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Ozonation of Metal-EDTA Chelates and Pesticides to Disinfect RO Brine

Background and Research Importance

Indirect potable reuse (IPR) is repurposing treated wastewater for future cleansing at a drinking water treatment plant. The Silicon Valley Advanced Water Purification Center is an advanced water treatment facility using microfiltration, reverse osmosis (RO), and ultraviolet light to purify wastewater. While the wastewater is pressurized through RO membranes, large dissolved molecules accumulate on the filters. The RO membranes are backwashed, producing the focus of this research: brine.

Brine is a saline liquid that contains dissolved metal-EDTA chelates, pesticides, and other contaminants.[1] Brine disposal is considered a deterrent of IPR because it cannot be directly released into the environment, per EPA guidelines. Additional treatment must be performed to remove metals and pesticides dissolved in brine. EDTA is a weak acid found in industry, such as paper milling. It encapsulates metals, making them unable to be filtered out of brine by precipitation (Figure 1). Pesticides, such as Fipronil (Figure 2), are also found in brine and are harmful to marine health.[2] Fipronil, and its derivatives (Fipronil sulfide, Fipronil sulfone, Fipronil desulfide, and Imidacloprid), are used in agriculture and tick/flea medicine. Stormwater causes EDTA and fipronil to enter the wastewater system. Learning how to remove metal-EDTA chelates and pesticides from brine will allow IPR to be a feasible water-reuse option.

Research Focus and Approach

Ozonation is the addition of ozone to break contaminants and organic pollutants, such as metal-EDTA chelates and pesticides. Ozone (O_3) is presumed to break the bonds of the EDTA molecule and the less electronegative element bonds of fipronil. During ozonation, hydroxyl radicals ($OH^{\cdot}$) are formed as a product of ozone.[3] Therefore, ozone and hydroxyl radicals both degrade disinfectants.

Nickel-EDTA, copper-EDTA, and zinc-EDTA were analyzed. All three metals are found in brine and form strong bonds with EDTA. All metal concentrations were held constant except when being examined. All filtration tests were analyzed using inductively coupled plasma mass spectrometry. Nickel used ion chromatography. Copper and pesticides were tested using high performance liquid chromatography. DI tests, including tert-butanol and perozone, were conducted with a constant ozone dose of 4 mg/L. The same tests in brine samples were conducted with a 20 mg/L ozone dose.

The first research focus is to understand how ozone reacts with metal-EDTA chelates and pesticides. This was better understood using per-ozone, tert-butanol, and filtration tests. The second research focus is to discover how well ozone and hydroxyl radicals can degrade these molecules. This was done with general ozone testing and filtration tests. The following sections will explain these tests in greater detail.

First Research Focus: How Ozone Reacts

Tert-butanol $(CH_3)_3COH$ is an alcohol that reacts with hydroxyl radicals, causing only ozone to remain. The higher the tert-butanol concentration, the lower the hydroxyl radical concentration. Figure 3 is the tert-butanol data. DI water had little percent change with the addition of tert-butanol. However, in brine samples, the addition of tert-butanol drastically increased the percent of Ni-EDTA remaining. At 100 mM tert-butanol, over 85% Ni-EDTA was remaining, or a 15% removal. Because DI samples were unaffected by the removal of hydroxyl radicals, ozone breaks most Ni-EDTA bonds in DI water. In brine, most Ni-EDTA bonds are broken by hydroxyl radicals.

Per-ozone testing is adding hydrogen peroxide (H_2O_2) and ozone to a solution. Contrarily to the tert-butanol tests, hydrogen peroxide reacts with ozone to produce high concentrations of hydroxyl radicals. Figure 4 is the change of adding just H_2O_2, just ozone, and both H_2O_2 and ozone in DI Water and brine samples. In DI water, just adding H_2O_2 is ineffective and no removal was observed. Adding ozone was effective with a percent remaining of under 40% Ni-EDTA. Adding H_2O_2 and ozone increased the Ni-

EDTA remaining almost 10%. Adding of H_2O_2 increased the hydroxyl radical concentration and decreased the ozone concentration, and those conditions are not favored in DI samples. These results correlate to the tert-butanol findings. Brine samples in Figure 4 show the same trend pattern, but Ni-EDTA in solution decreased with the addition of H_2O_2. Therefore, in brine, the perozone method does increase the removal of Ni-EDTA because brine favors the hydroxyl radicals.

