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Determination of Operating Conditions for Hydrogen Peroxide and Hydroxyl Radical Production in Electro-peroxone Process

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Abstract

Electro-peroxone (EPO) process is an enhanced ozonation process with a simple installation of electro-oxidation apparatus into the ozone reactor. It enables the use of excess oxygen gas caused by inefficient ozone generation by ozone generators. The sparged oxygen is reduced to form hydrogen peroxide (H_2O_2) on the cathode surface and then the electrogenerated H_2O_2 reacts with ozone to form hydroxyl radical (OH•). Thus, the highly oxidative species such as OH• and H_2O_2, are produced in the bulk solution. In this study, the effects of operating conditions such as reaction time, ozone flow rate and the applied current on the production of oxidant species were discussed. Response Surface Methodology (RSM) was used for the modeling of reaction conditions. The models employed were both significant for the production of OH• and H_2O_2. Reaction time is the most important factor in the production of oxidants. While the reaction time and ozone flow rate had a synergistic effect on OH• production, the interaction of the applied flow and the ozone flow rate affected H_2O_2 production. Optimum operating conditions were determined maximizing the OH• concentration. The short reaction time of the process may be preferred because OH• is inhibited by the electrogenerated H_2O_2 at advancing reaction times.

Keywords: Advanced oxidation processes, electro-peroxone, hydrogen peroxide, hydroxyl radical, response surface methodology.

1. Introduction

Electro-peroxone process (EPO) is an upgraded version of the conventional ozonation process when the electro-oxidation mechanism is used in the ozone reactor. Ozone generators have low transformation capacity to form aqueous ozone from the oxygen gas. The excessive oxygen gas in conventional ozonation is utilized to generate hydrogen peroxide (H_2O_2) in the EPO process. Here, the key point of the process is the usage of carbon-based electrodes such as carbon-polytetrafluoroethylene (carbon-PTFE), carbon felt, and carbon nanotubes for the cathode material [1]. The oxygen is reduced to form hydrogen peroxide on the cathode surface in the conformity with Eq. 1.1:

$$O_2+2H^{+}+2e^{-}\rightarrow H_2O_2 \qquad \textbf{(1.1)}$$

Then, the electro-generated H_2O_2 reacts with O_3 to form hydroxyl radical (OH•) according to Eq. 1.2:

$$O_3+H_2O_2\rightarrow OH\bullet+O_2^{-\bullet}+O_2 \qquad \textbf{(1.2)}$$

The relative oxidation power of H_2O_2 and OH• is 1.31 and 2.05, respectively [2]. Accordingly, highly oxidative media is formed during EPO process to oxidize target pollutants. The EPO process has been applied for the treatment of organic substances such as oxalic acid [3], 1,4-dioxane [4], amoxicillin [5], Orange II [6], diethyl phthalate [1] and some water matrixes such as laundry wastewater [7], landfill leachate [8], drinking water [9] and secondary effluents of wastewater treatment plants [10]. Most of the papers presented comparable results with conventional ozonation [11] and the removal of target organic substances is improved by the EPO process [7, 12]. . In addition, the formation of oxidant species during EPO, ozonation and electrooxidation processes was given comparatively [13]. Indeed, the oxidant species (i.e. OH• and H_2O_2) were generated in higher concentration during the EPO process than those of ozonation or electrooxidation processes. However, no evaluation has been made on the production of oxidant species in the EPO process, depending on operating conditions. In this paper, the main important factors such as reaction time, ozone flow rate and applied current are evaluated for the production of oxidant species. The formation of OH• and H_2O_2 was observed as dependent parameters in Response Surface Methodology (RSM), and the models were developed according to the experimental results.

