Comparing Aluminum and Iron Coagulants to Remove Organic Carbon, Color, and Turbidity from a Florida Slough

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Disinfection has been used to treat pathogenic microorganisms in the United States since 1908 (Environmental Protection Agency, 1999). Disinfectants such as chlorine and ozone are highly reactive chemicals, making them efficient for inactivating pathogens. In the mid-70s however, chemists in Rotterdam discovered that four trihalomethanes were observed to increase following chlorination of a surface water supply (Rook, 1974). In more recent times, ozone and other disinfectants have been shown to react with natural organic matter to form disinfection byproducts, or DBPs (Van Leeuwen, 2000; Kim Mi Hyung, 2005; Edzwald, 2011). Under the Stage 1 Disinfectants/Disinfection Byproducts Rule (D/DBPR), the U.S. Environmental Protection Agency (EPA) has regulated some DBPs such as trihalomethanes (THMs) and haloacetic acids, or HAAs (Lovins, Duranceau, Gonzalez, & Taylor, 2003). Strategies to maintain DBP rule compliance include either altering the disinfectant or removing the precursor matter. Efforts that focus on postformation treatment are limited to chloroform, which is a semi-volatile DBP that can, under certain conditions, be removed by stripping; however, this approach is limiting and does not address nonvolatile DBPs.

Natural organic matter (NOM) refers to complex organic chemicals present in natural waters originating from biological activity, decaying organic matter, excretions from aquatic organisms, and runoff from land (Crittenden, Trussell, Hand, Howe, & Tchobanoglous, 2005). It is of particular concern in drinking water treatment for both its effect on the aesthetic quality of the water and the fact that NOM serves as a surrogate for DBP precursors. In drinking water treatment, NOM and DBP precursors are often quantified by measuring the total organic carbon (TOC) or dissolved organic carbon (DOC), which is typically nonpurgeable (Wallace Brian, 2002). Although most groundwater has TOC concentrations less than 2 mg/L, surface water typically ranges from 1-20 mg/L. Swamps and highly colored surface water may have TOC concentrations as high as 200 mg/L (Crittenden et al., 2005). A common surface water treatment method for NOM removal includes coagulation, flocculation, sedimentation, and filtration (Crittenden et al., 2005).

Objective

The research for this article was conducted by the University of Central Florida (UCF) to assist Carollo Engineers with its efforts in the development of the Dona Bay Watershed Management Plan for Sarasota County and the Southwest Florida Water Management District (SWFWMD). Carollo Engineers identified six overall treatment objectives needed to achieve the treatment goals for the source water and meet drinking water standards. The overall objectives include treatment goals for total solids, natural organics, total dissolved solids (TDS), hardness, hydrogen sulfide (H_2S), synthetic organic compounds (SOCs), methyl-isoborneal (MIB), geosmin, iron, and manganese, and included disinfection evaluations (Carollo Engineers Inc., 2012). Iron and manganese control will be used to achieve possible odor and color treatment goals. Some form of stripping or aeration may be implemented to address odor concerns caused by H_2S if surrounding wells were to be incorporated as alternative sources to the Cow Pen Slough (CPS) overland flow. Solids and organics removal were critical in order to account for turbidity, TOC, and color issues.

The primary objective of research conducted by UCF's civil, environmental, and construction engineering (CECE) department was to conduct coagulant selection in support of the overall project by assessing the treatability of turbidity, color, and TOC through a bench-scale jar testing evaluation of conventional treatment. Information regarding coagulant dosages, type, optimum pH ranges, and percent removals were studied to compare the effectiveness of traditional coagulants with two coagulants less established in treating Florida surface water. Iron-based coagulants have often been used in conventional Florida drinking water plants and, although effective at removing organics, they can also add undesired color to the water. Aluminum sulfate provides a clear color alternative to the ferric based coagulants, but can add chemical costs due to the likely need for postcoagulation pH adjustment. Both aluminum chlorohydrate (ACH) and poly aluminum chloride (PACl) are advanced cationic and colorless chemicals designed to effectively treat industrial, municipal, and wastewaters at pH values near neutral, but have not previously been tested extensively on highly organic Florida surface water.

