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Effect of operating parameters on triclosan degradation by Fenton's reagents combined with an electrochemical system

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ABSTRACT

Triclosan is used as an antimicrobial in many processes. Fenton's reagents were used to degrade triclosan in combination with an electrochemical system, and the effects of operating parameters were investigated. The pH, current density, Fenton's reagents ratio, and H_2O_2 feeding modes were investigated to determine their effect on the process efficiency. The results showed that higher efficiency could be achieved by increasing the H_2O_2 concentration during Fenton's reagents ratio modification and by changing the H_2O_2 feeding mode development from a one-time initial feeding mode to a step feeding mode of operation. This could also reduce the toxicity potential of the one-time initial feeding mode. Under optimum pH, Fenton's reagents ratio, and electrical current density conditions, 1 mM triclosan could be completely removed in the initial H_2O_2 feeding operation. Additionally, the initial degradation rate for the first-order model and relative oxidation performance ratio was used to indicate process optimization. High performance liquid chromatography, ion chromatograph data, and gas chromatography-mass spectrophotometer confirmation results were used to identify the intermediates that comprised 2,4-dichlorophenol, 4-chloro-catechol, phenol, hydroquinone, p-benzoquinone, maleic, acetic, oxalic, and formic acids, that were present among the degradation reactions. The main oxidation intermediates present depended on the H_2O_2 operating feeding mode.

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Keywords: Fenton's reagents; Electrochemical; Triclosan; Hydroxyl radicals; Relative oxidation performance (ROP) ratio; H_2O_2 feeding mode

1. Introduction

In municipal raw and primary wastewaters, many antimicrobial agents can be detected in concentrations ranging from 0.5 to 5 μg L^{-1} [1]. Triclosan ($C_{12}H_7Cl_3O_2$), an antimicrobial agent widely used in a range of personal health care products, has been widely detected in wastewater. Triclosan is used in products such as toothpaste, soaps, deodorants, shampoos, and cosmetics, and also in consumer (e.g. plastic kitchenware and footwear) products. Although triclosan is largely removed from wastewater in sewage treatment plants, a considerable quantity of triclosan still remains in the effluent, thus, probably initiating widespread environmental contamination [2]. Triclosan is exposed to sunlight to become polychlorinated dioxin that is reported to be highly toxic to certain aquatic organisms, particularly to green algae [3,4]. Another concern about the presence of triclosan in surface water is the formation of more toxic by-products such as endocrine disruptor chemicals [5]. Aging stockpiles of triclosan often become contaminated by polychlorinated dioxins as a result of exposure to heat or ultraviolet light [6]. Triclosan is stable in acid solutions and during base hydrolysis which creates problems for the disposal of contaminated stockpiles from industries that use triclosan [7]. To control triclosan concentrations in wastewater, chemical oxidation using free chlorine, ozonation, or UV/TiO_2 photocatalysis has been successful [8,9]. However, use of free chlorine generates toxic by-products such as chlorinated phenphenoxy-phenols, chlorinated phenols, and trihalomethanes, which is a significant disadvantage [10]. Triclosan oxidation using alternative chemical oxidants like ferrate (K_2FeO_4), permanganate ($KMnO_4$), and manganese oxides (MnO_2) has also been reported [11,12], but the instability of ferrate in water and the violet coloration of water due to elevated manganese levels are drawbacks in practical applications. For all of these reasons, there is an urgent need to develop an effective method to treat these contaminants.

Advanced oxidation processes (AOPs) are alternative methods that can be used for the oxidation of refractory and hazardous organic compounds. The Fenton's process is one of the most powerful AOPs that can be used to oxidize the organic matter in water. This method uses Fenton's reagents to generates hydroxyl radicals ($^{\cdot}OH$) via the addition of a solution containing hydrogen peroxide (H_2O_2) and an iron catalyst (Fe^{2+}). In the Fenton's process, Fe^{2+} and H_2O_2 are externally applied, while an electrochemical system is used to help regenerate the ferrous ions on-site [13]. The integration of Fenton's reagents with an electrochemical system combines a series of reaction mechanisms that can occur in the Fenton's process with the reaction of the electrochemical system as shown below by reactions (1)–(8).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\cdot}OH + OH^- \tag{1}$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \tag{2}$$

