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OZONATION AND UV IRRADIATION: EFFECT ON OIL SHALE WASTEWATER BIOREFRACTORY ORGANIC SOLUTES

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ABSTRACT

Ozonation and ultraviolet (UV) irradiation were evaluated for their effects on the treatment of bicrefractory organic solutes in an oil shale process wastewater (Oxy-6 retort water). Direct mineralization of dissolved organic carbon (DOC) was determined for each method and for combined UV irradiation/ozonation, but emphasis was placed on the use of these oxidative methods to effect structural alterations, thereby promoting subsequent biooxidation. Short sequential or combined exposures to low dosages of UV and ozone did not effect mineralization of DOC nor did they promote biooxidation of previously biotreated (spent) retort water. Prolonged exposure to UV did not effect significant photochemical oxidation. In contrast, five hours of a high ozone dosage altered 14 percent of the recalcitrant DOC, thereby promoting subsequent microbial mineralization. Similar results were obtained after only three hours of combined high-dosage UV/ozone treatment; the trend of increasing biodegradability with increasing dosage, however, was reversed after three hours of treatment. Exhaustive biooxidation followed by extensive UV irradiation in combination with ozonation and by secondary biooxidation achieved total elimination of color and odor from Oxy-6 retort water, but more that 41 percent of the DOC was refractory to this series of treatments. Direct chemical and photochemical oxidation and the action of excited oxygen species, ozone decomposition products, and organic radicals are discussed; the ramifications of structural alterations of recalcitrant nitrogen heterocycles are considered.

INTRODUCTION

Microbial growth at the expense of the organic solutes in Oxy-6 oil shale retort water is limited by bioavailable carbon (Jones et al., 1982). Approximately 50 percent of the organic carbon is amenable to biological degradation; the remaining solutes are resistant to further mineralization. The extracellular fluid containing the refractory compounds that remain after exhaustive biooxidation is termed "spent" retort water (Jones et al., 1982). These refractory compounds are predominantly nitrogen and oxygen heterocycles and aromatic amines (Jones et al., 1982). Ozonation and ultraviolet (UV) irradiation can possibly enhance or augment biological treatment by either oxidative alteration or mineralization of the recalcitrant organic solutes. In addition to the possibility of aiding or supplementing microbial degradation, such chemical or photochemical processes might also hinder biotreatment by producing toxicants or by polymerizing the easily degradable solutes in raw retort water. These two effects, enhancement and impedance of biooxidation, should be considered in the evaluation of any treatment aid and are of special interest because the relatively high elevations of the western oil shale regions would allow substantial exposure to UV irradiation if the wastewaters are ponded before treatment, reuse, or codisposal.

UV Radiation

Irradiation by UV light may complement biotreatment by mineralizing the recalcitrant organic solutes that remain after extensive biooxidation. The degradation of organic solutes by exposure to UV radiation is accomplished by: (i) absorption of sufficient UV radiation to cleave intra-molecular bonds, producing lower-molecular-weight fragments, (ii) generation of organic free radicals, (iii) interaction of free radicals with oxygen to produce peroxy and hydroperoxy radicals, which are capable of structural alteration or complete mineralization of the lower-molecular- weight fragments by oxygenation, hydrogen abstraction or by the generation of radical chain reactions (Crosby, 1972; Manny, Miller, and Wetzel, 1971; Plimmer, 1972). In addition, it has been shown that the photolysis of endogenous organic compounds in natural waters generates hydroxyl radical (OH•) and singlet oxygen which are capable of subsequent transformation of synthetic organic solutes (Mill, Hendry, and Richardson, 1980).

In contrast to direct mineralization, a more efficient use of UV irradiation may be as an aid to biooxidation; the oxygenation of complex, refractory solutes or the production of low-molecular-weight products by UV radiation may make otherwise resistant molecules available for subsequent microbial attack. This has been implicated in the environmental degradation of pesticides (Crosby, 1972), in the biodegradation of certain synthetic polymers (Jones et al., 1974), and for the destruction of toxic wastes as reported by Kearney and coworkers (Anon., 1981). Photooxidation produces a family of products, each of which may vary in its susceptibility to microbial metabolism (Bull, 1980). This plethora of oxidation products is especially significant for the photooxidation of oil shale wastewaters. Two factors (Daughton, 1981) that exacerbate the refractory nature of the substituted heterocyclic compounds in spent retort water are (i) the presence of numerous homologs and variants, each of which often requires a specialized catabolic enzyme system, and (ii) the low individual heterocycle concentrations (see Raphaelian and Harrison, 1981), which are sufficiently below the affinity or threshold values for the requisite enzymes. Photooxidation may generate more degradable solutes but it may actually exacerbate the existing problem of enzyme specificity and threshold concentration effects.

The direct absorption of energy by chemical bonds is not the only route by which UV radiation can affect an organic compound. An appropriate chromophore or photosensitizer (such as riboflavin) can absorb light energy and transmit the energy to an ordinarily nonabsorbing species during its return to the unexcited state. Dye-sensitized energy transfer represents a highly specific means of introducing oxygen into an organic compound (Foote, 1968), and the resultant dissociation products may differ significantly from those of direct photolysis (Plimmer, 1972).

Molecular oxygen, itself, may be photochemically excited to a highly active state. The result of photosensitized energy transfer stimulated by near-UV irradiation of molecular oxygen is the highly reactive species called singlet oxygen (Crosby, 1972). In certain instances, singlet oxygen has been documented as the oxygenating species common to both metabolism and photolysis. A key function of metalloenzymes is, in theory, to induce singlet oxygen generation (Crosby, 1972); the oxygenation chemistry of several classes of oxygenases resembles the reactions of singlet oxygen (Foote, 1968). Therefore, the degree of mineralization or alteration of organic carbon mediated by the photochemical effects of singlet oxygen may predict the potential of microbial metalloenzymes; that is, if the appropriate enzyme system were available and if it could function in the defined environment, then the action of photochemical oxidation by UV irradiation may mirror the maximum effects achievable by microbial oxygenases. Photochemical transformations, including photolysis, oxidation, reduction, elimination, hydrolysis, and isomerization, are regarded as the most important abiotic activity affecting organic compounds, especially pesticides, in experimental and field applications (Bull, 1980). The interaction of UV energy with organic material in the presence of oxygen is summarized in Figure 1.

Ozonation

Ozone is a very selective and highly versatile oxidizing agent that has been used extensively in organic chemistry and has been promoted as a method of disinfection for potable water and as a wastewater treatment aid. Details on the specific effects of ozone on different classes of organic compounds can be found in an extensive two-volume review (Bailey, 1978; Bailey, 1982). Unfortunately, the majority of studies on the ozonation of organic substances have been conducted in nonprotic solvents, and these studies often are not directly applicable to the chemical pathways that develop from the ozonation of organic compounds in aqueous solutions (Bailey, 1972). The literature must be interpreted and applied judiciously because solvent effects can be profound. In an aqueous medium, for instance, the oxidative capacity of ozone appears to be dependent on pH, alkalinity, and the organic and inorganic solute concentrations. For acidic and neutral solutions (pH less than 9.0), ozone reacts predominantly as the parent ozone molecule; these reactions are relatively slow and highly specific depending on the class of organic compound and its bonding structure. Furthermore, it has been reported that oxidation by ozone is almost entirely ineffective in highly acidic aqueous solutions (pH below 2.0) (Suzuki, 1976). In contrast, ozone in basic solutions (pH greater than 10.0) is catalytically decomposed by hydroxide ion to a variety of products, including $OH^{\bullet}$, the most potent and effective oxidant known to occur in aqueous solutions (Hoigné and Bader, 1978a; Larson, 1978) and superoxide ion (Bailey, 1982; Hoigné and Bader, 1976; Weber, 1972). At a pH of 10.5, approximately one-half mole of $OH^{\bullet}$ is formed per mole of O_3 decomposed (Hoigné and Bader, 1978a). Hydroxyl radicals are extremely reactive and easily oxidize organic material and react with inorganic solutes with little substrate specificity. These radicals are quickly consumed (within microseconds), but their intense reactivity makes them critically important to aqueous ozone chemistry (Hoigne and Bader, 1979). Hydroxyl

radicals are vigorously scavenged by carbonate ion and, to a lesser extent, by bicarbonate species; the disproportionation of ozone is accelerated by increased alkalinity (Hoigné and Bader, 1976).

