



Project Summary

Pilot-Scale Evaluation of Photolytic Ozonation for Trihalomethane Precursor Removal

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Ozone used in combination with ultraviolet (UV) radiation was studied on the pilot scale for removing trihalomethane (THM) precursors from potable water. The effects of varying parameters such as ozone dose rate and UV intensity were first studied using a synthetic feedwater reconstituted from a humic concentrate. This concentrate was obtained by sodium hydroxide elution of granular activated carbon (GAC) columns used for the adsorption of humic material from water in a previous project. The pilot plant was then operated for 8 months at the Sabine River Water Treatment Plant in Longview, Texas.

A laboratory investigation was also conducted on the mechanism of the ozone/UV process. Kinetic analysis was performed on data collected during ozone photolysis experiments in the presence and absence of known hydroxyl radical scavengers. This analysis indicates that ozone photolysis in aqueous solution leads directly to the formation of hydrogen peroxide, which then produces hydroxyl radical by secondary reaction of peroxy anion (HO_2^-) and subsequent species with ozone.

The mechanistic results predict a maximum yield of $\frac{2}{3}$ hydroxyl radical for each ozone molecule used in the proposed mechanism. The mechanistic results also predict a plateau in treatment efficiency as a function of the fraction of ozone photolyzed and thus as a function of UV power input. A simple model was developed for ozone

mass transfer with chemical and photochemical reaction. Correlation of this model with mechanistic and pilot plant data is ongoing.

Operating data from the pilot plant and analysis of the residual trihalomethane formation potential (THMFP) after treatment provided the basis for projecting costs for removing THMFP by photolytic ozonation. At a 1-mgd plant capacity and an initial THMFP of $300 \mu\text{g/L}$, projected treatment costs were \$0.55, \$0.70, and \$0.91 per thousand gallons for 60%, 70%, and 80% THMFP removal, respectively, assuming an electrical cost of \$0.10 per kWh. At this capacity, projected treatment costs were still decreasing rapidly with increased plant capacity.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The chlorination of natural water for potable use is now known to produce trihalomethanes (THM's), which have been shown to be carcinogenic in laboratory animals. A preliminary laboratory study reported by this research group in 1980 (EPA-600/2-80-110) showed that the potential of natural waters for producing THM's upon chlorination could essentially be elimi-



nated by simultaneous treatment with ozone and ultraviolet (UV) radiation. However, the ozone doses required in the laboratory experiments were rather high. The present report describes an attempt to understand and refine the ozone/UV system; also described is a pilot-scale evaluation using photolytic ozonation to destroy THM precursors in water.

The project was conducted in four parts: (1) a laboratory and theoretical investigation of the mechanism of photolytic ozonation, (2) construction and initial testing of the pilot plant using a reconstituted lake water concentrate for feedwater consistency, (3) continuous operation of the pilot plant using feedwater from the Sabine River Water Treatment Plant located in Longview, Texas, and (4) a laboratory study of byproducts formed upon photolytic ozonation of natural waters. In addition to these four phases, a simple model for ozone mass transfer with photochemical reaction has been developed to use with the mechanistic results for interpreting the experimental results. Data obtained during pilot-scale operation were used in treatment cost projections for a full-scale system.

Procedures

Laboratory Study

Ozone photolysis was studied in the laboratory by monitoring the accumulation of ozone, hydrogen peroxide, and total oxidants in a laboratory scale, stirred-tank reactor, with and without irradiation by UV light and in the presence and absence of known hydroxyl radical scavengers. The experiment was set up so that the ozone concentration in the gas stream into and out of the reactor could be measured. The analyses indicated that in the absence of organic compounds, the total oxidant concentration was equal to the sum of the ozone and hydrogen peroxide concentrations. Ozone was measured using indigo disulfonate bleaching; hydrogen peroxide was measured by the colorimetric detection of the peroxide-titanium complex, and total oxidants by molybdate-catalyzed iodimetry.

Pilot-Scale Studies

Pilot studies were conducted in a pilot plant housed in a 42-ft-long drop-frame trailer. The plant had been previously used in a pilot study of ozonation combined with GAC for THM precursor removal. This facility was moved to the SumX Corporation in Austin, Texas, where it was modified by the addition of UV lamps to the existing ozone contactor

and the addition of tubular photochemical reactors (bubble columns with UV lamps installed in quartz lamp wells) for comparison studies.