$$Fe^{2+} + {}^{\cdot}OH \rightarrow Fe^{3+} + OH^- \tag{3}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\cdot} + H^+ \tag{4}$$

$$H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^- \tag{5}$$

$$H_2O_2 + \text{organic} \rightarrow \text{products} \tag{6}$$

$${}^{\cdot}OH + H_2O_2 \rightarrow HO_2^{\cdot} + H_2O \tag{7}$$

$${}^{\cdot}OH + \text{organic} \rightarrow \text{products} \tag{8}$$

For Fenton's reagents combined with an electrochemical system, Fe^{3+} can be directly reduced to Fe^{2+} by an electron supplied more effectively and rapidly by an electrical current [13]. This study aims to investigate the effect of operating parameters on the performance of triclosan removal by Fenton's reagents combined with an electrochemical system with continuous electroregeneration of ferrous ions. The effect of the operating parameters which were considered in this study on the performance of the system were operating pH, current density, Fenton's reagents ratio (H_2O_2: Fe^{2+} ratio), and H_2O_2 feeding mode of operation. Then, the optimal operating conditions were selected. Moreover, the intermediates from triclosan degradation were identified, and a degradation pathway was suggested.

2. Materials and methods

This experiment used 1 mM of triclosan synthetic wastewater prepared by dissolving triclosan with deionized water (Millipore system with a resistivity of 18.2 MΩ cm^{-1}) and adjusted to a pH of around 10 by 0.1 mM NaOH to dissolve triclosan and by 0.1 mM $HClO_4$ to return it to a desired pH. The required pH in each experiment was adjusted by addition of $HClO_4$ or NaOH as necessary. All high-purity grade chemicals were purchased from Merck. An acrylic reactor of 15 cm × 20 cm × 20 cm with 5 L of working volume was used for the experiments on the application of Fenton's reagents combined with an electrochemical system. The three cathode electrodes were stainless steel nets, while the two anode electrode nets were made from mesh-type titanium metal coated with IrO_2/RuO_2. Each electrode had a surface area of 600 cm^2, while the distance between each electrode was 1.5 cm. All electrodes were connected to a DC power supply which discharged electrical current constantly and maintained a constant voltage into the process during the reactions in each experiment. Two mixers were installed to provide complete agitation in the reactor. A calculated amount of catalytic ferrous sulfate was added as the source of Fe^{2+} in these experiments. H_2O_2 was added into the reactor, when the power supply was turned on to start the reaction. At selected time intervals of 90 mins, triclosan, chemical oxygen demand (COD), total organic carbon (TOC), Fe^{2+}, and H_2O_2 were measured to investigate the effect of the operating parameters on process performance. The collected samples were immediately injected into tubes containing NaOH solution to stop further reaction and then were filtered through 0.45-μm syringe microfilters to separate precipitated iron from the solution. Triclosan concentration was determined by high-performance liquid chromatography (HPLC Thermo SCIENTIFIC Model) equipped with a UV detector (FINNIGAN SPECTRA SYSTEM UV1000). The UV wavelength for detection was 220 nm. The separation column was a reverse-phase column (Zorbax XDB-C18 4.6 mm × 250 mm, 5 μm), and the flow rate was set at 1 mL min^{-1}. The mobile phase consisted of acetonitrile and acetic acid (65:35). The H_2O_2 concentration was measured by a spectrophotometer (Shimadzu UV-1201) at 400 nm wavelength, using $K_2Ti(C_2O_4)_3$ (analytical grade) as an indicator. The ferrous concentration was determined according to Standard Methods [14] by light absorbance measurement at 510 nm after complex with 1, 10-phenanthroline using a UV–vis spectrophotometer. Following the Standard Methods (APHA, 1992), a closed-reflux titrimetric method was used for COD measurement in samples that were left overnight to remove any residual H_2O_2 that might remain in the sample solutions [14]. TOC was measured by an Elementar-liquid TOC (Germany) analyzer with a high-temperature combustion method. A HPLC and ion chromatograph (IC) (Dionex DX-120) equipped with a RFC-30 EGCII (KOH), an IonPac® AG 11 guard column (4 mm × 50 mm), an IonPac® AS11 analytical column (4 mm × 250 mm), and an ASRS®-ULTRA II (4 mm) suppressor and conductivity detector was utilized to identify the intermediates that might be present during the reactions, while the results were confirmed by gas chromatography using a mass spectrophotometer (GC-MS). All experimental scenarios were duplicated, and the average value was reported.

