Formation, Destruction, and Adsorption of *N*-nitrosamines in Water Treatment Systems

by

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ABSTRACT

Modern water treatment seeks to mitigate micropollutant and pathogen contamination in drinking water, yet processes deployed for pathogen control can themselves generate micropollutant byproducts. This thesis focused on *N*-nitrosamines, an unregulated byproduct class whose carcinogenic risk extends to ng/L concentrations under chronic exposure, and whose formation, degradation, and removal each present distinct challenges for water treatment.

The first study identified a previously unrecognized route for nitrosamine formation during electrochemical water treatment. In a novel flow-through electrochemical cell, *N*-nitrosodimethylamine (NDMA), the most frequently detected nitrosamine in drinking water, formed via nitrite electro-oxidation in synthetic and spiked natural electrolytes, yielding 169–715 ng/L NDMA across various cell potentials. Formation occurred exclusively in cathode-to-anode flow and was undetectable in anode-to-cathode flow, consistent with a cathodic pH increase that deprotonates the amine precursor and enables its nitrosation by reactive nitrogen species generated from nitrite oxidation at the anode. This route is independent of the chloride-mediated byproduct pathways previously studied in electrochemical treatment. The flow-direction dependence indicates that the spatial separation of electrode processes in heterogeneous treatment creates both formation mechanisms and mitigation opportunities absent in conventional homogeneous oxidative treatment processes.

The second study defined kinetic parameters for a nitrosamine destruction approach: UV advanced oxidation using sulfate radicals. To improve degradation prediction for such radical systems, a sulfate radical exposure parameter was developed, linking steady-state sulfate radical concentrations to the UV fluence rate. This parameter, determined using a 96-well high-throughput photochemical workflow, accurately resolved differences in radical concentration across synthetic matrices and successive stages of a municipal drinking water treatment train. Bimolecular rate constants were determined for a suite of nitrosamines with sulfate radicals; larger nitrosamines were more reactive by factors of 1.2 to 9.7 relative to NDMA. Integrating radical exposure with compound-specific kinetics revealed that the choice between persulfate and peroxide depends on both the target nitrosamine and the water matrix; this framework enables that decision at the bench scale before process scale-up.

The third study evaluated activated carbon adsorption of nitrosamines at the point-of-use scale. Residual disinfectant concentrations maintained during distribution can produce nitrosamines after water leaves the treatment plant, creating an exposure route that centralized treatment alone does not address. Activated carbon has been deemed impractical for NDMA at larger treatment scales, but its efficacy at smaller scales had not been evaluated. Eight commercial pitcher filters challenged with 40 ng/L NDMA showed removal ranging from 39% to 97%. Equilibrium adsorption isotherms were measured for four nitrosamines on granular activated carbon at trace (µg/L) concentrations; at 1 µg/L in solution, the activated carbon-water partitioning coefficient spanned a 55-fold range across the four compounds, with NDMA the most weakly adsorbed. Adsorption broadly tracked molecular size rather than hydrophobicity. Three predictive approaches of varying methodology were each inaccurate, confirming that experimental determination is necessary. While performance is highly sensitive to device design, the measured isotherms coupled with packed-bed modeling suggest that point-of-use carbon devices can be feasibly engineered to achieve substantive removal of even NDMA, with larger nitrosamines more readily removable.

Byproduct discovery in water treatment typically lags behind process implementation; the identification of NDMA formation via nitrite electro-oxidation demonstrates the value of proactive byproduct screening in nascent treatment processes. Existing predictive frameworks for micropollutant reactivity and adsorption, developed for the larger, more hydrophobic contaminants that have historically driven water treatment research, consistently underperformed for nitrosamines, and the data generated here provide a basis for extending such frameworks to smaller, hydrophilic contaminants.

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