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DEGRADATION OF TRIETHYLENE GLYCOL DIMETHYL ETHER BY OZONATION COMBINED WITH UV IRRADIATION OR HYDROGEN PEROXIDE ADDITION

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ABSTRACT

Ozonation of pure aqueous solutions of the polar aliphatic refractory triethylene glycol dimethyl ether (TEGDME) which is a typical representative of organic solutes of oil reclaiming wastewaters does not lead to effective mineralization unless high ozone doses are applied. Small doses of UV irradiation do not markedly increase TEGDME mineralization by ozonation, but transformation to more oxidized products (mainly carboxylic acids containing methoxy and/or ethoxy groups) which are biodegradable to a higher degree than TEGDME. Addition of high concentrations of hydrogen peroxide during ozonation results in efficient increase of TEGDME mineralization, however. The presence of humic acids - which is a consequence of biological treatment of wastewaters containing biodegradable organic constituents - has a beneficial effect on transformation of TEGDME during ozonation or ozone/UV treatment because hydrogen peroxide is formed during ozonation of humic acid C-C double bonds. © 1997 IAWQ. Published by Elsevier Science Ltd

KEYWORDS

Ozonation; ozone/UV; ozone/hydrogen peroxide; triethylene glycol dimethyl ether; humic acid.

INTRODUCTION

Removal of organic pollutants in water for drinking, urban, agricultural and industrial purposes is of great importance in solving the problems of environment and health protection. Conventional methods, such as biological treatment, are not always able to attain the degree of purification desired by the quality standards. This is the case with some recalcitrant aliphatic compounds found in certain petrochemical wastewaters. A possibility for solving this problem is the application of ozonation as a method for degradation of such organics.

Usually biologically treated wastewaters also contain humic acids. It is interesting to study the effect of humic acid on the ozonation of the above mentioned pollutants because humic acids, being also pollutants, form hydrogen peroxide in presence of ozone, thus facilitating the degradation of organic compounds by a radical mechanism.

Generally, oxidation by ozone is accomplished by a radical mechanism forming oxygen containing compounds, including carboxylic acids as products. There are data on the ozonation of different organics converted to easily biodegradable products (Gulyas *et al.*, 1994a; Jones *et al.*, 1985). When aliphatic compounds are treated, more powerful oxidants are necessary. On the other hand, the necessity of higher ozone concentrations increases the price of the method making it unattractive from a practical point of view. Its combination with UV-irradiation gives some hope for enhancement of the method efficiency.

The purpose of the present paper is to study the possibilities of ozonation as a method for preliminary wastewater treatment on model compounds. This treatment could be solely ozonation or ozonation combined with another action, such as UV-irradiation or oxidation by hydrogen peroxide.

The main goals of our study were: i) comparative study of the rate and degree of degradation of a chosen polar aliphatic model compound, typical of oil reclaiming wastewaters, by ozonation combined with UV irradiation or hydrogen peroxide addition; ii) study of the effect of humic acids on the degradation with ozone of the same model compound; iii) check of the biodegradability of the products of ozonation.

The model organic compound to be degraded was triethylene glycol dimethyl ether (TEGDME), since it is a typical refractory found in oil reclaiming wastewaters (Gulyas *et al.*, 1994b). Another reason for this selection was the finding that TEGDME is not degradable by traditional biological treatment and not retained in biofilters. Moreover, oligo-ethoxylates are hardly sorbed to activated sludge or to activated carbon because of their polarity (Gulyas and Reich, 1996). In some experiments humic acid from lignite (as sodium salt) was added to the aqueous TEGDME solutions.

