Wat. Res. Vol. 24, No. 8, pp. 957–964, 1990
Printed in Great Britain.

0043-1354/90 $3.00 + 0.00

REMOVAL OF ORGANOHALOGENS AND ORGANOHALOGEN PRECURSORS IN RECLAIMED WASTEWATER—II

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(First received June 1989; accepted in revised form December 1989)

Abstract—Treatment, at bench scale, of filtered secondary effluent from an advanced wastewater reclamation facility indicated that carbon adsorption and advanced oxidation each provide significant reductions in concentrations of both total organic halogens (TOX) and TOX precursors (measured as NVTOC). Equilibria and batch dynamic data suggested that multicomponent adsorption of TOX and precursors was favorable and pH dependent. In addition to contact time, oxidation of TOX and precursors by ozone peroxide was highly dependent upon hydrogen peroxide dosages.

Key words—chlorination, halogens, disinfection, dechlorination, water reclamation

INTRODUCTION

In the past decade research has focused on treatment technologies concerning removal of organohalogen precursors from water following Rook's (1974) report of experimental evidence of the formation of haloforms from the chlorination of naturally occurring fulvic acids and results from the EPA's National Organic Reconnaissance Survey (Symons *et al.*, 1975) confirming ubiquity of halogenated organics in finished waters.

Much of this research has involved natural drinking water sources and has focused upon trihalomethane (THM) precursor removal. Recent research, however, has confirmed that THMs are only a fraction of the total organic halogen content of chlorinated waters (Becher and Carlberg, 1985; Johnson and Jensen, 1986). Furthermore, as the mutagenicity of drinking water has been associated with the higher molecular weight fraction of chlorinated organics (Bull, 1982), it seems prudent to consider total organic halogen content and precursors in the examination of water treatment processes.

Organohalogen, including total organic halogen (TOX) and trihalomethanes (THMs) (a subset of TOX), precursors are a complex mixture of natural organic substances. In natural water sources these include humic substances and other compounds implicated as potential precursors: chlorophyll (Morris and Baum, 1978), extracellular algal products (Briley *et al.*, 1979; Hoehn *et al.*, 1979), phenols and ketones (Onodera, 1984; Boyce *et al.*, 1983; Boyce and Honig, 1979), and free, proteinaceous and humic bound amino acids (Trehy *et al.*, 1986).

Industrial and municipal use of treated waters results in aqueous wastes with increased levels of dissolved organic substances that are potential organohalogen precursors. Much of this organic material is proteinaceous, fatty or carbohydrate-like —byproducts of microbial metabolism. Additionally, these waters contain background levels of organohalogens from industrial and municipal pollution including organic solvents, deodorants such as dichlorobenzene, pesticides, cresols and terpenoid wastes (Morris and Donovan, 1987) and toxic, mutagenic or carcinogenic chlorinated compounds classified by the U.S. EPA as priority pollutants (Council on Environmental Quality, 1978).

The city of San Diego (Calif., U.S.A.) has proposed to utilize reclaimed wastewater as a potential drinking water source. The proposal requires disinfecting and recycling effluent by mixing and storing, for 1 year in a reservoir, with natural source waters. The existing wastewater facility consists of primary treatment, secondary treatment, coagulation, flocculation, u.v. disinfection, reverse osmosis (RO), air stripping and carbon adsorption. Treatment would potentially be followed with disinfection by chlorination.

In an earlier paper (Bauman and Stenstrom, 1990) we investigated characteristics of the coagulated/flocculated/filtered secondary effluent that indicated that it may be suitably treated, before recycling, by simpler, more cost effective alternatives to the existing advanced treatment system. In addition to basic water quality parameters, alternative treatment systems would have to be capable of removing principle risk factors: bacteria, viruses, spores, protozoans, heavy metals, halogenated (ITOX) and nonhalogenated anthropogenic chemicals and organohalogen formation potentials (THMFP, TOXFP).

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Conceptual potential alternatives to the existing treatment facility include:

(1) carbon adsorption, ion-exchange, chlorine disinfection;
(2) ozone–peroxide oxidation, ion-exchange, chlorine disinfection;
(3) ozone–peroxide oxidation, carbon adsorption, ion-exchange, chlorine disinfection.

