Fluoride Removal in Small Water Systems: A Coagulation Approach

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Fluoride in Water

1945 - Fluoridation of drinking water begins in Grand Rapids, MI because of associated dental benefits

1974 – Fluoride identified by EPA as water contaminant through the SDWA

1986 – Fluoride MCL set at 4.0mg/L and secondary MCL set at 2.0mg/L

2006 – National Academies of Science review on fluoride data

2011 – HHS and EPA finalize risk and exposure assessments for fluoride

McGrady et al. BioMed Central Oral Health Journal, 2012.

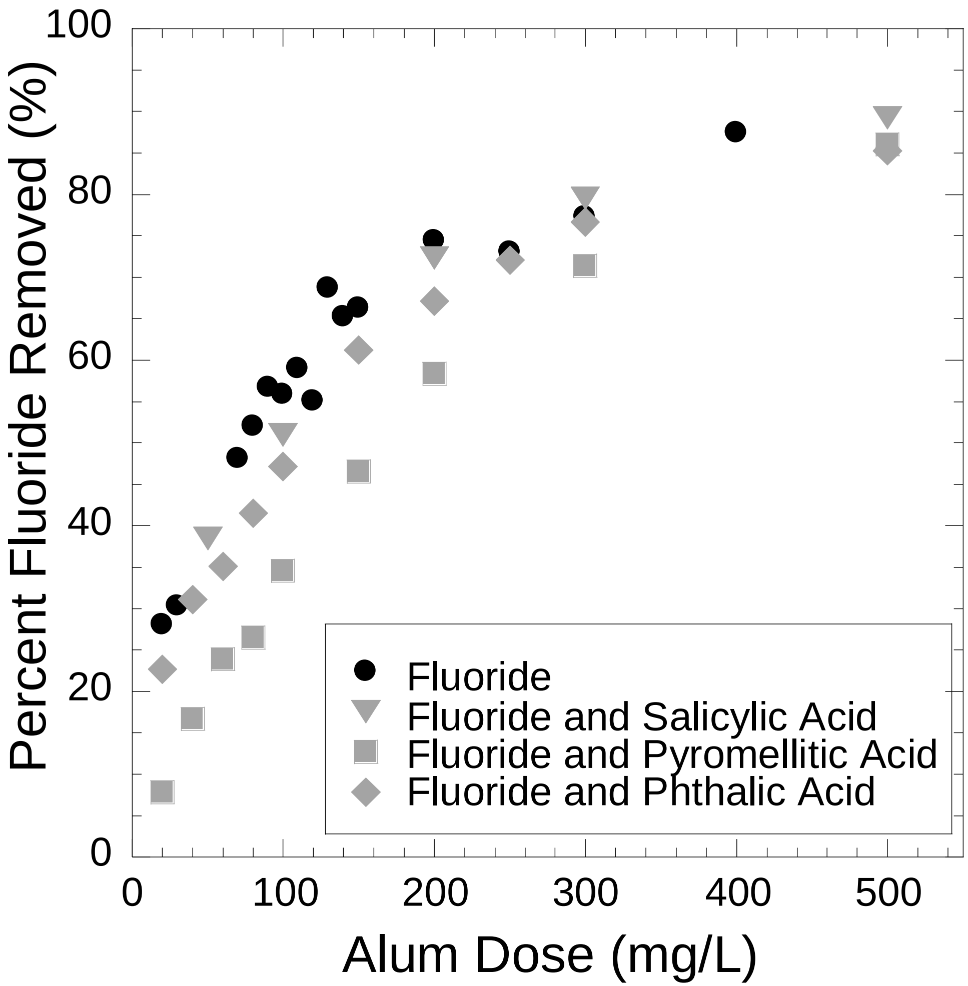
Research Objectives

1. Develop understanding of interactions among fluoride, organic ligands, and aluminum during coagulation process

2. Apply this understanding to waters containing NOM and further develop a set of treatment guidelines

3. Conduct pilot tests to validate guidelines

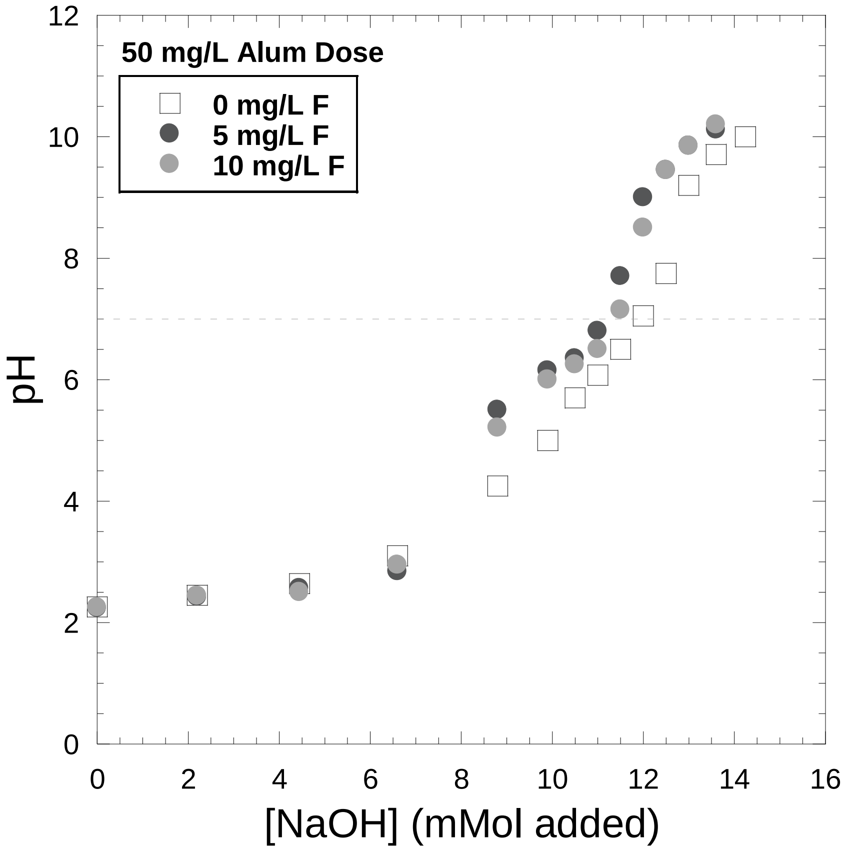
Fluoride Removal by Alum Coagulation

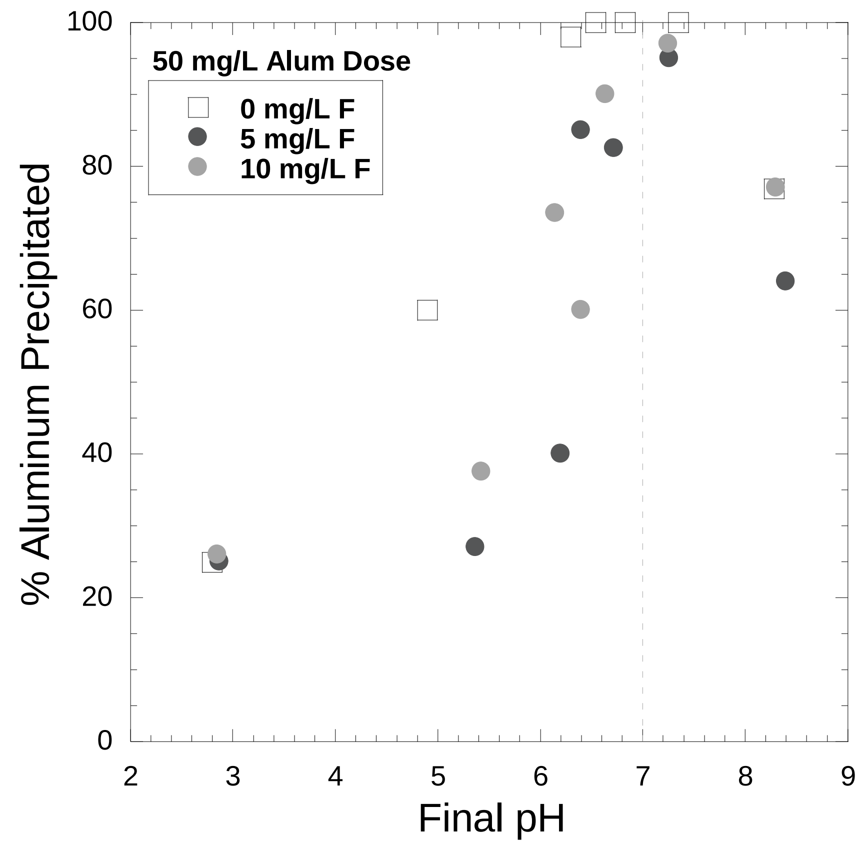


Impact of organic acids on the removal of fluoride at pH 6.5.

- Alum coagulation is an effective treatment process to remove fluoride
