

## Controlled release of iron for activation of persulfate to oxidize orange G using iron anode

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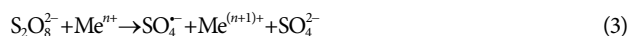
**Abstract**—Persulfate (PS) can be activated by transition metal to generate a sulfate radical and oxidize persistent organic pollutants. However, activation with excessive Fe(II) causes unnecessary self-degradation of PS. In this study, Fe(II) was slowly and continuously injected electrochemically using an iron anode to minimize the self-degradation of PS. Additionally, reaction rate was controlled by adjusting the current intensity applied to the system. Total organic carbon (TOC) was analyzed as an indicator of complete mineralization because the model pollutant, orange G (OG), produced secondary pollutants after disruption of the azo bonds. The removal rate of TOC was 1/10-th of that for OG. In addition, the effect of molar ratio of OG and PS was also studied to confirm the complete mineralization of OG.

Keywords: Persulfate, Transition Metals, Faraday's Law, Iron Anode, Current Intensity

### INTRODUCTION

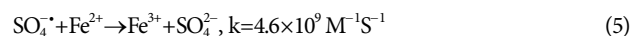
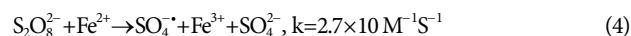
In recent years, the removal of non-biodegradable organic contaminants including hydrocarbons, chlorinated compounds, halogenated compounds, and dyes has gained increasing attention. Advanced oxidation processes (AOPs), including the Fenton Reaction [1-3],  $\text{TiO}_2$ -mediated photocatalysis [4,5], permanganate [6,7], electrochemical oxidation [8] and persulfate (PS) [9], have been studied to remove persistent organic contaminants.

PS is an attractive oxidant in environmental media because it is relatively soluble and stable [10]. The sulfate radical ( $\text{SO}_4^{\bullet-}$ ) is typically generated from PS. The hydroxyl radical ( $\text{OH}^{\bullet}$ ) is the most practical oxidant in AOPs due to its high oxidation potential (1.8 V-2.7 V), but the sulfate radical has higher oxidation potential (2.5-3.1 V) [11]. Moreover, the sulfate radical has a longer lifetime than the hydroxyl radical; therefore, it is an attractive oxidant to mineralize various organic contaminants [12-16]. PS can be activated into the persulfate radical by UV light, heat, and transition metals through the following reactions [17-20]:



However, heat and UV light are expensive methods and are too restrictive for field application [21]. Fe(II) is an effective transition metal for activating PS because it is cost effective and environmen-

tally friendly [22]. Reactions by Fe(II) are as follows:



As shown in Eqs. (4) and (5), Fe(II) can activate PS and simultaneously scavenge sulfate radicals [23]. To minimize the PS self-degradation reaction, suitable amounts of Fe(II) should be supplied. Electrochemical production using an iron anode is one way to provide a gradually increasing amount of Fe(II) [24-26]. At the same time, consumed Fe(III) can be reduced to Fe(II) by cathodic reaction (Eq. (7)), consequently reducing the overall consumption of Fe(II) [27,28].



Orange G (OG), an azo dye, is a representative non-biodegradable organic contaminant that has caused environmental contamination and affected human health, and the intermediates formed during its oxidation are toxic [29-31].

In this study, the oxidation characteristics of electrochemically activated sulfate radicals of OG were investigated. The PS activation rate was controlled by the current, and continuous generation of Fe(II) minimized PS consumption. Additionally, the oxidation rate constant of OG and complete mineralization rate constant were compared to evaluate potential intermediates of OG.

