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Furfural degradation using an electrochemical advanced oxidation process (EAOP): optimization of operating parameters using Taguchi approach

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ABSTRACT

The objective of this study was to investigate the efficiency of anodic oxidation (AO) for removing furfural from aqueous solutions. A Taguchi optimization approach was used to reduce the number of experiments and the time needed to find optimum conditions. Furfural and corresponding chemical oxygen demand (COD) reduction along with energy consumption of the process were also determined. The results showed that relative influence of the factors were as follows: furfural initial concentration > current density (CD) > operation time > pH. The contribution of the residual error to the furfural variability indicates a good fitting of the Taguchi design method. The initial furfural concentration of 500 mg/L, reaction time of 30 min, pH of 7, and CD of 71.43 mA/cm^2 were considered as Optimum 2 points with the predicted removal efficiency of 99.32%. A good agreement between experimental and predicted values was also observed. The amount of electrical energy consumption was obtained to be approximately 28 kWh/kg COD under the optimum experimental conditions and average applied voltage of 19.96 V. Several oxidation intermediate metabolites/by-products were identified using gas chromatography/mass spectrometry. Overall, the AO process can be applied as an efficient alternative process for degrading and mineralizing furfural-containing industrial wastewater.

Keywords: Electro-degradation process; PbO_2 electrodes; Energy consumption; Taguchi optimization; By-product detection.

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1. Introduction

Furfural ($C_5H_4O_2$) is a toxic, colorless, and soluble compound in water and has a pungent almond-like odor. It is used in solvent extraction processes and petroleum refining industry. It also has a wide variety of other applications such as an ingredient of phenolic resins, chemical intermediate and in the manufacture of pesticides and phenol furfural resins, and tetrahydrofuran. It is also used in many other fields such as food, antiseptic, disinfectant, insecticide, and dye industries [1]. Therefore, this compound may exist in considerable concentrations (500–1,700 mg/L) in effluents discharged from these industries [2,3].

Furfural can cause several problems for human health and the environment. Humans can be exposed to furfural in several routes such as ingestion, percutaneous, respiration, or via direct eye contact [4]. Acute exposure to furfural can damage the liver, kidney, and spleen, and chronic exposure may cause tumors and mutations [5]. Given the potential hazards of accidental exposure to this matter and minimization of these harmful effects, it is necessary to treat furfural-containing wastewaters through an

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appropriate method. A wide range of methods including physical [2,5–7], chemical [3,8–10], and biological [11–15] processes have been studied to remove furfural from water and effluents. Adsorption processes are commonly used to treat the polluted water and even air. The main challenges using these processes are as follows: they are merely a phase-transfer technique, which does not cause any change in the structure of the contaminant, and they produce high volume of concentrated contaminants, which requires specific consideration to be managed [13,16]. Biological processes are also preferred because of some of their advantages including flexibility, reliability, convenient operation and maintenance, capability to eliminate a lot of contaminants, economic benefits, environmental friendliness, degradation of contaminants to less toxic or harmful products, potential for full-scale applications, etc. [17]. However, these methods have some defects and disadvantages such as inefficiency at high concentrations of furfural because of the toxicity related to its ring structure, relatively high hydraulic retention time, which imposes larger reaction tank volumes resulting in more costs [12,18]. The applications of chemical and/or integrated techniques such as advanced oxidation processes (AOPs) are other alternatives that may be considered in these conditions [5]. The catalytic ozonation process (COP), which is of AOPs, has some drawbacks: ozone is highly corrosive and toxic, this process needs high energy consumption, there is need for off-gas destruction systems to remove ozone before being discharged into water bodies, etc. Therefore, these disadvantages could limit its applications [19,20].

Among the various AOP technologies, anodic oxidation (AO) (so-called electrochemical advanced oxidation processes [EAOPs]) has caused increasing interest for removing recalcitrant pollutants from water and wastewater [21,22] mainly owing to its ease of operation, no restrictions in terms of treatment conditions, environmental friendliness; also, no chemicals are used. In fact, only electrical energy is consumed for the mineralization of organic pollutants at the anodes [22–24].

