

original article

# Ultrasound-enhanced electrochemical mineralization of perfluorooctanoic acid in aqueous solutions: Assessed by response surface methodology

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## ABSTRACT

**Aims:** The sonoelectrochemical mineralization of the synthetic aqueous solution of the perfluorooctanoic acid (PFOA) on Ti/PbO<sub>2</sub> anode was investigated using the response surface methodology based on a central composite design (CCD).

**Materials and Methods:** The CCD was performed using three different variables such as current density (CD) (mA/cm<sup>2</sup>), pH, and supporting electrolyte (EL) concentration (mM). The total organic carbon (TOC) removal was determined as an indicator of PFOA mineralization. A Shimadzu TOC analyzer was used to measure the TOC of the samples. The Ti/PbO<sub>2</sub> electrode was prepared using the electrochemical deposition method. In order to enhance the electrochemical mineralization, ultrasonic (US) radiation was used. The US frequency was 20 kHz.

**Results:** The optimum conditions for PFOA mineralization in synthetic solution were EL concentration of 94 mM, pH of 2, and CD of 83.64 mA/cm<sup>2</sup>, which resulted in complete TOC removal. The results indicated that the most effective factor for PFOA mineralization was CD. Besides, the TOC removal efficiency significantly increased with increasing CD.

**Conclusions:** Under optimum conditions, the mineralization of PFOA was almost completed after 90 min of sonoelectrolysis. Therefore, sonoelectrolysis was found to be a more effective technique for mineralization of an environmentally persistent compound.

**Key words:** Central composite design, perfluorooctanoic acid, response surface methodology, sonoelectrochemical degradation, Ti/PbO<sub>2</sub>

## INTRODUCTION

Perfluorocarboxylic acids (PFCAs) and their salts have been extensively used as emulsifying agents in paper coatings, photolithography film, polymer synthesis, waxes, and polishes, due to their high surface active nature,

high thermal and chemical stabilities.<sup>[1,2]</sup> Conventional treatment methods are ineffectual for the degradation of PFCAs because it is intrinsically recalcitrant to biological

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and conventional chemical treatment.<sup>[1]</sup> The stability of perfluorinated compounds is ascribed to their strong C–F bond that makes them very persistent to most natural conditions.<sup>[2,3]</sup> Perfluorooctanoic acid (PFOA) is one of the PFCAs' families that have been universally detected in wildlife, water, and human body and is categorized as a likely potential carcinogen by the US-EPA's Science Advisory Board in 2006.<sup>[4]</sup> Lately, some chemical technologies for PFOA degradation have been reported, such as photocatalytic oxidation, direct photolysis, photochemical reduction, photochemical oxidation, thermally-induced reduction, and sonochemical pyrolysis. So far, most of the techniques could not effectively decompose PFOA.<sup>[5]</sup> The electrochemical oxidation is a technology that has presented its capacity to degrade refractory organic pollutants such as emerging contaminants contained in the secondary effluents of wastewater treatment plants.<sup>[6]</sup> Electrochemical techniques generally carried out oxidatively have the advantage of contaminant elimination without the addition of chemicals. The main disadvantage of these methods is energy consumption. Nevertheless, this disadvantage has been suppressed by the development of new anode materials.<sup>[7,8]</sup> Many researchers have investigated the usage of this technique for refractory pollutant removal from aquatic solution. For example, Sarafraz *et al.* used Ti/SnO<sub>2</sub>-Sb for electrochemical degradation of the acid orange 10 dye. They reported that decolorization of 100 mg/L dye was complete, and 61.3% and 43.9% chemical oxygen demand and total organic carbon (TOC) removal were recorded after 50 min of electrolysis, respectively.<sup>[9]</sup> PbO<sub>2</sub> is a low-cost electrode material that can be quickly and easily prepared, and is being used by many researchers for electro-oxidation of refractory pollutants in aquatic solutions.<sup>[10-13]</sup> During the process of oxidation of polluted waters, OH• specimen is generated on the PbO<sub>2</sub> electrode surface, and a mechanism for the electrochemical processes occurring in the gel-crystal structure of the PbO<sub>2</sub> layer of the electrode has been proposed.<sup>[14]</sup> The Pb\*O(OH)<sub>2</sub> active centers placed in the hydrated PbO<sub>2</sub> layer on the surface of the crystalline PbO<sub>2</sub> anode provide electrons to the Crystal district, becoming positively charged (Pb\*O(OH)<sup>+</sup> (OH)<sup>+</sup>). The OH• can depart from the active centers and react with the pollutant in the aqueous solution. Thus, the PbO<sub>2</sub> anode is expected to perform quite well in organic pollutant mineralization.<sup>[15]</sup> On the other hand, ultrasonic (US) treatment acts as cavitation, which not only generates plasma in water, and degrading molecules by pyrolysis, but also produces free radicals and other reactive types that can improve the amount of collisions between free radicals and contaminants. Recently, using the combination of US method and other techniques for the treatment of organic wastewater has been largely studied (e.g., phenol and pharmaceutical compounds).<sup>[16-18]</sup> Optimization of the operating conditions of an experimental system and recognition of the way in which the experimental parameters affect the final output of the system are realized using modeling techniques.<sup>[19]</sup> Besides, it is possible to determine the relationships and interactions between