The half-life of ozone also depends on the classes of organic solutes that are present in aqueous solutions. Upon ozonation, certain organic compounds form radical-type intermediates that subsequently oxidize other organic substrates and also catalyze the further decomposition of ozone (Hoigne and Bader, 1979). The presence of iron salts enhances the effect of ozone on the organic compounds in domestic wastewater (Shapiro et al., 1978). It is possible that ferric ion catalyzes the dismutation of ozone to its highly reactive decomposition product, hydroxyl radical. In addition, free ammonia can be oxidized to nitrate by ozone and OH•, although ammonia oxidation will only be a significant factor when ammonia is present in concentrations equal in magnitude to the concentrations of carbonate species and organic solutes (Hoigné and Bader, 1978b). The production of radicals and the presence of metal salts and coreacting or scavenging species, therefore, can mediate the effectiveness of oxidation by hydroxyl radical in a complex wastewater matrix. The reactions of ozone in aqueous solution are summarized in Figure 2.

Retort water often contains high ammonia and dissolved inorganic carbon (DIC) concentrations, both of which either react with or scavenge ozone or ozone-disproportionation products. Furthermore, substituted nitrogen heterocycles, a major biorefractory organic chemical class in spent retort water, are not particularly susceptible to attack by ozone. Whereas most aromatic heterocycles are readily oxidized by ozone, pyridine reacts extremely slowly and ozone preferentially attacks the carbocyclic ring of quinoline (Bailey, 1972). In contrast, OH• readily undergoes an addition reaction with pyridine to form an hydroxycyclohexadienyl radical (Dorfman and Adams, 1973), which subsequently decomposes at an equally rapid rate (Cercek and Ebert, 1967).

Partial oxidation or cleavage by ozonation of complex high-molecular-weight organic compounds, which are commonly biorefractory, into lower-molecular-weight fragments, can substantially affect biodegradability. Such partial treatment offers an alternative to the use of chemicals for the mineralization of solutes. The benefit of partial oxidation has been shown for nonbiodegradable water-soluble polymers (Suzuki, Nakagawa, and Ito, 1976; Suzuki, Hukushima, and Suzuki, 1978). Ozone pretreatment of polyethylene glycol, poly(vinyl alcohol), poly(vinylpyrrolidone), and sodium polyacrylate reduces the molecular weights and improves biooxidation. In addition, reactive oxygen species have been implicated in a variety of metabolic syntheses of oxygenated products (Larson, 1978). Superoxide ion, for instance, is postulated to be the active species of various monooxygenases (Jerina, 1973) and is considered to be the active oxygenating agent of cytochrome P-450 in microsomal systems (Larson, 1978). In addition, a group of copper proteins (erythrocuprein, hepatocuprein, and cerebrocuprein) have been found to catalyze the addition of oxygen via superoxide ion to organic substrates, yielding hydrogen peroxide and molecular oxygen (Cohen and Heikkila, 1974). It has been noted that oxidation of ferrocytochrome c by xanthine oxidase is dependent on OH• reactivity (Cohen and Heikkila, 1974); there is some evidence that this highly reactive radical is also involved in microsomal activity (Cohen and Cederbaum, 1979). In addition, there is evidence that some biological systems form OH• from the interaction of superoxide ion and hydrogen peroxide; it has been suggested that enzymatically-produced hydroxyl radicals may cause pathological reactions (Pryor, 1976).

Chemical oxidation by ozone or ozone-decomposition products could be used to predict the extent of oxidation of the biorefractory organic solutes in retort water that could possibly be realized by the appropriate bacteria with competent enzyme complements. Ozonation could therefore be viewed as an facile means for predicting the maximum theoretical degree of oxidation that could be effected by biological treatment.

Combined UV Irradiation/Ozonation

UV radiation catalyzes the disproportionation of ozone into OH• (Bailey, 1982; Prengle and Mauk, 1978; Sierka and Cowen, 1980) and superoxide ion, and it promotes the production of free organic radicals (Prengle et al., 1975). In contrast to hydroxide-ion mitigated ozone decomposition, ozone disproportionation by UV radiation is not restricted to the alkaline pH range. The existence of ozone decomposition products at a neutral pH minimizes the effects of carbonate scavenging and ammonia oxidation, thereby allowing the radicals to primarily oxidize organic compounds. This offers the major advantage of the combined UV irradiation/ ozonation approach for mineralization of contaminative solutes. The method of combined UV/ozone exposure has been reported to be superior to either treatment individually for the elimination of refractory organic impurities from water and for the treatment of industrial wastewaters (Bailey, 1982; Hoigné and Bader, 1976; Kuo, Chian, and Chang, 1977).

The destruction of biologically recalcitrant organic solutes by combined UV irradiation/ozonation complements the effects of activated sludge (Prengle and Mauk, 1978). Ultraviolet irradiation/ozonation pretreatment followed by second-stage biological treatment may offer a more economical approach than complete chemically-mediated mineralization of the refractory compounds. The structural alterations of the solutes effected by a short exposure to UV/ozone may be sufficient to allow an acclimated microbial community to mineralize a significant portion of the formerly recalcitrant solutes. Perhaps the major drawback to this approach as a pretreatment for biooxidation of oil shale wastewaters is that both ozonation and UV irradiation/ozonation, like UV photolysis, create multiple products from each oxidizable compound (Hoigné and Bader, 1976; Kolonko et al., 1979). In addition to its role as a treatment step complementary to biooxidation, the chemical alterations effected by UV/ozonation may also model microbial systems in a manner analogous to ozone-decomposition products. If extensive UV irradiation/ ozonation which results in the generation of OH• is unable to completely mineralize refractory organic solutes in a waste stream, then it would be unlikely for enzymatic microbial oxidation to be effective. The chemical decomposition products from UV irradiation of ozone and the resulting interactions with substrates are summarized in Figure 3.

Treatment of Retort Water

In the studies reported here, low dosages of either UV radiation or ozonation had negligible effects on the organic solutes in raw or spent Oxy-6 retort water. The solutes were neither mineralized nor sufficiently altered to permit renewed biooxidation by brief exposures. UV irradiation was also an ineffective oxidant when intensively applied; spent retort water was essentially unchanged by five hours of UV irradiation. In contrast, the effectiveness of ozone as an oxidant was entirely dependent on dosage. Five hours of ozonation successfully mineralized four percent of the dissolved organic carbon (DOC) and structurally altered a portion of the biorefractory organic solutes. Following ozone pretreatment, approximately 14 percent of the DOC became available to the acclimated microbial inoculum. Oxidation by ozone in combination with UV radiation was also a function of dosage. Low dosages of the combined treatment for short exposure intervals did not

mineralize or alter the solutes in raw or spent Oxy-6 retort water. Intensive UV/ozonation of spent retort water, however, was capable of mineralizing 20 percent of the DOC associated with biorecalcitrant solutes. Subsequent biological treatment indicated that this treatment scheme also chemically altered the nonmineralized solutes. After three hours of treatment, 15 percent of the DOC was biologically available. Further UV/ozonation (6 hours) eliminated the color and odor of retort water; the treated water, however, was not amenable to biodegradation. Forty-one percent of the DOC remained in the colorless, odorless extracellular fluid following exhaustive biooxidation, 6 hours of UV/ozone exposure, and secondary biological treatment. This implies that oxidative enzyme systems also may be incapable of promoting further alteration or mineralization of these recalcitrant solutes.

METHODS and MATERIALS

Oil shale wastewater from the pilot-scale modified in-situ (MIS) retort burn #6 (Oxy-6; Occidental Oil Shale, Inc., Logan Wash, CO) was used in all experimental work. Samples of this water were collected from the oil-water separator (sample point #2) (Farrier, 1979), composited (Daughton and Sakaji, 1980), and distributed for interlaboratory comparison studies. In experiments that used "raw" Oxy-6 retort water (experiments 1, 2, 3, and 6) the wastewater was not pretreated. "Spent" retort water, the extracellular fluid that remains after exhaustive biooxidation, was generated using a MagnaFerm Bench-top fermentor (model MA-107, New Brunswick Scientific Co., Inc., Edison, NJ). Approximately 3 L of 100 percent Oxy-6 retort water, amended with 5.0 mL of concentrated phosphoric acid (final concentration 26 mM P and pH 7.46), was inoculated with a highly acclimated microbial seed derived from sewage, soil, and industrial sources. The culture was aerated (2.5 L/min), mixed (500 rpm), and maintained at 30 °C. At the cessation of growth, the culture was centrifuged (13,330 x g at 4 °C for 30 min) and the supernatant fluid was filtered through a polycarbonate membrane (0.4-0.8-μm pore diameter; Bio-Rad, Richmond, CA). The filtrate, i.e., spent Oxy-6 retort water, was used in experiments 4, 5, 7, 8, and 9. Vigorous aeration during incubation in the fermentor effectively stripped ammonia from the spent retort water. The ammonia concentration after 100 hours of incubation was reduced from 86 mM to less than 2 mM. To eliminate the possibility of ozone consumption by ammonia oxidation, the residual ammonia was air-stripped in a bench-scale reboiler (experiment 5). Ammonia was quantitated using the phenol-hypochlorite colorimetric method adapted for oil shale wastewaters (Cantor et al., 1981).

