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REMOVAL OF 3,4-DICHLOROBUT-1-ENE USING OZONE OXIDATION

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Abstract—The efficiency of ozone oxidation in the removal of 3,4-dichlorobut-1-ene (3,4 DCB), a contaminant often present in the aqueous effluents generated by synthetic rubber processes, was studied. Ozone oxidation removed 3,4 DCB completely from the model solutions with initial concentrations ranging from 4 to 64 mg/l over a maximum ozonation time of 7 min. The complete oxidation of 3,4 DCB was mainly due to the direct reaction with ozone molecules at acidic and neutral pH. At alkaline pH ozone oxidation only reduced the 3,4 DCB concentration by 61% over 15 min of ozonation. Methanol used in preparing the 3,4 DCB solutions did not affect the ozone oxidation rate. Ozone oxidation of a 3,4 DCB/methanol solution with an initial 3,4 DCB concentration of 120 mg/l reduced 95% of the 3,4 DCB concentration but only 4% of the Chemical Oxygen Demand (COD) in the solution. The high COD value in the ozonated solution was probably due to the presence of methanol. Ozone degraded 3,4 DCB and chloroprene (CD) in the effluent samples from a synthetic rubber processing plant and resulted in the maximal reduction of the COD by 45%. © 2000 Published by Elsevier Science Ltd. All rights reserved

Key words—aqueous effluent, chlorinated hydrocarbons, synthetic rubber, 3, 4-dichlorobut-1-ene, chloroprene, ozonation

INTRODUCTION

The treatment of aqueous borne chlorinated hydrocarbon wastes is very important to a wide range of industrial processes including the fibres, plastics and polymers industries. Chlorinated hydrocarbon compounds are known to be recalcitrant, toxic and in some cases carcinogenic and discharge of the aqueous wastes can lead to the build up of significant amounts of chlorinated hydrocarbons in the environment.

Polychloroprene elastomer belongs to a group of products known as synthetic rubbers. During the course of its production aqueous effluent streams are generated which contain derivatives of dichlorobutene and chlorobutadiene. The synthetic rubber manufacturers are therefore obliged to find improved methods for treating their effluents to meet the criteria of Integrated Pollution Control, and in particular to demonstrate that the Best Available Techniques Not Entailing Excessive Cost (BATNEEC) criteria is fulfilled.

This paper discusses the efficiency of ozone oxidation in the removal of chlorinated hydrocarbons from both model solutions and effluent samples taken from a synthetic rubber processing plant.

OZONATION

Ozone applications

Ozone oxidation has been widely employed to disinfect potable water in several European countries (Rice and Netzer, 1984), however, in the UK it is primarily used for the removal of pesticides (Aeppli *et al*., 1997). Ozone oxidation is also used for treating waste waters from the electroplating, textile, pulp and paper, and petroleum industries (Rice, 1997). In recent years ozone oxidation has been studied for treating rubber additive waste waters, landfill leachates and municipal waste waters (Rice, 1997).

The advantages of ozone oxidation process are the ability to apply ozone directly in its gaseous state and a short reaction time between the ozone and effluent. Ozone application neither increases the volume of effluent nor results in formation of sludge. In addition, ozone reacts preferably with refractory substances. The disadvantages of ozone oxidation include the relatively high energy cost of producing ozone, the pH impact on its oxidation

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*Author to whom all correspondence should be addressed. Present address: 33 Ferrymoor, Ham, Richmond, Surrey, TW10 7SD, UK. Tel.: +44-181-940-3907; Fax: +44-181-940-3907; e-mail: maryam_at@hotmail.com potential, insignificant TOC reduction and possible development of more toxicity in the treated water than the unprocessed water (Heinzle *et al.*, 1992; Gähr *et al.*, 1994; Strickland and Perkins, 1995; Schroeder, 1996; Aeppli *et al.*, 1997; Hanmer, 1997).

Ozone reaction with organic compounds

Ozone (O_3) is an unstable reactive gas which is about 13 times more soluble in water than oxygen at standard temperature and pressure (Hill and Rice, 1982). At low pH, saturated olefins are essentially unreactive with ozone compared to their counterparts, the unsaturated olefins. Halogens directly attached to a double bond greatly deactivate the rate of ozone oxidation. In competitions between halogenated and non-halogenated double bonds, ozonolysis appears to occur exclusively at the latter (Bailey, 1978; Masten and Hoigné, 1992).