### MATERIALS AND METHODS

Orange G ( $\text{C}_{16}\text{H}_{10}\text{N}_2\text{Na}_2\text{O}_7\text{S}_2$ ) (Fig. 1), potassium persulfate ( $\text{K}_2\text{O}_8\text{S}_2$ ,

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$\geq 99\%$ ), sodium nitrate ( $\text{NaNO}_3$ ), sodium bicarbonate ( $\text{CH}_3\text{NaO}_3$ ), and 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-4', 4'-disulfonic acid sodium salt ( $\text{C}_{20}\text{H}_{13}\text{N}_4\text{NaO}_6\text{S}_2$ ,  $\geq 97\%$ ) were purchased from Sigma-Aldrich. Ammonium iron(II) sulfate hexahydrate ( $\text{FeSO}_4(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$ , 99%) was provided by Junsei Chemical Co., Ltd., Japan. Ammonium acetate ( $\text{CH}_3\text{COONH}_4$ ) was obtained from Samchun Co., Korea. All reagents were used after dissolution in deionized water. An iron plate and mesh type titanium electrode (35 mm length  $\times$  50 mm width  $\times$  4.5 mm thickness) were used as the anode and cathode, respectively. In a beaker of 1 L, 500 ml of OG solution was prepared, then direct current was applied with a normal power supply (P6015, Advantech, Korea), and PS was added the solution. The solution was continuously stirred during the experiment [26].

Sodium nitrite, a quenching agent, was used to stop the reaction by sulfate radicals [32]. Excess amounts of sodium nitrite were injected into the sample to quench radicals. The experimental conditions are summarized in Table 1. The current intensity was regulated by a DC power supply (Advantech@NTEK, P6015, Korea). The amount of Fe(II) was regulated by current intensity based on Faraday's Law.

OG was analyzed by using a UV/Visible spectrophotometer (HS3300, HUMAS, KOREA) at 478 nm [21], and PS concentration was estimated by analyzing the sulfate concentration by ion chromatography (Futecs Co., Korea) because PS is converted to sulfate. Ferrous was analyzed by the ferrozine method with a UV/VIS spectrophotometer at 562 nm [33,34]. Total iron was analyzed by using an inductive coupled plasma-optical emission spectrometer (720-ES, Agilent, USA). The intermediates were measured as total organic carbon (TOC) with a total organic carbon analyzer (H544352, Shimadzu, Japan).

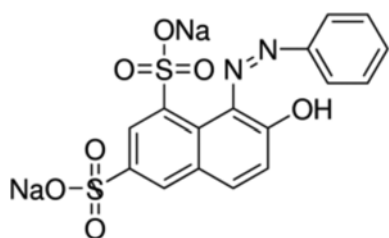


Fig. 1. Structure of Orange G.

Table 1. Experimental conditions used in this study

Exp. no.	OG (mM)	PS (mM)	Current intensity ( $\text{C}/\text{m}^3$ )	Time (min)
1	0	0	8.6 (10 mA)	120
2			8.6 (10 mA)	
3			43.2 (50 mA)	
4		1	86.4 (100 mA)	
5			129.6 (150 mA)	
6	0.05		172.8 (200 mA)	240
7		0.05	8.6 (10 mA)	
8		0.5	8.6 (10 mA)	
9		5	8.6 (10 mA)	

## RESULTS AND DISCUSSION

### 1. Electrochemical Activation of Persulfate

Fe(II), which was generated by an electrochemical process using an iron anode, activated persulfate to sulfate radicals. Based on

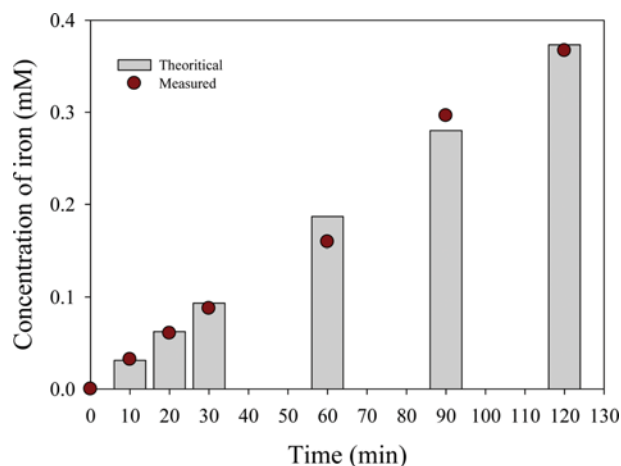


Fig. 2. Amounts of iron in the solution. Theoretical value was calculated by Faraday's law.