3. Results and discussion

3.1. Comparison of triclosan degradation by various processes

This experiment determined and compared the performance of various processes on triclosan degradation efficiency. The lonely electrochemical system with electrical current densities between 0.01 and 0.15 mA cm^{-2} has a low triclosan removal efficiency of about 2–4% (Fig. 1). In this experiment, the conventional Fenton's process and Fenton's reagents combined with an electrochemical system were able to remove triclosan at increased efficiencies of 41 and 67%, respectively. The results indicated that the electrical current with Fenton's reagents had an obvious influence on triclosan degradation efficiency. This can

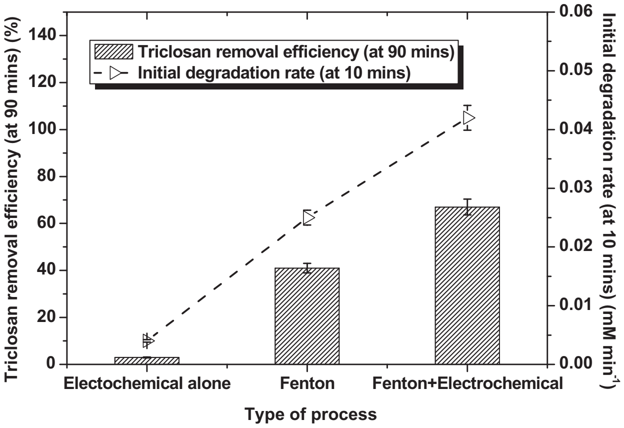


Fig. 1. Triclosan removal efficiency and initial degradation rate by various processes. ([Triclosan] = 1 mM, $[Fe^{2+}]$ = 0.1 mM, $[H_2O_2]$ = 1 mM, pH = 3, an electrical current of 0.15 mA cm^{-2} (Fenton's reagents combined with an electrochemical system using an electrical current of 0.15 mA cm^{-2}).

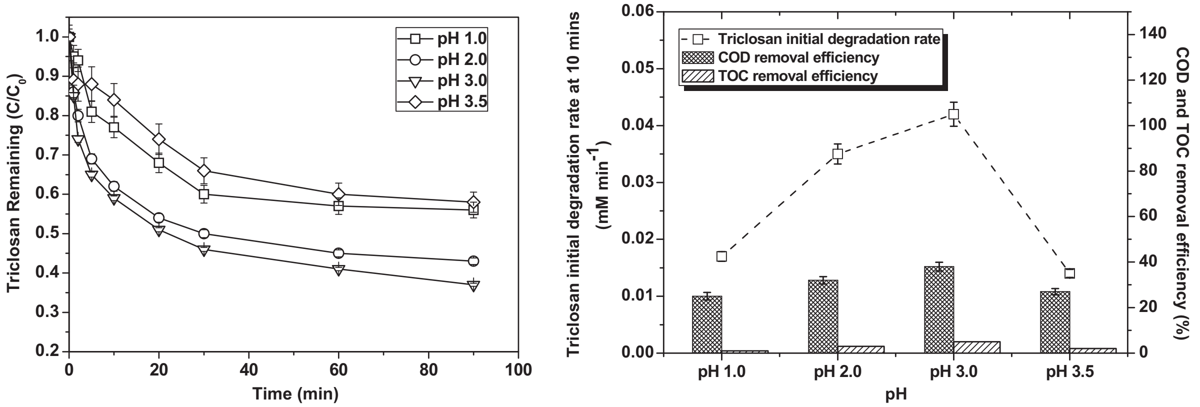
be seen from the low degradation efficiency of the process in the absence of Fenton's reagents, whereas the efficiency could be enhanced when Fenton's reagents were combined with the electrochemical process. The continuous generation of hydroxyl radicals in the Fenton's reagents combined with the electrochemical process appears to be the cause of the high degradation efficiency. This suggestion is confirmed by the resulting increase in the initial degradation rate from 0.004 to 0.042 mM min^{-1}.