the variables through these techniques. In this regard, statistical methodologies, such as the response surface methodology (RSM), are suitable for studying and modeling a particular system.<sup>[20]</sup> Since the sonoelectrochemical mineralization of PFOA using Ti/PbO<sub>2</sub> electrode was not reported in the literature, the aim of the present study was to investigate the electrochemical mineralization of PFOA as an emerging contaminant using Ti/PbO<sub>2</sub> anode coupled with US irradiation (sonochemical) and to determine the optimum conditions by RSM. The effects of current density (CD), pH of the solution, and supporting electrolyte (EL) concentration were evaluated in terms of TOC removal.

## MATERIALS AND METHODS

### Chemicals

Analytical-grade PFOA was purchased from Sigma Aldrich Co., USA, and used without further purification. Pb(NO<sub>3</sub>)<sub>2</sub> (Sigma Aldrich Co.), Triton X-100 (Merck Co., Germany), and CuSO<sub>4</sub>·5H<sub>2</sub>O (Merck Co.) were used for electrode preparation. Other chemicals were purchased from Merck Co. The initial pH of the solutions was adjusted using sodium hydroxide and sulfuric acid. The pH adjustment was done using an E520, Metrohm Herisau pH meter. Sodium sulfate was used as the supporting EL. All of the solutions were prepared using de-ionized water.

### Preparation of Ti/PbO<sub>2</sub> electrode

The Ti substrate with 2 mm thickness was cut into a strip (4.8 cm × 4 cm, 99.7% Aldrich) and pretreated according to the following procedures. The substrate was polished on 320-grit paper strips<sup>[21]</sup> to eliminate the superficial layer of TiO<sub>2</sub> (an electric semiconductor) and increase surface roughness (for efficient adherence of PbO<sub>2</sub>). Then, the substrate was degreased in an US bath of acetone for 10 min and then in distilled water for 10 min. Afterward, the substrate was etched for 1 h in a boiling solution of oxalic acid (10%) and rinsed with ultrapure water.<sup>[22]</sup> Finally, the cleaned Ti substrate was transferred to an electrochemical deposition cell, which contained 12% (w/v) Pb(NO<sub>3</sub>)<sub>2</sub> solution comprising 5% (w/v) CuSO<sub>4</sub>·5H<sub>2</sub>O and 3% (w/v) surfactant (Triton X-100). The role of the surfactant was to minimize the surface tension of the solution for better wetting of the substrate and also to increase the adhesion of PbO<sub>2</sub> to the Ti substrate. The electrode position of PbO<sub>2</sub> was performed at a constant anodic current of 20 mA/cm<sup>2</sup> for 60 min at 80°C with continuous stirring.<sup>[23]</sup> The X-ray diffraction (XRD) tests were performed using a Bruker, D8 Advance, Germany. The samples were scanned under Co K $\alpha$  radiation (wavelength: 1.7890 Å) at 40 kV and 40 mA. Scanning electron microscope (SEM; Philips XI30, The Netherlands) was employed to observe the surface morphology of the electrodes, which presented a typical pyramid shape similar to that reported in the literature.<sup>[24]</sup>

