

EVALUATION OF THE OPTIMAL OPERATION CONDITIONS USING RESPONSE SURFACE METHODOLOGY FOR THE AQUEOUS DMP SOLUTION BY ELECTROCOAGULATION

TÜNAY O.*
OLMEZ-HANCI T.
KABDAŞLI I.
ÇOŞKUN B.

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

Received: 20/09/2013

Accepted: 03/04/2014

Available online: 13/03/2015

*to whom all correspondence should be addressed:
e-mail: tunayol@itu.edu.tr

ABSTRACT

Phthalic acid esters, commonly called as phthalates, are of a common use in the industrial activities and are known with their hazardous impact on the environment and on humans such as endocrine disrupting agents, carcinogenic and toxic effects. These adverse effects have led to increasing interest and research on the treatment and control of phthalates. Over the past two decades, there has been growing interest in the use of electrochemical techniques such as electrocoagulation (EC) for the treatment of organic pollutants particularly toxic organics. During the course of EC, where iron or stainless steel electrodes are used as electrodes, different mechanisms are operative for the elimination of organic matter, namely (a) adsorption (b) direct anodic oxidation, and (c) indirect oxidation of pollutants in the bulk solution. A statistical-based technique named as response surface methodology (RSM) is a powerful tool for modeling the complex systems (such as EC), evaluating the simultaneous effects of several factors (independent variables), and thus searching optimum conditions for desirable responses (dependent variables). Until now, RSM has not been used as a modeling and optimization tool for the EC treatment of phthalates. In this study, EC treatment, using stainless steel anode, of dimethyl phthalate (DMP), was investigated and optimized via RSM, central composite design (CCD). Initial DMP concentration (DMP_0 ; 20-100 mg L⁻¹), current density (J_c ; 4.5-22.5 mA cm⁻²), electrolyte concentration (NaCl, 750-1750 mg L⁻¹), treatment time (t_r ; 60-180 min) were selected as critical process parameters while DMP, total organic carbon (TOC) removals and electrical energy consumption (EEC, in kWh m⁻³) values were selected as the responses. The EC process was optimized to improve the abatements of DMP and TOC and to reduce the EEC values. Separate validation experiments were conducted for each initial DMP concentrations at optimum EC conditions established by the software module to check the goodness of fit and quality of the regression models. According to the established second-order polynomial regression models, DMP, TOC removal efficiencies and EEC values were affected by the process variables in the following decreasing order; $J_c > t_r > DMP_0 > NaCl$ (negative impact), $t_r > DMP_0$ (negative impact) $> J_c > NaCl$ (negative impact) and $t_r > J_c > NaCl$ (negative impact) $> DMP_0$ (negative impact), respectively. Analysis of variance indicated that the experimental design models obtained for the EC treatment of aqueous DMP solutions in terms of the model pollutant and mineralization were statistically significant. The response surfaces of DMP established between initial DMP concentration and current density showed that DMP removal efficiencies can be enhanced by increasing the current density to a certain value indicating that an optimum value of current density exists for maximum DMP removal.

Keywords: Dimethyl phthalate; endocrine disrupter; electrocoagulation; response surface methodology, central composite design