3.2. Effect of operating pH

The operating pH is considered to be a significant parameter that can affect the efficiency of the Fenton's reaction. Here, the effect of the operating pH on triclosan removal by Fenton's reagents combined with the electrochemical process has been investigated. The results obtained from this experiment are shown in Fig. 2. From the results obtained here, pH 2 and 3, which have nearly the same removal performance, were the optimum conditions for triclosan, COD, and TOC removal by Fenton's reagents combined with an electrochemical system since they exhibited higher initial degradation rates than for pH 1.0 and 3.5. For the condition of very low pH, the formation of (Fe(II)(H_2O))$^{2+}$, which can react with hydrogen peroxide to generate hydrogen ions, was expected to occur. These might induced a hydroxyl radicals scavenging effect by hydrogen ions which could become a significant inhibitor for process efficiency. In addition, the solvation of peroxide into a high concentration of H^+ ions can produce oxonium ions to induce electrophilic activation of hydrogen peroxide and enhance its stability. Moreover, it can substantially reduce the process reactivity with ferrous ion. In contrast, at higher pH (above 3), the performance of the process was significantly decreased, mainly due to a decrease in the dissolved fraction of iron species [15,16]. Consequently, lower amounts of dissolved Fe(II) species could react with H_2O_2. The process performance was affected because a smaller continuous concentration of hydroxyl radicals was attained.

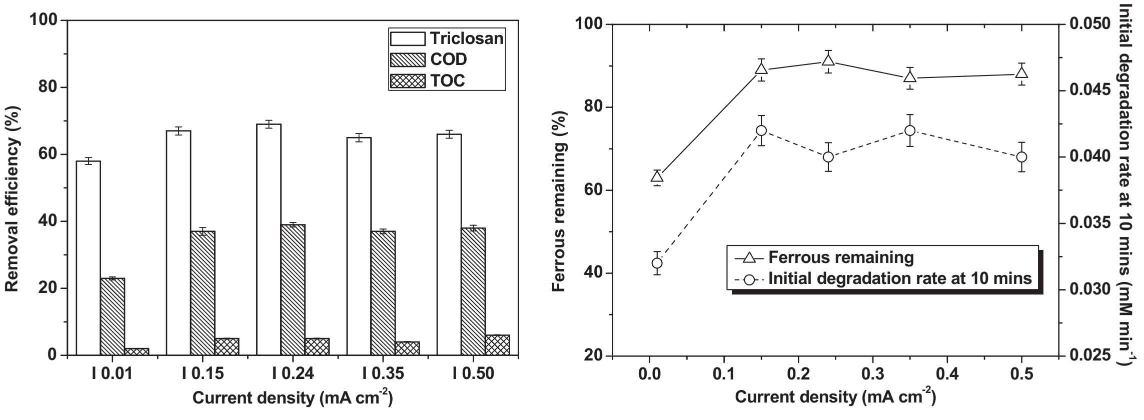
3.3. Effect of electrical current density

The electrical current density is one of the important parameters which influence the reaction rate of an electrochemical system. The effect of current density on the performance of triclosan, COD, and TOC removal by Fenton's reagents combined with an electrochemical system was investigated as shown in Fig. 3. The results demonstrated that an optimum current density maximizes the removal efficiency of the process. The optimum current density value for this experiment was 0.15 mA cm^{-2} for high triclosan, COD, and TOC removal efficiency, and for saving energy. The optimum current density helped to increase the process efficiency with a high initial degradation rate and optimized ferrous regeneration. Lower and higher current densities could induce the process to lower the degradation rate and the removal efficiency. The decrease in removal efficiency was probably due to fewer electrons for Fe^{2+} regeneration under low current conditions. In contrast, at higher current conditions, which promoted the regeneration of [Fe^{3+}] to [Fe^{2+}] continuously in the process, a scavenging effect from excess Fe^{2+} regeneration occurred which inhibited the process from being highly efficient. From the results, when increasing the current



(a) (b)

Fig. 2. Effect of operating pH on triclosan, COD and TOC removal by Fenton's reagents combined with an electrochemical system ([Triclosan] = 1 mM, [Fe^{2+}] = 0.1 mM, [H_2O_2] = 1 mM, an electrical current of 0.15 mA cm^{-2}).