The Taguchi model can predict influence and optimum levels of operating parameters via specific number of the experiments. The Taguchi's orthogonal array (OA) method has been employed to investigate the optimal design of experiments (DoEs) and the effects of multiple variables as well as interactions among them. It has the ability to minimize the whole testing time, thereby reducing significantly experimental costs to find optimum conditions. Therefore, it was used as an acceptable way to optimize design variables [25]. In this regard, the effects of initial concentrations, CD, operating time, supporting electrolyte, and pH were studied, as the controllable factors. An analysis of variance (ANOVA) was performed for the raw and signal-to-noise (S/N) ratio data in order to indicate the significant parameters affecting the process, and their effects on the response characteristics were quantified. Thus, the main focus of this work was to investigate the efficiency of the AO (Steel/Pb/PbO_2) process in the removal of furfural from synthetic wastewater using the Taguchi optimization approach to reduce the number of experiments and time needed to find the optimum conditions. Furthermore, chemical oxygen demand (COD) reduction, the extent of mineralization according to total organic carbon (TOC) measurement, degradation by-products, and energy consumption of the process were also determined.

2. Materials and methods

2.1. Materials

All chemicals used in this study were of the highest available quality and purchased from Merck (Darmstadt, Germany) and used without further purification. The aqueous solution of furfural with desired concentrations for the experiments was prepared by serial dilution of the stock solution (1%). Doubly deionized water (18 MΩ cm^{-1}) was used to prepare the solutions throughout all experiments.

2.2. Apparatus and experiments

A 100 mL polyvinyl chloride electrolytic cell with the working volume of 80 mL was used to perform electrolysis. In the AO reactor, the Pb/PbO_2 and stainless steel electrodes were used as anode and cathode, respectively. In order to prepare Pb/PbO_2, lead rods were placed in sulfuric acid (10%) and a CD of 10 mA was passed for 90 min at room temperature (25°C) for each cm^2 of the electrode surface; as a result, a PbO_2 layer was formed on the surface of the electrode according to Eqs. (1) and (2):

$$\mathrm{Pb} + \mathrm{SO_4^{2-}} \rightarrow \mathrm{PbSO_4} + 2\mathrm{e^-} \tag{1}$$

$$\mathrm{PbSO_4} + 2\mathrm{H_2O} \rightarrow \mathrm{PbO_2} + \mathrm{SO_4^{2-}} + 4\mathrm{H^+} + 2\mathrm{e^-} \tag{2}$$

Dimensions of each electrode were 10 cm×1 cm, which were used with a monopolar arrangement in the reactor. The effective electrode surface area was 21 cm^2. The distance separating the electrodes was fixed at 1.5 cm. They were connected to the terminals of a direct current power supply (Adak, ps–405, Hamadan Kit Co., Iran), which is characterized by the ranges 0–5 A for CD and 0–25 V for voltage. A constant stirring speed of 300 rpm was applied during all experiments for better dissolution of the electrolyte as well as increasing the chance of contact between the pollutant and the anode surfaces.

In order to adjust the pH of the solution, NaOH and H_2SO_4 were used. Na_2SO_4, 0.12 mol/L, was employed as the supporting electrolyte. The removal efficiency was studied in the electrolytic cell under the following conditions: initial furfural concentration = 300–2,000 mg/L, CD = 23.81–95.24 mA/cm^2, pH = 3–9, and operating time = 10–40 min. A very important point to make here is that all parameters were optimized with the Taguchi model. The efficiency of furfural removal and COD reduction were calculated by using Eq. (3) [26]:

$$R(\%) = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{3}$$

where C_0 and C_t are the measured variables (furfural concentration and COD) at the feed solution and reaction time t, respectively.

To calculate energy consumption (kWh /kg COD), Eq. (4) was used [26]:

$$\text{Energy consumption} = \frac{VIt}{3600 \times 10^3} \times \frac{1}{\Delta C \times V_R \times 10^{-6}} \quad (4)$$

where V is average cell voltage (V), V_R is the solution volume (L), ΔC is the difference in COD in mg/L, I is applied current (A), and t is the electrolysis time (s).

To measure the degree of furfural mineralization in AO process, some samples were analyzed to determine the TOC of the solution using a TOC analyzer (Vario TOC cube, Elementar, Hanau, Germany). The mineralization efficiency of furfural was calculated as follows:

$$\text{Furfural mineralization}(\%) = \frac{(\text{TOC}_i - \text{TOC}_e)}{\text{TOC}_i} \times 100 \quad (5)$$

where TOC_i and TOC_e are TOC concentrations in the influent and effluent, respectively.

