 amount was high, the highest level of the O_3 amount was chosen between 1.16 g/h and 4.14 g/h avoiding the excessive O_3 consumption, while the minimum amount was kept lower than 1.16 g/h.

3.2 Experimental design

3.2.1 Fractional factorial design for peroxone treatment of SRW

2-level fractional factorial design of peroxone treatment has been performed with SRW in order to determine the significant parameters that should be controlled for the RRW treatments. Initially, four variables as H_2O_2 amount, O_3 amount, time and pH change have been considered to examine closely. Three replications on the center points were also performed to ensure reproducibility and reliability of the results, requiring 11 experiments (2^{4-1}+3) in total. ***Table S2*** presents the set of experiments and the obtained response based on TOC removals.

The analysis of variance (ANOVA), given in ***Table S3***, indicated that neither pH nor the 2-way interactions betweenH_2O_2 concentration and time or pH were significant for the model. However, since pH was the main variable and it had an effect in terms of 4-way interactions, only the 2 way interactions that showed P-values higher than 0.05 have been excluded from the model, which is generally preferable to simplify the system whenever possible (Hayder et al., 2014).

Thus, the simplified model (with the ***equation 2***) presented a regression coefficient (R^2) of 99.95% and adjusted R^2 of 99.86%. P value of the lack-of-fit was also 0.681 (>0.05), which indicated that model and the data were well fitted and the variations around the model were negligible (Shafiei et al., 2018). On the other hand, 4-way interaction term was totally confounded with the center point term and its P value exhibits a significant curvature in the model.

$$\text{TOC Removal} = 84.467 + 1.988\,A + 4.637\,B + 19.512\,C - 0.488\,D - 3.312\,A{*}B - 21.629\,A{*}B{*}C{*}D \quad (2)$$

Residual plots presented in ***FigureS2*** showed normal distribution of the residuals that scattered randomly around zero.

3.2.2 Response surface methodology by Box-Behnken design for RRW1

Petroleum refinery effluents contain large variety of compounds from inorganic to organic that are poorly biodegradable(de Abreu Domingos and da Fonseca, 2018; Stepnowski et al., 2002). Due to the complex nature of the effluents, organic fractions are represented by bulk parameters such as TOC, COD and BOD, which are easier parameters to observe, rather than detailed analytical methods (Jafarinejad and Jiang, 2019).

In this study, TOC was chosen as the key parameter because of its simple and fast measurement. Besides, TOC is one of the common parameters that must be measured to determine the water quality before discharging or recycling through the processes. Although the target values are changeable depending on the plant, in our case, it was determined a final TOC value lower than 4 mg C/L to take the place of fresh water need of cooling/boiling tower after treatment.

According to the initial assessment of variables and their interactions by 2-level fractional factorial design, Box-Behnken design has been performed for RRW1 with three variables as H_2O_2 (mg/L), O_3 (g/h) and time. pH has been excluded to simplify the process since it was mainly found insignificant for the treatment. Experiments were conducted at its natural pH=8.2 according to the set of experiments proposed by the software, which are given in ***Table S4***.

ANOVA data of the design(***Table 3***) presented insignificant effects of 2-way interactions. However, although their P-value was higher than 0.05, in terms of the negative effect on S and R^2, they were kept in the model. Model contained two squared effects (A*A and C*C) with P-value< 0.05which showed the presence of curvature in the response surface.

Table 3 ANOVA obtained for RRW1 by Box-Behnken design with predicted Optimum conditions and the responses by the model.

Analysis of Variance					
Source	**DF**	**Adj SS**	**Adj MS**	**F-Value**	**P-Value**
Model	7	5085.53	726.5	34.61	0
Linear	3	3914.11	1304.7	62.15	0
A	1	2850.13	2850.13	135.78	0
B	1	168.91	168.91	8.05	0.025
C	1	895.07	895.07	42.64	0
Square	2	1007.32	503.66	23.99	0.001
A*A	1	897.63	897.63	42.76	0
C*C	1	158.42	158.42	7.55	0.029
2-Way Interaction	2	164.11	82.05	3.91	0.072
A*B	1	70.31	70.31	3.35	0.11
B*C	1	93.8	93.8	4.47	0.072
Error	7	146.94	20.99		
Lack-of-Fit	5	123.71	24.74	2.13	0.35
Pure Error	2	23.23	11.62		
Total	14	5232.47			

Levels			**Response Values**				
C_{H2O2} (mg/L)	***C_{O3} (g/h)***	***Time (min)***	***TOC Removal %***		***Final TOC (mg C/L)***	***Desirability value***	***TOC Removal observed SD%***
			Observed	***Predicted***			
70	0.9	60	77.08	81.16	3.51	1	0.58
47	0.9	60	77.68	75.26	3.3	1	0.2

$$\text{TOC Removal} = -42.0 + 1.622\,A + 19.22\,B + 1.868\,C - 0.01077\,A{*}A - 0.01290\,C{*}C - 0.1226\,A{*}B - 0.239\,B{*}C \quad (3)$$

Residual plots given in ***Figure 2*** showed normal distribution of the residuals that scattered randomly around zero. Contourplots present the effect of H_2O_2 amount (A), O_3 amount (B) and time (C) on the response. When time was set at its middle value, the amounts of H_2O_2 and O_3exhibit an opposite balance to reach the same TOC removal. That is, in case of increase in O_3 concentration, H_2O_2 dosing may be decreased and vice versa. On the other hand, when the O_3 amount was set at 1.8 g/h, optimum removal can be achieved with H_2O_2 amount between 40-80 mg/L by a 30-60 min treatment. ***Figure 3*** indicates how predicted values fitted with the responses achieved.