Filtration tests were also conducted. The data is found in Figures 5, 6, and 7. In brine samples, three tests were performed for each ozone doses of 0 mg/L, 12 mg/L, and 20 mg/L. The tests were: (1) Add Na_2CO_3; (2) Add CaO; (3) Add Na_2CO_3 and CaO. Na_2CO_3 and CaO will form metal precipitates in brine samples. Brine already contains carbonate, so test 1 is adding an overabundance of the molecule. Test two is adding the base calcium oxide, which increases the pH, forming more hydroxyl radicals. Test three is the addition of both these compounds. Figure 5 is the total Ni concentration in ppb. Adding Na_2CO_3 had little change in Ni concentration because the molecule was already present. Adding CaO has a decrease of 300 Ni ppb at an ozone dose of 20 mg/L. In test 3, there is an additional decrease in Ni concentration of 400 ppb. However, Cu (Figure 6) and Zn (Figure 7) have a different pattern. Adding CaO removed nearly all the Cu and Zn in the samples, regardless of ozone dose. This means that Ni can only be precipitated out of brine with large ozone doses with sodium carbonate and calcium oxide. Cu and Zn can be precipitated out of brine with no ozone and only calcium oxide.

Second Research Focus: How Well Ozone Degrades Pollutants

Filtration tests can also depict how well ozone degrades pollutants. In the Ni filtration data (Figure 5), adding ozone had a large effect on Ni removal. At ozone doses of 0 mg/L, there was no change between tests. In other words, the addition of sodium carbonate and calcium oxide is unsuccessful at removing Ni without ozone. Contrarily, Cu and Zn (Figures 6 and 7) showed total metal removal, regardless of the ozone dose. Cu and Zn can be removed from brine without ozone.

General ozone testing was performed in Ni and Cu samples (Figure 8) to see how metal-EDTA remained in solution with various ozone doses. At high ozone doses (>12 mg/L), Ni and Cu are nearly completely removed from solution in DI water. This is because the ozone has no interference and can react directly with metal-EDTA chelates. In brine samples, organics that cloud the water can also react with ozone, making it appear less efficient. When additional metals are in a solution, Ni-EDTA also showed a similar trend of higher Ni-EDTA remaining because there are other solutions that ozone could react with. Figure 9 shows the same ozone test with pesticides in DI water. Pesticides follow a similar removal to Ni-EDTA in brine solutions. Pesticides were also tested in brine samples at the same ozone doses, and no significant pesticide removal was noted. Pesticides are a more electron-withdrawing molecule (in comparison to metal-EDTA); therefore, it is harder for ozone and hydroxyl radicals to steal electrons from pesticides. The general ozone test shows that ozone is a powerful disinfectant to break these compounds.

Conclusions and Future Work

Freeing metal-EDTA chelates and pesticides from brine is a crucial step in IPR. The major findings were that brine samples use hydroxyl radicals to degrade pollutants, while DI water depended on ozone. Filtration tests also showed the different behavior of Ni to Cu and Zn. Cu and Zn required no ozone for metal filtration, but Ni needed ozone to be freed from the chelate. The Silicon Valley Treatment Center in California is utilizing this ozone research to remove these molecules in the RO brine in the most efficient way. Future work should include a more diverse understanding of Cu-EDTA, Zn-EDTA, and pesticides. These molecules should be tested at various ozone doses under many conditions like Ni-EDTA was.