1. Introduction

In 2001, the Stockholm Convention under the auspices of United Nation Environmental Program, specified a suite of persistent organic chemicals considered as potential endocrine disruptors (EDs) in the environment (UNEP, 2001). EDs can interfere with hormones by mimicking hormones, blocking hormone receptors, or altering hormone metabolism (Gilbert, 2006). The best known EDs are phthalic acid esters (PAEs), hexachlorocyclohexane (lindane), pentachlorophenol, dichlorodiphenyltrichloroethane (DDT), bisphenol A, atrazine, dioxins, furans, poly-chlorinated biphenyls, and also some heavy metals (Dyer, 2007). PAEs are commonly used as plasticizers in a variety of products, including soap; cosmetics; hair spray; flexible plastics, such as blood transfusion bags; plastic toys and containers; paints; and inks (Horn *et al.*, 2004). As a result, PAEs have been released into terrestrial and aquatic ecosystems through wastewater effluent from the plastics industry and by leaching from the wasted plastic products (Psillakis *et al.*, 2004). Numerous studies have shown that PAEs exert adverse effects on the environment and human health, such as inducing hepatic peroxisome proliferation, hormonal disorders, reproductive toxicity, and carcinogenicity (Rusyn *et al.* 2006, Babu and Wu, 2010). The short-chained PAEs such as dimethyl phthalate (DMP) is among the most frequently identified PAEs in diversified environmental samples including upper layer of marine water, surface waters and sediments. DMP, one of the priority pollutants listed by many regulatory agencies including the United States Environmental Protection Agency, is an ED which can disturb the endocrine system of humans and wildlife even at very low concentrations. DMP is widely used as plasticizer and is classified as hardly biodegradable (Wang *et al.*, 1998). DMP is found to be toxic to a variety of aquatic organisms, which are at the base of the food chain in both marine and surface water environments. Therefore, decomposition of DMP is not only of scientific interest but also of industrial and medicinal importance. Recently, treatability studies performed employing advanced oxidation process which provided total destruction of the phthalates (Xua *et al.* 2007; Kabdaşlı *et al.*, 2010; Olmez-Hanci *et al.* 2009; 2010; 2012; 2013). In these studies complete oxidation of phthalates was realized together with a high degree of mineralization. Among physical/chemical methods, electrocoagulation (EC) treatment is one of the advanced processes which offers high removal efficiencies in compact reactors with simple equipment for control and operation of the process. EC has recently received greater attention than conventional methods as a high-efficiency removal technique for water and wastewater treatment. EC, using iron based electrodes, has been effectively tested in the treatment of varieties of industrial wastewater (Apaydin *et al.*, 2009; Kabdaşlı *et al.*, 2009a, b; Soloman *et al.*, 2009; Dermentzis *et al.*, 2011). During the course of EC conducted with iron and stainless steel (SS) electrodes, different mechanisms are thought to be responsible for the elimination of organic matter, namely (a) adsorption and/or surface complexation of suspended/colloidal matter as well as soluble fraction of pollutants onto in-situ formed flocs; (b) direct anodic oxidation in which the pollutants adsorbed on the anode surface and destroyed by the anodic electron transfer reaction in the presence of chloride ions, (c) indirect oxidation of pollutants in the bulk solution mediated by the conversion of chloride ions originating from the electrolyte solution to chlorine gas that forms hypochloric acid in water (Chatzisyseon *et al.*, 2006; Moreno-Casillas *et al.*, 2006). The number of parameter involved in the design and operation of the EC process is relatively high with respect to other oxidation methods and an efficient design and operation of the EC call for a detailed and careful evaluation and optimization. The best approaches in the optimization of such systems are the use of a procedure relying on statistical evaluation. In conventional multifactor experiments (classical optimization method), optimization is usually carried out by varying a single factor while keeping all other factors fixed at a specific set of conditions. This is not only time-consuming, but also usually incapable of reaching the true optimum conditions due to ignoring the interactions among variables. On the other hand, the technique of the experimental design is an efficient method of indicating the relative significance of a number of variables and their interactions (Myers and Montgomery, 2002). Response surface methodology (RSM) is an effective statistical tool for collection of mathematical and statistical information that are useful for developing, improving and optimizing processes and can be used to evaluate the relative significance of several affecting factors even in the presence of complex interactions. The main advantage of RSM is the reduced number of experiments

needed to provide sufficient information to optimize the process. Several studies have already reported the combinative effects of process variables affecting the EC processes. In these researches, similar relationships for different industrial effluents and single model pollutants have been observed. However, until now, RSM has not been used as a modeling and optimization tool for EC treatment of phthalates such as DMP, taking into account the variations in initial organic pollution loads of phthalates that may differ appreciably from point source to point source. Besides, EC is an energy-intense process and, thus, a cost-driven approach should be employed for its optimization, considering its economical and technical feasibility.

In the present study, Central Composite Design (CCD) Response Surface Methodology (RSM) was used as a design framework to model and optimize the treatment of aqueous DMP by electrocoagulation with stainless steel electrodes. The individual and interactive effects of the key process variables such as initial DMP concentration (DMP_0), current density (J_c), electrolyte concentration (NaCl) and treatment time (t_r) on DMP and total organic carbon (TOC) removals as well as electrical energy consumption (EEC, the electrical energy required per unit volume effluent treated, in kWh m^{-3}) values were evaluated and mathematically modeled. The established mathematical models were validated by running separate experiments under EC conditions optimized for different initial DMP concentrations.

To the best of our knowledge, this is the first study of its kind that addressed the optimization of EC treatment of DMP via RSM.