Kinetics of ozonation

Ozone always reacts in two different mechanisms: direct reaction of ozone with organic compounds and indirect reaction by free hydroxyl radicals. The direct reactions are often rather slow but highly selective. The indirect reactions by free hydroxyl ions, on the other hand, are highly reactive but less selective (Aeppli *et al.*, 1997).

In the direct reaction, ozone molecule (O_3) oxidises the dissolved contaminant, M. The rate of the transformation of M with concentration of $[M]$, by the ozone molecule is assumed to be first order with respect to ozone. Masten and Hoigné (1992) expressed the kinetics of this reaction by the following equation:

$$-\left(\frac{\mathrm{d}[M]}{\mathrm{d}t}\right) = k_{\mathrm{O}_3,\,M}[\mathrm{O}_3][M] \qquad (1)$$

where t is the reaction time and $k_{\mathrm{O}_3,\,M}$ is the reaction rate constant for the direct reaction of ozone with the contaminant M. When the concentration of M is much greater than the ozone concentration the reaction rate becomes pseudo-first order. For such reactions the following has been formulated by Hoigné and Bader (1983):

$$-\log\left(\frac{(\mathrm{O}_3)_t}{(\mathrm{O}_3)_0}\right) = k_{\mathrm{o}_3}[M]_0^n t \qquad (2)$$

where $[O_3]_0$ and $[O_3]_t$ are concentrations of ozone at time zero and time t respectively. The rate constant can then be determined experimentally by measuring ozone concentrations during the reaction time t (Hoigné and Bader, 1983).

In the indirect reaction a part of the decomposed ozone converts to hydroxyl radical (HO·) and the logarithm of the relative residual concentration of M is a function of the amount of decomposed ozone and the reaction rate constant for the indirect reaction of (HO·) and M (Masten and Hoigné, 1992).

Parameters influencing oxidation rate

The oxidation potential of ozone ranges from around 2.08 V in acidic solutions to only 1.4 V in alkaline solutions. The pH therefore influences the relationship between oxidation potential and decomposition behaviour of Ozone. The oxidising agent in acidic solutions is the ozone molecule whereas in alkaline solutions it is the hydroxyl radical (Gähr *et al.*, 1994). In oxidising organic substances such as 1,1-dichloro-1-propene and 1,1-dichloroethylene increasing the pH resulted in an increase in the ozone dosage required for the former and decrease in the ozone dosage required for the latter substance (Masten and Hoigné, 1992).

Mass transfer of ozone

Mass transfer of ozone into aqueous solutions is important in both air and water pollution abatement. The overall mechanism of the gas-liquid reaction system consists of the following steps:

- diffusion of ozone into an interface between the gas and liquid phases;
- transport across the interface to the liquid phase boundary due to a concentration gradient;
- transfer into the bulk liquid.

The mass transfer rate is influenced by many factors, which can be divided into hydrodynamic and physicochemical effects. Hydrodynamic behaviour is concerned with the movement of the molecules. For example, bubbles rising slowly to the surface in a column of liquid have small interfacial areas, and therefore, mass transfer rates are generally low. If intense mixing is added, the bubbles are sheared and mixed thoroughly, increasing both interfacial area and contact time and therefore higher mass transfer rate. Physicochemical effects include decomposition reactions of ozone, temperature, pressure and chemical composition of the liquid (Kuo and Yocum, 1982).

EXPERIMENTAL PROCEDURES

Samples

Both model solutions and effluent samples from a synthetic rubber processing plant were investigated. The model solutions were made up using pure 3,4-dichlorobut-1-ene (3,4 DCB) which was dissolved in methanol (1:50 v/v). The 3,4 DCB solutions were prepared by diluting 3,4 DCB/methanol in double distilled water. The aqueous solution was stirred for one hour using a magnetic stirrer bar prior to ozonation. The effluent samples were transported to the laboratory and kept at 5°C. Prior to ozonation, the samples were filtered using filter papers (Whatman, grade 1) to remove suspended solids.

