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

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Background

Indirect Potable Reuse

IPR is repurposing wastewater for Drinking Water Treatment.

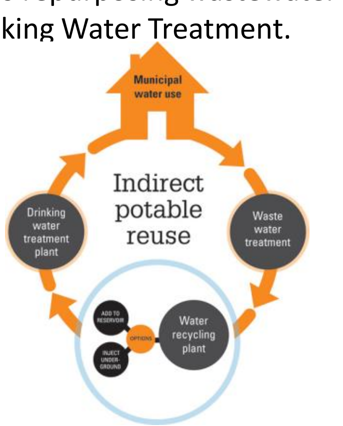


Figure 1: IPR cycle

Reverse Osmosis (RO)

RO is performed in IPR at the Water Recycling Plant, or Advanced Water Purification Center.

RO membranes remove organics and large dissolved molecules, such as pesticides.

Figure 2: Inside of an RO filter

Brine

Brine is a saline liquid produced from backwashing the RO filters.

It contains metal EDTA chelates, pesticides, and other organics.

Figure 3: Brine from the Silicon Valley Advanced Water Purification Center

Metal-EDTA Chelates and Pesticides

EDTA is a weak acid introduced to the environment through paper-milling. Metal-EDTA chelates consist of a metal (Ni, Cu, Zn) encapsulated by the EDTA molecule, making it dissolved.

Pesticides, such as fipronil, are used in agriculture and tick/flea medicine.

Stormwater causes EDTA and fipronil to enter the wastewater system, resulting in their presence in brine.

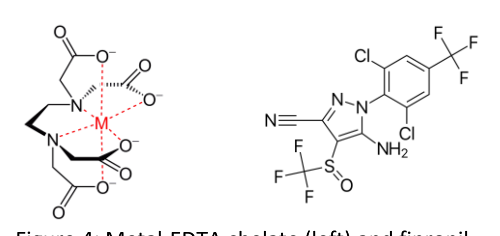


Figure 4: Metal-EDTA chelate (left) and fipronil molecule (right)

Feasible Solution: Ozone

Ozone (O_3) is presumed to break contaminants and organic pollutants in brine.
During ozonation, hydroxyl radicals (OH·) are formed as a product of ozone.
Ozone and hydroxyl radicals break the bonds of EDTA and fipronil.

Importance

Brine disposal is a deterrent of IPR because it can't be released into the environment.

Untreated brine is harmful to marine life as a result of high dissolved solids and pesticides.

Tests Performed and Results

General Ozone Testing

Adding various doses of ozone to brine and DI samples to degrade.

