



## Application of response surface methodology for dimethyl phthalate treatment via H<sub>2</sub>O<sub>2</sub>/UV-C process

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### ABSTRACT

In the present study, the reaction conditions required for the oxidation of dimethyl phthalate (DMP), being selected as a model endocrine disrupting compound, with the H<sub>2</sub>O<sub>2</sub>/UV-C treatment process were optimized using central composite design and response surface methodology (CCD–RSM). Initial DMP (DMP<sub>o</sub> = 20–100 mg/L) concentration, initial H<sub>2</sub>O<sub>2</sub> dosages (H<sub>2</sub>O<sub>2o</sub> = 5–45 mM), and treatment time ( $t_r$  = 2–18 min) were selected as critical process parameters (independent variables) while DMP and total organic carbon (TOC) abatements were chosen as the responses (dependent variables). Analysis of variance revealed that the variables “treatment time” and “initial DMP” were the process-independent parameters most positively and negatively affecting the treatment performance, respectively. According to the established polynomial regression models, for the degradation of the DMP at an initial concentration of 60 mg/L, the optimized treatment conditions were 25 mM of H<sub>2</sub>O<sub>2o</sub> and treatment time of 10 min. At these reaction conditions, complete DMP degradation and 28% TOC removal were obtained. By GC/MS analysis, phthalic acid and 4-hydroxy-1,2-benzoic dicarboxylic acid, dimethyl ester were identified as the aromatic oxidation intermediates.

*Keywords:* Dimethyl phthalate; Endocrine disrupting compounds; H<sub>2</sub>O<sub>2</sub>/UV-C process; Oxidation intermediates; Response surface methodology

### 1. Introduction

Phthalic acid diesters (PAEs), also known as dialkyl or alkyl aryl esters of 1,2-benzene di-carboxylic acid, are a group of compounds that have broad uses in a wide array of industrial applications such as plasticizers for plastics, nail polish, fishing lures, caulk, adhesives, dope, and paint industry [1]. PAEs are controversial because many phthalates are suspected to be mutagens, hepatotoxic agents, and

endocrine disruptors, and can lead to adverse effects on organisms even in a low concentration [2,3]. As one of the PAEs, dimethyl phthalate (DMP) is typically applied in cellulose ester-based plastics, such as cellulose acetate and butyrate [4]. As a result of its wide and large quantity use in industry, DMP has been recognized as a significant environmental pollutant and it has been detected in various environmental samples, such as surface waters, freshwaters, mineral waters, seawaters, urban lakes, sediments, and landfill leachate [5–8]. DMP has two carboxyl groups at the

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ortho-position on the aromatic ring and shows high water solubility (~4,000 mg/L) and it is volatile (with a Henry's law constant of  $1.1 \times 10^{-5}$  kPa). It is relatively hydrophilic ( $\log K_{ow}$ : 1.60) and has low tendency to adsorb on organic carbon ( $K_{oc}$ : 44–160 L/kg) [9]. Known as the endocrine-disrupting chemical, DMP may have the possibility of promoting chromosome injuries in human leucocytes and interfering with the reproductive systems and normal development of animals and humans [1]. Therefore, the US Environmental Protection Agency (USEPA) and European Union have classified DMP and some other phthalates (e.g. diethyl phthalate, dibutyl phthalate, di-(2-ethylhexyl) phthalate, and benzylbutyl phthalate) as priority environmental pollutants [10,11].

