

Continuous extraction and destruction of chloro-organics in wastewater using ozone-loaded Volasil™245 solvent

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Abstract

Extracting waterborne contaminants to ozone-loaded Volasil™245 (a siloxane solvent in which ozone is ten times more soluble than water) has been studied as a means of enhancing reaction kinetics and thus, providing more rapid wastewater decontamination. Investigation was carried out with respect to 2-chlorophenol and dichloromethane. Using a pilot scale continuous flow liquid–liquid/ozone water treatment system, 2-chlorophenol was extracted to the ozone-loaded solvent phase and considerable extents of destruction were achieved. However, the approach was demonstrated to yield slightly less destruction than direct gas contact for the same utilization of ozone and enhanced reaction kinetics were not shown to occur. This was suggested to be due to increased interfacial mass transfer resistance and/or the promotion of less destructive reaction pathways. Modification of the existing pilot system, by conversion from co- to counter-current solvent-loading, enabled greater dissolved ozone concentrations to be achieved within the solvent. Increasing the counter-current exchange column height to ~2.5 m was suggested for achieving a near optimum level of performance. The liquid–liquid/ozone approach was demonstrated to be an effective means of indirectly exposing wastewater contaminants to concentrated ozone. As such the technology may be applicable as an alternative to direct gas contact in instances where the avoidance of contaminant sparging is desired (i.e. where contaminants are highly volatile, pungent and/or toxic) or foaming occurs.

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1. Introduction

Ozone-based technologies have proved themselves very useful in meeting the challenge of improved industrial wastewater quality. Ozone is a powerful oxidising agent with a wide range of applications. These include the treatment of waters containing organic contaminants [1], predominantly for

- (i) the transformation of toxic or biocidal micro-pollutants (e.g. aromatic, chloro-aromatics and specifically, pesticides);
- (ii) the partial oxidation of biologically refractory compounds (mostly applied as a pre-treatment to biodegradation);
- (iii) the removal of colour.

In order for ozone to oxidise a wastewater contaminant, the respective substances must be mutually exposed. Conventional treatment systems dissolve ozone directly into wastewater using gas–liquid contacting devices (e.g. bubbling columns, jet ejectors, etc.). However, this approach incorporates two potentially serious limitations that may severely retard the oxidation process. Firstly, current ozone generating technology is incapable of producing gas concentrations of more than several percent (even when supplied with pure oxygen) and secondly, the solubility of ozone in water is relatively poor (~0.2 mg/L per mg/L in contacting gas phase at 20 °C [2]). These factors combine to ensure wastewater contaminants encounter relatively low ozone concentrations in solution and thus, may undergo slow rates of breakdown as a consequence.

It is proposed that oxidation kinetics may be improved by exposing contaminants to higher concentrations of ozone. The feasibility of using ozone-loaded solvents as a means of

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Nomenclature

C_g	concentration of ozone in gas phase (mg/L)
$C_{g\text{ in}}$	concentration of ozone in gas phase at inlet (mg/L)
$C_{g\text{ out}}$	concentration of ozone in gas phase at outlet (mg/L)
C_s	concentration of ozone in solvent phase (mg/L)
$C_{s\text{ in}}$	concentration of ozone in solvent phase at inlet (mg/L)
$C_{s\text{ out}}$	concentration of ozone in solvent phase at outlet (mg/L)
C_s^*	concentration of ozone in solvent phase at equilibrium with C_g (mg/L)
H	Henry constant (mg/L per mg/L)
H_{os}	height of each transfer unit (m)
N_{os}	number of transfer units
Z	height of packing (m)

achieving this has been investigated at bench scale [3–11]. The general process involves contacting contaminated water with an immiscible solvent containing a high concentration of dissolved ozone. Prior saturation, or loading, of the solvent is achieved by contact with ozone gas (in oxygen or air mixture). The loaded solvent is then contacted with the water phase in order to promote mass transfer of contaminants and/or ozone. The site of the reaction may depend upon the solvent/water distribution coefficient of the contaminants involved. Contaminants extracted into the solvent phase will encounter an oxidant-enriched environment and hence, have the potential to undergo more rapid degradation. Compounds resisting extraction may also be subject to accelerated oxidation, as ozone in the water is rapidly replenished from an elevated concentration within the solvent (i.e. enhanced ozone mass transfer). Following adequate contact time, the two immiscible phases can be separated by gravity and the solvent reloaded for re-use. The technique may be termed liquid–liquid/ozone water treatment.

The process has been suggested to improve the efficiency of ozonation by selectively extracting and oxidising target pollutants [6]. In conventional gas contact systems, the presence of free radical scavengers, such as carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) in the water phase, can further retard the oxidation of target compounds by the wasteful consumption of oxidant in preferential reactions. The selective extraction of contaminants to an ozone-plentiful, scavenger-free, phase may avoid this problem.

Another potential advantage of liquid–liquid/ozone treatment may lie in its ability to deliver ozone indirectly. The conventional approach of bubbling ozone gas through a wastewater (i.e. the direct contact method) may be problematic where contaminants possess high volatility (e.g. dichloromethane) as this could potentially result in sparging (i.e. the transfer and consequent escape of compounds to the exiting gas phase).

It may also be desirable to avoid sparging in cases where contaminants are particularly toxic and/or pungent. Indirect ozone contact methods have been reported [1]. However, these operate by mixing contaminated wastewater with prior ozone-loaded water. As discussed, achievable concentrations of ozone in water are relatively poor and hence, contact with a highly loaded solvent phase may prove a more effective means of indirect ozone delivery.

In selecting an appropriate solvent, ozone solubility is amongst the most important criteria. This must be significantly greater within the solvent than in water and thus, allow the achievement of a much higher dissolved concentration when exposed to ozone gas of a given partial pressure. Very low solubility of the solvent in water and non-toxicity are also needed. Previous work in this field has involved the fluorocarbon solvents FC40 and FC77 (3M Co.) [3–8]. However, more recent research has identified the heat exchange fluid VolasilTM245 (decamethylcyclopentasiloxane) (VWR International, UK) as a potential liquid–liquid/ozone solvent with distinct advantages over fluorocarbons [9]. Ward et al. [9] determined the solubility of ozone in VolasilTM245 to be 10 times greater than that found in water and hence, results in 10 times the dissolved concentration when exposed to ozone gas of a given partial pressure.

VolasilTM245 is considered additionally suitable as it possesses a low toxicity (LD_{50} oral rats = 2 g/kg), low water solubility (17 $\mu\text{g/L}$) and can hold in solution a wide variety of organic compounds. Furthermore, by exposing the substance to ozone for 100 h without noticeable detriment, Ward et al. [11] demonstrated VolasilTM245 to be resistant to ozone attack. Some general physical properties are given in Table 1.

The present cost of VolasilTM245 currently stands at approximately 7.5 €/L (VWR International, UK). However, as solvent is recovered and recycled through the liquid–liquid/ozone system, replacement costs may be minimised by careful handling of the material.

Further investigation by Ward et al. [12] has resulted in the development of a continuous flow VolasilTM245 liquid–liquid/ozone pilot rig and its demonstration with respect to various dye solutions. However, although dye destruction was effectively achieved within the system, it was concluded that the true potential of the process had not been

Table 1
General physical properties of VolasilTM245

Property	Quantity
Density (kg/m^3)	956 at 20 °C ^a
Viscosity (g/m s)	4.0 at 20 °C ^a
Molar mass (g/mol)	370 ^a
Flash point (°C)	72 ^a
Water solubility ($\mu\text{g/L}$)	17 at 20 °C ^a
Vapor pressure (mmHg)	<5.3 at 20 °C ^a
Interfacial tension with water (mN/m)	24 at 20 °C ^b
Henry's constant (Ozone) (bar/mole-fraction)	34 at 20 °C ^b

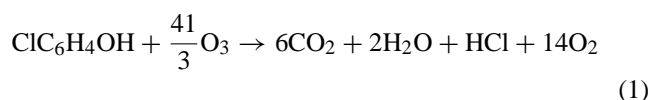
^a Manufacturer's product information (VWR International, UK).

^b Ward et al. [10].

fully explored due to: (a) the insolubility of the dyes within Volasil™245 (i.e. dyes were not extracted to the ozone rich phase) and (b) the less than adequate dissolved ozone concentrations achieved by the rig's co-current solvent loading system.