This article examines carbon adsorption and ozone–peroxide oxidation. These unit operations are most likely candidates for removal of halogenated organics (ITOX) and organic carbon in order to produce effluent which can be adequately chlorinated to remove biological risk factors with minimal disinfection byproduct (TOXFP) formation.

EXPERIMENTAL

Sampling and analytical protocol

Wastewater samples, taken from secondarily treated and coagulated/flocculated/filtered effluent were treated in the laboratory and analyzed for nonvolatile total organic carbon (NVTOC), u.v. absorbance, total organic halogen (TOX) or for organohalogen formation potentials (TOXFP). Detailed sampling and analytical procedures and a description of the wastewater facility are reported in a previous paper.

Isotherms and rate studies

Granular activated carbon (GAG; Calgon F-400; pore volume = 1.07 $cm^3 g^{-1}$; BET surface area = 1000–1200 $m^2 g^{-1}$) and activated alumina (AA; Alcoa F-1; pore volume = 0.4; BET surface area = 250) were used for equilibrium isotherm or rate studies. Both GAC and AA were prepared by pulverizing and sieving through a 100-mesh screen to increase surface area and minimize time required to reach equilibrium. Powdered carbon was successively washed in distilled reagent water and dried at 150°C to constant weight. Pulverized AA was allowed to equilibrate on a shaker table in a solution of 2 mM Ca^{2+}, 1.6 mM Mg^{2+} and 7.2 mequiv l^{-1} alkalinity for 2 days, filtered and dried to constant weight at 120°C prior to use.

Ultraviolet (u.v.) disinfected, coagulated/flocculated/filtered secondary effluent samples, obtained from the Aqua II treatment facility, were adjusted to several acidic, neutral and basic pHs with phosphate buffers and combined with accurately weighed portions of powdered carbon or AA in 50 and 100 ml glass bottles. For each group of samples a pH buffered sample, with no added carbon or AA, was included as a control. Samples were allowed to equilibrate for 6–7 days on a shaker table at room temperature (20–25°C). Equilibrated samples were then filtered through prewashed glass microfiber filters (Whatman GF/F; retention = 0.7 μm) to remove particulates and analyzed for NVTOC or TOX.

Rate studies were conducted using pH adjusted effluent samples in a completely mixed batch reactor. Powdered GAC (250 mg) was wetted with 10 ml distilled reagent water overnight to saturate the pores prior to mixing with 0.9 l. of filtered effluent. After mixing, sample aliquots were removed by syringe at various time intervals, filtered and analyzed for NVTOC.

Advanced oxidation

Ozonation and ozone–peroxide experiments were conducted using u.v. disinfected coagulated/flocculated/filtered secondary effluent obtained obtained from the Aqua II treatment facility. Untreated samples were returned to the laboratory and ozonated in a completely mixed batch reactor. The coagulated/flocculated/filtered effluent had a pH range of 6.6–7.0 and an alkalinity, as determined by duplicate titration, of 102.6 mg l^{-1} as $CaCO_3$. No pH adjustment was done prior to ozonation of the samples.

The ozone reactor consisted of a covered and vented 20 l. glass reactor with internal baffles to prevent vortexing. Mixing was effected with a Ruston stainless steel six-bladed impeller powered by a variable speed motor resulting in velocity gradients (G) of 257 and 545 s^{-1} for 9.0 and 16.0 l. samples, respectively. Ozone and carrier gas were injected into the reactor, adjacent to the impeller, through stainless steel tubing and a ceramic sparger. Ozone was generated from dried compressed ambient air using an OREC (Phoenix, Ariz.) Model O3V-10-AR corona discharge ozone generator (air flow = 2.0 l min^{-1}; ozone mass flow rate = 48.16 mg min^{-1}). Ozone concentration in the feed gas was determined directly by absorbance. Ozone was sampled from a small vessel, flushed with 20–30 vol of feed gas, with a fully evacuated 1 mm Supracil quartz cuvet. Absorbance was then directly determined, at 254 nm, using an HP diode array u.v. spectrophotometer. Replicate determinations yielded an average absorbance of 0.1521 ± 0.0028 corresponding to an ozone concentration of 24.08 mg l^{-1}. Hydrogen peroxide solutions, prepared from 30% reagent grade H_2O_2 and distilled water, were metered into the reactor with a calibrated feed pump.