Ozonation

The ozonation experiments were carried out using an ozone generator (Ozat®, type CF-0B, Ozonia Ltd). Oxy-

Table 1. The conditions under which the experiments were run

Gas flow (m^3/h)	0.18	0.18	0.18	0.18
Current (A)	0.8	0.9	1.0	1.1
Ozone concentration (wt%) (at t = 20°C, P = 1.3 bar)	2	3.5	4.8	5.8
Ozone production (g/h)	5	9	12	15

gen was used as the feed gas. The ozone reactor, a round glass vessel with an approximate volume of 6 l, was equipped with two taps from which aqueous samples were withdrawn. The ozone bearing gas (inlet gas) was delivered to the bottom of the vessel through a glass pipe 5 mm in diameter. The excess gas left the vessel through another glass pipe situated on top of the vessel. In each experiment a batch of 5 l of model solution or effluent sample was ozonated continuously in the system mentioned. During the ozonation the solution/effluent sample was stirred by means of a magnetic stirrer in order to increase the mass transfer rate between the ozone gas and solution. All the experiments were conducted at room temperature; 20 ± 2°C. The experimental conditions are summarised in Table 1.

The ozone production was calculated using the following equation:

$$V_n = \frac{100}{\rho}\frac{M_{O_3}}{C} \tag{3}$$

where V_n is the gas flow in m^3/h; ρ is the density of the feed gas at standard conditions ($\rho_{\text{Oxygen}} = 1.429$ kg/m^3 at 0°C and 1.013 bar); M_{O_3} is the ozone production in kg/h; and C is the ozone concentration in wt% corresponding to the adjusted current supply (Ozonia Operating Instructions, 1996).

The gas flow rate and the corresponding ozone concentrations were taken from the diagrams given in the Ozonia Operating Instructions, 1996.

Analytical procedures

3,4 DCB was analysed using a Pye Unicam gas-liquid chromatography system (Series 304 Chromatograph, Pye Unicam Ltd.), with a capillary column (Phase Sep 12 m × 0.22 mm OV-1) and with electron capture detection. The 3,4 DCB samples were extracted from the aqueous phase to the organic phase using tetrachloroethene in 2,2,4-trimethylpentane. The 3,4 DCB standard solutions used for calibration were treated the same way. The extracts (0.8 μl) were injected manually. The injection port and the detector were heated to 200°C whereas the column operated at 35°C. The effluent samples were extracted using 2,2,4-trimethylpentane. The extracts were analysed automatically by a Hewlett Packard chromatography system (Series II, 5890A GC) on a narrow bore capillary column.

The residual ozone in the ozonated solutions was measured following the Indigo Method (Method 8311 for water in the DR/2000 Spectrophotometer Handbook) using a DR/2000 spectrophotometer (HACH Systems, USA). Following this method 40 ml of the solution was brought into contact with an AccuVac Ampoule containing potassium acid malonate (HACH Systems, USA). The Indigo reagent when dissolved in ozone free water resulted in a deep blue colour solution whereas in contact with the ozonated sample the blue colour faded or disappeared. The difference in absorbency between a blank and a sample measured at 600 nm presented the residual ozone in the sample.

The Chemical Oxygen Demand (COD) was measured following the Reactor Digestion Method (Method 8000 for water, wastewater and sea water in the DR/2000 Spectrophotometer Handbook) using the DR/2000 spectrophotometer (HACH Systems, USA).

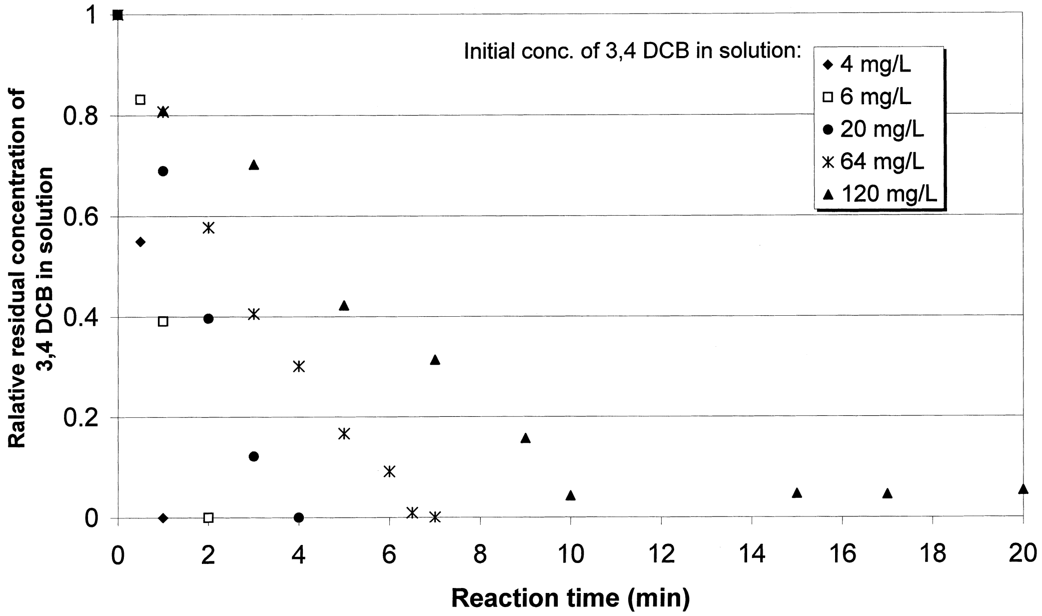

Fig. 1. The effect of initial concentration of 3,4 DCB on the oxidation rate at an ozone concentration of 4.8 wt%.

