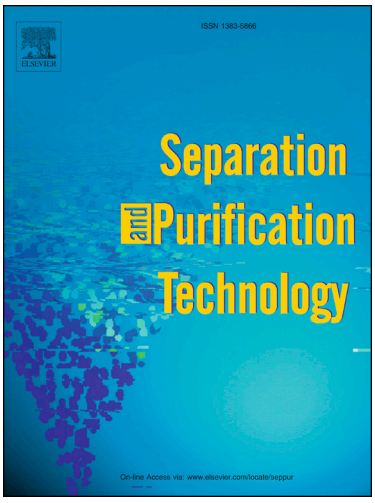

Enhanced mineralization of dimethyl phthalate by heterogeneous ozonation over nanostructured $(Cu_2O)_{0.5}$·CuO·Fe_2O_3 surfaces: Synergistic effect and radical chain reactions

Ying Liu, Deli Wu, Shuhan Peng, Yong Feng, Zhigang Liu

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Enhanced mineralization of dimethyl phthalate by heterogeneous ozonation over nanostructured $(Cu_2O)_{0.5}\cdot CuO\cdot Fe_2O_3$ surfaces: Synergistic effect and radical chain reactions

Ying Liu [a], Deli Wu [a], Shuhan Peng [a], Yong Feng [b], Zhigang Liu [a]*

[a] State Key Laboratory of Pollution Control and Resources Reuse, School of Environmental Science & Engineering, Tongji University, Shanghai 200092, P.R. China

[b] Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong

(* corresponding author)

Abstract: $(Cu_2O)_{0.5}\cdot CuO\cdot Fe_2O_3$ nanoparticles (CFO NPs), synthesized with zero-valent iron (ZVI) and $Cu(NO_3)_2$ as the metal precursors, were used to enhance ozonation to degrade dimethyl phthalate (DMP). Great DMP degradation and mineralization rates were achieved in a wide range of the initial pH values (3–9); the amount of ·OH in catalytic ozonation was much higher than that of O_3 alone at the initial pH of 5.70. The generation of hydroxyl radicals (·OH), methyl radicals ($\cdot CH_3$) and superoxide radicals ($O_2^{\cdot -}$) were identified and ·OH mainly contributed to DMP removal. The potential of ≡Fe(III)/≡Fe(II) and ≡Cu(II)/≡Cu(I) cycles have largely been overlooked, which was found to be the key for producing more ·OH in CFO/O_3 system. The underlying mechanisms were probably initiated by a chain reaction: initiated O_3 reaction with ≡Cu(I)/≡Fe(II)-OH to form ·OH and $O_2\cdot^-$, accelerated reaction between ≡Cu(II)/≡Fe(III) and the in situ generated $O_2\cdot^-$ with a relatively high reaction constant, redox reaction between ≡Cu(I) and ≡Fe(III), ·OH oxidizing reaction with DMP to produce $\cdot CH_3$.. This study sheds new light on the specific radical chain reaction mechanisms of catalytic ozonation.

Key word: Catalytic ozonation; Dimethyl phthalate; Hydroxyl radical; Superoxide radical; Methyl radical

1. Introduction

It is estimated that about 100 million tons of plastics have been generated every year around the world. The raw material phthalic anhydride of DMP is very cheap, therefore it is widely used as an indispensable additive in the plastic industry to improve flexibility and softness in China [1]. However, it has been proven to be slowly released directly or indirectly into wastewater and natural waters due to being not aggregated into a plastic matrix[2, 3]. What's more, the soluble phthalates