



Multivariate analysis of anionic, cationic and nonionic textile surfactant degradation with the H₂O₂/UV-C process by using the capabilities of response surface methodology

Tugba Olmez-Hanci*, Idil Arslan-Alaton, Gulcan Basar

Istanbul Technical University, Faculty of Civil Engineering, Department of Environmental Engineering, 34469 Maslak, Istanbul, Turkey

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ABSTRACT

Anionic, cationic and nonionic surfactants being frequently employed in the textile preparation process were subjected to H₂O₂/UV-C treatment. As a consequence of the considerable number of parameters affecting the H₂O₂/UV-C process, an experimental design methodology was used to mathematically describe and optimize the single and combined influences of the critical process variables treatment time, initial H₂O₂ concentration and chemical oxygen demand (COD) on parent pollutant (surfactant) as well as organic carbon (COD and total organic carbon (TOC)) removal efficiencies. Multivariate analysis was based on two different photochemical treatment targets; (i) full oxidation/complete treatment of the surfactants or, alternatively, (ii) partial oxidation/pretreatment of the surfactants to comply with the legislative discharge requirements. According to the established polynomial regression models, the process independent variables “treatment time” (exerting a positive effect) and “initial COD content” (exerting a negative effect) played more significant roles in surfactant photodegradation than the process variable “initial H₂O₂ concentration” under the studied experimental conditions.

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1. Introduction

Surfactants are widely used in household detergents, personal care products, paints, inks, polymers, pesticide formulations, pharmaceuticals, mining, oil recovery, pulp and paper, tannery and textile industries [1,2]. Surfactants enter the aquatic and terrestrial environment mainly through the discharge of sewage into receiving water bodies and the application of sewage sludge on land for soil fertilizing purposes [3,4]. A considerable number of commercial surfactants used today by different industries are only partially and slowly biodegradable in natural as well as engineered biological (mainly activated sludge) treatment systems [5,6] Due to their amphiphilic characteristics, surfactants tend to sorb and

hence accumulate onto sludge and soil sediments thus imparting serious ecotoxicological risks in the environment. As a consequence, more effective and at the same time economically feasible treatment processes have to be applied to alleviate the chronic problem of surfactant accumulation in the aquatic ecosystems. Moreover, the management of biologically difficult-to-degrade effluent discharges bearing surfactants remains an important challenge that has to be urgently solved to reduce the concentration of surfactants in effluent discharge at source.

Among different alternative treatment options, in particular chemical and photochemical advanced oxidation processes (AOPs) have proven to be good candidates for the destructive treatment of recalcitrant pollutants [7–9] and until now numerous studies have been devoted to the oxidative treatment of different surfactant types [10–16]. However, there are still some critical issues that need to be further addressed. For instance, several studies reported the advanced oxidation of anionic and nonionic surfactants or their mixtures, in particular alkyl (mainly octyl- and nonyl-) phenol ethoxylates which are also known as potential endocrine disrupting compounds [17,18]. Advanced oxidation of cationic surfactants that are consumed at relatively low amounts but are at the same time more toxic and essentially nonreplacable for some specific industrial applications remained almost untouched. In addition, according to our knowledge, there is no study available in the scientific literature dealing with the (i) kinetic evaluation and comparative application of AOPs for the treatment of different

Abbreviations: ANOVA, analysis of variance; AOP, advanced oxidation process; CCD, central composite design; COD, chemical oxygen demand (mg L⁻¹); COD_o, initial COD (mg L⁻¹); DAD, diode-array detector; DBAS, Disulphine Blue Active Substances; DOS, dioctyl sulfosuccinate; EHTH, quaternary ammonium ethoxylate; Exp, experimental; *F*-value, Fisher value; FLD, fluorescence detector; FO, full oxidation; HPLC, high performance liquid chromatography; H₂O₂, hydrogen peroxide; H₂O_{2o}, initial H₂O₂ concentration (mg L⁻¹); NPEO, nonyl phenol ethoxylate; PC, parent compound; Pred, predicted; PO, partial oxidation; PROB, probability; R², coefficient of variation; RSM, response surface methodology; *t_r*, reaction time (min); TOC, total organic carbon (mg L⁻¹).

* Corresponding author. Tel.: +90 212 285 65 79; fax: +90 212 285 65 45..

E-mail addresses: tolmez@itu.edu.tr, tolmez@ins.itu.edu.tr (T. Olmez-Hanci).

surfactant types as well as (ii) optimization and statistical analysis of major process variables affecting the partial and complete oxidation of different commercial surfactants by employing an experimental design approach.

Response surface methodology (RSM) is a collection of statistical and mathematical techniques that are employed for the development, improvement and optimization of certain processes in which a response of interest is affected by several process variables and the objective is to optimize this response [19]. RSM has a multitude of application ranges in the design, development and formulation of new processes and products, or the improvement of an existing product [20–25]. It defines single and combined effects of the process independent variables by the establishment of mathematical model equations that describe physical operations as well as chemical or biochemical processes [19,22,26]. RSM offers several advantages over classical experimental optimization methods in which a “one process variable at a time” approach, that is not fully correct, is applied. RSM provides more information from a relatively little number of experiments as compared with conventional optimization procedures, which is less expensive and time consuming [19]. In addition, empirical models developed by the application of RSM relate the response variables to the process independent parameters to obtain more information about the process or operation. In particular, in more complex treatment systems such as photochemical advanced oxidation processes, interactive and synergistic effects are quite common making these applications ideal candidates for RSM [27].

Considering the above mentioned facts, the present experimental study aimed at investigating the photochemical oxidation of commercially important anionic (a dioctyl sulfosuccinate), cationic (a quaternary ammonium ethoxylate) and nonionic (a nonyl phenol ethoxylate derivative) surfactant types being frequently employed in the textile preparation (scouring, bleaching, mercerizing) activities with the H_2O_2 /UV-C process. RSM–central composite design (CCD) was used to analyze, model and optimize surfactant (parent compound, PC) and organic carbon (chemical oxygen demand (COD) and total organic carbon (TOC)) removals during photochemical treatment. The experimental design approach differed from previously published, related work [16,20,21,23–25] in that (i) three different responses were modeled for three different pollutant types by using two different experimental ranges in terms of the independent variable “photochemical treatment time”, (ii) H_2O_2 /UV-C treatment was individually optimized for partial and full (complete) oxidation (PC, COD and TOC removals) at different initial COD values considering that effluent from the textile preparation stage may vary in its organic pollution load, (iii) separate validation experiments were conducted to confirm the model’s adequacy and fitness at the local optimum (initial surfactant) values as well as different photochemical treatment time intervals. Overall, the main objective of the present study was to develop a simple, reliable and COD-oriented model to optimize the effective treatment of wastewater bearing a similar group of industrial pollutants.

2. Materials and methods

2.1. Materials

The study focused on the photochemical treatment of three commercial surfactant types used in the textile preparation processes. For this purpose, anionic (a dioctyl sulfosuccinate; called DOS herein), cationic (a quaternary ammonium ethoxylate, called ETHHT herein, that is also its trade name) and nonionic (a nonyl phenol ethoxylate derivative, NP-10; called NPEO herein) surfactants were selected to assess the effect of surfactant structure and type on

the H_2O_2 /UV-C treatment rate and efficiency. The surfactants were obtained from a local company manufacturing textile auxiliaries and were of high purity (>90%). Aqueous solutions of the surfactants were prepared at concentrations being typical for effluents originating from the textile preparation activities. The physicochemical characteristics of the studied surfactants are summarized in Table 1. All other chemicals and reagents used were analytical grade and purchased from Fluka or Merck, Germany.

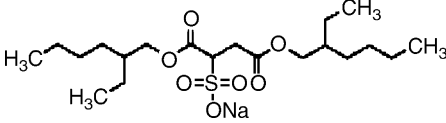
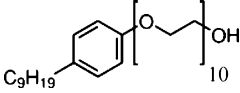
2.2. Photoreactor and UV light source

H_2O_2 /UV-C treatment experiments were performed at varying H_2O_2 concentrations (15–75 mM) and initial surfactant COD values (300–900 $mg\ L^{-1}$) for a treatment time of up to 100 min. At the studied initial COD values the range of surfactant concentrations were 200–600 $mg\ L^{-1}$ for DOS, 155–464 $mg\ L^{-1}$ for ETHHT and 147–441 $mg\ L^{-1}$ for NPEO. The pH and ionic strength of the surfactant samples was not controlled during photochemical treatment. The UV-C photoreactor was a 3250 mL-capacity batch stainless steel tube (length = 84.5 cm; width = 8 cm) with a 40 W low pressure, mercury vapor sterilization lamp that was located at the center of the photoreactor in a quartz sleeve. The incident light flux of the UV-C lamp at 253.7 nm was determined via H_2O_2 actinometry [28] as 1.603×10^{-5} einstein $L^{-1}\ s^{-1}$. The effective UV-C light path length was calculated as 5.14 cm by using the same analytical method. During a typical run, 3250 mL aqueous surfactant solution was continuously circulated through the reactor by means of a peristaltic pump at a rate of 400 $mL\ min^{-1}$, corresponding to a hydraulic retention time of 7.5 min in the photoreactor.