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Raw Water Quality

The CPS is a man-made canal in the Dona Bay watershed located along the western coastal region of central Florida in Sarasota County. The CPS is one of three main tributaries contributing to the Dona Bay. The water in the slough flows south and eventually converges with Fox Creek and Salt Creek before flowing into the Shakett Creek, and ultimately, Dona Bay. The CPS was originally constructed in 1966 as a drainage system for flood protection in the Myakka River basin (SWFWMD, 2009). Historical rainfall and stream flow data for the CPS describe flows ranging from 0 to 2,000 cu ft per sec (cfs), indicating widely variable and flashy flows corresponding to rainfall events. The size of the contributing catchment for the CPS is approximately 35,380 acres. Land-use data from the SWFWMD for the CPS basin is categorized into seven classes. The

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Figure 1. Photographic Comparison of the Cow Pen Slough

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data indicates that the CPS basin is dominated by agricultural and urban land use.

The natural organic content of Florida surface water is typically high, with TOC values often greater than 15 mg/L and true color values as high as 700 platinum-cobalt units (PCU). The water quality in the CPS is representative of typical Florida surface water. Water from the CPS contains high amounts of natural organic carbon, color, and suspended solids. The presence of trace levels of organic contaminants were found that included insecticides, herbicides, and petroleum hydrocarbons. Because the majority of the slough is bordered by fertilized agricultural lands, nutrient runoff from sheet flow over the agricultural lands has been observed during periods of heavy rainfall. Visual observations indicated that leaching of excess nitrates and phosphates from surrounding lands had caused algae blooms and nitrogen concentrations to spike within the slough. Figure 1 provides photographs taken during average conditions (left) and during a eutrophic event (right).

Table 1 compares the values from historical data to the values obtained during the 2012 UCF treatability study. Many of the 2012 values fall within the range of the historical data taken over the years 1963-2011. More recent data collected in 2012 indicated that DOC, sodium, strontium, TOC, and total suspended solids (TSS) had increased over time. This was not surprising as there were less than 30 historical samples taken for carbon and metals analyses. The maximum values for TSS corresponded to a eutrophic event; these numbers are shown in Figure 2. Because the historical data makes no mention of eutrophic events that cause increases in algae concentrations, it is possible that in the past samples were not taken for TSS during such occurrences.

Table 1. Comparison of Historical and UCF Raw Water Quality

		Historical Data (1963-2011)		UCF
Test	Units	Min	Max	Min
Alkalinity-total	mg/L as $CaCO_3$	10	195	167
Barium	mg/L	0.013	0.023	0.024
Calcium	mg/L	7.2	192	81
Chloride	mg/L	11	75	52
Conductivity	µS/cm	100	51695	354
DOC	mg/L	10.4	24.6	11.0
Iron-total	mg/L	0.16	1.66	0.071
Magnesium	mg/L	6.7	52.5	19.0
Mn-total	mg/L	0.01	0.04	0.004
pH	s.u.	5.8	11.5	6.34
Potassium	mg/L	0.2	8.6	2.52
Silica-total	mg/L	0.41	11.0	0.24
Sodium	mg/L	6.1	43.5	36.5
Strontium	mg/L	0.64	1.11	0.92
Sulfate	mg/L	15	526	116
TDS	mg/L	88	1000	470
Temperature	°C	9.0	34.4	18.1
TOC	mg/L	10.2	26	11.3
TSS	mg/L	1.20	19.4	1.5
Turbidity	NTU	0.40	23.0	1.39

Methods and Materials

Approach

Jar testing is considered to be an acceptable and economical method for simulating a full-scale coagulation, flocculation, and sedimentation (CFS) basin and was chosen to determine the effectiveness of each coagulant. For the purpose of this study, effectiveness was evaluated based on the removal efficiency of organics, color, and turbidity.