2. Materials and methods

2.1. Chemicals and reagents

DMP ($\text{C}_{10}\text{H}_{10}\text{O}_4$; molecular weight: 194 g mol^{-1} ; water solubility at 20 °C: 4.3 g l^{-1} ; CAS: 131-11-3; purity: >99%) was purchased from Sigma-Aldrich Chemicals (USA). NaCl (MERCK, Germany) was used as the electrolyte because it appeared to be the best electrolyte in our previous electrocoagulation study (Kabdaşlı *et al.*, 2009). Aqueous DMP solutions were prepared by dissolving a required amount of DMP in distilled water. The other chemicals used in the experiments were of analytical grade. When required, the pH of the solution was adjusted using H_2SO_4 (MERCK, Germany) and NaOH (MERCK, Germany) solutions. HPLC grade acetonitrile (MERCK, Germany) was used in the DMP analyses.

2.2. Experimental setup and procedure

A batch reactor with the dimensions of 19 cm×19 cm×29 cm and an effective working volume of 3 L was used for the EC experiments. A magnetic stirrer was used to agitate the reaction medium from the reactor bottom. The EC unit was equipped with eight monopolar, parallel connected 316 SS electrodes (four anodes and cathodes) making up a total effective surface area of 286.4 cm^2 (L: 11.9 cm; d: 1.02 cm). The distance between the electrodes was fixed at 3 mm. The electrodes were located at the bottom of the EC reactor. The current density was maintained constant by means of a precision digital direct current power supply (Maksimel Professional Systems UPS 023 model; E_{max} : 20 Volt; Current density: 2.25–88.00 mA cm^{-2}). After each experimental run, the EC reactor and electrodes were carefully rinsed according to the procedure given in Kabdaşlı *et al.* (2009a; b). In order to follow the performance of the electrocoagulation process, the samples were taken from the reactor at proper time intervals (foreseen by the model) during the course of electrocoagulation. Thereafter, the samples were allowed to settle for 30 min prior to vacuum filtration through Sartorius SM 11106 membrane filters with a pore size of 0.45 μm for the analyses of pH, DMP and TOC.

2.3. Analytical procedures

TOC analyses were carried out using a Shimadzu V_{CPN} model carbon analyzer (combustion method) equipped with an autosampler. The amount of DMP in the aqueous solution was measured by high performance liquid chromatography (HPLC, Agilent 1100 Series, USA) equipped with a Diode-Array Detector (DAD; G1315A, Agilent Series) and Atlantis C18 (3.9 × 150 mm, 5 mm, Waters) column. The mobile phase used was acetonitrile-water solution (40:60, v/v) with a flow rate of 1 mL min^{-1} . The elution

was monitored at 220 nm. The column temperature and injection volume were set as 30°C and 20 µL, respectively. The correlation coefficient of the established calibration curve for DMP was found as 0.999. The instrument detection limit and the limit of quantification were 1.5 mg L⁻¹ and 5 mg L⁻¹, respectively.

2.4. Experimental design and data analysis

RSM is a statistical method being useful for the optimization of chemical reactions and/or industrial processes and widely used for experimental design (Myers and Montgomery, 2002). Whenever multiple system variables may influence the outputs, RSM utilize to assess the relationship between dependent (response) and independent variables as well as to optimize the relevant processes (Bas and Boyaci, 2007). In order to explore the effect of independent process variables on the responses within the range of investigation, a CCD with four independent variables (X_1 , J_c (mA cm⁻²); X_2 , DMP₀ (mg L⁻¹); X_3 , t_r (min); X_4 , NaCl (mg L⁻¹)) was performed at five levels. The independent variables and their ranges were chosen based on our previous studies (Kabdaşlı *et al.*, 2009a). The whole design consisted of 26 experimental runs carried out in random order, which included 16 factorial points, 2 centre and 8 axial points. All experiments conducted at these points were done in duplicate. Table 1 shows the coded and actual values of the process independent variables at which the experiments were conducted to estimate the response variables DMP removal (Y_1 , (%)), TOC removal (Y_2 , (%)) and EEC values (Y_3 , kWh m⁻³). The EEC values were calculated as a function of 1 m³ treated volume of aqueous DMP solution during EC in kWh m⁻³ using the equation described in elsewhere (Kobya *et al.*, 2010).

Table 1: Ranges for coded and actual values of the selected process independent variables.