In last decade, considerable interest has been focused on the application of advanced oxidation processes (AOPs) for the treatment of DMP in water such as Fenton's reaction [12], electro-Fenton oxidation [13],  $TiO_2$ -UV, and Fe(VI)- $TiO_2$ -UV photocatalyst [14,15], ozone-based oxidation [16,17], and  $H_2O_2$ /UV-C oxidation [18,19]. Among the range of possible AOPs, homogeneous AOP employing hydrogen peroxide ( $H_2O_2$ ) with UV-C radiation ( $H_2O_2$ /UV-C process) is a relatively well-known and easy-to-operate treatment method. However, in the  $H_2O_2$ /UV-C treatment process, several process variables (reaction pH, treatment time, UV light intensity,  $H_2O_2$ , and target pollutant concentrations) affect the oxidation efficiency. Therefore, the optimization of the process for an effective treatment is crucial. Conventional and classical methods of optimizing a process by maintaining other factors involved at an unspecified constant level do not depict the combined effect of all the factors involved. This method is also time consuming and requires a number of experiments to determine optimum levels, which are unreliable [20]. A statistical-based technique commonly named the response surface methodology (RSM) as a powerful experimental design tool that has been used to optimize and understand the performance of complex systems using lesser number of experimental runs planned according to experimental design [21]. RSM is a combination of mathematical and statistical techniques used for developing, improving, and optimizing the processes and used to evaluate the relative significance of several affecting factors even in the presence of complex interactions [21]. The graphical representations of these equations are called a response surface contour that describes the cumulative interactions of the test variables on the response [22]. It is worthy to point out that the RSM does not elucidate the mechanism of the processes studied but only ascertains the effects of factors upon response and the interactions between the factors [23].

As aforementioned, several studies are available in the scientific literature reporting the effects of process variables on DMP degradation. However, until now, statistical design tools have not been used to model and optimize the DMP degradation with  $H_2O_2$ /UV-C process for different initial DMP concentrations.

Keeping the above-mentioned facts in mind, the present experimental study aimed at modeling and optimizing the  $H_2O_2$ /UV-C degradation of aqueous DMP solution using central composite design (CCD), the most widely used form of RSM. Initial DMP concentrations ( $DMP_0 = 20$ – $100$  mg/L), initial  $H_2O_2$  dosages ( $H_2O_{20} = 5$ – $45$  mM), and treatment time ( $t_r = 2$ – $18$  min) were selected as critical process parameters (independent variables), while DMP and total organic carbon (TOC) removal efficiencies were chosen as the responses (dependent variables).  $H_2O_2$ /UV-C oxidation experiments were carried out under relatively short treatment times since only parent pollutant oxidation was targeted. Separate validation experiments were conducted for each  $DMP_0$  at optimum reaction conditions established by the software module to check the goodness of fit and quality of the regression models. In order to elucidate the reaction mechanism, oxidation products identification was also undertaken qualitatively via gas chromatography/mass spectrometry (GC/MS).

## 2. Materials and experimental methods

### 2.1. Chemicals and reagents

DMP ( $C_{10}H_{10}O_4$ ; molecular weight: 194 g/mol; CAS: 131-11-3; purity: >99%) was purchased from Sigma-Aldrich Chemicals (USA). Aqueous DMP solutions were prepared in distilled water to attain different initial DMP concentrations in the range of 20–100 mg/L. 35% w/w  $H_2O_2$  (Fluka, USA) was used as received without dilution. Acetonitrile, ethyl acetate, and dichloromethane were of chromatography grade and purchased from Merck (Germany). All other reagents were of analytical grade. All experiments were carried out at room temperature and original pH of aqueous DMP solutions (pH 6.5).

### 2.2. $H_2O_2$ /UV-C experiments

$H_2O_2$ /UV-C experiments were performed according to experimental design given in Table 1. The pH and ionic strength of the aqueous DMP solutions were not controlled during irradiation. The UV-C photoreactor setup and important properties of the photoreactor and the UV-C light source were previously described elsewhere in detail [19]. Mixing inside the

Table 1

Process-independent design value ranges and coded values used in the factorial design for H<sub>2</sub>O<sub>2</sub>/UV-C treatment of aqueous DMP

Process variable (unit-code)	Real values of coded levels				
	-2	-1	0	+1	+2
$t_r$ (min- $X_1$ )	2	6	10	14	18
H <sub>2</sub> O <sub>2</sub> (mM- $X_2$ )	5	15	25	35	45
DMP <sub>o</sub> (mg/L- $X_3$ )	20	40	60	80	100

reactor was provided by circulating the reaction solution with a peristaltic pump (Meterpump Systems, Aripa) at a rate of 80 mL/min. For the H<sub>2</sub>O<sub>2</sub>/UV-C experiments, the aqueous DMP solution was first placed into the reactor. After adding the desired amount of H<sub>2</sub>O<sub>2</sub> into the solution, the lamp was turned on and the experiment was initiated. Samples were regularly withdrawn from the photoreactor during the experiments for the analyses of DMP, TOC, and pH.