2.3. Experimental design and analysis

2.3.1. Taguchi optimization method

The DoEs methodology has generally been adopted to optimize a predetermined response by controlling design variables. The Taguchi-type experimental designs are statistical-based methods applied for improving response rate. The Taguchi crossed array layout is composed of inner and outer arrays. The inner array is comprised of the OA selected from all possible combinations of the controllable factors. Using the OA, which is specially designed for the Taguchi method, the optimum experimental conditions can easily be determined. Therefore, an analysis of the S/N ratio is required to compute the experimental results. Three types of the S/N ratio analysis are used as follows: (1) the lower the better, (2) the nominal the best, and (3) the higher the better (HB) [27]. Because the target of this study was to maximize the removal efficiency, the S/N ratio with HB characteristics is required, which is given by Eq. (6) [28]:

$$\text{SNL} = -10\log\left(\frac{1}{n}\sum\nolimits_{i=1}^{n}\frac{1}{{y_i}^2}\right) \quad (6)$$

where SNL is the signal-to-noise ratio or the performance characteristics as 'the larger the better', y_i is the is the comparative variable in experiment i for a certain combination of control factor levels (response), and n is the number of replicate under the same experimental conditions. The range of the four controllable factors and four levels of them have been shown in Table 1.

Because the response (% efficacy) is skewed and bounded at 0 and 100, we decided to use logit transformation ($y^* = \log[y/(100-y)]$) of the response. The transformed response is unbounded with less asymmetric compared with the original response. Thus, when it is possible, the results have been presented in original scale.

Table 1
Controllable factors and their levels used for design of experiments

Factor	Level 1	Level 2	Level 3	Level 4
Initial furfural concentration (mg/L)	300	500	1,000	2,000
Operating time (min)	10	20	30	40
pH	3	5	7	9
CD (mA/cm^2)	23.81	47.62	71.43	95.24

2.3.2. Analysis

The initial and final concentrations of furfural in the solutions were determined at its maximum wavelength (278 nm) using a UV–vis spectrophotometer (model LAMBDA 25 UV–vis PerkinElmer, USA) [3,6]. The initial and final COD contents of the solutions were measured by the closed reflux method (method 5220 D) [29]. The pH values of the solutions were measured using a pH meter (Sense Ion 378, Hack, USA). The surface morphology of the electrodes was characterized by X-ray diffraction (XRD, Thermo ARL SCINTAG X'TRA, 45 kV and 40mA, Cu K) and scanning electron microscopy (SEM, Philips XL-30). Gas chromatography (GC) equipped with a mass spectrometry (GC–Mass, Model: Agilent 7890, USA) with HP-5MS capillary column (30 m × 0.25 mm × 0.25 µm film thickness, 5% phenyl–95% methyl siloxane phase) was used to detect the intermediates produced during the AO process.

3. Results and discussion

3.1. Results of Taguchi modeling

As mentioned above, a L_{16} (4^4) OA is designed, and the experimental conditions are obtained by combining Table 1 and the L_{16} (4^4) OA. The mean from duplicate measurements of the efficiency and S/N ratio for each test condition have been shown in Table 2. The maximum values of the S/N ratios among the 16 runs of the experiments have been highlighted in Table 3.

The ranking of the parameters (Table 3) showed that relative influences of the factors were as follows: initial furfural concentration > CD > operating time > pH. The ranking is based on the amount of delta (difference between maximum and minimum S/N ratio for each factor). The relative optimal conditions for furfural removal are achieved via the analysis of the S/N ratio. As presented in Table 3, the highest S/N ratio of each factor determines the best response, which confirms that the most influential factor is the initial furfural concentration ratio, with the delta value of 2.09, followed by CD (1.69). Reaction time and pH had a minor effect (with the delta values of 1.43 and 1.23, respectively). As seen in Table 4, the contribution of the residual error to the furfural variability (4.37%) indicates the goodness of the used experimental design.

Furthermore, different levels of the parameters had different effects on the efficiency. Thus, the best level of each parameter was predicted through the Taguchi model. The results of the S/N ratio for various designed experiments after ANOVA calculations have been shown in Fig. 1 and Table 5. As seen, the second level of initial furfural concentration (500 mg/L), the fourth level of reaction time (40 min), the first level of pH value (3), and the fourth level of CD (95.24 mA/cm^2) were considered as Optimum 1 conditions, in which the predicted removal efficiency was 99.87%. It should be noted that other optimum conditions (considered as Optimum 2) have also been given in Table 5. The amount of removal efficiency determined for Optimum 2 was 99.32%, which had little difference with the first optimum conditions, but it is of great importance in terms of operational point of view, especially regarding pH value, which it makes the treatment processes more cost-effective. When there was an increase in initial furfural concentration from Level 2 to 4 (Fig. 1), the S/N ratio also decreased, resulting in a rapid decrease in the removal efficiency. Similar trends were also observed in the removal efficiency by changing the levels of other parameters.