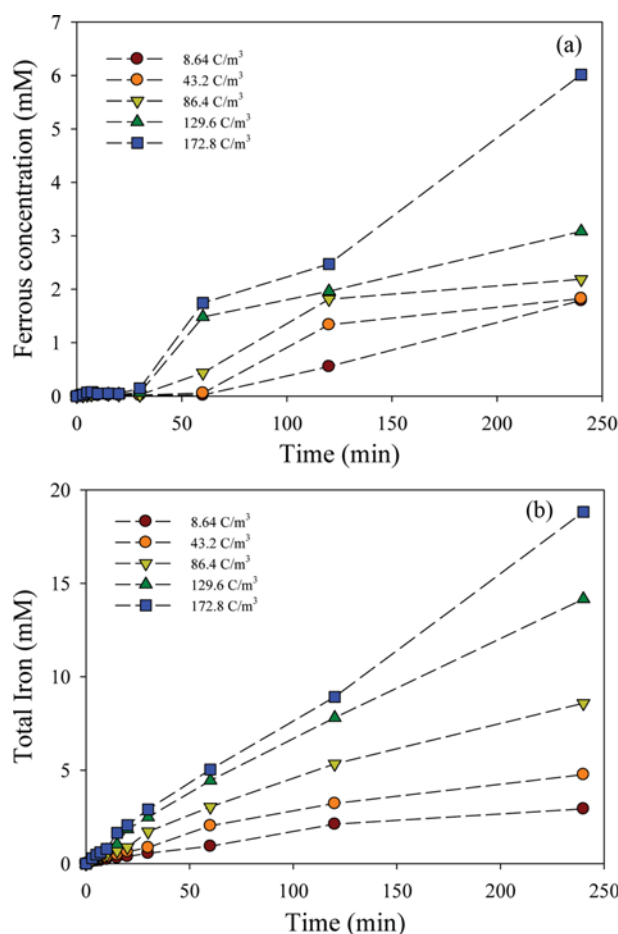


Fig. 3. Amounts of Fe(II) (a) and total Fe (b) in the aqueous phase by current intensity.

Faraday's law, the amount of Fe(II) electrochemically generated is estimated as follows [24]:

$$N = \frac{I \cdot t}{F} \times \frac{1}{Z} \left( F = \frac{96,485 \text{ C}}{\text{mol}} \right) \quad (9)$$

where  $N$  is the amount of transition metal produced,  $I$  is current intensity,  $F$  is Faraday's constant, and  $z$  is valance of the transition metal. The theoretical amounts of total Fe(II) based on Faraday's law were similar to the measured amounts (Fig. 2). This result

indicates that the amount of Fe(II) required to activate PS can be controlled by current intensity. The amounts of Fe(II) and total Fe are linearly proportional to current intensity (Fig. 3). Fe(II) was not observed in the system until 24 hours because its generating rate constants were  $3.1 \times 10^{-7} \sim 45.6 \times 10^{-7} \text{ M}^{-1} \text{ s}^{-1}$  and the PS consuming rate constant was  $2.7 \times 10 \text{ M}^{-1} \text{ s}^{-1}$  [23]. Electrochemically generated Fe(II) was immediately consumed by consuming reactions. Additionally, the voltage under constant current conditions gradually decreased, indicating that overall energy consumption decreased because the intermediates acted as electrolytes in the system.