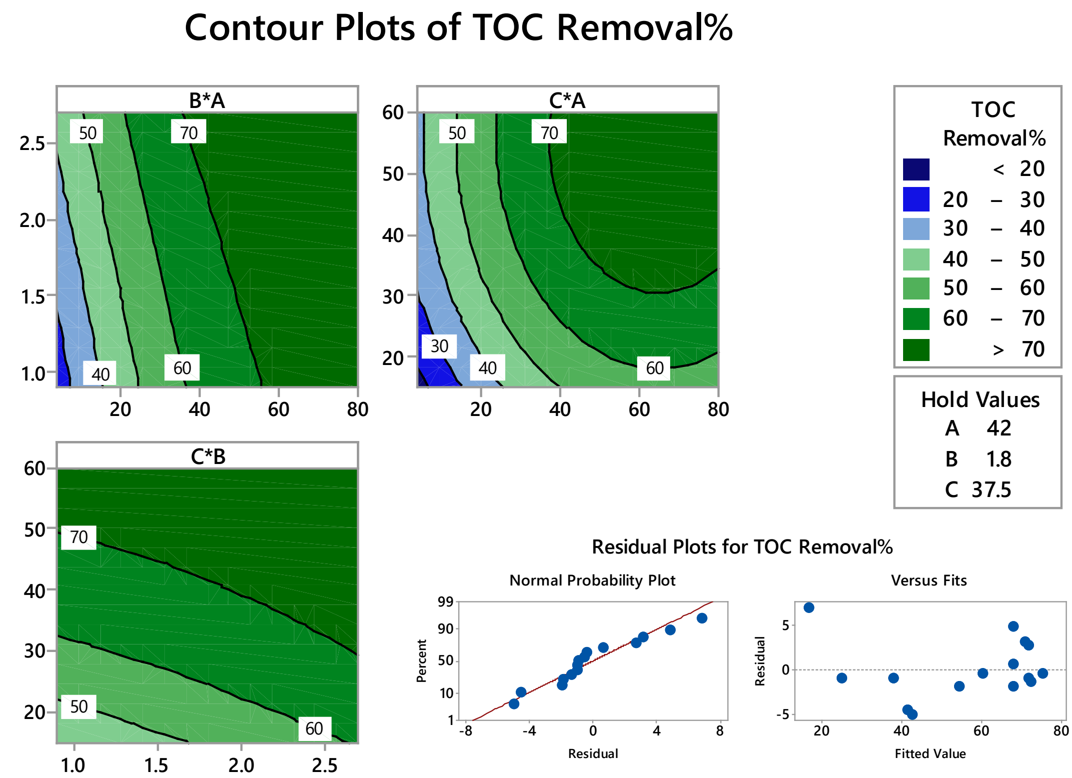

Figure 2 Residual and contour plots obtained by Box-Behnken design for RRW1, where A = the amount of H_2O_2 (mg/L), B= the amount of O_3 feed (g/h), C = time (min)

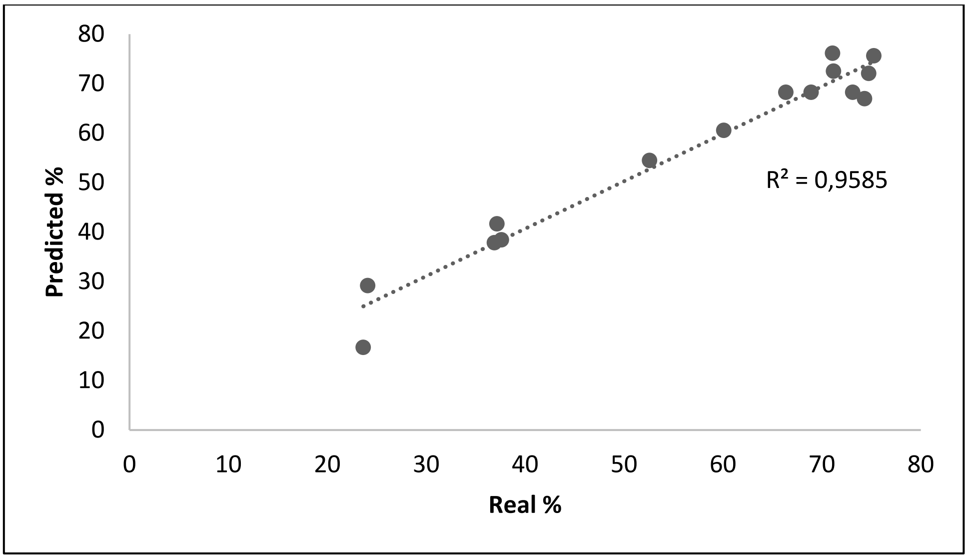

Figure 3 Experimental responses versus predicted responses by Box-Behnken design applied for RRW1

According to ***Table 3***, the quadratic model obtained by the Box-Behnken design (***equation 3***) with a Model F-value of 34.61 was considered significant. The lack of fit of 2.13 indicates that there is a good fit of the model relative to pure error. This is seen, in addition, with the regression coefficient (R^2) of 97.19%, adjusted R^2 of 94.38% and predicted R^2 of 82.43%that presents the adequate match of the model and the response. Therefore, the model was used to determine the optimized parameters for the current process. ***Table 3*** also presents the optimum conditions predicted by the model with the desirability of 1 and their responses either the observed or the predicted ones which had low standard deviation (SD) as expected.

