Combination of advanced oxidation processes and gas absorption for the treatment of chlorinated solvents in waste gases

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Abstract Treatment of chlorinated organic compounds in waste gases is difficult because of several reasons: these compounds are dioxin precursors when incinerated, and also biological treatment is difficult because of a limited number of suitable microbial degradation pathways. On the other hand, since the 1990s, a new generation of chemical oxidation techniques has been introduced in water treatment. Advanced Oxidation Processes (AOPs) are based on a combination of UV/H2O2, UV/O3 or H2O2/O3. The combinations result in the generation of OH-radicals, which subsequently attack the organic pollutants. In this work, the treatment of a gas stream (240 L/h) loaded with 20–40 ppmv trichloroethylene (TCE) is presented. Therefore, a combination of an absorption process in a bubble column with a liquid H2O2/O3 initiated oxidation, was investigated. Removal efficiencies, depending on the dosed H2O2 and O3, up to 94% were found. The production of chloride ions was investigated: the Cl-atoms from the removed TCE could be found back as chloride ions. Next to the experimental work, attention was paid to the mechanisms taking place in the proposed concept. Here, a simulation model was developed, considering gas/liquid mass transfer of TCE and ozone, axial liquid dispersion, advective gas and liquid transport and about 29 chemical reaction steps. The modelling allowed a better understanding of the technique and gives insight in its possibilities and limitations. Finally, it can be concluded that the proposed technique shows interesting perspectives: it is able to transform chlorine in chlorinated solvents into chloride ions effectively at ambient temperature conditions.

Keywords Advanced Oxidation Processes (AOP); gas absorption; peroxone; trichloroethylene (TCE); volatile organic compounds (VOC); waste gas

Introduction

Next to efficient operation and the use of sustainable material and energy resources (Dewulf et al., 2000), one of the main aspects in developing a sustainable technosphere, is that the emissions of it may not damage the ecosphere. In this view low cost and efficient end of pipe technologies have been developed in order to reduce the impact of waste streams as much as possible, or at least to reduce them to levels below emission limits stated in environmental regulations. With respect to volatile and chlorinated organic compounds, several degradation technologies have been developed for waste gas treatment during the last two decades (Dvorak et al., 1996; Cloud, 1998; Keller and Dyer, 1998).

Roughly, three groups of methods can be distinguished. In recovery technologies, a unit operation is introduced in order to recover the compounds, e.g. condensation, carbon adsorption, pressure-swing and temperature-swing adsorption, and membrane separation. Next, oxidation technologies are employed; they convert the environmentally harmful compounds into carbon dioxide, water and chloride. Mentioned operations in this field are thermal oxidation, flameless thermal oxidation, catalytic oxidation and microbial degradation (biofilters, biotrickling filters). Finally, disposal techniques can be used, e.g. granulated activated carbon (GAC) filters.

All of these techniques operate in a competitive way in a limited field of application. Of course, recovery techniques are the most favourable from an environmental point of view,
but in a number of applications, they are economically unsuitable. Disposal techniques are less favourable from the environmental point of view because the compounds are not degraded by the disposal operation. The operations in the oxidation option, all have some technological limitations, e.g. thermal oxidation can give rise to dioxins, catalytic oxidation can be hindered by chlorine gas, whereas biological treatment of chlorinated compounds often needs both anaerobic and aerobic pathways.

The limitations of each technique have resulted in a continuous search for new abatement techniques of gaseous pollutants. Techniques getting attention nowadays are electric discharge-based oxidation (Paur et al., 1995; Vitale et al., 1996; Kogelschatz, 1997) and photocatalytic oxidation (Nimlos et al., 1993; Luo and Ollis, 1996; Rajeshwar, 1996; Wang and Hsieh, 1998; Hager and Bauer, 1999).

