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Groundwater Remediation of Synthetic Phenolic Antioxidants via ZVI/PS: Geochemical Dynamics and Transformation Pathways

YUTENG WANG AND MR. HUI LIU
China University of Geosciences, Wuhan

Synthetic phenolic antioxidants (SPAs) are emerging organic contaminants in industrial groundwater, posing persistent risks due to their complex structures. To understand their remediation mechanisms, this study integrates experiments and theoretical calculations to elucidate the geochemical dynamics and transformation pathways of SPAs driven by the Zero-Valent Iron/Persulfate (ZVI/PS) system.

Initial investigations into AO2246 as the representative SPA demonstrated that the ZVI/PS process achieved 98.59% removal in 30 min under optimal conditions. However, this degradation is governed by interfacial geochemical speciation in complex aqueous matrices. Visual MINTEQ simulations demonstrate that alkaline conditions mitigate humic acid (HA) inhibition via electrostatic repulsion, whereas the coexistence of Mg^{2+} and HA triggers severe antagonism through cation bridging, passivating reactive surface sites.

Electron paramagnetic resonance and radical quenching identified $SO_4^{\cdot-}$ and ·OH as primary radicals. Structural Equation Modeling on eight SPAs revealed that $SO_4^{\cdot-}$-mediated oxidation is accelerated by higher Highest Occupied Molecular Orbital (HOMO) energy, whereas the ·OH pathway is enhanced by a narrower Energy Gap, with both facing steric suppression. This pattern is validated by a probe-based kinetic model that quantifies the fractional contributions of distinct radicals and reveals a general ·OH dominance. Specifically, the $SO_4^{\cdot-}$ contribution becomes negligible in BHT and AO425, whereas BHA's exceptional HOMO drives a unique inversion to a $SO_4^{\cdot-}$-dominant regime.

At the mechanistic level, Fukui function analyses localized the reactive sites on the methyl and hydroxyl carbons. Combined Density Functional Theory and LC-MS analyses revealed that ·OH exhibits non-selective reactivity in both Radical Adduct Formation (RAF) and Hydrogen Atom Abstraction (HAA) due to lower energy barriers and thermodynamic spontaneity. Conversely, the $SO_4^{\cdot-}$ RAF pathway avoids sterically hindered sites on bulky bis-phenols, forming adducts exclusively at the para-carbon. Furthermore, $SO_4^{\cdot-}$ exhibits no selectivity in electron transfer reactions. This mechanistic bifurcation is critical, as the ·OH-driven HAA route yields toxic quinones, while the $SO_4^{\cdot-}$-selective pathway promotes safer ring-cleavage products. Therefore, steering selectivity towards $SO_4^{\cdot-}$ is key to enhancing degradation efficiency and environmental safety. Ultimately, this work offers a theoretical basis for optimizing persulfate-based advanced oxidation processes for groundwater remediation of persistent organic contaminants.