### 2.3. Experimental design and statistical analysis

In order to explore the effect of independent process variables on the responses within the range of investigation, a CCD with three independent variables ( $X_1$ ,  $t_r$  (min);  $X_2$ , H<sub>2</sub>O<sub>2</sub> (mM);  $X_3$ , DMP<sub>o</sub> (mg/L)) was performed. The ranges and levels of each variable at which the experiments were conducted to estimate the response variables DMP and ( $Y_1$  (%)) and TOC ( $Y_2$  (%)) removals are given in Table 1. The range and central point values of these three independent process variables were based on the results of our previous study [19]. Experimental runs were randomized to minimize the effects of unexpected variations in the observed responses.

Each response was used to develop an empirical model which correlated the responses to the three process variables. The general equation of the empirical (second-order polynomial) regression model is presented in Eq. (1) given below [21]:

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

where  $Y$  stands for the predicted responses (percent DMP and TOC removals),  $b_0$  is the constant coefficient,  $b_i$ ,  $b_{ii}$  and  $b_{ij}$  are the regression coefficients that were estimated by least squares fitting of the model to the experimental results obtained at the design points and  $X_i$ ,  $X_j$  indicate the levels of the process-independent variables [21]. According to experimentally obtained

results, response surface plots were developed using the Design Expert® Software (Version 7.1.6) from Stat-Ease Inc., USA, and represented a function of two independent variables while keeping the other independent variable(s) at the zero level. Multiple regression analysis carried out by the least squares method generates the analysis of variance (ANOVA) data for verification of the robustness of the models (95% confidence level). The adequacy of the model was checked by evaluating the lack of fit, coefficient of determination ( $R^2$ ) and the Fisher test value ( $F$ -value) obtained from ANOVA [21]. The significances of all model terms in the polynomial equation were judged statistically by computing the  $F$ -value at a probability value (Prob. >  $F$ ) of 0.05. The optimum H<sub>2</sub>O<sub>2</sub>/UV-C treatment conditions for DMP and TOC removal efficiencies were estimated using the numerical and graphical optimization tool of Design Expert Software® at different initial DMP concentrations.

### 2.4. Analytical procedures

The concentration of DMP was determined by high performance liquid chromatography (HPLC, Agilent 1100 Series, USA) equipped with a Diode-Array Detector (DAD; G1315A, Agilent Series). Atlantis C18 (3.9 × 150 mm, 5 mm, Waters) column was used, and the analysis was carried out with a 40/60 (v/v) acetonitrile/water mobile phase at a flow rate of 1 mL/min. The elution was monitored at 220 nm. The column temperature was set at 30°C during the measurements. The instrument detection limit was 1.5 mg/L. The H<sub>2</sub>O<sub>2</sub>/UV-C oxidation intermediates were extracted by means of solid-phase extraction (SPE). The SPE cartridges (Oasis HLB, 6 mL, 250 mg) was pre-conditioned with 5 mL of ethyl acetate, 5 mL of dichloromethane, 5 mL of methanol, and 5 mL of ultrapure water. Then, the sample was passed through the SPE cartridges with a flow rate of 5 mL/min. When the extraction was complete, the cartridge was dried for 5 min under vacuum. The oxidation intermediates trapped in the SPE cartridges were eluted using 5 mL of ethyl acetate and 5 mL of dichloromethane. These two different fractions were used separately for analysis. The oxidation intermediates were identified by GC/MS with an Agilent Technologies (USA) system composed of a 5975C model GC connected to an Agilent capillary column (HP5-MS, 30 m × 0.25 mm), coupled with a 7890A model MS. Helium was used as the carrier gas at a flow rate of 1.5 mL/min. 2 µL sample aliquots were injected from the injection port (220°C) in splitless mode. For separation of the oxidation intermediates, the following temperature program was adopted; starting at 40–200°C (5°C/min),

200–210 °C (1 °C/min), 210–280 °C (20 °C/min), and 280 °C (3 min). Qualitative analyses were performed in the electron impact (EI) mode at 70 eV using the full scan mode. Unknown peaks were identified using the library of Agilent Technologies. TOC was determined by a Shimadzu V<sub>CPN</sub> model carbon analyzer (combustion method) equipped with an autosampler.