RESULTS AND DISCUSSION

Model solutions

Ozonation was carried out at a flow rate of 0.18 m^3/h and a current supply of 1 A. These resulted in an ozone concentration of 4.8 wt% equivalent to an ozone production of 12 g/h in the inlet gas. Figure 1 shows the reduction in the 3,4 DCB concentration as a function of time for the 3,4 DCB solutions with initial concentrations ranging from 4-120 mg/l.

The ozonation time required for oxidising 3,4 DCB increased with higher initial concentrations of 3,4 DCB as shown in Fig. 1. In solutions with low initial concentrations (4 and 6 mg/l), there was a rapid linear decrease in 3,4 DCB concentration. This suggests that the reaction between 3,4 DCB and ozone was a zero order reaction with respect to 3,4 DCB. In this case the reaction rate constant (k) equal to the gradient of the line, was 4.10^{-7} M/s.

For solutions with initial concentrations from 20 to 120 mg/l, the oxidation rate did not appear to be linear. This suggests that the order of the reaction between ozone and 3,4 DCB depends on the initial concentration of 3,4 DCB in the solution. Moreover, for the 3,4 DCB solution with an initial concentration of 120 mg/l, 10 min of ozonation removed only 95% of 3,4 DCB. After the ozonation was interrupted, the concentration of 3,4 DCB remained constant in the solution. The incomplete oxidation of 3,4 DCB suggests a rapid decomposition of ozone molecules in the solution.

As 3,4 DCB is highly volatile, the reaction between 3,4 DCB and ozone could also take place in the gas phase. Due to the lack of an appropriate analytical set up, it was not possible to study and analyse samples from the gas phase. Therefore the lowest flow rate provided by the ozone generator, 0.18 m^3/h, was chosen in order to minimise the evaporation of 3,4 DCB.

To determine the extent of the evaporation of 3,4 DCB during the experiments the following was carried out: a 3,4 DCB solution with an initial concentration of 20 mg/l was purged for 5 min at the preceding flow rate and a current supply of 0.3 A (at this current the inlet gas only contained oxygen). Under these conditions, the concentration of 3,4 DCB reduced by 12% (Fig. 2). To determine the effect of ozone dosage on the oxidation rate of 3,4 DCB, solutions with initial concentration of 20 mg/l were ozonated at various ozone concentrations as shown in Fig. 2. The ozone concentrations expressed in wt% correspond to ozone productions of 5, 9, 12 and 15 g/h in the gas phase (equation (3) and Table 1).

The reduction in 3,4 DCB concentration was slower at low ozone concentrations. Increasing the ozone production three fold from 5 to 15 g/h reduced the ozonation time required for complete oxidation of 3,4 DCB by 50% from 6 to only 3 min. At the highest ozone concentration (5.8 wt%), the ozone oxidation seemed to be a zero order reaction.

To determine the effect of methanol on the ozone oxidation rate, two 3,4 DCB solutions with initial concentrations of 120 mg/l were ozonated at an ozone concentration of 4.8 wt% over 10 min. One

