

Electrochemical Degradation of Chlorsulfuron Herbicide from Water Solution Using Ti/IrO₂-Pt Anode

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ABSTRACT

Chlorsulfuron (ChS) which is a nonbiodegradable herbicide was effectively removed using an electrochemical method at the Ti/IrO₂-Pt anode. The influences of current density, initial ChS concentration, initial solution pH and different NaCl dosages on electrochemical degradation of ChS were investigated. HOCl formed during electrolysis and quickly generated •OH radicals would likely play an important role in the electrochemical degradation of ChS with the presence of NaCl. At current density of 20 mA·cm⁻², ChS concentration decreased from 1 mg·L⁻¹ to 0 mg·L⁻¹ after 10 min electrolysis with 0.2 g·L⁻¹ NaCl dosage. It was found that the ChS removal rate increased with increasing current density and the ChS degradation was similar at different initial pH values, which means that Ti/IrO₂-Pt anode can be used in a wide pH range. The electrochemical performance of Ti/IrO₂-Pt anode for degradation of ChS will not decrease after serviced for a long time. These results reveal that an electrochemical approach would be a novel treatment method for effective and rapid degradation of ChS herbicide from aqueous solution.

Keywords: Electrochemical Degradation; Chlorsulfuron; Herbicide; Sodium Chloride

1. Introduction

Increased concerns about the herbicides in water have arisen because of the danger they pose to aquatic life and to any kind of life in contact with the polluted water. These compounds are mostly recalcitrant (nonbiodegradable) and can persist for long periods of time [1]. Sulfonylurea herbicides were developed in the 1970s, and first commercialized for wheat and barley crops in 1982. Their broad spectrum of action with a low application dose has led to a rapid acceptance of these compounds. However, their high phytotoxicity and relatively high solubility make them potential contaminants of groundwaters [2,3]. Furthermore, sulfonylurea compounds which are used as herbicides for agriculture undergo decomposition into, among others, simpler sulfonamides. Sulfonamides are polar, amphoteric substances that are readily-soluble in water. For this reason, they possess high migrationability in the environment [4]. Chlorsulfuron (ChS) whose chemical structure is shown in **Figure 1**, is a systemic sulfonylurea herbicide for the selective pre- and post-emergence control of broad-leaved and grass weeds in cereal crops.

Technologies able to convert ChS to non-toxic compounds are desirable, because contamination of ground-

water and drinking water could not be excluded. Urgent needs exist also for detoxification procedures of herbicide wastes [5]. Previous research showed that conventional process cannot effectively decrease the sulfonylurea herbicides in the water, such as nature photolysis, sorption and hydrolytic degradation [6-9]. Some researchers focus on the photocatalytic degradation of various pesticides herbicides especially the sulfonylurea herbicides using the TiO₂ photocatalyst [3-5,10-14]. It has been proved that photocatalytic method is a good method for removal persistent and nonbiodegradable contaminants in the water. However, only photons with energies greater than the band-gap energy (ΔE) can result in the excitation of valence band (VB) electrons which then promote the possible reactions with organic pollutants [14], which means that it is difficult for efficient degradation of the compounds under the visible light. Moreover, the recombination of photo-generated electron

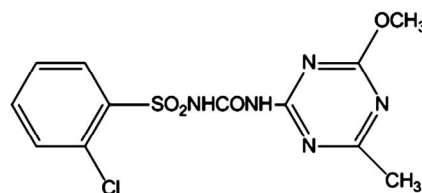


Figure 1. Structural formulae of Chlorsulfuron (ChS).

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and hole pairs is rapid without adding an oxidizing agent such as oxygen, which will decrease the photocatalytic reactivity. On the other hand, it is difficult for semiconductor photocatalyst powder to disperse and be recycled in aqueous solution, and the post-treatment recovery of the photocatalysts can be costly [15,16].