During an experiment the reactor was filled with 9.0–16.0 l. filtered effluent, and air sparged through the ozone generator and reactor. At time zero, voltage was applied to the generator and the hydrogen peroxide feed pump simultaneously started. At 5 or 10 min intervals, samples were taken for NVTOC, TOX, or u.v. absorbance analyses. During one 70 min run, 50 ml samples were taken at 5 or 10 min intervals, stored for several days to remove O_3 residuals and mixed with accurately weighed portions of powdered (100 mesh) F-400 (Calgon Corp.) carbon. After 2 days of mixing at room temperature, samples were filtered and measured for NVTOC to determine the adsorbability of the dissolved carbon. At the end of certain runs samples were taken for TOXFP analyses. The total volume removed by sampling during a run generally represented 2–3% of the initial volume. Total hydrogen peroxide addition accounted for between 0.5 and 2.2% of the total volume for 9 l. (40 min) runs and 5% of the total volume for 16 l. (70 min) runs.

Ozonation conditions employed in this study are summarized in Table 1. Ozone concentrations were not measured in the reactor off-gas, precluding an exact ozone mass balance. Ozone application rates were approx. 3.0 and 5.4 mg $O_3 l^{-1} min^{-1}$ for 16.0 and 9.0 l. reactor volumes, respectively, and are similar to others reported in the literature. Wallace *et al.* (1988), examining ozone peroxide for THMFP reduction, used application rates ranging from 2.5 to 3.7 mg $O_3 l^{-1} min^{-1}$ for 9.0 l. volumes. Ozone consumption rates ranged from 18 to 20%. Maximum overall dosages were 74 mg ozone/mg NVTOC. Duguet *et al.* (1985), ozonating drinking waters for u.v. and THMFP reduction, reported application rates near 4.3 mg $O_3 l^{-1} min^{-1}$ for 3.0 l. volumes and total applications of

Table 1. Terminal total applied ozone and hydrogen peroxide dosages

Volume (liters)	Duration (min)	mg/mg NCTOC		H_2O_2/O_3 (w/w)
		Applied O_3	Applied H_2O_2	
16.0	70	29.5	29.5	1.0:1.0
16.0	70	34.8	34.8	1.0:1.0
9.0	40	28.2	0	0.0:1.0
9.0	40	31.7	10.9	0.343:1.0
9.0	40	32.1	22.0	0.685:1.0
9.0	40	32.5	32.5	1.0:1.0
9.0	40	35.2	49.2	1.4:1.0

17 mg ozone/mg NVTOC. They reported ozone mass transfer increases from 25 to 47% by addition of peroxide.

Data in the literature indicate that adequate mixing further improves mass transfer. Nakayama *et al.* (1979), treating electrodeposition effluents with hydrogen peroxide, reported ozone consumptions of 180 mg l^{-1} for applied dosages of 200 mg l^{-1} in mixed reactors. Aieta *et al.* (1988) reported increases in mass transfer efficiencies from 25 to 87% (total applied ozone 10.9 mg l^{-1}) by mixing peroxide dosed reactors. Based on these data, relatively high ozone transfer efficiencies were expected under our experimental conditions.

RESULTS AND DISCUSSION

Carbon and activated alumina

Isotherm results for powdered F-400 carbon indicate favorable adsorption of NVTOC from Aqua II filter effluent. As previous results have indicated, NVTOC is an excellent predictor of THMFP and TOXFP for this water. Therefore carbon adsorption, by itself, provides an excellent method for reducing levels of organohalogen precursors.

Equilibrium data fit a modified linear isotherm (Cannon and Roberts, 1982) of the form:

$$q_e = K_L[C_e - C_n] \quad (1)$$

with equilibrium values

q_e = mass adsorbate/mass carbon (mg g^{-1})
K_L = coefficient (l g^{-1})
C_e = observed equilibrium DOC level (mg l^{-1})
C_n = nonadsorbable concentration of DOC (mg l^{-1}).

