Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.22264

115 (2018) 227–235
May

Mineralization of aniline in aqueous solution by cathodic reduction of peroxymonosulfate

Wen-Shing Chen*, Chi-Pin Huang, Sheng-Ci Shao

[a]*Department of Chemical and Materials Engineering, National Yunlin University of Science & Technology, 123 University Road, Section 3, Douliou, Yunlin 640, Taiwan, Tel. 886-5-534-2601x4624, Fax 886-5-531-2071, email: chenwen@yuntech.edu.tw (W.-S. Chen), D10015001@yuntech.edu.tw (C.-P. Huang), M10415004@yuntech.edu.tw (S.-C. Shao)*

Received 17 October 2017; Accepted 28 March 2018

ABSTRACT

Oxidative degradation of aniline in aqueous solution was performed using electrochemical oxidation coupled with peroxymonosulfate anions, wherein a dramatically synergistic effect was found. Experiments were carried out under the batch-wise mode to investigate the influence of various operation parameters on the electrolytic behavior, such as temperature, peroxymonosulfate anion concentration and acidity of aqueous solution. According to the poison effect of carbon monoxide, the principal oxidizing agents were presumed to be sulfate radicals, descended directly from cathodic reduction of peroxymonosulfate anions. Based on the results obtained from gas chromatograph-mass spectrometer, it was postulated that aniline was initially oxidized into iminobenzene radicals, followed with formation of azobenzene, nitrobenzene and nitrosobenzene respectively. Phenol was also detected as the degradation intermediate, leading to generation of hydroquinone and *p*-benzoquinone.

Keywords: Aniline; Peroxymonosulfate; Electro-activation; Sulfate radical; Cathodic reduction

1. Introduction

Aniline is an extremely important petrochemical compound due to its substantial demand for the synthesis of isocyanate, an essential intermediate for the production of polyurethane. Besides, aniline derivatives have been broadly used as precursors for the manufacture of accelerators and antioxidants in the rubber industry. The other fundamental applications include the manufacture of dyes, herbicides and pharmaceuticals [1]. However, due to its high toxicity and severe damage to the liver of animals, the wastewater effluent contaminated with aniline should be properly treated [2].

Several techniques have been developed to decompose aniline in wastewater due to its recalcitrance for biodegradation. Based on the results shown [3–6], the removal efficiency of aniline was significantly enhanced over the TiO_2 photocatalysts assisted with carbonate ions, which increased the number of active adsorption sites. The reaction pathway was proposed, wherein azobenzene and benzoquinone had been identified to be reaction intermediates. Alternatively, some researchers investigated oxidative degradation of aniline by means of ozonation [7,8], O_3/UV [9,10] and O_3/ultrasound method [11], wherein ozone could be substantially converted into hydroxyl radicals via cavitation microbubbles. For some publications, aniline was treated using electrochemical oxidation [12–15]. The electrode materials were improved with Ru-Cu catalysts supported on carbon nanotubes or boron doped mesoporous activated carbon, respectively. Further, many studies have been issued on the mineralization of aniline utilizing H_2O_2/SBA-15 [16], Fenton's reagent [17], electro-Fenton method [18–21] and fluidized-bed Fenton process [22,23].

Recently, sulfate radical-based oxidation processes have received much attention for oxidative degradation of aniline in wastewater. Experiments for decomposition of aniline through the thermally activated peroxydisulfate anions were conducted, wherein the degradation rate was proportional to the operating temperature [24]. In addition, per-

---

*Corresponding author.

oxydisulfate anions catalyzed with homogeneous ferrous ions were proved to be effective for abatement of aniline [25–27]. Co/N/graphene and Co_3O_4/N/carbon have been used as heterogeneous catalysts for activation of peroxymonosulfate anions during oxidation of aniline [28,29]. In our previous work [30,31], it was found that sulfate radicals formed via electrochemical activation of peroxydisulfate anions [shown as Eq. (1)] were viable for removal of aniline. Nonetheless, the yield of sulfate radicals depends intensely on the activity of cathodic reduction of peroxydisulfate anions.

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + SO_4^{-}\cdot \tag{1}$$

It has been reported that peroxymonosulfate anions accept electrons more easily than peroxydisulfate anions, due to the unsymmetrical structure for the former [32–34]. Therefore, the higher yield of sulfate radicals is expected to be produced from electrochemical activation of peroxymonosulfate anions, listed as following.

$$HSO_5^- + e^- \rightarrow SO_4^-\cdot + OH^- \tag{2}$$

According to the results shown [35–37], sulfate radicals could be formed via simply electro-activation of peroxymonosulfate anions or by way of electrochemical treatment of peroxymonosulfate anions with assistance of ferrous ions, whereas it has been not yet used to dispose wastewater contaminated with aniline. Consequently, this research devotes to assess the feasibility of mineralization of aniline in aqueous solution by electrochemical activation of peroxymonosulfate anions under a variety of operating variables, such as temperature, peroxymonosulfate anion concentrations, acidity of aqueous solution, dosages of nitrogen, oxygen and carbon monoxide gas respectively.

2. Experimental methods

2.1. Electrochemical activation of peroxymonosulfate oxidation testing

Experimental system was referred to our previous work [38]. The electrolytic cell was a glass jacket cylinder equipped with a magnetic stirrer (Heidolph MR 3001K Model). With regard to electrode materials used, the anode and cathode plates were made of platinum (99.9 wt%) with dimensions of 20 mm × 20 mm × 1 mm (PIIN JIA Technology Co.) [39]. Experiments were carried out in a batch mode under atmospheric pressure among the temperature range of 303–318 K. Prior to the testing, the wastewater feedstock (450 mL) at the aniline concentration of 2.74 mM, synthesized from deionized water and aniline (≥99.9%, Riedel-de Haen), and potassium peroxymonosulfate (≥98.0%, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, Riedel-de Haen) were blended well in the cell of which temperature was controlled through a thermostat (VWR Scientific Co. 1167 Model). In this research, the constant cell voltage mode was applied by means of a dc power supply (INS Power). For the duration of tests, periodic samples were withdrawn from the electrolytic cell, and placed in an ice bath (277 K) immediately to terminate oxidation of aniline [31]. Sequentially, the samples obtained were proceeded with total organic compound (TOC) analyses. The residual peroxymonosulfate concentration was determined by means of modified iodometric titration method [40]. In additional set of tests, nitrogen, oxygen and carbon monoxide gases measured with mass flow meters (BROOKS 5850E Model) were introduced into the wastewater respectively via a porous pipe-diffuser located under the cathode.