## 2. Influence of Current Intensity

Most OG was removed within 20 min at all current intensities due to breakage of the azo bonds. However, <50% of TOC was removed because secondary pollutants or partially oxidized intermediates were generated (Fig. 4). The PS degradation rate constants were 0.0216, 0.0302, 0.0338, 0.0540, and  $0.0630 \text{ min}^{-1}$  at a current intensity of 8.6, 43.2, 86.4, 129.6, and  $172.8 \text{ C/m}^3$ , respectively. However, the OG degradation rate constants were 0.1409, 0.1812, 0.2049, 0.3567, and  $0.3144 \text{ min}^{-1}$ , respectively, while the TOC degradation rate constants were 0.0284, 0.0296, 0.0419, 0.0447, and  $0.0395 \text{ min}^{-1}$ . The PS degradation rate constants were proportional to current intensity. Both OG and TOC degradation rate constants increased with current intensity, but decreased over  $129.6 \text{ C/m}^3$ . This difference indicates that the generated sulfate radicals were scavenged by excess iron (Eq. (2)).

It took 16, 13, 10, 7, and 7 min to remove >99% of OG at 8.6, 43.2, 86.4, 129.6, and  $172.8 \text{ C/m}^3$  (Fig. 5). The complete degradation time of OG decreased exponentially with current intensity, indicating that at least 4 min is required to remove more than 99% of OG based on the correlation.

$$\text{OG removal time} = 13.1239 (1 - \exp(-0.0097 \times \text{Current intensity})) + 4.07 \quad (10)$$

Above a certain current intensity, it is impossible to decrease the time required to remove 99% of OG. Therefore, an optimum current intensity is needed to minimize consumption of energy and materials. However, Eq. (10) is limited to this study, and the reac-

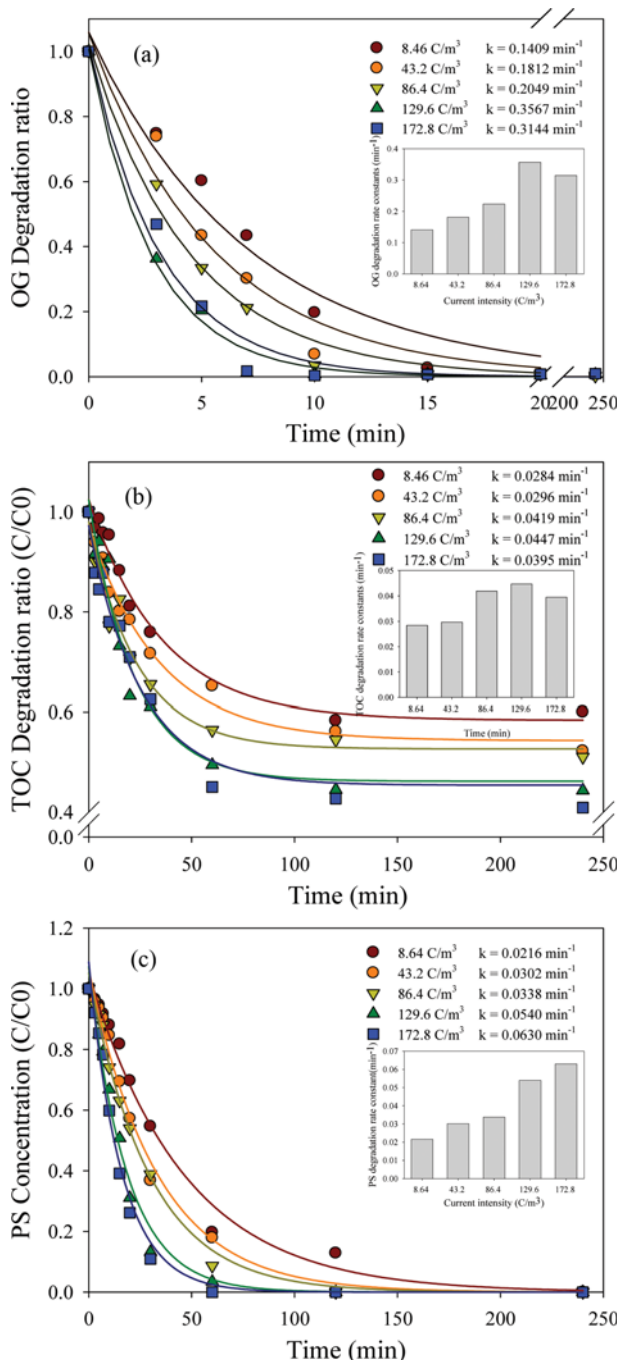


Fig. 4. Influence of current intensity on degradation kinetics of Orange G (a), total organic carbon (b), and persulfate (c).

