CONTENTS

The 5th International Symposium on Environmental Economy and Technology (ISEET-2012)

Sensitive voltammetric and amperometric responses of respiratory toxins at hemin-adsorbed carbon-felt
Yasushi Hasebe, Yue Wang ................................................................. 1055

Destruction of 4-phenolsulfonic acid in water by anodic contact glow discharge electrolysis
Haiming Yang, Baigang An, Shaoyan Wang, Lixiang Li, Wenjie Jin, Lihua Li ................................................................. 1063

Nitrous oxide emissions from black soils with different pH
Lianfeng Wang, Huachao Du, Zuoqiang Han, Xilin Zhang ................................................................. 1071

Coulometric determination of dissolved hydrogen with a multielectrolytic modified carbon felt
electrode-based sensor
Hiroaki Matsuura, Yosuke Yamawaki, Kosuke Sasaki, Shunichi Uchiyama ................................................................. 1077

Palladium-phosphinous acid complexes catalyzed Suzuki cross-coupling reaction of heteroaryl bromides
with phenylboronic acid in water/alcoholic solvents
Ben Li, Cuiping Wang, Guang Chen, Zhiqiang Zhang ................................................................. 1083

Aquatic environment

Organic matter produced by algae and cyanobacteria: Quantitative and qualitative characterization
Maud Leloup, Rudy Nicolau, Virginie Pallier, Claude Yéprémian, Geneviève Feuillade-Cathalifa ................................................................. 1089

Effects of environmental factors on sulfamethoxazole photodegradation under simulated sunlight irradiation:
Kinetics and mechanism
Junfeng Niu, Lilian Zhang, Yang Li, Jinbo Zhao, Sidan Lv, Keqing Xiao ................................................................. 1098

Irrigation system and land use effect on surface water quality in river, at lake Dianchi, Yunnan, China
Takashi Tanaka, Takahiro Sato, Kazuo Watanabe, Ying Wang, Dan Yang, Hiromu Inoue, Kunzhi Li, Tatsuya Inamura ................................................................. 1107

Temporal and spatial changes in nutrients and chlorophyll-α in a shallow lake, Lake Chaohu, China:
An 11-year investigation
Libiao Yang, Kun Lei, Wei Meng, Guo Fu, Weijin Yan ................................................................. 1117

Phosphorus speciation in the sediment profile of Lake Erhai, southwestern China: Fractionation and 31P NMR
Runyu Zhang, Liying Wang, Fengchang Wu, Baonan Song ................................................................. 1124

Effect of ammonium on nitrous oxide emission during denitrification with different electron donors
Guangxue Wu, Xiaofeng Zhai, Chengai Jiang, Yuntao Guan ................................................................. 1131

Adsorption of 2-mercaptobenzothiazole from aqueous solution by organo-bentonite
Ping Jing, Meifang Hou, Ping Zhao, Xiaoyan Tang, Hongfu Wan ................................................................. 1139

Differences in rheological and fractal properties of conditioned and raw sewage sludge
Hui Jin, Yili Wang, Ting Li, Yujing Dong, Junqing Li ................................................................. 1145

Competitive sorption between 17β-ethinyl estradiol and bisphenol A/ 4-n-nonylphenol by soils
Jianzhong Li, Lu Jiang, Xi Xiang, Shuang Xu, Rou Wen, Xiang Liu ................................................................. 1154

Determination of estrogens and estrogenic activities in water from three rivers in Tianjin, China
Kaifeng Rao, Bingli Lei, Na Li, Mei Ma, Zijian Wang ................................................................. 1164

Terrestrial environment

Adsorption and desorption characteristics of diphenylarsenicals in two contrasting soils
Anan Wang, Shixin Li, Ying Teng, Wuxin Liu, Longhua Wu, Haibo Zhang, Yujuan Huang, Yongming Luo, Peter Christie ................................................................. 1172