Factor	Variables	Unit	Range of actual and coded variables				
			-2	-1	0	1	2
X_1	J_c	mA cm ⁻²	4.5	9.0	13.5	18.0	22.5
X_2	DMP ₀	mg l ⁻¹	20	40	60	80	100
X_3	t_r	min	60	90	120	150	180
X_4	NaCl	mg l ⁻¹	750	1000	1250	1500	1750

Each response was used to develop an empirical model which correlated the responses to the four process variables. The empirical regression model is presented in Eq. (1) (Myers and Montgomery, 2002).

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

where Y stands for the predicted responses (percent DMP and TOC removals and EEC values), b_0 for the constant coefficient, b_i , b_{ii} and b_{ij} for 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 (Myers and Montgomery, 2002). Analysis of variance (ANOVA) for the model was also applied to deduce its statistical significance and reliability. The significances of all model terms in the polynomial equation were judged statistically by computing the F-value (Fisher variation ratio) at a probability value (Prob > F) of 0.05. The regression coefficients were then used to conduct statistical calculations and generated dimensional/contour maps from the regression models. The ANOVA and response surfaces were performed using the Design Expert Software (Version 7.1.5) from Stat-Ease Inc., USA. The EC conditions being optimized for DMP and TOC removals as well as EEC values at different initial DMP concentrations were estimated using the software's numerical and graphical optimization tools.

3. Results and discussion

3.1. Establishment of empirical regression models and ANOVA results

The relationships between process dependent and independent variables were established by using the experimental sets foreseen by the design tool. The obtained regression models (polynomial equations) are given below in terms of the coded values:

$$\text{DMP Removal (\%)} = 77 + 14.04 \times X_1 + 7.54 \times X_2 + 11.96 \times X_3 - 2.29 \times X_4 - 5.56 \times X_1 \times X_2 + 0.31 \times X_1 \times X_3 + 3.19 \times X_1 \times X_4 - 3.44 \times X_2 \times X_3 - 0.062 \times X_2 \times X_4 + 1.31 \times X_3 \times X_4 - 5.26 \times X_1^2 + 0.74 \times X_2^2 - 0.26 \times X_3^2 - 0.26 \times X_4^2 \quad (2)$$

$$\text{TOC Removal (\%)} = +5.00 + 1.61 \times X_1 - 2.93 \times X_2 + 3.35 \times X_3 - 0.18 \times X_4 + 4.52 \times X_1 \times X_2 + 3.11 \times X_1 \times X_3 - 0.86 \times X_1 \times X_4 + 1.02 \times X_2 \times X_3 - 3.27 \times X_2 \times X_4 + 0.14 \times X_3 \times X_4 + 1.14 \times X_1^2 + 2.54 \times X_2^2 + 1.54 \times X_3^2 + 0.79 \times X_4^2 \quad (3)$$

$$\text{EEC Values (kWh m}^{-3}\text{)} = +55.44 + 10.92 \times X_1 - 4.49 \times X_2 + 12.30 \times X_3 - 6.29 \times X_4 - 3.08 \times X_1 \times X_2 + 1.49 \times X_1 \times X_3 - 0.83 \times X_1 \times X_4 - 0.83 \times X_2 \times X_3 + 0.54 \times X_2 \times X_4 - 2.95 \times X_3 \times X_4 - 2.18 \times X_1^2 - 1.73 \times X_2^2 + 0.88 \times X_3^2 - 0.38 \times X_4^2 \quad (4)$$

for $-2 \leq X_i \leq 2$.

The actual design of CCD-RSM modeling, the results of the experimental study and the values predicted by using the above obtained empirical models are presented in Table 2. Closer inspection of Table 2 indicates that the experimentally obtained and predicted results (DMP and TOC removals and EEC values) were close to and in consistent with each other.

Table 2: The actual design of CCD-RSM modeling and comparison of responses predicted by CCD-RSM with those obtained from the experimental runs.