3.3 Treatment assessment by TOC

Considering the feasibility of the ozone-based treatment for the treatment of RRW1, the boundaries that were determined for the response surface methodology were kept reasonable in terms of the costs of the operation and the resources.

According to the optimized parameters presented in Table, it is possible to reach the final TOC requirements with the H_2O_2 amount down to 47 mg/L when the treatment lasts 60 min keeping the O_3 feed rate at 0.9 g/h. However, considering the cost of O_3 production, it can be more realistic to apply the parameters given in Run 15 in ***Table S4***, which could reduce the operation time down to 37.5 min rather than 60 min while increasing the H_2O_2 amount to 80 mg/L. Thus, some of the energy requirement for the O_3formation from O_2 and for other operations could be saved by increasing the consumption of the reagent. A comparison between these two cases was performed in terms of energy and reagent consumptions (***Table 4***). The calculation of electrical energy per order (EEO) for O_3 treatment was reported before by Jiménez et al. by the ***equation 4***, where the P is rated power, V is the volume of effluent treated, t is the treatment duration and TOC_i and TOC_f is initial and final TOC values(Jiménez et al., 2019).

$$EEO\ (\frac{kWh}{m^3}) = \frac{P(kW)*t(h)*1000}{V(L)*\log(\frac{TOC_i}{TOC_f})} \quad \textbf{(4)}$$

The rated power (P) was calculated as 0.19 kW including 0.002 kW of stirring, 0.008 kW for ozone measurer with O_3destruction catalyst and 0.009 kW for ozone generator, which was calculated by for the constant O_3 production of 0.9 kg/h that was used for the optimum conditions obtained by the model (ozone generator consumed around 10 kW/Kg O_3 according to the supplier).As the reagents,38,57 m^3/h of oxygen (with a unit price of 3 Eur/m^3 (Boconline, 2019))gas for O_3 generation and H_2O_2 with a unit price of 346 Eur/m^3 were consumed. Thus, 37% of total cost could be saved by changing parameters. Also, since the operation and reagent costs of the large-scale operations are lower than those of laboratory scale operations, the saving can be higher for scaled-up operations.

Table 4 Energy consumption comparison of different operation parameters

	Treatment Conditions					**Costs per unit**		
	C_{H2O2} (g/m³)	***Required 35% H_2O_2 (L/m³)***	***O_3 (kg)***	***Time (h)***	**EEO (kWh/m³)**	**O_2 (Eur/m3)**	**35% H_2O_2 Eur/m³**	**Cost of energy (Eur/kWh)**
Case 1	47	0.07	0.9	1	95.1	3	346	0.148
Case 2	80	0.12	0.56	0.625	67.1			

Calculated cost per treatment								
Case 1				***Case 2***				
35% H_2O_2 Eur/m³	**Energy (Eur/m³)**	**O_2 (Eur/m³)**	**Total (Eur/m³)**	**35% H_2O_2 Eur/m³**	**Energy (Eur/m³)**	**O_2 (Eur/m³)**	**Total (Eur/m³)**	**Cost save**
0.025	14	116	130	0.042	10	72	82	37%

In accordance with the treatment conditions and response of RWW1, RRW2 was treated within the parameter boundaries that were considered for RRW1 to compare the treatment impact depending on the changing characteristics. The initial treatment of RRW2 conducted with the optimized parameters of RRW1 (***Table 3***) resulted in an average TOC removal of 67%, by which final TOC reached ca. 9 mg C/L. Thus, although the boundaries for H_2O_2 and O_3 were kept at the same range, treatment time was enlarged up to 90 min rather than 60 min to check whether the target final TOC can be reached.

Figure 4presentsthe effect of H_2O_2 addition to the system. For all cases, most of the total organic carbon was removed in 30 min in the presence of H_2O_2. However, in the absence of H_2O_2 (***Figure 4a***), TOC removal reached up to 56% with an O_3dosing of 2.7 g/h after 90 min treatment, while the treatment efficiency of 1.8 g O_3/h was already 54%. Ozone depletion (calculated by residual O_3 measured during both experiments) was higher at the highest feed rate, indicating that even if ozone dissolved in RRW2 can be increased, reacted ozone does not increase, which showed the unnecessity of excessive amount of O_3 feed for the treatment. In the presence of H_2O_2, even with small addition of H_2O_2 (***Figure 4b***), TOC removal efficiency was slightly increased in 30 min (10% more than the treatment without

H_2O_2). When the H_2O_2/COD ratio (w/w) was increased to 1.05 (***Figure 4c***), 30-min treatment efficiency reached around 60% regardless to the O_3 feed amount, while that of the H_2O_2/COD ratio (w/w) 2 (***Figure 4d***) varied between 55% to 75% depending on the O_3 feed ratio. This behavior could be explained by the changes in radicals that competed to attack the organic contaminants faster than the other while changing the intermediate product. Thus, the reaction pathway may change depending on the by-products occurred during the treatment. Bourgin et al. explained the similar behavior of the selectivity of direct reaction of ozone and the O_3/H_2O_2treatment due to the hydroxyl radicals on the abatement of some micropollutants from water (Bourgin et al., 2017).