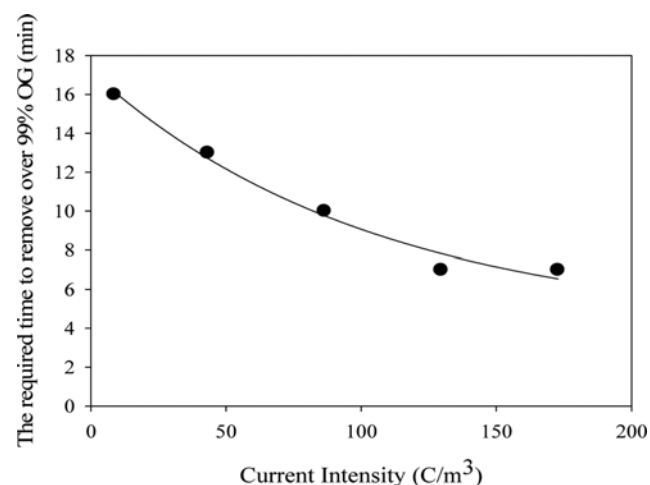


Fig. 5. Influence of current intensity on complete decolorization time of Orange G.

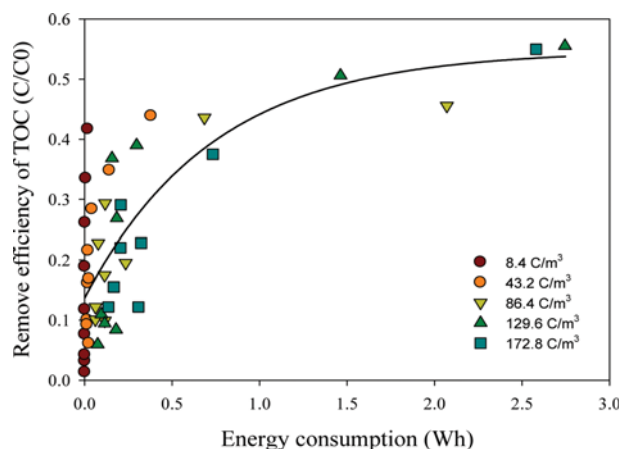


Fig. 6. Influence of energy consumption on removal of total organic carbon (TOC).

tion time might be affected by the surface area of the electrode as well.

Maximum removal of TOC was 60% (Fig. 6), although OG removal reached 100%. The TOC could not be completely removed by increasing the current intensity because excessively high current intensity decreased the degradation rate constant. The OG degradation rate constants were almost seven-times higher than those of PS self-degradation, while TOC degradation rate constants were similar or lower. The results indicate that relatively small amounts of PS were consumed to break azo bonds, but complete mineralization of OG (TOC removal) requires much more PS. However, when >50% of the TOC was removed, the residual intermediates were non-toxic, although they were not clearly identified [10]. TOC removal was dependent on current intensity, indicating that Fe(II) activated PS to sulfate radicals and acted as a scavenger for the radicals with faster reaction rate constants [14]. When current intensity was low, sulfate radicals were slowly generated. Therefore, the sulfate radicals were present in a low concentration in solution. Even though the same amounts of PS were added to the system, final removal of TOC was dependent on current intensity because Fe(II) consumed sulfate radicals.