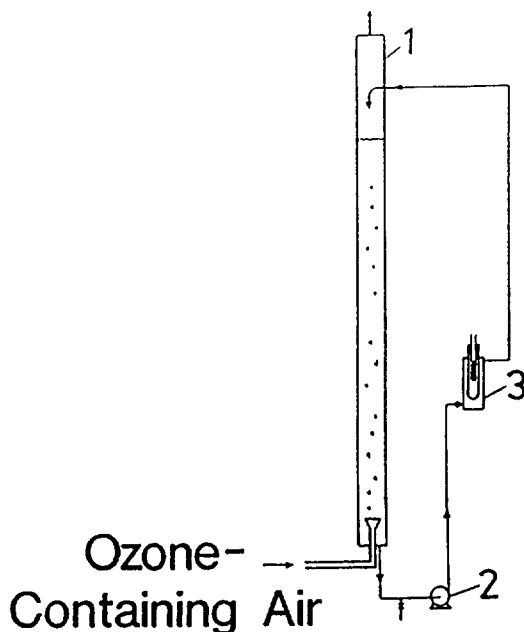


Figure 1. Bubble column reactor for treatment of model wastewaters with ozone and ozone/UV; 1: Bubble column; 2: Recirculation pump; 3: UV irradiation reactor.

EXPERIMENTAL PROCEDURES

Equipment. The experimental study of ozonation in combination with UV irradiation was accomplished in a bubble column reactor (Fig. 1) of 5 m height (4 m effective height) and 0.05 m I.D. The reactor was supplied with a closed loop for recycling the ozonated liquid (a total volume of 10 l) by pump 2 assuring a contact time of 8 min in the ozonation column. The duration of the experiments varied up to 22 hrs.

Ozone was produced from ambient air by a Trailgaz laboratory scale ozonator. The formed ozone/air mixture was supplied to the lower part of the reactor by a glass gas diffusor. Gas flow was 50 or 100 l/h and inlet ozone concentrations were 18 and 30 g/Nm³. Ozone concentrations in the gas phase (inlet and outlet concentrations) were determined iodometrically. When the effect of UV irradiation was studied, the 5 W UV lamp in chamber 3 was switched on.

Ozonation in combination with hydrogen peroxide was carried out in a stirred vessel reactor equipped with a gas distributor at the bottom and a paddle mixer (diameter: 8 cm; paddle width: 2 cm; 700 rpm) as described by Gulyas *et al.* (1995): liquid volume: 4.5 l; gas flow: 50 l/h; ozone concentration in the gas phase: 50 g/Nm³. Ozone concentration in the gas phase (inlet and outlet) was measured by a UV analyzer. In these investigations ozone was generated from pure oxygen in an ozone generator. Aqueous solutions of different concentrations (0.3, 3 and 7%) of hydrogen peroxide were continuously added by a membrane pump with a flow of 40 ml/h. At different times samples were taken from the reactor for analyses.

Model wastewater. Model wastewaters used for ozonation experiments were solutions of TEGDME (10 to 100 mg/l) and humic acid (0 to 50 mg/l) in distilled water.

Analytical Methods. TOC was analyzed by means of a Maihak TOC analyzer, COD by the classical dichromate standard method using cuvette tests which enabled analysis of small sample volumes, and BOD₅ using the standard method. Measurement of pH was performed by electrodes. UV absorption spectra were recorded with a Pye-Unicam UV/VIS spectrophotometer SP8-400.

TEGDME concentrations were quantified gas chromatographically after extracting a 40 ml sample or aqueous standard (10, 50 and 100 mg/l) three times with 5 ml dichloromethane. The collected extracts were dried with sodium sulfate and concentrated by vacuum evaporation to a few ml. These concentrates were further concentrated in a gentle stream of nitrogen to give a final volume of 0.5 ml. Some extracts were selected for GC/MS analyses following the method described elsewhere (Gulyas and Reich, 1996).

RESULTS AND DISCUSSION

Ozonation without UV. At lower ozone concentrations and small exposure time the effect of ozone was negligible (Fig. 2): decrease of COD (and also of TOC, data not shown) was very small, i.e. degradation of the model compound does not reach a sufficient degree of mineralization. Nevertheless, a small amount of TEGDME was transformed to biodegradable products by ozonation which is manifested by the increase of BOD₅, although the BOD₅ formed during ozonation was very small (below 5 mg/l). In a long time ozonation experiment (22 h, gas flow 100 l/h, ozone concentration in the gas phase 30 mg/l) COD was reduced below the detection limit (< 15 mg/l) and TOC to 2.4 mg/l even without UV irradiation, however (data not shown).