In the best of the cases giving the maximum removal, the final TOC reached for RRW2 was 5.15 mg C/L. This value was obtained by using the highest amounts of reagents after 90-min treatment, which were H_2O_2/COD ratio (w/w) of 2 and 2.7 g O_3/h. On the other hand, the target TOC (4 mg C/L) could only be reached by discontinuous addition of H_2O_2 rather than its initial addition at once. When the required amount of H_2O_2 (160 mg/L for the H_2O_2/COD ratio (w/w) of 2) was added at 4 times (40 mg/L for each addition in every 15 min), final TOC of 3.32 mg C /L was reached after 90-min treatment. This suggests that, in those cases where the $H_2O_2$is added at once for RRW2 treatment, there is an excessive H_2O_2 present in the solution which likely acts as a scavenger, thus consuming the HO· generated. Although the O_3 depletion (measured as the difference between feed rate and residual rate) is higher at higher concentrations of H_2O_2 (because of the interactions between them), the rate may vary due to the scavenging effect of excessive H_2O_2 (and hydroxyl ion) in reacting with hydroxyl radical, which negatively affects the organics degradation/mineralization.

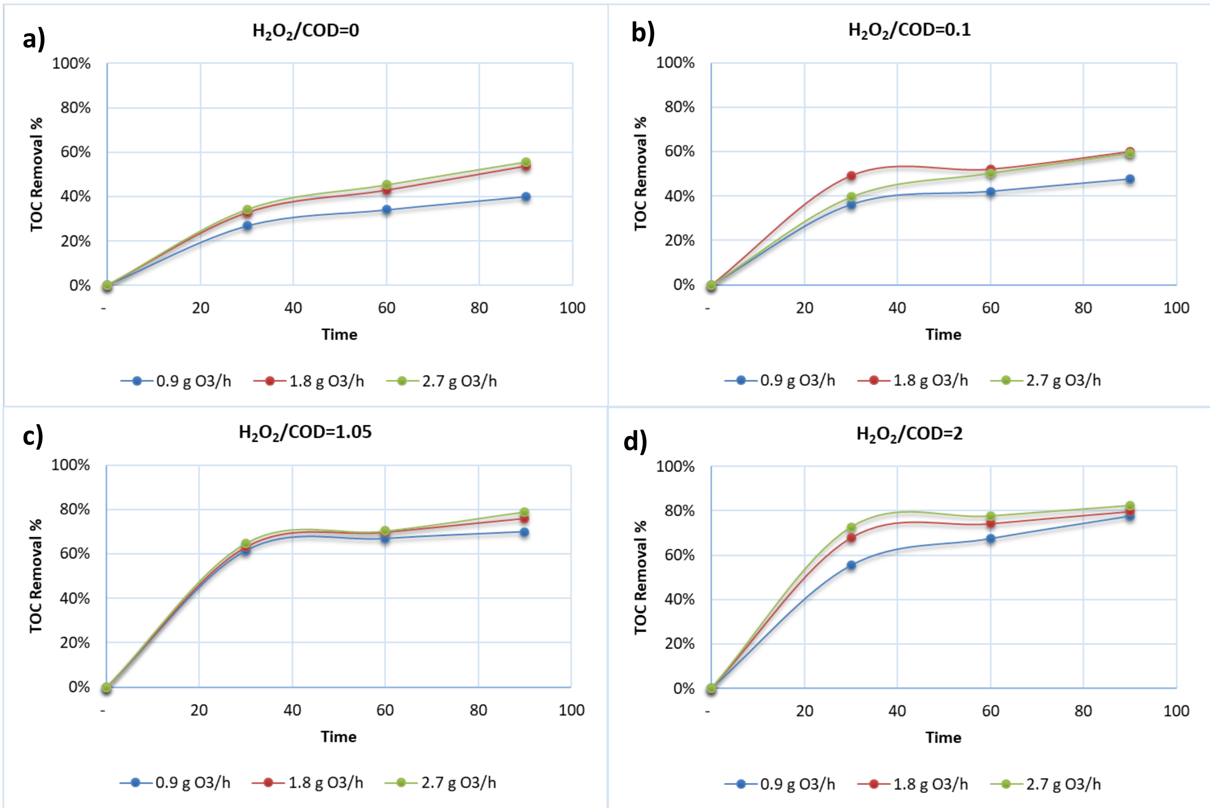

Figure 4RRW2 Treatment efficiencies of ozone-based studies depending on the varied H_2O_2/COD ratios (w/w) between 0-2.

Then, the compositional difference between RRW1 and RRW2 affects to the treatment efficiencies or required amounts of reagents. In this case, RRW2 present higher amount of recalcitrant products (likely saturated alkanes) than RRW1 having an inhibiting effect on the ozonation treatment. Thus, fluctuations in the water properties and components that can occur either during the production or in the different points of each plant pretreatment may affect to the ozonation efficiency to achieve the water requirements to reuse.

