



ANODIC OXIDATION OF PHTHALIC ACID IN EXTREMELY ACIDIC MEDIUM IN THE PRESENCE CrVI

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ABSTRACT

In this study, mineralization of phthalic acid added to chromium medium by electrochemical anodic oxidation method to represent organic residue in chromium medium were investigated. In anodic oxidation with BDD anode of phthalic acid (initial form potassium hydrogen phthalate, KHP) BDD anode in chromium and acidic media, the effects of cathode type, current density and electrolysis time were investigated. As a result of electrolysis experiments, stainless steel cathode was preferred in terms of persulfate production, cost and ease of use. After electrode selection, the effect of current density, amount of CrVI in solution and electrolysis time on KHP mineralization was realized by using response surface method and central composite design. The optimum parameters were determined as 70 mA/cm² current density, CrVI ratio 12.5%, and time 377 min, where 89.79% mineralization efficiency could be achieved with a desirability value of 1.00.

Keywords: *Phthalic acid, Anodic Oxidation, Mineralization, Chromium, Optimization*

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1. INTRODUCTION

The most important chemical species of chromium are trivalent and hexavalent chromium, which hexavalent chromium is more toxic due to its high solubility in aqueous media, resulting in a high mobility inside the environment. In contrast, trivalent chromium is much less toxic due its low solubility in water and lower mobility, besides this species has important functions in the metabolism of glucose (Almazán-Sánchez *et al.*, 2011). There are various chemical and physical means for separation and disposal of chromium (Lugo-Lugo *et al.*, 2010; Olmez, 2009).

When a concentrated and refinable chromium stream is achieved, it is possible to reuse these pretreated wastes as new products. In some cases, the existence of organic pollutants obstructs the reuse of the regenerated chromium materials. In this study the chromium species polluted with a representative refractory organic species (phthalic acid) is investigated by means of electro-oxidation with BDD anode.

The main advantage of electro oxidation technology is that no chemicals are used. In fact, only electrical energy is consumed for the mineralization of organic pollutants on high oxidation power anodes. The activity of the electro-generated hydroxyl radicals is strongly related to their interaction with the anode surface. As a general rule, the weaker the interaction, the lower is the electrochemical activity towards oxygen evolution (high O₂ over-voltage anodes) and the higher is the chemical reactivity toward organics oxidation. BDD provides highest O₂ over potential and is an excellent anode for any kind of organic compounds (Comninellis, 2008; Vatistas, 2012).

Electro-oxidation with BDD anode is an effective way to decompose persistent organic species through mineralization to carbon dioxide and water (Panizza *et al.*, 2008; Matzek and Carter, 2016). The •OH radicals are produced on BDD anode surface and sulfate radicals are formed directly or through interaction with •OH radicals as illustrated in Fig 1 and Eq. (1-5) (Lee *et al.*, 2018; Davis *et al.*, 2014):

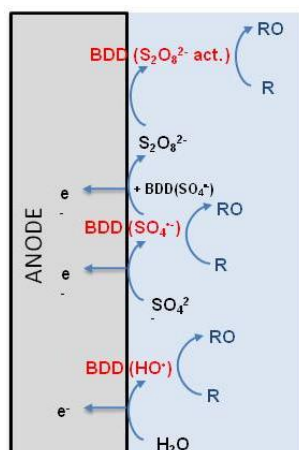
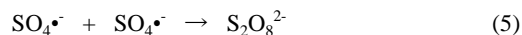
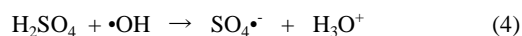
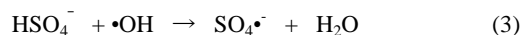
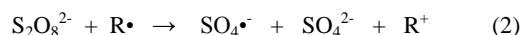
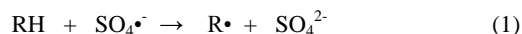


Fig. 1. Hydroxyl and sulfate radicals formation on BDD anode (Electron 4 water, 2019)



BDD electrodes have extreme stability under anodic polarization and high overpotential for water dissociation (Chaplin, 2014; Perez *et al.*, 2012). BDD anode can be used in conjunction with BDD cathode, however it has limitations due to cathode deposition and regeneration. Therefore, in this study BDD, 316-L steel and Titanium grade-2 cathodes are compared in terms of their persulfate production capacity and reusability. 316-L steel and Titanium grade-2 are easily available materials. 316-L is selected due to its low cost and high current efficiency, while Titanium grade-2 has modest cost and high resistivity at acidic media.