Removal of TOC is strongly related to energy consumption in electrochemical activation using an iron anode (Fig. 6). TOC removal is proportional to energy consumption, which was saturated to approximately 55% even at higher energy consumption.

$$\text{TOC removal} = 0.4098(1 - \exp(-1.3548 \times \text{Energy consumption})) + 0.1364 \quad (11)$$

Therefore, a current intensity of  $129.6 \text{ C/m}^3$  was optimal in this study because 55% of TOC was removed and Fe(II) consumption was minimized with these conditions.

For complete degradation of TOC, PS concentration during the activation process was achieved with OG to PS ratios of 1 : 1, 1 : 10, 1 : 20, and 1 : 100 (Fig. 7). The degradation ratio of OG and TOC was analyzed by using a difference ratio of PS to OG when  $8.6 \text{ C/m}^3$  was applied. The OG degradation rate constants were 0.0062, 0.0699, 0.1409, and 0.6792, and the TOC degradation rate constants were 0.0059, 0.0103, 0.0129, and  $0.0934 \text{ min}^{-1}$ , respectively.

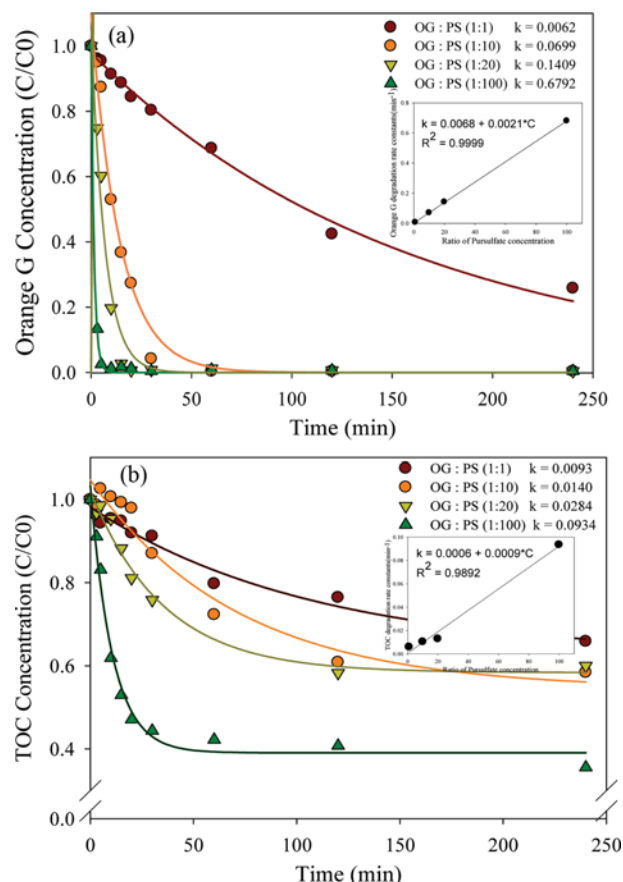


Fig. 7. Influence of persulfate dosage on degradation kinetics of Orange G (a) and TOC (b).

The degradation rate constant for OG was much higher than that of TOC because complete mineralization requires more PS. Although the removal of OG approached 100%, TOC removal was only 60%. The degradation rate constants for OG and TOC increased linearly with the molar ratio of OG to PS, indicating that complete mineralization of OG requires huge amounts of PS compared to breakage of azo bonds.

## CONCLUSIONS

Fe(II) was electrochemically produced from an iron anode based on Faraday's law and continuously supplied to the system. OG was used as a pollutant, most of which was removed within 20 min when treated with this electrochemical method. The removal of OG was much faster than that of TOC, because complete mineralization required more oxidants. Increased current intensity enhanced the reaction rate, but excessively high current intensity decreased the oxidation rate because Fe(II) electrochemically produced scavenged sulfate radicals with a greater reaction rate constant. Based on the reaction rate constants, energy consumption, and toxicity, there is an optimum current intensity even though the value can be changed by PS dosage and initial OG concentration. The oxidation rate constants of OG and TOC are linearly proportional to increases in PS dosage.

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