To generate ultraviolet light, a 450-W, medium-pressure, full-emission mercury-arc lamp was enclosed in a water-cooled quartz immersion well and placed directly in approximately 900 mL of retort water, which was held in a photochemical reactor (model #7840-185, Ace Glass, Inc., Vineland, NJ). The design of the apparatus permitted 40 to 50 percent of the total volume to be in the reactive area. The solution was stirred with a magnetic bar to ensure equal exposure of the wastewater to the photochemical reaction zone. The photoreactor was also used for the ozonation and UV/ozonation experiments.

Ozone for experiments 3 through 8 was produced using an ozone generator (model 1-T, Aqueonics Division, ARCO Environmental, Inc., Dublin, CA). For experiments 3 through 6, purified compressed air was used as feed gas for the production of ozone and for experiments 7 and 8 purified oxygen was used as feed gas. The gas flow rate to the ozone generator was maintained at 100 cm^3/min (STP) for experiments 3 through 8. The ozone production rate for experiments 3 through 6 was assumed to follow the manufacturer's specifications; with air (100 cm^3/min) as a feed gas the ozone production rate was 1.5 mg per minute. For experiments 7 and 8, the ozone production

rates were 6.36 and 6.53 mg/min, respectively. Ozone was introduced to the 900 mL of wastewater through 1/16-in O.D. Teflon tubing at the bottom of the reactor directly above the stirrer. The mean bubble diameter was approximately 2 mm.

The quantity of ozone consumed was estimated by subtracting the mass of ozone in the effluent (off-gas) of the photochemical reactor from the mass of ozone introduced into the wastewater. Ozone was measured using the starch/iodine method (Standard Methods..., 1981). Ozone from the generator and off-gas were sparged through a measured volume of 0.12 N potassium iodide solution. Ozone stoichiometrically oxidizes iodide to iodine. The concentration of ozone in the gas stream was determined from the volume of standardized thiosulfate solution required to titrate the iodine. Ozone consumed or solubilized in the reactor (grams of O_3 per liter of retort water) was calculated by difference, assuming a constant rate of production by the generator.

At hourly intervals, 25-mL samples were withdrawn from the photochemical reactor. Dissolved organic carbon concentration and absorbance were determined for each sample. To characterize color removal effected by UV or ozone treatments, absorbance spectra from 200 to 850 nm were obtained in 1-cm pathlength quartz cuvettes with a Bausch & Lomb 2000 UV-vis scanning spectrophotometer. From each time-course sample, 15 mL was diluted with 5.0 mL of 156 mM phosphate buffer, 9.5 mL of ASTM Type I water, and 0.5 mL of a trace nutrient solution (0.72 mM $FeSO_4 \cdot 7H_2O$ and 99.7 mM $MgSO_4 \cdot 7H_2O$); the wastewater served as sole sources of carbon and nitrogen for the 100-µL microbial inoculum that had been acclimated to 50-percent raw retort water. Residual ozone that may have been present was allowed to dissipate for 24 hours prior to inoculation. The cultures were incubated in either 125-mL or 250-mL baffled Erlenmeyer flasks (Bellco Glass, Inc., Vineland, NJ) at 120 rpm and 30 °C for 72 hours in a water bath shaker (model G76, New Brunswick Scientific, Co., Inc., Edison, NJ), The flasks were stoppered with cotton to minimize evaporation while allowing oxygen transfer. Samples from the outgrown cultures were filtered through 0.4-µm pore diameter polycarbonate membranes and the filtrates were analyzed for DOC concentration. Stationary phase was generally reached within 48 hours.

A UV-persulfate low-temperature oxidation unit (Langlois et al., 1982) was used to convert organic carbon in the filtered, acidified, and purged samples to CO_2. The evolved CO_2 was detected and quantitated by automatic coulometric titration.

The separation of the polar and nonpolar organic organic solutes in retort water was accomplished by a miniaturized reverse-phase fractionation (RPF) chromatographic technique (Daughton, Jones, and Sakaji, 1982). Polar organic solutes (the hydrophilic fraction; HpF) of the DOC pass through a reverse-phase cartridge and are collected with the aqueous effluent. Less-polar compounds (the lipophilic fraction; LpF) are retained by the packing material and can be subsequently eluted by methanol.

Methanolic eluates of the lipophilic fraction (LpF) of carbon from raw, spent, and UV/ozone-treated (360 min) spent Oxy-6 retort water were analyzed for volatile nitrogenous organic compounds with a Varian 3700 gas chromatograph equipped with a N/P thermionic detector. Samples (1-µL) were injected (split mode) into a 30-m SE-30 fused silica column. Isothermal operation at 50 °C for one minute was followed by temperature programming at 5 °C per minute up to 260 °C.

The UV irradiation and ozonation experiments were conducted at ambient temperature (23 °C); for the samples that included UV irradiation, the temperature increased to 28-30 °C, depending on the length of exposure. The pH of raw retort water used in these experiments was approximately 8.5; spent retort water pH was 9.7 initially, but following extensive ozonation or UV/ozonation (experiments 7 and 8), the pH was reduced to 8.6. The protocol for each experiment is given in Table 1.

RESULTS and DISCUSSION

Ozonation and UV irradiation were evaluated both for their ability to directly oxidize organic solutes and for their indirect influence on biodegradability through the alteration of refractory compounds in Oxy-6 retort water. Organic carbon determinations of the reverse-phase fractions of time-course samples yielded further insight into the possible mechanisms of organic solute alteration. The results from these experiments are summarized in Table 2. All DOC percentages are given on the basis of raw retort water.

Ultraviolet Radiation

Short exposure to intense UV radiation was insufficient to mineralize or alter the recalcitrant compounds in raw retort water (experiment 1). The results of extensive UV irradiation of spent Oxy-6 retort water followed by biological treatment (experiment 9) are presented in Figure 4. The lower graph is the cumulative UV energy supplied to the photoreactor. Each pair of bars represents a sample withdrawn from the reactor at hourly intervals. For each pair, the first bar is the DOC concentration that remained after UV irradiation, and the second bar is the DOC concentration after subsequent biological treatment. The solid portion of each bar is the DOC concentration of the HpF. Five hours of intensive UV irradiation of spent retort water did not mineralize a significant amount of the DOC (2 percent), remove the chromophoric substances that give retort water its characteristic color, or change the relative polarities of the organic constituents. Furthermore, UV irradiation did not appear to alter the biorefractory organic constituents. Biooxidation subsequent to photochemical pretreatment did not mineralize additional carbon compared with nonirradiated reinoculated control cultures (i.e., the difference in DOC for each pair of bars was equivalent to the control). Riboflavin, a photosensitizer, did not enhance the effects of UV irradiation on raw Oxy-6 retort water (experiment 2, Table 2).

The organic carbon remaining in either raw or spent retort water after ozonation at low dosages followed by ozone/UV treatment was not susceptible to mineralization by further UV radiation alone (experiments 3-6, Table 2). In addition, the solutes were not significantly altered by this series of low-dosage physicochemical treatments; an acclimated microbial inoculum was unable to effect any further DOC removal compared with nonirradiated control samples (experiments 3-5). In experiment 6, UV irradiation for 90 minutes subsequent to 20 minutes of ozone and 40 minutes of ozone/UV treatment appeared to slightly modify the organic solutes in raw retort water. An additional 8 percent of the DOC was made available to biooxidation compared with untreated retort water. These results, however, were not reproducible (viz. experiment 6 vs. experiment 3). The addition of riboflavin as a photosensitizer had no synergistic effect with UV irradiation under these conditions.

Ultraviolet radiation on its own may have been ineffective because of the presence of photooxidation inhibitors (Larson, 1978). Particulate and colloidal carbonates can protect organic species from the effects of UV irradiation (Manny et al., 1971); the high concentration of carbonates in

retort water may have prevented photoalteration.