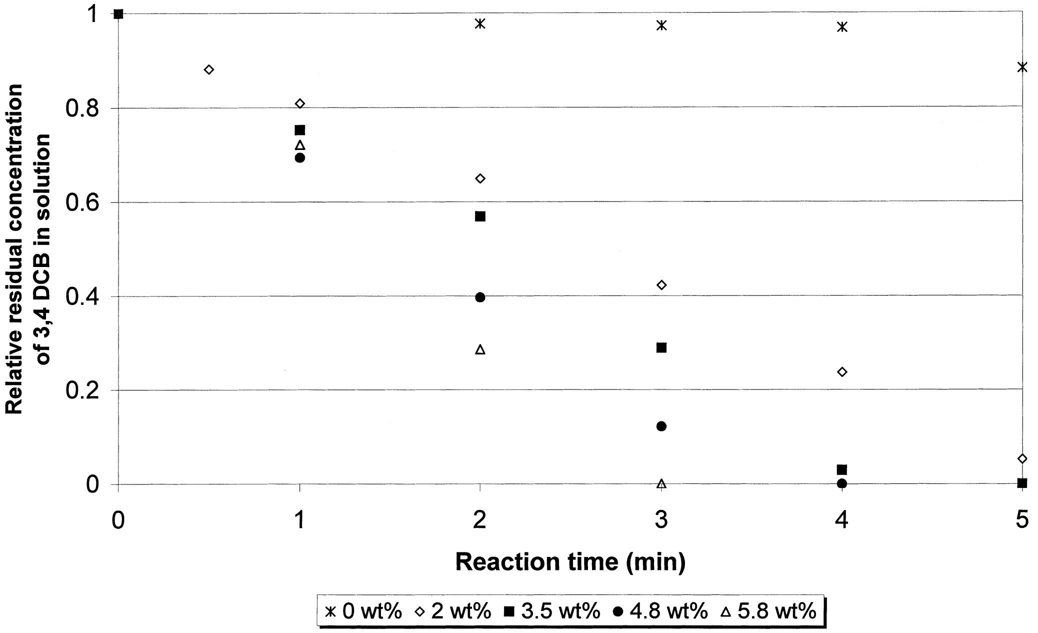

Fig. 2. The effect of ozone concentration on the oxidation rate of 3,4 DCB in solutions with initial concentration of 20 mg/l.

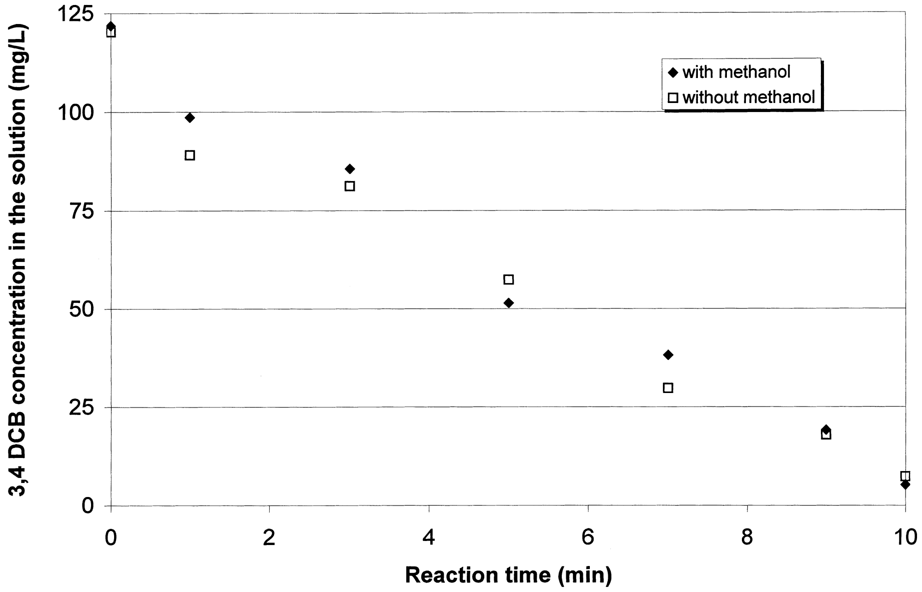

Fig. 3. The effect of methanol on the ozone oxidation rate.

solution was made following the procedure described in the Experimental Procedures section and one was made up without using methanol. The reduction of 3,4 DCB by 94–95% in both solutions is illustrated in Fig. 3.

The ozone oxidation rate in both 3,4 DCB solutions was the same and not affected by the presence of methanol. This may be explained by the low reaction rate constant ($k_{O_3} = 0.02$ M/s) for the ozone and methanol reaction in water (Hoigné, 1982). The effect of methanol on the COD value of the solution was also investigated. The COD of the 3,4 DCB solution made up with methanol was measured during the ozonation. The COD data were then compared with the COD values of a 3,4 DCB/water solution and a methanol/water solution with an initial concentration of 20 mg/l (Table 2).

The COD of the methanol/water solution was much higher than that of the 3,4 DCB/water solution (Table 2). Consequently, the high value of COD in the 3,4 DCB solution using methanol could be due to the presence of methanol in the solution. This may be supported by the fact that little changes were observed in the COD values after completing ozonation (10 min) during which 3,4 DCB concentration was reduced by 95% (Fig. 3). Despite the fact that COD has been used as the key parameter in the study of the ozone oxidation rate of organic pollutants in aqueous solutions (Preis *et al.*, 1988), this was not applicable due to the inaccuracy of the COD measurements.

