Advanced oxidative wastewater treatment using cavitational reactors

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I certify that this is a true and accurate version of the thesis approved by the examiners

Signed: [redacted] **Dated:** 16/6/08.

Director of studies

Declaration

I hereby declare that the work presented in this thesis was carried out by me at the University of Abertay Dundee, except where due acknowledgement is made, and has not been submitted for any academic award at this or any other University.

Signed: [redacted]
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Abstract

This thesis explores various novel ways of treatment of wastewater contaminated by toxic organic pollutants using single and combined advanced oxidative wastewater treatment technologies in conjunction with a variety of acoustic and hydrodynamic cavitational reactors. There have been many reports in the literature on the use of hydroxyl radicals as the core part of AOPs and hence, as the first objective, the amount of hydroxyl radical generation from different acoustic and hydrodynamic cavitational reactors was studied using the potassium iodide dosimeter. The results reveal that optimum concentrations of less toxic chloroalkanes (chloroform and dichloromethane) could be efficient alternatives to carbon tetrachloride for enhancement of hydroxyl radical generation in cavitational reactors. Increasing ultrasonic amplitudes and operating hydrodynamic cavitational pressures lead to higher rates of hydroxyl radical production. Having explored the efficiency of generation of hydroxyl radicals the capacity of the reactors to degrade the model pollutant phenol, via a modified classic Fenton reaction which uses zero valent iron catalysts (instead of iron salts) and hydrogen peroxide under acidic conditions was studied. This process, named the advanced Fenton process (AFP), is the main foundation of the phenolic wastewater treatment reported in this thesis.

Phenol degradation was assessed using different frequencies of ultrasound where a comparison between 20, 300 and 520 kHz ultrasonic reactors showed that 300 kHz was by far the most efficient US reactor resulting in 100% phenol removal and 37% total organic carbon (TOC) mineralization in 25 min.

The concept of Latent Remediation (LR) was discovered during investigations into innovative approaches towards development of cost/energy-effective methods to treat phenolic wastewater. LR consists of inputting only 15 min of either ultrasound or stirring to the reaction medium, which contains optimised amounts of hydrogen peroxide and iron catalyst, and then the silent–dark AFP phenol degradation was studied over 24 h. The excellent results revealed that >80% TOC mineralization was achieved after this time. It was also found that zero valent copper catalysts were effective for phenol degradation and offered an excellent alternative to iron in the AFP, however toxicity analysis on the 24, 48 and 72 h samples showed that zero valent iron exhibited decreased toxicity when compared to zero valent copper.

Conventional granular/powdered activated carbons were replaced with activated carbon cloth and investigations on the potential use of this material for phenol removal/decomposition was studied in detail at different operating pHs (3, 5.5 and 9), temperatures (20, 40 and 80 °C), oxidants (H_2O_2/O_3) in various reactors (pump, shaker and US bath).

Another aspect of the AOP application, disinfection of natural waters, was studied employing hydrodynamic cavitation and ozonation in a novel Liquid Whistle Reactor system. Model markers of faecal coliforms, *Escherichia coli,* were chosen for the study and the combined technologies of hydrodynamic cavitation and step-wise ozonation proved be highly beneficial, resulting in ~6 log bacterial reduction revealing 99.9999% disinfection efficiency of the process.

List of Abbreviations

AOP	Advanced Oxidation Processes
AC	Activated carbon
ACC	Activated carbon cloth
ACC-Std	Activated carbon cloth-standard construction (160×86): no impregnation
ACC-Cu	Activated carbon cloth-5.2% copper content on standard construction(160×86)
ACC-Ag	Activated carbon cloth-0.04% silver content on standard construction(160×86)
ACC-Extra-Cu	Activated carbon cloth-4.2% copper content on extra yarns (160×100)
ACC_0	Non-ozonised activated carbon cloth
ACC_{15}	15 min ozonised activated carbon cloth
ACC_{150}	150 min ozonised activated carbon cloth
ACF	Activated carbon fiber/felt
AFP	Advanced Fenton Process
BAC	Biological activated carbon
CCl_4	Carbon tetrachloride
CFU	Colony forming units
CP	Chlorophenol
$CHCl_3$	Chloroform
CH_2Cl_2	Dichloromethane
COD	Chemical oxygen demand
CWAO	Catalytic wet air oxidation
DCP	Dichloro-2-propanol
DDT	Dichlorodiphenyltrichloroethane
dH_2O	Distilled water
GAC	Granular activated carbon
GC	Gas Chromatography
GC–MS	Gas Chromatography–Mass Spectroscopy
H_2O_2	Hydrogen peroxide
HC	Hydrodynamic cavitation
HO	Hydroxyl
HTA	Hydroxyterephthalate acid
KI	Potassium iodide
LR	Latent Remediation
LWR	Liquid Whistle Reactor
MANOVA	Multiple analysis of variance
MTBE	Methyl *tert*-butyl ether
O_3	Ozone
RDX	Cyclotrimethylenetrinitramine
SOG	Surface oxygen groups
TCE	Trichloroethylene
TDS	Total dissolved solids
TIC	Total inorganic carbon
TiO_2	Titanium dioxide
TOC	Total organic carbon
TNT	Trinitrotoluene

US	Ultrasound or acoustic cavitation
UV	Ultraviolet
WAO	Wet air oxidation
ZVC	Zero valent catalysts
ZVCu	Zero valent copper
ZVCF	Zero valent copper flitters
ZVCP	Zero valent copper powder
ZVCT	Zero valent copper turnings
ZVI	Zero valent iron
ZVI-N	Zero valent iron (new powder)
ZVI-O	Zero valent iron (old powder)

List of Symbols

E_{bg}	Bandgap energy
I_3^-	Triiodide
C_{O_3}	Concentration of ozone in mg L^{-1}
ΔA	Difference in absorbance
f	Absorption coefficient for aqueous ozone (0.42)
b	Path length
V_T	Total volume of the volumetric flask
V	Volume of ozonated sample added
N_0	Initial microbial count
N	Represent microbial count at any given time
m	Mass of water (g)
c	Specific heat of water (4.186 joule g^{-1} $°C^{-1}$)
ΔT	Change in temperature (°C)
Δt	Change in time (s)
W	Watt
Q	Power dissipation
μ	Microns
***o*-**	ortho
***p*-**	para
C	Concentration at a given time
C_0	Initial concentration
g	Gram
L	Litre
M	Molar
m	Milli
°C	Degree centigrade
eq^-	Aqueous electron
w/v	Weight/volume
μM	Micro molar
O_2–O_3	Oxygen–ozone mixture
(^3P)	Protonated
kJ	Kilo Joule
kGy	Kilo Gray
atm	Atmospheres

Chapter 1

General introduction

1.1 Introduction

Access to fresh, clean, uncontaminated water is recognised as a universal need for all societies. This, combined with the global requirement to protect our environment, continues to motivate a legislative drive toward more stringent limits on the amount of pollutants present in industrial wastewater discharge. This new legislation, is forcing de-pollution measures and in order to meet this challenge, industrial demand has grown for innovative and improved water treatment solutions for both, disinfection and pollutant removal. Advanced oxidative disinfection and wastewater treatment technologies contribute a great deal in environmental friendly–economic–efficient water treatment methodologies in order to achieve complete mineralisation or convert highly toxic organic pollutants into less harmful compounds.

In industrial effluents, phenol is one of the most common toxic pollutants in wastewaters generated from petroleum refining, petrochemicals, pharmaceuticals, pesticides, dyes/paints and organic chemical manufacturing industries (Benitez *et al.*, 1999). To all living creatures, phenol is a prototype poison, which can coagulate protein and devitalise cells, especially the nervous system. It is believed that in high concentration, phenol can even lead to death, whereas lower concentrations could cause cumulative chronic intoxication. Therefore, this organic compound has been researched over several decades and the United States Environmental Protection Agency (US EPA) has listed it as one of the 129 priority pollutants (Chen *et al.*, 2003). Conventional treatment of phenolic wastewaters include recycling, incineration, activated carbon (AC) adsorption (Dabrowski *et al.*, 2005), biological treatment (Calvosa *et al.*, 1991) and chemical oxidation (Davis and Huang, 1990; Joglekar *et al.*, 1991; Weavers *et al.*, 1998), however with each methods are associated advantages and disadvantages. Therefore, the selection of an efficient technology depends on the: concentration of phenolic compounds in wastewaters, compositions of the wastewater and treatment cost.

Recent advances in science and technology have introduced a range of new techniques, termed as **A**dvanced **O**xidation **P**rocesses (AOP). Thus, a number of AOPs have been considered as an attractive way of treating phenolic compounds from effluent streams. Since the 1970s, AOPs have shown considerable potential for treating a variety of pollutants, with low to high concentrations of harmful to toxic organic compounds and for drinking waters to industrial wastewaters. The concept of 'AOPs' was described by Glaze *et al.* (1987) as a process which ''involves the generation of HO• in sufficient quantity to effect water purification''.

Table 1.1 lists AOPs and the area of opportunities for the variety of AOPs developed, or are under investigation, that could have possible applications in wastewater treatment technologies (Parsons, 2004).

Some of the widely used AOPs for phenol oxidation studies will be reviewed in detail with special emphasis on the use of single and combined processes of the Fenton reaction, cavitation (ultrasound and hydrodynamic), catalysis, peroxidation, ozonation and use of activated carbon cloth as emerging AOPs in phenolic wastewater and drinking water treatment.

AOPs	Catalysis Electrochemical Fenton's reagent Ferrate Ionising radiation Microwave Photo-Fenton's reagent Photocatalysis	Pulsed plasma Supercritical water oxidation Cavitation UV UV/H_2O_2 UV/H_2O_2/O_3 Vacuum UV Wet air oxidation
Opportunities for AOPs	Groundwater Odour and VOCs Surface water Swimming pools Water recycling Disinfection	Industrial wastewater Industrial sludge's Municipal wastewater Leachates Municipal sludge's Ultra pure water

Table 1.1: List of AOPs and its applications in water and wastewater treatment (Parsons, 2004).

In AOPs, the main aim of oxidation of pollutants is to mineralise or convert the reactants of the organic pollutants into relatively simpler inorganic molecules, mainly CO_2, H_2O and mineral salts (Parsons, 2004). The conventional oxidants such as hydrogen peroxide (H_2O_2) and ozone (O_3) have been focussed in this thesis and the hydroxyl radicals (HO•) generated from these oxidants, through chain reactions, give many AOPs its power to oxidise pollutants and enhance degradation rates. The efficiency of oxidising species in a reaction depends on its oxidation power and shown in Table 1.2 (Vogelpohl and Kim, 2004). However, the rate of oxidation depends on various factors such as radical/oxygen/pollutant concentrations and presence of scavengers, like bicarbonate ions. Physical parameters like pH, temperature, pollutant type also tend to affect the oxidation process.

Oxidation species	Relative oxidation power (V)
Hydroxyl radicals	2.05
Atomic oxygen	1.78
Ozone	1.52
Hydrogen peroxide	1.31
Permanganate	1.24
Chlorine	1.00

Table 1.2: Relative oxidation power of oxidising species (Vogelpohl and Kim, 2004).

Many strong oxidants mentioned above are 'free radicals' of which HO• radicals is the most powerful oxidising species after fluorine and is able to oxidise a wide range of pollutants (Parsons, 2004).

1.2 AOPs for wastewater treatment

Typical AOPs can be broadly categorised under photochemical and non-photochemical systems (Table 1.3) (Huang *et al.*, 1993). However, a set of advantages and disadvantages are associated with every system; the major advantages of the AOPs mentioned below are: high rates of toxic pollutant degradation, reduced-dimension reactor set-ups and flexible systems; whereas, high cost of operation, high energy requirements (use of UV lamps/electron beam/radioactive sources) and enhanced safety requirements due to the use of highly reactive chemicals like O_3 and H_2O_2 are some main disadvantages.

Photochemical oxidations	**Non-photochemical oxidations**
UV/H_2O_2	O_3/HO^-
UV/O_3	H_2O_2/O_3
$UV/H_2O_2/O_3$	US/O_3[a]
$UV/H_2O_2/Fe^{2+}$ (Photo-Fenton)	O_3/activated carbon
$UV/TiO_2/$	H_2O_2/Fe^{2+} (Fenton process)
$UV/H_2O_2/TiO_2$	Electro-Fenton
$UV/O_3/TiO_2$	Electron beam irradiation
UV/US	Cavitation oxidation (CAV–OX®)[a]
	Cavitation/H_2O_2
	Radiolysis
	US/Wet air oxidation (SONIWO)[a]

[a](Gogate and Pandit, 2004b).

Table 1.3: Different photochemical and non-photochemical oxidations (Huang *et al.*, 1993).

1.2.1 Photochemical oxidations

1.2.1.1 UV/H_2O_2, UV/O_3 and $UV/H_2O_2/O_3$ systems

UV photolysis of H_2O_2 generates HO• (Eq. 1.1). Photolysis of aqueous O_3 produces H_2O_2. The deprotonated form of H_2O_2 (HO_2^-) reacts with O_3 to produce ozonide (O_3^-) and then HO• (Eq. 1.2) (Huang *et al.*, 1993).

$$H_2O_2 + h\nu \longrightarrow 2HO\bullet \qquad (1.1)$$

$$O_3 + h\nu \longrightarrow H_2O_2 \longrightarrow HO_2^- + O_3 \longrightarrow O_3^- \longrightarrow HO\bullet \qquad (1.2)$$

The principle theory behind this combination of technologies exists in the enhanced free radical production from the dissociation of O_3 or H_2O_2. The technique is actually very similar to the system where $US/H_2O_2/O_3$ is used with the only difference being in supply of energy required for the dissociation of O_3 and HO•. In the case of US, the energy is provided by cavitation bubbles whereas in UV systems, the dissociation is supported by UV light (Gogate and Pandit, 2004b).

Gogate and Pandit (2004b) discussed some of the key optimal operating conditions in the UV/H_2O_2 system and refer to developing realistic kinetic models and optimisation of H_2O_2 dose, concentration of radical scavengers and pH for different types of pollutants. However, pH is one of the important factors considered in this UV/H_2O_2 system as the rate of reaction depends on the change of pH with time. Usually lower operating pH (2.5–3.5) is preferred as the effect of radical scavengers, i.e., carbonate and bicarbonate ions, is negligible leading to high rates of degradation. On the contrary, neutral to alkaline pH (7–8) is preferred in the UV/O_3 system. Also, reduced temperatures, lower initial concentration of pollutant and continuous ozonation are key parameters. Higher temperatures often reduce the O_3 solubility and thus affect the degradation process hence appropriate cooling units should be installed.

According to Huang *et al.* (1993), the UV/H_2O_2, UV/O_3 and UV/H_2O_2/O_3 systems are best suited for ground water and soil remediation, the reason being the activation energy between HO• and organics is close to zero and therefore oxidation is rapid. However, there are certain disadvantages that exist in the UV-based oxidation system:

1. UV/O_3: mass transfer between gaseous O_3 and aqueous medium is the limiting factor.
2. UV/H_2O_2: decomposition of H_2O_2 by UV is inefficient because the extinction coefficient of H_2O_2 at 254 nm is only 19.6 M^{-1} s^{-1} compared to 3000 M^{-1} s^{-1} for O_3.
3. Reactor design: inappropriate match between reactor size and UV penetration depth could lead to inefficient degradation of pollutants.
4. Physical parameters: turbidity and colour could also significantly reduce the efficiency of UV-based oxidation systems.

1.2.1.2 Photocatalytic systems

There have been a number of reviews concerning photocatalytic systems in the last ten years (Chapter 6; (Parsons, 2004)). Titanium dioxide (TiO_2) has been considered as the semi-conducting material for research in the field of semi-conductor photocatalysis for water purification, where, dissolved oxygen is the electron acceptor (A) and pollutant is the electron donor (D), the overall process could be defined as semiconductor photocatalysed oxidative mineralisation of the pollutant by dissolved oxygen and is represented by Eq. (1.3). TiO_2 has a large bandgap energy, $E_{bg} \cong 3.2–3.0$ eV and hence it is only able to absorb UV light, typically <380 nm but does not absorb visible light. Moreover, TiO_2 exists in three crystalline forms, namely anatase, rutile and brookite. However, the most photocatalytically active and easy to produce is anatase, therefore anatase-TiO_2 is the semiconductor used in various commercial photocatalytic systems for water purification.

$$\text{Pollutants} + O_2 \xrightarrow[h\nu \geq E_{bg}]{\text{semiconductor}} \text{minerals} \qquad (1.3)$$

Mills and Lee (Chapter 6; (Parsons, 2004) highlighted notable compounds treated by semiconductor photolysis are haloalkanes (chloroforms and tetracholoromethane); surfactants, hormones; herbicides; pesticides and dyes. The technology, utilising semiconductor TiO_2, is also very extensively used in bacterial/viral/mould destruction, where the mode of action is similar to the destruction of pollutants in which the photogenerated holes produce surface HO• species, which in turn destroy the cell wall of the biological material and they die quickly. This process is termed as photosterilisation or photodisinfection and can be represented as Eq. (1.4).

$$\text{Biological systems} + O_2 \xrightarrow{h\nu \geq E_{bg}} \text{dead systems} + CO_2 + H_2O \qquad (1.4)$$

Installation of the semiconductor photocatalytic oxidation systems in any wastewater treatment plant should consider the advantages and disadvantages associated with the reactor design and technology (Gogate and Pandit, 2004a). Some of the major advantages are: low cost of titania, total mineralisation for many toxic organic pollutants; system applicability for low concentrations; use of natural resources like sunlight and operation at room temperature and pressure. However, the main disadvantages that have been noticed with this technology on an industrial scale are mainly lack of engineering design and operation strategies for efficient use of reactors; relatively low reaction rates; time consuming and expensive processes; ineffective real industrial effluent treatment and finally, fouling of the photocatalysts with continuous use, retard the degradation rates.