Ozonation

Ozone applied to raw or spent retort water in low dosages (1.7 mg/L-min) for short periods (20 and 60 minutes) was sufficient to mineralize only up to three percent of the DOC. Furthermore, it appeared that these dosages of ozone did not significantly affect the structures of the organic solutes; biooxidation of the ozone-pretreated retort water was not enhanced compared with the untreated raw or spent retort water (experiments 3-6).

Five hours of ozonation at 7.1 mg/L-min resulted in only slight mineralization of the DOC (4 percent) in spent retort water (experiment 7). The small fraction of compounds that were mineralized or altered by ozonation was responsible, however, for the majority of the color of spent retort water; five hours of ozonation reduced the typical deep amber color of spent retort water to a very light straw hue (Fig. 5). Concomitant with this color reduction, filtration of the time-course samples was easier with increasing ozone dosage. In contrast to small dosages of ozone (i.e., experiments 4 and 5), intensive ozonation of spent retort water altered a significant fraction of the residual organic solutes; 14 percent of the DOC that was previously recalcitrant became amenable to microbial mineralizaton. Of the 380 mg/L of the DOC that was biologically oxidized, approximately 320 mg/L was at the expense of carbon in the HpF which was either created from LpF carbon by ozonation or resulted from altered refractory HpF carbon that became available as a carbon and energy source to the microbial inoculum. Of the original raw retort water DOC, 38 percent remained after treatment by exhaustive bio-oxidation, five hours of extensive ozonation, and second stage biooxidation; the organic carbon that remained after this series of treatments was evenly divided between HpF and LpF compounds. The effects of extensive ozonation of spent retort water are represented in Figure 6 in a manner analogous to Figure 4 except that the lower graph represents the cumulative amount of ozone consumed.

The ozone demand at each hourly interval was greatest initially, steadily declined until the four-hour sample, and then appeared to increase slightly in the five-hour sample (Fig. 7). This apparent increase may have been the result of an analytical error (one of the two ozone determinations for the four-hour sample was uncharacteristically high), incomplete mixing, or variations in the oxidative reaction rates. If this data point were disregarded, then the ozone demand would appear to plateau after four hours of intense ozonation.

We have repeatedly noted that foaming is a major drawback to ozonation of raw retort water. This intense foaming was not evident, however, when spent retort water was ozonated. This change may have been the result of the microbial mineralization of aliphatic carboxylic acids which can act as surfactants. We also noted that when compressed air was used as the feed gas (experiments 3-6), a dense, white fog accumulated at the liquid surface in the photoreactor. Weber (1972) has indicated that oxides of nitrogen are formed when air is used for ozone generation and, in fact, we did not observe this phenomenon when pure oxygen was the feed stock.

The alteration of the refractory organic compounds and the elimination of the chromophoric substances were most likely a result of direct oxidation by the parent ozone molecule; the solution pH precluded the catalytic decomposition of ozone by OH^- into its highly reactive radicals. Ozone is typified by slow, selective oxidation of organic compounds; this type of reaction could account for the experimental results. The susceptible solutes

were gradually modified until the solution was devoid of these compounds; at that point ozone was no longer an effective oxidant.

Combined UV Irradiation/Ozonation

Short intervals of exposure (30, 40, and 60 minutes) to low dosages of ozone (1.7 mg/L-min) coupled with UV radiation was incapable of mineralizing a substantial portion of the DOC in ozone-pretreated raw or spent retort water (experiments 3-6). Biooxidation of the ozone-UV/ozone treated samples did not effect DOC removals beyond those observed for untreated samples; the short contact time in combination with the low dosage was incapable of making the organic solutes in either raw or spent retort water more amenable to biooxidation (experiments 4-6). In contrast, 40 minutes of UV irradiation/ozonation following 20 minutes of ozonation (experiment 3) did appear to alter the organic constituents in raw retort water. The organic solutes that remained, however, were predominantly less available to the microorganisms; only 11 percent of the DOC was biologically oxidizable compared with 50-percent mineralization usually observed in untreated raw water. This effect was not observed in a replicate experiment (experiment 6).

Six hours of simultaneous ozonation and UV irradiation of spent retort water mineralized 20 percent of the organic carbon beyond the amount that could be initially biodegraded. At first, LpF compounds were either transformed into HpF solutes (oxidation would be expected to increase the polarity of compounds) or were mineralized. After three hours of ozonation, the LpF carbon continued to be mineralized, but further conversions to the HpF carbon pool were not observed. The intense color of spent retort water was almost entirely eliminated (Fig. 5). (The initial absorbance values for experiment 8 were approximately 2.5 times the absorbance values for experiment 7. This may have resulted from the anomalous initial DOC concentration of the spent retort water that was used in experiment 8.) The odor became almost undetectable. Ease of filtration, again, accompanied the observed color reduction. The particular batch of spent retort water that was used for this study had more DOC remaining than usual after exhaustive biooxidation (72 percent compared with 50 percent); the additional DOC appeared to be exclusively in the LpF. We have hypothesized that the excess LpF was either derived from an accumulation of retort water tarry materials in the fermentor or from compressor oil that entered the bioreactor during initial incubation. This retort water appeared to be truly spent, however, because reinoculation did not result in further DOC removal. Thirty minutes of UV irradiation/ozonation reduced the DOC by 50 mg/L, and biooxidation of this UV/ozonated water reduced the DOC by more than 300 mg/L to a value of 1438 mg/L. This value was within the range for spent retort water and was approximately the same value observed after biotreatment of spent retort water that was ozonated for 30 minutes (experiment 7). This additional biooxidation was primarily at the expense of the LpF carbon that was not degraded initially. From these results, we concluded that even though this particular batch of spent retort water contained more DOC initially, after initial treatment it appeared to behave identically to usual samples.

Three hours of intensive ozonation coupled with UV irradiation altered the organic solutes in spent retort water; an acclimated microbial seed was capable of utilizing approximately 400 mg/L of DOC that was generally unavailable prior to physicochemical treatment. This auxiliary biooxidation was entirely at the expense of HpF organic compounds. The composition of the retort water following the serial application of biooxidation, three hours of UV/ozonation, and exhaustive secondary biological treatment was similar to that of spent retort water after five hours of ozonation followed by biotreatment. The DOC remaining after the completion of each of the two

series of treatments was essentially the same, 1048 mg/L and 1068 mg/L, respectively. The ozone-pretreated retort water (experiment 7), however, contained approximately 5 percent more HpF carbon in the extracellular fluid than remained following UV/ozone pretreatment and second-stage biooxidation (experiment 8).

Simultaneous UV/ozone treatment of spent water beyond three hours of exposure, resulted in a reversal of the trend of increasing biodegradability with increasing dosage. After six hours of combined UV/ozone treatment, only one percent of the DOC was susceptible to microbial attack. The overall removal was 59 percent compared with 63 percent after only three hours of UV/ozone and biooxidation. After six hours of simultaneous UV/ozone exposure, no new HpF compounds were generated in comparison with the three-hour treatment. The microbial assemblage that was introduced into the treated water modified the existing LpF compounds into nondegradable HpF compounds. The six-hour time-course sample typified this effect. The portion of HpF was larger after biological treatment than it was before; the bacteria were growing at the expense of the LpF carbon and altering a portion of this carbon to refractory HpF compounds. The effects of the different treatment steps are represented in Figure 8 in a manner analogous to Figure 4 except that the lower graph represents both the cumulative amount of ozone consumed and UV energy supplied.

Ozone consumption appeared to decline more rapidly for the simultaneous UV/ozone treatment process (Fig. 7) compared with unassisted ozonation. After three hours, however, the ozone demand suddenly increased and after six hours reached a level equal to the one-hour demand. This decline, followed by an increasing demand, may have been a function of a number of features of ozone chemistry. In a concentrated organic waste, the oxidation rate for ozone is limited by the transfer of ozone from the gas to the liquid (Prengle and Mauk, 1978), whereas the chemical reaction rate limits the oxidation rate in dilute solutions. Perhaps the increasing ozone demand after three hours of treatment was a reflection of the changing solute concentrations. A second explanation for the fluctuating ozone demand is that the initial reactions were a result of ozone oxidations alone because UV radiation could not penetrate the solution sufficiently to decompose the ozone molecule into its radical components. After three hours, the color of the solution was significantly reduced, and UV radiant energy might then have been able to interact with ozone, creating hydroxyl radical, which rapidly and nonspecifically altered the remaining compounds. This explanation could account for both the increase in ozone demand and the qualitative changes that were observed in the residual solutes. The use of UV radiation in conjuction with low-level ozonation (experiments 3-6) was ineffectual perhaps because of the inability of the light to penetrate the intensely colored water and to interact with the ozone molecule.

