

Synergetic Effects of UV/Fe³⁺ Combined with Electrocatalysis for *p*-Nitrophenol Degradation

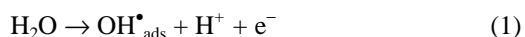
Ming Hua ZHOU, Zu Cheng WU*, Da Hui WANG

Department of Environmental Science and Engineering, Zhejiang University, Hangzhou 310027

Abstract: Synergetic effects for *p*-nitrophenol degradation were observed in the combination of two-advanced oxidation processes, UV/Fe³⁺ and electrocatalysis. The enhancement of removal rate for *p*-nitrophenol and COD was around 123% and 278%, respectively. The possible contributions for the synergetic effects were the electrochemically regeneration of ferric ion and the role of the oxygen that formed on the anode.

Keywords: UV/Fe³⁺, electrocatalysis, synergetic effect, *p*-nitrophenol degradation, AOPs.

Advanced oxidation processes (AOPs), generating high reactive and non-selective hydroxyl radicals in aqueous solution, have attracted considerable interest for destructing toxic or biorefractory organics in wastewater. AOPs such as photocatalysis, electrocatalysis, ozonation, and wet air oxidation have been extensively studied. In recent years, it has been a trend to develop combined processes with one or more kinds of AOPs such as UV / H₂O₂, O₃ / UV, H₂O₂ / O₃, UV / Fe³⁺, UV / Fe²⁺ (Fe³⁺) / H₂O₂ which have been found existing synergetic effects. However, the combined processes with electrocatalysis and other forms of AOPs were seldom reported in literature. Electrocatalysis is one of the recently-developed AOPs, characterized by amenability to automation, high efficiency and environmental compatibility¹. Hydroxyl radical can be produced by means of anodic oxidation on high over-voltage anodes such as lead dioxide².



The object of this work was to explore if there existed synergetic effects in the combined process with electrocatalysis and UV/Fe³⁺, and to probe the possible mechanism chemically. *p*-Nitrophenol (PNP), one of the priority toxic pollutants by U.S. EPA, was selected as the model pollutant due to its wide presence in many wastewaters such as pesticides and dyes.

Simulated wastewater, a certain amount of PNP and 10 g·L⁻¹ K₂SO₄, was circulated between photolysis reactor and the electrolytic cell by a circulated pump. The anode

* E-mail: wuzc@che.zju.edu.cn

adopted in this work was a β -PbO₂/ceramic anode modified by fluorine resin, which had showed promising application for treating phenolic wastewater of high salinity and of high acidity³. The anode and the cathode of Ni-Cr-Ti alloy net (grid 1 × 1 mm) were concentrically assembled into the electrolytic cell. A mercury lamp with main wavelengths 254 nm was employed in the photolysis reactor (ϕ 20 × 250 mm). The temperature of the solution was maintained at about 25°C in water bath. Iron (III) sulfate (5 mmol/L) was introduced into the solution at the beginning and the UV light was simultaneously turned on. The determination of PNP and its degradation intermediates were carried out on high-performance liquid chromatograph (HPLC, Gilson) by comparing the retention time of the standard compounds. Organic acids were determined by ion chromatography (Alltech, USA). The chemical oxygen demand (COD) was measured by the standard method⁴. The concentration of ferrous and ferric concentration was determined by phenanthroline method.

A systematic comparison on PNP degradation, COD removal and their principal intermediates was carried out among the UV/Fe³⁺, electrocatalysis, and their combined process. **Figure 1** shows the typical results, (a) for the COD removal and (b) for PNP removal, suggesting that their removals in three processes fit well as the following pseudo-first-order kinetic,

$$\ln(c_0/c) = k t \quad (2)$$

where, c_0 and c is the concentration of COD or PNP at the initial time ($\text{mg} \cdot \text{L}^{-1}$) and at the reaction time t , respectively; k is the pseudo-first-order reaction rate constant (s^{-1}). The simulated reaction rate constants are listed in **Table 1**.

It is evident that the combined process has synergetic effects in enhancing the removal rate of both COD and PNP in comparison with the individual photolysis or electrocatalysis. k for PNP removal, for example, in the combined process ($1.07 \times 10^{-3} \text{ s}^{-1}$) is much greater than the addition of the value of k obtained in the individual photolysis process ($0.19 \times 10^{-3} \text{ s}^{-1}$) and in individual electrocatalysis process ($0.36 \times 10^{-3} \text{ s}^{-1}$). To evaluate the enhancement on the removal rate, the promoted factor (f) is estimated about 123% using the following definition,