### 3. Results and discussion

#### 3.1. Application of CCD and fitted regression models as related to the DMP and TOC removals

A five-level full-factorial central composite statistical experiment design and a second-order RSM were applied to observe the effect of the three independent variables on the response function and to confirm the optimal conditions for the maximized removal efficiencies of DMP ( $Y_1$  (%)) and TOC ( $Y_2$  (%)). The treatment time ( $X_1$ ,  $t_r$  (min)), initial H<sub>2</sub>O<sub>2</sub> dosage ( $X_2$ , H<sub>2</sub>O<sub>2o</sub> (mM)), and initial DMP concentration ( $X_3$ , DMP<sub>o</sub> (mg/L)) were chosen as independent variables. The CCD model can enable the development of mathematical equations from which each response  $Y = f(X)$  was estimated as a function of  $X_1$ ,  $X_2$ , and  $X_3$  and calculated as the sum of a constant, three first-order effects ( $X_1$ ,  $X_2$ ,  $X_3$ ), three interaction effects ( $X_1X_2$ ,  $X_1X_3$ ,  $X_2X_3$ ), and three second-order effects ( $X_1^2$ ,  $X_2^2$ ,  $X_3^2$ ) using Eq. (1). Table 2 presents the responses and independent variables and the results of both experimentally observed and predicted responses. From the experimental design and the obtained results listed in

Table 2, the second-order polynomial regression models representing DMP and TOC removals (responses) can be expressed as a function of three investigated H<sub>2</sub>O<sub>2</sub>/UV-C operating parameters (independent variables). The relationships between responses and independent variables were obtained for coded factors as follows:

$$\begin{aligned} \text{DMP removal (\%)} = & 100.94 + 11.63X_1 - 0.50X_2 \\ & - 0.63X_3 + 2.50X_1X_2 - 1.00X_1X_3 \\ & + 2.75X_2X_3 - 8.00X_1^2 - 2.00X_2^2 \\ & - 1.13X_3^2 \end{aligned} \quad (2)$$

$$\begin{aligned} \text{TOC removal (\%)} = & 23.92 + 11.23X_1 + 2.06X_2 - 8.91X_3 \\ & + 0.59X_1X_2 - 3.50X_1X_3 + 0.39X_2X_3 \\ & - 0.49X_1^2 - 0.86X_2^2 + 4.07X_3^2 \end{aligned} \quad (3)$$

In Eqs. (2) and (3), the coefficients 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. A positive effect of a factor means that the response is improved when the factor level increases and a negative effect of the factor reveal that the response is inhibited when the factor level increases [24]. For instance, it is evident that from Eqs. (2) and (3), the linear effect of variable  $t_r$  coded as  $X_1$  exhibited the highest positive influence on DMP and TOC removals. The variable H<sub>2</sub>O<sub>2o</sub> (coded as  $X_2$ ) exhibited negative influence on

Table 2  
CCD design matrix for independent variables along with the experimentally observed and predicted responses

Exp. no.	$t_r$ ( $X_1$ ) (min)	H <sub>2</sub> O <sub>2o</sub> ( $X_2$ ) (mM)	DMP <sub>o</sub> ( $X_3$ ) (mg/L)	DMP removal ( $Y_1$ ) (%)		TOC removal ( $Y_2$ ) (%)	
				Observed	Predicted	Observed	Predicted
1	10	25	100	92	95	18	22
2	14	15	80	98	95	32	22
3	10	25	60	100	100	20	24
4	10	5	60	89	94	11	16
5	6	15	80	84	79	8	8
6	6	35	40	71	72	20	22
7	14	35	40	99	100	61	52
8	18	25	60	100	92	35	44
9	14	35	80	97	100	33	28
10	10	25	20	99	98	54	58
11	10	45	60	95	92	22	25
12	6	15	40	93	84	23	20
13	2	25	60	36	46	1	0
14	10	25	60	100	100	20	24
15	14	15	40	98	100	53	48
16	6	35	80	86	78	14	12