Another conclusion to be drawn is that there is no marked difference between the data at different gas flow rates and inlet ozone concentrations, i.e. there is no mass transfer resistance in the gaseous phase.

During ozonation a decrease of pH took place which was caused by the formation of acidic products. This conclusion was confirmed by the UV spectra showing that a new UV absorbance maximum occurred at 205 nm (Fig. 3) which is typical for carboxylic groups. These maxima were observed during all experimental runs - both with and without UV irradiation, with and without addition of humic acid. Organic acid formation was also confirmed by HPLC analyses (data not shown). By GC/MS four new compounds

formed during ozonation were detected, but not identified. They were characterized as methoxy ethoxy compounds.

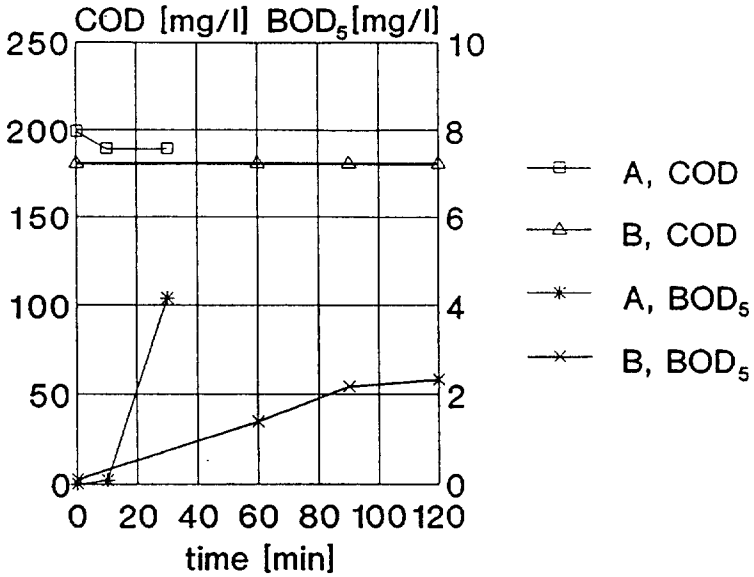


Figure 2. COD and BOD₅ of an aqueous TEGDME solution (100 mg/l) during ozonation; A: Gas flow: 100 l/h, O₃ concentration in the gas: 18 mg/l; B: Gas flow: 50 l/h, O₃ concentration in the gas: 30 mg/l.

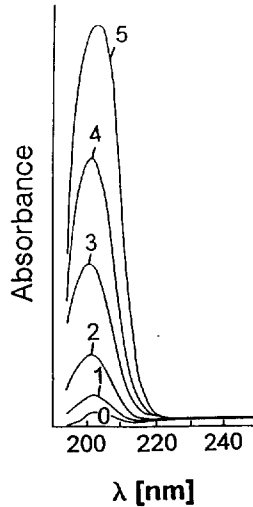


Figure 3. UV spectra of aqueous solutions of TEGDME (100 mg/l) after different ozonation times (0: No ozonation; 1: 2 h; 2: 4 h; 3: 6 h; 4: 10 h; 5: 22 h); Gas flow: 100 l/h, O₃ concentration in the gas: 30 mg/l.

Ozonation combined with UV irradiation. Irradiation has a beneficial effect on acidic products formation during ozonation (as pH decreases, Fig. 4a) with a better biodegradability (increase of BOD₅, Fig. 4b). Acid products formation could be monitored by the UV absorption maximum at 205 nm as well (data not shown). However, no total mineralization at shorter exposure times (up to 30 min) occurred, since COD (Fig. 4b) and TOC (data not shown) remained almost the same as in the starting solutions. Measured TEGDME concentrations decreased during ozonation, but were only slightly affected by additional UV irradiation

(data not shown). The modest effect on mineralization and TEGDME removal can be explained by the low power of the available UV lamp.