- Fluoride removal is negatively impacted by the presence of organic ligands during coagulation
- Fluoride is anticipated to adsorb to aluminum precipitate surface or be incorporated into its structure

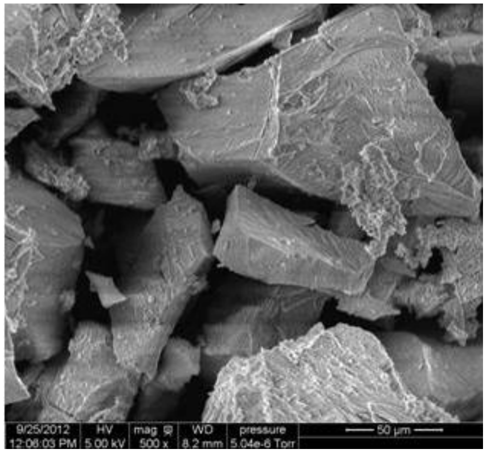
Titrations of Precipitates and the Impact of Fluoride



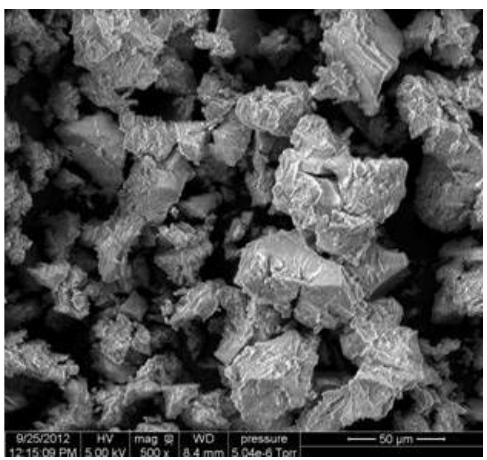


- Dashed line indicates >95% aluminum precipitation.
- Differences in titration curves above this line indicate changes within the precipitate and suggest incorporation of fluoride into the precipitate structure.