2. Materials and Methods

2.1. E-peroxone Process Setup

The EPO system included a reserved Plexiglass reactor, DC power supply, ozone generator and online analyzer for the H_2O_2 measurement. The reactor with 2000 ml capacity was installed with electrode plates and ozone diffuser on the bottom of it. Carbon PTFE electrodes (2 pieces) were used as a cathode with the dimension 0.3 x 2 x 15 cm of each. Anode electrode was a platinum sheet with the dimension of 0.1 x 1 x 15 cm. Sodium sulphate as supporting electrolyte was used in the concentration of 0.05 M. Ozone gas fed into the reactor with the desired concentration after becoming a stable trend. DC power supply and the ozone generator were turned on simultaneously for the EPO treatment. The generation of H_2O_2 was observed online during the reaction. The OH• concentration was determined through the terephthalic acid (TA) cumulative protocol [14]. In this case, TA was added to the reactor instead of sodium sulfate to capture the formed OH• radical in the form of hydroxyterephthalic acid (HTA).

2.2. Statistical Analysis

Design expert, version 8.0.4.1 (STAT-EASE Inc., Minneapolis, USA) was operated for the statistical analysis in this study. Box-Behnken design with three independent parameters was established for modeling the production of oxidants in the EPO process. The concentrations of oxidant species (i.e. OH• and H_2O_2) were recorded as the responses of the model. The values of the independent parameters and the results of the responses are given in Table 1.

The production of oxidant species was fitted to a general function of the second-order polynomial equation. The employed model of the second order polynomial is:

$$R=\beta_o+\sum\beta_i X_i+\sum\beta_{ii} X_i^2+\sum\beta_{ij} X_i X_j \qquad \textbf{(2.1)}$$

where R is the predicted response, X_i and X_j are independent factors, β_o is the intercept, β_i is the linear coefficient, β_{ii} is the quadratic coefficient and β_{ij} is the interaction coefficient.

Table 1. Operating levels of independent parameters.

Run Number	**A: Reaction time**	**B: Ozone flow rate**	**C: Applied current**	**R1: OH• radical concentration**	**R2: H_2O_2 concentration**
	(min)	**(L/h)**	**(A)**	**(µM)**	**(mg/L)**
1	5.00	200	0.6	11.09	3508.8
2	5	120	0.2	9.695	5997.5
3	45	200	0.6	0.020	6362.0
4	25	120	0.6	3.548	5409.5
5	45	120	0.2	1.026	6498.8
6	25	120	0.6	0.046	5482.1
7	25	120	0.6	0.155	4593.5
8	45	120	1.0	0.001	4124.8
9	45	40	0.6	1.567	6073.4
10	25	40	1.0	0.004	3174.6
11	25	120	0.6	1.431	5070.4
12	25	40	0.2	0.456	7233.2
13	25	200	1.0	0.587	4331.6
14	5	120	1.0	9.061	1405.8
15	25	200	0.2	0.595	4178.4
16	25	120	0.6	0.937	4729.3
17	5	40	0.6	6.272	2813.6

ANOVA analysis was employed to reveal the significance and applicability of each model. Perturbation plots and 3D surface graphs were used to evaluate the effect of the variables on the production of OH• and H_2O_2.

3. Results and Discussion

3.1. The significancy of the employed models

The model F-ratio (Fisher variation ratio), the probability value (prob>F) and adequate precision are the main indicators donating the significancy and acceptability of the model employed. Statistical values of the employed model obtained from ANOVA analysis are given in Table 2.

The models employed based on the F- ratio were significant. On the other hand, lack of fit is desired to be non-significant for a fit model. The value of R square (R^2) indicates the correlation between the predicted and actual values of parameters. A high value of R^2 was acquired for the models of OH•, while a low R^2 was obtained in the case of H_2O_2.

Table 2. Statistical values of the model employed according to ANOVA Analysis.

Response	**OH• production**	**H_2O_2 production**
F value	18.16	11.40
Significant model terms*	A, AB, A^2	A, C, BC
Lack of fit significance**	0.24 non-significant	4.22 non-significant
R square	0.95	0.87
Predicted R^2	0.84	0.46
Adjusted R^2	0.90	0.79
Adequate Precision	12.95	12.87

*p value < 0.0500
**It is desired to be "non-significant"

It is expected that the difference between predicted and adjusted R^2 should be less than 0.2. In view of that, the differences between them were in reasonable agreement for the models of OH• production. However, the predicted R^2 was also quite low for H_2O_2 production. The hydrogen peroxide was the most abundant species in EPO reactions. Hydrogen peroxide concentration increased rapidly in the first minutes of the reaction, and it reached a steady state after a while. Therefore, the R^2 value of the model remained relatively low compared with the model of OH•.