DMP removal while it affected the TOC removal positively. In other words, initial  $\text{H}_2\text{O}_2$  dosage negatively influenced the DMP removal indicating that the initial  $\text{H}_2\text{O}_2$  dosage range selected for the degradation of the DMP was excessive. However, the positive influence of the variable  $\text{H}_2\text{O}_{20}$  on TOC removal indicates that the mineralization of aqueous DMP solution is more difficult to achieve than DMP removal and requires higher  $\text{H}_2\text{O}_{20}$ . The initial DMP concentration (coded as  $X_3$ ) exhibited negative effect on DMP and TOC removals.

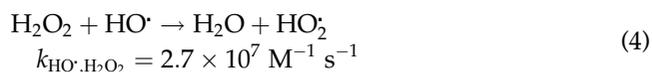
The experimental data were fitted to a polynomial second-order regression model and the correctness/fitness of the established models was statistically confirmed via ANOVA. Table 3 displays the ANOVA results for the full second-order polynomial regression models generated for DMP and TOC removals obtained with the  $\text{H}_2\text{O}_2/\text{UV-C}$  treatment. The correctness and fitness of the models were examined by the  $R^2$  which was found as 0.8779 and 0.9054 for DMP and TOC removals, respectively. The values of  $R^2$  indicated that only 12.21 and 9.46% of the total variation could not be explained by the empirical models and expresses good enough quadratic fits to navigate the design space for DMP and TOC removals, respectively. The adequate precision measures the signal-to-noise ratio and a ratio greater than 4 is usually desirable. Therefore, the ratios of 8.249 and 8.908 both being greater than 4 indicated adequate signals. Prob. > F values less than 0.05 imply that the model is statistically significant and can be used to navigate the design space, whereas values greater than 0.10 are usually considered as insignificant. As can be seen from Table 3, Prob. > F values were 0.035 and 0.018 for the models describing DMP and TOC removals. According to the ANOVA, the model F-values determined as 4.79 and 6.38 for DMP and TOC removals, respectively, the model terms were significant.

### 3.2. Interactive effects of process-independent variables

Response surface 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 center (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. In the present study, it was decided to focus on the dual effect of the parameters “DMP<sub>0</sub>” and “ $\text{H}_2\text{O}_{20}$ ” on the DMP and TOC removal efficiencies for further assessment and elucidation. Percentage of DMP and TOC removals as a function of DMP<sub>0</sub> and  $\text{H}_2\text{O}_{20}$  are depicted in Fig. 1(a) and (b) on the basis of response surfaces, respectively, for a fixed treatment time of 10 min. Fig. 1(a) and (b) reveals that an increase in the DMP<sub>0</sub> results in a decrease in both DMP and TOC removal efficiencies for the DMP<sub>0</sub> range selected in the present study. For instance, for DMP<sub>0</sub> = 20 mg/L, complete DMP removal together with 52% TOC removal were obtained at  $\text{H}_2\text{O}_{20}$  = 5 mM and  $t_r$  = 10 min. Under the same initial  $\text{H}_2\text{O}_2$  dosage and treatment time, for increased initial DMP concentration of 100 mg/L, the DMP and TOC removals were decreased to 77 and 13%, respectively.