For the purpose of evaluating the influence of acidity of aqueous solution on the degradation of aniline, four tests including a variety of initial pH values (3.0–7.0) were performed. To explore the effect of peroxymonosulfate anion concentrations on the decomposition of aniline, a series of tests under various peroxymonosulfate anion concentrations between 24.4 and 48.8 mM were carried out. Moreover, the electro-activated peroxydisulfate oxidation test was undertaken as well for comparison with that by electro-activated peroxymonosulfate oxidation. To gain an insight on the directly anodic oxidation process, the electrolysis was also conducted with an internal distance of 40 mm between the cathode and anode plates [41]. In this study, all the tests were undergone at least in duplicate to confirm the data obtained.

2.2. Total organic compounds (TOC) analysis

In the course of electro-activated peroxymonosulfate oxidation tests, the wastewater was periodically sampled from the electrolytic cell and directly measured utilizing a TOC analyzer (Tekmar Dohrmann Phoenix 8000 Model) equipped with both ultra-violet (UV) reactor and nondispersive infrared (NDIR) detector. Based on the quantity of carbon dioxide generated from oxidation of organics by sodium peroxydisulfate assisted intensely with UV irradiation, the organic compound extent in the solution was determined. In contrast, the inorganic compounds which were acidified by phosphoric acid would be eliminated in the form of carbonic acid. For quantitative analyses of organic compound concentrations in samples, the calibration curve was established at the range of 0–300 mg L^{-1} utilizing the potassium hydrogen phthalate standard solutions.

2.3. Hydrogen peroxide concentration analysis

It has been well recognized that sulfate radicals could be transformed into sulfate ions, leading to generation of hydroxyl radicals [Eq. (3)], of which rate constant has been determined to be 60 $M^{-1} s^{-1}$ [42]. Sequentially, hydroxyl radicals in aqueous media would recombine quickly to form hydrogen peroxide [Eq. (4)], of which rate constant has been estimated to be 6×10^9 $M^{-1} s^{-1}$ [43]. In other words, the hydrogen peroxide concentration gives an indication on the yield of sulfate radicals produced by electrochemical activation of peroxymonosulfate anions in the absence of organics. Therefore, the yield of hydrogen peroxide generated in the electro-activated peroxymonosulfate process with the deionized water instead of wastewater was measured using a titanic sulfate method [44]. The main absorbance peak (410 nm) reflected by a titanic-hydrogen peroxide complex was detected by an UV-Vis spectrophotometer (LAMBDA 850 Model, Perkin- Elmer). The aliquots (ca. 4 mL) of the solution periodically withdrawn from the electrolytic cell were analyzed among the range of 0–200 mg L^{-1}, calibrated in advance by the hydrogen peroxide standard solutions.

$$SO_4^{-}\cdot + H_2O \rightarrow OH\cdot + SO_4^{2-} + H^+ \tag{3}$$

$$OH\cdot + OH\cdot \rightarrow H_2O_2 \tag{4}$$

2.4. Gas chromatograph-Mass spectrometer analysis (GC-MS)

After 4 h test operation of electro-activated peroxymonosulfate oxidation, the sample solution withdrawn (ca. 50 mL) was situated on the hot plate equipped with a magnetic stirrer at a speed of 150 rpm. The solid phase microextraction fiber (carboxen/polydimethylsiloxane, 75 µm, SPME, Supelco.) was directly immersed in the solution to adsorb and concentrate the dissolved organic compounds. Until the extraction process performed for 2 h, the fiber was retracted into a protective needle and removed from the solution. Afterwards, the SPME needle was injected into the injection port of gas chromatograph-mass spectrometer (Hewlett Packard 59864B/HP 5973 MASS) fitted with a capillary column (Metal ULTRA ALLOY UA-5, 30 m × 0.25 mm, film thickness 0.25 µm). Helium gas served as carrier gas and the oven was programmed from 303 to 573 K at the raising rate of 20 K min^{-1}. The mass spectra obtained were compared with those of the authentic standard compounds in database (Wiley 275L). Thus, most of aniline degradation intermediates were identified.

3. Results and discussion

3.1. Comparison of anodic oxidation, peroxydisulfate, peroxymonosulfate, electro-activated peroxydisulfate and peroxymonosulfate oxidation

The time-dependent patterns of TOC removal percentage by means of peroxydisulfate, peroxymonosulfate, electro-activated peroxydisulfate and electro-activated peroxymonosulfate oxidation respectively are demonstrated in Fig. 1. It clearly indicates that TOC removal rate via electro-activated peroxydisulfate oxidation was higher than that via peroxydisulfate oxidation alone. This phenomenon could be ascribed to generation of stronger oxidants of sulfate radicals (E° = 2.6 V) by means of reduction of peroxydisulfate anions (E° = 2.01 V) at the cathode [30,31]. A similar outcome was also observed upon comparison the TOC removal rate via electro-activated peroxymonosulfate oxidation with that via only peroxymonosulfate oxidation. The results could be likely attributed to production of sulfate radicals through reduction of peroxymonosulfate anions, of which redox potential was estimated to be 1.85 V [45]. It deserves to note that TOC removal percentage via electro-activated peroxymonosulfate oxidation (64%) is significantly higher than that via electro-activated peroxydisulfate oxidation (23%). The observation could be interpreted with easier acceptance of electrons from the cathode for peroxymonosulfate anions, due to their unsymmetrical structure of the peroxide bond [32–34]. Another possible explanation is that the peroxide bond length of peroxymonosulfate (1.463 Å) is shorter than that of peroxydisulfate anions (1.497 Å), which makes the former more susceptabile to adsorb on the cathode [46]. As regards anodic oxidation of aniline on the surface of Pt anode, the result showed a low degradation percentage, consistent with some literature [47,48]. Thus, decomposition of aniline by way of directly anodic oxidation [40,49] or via adsorbed hydroxyl radicals [50–52] at the Pt anode is insignificant in this work. Obviously, a synergistic effect was found as electrochemical oxidation was coupled with peroxymonosulfate oxidation due to the dramatic generation of sulfate radicals.

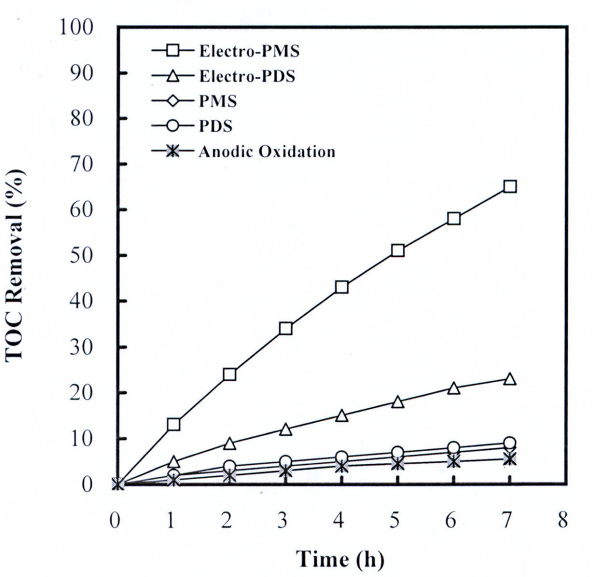

Fig. 1. Time-dependent patterns of TOC removal percentage by means of peroxydisulfate alone, peroxymonosulfate alone, anodic oxidation, electro-activated peroxydisulfate and electro-activated peroxymonosulfate oxidation respectively under the conditions of electrode potential = 6 V, T = 303 K, peroxydisulfate anion concentration = 105.0 mM, peroxymonosulfate anion concentration = 40.7 mM and initial pH = 3.0.