Adequate precision determines a signal to noise ratio, and a value greater than four is desirable. The entire models employed showed adequate signals. Significant model term of OH• production was just the reaction time. The synergistic effect of reaction time and ozone flow rate of OH• production also can be seen from Table 2. The reaction time and the applied current affected the H_2O_2 production individually, and the intersection of the applied current and ozone flow rate had an impact on the production of H_2O_2. Eventually, the reaction time was the major parameter that affected all responses.

3.2. The evaluation of hydroxyl radical production

Perturbation plot gives the individual effect of the independent parameters on the response. Coded units from -1.000 to 1.000 signify the range between minimum and maximum values of independent parameters. As seen in Figure 1, OH• concentration was mostly affected by changes in the reaction time (A). The applied current (C) and ozone flow rate (B) had no significant effect on the production of OH•.

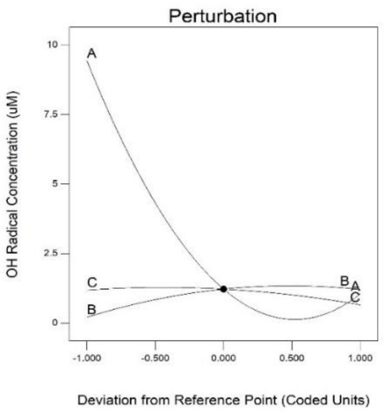

Figure 1. The perturbation plot of the OH• production (The applied current of 0.6 ampere, the reaction time of 25 min, the ozone flow rate of 120 L/h).

The production of OH• was seen to be a time-dependent process according to these results. Furthermore, it was also dependent on the reactions between the species produced during the process. At the beginning of the reactions, aqueous ozone and hydrogen peroxide were available in the solution to produce OH• upon Equation 1.2. Subsequently, H_2O_2 was produced excessively in the bulk solution and it inhibited the formation of OH•. Furthermore, hydrogen gas formation on the cathode surface may cause the formation of hydrogen bubbles covering the electrode surface, and this can be resulted in a reduced transfer area. The decrease of A-curve seen in Figure 1 tells about this phenomenon.

The synergistic effect of independent parameters is shown in Figure 2. The applied current did not affect the production of OH• as seen in Figure 2a. Besides, the interrelation between the applied current and the reaction time was insignificant. The increase of the applied current did not cause to further removal of the organics as reported in the literature [5, 13]. It is considered that OH• radical, which provides effective organic abatement, could not produce sufficiently as the applied current increased. On the other hand, the change of ozone flow rate was influential on OH• production just within shorter reaction time (i.e. 5-20 minutes) as seen in Figure 2b. It is because of that the increase of the ozone flow rate does not state to the formation of aqueous ozone concentration. Ozone is poorly soluble in water and the rate of autodecompsozition of ozone is higher than the rate of mass transfer of the gaseous ozone [15]. In our cases, ozone can transform into the aqueous form from gaseous at the beginning of the reaction, but in time, it was probably decomposed and used for further reactions to generate OH• radicals.

The ozone flow rate and the reaction time affected synergistically OH• production. Accordingly, OH• concentration can be stated as the following equation based on the RSM model.

$$\text{OH• concentration } (\mu M) = 1.22 - 4.19A - 1.60AB + 4.02A^2 \qquad \textbf{(3.1)}$$