(a) **(b)**

Fig. 3. Effect of electrical current density on triclosan, COD, and TOC removal and ferrous regeneration in Fenton's reagents combined with an electrochemical system ([Triclosan] = 1 mM, [Fe^{2+}] = 0.1 mM, [H_2O_2] = 1 mM, pH = 3).

density over 0.15 mA cm^{-2} up until 0.50 mA cm^{-2}, the removal efficiency and the ferrous regeneration rate was almost the same. This might be due to the occurrence of the following at higher current density hydrogen peroxide is anodically oxidized to yield the intermediate $HO_2\cdot$ radical; Fe^{2+} present in the solution is anodically oxidized to Fe^{3+}; and the hydroxyl radical is dimerized to hydrogen peroxide, and there is destruction of hydrogen peroxide. In addition, it is advisable to limit the current density to avoid adverse effects such as higher power consumption.

3.4. *Effect of the Fenton's reagents ratio in terms of the H_2O_2 to Fe^{2+} ratio (H/F ratio)*

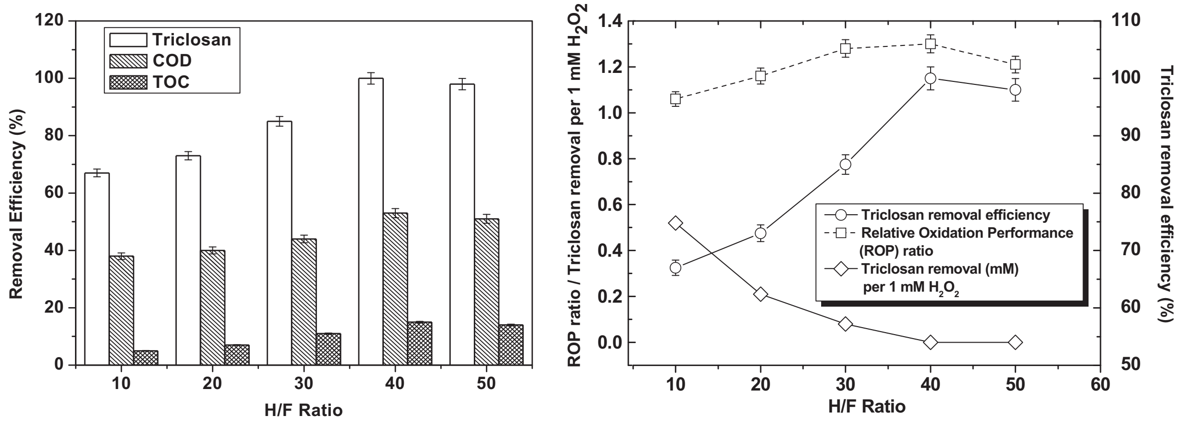
The effect of the Fenton's reagents ratio in terms of the H_2O_2/Fe^{2+} (H/F) ratio (mM/mM) was investigated for triclosan, COD, and TOC removal efficiency in this experiment as was shown in Fig. 4. The experimental results showed that increasing the H/F ratio could induce the removal efficiency to accelerate and reach the maximum level. In this experiment, a H/F ratio of 40 was found to be the most effective ratio as a 100% removal efficiency could be achieved for 1 mM triclosan by the addition of Fenton's reagents combined with an electrochemical system. Increasing H/F ratios more than 40 was not effective for removal efficiencies. Reaching maximum efficiency, when using H/F ratio of more than 40 indicated that the chemical reagents might be in excess of process requirements. The decrease in the performance of triclosan removal by 1 mM of H_2O_2 with increasing H/F ratio confirms that increasing the H/F ratio did not improve performance. It is reasonable to expect that an increase in the H/F ratio might result in more hydrogen peroxide than the process required and might scavenge other pollutants in the process. Moreover, such an input-response correlation might not be a linear relationship because other side reactions that occur simultaneously might also favor a high concentration of H_2O_2.

