Co-Removal of Energetics and Oxyanions via In Situ Coupling of Catalytic and Enzymatic Destructions: A Solution to Ammunition Wastewater Treatment

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Background/Objectives. The treatment of ammunition wastewater is challenged by the presence of mg/L-level munition residues -- defined as energetics -- in the typical form of nitrated organic compounds, such as RDX (1,3,5-trinitro-1,3,5-triazacyclohexane). Due to its adverse effects on the central nervous system, RDX was listed by United States Environmental Protection Agency (U.S. EPA) as a priority pollutant with a health advisory of 0.1 mg/L in drinking water. A further challenge for ammunition wastewater treatment is that the energetics usually occur in mixtures with abundant (usually hundreds of mg/L) toxic oxyanions including perchlorate (ClO_4^-, used as energetics booster) and nitrate (NO_3^-, used as propellant oxidizer). Therefore, a practical and sustainable solution for treating ammunition wastewater with a chemical unit specific for RDX removal and a biological unit specific for oxyanion removal.

The overall objectives of this research were to document the ability of a Pd-biofilm to reductively denitrate RDX while bio-reducing nitrate and perchlorate and then to evaluate its capability for continuous RDX and oxyanions removals. Specific objectives were to integrate information on RDX-reduction intermediates, biofilm community structure, and functional genes to determine the mechanism of RDX mineralization, as well as its interactions with biofilm denitrification and perchlorate reduction.

Approach/Activities. We proposed a solution featuring an in situ combination of chemical reduction of RDX and enzymatic reduction of oxyanions in a single unit in which active Pd nanoparticles (PdNPs) capable of RDX denitration were synthesized and stabilized as an extracellular layer on microorganisms capable of NO_3^- and ClO_4^- reductions.

Results/Lessons Learned. After a nitrate- and perchlorate-reducing biofilm incapable of RDX biodegradation was coated with palladium nanoparticles (Pd0NPs), RDX was rapidly denitrated with a specific catalytic activity of 8.7 $gcat^{-1}$ min^{-1}, while biological reductions of nitrate and perchlorate remained efficient. In the subsequent 30-day continuous test, >99% of the RDX, nitrate, and perchlorate were co-removed and their effluent concentrations were below their respective regulation levels. Up to 1 mmol/L ClO_4^- and 2 mmol/L NO_3^- were rapidly reduced in the Pd-biofilm reactor. Based on detected intermediates, community structure, and functional genes, RDX ultimately could be mineralized to CO_2, N_2, and NH_4^+ via intermediates methylene imine, formaldehyde, and formate by bacteria carrying out denitrification.

By coupling Pd-based reductive denitrations and microbial reductions of nitrate and perchlorate, the palladized biofilm reactor can be an efficient, low-cost, and sustainable means to treat the co-contaminating energetics and oxyanions commonly present in ammunition wastewater.