The influence of pH on the oxidation rate of 3,4 DCB was determined by oxidising alkaline and acidic 3,4 DCB solutions. Prior to ozonation, the pH values of the solutions were adjusted to 3–4 using HCl and 9–10 using NaOH, respectively. A comparison between the ozonation time required for these solutions is shown in Fig. 4.

In the acidic and neutral solutions, 3,4 DCB was oxidised completely after four minutes ozonation whereas in the alkaline solution, the relative residual concentration of 3,4 DCB was as high as 39% after 15 min ozonation. The final pH-values of all the solutions remained the same as the start values. The residual ozone was measured in the alkaline and neutral solutions. As expected, there was no residual ozone detected in the alkaline solution whereas the residual ozone was 1.29 mg/l in the neutral solution after 4 min ozonation.

An increase in pH of the solution resulted in a significant increase in the reaction time required to complete oxidation of 3,4 DCB. This suggests that

Table 2. The COD of the samples taken from 3,4 DCB solutions made up with and without methanol

Ozonation Min	3,4 DCB solution using methanol (120 mg/l) COD ± SD (mg/l)	3,4 DCB/water solution (20 mg/l) COD ± SD (mg/l)	Methanol/water solution (20 mg/l) COD ± SD (mg/l)
0	5083 ± 34	183 ± 18	4040 ± 259
10	4893 ± 31		
15	4895 ± 5		
20	4840 ± 10		

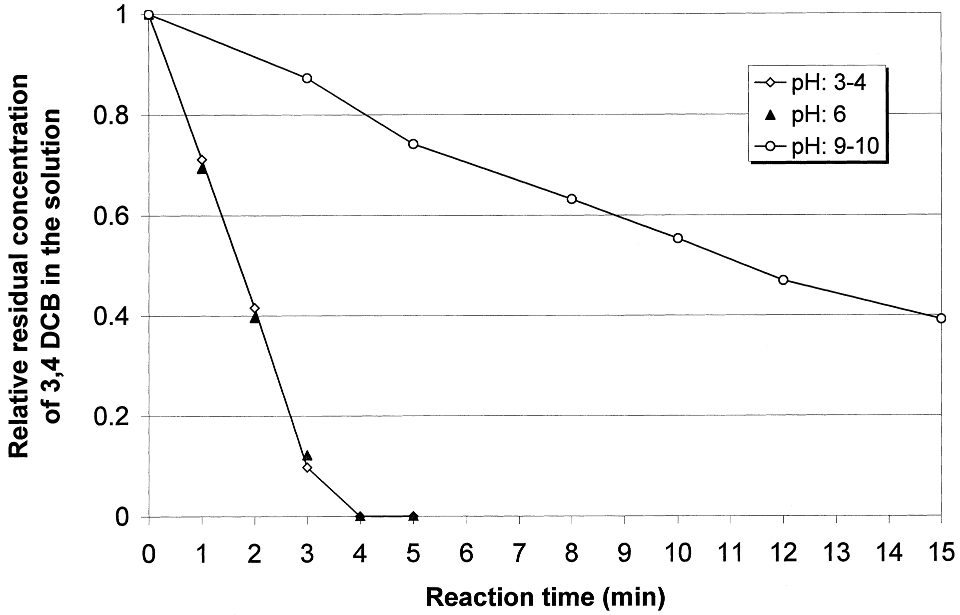

Fig. 4. The influence of pH on the oxidation rate of 3,4 DCB in the solutions with initial concentration of 20 mg/l.

the 3,4 DCB oxidation by ozone molecules is much faster than the 3,4 DCB oxidation by hydroxyl radicals formed in the alkaline solution. It is assumed that the reaction between the hydroxyl radicals and the methanol present in the solution took place at a faster rate. Changes in the COD values of the solution before and after ozonation could have supported this assumption.