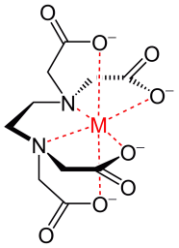

Figure 1: Metal-EDTA Chelate

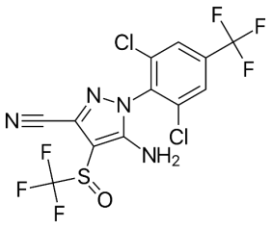

Figure 2: Fipronil molecule

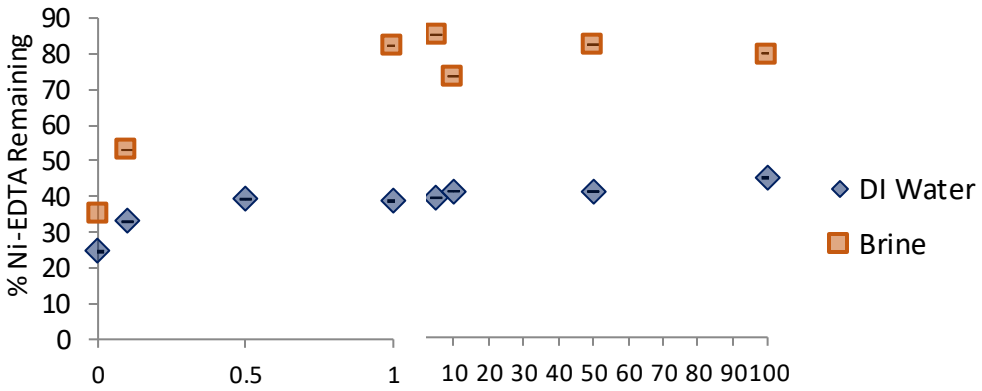

Figure 3: Ni-EDTA Tert-Butanol Test in DI Water and Brine

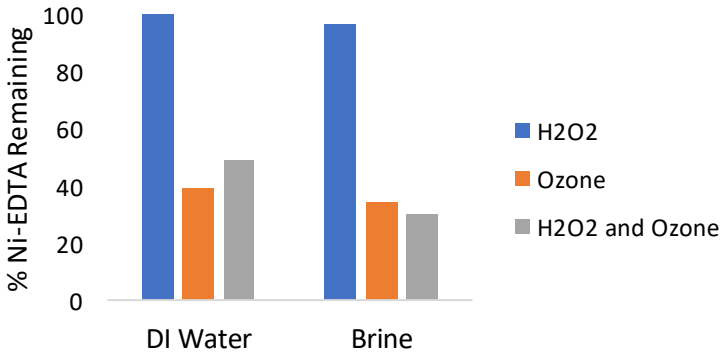

Figure 4: Ni-EDTA H2O2 Test in DI Water and Brine

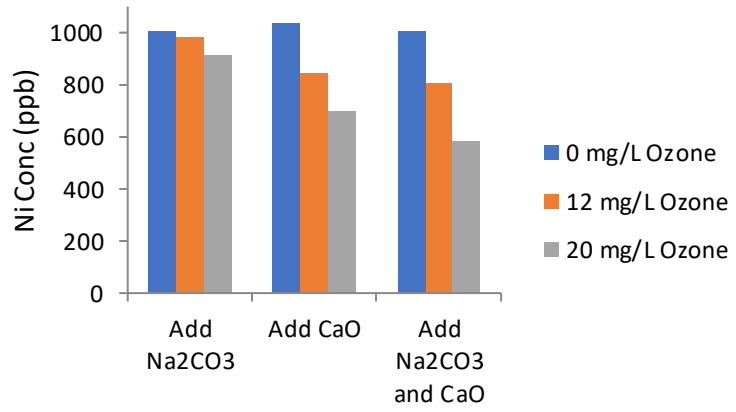

Figure 5: Ni Filtration Test in Brine at Various Ozone Doses

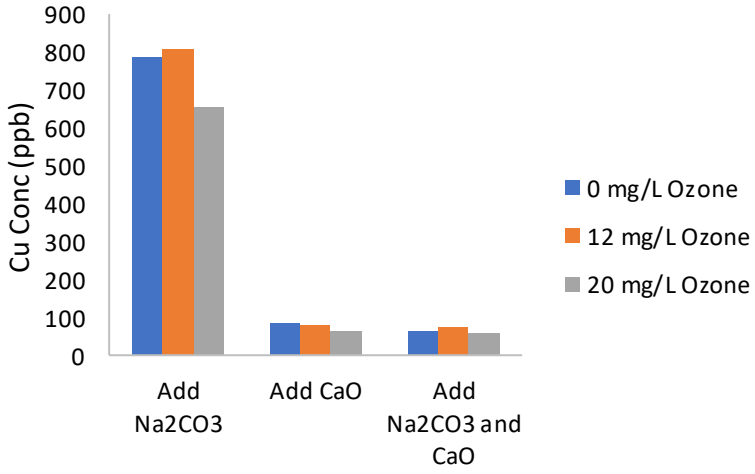

Figure 6: Cu Filtration Test in Brine at Various Ozone Doses

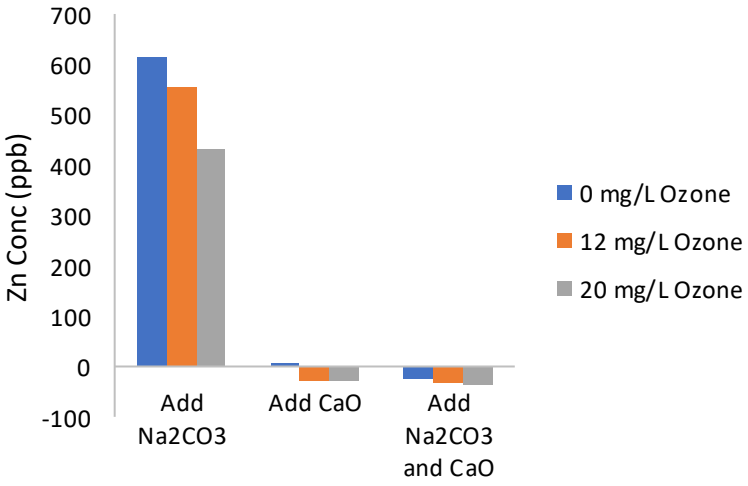

Figure 7: Zn Filtration Test in Brine at Various Ozone Doses

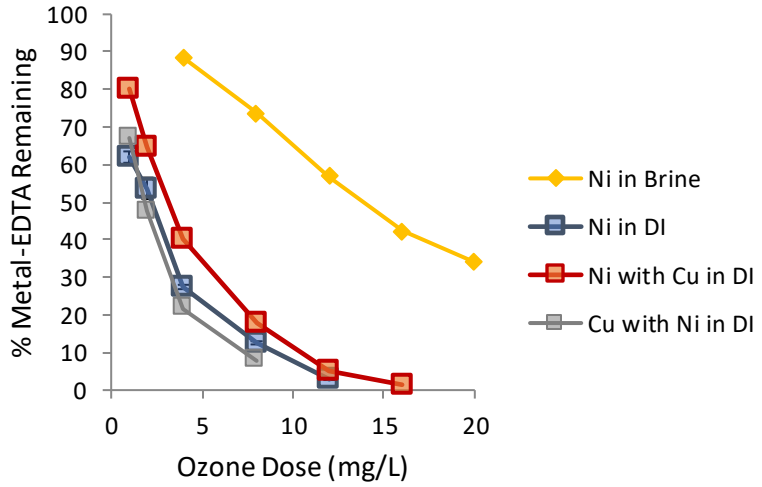

Figure 8: Ni and Cu in DI Water and Brine