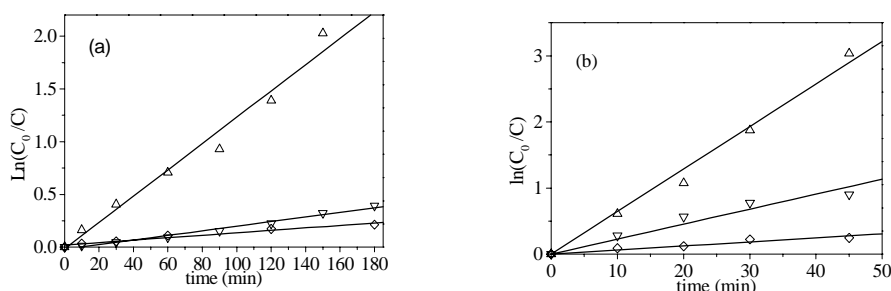
$$f = [k_{\text{PE}} / (k_{\text{P}} + k_{\text{E}}) - 1] \times 100\% \quad (3)$$

where, k_{PE} , k_{P} , and k_{E} represents the reaction rate constant in the photo-electrocatalysis process, photolysis process and electrocatalysis process, respectively. Similarly, the promoted factor of removal rate on COD is as high as 278%, which is even much greater than that of the PNP. However, the result indicates that the evolution of intermediates during PNP degradation be significantly accelerated in the combined process.

Table 1 Reaction rate constant (k) for COD and PNP removal

	k for COD (10 ⁴ s ⁻¹)	k for PNP (10 ³ s ⁻¹)
Photo-electrocatalysis	2.08	1.07
Electrolysis	0.36	0.38
Photolysis	0.19	0.10

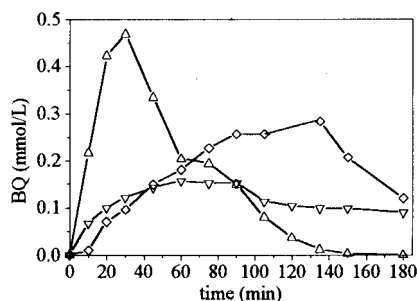
Figure 1 COD and PNP removal in the three processes



Δ: Photo-electrolysis; ∇: Electrolysis; ◇: Photolysis

This speculation above was confirmed by determining the intermediates during PNP degradation. Aliphatic carboxylic acids such as maleic acid and oxalic acid, and the ring-contained intermediates mainly benzoquinone (BQ) are identified in three processes. As shown in **Figure 2**, the comparison of BQ evolutions in three processes were made because BQ was known as one of rather persistent byproducts and indicated the difficulty of the ring opening⁵. The results showed that the concentration of BQ increased initially, and then decreased after reaching maximum concentration in all three processes. In electrocatalysis, BQ formed rather slowly. After gradually elevating the maximum at the period of 60 min, it began to decrease even much more slowly. In photocatalysis, it took much more time for BQ to rise at its maximum, however, it vanished much more rapidly. In the combined process, both the formation and the disappearance of BQ were greatly accelerated. It ascended the top at almost 0.48 mmol/L in no more than 30 min and was almost completely removed within not more than 150 minutes.

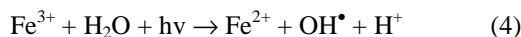
Figure 2 Evolution of BQ in three processes



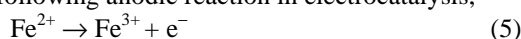
Δ: Photo-electrolysis; ∇: Electrolysis; ◇: Photolysis

The mechanism for the synergetic effects of the combined process would be complicated. As known, in the individual photolysis process (UV/Fe³⁺), the degradation

of organic compounds mainly depends on the hydroxyl radical based on the following mechanism⁶



This process is very simple and does not need the addition of expensive oxidant such as H_2O_2 . However, one drawback is that the efficiency of the treatment will be slow down with the conversion of ferric ion to ferrous ion. While in the combined process, the rapid depletion of ferric ion would be improved due to the regeneration of ferric ion by the following anodic reaction in electrocatalysis,

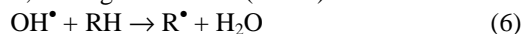


The regeneration of ferric ion was proved in **Table 2**. Fe (III) dramatically drop from 5 mmol/L to about 0.5 mmol/L in the period of 10 min till it reached the minimum at time 30 min, then it increased and finally maintained at about 2.7 mmol/L. Consequently, the mineralization of PNP has been accelerated due to the regeneration of ferric ion, which can continuously promote reaction (4) to form hydroxyl radicals.

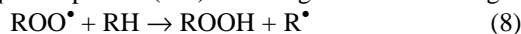
Table 2 Variation of ferric concentration against time

Time (min)	0	10	30	60	90	120	150	180
Ferric (mmol/L)	5.00	0.50	0.32	0.72	1.39	3.09	2.70	2.69

Another enhancement factor in the combined process is attributed to the fully utilizing of oxygen, one of the side-reaction products of electrocatalysis. It was reported that oxygen could accelerate organic compounds degradation in photocatalysis^{7,8}. In the presence of oxygen, the organic radical (ROO^\bullet) evolves as follows^{9,10}



giving rise to a peroxy-organic radical that in turn can participate in another series of reaction to drive *p*-nitrophenol (RH) to be degraded into the organic peroxide (ROOH)



As demonstrated in this work, the combined process provided a novel alternative to promote the degradation of the biorefractory compounds for wastewater treatment. Using a combinative AOPs approach is certainly a positive method to achieve quick mineralization. It will be expected to be valuable for environmental research and application.

References

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