Next to these more recently introduced degradation techniques, potential for developing new waste gas treatment techniques may be found in recent oxidation technologies for water treatment. In this field, Advanced Oxidation Processes (AOPs) have shown great potential as oxidation technologies for organics at ambient temperature (Glaze et al., 1992; Masten and Hoigné, 1992; Legrini et al., 1993; von Sonntag et al., 1993; Glaze, 1994; Beltran et al., 1995, 1996; Peyton et al., 1995; Hirvonen et al., 1996; Kuo and Chen, 1996; Prousek, 1996; von Sonntag, 1996; Weir et al., 1996; Gulyas, 1997; Luck et al., 1997; Mansilla et al., 1997; Masten et al., 1996, 1997; Ormad et al., 1997; Pedit et al., 1997; Sapach and Viraraghavan, 1997; Hoigné, 1998; Oppenländer, 1998). The AOPs rely on a two step process. First, hydroxyl radicals in the aqueous phase are generated by a combination of $\text{O}_3/\text{H}_2\text{O}_2$ (peroxone process), $\text{O}_3/\text{UV}$ or $\text{H}_2\text{O}_2/\text{UV}$. Secondly, the radicals react in a fast way with all compounds which can be oxidised.

In this work the use of the peroxone process in combination with gas absorption was evaluated in order to investigate the potential of AOPs in waste gas treatment. Therefore, a simple bubble column was used for the treatment of trichloroethylene (TCE) as a model compound. Modelling including reaction and mass transfer kinetics, was established in order to enhance the insight in the potential of the AOP technique for waste gas treatment.

**Methods**

**Reactor set-up and experiments**

A reactor was built as presented in Figure 1. A Plexiglas column (length 1 m, I.D. 0.193 m, wall thickness 3 mm) was mounted on a PVC bottom covered with a membrane foil (Trevi, J. Dewulf et al. 174

**Figure 1** Experimental set-up: (1) $\text{N}_2$ inlet at 1.8 bar (absolute pressure); (2) $\text{O}_2$ inlet at 1.3 bar (absolute pressure); (3) thermostatic water bath at 25°C; (4) bubble flask with pure TCE; (5) mass flow controller; (6) sampling point for measurement of ingoing TCE; (7) gas valve; (8) perforated foil; (9) teflon foil; (10) combined liquid and gas outlet; (11) aqueous output sample collection; (12) $\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NaOH}$ delivery; (13) pump; (14) sampling point for measurement of outgoing TCE; (15) reactor column; (16) rotameter; (17) mixing chamber; (18) ozone generator

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Ghent, Belgium). Input gases were supplied through the perforated foil, input liquids just above this foil. The top of the column was sealed with Teflon foil. At the top aqueous and gaseous output samples were collected. A nitrogen gas stream, maintained at 3 ml min\(^{-1}\) by means of a mass flow controller (Brooks model 5850), was delivered to the reactor at 0.8 bar, after supply with TCE. TCE was dosed by means of a bubble flask kept at 25.0 ± 0.1ºC. Next, an oxygen stream (0.3 bar) was delivered at 240 L h\(^{-1}\) after ozonation through an ozone generator (nominal capacity 1.2 g h\(^{-1}\), Litha, Germany). The gas flow rate was controlled by means of a rotameter (Bailey Fisher Porter, Germany). The ozonation resulted in an ozone concentration of 0.5 to 6% (w/w) in the gas stream entering the reactor. Demineralized water with hydrogen peroxide was supplied to the reactor at a flow rate of 2 L h\(^{-1}\) (Chemap AG-Ismatec pump). Before each experiment, the reactor column was filled up with this same solution. Solutions were prepared with demineralised water and a 30% \(\text{H}_2\text{O}_2\) in water solution, obtained from Fluka. For alkaline solutions, sodium hydroxide was dosed. Oxidation experiments were carried out during a 2 hour period.