Although electrochemical oxidation tests were performed in the absence of oxygen gas feedstock, a small amount of hydrogen peroxide may be generated through cathodic reduction of oxygen, descended mainly from anodic oxidation of water shown as follows [53,54]:

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \tag{5}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{6}$$

Alternatively, in the electro-activated peroxymonosulfate process, peroxymonosulfate anions and oxygen would be competitively adsorbed on the surface of cathode and transformed into sulfate radicals and hydrogen peroxide individually [Eqs. (2) and (5)]. That is, mineralization of aniline would be mostly contributed by sulfate radicals and electrogenerated hydrogen peroxide. The oxidizing ability of sulfate radicals has been recognized to be stronger than that of hydrogen peroxide. Consequently, the main oxidant in the electro-activated peroxymonosulfate process could be reasonably proposed to be sulfate radicals.

3.2. Effect of operating temperature on electro-activated peroxymonosulfate oxidation

As far as electrochemical engineering is considered, it is essential to determine the appropriate operating temperature, at which the higher removal rate of aniline is achieved. Fig. 2a illustrates the time-dependent patterns of TOC removal percentage as a function of reaction temperature. It is apparent that the decomposition rate of TOC at 318 K was higher than that at 313 K in the course of electro-activated peroxymonosulfate process. Likewise, analogous degradation behaviors were also observed in comparison with the data of 308 K and that of 303 K. Higher reaction temperature seems to be favorable for mineralization of aniline. Owing to suppression of oxygen solubility in aqueous solution at higher temperature [55], leading to lower yield of electrogenerated hydrogen peroxide [Eq. (5)], the principal oxidant for mineralization of aniline could be ascribed to sulfate radicals.

Despite of less oxygen gas dissolved in aqueous solution at higher temperature, the total yield of hydrogen peroxide was dramatically increased with an increase of reaction temperature (shown in Fig. 2b). The increment of hydrogen peroxide concentration could be attributed to generation of sulfate radicals which were transformed into hydroxyl radicals and hydrogen peroxide sequentially [Eqs. (3), (4)]. The outcomes support previous hypothesis that sulfate radicals were chiefly responsible for destruction of aniline.

3.3. Effect of dosage of nitrogen, oxygen, carbon monoxide gases on electro-activated peroxymonosulfate oxidation

With a view to promote generation of sulfate radicals, nitrogen gas was introduced into wastewater. Fig. 3 presents the influence of injection of nitrogen gas on the electro-activated peroxymonosulfate process. Apparently, the removal rate of TOC raises upon dosages of nitrogen gas. It could be interpreted with enhancement on the amounts of sulfate radicals descended from peroxymonosulfate anions. On influx of nitrogen gas, partial oxygen gas dissolved would be repelled from the aqueous solution, resulting in more peroxymonosulfate anions adsorbed on the cathode. Instead, upon injection of oxygen gas into wastewater, TOC removal percentage decreases conversely in the electro-activated peroxymonosulfate process. The observation may be partially ascribed to more oxygen molecules dissolved, which intensely compete with peroxymonosulfate anions for cathodic reduction, leading to diminution in sulfate radical production. Particularly, the destruction rate of TOC decreases significantly in the presence of carbon monoxide. It could be attributed to the Pt cathode poisoned by carbon monoxide molecules [56,57], which obviously inhibited peroxymonosulfate anions from adsorption on the surface of cathode. The results imply that cathodic reduction of peroxymonosulfate anions into sulfate radicals plays an important role for oxidative degradation of aniline.

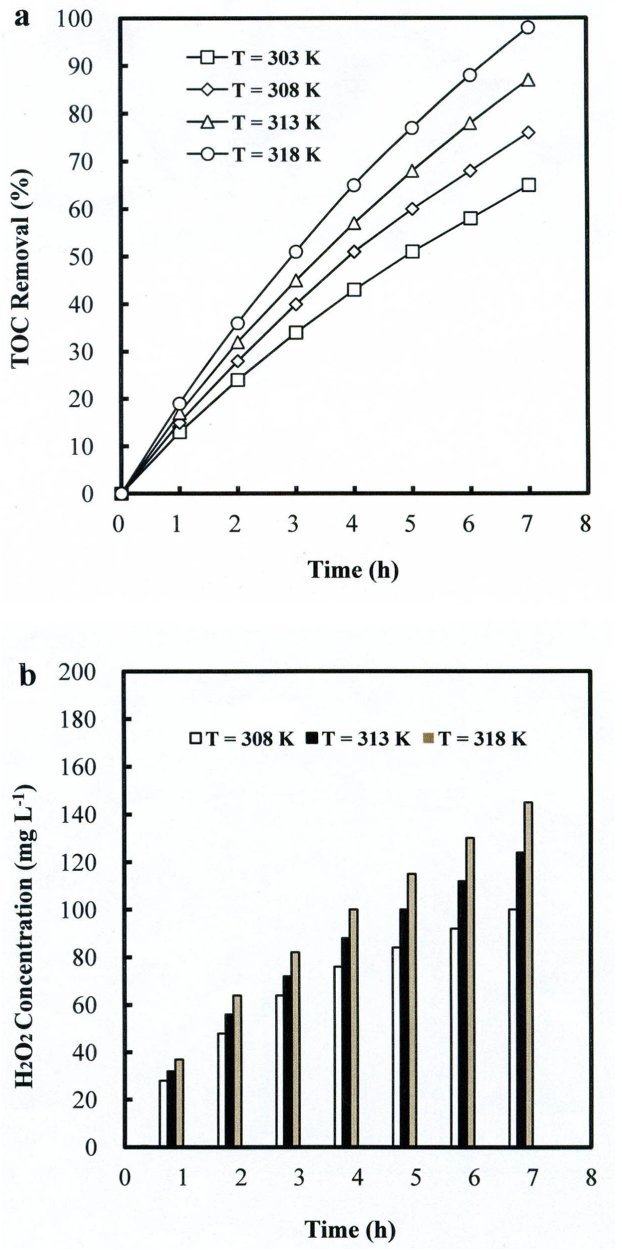

Fig. 2. (a) Effect of temperature on the TOC removal percentage by electro-activated peroxymonosulfate oxidation under the conditions of electrode potential = 6 V, peroxymonosulfate anion concentration = 40.7 mM and initial pH = 3.0. (b) Hydrogen peroxide concentrations generated in deionized water by electro-activated peroxymonosulfate anions with various operating temperature under the conditions of electrode potential = 6 V, peroxymonosulfate anion concentration = 40.7 mM and initial pH = 3.0.