3.4 Oxidant consumption

The contour plots present a relationship between H_2O_2 and O_3 (***Figure 2***), which motivates further attention to oxidant consumption behavior during the treatments. Thus, initially, ozone consumption (calculated from residual monitored during the reactions) has been considered as a significant indicator to find the optimized amount of oxidant to be fed into the system. ***Figure S3*** shows the importance of the initial O_3 feed rate recorded during the experiments conducted with RRW1. The time factors have been selected according to the case of reaching to 0.9 g feed (Feed(g) = O_3 dose (g/h)*t (h)). Thus, O_3 dosing was performed during 60 min, 30 min and 20 min for 0.9 g/h, 1.8 g/h and 2.7 g/h O_3 feed, respectively. According to the obtained results, when the feed rate was kept at 0.9 g/h, increasing H_2O_2 amount did not change the O_3consumption rate, which reached only up to 9% of the feed amount. However, when the feed rate increased to 1.8 g/h and 2.7 g/h, consumed amount of O_3increased to 25% when the O_3feed reached to 0.9 g. Besides, increasing the feed rate from 1.8 g/h to 2.7 g/h did not change either the O_3consumption or the TOC removal significantly, which presented the high amount of O_3 feed to be redundant.

Khuntia et al., reported the similar consumption increase with increasing O_3 dose (Khuntia et al., 2018).

Figure 5 exhibits the significance of the optimum oxidant feed for the maximum TOC removal for the experiments conducted with RRW1 during 37.5 min. The number of run represents the conditions of the experiments given in ***Table S4*** previously. The green data present the ratio of consumed O_3 amount calculated based on the ***equation 1***to remove TOC (mole/mole), while the purple data present the ratio between consumed O_3 and consumed H_2O_2 (mole/mole). The consumed amount of H_2O_2 was determined by the semi-quantitative strips that gives a range of concentration in mg/L. In case of any detected H_2O_2 amount in the samples, calculations were made based on the lower scale of the range assuming the higher amount of reagent consumption. Notably, when an insufficient amount of H_2O_2 was added to the reactor (i.e. 4 mg/L) as in the case of Run 2 and 4, most of the O_3seems not to react with the organic matter, reaching a low %TOC removal and, therefore, being ineffective treatment conditions. On the other hand, when higher amount of H_2O_2(i.e. 80 mg/L) was fed as in the cases of Run 1 and Run 15, the oxidants resulted more efficient in removing the carbon content. In these cases, both the O_3cons/TOC and O_3cons/H_2O_2cons ratios decrease compared to the former cases. Indeed, conditions used in Run 15 were markedly more efficient in terms of effective consumption of oxidants reaching the higher TOC removal while reducing the unreacted oxidant amount. This result totally agrees with the optimized conditions found previously through box-Behnken response surface methodology to achieve lower costs maintaining high TOC removal, as presented in section 3.3.

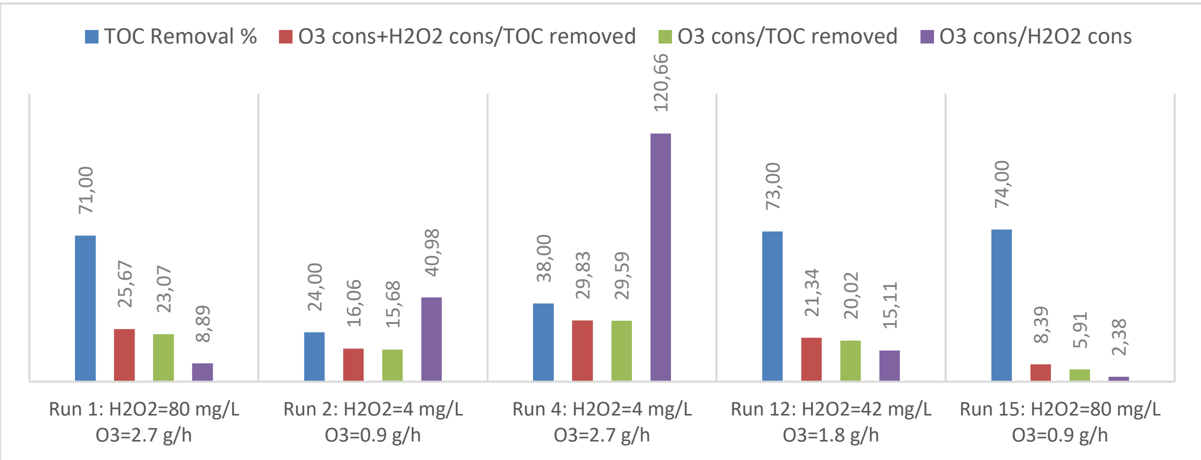

Figure 5 The oxidant consumption ratios (mole/mole) compared to TOC removal % for RRW1 treatment during 37.5 min

In case of the treatment of RWW2, similar consumption behavior was obtained. When the treatment ends in 30 min (***Figure 6a***), the most effective reagent consumption was achieved with 160 mg/L of H_2O_2 and 0.9 g/h O_3(E7) reaching 55% of TOC removal. The increase in O_3 dose resulted in higher TOC removal; however, this also cause an increase in O_3 wastage. On the other hand, increasing the reaction time to 90 min (***Figure 6c***) led to higher TOC removals still preserving the effective consumption of the reagents. Nevertheless, again the optimum conditions can be determined according to the cost analysis for each case.