Organic content was measured in terms of nonpurgeable dissolved organic carbon (NPDOC; herein after referred to as DOC) which assumes filtration will be implemented after the sedimentation process, and is defined as the fraction of organic carbon remaining that has the potential to act as a DPB precursor. The CFS removal efficiency is a function of many parameters, including mixing intensity, mixing times, chemical addition, pH, temperature, etc. Variables such as mixing intensity and mixing times were held constant and did not change during the study. Coagulant concentrations ranged from 80 mg/L to 240 mg/L and were increased in increments of 20 mg/L for each coagulant. The established effective testing range for pH was 4.0 to 8.0 and pH was measured in increments of 0.5 pH units. By varying pH and coagulant concentrations, effective removals were determined for a wide range of concentrations and pH values. Table 2 provides descriptions of the five coagulants under investigation.

Table 2. List of Coagulants

Chemical	Description
Aluminum Chlorohydrate (ACH)	SG = 1.35, Dry Weight = 45.6 percent Basicity = 80 percent
Aluminum Sulfate (Alum	SG = 1.34, Dry Weight = 48.5 percent
Ferric Chloride (FC)	SG = 1.41, Dry Weight = 40 percent
Ferric Sulfate (FS)	SG = 1.59, Dry Weight = 60 percent
Poly Aluminum Hydroxychloride (PACl)	SG = 1.32, Dry Weight = 50 percent Basicity = 45- 55 percent

SG = specific gravity

Table 3. Summary of Data

Parameters	ACH	Alum	Ferric Chloride	Ferric Sulfate	PACl
Coagulant Dosage (mg/L)	80 – 100	180 – 200	100 – 120	160 – 180	100 – 120
DOC Removal (filtered)	60 – 70 percent	50 – 55 percent	80 – 85 percent	65 – 70 percent	50 – 55 percent
Color Removal (filtered)	76 – 97 percent	75 – 83 percent	65 – 98 percent	48 – 81 percent	68 – 96 percent
Turbidity Removal (settled water)	40 – 50 percent	< 10 percent	< 5 percent	< 5 percent	40–63 percent

Procedures

Raw field samples were collected from a sampling bridge by repetitively lowering 5-gal buckets from the bridge into the slough. Raw samples were transferred into 15-gal drums for transportation and storage. Field parameters, including turbidity, pH, temperature, and conductivity, were measured on site during sampling and 1-L amber sample bottles were filled for laboratory analyses for each drum. Titrations curves were developed on the raw water to determine the appropriate volume and normality of pH adjusting chemicals, which were necessary to obtain the target pH values for each coagulant dose. After determining the appropriate caustic or acid dosages for each coagulant dose, coagulant concentrations could be varied and interference from varying pH and temperature values could be minimized.

The jar testing equipment was programmed using the American Society for Testing and Materials (ASTM) standard jar testing sequence of 120 revolutions per min (rpm) for 1 min, 50 rpm for 20 min, and 0 rpm for 15 min (ASTM, 2003). The proper volume of coagulant and corresponding caustic or acid volume was measured and delivered onto septas using a pipette. To minimize variation among coagulated samples and obtain equal reaction times, the septas were simultaneously dropped into the jars once the jar testing sequence was initiated. During the flocculation stage of jar testing, the pH and temperature were recorded. At the end of the settling period, 450 mL of each settled sample was collected and tested for turbidity and filtered for DOC and color analysis.

Extensive field and laboratory quality control measures were taken throughout this study. To assess the consistency of the precision of the analytical instrumentation, duplicate measurements were taken. For field measurements, duplicates were taken every six samples. During the bench-scale testing, duplicates were prepared for each jar test run, as well as for each metal and anion analyses. To assess the consistency of the accuracy of the TOC analyzer, one out of every five samples was spiked with 1 mL of 200 parts per mil (ppm) TOC solution created monthly for DOC analysis. Quality control requirements for field data were followed according to the analytical methods listed in the laboratory quality assurance procedures for the UCF Environmental Systems Engineering Institute (ESEI) housed within the CECE department (Real-Robert, 2011). Quality control measures for laboratory data collection were performed according to the *Standard Methods for the Examination of Water and Wastewater* (Eaton, Clesceri, Rice, & Greenberg, 2005) and EPA's *Handbook of Analytical Quality Control in Water and Wastewater Laboratories.*