Operating parameters were varied in the initial phase, which used synthetic lake water reconstituted from a concentrate. The concentrate was obtained by sodium hydroxide elution of several GAC columns that had been used for several weeks to treat water with a high natural organic content. The consistency of feedwater provided by this concentrate during a several-month study to determine optimum treatment parameters outweighed arguments about the concentrate's representative nature. A stirred-tank reactor equipped with a turbine contactor was compared with the tubular photochemical reactors (TPR's) while the ozone dose rates and UV intensities were varied in both.

Following the study to determine optimum treatment parameters, the pilot plant was moved to the Sabine River Water Treatment Plant in Longview, Texas, and operated for 8 months. Feedwater was of two types: alum-settled water before and after lime clarification. The stirred-tank reactor and the TPR's were compared while ozone dosages and UV intensities were varied. Treatment effectiveness of various configurations was evaluated by withdrawing water samples after treatment, chlorinating them for 7 days in the laboratory at an applied chlorine dose of 30 mg/L, and measuring them for THM formation by liquid-liquid extraction and gas chromatography/electron capture detection (GC/ECD) analysis.

Byproduct Studies

Treated and untreated water samples from the pilot plant were passed through columns of the macroreticular resins XAD-4 and XAD-8 to trap organic byproducts of photolytic ozonation. In the first of two experiments, the water was acidified to pH 1.8, a water-to-resin volume ratio of 20 was used, and the resin was eluted with methanol. To derivatize carboxylic acids, the sample was evaporated to dryness by gentle warming in a stream of inert gas after adding tetrabutylammonium hydroxide (TBAH) to pH 9. The residue was taken back up in a small quantity of acetonitrile containing a slight excess (based on TBAH) of ethyl bromide and allowed to stand at room temperature for 1 hour or longer. This procedure produces the ethyl esters of carboxylic acids.

In the second experiment, the water was passed through the resins after it was adjusted to pH 10, the resin was eluted with ethyl ether, the water was adjusted to pH 2 and put back through the column, and the column was again eluted with ether. Extracts from both experiments were analyzed by capillary gas chromatography/flame ionization detection (GC/FID) and by gas chromatography/mass spectrometry (GC/MS) at overall concentration factors of 1300 and 1200, respectively, for the first and second experiments.

Results and Discussion

Laboratory Study of Active Species

The main thrust of this portion of the project was to identify the principal active specie(s) in photolytic ozonation and, if possible, to determine the reaction mechanism. The primary barrier to elucidating the mechanism was identifying the products of the first step, ozone photolysis. The literature indicated that this reaction would produce either two hydroxyl radicals or hydrogen peroxide, followed in either case by a complex network of secondary reactions.

Ozone photolysis studies were designed to differentiate between the two possibilities for the primary step in photolytic ozonation. The studies led to conflicting results when two different known hydroxyl radical scavengers were used. When 0.015M acetic acid/acetate was present, hydrogen peroxide accumulated in solution upon continued ozonation and irradiation at pH values in the range of 3 to 8. However, peroxide levels were too low to be quantified in the presence of 0.015M sodium bicarbonate at pH 7. Experiments run in distilled water with no scavenger added gave results intermediate between the two scavenger experiments, indicating the presence of some additional complicating effect in at least one set of experiments. Kinetic analysis of the complex reaction system, using rate constants from the literature and assuming first one initiation step and then the other, indicated that the initial step of the reaction mechanism is the photolysis of aqueous ozone to produce hydrogen peroxide. The ensuing secondary reaction system is primarily that of the ozone/hydrogen peroxide system. This system includes the dissociation of hydrogen peroxide to yield the anion, which in turn reacts with ozone to yield hydroxyl radical and superoxide (O_2^-).

Superoxide reacts very quickly with additional ozone to yield ultimately another hydroxyl radical. Thus in the net reaction, three ozone molecules and one photon yield two hydroxyl radicals. The implication of this net reaction stoichiometry is that, in a system where the hydroxyl radical is effectively scavenged by the substance to be destroyed (organic substrates), the optimum hydroxyl radical yield is achieved when one-third of the ozone transferred into solution is photolyzed. On the other hand, if ozone photolysis resulted directly in the production of two hydroxyl radicals, the maximum yield would be realized when all the transferred ozone was photolyzed.

Pilot Studies

The studies to determine optimum operating parameters indicated that the stirred-tank reactor performed better than the tubular photochemical reactors, even on the basis of ozone consumed. Thus the greater effectiveness in the former case was not simply the result of better mass transfer. These studies also indicated that an optimum level of UV power existed, above which performance increased very little. These data support the proposed mechanism.