Whilst reporting on a series of bench scale liquid–liquid/ozone tests, Ward et al. [11] demonstrated 2-chlorophenol (2-CP) to possess a Volasil™245/water distribution coefficient of 4 (between pH 3 and 7). Along with similar compounds, 2-CP is considered a List 2 Dangerous Substance by the EC Dangerous Substances Directive (annual average freshwater limit = 50 µg/L) (76/464/EEC). The substance can be found in many industrial effluent streams, including those arising from pesticide manufacture. Thus, 2-CP was considered a good candidate with which to demonstrate the effectiveness of the Volasil™245 liquid–liquid/ozone pilot rig.

Eq. (1) gives the overall ozonation reaction that can be expected for 2-CP. As can be seen, 41/3 mol of ozone are suggested to totally destroy 1 mol of 2-CP:



The EC Water Framework Directive (2000/60/EC) includes dichloromethane (DCM) on a Priority List of dangerous substances that are considered to present a significant risk to or via aquatic environments. DCM is highly soluble in water (20 g/L at 20 °C [13]) and can be expected to occur in the effluent streams of users and manufacturers of paint, paint stripper and adhesives. As discussed, the compound is highly volatile (vapour pressure = 475 hPa at 20 °C) and therefore, may be prone to sparging from wastewater (rather than destruction) if subjected to direct ozone gas contact. Hence, a demonstration of indirect ozone contact using the liquid–liquid/ozone approach in relation to DCM was considered worthy of investigation. Eq. (2) shows the overall reaction assumed for the total destruction of DCM by ozone. If correct, then 2 mol of ozone are required to destroy 1 mol of DCM:



In order to promote a better understanding of Volasil™245 liquid–liquid/ozone water treatment, this paper will comment upon:

- the design, construct and optimisation of a new counter-current ozone-loading system;
- the effectiveness of counter-current ozone solvent-loading as compared to co-current;
- the effectiveness of liquid–liquid/ozone treatment with regards to the destruction of 2-CP in water and associated reductions in TOC and COD;
- the effectiveness of liquid–liquid/ozone water treatment as compared to direct (i.e. conventional) wastewater contact with gas phase ozone;

- the effectiveness of liquid–liquid/ozone treatment with regard to the destruction of DCM in water.

In addition, this paper also comments upon a series of bench-scale tests aimed at assessing the feasibility of the liquid–liquid/ozone approach with regard to waters contaminated with surfactant.

2. Liquid–liquid/ozone rig design and modification

A schematic diagram showing the continuous flow Volasil™245 liquid–liquid/ozone pilot rig developed by Ward et al. [12] is given in Fig. 1. This comprised four sections: (i) ozone generation; (ii) solvent-loading; (iii) solvent–water contact; (iv) off-gas cleaning.

2.1. Ozone generation section

Ozone gas was produced using a LAB2B Ozone Generator (Ozononia Triogen Ltd., UK) fed with dry oxygen from a pressurized cylinder. A flow meter, pressure gauge and valve was used to regulate/measure gas stream conditions before entry into the solvent-loading section. To determine the ozone gas concentration, a flow sample was diverted through an ultraviolet ozone analyzer (model BMT963, BMK Messtechnik, Germany).

2.2. Solvent-loading section

The purpose of this section was to achieve a dissolved concentration of ozone within the solvent. The system initially comprised 4 m × 1 m vertically mounted glass tubes connected by U-bends (QVF Process Systems Ltd., UK), the tube diameter being approximately 0.015 m throughout (i.e. DN15). Gas and solvent were passed through the system co-currently. For the promotion of contact, SMV static mixing elements (Sulzer (Chemtech) Ltd., UK) were mounted at the base of each tube carrying upward flow (to generate bubbles); tubes carrying downward flow were packed with 6 mm glass beads. At the section exit, gas and ozone-loaded solvent were disengaged by gravity in a gas/liquid separator. Spent gas was drawn off at the top of the separator (via a glass wool demister for the removal of solvent droplets), from where it passed into the off-gas cleaning section. Loaded-solvent was allowed to flow under head pressure from the base of the separator and directly into the solvent–water contact section.

2.3. Solvent–water contact section

This section contacted ozone-loaded solvent with contaminated water and allowed exchange and/or oxidation reactions to occur. The section consisted of 15 m × 1 m vertically mounted glass tubes (0.015 m diameter, DN15) connected with U-bends (QVF Process Systems Ltd., UK). Water and solvent flowed co-currently through the system. In order to

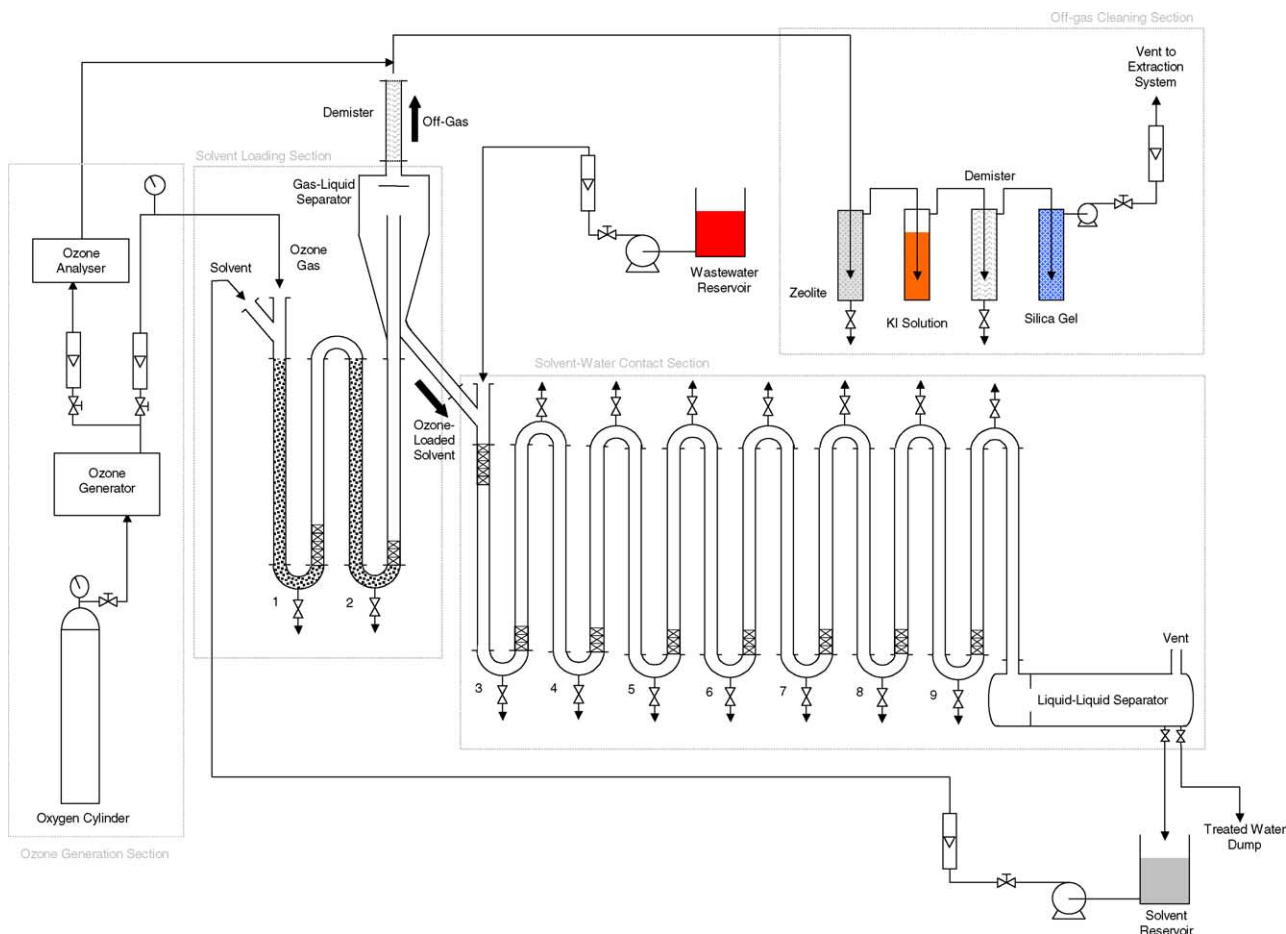


Fig. 1. Schematic diagram showing the liquid–liquid/ozone pilot rig with co-current ozone-loading arrangement.

encourage mixing of the two liquid phases, each alternate tube was fitted at the base with a SMV static mixing element (Sulzer (Chemtech) Ltd., UK). Passage of the liquids through the static mixers created and maintained a dispersion of solvent droplets. Lower U-bends were fitted with drain valves to allow the extraction of point samples. Valves fitted to the upper U-bends allowed the build-up of any gas to be vented if required. Solvent/water separation was achieved by means of a cylindrical gravity separation tank ($L=0.9$ m, $D=0.1$ m). The solvent, being the lighter phase, separated as a supernatant layer and was selectively drained off and recycled through the system. The water phase (i.e. the subnatant) was allowed to drain to a treated water holding tank for sampling and/or disposal.