3.4. Effect of peroxymonosulfate anion concentrations on electro-activated peroxymonosulfate oxidation

From the viewpoint of economics, an optimal concentration of peroxymonosulfate anions should be found. Fig. 4a presents the influence of peroxymonosulfate anion concentrations on the electro-activated peroxymo-

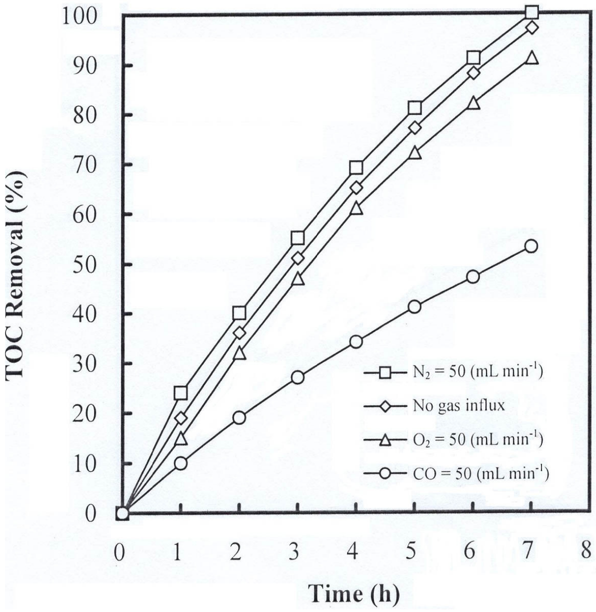

Fig. 3. Effect of dosage of nitrogen, oxygen and carbon monoxide gases on the TOC removal percentage by electro-activated peroxymonosulfate oxidation under the conditions of electrode potential = 6 V, T = 318 K, peroxymonosulfate anion concentration = 40.7 mM and initial pH = 3.0.

nosulfate process. It is transparent that the TOC removal percentage raised with increasing peroxymonosulfate anion concentrations. This phenomenon could be interpreted with significant elevation on the number of sulfate radicals. Nonetheless, under the condition of excess peroxymonosulfate anions (48.8 mM), TOC degradation percentage was decreased, due to elimination of sulfate radicals by residual peroxymonosulfate anions [Eq. (7)] [35,58]. Furthermore, the yield of hydrogen peroxide was determined in the deionized water instead of wastewater under various concentrations of peroxymonosulfate anions in the electro-activated peroxymonosulfate process (shown in Fig. 4b). It clearly indicates that hydrogen peroxide concentrations increase with an increment of peroxymonosulfate anion concentrations (or sulfate radical concentrations), whereas excess peroxymonosulfate anion concentrations (48.8 mM) retard formation of hydrogen peroxide. That could be probably interpreted with side reactions between residual peroxymonosulfate anions and sulfate radicals as mentioned. In fact, the total yield of hydrogen peroxide presents an identical tendency with TOC removal percentage at a variety of peroxymonosulfate anion concentrations. However, electrogenerated hydrogen peroxide made minor contributions for the yield of hydrogen peroxide. Therefore, the results provide an evidence on our previous inference that sulfate radicals were main oxidizing agents.

$$SO_4^- \cdot + HSO_5^- \rightarrow SO_4^{2-} + SO_5^- \cdot + H^+ \tag{7}$$

Fig. 5 depicts the decomposition efficiency of peroxymonosulfate anions in a variety of peroxymonosulfate concentrations during the experiments. Obviously, the decomposition rate of peroxymonosulfate anions increased with increasing peroxymonosulfate concentrations. It may be ascribed to generated sulfate radicals accelerating the decomposition of peroxymonosulfate anions, consistent with the results by Wang and Wang [59]. Nevertheless, excess peroxymonosulfate anions (48.8 mM) would

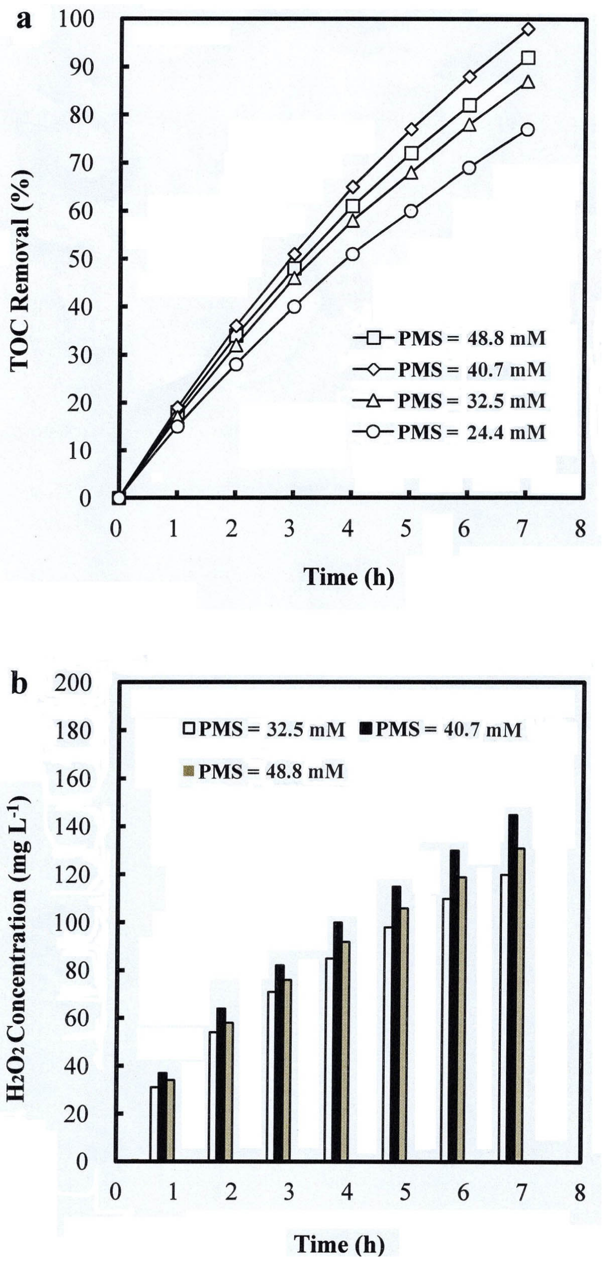

Fig. 4. (a) Effect of peroxymonosulfate anion concentrations on the TOC removal percentage by electro-activated peroxymonosulfate oxidation under the conditions of electrode potential = 6 V, T = 318 K and initial pH = 3.0. (b) Hydrogen peroxide concentrations generated in deionized water by electro-activated peroxymonosulfate anions with various peroxymonosulfate anion concentrations under the conditions of electrode potential = 6 V, T = 318 K and initial pH = 3.0.