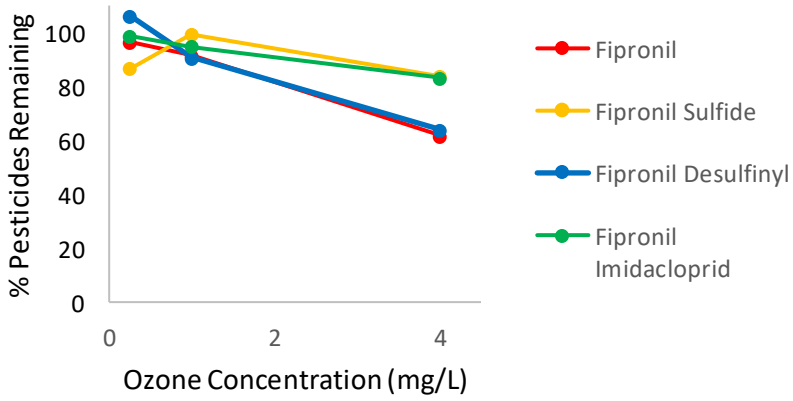

Figure 9: Pesticide Removal in DI Water

References

(1) Bedsworth, William W, and David L Sedlak. "Sources and environmental fate of strongly complexed nickel in estuarine waters: The role of ethylenediaminetetraacetate." *Environmental Science and Technology*, ACS Publications, Feb. 1999.

(2) da Costa Filho, Batuira Martins, et al. "Coupling coagulation, flocculation and decantation with photo-Fenton process for treatment of industrial wastewater containing fipronil: biodegradability and toxicity assessment." *Journal of environmental management*, 2016: 71-78.

(3) Hoigne, J., and H. Bader. "The role of hydroxyl radical reactions in ozonation processes in aqueous solutions." *Water Research*, 1976) 377-386