Six hours of UV/ozonation eliminated most of the lower- and higher-molecular weight volatile nitrogen-containing compounds from the LpF (Fig. 9). In addition, the concentration of the intermediate-molecular-weight nitrogenous compounds in the LpF was greatly reduced. These compounds were either mineralized or were transformed into HpF nitrogen-bearing compounds.

Biooxidation

The data from the biooxidation of the ozonated and UV-irradiated waters supports the following scenario (Daughton, unpublished observations) for explaining the extremely biorefractory nature of a large portion of retort water organic solutes. Each factor serves to compound and exacerbate the

effects of the others. (1) Although the DOC of spent retort water is high, it probably comprises a multitude of organic compounds, especially nitrogenous heterocycles and their respective isomers, homologs, etc., each present at low (ppm) concentrations. Ironically, although the DOC is high, carbon is the limiting nutrient. (ii) Bacterial enzyme specificity for these compounds may be sufficiently high, so as to necessitate the acclimation of numerous bacterial species in order to effect a significant diminution of DOC. (iii) Each heterocycle may be present at concentrations sufficiently below the affinity constants of the requisite enzymes so that even if an assemblage of competent bacteria were available, degradation would be effectively inhibited. (iv) UV radiation/ozonation, as a pretreatment to biooxidation, probably creates multiple products from each oxidizable heterocycle (Hoigné and Bader, 1976), thereby compounding the low concentration problem. (v) Oxygenated heterocycles may be less biodegradable than the parent compounds. Therefore, nonselective oxidation of retort water organic solutes (i.e., ozonation at high pH, or UV/ozone treatment at neutral pH) may amplify the conditions that lead to the apparent biorefractory nature of the majority of retort water compounds. This condition could be circumvented only by ensuring that the oxidative process accomplished complete mineralization of these compounds.

In addition to this scenario, the production of toxicants by extensive chemical oxidation was a possibility that may have precluded further microbial oxidation. This proposal was not addressed and may require more extensive research.

Although the production of activated oxygen species other than ozone was never verified in this investigation, their presence could be reasonably assumed. The gross inability of these powerful oxidants to effect significant mineralization or structural alterations of the biorefractory solutes is strong evidence that biooxidative potential may not suffice for these compounds. Although chemical oxidation cannot strictly model the activity of oxygenases, these data indicate that successful biotreatment of retort water may also require reductive reactions.

SUMMARY

UV radiation in low or high dosages (1×10^6 - 10×10^6 J/L) did not mineralize a significant portion of organic carbon in retort water. UV radiation also did not alter the structure of the biorefractory compounds; the organic solutes in spent retort water remained unavailable to acclimated microorganisms.

Low dosages of ozone for short exposure intervals were insufficient to either mineralize or alter the biorecalcitrant solutes in raw or spent retort water. In contrast, extensive ozonation of spent retort water mineralized four percent of the DOC and altered a portion of the remaining organic solutes; approximately 14 percent of the DOC became available to biological degradation. It was postulated that the observed alterations were a result of the activity of the highly specific parent ozone molecule and not of its extremely reactive decomposition products.

Low dosages of ozone coupled with UV irradiation for short exposure intervals was an ineffective treatment agent for spent or raw retort water. The combined treatments did not effect the elimination or alteration of DOC from exposed wastewater samples. These results were merely the result of dosage. Intensive UV/ozone treatment for an extended exposure interval mineralized 20 percent of the carbon from spent retort water. For up to three

hours of combined treatment, the residual organic solutes became more biodegradable with increasing exposure. This trend was reversed, however, with further UV/ozone treatment. The effect of ozone appeared to be enhanced and accelerated by UV radiation; this was probably the result of UV-catalyzed disproportionation of ozone into its highly reactive, nonspecific free-radical decomposition products.

The nonspecific application of these oxidants may exacerbate the problems of bacterial enzyme specificity and solute threshold concentration effects by producing a multitude of oxidation products, each of which varies in its susceptibility to microbial attack. UV radiation and ozonation should be judged for their combined abilities to mineralize organic material, but their effect on the subsequent biotreatability of residual solutes should not be neglected.

RECOMMENDATIONS

The following should be incorporated or investigated in future experimentation:

1. all spent retort water should be pooled prior to a series of experiments to guarantee uniformity of initial conditions

2. additional parameters that should be monitored include: pH, dissolved inorganic carbon, chemical oxygen demand, ammonia, and organic nitrogen

3. experiments 7, 8, and 9 should be repeated using bacteria specifically acclimated to the pretreated water rather than to raw retort water for secondary treatment

4. longer ozonation time should be incorporated to estimate maximum achievable oxidation

5. combined treatment with H_2O_2 and UV for the production of $OH^{\bullet}$

6. Fenton reaction for $OH^{\bullet}$ production

7. UV irradiation/ozonation followed by powdered activated carbon treatment or combined spent shale and biotreatment

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Table I. Experimental Protocols

Experiment #	Type of Oxy-6 retort water treated	Sequential Treatment Duration (min)[1]			
		Ozone	UV/Ozone	UV	UV + riboflavin[2]
1	100 % raw	–	–	120	–
2	50 % raw	–	–	–	190
3	100 % raw[3]	20	40	60	–
4	100 % spent[4]	60	60	30	60
5	100 % spent (NH_3-stripped)[5]	60	30	60	–
6	100 % raw[4]	20	40	90	–
7	100 % spent[5]	300	–	–	–
8	100 % spent[5]	–	360	–	–
9	100 % spent[5]	–	–	300	–

[1] order of treatment from left to right
[2] 3 mg/L
[3] filtered through 0.25-um cellulose-acetate membrane
[4] filtered through 0.4-um polycarbonate membrane
[5] filtered through 0.8-um polycarbonate membrane

Table II. Cumulative Percent DOC Removal from Oxy-6 Retort Water by Chemical Oxidation or Photooxidation in Combination with Biological Treatment

cumulative step	Experiment #[a] 1	2	3	4[b]	5[b]	6	7[b]	8[b]	9[b]
primary biooxidation	-[c]	-	-	49 (50)	44 (46)	-	44 (48)	38 (38)	36 (43)
ozonation	-	-	3 (51)	49 (50)	45 (49)	0 (50)	48 (62)	-	-
UV-irradiation/ ozonation	-	-	2 (11)	51 (52)	47 (53)	1 (51)	-	48[d] (63) 58[e] (59)	-
UV-irradiation	5 (48)	-	1 (45)	50 (51)	47 (55)	1 (58)	-	-	38 (45)
UV-irradiation & riboflavin	-	3 (49)	-	51 (53)	-	-	-	-	-

[a] the results from each experiment are sequential from top to bottom row and the value in parenthesis is the cumulative % DOC removed by microbial mineralization following each treatment step