Several researchers evaluated the effect of initial  $\text{H}_2\text{O}_2$  dosage for  $\text{H}_2\text{O}_2/\text{UV-C}$  process on oxidation rates for organic pollutants. They reported that there is an optimum  $\text{H}_2\text{O}_2$  dosage for the process [25,26]. The oxidation rates of organic pollutants increase at higher  $\text{H}_2\text{O}_2$  dosages up to an optimum value, beyond which the rates decrease due to the well-known HO· scavenging effect of excessive  $\text{H}_2\text{O}_2$  concentrations which can be expressed by the following reaction [27]:



As delineated in Fig. 1(a) for DMP<sub>0</sub> ≤ 40 mg/L, an optimum initial  $\text{H}_2\text{O}_2$  dosage existed around 20 mM (where complete DMP removals were achieved) and an increase in the initial  $\text{H}_2\text{O}_2$  dosage above this value, the inhibitory effect of  $\text{H}_2\text{O}_2$  started to show up especially for lower initial DMP concentrations. By increasing the  $\text{H}_2\text{O}_{20}$  to 32 mM, DMP removals decreased to 92 and 97% for initial DMP concentrations of 20 and 40 mg/L, respectively. At initial  $\text{H}_2\text{O}_2$  dosage of 32 mM, complete DMP removals were observed for initial DMP concentrations between 60 and 80 mg/L which emphasized that a higher optimum initial  $\text{H}_2\text{O}_2$  dosage existed for higher initial

Table 3  
ANOVA results for the regression models established for  $\text{H}_2\text{O}_2/\text{UV-C}$  treatment of aqueous DMP solutions

Response (%)	$R^2$	Adequate precision	F-value	$p > F$
DMP removal	0.8779	8.249	4.79	0.035
TOC removal	0.9054	8.908	6.38	0.018

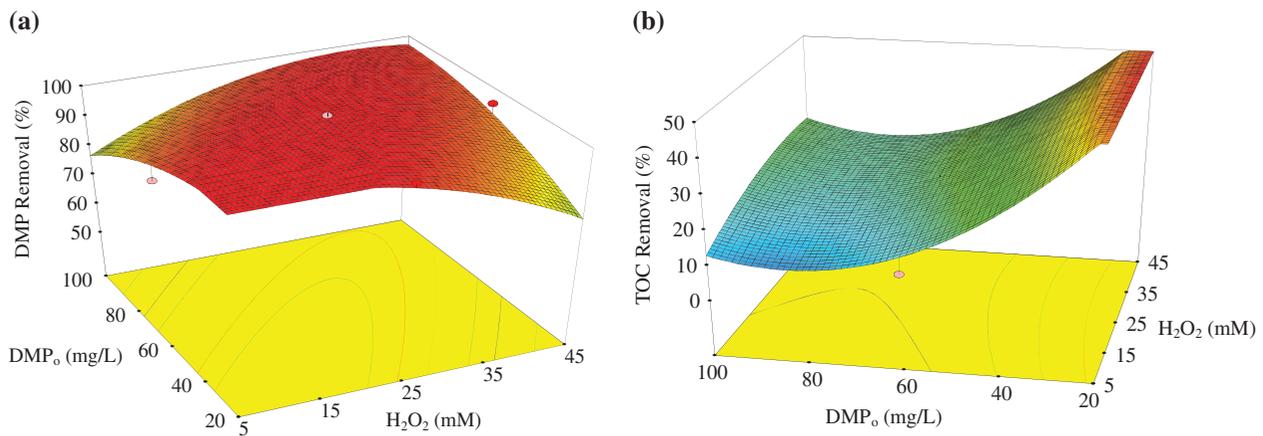


Fig. 1. Response surface plots for the effects of initial DMP concentrations and initial H<sub>2</sub>O<sub>2</sub> dosages on DMP (a) and TOC (b) removals at treatment time of 10 min.