2.4. Off-gas cleaning section

To facilitate destruction of any residual ozone in the exiting oxygen of the solvent-loading section (and ozone analyser), off-gas was channelled through a series of cleaning stages before being safely delivered to the laboratory air extraction system. Ozone destruction was achieved by passage through firstly, a bed of zeolite pellets (aluminium oxide, 3 mm sieve) and then a solution of potassium iodide

(KI) (Avocado Research Chemicals Ltd., UK). A demister of glass wool subsequently removed any entrained droplets of KI solution before the gas was dried by means of silica gel (to prevent moisture build-up in pump and flow meter). A diaphragm pump was used to draw the gas through the system under negative pressure and so minimise the possibility of ozone escape to the laboratory atmosphere. A TX2000 personal ozone monitor (Oldham s.a., France) was used to check that safe limits were not exceeded in the working area.

2.5. Modification of the solvent-loading section

In a series of experiments, Ward et al. [12] investigated the behaviour of the co-current solvent-loading system over a range of inlet conditions. Table 2 gives the test conditions and results of this investigation. Although designed to offer ease of construction and operation, the arrangement was concluded to be an inefficient means of solvent-loading. As can be seen from Fig. 2 [12], depending on the solvent-to-gas volumetric flow ratio, the co-current system either achieves poor ozone utilisation (i.e. minor fraction of available ozone mass dissolved in solvent—with the balance wasted) or poor ozone concentrations within the solvent. These limitations

Table 2
Solvent-loading conditions applied and achieved by Ward et al. [12] using a co-current system

Flow condition	Gas inlet flow (L/min)	Solvent inlet flow (L/min)	Gas/solvent volume flow ratio	Ozone-in-solvent (mg/L)		
				20 mg/L gas inlet	40 mg/L gas inlet	60 mg/L gas inlet
A	1.5	0.6	2.5	21	43	63
B	1.5	0.3	5	30	56	79
C	3.0	0.3	10	33	63	91

are symptomatic of a co-current system; dissolved equilibrium is achieved with the ozone depleted exit gas, rather than the ozone-rich inlet gas. Such a wasteful arrangement cannot be considered economically acceptable. A second co-current contact could be used to absorb more ozone, however, the engineering becomes more complicated. Only if the Henry constant was very much greater (requiring the use of another solvent) could a single co-current contact probably be made acceptable.

It was proposed that the rig be modified to incorporate a counter-current solvent-loading system. Such an arrangement should encourage dissolved equilibrium to be achieved with the ozone rich inlet gas and hence, result in greater loading concentrations and improved ozone utilisation. Earlier investigations by Ward et al. [10] showed that at equilibrium, the concentration of dissolved ozone acquired by Volasil™245 was approximately two times that of the contacting gas phase (using an absolute pressure of ~ 1.2 bar absolute pressure and a solvent temperature of ~ 25 °C). Hence, by employing a counter-current system (and operating conditions similar to Ward et al. [10]) dissolved concentrations of near double that of the inlet gas phase should potentially be achievable.

A schematic diagram of the developed counter-current loading system can be seen in Fig. 3. This was integrated into the overall liquid–liquid/ozone rig design (Fig. 1)

and replaced the co-current arrangement. It consisted of a ~ 1.7 m glass column (QVF Process Systems Ltd., UK) with an approximate internal diameter of 0.055 m (i.e. DN50 specification). Solvent was added near the top of the column and allowed to flow downwards under the influence of gravity. The column was permitted to flood to a height and head-pressure sufficient to drive loaded-solvent into the adjoining solvent/water contact section. Ozone gas was introduced near the base of the column (via a glass-sintered frit) and allowed to bubble upwards, against the solvent flow. After passage through the column, spent gas was drawn off via a glass-wool demister before entering the gas cleaning section. In order to encourage good contact between gas and solvent, the column was randomly packed to a depth of 1 m with glass tube sections (0.8 cm diameter, 2 cm length).

3. Experimental method

3.1. Solvent-loading tests

In order to compare co- and counter-current solvent-loading systems, the operating conditions applied by Ward et al. [12] in assessing the effectiveness of the co-current arrangement were applied to the new counter-current system

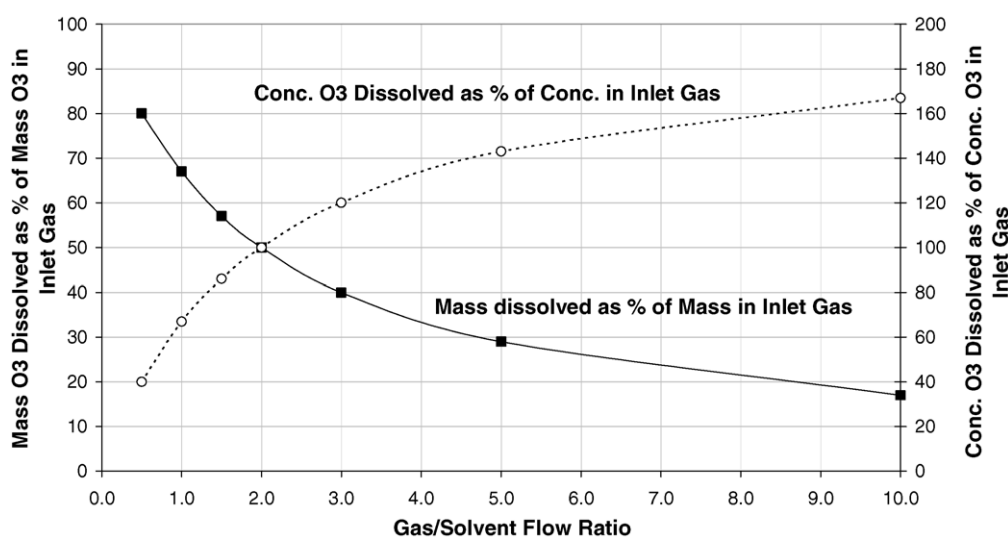


Fig. 2. Predicted variation in 'mass% dissolved' and 'dissolved concentration%' achieved' with gas/solvent volume flow ratio [12].

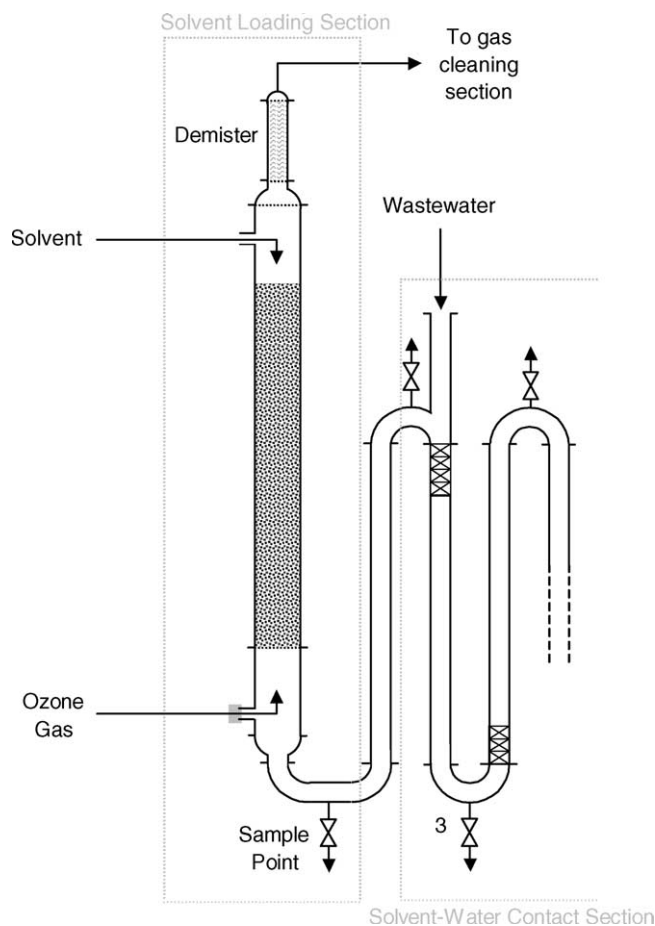


Fig. 3. Schematic diagram showing the modified counter-current ozone-loading system for the liquid–liquid/ozone pilot rig.