Measurement techniques
Ozone in inlet and outlet gas streams was measured by a iodometric standard method (Standard Methods for the Examination of Water and Wastewater, 1981). TCE in ingoing and outgoing gas streams was determined by gas chromatography. Samples taken by a Pressure Lok 1.0 ml gas syringe were injected into a Varian 3700 gas chromatograph, equipped with a capillary column (Chrompack CP-SIL 5, 100% poly dimethyl siloxane, 30 m, 0.53 mm, film thickness 5 \(\mu\) m or a J&W DB-5, 5% poly fenyl/95% polyethyl siloxane, 30 m, 0.53 mm, 1.5 \(\mu\) m) and a FID detector. Gases supplied to the chromatograph were helium as carrier gas (6.4 mL min\(^{-1}\)), and air (244 mL min\(^{-1}\)) and hydrogen (35 mL min\(^{-1}\)), feeding the detector. Calibration of the GC was done by taking headspace of a closed equilibrated air/water system (Dewulf et al., 1996). Analyses were performed isothermally at 80ºC, integration was done by HP 3388A or Nelson integration systems. Before starting the oxidation experiments initiated by \(\text{H}_2\text{O}_2\) and ozone, TCE was fed to the reactor in the same conditions as in the subsequent experiment, but without supply of \(\text{H}_2\text{O}_2\) and \(\text{O}_3\). It was found in this blank experiment that TCE concentration leaving the reactor reached the input concentration level (95.1 ± 9.0%, \(n=3\)).

Aqueous hydrogen peroxide concentrations in the mM range were determined by a iodometric titration, catalysed by ammonium molybdate (Fritz and Hammond, 1957). In the \(\mu\)M range, concentrations were determined by a spectrophotometric method based on DMP (2,9-dimethyl-1,10-fenantroline) and Cu(II) (Kosaka et al., 1998). Chloride concentrations were measured by ion chromatography with electroconductivity detection. Gas and liquid flow rates were 240 and 2 L/hr\(^{-1}\), respectively. Measurement of pH values were done by a Jenway 3310 electrode.

Results and discussion
Experimental results
Four degradation experiments were conducted under different conditions. The experimental conditions are presented in Table 1. The obtained removal efficiency is given in Table 2. It can be seen that the removal efficiency increases from 48.7 to 50.3% in experiments 1 and 2, over 63.2% in Experiment 3 and up to 93.8% in Experiment 4.

In experiment 1 and 2, high concentrations of \(\text{H}_2\text{O}_2\) (8.5 to 9.0 mM) were applied, resulting in lower TCE removal efficiencies. This can be explained by the reaction kinetics of the \(\text{HO}_2^-\) ion with OH-radicals \((k=7.5 \times 10^8 \text{ M}^{-1} \text{s}^{-1})\), resulting in a competition with TCE \((k=4.0 \times 10^9 \text{ M}^{-1} \text{s}^{-1})\). The effect of change in pH in the incoming liquid on the removal rate at high pH values is limited. In Experiments 3 and 4, the \(\text{H}_2\text{O}_2/\text{O}_3\) ratio was near to the...
ratio of the overall peroxone reaction. It can be seen that the removal efficiency significantly increases. Here the effect of pH becomes important: the initial step of the process, i.e. the reaction of HO₂⁻ with ozone, is favoured. It has to be mentioned that for Experiment 4 the load of TCE was also lower than in the other experiments.

The hydrogen peroxide at the exit was increased up to 355 ± 9 M. This can be explained by the domination of the production reactions (Pedit et al., 1997) over the hydrogen peroxide consumption reactions:

\[ \text{HO}_2^+ + \text{HO}_2^+ \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \]  

\[ \text{H}_2\text{O} + \text{HO}_2^+ + \text{O}_2^\cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^- \]  

Based on the measurements of chloride ions at the outlet liquid, a chloride production rate of 33 mg h⁻¹ was calculated for Experiment 3. This is in the same order of magnitude as the amount of Cl⁻-atom removal rate due to TCE breakdown (24 mg h⁻¹), indicating that TCE is oxidised to carbon dioxide and chloride, and explaining partially the pH drop. The observed chloride production rate in Experiment 4, 19 mg h⁻¹, matched the amount of chlorine from TCE removal. Also during this experiment, a drop in pH down to 7.1 at the end of the experiment was observed.