Evaluation of remediation process with soapberry derived saponin for removal of heavy metals from
contaminated soils in Hai-Pu, Taiwan
Jyoti Prakash Maity, Yuh Ming Huang, Cheng-Wei Fan, Chien-Cheng Chen, Chun-Yi Li, Chun-Mei Hsu, Young-Fo Chang, Ching-I Wu, Chen-Yen Chen, Jiin-Shuh Jean ................................................................. 1180
Environmental biology

Vertical diversity of sediment bacterial communities in two different trophic states of the eutrophic Lake Taihu, China (Cover story)
Keqiang Shao, Guang Gao, Yongping Wang, Xiangming Tang, Boqiang Qin ................................................................. 1186
Abundance and diversity of ammonia-oxidizing archaea in response to various habitats in Pearl River Delta of China, a subtropical maritime zone
Zhixin Li, Wenbiao Jin, Zhaoyun Liang, Yangyang Yue, Junhong Lv ................................................................. 1195

Environmental catalysis and materials

Effect of pretreatment on Pd/Al2O3 catalyst for catalytic oxidation of α-xylene at low temperature
Shaoyong Huang, Changbin Zhang, Hong He ................................................................. 1206
Efficient visible light photo-Fenton-like degradation of organic pollutants using in situ surface-modified BiFeO3 as a catalyst
Junjian An, Lihua Zhu, Yingying Zhang, Heqing Tang ................................................................. 1213
Basic properties of sintering dust from iron and steel plant and potassium recovery
Guang Zhan, Zhancheng Guo ................................................................. 1226
Degradation of direct azo dye by Cucurbita pepo free and immobilized peroxidase
Nabila Boucherit, Mahmoud Abouseoud, Lydia Adour ................................................................. 1235

Environmental analytical methods

Determination of paraquat in water samples using a sensitive fluorescent probe titration method
Feihu Yao, Hailong Liu, Guangquan Wang, Liming Du, Xiaofen Yin, Yunlong Fu ................................................................. 1245
Chemically modified silica gel with 1-f4-[(2-hydroxy-benzylidene)amino]phenylgethanone: Synthesis, characterization and application as an efficient and reusable solid phase extractant for selective removal of Zn(II) from mycorrhizal treated fly-ash samples
R. K. Sharma, Aditi Puri, Anil Kumar, Alok Adholeya ................................................................. 1252

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Destruction of 4-phenolsulfonic acid in water by anodic contact glow discharge electrolysis

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Abstract
Destruction of 4-phenolsulfonic acid (4-PSA) in water was carried out using anodic contact glow discharge electrolysis. Accompanying the decay of 4-PSA, the amount of total organic carbon (TOC) in water correspondingly decreased, while the sulfonate group of 4-PSA was released as sulfate ion. Oxalate and formate were obtained as minor by-products. Additionally, phenol, 1,4-hydroquinone, hydroxyquinol and 1,4-benzoquinone were detected as primary intermediates in the initial stages of decomposition of 4-PSA. A reaction pathway involving successive attacks of hydroxyl and hydrogen radicals was assumed on the basis of the observed products and kinetics. It was revealed that the decay of both 4-PSA and TOC obeyed a first-order rate law. The effects of different Fe ions and initial concentrations of 4-PSA on the degradation rate were investigated. It was found that the presence of Fe ions could increase the degradation rate of 4-PSA, while initial concentrations lower than 80 mmol/L had no significant effect on kinetic behaviour. The disappearance rate of 4-PSA was significantly affected by pH.

Key words: 4-phenolsulfonic acid; destruction; contact glow discharge electrolysis; first-order rate law; Fenton reaction
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Introduction
The continuing emission of hazardous organic compounds in wastewaters and drainage as a result of industrial and agricultural human activities is of grave environmental concern (Marye et al., 1993; Ollis et al., 1993). 4-Phenolsulfonic acid (4-PSA) is an important intermediate/component of detergents, medicines, agrochemicals, colouring agents and surfactants. In addition, the compound was used in electrolytic galvanizing baths for tin plate production and in electrolytic refining for the purification of crude tin (Pujara et al., 2007). 4-PSA is found in most global groundwater sources, due in part to its high water solubility. Nowadays, it is well known that 4-PSA is a highly toxic compound and it has been classified as a “priority pollutant” by the U.S. Environmental Protection Agency since 1976 (Luise et al., 2000). Considering the toxicity of 4-PSA toward microbiological processes, efforts aimed at developing advanced oxidation processes (AOPs) for the destruction of 4-PSA in water sources are underway. TiO₂ (Pujara et al., 2007) and Fenton reactions using Fe²⁺/H₂O₂ systems (Qu, 2002) have previously been employed to degrade 4-PSA. In each case, it has been postulated that hydroxyl radical generated under the reaction conditions might play a crucial role as a potent oxidizing species.