(see Table 2). In addition, inlet gas pressure and solvent temperature were likewise regulated to 1.2 ± 0.2 bar (absolute) and 25 ± 2 °C, respectively.

The concentration of ozone loaded into the solvent was determined as described by Ward et al. [12]. Solvent samples taken from the rig (sample point beneath column—see Fig. 3) were subjected to UV absorption analysis at 254 nm. Interpretation of absorption data in terms of dissolved ozone concentration was achieved with the assistance of a predetermined calibration curve.

Under each set of operating conditions, solvent samples were collected after 5 min intervals until three equal and consecutive results had been obtained. At this point steady-state ozone-loading was considered to have been achieved. In each case, approximately 15 min of stable inlet conditions were required in order to yield a steady-state ozone concentration at the solvent outlet.

To prevent dissolved ozone from being recycled through the rig system (and thus, falsely elevate loading concentration on subsequent passages), solvent entering the solvent/water contact section was depleted of ozone by contact/reaction with an excess amount of Drimarene Brilliant Red K-4BL dye (colour index no. 147)(Clariant UK Ltd.) in aqueous solution.

3.2. Quantitative 2-CP analysis

The following section describes the methods employed throughout this investigation for the quantitative analysis of 2-CP in both aqueous and Volasil™245 phases.

3.2.1. Analysis of 2-CP in the aqueous phase

Aqueous 2-CP concentration was determined using a Hewlett-Packard 5890 series II Gas Chromatograph and Quadrupole 5971 series Mass Selective Detector. Contaminant identification was achieved using a NIST/EPA/MSDC 49 K mass spectral database. Sample preparation was carried out as described by Ward et al. [11]. This basically involved extracting the 2-CP to toluene and spiking with an internal standard of phenol.

3.2.2. Analysis of 2-CP in the Volasil™245 phase

The determination of solvent 2-CP concentration was based on UV absorbance and carried out using a Hewlett-Packard 8451A Diode Array Spectrophotometer. Prior analysis of standard solutions containing 10, 25, 50, and 75 and 100 mg/L 2-CP (over the 190–400 nm range and using a 5 mm path length quartz cell) revealed the compound to produce a prominent and consistent UV absorption peak at 276 nm.

Plotting concentration (mg/L) against absorption at 276 nm was found to yield a linear relationship ($y = 58x$, $R^2 = 0.99$) and thus, showed 2-CP to obey the Beer–Lambert law (i.e. concentration is directly proportional to absorbance). Hence, solvent samples collected throughout this investigation were subjected to UV absorption analysis at 276 nm and the results interpreted as 2-CP concentration by means of the above described calibration curve.

It is conceivable that the products and intermediates of 2-CP ozonation (potentially organic acids) may also absorb UV light at 276 nm and thus, cause analytical interference. The determined 2-CP solvent concentrations should be considered as potential maximums, rather than absolute quantities.

3.3. 2-CP bench scale tests

Bench scale preliminary tests were carried out in order to gain a basic understanding of 2-CP behaviour in a liquid–liquid/ozone system and thus, allow the informed selection of pilot rig operating conditions. Specifically, such tests were devised to determine: (i) the destructive extent (i.e. 2-CP fraction destroyed) and (ii) the rate of destruction (i.e. 2-CP reaction kinetics with ozone). In addition, tests were also performed with the intent of gathering data by which the effectiveness of liquid–liquid/ozone contact could be directly compared to that of conventional liquid–gas/ozone contact.

Ward et al. [11] reported a similar bench-scale investigation to that described above. However, solvent phase 2-CP analysis was not carried out and therefore, such investigation was unable to reliably determine the extent of 2-CP destruction.

3.3.1. Liquid–liquid/ozone contact tests

Using an aqueous solution containing 2-CP (made up using distilled water), two sets of duplicate tests were performed in which molar contact ratios (moles ozone:moles 2-CP) of 4:1 and 6:1 were respectively applied. Each test involved contacting 200 mL of ozone-loaded Volasil™245 with an equal volume of aqueous 2-CP solution. Contact was carried out within a 250 mL separating funnel (max. capacity of 400 mL). Agitation of the two phases was achieved by means of a motorised impeller. Table 3 summarises the respective concentrations applied to each set of tests.

Ozone-loading of the solvent was carried out in a 250 mL Dreschel bottle supplied with ozone-enriched gas (0.4 L/min, 1.2 bar absolute pressure and $\sim 25^\circ\text{C}$). Ozone was produced using a BMT 803 generator (BMK Messtechnik, Germany) fed by pure oxygen. Gas exiting the Dreschel bottle was passed through an ultra-violet ozone analyzer (model BMT963, BMK Messtechnik, Germany). Dissolved ozone concentration in the solvent was determined by applying Henry's law ($H = 34$ bar/mole-fraction [10]).

Following initial contact, ~ 10 mL samples were drained from the reactor after intervals of 0.5, 1, 2, 5, 10, and 30 min. Each sample was collected in a 10 mL glass vial, prior

Table 3
GC–MS operating conditions used for 2-CP analysis of prepared sample

Gas chromatograph	
Injector port	
Oven temperature	250 °C
Carrier gas	
Gas	He
Flow rate	1 mL/min
Pressure	3 psi
Capillary column	
Type	30 m BPX5
Oven program	40 °C for 3 min 40–100 °C at 8 min ⁻¹ 100–300 °C at 25 min ⁻¹ Hold 2 min
Mass spectrometer	
Solvent delay	7 min
MS scan parameters	
Low mass	50 m/z
High mass	150 m/z

charged with ~ 20 μL sodium hydrogen sulphite solution (Na_2HSO_3 , 39%) (VWR International Ltd., UK). Na_2HSO_3 was added to destroy any residual ozone remaining in the sample and thus, halt the reaction at the moment of collection. Samples were then left to stand for 30 min to allow phase separation to occur. After this period, 2 mL sub-samples were taken from the solvent and aqueous phases and submitted for respective 2-CP analysis.

3.3.2. Direct ozone gas contact tests

Direct gas contact tests were carried out so as to provide data by which the effectiveness of liquid–liquid/ozone contact could be compared. Duplicate tests were conducted using a molar contact ratio of 4:1. In each test, ozone-in-oxygen was delivered to a 250 mL separating funnel containing an aqueous solution of 2-CP (100 mL at 100 mg/L). Gas was not bubbled through the liquid, but flooded (400 mL/min at 1.2 bar) into the reactor headspace above the aqueous solution (300 mL). The ultra-violet ozone analyzer was connected to the reactor outlet and was used to determine the headspace concentration. Upon reaching the desired gas concentration (49 mg/L), the reactor was sealed and vigorously shaken by hand for 30 min. During this time, 5 mL samples were drained from the reactor after 0.5, 1, 2, 5, 10, and 30 min. Samples were collected in a similar manner to as described in the above liquid–liquid/ozone tests. At the end of the test, 2 mL sub-samples were taken for 2-CP analysis.

3.4. 2-CP liquid–liquid/ozone rig tests

Tests involving operation of the continuous flow liquid–liquid/ozone pilot rig were carried out in duplicate using co-current and counter-current solvent-loading systems. In order to compare the effectiveness and efficiency of 2-CP destruction under each loading arrangement, identical inlet conditions were applied throughout (see Table 4).

Table 4
Concentrations applied in liquid–liquid/ozone bench scale contact tests

O ₃ :2-CP molar ratio	2-CP-in-water (mg/L)	O ₃ -in-solvent (mg/L)
4:1	100	150
6:1	75	165

In each test the rig was operated for 45 min, after which 20 mL samples were collected from the sampling ports installed in the lower U-bends of the solvent–water contact section (see Fig. 1, ports 3–9). Similar to bench scale tests, samples were collected in glass vials prior charged with ~20 µL sodium hydrogen sulphite solution (Na₂H₂SO₃, 39%) (VWR International Ltd., UK). Samples were then left to stand for 30 min. Following this time, 2 mL sub-samples were taken from the solvent and aqueous phases and submitted for 2-CP analysis.

The concentration of ozone loaded into the solvent was monitored throughout each test. This was carried out as described in the solvent-loading tests (see above).