3.2. Application of the optimized procedure

As suggested by Taguchi as a crucial step, the confirmation test is conducted to verify the experimental results. As can be verified in Fig. 1 and Table 5, the optimum combinations of factor levels were not previously tested, thus, a series of checking experiments were carried out by using the initial solution and the different noise levels, as well as solutions from student laboratories in order to check their reliability. The treatment efficiency, in terms of the observed efficiency, was found to be 96.34%, as an average value, which validates the proposed conditions.

3.2.1. Analysis of variance

The contribution of individual factors is the deciding control key to be enforced to attain high wastewater treatment efficiency. In Taguchi approach, the main purpose of the ANOVA was to assess the effect of each parameter on the variance of the OA experiments results to determine

Table 3
Estimated factors affecting (logit of) furfural removal

Level	Furfural concentration (mg/L)	Operation time (min)	pH	CD (mA/cm^2)
1	39.44	38.26	**39.53**	37.94
2	**39.67**	38.26	39.42	38.67
3	39.13	39.59	38.30	**39.63**
4	37.57	**39.69**	38.56	39.56
Delta	**2.09**	**1.43**	**1.23**	**1.69**
Importance of parameters	**1**	**3**	**4**	**2**

The bolded values exhibits the highest value of each parameter and the corresponding level.

Table 2
Taguchi L_{16} (4×4) OA design and the results

Accidental experiment	Experiment number	Level of experiment design				S/N ratio	Efficiency (%)
		Furfural concentration (mg/L)	Operating time (min)	pH	Current density (mA/cm^2)		
3	1	300	10	3	23.81	5.38	86.75
16	2	300	20	5	47.62	7.16	90.72
14	3	300	30	7	71.43	13.41	98.94
12	4	300	40	9	95.24	14.07	99.36
1	5	500	10	5	71.43	10.27	96.31
10	6	500	20	3	95.24	15.35	99.69
8	7	500	30	9	23.81	7.00	90.38
9	8	500	40	7	47.62	13.10	98.92
6	9	1,000	10	7	95.24	4.78	85.38
7	10	1,000	20	9	71.43	7.22	90.88
2	11	1,000	30	3	47.62	9.80	95.65
13	12	1,000	40	5	23.81	7.06	90.61
4	13	2,000	10	9	47.62	–5.48	63.27
15	14	2,000	20	7	23.81	–14.59	54.73
5	15	2,000	30	5	95.24	10.78	96.95
11	16	2,000	40	3	71.43	11.35	97.57

the variation in the contribution of each factor with respect to total variance of all the parameters. From the calculated ratios (*F*) (Table 4), it can be concluded that all factors and interactions considered in the experimental design are statistically significant at a 95% confidence limit, indicating that the variability of the experimental data can be explained in terms of significant effects. The general trend of influencing factors can be characterized by studying the main effects of each factor. Table 4 depicts the results of the ANOVA analysis, with the percentage contribution of each factor, which was calculated by the ratio of the sum of squares of that factor to the total sum of squares, and their interactions.

Table 4
Analysis of variance for mean (logit of) furfural removal efficiencies

Variation source	DoF	Sum of squares	Variance ratio (*F*)[a]	Contribution (%)[b]
Furfural concentration	3	784.5	7.15	31.24
Operating time (min)	3	641.4	5.85	25.54
pH	3	332.6	3.03	13.24
CD (mA/cm^2)	3	643.2	5.86	25.61
Residual	**3**	**109.7**	–	**4.37**
Total	**15**	**2,511.5**	–	**100.00**

DoF, Degrees of freedom.

[a] 95th percentile of the *F* distribution with 3 and 3 degrees of freedom is 5.39.

[b] Defined as 100× (sum of squares/total sum of squares).

