

Experimental Analysis and DFT Simulation for Phenolic Compounds Degradation by Free Radicals in EAOP

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1. Introduction

Coal chemical industry wastewater is discharged in the process of coal gasification and coal production, the composition of which is very complex, containing low concentration refractory organics and high salinity^[1]. Recently, the electrochemical advanced oxidation process (EAOP) has received great attention for refractory organics treatment. However, the unclear mechanism of EAOP, the toxic by-product formation and low current efficiency are the potential obstacles for plant scale^[2]. In this paper, pNitrophenol (PNP) was used as research object to compare degradation effects of direct electro transfer and free radicals such as •OH or reactive chlorine species (RCS). In addition to identification of intermediates by experimental analysis, the related degradation process was also simulated to provide potential degradation pathways of PNP oxidized by free radicals.

2. Experimental

The kinetics of direct electron transfer and free radicals during PNP degradation were determined by scavenging test based on steady-state assumption. The contributions of two degradation pathways were systematically studied as well under different electrolyte type, initial pH value, current density and dosages of reactive species (H₂O₂ and NaClO). The second-order reaction rate constant of PNP reacting with •OH was obtained. Furthermore, the identification of intermediates was conducted by SPME-GCMS and pathways for intermediates formation and PNP degradation were simulated in DFT theory using Gaussian software.

3. Results and Discussion

The results demonstrate that the PNP was more easily degraded in NaCl electrolyte than Na₂SO₄ electrolyte, and 80% of degradation was completed by direct electron transfer in both electrolytes. The main free radical in Na₂SO₄ and NaCl were •OH and RCS, respectively, but the reaction rate constant in NaCl was higher than Na₂SO₄ due to the oxidative selectivity of RCS to benzoic ring. It was investigated that the effect of Initial pH value(3~11) and current density(0.004 to 0.060 A·cm⁻²) on degradation, and it shows that the more free radicals were generated in the acid environment and the proportion of direct electron transfer degradation was linearly increased with the enhancement of current density. Although the steady-state concentration of free radicals could be increased by H₂O₂ and NaClO, direct electron transfer still was the main degradation way for overall kinetics. The attack order of PNP by •OH and •Cl was hydroxyl-group>nitro-group>benzene ring, and small molecule organic acids were produced after reactions. **4.**

Conclusions

- (1) PNP was more easily degraded in coal chemical industry wastewater containing concentrated NaCl due to oxidative selectivity of RCS.
- (2) The second-order reaction rate constant of PNP reacting with •OH was measured to be $2.1 \times 10^9 \text{ M}^{-1} \cdot \text{s}^{-1}$.
- (3) Direct electron transfer played a dominating role in EAOP, and the effect of that was related to initial pH, current density and dosage of reactive species.
- (4) The order of attacked position of PNP by free radicals was hydroxyl-group, nitro-group, finally benzene ring, and the broken rings formed small molecule organic acids.

5. References

- [1] Baolin Hou, Hongjun Han, Shengyong Jia, et al. *Journal of Environmental Sciences*, **26**(5), (2014) p.1015. Justin T. Japer, Yang Yang, Michael R. Hoffmann. *Environment Science and Technology*, **51**, (2017) p. 7111.