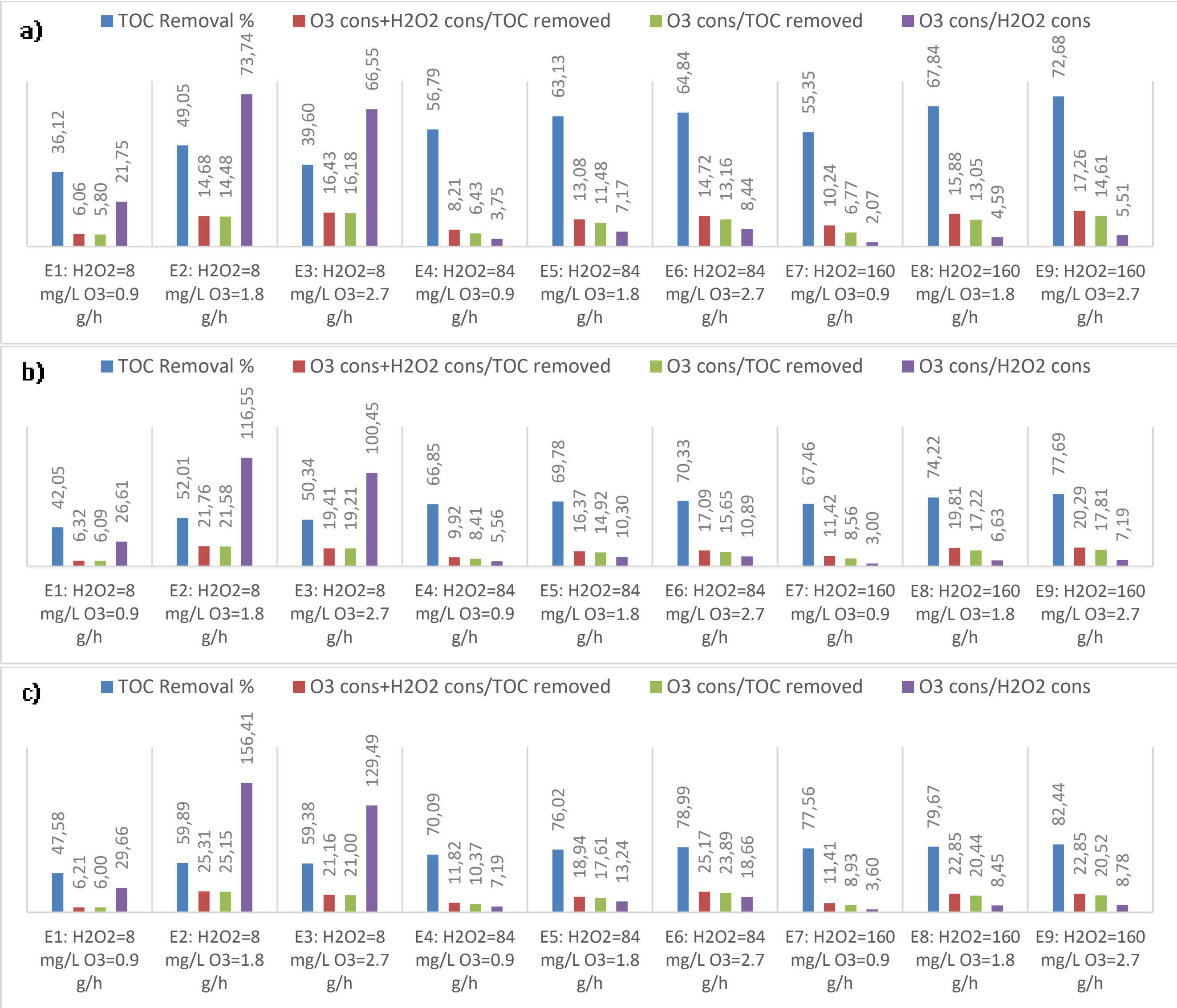

Figure 6 The oxidant consumption ratios (mole/mole) compared to TOC Removal % for RRW2 treatment a) 30 min, b) 60 min, c) 90 min

4. Conclusions

This study presented the ozone-based treatment of effluents from a petroleum refinery in Turkey. The selection of optimal conditions for effective degradation oftwo wastewater effluents after biological treatment was studied using fractional factorial design; whereas, the optimization of the significant parameters was performed by Box-Behnken response surface methodology.

According to the screening results obtained by the fractional factorial design, it was found that both the reagents concentration used for the treatment and the time were very significant for the treatment efficiency, while pH was found insignificant in terms of its effect on TOC removal. The optimized parameters by Box-Behnken design indicated that it is possible to reach the TOC requirements for reuse purposes by adjusting the amount of $H_2O_2$and reaction time at low feed O_3 rates. Thus, optimization allows reducing operational costs maintaining the process effectiveness to reach the stablished target. The ratio between consumed O_3 and H_2O_2 played a crucial role for an optimum treatment either in terms of efficiency or for the operation costs. However, the effect of initial characteristics of the effluents must be taken into account to determine the appropriate oxidant feed.

According to local water specifications for reclamation, peroxone treatment appears as a promising technique for water polishing allowing water recycling in refineries. The final characteristics of the treated water make it suitable to be reused in the plant's cooling towers or stored for fire extinction or cleaning purposes, which are the major water consumption sources of a refinery. This allows decreasing substantially the raw water consumption and generates a positive impact at different levels: social, economic and environmental.