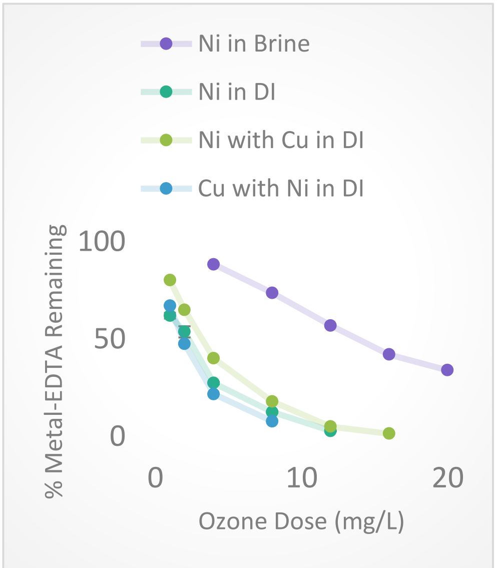


Figure 5: Ni and Cu in DI Water and Brine

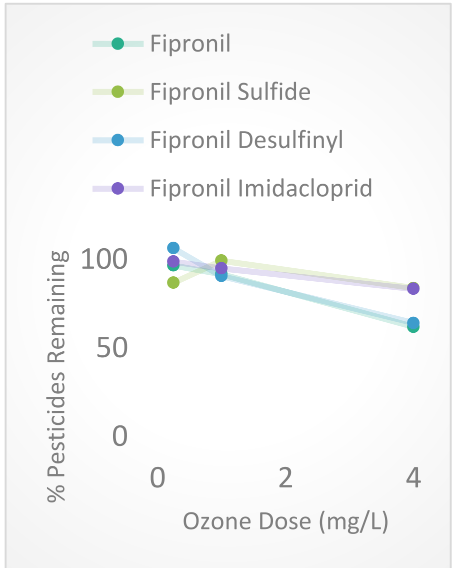
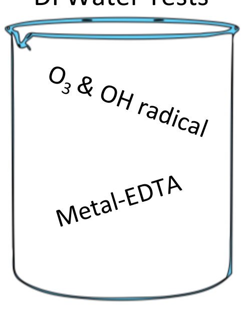
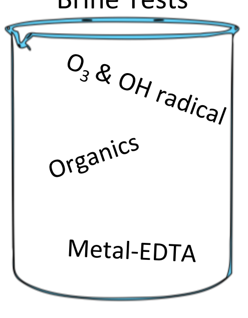


Figure 6: Pesticide Removal in DI Water

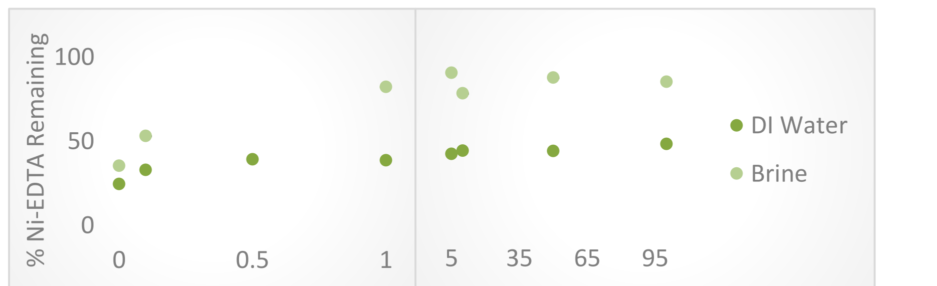




Ozone degrades Ni-EDTA most effectively in DI water (Figure 5). In brine, organics cloud the water and also react with ozone, making it appear less efficient. At an ozone dose of 20 mg/L, ozone degraded almost 65% of the Ni-EDTA in brine.
Pesticides (Figure 6) show a similar trend to Ni-EDTA and Cu-EDTA brine data. Future tests will be performed at higher ozone doses to determine pesticide's pattern.

Tert-Butanol Testing

Tert-butanol $(CH_3)_3COH$ is an alcohol that reacts with hydroxyl radicals, causing only ozone to remain. This tests shows how ozone and hydroxyl radicals work independently of one another.



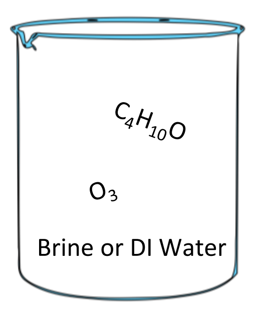
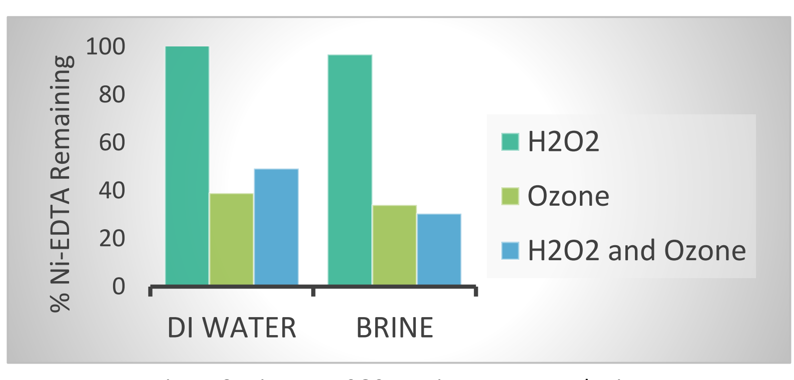


Figure 7: Ni-EDTA Tert-Butanol Test in DI Water and Brine

DI water had little change with tert-butanol addition. In brine samples, tert-butanol caused an increase in the percent of Ni-EDTA remaining. 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

Per-ozone testing is adding hydrogen peroxide (H_2O_2) and ozone to a solution. Hydrogen peroxide removes ozone, leaving high concentrations of hydroxyl radicals.