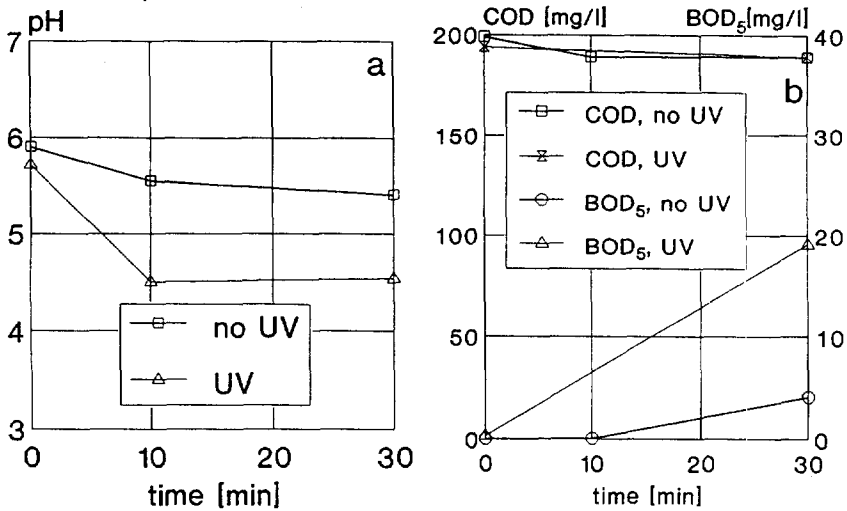


Figure 4. Influence of UV irradiation on pH (a) and on COD and BOD₅ (b) During ozonation of an aqueous solution of TEGDME (100 mg/l); Gas flow: 100 l/h; O₃ concentration in the gas phase: 18 mg/l.

Ozonation in the presence of humic acids. If no UV irradiation is applied, mineralization velocity during ozonation is nearly unaffected by humic acid concentrations as shown by TOC measurements (Fig. 5a). However, initial velocity of COD elimination is higher in TEGDME solutions containing high humic acid concentrations (Fig. 5b) indicating enhanced OH radical formation in the presence of humic acid.

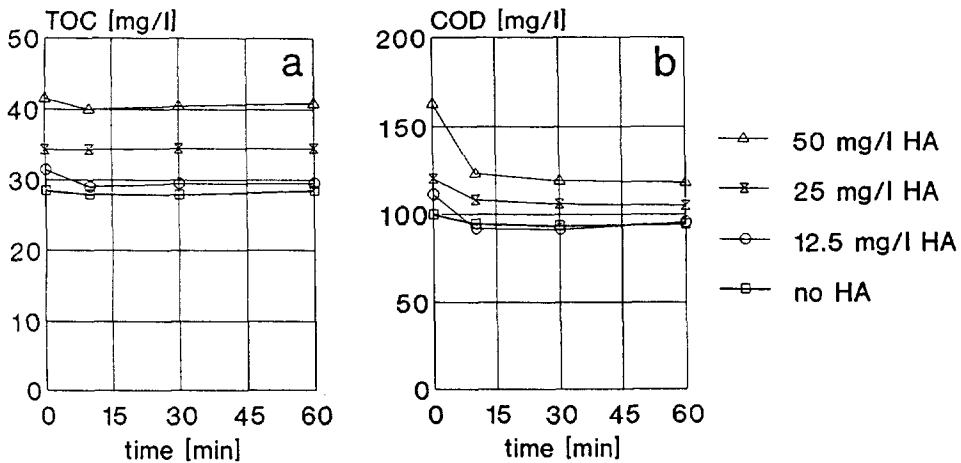


Figure 5. Influence of initial humic acid concentration on TOC (a) and COD (b) during ozonation of aqueous solutions containing humic acid and TEGDME (50 mg/l); Gas flow: 100 l/h; O₃ concentration in the gas phase: 30 mg/l.

Also the TEGDME concentrations measured in the presence of different initial humic acid concentrations suggest enhanced TEGDME transformation because of increased OH radical formation. After a 1 hr

ozonation period in the presence of 50 mg/l humic acids the TEGDME concentration is only one third compared to the absence of humic acids (Fig. 6).