### Sonoelectrochemical mineralization of perfluorooctanoic acid

Synthetic wastewater was prepared by dissolving PFOA in distilled water at a concentration of 50 mg/L. The sonoelectrochemical mineralization of PFOA was performed in a temperature-controlled water batch reactor (0.45 L) equipped with an ultrasonic probe (Bandelin SONOPULS, UW 3200, TT 13, Germany), a 41.12 cm<sup>2</sup> Ti/PbO<sub>2</sub> as the anode and a 80.32 cm<sup>2</sup> stainless steel plate as the cathode in conjunction with an adjustable power supply unit (HANI, Iran). The gap between the anode and cathode was 1 cm. The temperature of the reaction solution was kept constant at 25 ± 1°C. The duration of all the electrolysis experiments was 90 min. The reactor was placed on a magnetic stirrer for mixing its content during the experiment to maximize mass transport [Figure 1].

### Analytical procedure

The performance of sonoelectrochemical mineralization of PFOA was evaluated on the basis of TOC removal. A Shimadzu TOC-VCSH analyzer (Japan) was used to measure the TOC of the samples. The TOC removal efficiency was calculated Eq. (1) as follows:

$$\text{TOC removal (\%)} = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where C<sub>0</sub> and C<sub>t</sub> are the TOC of the solution before and after electrolysis for t minutes, respectively.

### Experimental design

The central composite design (CCD) technique coupled with RSM has been opted for modeling and design of experimental tests.<sup>[25]</sup> The CD, EL, and pH parameters were selected as input variables. The rotatable experimental plan was performed with the three variables at five levels (-1.68, -1, 0, 1, and 1.68). Table 1 shows the values and levels of the variables. Five replications were done at the center point of the design to evaluate the pure error and

consequently the lack of fit. Table 2 shows the CCD matrix of the mineralization experiments.

The relationship between response Y and the three independent variables X<sub>1</sub>, X<sub>2</sub>, and X<sub>3</sub> could be approximated by quadratic polynomial Eq. (2) as follows:

$$Y = b_0 + b_1X_1 + b_2X_2 + b_3X_3 + b_{11}X_1^2 + b_{22}X_2^2 + b_{33}X_3^2 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{23}X_2X_3 \quad (2)$$

where Y is the predicted response, b<sub>0</sub> is a constant, b<sub>1</sub>, b<sub>2</sub>, and b<sub>3</sub> are the linear coefficients, b<sub>12</sub>, b<sub>13</sub>, and b<sub>23</sub> are the cross-product coefficients, and b<sub>11</sub>, b<sub>22</sub>, and b<sub>33</sub> are the quadratic coefficients. In the present study, backward variable selection was used for multiple regression modeling.<sup>[26]</sup> The assumption of final regression model was verified using the Anderson–Darling test for normality of residuals,<sup>[27]</sup> Breusch–Pagan test for constant variance of residuals,<sup>[28]</sup> and Durbin–Watson test for independence of residuals.<sup>[29,30]</sup> Lack of fit test was performed to assess the fit of the final model. Validation of the final model was established using predicted R-squares (R<sup>2</sup>), which estimates the prediction power of the model with new observations based on the leave-one-out technique.<sup>[31]</sup> The optimum values of the final model were calculated using numerical methods. In this