2.3. Experimental design

The present work consisted of four main stages. Firstly, preliminary baseline experiments were conducted in which the levels and ranges of some important variables of the H_2O_2 /UV-C treatment process were established. The second stage comprises the design of photochemical treatment conditions for each individual surfactant formulation by employing RSM. In this respect, the polynomial model equations generated by the factorial design tool were statistically analyzed for their correctness, fitness and reliability. In the third stage of the study, optimum local conditions were determined for different initial COD (COD_0) values. For this COD (pollution load)-oriented process optimization, different treatment targets were set, namely (i) partial oxidation (PO) to a specific discharge limit value in terms of the COD parameter accompanied with complete surfactant degradation; (ii) full oxidation (FO) where complete surfactant treatment accompanied with maximized COD and TOC removals were achieved. In the final stage of the present work, separate validation experiments were conducted a local optimum points (varying initial COD values) in order to confirm the correctness and fit of the proposed polynomial regression models and to describe the photochemical treatment of the surfactant formulations at different time intervals of H_2O_2 /UV-C oxidation. Herein it should be emphasized that PC (surfactant) degradation was appreciable faster than organic carbon (COD and TOC) abatement for all studied surfactants. As a consequence, the treatment conditions and hence values of the process independent variable “reaction time – t_r ” was split into two separate ranges; (1) between 2–18 min, 2–18 min and 10–30 min for DOS, ETHHT and NPEO removals, respectively, and (2) 20–100 min for organic carbon (COD and TOC) removal efficiencies for the same surfactant formulations. For three process independent variables ($n = 3$), a total number of experiments was 16 as determined by the expression: $2n (2^3 = 8; \text{factor points}) + 2n (2 \times 3 = 6; \text{axial points}) + 2$ (center points, two replications). Table 2 presents the experimental design matrix established by the CCD, with the coded values

Table 1
Physicochemical properties of the studied anionic (DOS), cationic (ETHT) and nonionic (NPEO) textile surfactants.

	DOS	ETHT	NPEO
Molecular formula	C ₂₀ H ₃₇ NaO ₇ S	C _{36.4} H _{76.8} NCl	C ₉ H ₁₉ C ₆ H ₄ (OCH ₂ CH ₂) ₁₀ OH
Molecular weight (g mol ⁻¹)	444	563	660
g COD (g PC) ^{-1a}	1.50	1.94	2.04
g TOC (g PC) ^{-1a}	0.69	0.55	0.51
Molecular structure		Confidential (protected by patent)	

^a Experimental values obtained from the calibration curves.

(in brackets, minimum (-2), maximum (2) and the central point (0)) and their corresponding process parameters and values. The range and levels used in the experiments are also given in Table 2 in which X_1 denotes the reaction time (t_r , min), X_2 the initial COD value (COD₀, mg L⁻¹) and X_3 the initial H₂O₂ concentration (H₂O₂₀). Based on Table 2, the experiments were conducted to obtain the responses percent PC, COD and TOC removal efficiencies, at the corresponding independent variables addressed in the design matrix. The sequence of experiments was randomized in order to minimize the effects of uncontrolled factors. In general, the response for the quadratic polynomial is described in Eq. (1);

$$Y = b_0 + \sum b_i X_i + \sum b_{ii} X_i^2 + \sum b_{ij} X_i X_j \quad (1)$$

where Y is the predicted response, b_0 the intercept coefficient, b_i the linear terms, b_{ii} the squared terms, b_{ij} the interaction terms, and X_i and X_j represent the coded independent variables [19]. In the present work the analyses of variance (ANOVA) and response surface plots were performed using the Design Expert Software (version 7.1.5) from Stat-Ease Inc., USA.

2.4. Analytical procedures

Sample aliquots were taken against photochemical treatment time (0–100 min) for PC, COD, TOC, residual H₂O₂ and pH analyses. Before conducting the measurements, the pH of the samples was adjusted to 6.5–7.5 followed by catalase enzyme addition, whereas residual (unreacted) H₂O₂ was measured directly after pH adjustment. DOS was measured via high performance liquid chromatography (HPLC; Agilent 1100 series, USA) equipped with a fluorescence detector (FLD; $\lambda_{ex} = 225$ nm, $\lambda_{em} = 295$ nm)

and a C8 column. 3 mM NaCl/CH₃CN (80:20, v/v) served as the mobile phase (flow rate of 1.5 mL min⁻¹). The instrument detection limit for DOS (1.5 mg L⁻¹) was determined as the lowest injected standard that gave a signal-to-noise ratio of at least 3 and an accuracy of 80–95%. NPEO was also measured via HPLC (Agilent 1100 Series, USA) equipped with a Diode-Array Detector (DAD, G1315A, Agilent Series) and a Novapack reverse phase C18 column (3.9 mm × 150 mm, 5 μm, Waters). The detector was adjusted to 280 nm. A mixture of CH₃OH/H₂O (80:20, v/v) was used as the mobile phase at a flow rate of 1.1 mL min⁻¹. For both surfactant analyses, the column temperatures were fixed at 25 °C and the injection volumes were selected as 50 μL. The quantification limit for both surfactants was calculated as 10 times of the signal-to-noise ratio and found to be 5 mg L⁻¹. For the determination of ETHT concentrations the Disulphine Blue Active Substances (DBAS) colorimetric method [29] was chosen due to its high sensitivity for this cationic surfactant type.

Optimization of photochemical surfactant removal on the basis of two different oxidation targets was mainly evaluated in terms of the collective environmental parameter COD. COD values in all reaction samples were determined by the closed reflux titrimetric method according to ISO 6060 [30]. Residual (unreacted) H₂O₂ was traced by employing the molybdate-catalyzed iodometric method during the course of reaction [31]. Any remaining H₂O₂ was immediately destroyed thereafter by the addition of enzyme catalase made from *Micrococcus lysodeikticus* (200181 AU/mL, Fluka) to prevent positive interferences with COD analysis. The TOC of the samples was monitored on a Shimadzu V_{PCN} carbon analyzer equipped with an autosampler. The pH of reaction samples during photochemical treatment was followed by an Orion 720⁺ model pH-meter. All measurements were carried out in duplicate and

Table 2
Experimental design matrix of process independent variables established for photochemical treatment of aqueous DOS, ETHT and NPEO textile surfactants for the responses percent PC, COD and TOC removals.

Experiment no.	Organic carbon			(COD and TOC) $X_1 - t_r$ (min)	All responses	
	DOS $X_1 - t_r$ (min)	ETHT $X_1 - t_r$ (min)	NPEO $X_1 - t_r$ (min)		$X_2 - \text{COD}_0$ (mg L ⁻¹)	$X_3 - \text{H}_2\text{O}_{20}$ (mM)
1	2 (-2)	10 (0)	2 (-2)	100 (+2)	600 (0)	45 (0)
2	14 (+1)	15 (-1)	14 (+1)	80 (+1)	750 (+1)	60 (+1)
3	18 (+2)	20 (0)	18 (+2)	60 (0)	600 (0)	45 (0)
4	14 (+1)	25 (+1)	14 (+1)	40 (-1)	450 (-1)	30 (-1)
5	10 (0)	20 (0)	10 (0)	60 (0)	600 (0)	75 (+2)
6	10 (0)	30 (+2)	10 (0)	60 (0)	600 (0)	45 (0)
7	14 (+1)	25 (+1)	6 (-1)	40 (-1)	450 (-1)	60 (+1)
8	6 (-1)	15 (-1)	14 (+1)	80 (+1)	450 (-1)	60 (+1)
9	6 (-1)	15 (-1)	6 (-1)	80 (+1)	450 (-1)	30 (-1)
10	10 (0)	20 (0)	10 (0)	60 (0)	300 (-2)	45 (0)
11	10 (0)	20 (0)	10 (0)	60 (0)	900 (+2)	45 (0)
12	14 (+1)	25 (+1)	14 (+1)	80 (+1)	750 (+1)	30 (-1)
13	10 (0)	20 (0)	10 (0)	60 (0)	600 (0)	15 (-2)
14	6 (-1)	25 (+1)	6 (-1)	40 (-1)	750 (+1)	60 (+1)
15	6 (-1)	25 (+1)	6 (-1)	40 (-1)	750 (+1)	30 (-1)
16	10 (0)	20 (0)	10 (0)	20 (-2)	600 (0)	45 (0)

arithmetic averages were taken throughout the data analysis and calculations. Variation coefficients for COD measurements were $<\pm 10\%$ and $<\pm 5\%$ for surfactant and TOC measurements.