Results

Ferric Chloride

The maximum removal obtained using ferric chloride was 89 percent, yielding a treated water DOC concentration of 2.90 mg/L. Consistent DOC removals of 80 percent were observed in the ferric chloride concentration range of 100 to 240 mg/L. This broad variation in ferric chloride concentration suggests that there is a low correlation between coagulant dose and the removal efficiency. Consistent DOC removals of 80 percent were observed within the pH range of 4.0 to 5.0. This narrow range of pH suggested a correlation between pH and DOC removal efficiency. Color removal appears correlated to the DOC removals achieving higher removals at lower pH values. Final color readings varied from 21 PCU to < 5 PCU, with an average value of 8 PCU achieving the maximum containment level goal (MCLG) of 15 PCU.

Ferric Sulfate

The DOC removals between 60 and 65 percent were achieved at concentrations as low as 80 mg/L with treatment using ferric sulfate. Doubling the dosage to 160 mg/L was required to reach the maximum DOC percent removal of 71 percent. Ferric sulfate does show a similar correlation to that of ferric chloride at pH values above 5.5, in that increasing the pH caused a decrease in DOC removals. However, unlike ferric chloride, at pH values above 6.5, increasing the ferric sulfate dosages did not produce a significant response in DOC removals. Only a 10 percent increase in DOC removal was achieved by raising the pH above 6.5. The maximum DOC removal was 71 percent and resulted in a final DOC concentration of approximately 3.5 mg/L. The required coagulant concentration of ferric sulfate is 50 percent higher and removed nearly 15 percent less DOC than that of ferric chloride. Ferric sulfate was also less effective for color treatment as only 16 percent of the samples achieved the MCLG of 12 PCU.

Aluminum Sulfate

Aluminum sulfate correlates well with the ferric sulfate results, even though the optimum pH and coagulant ranges are more constrained. Only at a pH range of 4.5 to 5.5 and by dosing alum to a concentration of 180 mg/L was a 55 percent removal of DOC observed. At 55 percent removal, final DOC values ranged from 5.5 to 7.5 mg/L. At pH values higher than 6.5, increasing the alum concentration has little effect on DOC percent removals, yielding the lowest DOC removals relative to the other coagulants. However, on average, alum was 82 percent efficient at removing color, yielding 95 percent of the values below 12 PCU.

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Poly Aluminum Hydroxychloride

The PACl achieved similar DOC removals to alum ranging from the lower 60s to the lower 20s, but with a less constrained effective pH range of 4.0 to 5.5. The DOC removals in the lower 50 percent range were observed at PACl concentrations of 100 mg/L, with a maximum DOC removal of 61 percent at 240 mg/L. Raw water DOC values were 16 mg/L for the jar tests conducted using PACl. Post-CFS DOC values were observed as low as 5.29 mg/L. Color removal was relatively high as compared to the other coagulants, with an average value of 71 percent. Turbidity removals ranged from 30 to 60 percent in the pH range of 4.0 and 5.5.

Aluminum Chlorohydrate

Aluminum chlorohydrate achieved consistent DOC removals of over 60 percent within a pH range of 6.0 to 7.0. A strong correlation between pH and DOC removal exists with ACH, while ACH concentration seems to have a minimal effect on overall DOC removal. Removals from 60 to 70 percent were observed at nearly neutral pH and ACH dosages of 80 mg/L. The raw water DOC concentration within these ranges was 30 mg/L. Maximum DOC removals were observed in the lower 80s, with post-CFS DOC readings ranging between 5 and 6 mg/L. The ACH effectively removed color, with 33 percent of the samples showing color values under 5 PCU and 80 percent of the values meeting the MCLG of ≤12 PCU. The ACH achieved an average turbidity removal of 46 percent within this pH range. Table 3 provides the ranges for each coagulant dose observed to obtain optimal removals of DOC, color, and turbidity.