Exp.No	DMP ₀ (X ₁)	J _c (X ₂)	NaCl (X ₃)	t _r (X ₄)	DMP Removal (%)		TOC Removal (%)		EEC (kWh m ⁻³)	
	(mg l ⁻¹)	(mA cm ⁻²)	(mg l ⁻¹)	(min)	Exp.	Pred.	Exp.	Pred.	Exp.	Pred.
1	20	13.5	1250	120	76±4	65	18±2	21	48	57
2	40	9.0	1000	90	33±2	36	14±1	14	32	34
3	40	9.0	1000	150	71±4	64	16±2	12	65	63
4	40	9.0	1500	90	23±1	23	21±2	21	31	28
5	40	18.0	1000	90	63±3	69	8±1	4	63	61
6	40	9.0	1500	150	46±2	56	25±3	20	47	45
7	40	18.0	1000	150	96±5	97	13±1	14	102	96
8	40	18.0	1500	90	59±3	68	8±1	8	61	51
9	40	18.0	1500	150	99±1	100	18±2	19	76	75
10	60	13.5	750	120	73±4	81	4±0	9	68	66
11	60	4.5	1250	120	23±1	28	1±1	6	30	25
12	60	13.5	1250	60	59±3	52	3±1	4	30	34
13	60	13.5	1250	120	77±4	77	5±1	5	55	55
14	60	13.5	1250	120	77±4	77	5±1	5	55	55
15	60	13.5	1250	180	96±4	100	14±1	18	83	84
16	60	22.5	1250	120	92±5	84	13±1	13	59	69
17	60	13.5	1750	120	82±4	71	7±1	8	35	41
18	80	9.0	1000	90	76±4	70	8±1	3	32	32
19	80	9.0	1000	150	86±4	83	7±1	6	51	58
20	80	9.0	1500	90	51±3	56	1±1	0	25	28
21	80	9.0	1500	150	84±4	75	1±1	1	41	42
22	80	18.0	1000	90	83±4	80	8±1	11	48	46
23	80	18.0	1000	150	98±2	95	30±3	26	76	78
24	80	18.0	1500	90	75±4	79	2±1	2	38	39
25	80	18.0	1500	150	96±4	99	19±2	18	64	59
26	100	13.5	1250	120	87±4	95	7±1	9	45	40

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 (Cruz-González *et al.*, 2010). For instance, it is evident that from Eqs. (2)-(4) the J_c (current density, X_1) and t_r (treatment time, X_3) had positive influence both on DMP and TOC removals as well as EEC values. According to the established empirical regression models, DMP, TOC removals and EEC values were affected by the process variables in the following decreasing order; $J_c > t_r > \text{DMP}_0 > \text{NaCl}$ (negative impact), $t_r > \text{DMP}_0$ (negative impact) $> J_c > \text{NaCl}$ (negative impact) and $t_r > J_c > \text{NaCl}$ (negative impact) $> \text{DMP}_0$ (negative impact), respectively. The above mentioned rankings among the examined process independent variables imply that the factors influencing DMP degradation and TOC removal (in other words level of mineralization) may differ from each other.

The correctness and suitability of the established empirical regression models were statistically confirmed via ANOVA. The significance of the models and model terms (independent process variables) can be determined based on the F or Prob value (also called the “Prob>F” value). A “Prob>F” value less than 0.05 indicates that the design model and model terms are statistically significant (Körbahti and Rauf, 2008). ANOVA results obtained for the empirical regression models describing DMP and TOC removals and EEC values are presented in Table 3. It is evident from Table 3 that the Prob>F values of the models were 0.0004, 0.0049 and ≤ 0.0001 for DMP and TOC removals and EEC values, respectively, implying that the observed models were significant. The correctness and fitness of the models were examined by the coefficient of variation (R^2) which was found as 0.9196, 0.8669 and 0.9404 for DMP and TOC removals and EEC values, respectively. From these values it is evident that 91.96%, 86.69% and 94.04% of the variability in the responses could be explained by the regression models. The adequate precision values measure the signal-to-noise ratio (Körbahti and Rauf, 2008). A ratio greater than 4 is desirable for an appropriate model. In the present study, the adequate precision values were obtained as 10.986, 8.490 and 13.346 for DMP and TOC removals and EEC values, respectively. These values indicate an adequate signal and suggest that the regression models can be used to navigate the design space for the EC treatment of aqueous DMP solutions.

Table 3: ANOVA results of the empirical regression models

Responses	R^2	Adequate Precision	F value	Prob>F
DMP removal (%)	0.9196	10.986	8.99	0.0004
TOC removal (%)	0.8669	8.490	5.12	0.0049
EEC (kWh m ⁻³)	0.9404	13.346	12.4	≤ 0.0001