**Table 1: The range and codification of the independent variables (X<sub>i</sub>) used in the experimental design**

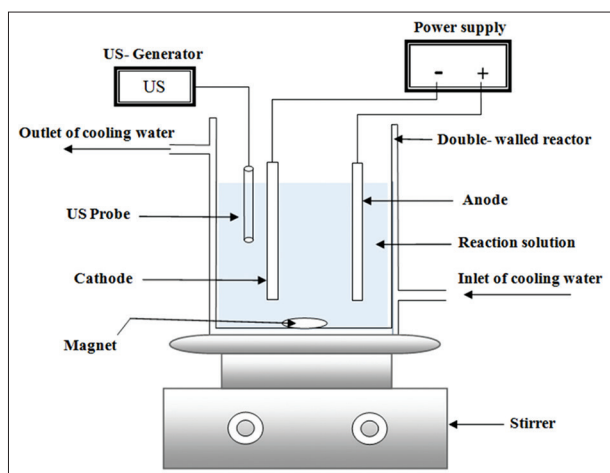
Variables	Actual values of the coded values				
	- 1.68	- 1	0	1	1.68
pH (X <sub>1</sub> )	1.95	4	7	10	12.05
EL (mM) (X <sub>2</sub> )	32.96	50	75	100	117.04
CD (mA/cm <sup>2</sup> ) (X <sub>3</sub> )	16.36	30	50	70	83.64

EL: Electrolyte, CD: Current density

**Table 2: CCD matrix of sonoelectrochemical mineralization of PFOA**

Experimental number	pH	EL	CD	TOC removal (%)	
				Observed	Predicted
1	4.00	50.00	30.00	57.41	57.43
2	4.00	50.00	70.00	92.70	92.19
3	4.00	100.00	30.00	60.92	59.72
4	4.00	100.00	70.00	94.15	94.49
5	10.00	50.00	30.00	55.00	54.02
6	10.00	50.00	70.00	90.68	88.78
7	10.00	100.00	30.00	54.55	56.32
8	10.00	100.00	70.00	92.71	91.08
9	1.95	75.00	50.00	80.25	80.73
10	12.05	75.00	50.00	73.78	74.99
11	7.00	32.96	50.00	73.27	74.78
12	7.00	117.04	50.00	78.72	78.65
13	7.00	75.00	16.36	39.99	39.74
14	7.00	75.00	83.64	96.51	98.21
15	7.00	75.00	50.00	78.78	78.90
16	7.00	75.00	50.00	80.04	78.90
17	7.00	75.00	50.00	79.14	78.90
18	7.00	75.00	50.00	78.25	78.90
19	7.00	75.00	50.00	78.78	78.90

EL: Electrolyte, CD: Current density, TOC: Total organic carbon, PFOA: Perfluorooctanoic acid, CCD: Central composite design



**Figure 1: Schematic of the experimental setup**

regard, the experimental range predictors were divided into a grid and then the final model was calculated for all possible combinations of predictors in the grid.

## RESULTS

### Characterization of the Ti/PbO<sub>2</sub> electrode

XRD pattern of the Ti/PbO<sub>2</sub> electrode is shown in Figure 2. It can be observed that PbO<sub>2</sub> was deposited in the form of two known polymorphs, namely, orthorhombic α-PbO<sub>2</sub> and tetragonal β-PbO<sub>2</sub>, which occur naturally as scrutinyite and plattnerite, respectively. Figure 3 shows the SEM image of the surface microstructure of the Ti/PbO<sub>2</sub> electrode. It can be observed that the PbO<sub>2</sub> layer is crack free and composed of packed faceted microcrystallites. Such morphology verifies that only PbO<sub>2</sub> is involved in the electrochemical mineralization of the PFOA and protects the surface of the Ti substrate. Furthermore, energy-dispersive X-ray spectroscopy analysis (data not shown) confirmed the presence of lead and oxygen atoms on the surface of the Ti/PbO<sub>2</sub> electrode.