In a typical electrolysis process – where a thin wire anode is in contact with the electrolyte surface – if the applied voltage is sufficiently high, one can observe the formation of a sheath of vapour in the form of a glow discharge around the electrode through which current flows, even at atmospheric pressure. This phenomenon is specifically termed contact glow discharge electrolysis (CGDE) (Hickling and Ingram, 1964; Hickling, 1971; Sengupt and Singh, 1991; Gangal et al., 2009). In anodic CGDE processes, the ionic species in the gaseous discharge are accelerated due to the steep potential gradient, and pass into the solution with a high enough energy distribution to bring about chemical changes in the solution. In the reaction zone, ionized and/or activated water molecules resulting from the collisions of bombarding ions may possibly react with other water molecules to produce both hydroxyl and hydrogen radical species. One possible pathway would involve reaction of two hydrogen radicals, resulting in the formation of hydrogen. Hydrogen peroxide, an oxidant, is one of the main products of anodic CGDE in a solution of inert electrolytes, and is formed by the recombination of two hydroxyl radicals during the process (Hickling, 1971;
Mazzocchin et al., 1973; Almubarak and Wood, 1977; Bullock et al., 1980; Sengupta and Singh, 1994; Sengupta et al., 1998a, 1998b; Gangothi et al., 2010).

On the basis of a series of studies on degradation of aromatic compounds by anodic CGDE, it was assumed that hydroxyl radicals would act as the primary species responsible for breakdown of the benzene nucleus (Tezuka and Iwasaki, 1997, 1999; Tezuka et al., 2001; Amano et al., 2004; Amano and Tezuka, 2006; Yang et al., 2009; Yang and Tezuka, 2011a, 2011b). Since anodic CGDE has proven to be one of the promising AOPs (Gao et al., 2003a, 2003b; Wang and Jiang, 2008), it appears opportune to acquire practical knowledge of the aqueous degradation of 4-PSA induced by anodic CGDE. In the present article, the comprehensive destruction of 4-PSA dissolved in a neutral phosphate buffer solution by anodic CGDE is described in terms of both mechanistic and kinetic aspects.

1 Experimental

The reaction apparatus for the anodic CGDE experiments is illustrated in Fig. 1. A cylindrical glass cell was employed. The anode, a platinum wire of 0.6 mm diameter sealed within a glass tube, was introduced into the cell. The cathode employed was a stainless-steel plate (35 mm × 10 mm × 2 mm) and placed in another glass tube, with its lower end plugged by a sintered glass disk of medium porosity, and immersed in 70 mL of an aqueous phosphate solution (8.7 mmol/L potassium dihydrogenphosphate and 30.4 mmol/L disodium hydrogenphosphate, pH = 7.4) or 40 mmol/L sodium sulfate solution.

Because Fe ions precipitated on addition to the phosphate solution, sodium sulfate solution was employed in place of phosphate solution to investigate the effects of Fe ions on the disappearance rate of 4-PSA. For the source of Fe ions, either ferrous or ferric sulfate was used.

A voltage of 500 V from a DC power supplier was applied between the electrodes. The depth of the discharge electrode (anode) in the solution was ca. 1 mm, and adjusted so that the average current could be maintained at approximately 70 mA. The total electricity passed during CGDE was measured by a digital coulomb-meter. During CGDE, the solution was gently stirred with a Teflon-coated magnetic bar and the cell was placed in an ice-water bath to hold the temperature of the bulk solution at about 20°C.