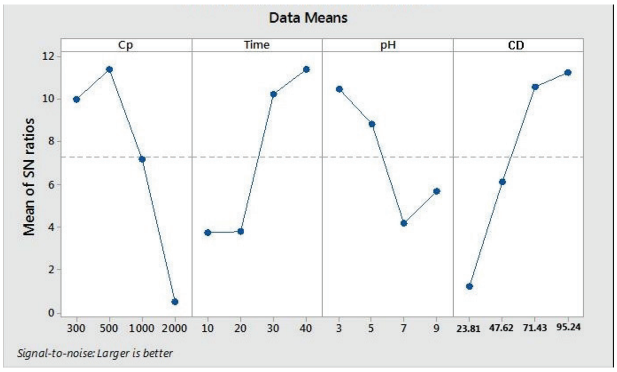

Fig. 1. Calculated S/N ratio for furfural removal at the determined level of furfural concentration (Cp), operating time, pH, and current density.

3.3. SEM and XRD characterization

Fig. 2(a) presents the SEM of the PbO_2 electrode with magnification of 5,000 times. As can clearly be seen, the electrode had small-sized particles and a very compact crystalline structure which, in turn, provided more specific surface area and better physical performance for the electrochemical degradation of furfural. Furthermore, the XRD patterns of the electrode (Fig. 2(b)) demonstrated the characteristic reflections of β-PbO_2 with crystal planes at 25°, 32°, and 49°, respectively.

3.4. Effects of operating parameters

3.4.1. Effect of initial furfural concentration

As shown previously, the initial concentration of furfural had the most impact on process effectiveness followed by CD, reaction time, and pH. In addition, furfural removal

Table 5
Optimum conditions form analyzed S/N

Parameter	Level	
	Optimum 1	Optimum 2
Furfural concentration (mg/L)	500	500
Operating time (min)	40	30
pH	3	7
CD (mA/cm^2)	95.24	71.43
Predicted efficiency (%)	99.87	99.32
Observed efficiency (%)	98.59	96.34

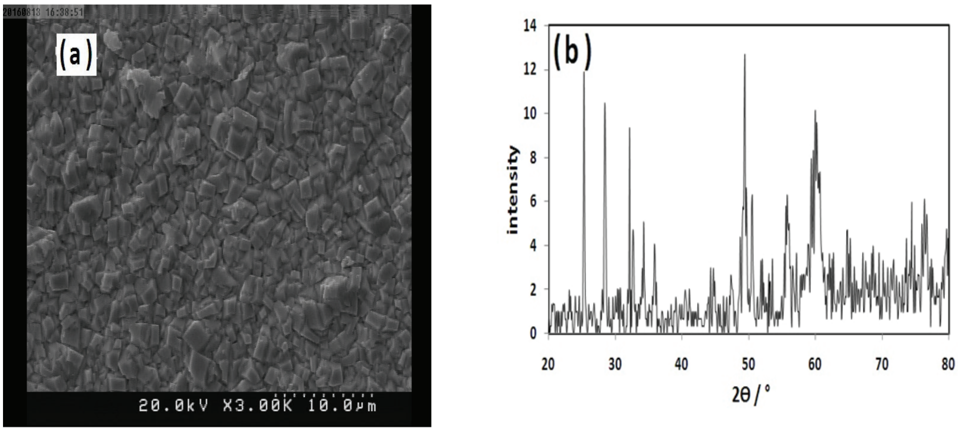

Fig. 2. (a) Scanning electron microscopy (SEM), and (b) XRD patterns of PbO_2 anode.

rates were high at low concentrations but the amount of its removal was low and vice versa. For example, an increase in initial concentration from 300 to 2000 mg/L (at the optimized conditions) declined the removal efficiency from 99.36% to 97.27 %. This is also accompanied by S/N changes, as a rise in initial furfural concentration from 500 to 2000 mg/L decreased the S/N ratio from about 11.75 to 0.5. This marginal reduction could be attributed to the reduction of $OH^{\bullet}$/furfural ratio [30]. Furthermore, at low concentrations, electrochemical reactions occur faster than diffusion reactions, and it is expected that the pollutant is completely destroyed at the interface. However, more amount of furfural removal was expected with increasing furfural concentration as a result of significant effect of mass transfer mechanism in the process; this, in turn, causes higher amounts of organic materials to be transmitted to the electrode surface. Hence, the efficiency of CD also increased. However, due to the lack of anodic hydroxyl radical generated on the electrode surface at higher concentration, the removal efficiency was low. These results are in accordance with the findings of the study by An et al. [31].