### Central composite design analysis and modeling

The initial model using linear and quadratic forms, as well as the interactions between pH, EL and the CD was created. The determination coefficient for the initial model was 97.4%. Eq. (3) represents the first model that was developed with all linear, quadratic, and two-way interaction of predictors:

$$Y = 5.482 + 0.1148 \times \text{pH} + 0.25671 \times \text{EL} + 1.5402 \times \text{CD} - 0.006450 \times \text{pH} \times \text{EL} + 0.009062 \times \text{pH} \times \text{CD} + 0.0002675 \times \text{EL} \times \text{CD} - 0.04520 \times \text{pH}^2 - 0.0011974 \times \text{EL}^2 - 0.0079632 \times \text{CD}^2 \quad (3)$$

The backward method was used to remove insignificant variables. In the first step, linear form of pH was removed from the initial model ( $P = 0.959$ ). In three following steps, interactions of  $\text{EL} \times \text{CD}$  ( $P = 0.908$ ),  $\text{pH} \times \text{EL}$  ( $P = 0.239$ ),

and  $\text{pH} \times \text{CD}$  ( $P = 0.201$ ) were removed from the model. The final model was obtained by removing the four waste predictors which have prediction coefficient of 98.6% as shown in Table 3. The final model was as in Eq. (4):

$$Y = 5.113 + 0.23125 \times \text{EL} + 1.74595 \times \text{CD} - 0.040573 \times \text{pH}^2 - 0.0012352 \times \text{EL}^2 - 0.008768 \times \text{CD}^2 \quad (4)$$

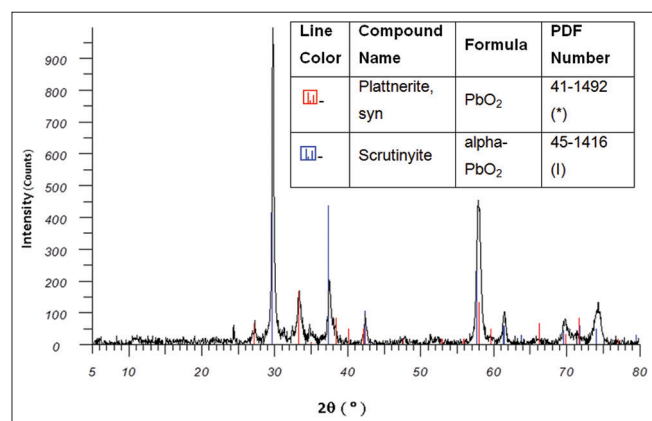
A partial F-test was performed for comparison between first model and the final model. The difference of these two models was not significant ( $P = 0.603$ ), although the final regression model (Eq. 4) had four predictors less than the initial model (Eq. 3). Figure 4 shows surface plot of final model for the TOC removal as a function of CD and pH. Table 3 represents the final regression model for PFOA mineralization. Regression model assumptions were also considered. The normality of model residual was approved using Anderson–Darling test ( $P = 0.796$ ). Independency of residuals (nonauto-correlation) was confirmed by Durbin–Watson test ( $P = 0.538$ ) and Breusch–Pagan score test approved the constant variances of residuals ( $P = 0.563$ ). Moreover, the lack of fit test of the final model was insignificant, which confirms the goodness of fit for this model ( $P = 0.072$ ).

The final model was validated using the leave-one-out technique. Predicted  $R^2$  was 98.6% that confirmed external

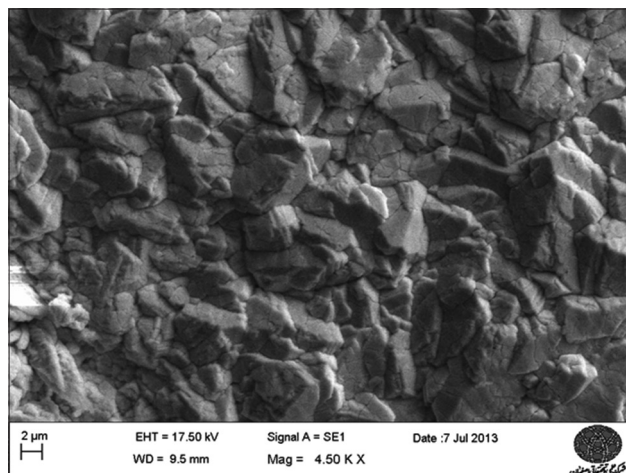
**Table 3: Final regression model for TOC removal**