Following shutdown, an additional 1 L water sample was taken from the liquid–liquid separator for chemical oxygen demand (COD) and total organic carbon (TOC) analysis. Such parameters are commonly used to determine the quality of industrial wastewaters and therefore, were considered useful measures of process effectiveness.

COD measurement was carried out in accordance with US EPA 8000 using a HACH reactor, digestion equipment (0–150 mg/L detection range) and colorimeter (model DR/890)(Camlab Ltd., UK). Duplicate 2 mL sub-samples were submitted for COD analysis. TOC was determined using an Isco TOC Analyser (Isco Inc., USA). Approximately 300 mL of sample was passed through the instrument in order to ensure a stable reading.

3.5. Dichloromethane tests

Tests involving the treatment of DCM contaminated water using the liquid–liquid/ozone approach were carried out at bench scale. Using distilled water, a solution of DCM in water was made up to 50 mg/L and sealed in a 2 L volumetric flask. So as to minimise any losses of DCM to atmosphere while decanting, the solution was chilled to approximately 4 °C. Two sets of duplicate tests were performed in order to determine: (i) the distribution coefficient of DCM between water and VolasilTM245 and (ii) the effectiveness of liquid–liquid/ozone in destroying DCM in solution.

Tests to determine the distribution coefficient were carried out by mixing equal volumes (60 mL) of VolasilTM245 and aqueous DCM solution within 100 mL separating funnels. So as to eliminate air space (and therefore, a third gas phase into which DCM could volatilise), each funnel was filled to capacity. Funnels were then sealed and shaken vigorously by hand for 30 min. Following this period, the liquids were allowed to stand for 2 h within a refrigerator at ~4 °C in order to allow

separation and chilling. A 40 mL aqueous sample was drained from each separator funnel and collected in prior-chilled glass receptacles. Each receptacle was filled to capacity, sealed and submitted for DCM analysis using GC–MS (Alcontrol Laboratories, UK). Analysis of the VolasilTM245 phase was not carried out as the solvent was incompatible with the analytical methodology.

Tests aimed at demonstrating DCM destruction by means of liquid–liquid/ozone contact were conducted as above but using ozone-loaded VolasilTM245. Loading of the solvent was carried out as described above (i.e. 2-CP liquid–liquid/ozone bench tests). The concentration of ozone achieved in the solvent was 150 mg/L; giving a molar contact ratio of 5.5:1 (moles ozone:moles DCM).

3.6. Chemical surfactant effects

It was postulated that the liquid–liquid/ozone process could, foreseeably, be undermined by effluent streams containing surfactants (or contaminants with surfactant properties). In significant concentration, the presence of a surfactant could work to significantly decrease the interfacial tension existing between the water and solvent phases. All but the most careful of mixing may result in the creation of unrecoverable microdroplets and thus, lead to solvent losses and the consequent contamination of the treated water outlet.

In order to determine the behavior of VolasilTM245 liquid–liquid contact in the presence of a surfactant, a series of simple tests were performed. Aqueous solutions containing an established surfactant compound, sodium dodecyl sulphate (SDS)(Avocado Research Chemicals, UK), were made up to concentrations of 0, 50, 100, 250, and 500 mg/L (distilled water). Using a Krüss K10ST Digital Tensiometer and Ring Method, the interfacial tensions existing between each solution and VolasilTM245 were measured.

4. Results and discussion

4.1. Solvent-loading tests

Counter-current ozone-loading results are given in Fig. 4, and are compared with those reported by Ward et al. [12] for the co-current system operating under identical inlet conditions (see Table 2). As can be seen, counter-current operation was demonstrated to produce superior dissolved ozone concentrations within the solvent. This was particularly the case for flow condition A, under which the counter-current system was shown to yield a ~40% improvement (~1.5 times the gas inlet concentration). However, counter-current operation under flow conditions B and C was shown to give only modest improvement (10–20%).

The process of loading ozone into the solvent can be represented diagrammatically by Fig. 5. With regard to this figure, the limitations of co-current loading and the requirements of counter-current loading can be appreciated.

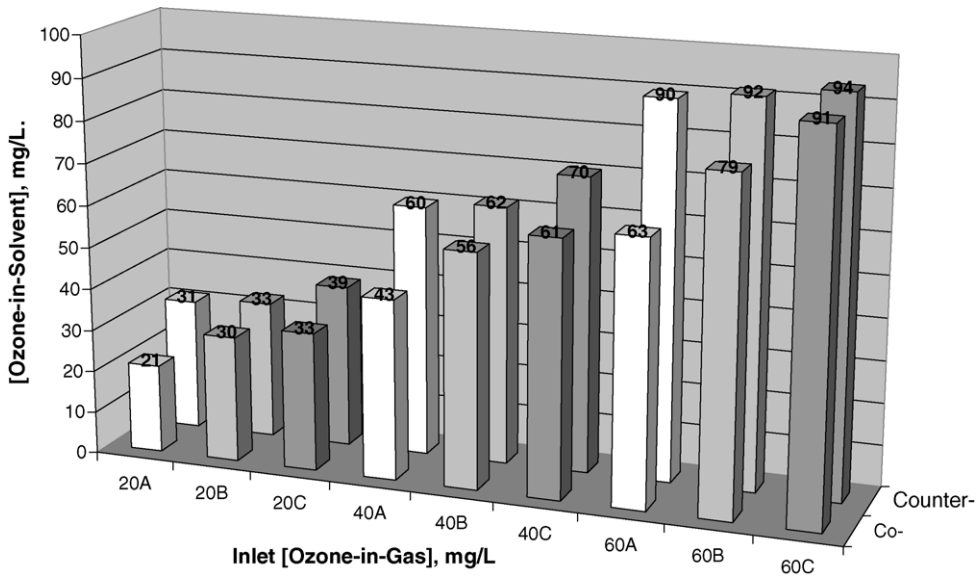


Fig. 4. Comparison of co- and counter-current ozone-in-solvent concentrations obtained under flow conditions A–C.

The equilibrium relationship (i.e. line—equilibrium line) is an expression of Henry’s law (see Eq. (3)). Expressed in terms of mg/L ozone in the Volasil™245 phase per mg/L in the contacting gas phase, investigation by Ward et al. [10] determined the Henry constant (*H*) to be approximately 2 at 298 K and 1.2 bar (absolute pressure). As can be seen for the co-current system operated under flow conditions 60A (i.e. line—60A Co-Current Test), the ozone loading process began with 60 mg/L in the gas phase and zero in the feed solvent. Within the allowed contact time an equilibrium condition was closely approached at the exit. However, this was only about half the potential maximum solvent-loading concentration (and only about half the available ozone was absorbed from the gas phase). Operation of the counter-current system under flow conditions 60A showed better ozone absorption (line—60A counter-current test) and scope

for further improvement. This could be achieved by employing a taller packed column which consequently, would give more transfer units and thus, enable greater solvent-loading concentrations by allowing opportunity for more ozone to be absorbed.

Using the height of the existing packed column, 1.0 m, the solvent-based transfer unit height (*H*_{OS}) was calculated for each set of flow conditions and loading test results using Eqs. (3)–(6). Since the equilibrium line is straight, the log mean driving force can be calculated easily and hence, so can the number of transfer units *N*_{OS}. Table 5 gives each calculated transfer unit height.

Equilibrium line

$$HC_s^* = C_g \tag{3}$$

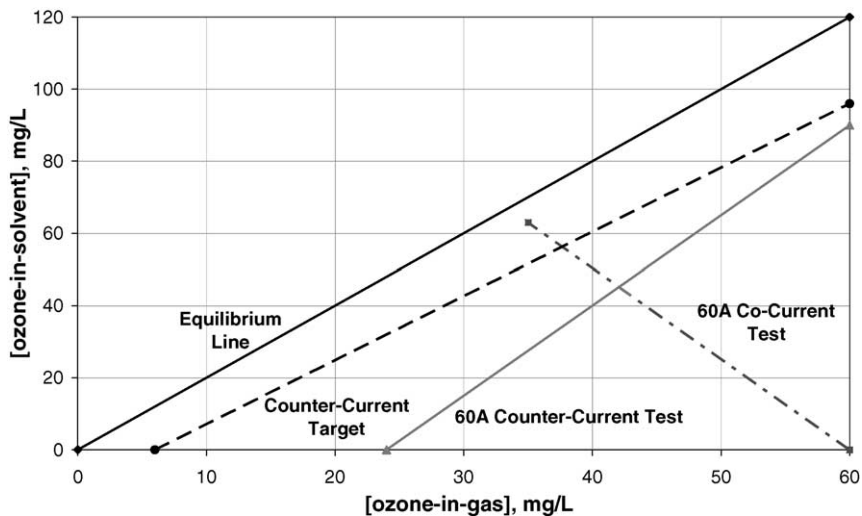


Fig. 5. Representation of co- and counter-current solvent-loading process behaviours using flow condition A and an ozone-in-gas concentration of 60 mg/L.