Imaging of Precipitates



Aluminum precipitates

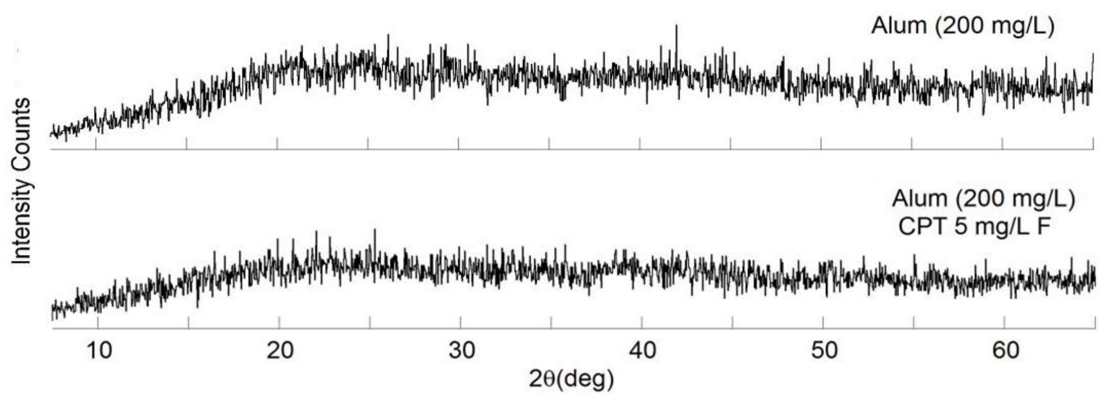


Aluminum precipitates
with fluoride

- SEM imaging of aluminum hydroxide precipitates reveals impact of fluoride on precipitate structure

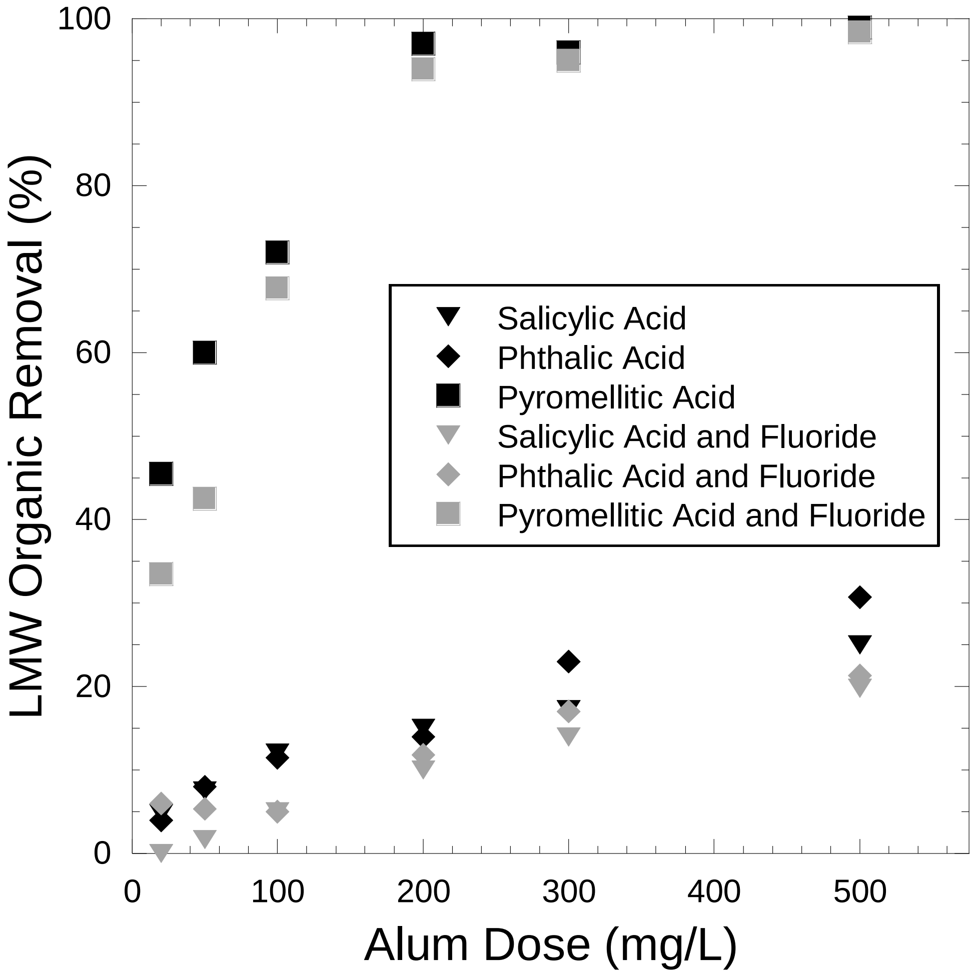
- Smaller precipitate sizes indicate fluoride incorporation into the precipitate structure.