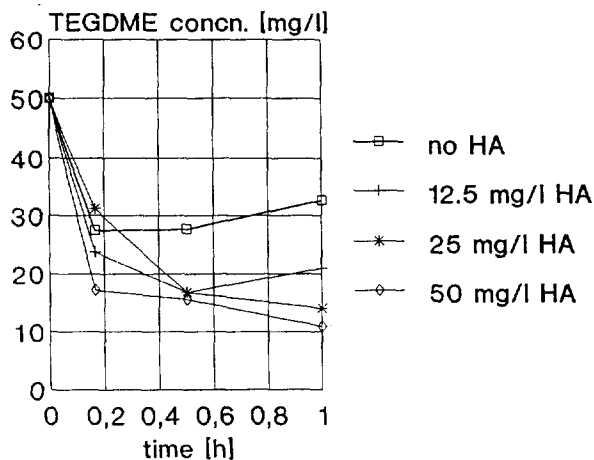


Figure 6. Influence of initial humic acid concentration on TEGDME concentrations during ozonation of aqueous solutions containing humic acid and TEGDME (50 mg/l); Gas flow: 100 l/h; O_3 concentration in the gas phase: 30 mg/l.

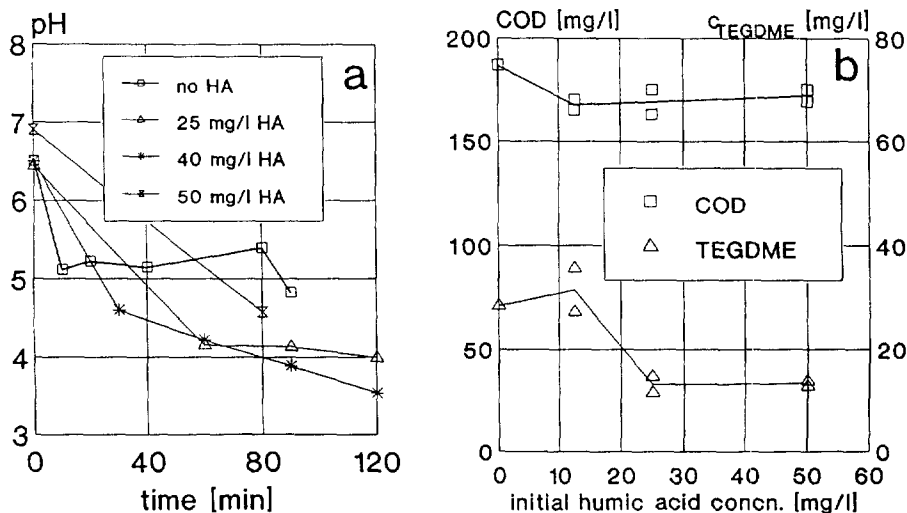


Figure 7. Effect of initial humic acid concentration on pH of aqueous TEGDME solutions during O_3/UV treatment (a) and on COD and residual TEGDME concentration after 2 hours O_3/UV treatment (b) (gas flow: 50 l/h, initial O_3 concentration in the gas phase 30 mg/l).

Presence of humic acids during simultaneous ozone/UV treatment resulted in an enhanced decrease of pH (Fig. 7a). Although initial COD was higher in solutions containing more humic acid, the COD after 2 hr ozone/UV treatment of solutions with humic acid was lower than COD of the treated pure TEGDME solution (Fig. 7b). TOC values of all treated solutions show that mineralization increased (up to 18%) with initial humic acid concentration (data not shown). Thus, humic acids enhance organic solute mineralization during ozonation rather than to compete with other organic solutes. The explanation of these effects could be sought in the presence of the humic acids, which facilitates the formation of OH radicals which support

TEGDME oxidation to carboxylic acids and even to carbon dioxide. This explanation is confirmed by the observed UV spectra (Fig. 8.). As one can see TEGDME absorbs light at lower wave lengths ($\lambda = 190$ nm) while at 205 nm only the ozonation products show absorption but not TEGDME. However, there is also some absorption of humic acids at 205 nm. During the first 30 min a decrease of the height of UV absorption maximum takes place because of humic acid transformation. Then the height of the maximum increases because of TEGDME degradation which leads to carboxylic acid formation.