3.2. Interactive effects of process independent variables

Figure 1 displays the 3-D plots generated for EC treatment of aqueous DMP solution in terms of removals of DMP (a) and TOC (b) and EEC values (c) by the Design-Expert® software. In the present study it was decided to focus on the dual effect of the parameters “ DMP_0 ” and “ J_c ” on the treatment efficiencies and EEC values for further assessment and elucidation. The 3D response surface plots were established for a fixed NaCl concentration of 1250 mg L⁻¹ and a t_r of 120 min. Figure 1 (a) reveals that an increase in the DMP_0 appears to enhance the DMP removals. For instance for $J_c = 9 \text{ mA cm}^{-2}$ increasing the DMP_0 from 40 to 80 mg L⁻¹ increased the DMP removals from 47% to 70%. However, this enhancement is only dramatic up to a certain J_c ($\leq 13.5 \text{ mA cm}^{-2}$). Even more at the highest J_c of 22.5 mA cm^{-2} DMP removals tend to decrease by increasing the DMP_0 . As can be seen from Figure 1 (b) the highest TOC removals ($>25\%$) for t_r of 120 min were obtained at two regions where $\text{DMP}_0 < 40 \text{ mg L}^{-1}$, $J_c < 12.5 \text{ mA cm}^{-2}$ and $\text{DMP}_0 > 80 \text{ mg L}^{-1}$, $J_c > 17.5 \text{ mA cm}^{-2}$. As aforementioned, the relative contribution of each factor to each dependent variable (DMP and TOC removals) was directly measured by the respective coefficients in the fitted model. The coefficients of J_c on DMP and TOC removals were +14.04 and +1.61, respectively, which revealed that the sensitivity of DMP removal to J_c was more pronounced than in the case of TOC removal. This might be due to the fact that ultimate oxidation is more difficult to achieve than DMP degradation. It should be also

emphasized here that in order to achieve complete DMP degradation and TOC removals higher than 35%, the t_r had to be longer than 120 min. A technically efficient process also requires to be economically feasible with regard to its capital as well as operating expenses. From Figure 1 (c) it is obvious that EEC values increase continuously and gradually by increasing the current density at a fixed t_r of 120 min. For instance for a DMP_0 value of 60 mg L^{-1} , EEC values were obtained as 25, 55 and 69 kWh m^{-3} for the current densities 4.5, 13.5 and 22.5 mA cm^{-2} .

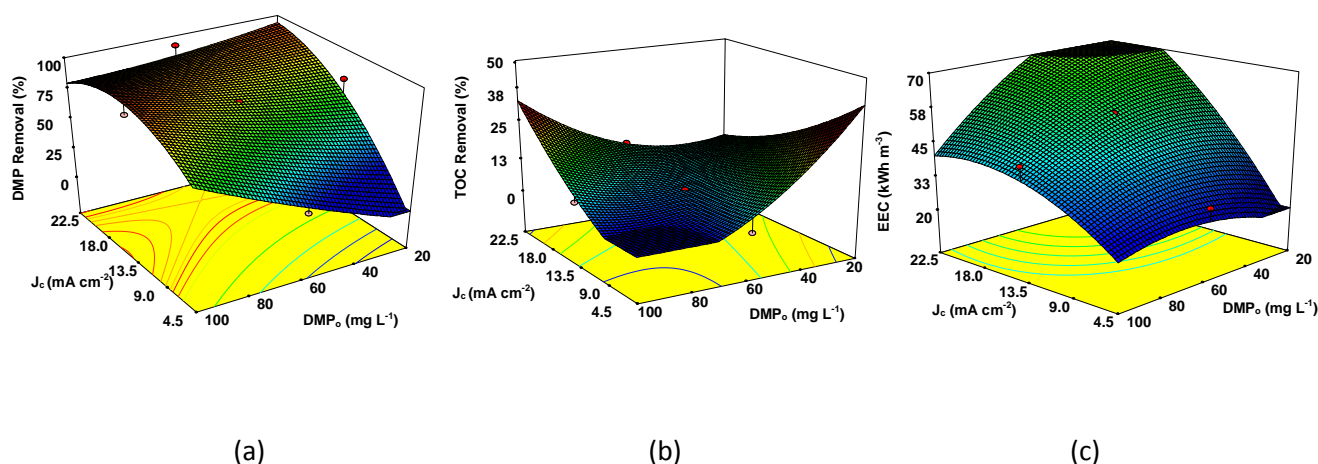


Figure 1. 3D plots for DMP_0 - J_c -percent DMP (a) and TOC (b) removals and EEC values (c) relationships. (Experimental conditions: $t_r = 120 \text{ min}$; $NaCl = 1250 \text{ mg L}^{-1}$)

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 the EC process.