- XRD analysis confirms that precipitates are amorphous (non-distinguishable peaks)



XRD analysis of precipitates from 200mg/L alum dose

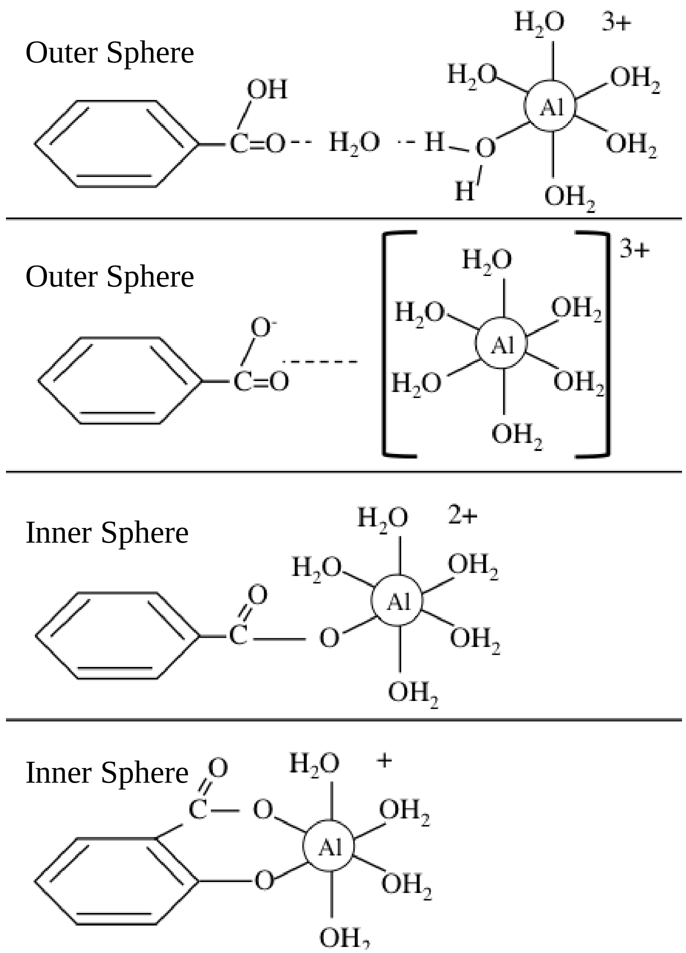
Organic Removal by Alum Coagulation



Impact of fluoride on the removal of organic ligands at pH 6.5.

- Alum coagulation is an effective treatment process to remove organic ligands
- Organic ligand removal is negatively impacted by the presence of fluoride during coagulation
- Differences in organic ligand removal are expected to be the result of differences in their functionality

Ligand Interactions and Coagulation



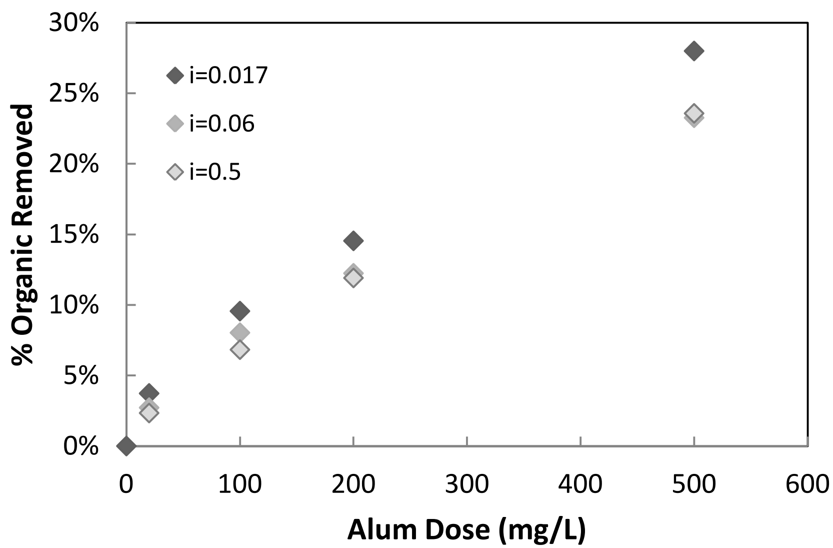
Proposed complexation models for organics and aluminum precipitates