[b] initial DOC of Oxy-6 retort water assumed to be 2800 mg/L

[c] not applicable

[d] after 180 minutes

[e] after 360 minutes

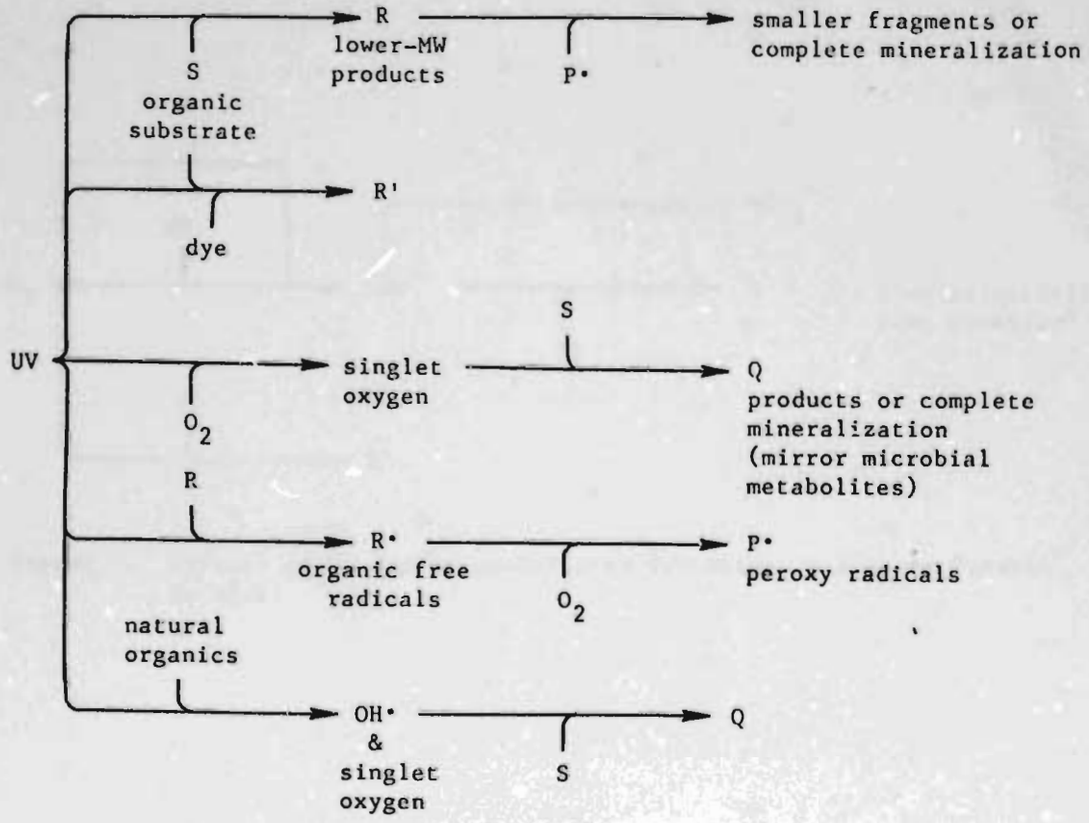


Figure 1. Interactions of UV Irradiation with Organic Material in the Presence of Oxygen.

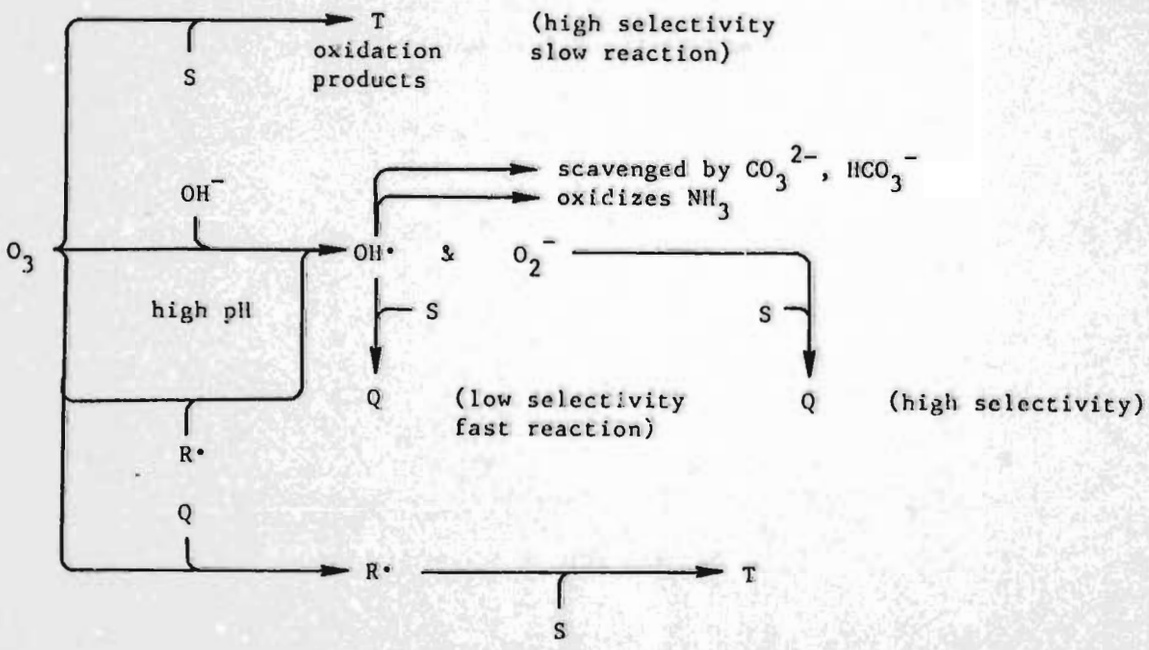


Figure 2. Summary of the Reactions of Ozone with Organic Compounds in Aqueous Solution (modified from Hoigné and Bader, 1976).

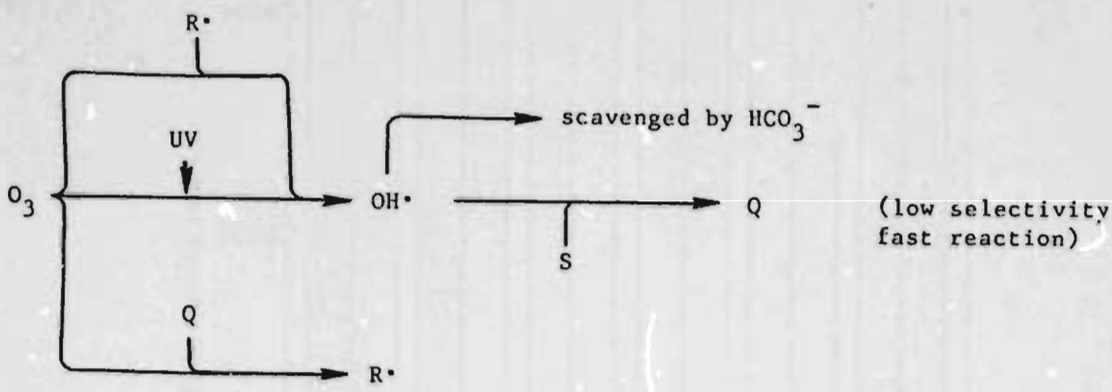


Figure 3. Effects of UV-Radiation-Mediated Ozonation on Aqueous Organic Solutes.

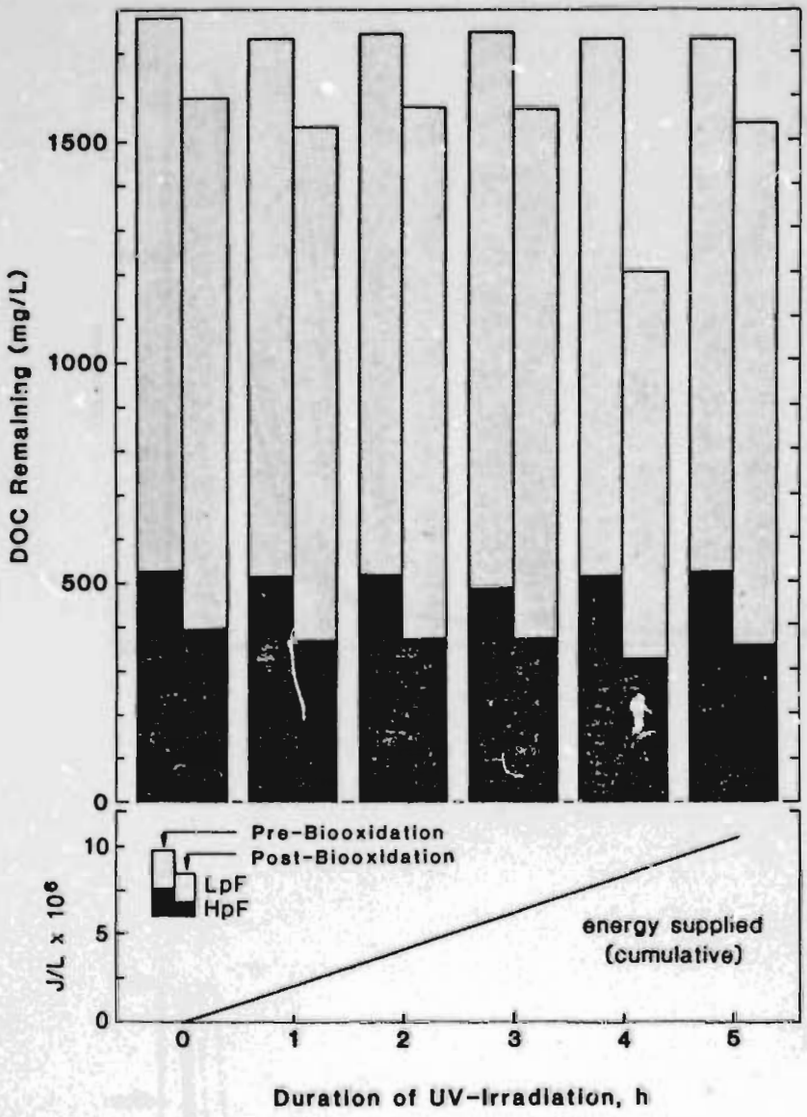
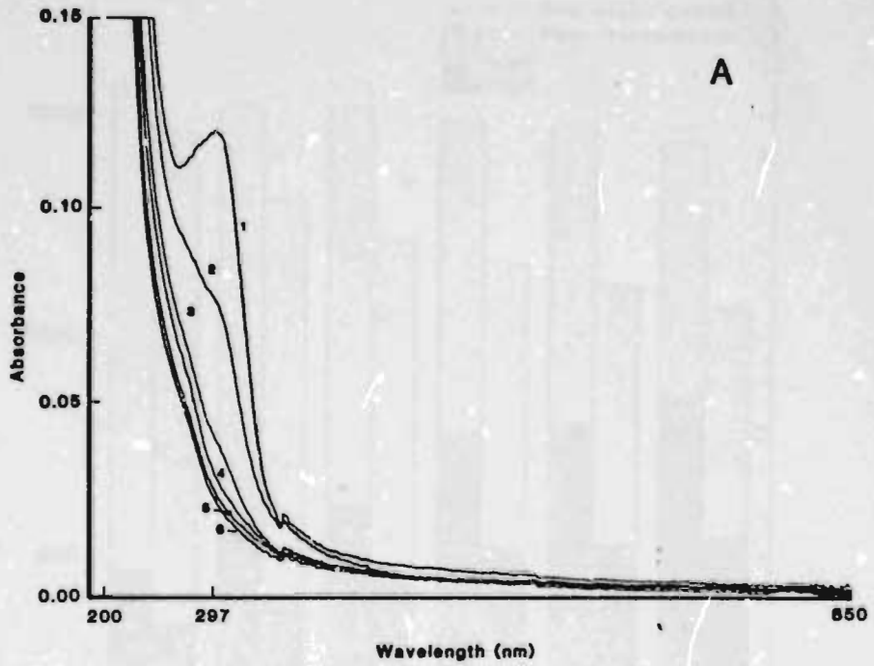