The objectives of this study is to determine a suitable cathode for mineralization of phthalic acid in solutions containing sulfate at and use surface response method to investigate the effect of factors namely current density, percentage of CrVI/Total chromium and time during mineralization of phthalic acid at chromium and sulfate rich acidic solutions.

2. MATERIALS AND METHODS

2.1. Anodic Oxidation Experiments

In the experiments, approximately 10 μm boron doped diamond coated niobium electrode (BDD, Condias GmbH) was used as an anode. Different types of electrodes were used as cathodes (stainless steel 316L, titanium grade 2, BDD). The combined electrode set (CONDIACELL® Stack Modell EAOP® Testkit) with 3 anodes and 2 cathodes provides an impact surface of approximately 200 cm². The system where electro oxidation experiments were performed was given in the Fig 2.

Synthetic solutions containing total chromium around 4% in terms of Cr₂O₃, app. 10% Na₂SO₄, 20 g potassium hydrogen phthalate (KHP) per 1232 g solution, various Na₂Cr₂O₇ and initial pH adjusted to 1.8-2.0 were studied. Solutions described above weighs approximately 1230 g and 1L of this solution was transferred to conduct electro oxidation experiment and remaining was stored as initial sample. Total chromium levels were selected so that the conductivity was around 50 mS/cm, which can be a level useful for industrial applications. Total chromium and sulfate input was provided by addition of Cr(OH)SO₄. The pH was adjusted by adding 1:1 H₂SO₄ (app.15-20 g).

The apparatus used at electrolysis experiments is given in Fig 2.



Fig. 2. Electro-oxidation test apparatus

The direct current source has 20V and 50A limits. The borosilicate glass reaction vessel was specially designed to provide full accommodation of the electrodes and supply efficient mixing with magnetic stirrer. The peristaltic pump equipped with a sintered glass opening onto the surface of the solution provided the ceasing of the bubbles encountered especially at the initial steps of the experiments.

2.2. Methods of Analysis

Total Organic Carbon (TOC) analyzes were performed with a TOC analyzer (Shimadzu) containing Solid Incineration Module (SSM), since the samples were not prone to liquid injection.

Cr (III) and Cr (VI) content were determined by potentiometric titration. If both Cr species were present at the same time and in high amounts, the amount of Cr (VI) was found by direct titration with FeSO_4 ; after oxidation and removal of the oxidant, total Cr content was determined by titration with FeSO_4 and Cr (III) amount was calculated from the difference. In case Cr (VI) was found in trace levels, UV-VIS photometric method was used which works with diphenyl carbazide staining principle.

In the persulfate (PS) analysis, calibration was prepared at 352 nm with PS standards in the 0.5 - 20 mg/L concentration range using 0.02 M sodium PS ($\text{Na}_2\text{S}_2\text{O}_8$ corresponding to 4760 mg/L) stock solution to prepare calibration standards. In the method, 5 g of KI and 0.3 g of NaHCO_3 were dissolved in 50 ml volumetric flask for calibration standards and sample, the standard or sample was added, followed by stirring to 50 mL, waiting for 15 minutes and measured on the spectrophotometer.

2.3. Experimental Design and Optimization

The effects of three independent variables (current density, CrVI%, and time) on electro-oxidation of KHP solution were studied by central composite design (CCD) at five levels ($-\alpha$, -1, 0, +1, $+\alpha$) using Design Expert 11.

The process was optimized and the effect of current density (60–80 mA/cm^2), CrVI% (5–20), and time (120–360 min) was investigated (labeled as X_1 , X_2 , and X_3 , respectively).

3. RESULTS AND DISCUSSION

It was aimed to use persulfate oxidant produced from sulfate ions in mineralization of phthalic acid solution in acidic medium containing chromium species by anodic oxidation method. For this reason, firstly, the electrolytic persulfate (PS) formation performance of cathode species was evaluated.