Despite the above mentioned drawbacks the photocatalytic oxidation can be effectively and economically used in conjunction with other AOPs such as ultrasound, with H_2O_2, O_3 and Fenton like reactions (Andreozzi *et al.*, 2001a; Andreozzi *et al.*, 2001b; Beltran *et al.*, 1999; Beltran *et al.*, 1996a, 1996b; Benitez *et al.*, 1999).

1.2.1.3 Photosono-catalytic systems

The photocatalytic oxidation system in continuous operations, in either slurry or immobilised catalyst type reactors, results in adsorption of the contaminant on the catalyst which blocks the UV activation sites and results in reduced degradation efficiency. To overcome this limitation, ultrasonic irradiation is the only technique that can be used successfully and simultaneously with photocatalytic operations. The UV–US integrated systems have a great deal of synergism which leads to enhanced generation of free radical species and effective degradation rates with low maintenance cost and energy inputs. Cavitation contributes to cleaning of the catalysts throughout the process; increased mass transport of reactant and products to the catalyst by shockwave propagation; increased catalyst surface area; better formation of radical intermediates for pollutant degradation and enhanced reaction rates. However, while designing an efficient photosono-catalytic reactor, the following important factors should be taken into account (Gogate and Pandit, 2004b):

1. UV–US integrated systems should be installed to operate simultaneously rather than sequentially because such operation may help in continuous cleaning of the photocatalyst and also enhanced HO• generation, thereby increasing rates of degradation.
2. Catalyst shape, size and structure are crucial in the photocatalytic processes, therefore appropriate catalyst support that can withstand high acoustic turbulence should be constructed in the reactor.

3. For wastewater treatment in photosono-catalytic reactors, it is suggested that continuous reactors are better than batch reactors or those operating in re-circulating mode in order to treat huge quantities of effluents.
4. While combining, the photosono-catalytic reactors, uniformity in power distribution by ultrasonic irradiation and uniformity in receiving the irradiation by the photocatalysts, should always be taken in account to achieve maximum pollutant degradation.

1.2.1.4 Photo-Fenton systems

The process of photo-Fenton is the combination of H_2O_2 and UV radiation with Fe^{2+} and Fe^{3+} ions, which tends to produce more HO• and promote pollutant degradation. The reaction mechanism of production of HO• and degradation of pollutants by simultaneous Fenton reactions and photo-Fenton reaction is shown in Fig. 1.1. In the photo-Fenton process, H_2O_2 is utilised by three different mechanisms: direct Fenton reactions, photoreduction of Fe^{3+} to Fe^{2+} and H_2O_2 photolysis. High rates of contaminant removal in photo-Fenton processes can be achieved by appropriate selection and loading of iron salt and H_2O_2, aeration, optimal dilutions and acidic pH (usually pH 2.8). The process could be more energy efficient on a large scale if sunlight is used for photoactivation (Gogate and Pandit, 2004b).

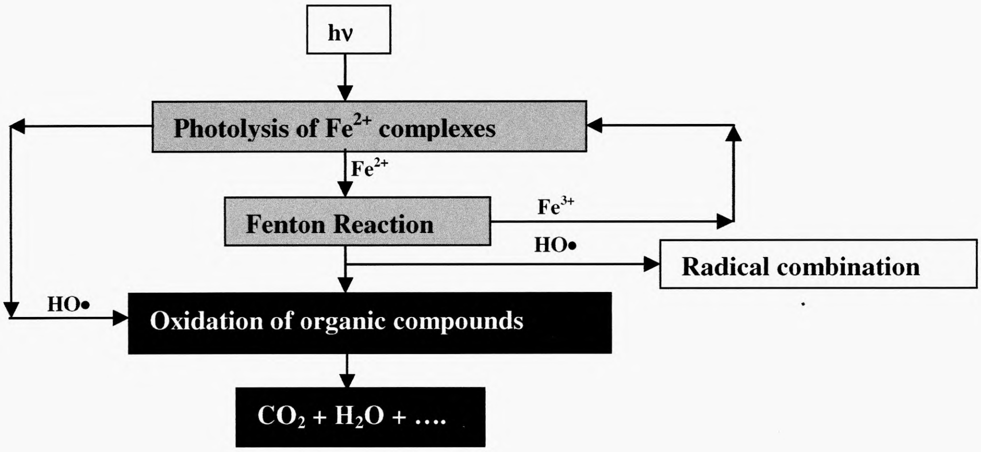


Figure 1.1: Reaction pathways in photo-Fenton process (Vogelpohl and Kim, 2004).

1.2.2 Non-photochemical oxidations

1.2.2.1 Fenton oxidation

According to Wadely and Waite (Chapter 5; (Parsons, 2004)), the Fenton reaction is used extensively in the treatment of contaminated water and soil and has been categorised into light- and dark-Fenton processes. The light-Fenton process is often termed as the photo-assisted Fenton process whereas, the dark-Fenton process involves one or more oxidising agents, usually H_2O_2 and/or oxygen and a catalyst (usually iron metal salt or oxide). The contaminant degradation is normally catalysed by the reduction of Fe^{3+} to Fe^{2+} and leads to the formation of a range of free radical species, including highly reactive HO• which helps in efficient pollutant removal. The Fenton reaction involves three main radical species, two of which are HO• and the third is an aquo or organo complex of high valence iron, called the ferryl ion (Sauer and Ollis, 1996). These coexisting radical species predominate over each other depending on substrate nature, metal–peroxide ratio, scavenger addition, etc. The Fenton oxidation system is highly applicable in removing colour and odour from wastewater with good energy efficiency and can be effectively used in treating toxic and non-biodegradable wastewaters making it suitable for secondary biological treatment (Chen and Pignatello, 1997).

Optimum operating conditions in the Fenton oxidation system have been summarised in a review by (Gogate and Pandit, 2004a):

1. pH: the optimum pH recommended for Fenton reactions is 3, however at pH <3, the formation of $[Fe(II).(H_2O)]^{2+}$ occurs, which reduces HO• production thereby decreasing the degradation rates, similarly, at pH >4, the degradation rate often tends to fall mainly due to formation of Fe^{2+} complexes with the buffer which in turn inhibits the free radical formation and enhances ferric oxyhydroxide precipitation.
2. Ferrous ions: the rate of pollutant degradation increases with increasing ferrous ion concentration; however enormous quantities may remain unutilised and may eventually increase the total dissolved solids load in the effluent stream.
3. H_2O_2: the efficacy of Fenton oxidation greatly depends on the oxidant dose and generally the pollutant degradation increases with the increased H_2O_2

dosage. However, selecting an optimum oxidant concentration is important as the residual H_2O_2 concentration influences the chemical oxygen demand (COD) levels and therefore excess amount is not recommended.

4. Pollutant concentration: lower initial pollutant concentration is favoured.
5. Operating temperature: usually 10–40 °C have been reported to be the range of temperatures that does not affect the degradation efficiency. Above this range, cooling units should be installed in the reactor design.

Fenton oxidation systems can also be greatly enhanced by combination with other AOPs, like UV, cavitation, catalysis and ozonation.

1.2.2.2 Oxidation using oxidants

The two most extensively used oxidants in AOPs are O_3 and H_2O_2. The combination of the two oxidants (H_2O_2/O_3) leads to synergy in the treatment of chemicals such as organophosphoric acid triesters, clofibric acid, ibuprofen, tetrachloroethylene, which show less reactivity towards direct oxidation with O_3 alone (Echigo *et al.*, 1996; Glaze and Kang, 1989a, 1989b; Zwiener and Frimmel, 2000).

1.2.2.2.1 Ozone

O_3 is an unstable gas and a highly powerful oxidising agent ($E° = +2.07$ V). The main areas where O_3 has been used extensively are:

i. Disinfection
ii. Oxidation of organic and inorganic compounds
iii. Particle and taste/colour/odour removal

O_3 has a high potential to react with multiple bonds species, i.e., C=C, C=N, N=N, etc., however it has a reduced potential to react with single-bonded species, i.e., C–C, C–O and O–H.

O_3 transfer in the aqueous medium is one of the key factors controlling disinfection and degradation rates. Literature supports the use of small size O_3 diffusers such as porous disks, porous glass diffusers, bubble columns, packed and plate columns, static mixers, jet reactors and agitated vessels. These have all been shown to be effective in increasing the interfacial area of contact of O_3 in aqueous medium (Glaze, 1987). Martin and Galey (1994) studied the use of static mixers in oxidation and disinfection and reported that the mass transfer coefficient of O_3 increases with a decreasing static mixer's flowrate and increasing gas flowrate.

A list of operating conditions to achieve the maximum extent of degradation along with high energy efficiency has been recommended (Beltran *et al.*, 1997; Beltran *et al.*, 1994; Beltran *et al.*, 1992; Glaze, 1987; Martin and Galey, 1994):

1. Higher pH values.
2. Increased O_3 partial pressure.
3. Use of static mixers.
4. Temperatures 5–20 °C.
5. Presence of catalyst: TiO_2, Fe (II), Mn (II), etc.

A major drawback of using ozonation technology on larger scale operations is the high cost of generation and gas–liquid mass transfer. However, such difficulties could be partially tackled with a combination of ozonation with other existing AOPs such as ultrasound; UV; H_2O_2 and efficient reactor design, with lower cost of treatment (Gogate and Pandit, 2004a).

1.2.2.2.2 Hydrogen peroxide

H_2O_2 has been found to be effective in treating wastewater which require less stringent oxidation conditions (Ayling and Castrantas, 1981). There are three different concentrations normally recommended for the treatment of wastewater: 35%, 50% and 70%, of which, 35% is the safest to use while 70% may produce detonable mixtures with many organic compounds. The reaction rate between H_2O_2 and the pollutant often decides where H_2O_2 should be added in the pollutant stream. According to Gogate and Pandit (2004a), the simplest, fastest and cheapest method for injection of H_2O_2 is a gravity feed system.

No reports so far state the usage of H_2O_2 alone for effective wastewater treatment. Moreover, stability of this oxidant is always a limitation in any reaction system. Interestingly, H_2O_2 could act as an additional pollutant if added in excess to the reaction system or if formed by recombination of dissociated HO•. Either of the above processes could result in decreased overall degradation rates.

However, the above limitations can be tackled by involving H_2O_2 in other hybrid AOP systems such as ultrasound, UV, the Fenton reaction, catalysis and ozonation. Such alternatives might also lead to enhanced oxidation rates at low cost and energy consumption.

1.2.2.2.3 Ozone/hydrogen peroxide

The addition of H_2O_2 at a O_3/H_2O_2 ratio of 2:1 to ozonation processes, increases the decomposition of O_3 molecules thereby enhancing the formation of HO• in the reaction medium (Vogelpohl and Kim, 2004). The reaction mechanism has been studied and is shown in Eq. 1.5–1.12 (Buhler *et al.*, 1984; Forni *et al.*, 1982; Sehested *et al.*, 1982).

H_2O_2 can form the hydroperoxide ion HO_2^- and an H^+:

$$H_2O_2 \longrightarrow HO_2^- + H^+ \qquad (1.5)$$

The hydroperoxide ion reacts with O_3 to produce the ozonide ion (O_3^-) and hydroperoxide radical ($HO_2\bullet$):

$$HO_2^- + O_3 \longrightarrow O_3^- + HO_2\bullet \qquad (1.6)$$

Chain reactions of these products (O_3^- and $HO_2\bullet$) form HO•:

$$HO_2^- \longrightarrow H^+ + O_2^- \qquad (1.7)$$
$$O_2^- + O_3 \longrightarrow O_3^- + O_2 \qquad (1.8)$$
$$O_3^- + H^+ \longrightarrow HO_3 \qquad (1.9)$$
$$HO_3 \longrightarrow HO\bullet + O_2 \qquad (1.10)$$

Once HO• are formed, the following propagation steps generate HO• by an autocatalytic mechanism:

$$O_3 + HO\bullet \longrightarrow O_2 + HO_2\bullet \qquad (1.11)$$
$$O_3^- + HO_2\bullet \longrightarrow 2O_2 + HO\bullet \qquad (1.12)$$

The chain mechanism generates HO• by consuming H_2O_2 and O_3 and the sequence is terminated by recombination of different radicals.

(Gogate and Pandit, 2004b) highlighted the following important considerations for the use of the hybrid H_2O_2/O_3 technology in wastewater treatment:

1. The combined technology will be particularly helpful for pollutants showing less reactivity towards molecular O_3 attack and where radical chain initiators are present in low concentrations.
2. The optimum operating conditions in order to achieve enhanced degradation from this combined technology can be given as: optimum O_3 and H_2O_2 dosage, neutral pH, low pollutant concentration and pre-treatment of wastewaters.
3. Increasing the O_3 utilisation in the reactions is another important factor that should be taken into account in reactor design.
4. Instead of using reactors in series, multiple point injection of H_2O_2 and addition of O_3 in steps is a promising technique rather than single point injection/addition.

1.2.2.3 Radiation-based oxidation

Parsons (Chapter 9; 2004) suggests that ionising radiation is "an excellent source of both reducing and oxidising radicals for water treatment". Thus, the simultaneous generation of both oxidising and reducing species allows a versatile approach towards treatment of a variety of pollutants. Irradiation of water with electron beams or γ-rays results in formation of electronically-excited states, free radicals and ions, which attack and decompose pollutants. Table 1.4 provides an estimate of the concentrations of the reactive species in aqueous solution. The three most reactive products formed in radiolysis of water are: oxidising HO•; the reducing aqueous electron (e_{aq}^-) and the hydrogen radical (H•). Oxidising and reducing species are formed in approximately equal amounts and these are the products which are highly involved in any wastewater treatment.

Dose (kGy)	Concentration (mM)			
	e_{aq}^-	H•	HO•	H_2O_2
1	0.27	0.06	0.28	0.07
5	1.4	0.3	1.4	0.4
10	2.7	0.6	2.8	0.7

Table 1.4: Estimated concentrations of reactive species in pure water at several doses using high energy electron irradiation.

Although aqueous electron (e_{aq}^-) and HO• have similar *G* values, the former is less available for reaction due to scavenging by hydronium ion (H_3O^+) in acidic water and oxygen in aerated solutions. Likewise, though H• is less abundant than e_{aq}^-, the former has a relatively small reaction rate with common radical scavengers found in natural water which makes it important for some pollutant removal. However, such limitations do not exist with the HO•, therefore it can participate in several types of reactions (Parsons, 2004).

The rate of reaction in radiation processes is controlled by several factors, namely ionising radiation (electron beam or γ-radiation energy, absorbed dose and dose rate), nature and concentration of pollutants and presence of scavengers and additives. The effect on treatment efficiency is especially noticeable at low pollutant concentrations. Irradiations of some systems have a dual impact on the treatment system: on the one hand it degrades the pollutant whereas on the other it changes the physico-chemical properties of the system which again contributes to pollutant removal process. Highly concentrated pollutants require large absorbed doses for their purification. Therefore, a cost-effective approach in irradiation treatment would be to combine this technology with other conventional technologies, such as ozonation, floatation, adsorption, coagulation or biological treatment (Woods and Pikaev, 1994).

1.2.2.4 Wet air oxidation

The application of wet air oxidation (WAO) for the treatment of industrial wastewaters began to be commercialised in the 1970s (Mishra *et al.*, 1995). Nearly 100 WAO plants are operating commercially mostly to treat wastewaters generated from petrochemical, chemical and pharmaceutical industries as well as residual sludge from wastewater treatment plants. WAO is an aqueous phase process, where water is an integral part of the reaction. The process is defined as 'the oxidation of organic and inorganic compounds in an aqueous media by means of oxygen/air at elevated temperatures' (Chapter 9; (Parsons, 2004)). Typical operating temperature range for WAO varies from 100 °C to 372 °C (subdivided into: lower, 100–200 °C; medium, 200–260 °C; higher, 260–320 °C; highest, 320–

372 °C) at elevated pressures to maintain water in the liquid phase and ensure oxidation reactions take place in the liquid phase. However, due to high capital cost, high temperature systems, i.e., 320–372 °C, are rarely used. Residence time may vary between 15 and 120 min, leading to 75–90% COD removal. Insoluble organic matter is converted to small organic compounds and eventually to carbon dioxide and water without emission of NO*x*, SO*x*, HCl, dioxins, furans, fly ash, etc. WAO plants either aim for complete oxidation or partial oxidation prior to treatment by conventional biological processes.