Modelling

In the modelling, the following physical chemical processes have to be considered: gas/liquid exchange, aqueous phase reaction kinetics and advective and dispersive transport in both the liquid and gas phase. Acid dissociation equilibria to be considered are those of H₂O, HO₂⁻ (pKₐ = 4.8), H₂O₂ (pKₐ = 11.7), H₂CO₃ (pKₐ = 6.3) and HCO₃⁻ (pKₐ = 10.3) (Pedit et al., 1997). The global change of the liquid phase concentration of a species \( i \) in a layer \( j \) (\( c_i(j) \) in the reactor becomes:

\[
V_w \frac{d c_{w,i}(j)}{dt} = V_w \sum_{m=1}^n k_{i,m} c_{w,i}(j) + Q_w \left[ \frac{c_{w,i}(j) + c_{w,i}(j-1)}{2} \right] \left[ \frac{c_{w,i}(j+1) + c_{w,i}(j)}{2} \right] \\
+ K_{f,a} (c_{w,i} - c_{w,i}) A_d \left[ \frac{c_{w,i}(j+1) - c_{w,i}(j) - 1}{2} \right] A D \left[ \frac{c_{w,i}(j) + c_{w,i}(j-1)}{2} \right] A
\]  

### Table 1

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Ozone in</th>
<th>Ozone out</th>
<th>H₂O₂ in</th>
<th>H₂O₂ out</th>
<th>pH in</th>
<th>pH out</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>0.46 ± 0.06</td>
<td>0.06 ± 0.03</td>
<td>8.97</td>
<td>8.1 ± 0.8</td>
<td>7.1</td>
<td>6.5 ± 0.3</td>
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<td>2</td>
<td>0.53 ± 0.07</td>
<td>0.11 ± 0.01</td>
<td>8.53</td>
<td>8.7 ± 0.5</td>
<td>8.7</td>
<td>7.4 ± 1.2</td>
</tr>
<tr>
<td>3</td>
<td>0.85 ± 0.12</td>
<td>0.46 ± 0.07</td>
<td>0.326</td>
<td>0.388 ± 9</td>
<td>5.5</td>
<td>3.4 ± 0.1</td>
</tr>
<tr>
<td>4</td>
<td>0.87 ± 0.03</td>
<td>0.18 ± 0.02</td>
<td>0.385</td>
<td>0.300 &lt;0.010</td>
<td>10.0</td>
<td>7.4 ± 0.7</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Input C (ppmv)</th>
<th>Input sd</th>
<th>Input n</th>
<th>Output C (ppmv)</th>
<th>Output sd</th>
<th>Output n</th>
<th>Removal Efficiency R (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>33.9</td>
<td>1.0</td>
<td>5</td>
<td>17.4</td>
<td>0.5</td>
<td>7</td>
<td>48.7</td>
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<td>2</td>
<td>39.8</td>
<td>4.6</td>
<td>6</td>
<td>19.8</td>
<td>0.6</td>
<td>4</td>
<td>50.3</td>
</tr>
<tr>
<td>3</td>
<td>38.0</td>
<td>5.5</td>
<td>9</td>
<td>14.0</td>
<td>1.2</td>
<td>8</td>
<td>63.2</td>
</tr>
<tr>
<td>4</td>
<td>19.2</td>
<td>3.1</td>
<td>10</td>
<td>1.2</td>
<td>0.7</td>
<td>9</td>
<td>93.8</td>
</tr>
</tbody>
</table>

J. Dewulf et al.
In this equation $k_{i,m}$ represents the reaction of species $i$ with species $m$, $n$ is the number of species, $Q_w$ the liquid flow rate (m$^3\cdot$s$^{-1}$) and $D$ the axial diffusion coefficient (m$^2\cdot$s$^{-1}$). $A$, $V_w$ and $d$ are the cross section, volume and thickness of the considered layer, respectively. The right hand terms represent the reaction kinetics, the advective flow, the gas to liquid mass transfer and the axial dispersion, respectively. The equation has to be applied for the species ozone, TCE, $H_2O_2$, $H_2CO_3$, $O_3^-$, $HO_2^-$, $HO_3^-$, $OH^-$, $CO_3^{2-}$ and Na$^+$ (if NaOH was added).