3.1. Persulfate Production of Different Cathodes at Constant Current Density

Persulfate measurement experiments covered a period of 480 minutes and the solution to be electrolyzed contained 100 g/L Na_2SO_4 solution adjusted to pH 1.8 by adding 40 mL H_2SO_4 . Analysis results with BDD, Ti Gr-2 and 316 SS cathodes at 50 mA/cm^2 current density are given in Fig. 3.

Fig. 3 showed that the highest persulfate formation is obtained in BDD/SS electrode pair. During electrolysis, the pH and temperature of the medium were also monitored and the temperature increased to $\sim 50^\circ\text{C}$ after 120 minutes at all electrodes and increased to 59°C , 56°C and 51°C for BDD, Ti-Gr 2 and SS, respectively, as the electrolysis time increased.

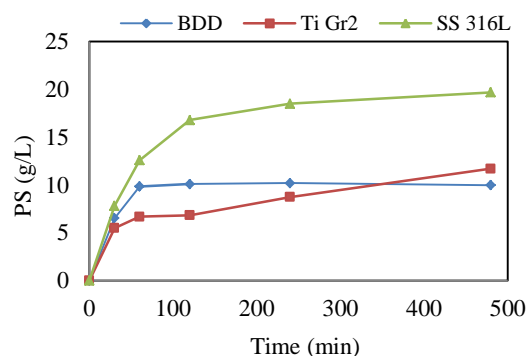


Fig. 3. Persulfate formation when 2 cathodes were used against 3 BDD anodes, $j = 50 \text{ mA}/\text{cm}^2$

3.2. Optimization of Mineralization

The TOC Removal of KHP was carried out by the electro-oxidation experiments at acidic condition, and the results were given in Table 1. The model fitted was observed to be quadratic model. The quality of the model fitted was evaluated by analysis of variance (ANOVA).

When the results of ANOVA of the models were examined (Table 2), it was observed that the F values of the model was higher than the tabulated F value [$F_{0.05, d(f) - (dF+1)}$] with a very low p values (< 0.0001). A small p value ($\text{Prob} > F$) indicated that the terms have improved the model.

Table 1. Central composite experimental design and results of electro-oxidation of KHP

Run	Parameters			Response
	J (mA/cm ²)	CrVI (%)	Time (min)	TOC Removal (%)
1	80	20	360	92,0
2	70	12,5	240	61,2
3	60	5	360	78,2
4	86,8	12,5	240	75,5
5	70	25,1	240	61,7
6	70	12,5	240	62,6
7	70	12,5	240	61,7
8	80	5	120	30,5
9	53,2	12,5	240	46,3
10	70	12,5	240	61,5
11	60	20	360	81,1
12	70	12,5	441,8	94,4
13	60	20	120	30,2
14	80	20	120	39,1
15	70	12,5	240	67,4
16	70	0	240	41,9
17	70	12,5	38,2	8,9
18	70	12,5	240	68,7
19	60	5	120	20,4
20	80	5	360	91,9

Table 2. Analysis of variance results for the validation of the quadratic model proposed

Source	Sum of Squares	df	Mean Square	F-value	p-value
Model	11060	9	1229	64.64	0.0001
X ₁ :J	632	1	632	33.24	0.0002
X ₂ :CrVI%	222	1	222	11.68	0.0066
X ₃ :time	9851	1	9851	518.12	0.0001
X ₁ X ₂	2.07	1	2,07	0.1090	0.7481
X ₁ X ₃	3.90	1	3,90	0.2054	0.6601
X ₂ X ₃	29.59	1	29.59	1.56	0.2406
X ₁ ²	0.9491	1	0.9491	0.0499	0.8277
X ₂ ²	174	1	174	9.13	0.0129
X ₃ ²	179	1	179	9.40	0.0119
Residual	190	10	19.01		
Lack of Fit	136	5	27.23	2.52	0.1663
Pure Error	53.95	5	10.79		
Cor Total	11251	19			

The experimental data provided the input for the polynomial second degree model (Eq. (6)).

$$TOC\ Removal\ \% = +63.72 + 6.80 X_1 + 4.04 X_2 + 26.86 X_3 - 0.5089 X_1 X_2 + 0.6986 X_1 X_3 - 1.92 X_2 X_3 - 0.2566 X_1^2 - 3.5 X_2^2 - 3.52 X_3^2 \quad (6)$$

In this study the following parameters were the most influential (in order of decreasing significance): time > current density > CrVI%. The quality of the fit of the model was expressed by the correlation coefficient (R²)

of 0.9831 which is used to check the correlation between the experimental data and predicted responses (Fig. 4).