Data were fit with least square linear regression equations and a one-sided test used to determine significance (Table 2). Slope of the isotherms increased with decreasing pH (Fig. 1). Cannon and Roberts (1982) observed K_L values, for Palo Alto secondary effluent at pH 7.5–8.0 and F-400 carbon, of 11.4 ± 2.0 (l g^{-1}) and a C_n of 0.95 mg l^{-1}. Similar values were observed in this study at alkaline pH. At lower pH a 3-fold increase in the slope of the isotherm and an almost 50% reduction of the "nonadsorbable" fraction of the TOC was observed. Chen *et al.* (1987), using groundwater fulvic acids with F-400 and NORIT carbons, noted an increase in adsorptive capacity with decreasing pH. The importance of pH as a factor influencing adsorption isotherms is also documented by Ford (1981).

The nonadsorbable fraction of NVTOC was confirmed by larger equilibrium dosages of powdered F-400 carbon. Dosages as high as 16.61 g l^{-1} failed to reduce equilibrium NVTOC levels below C_n levels observed above.

Table 2. Modified linear adsorption model coefficients for filtered secondary effluent

Sample pH	C_n (mg l^{-1})	K_L (l g^{-1})	Correlation coefficient	Level of significance
3.22	0.496	57.34	0.990	0.005
7.08	0.682	25.68	0.998	0.005
10.25	0.946	18.53	0.987	0.005

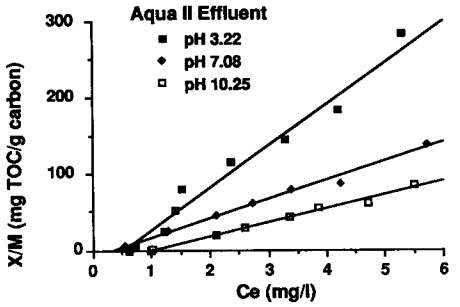

Fig. 1. Carbon (Calgon F400) equilibrium isothers for NVTOC in Aqua II effluent.

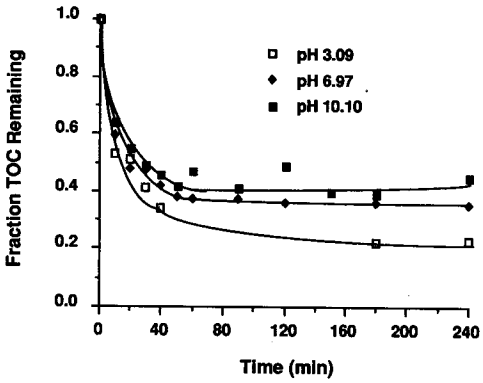

Fig. 2. Sorption of NVTOC in Aqua II effluent on activated carbon (Calgon F400).

Rate studies using powdered GAC indicate initial NVTOC removal at various pHs (Fig. 2). A plot of surface concentration (q_e) vs $t^{1/2}$ for the first 50 min of contact yields nearly linear relationships. Slopes provide comparative removal rates (Faust and Aly, 1987). Slopes were 2.4 [(mg g^{-1} $min^{-1/2}$)] for pHs 3.09 and 6.97 and 2.1 [(mg g^{-1} $min^{-1/2}$)] for pH 10.1. Hand *et al.* (1983) have developed a user-oriented method using batch reactors to obtain surface diffusion coefficients for the homogeneous surface diffusion model. Results can be used for fixed bed predictions. However, liquid diffusivity of the adsorbate D_l, requiring knowledge of molecular weight, radius or molal volume at boiling point, is needed for an accurate estimate. These parameters are unknown for the NVTOC in the Aqua II effluent.

Equilibrium TOX data were fit to the Freundlich isotherm and provide for estimates of background halogenated organic removal by carbon. Freundlich isotherm parameters were determined: $K = 2.294$; $n = 0.556$. Initial TOX levels were 69.22 μg l^{-1} and required dosages were, at pH 3.0, 0.176 and 2.49 g l^{-1} to reduce terminal levels to 12.8 and 3.9 μg l^{-1}, respectively. TOX removal must be considered multicomponent as NVTOC levels of approx. 7 mg l^{-1} in the samples; NVTOC is adsorbed simultaneously with the TOX. It is expected that the column mode

of operation would improve TOX, as well as NVTOC, removal efficiencies. Quinn and Snoeyink (1980) used a TOX parameter to monitor removal of products from chlorinated humic substances at the laboratory scale and removal of halogenated organics from Mississippi River water at full scale. For both studies it was found that TOX buildup within the adsorbers was graded and consistent, and that a TOX profile within the adsorber can be used to determine replacement or regeneration.