Organic Acid	Proposed Adsorption Complex	pKa's
Salicylic Acid	Inner Sphere	2.88 13.56
Phthalic Acid	Outer Sphere	2.87 5.23
Pyromellitic Acid	Inner Sphere	1.52 2.95 4.65 5.89

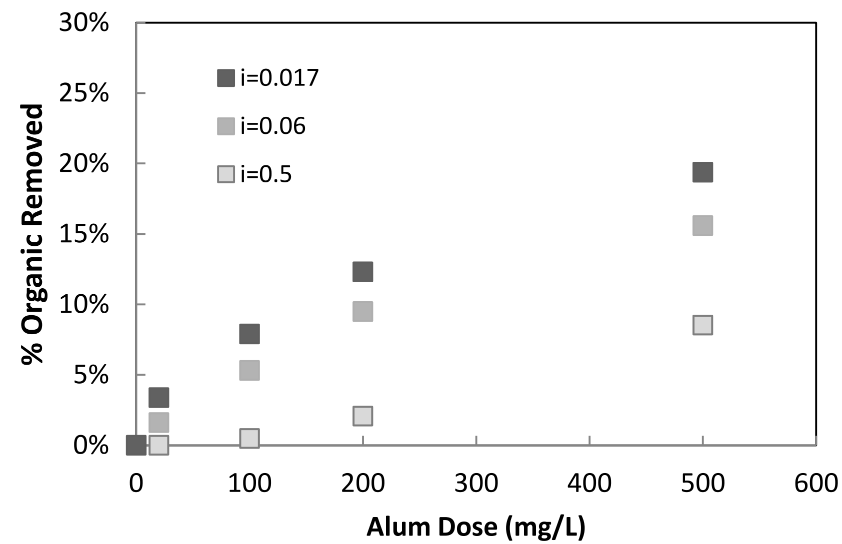
- Complexation of organics is a function of acidity of functional groups and bonding mechanism
- Inner-sphere sorption can lead to ligand-promoted dissolution while outer sphere adsorption prevents dissolution