Electrochemistry is a promising method for the water and wastewater treatment and has received considerable attention recently. Electrochemical method applied in water treatment has been investigated by many researchers [17-23]. Toxic organics can be effectively oxidized by the electrochemical method [1,18,21,24-29], demonstrating that this approach may be feasible for sulfonylurea herbicides. Because of the simply in structure and operation, it is possible that the electrochemical method can be developed as a cost-effective technology for the treatment of aromatic pollutants [24]. The efficiency and selectivity of electrochemical oxidation of organic compounds are mainly effected by the nature of the electrodes that are used in the process [25,26]. Martinez *et al.* [1] have demonstrated that the removal of chlorbromuron urea herbicide achieved by the processes of electro-Fenton with a stainless steel anode is regarded as high degree of mineralization by the Fenton chemistry. However, ferricirons are required to be in the solution for the electro-Fenton reaction, and it is too sensitive to pH. Dimensionally stable anode (DSA), made by the deposition of a thin layer of metal oxides on a base metal, usually titanium, have been proved to be effective in organic degradation [18,24-26,29]. Nowadays, IrO₂-based type DSA has been proved to maintain good catalytic activity and dimensional stability for oxygen evolution reaction (OER) [21,30-32], and has excellent performance for degradation of organic compounds [24,25]. Electrode of Ti coated with IrO₂ and doped with Pt (Ti/IrO₂-Pt), as one of the practical anodes, has been widely used as anode in electrochemical treatment of contaminated water, which has good performance for degradation of organic compounds and long service life [24,25].

To our best knowledge, there is little information about the electrochemical degradation of ChS herbicide using Ti/IrO₂-Pt anode in previous studies [1,3,5,12]. The main aim of this study is to evaluate the electrochemical degradation of ChS herbicide using Ti/IrO₂-Pt anode. In order to investigate the ChS degradation effect and related reaction mechanisms, current density, initial ChS concentration, initial pH value of the solution, NaCl dosage, free radicals and oxidizing substance were measured, and the role of hypochlorous acid formed during electrolysis was also analyzed.

2. Materials and Methods

2.1. Materials

All chemicals were used as received without further pu-

rification. Chlorsulfuron (ChS) standard material (99.0%) used in this study was purchased from WAKO Pure Chemicals Ltd. Japan. 10 mg of ChS was dissolved in 10 mL of methanol (HPLC grade, WAKO Pure Chemicals Ltd. Japan) to be the stock solution, and stored in the dark at 4°C prior to use. They were diluted with Milli-Q water (resistivity 18.2 MΩ cm at 25°C) prepared with a water purification system (Purelite PRB-001A/002A) to the desired concentration required for each experiment and or analysis.

A simple cubic electrochemical cell was designed with a working volume of 100 mL. A DC potentiostat (GW INSTEK, GPS-183000) with a voltage range of 0 - 18 V and a current range of 0 - 3 A was employed as power supply. A Ti/IrO₂-Pt electrode (TohoTech Company, Japan) of 51.6 cm² (4.3 × 12 cm²) was used as the anode and a Ti electrode with the same area was used as the cathode, and a distance of 1 cm between the two electrodes was set. The immersed areas of the anode and cathode in the treated solution were the same at 25 cm².

2.2. Methods

In the present study, all of the electrolysis experiments were performed under galvanostatic control at different current densities of 10, 20, 40 and 60 mA·cm⁻², respectively. ChS solution with different initial concentration of 0.5, 1.0, 2.0 and 5.0 mg·L⁻¹ were prepared for electrolysis experiments. In all of the electrolysis processes, 1.5 g·L⁻¹ Na₂SO₄ was added into the solution in order to enhance the conductivity of the solution. Different initial pH (3, 7, 11) of ChS solution was also investigated. Various concentration of sodium chloride (0.1, 0.2, 0.5 g·L⁻¹) was added into the ChS solution to investigate the degradation performance, respectively. A 100 mL of synthetic ChS solution with different initial concentration prepared with the stock solution and distilled water was transferred into the electrochemical cell, and then the electrolysis began with different current density. Samples were taken from the electrochemical cell with different interval (15, 30, 60, 90, 120 min) for analysis.

2.3. Detection of Free Radicals Species

To investigate the production of free radicals species and oxidizing substance generated during the electrolysis, 0.005 mmol·L⁻¹ sulforhodamine B (SRB) was used for the electrolysis. Because the SRB rapidly reacts with the hydroxyl radicals, and the changes in absorbance, ΔA, corresponding to color intensity change of SRB can be measured at λ 565 nm, so the amount of free radicals and oxidizing substance produced can be determined indirectly [33]. Samples were taken at intervals of 1, 2, 5 min and absorbance of SRB was measured by UV-vis spectrophotometer (UV-1600, Shimadzu).