Reagent-grade 4-PSA was used without further purification. Identities of the products, as well as unreacted starting material, were determined by high-performance liquid chromatography (HPLC; Shimadzu LC10A). For the quantification of 4-PSA, a GL Sciences Inertsil ODS-4V column (5 mm, 4.6 × 150 mm) connected to an ultraviolet (UV)-Visible detector (Shimadzu SPD-M10A) was used; the eluent used was 0.1 mol/L ammonium dihydrogenphosphate, adjusted to pH 2.5 by KOH. A Shodex Ionpak KC-811 column (8 × 300 mm) with an eluent composed of 0.5 mmol/L and 15 mmol/L perchloric acid + acetomitrile (85:15, V/V) was used together with a conductivity detector (Shimadzu CDD-6A) for the analysis of formate and oxalate. In addition, a HAMILTON PRP-X100 column (10 mm, 4.1 × 150 mm) with an eluent of 4 mmol/L p-hydroxybenzoic acid (+2.5% methanol) was used together with a conductivity detector for the analysis of sulfate. The amount of total organic carbon (TOC) in the solution was measured by a TOC analyser (Shimadzu TOC-VF). In order to identify the minor intermediate products, the reaction solution after 20 min of CGDE was extracted with ethyl acetate. The extract was dried with anhydrous sodium sulfate, filtered, and concentrated by rotary evaporation at 35°C. Then, the sample was analysed by gas chromatography-mass spectrometry using a Shimadzu GC17A/QP5050A GC/MS combination. The GC17A was equipped with a low polarity (5% phenylsiloxane, 95% methyl-siloxane) capillary column (30 m length, 0.25 mm ID, 0.25 μm film thickness, 10 m length guard column). The injector temperature was maintained at 280°C and the transfer interface at 280°C. The oven temperature was ramped from 60°C to 280°C at a rate of 10°C/min. The QP5050A is an EI quadrupole-based mass spectrometer with a maximum scan range of 900 amu and ionizing electron energy of 70 eV. For the determination of hydrogen peroxide in the absence of 4-PSA, titration with permanganate was executed; iodometry using sodium iodide in 2-propanol was adopted for the fractional detection of hydrogen peroxide in solutions containing 4-PSA, where iodine liberated through the redox reaction involv-
ing hydrogen peroxide was back-titrated with thiosulfate.

2 Results and discussions

2.1 Decomposition of 4-PSA

When anodic CGDE was applied to an aqueous phosphate solution containing 4-PSA (an initial concentration of 5.0 mmol/L, corresponding to 360 mg/L of TOC, as shown in Fig. 2), both the 4-PSA and TOC concentrations in the solution were found to decrease over the course of the reaction. It should be noted that the decrease in TOC corresponds to the formation of inorganic carbon. In addition, it was also observed that the sulfonate group of 4-PSA was liberated as sulfate ion.

The course of decomposition of 4-PSA by anodic CGDE is depicted in Fig. 2; the variations in concentrations of 4-PSA, TOC, and sulfate ions as a function of discharge time are indicated. At the beginning of reaction, the concentrations of both 4-PSA and TOC decreased monotonously with discharge time. After 240 min, 4-PSA was completely consumed and most of the TOC had disappeared. This observation indicates that anodic CGDE is effective in the conversion of carbon atoms of the benzene nucleus to IC, which may then exist in solution as hydrogencarbonate, or as carbon dioxide in the gas phase. Furthermore, the sulfonic acid/sulfonate functionality of 4-PSA was almost quantitatively liberated as the corresponding sulfate ion. Peroxodisulfate (persulfate) ion was not detected during degradation of 4-PSA, an observation in good agreement with the CGDE study of a dilute sulfuric acid solution (Tezuka, 1993; Amano et al., 2004). The power consumption of CGDE was 35 W and the energy efficiency for 4-PSA degradation was 1.63 g kWh calculated by the equation employed by other researchers (Malik M A, 2010). And these results were better than those observed in a similar reaction using UV (Pujara et al., 2007), or at least comparable to them.