3. Results and discussions

3.1. $H_2O_2/UV-C$ oxidation of textile surfactants: preliminary treatment performance assessment

The $H_2O_2/UV-C$ treatment process is affected by numerous parameters such as reaction time, pH, initial H_2O_2 and pollutant concentrations, temperature as well as intensity of the UV-C light source [7]. Since it is too complicated to consider all process variables, the selection of those variables having a significant influence on treatment performance becomes important. Hence, preliminary baseline experiments are generally very useful to identify the major process variables and to decide for their most appropriate levels and ranges. In the present study, the initial pH of the $H_2O_2/UV-C$ experiments was selected as 10.5 mainly because the pH of typical textile preparation effluent is usually in the range of 10–11 [32]. Besides, in our previous studies, surfactant treatment with the $H_2O_2/UV-C$ process appeared to be practically pH-independent in the range of 3–11 [11,16]. Hence, reaction pH was not considered as an independent process variable in the present study and adjusted to an initial value of 10.5 in all experiments. Preliminary $H_2O_2/UV-C$ experiments were carried out at $COD_0 = 450 \text{ mg L}^{-1}$ and $pH_0 = 10.5$ with an initial H_2O_2 concentration of 30 mM which was close to the stoichiometric oxygen equivalent of the initial COD values of surfactant solutions ($=450 \text{ mg L}^{-1} \text{ COD} \times 2.12 \text{ mg } H_2O_2 (\text{mg } O_2)^{-1} = 954 \text{ mg L}^{-1} H_2O_2 = 28 \text{ mM } H_2O_2$) and was thought to be a good starting concentration considering our previous experiments conducted with industrial pollutants including surfactants having the same initial COD levels [16,33,34].

Fig. 1 presents the results of the preliminary experiments obtained for $H_2O_2/UV-C$ treatment of the anionic, cationic and nonionic textile surfactants in terms of parent compound (PC) (a), COD (b) and TOC (c) abatement rates. A general remark could be that the abatement of the PC is fastest, followed by COD (oxidation) and TOC (mineralization) abatements as typically being expected for photochemical AOPs [7]. Fig. 1(a) depicts DOS, ETHT and NPEO abatement profiles as a function of photochemical treatment time. From Fig. 1(a) it is apparent that surfactant degradation is fast and practically complete within a treatment period of only 15–20 min for NPEO and 30 min for the cationic surfactant ETHT, whereas complete DOS degradation required a slightly longer treatment period, although practically 90% was already degraded after 20–25 min $H_2O_2/UV-C$ treatment. As is evident in the insert of Fig. 1(a) depicting surfactant abatements versus photocatalytic treatment time, the degradation of all studied surfactant types via $H_2O_2/UV-C$ process followed pseudo-first order kinetics with respect to the surfactant concentrations with high correlation coefficients ($R^2 \geq 0.98$). The surfactant abatement rates were established in the following decreasing order; NPEO (0.221 min^{-1}) > ETHT (0.165 min^{-1}) > DOS (0.081 min^{-1}).

The differences in surfactant degradation rates were mainly attributable to the structural and charge differences between the studied textile surfactant types [35]. According to Brand et al. [36] the ethoxy functional groups of alkyl phenol ethoxylate type nonionic surfactants are very prone to HO^\bullet attack. Therefore, the primary step of NPEO oxidation is thought to involve hydrogen abstraction of one carbon atom of the ethoxy moiety and the immediate cleavage of the ethoxylated chain. In the case of the anionic surfactant (DOS), HO^\bullet attack occurs at two sites; the CH_3- groups located at the end of the ethoxy chain as well as the CH_2- groups in the intermediate position [37]. As a conse-

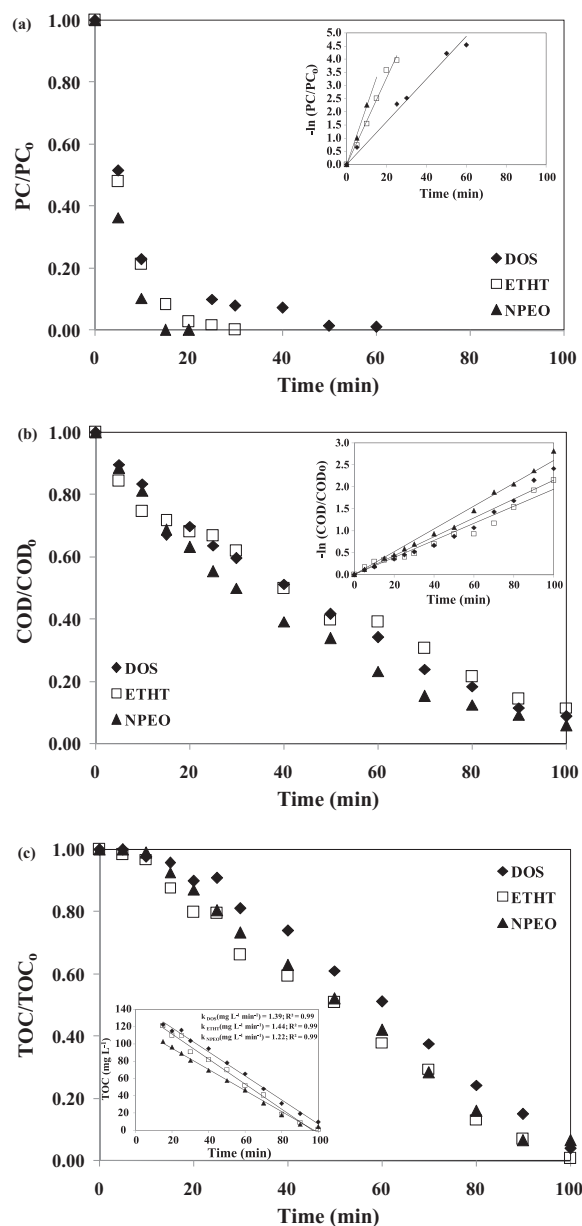


Fig. 1. Normalized PC (a), COD (b) and TOC (c) abatements versus photochemical treatment time for DOS, ETHT and NPEO. Experimental conditions: $COD_0 = 450 \text{ mg L}^{-1}$, $DOS_0 = 300 \text{ mg L}^{-1}$; $ETHT_0 = 232 \text{ mg L}^{-1}$; $NPEO_0 = 220 \text{ mg L}^{-1}$; $H_2O_2_0 = 30 \text{ mM}$; $pH_0 = 10.5$.

quence of the hydrogen abstraction reactions, alkyl radicals (R^\bullet) are formed during the oxidation of the anionic surfactants. These organic radicals may react with another HO^\bullet to form low molecular weight degradation intermediates including alcohols [37]. A possible explanation for the deviation of the degradation pattern for the anionic surfactant DOS could be explained by the prompt reaction of formed organic radicals and/or degradation intermediates with the HO^\bullet thus competing with the parent pollutant (DOS) for active oxidizing agents and thereby retarding its degradation. Fig. 1(b) presents COD evolutions as a function of photochemical treatment time. From the semi-logarithmic plots obtained for COD abatements versus photochemical treatment time it is evident that COD abatements followed pseudo-first order kinetics with respect to surfactant CODs exerting high correlation coefficients ($R^2_{DOS \text{ and } ETHT} = 0.96$; $R^2_{NPEO} = 0.99$) for the whole photochemical treatment period. The COD abatement rate coefficients were

Table 3

Experimental results (responses: percent PC, COD and TOC removal efficiencies) obtained by using the design layout proposed by the RSM tool.