$$\text{ROP ratio} = \frac{\%\ \text{pollution removal}}{\%\ H_2O_2\ \text{consumed}} \tag{9}$$

In this section, the relative oxidation performance (ROP) ratio was developed as described by Eq. (1) [17]. It was used to indicate the oxidation or degradation efficiency related to H_2O_2 consumption as shown by the dashed line in Fig. 4. The ROP ratio indicated that the oxidation power of the process increased, when the H/F ratio was less than 40 and it decreased when the ratio was more than 40. The real performance in triclosan, COD, and TOC removal efficiency did not increase when the H/F ratios were above 40 which might be due to excessive H_2O_2 molecules in the process. This condition makes the activity of H_2O_2 to react with hydroxyl radicals that were scavenging in the process by producing $HO_2^{\cdot}$ via the reaction as can confirm by the decrease in amount of triclosan removal performance by 1 mM of H_2O_2 in the process. In addition, the generated $HO_2^{\cdot}$ can participate in propagating radical chain reactions by reducing ferric to ferrous ion that can induce increased ferrous scavenging. The data for process removal efficiency and the ROP ratio confirm that the Fenton's reagents ratio was the major critical parameter for this process.

3.5. *Effect of H_2O_2 operational feeding mode*

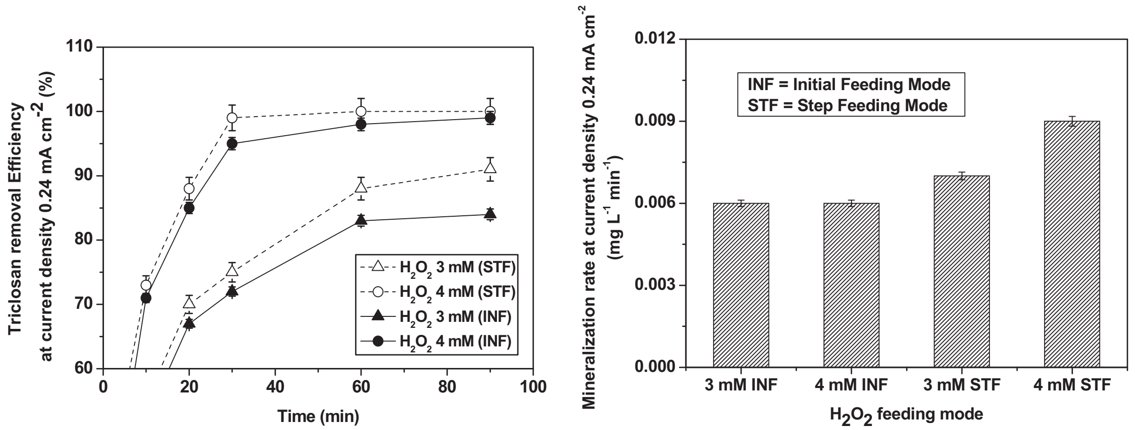
Two different H_2O_2 operational feeding modes, a one-time initial feeding mode and a step feeding



(a) (b)

Fig. 4. Effect of Fenton’s reagents ratio in terms of H_2O_2 to Fe^{2+} ratios (H/F) on triclosan, COD, and TOC removal efficiency by Fenton’s reagents combined with an electrochemical system ([Triclosan] = 1 mM, [Fe^{2+}] = 0.1 mM, pH = 3, an electrical current of 0.15 mA cm^{-2}).