WAO can be divided into two types:

1. Non-catalytic WAO
2. Catalytic WAO (CWAO)
    i. Heterogeneous CWAO
    ii. Homogeneous CWAO

In case of non-catalytic WAO, the free radical chain mechanism involves the formation of hydroperoxides and oxyradicals. The two-step non-catalytic WAO degradation mechanism is as follows:

Step 1: hydrogen abstraction from the α-, β- and γ-CH_2 groups of carboxylic acids by O_2 results in the formation of free radicals which react immediately with O_2 to form peroxy radicals.

Step 2: the peroxy radicals can lead to the decarboxylation and formation of CO_2 by H abstraction from the —COOH group of another molecule of carboxylic acid.

A generalised kinetic model based on a simplified reaction scheme with acetic acid as the rate-limiting intermediate was proposed by (Li *et al.*, 1991). This kinetic model is usually used to represent the WAO reactions and shows a reasonably good fit with experimental data.

With the high thermal efficiency of WAO and utilisation of direct chemical oxidation processes, it offers an economical alternative to liquid waste incineration. Higher efficiencies have also been achieved by addition of a catalyst to WAO which in turn reduces the energy consumption in the process and proves out to be a cost-effective process for the treatment of organic sludge and refractory industrial wastewater.

Furthermore, hybrid technologies like SONIWO (sonication followed by WAO) have proved to be outstanding in achieving high degradation rates with enhanced efficiency at comparatively milder temperature and pressure conditions as compared to WAO alone (Dhale and Mahajani, 2001; Ingale and Mahajani, 1995). The WAO has certain limitations with respect to treating complex materials, e.g., polychlorinated biphenyls and polyaromatics along with requirements of severe conditions of temperature and pressure which may lead to high operating cost and therefore affect the overall economic values of the treatment system. In such situations SONIWO has a great advantage as the hybrid technology, involving sonication, may first used to pre-treat the wastes and convert the toxic complex mixtures to smaller fragmented molecules and further processing can easily be carried out by WAO, thereby achieving efficient degradation at comparatively less severe conditions of temperature and pressure.

Some laboratory scale studies suggest that hybrid technologies such as membrane/sonication/WAO, can lead to 80–90% dye degradation in a residence time of 120 min at neutral pH (Dhale and Mahajani, 1999). Also, catalysts like $CuSO_4$ and $NiSO_4$; small amounts of phenol; acidic pH; pre-treatment such as adsorption by activated carbon and membrane separation, could be other hybrid alternative ways in treating toxic wastes along with WAO (Gogate and Pandit, 2004b).

1.2.2.5 Catalytic oxidation

Some of the catalytic oxidations such as photocatalytic oxidation and use of iron salts and iron oxides in Fenton reactions have been discussed earlier. Solid catalysts have also been reported to enhance the rate of degradation when combined with other AOPs like, ozonation and cavitation. This part of the Introduction will mainly concentrate on the use of catalysts in ozonation and cavitation processes and their effect on the oxidation rates.

1.2.2.5.1 Catalysts in sonochemical reactions

The presence of solid catalysts in the form of the particles in sonochemical reactors increases the collapse events, thereby increasing the number of free radical formation. Also, by the action of ultrasound the solid catalysts are continuously polished and reduction in particle size due to mechanical action provides large surface areas for pollutants to react. Hung and co-workers discussed the enhanced reductive degradation of CCl_4 and nitrobenzene by elemental iron during sonication (Hung and Hoffmann, 1998; Hung *et al.*, 2000). The presence of solid catalysts in sonochemical reactors also alters the physical properties of the liquid medium, viz., vapour pressure and surface tension, which results in greater cavity collapse and intense radical species formation available for pollutants (Gogate and Pandit, 2004b). The use of NaCl as an additive for the enhanced degradation of aqueous pollutants has been reported (Seymour and Gupta, 1997). The presence of NaCl and $NaNO_2$ alters the distribution of the aqueous and organic phases by changing the partition coefficient due to which the concentration of organics increases at the gas–liquid interfaces, subsequently increasing the degradation rates. Moreover, salts are known to increase the surface tension of liquids and in doing so in the presence of cavitational activity, much violent cavity collapse occurs (Mahamuni and Pandit, 2006). However, the concentration of salts, the pollutant concentration, power density and operating frequency should always be considered before application (Gogate and Pandit, 2004a).

1.2.2.5.2 Catalysts in ozonation reactions

(Ma and Graham, 1997, 2000) discussed in detail the use of manganese ions in an ozonation process as a promising catalyst for enhanced degradation rates. They reported that in the presence of Mn ions, the O_3 is utilised efficiently by the Mn(II) ions and assist subsequent degradation and the catalyst may promote the formation of free radicals from O_3 since Mn(IV) acts as catalyst in O_3 decomposition. A small dose of Mn(II) is often recommended, however as the free radical attack is the driving mechanism in catalytic ozonation, the naturally occurring material present in effluents is always a deciding factor. In a similar study Andreozzi and co-workers (Andreozzi *et al.*, 2000a; Andreozzi *et al.*, 1998; Andreozzi *et al.*, 2001b; Andreozzi *et al.*, 1992; Andreozzi *et al.*, 2000b) studied catalytic ozonation in the presence of Mn catalyst for degradation of pyruvic and oxalic acid and reported that pH is the controlling factor in catalytic action. At pH 10, conversion of Mn(II) to Mn(III) via Mn(IV), initiates free radical formation, whereas at pH 4.7, the Mn(III)–oxalate complex is formed, which acts as a free radical chain initiator.

The above study could be adapted to provide guidelines in developing similar kinetic models for different reaction systems involving catalysts and O_3 in order to achieve high degradation rates. Moreover, optimum conditions such as O_3/catalyst loading and lower pH/temperatures/naturally occurring materials/radical scavengers may also contribute towards efficient degradation. Also, the use of hybrid AOP technologies like ultrasound, in conjunction with catalytic ozonation, offers an attractive alternative in pollutant removal.

1.2.2.5.3 Catalytic oxidation by activated carbon

Granular activated carbon (GAC) has gained immense importance for removal of organic pollutants, however use of activated carbon cloth (ACC) in removal processes showed similar or higher adsorption capacities (Brasquet *et al.*, 1999). Catalytic oxidation for wastewater treatment has also been extensively studied in the integrated processes such as metal oxide catalyst/GAC/H_2O_2 for dye wastewater (Lin and Lai, 1999); GAC/H_2O_2 treatment of 4-chlorophenol (Huang *et al.*, 2003); AC/O_3 treatment for gallic water (Beltran *et al.*, 2006) and bagasse ash and wood charcoal ACs have been effectively used to remove phenol (Mukherjee *et al.*, 2007). Combined AOPs such as O_3–BAC (biological AC), UV/O_3–BAC, TiO_2/UV/O_3–BAC (Li *et al.*, 2005) and CWAO–Fe/AC (Quintanilla *et al.*, 2007) for removal of organic pollutants from secondary effluents have also been reported in recent literature.

Pre-treatment of AC by oxidants like, H_2O_2/HNO_3 on pentachlorobenzene (P5CBz) was studied and results suggest that certain functional groups such as carboxyl and hydroxyl were formed on the surface of the AC. It was inferred that the hydroxyl groups act on the dechlorination of P5CBz and the oxygen functional groups arising from the HNO_3 treatment helps in the destruction of P5CBz (Takaoka *et al.*, 2007). Similarly, when AC is pre-treated with O_3 the chemical and textural properties are altered. Also, as a rule the O_3 treatment, at room (25 °C) or even higher (100 °C) temperatures give rise to the surface oxygen groups (SOG). However, at the same time it is worth noting that at 25 °C, only primary carboxylic acids are formed on the surface of AC but at higher temperatures (100 °C), a more homogeneous distribution of carboxylic, lactonic, hydroxyl and carbonyl group formation, which in turn increases the adsorptive capacity of AC at elevated temperatures, has been reported (Alvarez *et al.*, 2005).

The complete reaction mechanism of action of HO• formed on the surface of AC by AC/H_2O_2 for organic contaminant removal has been proposed (Georgi and Kopinke, 2005). AC is known to decompose H_2O_2 and subsequent reactions lead to formation of HO• (Eq. 1.13 and 1.14).

$$\text{AC–OH} + \text{H}^+\text{OOH}^- \longrightarrow \text{AC–OOH} + H_2O \qquad (1.13)$$
$$\text{AC–OOH} + H_2O_2 \longrightarrow \text{AC–OH} + H_2O + O_2 \qquad (1.14)$$

Apart from the decomposition reaction, H_2O_2 can be activated on the AC surface involving the formation of free radicals (Eq. 1.15). Similar to the Haber–Weiss reaction in the Fenton reaction, AC is considered to function as an electron-transfer catalyst. In such a case, AC and AC^+ act as the oxidised and reduced catalyst state and catalyse the decomposition of organics (Eq. 1.16).

$$\text{AC} + H_2O_2 \longrightarrow \text{AC}^+ + \text{OH}^- + \text{OH}\bullet \qquad (1.15)$$
$$\text{AC}^+ + H_2O_2 \longrightarrow \text{AC} + \text{HO}_2\bullet + \text{H}^+ \qquad (1.16)$$

1.2.2.6 Cavitation

Cavitation is the phenomenon of 'formation–growth–implosive collapse of gas or vapour-filled liquids' occurring in milliseconds and releasing energy in small pockets, called 'hotspots', at multiple locations within the liquid stream of cavitational reactors (Doktycz and Suslick, 1990; Mason and Lorimer, 1988; Suslick, 1988; Suslick, 1990; Suslick *et al.*, 1990). Although cavitation, has been classified as: acoustic, hydrodynamic, optic and particle; only acoustic and hydrodynamic cavitation have been reported for inducing effective chemical changes in any reaction. In cavitational processes, chemical degradation of pollutants occurs via two pathways:

1. Free radical attack
2. Pyrolysis

This thesis mainly concentrates on the utilisation of acoustic and hydrodynamic cavitation, as one of the major AOPs, for degradation and disinfection studies, respectively; therefore the two effective cavitation types only will be discussed in great detail in the following sections. However, the work on phenol degradation with different frequency acoustic cavitation reactors and the disinfection studies by hydrodynamic cavitation and ozonation will be dealt as separate chapters.

1.2.2.6.1 Acoustic cavitation

Acoustic cavitation is the phenomenon where cavitation is generated by the action of high frequency sound waves, usually ultrasound. The activity of compression and rarefaction cycles of the sound waves leads to formation–growth–collapse of cavitational bubbles, releasing large amounts of high temperature and high pressure zones, termed as 'hotspots'. In the literature, the range of frequencies reported for ultrasound used in degradation studies is 16 kHz–100 MHz. Based on previous research, if certain operating conditions are considered while designing a treatment technology using ultrasound, the process can be highly effective and economical for contaminant removal from wastewaters. The optimum operating conditions suggested are:

1. High ultrasonic frequencies are best suited for effective pollutant destruction, however continuous operation at high frequencies may lead to erosion of the transducers and the power input may considerably increase which may act as a limitation in large scale operations and make the process uneconomical (Francony and Petrier, 1996; Hua and Hoffmann, 1997; Hung and Hoffmann, 1999; Petrier *et al.*, 1996; Petrier and Francony, 1997a, 1997b). Multiple transducers attached on the opposite faces and irradiating with multiple frequencies produces results in higher yields of transformation. Also, dual or triple frequency US reactors minimise the problem of erosion as the cavitational collapse occurs away from the transducer surface, hence

this way multiple transducers can be placed in large volume reactors which can treat larger volumes of effluents (Sivakumar *et al.*, 2002).

2. Greater cavitational events can be achieved using ultrasonic probes with higher irradiating surfaces (Gogate *et al.*, 2001).
3. The physico-chemical properties of the liquid medium should be adjusted in such a way that the reactors produce cavitation easily and also generate cavities with lower initial size (Gogate, 2002; Gogate and Pandit, 2000).
4. Large quantities of pollutants can easily be treated with high rates at lower initial pollutant concentration, hence dilution factors should be considered before subjecting the effluent to treatment (Sivakumar and Pandit, 2001).
5. The inclusion of catalysts: TiO_2, $NiSO_4$, CCl_4, Fe^{2+}/Fe^{3+}, $CuSO_4$, NaCl and presence of gases: air, O_3, oxygen and Ar/O_3 mixtures, enhances the cavitational events by providing additional nuclei and also blocks sound wave propagation, thereby, reducing the energy dissipation into the system (Hart and Henglein, 1985; Hung and Hoffmann, 1998; Ingale and Mahajani, 1995; Seymour and Gupta, 1997; Sivakumar and Pandit, 2002).
6. Lower temperatures are often effective for cavitational events, therefore a range of 10–15 °C is preferred (Suslick *et al.*, 1997).

Although sonochemical reactors have been reported to be effective for degradation of pollutants in laboratory scale studies, degradation of real effluents on large/industrial scale by sonochemical reactors still needs a large amount of research in terms of design strategies for scale up.

1.2.2.6.2 Hydrodynamic cavitation

Hydrodynamic cavitation is the phenomenon where cavities are generated by the passage of liquid through a constriction/orifice, which creates large pressure differentials within the moving liquid and is accompanied by a number of physical effects (Gogate and Pandit, 2001; Suslick *et al.*, 1997).

Pandit, Gogate and co-workers (Gogate, 2001; Gogate, 2002; Gogate and Pandit, 2001; Gogate *et al.*, 2001) have carried out in-depth research on hydrodynamic cavitational reactors and reported that intensities generated by hydrodynamic cavitation are lower than for acoustic cavitational reactors but the design offers much more flexibility as compared to sonochemical reactors. A variety of orifice plate configurations, differing in number/size/type of holes can be used to suit a particular application of treatment. Recently, effective and economical degradation and disinfection systems have been reported where hydrodynamic cavitation is used in conjunction with other AOPs like Fenton reactions and ozonation (Chakinala *et al.*, 2007a; Chakinala *et al.*, 2008a; Chand *et al.*, 2007).

Some important optimisation parameters related to hydrodynamic cavitation are as follows (Gogate, 2002; Gogate and Pandit, 2000, 2001; Vichare *et al.*, 2000):

1. The inlet pressure into the system.
2. Geometry of the constriction/orifice.
3. Physico-chemical property of the aqueous medium.

There are not many reports regarding the use of hydrodynamic cavitation as a technology in wastewater treatment, however these equipment offer higher energy efficiencies; more flexibility in design and have higher potential for scale up compared to acoustic cavitational reactors. Despite its high industrial value, only one commercial plant, namely CAV–OX®, introducing hydrodynamic cavitation along with UV/H_2O_2 has been established by Magnum Water Technology Inc., California (http://www.epa.gov/ORD/SITE/reports/540ar93520/540ar93520.pdf) (Gogate and Pandit, 2004a).

Researchers suggest that more theoretical and experimental work is needed in this field in order to make the use of hydrodynamic cavitation a commercially feasible technology (Gogate and Pandit, 2004a). The use of modern sophisticated Computational Fluid Dynamics (CFD) to study the mean/fluctuating velocity components, Reynolds stresses, turbulent pressure fluctuations, etc. need to be investigated further. Such CFD simulations could then be used to understand the role of the above mentioned parameters in altering the cavity dynamics in hydrodynamic cavitational processes.

Overall, pilot scale case studies have shown that the process is effective enough in treating a wide range of effluents containing pentachlorophenol, benzene, toluene, ethyl benzene, xylenes, phenols and pesticides, like atrazine, but very few studies report the use of hydrodynamic cavitation in treating complex mixtures of effluents and/or real industrial wastewaters. Conclusively, it can be said that cavitation technology on its own has great potential in treating toxic pollutants where the majority of other conventional oxidation technologies fail to do so.

1.3 AOPs used in chemical oxidation of phenol

The major part of this thesis focuses on the phenol oxidation by single and combined oxidation technologies. Henceforth, a review on phenol degradation by varieties of AOP's is presented in Table 1.5 to focus on the research carried out in the past two decades and to lay the background for this novel research. Furthermore, the detailed information on the innovative technologies for phenol removal used in this study will be later discussed in separate chapter introductions.

Apart from the individual work mentioned in Table 1.5, there are some overall conclusions derived from different studies related to phenol oxidation by single and/or integrated approaches of AOPs. Photochemistry of phenol is pH dependant, given the acid–base equilibria in which these compounds are involved. Among the primary phenol photoproducts are tri-, tetra-dihydroxyphenyls, quinines and diphenols. The literature suggests that phenol photolysis at pH 3–8 over a wide light frequencies (Xe flashlamp), does not depend on the irradiation wavelength but on pH (Ho *et al.*, 1996). Recently, reported phenol degradation studies suggest that, among various AOPs, UV/H_2O_2 processes have highest rates and also phenol removal depends on pH alone with low rates in alkaline media (Esplugas *et al.*, 2002). Recently, laser-based photocatalytic oxidation using a P-type NiO semiconductor catalyst was reported for efficient fast phenol removal (0–60 min) (Gondal *et al.*, 2008). Almost complete sono-electrochemical destruction of phenol can be achieved in an aqueous medium containing 0.5 g L^{-1} NaCl at pH 6 within 20 min at 25 °C. The reaction was shown to proceed via intermediate chlorinated phenols (Parsons, 2004).

