

A Novel Electrocatalysis Method for Organic Pollutants Degradation

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

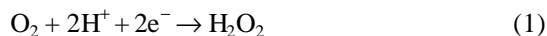
Department of Environmental Science and Engineering, Zhejiang University, Hangzhou 310027

Abstract: A novel electrocatalysis, ferrous ion catalyzed anodic-cathodic electrocatalysis (FACEC), was developed for organic pollutants degradation, which could promote the degradation by achieving synergetic effects of both anodic oxidation and cathodic indirect oxidation. The degradation rate of model pollutants — phenol by FACEC could increase by nearly 30% comparing with that of anodic electrocatalysis, and the current efficiency could reach 67%.

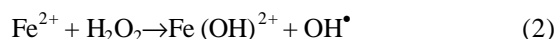
Keywords: Electrocatalysis, synergetic effect, phenol degradation.

As typical contaminants, phenolic pollutants are wide spread and are toxic to aquatic life. Thus the demand for new technology to remove or detoxify such organics should be widely recognized.

Recently, electrochemical method has attracted a great deal of attention for treating such kinds of wastewater, mainly because of its amenability to automation, high efficiency and environmental compatibility¹. Various electrochemical processes have been developed and anodic oxidation might be the most widely studied one²⁻⁵. High oxygen over-voltage anodes (PbO₂, doped PbO₂ and SnO₂) were very often employed for their good effectiveness in low pH solution though they possessed the disadvantage of anode inhibition⁵. Now, attention has been turned towards electrogenerated reagents such as hydrogen peroxide, which is formed on graphite or reticulated vitreous carbon cathodes by the two-electron reduction of sparged air.



In the presence of ferrous ions, Electro-Fenton process developed in which the oxidation power of H₂O₂ would be enhanced significantly due to the formation of hydroxyl radicals (OH•)⁶:



Although there was an ever-increasing interest in developing effective electrochemical methods either by anodic oxidation or cathodic process, there was almost no work both on anodic and cathodic electrocatalysis simultaneously for organics treatment.

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

In the present work, a new PbO_2 anode, $\beta\text{-PbO}_2$ /ceramic anode modified by fluorine resin, was adopted. This anode has similar electrocatalytic ability with Pt and can overcome anode inhibition due to its perfect resistance against high acidity⁷. Simultaneously, cheap air was sparged and ferrous ion was added into the electrolyte. The objective of this work was to explore if there existed the synergetic effects of such an anodic-cathodic electrocatalysis process.

As a sample pollutant, phenol degradation was carried out on an undivided cell composed of a $\beta\text{-PbO}_2$ /ceramic anode modified by fluorine resin and a Ni-Cr-Ti alloy cathode. The simulated wastewater ($10 \text{ gL}^{-1} \text{ K}_2\text{SO}_4$ and a certain amount of phenol) was pumped through the electro-reactor and then returned to the reservoir for recycling. The electro-reactor was placed in the water bath to maintain the reaction temperature 25°C . Constant current was maintained at the desired level with only minor adjustments of the applied voltage. Air was sparged into the electrolyte at a rate $6.78 \text{ mL}\cdot\text{s}^{-1}$. Iron(II) sulfate (0.5 mM) was added into the solution at the beginning. The determination of phenol and its oxidation products was carried out on high-performance liquid chromatograph (Gilson HPLC system, France), running with a mobile phase of acetonitrile/water (v/v) at 58/42. The separation was performed by using an ODS-18 reversed phase column at the flowrate of $1.5 \text{ mL}\cdot\text{min}^{-1}$ and column temperature of 25°C . Organic acids were determined by ion chromatography (Alltech, USA). The COD was measured by the standard method (closed reflux)⁸. The instantaneous current efficiency (ICE) during the phenol degradation was determined according to COD method⁹. The measurement of ferrous and ferric concentration was determined by phenanthroline method.

Figure 1 shows the difference of phenol removal rate by three kinds of processes: anodic electro-oxidation (AEC), anodic-cathodic electro-catalysis (ACEC) and anodic-cathodic electro-catalysis in the presence of ferrous ion (FACEC). The principal differences of the processes on operating conditions were the concentration of ferrous ion and the rate of sparged air. When phenol was 90% removed, the time for AEC was around 90 minutes, for ACEC it was 60 minutes, while for FACEC it was only 30 minutes. Consequently, the improvement of this process is significant. Comparing phenol degradation rate of ACEC with that of AEC, the contribution of the cathode was found to be in the range of 12-13%. In the presence of ferrous ion, ACEC changed into FACEC and the improvement of phenol degradation rate was around 12-15%. Thus the enhancement on phenol degradation rate of FACEC was around 24-28% comparing with that of AEC, which showed that the synergetic effect by FACEC was great which would make the process more effective though anodic oxidation still played much more important role in the role of anode and cathode.

To confirm the role of the reduction of oxygen at the cathode, the oxidation of phenol by sparged air without electrocatalysis was carried out in the same apparatus. Seen from **Figure 1**, after 2.0 hrs treatment, the removal rate of phenol was still not more than 5%. The main intermediates detected were the aromatic substrates such as hydroquinone, benzoquinone rather than aliphatic carboxylic acids. These show that the oxidation of air was weak and its ability was not strong enough to break down the benzene ring. Comparing FACEC with AEC, at the first reaction period of 45 mins, the

enhancement on phenol degradation rate was around 26% on the average, even took the role of direct oxidation by air as 5% in the electrolysis, the proportion is only 19% (=5%/26%). Thus it may be concluded that the direct oxidation by air in the electrocatalysis of phenol is insignificant. Therefore there must exist a strong role at the cathode related with the sparged air through which the rate of phenol degradation was promoted.