3.4.2. Effect of CD

Previous studies have illustrated that CD has a positive impact on the removal of organic compounds [30,32]. As can be seen in Fig. 1, with increasing CD from 23.81 to 95.24 mA/cm^2, the S/N ratio increased and the highest S/N ratio (≈11.7) was observed at the CD of 95.24 mA/cm^2. The reason behind is that, when CD was raised, the production rate of oxidizing agents (hydroxyl radical) on the electrode surface increases, leading to the enhancement of the efficiency, as well as COD reduction. Nevertheless, when this parameter exceeded the optimum amount (71.43 mA/cm^2, Table 5), the efficiency declined. It could be said that as the diffusion mechanism plays an important role in the transfer of pollutants to the electrode surface, which itself is affected by CD; hence, if CD is higher than the optimum value, the content of the pollutant reaches to the electrode surface declines. As a result, CD is consumed in useless and adverse reactions such as oxidation of water on both the anode and the cathode [32], according to Eqs. (7 and 8):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{7}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{8}$$

3.4.3. Effect of operating time

The results illustrated that the efficiency went up by increasing operating time, which reached 99.32% in 30 min (Table 5). It should be pointed out that the main upside of the process compared with traditional methods is its low reaction time, thereby reducing the costs of construction and operation. It was also found that the efficiency dropped at reaction times more than 30 min. Generally, reaction times over the optimum point can only result in more energy consumption without any significant increases in removal efficiency [26,33].

3.4.4. Effect of pH

In this study, the maximum efficiency of furfural removal was obtained under acidic conditions (pH = 3), with the corresponding S/N ratio of about 10.5. The most possible reason for this observation is that furfural degradation by hydroxyl radical is the main mechanism of degradation through joining to the organic compound molecule such a furfural, in which hydroxyl radical has better oxidation property in acidic pH than to neutral and alkaline pHs. In addition, at high pHs, hydroxyl radicals are converted to alkaline $^{o}O^{-}$, which has lower oxidation potential in comparison with $OH^{\bullet}$. Nevertheless, in pHs lower than 2, hydroxyl radical reacts with hydrogen ion, which the latter acts as $OH^{\bullet}$ scavenger [26].

3.5. Reaction pathways, COD reduction, mineralization of furfural, and degradation by-products

The understanding of removal mechanisms and degradation pathways of any organic compounds is of great importance. Several mechanisms have been proposed to remove organic compounds such as furfural in semi conductive reactor such as the AO process: (1) indirect AO on the Pb/PbO$_2$ surface mediated based on the electrogeneration of physisorbed $OH^{\bullet}$ at the anode surfaces (Eqs. (9) and (10)); (2) indirect electrochemical oxidation is mediated by electrogenerated oxidants such as active chlorine (in the presence of Cl^-) (Eqs. (11)–(13)); and (3) direct AO on the electrode surface through electrocatalytic activity (Eq. (14)) [22].

$$PbO_2 + H_2O \rightarrow PbO_2(^{\bullet}OH) + H^+ + e^- \tag{9}$$

$$C_5H_4O_2 + 5PbO_2(^{\bullet}OH) \rightarrow 5CO_2 + H_2O + PbO_2 \tag{10}$$

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{11}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{12}$$

$$\text{Furfural} + OCl^- \rightarrow CO_2 + H_2O + Cl^- \tag{13}$$

$$\text{Furfural}_{red} + \text{Furfural}_{ox} \rightarrow CO_2 + ne^- \tag{14}$$

Hydroxyl radicals can recombine into oxygen and water. In the presence of organic compounds such as furfural, a competitive process takes place, which, in turn, adsorbed on the electrode surface where radicals react with the organic compound to degrade it [34].

It is also important to know the effectiveness of the AO in COD reduction and mineralization of furfural. Thus, after determination of the optimum experimental conditions via the Taguchi method, for which the AO achieved the highest furfural removal, the degree of COD reduction and mineralization were evaluated. Fig. 3 illustrates the degradation of furfural and its corresponding COD reduction in AO process. After 10 min, approximately 49% of furfural was removed, but this value was 42% for COD reduction, and increased up to 100% and 95% after 50 min of reaction time for furfural removal and COD reduction, respectively. As can also be observed in Fig. 3, the removal of COD in the AO followed almost the same trend like furfural degradation, even with a lower rate. Thus, it should be noted that for the optimum reaction time (30 min) 95.58% and 92.02% efficiencies were obtained for furfural removal and COD reduction, respectively. It is revealed that the process developed in the study was more efficient than the COP [5], combined adsorption and Fenton-like oxidation processes [8] in furfural removal. The results also indicated that TOC_i and TOC_e were 128.17 and 14.89 mg/L, respectively, under the optimum conditions. The difference between the value of furfural and COD/TOC removal at each reaction time equals the intermediates formed during furfural degradation, which were still measured as COD. Furthermore, the UV–vis absorbance characteristics of the solution during various electrochemical degradation times were investigated from 200 to 480 nm (Fig. 4). The maximum absorbance peaked at ~278 nm, representing furfural, disappears gradually during the electrochemical oxidation process confirming the complete degradation of initial furfural in the solution.