Except for the samples taken from the alkaline 3,4 DCB solutions, two main peaks were always recognised in the GC analysed samples. These included one with a retention time of 0.8 min (eluting before 3,4 DCB) and one with retention time of 2.2 min (eluting just before the internal standard). In order to identify the intermediates formed due to ozonation, samples taken prior and following ozo-

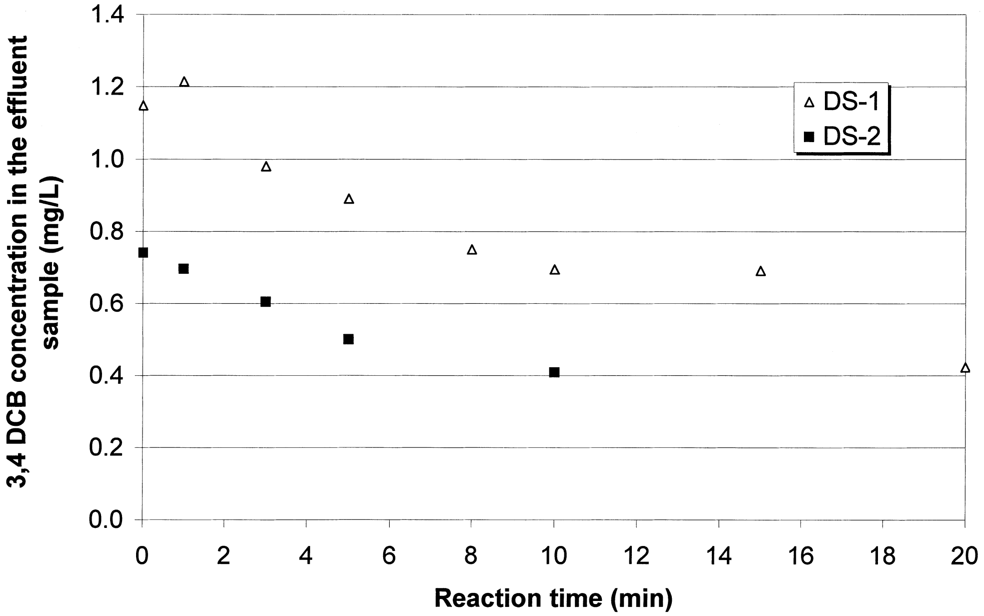

Fig. 5. The reduction in the 3,4 DCB concentration in the effluent samples DS-1 and DS-2 as a function of ozonation time.

nation were extracted using hexane, ether and 2,2,4-trimethylpentane. The extracts were analysed on a GC-MS using a flame ionisation detector. Unfortunately, none of these attempts gave satisfying results, as the peaks of the solvents in all the cases were more dominant than the actual intermediates. Purge and trap method was used in analysing water samples withdrawn from a 3,4 DCB solution with initial concentration of 20 mg/l prior and following ozonation. A comparison between the spectra of the intermediates and known organic compounds suggested formation of 2,3-dichlorobutane due to ozonation. Formation of a chlorinated alkane suggests that ozonation is more reactive towards the C—C double bond than the C—Cl bonds in 3,4 DCB. Using advanced oxidation processes or catalytic ozonation could more likely provide stronger oxidants for oxidising C—Cl bonds.

Effluent samples

Preliminary ozone oxidation experiments were carried out on two samples; DS-1 and DS-2 taken from the effluent generated by a synthetic rubber plant. Unfortunately, the production plant was shut down shortly after we obtained the preliminary results and therefore it was impossible to carry out further studies on the effluent. Since the pH and composition of the effluent generated by the plant varied greatly with time, the composition and pH of the effluent samples were different from those of the model solutions. The effluent samples were alkaline with a pH of 13 and contained low concentrations of derivatives of dichlorobutene, chloroprene (CD) and traces of other chlorinated organic compounds.

Table 3. The COD of the effluent samples prior and following ozonation

Sample	Time after starting ozonation (min)	COD ± SD
DS-1	1	1377 ± 110
	20	759 ± 65.5
DS-2	1	1394 ± 38
	15	1154 ± 19

Prior to ozonation, the effluent samples were filtered in order to remove the suspended solids. The CD concentration was reduced by 40–45% in the filtered samples. The 3,4 DCB concentration was reduced by 40% in the filtered DS-1 sample but it could not be determined for DS-2 due to an error in the analytical results. The reduction in the concentrations of 3,4 DCB and CD was probably due to both filtration and evaporation.

The filtered DS-1 and DS-2 samples were ozonated at a flow rate of 0.18 m^3/h and an ozone concentration of 2 wt% for 20 and 10 min, respectively. The ozone oxidation was carried out at the lowest ozone concentration due to the low concentration of 3,4 DCB in the samples. The reductions in the 3,4 DCB and CD concentrations are shown in Figs 5 and 6.

