Accessory publication

Monitoring advanced oxidation of Suwannee River fulvic acid

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Experimental design

A 2^k factorial experimental design, where k is the number of primary factors tested ($k = 2$), was used to determine if the primary factors, pulse frequency and applied energy, significantly affected the dependent variables. The effects of frequency and energy on the dependent variables, ultraviolet absorbance (UV_{254}), fluorescence emission ($EX_{254}EM_{460}$ and $EX_{328}EM_{460}$), dissolved organic carbon (DOC), and trihalomethane formation potential (THMFP), were examined. The dependent variables were selected as surrogate measures of Suwannee River Fulvic Acid (SRFA). The results were evaluated during a 60-min period. Each independent variable was evaluated at a high (+) level and a low (–) level. Four sets of tests ($k = 2$) were conducted. A set consisted of a control sample (without SRFA) and a test sample (with SRFA). To provide background information, control solutions were subjected to variation in all experimental conditions (time, frequency, energy) in the pulsed electrical discharge system in the same manner as were test solutions. Data generated in this research are published in Smith.[1]

Sample matrix

Control and test solutions were prepared in distilled de-ionised water that was buffered to pH 7 using a phosphate buffer. While it has been speculated[2] that phosphate may be a radical scavenger during electrical-based corona reactions, for hydroxyl radicals, scavenging by

phosphate is highly unlikely.[3] Regardless, control of pH was deemed necessary to this research. The phosphate buffer was maintained at 0.01 M in control and test solutions. The phosphate buffer was prepared according to the recommended procedure for the THMFP protocol (*Standard Method* 5710–00)[4] in order that samples extracted from the pulsed electrical discharge system were compatible with THMFP analyses.

A stock solution was prepared by reconstituting 200 mg of SRFA (1S0F1, International Humic Substances Society Standard, Georgia Tech University, Atlanta, Georgia) in 100 mL D^2H_2O. The solution was stirred overnight and filtered using nitrogen-positive pressure filtration through a 0.45-μm pore, plain, nylon-supported membrane (Osmonics, Inc.). Dilution of the stock solution with phosphate buffer was monitored by DOC analysis to provide an initial concentration of 5.2 ± 0.1 mg L^{-1} DOC for SRFA test solutions.

Sampling techniques

Samples for analysis were obtained through the sampling port after discarding ~50 mL. After sampling was complete for each time interval, the remainder of the treated water was discarded.

Preliminary testing with the PulsePower™ system was performed to determine the amount of quenching agent, Na_2SO_3, required to terminate oxidation reactions occurring in samples. Appropriate amounts in excess were added to all sample collection receptacles to stop any oxidation reactions that might have proceeded otherwise from sampling time until analysis. All samples were maintained in a headspace-free glass container fitted with Teflon®-lined caps and stored in darkness at 4°C and analysed as soon as possible. Analysis was performed within the maximum holding times specified in each standardised methods discussed following.

Sample analyses

Temperature, conductivity, pH, and DOC

Temperature and conductivity were determined with an Orion Model 122 probe and pH with a pHTestr3+ probe according to standard laboratory operating procedures. DOC concentrations were determined using a Shimadzu TOC-V CSN Total Organic Carbon Analyzer according to *Standard Method* 5310B-00.[4]

Metals

Analyses for trace metals were conducted because the copper-tungsten cathode was susceptible to erosion during the electrical discharge. Samples for metals analyses were preserved by adding nitric acid and were stored at 4°C until processed. Samples were digested using EPA Method 3015[5] and analysed by EPA Method 200.7[6] using a Perkin Elmer Optima 3000XL ICP.

THMFP

In accordance with *Standard Method* 5710B-00,[4] THMFP was measured as the difference between the final (Day 7) and initial (Day 0) concentrations of trihalomethanes (THMs) formed. A diluted solution of Clorox® bleach was used as the source of hypochlorite ion for the chlorine-dosing solution. The chlorine concentration was determined by titration to the starch-iodide endpoint (*Standard Method* 4500-Cl^-00).[4] The solution was maintained in an amber glass bottle with Teflon septa, headspace-free, at 4°C until used.