DMP concentrations. For DMP<sub>0</sub> = 100 mg/L, the maximum DMP removal of 98% was observed at H<sub>2</sub>O<sub>2,0</sub> = 32 mM. Elevating the initial H<sub>2</sub>O<sub>2</sub> dosage to 45 mM decreased the DMP removals to 78, 87, 92, 96, and 97% for 20, 40, 60, 80, and 100 mg/L DMP<sub>0</sub>, respectively. From these results, it can be concluded that the scavenging effect of excessive H<sub>2</sub>O<sub>2</sub> dosages were more pronounced for initial DMP concentrations lower than 40 mg/L at the investigated experimental design matrix. As aforementioned, initial H<sub>2</sub>O<sub>2</sub> dosage had a negative influence on DMP removals while it had a positive influence on TOC removals. As is evident from the Fig. 1(b), an increase in initial H<sub>2</sub>O<sub>2</sub> dosages, for *t<sub>r</sub>* of 10 min, improved the system performance in terms of TOC removal efficiencies. For instance, at DMP<sub>0</sub> of 20 and 100 mg/L, increasing the H<sub>2</sub>O<sub>2,0</sub> from 5 to 45 mM slightly increased the TOC removal efficiencies from 52 to 58% and 13 to 24%, respectively. Upon comparison of the dependency of TOC removals on DMP<sub>0</sub> and initial H<sub>2</sub>O<sub>2</sub> dosages shown in Fig. 1(b), it can be concluded that the initial DMP dosages had higher influence on TOC removals than initial H<sub>2</sub>O<sub>2</sub> dosages as was also obvious from the second-order polynomial regression models (Eqs. (2) and (3)). This effect may be attributed to oxidation of the reaction products that are more readily oxidized than DMP.

### 3.3. Process optimization and validation experiments

The major goal of this study was to establish optimum values of the selected process parameters in order to achieve the maximum DMP removal at different initial DMP concentrations by H<sub>2</sub>O<sub>2</sub>/UV-C process. According to the optimization step of the

program, the desired goal for each independent variable and responses should be chosen. The desired goals for *t<sub>r</sub>* and H<sub>2</sub>O<sub>2,0</sub> were defined as “keep in range”, while for responses DMP and TOC removals as “maximize” and “keep in range”, respectively. It should be emphasized here that in the present study, only DMP removal was adjusted to maximize. Several scenarios were examined in order to find the optimum reaction conditions for different initial DMP concentrations and these conditions are shown in Table 4. Verification experiments performed at the optimum conditions derived through the optimization step of the program demonstrated that the experimental values were reasonably close to the predicted values, indicating the validity and adequacy of the predicted models. Moreover, the verification experiments also proved that the predicted values of the DMP removal could be achieved within 95% confidence interval of the experimental values.

### 3.4. Identification of oxidation intermediates

An attempt was made to identify the intermediates formed in the H<sub>2</sub>O<sub>2</sub>/UV-C treatment of DMP using GC/MS. The nature of intermediates was investigated by degrading a 100 mg/L aqueous DMP solution at an initial H<sub>2</sub>O<sub>2,0</sub> dosage of 35 mM and at pH 6.5 (original pH of aqueous DMP solutions) for treatment times of 2, 6, 10, 18, and 30 min. The products were identified based on their molecular ion and mass spectrometric fragmentation peaks compared with the chemical standards. Many researchers reported that the oxidation mechanism of aromatic compounds by HO• is expected to start with HO• attack to the aromatic ring leading to the formation of hydroxylated

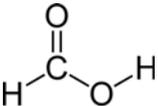
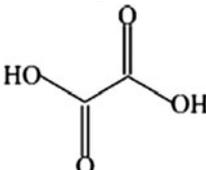
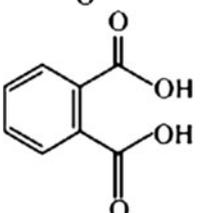
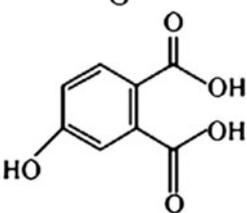
Table 4

Optimization results and comparison of the process responses predicted by CCD with those obtained from the experimental runs

Exp. no.	$t_r$ (min)	$H_2O_{2o}$ (mM)	$DMP_o$ (mg/L)	DMP removal (%)		TOC removal (%)	
				Observed	Predicted	Observed	Predicted
1	14	35	100	97	100	25	29
2	14	35	80	100	100	28	28
3	10	25	60	100	100	28	24
4	14	15	40	100	100	43	48
5	10	5	20	100	100	53	52

Table 5

Oxidation intermediates identified for aqueous DMP treatment by  $H_2O_2$ /UV-C process