Table 5: Experimentally obtained and predicted DMP and TOC removals and EEC values

DMP_0 (mg L^{-1})	J_c (mA cm^{-2})	$NaCl$ (mg L^{-1})	t_r (min)	DMP Removal (%)		TOC Removal (%)		EEC (kWh m^{-3})	
				Exp.	Pred.	Exp.	Pred.	Exp.	Pred.
20	13.5	1250	180	99±1	100	26±3	30	82	89
40	18.00	1500	150	99±1	100	18±2	19	76	75
60	13.50	1250	180	96±4	100	14±1	18	83	84
80	18.00	1000	150	98±2	95	30±3	26	76	78
80	18.00	1500	150	96±4	99	19±2	18	64	59
100	13.50	1250	120	87±4	95	7±1	9	45	40

For the optimization of the responses, the program randomly picks a set of reaction conditions from which to start its search for desirable results. According to the optimization step of the program, the desired goal for each independent variable (in our case current density, treatment time and electrolyte concentration) and responses (in our case DMP and TOC removals and EEC values) should be chosen. For the optimization of DMP treatment by EC process, a cost driven approach was preferred. Therefore, in the optimization procedure, the desired goals for all independent variables and TOC removal were defined as “keep in range” while the DMP removal as “maximize” and EEC values as “minimize”. Table 4 summarizes the experimental conditions required to achieve the targeted responses at varying DMP_0 . Table 4 also presents achievable treatment goals and options foreseen by the established empirical

regression models for removals of DMP and TOC and EEC values together with the experimentally obtained results. Upon comparison of the predicted and observed results it is evident that the values obtained for the foreseen treatment targets were close to each other. These results testify that the independent variables and their ranges as well as the selected optimization targets were satisfactory in terms of all studied responses and also prove that the CCD-RSM is a powerful tool for optimizing the operational conditions of EC for DMP removal.

4. Conclusions

In the present study, the performance of electrocoagulation on the treatment of aqueous DMP solutions, an endocrine disruptor, was investigated focusing on the influence of major operating parameters by using Response Surface Methodology with Central Composite Design. Analysis of variance indicated that the established factorial design models were statistically significant and described removals of DMP and TOC and EEC values at satisfactory levels. From the established polynomial regression models it was evident that the initial DMP concentration, current density and treatment time had significant effects on treatment performance. The results obtained from the present study proved that RSM was a suitable method to optimize the operating conditions of EC for DMP removal. EC treatment of DMP containing surface water or/and industrial wastewaters may be resulted in lower DMP and TOC abatements since they may also contain some organic (such as humic acids) and inorganic chemicals (such as carbonate and bicarbonate) which may modify the electrocoagulation mechanism. Thus, similar modelling and optimization studies for EC treatment of DMP containing surface water or/and industrial wastewaters should also be performed.

Acknowledgements

The authors acknowledge the financial support of the İstanbul Technical University Research Foundation under project number 33380.

References

- Apaydin O., Kurt U. and Gonullu M.T. (2009), An Investigation on the treatment of tannery wastewater by electrocoagulation, *Global Nest J.*, **11**, 546-555.
- Babu B. and Wu J.T. (2010), Biodegradation of Phthalate Esters by Cyanobacteria, *J. Phycol.*, **46**, 1106-1113.
- Bas D. and Boyaci I.H. (2007), Modeling and optimization I: usability of response surface methodology, *J. Food Eng.*, **78**, 836-845.
- Chatzisyneon E., Xekoukoulotakis N.P., Coz A., Kalogerakis N. and Mantzavinos D. (2006), Electrochemical treatment of textile dyes and dyehouse effluent, *J. Hazard. Mater.*, **137**, 998-1007.
- Cruz-González K., Torres-Lopez O., Garcia-Leon A., Guzman-Mar J.L., Reyes L.H., Hernandez-Ramirez A. and Peralta-Hernandez J.M. (2010), Determination of optimum parameters for Acid Yellow 36 decolorization by electro-Fenton process using BDD cathode, *Chem. Eng. J.*, **160**, 199-206.
- Dermentzis K., Christoforidis A., Valsamidou E., Lazaridou A. and Kokkinos N. (2011), Removal of hexavalent chromium from electroplating wastewater by electrocoagulation with iron electrodes, *Global Nest J.*, **13**, 412-418.
- Dyer C.A. (2007), Heavy metals as endocrine disrupting chemicals, endocrine disrupting chemicals: from basic research to clinical practice. Humana Press Inc, Totowa, NJ, pp 111-133, Chapter 5.
- Gilbert S.F. (2006). Developmental biology, Eight Edition, Sinauer Associate Inc., Chapter 21.
- Horn O., Nalli S., Cooper D. and Nicell J. (2004), Plasticizer metabolites in the environment, *Water Res.*, **38**, 3693-3698.
- Kabdaşlı I., Coşkun B., Ölmez-Hancı T., Tünay O. and Arslan-Alaton I. (2010), Treatment of aqueous dimethyl phthalate by the combined electrocoagulation/Fenton process, *Fresen. Environ. Bull.*, **19**, 1677-1681.

