STEVENS
INSTITUTE OF TECHNOLOGY
1870

Ph.D. DISSERTATION DEFENSE

Candidate: Bo Zhao
Degree: Doctor of Philosophy
School/Department: Charles V. Schaefer, Jr. School of Engineering and Science/Civil, Environmental & Ocean Engineering
Date: Wednesday, April 22nd, 2026
Time/Location: 11:00 am, Babbio 202
Title: Alkaline Hydrolysis of Polychlorinated Polynitrobenzenes: Mechanistic Elucidation, Deprotonation Effects, and Environmental Implications

Chairperson: Dr. Christos Christodoulatos, Department of Civil, Environment & Ocean Engineering

Committee Members:
Dr. Xiaoguang Meng, Department of Civil, Environmental & Ocean Engineering
Dr. Tsan-Liang Su, Department of Civil, Environmental & Ocean Engineering
Dr. Tao Ye, Department of Civil, Environmental & Ocean Engineering
Dr. Hongjun Wang, Department of Biomedical Engineering

ABSTRACT

Large-scale production of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) generates concentrated spent sulfuric acid containing toxic polychlorinated polynitrobenzenes (PCPNBs). Conventional NaOH neutralization is costly and mainly removes acidity, while the transformation behavior of PCPNBs during treatment remains unknown. This dissertation investigates lime neutralization as an alternative strategy and elucidates the hydrolysis behavior and molecular-level mechanisms of PCPNBs.

The dissertation first examined the hydrolysis of 1,3,5-trichloro-2,4,6-trinitrobenzene (TCTNB), the major PCPNB byproduct in TATB spent acid, during lime neutralization. TCTNB was efficiently hydrolyzed, and the reaction was strongly accelerated by increasing pH and temperature, whereas Ca^{2+} and SO_4^{2-} showed no obvious effect. Field-scale neutralization confirmed complete reduction of TCTNB and 1,3,5-trichloro-2,4-dinitrobenzene (T3), together with effective acid neutralization and compliance of regulated metals in treated leachates. Product identification and ion-release analysis showed selective hydrolysis, with dechlorination favored over denitration and mono- and di-substituted phenolic derivatives dominating. Hydrolysis also reduced acute ecotoxicity, as luminescence suppression of *A. fischeri* decreased from 64.4% for TCTNB to 40.4% for the hydrolysis products. These results demonstrate that lime neutralization is an effective front-end treatment for rapid parent-burden reduction and partial detoxification.

To verify whether such selective and incomplete hydrolysis is a general feature of PCPNBs and to clarify its deeper mechanism, hydrophobic T3 was used as a model compound. Hydrolysis was strongly phase-state dependent, showing that dissolution and mass transfer constrain transformation of poorly soluble PCPNBs.

Experiments further confirmed selective and limited hydrolysis, releasing 0.97 mM Cl but only 0.16 mM NOx per mM T3 after 14 d at 95 °C. DFT calculations showed that dechlorination is kinetically favored because Cl-bearing sites are more electrophilic, possess weaker C–Cl bonds, and experience lower steric hindrance. More importantly, UV–vis and DFT calculations showed that deprotonation of phenolic intermediates sharply increased the barriers for subsequent substitution (e.g. from 14.4 to 31.1 kcal/mol). This increase arose from enhanced electrostatic repulsion and diminished resonance stabilization in the aromatic transition state. Deprotonation therefore acts as a kinetic bottleneck that suppresses continued hydrolysis. This work provides a mechanistic basis for evaluating treatment performance and the environmental fate of hydrophobic PCPNBs and their phenolic derivatives under alkaline conditions.