Furthermore, to elucidate the routes through which furfural is converted to some reaction intermediate metabolites/by-products and eventually to end-products, besides the TOC reduction, the samples were subjected to GC/Mass to identify the major intermediates. Fig. 5 shows the proposed degradation pathway of furfural. The main identified oxidation intermediate metabolites/by-products included: (1) 2-ethylhexyl alcohol, (2) furan-3-carboxylic acid, (3) behenic alcohol, (4) 2-ethyl propane-1,3-diol, (5) tetrahyrofuran-3-caboxylic acid, (6) tetrahyrofuran-3-methanol, and (7) 2-methyl butanoic acid. It should be noted that the measured concentrations of the identified intermediate metabolites/by-products are low, which also are in agreement with high COD and TOC removal efficiencies. This indicates the effect of the AO process toward simplifying the nature of furfural and its conversion to more simple and degradable compounds.

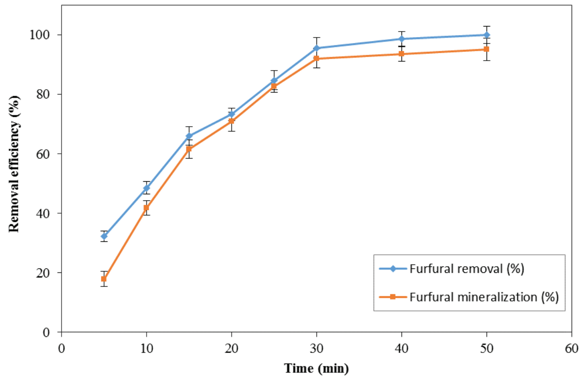

Fig. 3. Profile of furfural and COD removal efficiencies of the AO process under second optimum conditions (pH = 7, initial furfural concentration = 500 mg/L, and CD = 71.43 mA/cm^2).

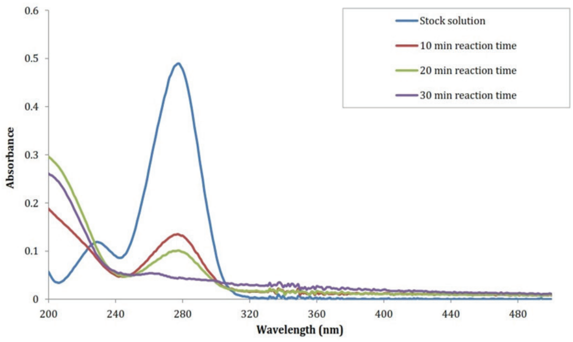

Fig. 4. The time-dependent UV–visible wavelength scan of furfural solution in the optimum conditions (pH = 7, initial furfural concentration = 500 mg/L, and current density = 71.43 mA/cm^2).

Moreover, average oxidation state (AOS) and carbon oxidation state (COS) which have been considered as good indicators of changes in relative composition of dissolved organic matter and might also involve changes in toxicity/biodegradability of wastewater were calculated using Eqs. (15) and (16), based on the COD and TOC results [35,36]:

$$AOS = 4 - 1.5(COD / TOC) \tag{15}$$

$$COS = 4 - 1.5(COD / TOC_0) \tag{16}$$

where TOC, COD, and TOC_0 are, respectively, the total organic carbon, the chemical oxygen demand of the solution (as mg/L) at the sampling time, and TOC that is determined at the beginning of the experiment.

AOS and COS vary between +4 for the most oxidized state for C, that is, CO_2, and –4 for the most reduced state, that is, CH_4 [37]. The AOS value of the feed solution to the reactor was –0.55 and increased to +1.28 after 30 min; this means that more oxidized intermediates were formed. The same value (–0.55) was calculated for COS, but this value also raised up to +2.56 at the end of the experiment indicating strong mineralization and formation of some highly oxidized intermediate metabolites and enhancement of the biodegradability of the raw wastewater.