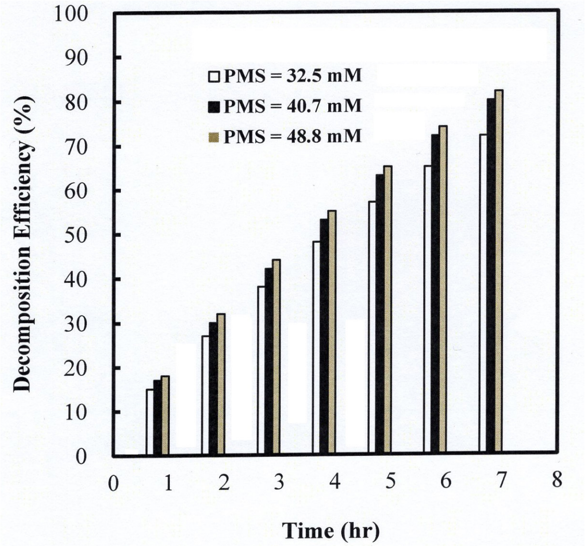

Fig. 5. Decomposition efficiency of peroxymonosulfate anions in a variety of peroxymonosulfate concentrations during the experiments under the conditions of electrode potential = 6 V, T = 318 K and initial pH = 3.0.

consume more sulfate radicals, leading to lower TOC degradation percentage. In this work, the optimal peroxymonosulfate concentration was 40.7 mM for the removal of aniline.

3.5. Effect of initial pH values of aqueous solution on electro-activated peroxymonosulfate oxidation

For the sake of promotion on the degradation percentage of aniline, the acidity of aqueous solution was usually adjusted practically. Fig. 6a illustrates the time-dependent patterns of TOC removal percentage as a function of initial pH values. As can be seen, the removal rate of TOC increases with a decrease of pH values. The observation may be partially attributed to reduction on the solubility of oxygen gas in aqueous solution under stronger acid conditions [30], which instead facilitates the adsorption of peroxymonosulfate anions on the cathode and sequential formation of more sulfate radicals.

Because of less oxygen gas dissolved in aqueous solution at low pH values, the yield of electrogenerated hydrogen peroxide derived from cathodic reduction of oxygen would decrease. Nevertheless, the total yield of hydrogen peroxide was theatrically raised with increasing the acidity of aqueous solution (shown in Fig. 6b). The increment of hydrogen peroxide is likely contributed by considerable amounts of sulfate radicals formed [Eqs. (3) and (4)]. As a consequence, it reveals again that sulfate radicals were main oxidants in the electro-activated peroxymonosulfate process.

3.6. Reaction pathways of aniline by electro-activated peroxymonosulfate oxidation

For the insight of oxidative degradation pathways of aniline in the course of electro-activated peroxymonosulfate process, the reaction intermediates extracted through

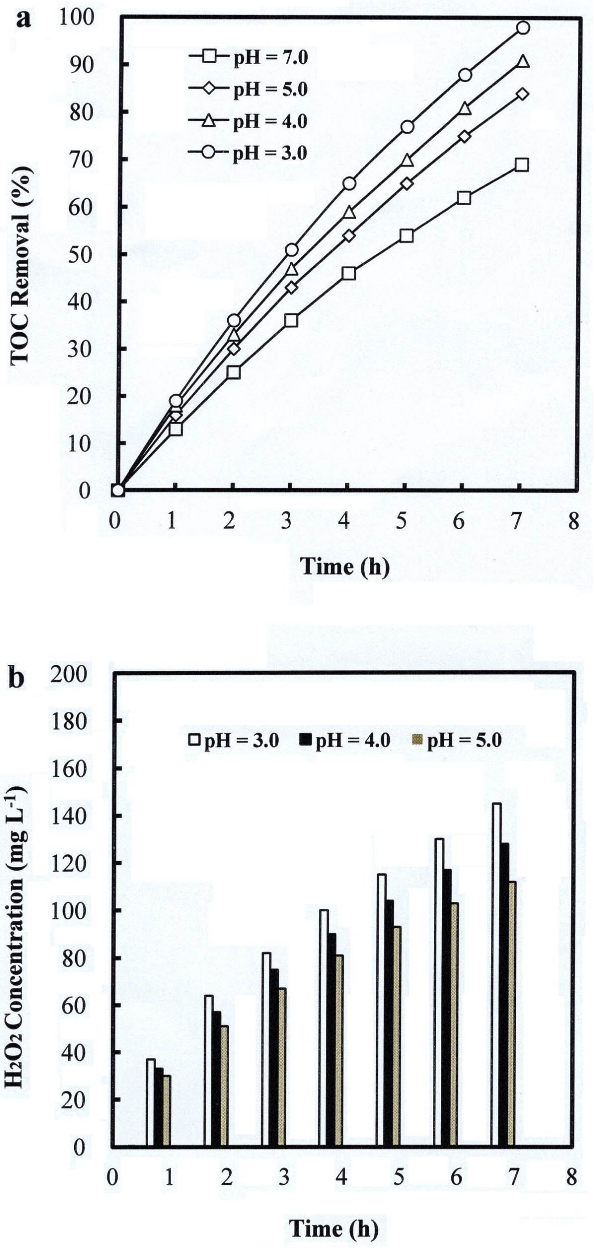

Fig. 6. (a) Effect of initial pH values of aqueous solution on the TOC removal percentage by electro-activated peroxymonosulfate oxidation under the conditions of electrode potential = 6 V, T = 318 K and peroxymonosulfate anion concentration = 40.7 mM. (b) Hydrogen peroxide concentrations generated in deionized water by electro-activated peroxymonosulfate anions with various pH values of aqueous solution under the conditions of electrode potential = 6 V, T = 318 K and peroxymonosulfate anion concentration = 40.7 mM.