There are various other AOPs, which contribute towards effective phenol removal from water. Some of the extensively used AOPs utilised in phenol oxidation in a variety of reactor set-ups have been outlined in Table 1.5. Moreover, there have been several other AOPs which have also been suggested in the literature for effective phenol degradation: photocatalytic oxidation using titania-clay composites (Menesi *et al.*, 2008); enzyme catalysed conversion by using immobilised horseradish in a membrane-less electrochemical reactor (Cho *et al.*, 2008); use of multiwalled carbon nanotubes in CWAO (Yang *et al.*, 2007); photodegradation by phthalocyanines (Kluson *et al.*, 2008); electrochemical degradation using Gd-doped Ti-based Sb–SnO_2 anodes (Feng *et al.*, 2008); laser-enhanced photocatalytic process using semiconductor catalysts (Fe_2O_3, NiO, WO_3, TiO_2) (Gondal *et al.*, 2007); by adsorption (Ahmaruzzaman and Sharma, 2005; Vazquez *et al.*, 2007); wet H_2O_2 catalytic oxidation with Cu-zeolite and Cu-pillared clay catalyst (Giordano *et al.*, 2007); simultaneous use of O_3 with silica gel and zeolite (Sano *et al.*, 2007); by electrocoagulation (Ugurlu *et al.*, 2008); use of combined biological and photocatalytic treatment (Suryaman *et al.*, 2006); microwave-enhanced catalytic degradation over nickel oxide (Lai *et al.*, 2006); oxidative decomposition by microwave irradiation in UV/H_2O_2 process (Han *et al.*, 2004); photo-Fenton oxidation in solar reactors (Will *et al.*, 2004); solar-activated ozonation (Sanchez *et al.*, 2003); ultrasound-assisted CWPO (Nikolopoulos *et al.*, 2006); carbon-coated anatase adsorption and decomposition (Tryba *et al.*, 2004); catalytic oxidation under low temperature iron-modified cobalt oxide system (Christoskova *et al.*, 2001); by soybean peroxidase treatment (Wright and Nicell, 1999); photo-oxidation in oxygen saturated aqueous solutions by different sensitisers (Gerdes *et al.*, 1997); by homogeneous photo-oxidation in the presence of metals (Sykora *et al.*, 1997); by high energy electron-beam irradiation (Lin *et al.*, 1995); H_2O_2-mediated photodegradation studied by flash photolysis/HPLC technique (Lipczynska-Kochany, 1993).

S. no.	Reference	Oxidation Process	Highlights of the work
1.	(Bremner *et al.*, 2006)	The Advanced Fenton Process (AFP) (zero valent iron (ZVI) bars/H_2O_2)	High amounts of H_2O_2/acid/ZVI leads to extremely rapid phenol removal. 25 min was sufficient time observed in this study to remove total phenol. The AFP is a novel system of generating highly reactive HO•. During the reaction, an unknown product, tentatively named as iron-catechol salt was found to be quite resistant to further oxidation, needs further research.
2.	(Chakinala *et al.*, 2007a)	The AFP (hydrodynamic cavitation (HC)/L-shaped ZVI pieces/H_2O_2)	50–60% TOC (total organic carbon) removal after 105 min treatment time was observed by the modified AFP with an optimal 2000 mg L^{-1} H_2O_2 (oxidant) concentration and 50 pieces of L-shaped ZVI catalyst. The oxidant concentration plays a major role than the catalyst in the modified AFP. HCAFP offers a promising technology for industrial wastewater treatment on pilot scale.
3.	(Kidak and Ince, 2007)	US/O_3/UV	Order of degradation of phenol by single and combined reactions at different pH: pH 2: US/UV/O_3 >> O_3/UV > US/O_3 > US/UV > O_3 > US > UV pH 9: US/UV/O_3 > O_3/UV > O_3> US/O_3 >US/UV > UV > US
4.	(Silva *et al.*, 2007)	Sono-photocatalytic (US/UV)/H_2O_2 system	Combined process more effective than individual sonolysis and photocatalysis. Process efficiency enhanced in the presence of H_2O_2. Ultrasound induces de-aggregation of the catalysts, thereby increasing BET surface area of the catalysts, and also accelerates mass transfer of reagents on TiO_2 catalyst and polish the catalyst surface. Enhanced HO• production due to sonolysis and H_2O_2 cleavage supports degradation.
5	(Wu *et al.*, 2001)	Photosonochemical (UV/US)/Fe^{2+}	TOC removal results reveal the synergistic effect of UV light and US. Fe^{2+} present in aq. phenol solution enhanced the TOC removal. The rate of phenol degradation increased with decreasing pH and increasing dissolved oxygen. Intermediate product formation, catechol/benzoquinone/resorcin, indicated involvement of HO• in degradation mechanism.
6.	(Entezari *et al.*,	Sonochemical	Fenton like reactions were found to be more pronounced in degradation as

	2003)	oxidation in new cylindrical reactor	compared to when H_2O_2 added alone. The order of reactivity for phenol oxidation by the combined method was 35>500>20 kHz. Thus, it can be seen that degradation rate is more by cylindrical reactor at lower frequency. Therefore, it is recommended that geometrical parameters in overall efficiency should be taken into account in general assessment of process. 20/500 kHz take 200–360 min and 35 kHz take 80–240 min time to completely degrade phenol and its by-products, respectively.
7.	(Mahamuni and Pandit, 2006)	US/O_3/additives (NaCl, CCl_4)	Additives like salts and CCl_4 enhance rates of phenol degradation. Pollutants, phenol and CCl_4, are degraded simultaneously with higher rate of overall COD reduction. Enhanced rates can be achieved when higher amounts of additives used. The additives break the phenol to easily degradable products. In US/O_3 process, the degradation rate is much faster with ozonation alone.
8.	(Beltran *et al.*, 2003)	Heterogeneous catalytic ozonation	Fe, Ti and Co metal catalyst on alumina prepared by impregnation/calcination leads to complete TOC mineralisation in 5 h during catalytic phenol ozonation. Co/Al_2O_3 led to fastest mineralisation rate. However, leaching of the metal is the biggest limitation in their use. In the AC–O_3 process, the rate of TOC mineralisation was same as Fe and Ti catalysts in 5 h. However, increase in temperature, gas concentration and mass of carbon may lead to increased TOC mineralisation. The reaction mechanism proceeds by the formation of HO• in solution, generated from adsorbed entities on the AC.
9.	(Polaert *et al.*, 2002)	Adsorption–oxidation process on activated carbon	The activated carbon used in the study acts as adsorbants in the first step and as oxidants in the second step of the study at moderate temperatures for treating highly concentrated effluents. However, the integrated system offers great potentials in treating diluted phenolic wastewaters. Presented studies are relevant for moderate flowrates, therefore much optimisation is needed for the high flowrate when the adsorption is still in process. In order to make this process industrially feasible, economical aspects should be taken into account.

Table 1.5: Review of current research on phenol oxidation studies with single and combined AOPs.

1.4 Aims and objectives of this thesis

The aim of most AOPs is to produce HO• in water and the amount and types of generation of these free radicals is mainly dependent on the single and combined AOPs, e.g., the oxidation of wide range of organic compounds by HO• is 10^9 faster than O_3. Once the free radicals are introduced to the system by photolysis, O_3, H_2O_2, heat ultrasound, etc., a series of chain reactions is initiated which makes the system more complex and prediction of all the products of oxidation becomes difficult. Therefore, in order to understand the radical formation and associated chemistry in sonochemical and hydrodynamic cavitational reactors, extensively studied in the work, the first objective was to estimate the HO• production in these cavitational reactors.

Secondly, the potential use of zero valent metal powdered/solid catalysts (instead of classical iron salts) in Fenton-type reactions, termed the Advanced Fenton Process (AFP) (Bremner and Burgess, 2004; Namkung *et al.*, 2006), which has recently been patented and reported in the literature for phenol oxidation, has been explored in this work with the novel approach of usage of types of zero valent catalysts ZVC (i.e., iron (ZVI) and copper (ZVCu)). Also, the use AFP has been extensively studied in sonochemical and silent reactions and a number of novel reaction mechanisms and hypotheses have been proposed.

Thirdly, the use of activated carbon cloth (ACC) in phenol adsorption–oxidation is explored in conjunction with oxidants such as O_3 and H_2O_2 and variety of reactor set-ups.

Finally, the use of hydrodynamic cavitation and ozonation were employed to study natural water disinfection in a newly designed Liquid Whistle Reactor (LWR) set-up.

Thus, the presented thesis mainly focuses on three **D's**: **D**osimetry (Chapter 3), **D**egradation (Chapter 4–6) and **D**isinfection (Chapter 7). The research described herein may be considered interdependent.

Specific contents/objectives of each Chapter are:

Chapter 2: General experimental

- synthetic wastewaters for degradation and disinfection
- laboratory scale cavitational reactor set-ups
- analytical methods: triiodide; phenol; TOC; pH; GC–MS; UV–vis; H_2O_2; O_3; bacterial plate count

Chapter 3: Dosimetry: Investigation of oxidation intensities in cavitational reactors

- to study the oxidation capacity of different chloroalkanes (CH_2Cl_2, $CHCl_3$, $CHCl_4$; 5.25 g L^{-1}), chloroalkane concentrations and different pressures (500, 1000, 1200, 1500 psi) in the LWR
- to study the effect on oxidation rates of different concentrations of CH_2Cl_2 in US bath
- to study the oxidation capacity of different chloroalkanes (CH_2Cl_2, $CHCl_3$, $CHCl_4$; 7 g L^{-1}; 50% amplitude) and oxidation capacity of CH_2Cl_2 (5.25 g L^{-1}) under different amplitudes (25%, 50%, 75%) in an US probe reactor
- to carry out a comparative study between US and HC reactors for oxidation capacities

Chapter 4: Degradation I: Phenol removal using multiple frequency US reactors

- assess the H_2O_2 production in the chosen low-and high-frequency US reactors
- optimisation of parameters for enhanced phenol degradation in the presence and absence of air, H_2O_2, US, ZVI
- assess the efficacy of different ZVI and ZVCu catalysts in conjunction with H_2O_2 and ultrasound (20, 300 and 520 kHz) in the process of phenol degradation
- compare the efficiency of oxidants, H_2O_2 and O_3 with the AFP for phenol degradation in high frequency US (300 and 520 kHz) reactors

Chapter 5: Degradation II: Latent Remediation using the Advanced Fenton Process

- to study the effect of low and high frequencies (20, 300 and 520 kHz)
- to assess the presence and absence of oxidant (H_2O_2) and catalysts (ZVI and ZVCu)
- to compare the effects of ZVI and ZVCF, ZVCT, ZVCP catalysts
- to study the effects of low (0.6 g L^{-1}) and high (5 g L^{-1}) catalysts amounts
- to assess the US irradiation and stirring input time (15–30 min)
- to assess the efficacy of filtered and unfiltered catalyst LR reactions

Chapter 6: Degradation III: Investigation of activated carbon cloth and oxidants for phenol removal via adsorption/oxidation

- to study the effect of reactor performances (peristaltic pumps, shaker bath and US bath) for ACC/oxidant systems
- to compare ACC types and amounts (ACC-Std, ACC-Cu, ACC-Ag, ACC-extra)
- to study the effect of different concentrations of hydrogen peroxide (H_2O_2: 1.19, 2.38 and 4.76 g L^{-1})
- to explore the effect pH (3, 5.5 and 9) and temperature (20, 40, 80 °C)
- to investigate types and duration of ozone (O_3) treatments (bulk and/or step-wise ozonation)
- to examine thermal regeneration and reuse

Chapter 7: Disinfection: Bacterial inactivation using cavitation and ozonation in a novel Liquid Whistle Reactor

- to study the effect of the inlet pressure into the LWR (over a range 500–1500 psi)
- to assess the effect of O_3 dosages (time of ozonation and flowrates)
- to study the effect of individual technology: HC and ozonation
- to study the effect of combined technology: HC + (single/double) ozonation
- to assess O_3 decomposition in the LWR

Chapter 2

General experimental

2.1 Dosimetry

Hydroxyl radical (HO•) generation in acoustic and hydrodynamic cavitational reactors was measured by iodide dosimeter (Chapter 3). In a typical run, 20 g L^{-1} KI solution in distilled water (dH_2O) was prepared in different volumes for the various experimental studies. Measurement of HO• in reactors was carried out with and without addition of chloroalkanes, namely chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2) and carbon tetrachloride (CCl_4), in various concentrations. The effectiveness of different chloroalkanes in terms of degree of intensification achieved was quantified by means of I^-/I_3^- dosimeter. The temperature was maintained constant at 35 ± 3 °C and 23 ± 2 °C in hydrodynamic and acoustic cavitational reactors, respectively. An external cooling bath with ice was used in order to maintain the temperatures.

2.2 Synthetic wastewaters

2.2.1 Degradation

The model pollutant phenol was chosen to create synthetic wastewater for laboratory scale degradation studies (Chapters 4–6). Throughout the study, concentration of the phenol solution was 2.5 mM prepared in dH_2O with analytical grade phenol (Fluka). The degradation rates were measured by total organic carbon (TOC) analysis (Chapters 4–6), gas chromatography (Chapter 4) and GC–MS (Chapter 6). Materials and methods for different chapters have been discussed in detail in the experimental section of individual chapters.

2.2.2 Disinfection

A dominant marker of faecal coliforms, *Escherichia coli* was chosen as the model bacterium for the disinfection studies (Chapter 7). Stock cultures were maintained by repeated subculturing on nutrient agar (CM3; Oxoid Basingstoke, UK) at 37 °C and used for viable counts. It was observed that nutrient broth with a cell concentration 6×10^7 CFU mL^{-1} (on inoculation) reached the stationary phase in 9 h as shown in growth curve (Fig. 2.1). Therefore, standard experimental cultures were prepared by loop inoculation of a colony from a source plate of the *E. coli* on 400 mL of sterile nutrient broth (CM1; Oxoid Basingstoke, UK), in a 1 L conical flask and incubated overnight at 37 °C on an orbital shaker (GallenKamp) at a speed of 180 rpm. The overnight cloudy bacterial solution (400 mL) was then mixed with dH_2O (3600 mL) to create 4 L of synthetic wastewater for disinfection studies. The viability count for every treatment was carried out by preparing the plates in triplicates using the spread plate technique.

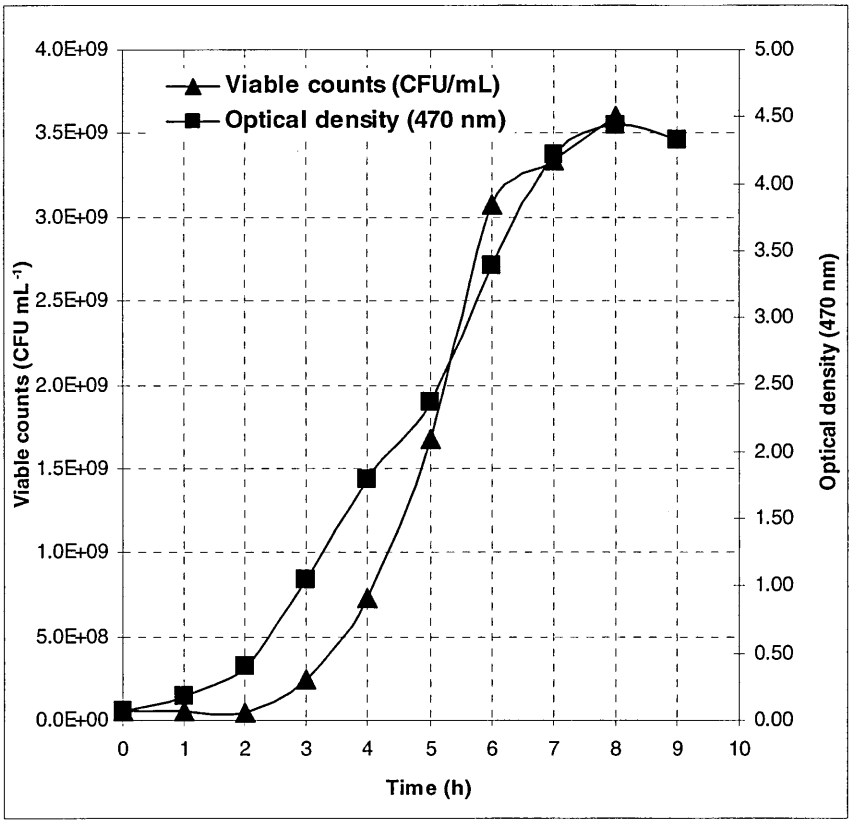


Figure 2.1: Standard growth curves of *Escherichia coli*.

2.3 Cavitational reactors

2.3.1 Liquid Whistle Reactor

The Liquid Whistle Reactor (LWR) used, for dosimetry (Chapter 3) and disinfection (Chapter 7) studies was a Benchtop Sonolator™ 2000 (Sonic Corp., CT, USA) comprising a Model A CIP Sonolator™; a plunger pump, a 2 HP motor, an Hitachi VFD inverter and a controller unit (www.sonicmixing.com). The LWR consists of a feed vessel tank with a 5 L capacity, a plunger pump (Giant Industries, Model P220A, USA) with a power consumption of 3.6 kW and having a speed of 1750 rpm and a mixing chamber comprising of an orifice (orifice area, 0.0012 sq. in.) and a blade (length, 26.8 mm; width, 22.2 mm; thickness, 1.5 mm). The pump has a maximum discharge pressure of up to 2000 psi. An acoustic intensity meter is connected to the mixing chamber to give a measure of the level of cavitation inside the chamber. The distance between the orifice and blade is adjustable and the backpressure valve connected at the end of the mixing chamber influences the inlet pressure into the system (Fig. 2.2).