Experiment no.	Surfactant type								
	DOS			ETHT			NPEO		
	PC (%)	COD (%)	TOC (%)	PC (%)	COD (%)	TOC (%)	PC (%)	COD (%)	TOC (%)
1	7 ± 0.4	90 ± 9.0	96 ± 4.0	75 ± 3.8	96 ± 4.0	97 ± 3.0	6 ± 0.3	86 ± 8.6	83 ± 8.3
2	89 ± 4.5	72 ± 7.2	73 ± 7.3	68 ± 3.4	84 ± 8.4	85 ± 8.5	74 ± 3.7	68 ± 6.8	45 ± 4.5
3	87 ± 4.4	73 ± 7.3	62 ± 6.2	91 ± 4.6	78 ± 7.8	69 ± 6.9	95 ± 5.0	61 ± 6.1	41 ± 4.1
4	95 ± 5.0	62 ± 6.2	47 ± 4.7	99 ± 1.0	67 ± 6.7	50 ± 5.0	95 ± 5.0	55 ± 5.5	34 ± 3.4
5	44 ± 2.2	63 ± 6.3	50 ± 5.0	82 ± 4.1	78 ± 7.8	62 ± 6.2	77 ± 3.9	64 ± 6.4	39 ± 3.9
6	77 ± 3.9	73 ± 7.3	62 ± 6.2	97 ± 3.0	78 ± 7.8	69 ± 6.9	83 ± 4.2	61 ± 6.1	41 ± 4.1
7	75 ± 3.8	60 ± 6.0	38 ± 3.8	92 ± 4.6	69 ± 6.9	51 ± 5.1	62 ± 3.1	62 ± 6.2	28 ± 2.8
8	54 ± 2.7	82 ± 8.2	91 ± 9.0	80 ± 4.0	97 ± 3.0	97 ± 3.0	95 ± 5.0	86 ± 8.6	78 ± 7.8
9	64 ± 3.2	95 ± 5.0	97 ± 3.0	95 ± 4.8	94 ± 6.0	93 ± 7.0	69 ± 3.5	86 ± 8.6	84 ± 8.4
10	61 ± 3.1	83 ± 8.3	78 ± 7.8	90 ± 4.5	93 ± 7.0	92 ± 8.0	95 ± 5.0	84 ± 8.4	65 ± 6.5
11	78 ± 3.9	59 ± 5.9	39 ± 3.9	86 ± 4.3	55 ± 5.5	41 ± 4.1	56 ± 2.8	42 ± 4.2	31 ± 3.1
12	74 ± 3.7	52 ± 5.2	67 ± 6.7	93 ± 4.7	53 ± 5.3	46 ± 4.6	83 ± 4.2	45 ± 4.5	26 ± 2.6
13	95 ± 5.0	47 ± 4.7	17 ± 1.7	91 ± 4.6	40 ± 4.0	24 ± 2.4	84 ± 4.2	42 ± 4.2	31 ± 3.1
14	61 ± 3.1	45 ± 4.5	26 ± 2.6	84 ± 4.2	50 ± 5.0	35 ± 3.5	37 ± 1.9	54 ± 5.4	30 ± 3.0
15	50 ± 2.5	33 ± 3.3	17 ± 1.7	93 ± 4.7	40 ± 4.0	29 ± 2.9	35 ± 1.8	39 ± 3.9	20 ± 2.0
16	77 ± 3.9	29 ± 2.9	11 ± 1.1	93 ± 4.7	34 ± 3.4	21 ± 2.1	83 ± 4.2	24 ± 2.4	11 ± 1.1

calculated as 0.021 min^{-1} , 0.019 min^{-1} and 0.026 min^{-1} for DOS, ETHT and NPEO, respectively. The highest COD degradation rate coefficient was obtained for NPEO revealing that the intermediates formed during $\text{H}_2\text{O}_2/\text{UV-C}$ treatment of the nonionic surfactant (NPEO) were more readily oxidized than those formed during the photochemical degradation of the surfactants DOS and ETHT. After 60 min photochemical treatment, COD removal efficiencies were obtained as 66%, 61% and 77% for DOS, ETHT and NPEO, respectively. Increasing the photochemical treatment time to 100 min resulted in over 90% COD removal efficiencies for all studied textile surfactants.

An important measure of AOP performance is the degree of mineralization achieved for the target pollutants because it signifies the overall destruction of potentially toxic organic intermediates to environmentally benign end products. In this respect, Fig. 1(c) displays TOC abatements throughout photochemical treatment of the textile surfactant solutions. Upon closer inspection of the TOC abatement profiles, it is evident that during the first 10 min of the reaction, practically no TOC removal was recorded and after this brief induction period, mineralization started and reached nearly 90% at the end of the treatment period. It is expected that mineralization occurs at the later stages of oxidation and thus it is not surprising that an initial lag-phase was observed although rapid surfactant transformation of the PC as well as COD abatements started right at the beginning of the photochemical reaction [16,38,39]. As can be clearly seen from the insert in Fig. 1(c), TOC removals did not obey first order kinetics, but could be satisfactorily fitted to zero-order kinetics ($d\text{TOC}/dt = k_{\text{TOC}}$) for the treatment period observed after the lag-phase (10–100 min). The calculated rate coefficients exhibited the following increasing order; NPEO ($1.22 \text{ mg L}^{-1} \text{ min}^{-1}$) < DOS ($1.39 \text{ mg L}^{-1} \text{ min}^{-1}$) < ETHT

($1.44 \text{ mg L}^{-1} \text{ min}^{-1}$). TOC removals achieved after 100 min photochemical treatment were 96%, 99% and 93% for DOS, ETHT and NPEO, respectively. Information about the rate and degree of ultimate oxidation can be derived from the TOC data, representing mineralization of the original pollutants and their photodegradation products to oxidation end products [39]. As apparent from the calculated PC and TOC removal kinetics, NPEO was relatively rapidly degraded but rather slowly mineralized. Nevertheless, these results clearly demonstrate that $\text{H}_2\text{O}_2/\text{UV-C}$ process can be efficiently used for photocatalytic mineralization of both anionic, cationic and nonionic surfactants.

H_2O_2 consumption rates were also monitored throughout the course of the $\text{H}_2\text{O}_2/\text{UV-C}$ oxidation experiments for all three surfactants (data not shown). As can be seen from Fig. 1(b) and (c), the oxidation of the surfactants continued during the course of $\text{H}_2\text{O}_2/\text{UV-C}$ treatment (till 100 min) and even at the end of the photochemical treatment time there was still H_2O_2 present in the reaction solution. According to the obtained data, 98% of the initially added H_2O_2 was consumed at the end of the treatment period (=100 min) for all studied surfactant formulations. Changes in pH were also followed during $\text{H}_2\text{O}_2/\text{UV-C}$ treatment of the studied surfactants (data not shown); the reaction pH slowly decreased from its original value being 10.5 to around 3.5–3.6 during the first 50 min of photochemical treatment, most probably due to the formation of acidic oxidation intermediates (carboxylic acids). After approximately 50 min, the pH started to increase because of the generated CO_2 that was subsequently released from the reaction solution and finally reached pH 4.7, 5.5 and 5.9 for DOS, ETHT and NPEO at the end of the 100 min reaction time, respectively, depending upon the degradation intermediates and kinetics of each surfactant type.

Table 4

Quadratic models obtained for percent PC, COD and TOC removal efficiencies in terms of coded factors.