Equilibrium data obtained for pulverized activated alumina (AA) indicated that it exhibited extremely poor adsorption characteristics. Virtually no reduction in equilibrium NVTOC levels was observed except for the highest dose of $3\,g\,l^{-1}$ for filtered secondary effluent samples with an average NVTOC of $6.4 \pm 0.32\,mg\,l^{-1}$. Surface concentrations of NVTOC ($mg\,g^{-1}$) were then only a fraction of those on carbon: pH 3, 6.1%; pH 7, 3.0; pH 10, 16.2%. Chen *et al.* (1987), using granular AA with groundwater fulvic acid, noted nonlinear isotherms with comparatively poor adsorptive characteristics. They demonstrated an improvement by ozonating samples prior to adsorption. The presence of amphoteric hydroxyl groups on the surface of AA was used to explain adsorption of anionic humates at positively charged sites at low pH. They note that pulverization increases adsorptive capacities of AA capacities up to 80% or more. The use of pulverized AA, in this study, did not, however, result in significant adsorption. The high fraction of hydrophilic NVTOC in the filtered Aqua II effluent may account for the poor adsorption observed.

Advanced oxidation

Substantial oxidation of NVTOC to mineral products was effected by treatment of filtered secondary effluent (Aqua II). Ozone in combination with hydrogen peroxide was shown to increase greatly the concentration of hydroxy radicals formed during ozonation (Staehelin and Hoigne, 1982), giving an approximate stoichiometry:

$$2O_3 + H_2O_2 \rightarrow 2(\cdot OH) + 3O_2. \quad (2)$$

Although complex, the reaction of ozone and hydroxyl radicals with an organic contaminant(s) may be represented:

$$C_0 + O_3 \rightarrow C_{oxid'} + C_{oxid''} + \cdots \quad (3)$$

$$C_0 + \cdot OH \rightarrow C_{oxid'} + C_{oxid''} + \cdots \quad (4)$$

where C_0 is the substrate and $C_{oxid'}$ and $C_{oxid''}$ are the oxidation products.

The corresponding rate expression for decay of the organic(s) can be expressed (Glaze and Kang, 1988):

$$\frac{-d(\ln C)}{dt} = K_0[O_3] + K_1[\cdot OH] = K_{ps} \quad (5)$$

where K_0 and K_1 are the rate constants for the oxidation of C_0 by ozone and hydroxyl radicals, respectively; and K_{ps} the pseudo first-order assuming steady-state ozone and hydroxyl radical concentrations.

Treatment of Aqua II filter effluent with ozone–hydrogen peroxide (O_3/H_2O_2) at a dosage ratio of 1:1 resulted in pseudo first-order decay ($K = 2.079 \times 10^{-2}\,min^{-1}$, correlation coefficient = 0.995) of NVTOC for the initial 30 min of contact time and resulted in a 45.4% removal of substrate. Rate of decay then slowed and deviated from pseudo first-order. An additional 40 min of contact time resulted in terminal removals of 67.7% of initial NVTOC levels. The observed decrease may have been due to recalcitrant materials initially present in the effluent, or may be due to the formation of oxidation and cleavage products which are resistant to further oxidation by hydroxyl radicals or ozone.

It is likely that the latter speculation best describes the process. It is well documented that ozonation, without peroxide, can result in the formation of products that are resistant to further oxidation. Ozonation of natural organic substances dissolved in water results primarily in a change in molecular structure (Maier, 1982). The ozonation of phenol results in the production of hydroquinone + catechol, glyoxylic acid, glyoxal and finally oxalic acid. The ozonation of 2-propanol results in its total decay with the subsequent production of acetone. An overall NVTOC reduction of only about 15% is seen. The u.v.-ozonation of acetic acid results in the formation of oxalate which is fully oxidized only after 120 min of contact time (Bollyky, 1977).