The LWR is an in-line homogenizing device that employs high pressures and ultrasonic cavitational energy generated within the liquid stream by a physical phenomenon known as "jet-edge tone" (www.sonicmixing.com). A stream of process liquid is subjected to extreme pressure and shear when forced to pass through a specially engineered lip-shaped orifice and blade and the jet of liquid sheds vortices perpendicular to the original flow vector which creates oscillations similar to that generated due to ultrasound within the liquid, causing the fluid to cavitate.

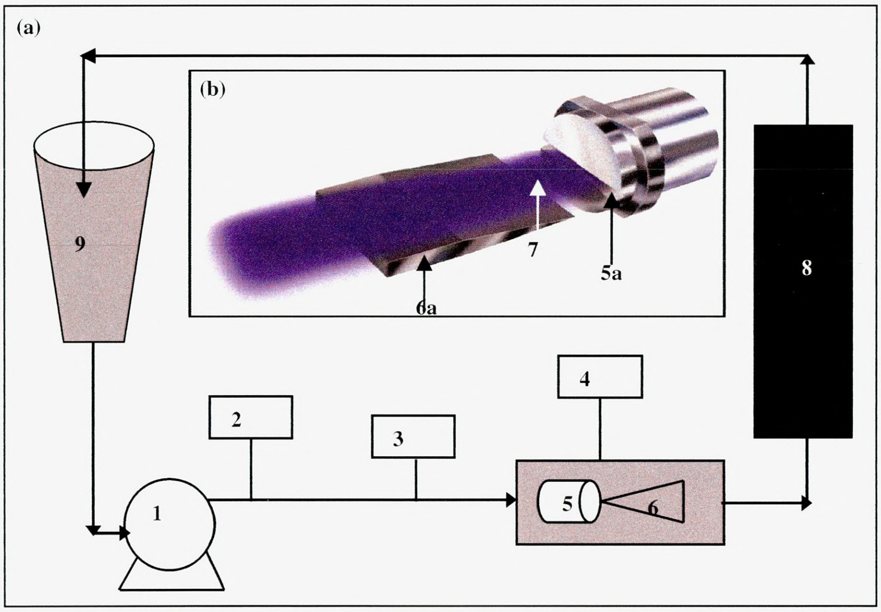


Figure 2.2: Schematic representation of (a) the LWR and (b) an expanded view of the arrangement of orifice and blade (www.sonicmixing.com): 1, Plunger pump; 2, PLC board; 3, Pressure guage (digital); 4, Pressure guage (analog); 5, Orifice; 5a, Orifice high pressure zone (expanded view); 6, Blade; 6a, Blade (expanded view); 7, Cavitation zone; 8, Cooling bath; 9, Feed tank (5 L).

2.3.2 Ultrasonic reactors

2.3.2.1 Low frequency ultrasonic probe (20 kHz)

There were two different kinds of low frequency 20 kHz US reactors were used in various studies, Unit (i) was used at the Bogazici University, Turkey and (ii) was used at the University of Abertay Dundee:

i. Sono-Fenton studies were carried out in the presence of zero valent metal/powdered catalysts (Chapter 4) in a horn type sonicator (tip diameter 12 mm) connected to a 20 kHz Bandelin Sonoplus HD2200 generator with a capacity of 180 W. The tip of the horn was submersed into the liquid from the top of an 80 mL cylindrical glass reactor. The cell was equipped with a water cooling jacket to maintain constant liquid temperature and the entire reactor set-up was enclosed in a sound proof box (Fig. 2.3).
ii. Dosimetry (Chapter 3) and Latent Remediation (Chapter 5) were performed in a commercial ultrasonic (US) processor (Cole Parmer, 400 W Model) equipped with a titanium probe (1 cm diameter) capable of operating either continuously or in a pulse mode at a fixed frequency of 20 kHz. Most of the experiments were carried out with the probe working in pulses, 4 s on and 2 s off, which allows the system to dissipate some of the heat generated by the US waves. The experiments were carried out at variable US power amplitudes (25%, 50% and 75%).

2.3.2.2 High frequency ultrasonic probes

The high frequency US reactors (300 and 520 kHz), used to study the phenol degradation in the presence of zero valent metals (Chapter 4) were used at the Bogazici University, Turkey.

2.3.2.2.1 300 kHz

A 300 kHz piezo-electric transducer located at the bottom of a 150 mL cell was connected to a generator with a maximum capacity of 25 W (UNDATIM ULTRASONICS). The cell was equipped with a water cooling jacket to maintain constant liquid temperature (Fig. 2.4).

2.3.2.2.2 520 kHz

The 520 kHz US reactor consisted of a peizo-electric transducer mounted on a titanium plate at the bottom of a cylindrical Pyrex reactor (1200 mL) with a generator capacity of 100 W (UNDATIM ULTRASONICS). The cell was equipped with a water cooling jacket to maintain constant liquid temperature (Fig. 2.5).

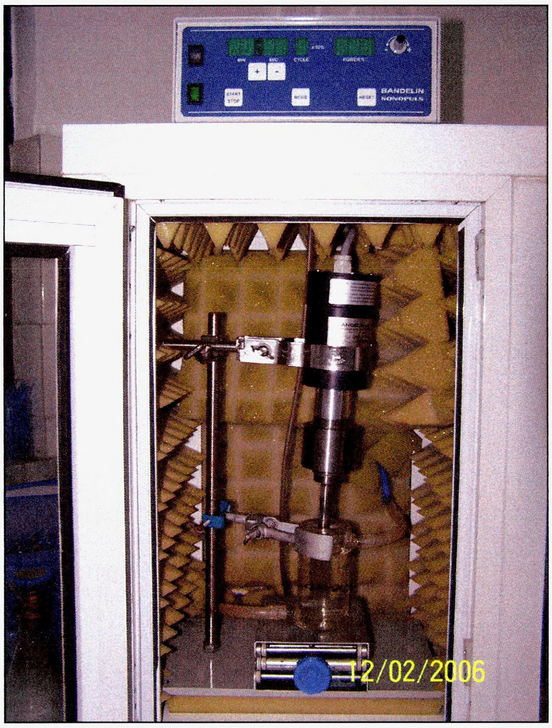


Figure 2.3: Low frequency (20 kHz) US reactor (Bogazici University, Turkey).

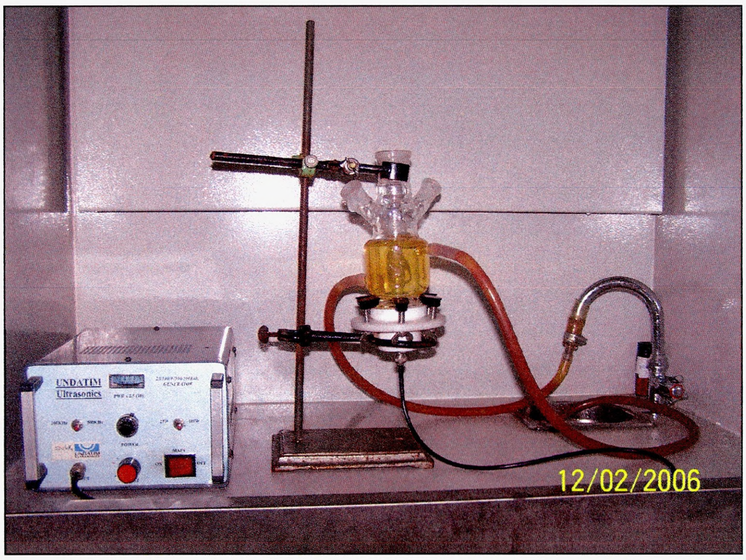


Figure 2.4: High frequency (300 kHz) US reactor (Bogazici University, Turkey).

Figure 2.5: High frequency (520 kHz) US reactor with an overhead stirrer (200 rpm) (Bogazici University, Turkey).

2.4 Analytical methods

2.4.1 Triiodide (I_3^-)

The amount of triiodide (I_3^-) production in the acoustic and hydrodynamic cavitational reaction was determined by withdrawing 2 mL samples at set times during the reaction and analysed using UV–vis spectrophotometer (Jenway 6300). Samples were returned back to reaction vessel soon after measurement. The amount of I_3^-production was determined using the molar absorptivity at 355 nm. In the case of high absorbance, the samples were diluted 5 times and absorbance was measured quickly and these diluted samples were not returned back to the reaction vessel.

2.4.2 Phenol

2.4.2.1 Quantitative analysis

2.4.2.1.1 Total organic carbon (TOC)

The removal of organic carbon was measured using a TOC analysers: TOC-VCHS (Shimadzu) in Chapter 4, whereas for Chapters 5 and 6, Model 1020A Combustion TOC (O.I. Analytical; furnace temperature, 680 °C; sample introduction loop volume, 92 μL; washing reagents: 5% v/v 85% H_3PO_4 and reagent water (dH_2O); IR signal >10000) were used.

Prior to analysis, sample (5–10 mL) was withdrawn from the reaction vessel through a 10 mL syringe and filtered using Whatman cellulose nitrate membrane filters (Schleicher and Schuell, CAT No. 7184-200; 25 mm diameter) fitted in filter holder (Fig. 2.6).

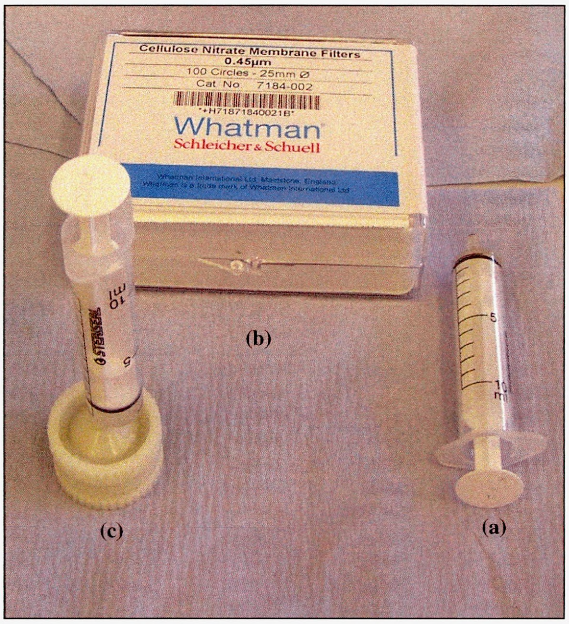


Figure 2.6: (a) Sample collection using 10 mL syringe; sample (b) filtration using Whatman cellulose membrane filters and (c) fitted on syringe and filter holder.

2.4.2.1.2 Gas Chromatography (GC)

Phenol degradation studies were also carried out using the GC analysis (Chapter 4) (Agilent Technologies, Model 6890N). Column specification: HP-5 5% Phenyl Methyl Siloxane (Aligent Cat No. 19091J-413); dimensions, 30 m (length) × 0.32 mm (inner diameter) × 0.25 μm (film thickness). Back detector, flame ionisation detector (FID); temperature, 300 °C; mode, splitless; hydrogen flow, 30 mL min^{-1}; makeup gas type, Helium.

Prior to analysis a sample (1 mL) was withdrawn from the reaction and mixed with dichloromethane (50 μL) for 3 min in a 2 mL standard GC vial which was then placed on the autosampler of the GC Machine. The extracted liquid, which settled at the bottom of the vial, was subsequently taken up by 10 μL syringe for injection into the

GC. A calibration curve (Fig. 2.7) was first constructed based on which actual phenol concentrations were estimated.

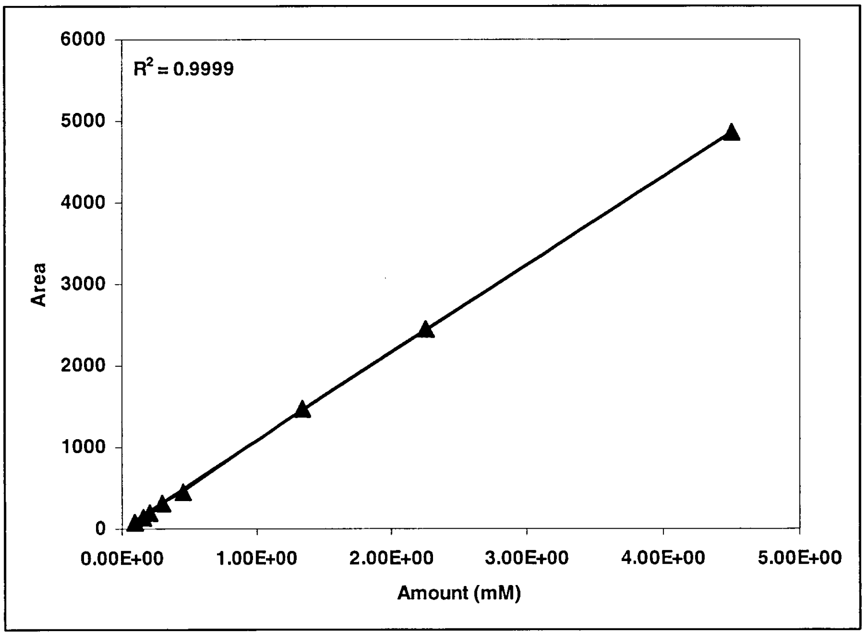


Figure 2.7: GC calibration curve for phenol analysis.

2.4.2.2 Qualitative analysis (GC–MS)

Qualitative analysis of phenol and its by-products were performed by gas chromatography–mass spectroscopy using a Shimadzu GC-2010 and GC–MS-QP2010 with autosampler (Chapter 6). The column was 35 m (length) × 2.5 mm (internal diameter) and had a 5% phenyl 95% dimethylsiloxane film coating. For aqueous phase analysis: column oven temperature, 40 °C; injection temperature, 240 °C; injection mode, splitless; end time, 17 min. GC–MS was mainly used to estimate by-products formation on phenol oxidation (if any) using activated carbon cloth in aqueous medium. Therefore, for aqueous phase analysis filtered reaction sample (1 mL) in a 2 mL standard vial, was used.

2.4.3 Hydrogen peroxide

Hydrogen peroxide was spectrophotometrically determined by the I_3^- method at 351 nm (Klassen *et al.*, 1994). For the I_3^- method, solutions A and B were prepared.

- Solution A: KI (33 g), NaOH (1 g) and ammonium molybdate tetrahydrate (0.1 g) were diluted to 500 mL dH_2O. The solution was stirred for 10 min to dissolve the molybdate and was stored in the dark to avoid oxidation.
- Solution B: this is an aqueous buffer prepared by 10 g of K_2HPO_4 per 500 mL.

The I_3^- method consists of mixing equal volumes of A and B, followed by addition of the H_2O_2 experimental solution. The absorbance of the resulting solution was measured at 351 nm in a 1 cm cuvette. In this study, 2.5 mL of A and B each was mixed in a 10 mL volumetric flask and 1 mL of H_2O_2 experimental solution was added to the mixture and volume was made up to the mark with dH_2O. Hydrogen peroxide concentration in mg L^{-1} was measured using the equation obtained from the calibration curve (Fig. 2.8).

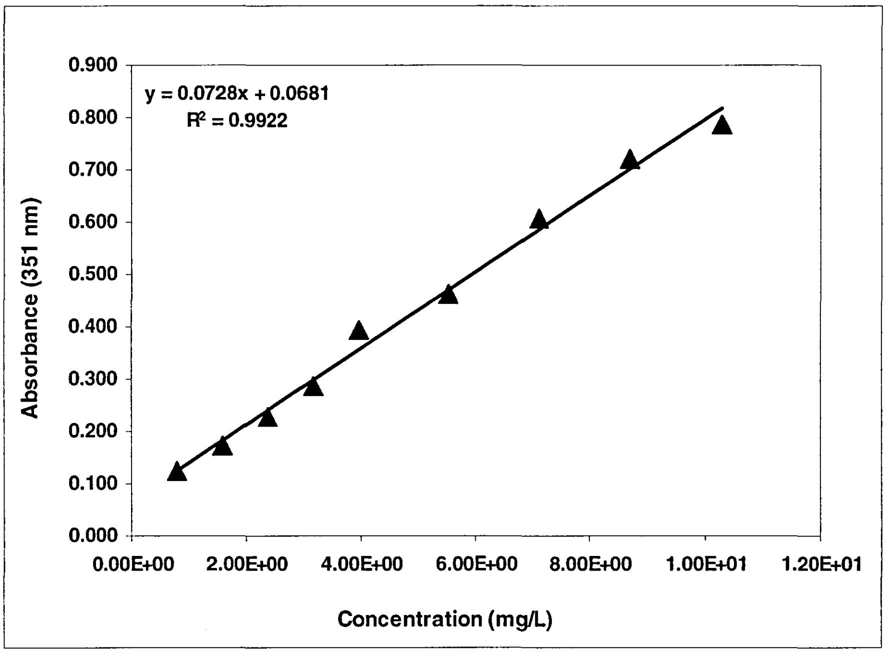


Figure 2.8: Calibration curve for hydrogen peroxide analysis.

