Humic Substance Removal and Minimization of Trihalomethanes by Ferric Chloride Coagulation [Project #531]

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BACKGROUND
Many water utilities will be significantly affected by the proposed drinking water regulations in the Disinfectants/Disinfection By-products (D/DBP) Rule. Humic substances are the primary constituent of natural aquatic dissolved organic matter (DOM), and some constituents of DOM form trihalomethanes (THMs) when chlorination is used as the disinfection process in water treatment. Coagulation is considered one of the most effective means of removing DOM during water treatment and hence of minimizing the production of THMs during chlorination. The extent of removal of DOM and total organic carbon (TOC) is of critical importance under the D/DBP Rule. This report discusses research conducted to determine the maximum removal of humic substances from two natural water sources by coagulation with ferric chloride. Some limited experiments conducted with alum coagulation are also discussed.

APPROACH
Coagulation studies were completed using jar test procedures with DOM that had been isolated from (1) the Suwannee River and (2) Lake Allatoona using reverse osmosis procedures. The DOM extracted from the first source is used currently as the International Standard for Humic Substances. The second source supplies water to a county in the metropolitan Atlanta area.

During the first phase of the research, the efficiencies of removal of DOM by coagulation were identified based on the initial concentration of DOM (2.3 to 13 mg C/L), the coagulant dosage (10 to 100 mg/L as FeCl₃×6H₂O [ferric chloride]), and the pH value (3 to 8). The removal efficiencies were determined using ultraviolet (UV) absorbance measurements. The results are presented in the form of operational coagulation diagrams.

During the second phase of the research, the settled supernatant in the jar tests was filtered and chlorinated. The THM production was measured as THM formation potential (THMFP) using a packed column in a gas chromatograph equipped with an electron capture detector. Operational coagulation diagrams for THM production were generated in terms of pH and coagulant dosage.

Fast atom bombardment mass spectrometry (FABMS) was used to characterize the molecular weight distributions of the DOM before and after coagulation. This research represents only the second time that this analytical technique has been used to characterize the molecular weight distribution of natural DOM. The spectra obtained provided comparative information on the molecular weight distribution of the organics remaining after coagulation conducted with various treatment conditions.

CONCLUSIONS
For the Suwannee River DOM, well-defined regions of removal were identified. Removal efficiencies of 95 percent of DOM based on UV-absorbance and nearly 85 percent of nonpurgeable organic carbon (NPOC) were obtained for
each of the DOM concentrations tested. Removal occurred only under specific pH and coagulant dosages. The regions of effective removal were typically within the pH range of 4 to 6 with coagulant doses ranging from 10 to 100 mg/L of ferric chloride

The DOM from Lake Allatoona did not coagulate as predictably as that from the Suwannee River. Removal efficiencies typically ranged from 15 to 35 percent for both DOM based on UV-absorbance and NPOC over the effective pH range of 5 to 6. However, the results agreed closely with those obtained by other researchers for similar surface waters.

Comparison of the raw waters for these two sources of DOM suggests that the composition and the character of the DOM are different. The most significant differences between the waters were their pH and organic carbon concentrations. The isolation techniques used probably did not remove nonhumic, neutral, nonpolar, organic components, which are commonly not removed effectively by coagulation.

Fast atom bombardment mass spectrometry (FABMS) indicated that the molecular weight distribution for Suwannee River humics generally ranged from 200 to 500 daltons; no values exceeded 1,000 daltons. Qualitative differences in the spectra were noted when the coagulation conditions were altered from underdosing to overdosing of coagulant.

Maximum UV absorbance removal efficiencies and minimum THMFPS occurred almost concurrently. Removal of humic material by optimized coagulation simultaneously removed DOM and lowered THMFPS. Increased initial DOM concentrations resulted in higher THMFPS. If the THM maximum contaminant level (MCL) is lowered to 40 mg/L in the United States as proposed under Stage II of the Disinfectants/Disinfection By-Products (D/DBP) Rule, treatment plants with raw water sources having high DOM concentrations will have difficulty meeting the standard by conventional treatment and chlorination alone.

The important conclusion for practice is that minimum THMFP for a particular water occurred under specific conditions of dosage and pH. Thus, treatment schemes to reach this minimum THM level may require pH adjustment and laboratory- or pilot-scale testing to determine the optimal conditions. The coagulation diagrams developed in this research may be used to predict the general domain in which minimum THMs will be formed when ferric chloride coagulation is used. Water utilities attempting to maximize DOM removal and minimize THMs may use the approach indicated in this report by plotting their data on an iron coagulation diagram to determine the optimal chemical conditions for treatment.