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Ultrasound-enhanced Nanosized Zero-valent Copper Activation of Hydrogen Peroxide for the Degradation of Norfloxacin

Xiaoyan Ma[1], Yongqing Cheng[1], Yongjian Ge[1], Huadan Wu[1], Qingsong Li[2], Naiyun Gao[3], Jing Deng[1*]

(1. College of Civil Engineering and Architecture, Zhejiang University of Technology, Hangzhou 310014, China;

2. College of Environmental Science and Engineering, Xiamen University of Technology, Xiamen 361024, China;

3. State Key Laboratory of Pollution Control and Resource Reuse, School of Environmental Science and Engineering, Tongji University, 200092, Shanghai, China)

Abstract: Commercial nanosized zero-valent copper (nZVC) was used as hydrogen peroxide (H_2O_2) activator in conjunction with ultrasonic irradiation (US) for the oxidative degradation of norfloxacin (NOR) in this study. Compared with silent degradation system, a significantly enhanced NOR removal was obtained in sono-advanced Fenton process, which involved a synergistic effect between sonolysis and Fenton-like reaction. Almost complete removal of NOR was achieved at 30 min when the operating conditions were 0.25 g/L nZVC and 10 mM H_2O_2 with ultrasound power of 240 W at 20 kHz. The released Cu^+ during the nZVC dissolution was the predominant copper species to activate H_2O_2 and yield hydroxyl radicals ($\cdot OH$) in US/nZVC/H_2O_2 system. According to the radical quenching experiments and electron paramagnetic resonance technique, hydroxyl radicals in solution ($\cdot OH_{free}$) were verified as the primary reactive species, and superoxide anion radicals ($\cdot O_2^-$) were regarded as the mediator for the copper cycling by reduction of Cu^{2+} to Cu^+. NOR removal efficiencies were improved in various degrees when increased nZVC dosage, ultrasound power, hydrogen-ion amount and H_2O_2 concentration. Moreover, the inhibitory effect of different inorganic salts on NOR degradation followed the sequence of Na_2SO_4 > $NaNO_3$ ≈ no salt > NaCl > $NaHCO_3$. Finally, eleven intermediates were identified and five oxidation pathways were proposed, the cleavage of piperazine ring and transformation of quinolone group seemed to be the major pathway.

Keywords: Ultrasound; Nanosized Zero-valent Copper (nZVC); Hydrogen Peroxide; Norfloxacin;

[*]Corresponding author at: College of Civil Engineering and Architecture, Zhejiang University of Technology, Hangzhou 310014, China. Tel./fax: +86 57187952015

E-mail address: zjut_djing@163.com (J. Deng)