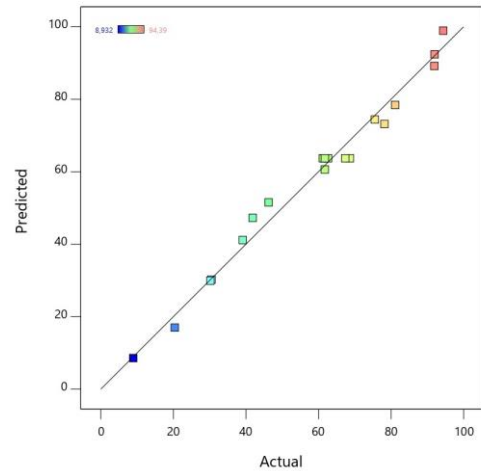


Fig. 4. Predicted vs experimental plot

The combined effect of time and initial CrVI % on mineralization of KHP, while holding other variable constant, is shown in Fig. 5.

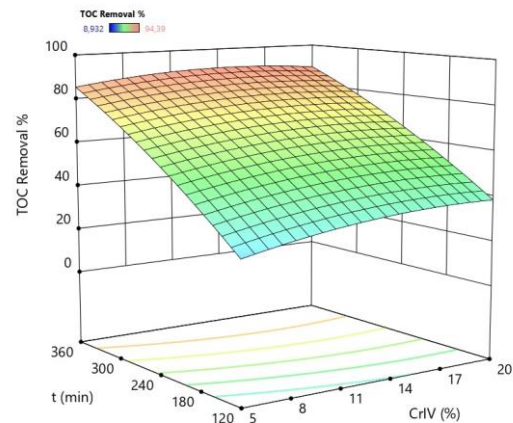


Fig. 5. Three-dimensional response surface plots showing the effects of significant interactions between time and CrVI% (J=75 mA/cm²)

The electrolysis time is an important parameter and in order to obtain 90% mineralization, a 360 min (6 hours) electrolysis time is required. However, since the initial TOC of the solution is too high (9400 mg/L), this time is considered reasonable. When we look at the effect of the amount of CrVI in the medium, it can be said that the presence of 12.5% CrVI catalyzes the mineralization.

Fig. 6 presents the effect of time and current density on the mineralization efficiency of KHP at constant CrVI % value. High current density is required for effective mineralization, but is not applicable as the medium is exposed to overheating when 80 mA/cm² is applied.

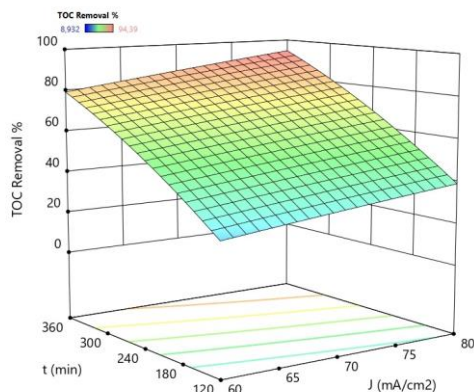


Fig.6. Three-dimensional response surface plots showing the effects of significant interactions between time and current density (CrVI%=12.5)

Within the experimental range for each variable and by setting 90% as the minimum acceptable TOC removal %, the optimum parameters were determined as 70 mA/cm² current density, CrVI 12.5%, and time 377 min, where 89.79% mineralization efficiency could be achieved with a desirability value of 1.00.

4. CONCLUSION

In this study, TOC removal of an synthetic KHP solution with high TOC content was investigated by using anodic oxidation which is one of the electro oxidation methods. The production of persulfate from the sulfate ions present in the solution prepared under highly acidic conditions was targeted. It was determined that KHP was effectively mineralized by sulfate radicals obtained from the activation of persulfate (electrolysis or metal catalyzed). Optimum working conditions; 70 mA/cm² current density, 377 min electrolysis time and 12.5% CrVI were found.

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