Terms	Co-efficient	SE co-efficient	T statistic	P
Constant	5.113	3.844	1.33	0.206
EL	0.23125	0.08276	2.79	0.015
CD	1.74595	0.08669	20.14	<0.001
pH <sup>2</sup>	-0.040573	0.007992	-5.08	<0.001
EL <sup>2</sup>	-0.0012352	0.0005441	-2.27	0.041
CD <sup>2</sup>	-0.0087680	0.0008498	-10.32	<0.001

$R^2 = 99.5\%$ ; Adjusted  $R^2 = 99.3\%$ ; Predicted  $R^2 = 98.6\%$ . TOC: Total organic carbon, SE: Standard error, EL: Electrolyte, CD: Current density



**Figure 2:** X-ray diffraction pattern of the prepared PbO<sub>2</sub> electrode



**Figure 3:** Scanning electron microscope micrograph of the surface of the Ti/PbO<sub>2</sub> electrode



validity of the final model. Leave-one-out prediction of the final model versus observed values of response represented in Figure 5.

The final model was evaluated through the range of experimental predictors with a numerical method. The grid combination of predictors was ranged between 2 and 12 with 0.1 increments for pH, from 33 to 117 with 1 increments for EL and from 16 to 85 with 1 increments for CD. Model prediction was calculated for 5,712,000 different combination of predictors and optimum values of input parameters were pH = 2, EL = 94, and CD = 83.64 which resulted in complete TOC removal. Effects of pH, EL, and CD on PFOA mineralization can be investigated independently because there is no interaction effect in the final model. Figures 6-8 show effects of pH, CD, and EL on TOC removal, respectively when other factors were at optimum values. The CCD design matrix, the observed TOC removal values, and predicted results for

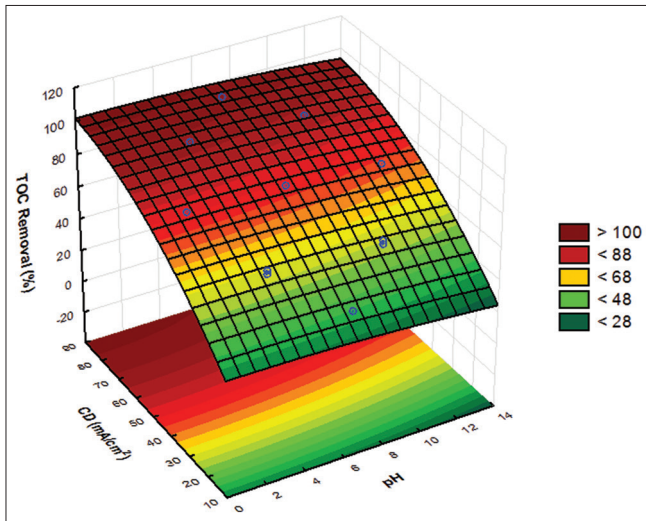
the sonoelectrochemical mineralization of PFOA are shown in Table 2.

## DISCUSSION

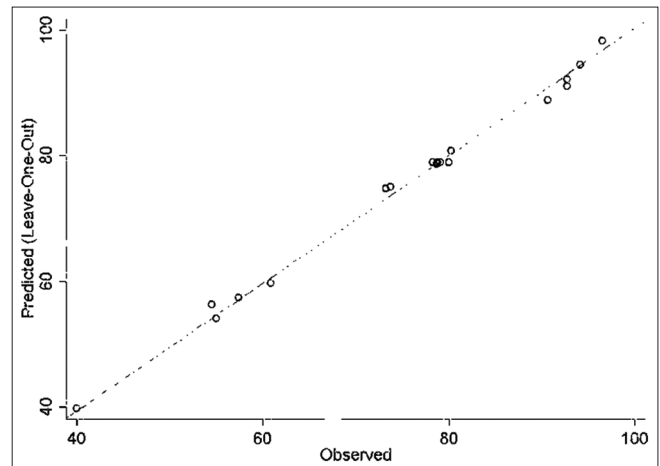
### Effect of initial pH

Figure 4 shows the effect of initial pH of the solutions on TOC removal that has been adjusted to the following values: 1.95, 4, 7, 10, and 12.05. There are many disagreements about the mechanism of influence of pH in the literature that is due to diversity of the organic structures and electrode materials; however, the initial pH is one of the main factors in the oxidation process.<sup>[24]</sup>