The gap between the decay curves of 4-PSA and TOC is indicative of the presence of organic intermediate products. In the reaction mixture, various organic substances possessing carboxylate functionalities were detected; however, because of their lability and low concentrations in solution, the identities of most of these species have not been determined. Only oxalate and formate carboxylate species were formed in amounts worth quantifying. The variations in oxalate/formate concentration as a function of discharge time are shown in Fig. 3. The concentration of oxalate culminated at 60 min, and then decreased gradually, whereas formate concentration rose in the starting 210 min, and then held steady for the duration of the reaction. It should be noted that oxalate was formed more rapidly than formate, while the increase in formate concentration appeared relatively stable under the conditions. However, it seems improbable that formate might result from the decomposition of oxalate, since formate is not obtained in the CGDE reaction of oxalate alone (Amano and Tezuka, 2006).

The elemental yields of the aforementioned products, namely inorganic carbon, oxalate, formate, and SO$_4^{2-}$, as well as the conversion of 4-PSA, are tabulated in Table 1. The yield was defined as the percentage of moles of a certain element (C or SO$_4^{2-}$) in each product per initial number of moles of that element in the starting material. The yields of undetermined intermediates, specified as not determined, were estimated so as to balance the sum of yields with respect to 4-PSA conversion. Particularly in the earlier stage of a run, not determined was noticeable, but steadily lowered as the conversion went up. It was ascertained that not determined products associated with SO$_4^{2-}$ and C declined to 0% and 3%, respectively, at a discharge time of 240 min.

2.2 Intermediates in anodic CGDE of 4-PSA

It is important to determine intermediate identities to aid elucidation of the degradation mechanism of 4-PSA. Emphasis was placed on the search for primary products, which may be formed only in the initial stages of de-

![Fig. 2](image1.jpg) Decomposition of 4-PSA ($C_0$: 5.0 mmol/L) by anodic CGDE.

![Fig. 3](image2.jpg) Carboxylates from anodic CGDE of 4-PSA ($C_0$: 5.0 mmol/L).
Table 1  Elemental yields of products from anodic CGDE of 4-PSA at initial concentration of 5.0 mmol/L

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>4-PSA conversion (%)</th>
<th>Sulfur</th>
<th>Product yield (%)</th>
<th>Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>SO(_4^{2-})</td>
<td>Not determined</td>
<td>Formate</td>
</tr>
<tr>
<td>30</td>
<td>48</td>
<td>38</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>60</td>
<td>71</td>
<td>62</td>
<td>9</td>
<td>4</td>
</tr>
<tr>
<td>90</td>
<td>84</td>
<td>82</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>120</td>
<td>91</td>
<td>90</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>150</td>
<td>96</td>
<td>95</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>180</td>
<td>99</td>
<td>97</td>
<td>1</td>
<td>6</td>
</tr>
<tr>
<td>210</td>
<td>100</td>
<td>100</td>
<td>0</td>
<td>7</td>
</tr>
<tr>
<td>240</td>
<td>100</td>
<td>100</td>
<td>0</td>
<td>7</td>
</tr>
</tbody>
</table>

composition, in the reaction solution at discharge times of 10–30 min. As a result of the intermediate instability under the reaction conditions, very few species could be satisfactorily identified by HPLC (Fig. 4) and GC-MS analysis (Fig. 5). 1,4-Hydroquinone (2), 1,4-benzoquinone (3), hydroxyquinol (4), and phenol (1) were detected as primary intermediates. Compounds (2)–(4) can be described as the products formed by the attack of a hydroxyl radical at the para-position of the phenolic OH group in 4-PSA; these results confirmed that the species responsible for oxidation in aqueous media by anodic CGDE was in fact the hydroxyl radical (Sengupta and Singh, 1994; Sengupta et al., 1995, 1998a, 1998b; Gangal et al., 2010). Phenol (1) appears to be the result of reduction of 4-PSA by a hydrogen radical, generated by anodic CGDE. The possible formation pathways of (1)–(4) are depicted in Scheme 1.