Surfactant type	Quadratic regression models
DOS	PC (%) = $79.25 + 16.81 \times X_1 + 0.94 \times X_2 - 7.56 \times X_3 - 0.62 \times X_1 \times X_2 - 1.37 \times X_1 \times X_3 + 7.63 \times X_2 \times X_3 - 7.50 \times (X_1)^2 - 1.87 \times (X_2)^2 - 1.25 \times (X_3)^2$ COD (%) = $72.31 + 14.25 \times X_1 - 9.38 \times X_2 + 2.75 \times X_3 - 1.75 \times X_1 \times X_2 + 6.50 \times X_2 \times X_3 - 1.00 \times X_1 \times X_3 - 3.37 \times (X_1)^2 - 0.50 \times (X_2)^2 - 4.50 \times (X_3)^2$ TOC (%) = $64.56 + 23.12 \times X_1 - 10.50 \times X_2 + 4.13 \times X_3 + 10^{-3} \times X_1 \times X_3 - 0.75 \times X_1 \times X_2 + 3.75 \times X_2 \times X_3 - 2.12 \times (X_1)^2 - 0.87 \times (X_2)^2 - 7.12 \times (X_3)^2$
ETHT	PC (%) = $90.81 + 5.51 \times X_1 - 2.91 \times X_2 - 3.86 \times X_3 + 1.41 \times X_1 \times X_2 - 0.14 \times X_2 \times X_3 + 1.64 \times X_1 \times X_3 - 1.36 \times (X_1)^2 - 0.96 \times (X_2)^2 - 1.25 \times (X_3)^2$ COD (%) = $77.90 + 14.11 \times X_1 - 10.88 \times X_2 + 7.67 \times X_3 - 1.04 \times X_1 \times X_2 + 4.59 \times X_2 \times X_3 + 2.74 \times X_1 \times X_3 - 3.22 \times (X_1)^2 - 0.86 \times (X_2)^2 - 4.70 \times (X_3)^2$ TOC (%) = $69.53 + 19.30 \times X_1 - 12.26 \times X_2 + 7.89 \times X_3 - 2.85 \times X_1 \times X_2 + 4.93 \times X_2 \times X_3 + 4.52 \times X_1 \times X_3 - 2.55 \times (X_1)^2 - 0.59 \times (X_2)^2 - 6.47 \times (X_3)^2$
NPEO	PC (%) = $81.19 + 21.37 \times X_1 - 11.88 \times X_2 - 1.75 \times X_3 + 2.0 \times X_1 \times X_2 - 0.5 \times X_1 \times X_3 + 10^{-2} \times X_2 \times X_3 - 7.50 \times (X_1)^2 - 1.25 \times (X_2)^2 - 0.63 \times (X_3)^2$ COD (%) = $63.50 + 12.44 \times X_1 - 10.44 \times X_2 + 6.69 \times X_3 - 4.37 \times X_1 \times X_2 + 0.12 \times X_1 \times X_3 + 3.38 \times X_2 \times X_3 - 1.50 \times (X_1)^2 + 0.50 \times (X_2)^2 - 3.12 \times (X_3)^2$ TOC (%) = $42.50 + 16.56 \times X_1 - 10.69 \times X_2 + 4.69 \times X_3 - 9.99 \times X_1 \times X_2 + 1.12 \times X_1 \times X_3 + 5.13 \times X_2 \times X_3 + 1.50 \times (X_1)^2 + 1.75 \times (X_2)^2 - 4.12 \times (X_3)^2$

Table 5

ANOVA results obtained for the quadratic models established for H₂O₂/UV-C treatment of aqueous DOS, ETHT and NPEO surfactants in terms of the process responses percent PC, COD and TOC removal efficiencies.

Response type	Surfactant type		
	DOS	ETHT	NPEO
PC removal efficiency (%)			
R ²	0.8612	0.8883	0.9838
Lack-of-fit	1127.31	115.31	177.56
F-value	4.14	5.30	40.58
Adequate precision	7.94	7.04	22.53
Prob > F	0.049	0.0276	0.0001
COD removal efficiency (%)			
R ²	0.9488	0.9751	0.9486
Lack-of-fit	182.56	171.33	296.31
F-value	12.34	26.08	12.29
Adequate precision	11.35	15.46	10.64
Prob > F	0.0031	0.0004	0.0032
TOC removal efficiency (%)			
R ²	0.9631	0.9844	0.9695
Lack-of-fit	447.06	167.71	260.81
F-value	17.42	42.16	21.16
Adequate precision	13.56	19.40	12.71
Prob > F	0.0012	<0.0001	0.0007

Several control experiments were also conducted to verify the reaction mechanism of surfactant degradation. The absence of UV-C light irradiation (mere H₂O₂ oxidation) did not cause any DOS, ETHT and NPEO degradation. Less than 10% PC abatements without any changes observed in the parameters COD and TOC were observed as a consequence of direct UV-C photolysis of the textile surfactants in the absence of H₂O₂ (data not shown).

3.2. Results of the central composite design experiments: establishment of polynomial regression models

Experimental data shown in Table 3 were used to establish the second-order response surface models for photochemical PC, COD and TOC removals. The coefficients of the model for the responses were estimated using the multiple regression analysis technique included in the RSM. The quadratic models obtained in terms of percent PC and organic carbon (COD and TOC) removals are given in Table 4 in terms of coded factors. The algebraic sign and the value in front of the coded model terms indicate the intensity and direction (positive or negative) of the influence of that process independent variable on the response [40]. The “+” sign in front of the term indicates positive influence, where as “-” sign indicates a negative influence. The linear effects of process independent variables on PC, COD and TOC removals (responses) are schematically displayed in Fig. 2(a), (b) and (c), respectively. As can be seen from Fig. 2, the variable t_r coded as X_1 exhibited the highest positive influence on PC and COD–TOC removals. The initial COD content (variable X_2) of the surfactants exhibited relatively high negative influence on COD and TOC removals. In other words, increasing the initial COD content of the surfactant formulations decreased the oxidation efficiency that can be explained by the fact that less active oxidant (HO[•]) is available to perform COD and TOC abatements. The same trend was also observed for PC removals at a lesser extent except for the anionic surfactant formulation (DOS) that occurred more promptly compared with the other surfactant types. Moreover, in the case of H₂O₂/UV-C oxidation of the anionic surfactant, increasing the initial COD content had a slight positive effect on PC removal. The influence of H₂O₂ concentration (variable X_3) on the responses PC, COD and TOC removals exhibited a different pattern. As can be seen from Table 3 H₂O₂ concentration (variable X_3) negatively influenced the PC removals indicating that the H₂O₂ concentration range selected for the degradation of the

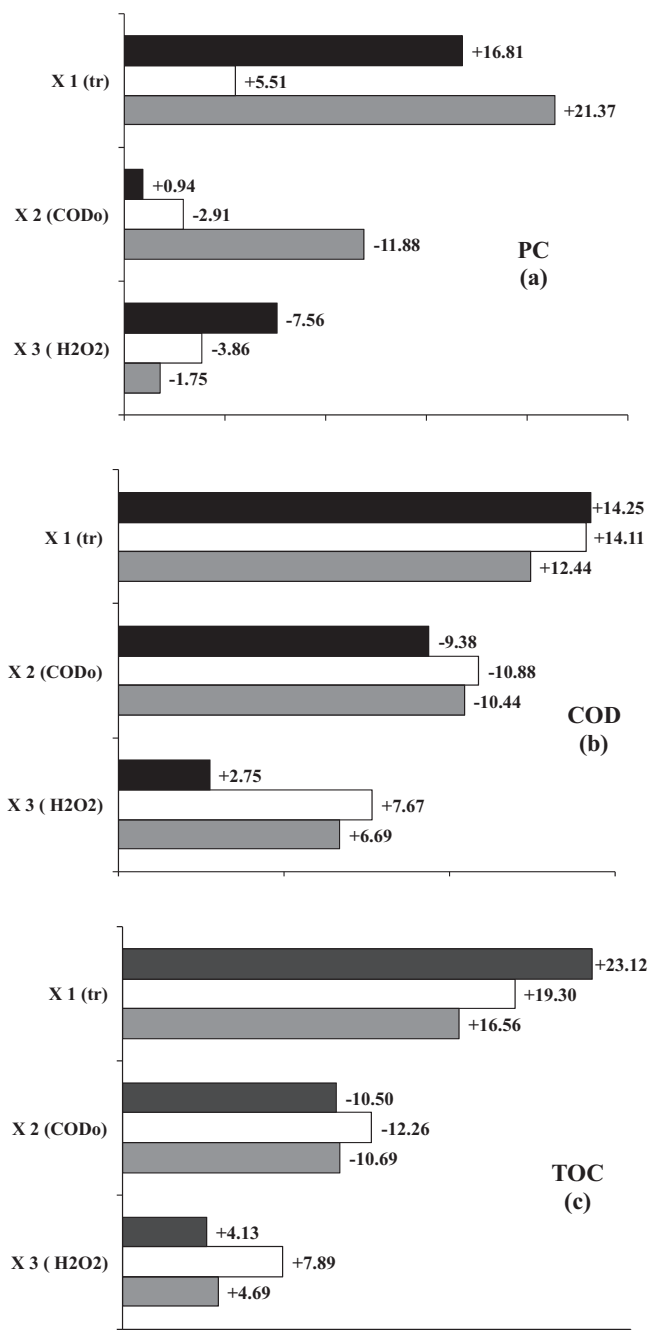


Fig. 2. Elucidation of the relative contribution intensities and signs (indicating positive/negative impacts) for the coefficients of each process independent variables affecting the responses percent PC (a), COD (b) and TOC (c) removal efficiencies obtained for the polynomial regression models describing H₂O₂/UV-C treatment of the textile surfactants DOS (■), ETHT (□) and NPEO (▒).

surfactants was excessive. However, the positive influence of H₂O₂ concentration (variable X_3) on COD and TOC removals indicates that the oxidation and mineralization of all surfactants solutions is more difficult to achieve than parent compound abatements and requires higher H₂O₂ concentration than the PC [16,41]. As is obvious from Fig. 2(a), (b) and (c), the effects of H₂O₂/UV-C process parameters under investigation had disparate effects on different surfactant formulations. The intensity (level) of these process parameters varied again as a consequence of the differences in molecular structure of different surfactant types as well as the quantity of degradation intermediates formed during H₂O₂/UV-C oxidation.