To confirm the free radicals species generated during the electrolysis, a photoluminescence (PL) technique was applied. Terephthalic acid as a probe molecule easily reacts with $\bullet\text{OH}$ to form highly fluorescent product, 2-hydroxyterephthalic acid. This technique has been widely used in radiation chemistry, biochemistry, and sonochemistry for the detection of $\bullet\text{OH}$ generated in water [34]. The intensity of the PL peak of 2-hydroxyterephthalic acid is in proportion to the amount of $\bullet\text{OH}$ radicals produced in water. The optimal concentration of terephthalic acid solution was about $5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ in a diluted NaOH aqueous solution ($2 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$) for the electrolysis. PL spectra of the generated 2-hydroxyterephthalic acid were measured on a fluorescence spectrophotometer (F-4500, Hitachi) at 425 nm excited by 315 nm light of 2-hydroxyterephthalic acid.

2.4. Analysis

The concentrations of ChS were determined by means of HPLC (Jusco, Japan) with an auto sampler model. The column was 5 C₁₈-AR-II, $4.6 \times 150 \text{ mm}$. The flow rate was $1.0 \text{ mL}\cdot\text{min}^{-1}$ and the injection volume was $50.0 \mu\text{L}$. The mobile phase was the mixture of methanol and water (1:1), whose pH was adjusted to 2.80 by using H_3PO_4 . The solution pH was measured by pH/iron meter (Mettler-Toledo AG 8603, Schwerzenbach, Switzerland). Surface morphology of anode was characterized by scanning electron microscope (SEM) (JSM-5600).

3. Results and Discussion

3.1. Effect of Current Density

At different current density of 10, 20, 40 and $60 \text{ mA}\cdot\text{cm}^{-2}$, ChS concentration decreased from $1.00 \text{ mg}\cdot\text{L}^{-1}$ to 0.32, 0.19, 0.02 and $0.00 \text{ mg}\cdot\text{L}^{-1}$, respectively after 120 min electrolysis (**Figure 2(a)**). The mechanism of ChS degradation at different current densities was demonstrated to be pseudo-first-order. The data showed that the rate of degradation of ChS increased with the increasing of current density. The rate constants are 0.0092 min^{-1} ($R^2 = 0.953$) at $10 \text{ mA}\cdot\text{cm}^{-2}$, 0.0137 min^{-1} ($R^2 = 0.998$) at $20 \text{ mA}\cdot\text{cm}^{-2}$, 0.0342 min^{-1} ($R^2 = 0.976$) at $40 \text{ mA}\cdot\text{cm}^{-2}$ and 0.0424 min^{-1} ($R^2 = 0.950$) at $60 \text{ mA}\cdot\text{cm}^{-2}$, respectively (**Figure 2(b)**). High current density is benefit for the electrochemical degradation of ChS, and complete ChS removal was achieved after 90 min electrolysis at current density of $60 \text{ mA}\cdot\text{cm}^{-2}$. As a higher current density enhances hydroxyl production, more ChS is likely to be oxidized. However, increasing the current density is an easy approach of improving the degradation reaction that is usually accompanied by a decrease in both the current efficiency and selectivity [35].

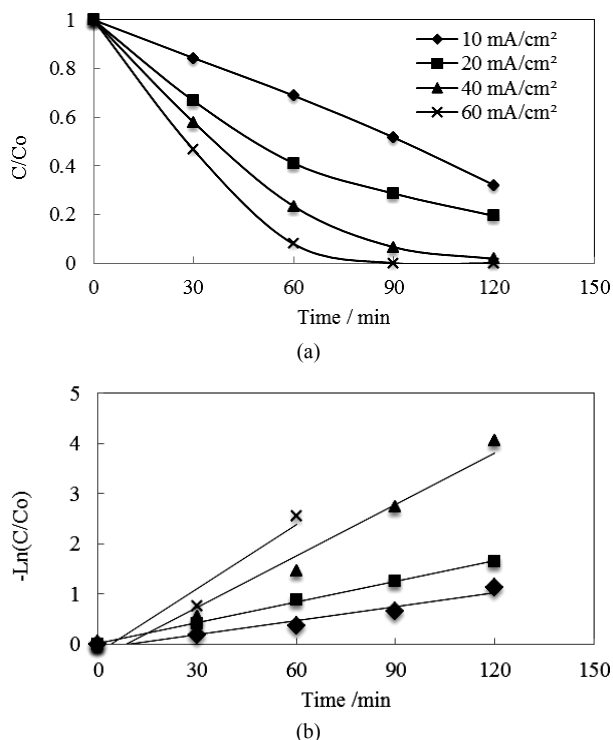


Figure 2. (a) Performance of ChS degradation with different current densities; (b) Pseudo-first-order kinetic plot using (a) data.