Based on a survey of the intermediates, it is hypothesized that degradation of aqueous 4-PSA by anodic CGDE proceeds in a successive manner as follows: (I) the reduction of 4-PSA to form phenol (1) is accompanied by hydroxylation of the benzene nucleus, giving rise to (2) and (3); (II) oxidative ring cleavage leads to the formation of carboxylates–oxalate and formate; and (III) mineralization to IC and SO\(_4^{2-}\). The desulfurization of 4-PSA should take place through all the steps mentioned above.

2.3 Kinetics of 4-PSA decomposition

Since the decay curves of 4-PSA and TOC (Fig. 2) appeared to be exponential during the reaction, it was decided to apply the data associated with this decay to the integral formula for the first-order rate law (Eq. (1)):

\[
\ln(C_0/C) = kt
\]

where, \( C \) and \( C_0 \), denote the concentration of 4-PSA or TOC at the given reaction time and that at reaction time \( t = 0 \), respectively, \( k \) represents the rate constant.

For each set of data, a straight line with good correlation was obtained (Fig. 6). This result implies that both 4-PSA and TOC reacted in accordance with the first-order rate law. The apparent rate constants, \( k_{4\text{PSA}} \) and \( k_{\text{TOC}} \), for the decay of 4-PSA and TOC were calculated from the slope of each line to be \( 2.13 \times 10^{-2} \text{ min}^{-1} \) \( (R^2 = 0.996) \) and \( 0.72 \times 10^{-2} \text{ min}^{-1} \) \( (R^2 = 0.996) \), respectively.

The main chemical reactions in the solution during anodic CGDE in the absence of Fe ions and organics are described as follows (Hickling, 1971; Gao et al., 2001, 2006; Gong et al., 2008):

\[
\text{H}_2\text{O} \xrightarrow{\text{CGDE}} \cdot\text{H} + \cdot\text{OH} \quad (2)
\]

\[
\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2 \quad (3)
\]

\[
\cdot\text{H} + \cdot\text{H} \rightarrow \text{H}_2 \quad (4)
\]

\[
2\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \quad (5)
\]
Among the oxidants formed during anodic CGDE (Reactions (2)–(5)), the hydroxyl radical was the strongest and thus was proposed to be the main species responsible for the degradation of organics, as shown in Reaction (6) (Tezuka and Iwasaki, 1997, 1999, 2001; Amano et al., 2004; Amano and Tezuka, 2006; Yang et al., 2009; Yang and Tezuka, 2011a, 2011b).

**Organics + ·OH → Product**  \hspace{1cm} (6)

In addition, hydrogen peroxide, a much weaker oxidant, was simultaneously produced, consuming two hydroxyl radicals, as shown in Reaction (3). In the first 15 min the concentration of hydrogen peroxide increased steadily to 4.41 mmol/L at a rate of $4.9 \times 10^{-3}$ mmol/sec without 4-PSA. Following this, the rate decreased slowly with increasing reaction time. This result might be explained by the instability of hydrogen peroxide, as shown in Reaction (7). When the initial concentration of 4-PSA was set to 5 mmol/L, the rate of hydrogen peroxide formation decreased to $3.5 \times 10^{-3}$ mmol/sec in the first 15 min, with a measured concentration of 3.24 mmol/L at 15 min. When the destruction of 4-PSA was allowed to continue for more than 15 min, the color of the reaction solution became deep brown. Thus, the concentration of hydrogen peroxide was difficult to obtain by iodometry.

With regard to hydroxyl radicals generated from hydrogen peroxide, Fe ions could possibly affect this generation reaction via the Fenton reaction. The effect of Fe ions on the disappearance rate of 4-PSA was investigated by adding different types and concentrations of Fe ions to the electrolytic solution. In order to avoid the formation of Fe ion precipitates, sodium sulfate solution was employed in place of phosphate solution. The experimental results are listed in Table 2.