A chlorine-demand test was performed to determine whether the addition of quenching agent to samples collected from the pulsed electrical discharge system would affect the chlorine demand required for THMFP analysis. The resulting chlorine concentration was determined, using *Standard Method* 4500-Cl^-G-00,[4] after 4 h of chlorination. The dose recommended by *Standard Method* 5710B-00[4] for chlorine demand resulted in no chlorine residual after 4 h. Therefore, testing was repeated to determine the sufficient chlorine-dosing solution. From this analysis, addition of 2.3 mL of chlorine dosing solution was determined to be required for the sample. After adding the chlorine-dosing solution, samples were transferred to the incubator and maintained in darkness at 25°C for 7 days.

After the 7-day incubation period, the test samples were removed from the incubator, and an aliquot of the sample was collected for residual chlorine analysis according to *Standard Method* 4500-Cl^-G-00.[4] The remainder of the sample was tested for pH, and sodium sulfite solution was added to each vial to stop the chlorination. THM analysis was performed within the accepted 7-day holding time after reaction quenching.

Day-0 and Day-7 samples were analysed for THMs by liquid-liquid extraction and gas chromatography (Hewlett Packard 5890A gas chromatograph with electron capture detector [GC/ECD]). An HP-1 cross-linked methyl silicon gum stationary phase (film thickness: 30 m × 0.53 mm × 2.65 μm) was used for analysis according to *Standard Method* 6232B-00.[4] THM standard reference materials (Ultra Scientific, THM-501N) were processed for calibration. Duplicate injections were performed for all samples, standards, and quality checks. Standard solutions (Ultra Scientific QCM-120) were used for quality control of the extraction and GC/ECD procedures. For additional details regarding analysis of THMFP in this laboratory, refer to Smith[1] and Aboul Eish and Wells.[7]

Ultraviolet-visible (UV-visible) and excitation emission matrix (EEM) spectroscopy

UV-visible spectra were measured using a Varian UV-visible spectrophotometer, and EEM spectra were obtained using a Varian Eclipse Fluorescence Spectrophotometer. UV-visible spectra were obtained between 200 and 500 nm. Three-dimensional EEM spectra were obtained by scanning excitation wavelengths from 200 to 400 nm with an excitation slit of 10 nm while emission wavelengths were scanned between 290 to 600 nm with an emission slit of 10 nm. Data were recorded at 1-nm intervals.

UV-visible and EEM spectra were obtained for each set of data consisting of a control sample (without SRFA) and a test sample (with SRFA), under varying conditions of time, frequency, and energy. Each EEM spectrum (test or control) was corrected for primary and secondary inner filtering effects by applying the UV-visible data according to procedures given in Tucker *et al.*[8] using Matlab® programs written in-house. After each control and test spectrum was corrected for inner filtering effects, Matlab was also used to subtract the entire EEM spectrum of the appropriate control sample from the corresponding test sample, thereby simultaneously removing background fluorescence and correcting for the Raman spectrum of water. From the corrected three-dimensional spectra, two EEM wavelength pairs were selected as dependent variables: $EX_{254}EM_{460}$ and $EX_{328}EM_{460}$.

Statistical analyses

The Statistical Analysis System (SAS®, Version 9.1, SAS Institute Inc., Cary, NC) was used to evaluate the data. Statistical analysis of variance (ANOVA) of the factorial design was conducted to determine if the primary factors (time, energy, frequency) significantly affected the results (THMFP, $EX_{254}EM_{460}$, and $EX_{328}EM_{460}$). Student's two-tailed *t* test, in the form of Eqn A1 (where *s* is the standard deviation of *n* observations whose mean is $\overline{X}$; μ is the parameter being compared to the population represented by $\overline{X}$; and d.f. represents the degrees of freedom), was used as the appropriate test statistic to determine if a parameter measured at time *t* falls within the sample population measured at time 0 (95%).

$$t = \frac{\overline{X} - \mu}{s}; \text{ d.f.} = n - 1 \quad \text{(A1)}$$

References

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