SPME method were identified by a GC-MS analyzer. Table 1 summarizes the results acquired, wherein the compositions include aniline, azobenzene, nitrosobenzene, nitrobenzene, 2-nitrophenol, phenol, hydroquinone and *p*-benzoquinone. As far as azobenzene is concerned, it could be originated from iminobenzene radicals, corresponding to the reports by Kumar and Mathur [5]. Additionally, the imino radicals

Table 1
Compositions of feedstock and reaction intermediates identified by GC-MS

Component	m/z (relative abundance, %)
Feedstock	
Aniline	39 (6.0), 46 (3.1), 52 (3.3), 63 (3.5), 65 (14.0), 66 (27.3), 67 (3.6), 92 (11.0), 93 (100), 94 (6.7)
Reaction intermediate	
Azobenzene	50 (4.7), 51 (18.8), 77 (100), 78 (6.7), 105 (20.4), 151 (2.6), 152 (11.2), 153 (6.8), 182 (35.8), 183 (4.8)
Nitrobenzene	50 (15.0), 51 (37.2), 65 (12.8), 74 (8.1), 75 (4.6), 77 (100), 78 (6.7), 93 (16.3), 123 (69.4), 124 (5.1)
2-Nitrophenol	39 (15.1), 53 (8.7), 63 (19.4), 64 (13.2), 65 (24.8), 81 (19.0), 93 (7.3), 109 (17.4), 139 (100), 140 (7.0)
Phenol	38 (4.4), 39 (11.7), 40 (6.1), 50 (3.9), 55 (5.7), 63 (5.7), 65 (20.3), 66 (26.7), 94 (100), 95 (6.8)
Hydroquinone	39 (6.2), 53 (13.7), 54 (12.0), 55 (9.7), 81 (24.8), 82 (11.4), 110 (100), 111 (5.4), 115 (5.0), 143 (8.8)
p-Benzoquinone	26 (17.3), 50 (6.2), 52 (17.0), 53 (16.4), 54 (62.7), 80 (27.7), 82 (35.4), 108 (100), 109 (7.3), 110 (11.3)
Nitrosobenzene	50 (15.1), 51 (45.7), 63 (3.5), 74 (7.0), 75 (3.7), 77 (100), 78 (7.3), 93 (9.4), 107 (82.3), 108 (5.7)

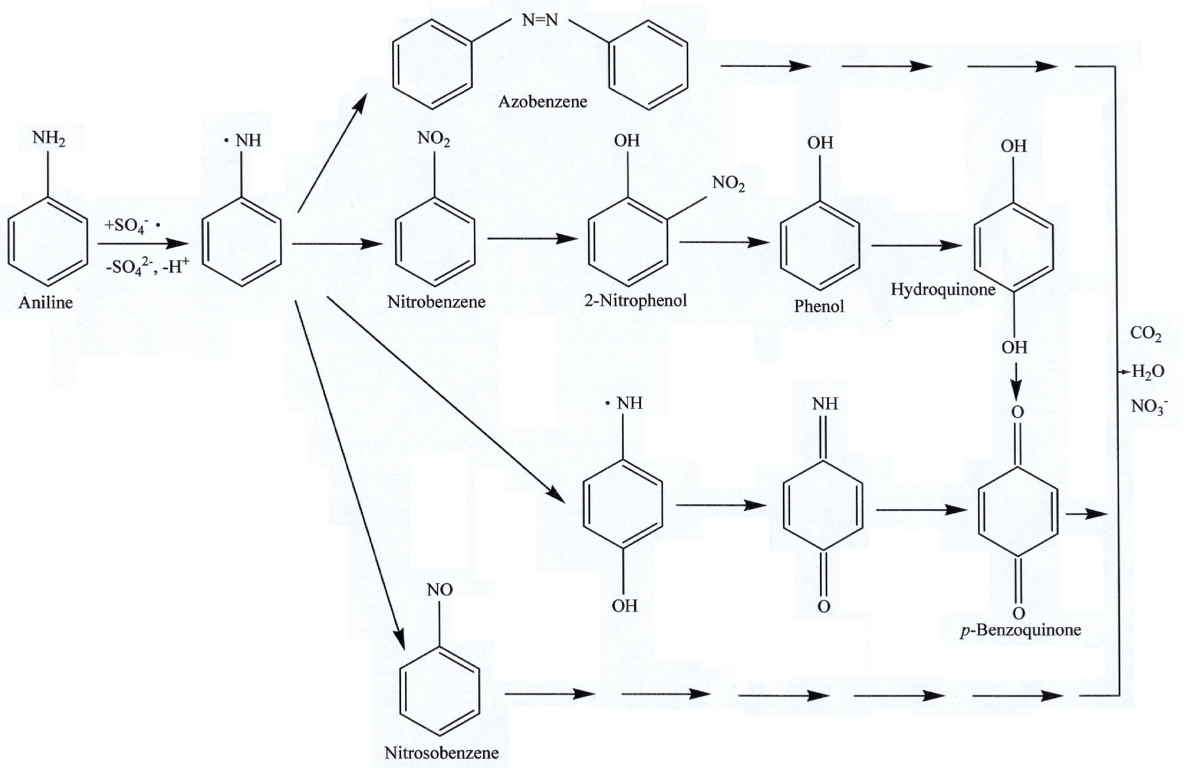

Fig. 7. Plausible reaction pathways of aniline in aqueous solution by electro-activated peroxymonosulfate oxidation.

could be transformed into nitrobenzene, which is sequentially oxidized to 2-nitrophenol. The detection of phenol implies the occurrence of denitration of 2-nitrophenol. Afterwards, oxidation of phenol gives rise to generation of hydroquinone, which would undergo further oxidation step to form benzoquinone via abstraction of hydrogen. Alternatively, the imino radicals may proceed other oxidation reactions, leading to production of nitrosobenzene and benzoquinonimine, which could also result in formation of benzoquinone, consistent with the publication by Brillas et al. [19]. Finally, mineralization of aniline would result in the ultimate products of carbon dioxide, water and nitrate ions, proved by the UV-Vis spectrophotometer at the wavelength of 313 nm. On the basis of reaction intermediates involved in the aqueous solution, the plausible degradation pathways of aniline in an electro-activated peroxymonosulfate process could be illustrated in Fig. 7.

4. Conclusions

Based on above discussion, it is obvious that aniline contaminants in wastewater would be mainly decomposed by sulfate radicals via electro-activated peroxymonosulfate anions. Carbon monoxide intensely diminished aniline removal rate, indicating that sulfate radicals were descended directly from cathodic reduction of peroxymonosulfate anions. According to the spectra obtained from GC-MS analyses, the possible reaction pathways of aniline are proposed as follows. Aniline was preliminarily oxidized into iminobenzene radicals, subsequently transformed to azobenzene, nitrobenzene and nitrosobenzene respectively. Phenol was also observed as one of degradation intermediates, leading to formation of hydroquinone and *p*-benzoquinone. Eventually, aniline would be mineralized into carbon dioxide, water and nitrate. It is remarkable that aniline in aqueous solution could be almost thoroughly removed in this work. The outcomes convince us that the electro-activated peroxymonosulfate process may be a promising manner for disposal of aniline in wastewater.

References

[1] K. Weissermel, H.-J. Arpe, Industrial Organic Chemistry. Ullmann's Encyclopedia of Industrial Chemistry, VCH, Weinheim, New York, p.327–330. 1972.

[2] A. Messeguer, Potential implication of aniline derivatives in the toxic oil syndrome (TOS), Chem. Biol. Interact., 192 (2011) 136–141.