An important point concerns to the fluctuation in the characteristics of the effluent, which was found rather significant in the treatment efficiency and the operational conditions that should be adjusted. This is especially important for real applications in situ, since the water variability in the refinery is highly expected with time and season. However, we have shown here that this problem may be overcome by means of detailed statistical approaches, which may be extrapolated to a refinery scenario through the development of a decision support system.

Acknowledgements

This project has received funding from the European Union’s Horizon 2020 research and innovation program under grant agreement No 688989. Authors acknowledge Universitat Rovira i Virgili for the doctoral fellowship, Marti-Franques Research Grant (2016PMF-PIPF-30).

References

Al Zarooni, M., Elshorbagy, W., 2006. Characterization and assessment of Al Ruwais refinery wastewater. J. Hazard. Mater. 136, 398–405. https://doi.org/10.1016/j.jhazmat.2005.09.060

Beltran, F.J., 2004. Ozone reaction kinetics for water and wastewater systems. Lewis Publishers, Boca Raton.

Boconline, 2019. Boconline [WWW Document]. URL https://www.boconline.co.uk/shop/en/uk/gas-a-z/oxygen/oxygen-cylinder (accessed 10.3.19).

Boczkaj, G., Fernandes, A., 2017. Wastewater treatment by means of advanced oxidation processes at basic pH conditions: A review. Chem. Eng. J. 320, 608–633. https://doi.org/10.1016/j.cej.2017.03.084

Boczkaj, G., Fernandes, A., Makos, P., 2017. Study of different advanced oxidation processes for wastewater treatment study of different advanced oxidation processes for wastewater treatment from petroleum bitumen production at basic pH. Ind. Eng. Chem. Res. 56, 8806–8814. https://doi.org/10.1021/acs.iecr.7b01507

Bourgin, M., Borowska, E., Helbing, J., Hollender, J., Kaiser, H., Kienle, C., Mcardell, C.S., Simon, E., Gunten, U. Von, 2017. Effect of operational and water quality parameters on conventional ozonation and the advanced oxidation process O3/H2O2 : Kinetics of micropollutant abatement, transformation product and bromate formation in a surface water. Water Res. 122, 234–245. https://doi.org/http://dx.doi.org/10.1016/j.watres.2017.05.018

Bustillo-Lecompte, C.F., Knight, M., Mehrvar, M., 2015. Assessing the performance of UV/H2O2 as a pretreatment process in TOC removal of an actual petroleum refinery wastewater and its inhibitory effects on activated sludge. Can. J. Chem. Eng. 93, 798–807. https://doi.org/10.1002/cjce.22180

Chen, C., Chen, H., Guo, X., Guo, S., Yan, G., 2014. Advanced ozone treatment of heavy oil refining wastewater by activated carbon supported iron oxide. J. Ind. Eng. Chem. 20, 2782–2791. https://doi.org/10.1016/j.jiec.2013.11.007

Coelho, A., Castro, A. V., Dezotti, M., Sant'Anna Jr., G.L., 2006. Treatment of petroleum refinery sourwater by advanced oxidation processes. J. Hazard. Mater. 137, 178–184. https://doi.org/10.1016/j.jhazmat.2006.01.051

de Abreu Domingos, R., da Fonseca, F.V., 2018. Evaluation of adsorbent and ion exchange resins for removal of organic matter from petroleum refinery wastewaters aiming to increase water reuse. J. Environ. Manage. 214, 362–369. https://doi.org/10.1016/j.jenvman.2018.03.022

Deligiorgis, A., Xekoukoulotakis, N.P., Diamadopoulos, E., Mantzavinos, D., 2008. Electrochemical oxidation of table olive processing wastewater over boron-doped diamond electrodes: Treatment optimization by factorial design. Water Res. 42, 1229–1237. https://doi.org/10.1016/j.watres.2007.09.014

Demir-Duz, H., Ayyildiz, O., Aktürk, A.S.A.S., Álvarez, M.G.M.G., Contreras, S., 2019. Approaching zero discharge concept in refineries by solar–assisted photo-Fenton and photo-catalysis processes. Appl. Catal. B Environ. 248, 341–348. https://doi.org/10.1016/j.apcatb.2019.02.026

Dias, I.N., Cerqueira, A.C., Sant'Anna Jr., G.L., Dezotti, M., 2012. Oil refinery wastewater treatment in biofilm reactor followed by sand filtration aiming water reuse. J. Water Reuse Desalin. 2, 84–91. https://doi.org/10.2166/wrd.2012.022

El-Naas, M.H., Alhaija, M.A., Al-Zuhair, S., 2014. Evaluation of a three-step process for the treatment of petroleum refinery wastewater. J. Environ. Chem. Eng. 2, 56–62. https://doi.org/10.1016/j.jece.2013.11.024

Escudero, C.J., Iglesias, O., Dominguez, S., Rivero, M.J., Ortiz, I., 2017. Performance of electrochemical oxidation and photocatalysis in terms of kinetics and energy consumption. New insights into the p-cresol degradation. J. Environ. Manage. 195, 117–124. https://doi.org/10.1016/j.jenvman.2016.04.049

Hayder, G., Ramli, M.Z., Malek, M.A., Khamis, A., Hilmin, N.M., 2014. Prediction model development for petroleum refinery wastewater treatment. J. Water Process Eng. 4, 1–5. https://doi.org/10.1016/j.jwpe.2014.08.006

IFP Energies nouvelles, 2010. Water in fuel production [WWW Document]. Panaroma 2011. URL https://www.researchgate.net/publication/276292861_Water_in_fuel_production_Oil_production_and_refining (accessed 9.28.19).