The studies of optimum operating parameters also indicated that in the stirred tank with 0.1 to 0.3 watt/L of applied UV radiation, an ozone dose of 30 mg/L was required to reduce the total trihalomethane formation potential (TTHMFP) of the reconstituted lake water concentrate to 1/e (37%) of its original value. (Original THMFP values ranged from 106 to 192 µg/L in this phase of the study). In the tubular photochemical reactors, 40 mg/L ozone was required to achieve the same extent of removal, using applied UV radiation of 0.5 to 0.7 watt/L of reactor volume. It was found in most cases that upon ozone/UV treatment, the THMFP first increased from its initial value, then dropped exponentially with continued treatment. This is attributed to the formation of precursor sites from nonprecursor organic material. During pilot operation in Longview, the stirred tank also proved superior to the tubular photochemical reactor. In an attempt to test whether gas-phase ozone photolysis was detrimental to process efficiency, delayed irradiation (DI) configurations were also tested. In these configurations, ozone contacting took place in the stirred tank reactor, followed by ozone photolysis in a separate vessel.

The DI configurations were less effective than simultaneous ozone contacting and photolysis in the stirred tank, but more effective than the tubular reactors alone, based on the amount of ozone removed from the gas stream. The ozone doses required for TTHMFP removal to 1/e of the original value are listed in Table 1, along with those required for the reconstituted lake water used in the parameter studies. Correspondence of results obtained on the two different feedwaters is good when expressed in terms of the ozone dose required to reach a particular extent of removal. Note that the desired TTHMFP removal could be reached using ozone alone, but that the required ozone dose is prohibitive.

The pilot-scale operation at Longview also showed that the lowest dose rate that could achieve the desired removal proved to be the most efficient. In addition, the efficiency with which ozone was used in the ozone/UV reactions was relatively insensitive to pH and other matrix components in clarified, filtered Sabine River water.

Cost Analysis

Data for removing 60%, 70%, and 80% of the TTHMFP in the optimum configuration was used to project an approximate treatment cost, using cost data supplied by the U.S. Environmental Protection Agency (EPA) for small systems (0.1 and 0.5 mgd). These data were extrapolated to other system sizes using the equation $T = LQ^n$, where T is the cost, Q is the plant or unit capacity, and L and n are parameters evaluated by fitting the equation to the EPA-supplied data for capital and operating costs for ozone generation and feed, UV light, stirring, etc., at 0.1- and 0.5-mgd capacities. Capital costs were subjected to a multiplicative factor of 1.4

to cover engineering, contractors, overhead and profit, site preparation, interest during construction, and legal and administrative fees. An interest rate of 8% was assumed over 20 years.

Cost projections for various levels of removal strongly depended on plant capacity in the 0.1- to 0.5-mgd range, and a method was sought to estimate treatment costs over a larger range of plant size. To assess the validity of extrapolation to larger systems, suppliers of ozonation equipment were contacted and asked about ozone generation and feed equipment costs for systems in the size range of 20 to 1000 lb/day. The hardware costs thus obtained were fit to the same exponential equation given above and then extrapolated upwards (in plant capacity) for comparison with the installed costs for actual large systems installed in recent years. A ratio of hardware costs to installed costs for large systems was obtained from this comparison. When this ratio was applied to the manufacturer-supplied hardware costs applicable to 0.1- and 0.5-mgd plants, the resulting value predicted the EPA-supplied cost figures (including the factor of 1.4) within 10% to 15%, thus indicating the validity of the above extrapolation. Projected treatment costs are given in Table 2 for 0.1- to 5.0-mgd capacities. Treatment costs are still strongly capacity-dependent in the range of 5.0-mgd capacity.

Byproduct Study

The methanol extract derived from the first experiment was analyzed by GC/FID and GC/MS. Several peaks were reduced to a few percent of their original size by ozone/UV treatment (17.7 mg/L of ozone used), and only two new peaks were found. The latter corresponded with 9 and

Table 1. Ozone Dose Required to Reduce TTHMFP of Sabine River Water and Reconstituted Lake Water to 1/e of Its Original Value*

Reactor	Mode	Ozone Dose	
		Sabine River Water, Longview, Texas	Reconstituted Lake Water
Stirred Tank	O ₃ /UV-CP†	27 mg/L	30 mg/L
Stirred Tank	O ₃ /UV-DI‡	34 mg/L	§
Tubular	O ₃ /UV-CP†	41 mg/L	40 mg/L
Stirred Tank	Ozone only	48 mg/L	§

* 1/e = 37%; initial THMFP values ranged from 106 to 192 g/L in reconstituted lake water and 120 to 437 g/L in Sabine River water.

† CP = simultaneous ozone contacting and photolysis.

‡ DI = ozone contacting followed by photolysis in a separate vessel.

§ Not run.