[3] L. Sánchez, J. Peral, X. Domènech, Photocatalyzed destruction of aniline in UV-illuminated aqueous TiO_2 suspensions, Electrochim. Acta, 42 (1997) 1877–1882.

[4] A. Kumar, N. Mathur, Photocatalytic oxidation of aniline using Ag^+-loaded TiO_2 suspensions, Appl. Catal. A: General, 275 (2004) 189–197.

[5] A. Kumar, N. Mathur, Photocatalytic degradation of aniline at the interface of TiO_2 suspensions containing carbonate ions, J. Colloid Interface Sci., 300 (2006) 244–252.

[6] J. Anotai, A. Jevprasesphant, Y.M. Lin, M.C. Lu, Oxidation of aniline by titanium dioxide activated with visible light, Sep. Purif. Technol., 84 (2012) 132–137.

[7] J. Sarasa, S. Cortés, P. Ormad, R. Gracia, J.L. Ovelleiro, Study of the aromatic by-products formed from ozonation of anilines in aqueous solution, Water Res., 36 (2002) 3035–3044.

[8] P.C.C. Faria, J.J.M. Órfão, M.F.R. Pereira, Ozonation of aniline promoted by activated carbon, Chemosphere, 67 (2007) 809–815.

[9] R. Sauleda, E. Brillas, Mineralization of aniline and 4-chlorophenol in acidic solution by ozonation catalyzed with Fe^{2+} and UVA light, Appl. Catal. B: Environ., 29 (2001) 135–145.

[10] C.A. Orge, J.L. Faria, M.F.R. Pereira, Removal of oxalic acid, oxamic acid and aniline by a combined photolysis and ozonation process, Environ. Technol., 36 (2015) 1075–1083.

[11] S. Song, Z.Q. He, J.M. Chen, US/O_3 combination degradation of aniline in aqueous solution, Ultrason. Sonochem., 14 (2007) 84–88.

[12] Y.J. Li, F. Wang, G.D. Zhou, Y.M. Ni, Aniline degradation by electrocatalytic oxidation, Chemosphere, 53 (2003) 1229–1234.

[13] M. Mitadera, N. Spataru, A. Fujishima, Electrochemical oxidation of aniline at boron-doped diamond electrodes, J. Appl. Electrochem., 34 (2004) 249–254.

[14] M. Ferreira, M.F. Pinto, I.C. Neves, A.M. Fonseca, O.S.G.P. Soares, J.J.M. Órfão, M.F.R. Pereira, J.L. Figueiredo, P. Parpot, Electrochemical oxidation of aniline at mono and bimetallic electrocatalysts supported on carbon nanotubes, Chem. Eng. J., 260 (2015) 309–315.

[15] S. Karthikeyan, K. Viswanathan, R. Boopathy, P. Maharaja, G. Sekaran, Three dimensional electro catalytic oxidation of aniline by boron doped mesoporous activated carbon, J. Ind. Eng. Chem., 21 (2015) 942–950.

[16] L. Kong, X. Zhou, Y. Yao, P. Jian, G. Diao, Catalytic wet peroxide oxidation of aniline in wastewater using copper modified SBA-15 as catalyst, Environ. Technol., 37 (2016) 422–429.

[17] M.C. Lu, Y.F. Chang, I.M. Chen, Y.Y. Huang, Effect of chloride ions on the oxidation of aniline by Fenton's reagent, J. Environ. Manage., 75 (2005) 177–182.

[18] E. Brillas, E. Mur, J. Casado, Iron (II) catalysis of the mineralization of aniline using a carbon-PTFE O_2-fed cathode, J. Electrochem. Soc., 143 (1996) L49–L53.

[19] E. Brillas, E. Mur, R. Sauleda, L. Sánchez, J. Peral, X. Domènech, J. Casado, Aniline mineralization by AOP's: anodic oxidation, photocatalysis, electro-Fenton and photoelectro-Fenton processes, Appl. Catal. B: Environ., 16 (1998) 31–42.

[20] E. Brillas, J. Casado, Aniline degradation by electro-Fenton and peroxi-coagulation processes using a flow reactor for wastewater treatment, Chemosphere, 47 (2002) 241–248.

[21] J. Anotai, M.C. Lu, P. Chewpreecha, Kinetics of aniline degradation by Fenton and electro-Fenton processes, Water Res., 40 (2006) 1841–1847.

[22] J. Anotai, C.C. Su, Y.C. Tsai, M.C. Lu, Effect of hydrogen peroxide on aniline oxidation by electro-Fenton and fluidized-bed Fenton processes, J. Hazard. Mater., 183 (2010) 888–893.

[23] J. Anotai, C.C. Su, Y.C. Tsai, M.C. Lu, Comparison of aniline oxidation by electro-Fenton and fluidized-bed Fenton processes, J. Environ. Eng., 137 (2011) 363–370.

[24] X.F. Xie, Y.Q. Zhang, W.L. Huang, S.B. Huang, Degradation kinetics and mechanism of aniline by heat-assisted persulfate oxidation, J. Environ. Sci., 24 (2012) 821–826.

[25] Y.Q. Zhang, W.L. Huang, D.E. Fennell, In situ chemical oxidation of aniline by persulfate with iron (II) activation at ambient temperature, Chinese Chem. Lett., 21 (2010) 911–913.

[26] J. Anotai, W. Bunmahotama, M.C. Lu, Oxidation of aniline with sulfate radicals in the presence of citric acid, Environ. Eng. Sci., 28 (2011) 207–215.

[27] J. Anotai, N. Masomboon, C.L. Chuang, M.C. Lu, Persulfate oxidation for the aniline degradation in aqueous systems, Water Sci. Technol., 63 (2011) 1434–1440.

[28] X. Qin, S. Fang, L. Zhao, P. Shi, J. Fan, Y. Min, Q. Xu, W. Yao, Cobalt super-microparticles anchored on nitrogen-doped graphene for aniline oxidation based on sulfate radicals, Sci. Total Environ., 601–602 (2017) 99–108.

[29] Q. Huang, J. Zhang, Z. He, P. Shi, X. Qin, W. Yao, Direct fabrication of lamellar self-supporting Co_3O_4/N/C peroxymonosulfate activation catalysts for effective aniline degradation, Chem. Eng. J., 313 (2017) 1088–1098.

[30] W.S. Chen, C.P. Huang, Mineralization of aniline in aqueous solution by electrochemical activation of persulfate, Chemosphere, 125 (2015) 175–181.

[31] W.S. Chen, C.P. Huang, Mineralization of aniline in aqueous solution by electro-activated persulfate oxidation enhanced with ultrasound, Chem. Eng. J., 266 (2015) 279–288.