Figure 4. Biooxidation of UV-Pretreated Spent Oxy-6 Retort Water.



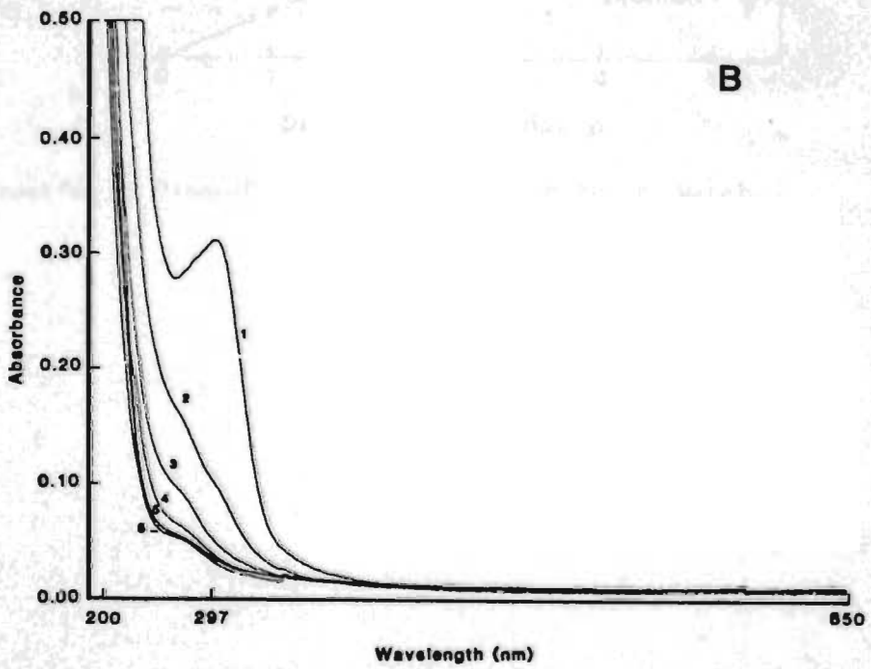


Figure 5. UV Absorbance Spectra; Labels 1-6 correspond to treatment times of 0, 1, 2, 3, 4, and 5 hours, respectively.
A. Absorbance of Ozone-Treated Spent Oxy-6 Retort Water.
B. Absorbance of UV/Ozone-Treated Spent Oxy-6 Retort Water.

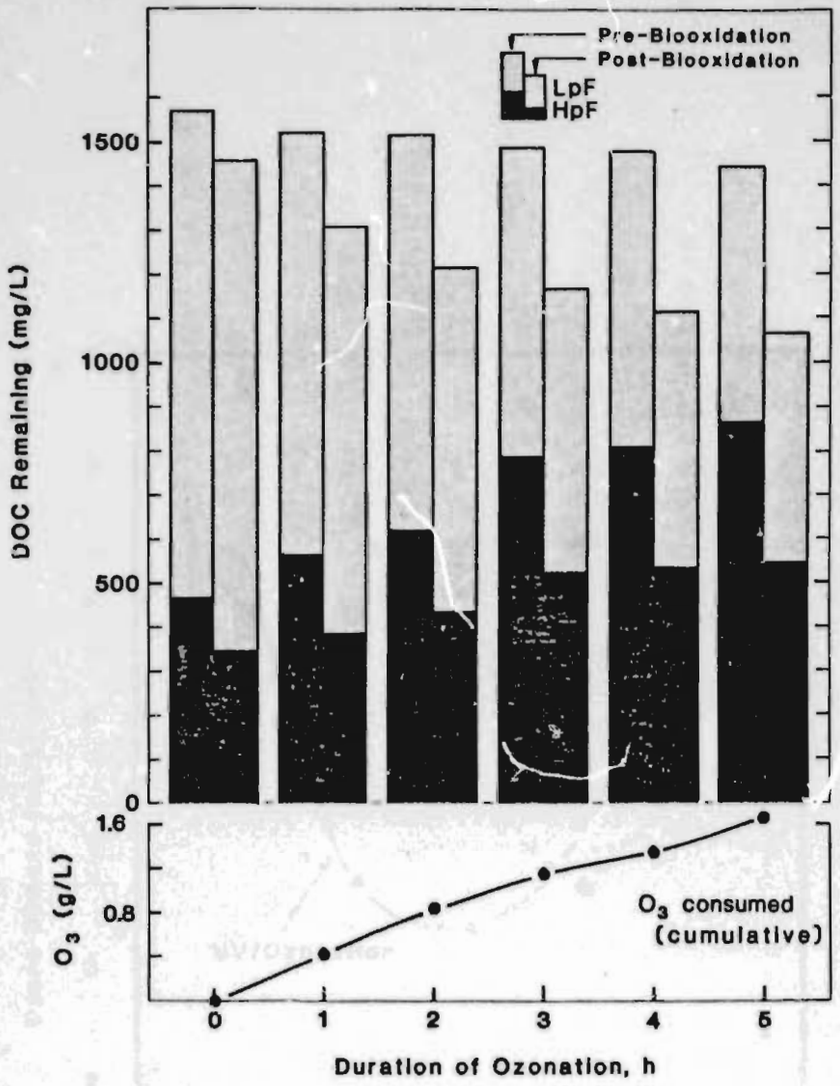


Figure 6. Biooxidation of Ozone-Pretreated Spent Oxy-6 Retort Water.