Jafarinejad, S., Jiang, S.C., 2019. Current technologies and future directions for treating petroleum re fi neries and petrochemical plants (PRPP) wastewaters. J. Environ. Chem. Eng. 7, 103326. https://doi.org/https://doi.org/10.1016/j.jece.2019.103326

Jamshidnezhad, M., 2015. Experimental design in petroleum reservoir engineering, in: Experimental Design in Petroleum Reservoir Studies. Gulf Professional Publishing, Waltham.

Jia, X., Li, Z., Tan, R.R., Foo, D.C.Y., Majozi, T., Wang, F., 2019. Interdisciplinary contributions to sustainable water management for industrial parks. Resour. Conserv. Recycl. 149, 646–648. https://doi.org/https://doi.org/10.1016/j.resconrec.2019.06.034

Jiménez, S., Andreozzi, M., Micó, M.M., Álvarez, M.G., Contreras, S., 2019. Produced water treatment by advanced oxidation processes. Sci. Total Environ. 666, 12–21. https://doi.org/10.1016/j.scitotenv.2019.02.128

Khuntia, S., Kumar Sinha, M., Saini, B., 2018. An approach to minimize the ozone loss in a series reactor: A case of peroxone process. J. Environ. Chem. Eng. 6, 6916–6922. https://doi.org/10.1016/j.jece.2018.10.069

Montgomery, D.C., 2017. Design and analysis of experiments, Eighth. ed. John Wiley & Sons, Inc., Hoboken.

Mota, A.L.N., Albuquerque, L.F., Beltrame, L.T.C., Chiavone-Filho, O., Machulek Jr., A., Nascimento, C.A.O., 2008. Advanced oxidation processes and their application in the petroleum industry: a review. Brazilian J. Pet. Gas 2, 122–142. https://doi.org/10.5419/bjpg.v2i3.57

Narenderan, S.T., Meyyanathan, S.N., Karri, V.V.S.R., 2019. Experimental design in pesticide extraction methods : A review. Food Chem. 289, 384–395. https://doi.org/10.1016/j.foodchem.2019.03.045

Rajasekhar Pullabhotla, V.S.R., Southway, C., Jonnalagadda, S.B., 2008. Ozone initiated oxidation of hexadecane with metal loaded γ-Al2O3 catalysts. Catal. Lett. 124, 118–126. https://doi.org/10.1007/s10562-008-9434-4

Ribeiro, A.R., Nunes, O.C., Pereira, M.F.R., Silva, A.M.T., 2015. An overview on the advanced oxidation processes applied for the treatment of water pollutants defined in the recently launched Directive 2013/39/EU. Environ. Int. 75, 33–51. https://doi.org/10.1016/j.envint.2014.10.027

Rodríguez-Chueca, J., Amor, C., Fernandes, J.R., Tavares, P.B., Lucas, M.S., Peres, J.A., 2016. Treatment of crystallized-fruit wastewater by UV-A LED photo-Fenton and coagulation-flocculation. Chemosphere 145, 351–359. https://doi.org/10.1016/j.chemosphere.2015.11.092

Sahu, P.K., Ramisetti, N.R., Cecchi, T., Swain, S., Patro, C.S., Panda, J., 2018. An overview of experimental designs in HPLC method development and validation. J. Pharm. Biomed. Anal. 147, 590–611. https://doi.org/10.1016/j.jpba.2017.05.006

Shafiei, S., Ebadi, A., Kiadehi, A.D., Aghaeinejad-Meybodi, A., Khataee, A., 2018. Degradation of Fluoxetine using catalytic ozonation in aqueous media in the presence of nano-γ-alumina catalyst: Experimental, modeling and optimization study. Sep. Purif. Technol. 211, 551–563. https://doi.org/10.1016/j.seppur.2018.10.020

Souza, B.M., Souza, B.S., Guimarães, T.M., Ribeiro, T.F.S., Cerqueira, A.C., Sant'Anna, G.L., Dezotti, M., 2016. Removal of recalcitrant organic matter content in wastewater by means of AOPs aiming industrial water reuse. Environ. Sci. Pollut. Res. 23, 22947–22956. https://doi.org/10.1007/s11356-016-7476-5

Srikanth, S., Kumar, M., Puri, S.K., 2018. Bio-electrochemical system (BES) as an innovative approach for sustainable waste management in petroleum industry. Bioresour. Technol. 265, 506–518. https://doi.org/https://doi.org/10.1016/j.biortech.2018.02.059

Stepnowski, P., Siedlecka, E.M., Behrend, P., Jastorff, B., 2002. Enhanced photo-degradation of contaminants in petroleum refinery wastewater. Water Res. 36, 2167–2172. https://doi.org/10.1016/S0043-1354(01)00450-X

Ziabari, S.S.H., Khezri, S.M., Kalantary, R.R., 2016. Ozonation optimization and modeling for treating diesel-contaminated water. Mar. Pollut. Bull. 104, 240–245. https://doi.org/10.1016/j.marpolbul.2016.01.017