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ACCEPTED MANUSCRIPT

Monuron photodegradation using peroxymonosulfate activated by non-metal-doped

TiO₂ under visible LED and the modeling via a parallel-serial kinetic approach

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ABSTRACT: N-doped TiO₂ (NT) was proven to be efficient for monuron decay via

peroxymonosulfate (PMS) activation under visible LED (Vis LED). The activation

mechanism revealed that 'OH and SO₄-' have a critical role in the monuron decay with a

ratio of about 3 to 1, respectively; and the holes at the catalyst surface are the main

precursors in forming SO₄^{-•}. The NT/PMS/Vis LED hybrid process was found to be an

effective approach under a wide solution pH range of 2.5-9.2 (> 80% decay).

Interestingly, the highest efficiency was observed at pH 9.2 due to the contribution of

PMS/Vis LED process by generating both 'OH and SO₄- at alkaline pH. However, the

decay rate of monuron was inhibited at pH 11.6 due to the dissociation of 'OH into O'

and the electrostatic repulsion among reagents. The process was also suitable for ion-rich

wastewater since no significant reduction in the performance was induced in the presence

of high concentrations of inorganic anions. Furthermore, the process was proven to be a

promising approach for mineralization of monuron and its intermediates. Twenty reaction

intermediates were detected and five of them are newly reported. A novel mathematical

model was established based on reaction intermediates using a parallel-serial-irreversible

reaction approach, which is helpful in predicting the detoxification extent of hazardous

intermediates.

Keywords: Photodegradation; Herbicides; PMS activation; Mathematical model; visible LED

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