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Case Study

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OZONATION OF SYNTHETIC COMBINED SEWER OVERFLOW: IMPACT ON THE FATE OF SILVER NANOPARTICLES

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1 PROJECT OVERVIEW

A Wastewater Treatment Plant (WWTP) in Alberta is working in collaboration with a research team at the University of Alberta on improving the treatment of its Combined Sewer Overflow (CSO) to maximize the removal efficiency of common regulated parameters, microorganisms, micropollutants and nanoparticles before the final discharge. All efforts employed by the WWTP to optimize its current CSO Enhanced Primary Treatment (EPT) converge to reduce the emission of any potentially toxic material into the North Saskatchewan River and ultimately protect the environment and public health.

2 INNOVATION

Recent developments in nanotechnology allowed the introduction of many nanomaterials in regular consumer products. Among those nanomaterials, Silver Nanoparticles (AgNPs) are the most commonly used because of their size, high surface area and antimicrobial properties, yet not the most abundantly produced (Vance et al., 2015). They are generally found in textile and medical and household products and eventually find their way to the wastewater network. Researchers were able to ascertain the bioavailability of AgNPs in wastewater to fish like juvenile rainbow trout (Bruneau et al., 2016) and to depict a dose-dependent toxic effect of AgNPs in zebrafish embryos (Asharani et al., 2008). This potential risk of AgNPs necessitates the consideration of treatment techniques that guarantee their removal from effluents before discharge. Accordingly, optimizing the EPT of CSO at the Alberta WWTP by adding a treatment step to the current coagulation/flocculation/settling process, can either jeopardise or boost the removal of AgNPs. This study, will test in particular the addition of ozonation to the EPT. A preliminary bench scale experiment is designed to test the impact of ozone (O_3) application on AgNPs in raw and treated synthetic CSO.

3 METHODOLOGY

A sample of raw primary influent was collected from the Alberta WWTP, under dry weather conditions. The sample was diluted with deionized water to mimic a wet weather CSO and is denoted as synthetic CSO. A jar test was conducted using 2 liters of synthetic CSO per jar and a coagulation/ flocculation/settling process was initiated with a blank for reference, and 3 different coagulants: Alum at 10.4 mg Al/L, Ferric Chloride ($FeCl_3$) at 20.95 mg Fe/L and Polyaluminum Chloride (PACl) at 10.4 mg Al/L that were added with 1.25 mg/L cationic polymer. Fast mixing was performed at 150 rpm for 1 min, followed by slow mixing at 15 rpm

for 10 min and settling for 1 hr. Samples were collected from the supernatant and stored in dark glass bottles at 4°C. Equal volumes of raw and treated synthetic CSO were added in 23 mL amber glass reactors and topped up with a fixed dose of applied O_3 (17.26 mg O_3/L). Upon the addition of O_3 stock solutions, all reactors were subjected to 20 min shaking at 203 rpm, after which O_3 residual was measured with the Indigo Method. Samples were then stored in amber glass vials at 4°C for AgNP analysis by Inductively Coupled Plasma – Mass Spectrometry (ICP-MS) and results are reported as concentration of ^{107}Ag.

4 RESULTS AND DISCUSSION

Experimental results unveil the ability of the primary treatment of synthetic CSO to enhance the removal of AgNPs. In fact, the concentration of AgNPs dropped by 15% through settling alone, by 80% through the addition of $FeCl_3$, and by 89% through the addition of either alum or PACl. On the other hand, ozonation of raw and treated synthetic CSO considerably increased Ag concentrations in all tested samples (by 86% in synthetic CSO, 93% in blank jar, 99% in all 3 jars treated with alum, $FeCl_3$ and PACl) with a utilized O_3 dose equivalent to applied O_3. This increase does not coincide with the results of similar ozonation experiments performed on synthesized AgNP stock solutions in MilliQ water that showed merely 5% decrease in AgNP concentration. This small drop can be probably attributed to the inability of silver oxide, the likely product of AgNP ozonation, to settle out of solution (feature of its solubility product), and thus the persistence of Ag for detection by ICP-MS. Based on the observed impact of ozonation on samples of synthetic CSO, it can be speculated that both high organic matter present in wastewater matrices and flocs obtained during primary treatment processes form strong complexes with colloidal Ag and settle out as aggregates leading to less detectable Ag in solution. It is also possible that chlorine ions (Cl^-) that were added with $FeCl_3$ and PACl might have disturbed the stability of AgNP and simulated the formation of silver chloride precipitate decreasing the detectable Ag in solution. In a complex wastewater matrix, O_3 might have preferentially oxidized the organic matter releasing embedded Ag and thus provoking higher Ag concentrations as measured by ICP-MS.

5 LESSONS LEARNED AND FUTURE WORK

This preliminary experiment showed that the ozonation of synthetic CSO, in a raw condition or after primary treatment, increases the final concentration of silver. While the scope of this work did not provide evidence on the exact AgNP transformations, it still gave some insight on newly explored impacts of wastewater ozonation that involve nanoparticles. As such, the mechanisms for AgNP transformations evoked during ozonation along with the kinetics, competing agents in wastewater matrices and oxidation by-products will be the core of future studies.

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