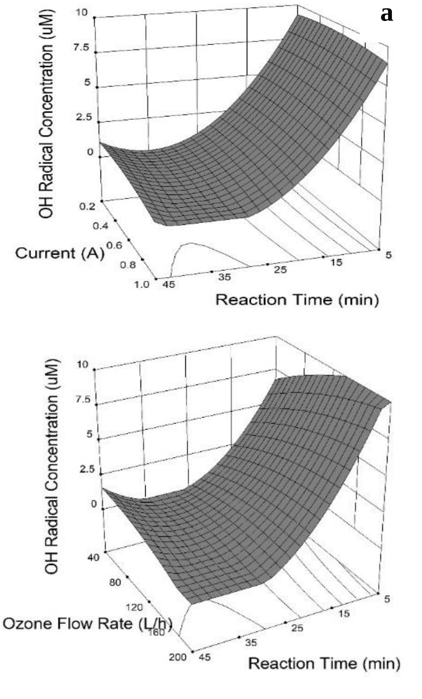

Figure 2. a) The applied current and the reaction time interrelation b) the ozone flow rate and the reaction time interrelation for the production of OH•.

If appropriate reaction conditions are to be determined, OH• radical concentration is desired to be maximized within oxidation processes. According to these results, low reaction time of 5 minutes and ozone flow rate of about 150 L/h are found effective to acquire high OH• concentration.

3.3. The evaluation of hydrogen peroxide production

The individual effect of the applied current, reaction time and ozone flow rate of H_2O_2 production can be seen in Figure 3. B-curve, namely the ozone flow rate, had no impact on the H_2O_2 concentration. Whereas reaction time (A-curve) affected positively, the applied current (C-curve) showed a negative impact on the production of H_2O_2. In other words, the increase in current caused a decrease in the H_2O_2 concentration. The higher current accelerated anodic reactions in the bulk solution, and H_2O_2 could be decomposed at the anode surface according to Eq. 3.2. Furthermore, the H_2O_2 concentration may decrease due to the self-decomposition of H_2O_2 based on Eq.3.3.[16].

$$H_2O_2 \rightarrow 2H^+ + O_2 + 2e^- \qquad \textbf{(3.2)}$$

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad \textbf{(3.3)}$$

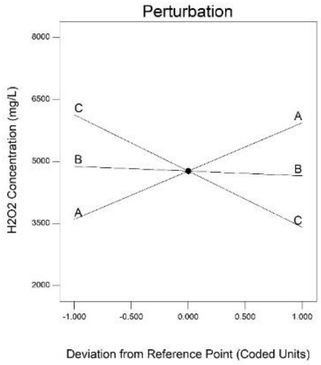

Figure 3. The perturbation plot of the H_2O_2 production (The applied current of 0.6 ampere, reaction time of 25 min, ozone flow rate of 120 L/h).

Ozone and the sparged oxygen gases fed into the reactor during the process. The sparged O_2 from the ozone generator can be utilized to form H_2O_2. The EPO process provides *in-situ* H_2O_2 generation by means of cathodic reduction of O_2 on the cathode surface. As seen in Figure 3, H_2O_2 was generated properly as the time increased by using the sparged O_2. Some of the H_2O_2 produced was consumed to produce OH• radical based on Eq. (1.2). However, it is not desired a high concentration of H_2O_2 for production of OH•, since H_2O_2 can limit OH• as stated before. On the other hand, the aqueous ozone concentration was also observed as a control parameter during the EPO process (Data not shown). It was not included in the model, because . ozone is consumed in such ways in the EPO system *i*) to form OH• radicals based on Eq. (1.1 and 1.2) *ii*) to form conjugate base of hydrogen peroxide (HO_2^-) (Eq. 3.3) and other radical species (Eq. 3.4 and 3.5). Indeed, ozone concentration covaried by the production of H_2O_2 and OH• during the EPO process. The ozone gaseous fed into the reactor transforms into the aqueous form of ozone and then participates through the aforementioned reactions. Here, the important factor is to provide efficient mass transfer for a gaseous form of ozone to aqueous form by dispersing ozone gaseous in the bubble with an optimum gas flow rate.

$$O_3 + OH^- \rightarrow HO_2^- + O_2 \qquad \textbf{(3.4)}$$

$$HO_2^- + O_3 \rightarrow OH\bullet + \bullet O_2^- + O_2 \qquad \textbf{(3.5)}$$

$$HO_2^- + OH\bullet \rightarrow \bullet O_2H + OH^- \qquad \textbf{(3.6)}$$

The synergistic effect of independent parameters is shown in Figure 4. There was no significant interaction between the applied current and reaction time as seen in Figure 4a. However, the increase in the time provided an increase in H_2O_2 concentration for all values of the applied current. The increment in H_2O_2 was more notable for higher applied current values.