An approximate 35% reduction in u.v. absorbance (254 nm) was observed during the initial 10 min of O_3/H_2O_2 treatment. Ultraviolet absorbance at this wavelength has been correlated with the presence of humic substances. No significant reduction in absorbance at this wavelength was observed for the additional 60 min of contact time. Duguet *et al.* (1985) observed a much more dramatic removal of $u.v._{.254}$ absorbance when treating lake water with O_3/H_2O_2. However, the initial optical densities in the lake water were much higher than the Aqua II filter effluent used here. A u.v./visible scan of the water after 70 min of treatment indicated a slight reduction in u.v./violet (~250–425 nm) absorption. Bourbigot and Dore (1982) suggest that the oxidation of aromatic compounds is evidenced by a reduction in u.v. absorbance between 254–270 nm.

Samples were taken, at 5 and 10 min intervals, from an O_3/H_2O_s run (34.8 mg O_3/mg NVTOC and 45.8 mg H_2O_2/mg NVTOC dose) to determine carbon adsorbability of the dissolved organic material as a function of O_3/H_2O_2 contact time (Fig. 3). The plot includes equilibrium NVTOC observed after adsorption (C_e observed), surface concentrations observed (X/M observed), and equilibrium concentrations that would occur for a sample of filtered effluent that had the same NVTOC as the sample in question, but had not been treated with O_3/H_2O_2 (C_e calc.). This value

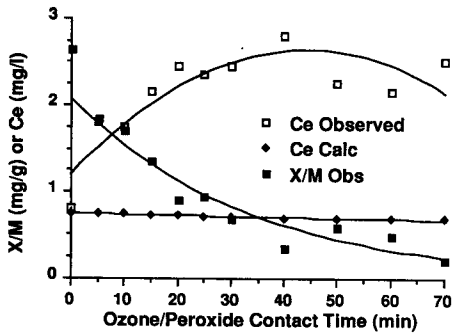

Fig. 3. Relative adsorption of NVTOC in Aqua II effluent as a function of dose (pH 6.65–7.55).

was calculated from a mass balance utilizing the linear isotherm developed for filtered effluent at neutral pH.

Although the NVTOC declined steadily throughout the experiment, it can be clearly seen that carbon adsorbability of the dissolved organic material decreases with increasing O_3/H_2O_2 dose. Much lower NVTOC levels are observed after carbon treatment for the unozonated water than for O_3/H_2O_2 treated samples. Clearly, a trade-off exists between physical removal vs oxidation of NVTOC. It should be noted, however, that research has shown that ozonation improves the removal of dissolved organic material on carbon that has been colonized by bacteria (Bourbigot and Dore, 1982).

The effect of H_2O_2 dose on ozonation of the filtered effluent was examined using five different peroxide dosages (see Table 1). The use of ozone without peroxide resulted in an overall NVTOC removal of 18.3%. The addition of peroxide at a $H_2O_s:O_3$ (w/w) ratio of 0.343:1 dramatically improved NVTOC mineralization to 65.4%. An increase in peroxide dosage at H_2O_2/O_3 (w/w) ratios of 0.685:1.0, 1.0:1.0 and 1.4:1.0 reduced terminal NVTOC removals to 54.1, 40.6 and 34.7%. The effect of peroxide dosage on pseudo first-order rate constants is shown in Fig. 4. All regressions used to obtain rate constants were significant at the 0.005 level except for the experiment without peroxide. Glaze and Kang (1988), using O_3/H_sO_2 to oxidize TCE and PCE in groundwater, determined that maximum oxidation rates were observed for $H_2O_2:O_3$ (w/w) ratios of 0.7–1.0, respectively. Aieta *et al.* (1988), conducting pilot studies on removal of TCE and PCE, suggested optimum $H_2O_2:O_3$ ratios (w/w) of 0.5. While a given amount of peroxide can catalyze the production of hydroxyl radicals, an excess results in radical quenching (Brunet *et al.*, 1984). The optimum ratio, for NVTOC removal, obtained here is near the stoichiometric ratio of 0.35 (w/w) for the production of hydroxyl radicals. However, as ozone levels in off-gases were not measured in this study, actual H_2O_2/O_3 ratios may have been somewhat higher.

