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PII: S1385-8947(17)31284-6
DOI: http://dx.doi.org/10.1016/j.cej.2017.07.137
Reference: CEJ 17403

To appear in: *Chemical Engineering Journal*

Received Date: 23 May 2017
Revised Date: 21 July 2017
Accepted Date: 22 July 2017

Please cite this article as: J. Deng, Y. Ge, C. Tan, H. Wang, Q. Li, S. Zhou, K. Zhang, Degradation of Ciprofloxacin Using α-MnO_2 Activated Peroxymonosulfate Process: Effect of Water Constituents, Degradation Intermediates and Toxicity Evaluation, *Chemical Engineering Journal* (2017), doi: http://dx.doi.org/10.1016/j.cej.2017.07.137

Degradation of Ciprofloxacin Using α-MnO_2 Activated Peroxymonosulfate Process: Effect of Water Constituents, Degradation Intermediates and Toxicity Evaluation

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Abstract: Nanoscale α-MnO_2 with different morphologies (nanoparticles, nanoflowers and nanorods) were synthesized via a facile hydrothermal method and tested in peroxymonosulfate (PMS) activation for ciprofloxacin (CIP) degradation. The catalytic activity of α-MnO_2 mainly relied on the specific surface area and crystallinity, and followed the order of α-MnO_2 nanoflowers > α-MnO_2 nanorods > α-MnO_2 nanoparticles > commercial MnO_2. Acidic condition was more beneficial to CIP removal than neutral condition, and the degradation would be greatly accelerated in alkaline circumstance. The introduction of chloride and bicarbonate displayed concentration-dependent dual effect. The presence of natural organic matter (NOM) exerted the detrimental effect on CIP degradation. Eleven oxidation products were identified by UPLC-MS/MS and the changes of their concentrations were monitored, five products showed monotonous uptrend while four intermediates present monotonous downtrend once they were generated. Piperazine ring cleavage, hydroxylation and F/OH substitution were found to be the important oxidation pathways. The acute toxicity of resulted solution gradually decreased with the lapse of time, and higher PMS concentration favored the detoxification. The CIP removal in α-MnO_2/PMS process was also efficient under the actual water background, which was testified by the results of fluorescence excitation-emission matrix (EEM).

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