Table 6

Summary of numerical optimization outputs and comparison of the process responses predicted by CCD with those obtained from the experimental runs.

	t_r (min)	H_2O_2 (mM)	COD removal efficiency (%)		TOC removal efficiency (%)		PC removal efficiency (%)	
			Pred	Exp	Pred	Exp	Pred	Exp
DOS								
300 – FO	74	35.3	100	95 ± 5.0	98	99 ± 1.0	100	95 ± 5.0
450 – FO	80	41.7	61	68 ± 6.8	43	39 ± 3.9	100	95 ± 5.0
450 – PO	40	32.8	95	90 ± 9.0	96	95 ± 5.0	100	95 ± 5.0
600 – PO	62	34.9	70	70 ± 7.0	61	63 ± 6.3	100	95 ± 5.0
750 – PO	80	58.8	75	86 ± 8.6	75	82 ± 8.2	100	95 ± 5.0
900 – PO	80	60.0	69	80 ± 8.0	64	73 ± 7.3	100	95 ± 5.0
ETHT								
300 – FO	67	37.4	96	95 ± 5.0	99	95 ± 5.0	100	95 ± 5.0
450 – FO	75	45.2	98	96 ± 4.0	97	93 ± 7.0	100	95 ± 5.0
450 – PO	40	30.0	64	57 ± 5.7	52	39 ± 3.9	100	95 ± 5.0
600 – PO	60	34.3	70	71 ± 7.1	61	58 ± 5.8	100	95 ± 5.0
750 – PO	70	50.0	76	84 ± 8.4	69	73 ± 7.3	100	95 ± 5.0
900 – PO	90	60.0	80	92 ± 8.0	75	88 ± 8.8	100	95 ± 5.0
NPEO								
300 – FO	66	40.4	92	90 ± 9	82	80 ± 8.0	100	95 ± 5.0
450 – FO	92	41.0	95	90 ± 9	99	96 ± 4.0	100	95 ± 5.0
450 – PO	50	30.0	60	56 ± 5.6	40	44 ± 4.4	100	95 ± 5.0
600 – PO	71	45.0	70	68 ± 6.8	54	53 ± 5.3	100	95 ± 5.0
750 – PO	80	60.0	66	67 ± 6.7	50	56 ± 5.6	100	95 ± 5.0
900 – PO	80	60.0	56	61 ± 6.1	39	41 ± 4.1	100	95 ± 5.0

3.3. Statistical evaluation of the central composite design models

In order to ensure a good model fit, the significance of the regression model and the lack-of-fit need to be questioned [22,26,40,41]. Normally, the significance of the model can be determined based on the F or P value (also called the $\text{Prob} > F$ value). The larger the magnitude of the F -value and correspondingly the smaller the “ $\text{Prob} > F$ ” value, the more significant is the established regression model. A “ $\text{Prob} > F$ ” value less than 0.05 indicates that the design model is statistically significant. ANOVA results obtained for the polynomial equations describing PC, COD and TOC removals are presented in Table 5. From Table 5 it is evident that the $\text{Prob} > F$ values of the models are varying between 0.0001 and 0.0490, implying that the models observed for the surfactants DOS, ETHT and NPEO are significant. The precision of a model can be checked by the determination of the coefficient of variation (R^2). The R^2 values for DOS, ETHT and NPEO removal efficiencies were calculated as 0.8612, 0.8883 and 0.9838, respectively. The values of the coefficient of variation for PC removals indicates that about 13.88%, 11.17% and 1.62% of the total variations for DOS, ETHT and NPEO were not satisfactorily designed by the proposed models. The R^2 values of COD and TOC removals are very close to 1 implying that less than 5% of the total variations could not be explained by the models for all studied surfactant formulations. This finding revealed that the accuracy and general ability of the polynomial models obtained for percent COD and TOC removals were appropriate and satisfactory. The obtained adequate precision of the models compares the range of the predicted values at the design points to the average prediction error. That is to say, it measures the signal-to-noise ratio [19] and a ratio greater than 4 is desirable. In our case, the obtained values indicate an adequate signal and suggest that the models can be used to navigate the design spaces.

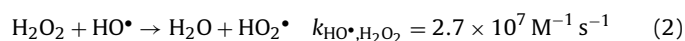
3.4. Interactive effects of process independent variables

3.4.1. Interactive effects of two design variables

Response surface and contour plots were also generated using the same software for different interactions of any two independent variables, while holding the value of the third variable constant at the central (0) level. Such three-dimensional surfaces could yield accurate geometrical representation and provide useful information about the behavior of the system within the experimental

design. On the basis of quadratic polynomial equations presented in Table 4, the effect of the interacting variables reaction time, initial COD value and H_2O_2 concentration on the degradation of anionic (DOS), cationic (ETHT) and nonionic (NPEO) surfactant formulations were analyzed. The effect of COD_0 and H_2O_{20} on percent COD removals are shown in Fig. 3(a), (b) and (c) for DOS, ETHT and NPEO, respectively. In Fig. 3, the effect of process variables is only exemplified in terms of the response “COD removal efficiency” considering that the present work was COD-oriented. From Fig. 3 it is obvious that COD_0 values had a dramatic negative effect on COD abatements of all surfactant formulations. Increasing the COD_0 of the surfactant solutions resulted in a reduction of COD removal efficiencies in the investigated COD_0 ranges. As an example, for $COD_0 = 300 \text{ mg L}^{-1}$, COD removals were obtained as 89%, 96% and 86% for DOS, ETHT and NPEO, respectively ($H_2O_{20} = 45 \text{ mM}$ and $t_r = 60 \text{ min}$). At the same H_2O_{20} and t_r , increasing COD_0 to 900 mg L^{-1} decreased the COD removals down to 51%, 52% and 45% for DOS, ETHT and NPEO, respectively.

In theory, the increase in H_2O_2 concentration applied in the $H_2O_2/UV-C$ process can be beneficial to the oxidation system up to certain level, where further increase (use of excessive concentrations) will have negative influence lowering the HO^\bullet concentration available for the degradation of organics throughout unwanted side reactions [42,43].



As delineated in Fig. 3, elevating the initial H_2O_2 concentration generally improved the COD removal efficiencies obtained for all surfactant types. For the anionic surfactant (DOS), at COD_0 values below 450 mg L^{-1} , elevating H_2O_{20} to 40 mM increased the COD removal efficiencies. However, an increase of H_2O_{20} above this value did not further improve COD removal rates. The same profile was observed for the cationic (ETHT) and nonionic (NPEO) surfactants. However, these critical optimum H_2O_{20} concentrations differed appreciably from each other, depending upon the surfactant type and the degradation profiles observed. In the case of cationic and nonionic surfactants (ETHT and NPEO, respectively) a critical optimum H_2O_{20} existed around 50 mM for COD_0 values $< 450 \text{ mg L}^{-1}$, whereas the optimum H_2O_{20} concentration was lower for the anionic surfactant DOS.