Aqua II filter effluent samples were treated with O_3/H_2O_2 at an applied dose of 34.8 mg O_3/mg NVTOC and a $H_2O_2:O_3$ dose of 1.0:1.0 (w/w) to determine effects of the oxidation process on background organohalogen concentrations. Samples removed for TOX analyses indicate that TOX values, while generally decreasing, fluctuate during the process (Fig. 5). The increase in TOX, after an initial reduction, may be due to the presence and oxidation of bromide (and possibly chloride) ions to hypohalous acids which can then react with chlorinated substances to form additional TOX. Comparing the relative redox potentials of the couples $O_3/O_2 = 2.07$ V, $HOCl/Cl^- = 1.49$ V and $HOBr/Br^- = 1.33$ V, to that of the redox potential of the hydroxyl radical = 2.8 V, it is apparent that ozone and hydroxyl radicals could oxidize chlorides or bromides in water.

Hoigne *et al.* (1985) report rate constants for the consumption of ozone by the halogens: for Cl^-, $K = 0.003\ M^{-1}s^{-1}$ and for Br^{-1}, $K = 160 \pm 2\ M^{-1}s^{-1}$, at pH 8 and 20–23°C. Thus, it may be the production of hypobromous acid that is responsible for the observed fluctuations in TOX. Indeed, the formation of bromoform has been observed in the ozonation of seawater (Dore, 1982).

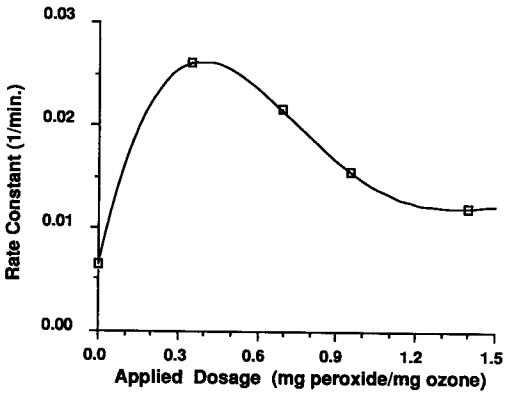

Fig. 4. Effect of hydrogen peroxide dose on pseudo-first-order rate constant at an applied azone dose of 31.94 mg O_3 1 mg NVTOC (average).

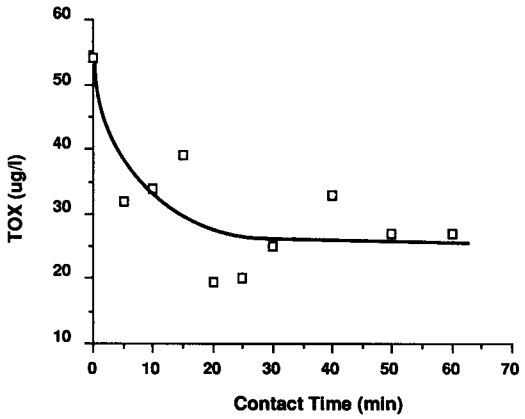

Fig. 5. Oxidation of TOX by ozone–peroxide.

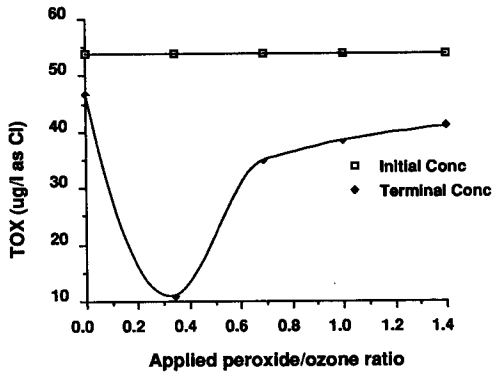

Fig. 6. Effect of hydrogen peroxide dose on ozonation of TOX in Aqua II effluent.

Applied peroxide doses (40 min, 34.8 mg O_3/mg NVTOC) markedly effect total terminal reductions in TOX levels upon ozonation (Fig. 6). Ozonation alone removes only 13.9% of the initial TOX, while the addition of hydrogen peroxide at a H_2O_2:O_3 ratio (w/w) of 0.343 reduces TOX by 79.1%. Increases in H_2O_2 addition to a ratio of 1.40 results in consistently inferior removals of TOX.