Table 5
Inlet conditions applied throughout liquid–liquid/ozone rig tests

Inlet flows (L/min)			Inlet concentrations (mg/L)	
Gas	Solvent	Water	O ₃ -in-gas	2-CP-in-water
1.5	0.5	0.3	60	50

Transfer units

$$Z = H_{os}N_{os} \quad (4)$$

where

$$N_{os} = \int_{in}^{out} \frac{dC_s}{C_s - C_s^*} = \frac{C_{s,in} - C_{s,out}}{\Delta C_s \log \text{mean}} \quad (5)$$

and

$$\Delta C_s \log \text{mean} = \frac{(C_{s,out} - HC_{g,in}) - (C_{s,in} - HC_{g,out})}{\ln \left[\frac{(C_{s,out} - HC_{g,in})}{(C_{s,in} - HC_{g,out})} \right]} \quad (6)$$

As liquid height in the column is allowed to vary naturally (depending on operating conditions) and as there exists a ~ 0.1 m unpacked column distance between the distributor and the bottom of the packing, so the determined transfer unit heights given in Table 5 should be considered as approximate values.

Assuming a target operation of 80% loading of the solvent (i.e. relative to the equilibrium concentration) and 90% absorption from the gas phase (see Fig. 5, line—counter-current target), 5.6 transfer units (N_{os}) and a gas/solvent flow ratio of 1.8 would thus, be required. Hence, if the height of each transfer unit was taken to be ~ 0.45 m then, the required packed column height would be ~ 2.5 m. This column height presents no difficulties. However, if the present design arrangement of allowing column head pressure to drive loaded solvent through the system is maintained then, consideration must be given to sustaining a sufficient liq-

uid head height (i.e. height above the upper U-bends of the solvent–water contact section). Although this height was observed to vary with operating conditions, a head of ~ 0.5 m was found to be sufficient.

It is therefore clear that counter-current ozone loading of solvent is the preferred and a feasible system. It will have a marked beneficial financial impact on performance without introducing engineering difficulties.

4.2. 2-CP bench scale tests

4.2.1. Liquid–liquid/ozone contact tests

The results of 4:1 and 6:1 mol ratio tests are shown in Figs. 6 and 7, respectively. Duplication of each test yielded similar results. Significant 2-CP destruction was achieved in both cases (approximately 70 and 96%, respectively). Conclusion of the reaction was shown to take place within 2 min of contact in both cases. Hence, the solvent/water contact time afforded by the pilot rig must be at least this duration.

4.2.2. Direct ozone gas contact tests

Fig. 8 compares liquid–liquid/ozone test 2-CP destruction to that achieved by direct ozone gas contact tests (both using 4:1 molar contact ratios). As can be seen, similar 2-CP destruction was achieved within the first minute of contact ($\sim 70\%$). However, beyond this time little further destruction was accomplished by the liquid–liquid/ozone approach. Destruction by direct gas contact, on the other hand, was shown to continue until only a trace of the original concentration ($\sim 1\%$) was remaining after 5 min. This suggests that liquid–liquid/ozone contact is a less effective process.

Unfortunately, this comparison would suggest liquid–liquid/ozone treatment to hinder rather than enhance the ozonation process. As suggested by Ward et al. [11], this

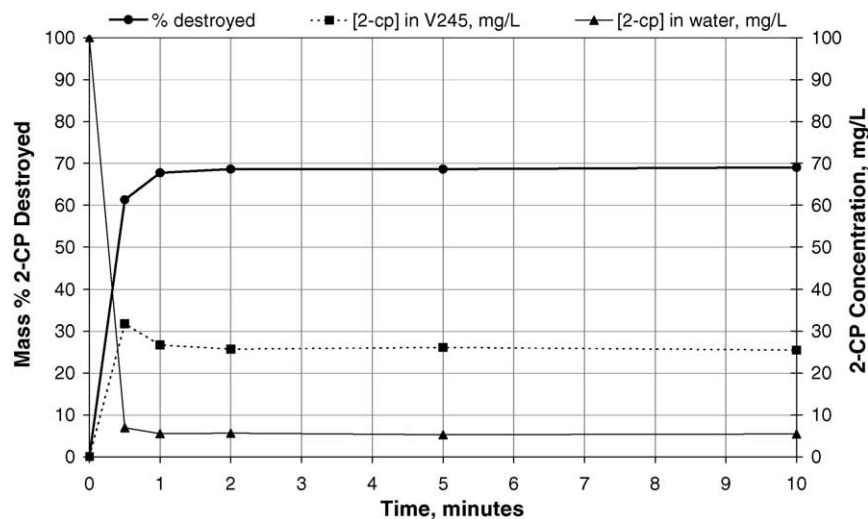


Fig. 6. Results of 4:1 mol ratio liquid–liquid/ozone bench scale 2-CP test.

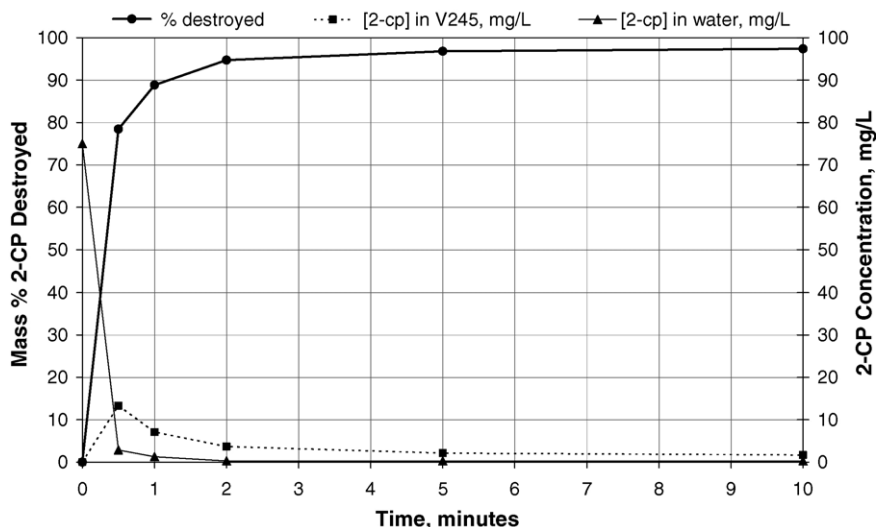


Fig. 7. Results of 6:1 mol ratio liquid-liquid/ozone bench scale 2-CP test.

may be due to a combination of two factors: (i) interfacial mass transfer resistance and (ii) the promotion of less effective chemical reaction pathways.

To overcome the interfacial mass transfer resistance and thus, migrate to the alternate phase, reactants must rely upon the existence of a sufficiently severe concentration gradient across the phase boundary—as can be expected at the initial moment of phase contact. However, with prolonged contact, concentration gradients can be expected to decline due to the progression of mass transfer and ozonation reactions. As such, a situation may arise where respective gradients are so diminished as to be incapable of providing reactants with sufficient potential to overcome the interfacial resistance. This would result in reactants remaining within their respective phases and thus, prevented from interaction by mutual isolation. If the interfacial mass transfer resistance experienced at the VolasilTM245/water boundary is signifi-

cantly greater than that experienced between oxygen/water, this may explain the observed discrepancy between the fractions of 2-CP destroyed (~70% liquid-liquid/ozone, ~100% direct gas contact). Where more ozone was applied in liquid-liquid/ozone tests (i.e. 6:1 mol ratio), the mass fraction of 2-CP destroyed was increased to 96%. The benefit of this additional ozone may have been to maintain the interfacial ozone concentration gradient above that required to sustain mass transfer. Hence, ozone supply to the aqueous phase was maintained and more 2-CP destroyed as a consequence.