3.6. Energy consumption and Pb corrosion issues

In this study, energy consumption was calculated using Eq. (4), and the results have been given in Fig. 6.

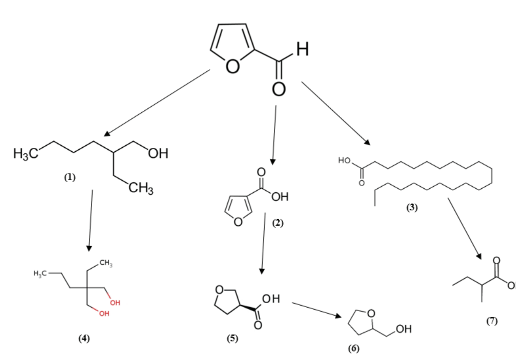

Fig. 5. Proposed reaction pathways for furfural degradation in EAOP in the optimum condition.

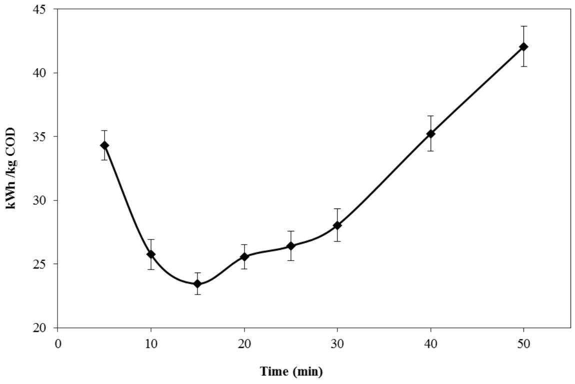

Fig. 6. The energy consumption for anodic oxidation of furfural in Optimum 2 conditions (pH = 7, initial furfural concentration = 500 mg/L, and current density = 71.43 mA/cm^2).

In electrochemical cells, the energy consumption is influenced by four important parameters: CD, average input voltage to the cell, retention time, and organic loading rate. Therefore, under the optimum points CD 71.43 mA/cm^2, reaction time 30 min, and average applied voltage 19.96 V, the amount of electrical energy consumption was found to be approximately 28 kWh/kg COD. As can be clearly seen in the optimum time of the process (30 min for Optimum 2 conditions), approximately 30 kWh was needed per kg of COD degraded and the consumed energy increased with increasing operating time. Thus, the highest energy consumption (about 42 kWh/kg COD) was required for the oxidation time of 50 min. One of the main arguments on electrochemical reactors is the electrical energy consumption of the system. Because the operating time was very low (about 30 min), it can be claimed that this method is preferable to other processes in terms of energy consumption and, surely, it is suitable for industries with very low volume of wastewater. Furthermore, according to the study by Zhou and He [38], if the energy consumption of an electrochemical process is less than 40–50 kWh/kg COD, it can compete with other AOPs.

Regarding some issues about Pb corrosion and its entrance into wastewater or to the environment, it should be noted that the pure Pb was covered by the formation of the PbO_2 layer, which, in turn, increased the resistance against corrosion. Furthermore, corrosion is usually more at high CDs and high pHs, but lower ranges of these parameters were used in this study, which logically resulted in little corrosion [30,32]. To confirm this, we measured Pb content in the effluent, which was 0.35 mg/L. It should be pointed that this concentration is well below the U.S. EPA recommended limit of 5 mg/L [39].

4. Conclusions

The AO process using the Pb/PbO_2 electrode led to the effective removal of furfural from aqueous solutions. An L_{16} OA was applied to investigate the effect of main operational parameters such as initial furfural concentration, CD, operation time, and pH on furfural removal efficiency. According to the Taguchi model through few numbers of well-defined experimental sets, as well as the results obtained from the evaluation of each parameter effect using ANOVA, initial furfural concentration and solution pH had, respectively, the most and least contribution to the furfural degradation by the AO. The removal efficiency of about 96.5% was achieved under the optimal conditions after nearly 30 min of reaction time. The COD measurements showed that wastewater-containing furfural underwent effective COD reduction by means of the AO process without using any extra chemicals. Ease of operation and not being affected by environmental conditions make this system a potent alternative. Therefore, this method could successfully be applied to treat the wastewater-containing furfural and similar compounds. Finally, the detection of by-products illustrated that some intermediates, which are easily oxidizable, were formed over the reactions.

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Conflict of interest

The authors declare they have no conflict of interest.

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