Ionic Strength Effects on Organics Removal

Salacylic Acid

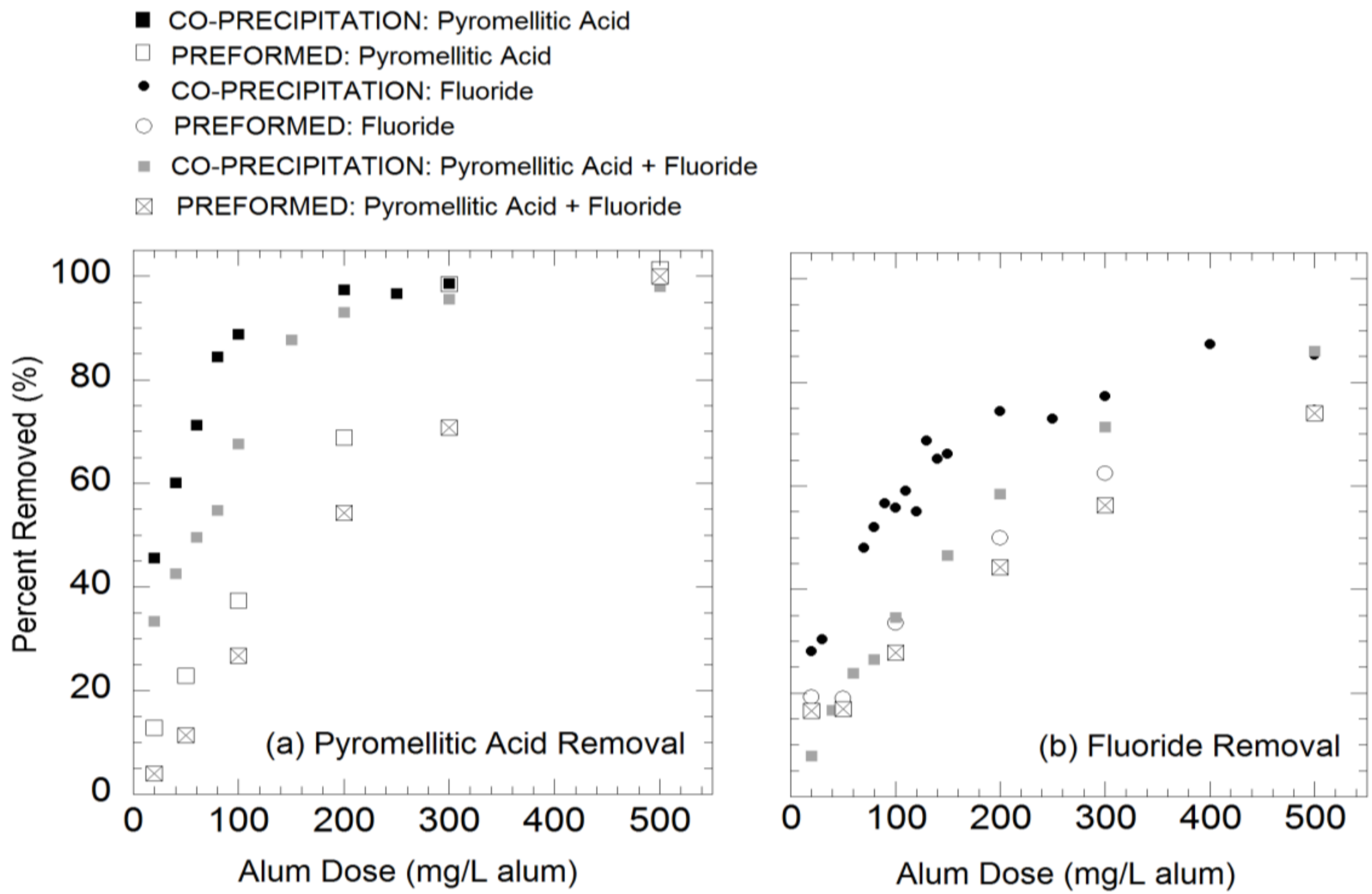


Phthalic Acid



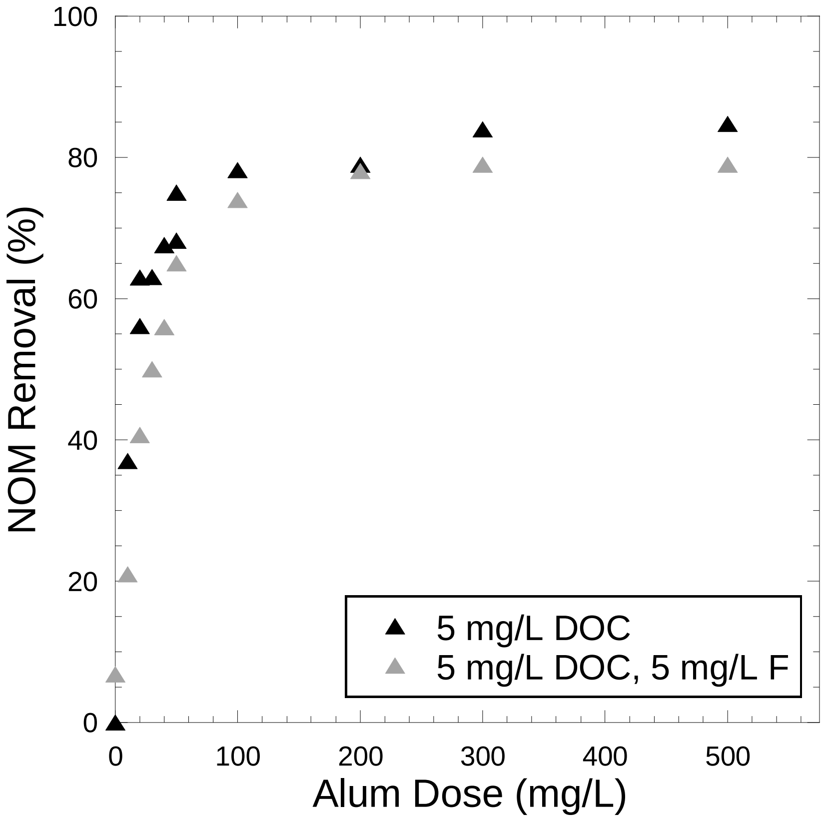
- Inner sphere complexes are not very dependent on ionic strength (Salacylic Acid)
- Outer sphere complexes are quite dependent on ionic strength (Phthalic Acid)