2.4.4 Ozone

Ozonator was used from Ozone Services (Yanco Industries Ltd.) at Bogazici University (Chapter 4) and ozonator Lab2B Laboratory Ozone Generator (Ozone Engineering CA, USA; http://www.ozone-engineering.com) at University of Abertay (Chapters 6 and 7). In both the ozonators, ozone was generated by the corona discharge method with pure oxygen as feed gas. Ozone concentrations were determined by the user manuals provided by companies, whereas in different reactions, ozone concentrations were determined by indigo method (details below).

The ozone concentration in the aqueous phase was measured using the indigo-trisulfonate method (Bader and Hoigne, 1981, 1982). The proportionality constant, which is the maximum absorbance of the indigo solution at 600 nm, is 0.42 ± 0.01 L cm^{-1} mg^{-1} giving a range of application of this method of 0.05 to 0.6 mg L^{-1}. The indigo method is based on the principle that in acidic solution, potassium indigo-trisulfonate ($C_{16}H_7N_2O_{11}S_3K_3$) (Riedel-de Haën) is discoloured by aqueous ozone and the degree of discoloration is compared to a blank solution of the dye. The decrease in absorbance is linear with increasing ozone concentration.

Indigo stock solution was prepared by adding dH_2O (500 mL), conc. phosphoric acid (85%; 1 mL) and potassium indigo trisulfonate (0.770 g) to a volumetric flask and diluting to 1 L with dH_2O. A 1:100 dilution exhibits an absorbance of 0.20 ± 0.010 cm^{-1} at 600 nm and this stock solution is stable for about 4 months when stored in the dark (Bader and Hoigne, 1981, 1982).

The working solution was made up immediately before use by dilution of 25 mL of the above indigo stock solution to 250 mL with dH_2O containing 2.5 g of analytical grade sodium phosphate monobasic monohydrate (ACS Reagent 98–102%; Sigma-Aldrich) and 1.75 mL of analytical grade 85% H_3PO_4.

In the actual method of analysis, two volumetric flasks (50 mL) were taken and 5 mL of working solution was introduced into each. One flask was then filled with ozone-free water and the other with 3 mL of the ozone sample and then filled to the mark with dH_2O. The ozone sample was introduced by immersing the pipette to the bottom of the flask and gently shaking so that no ozone degassing occurred. The difference in absorption of light at 600 nm between the blank and sample was measured, within 4 h, using a UV–vis spectrophotometer (Perkin-Elmer Lambda 2) and the ozone concentration was then determined using Eq. 2.1:

$$C_{O_3} = (\Delta A \cdot V_T)/(f \cdot b \cdot V) \qquad (2.1)$$

where C_{O_3} is concentration of ozone in mg L^{-1}; ΔA, the difference in absorbance; f = 0.42 (corresponding to the absorption coefficient for aqueous ozone); b, path length (4 cm); V_T and V, the total volume (50 mL) and volume of sample added (3 mL), respectively.

2.4.5 Microorganism identification

Prior to the disinfection studies, the bacteria to be used for all the experiments was confirmed by carrying out the API 20 E test on the subcultures of *E. coli* NCIMB 10000 obtained from National Collection of Industrial, Food and Marine Bacteria (Aberdeen, UK). Using the API 20 E Test, it was found the bacteria consisted *E. coli.*

2.4.6 Viable count

The bacterial numbers in this study were determined using the viable plate count method and spectrophotometric (420 nm) (turbidimetric) analysis methods were employed. Although the two methods are somewhat similar in the results they yield, there are distinct differences. For example, the standard plate count method is an indirect measurement of cell density and reveals information related only to live bacteria. The spectrophotometric analysis is based on turbidity and indirectly measures all bacteria (cell biomass), dead or alive. The standard plate count method used in the study to estimate bacterial killing due to hydrodynamic cavitation and/or ozonation (Chapter 7), employed diluting a sample with sterile saline diluent until the bacteria are dilute enough to count accurately. That is, the final plates in the series should have between 30 and 300 colonies. Fewer than 30 colonies are not acceptable for statistical reasons and more than 300 colonies on a plate are likely to produce colonies too close to each other to be distinguished as distinct colony-forming units (CFUs). The assumption is that each viable bacterial cell is separate from all others and will develop into a single discrete colony. Thus, the number of colonies should give the number of bacteria that can grow under the incubation conditions (37 °C) employed. A wide series of dilutions (e.g., 10^{-2} to 10^{-10}) were plated because the exact number of bacteria was usually unknown. Greater accuracy was achieved by plating duplicates or triplicates of each dilution. After 24 h incubation period, the 30–300 CFU plates were separated and surviving bacterial colonies were carefully counted by placing the plate on a colony counter. The percentage disinfection was calculated as described in Eq. 2.2.

$$\text{percentage disinfection} = \log\left((N_0 - N)/N\right) \times 100 \qquad (2.2)$$

where, N_0 represent initial microbial count and N represent microbial count at any given time.

2.4.7 Power measurement

Approximate power measurements in the US reactors were carried out without any cooling system and measuring the temperature rise on irradiation for a specific time period ($\Delta T/\Delta t$). The slope of the graph (time vs temperature) was used in Eq. 2.3 to calculate power (Watts) dissipation in US reactors. The power (Q) was calculated using formula shown in Eq. 2.3:

$$Q = cm\,(\Delta T/\Delta t) \qquad (2.3)$$

where, m is mass of water (g); c is specific heat of water (4.186 joule g^{-1} $°C^{-1}$); ΔT is change in temperature (°C) and Δt change in time (s). Unit is Watt (W). The values obtained in watts were divided by the volume of the reactant used, which finally gives the final power output (heat dissipation) in Watt per millilitre (W mL^{-1}).

2.4.8 Toxicity analysis

Toxicity evaluation was carried out on some samples (in Chapter 5) by Dr. Andreas Tiehm's team at Karlsruhe University, Germany. They determined the toxicity through (i) the bioluminescence test and (ii) by monitoring biological oxygen consumption of sonicated samples. (i) The bioluminescence test was performed with *Vibrio fisheri* according to the European standard procedure EN ISO 11348. The marine bacterium *V. fisheri* emits light during physiological activity. A decreasing light intensity is correlated with an increasing toxicity of the sample tested. (ii) In order to study the biodegradability of the sonicated samples, mineral salts suitable for microbial growth were added and the pH was adjusted to 7.0. Inoculation was done with activated sludge obtained from a municipal waste water treatment plant, and biological degradation was monitored in a respirometer at 20 °C. Toxicity of the sonicated samples was measured by diluting the samples. The dilution factor resulting in a 20% and 50% reduction (EC20 and EC50) of bioluminescence was determined. A higher EC20 or EC50 corresponds to a lower toxicity (Tiehm and Neis, 2005).

2.4.9 Statistical analysis

All experiments were performed in duplicates and/or triplicates and the average results were recorded. Standard deviation of the data points from the mean was also calculated. Multiple analysis of variance (MANOVA) was performed for multiple comparisons. *P*-values <0.05 were considered significant. MANOVA was carried out using MINITAB 15 software.

2.4.10 Cost and energy consumption analysis

This study is presented as an Appendix A and attached at the back of the thesis. This includes the formula, calucations and estimated cost and energy used in the cavitational reactors while carrying out **D**osimetry, **D**egradation and **D**isinfection studies. The cost is estimated in the form of cost per unit volume (£/L) and cost per unit generation/reduction/Log_{10} reduction presented as £/HO• generation, £/g TOC reduction and £/Log_{10} reduction, respectively.

Chapter 3

Dosimetry: Investigation of oxidation intensities in cavitational reactors

Published paper (Appendix B)

Chakinala, A.G., Gogate, P.R., Chand, R., Bremner, D.H., Molina, R. and Burgess, A.E. 2008. Intensification of oxidation capacity using chloroalkanes as additives in hydrodynamic and acoustic cavitation reactors. *Ultrasonics Sonochemistry*. 15(3): pp.164-170.

Platform presented paper: UK National Conference

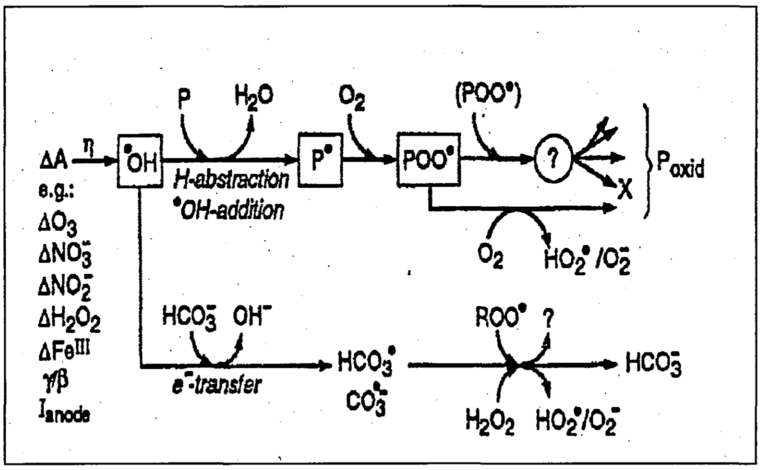
Chand, R. (18–20th April 2007). Enhanced oxidation using haloalkanes as additives in hydrodynamic and acoustic cavitational reactors. *8th IWA UK Young Water Professional Conference*. University of Surrey, Guildford, England.

3.1 Introduction

Hydroxyl radicals (HO•) are the most potent oxidants that control virtually all AOPs currently applied in wastewater technologies. HO• are produced in-processes such as:

- photolysis of hydrogen peroxide (H_2O_2), aqueous chlorine, nitrate, nitrite or dissolved aqueous iron (III) ions
- Fenton reactions or by ionising radiation
- decomposition of aqueous ozone by radical type chain reactions

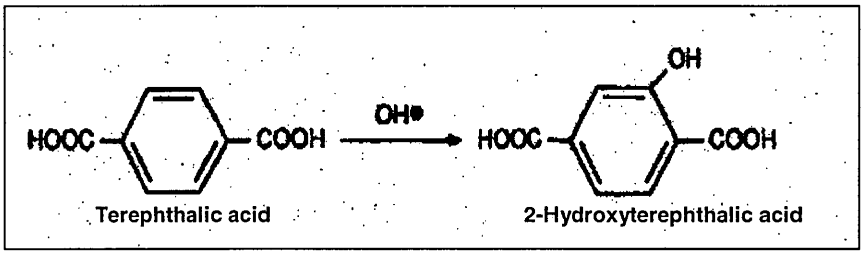
Aqueous HO• is non-selective and reacts with most organic and inorganic solutes with very high rate constants. In natural water and wastewater, they are consumed mostly through competitive reactions with a variety of natural organic matter, bicarbonate, carbonate, bromide and, even by, H_2O_2 (Hoigne, 1997). Organic radicals formed by any of these reactions may add a dissolved oxygen molecule to form peroxy type intermediates. These react further to form hydroperoxyl radicals, H_2O_2 and a series of different peroxides, aldehydes, acids, etc., thereby enhancing the oxidation rates and degradation of organic molecules (Von Sonntag and Schuchmann, 1991). In natural waters and most drinking waters, HO• are consumed with a rate constant of about 10^5 s^{-1}, i.e., the mean lifetime is only about 10 μs. Hoigne (1997) also explained the reaction kinetics through which the HO• can oxidise inorganic or organic compounds (Scheme 3.1), however the formation of the final oxidation products will depend on many different parameters.



Scheme 3.1: Hydroxyl radical initiated chains of reactions (Hoigne, 1997).

Several methods such as iodimetry (Weissler *et al.*, 1950); ESR spin trapping (Christman *et al.*, 1987); Fricke dosimeter (Miller, 1950; Price and Lenz, 1993), terphthalic acid dosimeter (Anbar *et al.*, 1966; Barreto *et al.*, 1994; Brandenburg and Moll, 1984; Mason *et al.*, 1994; Mclean and Mortimer, 1988; Mishin and Thomas, 2004; Price *et al.*, 1997), salicylic acid dosimeter (Blandini *et al.*, 1999; Chakinala *et al.*, 2007b; Floyd *et al.*, 1986; Luo and Lehotay, 1997; Teismann and Ferger, 2000), electrochemical and fluorescence detection (Liu, 1993; Mccabe *et al.*, 1997) have been proposed in order to monitor the production of HO• in aqueous media. The most generally used method for the estimation of H_2O_2 is by iodimetry, whereas ESR Spin, Fricke and terephthalate ion dosimeter is normally used for the estimation of the radical species themselves (Mason *et al.*, 1994). Moreover, in recent decades, a number of fluorescent probes such as *p*-chlorobenzoic aci (*p*CBA) (Sánchez-Polo *et al.*, 2005b) and coumarin (Louit *et al.*, 2005) have been used to monitor the HO• in various reactions involving ozone, activated carbon and radiolysis. Other recent techniques involves radical measurement by novel chemiluminescence method (Hu *et al.*, 2008).

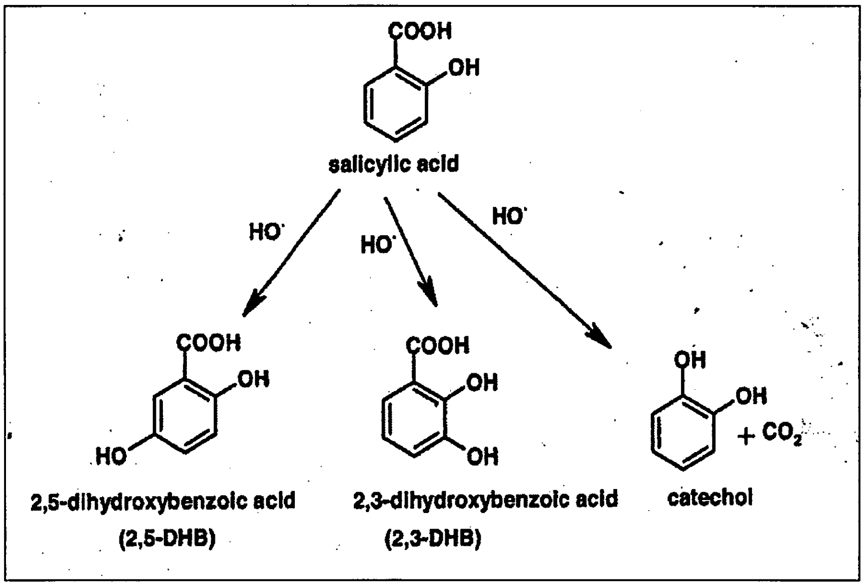
Research has been carried on the use of various dosimeters in the measurement of HO• generation in different sonochemical reactors and different reaction schemes had been proposed in the literature and presented in this study with the help of schemes taken from various research reports: terephthalic acid (Scheme 3.2) and Fricke (Fe^{2+}/Fe^{3+}) system (Scheme 3.3) (Mark *et al.*, 1998; Mason *et al.*, 1994; Price and Lenz, 1993) and salicylic acid dosimeter in acoustic (US) and hydrodynamic cavitational (HC) reactors (Arrojo *et al.*, 2007; Chakinala *et al.*, 2007b) (Scheme 3.4).



Scheme 3.2: Mechanism of the formation of 2-hydroxyterephthalic acid (HTA) from oxidation of terephthalic acid (Price and Lenz, 1993).

$$\begin{aligned}
&OH\bullet + Fe^{2+} + H^{+} \longrightarrow H_2O + Fe^{3+}\\
&H_2O_2 + Fe^{2+} + H^{+} \longrightarrow H_2O + Fe^{3+} + HO\bullet\\
&H\bullet + O_2 \longrightarrow HO_2\bullet\\
&HO_2\bullet + Fe^{2+} + H^{+} \longrightarrow H_2O_2 + Fe^{3+}
\end{aligned}$$

Scheme 3.3: Reaction mechanisms in Fricke (Fe^{2+}/Fe^{3+}) dosimeter (Mark *et al.*, 1998).



Scheme 3.4: Mechanism of the formation of 2,3- and 2,5-dihydroxybenzoic acid from oxidation of salicylic acid (Chakinala *et al.*, 2007b).

Ultrasonic irradiation in water forms HO• and H• as a result of high energies generated due to cavitational collapse and the number of these radicals depends on the cavitational energy of the system (Eq. 3.1–3.4) (Weissler, 1948).

$$H_2O \longrightarrow H\bullet + HO\bullet \tag{3.1}$$
$$H\bullet + O_2 \longrightarrow HO_2\bullet \tag{3.2}$$
$$HO_2\bullet + HO_2\bullet \longrightarrow H_2O_2 + O_2 \tag{3.3}$$
$$HO\bullet + HO\bullet \longrightarrow H_2O_2 \tag{3.4}$$

Cavities formed upon sonication of the liquid, oscillate in the sonic field and can reach very high temperatures during the compression phase or cavitational collapse as a result of which the dissolved gases, volatile material and water vapour may suffer thermal decomposition, Eq. 3.1, 3.5 and 3.6.

$$H_2O \longrightarrow O + H_2 \tag{3.5}$$
$$H\bullet + H_2O \longrightarrow H_2 + HO\bullet \tag{3.6}$$

It has been observed that among the water radicals in the solution, i.e., H• and HO•, HO• dominate over the H atoms (Hart and Henglein, 1985). This is attributed to the reaction of the hot H atoms with water vapour in the gaseous phase, which is an endothermic reaction. Due to cavitational activity, the water molecules in the cavitating bubble reacts with the originally formed H atoms and assumed to be converted to HO• (Eq. 3.6) (Hart and Henglein, 1986b) which participate in the reacting medium.