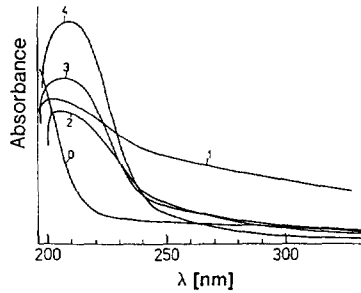


Figure 8. UV spectra of TEGDME solution (100 mg/l) during ozone/UV treatment in the presence of humic acid (50 mg/l); gas flow: 50 l/h; initial O_3 concentration in the gas phase 30 mg/l; TEGDME/humic acid mixture before (1), and after 60 min (2), 90 min (3), 120 min (4) ozonation; 0: pure TEGDME solution.

Treatment with ozone/hydrogen peroxide. In these experiments an aqueous solution containing 10 mg/l TEGDME and 50 mg/l humic acid were treated in a stirred vessel reactor. Fig. 9 clearly shows that hydrogen peroxide addition increases the efficiency of organic solute removal by ozonation. While ozonation without addition of hydrogen peroxide only removed about half of the initial TOC within 5 hr the continuous addition of the highest concentration of hydrogen peroxide (7%) resulted in the formation of such an amount of OH radicals that more than 85% of the initial TOC was removed within 80 min.

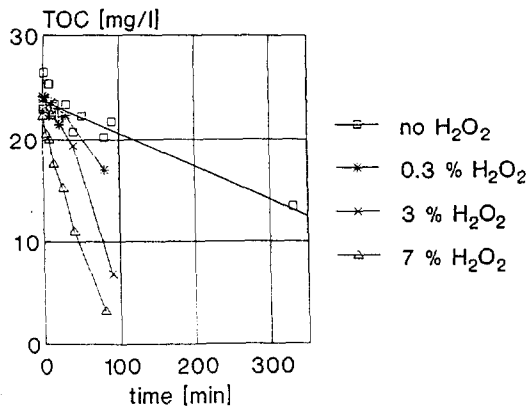


Figure 9. TOC removal from an aqueous solution containing 10 mg/l TEGDME and 50 mg/l humic acid by ozonation and simultaneous addition (40 ml/h) of aqueous solutions with different concentrations of H_2O_2 .

Data of TEGDME removal during these experiments are published elsewhere (Gulyas *et al.*, 1995). The substance TEGDME disappeared rapidly from the solution. Without addition of hydrogen peroxide after 25 min more than 90% of the substance was transformed to other products while at this time only less than 5% of the TOC was removed without hydrogen peroxide addition. If hydrogen peroxide solution with a concentration of 3% was continuously added, no more TEGDME was detectable after 20 min, and if a 7% hydrogen peroxide solution was added, already after 5 min no more TEGDME was detected.

CONCLUSIONS

Ozonation of pure aqueous TEGDME solutions is inefficient unless high doses of ozone are consumed which is uneconomic. However, acidic products are formed as intermediates before partial mineralization of organic constituents of the test solutions takes place. Formation of these compounds is correlated with an increase of BOD.

Simultaneous UV irradiation with a very small UV lamp increases TEGDME transformation (leading to higher biodegradability), but not mineralization. For enhancement of mineralization higher UV irradiation doses are required than realized in these experiments.

The studied process of degradation is enhanced in the presence of humic acids because of increased free radical formation by hydrogen peroxide production during ozonation of C-C double bonds of humic acids. This shows a beneficial effect of biological wastewater treatment prior to ozonation because humic acids are formed during biodegradation of organics. A further enhancement of TOC reduction is observed when hydrogen peroxide is added during ozonation confirming the hypothesis of the role of free radicals.

Advanced oxidation processes such as ozone/UV or ozone/hydrogen peroxide can be looked at as suitable processes for the removal of aliphatic polar refractories from wastewaters with relatively low concentrations of organics.

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