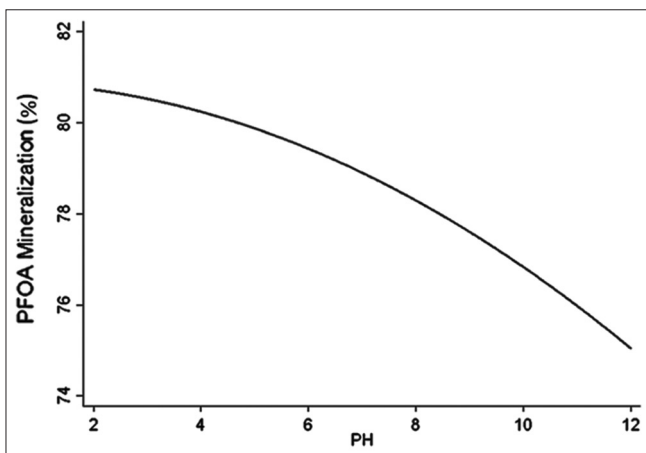
As shown in Figure 4 and by Eq. (4), the TOC removal efficiency was increased with decrease of pH. From Eq. (3), the highest and the lowest level of PFOA mineralization efficiency can be reached at an acidic (pH = 2) and alkaline (pH = 12) conditions, respectively. An increase in



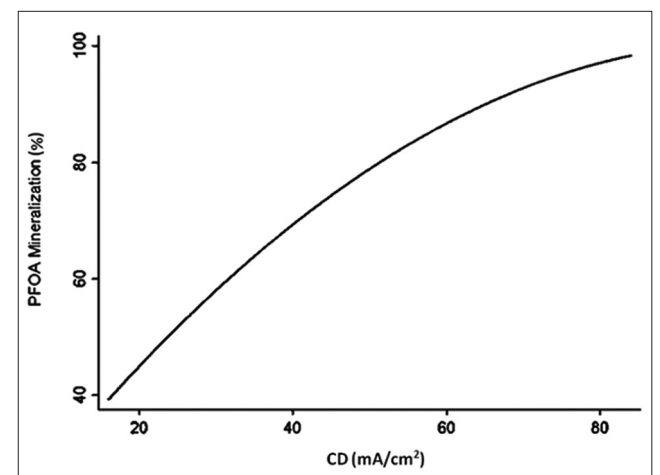
**Figure 4:** Three-dimensional surface plot for the total organic carbon removal as a function of current density and pH



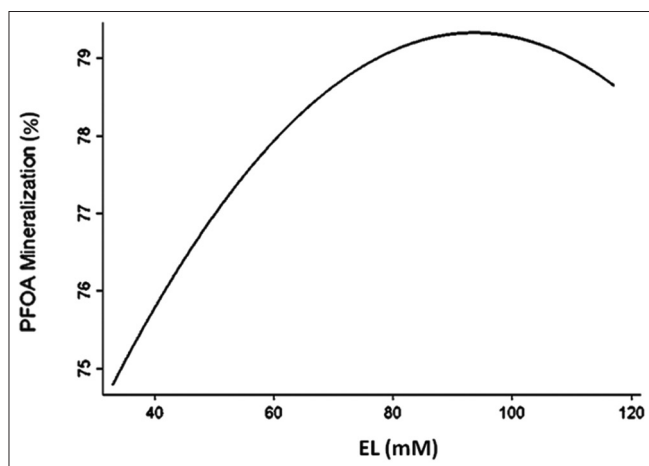
**Figure 5:** Leave-one-out prediction of the final model versus observed for perfluorooctanoic acid mineralization



**Figure 6:** Predicted perfluorooctanoic acid mineralization using the final model versus pH, when electrolyte = 94 mM and current density = 83.64 mA/cm<sup>2</sup>



**Figure 7:** Predicted perfluorooctanoic acid mineralization using the final model versus current density, when pH = 2 and electrolyte = 94 mM



**Figure 8:** Predicted perfluorooctanoic acid mineralization using the final model versus electrolyte, when pH = 2 and current density = 83.64 mA/cm<sup>2</sup>

the PFOA mineralization with the decreasing pH can be explained as the followings.