An alternative (or complementary) explanation may lie in the reaction pathways encouraged by the two contact approaches. If sufficiently less reactive oxidation pathways predominate within the VolasilTM245 phase, then despite a greater concentration of ozone being present, contaminant destruction may be inhibited rather than enhanced. The VolasilTM245 phase would inadvertently become a haven

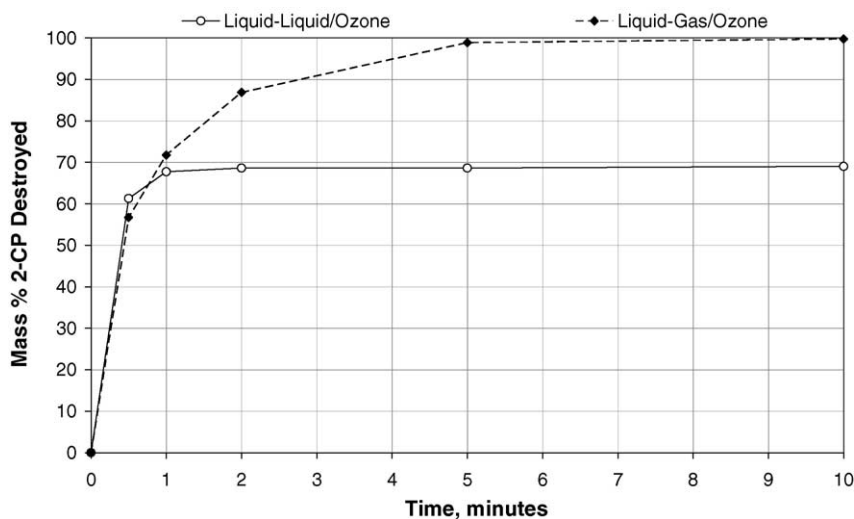


Fig. 8. Comparison of 4:1 mol ratio liquid-liquid/ozone and liquid-gas/ozone bench scale 2-CP test results.

Table 6
Solvent-based transfer unit heights determined for each flow condition

Flow condition	Solvent-based transfer unit height (H_{os}) (m)		
	20 mg/L gas inlet	40 mg/L gas inlet	60 mg/L gas inlet
A	0.38	0.43	0.43
B	0.45	0.54	0.55
C	0.23	0.42	0.59

from the more virulent oxidation reactions taking place within the water phase. For example, the OH^\bullet radical (an intermediate of ozone breakdown in water) is said to play an important role in scavenger-free water systems at $\text{pH} > 4$ [1] and is a more potent oxidant than the parent ozone molecule (oxidation potential of 2.76 V versus 2.08 V for molecular ozone [14]). However, following contaminant extraction, reactions occurring in the VolasilTM245 phase can be expected to take place in the absence of OH^\bullet radicals and thus, purely by means of the less reactive ozone molecule.

4.3. Liquid–liquid/ozone rig tests

Table 6 compares the ozone-loading conditions achieved during both co- and counter-current 2-CP tests. Despite the use of identical inlet conditions (see Table 4), the counter-current system was again demonstrated to yield improved solvent-loading and thereby, more efficient use of the ozone generated.

2-CP test results involving co- and counter-current operation of the continuous flow liquid–liquid/ozone rig can be seen in Figs. 9 and 10, respectively. Duplicate tests yielded similar results. Assuming plug flow, residence times were calculated based on recorded volumetric inlet flow, reactor tube dimensions and the location of each sample point.

Significant levels of 2-CP destruction were demonstrated whilst using either solvent-loading technique (approximately

85 and 95%, respectively). However, due to its marginally better loading performance (see Table 5), counter-current operation was seen to produce the greater destructive yield. In terms of water quality, all tests produced a treated outflow concentration of ≤ 1 mg/L 2-CP from a feed of 50 mg/L.

It is important to consider the destiny of contaminant residues persisting in the solvent after passage through the solvent–water contact section (≤ 4 mg/L 2-CP in the above rig tests). If not eliminated, such residues will be recovered along with the solvent and eventually re-introduced to the solvent-loading section. Reloading of the solvent and the consequent re-exposure to ozone should provide opportunity for their destruction, thus preventing residue recycle and build-up within the system.

COD and TOC results are given in Table 7. Treatment under the conditions applied resulted in COD and TOC reductions of ~ 50 and 30%, respectively. Although significant, these reductions are less substantial than that achieved for water phase 2-CP concentration (i.e. $\sim 99\%$). Typical of ozone water treatment in general, this would suggest the process to be more effective in reducing the concentration of specific toxins rather than generic parameters such as COD and TOC.

The persistence of significant COD and TOC residues would suggest complete 2-CP oxidation was not wholly achieved and that intermediate reaction products were formed (i.e. all 2-CP was not completely degraded to CO_2 , H_2O and HCl). This is not surprising as in each test, less than the stoichiometric ozone requirement for complete oxidation was added (i.e. less than $41/3$ mol ozone to 1 mol 2-CP. see Eq. (1)). The presence of intermediates was also suggested by the behaviour of water phase pH, which saw a decline from 7 (untreated) to approximately 3 (treated). In addition to HCl formation, this may indicate the formation of organic acids (e.g. carboxylic, oxalic, malic and/or chlorendic acid—as found in related studies [6,8,9]). In order to find further evidence of potential reaction products, the chromatograms and

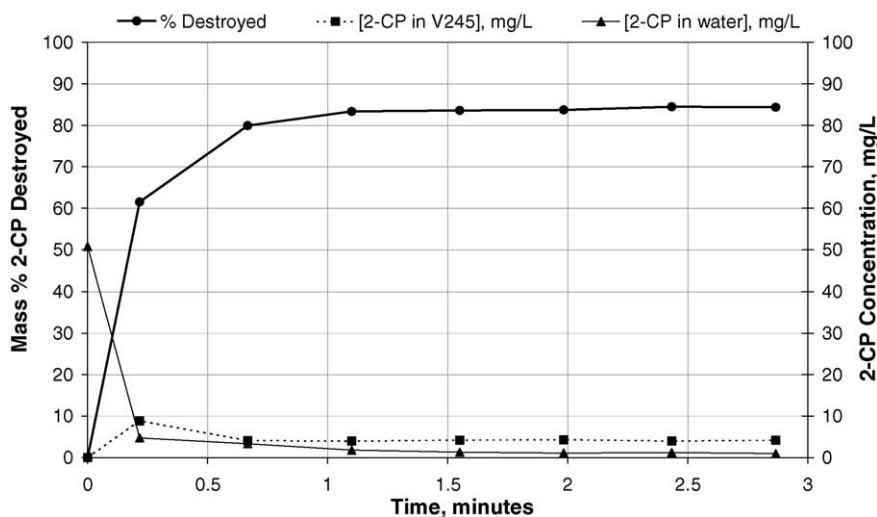


Fig. 9. 2-CP destruction in a continuous flow liquid–liquid/ozone pilot rig using co-current solvent-loading.

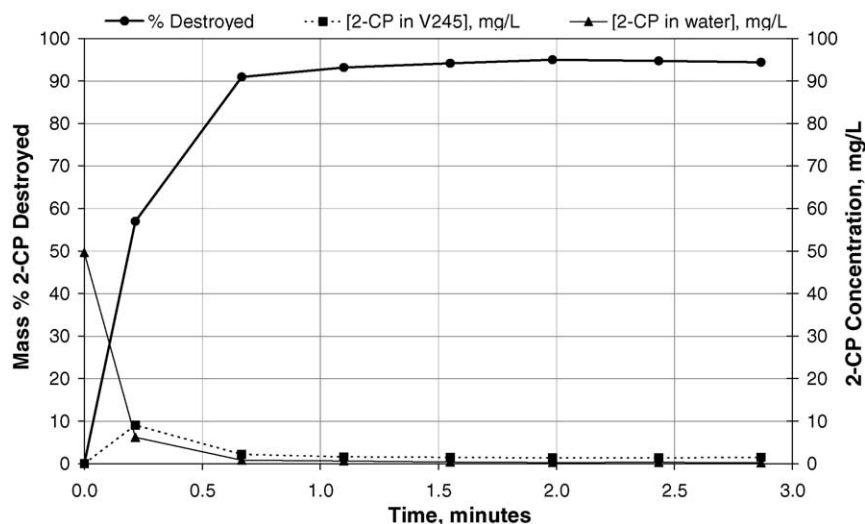


Fig. 10. 2-CP destruction in a continuous flow liquid–liquid/ozone pilot rig using counter-current solvent-loading.

mass spectra generated as a consequence of aqueous sample analysis were thoroughly scrutinised. However, no such presence was detected. It is possible such reaction products failed to be extracted to toluene during sample preparation and hence, fail to reach the GC–MS instrument. Analysis without preparatory extraction would have required use of a liquid chromatography instrument and none were available to this investigation.