3.2. Influences of Initial ChS Concentration

The expected concentration of ChS in drinking water was less than $0.04 \text{ mg}\cdot\text{L}^{-1}$ [36]. However, the concentration of ChS could be greater than $1.5 \text{ mg}\cdot\text{L}^{-1}$ for the short-term or chronic exposure. In order to investigate the treatment efficiency on different initial concentrations of ChS, the electrochemical degradation of 0.50, 1.00, 2.00 and $5.00 \text{ mg}\cdot\text{L}^{-1}$ ChS solution were carried out at a current density of $20 \text{ mA}\cdot\text{cm}^{-2}$. It is obvious from **Figure 3(a)** that at a current density of $20 \text{ mA}\cdot\text{cm}^{-2}$ with $1.5 \text{ g}\cdot\text{L}^{-1}$ Na_2SO_4 as supporting electrolyte, the ChS concentration decreased from around 0.50, 1.00, 2.00 and $5.00 \text{ mg}\cdot\text{L}^{-1}$ to 0.06, 0.19, 0.31 and $1.01 \text{ mg}\cdot\text{L}^{-1}$ after 120 min electrolysis. And with 1 kWh of the electricity power consumption, about 73.3 mg, 135.0 mg, 281.7 mg, and 665.0 mg ChS can be removed, respectively. The removal rate was relatively high at high ChS concentration. Therefore, the Ti/IrO₂-Pt anode performed well for electrochemical degradation of low and high concentration ChS solutions with appropriate current density.

3.3. Effect of Initial pH

Three different initial pH values (3, 7 and 11) of ChS solution were set to investigate the effect on ChS electrochemical removal. As shown in **Figure 3(b)**, the similar trend of the ChS degradation was observed at the

current density of $20 \text{ mA}\cdot\text{cm}^{-2}$ with $1.5 \text{ g}\cdot\text{L}^{-1}$ Na_2SO_4 as supporting electrolyte. ChS concentration decreased from around $1.00 \text{ mg}\cdot\text{L}^{-1}$ to about $0.20 \text{ mg}\cdot\text{L}^{-1}$ after 120 min electrolysis, which revealed almost the same degradation efficiency. It means that the electrochemical degradation of ChS could be used in a large range of pH, and pH is not a limiting factor. As we know, some organic material degradation methods are sensitive to pH in the solution. Martínez *et al.* [1] used a stainless steel anode for removal chlorbromuron urea herbicide by electro-Fenton method. However, for the removal of the organic substrate depends on the pH of the aqueous solution as the pH influences the production of H_2O_2 and Fe^{2+} , the pH of the solution have to be lower than 5. Therefore, the electrochemical degradation method at Ti/IrO₂-Pt anode gives us another approach for the degradation of ChS solution with a wide pH range.

3.4. Effect of NaCl Dosages

The degradation efficiency of some organic materials was significantly enhanced with the presence of NaCl in some researchers [2,15,26]. In the present experiment, three different NaCl dosages of 0.1, 0.2 and $0.5 \text{ g}\cdot\text{L}^{-1}$ were added into the ChS solution for ChS electrochemical degradation. Meanwhile, $1.5 \text{ g}\cdot\text{L}^{-1}$ Na_2SO_4 was used as supporting electrolyte. As shown in the Figure 4(a),