According to the results, the disappearance of 4-PSA in sodium sulfate solution also followed a first-order rate law; the disappearance rate constants in two experimental runs of electrolytic solutions without Fe additives were in agreement ($2.13 \times 10^{-2}$ min$^{-1}$ in phosphate solution, 2.15 $\times 10^{-2}$ min$^{-1}$ in sodium sulfate solution). Remarkably, the disappearance rate constant was significantly enhanced up-
in Table 3. This means that a greater amount of 4-PSA could be removed from solutions with higher initial concentrations. According to other studies (Tomizawa and Tezuka, 2006, 2007), when the initial 4-PSA concentration is high enough (above 80 mmol/L), the kinetics for the decomposition of 4-PSA might be shifted from a first-order to a zero-order rate law. A thorough investigation of this change in initial concentration on the impact of 4-PSA degradation is in progress. The apparent rate constants for the disappearance of 4-PSA decreased significantly from $2.15 \times 10^{-2}$, $1.84 \times 10^{-2}$ to $1.37 \times 10^{-2}$ with a rise in pH from 7.4, 9.4 to 12.1, respectively. This may be interpreted by invoking the fact that the reduction potential of hydroxyl radicals declines with the basicity of the solution (Buxton et al., 1988).

### 3 Conclusions

The exposure of 4-PSA in aqueous solution to anodic CGDE promoted exhaustive breakdown of the compound, with most of the TOC eventually converted to IC. The sulfonate group of 4-PSA was quantitatively liberated as the corresponding sulfate ion. The initial reaction stages are hypothesized to involve the attack of a hydroxyl radical at the phenolic para-position, as well as 4-PSA reduction by a hydrogen radical. The experimental results could be rationalized by assuming that the decomposition pathway of 4-PSA cascades through a sequence of hydrogenation events, resulting in phenol, and subsequent hydroxylation of the benzene nucleus to provide the corresponding hydroquinones and benzoquinones. Subsequent oxidative ring cleavage would lead to the formation of formate and oxalate species, followed ultimately by mineralization to inorganic carbon, $\text{H}_2\text{O}$, and $\text{SO}_4^{2-}$. When the initial concentration of 4-PSA was lower than 80 mmol/L, consumption of both 4-PSA and TOC obeyed a first-order rate law. Both $\text{Fe}^{2+}$ and $\text{Fe}^{3+}$ ions were shown to enhance the disappearance rate constant of 4-PSA due to the catalytic action of $\text{Fe}^{2+}$ in hydroxyl radical formation from hydrogen peroxide via the Fenton reaction.

### Acknowledgments

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### Table 2

<table>
<thead>
<tr>
<th>Fe ion added (mmol/L)</th>
<th>$k_{\text{dPSA}}$ ($\times 10^{-2}$ min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$^{2+}$ 0.00</td>
<td>2.15</td>
<td>0.996</td>
</tr>
<tr>
<td>Fe$^{2+}$ 0.25</td>
<td>3.23</td>
<td>0.997</td>
</tr>
<tr>
<td>Fe$^{2+}$ 0.50</td>
<td>3.31</td>
<td>0.996</td>
</tr>
<tr>
<td>Fe$^{2+}$ 1.00</td>
<td>3.38</td>
<td>0.998</td>
</tr>
<tr>
<td>Fe$^{2+}$ 2.00</td>
<td>3.41</td>
<td>0.997</td>
</tr>
<tr>
<td>Fe$^{3+}$ 2.00$^{a}$</td>
<td>3.15</td>
<td>0.998</td>
</tr>
<tr>
<td>Fe$^{3+}$ 4.00</td>
<td>3.40</td>
<td>0.996</td>
</tr>
</tbody>
</table>

$C_0$: 5.0 mmol/L.

on addition of Fe$^{2+}$ ions; however, no significant increase was observed by increasing the Fe$^{2+}$ ion concentration. These results can be explained by chemical reactions of Fe$^{2+}$ ions during anodic CGDE (Reactions (8)–(10)) (Davies and Hickling, 1952, 1958; Gao et al., 2001, 2003, 2006; Tomizawa and Tezuka, 2006, 2007; Gong et al., 2008):

\[
\begin{align*}
\text{H}_2\text{O}_2 & \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \quad (7) \\
\text{Fe}^{2+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH} \quad (8) \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{HO}_2^- \quad (9) \\
\text{Fe}^{3+} + \cdot\text{OH} & \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (10) \\
\text{Fe}^{3+} + \text{OH}_2^- & \rightarrow \text{Fe}^{2+} + \text{H}^+ + \text{O}_2 \quad (11) \\
\text{Fe}^{3+} + \cdot\text{H} & \rightarrow \text{Fe}^{2+} + \text{H}^+ \quad (12)
\end{align*}
\]