For the gas phase, the mass balance for ozone and TCE over a layer $j$ takes into account advective transport and gas/liquid exchange:

$$
V_g \frac{d C_{g,i}(j)}{dt} = Q_g \left[ C_{g,i}(j) + C_{g,i}(j-1) \right] - K_{L,a}(C_{w,i}^* - C_{w,i}) A d x
$$

with $C_{g,i}(j)$ the concentration in gas phase of compound $i$ in layer $j$; $V_g$ and $Q_g$ are the volume and flow rate of gas. The volume of gas and liquid are calculated on the measurement of the gas fraction, being 0.0142.

The equations were modelled in a Fortran programme, based on a fourth order Runge Kutta approach. Involved reaction kinetics were those as presented by Pedit et al. (1997), whereas axial diffusion and mass transfer coefficients were based on data from Deckwer and Schumpe (1993). At hydrogen peroxide concentrations of 8.9 mM and pH=7, a simulated TCE removal efficiency of 87.7% was obtained, whereas experimentally a removal efficiency of 48.7 ± 2.2% was observed (Dewulf et al., 1999). This overestimation can be due to the fact that the reaction scheme does not take into account the further degradation of intermediates, which also requires oxidants as OH radicals. Therefore, next to the reactions at the beginning of the oxidation pathway as described by Pedit et al. (1997), a more elaborated reaction scheme was proposed. In this scheme, reactions involved were: (1) reactions analogous to the oxidation of tetrachloroethylene with OH radicals as presented by Von Sonntag and Schuchmann (1997), leading to $Cl_2C(OO^2-)CH=O$; (2) oxidation of $Cl_2C(OO^2-)CH=O$ by OH-radicals as observed in atmospheric chemistry resulting in formic acid (Tuazon et al., 1988); (3) oxidation of formic acid by OH-radicals into carbon dioxide, water and peroxide (McElroy and Waygood, 1991). The implementation of this more detailed reaction scheme resulted in higher simulation capacity requirements. Despite this hindrance, it was found that the extended reaction scheme now showed a removal efficiency of 69%, which is closer to the observed removal efficiency, although it still shows an overestimation of 20%. From the simulation, it was concluded that new simulation approaches based on implicit integration methods instead of explicit methods will allow a faster simulation, providing a better understanding of the combination of gas absorption and the peroxone process.

Conclusions

The experiments presented here show that gas absorption combined with aqueous phase AOP reactions has potential to degrade volatile chlorinated compounds. In Experiment 4, the removal efficiency by this mechanism was 93.8%. The oxidation is carried out at ambient temperature, giving a number of advantages compared to high temperature oxidation technologies, e.g. lower power needs, no need of expensive catalysts. Moreover, undesired by-products formed at higher temperatures, e.g. dioxins, may be avoided. The chemicals used in this oxidation process are usually easily available products.

To our knowledge, this is one of the first reports investigating the combination of gas absorption with AOP in waste gas treatment. Sjöberg et al. (1997) concluded from a similar
type of experiment, with toluene as model the compound, that this AOP technique combined with biological processes is not to be expected to improve removal efficiencies when compared to biological processes. On the other hand, Lawson and Adams (1999) recently reported a similar process with a scrubber unit. They observed enhanced scrubbing efficiency of volatile organic compounds due to the implementation of the peroxone process, when compared to simple gas absorption.

This paper gives rise to a series of new possibilities. First, other model compounds can be investigated. Further, insight in the reaction kinetics of degradation products can enhance the predictive modelling. Finally, economic considerations can give incentives to improve the feasibility in full scale operations. In this view, more efficient H₂O₂ and ozone dosages, efficient ozone production, and implementation of reactors with lower pressure drops, e.g. shorter bubble columns or packed absorption towers, may be investigated.

References