4.4. Dichloromethane tests

The distribution coefficient of DCM between water and VolasilTM245 phases was determined as 8.5. Duplicate tests gave similar results. Hence, DCM was demonstrated to possess a significantly stronger affinity for VolasilTM245 than water.

Less encouraging were the results of tests aimed at demonstrating DCM destruction by liquid–liquid/ozone contact. Such destruction was estimated at a mere 18%. Assuming Eq. (2) to be an accurate description of overall DCM ozona-

tion, then significant ozone excess was afforded (i.e. 175%). However, despite this, only a modest level of destruction was accomplished. This would suggest DCM not to be susceptible to ozone attack and therefore, not a suitable candidate for treatment by liquid–liquid/ozone contact.

4.5. Effect of surfactants on the liquid–liquid/ozone process

Test results concerning the effect of SDS surfactant on the VolasilTM245/water interfacial tension are given in Table 8. Triplicate tests gave similar results. The system is not particularly sensitive since a relatively large concentration of SDS does not reduce interfacial tension to extremely low levels which might induce operating difficulties with very small drops.

To determine if SDS was extracted into the solvent phase, a 10 mL sample of the 500 mg/L solution was contacted with an equal volume of VolasilTM245 and shaken by hand for 3 min. UV absorption analysis of the aqueous phase before con-

Table 7

Solvent-Loading conditions experienced using identical inlet conditions during co- and counter-current 2-CP rig tests

Loading system	O ₃ -in-solvent (mg/L)	O ₃ :2-CP mole ratio	O ₃ -in-off-gas ^a (mg/L)	Mass O ₃ dissolved as% of total inlet mass ^a
Co-current	80	7.3	33	44
Counter-current	95	8.6	30	50

^a Determined by mass balance.

Table 8

COD and TOC reductions achieved by treatment of a 50 mg/L 2-CP solution in liquid–liquid/ozone rig tests

Loading system	COD			TOC		
	Untreated (mg/L)	Treated (mg/L)	Reduction (%)	Untreated (mg/L)	Treated (mg/L)	Reduction (%)
Co-current	85	44	48	24	17	29
Counter-current	85	41	52	24	16	35

Table 9
Volasil™245/water interfacial tensions at various water phase SDS surfactant concentrations

SDS concentration (mg/L)	Volasil™245 interfacial tension ^a (mN/m)
0	24
50	23
100	29
250	17
500	12

^a Triplicate average.

tact reveals that SDS produces a prominent peak at 192 nm. Identical analysis of the Volasil™245 phase after contact reveals no such peak, suggesting that SDS resists extraction and remains in the aqueous phase (Table 9).

5. Conclusions

Using Volasil™245 solvent, this investigation has successfully applied a continuous liquid–liquid/ozone treatment system to the purification of 2-CP contaminated water. 2-CP extraction to the ozone-loaded solvent phase was demonstrated to occur and considerable levels of contaminant destruction were achieved. Significant, though less dramatic, reductions in COD and TOC were also achieved. Completion of the reaction was shown to occur within ~2 min of liquid–liquid contact time. Mixing and dropletisation of the solvent within the water phase was achieved using Sulzer in-line SMV static mixers. Following contact, the two phases were disengaged and the solvent repeatedly recycled through the system.

In order to improve the performance of the previously reported liquid–liquid/ozone rig, the unit was modified to incorporate a counter-current solvent-loading arrangement. Design, installation and operation of the new section was successfully achieved. In comparison with the previous co-current system, the new counter-current assembly was demonstrated to yield: (i) greater concentrations of ozone within the solvent and (ii) more efficient ozone usage. Increasing the packed column height to ~2.5 m was suggested to improve counter-current design and thus, yield a near optimum level of performance.

The effectiveness of 2-CP destruction by liquid–liquid/ozone was compared to that achieved by the conventional approach of direct ozone gas contact. Unfortunately, liquid–liquid/ozone seems to be an inferior technique. The expected acceleration of reaction kinetics was not shown to occur and the fraction of 2-CP eventually destroyed by liquid–liquid/ozone was slightly reduced for the same utilization of ozone. It was postulated that this retardation might be the result of: (i) reactant isolation due to liquid–liquid mass transfer resistance and/or (ii) the promotion of less effective reaction pathways. Although contaminants other than 2-CP may behave differently, the

results of this investigation suggest the liquid–liquid/ozone technique to hinder rather than enhance the ozonation process.

Despite the modest levels of DCM destruction yielded by bench scale tests, the liquid–liquid/ozone technique has been shown an effective means of indirectly exposing waterborne contaminants to a concentrated source of ozone. Hence, the technology could still prove applicable in situation where the conventional approach of direct gas contact is to be avoided due to the consequences of sparging. As discussed above, this may be desirable where contaminants are volatile, highly toxic and/or pungent or foaming occurs. The presence of SDS surfactant does not introduce operating difficulties into the Volasil™245 system.

Further investigation is required in order to determine the fate of intermediate reaction products. These are expected to be either returned to the water phase or destroyed within the solvent on it being recycled and reloaded.

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References

- [1] C. Gottschalk, J.A. Libra, A. Saupe, *Ozonation of Water and Waste Water*, Wiley/VCH, Weinheim, Germany, 2000, pp. 30 and 69.
- [2] B. Langlais, D.A. Recklow, D.R. Brink, *Ozone in Water Treatment Application and Engineering*, Lewis Publishers, USA, 1991, p. 113.
- [3] D. Bhattacharyya, C.E. Hamrin Jr., R.P. Northey, Oxidation of hazardous organics in a two-phase fluorocarbon–water system, *J. Hazard. Waste Hazard. Mater.* 3 (4) (1986) 405–427.
- [4] F.A. Stich, D. Bhattacharyya, Ozonolysis of organic compounds in a two-phase fluorocarbon–water system, *Environ. Prog.* 6 (4) (1987) 224–229.
- [5] C.Y. Changand, J.N. Chen, Ozonolysis of 2,4-dichlorophenol in a two-phase solvent/water system, *Water Sci. Technol.* 29 (9) (1994) 343–346.
- [6] D. Bhattacharyya, T.F. Van Dierdonck, S.D. West, A.R. Freshour, Two-phase ozonation of chlorinated organics, *J. Hazard. Mater.* 41 (1995) 73–93.
- [7] A.K. Guha, P.V. Shanbhag, K.K. Sirkar, D.A. Vaccari, D.H. Trivedi, Multiphase ozonolysis of organics in wastewater by a novel membrane reactor, *Am. Inst. Chem. Eng. J.* 41 (1995).
- [8] A.R. Freshour, S. Mawhinney, D. Bhattacharyya, Two-phase ozonation of hazardous organics in single and multicomponent systems, *Water Res.* 30 (9) (1995) 1949–1958.
- [9] O.J. Jung, Destruction of 2-chlorophenol from wastewater and investigation of by-products by ozonation, *Bull. Korean Chem. Soc.* 22 (8) (2001) 850–856.
- [10] D.B. Ward, C. Tizaoui, M.J. Slater, Ozone-loaded solvents for use in water treatment, *Ozone Sci. Eng.* 25 (6) (2003) 485–495.
- [11] D.B. Ward, C. Tizaoui, M.J. Slater, Extraction and destruction of organics in wastewater using ozone-loaded solvent, *Ozone Sci. Eng.* 26 (2004) 475–486.

- [12] D.B. Ward, C. Tizaoui, M.J. Slater, Wastewater dye destruction using ozone-loaded Volasil™245 in a continuous flow liquid–liquid/ozone system, *Chem. Eng. Proc.*, March 2005, accepted for publication.
- [13] C.N. Sawyer, P.L. McCarty, G.F. Parkin, *Chemistry for Environmental Engineers*, 4th ed., McGraw-Hill, 1994, p. 269.
- [14] Water Quality Association Ozone Task Force, *Ozone for Point-of-entry, and Small Water Systems, Water Treatment Application, A Reference Manual* Lisle, Water Quality Association, Illinois, USA, 1997, p. 12.

Glossary

2-CP: 2-chlorophenol
COD: chemical oxygen demand
DCM: dichloromethane
LD: limit of detection
SDS: sodium dodecyl sulphate
TOC: total organic carbon