The Fe$^{2+}$ ion is thought to play the role of catalyst for the regeneration of hydroxyl radicals from hydrogen peroxide in solution, as shown in Reactions (8)–(9). The observed increase in the disappearance rate constant of 4-PSA by addition of Fe$^{2+}$ ion supports the idea that hydroxyl radicals are probably the main species responsible for 4-PSA degradation during anodic CGDE. Upon further Fe$^{2+}$ addition, it is thought that Fe$^{2+}$ functions as a consumer of hydroxyl radicals, according to Reaction (10). When Fe$^{3+}$ was added in place of Fe$^{2+}$, an increase in the disappearance rate constant of 4-PSA could also be observed ($C_0$: 2.00 mmol/L Fe$^{3+}$; $k = 3.15 \times 10^{-2}$ min$^{-1}$), which was a little less than that of 2.00 mmol/L Fe$^{2+}$ ion (3.40 $\times 10^{-2}$ min$^{-1}$). This result can be rationalized by the formation of Fe$^{3+}$ ions from Fe$^{2+}$ ions through reduction reactions, as shown in Reactions (9), (11) and (12); subsequent hydroxyl radical regeneration would then be able to occur via the Fenton reaction, using catalytic Fe. In these processes, the Fe$^{3+}$ ion was not a catalytic species, but a precursor of Fe$^{2+}$ ion. With this in mind, the experimental results mentioned above could be understood.

In order to get further kinetic information, the degradation of 4-PSA at various initial concentrations up to 80 mmol/L was examined in detail. The consumption of 4-PSA for each initial concentration was also determined to follow the first-order rate law. In addition, the disappearance rate constants were nearly identical, as shown in Table 3.

### Table 3

<table>
<thead>
<tr>
<th>$C_0$ (mmol/L)</th>
<th>$k_{dPSA}$ ($\times 10^{-2}$ min$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.15</td>
<td>0.999</td>
</tr>
<tr>
<td>5</td>
<td>2.13</td>
<td>0.998</td>
</tr>
<tr>
<td>10</td>
<td>2.12</td>
<td>0.997</td>
</tr>
<tr>
<td>20</td>
<td>2.15</td>
<td>0.997</td>
</tr>
<tr>
<td>40</td>
<td>2.14</td>
<td>0.996</td>
</tr>
<tr>
<td>80</td>
<td>2.17</td>
<td>0.996</td>
</tr>
</tbody>
</table>

The exposure of 4-PSA in aqueous solution to anodic CGDE promoted exhaustive breakdown of the compound, with most of the TOC eventually converted to IC. The sulfonate group of 4-PSA was quantitatively liberated as the corresponding sulfate ion. The initial reaction stages are hypothesized to involve the attack of a hydroxyl radical at the phenolic para-position, as well as 4-PSA reduction by a hydrogen radical. The experimental results could be rationalized by assuming that the decomposition pathway of 4-PSA cascades through a sequence of hydrogenation events, resulting in phenol, and subsequent hydroxylation of the benzene nucleus to provide the corresponding hydroquinones and benzoquinones. Subsequent oxidative ring cleavage would lead to the formation of formate and oxalate species, followed ultimately by mineralization to inorganic carbon, $\text{H}_2\text{O}$, and $\text{SO}_4^{2-}$. When the initial concentration of 4-PSA was lower than 80 mmol/L, consumption of both 4-PSA and TOC obeyed a first-order rate law. Both Fe$^{2+}$ and Fe$^{3+}$ ions were shown to enhance the disappearance rate constant of 4-PSA due to the catalytic action of Fe$^{2+}$ in hydroxyl radical formation from hydrogen peroxide via the Fenton reaction.

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