[32] A.G. Miroshnichenko, V.A. Lunenok-Burmakina, A quantum-mechanical study of the structure of inorganic derivatives of hydrogen peroxide, Theor. Experim. Chem., 11 (1976) 320–325.

[33] M.G. Antoniou, A.A. Dela Cruz, D.D. Dionysiou, Degradation of microcystin-LR using sulfate radicals generated through photolysis, thermolysis and e^- transfer mechanism, Appl. Catal. B: Environ., 96 (2010) 290–298.

[34] F. Ghanbari, M. Moradi, Application of peroxymonosulfate and its activation methods for degradation of environmental organic pollutants: Review, Chem. Eng. J., 310 (2017) 41–62.

[35] Y.R. Wang, W. Chu, Degradation of 2,4,5-trichlorophenoxy acetic acid by a novel Electro-Fe(II)/Oxone process using iron sheet as the sacrificial anode, Water Res., 45 (2011) 3883–3889.

[36] N. Jaafarzadeh, F. Ghanbari, M. Alvandi, Integration of coagulation and electro-activated HSO_5^- to treat pulp and paper wastewater, Sustain. Environ. Res., 27 (2017) 223–229.

[37] H. Lin, J. Wu, H. Zhang, Degradation of clofibric acid in aqueous solution by an EC/ Fe^{3+}/ PMS process, Chem. Eng. J., 244 (2014) 514–521.

[38] W.S. Chen, Y.C. Jhou, C.P. Huang, Mineralization of dinitrotoluenes in industrial wastewater by electro-activated persulfate oxidation, Chem. Eng. J., 252 (2014) 166–172.

[39] G. Chen, Electrochemical technologies in wastewater treatment, Sep. Purif. Technol., 38 (2004) 11–41.

[40] S. Wacławek, K. Grübel, M. Černík, Simple spectrophotometric determination of monopersulfate, Spectrochim. Acta A, 149 (2015) 928–933.

[41] I. Sirés, P.L. Cabot, F. Centellas, J.A. Garrido, R.M. Rodríguez, C. Arias, E. Brillas, Electrochemical degradation of clofibric acid in water by anodic oxidation Comparative study with platinum and boron-doped diamond electrodes, Electrochim. Acta, 52 (2006) 75–85.

[42] Y.C. Lee, S.L. Lo, J. Kuo, Y.L. Lin, Persulfate oxidation of perfluorooctanoic acid under the temperatures of 20–40°C, Chem. Eng. J., 198–199 (2012) 27–32.

[43] Y. Jiang, C. Pétrier, T.D. Waite, Effect of pH on the ultrasonic degradation of ionic aromatic compounds in aqueous solution, Ultrason. Sonochem., 9 (2002) 163–168.

[44] M. Sudoh, H. Kitaguchi, K. Koide, Electrochemical production of hydrogen peroxide by reduction of oxygen, J. Chem. Eng. Jpn., 18 (1985) 409–414.

[45] P.A.G. O´hare, L. Basile, E.H. Appelman, Thermochemistry of inorganic sulfur compounds V. Peroxymonosulfate revisited: standard molar enthalpies of formation of $KHSO_5^-H_2O$, $KHSO_5$, and HSO_5^-, J. Chem. Thermodynamics, 17 (1985) 473–480.

[46] J.A. Khan, X. He, N.S. Shah, H.M. Khan, E. Hapeshi, D. Fatta-Kassinos, D.D. Dionysiou, Kinetic and mechanism investigation on the photochemical degradation of atrazine with activated H_2O_2, $S_2O_8^{2-}$ and HSO_5^-, Chem. Eng. J., 252 (2014) 393–403.

[47] B.G. Pollet, J.P. Lorimer, J.-Y. Hihn, S.S. Phull, T.J. Mason, D.J. Walton, The effect of ultrasound upon the oxidation of thiosulphate on stainless steel and platinum electrodes, Ultrason. Sonochem., 9 (2002) 267–274.

[48] X. Zhu, M. Tong, S. Shi, H. Zhao, J. Ni, Essential explanation of the strong mineralization performance of boron-doped diamond electrodes, Environ. Sci. Technol., 42 (2008) 4914–4920.

[49] K. Serrano, P.A. Michaud, C. Comninellis, A. Savall, Electrochemical preparation of peroxodisulfuric acid using boron doped diamond thin film electrodes, Electrochim. Acta, 48 (2002) 431–436.

[50] G. Zhao, X. Cui, M. Liu, P. Li, Y. Zhang, T. Cao, H. Li, Y. Lei, L. Liu, D. Li, Electrochemical degradation of refractory pollutant using a novel microstructured TiO_2 nanotubes/Sb-doped SnO_2 electrode, Environ. Sci. Technol., 43 (2009) 1480–1486.

[51] G. Zhao, P. Li, F. Nong, M. Li, J. Gao, D. Li, Construction and high performance of a novel modified boron-doped diamond film electrode endowed with superior electrocatalysis, J. Phys. Chem. C, 114 (2010) 5906–5913.

[52] J. Fan, G. Zhao, H. Zhao, S. Chai, T. Cao, Fabrication and application of mesoporous Sb-doped SnO_2 electrode with high specific surface in electrochemical degradation of ketoprofen, Electrochim. Acta, 94 (2013) 21–29.

[53] W.S. Chen, J.S. Liang, Decomposition of nitrotoluenes from trinitrotoluene manufacturing process by electro-Fenton oxidation, Chemosphere, 72 (2008) 601–607.

[54] W.S. Chen, S.Z. Lin, Destruction of nitrotoluenes in wastewater by electro-Fenton oxidation, J. Hazard. Mater., 168 (2009) 1562–1568.

[55] D. Tromans, Temperature and pressure dependent solubility of oxygen in water: a thermodynamic analysis, Hydrometallurgy, 48 (1998) 327–342.

[56] H. Ren, M.P. Humbert, C.A. Menning, J.G. Chen, Y. Shu, U.G. Singh, W.C. Cheng, Inhibition of coking and CO poisoning of Pt catalysts by the formation of Au/Pt bimetallic surfaces, Appl. Catal. A: General, 375 (2010) 303–309.

[57] T.V. Reshetenko, K. Bethune, M.A. Rubio. R. Rocheleau, Study of low concentration CO poisoning of Pt anode in a proton exchange membrane fuel cell using spatial electrochemical impedance spectroscopy, J. Power Sources, 269 (2014) 344–362.

[58] K. Govindan, M. Raja, M. Noel, E.J. James, Degradation of pentachlorophenol by hydroxyl radicals and sulfate radicals using electrochemical activation of peroxomonosulfate, peroxodisulfate and hydrogen peroxide, J. Hazard. Mater., 272 (2014) 42–51.

[59] S.Z. Wang, J.L. Wang, Degradation of carbamazepine by radiation-induced activation of peroxymonosulfate, Chem. Eng. J., 336 (2018) 595–601.