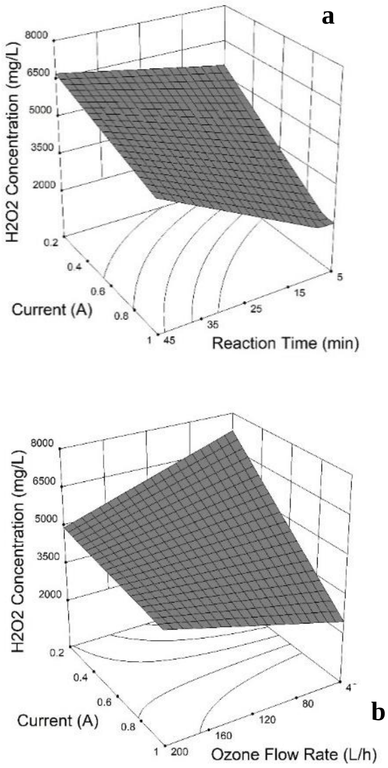

Figure 4. a) The applied current and reaction time interrelation b) The applied current and ozone flow rate interaction for the production of H_2O_2.

Figure 4b shows the interrelation between the applied current and ozone flow rate. The lower values of these independent parameters provided a higher production of H_2O_2. When the ozone flow rate is low, adequate ozone gaseous transforms into aqueous ozone. Eventually, the model equation for the H_2O_2 concentration became as below;

$$H_2O_2 \text{ concentration (mg/L)} = 4763.97 + 1166.68A - 1358.88C + 1052.95BC \qquad \textbf{(3.7)}$$

Hydrogen peroxide is produced electrochemically on the cathode surface in the EPO process. Its concentration increased sharply and exceeded 2000 mg/l within 5 minutes of the reaction at any other operating conditions. However, the huge amount of H_2O_2 is not desired to avoid the inhibition of OH• production. Therefore, short reaction time with an average ozone flow is also convenient for the H_2O_2 production.

4. Conclusion

EPO process is a new and superior oxidation technique. This has been successfully applied to remove some contaminants from the water. In this paper, it has been considered that how OH• and H_2O_2 formation dominate the oxidation features of the EPO process. The concentrations of these oxidants may vary depending on operating conditions such as reaction time, ozone flow rate and applied current. The production of OH• and H_2O_2 was modeled through the RSM, and operating conditions were discussed. The models employed for OH• and H_2O_2 production were statistically significant. Mostly, reaction time governed the oxidation features of the EPO process. According to the results, reaction time and ozone flow affected the OH• production efficiency together. The applied current and ozone flow rate had a synergistic effect of H_2O_2 production. The production OH• peaked in the first minutes of reaction, and then decreased, due to the inhibition effect of excessive H_2O_2. Because of abundant H_2O_2 generation, OH• production is the main factor to obtain desired operating conditions. Due to the inhibition and decomposition of oxidant species during the subsequent reaction times, a short reaction time of the process may be preferred.

EPO process enables the production of major oxidant species in itself within a short time. The process is also cost-effective due to utilization of excessive oxygen during ozone generation. EPO process can take the place of conventional ozonation with a simple system change in the near future.

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Author’s Contributions
Özge Dinç: Drafted and wrote the manuscript, developed the model and interpreted the results.
Zeynep Girgin Ersoy: Supplied all the equipment and chemicals and designed the experimental setup.
Hazal Öztürk: Performed the experiments and reported the results.
Sibel Barışçı: Assisted in data interpretation and helped in manuscript preparation.

Ethics
There are no ethical issues after the publication of this manuscript.

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