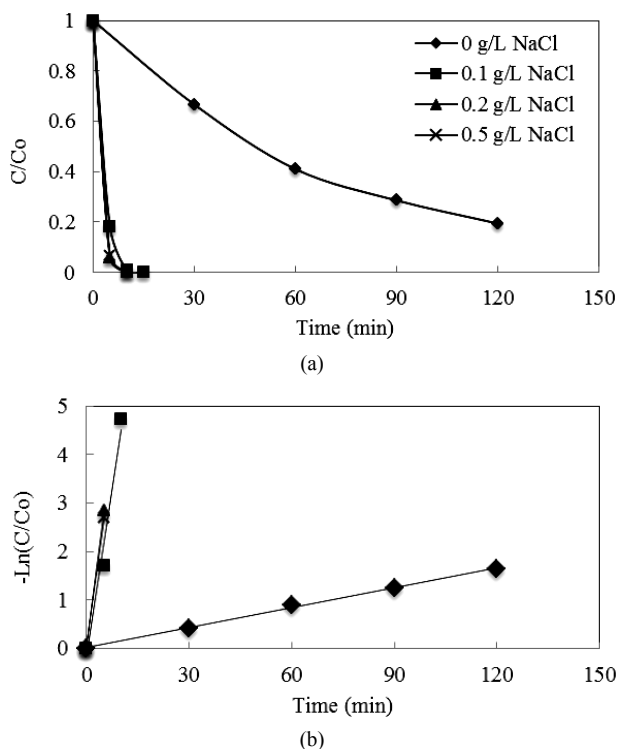


Figure 3. (a) Effect of initial concentration on the degradation efficiency; (b) Effect of initial pH on the removal of ChS.

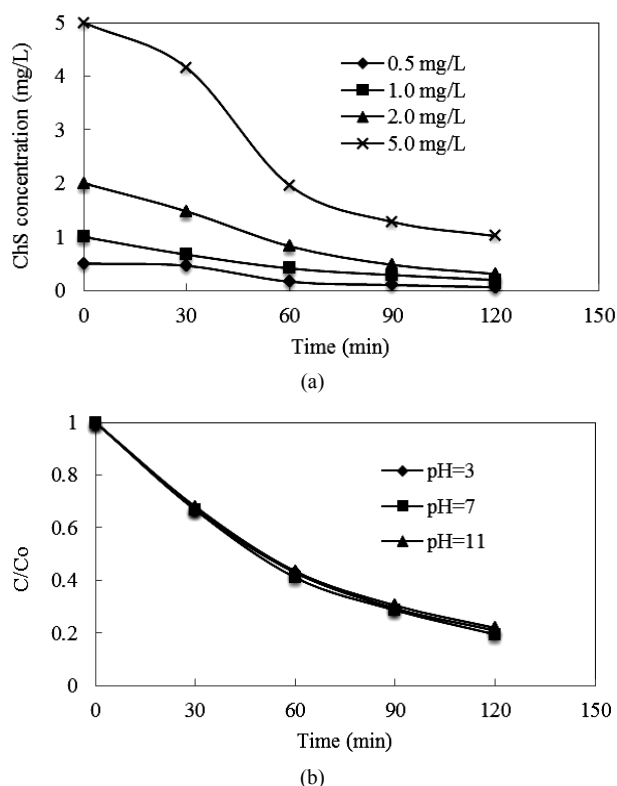
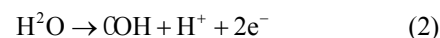
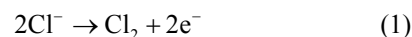


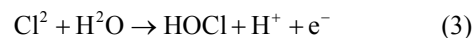
Figure 4. (a) Performance of ChS degradation with different NaCl dosages; (b) Pseudo-first-order kinetic plot using data from (a).

ChS concentration decreased sharply with the presence of NaCl, from around $1 \text{ mg}\cdot\text{L}^{-1}$ to 0.01 , 0.00 , $0.00 \text{ mg}\cdot\text{L}^{-1}$ with the presence of NaCl dosages of 0.1 , 0.2 , $0.5 \text{ g}\cdot\text{L}^{-1}$, respectively, at a current density of $20 \text{ mA}\cdot\text{cm}^{-2}$ at the beginning 10 min electrolysis. However, the degradation of ChS was much slower without NaCl addition. It was suggested that NaCl, which could be oxidized to form a strong oxidant of HOCl, could promote the degradation of ChS. The possible process was listed below [2]:

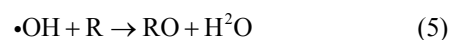
1) Anode reaction:



2) Hydrolysis reaction:



3) Degradation reaction:



Furthermore, with the presence of NaCl, the ChS concentration decreased rapidly. After the beginning 10 min electrolysis, ChS was almost completely removed, which proved that the Equations (4), (5) were rapid. It was a little different from study of Li *et al.* [25], who found that

with the presence of $0.1 \text{ g}\cdot\text{L}^{-1}$ NaCl, at the initial 5 min, the phenol concentration almost did not decrease. The reason could be that in his study, the concentration of treated materials was $8 \text{ mg}\cdot\text{L}^{-1}$, which was much higher than the present experiment. And HOCl could not be enough produced with lower NaCl at the beginning, consequently, the phenol concentration did not decrease obviously at the initial 5 min, and then was degraded sharply. The electrochemical degradation of ChS at different NaCl dosages occurred via a pseudo-first-order mechanism (**Figure 4 (b)**), with rate constants of 0.0137 min^{-1} ($R^2 = 0.999$) without adding NaCl, 0.4742 min^{-1} ($R^2 = 0.975$) at $0.1 \text{ g}\cdot\text{L}^{-1}$ NaCl, 0.5710 min^{-1} ($R^2 = 0.999$) at $0.2 \text{ g}\cdot\text{L}^{-1}$ NaCl, 0.5404 min^{-1} ($R^2 = 0.999$) at $0.5 \text{ g}\cdot\text{L}^{-1}$ NaCl. It was revealed that NaCl existence is a significant factor for efficient removal of ChS.

To investigate the generation of free radicals species and oxidizing substance generated during the electrolysis, $0.005 \text{ mmol}\cdot\text{L}^{-1}$ sulforhodamine B (SRB) solution was used for the electrolysis. It was clear from **Figure 5** that the absorbance of SRB solution sharply decreased in the initial 10 min at $20 \text{ mA}\cdot\text{cm}^{-2}$ with $0.2 \text{ g}\cdot\text{L}^{-1}$ NaCl dosage, and discoloration rate was up to 98.6%. However, no obvious discoloration was observed without NaCl dosage, indicating that formation of hypochlorous acid was an important bleaching factor during the electrolysis. Comninellis [6] and Xue [24] got the similar results using RNO as the material. Comninellis [6] suggested that hydroxyl radicals reacted selectively with RNO, but hypochlorous acid played a very important role in the RNO bleaching from the present study, which would enhance the ChS degradation. To confirm that the NaCl dosage promoted the formation of hydroxyl radical, the PL emission spectra excited at 315 nm from terephthalic acid solution were measured under the $0.2 \text{ g}\cdot\text{L}^{-1}$ NaCl and no NaCl dosage at $20 \text{ mA}\cdot\text{cm}^{-2}$. **Figure 6** shows the PL spectra from $5 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ terephthalic acid solution in $2 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$ NaOH after 1 min electrolysis under the NaCl dosage and after 20 min electrolysis under no NaCl addition. It can be seen that an obvious peak was observed under the NaCl dosage only after 1 min electrolysis, however, under no NaCl addition only an inconspicuous peak was observed after 20 min electrolysis at about 425 nm. This suggests that the fluorescence is caused by chemical reactions of terephthalic acid with $\cdot\text{OH}$ formed during the electrolysis. Consequently, it can be inferred that the hypochlorous acid which was generated in the solution can promote the formation of hydroxyl radicals, which was beneficial to degradation of ChS. Therefore, NaCl existence is a significant factor for efficient removal of ChS.

3.5. Electrode Surface

As shown in **Figure 7**, the surface of the Ti/IrO₂-Pt anode remains unchanged after more than 50 h electro-

chemical degradation of ChS. Furthermore, no formation of polymeric film was observed, implying that the electrochemical degradation efficiency of Ti/IrO₂-Pt anode did not decrease after repeated use under the same experimental condition (data not shown). Therefore, Ti/IrO₂-Pt anode has good performance for degradation of ChS and long service life, which demonstrates that it was suitable for ChS removal.

4. Conclusions

The electrochemical method is a novel approach for effective removal of ChS. In the present research, the effluence of current density, initial ChS concentration, initial solution pH and different NaCl dosage on the performance of electrochemical degradation of ChS were investigated using aTi/IrO₂-Pt anode. The electrochemical method is a novel approach for effective removal of ChS. In the present research, the effluence of current density, initial ChS concentration, initial solution pH and different NaCl dosage on the performance of electrochemical degradation of ChS were investigated using aTi/IrO₂-Pt anode.