Due to limitations on the use of ultrasound on an industrial scale, hydrodynamic cavitation (HC) has been investigated as an alternative for organic pollutant degradation in variety of wastewaters. In HC, a liquid (usually water) is forced to pass through a small constriction with high velocities leading to HO• formation (Suslick *et al.*, 1997). Detailed information on the use of HC reactors and its ability to generate HO• and simultaneously degrade/disinfect wastewaters has been studied by Arrojo, Pandit, Bremner and co-workers (Arrojo *et al.*, 2007a; Arrojo *et al.*, 2007b; Bremner *et al.*, 2008; Chakinala *et al.*, 2007a; Chakinala *et al.*, 2008a; Chakinala *et al.*, 2008b; Gogate, 2001; Gogate, 2002; Gogate and Pandit, 2000; Gogate and Pandit, 2005; Gogate *et al.*, 2001; Jyoti and Pandit, 2003; Pandit *et al.*, 2005; Save *et al.*, 1997; Senthil Kumar *et al.*, 2000; Sivakumar and Pandit, 2002; Suslick *et al.*, 1997; Vichare *et al.*, 2000)

Chloroalkanes, mainly carbon tetrachloride, have been found to enhance the efficacy of both US and HC when the controlling mechanism is free radical attack (Chendke and Fogler, 1983; Mahamuni and Pandit, 2006; Parke and Taylor, 1956; Wang *et al.*, 2007; Weissler *et al.*, 1950; Zheng *et al.*, 2005). Chendke and Fogler (1983) discovered that the sonoluminescence intensity was found to increase linearly with increasing percentage saturation of CCl_4 in water. Similarly Mahamuni and Pandit (2006) reported that the use of simple additives such as salt and CCl_4 acted as process intensifying parameters, thereby reducing operational time and cost. Reports also addressed that oxidation due to ultrasonic waves increased linearly with time of irradiation in the solutions: O_2-H_2O, O_2-KI-H_2O, air-KI-CCl_4-H_2O, Ar-H_2O, N_2-H_2O, while for the first three, the rate of oxidation increased linearly with both ultrasonic power and the intensity of sonoluminescence (Parke and Taylor, 1956). Presence of

CCl_4 and perflurohexane as additives have also been found to be useful in improving pollutant degradation efficiency or improving synthetic processes that rely on HO• as a key intermediate (Zheng *et al.*, 2005). However, considering the toxicity and carcinogenicity of CCl_4, this study demonstrates the use of less toxic chloroalkanes and its comparison with CCl_4 in cavitational reactors.

As described above, over the decades various methods have been adapted to monitor the HO• in aqueous media however iodimetry has gained the most interest in indirect estimation of HO• by monitoring triiodide (I_3^-) production from potassium iodide oxidation. Likewise, in this study iodimetry and terephthalic acid dosimeter has been adopted as tools to determine the oxidation intensities in cavitational reactors. The effect of different chloroalkanes (chloroform ($CHCl_3$), dichloromethane(CH_2Cl_2) and carbon tetrachloride (CCl_4)) on KI oxidation in cavitational reactors has been investigated, and simultaneously a variety of reaction mechanisms have been proposed with respect to KI oxidation due to the presence of chloroalkanes in US (ultrasonic bath and probe) and HC (Liquid Whistle Reactor; LWR) reactors at different amplitudes (25%, 50% and 75%) and pressures (500, 1000, 1200 and 1500 psi), respectively. The scope of this study has been listed below.

Hence, the main objectives of the study were as follows:

- to study the oxidation capacity of different chloroalkanes (CH_2Cl_2, $CHCl_3$, $CHCl_4$; 5.25 g L^{-1}), chloroalkane concentrations and different pressures (500, 1000, 1200, 1500 psi) in the LWR
- to study the effect on oxidation rates of different concentrations of CH_2Cl_2 in US bath
- to study the oxidation capacity of different chloroalkanes (CH_2Cl_2, $CHCl_3$, $CHCl_4$; 7 g L^{-1}; 50% amplitude) and oxidation capacity of CH_2Cl_2 (5.25 g L^{-1}) under different amplitudes (25%, 50%, 75%) in an US probe reactor
- to carry out a comparative study between US and HC reactors for oxidation capacities

3.2 Experimental

3.2.1 Hydrodynamic cavitation (HC)

3.2.1.1 Liquid Whistle Reactor (LWR)

The LWR has a feed tank capacity of 5 L, therefore 4 L of KI solution (20 g L^{-1}) was prepared in distilled water (dH_2O) and pumped through the orifice at selected pressures. The pressures chosen for the study were 500, 1000, 1200 and 1500 psi. The additives, CH_2Cl_2, $CHCl_3$ and CCl_4 were used for the study in concentrations of 5.25 g L^{-1}. However, for the comparative study at 1500 psi, high and low concentrations of additives (CH_2Cl_2, 7g L^{-1} and $CHCl_3$, 1.75 g L^{-1}) were selected. In each 90 min reaction time, aliquots (2 mL) were withdrawn every 10 min and the rate of I_3^- production was determined using a UV–vis spectrophotometer at 355 nm. Temperatures of 35 ± 3 °C were maintained using an external cooling water/ice bath. Reported results are average values of triplicates and the experimental error was in the range of ±5%.

3.2.2 Acoustic cavitation (US)

3.2.2.1 Ultrasonic bath

Experiments were carried out using a commercial US bath (Kerry Ultrasonics Ltd., England) capable of operating at a fixed frequency of 38 kHz. In the present work, experiments were carried out in 300 mL glass beaker, immersed partially in the US bath containing cold water and ice mixture as a cooling unit and maintaining a constant temperature of 23 ± 2 °C. The reaction solution in the glass beaker contained 200 mL KI (20 g L^{-1}) solution. Only dichloromethane (CH_2Cl_2) at different concentrations (1.4–7 g L^{-1}) was used as an additive for the study and results were compared with reactions carried out without additives. In a reaction time of 70 min for each experiment, aliquots of 2 mL were withdrawn every 10 min and I_3^- concentrations were determined using UV–vis at 355 nm. Results produced are the average values of experiments carried out in triplicates and the errors were in the range of ±5%.

3.2.2.2 Ultrasonic probe

Experiments were carried out using a commercial US probe (Cole Parmer) capable of operating at a fixed frequency of 20 kHz. In the present work, experiments were carried out in 300 mL glass beaker containing 200 mL KI (20 g L^{-1}) solution. A temperature of 23 ± 2 °C was maintained throughout the reaction with the help of ice. Different chloroalkanes, i.e., dichloromethane (CH_2Cl_2); chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) were used as additives in different concentrations (1.4–7 g L^{-1}) at three different amplitudes (25%, 50% and 75%) and results were compared with reactions containing no additives. In a reaction time of 70 min, aliquots of 2 mL were withdrawn every 10 min and I_3^- concentrations (μM) were analysed using UV–vis at 355 nm. Results reported are average values of triplicate experiments and the errors were in the range of ±5%.

3.3 Results and discussion

In wastewater treatment the destruction of volatile organic compounds can be considered to occur inside the cavitating bubble which acts as a micro-reactor. The cavities may also be considered to be a source of H•, HO•, HOO• and H_2O_2 (Eq. 3.1–3.4), which further reacts with toxic pollutants and enhances degradation rates in the bulk of the solution (Riesz *et al.*, 1985; Riesz and Kondo, 1992; Sehgal and Wang, 1981). The process of pollutant degradation and oxidant generation is further enhanced by the addition of chlorinated compounds, e.g., CCl_4 and $CHCl_3$ (Korn *et al.*, 2004); NaCl and CCl_4 (Mahamuni and Pandit, 2006) and related reaction mechanisms had been proposed showing pollutant (phenol) degradation (Eq. 3.1 and 3.7–3.13).

$$CCl_4 \longrightarrow Cl\bullet + CCl_3\bullet \tag{3.7}$$
$$CCl_3\bullet + Cl\bullet \longrightarrow \bullet\bullet CCl_2 + Cl_2 \tag{3.8}$$
$$CCl_3\bullet + CCl_3\bullet \longrightarrow C_2Cl_6 \tag{3.9}$$
$$\bullet\bullet CCl_2 + \bullet\bullet CCl_2 \longrightarrow C_2Cl_4 \tag{3.10}$$
$$\text{Phenol} + Cl\bullet \longrightarrow o\text{-Chlorophenol and } p\text{-Chlorophenol} \tag{3.11}$$
$$o\text{-Chlorophenol and } p\text{-Chlorophenol} + HO\bullet \longrightarrow \text{Dihydroxybenzenes} \tag{3.12}$$
$$\text{Dihydroxybenzenes} + HO\bullet \longrightarrow \text{Small organic acids} \longrightarrow CO_2 + H_2O \tag{3.13}$$

In a separate study the effect of CCl_4 and other salts, like $MgCl_2$, have also been studied using I_3^- production from aqueous NaI solution, instead of KI solution, in the presence of high frequency ultrasonic reactors (1 MHz) (Gutierrez *et al.*, 1995) and it was reported that in the absence of CCl_4, the yield was not affected upto 1 M, however, with higher $MgCl_2$ concentrations, the I_3^- yields rapidly decreased owing to the increased viscosity of the solution. The above studies reveal that much of the research involves CCl_4 as an additive for enhancing radical generation and pollutant removal, however due to its toxicity, it is important to use an optimum concentration which is degraded on reaction completion. Consequently, the use of other additives such as $CHCl_3$ and CH_2Cl_2 has been investigated in this study. Literature suggests that addition of chloroalkanes (Hua and Hoffmann, 1996; Rajan *et al.*, 1998) enhances the radical generation through its own degradation under cavitating conditions to generate Cl• which then participates in the process of pollutant removal. The Cl• undergoes a series of recombination reactions as a result of which there are additional oxidising agents such as Cl_2 and HOCl produced which take part in the process of oxidation (Rajan *et al.*, 1998). These supplementary oxidising agents, are supposedly more stable than the free radicals hence their contribution to the process of oxidation is greater. Possible reaction mechanisms taking place due to the action of chloroalkanes under cavitating conditions and responsible for KI oxidation has been proposed as follows (Eq. 3.7, 3.14–3.21) (Chakinala *et al.*, 2008b):

$$CCl_4 \longrightarrow Cl\bullet + \bullet CCl_3 \tag{3.7}$$
$$CHCl_3 \longrightarrow Cl\bullet + \bullet CHCl_2 \tag{3.14}$$
$$CH_2Cl_2 \longrightarrow Cl\bullet + CH_2Cl \tag{3.15}$$
$$CCl_4 + Cl\bullet \longrightarrow Cl_2 + \bullet CCl_3 \tag{3.16}$$
$$Cl_2 + H_2O \longrightarrow HOCl + HCl \tag{3.17}$$
$$I^- + Cl\bullet \longrightarrow I\bullet + Cl^- \tag{3.18}$$
$$Cl^- + Cl^- \longrightarrow Cl_2 \tag{3.19}$$
$$I\bullet + I\bullet \longrightarrow I_2 \tag{3.20}$$
$$I_2 + I^- \longrightarrow I_3^- \tag{3.21}$$

The reactions in Eq. 3.7 and 3.14–3.17 are initiation reactions which contribute additional oxidising agents to the system, however Rajan et al. (1998) discussed detailed reactions mechanisms involving KI oxidation in the presence of CCl_4 and reported that the sonolysis of KI solution containing CCl_4 acts as a separate phase resulting in the formation of I_2, revealing characteristics different from those observed when KI solution was sonicated alone. The reports also accounted that the addition of CCl_4, enhanced the rate by two orders of magnitude and the rate became independent of KI concentration, the effect of gas atmosphere was reported to be less pronounced and the rate was time-dependent. Rajan also explained that the significant increase in the oxidation rate was found to be due to release of Cl_2, Cl and HOCl which acted as separate source of reactants to yield I_2 and all these quantitatively reacted in the reactor with KI, turning the rate independent of KI concentration. From the above reactions, it was confirmed that ultrasonication of aqueous KI solution is known to yield I_2 due to reaction of iodide ions with HO•, which in turn are generated due to cavitation. Based on this conceptual framework, a model has also been developed to predict the rate of iodine formation for KI solutions of various concentrations under different gas atmospheres (Naidu *et al.*, 1994). Naidu explained this with the help of the model following the growth and collapse of a gas–vapour cavity using the Rayleigh–Plesset bubble dynamics equation. His explanation suggests that the bubble is assumed to behave isothermally during its growth phase and a part of the collapse phase. Thereafter, it is assumed to collapse adiabatically, yielding high temperatures and pressures. Thermodynamic equilibrium is assumed in the bubble at the end of collapse phase. The contents of the bubble are assumed to mix with the liquid, and the reactor contents are assumed to be well stirred. The model was verified by conducting experiments with KI solutions of different concentrations and using different gas atmospheres.

3.3.1 Liquid Whistle Reactor

The capacity of a LWR to generate oxidising radicals in the presence of CH_2Cl_2 was studied at different pressures (500, 1000, 1200 and 1500 psi), however initial studies at the highest pressure of 1500 psi and no addition of chloroalkanes, showed no oxidation of I^- to I_3^-. This can be attributed to the fact that 1500 psi in the LWR is an insufficient a pressure for generating enough HO• required for KI oxidation. Suslick et al. (1997) reported that no liberation of iodine was observed below ~2200 psi even in CCl_4 saturated bulk solution which means there has to be minimum intensity of cavitation for the onset of oxidation. However, Pandit and co-workers reported a high degree of cavitation at low pressures of 14.5–101.5 psi, using a multiple orifice plate with an advanced by-pass flow system in their HC reactor set-up. They postulated that the high flowrates induced increased cavitational activity leading to higher contact of the bulk liquid with the cavitating bubbles and contributing towards enhanced oxidation (Gogate *et al.*, 2001; Senthil Kumar *et al.*, 2000; Vichare *et al.*, 2000). In the present LWR set-up, no by-pass flow line was constructed which could be a reason for reduced diffusion and mixing rates and hampered the rates of oxidation of KI in the absence of chloroalkanes. This study suggests that the design of HC reactors is crucial in achieving high rates of oxidation/degradation and also minimisation of energy consumption and cost of operation, e.g., by-pass flow and use of multiple orifice plates allowed low pressure inputs to achieve a high degree of oxidation.

The rates of KI oxidation in the presence of CH_2Cl_2 at different pressures showed a trend of increased oxidation capacity with increasing pressure (Fig. 3.1). Although the extent of oxidation seen at 500 psi was much lower than that of 1500 psi the study confirms that addition of CH_2Cl_2 in cavitating conditions has the capacity to enhance overall oxidation rates by generating HO• and other additional chlorinated oxidising species. Thus, the first objective, in this study, of introducing a less toxic chloroalkane (CH_2Cl_2), other than CCl_4, for enhancing oxidation rates proved to be successful as the amount of I_3^- production increased with increasing pressures.

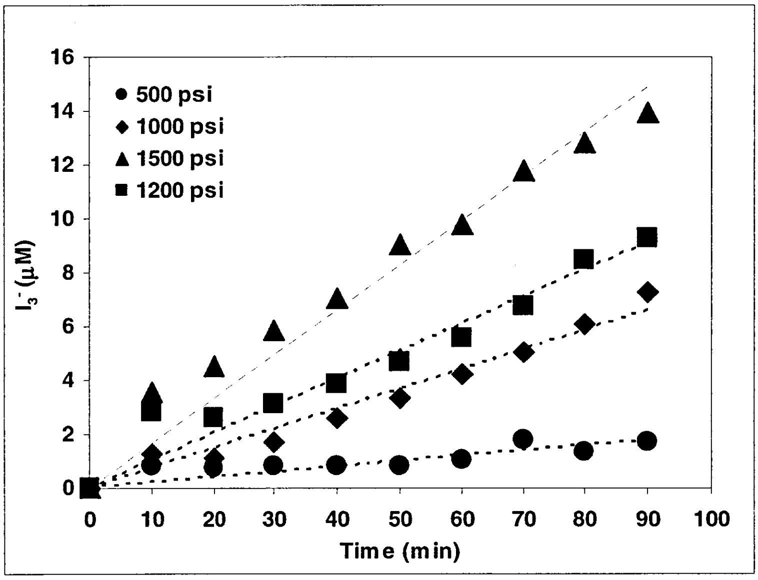


Figure 3.1: Effect of CH_2Cl_2 (5.25 g L^{-1}) on the oxidation of I^- to I_3^- in the LWR at different pressures (500, 1000, 1200 and 1500 psi). Experimental conditions: reaction volume, 4 L; KI, 20 g L^{-1}; temperature, 35 ± 3°C.