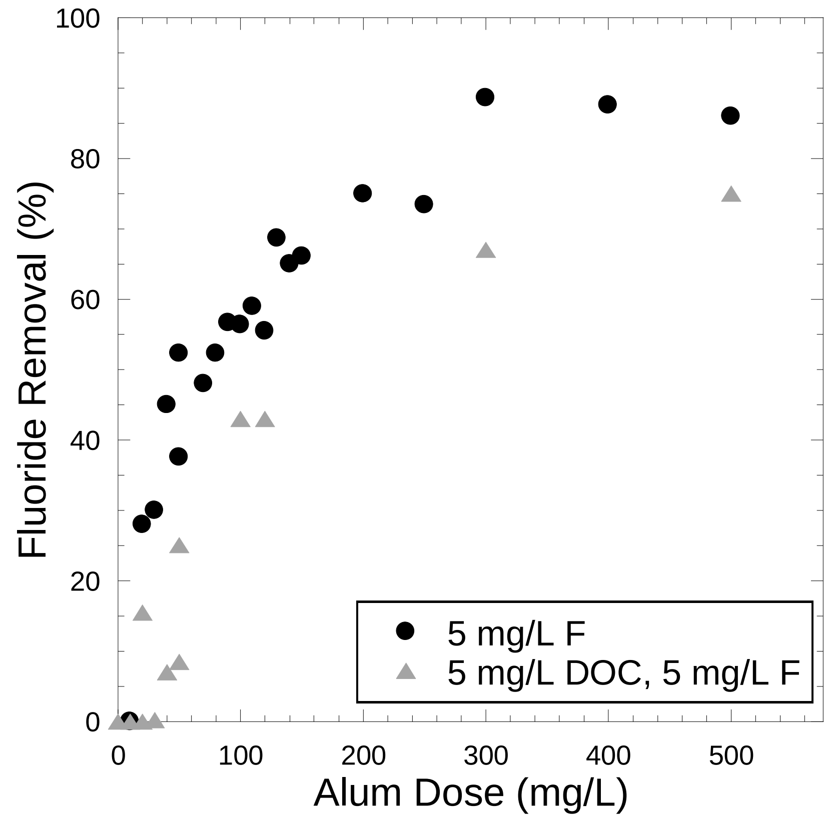
Removal of ligands by Co-precipitaton and Adsorption



- Jar tests were conducted such that either co-precipitation or adsorption of ligands onto pre-formed floc occurred
- Co-precipitation improved removals of both fluoride and organics ligands

NOM Experimental Results





- Negative impacts on NOM removal associated with the presence of fluoride were especially observed at the lower doses of alum (0 – 100 mg/L)
- The presence of 5 mg/L F doubled the alum dose required for adequate NOM and turbidity removal and also made aluminum more soluble; the presence of NOM diminished F removal at comparable alum doses

Future Work

- Confirming results with field waters that have high fluoride and reasonable NOM concentrations
- Objective 3 – Conduct pilot tests to further develop a treatment model and guidelines

Acknowledgements

The United States Environmental Protection Agency for providing funding through a STAR grant for the Research and Demonstration of Innovative Drinking Water Treatment Technologies in Small Systems (2011)

The University of Texas at Austin for providing general support, facilities, and equipment for this research