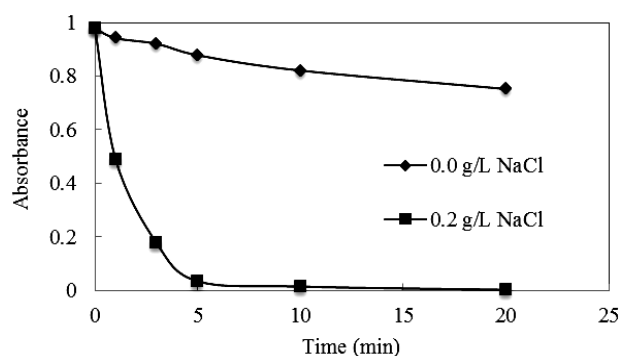


Figure 5. Electrochemical bleaching of 0.005 mmol/L SRB solution at $20 \text{ mA}\cdot\text{cm}^{-2}$.

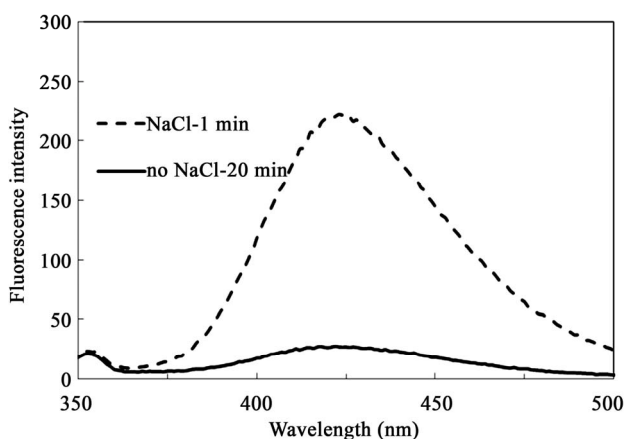
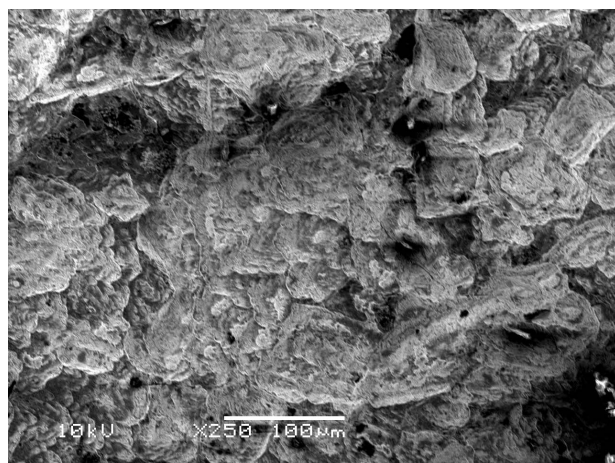
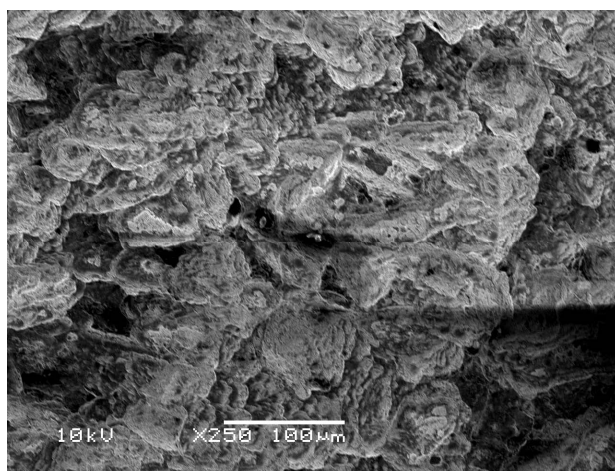


Figure 6. Effect of NaCl dosages on PL spectral.



(a)



(b)

Figure 7. SEM photograph of (a) unused (b) more than 50 h used for electrolysis Ti/IrO₂-Pt anode.

It was found that the ChS removal rate increased with increasing current density and the ChS degradation was similar at different initial pH values, which means that Ti/IrO₂-Pt anode can be used with a wide pH range. HOCl quickly formed during electrolysis would likely play an important role in the electrochemical degradation of ChS with the presence of NaCl. At 20 mA·cm⁻² ChS concentration decreased from 1 mg/L to 0 mg·L⁻¹ after 10 min electrolysis with 0.2 g·L⁻¹ NaCl dosage. The electrochemical performance of Ti/IrO₂-Pt anode for degradation of ChS will not decrease after serviced for long time.

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