Analysis of the above samples for TOX formation potentials (TOXFP) indicate that the ozone–peroxide method is highly effective in removing these substances (Fig. 7). Treatment with ozone alone causes an increase of TOXFP by 21.2% and an increase in the ratio of TOXFP/NVTOC of 39.6% when compared to unozonated filtered secondary effluent. This phenomena may be due to the cleavage of larger molecules into subunits more susceptible to halogen addition and substitution reactions. Addition of peroxide to ozonation, at a H_2O_2:O_3 ratio (w/w) of 0.343, results in a 90.8% removal of TOXFP and a 72.2% reduction in the TOXFP/NVTOC ratio when compared to unozonated effluent. The overall reduction in TOXFP is likely due to oxidation of NVTOC. The marked decrease in the observed TOXFP/NVTOC ratio may be explained by the fact that the remaining NVTOC may have been partially oxidized by hydroxyl radicals or ozone, making it resistant to further electrophilic attack by chlorine. The ozone–peroxide treatment compares favorably, with respect to these parameters, with the Aqua II final effluent (99.3% removal of TOXFP and 80.6% reduction in TOXFP/NVTOC ratio compared to unozonated) which, after filtration, has been treated with reverse osmosis, air stripping and carbon adsorption.

CONCLUSION

Results from this investigation demonstrate that direct carbon or ozone–peroxide treatment of coagulated/flocculated/filtered secondary effluent can result in significant removal of background ITOX and dissolved organic material implicated as TOXFP.

Important operation parameters for carbon were identified as follows:

NVTOC, a predictor of TOXFP, isotherms fit both modified linear and Freundlich isotherm models. Slopes of the isotherms increase with decreasing pH. At low pH a 3-fold increase in the slope of the isotherm and an almost 50% reduction of the "nonadsorbable" fraction of the TOC was observed.

Kinetic studies using powdered activated carbon indicated NVTOC removal rates also decrease with pH.

Equilibrium ITOX data modeled by the Freundlich isotherm provided estimates of background halogenated organic removal by carbon.

Ozone–peroxide treatment of coagulated/flocculated/filtered secondary effluent results in oxidation of NVTOC and TOX to mineral products, and the following conclusions are made:

Ozone–peroxide oxidation of NVTOC was pseudo-first-order. Derived constants provide for estimates of organic halogen precursor removal.

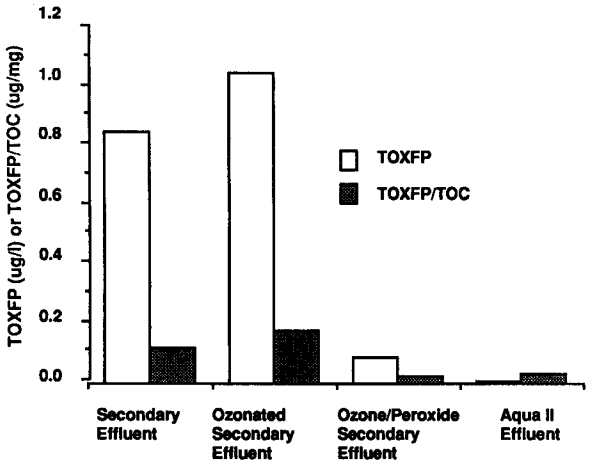

Fig. 7. TOXFP of treated and untreated Aqua II effluent.

Optimal peroxide to ozone (O_3/H_2O_2) dosage ratios were 0.343:1 (w/w).

Optimally catalyzed applied ozone dosages of 31.7 mg O_3/mg NVTOC resulted in 65.4% mineralization of NVTOC and 79.1% of ITOX.

Carbon adsorbability of remaining NVTOC decreases with O_3/H_2O_2 dose. Result indicates a trade-off exists between physical removal by carbon versus oxidation of NVTOC.

Pilot plant studies are recommended to assess cost effectiveness of these alternative treatment technologies for reclamation of secondary effluent.

Acknowledgement—This work was supported in part by the California Department of Water Resources under Contract B56726.

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