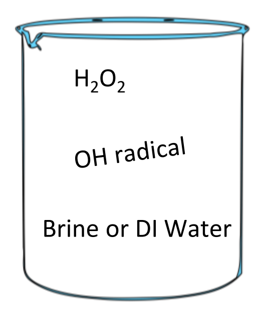
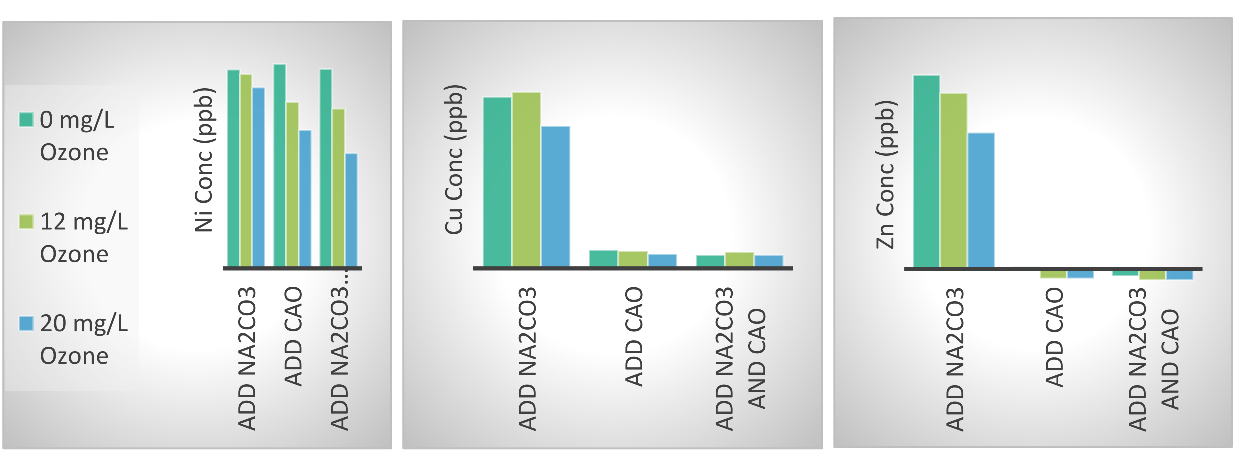


Figure 8: Ni-EDTA H2O2 Test in DI Water and Brine

In DI Water and brine samples, adding only H_2O_2 is ineffective. In DI water, adding H_2O_2 and ozone increased the Ni-EDTA remaining 10%. Adding H_2O_2 increased the hydroxyl radical concentration and decreased the ozone concentration, an unfavored condition in DI samples. In Ni-EDTA brine samples, adding H_2O_2 and ozone decreased the percentage of Ni-EDTA remaining. These results correlate to the tert-butanol findings.

Filtration Testing

Filtration tests can also depict how well ozone degrades pollutants. Three tests were performed at 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.



Figures 9, 10, and 11: Ni, Cu, and Zn Filtration Tests in Brine at Various Ozone Doses

Brine contains carbonate, so test 1 is adding an overabundance of the molecule. Adding CaO removed Cu and Zn, regardless of the ozone dose. Ni can only be precipitated out of brine with large ozone doses, sodium carbonate, and calcium oxide. Cu and Zn can be precipitated out of brine with calcium oxide and no ozone.
Ni filtration data (Figure 9) shows with increased ozone dose, there's an increases of 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 10 and 11) showed total metal removal, regardless of the ozone dose. Cu and Zn can be removed from brine without ozone.

Conclusions

Freeing metal-EDTA chelates and pesticides from brine is a crucial step in IPR.
There were two major findings. First, brine samples use hydroxyl radicals to degrade pollutants, while DI water depends on ozone. Second, filtration tests showed the different behavior of the metals. Cu and Zn required no ozone for filtration, but Ni required ozone to be removed. The Silicon Valley Treatment Center is utilizing this ozone research at their own treatment facility to remove pesticides and dissolved metals from brine.

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.