First, the enhancement of the TOC removal efficiency at pH values lower than neutral is due to the increase in oxygen over-potential that abate the anodic oxygen evolution reaction and favors the production of more OH radicals, which other studies confirmed it.<sup>[32-34]</sup> Second, micro bubbles formed at alkaline pH in the aqueous solution in contrast with the amounts of bubbles formed at acidic pH. This situation leads to adherence of bubbles to the Sonicator's probe and, therefore, restrict ultrasound energy distribution through the bulk of solution.<sup>[35]</sup>

However, in the strong acidic solutions, the life of anode decreases.<sup>[36]</sup> As a result, in the present study, a pH of 2 was found as the optimum pH value for maximum TOC removal. Eq. (4) and Figure 6 show that the difference between the minimum and maximum PFOA mineralization efficiency related to pH is 5.68%, which indicates that sonoelectrochemical mineralization of PFOA using PbO<sub>2</sub> anode is not very sensitive to the initial pH and PFOA could be mineralized under a broad range of pH.

### Effect of current density

In the present study, the effect of CD was investigated at five levels (16.36, 30, 50, 70, and 83.64 mA/cm<sup>2</sup>) in combination with pH and EL [Figure 4]. As shown in this figure, which is the output of the CCD, the TOC removal efficiency significantly increased with the increasing CD. Respect to Eq. (4), the maximum TOC removal efficiency was obtained at the CD of 83.64 mA/cm<sup>2</sup> in the range of investigation. Eq. (4) and Figure 7 show that the difference between the minimum and maximum PFOA mineralization efficiency related to CD is 59.1%, indicating that the most important variable for the enhancement of TOC removal was CD. The main reason for the increase in efficiency with increasing CD can be attributed to increasing the number of OH specimen

produced which is in well agreement with other studies.<sup>[33,36,37]</sup> As a result, in the present study, a CD of 83.64 mA/cm<sup>2</sup> was chosen as the optimum CD value for maximum PFOA mineralization.

### Effect of electrolyte

The effect of EL was investigated at five levels (32.96, 50, 75, 100, and 117.04 mM) in combination with pH and CD. It can be concluded from Figure 8, despite increasing PFOA mineralization with increasing the concentration of the EL, its impact is not significant. This negligible raise in the efficiency with increasing the concentration of the EL can be explained by increasing the concentration of sulfate radicals, which are generated through the irradiation of sulfate ions by US EL.<sup>[38]</sup> Change the EL concentration in the range of tests, leading up to a 4.54% change in the PFOA mineralization efficiency [Figure 8].

## CONCLUSIONS

In the present study, sonoelectrochemical mineralization of the PFOA as a term of TOC removal was investigated and modeled by employing CCD coupled with RSM for the prediction and optimization of the PFOA mineralization in synthetic wastewater using Ti/PbO<sub>2</sub> as the anode and stainless steel as the cathode. The use of RSM based on CCD allowed determination of the behavior of the sonoelectrolysis on mineralization without requiring large number of experiments, and provided sufficient information. Moreover, the CCD is facilitated in detecting the optimum conditions for PFOA mineralization. The final model was validated using the leave-one-out technique, and the predicted R<sup>2</sup> was 98.6%, which confirmed the external validity of the model. Also, lack of fit test was nonsignificant with a *P* value of 0.072, which confirmed the fit of the final model. The results of the present study demonstrated that sonoelectrolysis is a suitable and an environment-friendly method for the mineralization of refractory PFOA in aqueous solution.

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### Conflicts of interest

There are no conflicts of interest.

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