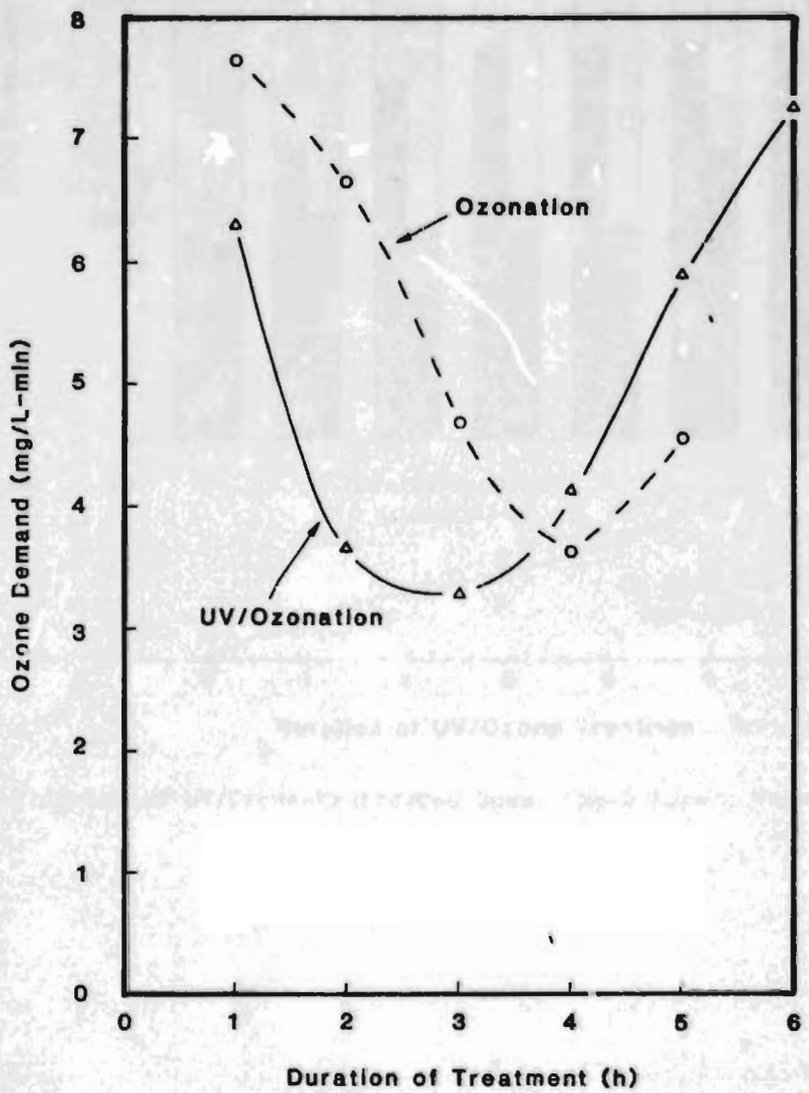


Figure 7. Ozone Demand during Ozonation and Combined UV-Irradiation/ Ozonation of Spent Oxy-6 Retort Water.

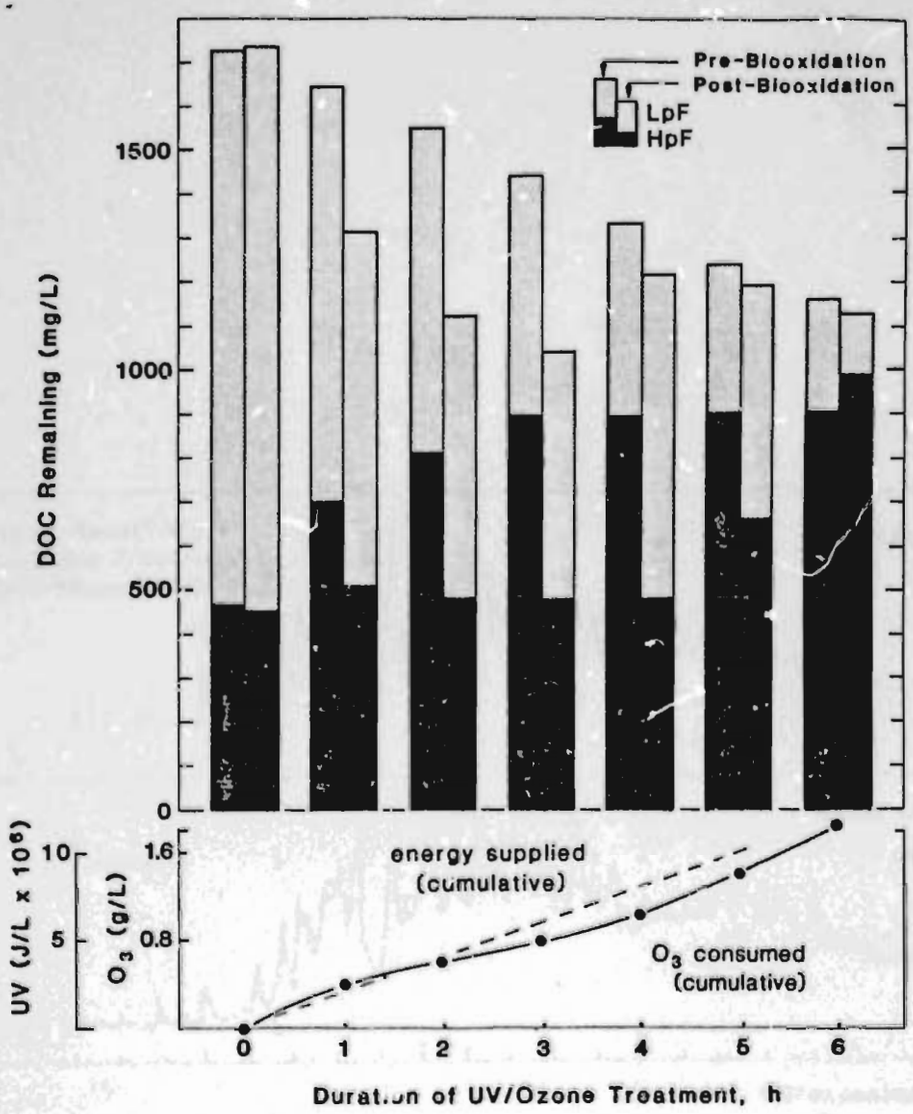


Figure 8. Biooxidation of UV/Ozone-Pretreated Spent Oxy-6 Retort Water.

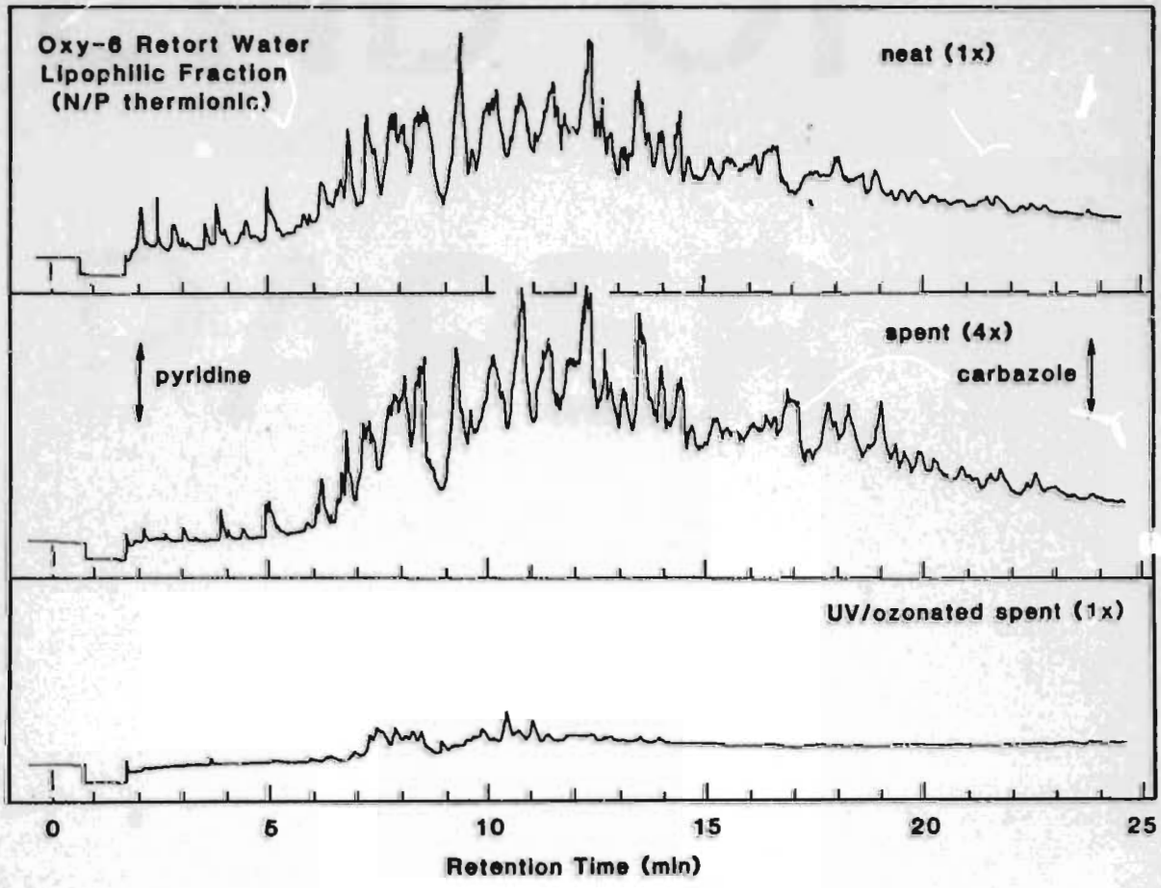


Figure 9. Gas Chromatograms of Raw, Spent, and UV/Ozone-Treated Spent Oxy-6 Retort Water (nitrogen selective detection).

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