Discussion

Due to the variability in raw water quality over time it is necessary to consider the water quality at the particular date of sampling. The sampled raw water contained DOC concentrations ranging from 10 mg/L to 30 mg/L and color units ranging from 28 PCU to 275 PCU. It was observed that ferric-based coagulants were less effective for removing turbidity, oftentimes adding to the turbidity of the water, whereas aluminum-based coagulants (specifically PACl and ACH) proved effective at decreasing turbidity.

The data collected during this study indicate that the water quality of the CPS is poor relative to other Florida surface water. Organic content in the CPS was found to be generally high, with TOC values averaging above the typical surface water range of 1 to 20 mg/L. Oftentimes the TOC concentration was 50 percent higher than representative Florida surface water, reaching concentrations over 30 mg/L. Raw turbidity concentrations over 5 nephelometric turbidity units (NTU) were consistently observed, with turbidity spikes as high as 23 NTU. Additionally, field observations revealed that the apparent color of the water was dark. True color values in the CPS ranged from 30 to 280 PCU, reflecting characteristics of swamplike waters. At least one instance of an algae bloom was observed. Each of these factors suggested that the water would be difficult to treat.

The factors that appear to have contributed to the poor quality of water include the surrounding land use and the variable environmental conditions. The CPS was originally designed as a drainage system for flood protection and consequentially contains high amounts of debris, vegetation, suspended solids, color, and organic content. The CPS catchment mainly consists of land classified as agricultural, urban, and nonforested wetland. The occurrences of algae blooms in the CPS suggest agricultural and urban runoff has had a negative effect on the water quality of the slough.

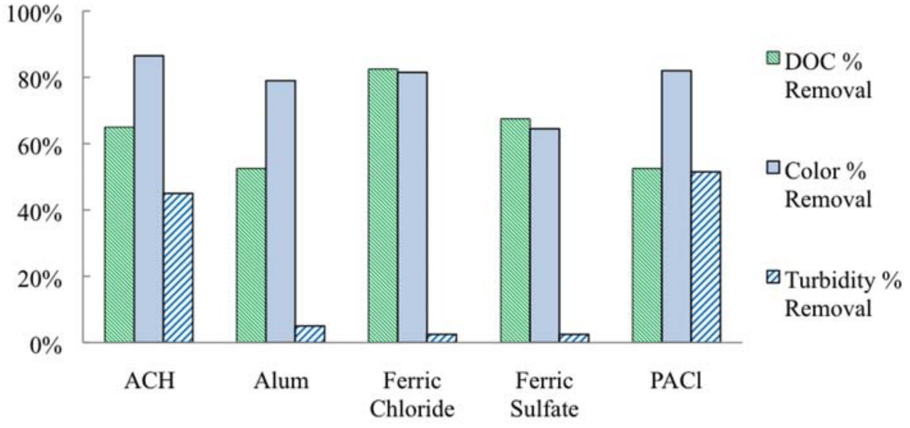

Figure 2. Coagulant Comparison Chart

From the bench-scale jar testing evaluation, the MCLGs and maximum containment levels (MCLs) for turbidity and organics removal were not attainable with the use of CFS alone. For example, the lowest turbidity achieved after CFS was 0.49 NTU and the MCLG for turbidity was 0.3 NTU. Therefore, traditional filtration techniques or membrane filtration may need to be supplemented to meet EPA regulations. Specifically the results of the jar testing evaluation indicated that ferric chloride and ACH were the most effective coagulants at DOC and color removal at the lowest dose concentrations.

Ferric sulfate was effective at DOC removal but required a higher concentration of coagulant and was the least effective coagulant at removing color depicted in Figure 2. The traditional iron-based coagulants and alum had low turbidity removals and they were often observed to add turbidity to the water. The PACl and ACH had similar percent removals for color and turbidity achieving consistent percent removals of 95 percent and 45 percent, but PACl was less effective than ACH at removing organics. Alum was the least effective at removing organics and was the second least effective coagulant for removing color. This study of nontraditional coagulant performance revealed that ACH was more efficient at removing DOC, color, and turbidity under the conditions tested in this evaluation than the other coagulants evaluated.

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