mode at 2 min interval was performed to investigate the effect on process efficiency by Fenton’s reagents combined with an electrochemical system as shown in Fig. 5. The results show that the feeding mode was the dominating effect with increasing current density (0.15–0.24 mA cm^{-2}). The reason might be that the higher current density condition resulted in a greater electron supply for Fe^{2+} regeneration which induced a faster regeneration rate than lower current conditions. In this experiment, the best degradation efficiency was obtained by using a step feeding operation because it could generate ·OH continuously and homogeneously. The step feeding mode could also help avoid the presence of excessive ·OH concentrations during the earlier oxidation stages and provide better ability of this species throughout the whole oxidation process [17]. A sufficient H_2O_2 concentration in the step feeding operation, as well as an optimal ratio of substrate to H_2O_2 consumption reduced the extension of scavenging reactions involving H_2O_2 and ·OH, thus minimizing the inefficient consumption of H_2O_2. On the other hand, the Fe^{2+} regeneration to H_2O_2 ratio was also higher, thus favoring the decomposition of H_2O_2 mostly into ·OH instead of O_2. At the lower current density (at 0.15 mA cm^{-2}), the effect of both operation feeding modes did not make any significant difference to degradation efficiencies. This might be caused by the similarly in the ferrous regeneration rate of both



(a) (b)

Fig. 5. Effect of H_2O_2 operational feeding mode (step feed; STF, initial feed; INF) on triclosan removal and mineralization by Fenton’s reagents combined with an electrochemical system ([Triclosan] = 1 mM, [Fe^{2+}] = 0.1 mM, [H_2O_2] = 3 and 4 mM, an electrical current of 0.24 mA cm^{-2}, pH = 3).

Table 1
COD and TOC removal efficiency by Fenton's reagents combined with an electrochemical system ([Triclosan] = 1 mM, pH 3)

Electrical current (mA cm^{-2})	Fe^{2+} (mM)	H_2O_2 (mM)	COD removal (%)	TOC removal (%)
0.15	0.1	4	53	16
0.15	1	50	59	33
0.24	1	50	70	47

feeding modes at lower currents. On the other hand, the mineralization rate increased which confirmed that the step feeding operation mode was also better than the initial feeding mode in mineralization.

3.6. *Effect of various conditions on COD and TOC removal*

The triclosan removal efficiencies for COD and TOC removal by Fenton's reagents combined with an electrochemical system were investigated at various operating conditions as reported in Table 1. The data from the experiment show that under the conditions of current density 0.15 mA cm^{-2} with initial Fe^{2+} and H_2O_2 0.1 and 4 mM, respectively, at pH 3, the process