Figure 1 Phenol degradation by different processes

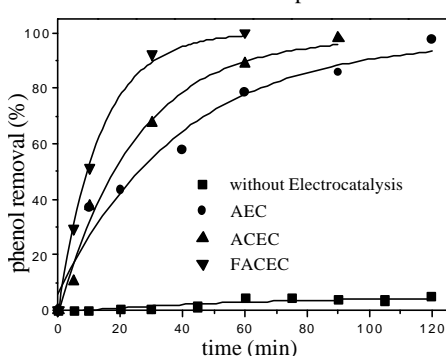
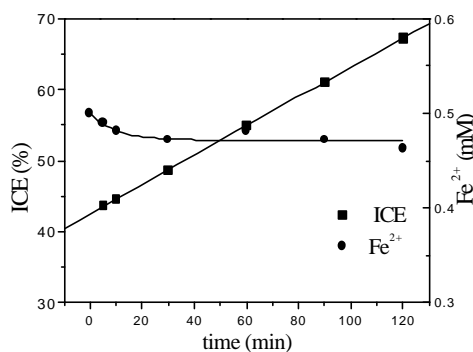


Figure 2 Evolution of ICE and Fe^{2+} concentration



To evaluate the effectiveness of FACEC, the variation of instantaneous current efficiency (ICE) during degradation was shown in **Figure 2**. To our surprise, ICE was rather high and almost linearly increased from 42% to 67%, which might indicate the promising of the process for industrial wastewater treatment. We speculated the increase of ICE with time might have something to do with the ferrous ion. As shown in **Figure 2**, the concentration of ferrous ion remained almost unchanged during electrocatalysis. These indicated that ferrous ion must be regenerated on the cathode by reduction of ferric ion.

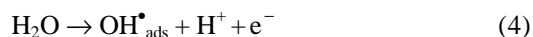


Therefore reaction (2) could be continuously catalyzed by the supply of the ferrous ion and hydroxyl radicals would be continuously formed, which would propagate the degradation of organic compounds. Therefore ICE was fair high and increased with time.

For better understanding the mechanism of the process, a comparative study was undertaken between FACEC and conventional Fenton's reaction under similar conditions. The degradation intermediates in the two techniques were almost the same and benzoquinone, fumaric acid, oxalic acid were also detected. Consequently, both reactions in the two techniques probably occurred by the same mechanism. It is well known that the mechanism of the chemical oxidation with Fenton's reagent is generation of hydroxyl radicals in the solution. Therefore in FACEC process, hydroxyl radical might also be the main oxidizing reagent.

Thus we might know the rough mechanism of the synergetic effects of FACEC though it needs further study. On the anode, OH^{\bullet} radicals were generated at the anode

by the oxidation of water¹⁰.



On the cathode, hydrogen peroxide was continuously produced by reduction of sparged air according to reaction (1), in presence of ferrous ion, hydroxyl radicals was generated according to reaction (2). There also existed the reduction of ferric ion to ferrous ion on the cathode, which kept the ferrous ion almost unchanged and continuously catalyzed the reaction (2). Therefore, with the role of hydroxyl radical generated both on the anode and indirectly on the cathode, phenol degradation was greatly accelerated.

In conclusion, FACEC has showed higher effectiveness than AEC for phenol degradation. The degradation mechanism is proved to be the generation of hydroxyl radicals that involved the two electrodes. It would be a cost-effective process for practical wastewater treatment and is necessary to undertake full research. To get a full knowledge of the synergetic effects of the process, it needs further study on the effects of the concentration of ferrous ion, the rate of sparged air and other electrocatalysis conditions such as current density as well.

References

1. K. Rajeshwar, J. G. Ibanex, G. M. Swain, *J. Appl. Electrochem.*, **1994**, *24*, 1077.
2. M. Gattrell, D. W. Kirk, *Can. J. Chem. Eng.*, **1990**, *68*, 997.
3. C. Comminellis, C. Pulgarin, *J. Appl. Electrochem.*, **1991**, *21*, 703.
4. B. N. Tahar, A. Savall, *J. Appl. Electrochem.*, **1999**, *29*, 227.
5. Y. M. Awad, N. Abuzaid, *Sep. Sci. Technol.*, **1999**, *34*, 699.
6. A. G. Alberto, D. Pletcher, *Electrochim. Acta*, **1999**, *44*, 2483.
7. C. A. Ma, R. K. Wang, S. P. Tong, *Fine chemicals* (in Chinese). **1996**, *13*, 96.
8. APHA, AWWA, WEF, *Standard Method for the Examination of Water and Wastewater*, 19th ed., Washington, DC, **1995**, p.515-516.
9. C. Comminellis, A. Nerini, *J. Appl. Electrochem.*, **1995**, *25*, 23.
10. B. Flesazr, J. Ploszynska, *Electrochim. Acta*, **1985**, *30*, 31.

Received 14 March, 2001