- Kabdaşlı I., Keleş A., Ölmez-Hanci T., Tünay O. and Arslan-Alaton I. (2009a), Treatment of phthalic acid esters by electrocoagulation with stainless steel electrodes using dimethyl phthalate as a model compound, *J. Hazard. Mater.*, **171**, 932-940.
- Kabdaşlı I., Vardar B., Arslan-Alaton I. and Tünay O. (2009b), Effect of dye auxiliaries on color and COD removal from simulated reactive dyebath effluent by electrocoagulation, *Chem. Eng. J.*, **148**, 89-96.
- Kobyas M., Demirbas E. and Sözbir M. (2010), Decolorisation of aqueous reactive dye Remazol Red 3B by electrocoagulation, *Color. Technol.*, **126**, 282-288.
- Körbahti B.K. and Rauf M.A. (2008), Application of response surface analysis to the photolytic degradation of Basic Red 2 dye, *Chem. Eng. J.*, **138**, 166-171.
- Moreno-Casillas H.A., Cocke D.L., Gomes J.A.G., Morkovsky P., Parga J.R. and Peterson E. (2007), Electrocoagulation mechanism for COD removal, *Sep. Purif. Technol.*, **56**, 204-211.
- Myers R.H. and Montgomery D.C. (2002), Response Surface Methodology: Process and Product Optimization using Designed Experiments, 2nd ed., John Wiley & Sons, New York.
- Ölmez-Hanci T., Imren C., Arslan-Alaton I., Kabdaşlı I. and Tünay O. (2009), H₂O₂ /UV-C oxidation of potential endocrine disrupting compounds: A case study with dimethyl phthalate, *Photoch. Photobio. Sci.*, **8**, 620-627.
- Ölmez-Hanci T., Dalmaz B., Arslan-Alaton I., Kabdaşlı I. and Tünay O. (2010), Kinetic modeling and toxicity assessment of diethyl phthalate treated by H₂O₂/UV-C process, *Ozone Scie. Eng.*, **32**, 238-243.
- Ölmez-Hanci T., Kabdaşlı I., Tünay O., Imren C. and Gülhan D. (2012), Treatment of aqueous dimethyl phthalate solution by Fenton and photo-Fenton processes, *Fresen. Environ. Bull.*, **21**, 3136-3141.
- Ölmez-Hanci T., Kabdaşlı I., Tünay O., Ecer C. and Aydın B., (2013), A statistical experimental design approach for mineralization and detoxification of diethyl phthalate by H₂O₂/UV-C process, *Water Sci. Technol.*, **68**, 856-862.
- Psillakis E., Mantzavinos D. and Kalogerakis N. (2004), Monitoring the sonochemical degradation of phthalate esters in water using solid-phase microextraction, *Chemosphere*, **54**, 849-857.
- Rusyn I., Peters J.M. and Cunningham M.L. (2006), Modes of action and species-specific effects of di-(2-ethylhexyl) phthalate in the liver, *Crit. Rev. Toxicol.*, **36**, 459-479.
- Soloman P.A., Ahmed Basha C., Velan M., Balasubramanian N. and Marimuthu P. (2009), Augmentation of biodegradability of pulp and paper industry wastewater by electrochemical pre-treatment and optimization by RSM, *Sep. Purif. Technol.*, **69**, 109-117.
- UNEP (2001). Stockholm convention on persistent organic pollutants. Stockholm: United Nation Environmental Program.
- Wang J.L., Liu P., Shi H.C. and Qian Y. (1998), Kinetics of biodegradation of di-n-butyl phthalate in continuous culture system, *Chemosphere*, **37**, 257-264.
- Xua B., Gao N.Y., Sun X.F., Xia S.J., Rui M., Simonnot M.O., Causserand C. and Zhao J.F. (2007), Photochemical degradation of diethyl phthalate with UV/H₂O₂, *J. Hazard. Mater.*, **B139**, 132-139.