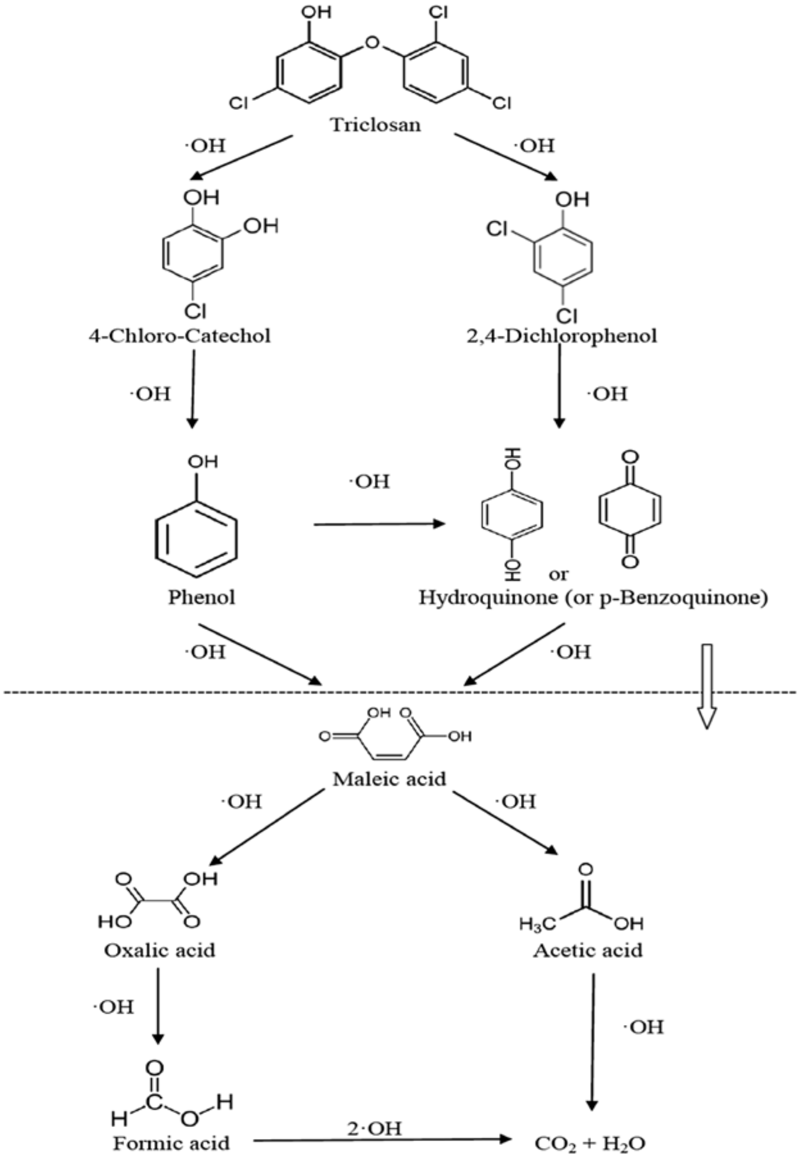


Fig. 6. Proposed reaction pathway for intermediates detected during triclosan degradation by Fenton's reagents combined with an electrochemical system.

resulted in up to 53% of COD and 16% of TOC removal for 1 mM of triclosan. However, the data in Table 1 also shows that 70% of COD and 47% of TOC removal was obtained, when the current density was increased to 0.24 mA cm^{-2} and Fe^{2+} and H_2O_2 up to 1 and 50 mM, respectively. It can be concluded from this section that the various operating parameters had effects on the degree of triclosan, COD, and TOC removal.

3.7. Proposed reaction pathways of triclosan degradation by Fenton's reagents combined with an electrochemical system

The reaction pathway of triclosan degradation by Fenton's reagents combined with an electrochemical system as proposed here is shown in Fig. 6. HPLC and IC were applied to identify and propose the intermediates that might occur in the reactions which were then confirmed by GC-MS. The proposed pathway is as follows: triclosan was separated in two ways, first to form 2,4-dichlorophenol which can oxidize to hydroquinone in the next step. The second way was to form 4-chloro-catechol which subsequently continued to oxidize to phenol. Then, the phenol was oxidized to hydroquinone by hydroxylation on the C (4)-position of phenol. The pathway was dehydrogenated from phenol or 2,4-dichlorophenol to p-benzoquinone, which is a known toxic compound, was occurred in the initial H_2O_2 feeding condition. In this condition, where the $^{\cdot}OH$ might be insufficient during the degradation, the dehydrogenation of hydroquinone to p-benzoquinone dominated. On the other hand, the formation of hydroquinone, which can oxidize continuous to form aliphatic carboxylic acid directly, occurred during the H_2O_2 step feeding condition. It can be inferred from this pathway that the step feeding of H_2O_2 might reduce the potential toxicity more than in the initial H_2O_2 feeding method. After that, the ring cleavage to the formation of maleic acid, the degradation may separate in two paths. The first direction is acetic acid formation. The second direction is the formation of oxalic acid and formic acid by hydrogen abstraction. In both degradation pathways, it is directly converted to carbon dioxide and water as final products.

4. Conclusions

The operating parameters affected the performance of a combined process using Fenton's reagents and an electrochemical system that was utilized to study the efficiency of triclosan degradation. The efficiency of degradation could be enhanced by changing the H_2O_2 operation mode from a one-time initial H_2O_2 feeding mode to a step feeding mode. The step feeding operation could reduce the scavenging effect of the reaction process and decrease the possibility of toxic compound formation from intermediates. In this experiment, the optimum operating conditions were found to be an operating pH of 3, an electrical current density of 0.15 mA cm^{-2}, and a H_2O_2 to Fe^{2+} ratio of 40 for complete oxidation of 1 mM of triclosan. A degradation pathway for triclosan removal was proposed on the basis of detected intermediate compounds. These intermediates, which depended on the process conditions, were 2,4-dichlorophenol, 4-chloro-catechol, phenol, hydroquinone, p-benzoquinone, maleic, acetic, oxalic, and formic acids.

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