Table 2. Projected Treatment Costs for THM Precursor Destruction Using Photolytic Ozonation*

Plant Capacity	Dollars/1000 gallons		
	60% Removal	70% Removal	80% Removal
0.1 MGD	\$ 2.16	\$ 2.43	\$ 2.75
0.5 MGD	0.83	1.02	1.27
1.0 MGD	0.55	0.70	0.91
5.0 MGD	0.21	0.29	0.42

* An electrical cost of \$0.10 per kWh was used, but costs are only 5% to 10% lower at an electrical cost of \$0.05 per kWh.

2 $\mu\text{g/L}$, assuming compound response factors equal to that of the internal standard d_{10} -anthracene. In the second experiment, GC/FID analysis of the ether extract revealed several compounds in the treated water that were not present in the untreated sample. The concentration of these compounds ranged from a few $\mu\text{g/L}$ to several tens of $\mu\text{g/L}$, assuming response factors equal to that of the internal standard. No GC/MS identification of these compounds has yet to be made.

Also in that sample, a small group of peaks present in the untreated water disappeared upon treatment, reconfirming the ability of the ozone/UV process to remove trace quantities of potentially harmful organic pollutants during treatment for THM precursors. Comparison with the internal standard indicated that the compounds were originally present in the water at less than 1 ppb. The mass spectra indicated that the compounds were probably a homologous series of alkyl benzenes. Further analysis of the GC/MS data reported here is ongoing.

Conclusions

The laboratory study shows that the primary mechanism of photolytic ozonation with UV irradiation at 254 nm is the photolysis of ozone to produce hydrogen peroxide, which dissociates to some degree to produce peroxy anion. The reaction between peroxy anion (and in a later step, superoxide) and ozone produces hydroxyl radical, which is the primary active species of the ozone/UV process. The above conclusions predict that (1) the maximum yield of hydroxyl radical per ozone molecule is $\frac{2}{3}$, and (2) when more than $\frac{1}{3}$ of the available ozone is photolyzed, little or no increase in hydroxyl radical production should be obtained.

In the pilot-scale study, an ozone dose of 27 mg/L (transferred from the gas phase to the liquid) was sufficient to reduce the THMFP of clarified and filtered

Sabine River water to $1/e$ (37%) of its original value (300 $\mu\text{g/L}$) using a stirred tank reactor with 0.27 watts of UV/L applied in the reactor. If UV application was delayed until after initial ozone contacting, or if the stirring or UV was omitted, required dosages (still based on that amount of ozone transferred out of the gas) were 34, 41, and 48 mg/L, respectively. The experimental data supported the concept of minimal increase in treatment efficiency above a certain UV intensity. The lowest rate of ozone addition that effected the desired THMFP removal was the most efficient in terms of ozone used.

The projected treatment costs of the process at a 1-mgd plant for 60%, 70% and 80% THMFP removals from clarified Sabine River water were \$0.55, \$0.70, and \$0.91 per thousand gallons, respectively, at an assumed electrical cost of \$0.10 per kWh. Treatment costs still strongly depended on plant capacity at this size. The increase in process efficiency by the addition of stirring and UV greatly outweighed the increased cost over ozonation alone in these cost projections. The dominant term (65%) in the projected treatment cost is the amortized capital cost of the ozone generation and feed equipment.

Recommendations

Further laboratory-scale investigations should be made of several points that were either beyond the scope of this study or emerged too late in the study to be systematically investigated. Ozonation of natural organics in water should be studied to determine how or whether it is possible to suppress the formation of new THM precursor material during the destruction of that material initially present. If that could be accomplished, the possibility would exist for considerably lowering the ozone dose requirement for satisfactory THMFP removal. The model developed for mass transfer with simultaneous chemical and photochemical reaction should be verified in the labora-

tory under conditions where careful oxidant measurements can be made. The use of a simple model substrate rather than natural organic material would increase the probability of success, as would the use of a photolyte that is less susceptible to side reactions than is ozone. Finally, a survey of ozone dose requirements for water samples from different geographical locations would provide information concerning the transferability of projected treatment costs from one water source to another.

Two further studies are necessary before photolytic ozonation can be recommended as a potable water treatment process. Thorough toxicity and mutagenicity testing should be done on concentrates of treated and untreated water from several different water sources to help ensure that public health problems do not arise later. The process itself should be tested at the field scale to verify ozone and UV dose requirements in larger systems and to address the problems associated with scale-up of the complicated, photochemically initiated reaction.

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The complete report, entitled "Pilot Scale Evaluation of Photolytic Ozonation for Trihalomethane Precursor Removal," (Order No. PB 84-234 517; Cost: \$20.50, subject to change) will be available only from:

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