It should be emphasized here that, as aforementioned, H_2O_{20} concentration had a negative influence on PC removals and a

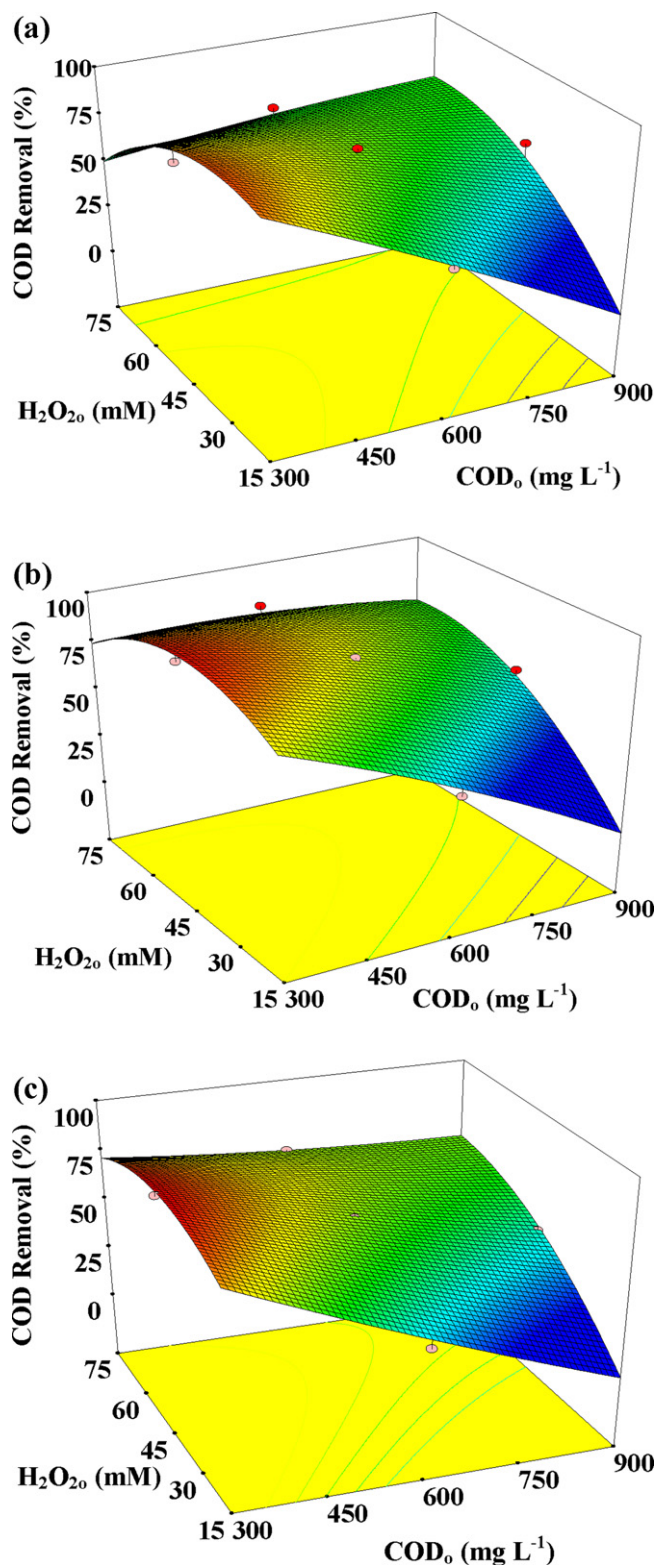


Fig. 3. Interactive effects of varying COD_0 and H_2O_{20} values on percent COD removal efficiencies for aqueous DOS (a), ETHT (b) and NPEO (c). Experimental conditions: DOS = 200–600 mg L^{-1} ; ETHT = 155–464 mg L^{-1} ; NPEO = 14–441 mg L^{-1} ; t_r = 60 min; pH_0 10.5.

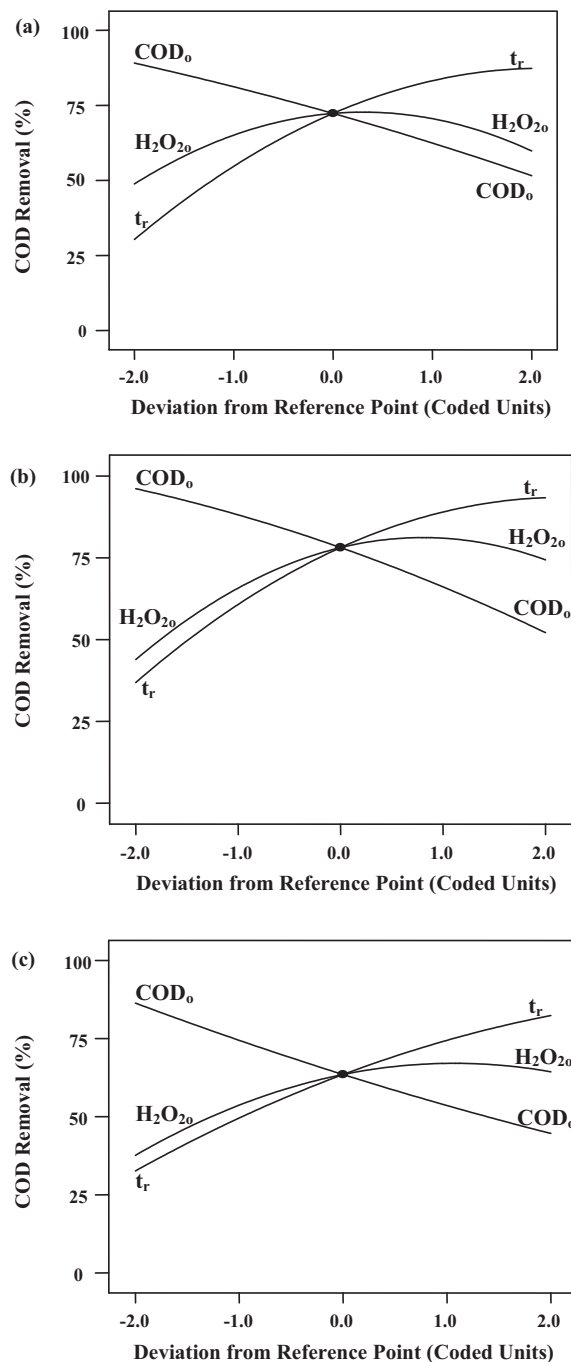


Fig. 4. Overlay plot perturbation of independent variables on percent COD removal efficiencies for aqueous DOS (a), ETHT (b) and NPEO (c). Experimental conditions: COD_0 = 600 mg L^{-1} ; DOS_0 = 400 mg L^{-1} ; ETHT_0 = 309 mg L^{-1} ; NPEO_0 = 294 mg L^{-1} ; H_2O_{20} = 45 mM; t_r = 60 min; pH_0 10.5.

positive influence on organic carbon removal (see Fig. 2). The observed critical H_2O_2 concentrations were significantly lower for PC removals than for COD removals. When the COD_0 of the surfactant solutions were between 300 and 450 mg L^{-1} , $\geq 95\%$ PC removals were obtained even at a H_2O_2 concentration of 15 mM at t_r = 10 min for DOS and NPEO, and t_r = 20 min for ETHT. On the other hand, beyond a critical H_2O_{20} concentration, the PC removals were retarded at COD_0 values ranging between 450 and 900 mg L^{-1} for ETHT (H_2O_{20} > 30 mM) and NPEO (H_2O_{20} > 45 mM), which can be attributed to the HO^\bullet scavenging effect of excessive H_2O_2 concentrations according to Eq. (2). In the case of DOS, at t_r = 10 min, the inhibitory effect of H_2O_2 is dominant in the

COD₀ range of 450–600 mg L⁻¹ and at COD₀ > 600 mg L⁻¹, increasing the H₂O₂ concentration improved DOS removals appreciably. Fig. 3(a), (b) and (c) indicates that COD₀ values of the surfactant solutions had higher influence on COD removals than H₂O₂ concentrations exhibiting distinct and surfactant-specific optimum values.

3.4.2. Interactive effects of three design variables

In order to evaluate the interactive effects of the studied independent variables on COD removals for all three surfactant formulations under study at a time, perturbation graphs were established and depicted in Fig. 4(a), (b) and (c), for DOS, ETHT and NPEO, respectively. The perturbation plots illustrate responses as each independent variable moves from the preferred reference with all other variables held constant at the middle of the design space (the coded zero level). A steep slope or curvature in an independent variable indicates that the response is sensitive to the variable, whereas a relatively flat line indicates insensitivity to change in the variable under consideration. The perturbation plots shown for COD removal of aqueous DOS, ETHT and NPEO against all three investigated independent process variables (t_r , COD₀ and H₂O₂) implies the contribution of each factor to the H₂O₂/UV-C oxidation process. As illustrated by the perturbation plots in Fig. 4(a), (b) and (c), all three independent variables have a major influence on the COD removal of studied surfactant formulations. The curve with the most prominent change was the perturbation curve of COD₀ compared to those of the other independent variables fixed at their maximum levels. Thus, COD₀ was the most significant factor that contributed to the removal of surfactant formulations by the H₂O₂/UV-C photochemical process.