A 20 min ozonation of the DS-1 sample reduced the concentrations of 3,4 DCB and CD by 70 and 63%, respectively. In the DS-2 sample these reductions were 49 and 45% over 10 min ozonation, respectively. The higher reductions in DS-1 could be due to the longer ozonation time. Unfortunately,

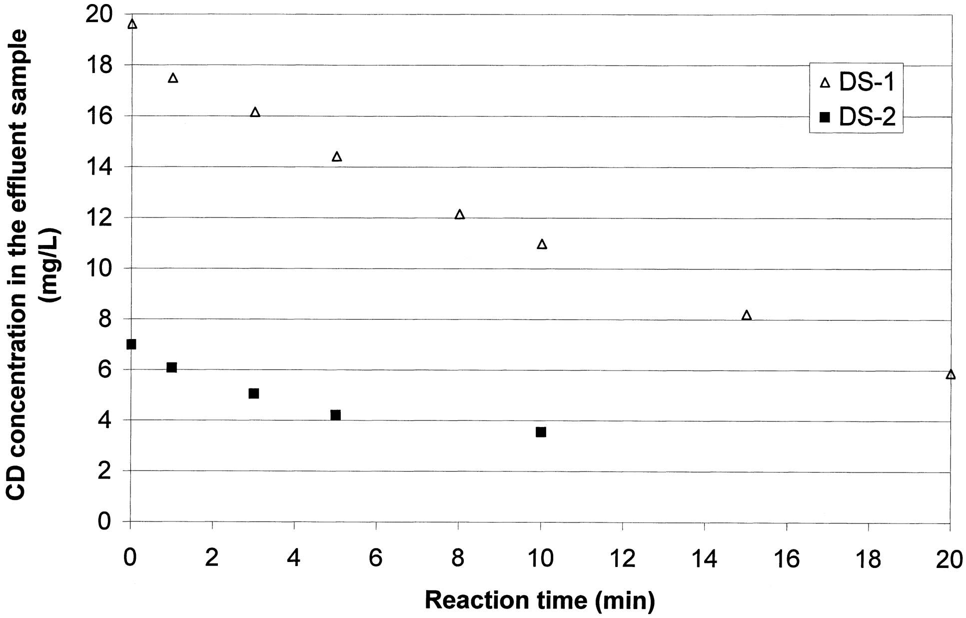

Fig. 6. The reduction in the CD concentration of the effluent samples DS-1 and DS-2 as a function of ozonation time.

the reduction of the chlorinated hydrocarbons as a result of evaporation could not be determined due to the limited volumes of samples.

The final pH values of both effluent samples did not change due to ozonation. The COD was measured in both effluent samples before and after ozonation (Table 3).

Ozonation reduced the COD of the DS-1 and DS-2 samples by 45 and 17%, respectively. The accuracy of the COD data is, however, not certain as mixing the effluent samples with the COD reagent resulted in precipitation in the samples.

CONCLUSIONS

- Ozone oxidation degraded 3,4 DCB. The ozonation time required to oxidise 3,4 DCB was longer for the solutions with higher initial concentration of 3,4 DCB.
- The reaction between ozone and 3,4 DCB was a zero order reaction with a reaction rate constant of 4×10^{-7} M/s with respect to 3,4 DCB in solutions with low initial 3,4 DCB concentrations (4 and 6 mg/l). On the other hand, a zero order reaction was not observed for the 3,4 DCB solutions with higher initial concentrations from 20 to 120 mg/l.
- At low ozone concentration the oxidation rate of 3,4 DCB was completed after 6 min. Increasing the ozone production by 3-fold reduced the ozonation time by 50% for the same solution with an initial 3,4 DCB concentration of 20 mg/l.
- The presence of methanol in the 3,4 DCB solutions did not affect the ozone oxidation rate. Ozonation of a 3,4 DCB/ methanol solution with an initial 3,4 DCB concentration of 120 mg/l at an ozone concentration of 4.8 wt% over 10 min reduced 95% of the 3,4 DCB but only 4% of the COD in the solution.
- 3,4 DCB was oxidised completely at neutral and acidic pH after only 4 min ozonation. In the alkaline solution, 39% of 3,4 DCB was still in the solution in spite of 15 min ozonation. Evidently, the oxidation took place following a direct reaction with ozone molecules in the neutral and acidic solutions rather than hydroxyl radicals present in the alkaline solution.
- Preliminary ozone oxidation experiments showed reduction in the 3,4 DCB and CD concentrations in the effluent samples but did not remove them completely.

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