Compound	Structure	Formula
Formic acid		$CH_2O_2$
Oxalic acid		$C_2H_2O_4$
Phthalic acid		$C_8H_6O_4$
4-hydroxy-1,2-benzoic dicarboxylic acid dimethyl ester		$C_8H_6O_5$

derivatives [28]. In  $H_2O_2$ /UV-C oxidation of DMP, the reaction was first initiated with demethylation of DMP to give phthalic acid, which was also reported by previous researchers [29,30]. The formed phthalic acid then underwent a possible attack of  $HO^\bullet$  on its C(4) position yielding 4-hydroxy-1,2-benzoic dicarboxylic acid dimethyl ester [30]. The continuing oxidation of 4-hydroxy-1,2-benzoic dicarboxylic acid dimethyl ester, after ring opening, then led to the formation of aliphatic carboxylic acids which might then converted to carbon dioxide and water by  $HO^\bullet$  gradually in the

oxidation process. In the literature, the formed carboxylic acid has been reported as formic, mesoxalic, oxalic, malonic, succinic, and maleic acids. In our case, formic and oxalic acids were identified by GC/MS analysis. The information of the identified oxidation intermediates are summarized in Table 5 and the proposed degradation pathway is shown in Fig. 2. The present analytical results of the oxidation intermediates of DMP degradation by  $H_2O_2$ /UV-C process generally agree with results reported previously [29,30].

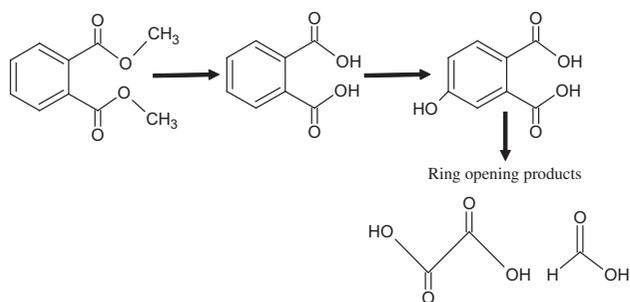


Fig. 2. Proposed degradation pathway of DMP for H<sub>2</sub>O<sub>2</sub>/UV-C process.

#### 4. Conclusions

In the present study, CCD coupled with RSM was applied to model and optimize process parameters in the H<sub>2</sub>O<sub>2</sub>/UV-C treatment of aqueous DMP solution.

The responses of the experimental runs foreseen by the experimental design tool were used to establish second-order polynomial regression models that described DMP and TOC removal efficiencies as a function of the selected critical process variables of H<sub>2</sub>O<sub>2</sub>/UV-C oxidation, namely treatment time, initial DMP concentrations, and initial H<sub>2</sub>O<sub>2</sub> dosages. The following conclusions can be drawn from the present study:

- (1) The experimental results indicated that photochemical treatment of the aqueous DMP solutions with the H<sub>2</sub>O<sub>2</sub>/UV-C process is an efficient method to completely degrade the parent pollutant as well as reducing its organic matter content.
- (2) From the established second-order polynomial regression models, it was evident that the DMP and TOC removal efficiencies were positively influenced by treatment time, whereas the initial DMP concentration had negative influence on treatment efficiencies. Initial H<sub>2</sub>O<sub>2</sub> dosage had positive effect on TOC removal efficiencies while it influenced the DMP removal negatively. The initial H<sub>2</sub>O<sub>2</sub> dosage plays a more important role in mineralization that is harder to achieve than target pollutant removal.
- (3) The second-order polynomial regression models developed in this study showed the presence of a high correlation between observed and predicated values and ANOVA results revealed that the established design models were statistically significant. Three-dimensional surface plots have found to be a good-driven

approach for visualizing the parameter interactions for complex systems.

- (4) The oxidation intermediates determined by GC/MS analysis indicated that the mineralization process started with the formation of phthalic acid then after followed by HO-addition to the aromatic ring leading to formation of 4-hydroxy-1,2-benzoic dicarboxylic acid dimethyl ester. The continuing oxidation of hydroxylated oxidation intermediate led to the ring opening reaction to form aliphatic carboxylic acids such as formic and oxalic acids.

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