3.5. Initial COD-based optimization of the H₂O₂/UV-C treatment process

As aforementioned, H₂O₂/UV-C treatment of aqueous textile surfactants was individually optimized at different initial COD values for PO to a specific discharge limit value (≤ 200 mg L⁻¹) in terms of the COD parameter according to national discharge limits [44] accompanied with complete surfactant degradation and FO where complete surfactant and the highest possible COD, TOC removals achieved. For the optimization of the responses, the program randomly picks a set of reaction conditions from which to start its search for desirable results. Multiple cycles improve the odds of finding multiple local optimums, some of which will be higher in desirability than others. According to the optimization step of the program, the desired goal for each variable (COD₀, H₂O₂ and t_r) and responses (percent PC, COD and TOC removals) should be chosen. The desired goals for all independent variables, percent PC and TOC removals were defined as “keep in range” while for percent COD removal as “maximize” for FO target and to the required percent COD removal for a COD value of 180 mg L⁻¹ (below 200 mg L⁻¹). Several scenarios were examined in order to find the optimum reaction conditions for different initial COD values of each surfactant formulation for the PO and FO targets and the optimization conditions shown in Table 6. Model-predicted and experimentally obtained results at these optimum conditions with relative experimental error ranges are also given in Table 6 for DOS, ETHT and NPEO surfactant formulations. As can be seen from Table 6, the predicted and experimental results were in good agreement for all studied surfactant formulations. These results testify that the RSM is a powerful tool for optimizing the operational conditions of H₂O₂/UV-C photochemical process for surfactant formulations in terms of parent compound and organic carbon removal.

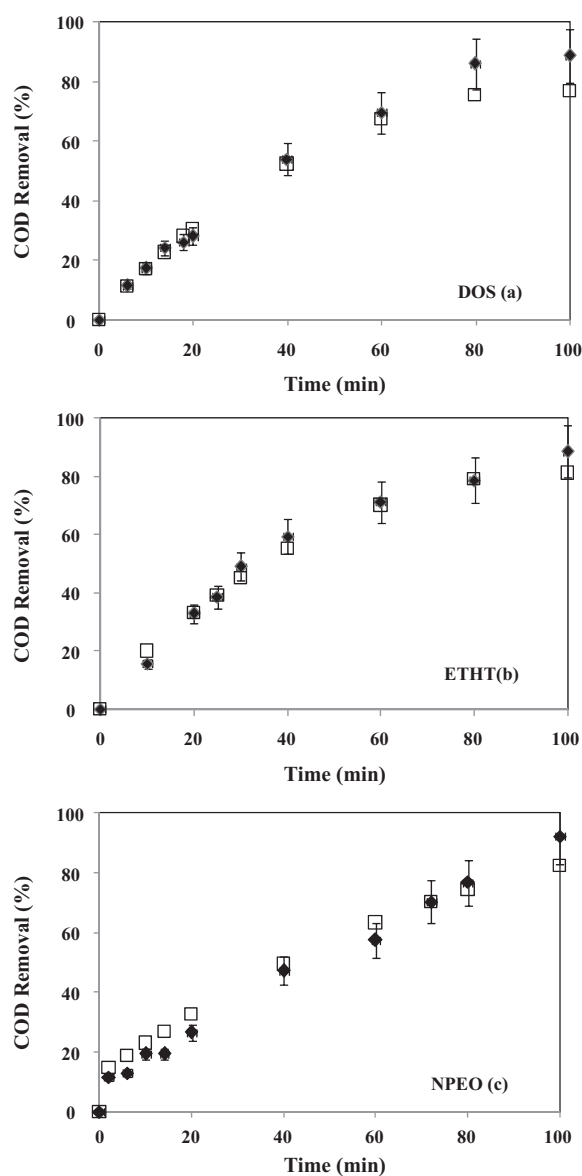


Fig. 5. Comparison of predicted (□) and experimentally obtained (◆) results for photochemical treatment at COD₀ = 600 mg L⁻¹ for DOS (a), ETHT (b) and NPEO (c). Error bars represent the individual precisions of each analytical method. Experimental conditions: DOS₀ = 400 mg L⁻¹; ETHT₀ = 309 mg L⁻¹; NPEO₀ = 294 mg L⁻¹; H₂O₂DOS = 34.9 mM; H₂O₂ETHT = 34.3 mM; H₂O₂NPEO = 45 mM; pH₀ 10.5.

3.6. Elucidation of validation experiments conducted for local optima based on initial surfactant COD

It should be pointed out here that it is important to question the applicability of the proposed quadratic models, in terms of PC, COD and TOC removals, not only for one single optimum reaction time (UV-C dose) but for the entire selected treatment period. The adequacy check of the models throughout the H₂O₂/UV-C treatments was accomplished by running additional experiments that were performed under the projected optimal reaction conditions based on the results from the models that are listed in Table 6. Fig. 5(a), (b) and (c) depicts COD removal efficiencies experimentally obtained together with the results predicted by the regression models for a COD₀ value of 600 mg L⁻¹ and a function of H₂O₂/UV-C treatment time for DOS (a), ETHT (b) and NPEO (c) surfactant formulations. The experimental and model results shown in Fig. 5 reveal that the model predictions for all studied surfactants were satisfactory

during the whole treatment period indicating that the RSM was a suitable method to optimize the operating conditions of H₂O₂/UV-C photochemical process for surfactant formulations treatment.

4. Conclusions

Commercial surfactants are difficult to treat by employing biological processes because they are only partially and slowly biodegradable in engineered biological treatment systems. Advanced oxidation processes including H₂O₂/UV-C treatment offer efficient solutions for the partial and full degradation of recalcitrant and/or toxic industrial pollutants. In the present study, multivariate analysis was employed to experimentally design the photochemical treatment of three different commercial textile surfactants. The following conclusions could be drawn from the present experimental study:

- In the preliminary baseline experiments, rapid degradation of all studied textile surfactant solutions accompanied with high COD and TOC removals was observed. Surfactant abatements were complete within 15–20 min photochemical treatment, whereas over 90% COD and TOC removals could be achieved after prolonged oxidation periods for an initial surfactant COD of 450 mg L⁻¹ and an initial pH of 10.5. The molecular structure and type of the surfactant played a significant role in the obtained photochemical degradation rates. The fastest abatement was observed for the aromatic nonionic surfactant, and the removal of the anionic surfactant was relatively slow. The responses of the experimental runs foreseen by the experimental design tool were used to establish second-order polynomial equations that described percent surfactant (parent compound), COD and TOC removal efficiencies as a function of the selected critical process variables of H₂O₂/UV-C oxidation. The absolute factors and signs in front of the design variables in the regression models indicated that the efficiency of the photochemical treatment process was appreciably influenced by all selected process outputs in the following decreasing order; photochemical treatment time (positive effect) > initial COD content of the surfactant formulation (negative effect) > initially added H₂O₂ concentration (positive effect, except for parent compound removals, that required low concentrations compared to organic carbon abatements).
- Analysis of variance revealed that the established factorial design models were statistically significant and described parent compound, COD and TOC removals at satisfactory levels. The highest correlation coefficients were obtained for TOC removals (surfactant mineralization rates).
- From the three-dimensional plots presenting the interactive relationships between COD removal efficiencies, initial COD's and H₂O₂ concentrations, it was evident that the photochemical treatment system was dramatically retarded by increasing the initial COD content of the surfactant formulations. At initial CODs > 600 mg L⁻¹, increasing the applied H₂O₂ concentration was not capable of compensating the negative impact of increasing the initial COD content of aqueous surfactant solutions and the obtained removal efficiencies were drastically reduced from 95% down to 25%. At relatively low CODs (<450 mg L⁻¹) on the other hand, a surfactant-specific optimum H₂O₂ concentration existed above which treatment efficiencies were negatively affected due to free radical scavenging effects as a consequence of H₂O₂ overdosing.
- The established response surface models could be used to precisely optimize specific photochemical treatment targets for full and partial (pre-) treatment of different types of surfactants. The experimental design models were also capable of predicting

advanced oxidation efficiencies at different photochemical treatment durations and varying initial CODs of the aqueous surfactant solutions.

- The independent variables and their ranges selected upon consideration of the preliminary experimental results were satisfactory in terms of all studied process responses. However, the initial H₂O₂ concentration could have been chosen at a narrower range in terms of PC removal, in order to increase the accuracy of the model predictions. Besides, it should also be pointed out that the developed response surface models are of rather empirical nature and thus only valid within the selected ranges of the process independent variables.

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