High rates of oxidation at 1500 psi can directly be contributed to high rates of cavitational events that occur at this pressure and leads to formation of more HO•, as well as formation of additional oxidants such as Cl•, Cl_2, HOCl. Thus, all the oxidising species formed in the bulk solution through different sources intensifies the oxidation of I^- to I_3^-. Moreover, higher rates of oxidation were observed during the first 10 min of the experiment because of the presence of gases which gradually degassed due to the cavitational activity. Also, at high pressures, large amounts of bubble formation and high temperatures and pressures dissociate the water and chloroalkanes in the bulk medium leading to the release of the radical species required for oxidation. The flowrate at different pressures affects the diffusion and mixing rates, thus high flowrates at 1500 psi (5.4 L min^{-1}) increases the number of passes around the cavitation zone, whereas lower pressures 500, 1000 and 1200 psi and their respective flowrates, 3.5, 4.7 and 4.9 L min^{-1}, have a milder effect on the mixing rates. Hence, contact of the radical species with the bulk solution is lowered thereby reducing oxidation rates; the rate of oxidation was 8 times higher in case of 1500 psi as compared to 500 psi

In a separate study, the effect of other chloroalkanes, i.e., CCl_4 and $CHCl_3$ were compared with CH_2Cl_2, under similar concentration (5.25 g L^{-1}) and pressure (1500 psi) conditions in the LWR (Fig. 3.2) The high rates of oxidation due to CCl_4 under similar concentration and pressure conditions in the LWR can be attributed directly to the availability of Cl• rather than HO• because at this pressure KI oxidation is supported by the same amount of HO• generated due to HC, however the dissimilarity in the amount of chlorine molecules among the chlorinated compounds used is the only factor accounting for the higher amount of additional free radicals available for oxidation in case of CCl_4 over $CHCl_3$ and CH_2Cl_2. Therefore, the rate of I_3^- production in case of CCl_4 is 2 and 6 times higher than the $CHCl_3$ and or CH_2Cl_2, respectively.

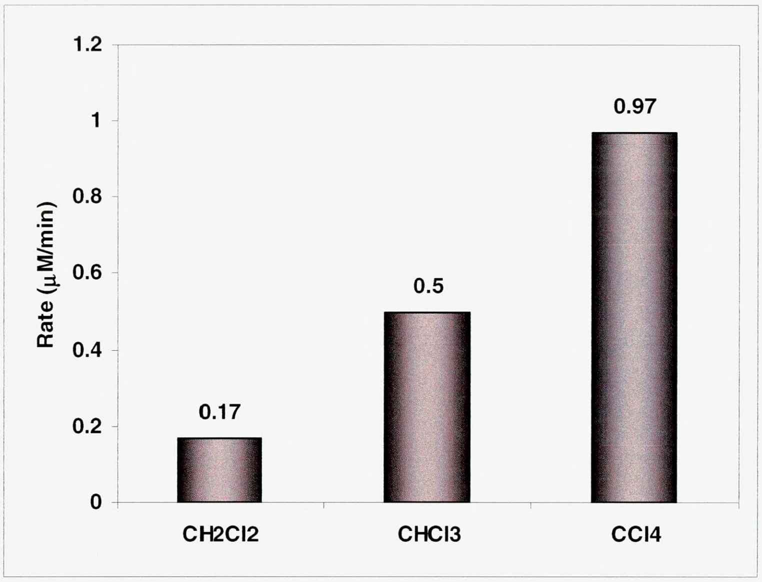


Figure 3.2: Comparative study of different chloroalkanes (CH_2Cl_2, $CHCl_3$, CCl_4; 5.25 g L^{-1}) on the oxidation of I^- to I_3^- in the LWR at 1500 psi. Experimental conditions: reaction volume, 4 L; KI, 20 g L^{-1}; temperature, 35 ± 3°C.

Use of the chosen chlorinated additives for this study is subject to environmental regulations in different countries. The study clearly shows that high rates of oxidation could be attained with CCl_4 but in the UK, it is considered to be a priority toxic pollutant and its usage is not permitted, therefore for our purposes, the use of less toxic additives such as CH_2Cl_2 could be a possible alternative for industrial purposes. However, as suggested earlier, advanced design of the HC reactors could also help in achieving higher oxidation rates (Senthil Kumar *et al.*, 2000). This would also minimise toxic chemical usage, operation cost and energy consumption in large scale operations.

As the above results reveal that CCl_4 at a concentration of 5.25 g L^{-1} lead to high rates of oxidation as compared to the other two additives, higher concentrations of CH_2Cl_2 (7 g L^{-1}) were investigated to determine if a similar degree of oxidation as CCl_4 could be achieved. Also, low concentrations of $CHCl_3$ (1.75 g L^{-1}) were compared with 5.25 g L^{-1} $CHCl_3$ to study the impact of the chosen amounts of additives on oxidation efficiencies (Fig. 3.3). Results showed that CH_2Cl_2 used in concentrations 5.25 and 7 g L^{-1} had no difference on the I_3^- production rates which directly refers to the amount of availability of Cl•. However, even lower concentrations of $CHCl_3$ (1.75 g L^{-1}) lead to increased I^- oxidation but after 30 min of reaction time, the reaction stopped probably due to exhaustion of Cl• desired for oxidation, which also indicates that additives degrade during the process of oxidation. Thus, concentrations of additives should be adjusted in such a way that it operates the dual mechanism of optimum oxidation and self-degradation, so that the treated effluent contains no residual chloroalkanes. When the above results were compared with $CHCl_3$ in 5.25 g L^{-1} concentration, the oxidation rates increased continuously probably due to availability of enough Cl• needed to maintain the continuity of I^- oxidation to I_3^- in the specified reaction time.

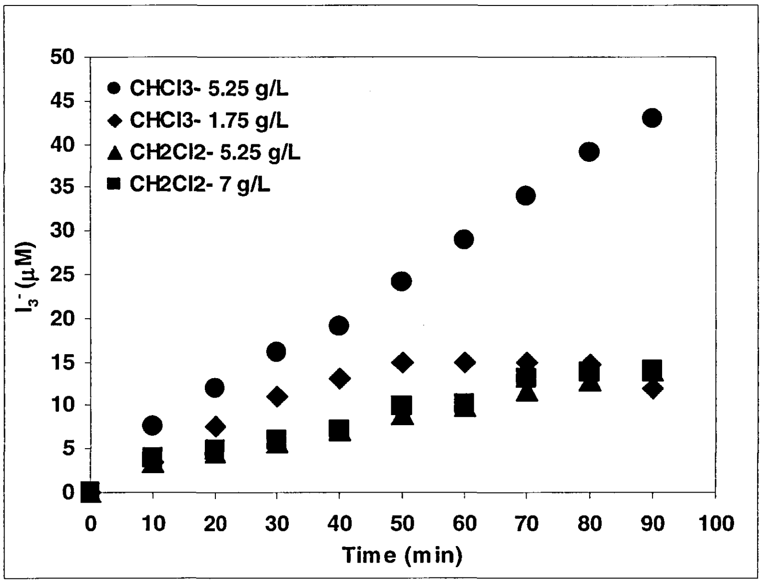


Figure 3.3: Comparative study of effect of different amounts of chloroalkanes ($CHCl_3$, 1.75 and 5.25 g L^{-1}; CH_2Cl_2, 5.25 and 7 g L^{-1}) on the oxidation of I^- to I_3^- in the LWR at 1500 psi. Experimental conditions: reaction volume, 4 L; KI, 20 g L^{-1}; temperature, 35 ± 3°C.

3.3.2 The ultrasonic bath

A US bath operating at 38 kHz inputs much less power compared to the LWR and/or US probe. Since the ultrasonic irradiations are not in direct contact with the reaction liquid, there is a reduced potential for cavitation and hence oxidation. However, studies carried out with US bath with different amounts of CH_2Cl_2 (1.4–7 g L^{-1}) showed similar results to the LWR for similar reasons as discussed above in that higher loadings of the chlorinated compound does not increase the rate of I_3^-

production (Fig. 3.4). Results also reveal that higher concentrations may lead to a decrease in I_3^- production; with increasing concentrations, the rate of I_3^- production decreased from 0.35 μM min^{-1} to 0.22 μM min^{-1}.

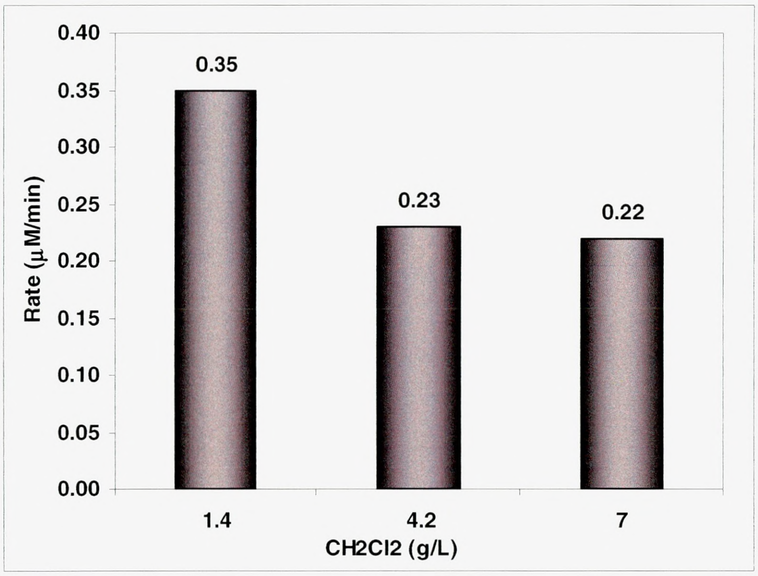


Figure 3.4: Comparative study of effect of different amounts of CH_2Cl_2 (1.4–7 g L^{-1}) on the oxidation of I^- to I_3^- in the US bath. Experimental conditions: reaction volume, 200 mL; KI, 20 g L^{-1}; temperature, 23 ± 2 °C.

Previous research in cavitational reactors reveals that other oxidants, e.g., H_2O_2, in optimum concentrations (not necessarily the highest concentrations) lead to enhanced degradation rates (Gogate and Pandit, 2004b). The reason proposed for the higher concentration of oxidants not increasing the oxidation rates was that the higher amount of unreacted H_2O_2 itself acts as a free radical scavenger thereby reducing the reaction rates. The cavitational activity in the US bath is very low, which could also be one of the reasons of lower dissociation rates of CH_2Cl_2 which contribute free radicals for I^- oxidation. Therefore, the study suggests that CH_2Cl_2 could be used as a potential additive in oxidation reactions but its usage in optimum concentration could lead to enhanced degradation rates.

3.3.3 The ultrasonic probe

3.3.3.1 Effect of US amplitudes

The US probe was operated at three different amplitudes (25%, 50% and 75%) and the results show that the rate of I_3^- production was directly proportional to the increasing amplitudes of the US probe. Initial studies were carried out with CH_2Cl_2 at the chosen concentrations and amplitudes and the results are shown in Fig. 3.5.

The results obtained with the US probe are very much in line with that of the LWR which showed that as the pressure increased in the LWR, the rate of I_3^- was increased simultaneously. Higher cavitational activities at higher frequencies and pressures contribute higher amounts of free radicals in cavitational reactors (Gogate and Pandit, 2004a). Thus, higher rates of oxidation of I^- could be attributed to the same fact. The greater rate of production of I_3^- at higher amplitudes could also be the result of the large amount of HO• production occurring due to dissociation of water molecules. Simultaneously, higher temperatures and pressures occurring due to bubble collapse in such conditions could lead to enhanced dissociation of CH_2Cl_2 and generation of additional free radicals in the system which participates in the process of oxidation. However, the results seen with three different concentrations (1.4–7 g L^{-1}) showed variable trends at different amplitudes, therefore all the results were compared at the highest chosen concentration (7 g L^{-1}) in order to estimate the effect of the chosen amplitudes as shown in Fig. 3.6 which clearly shows the KI oxidation increased with increasing amplitudes.

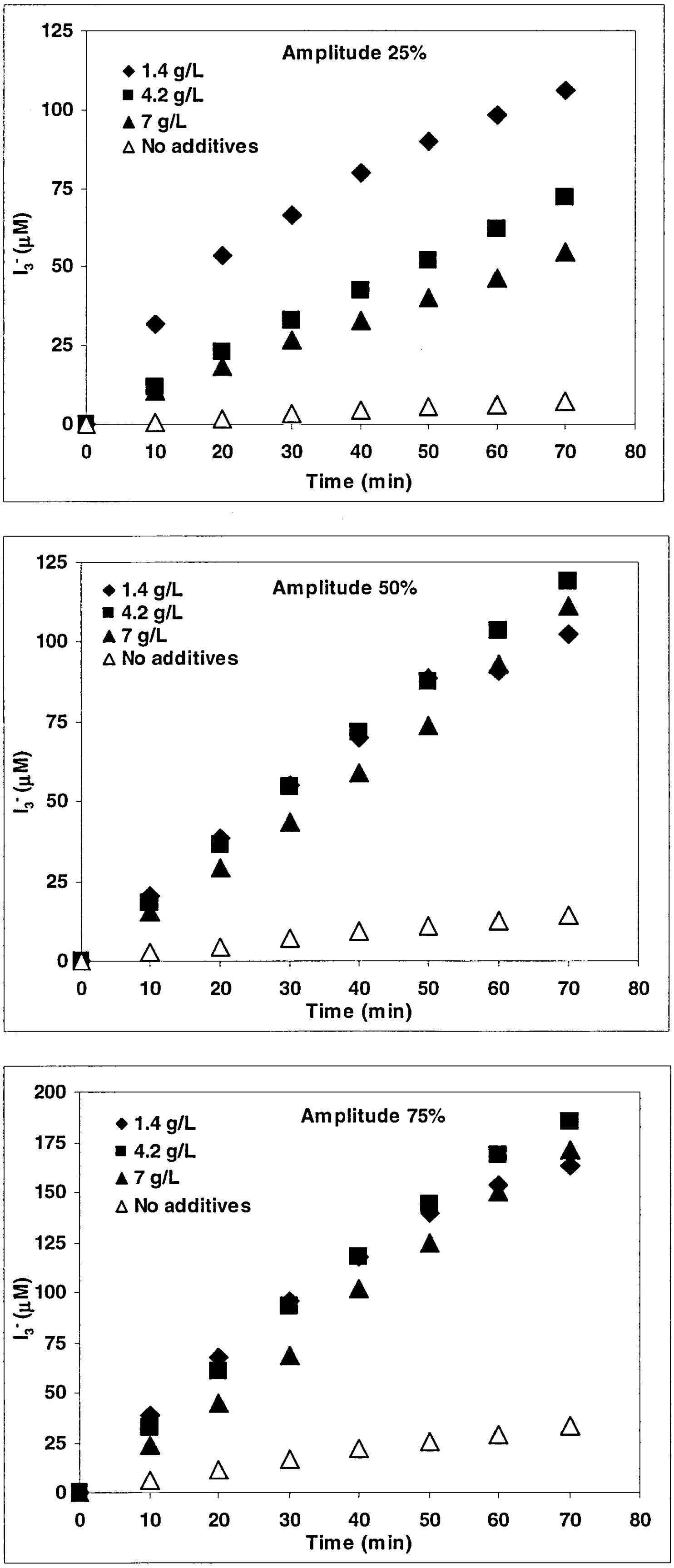


Figure 3.5: Comparative study of effect of different amplitudes (25–75%) and different concentration of CH_2Cl_2 (1.4–7 g L^{-1}) on the oxidation of I^- to I_3^- using an US probe. Experimental conditions: reaction volume, 200 mL; KI, 20 g L^{-1}; temperature, 23 ± 2 °C.

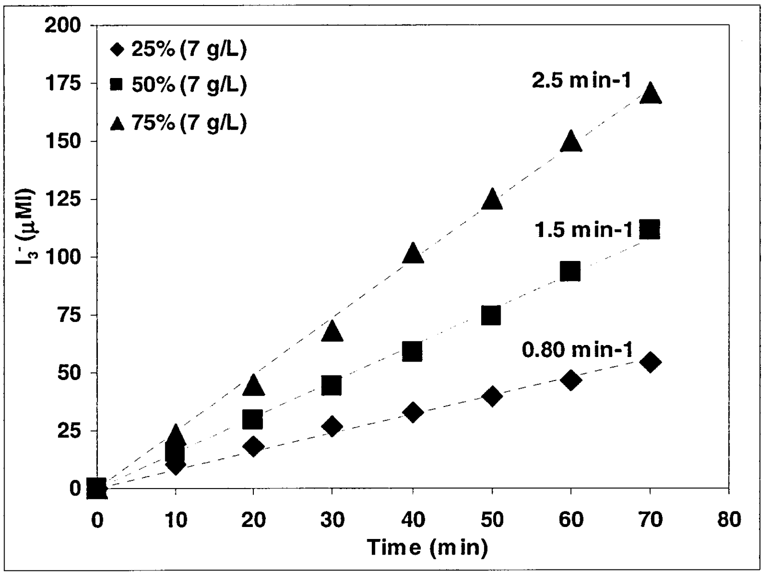


Figure 3.6: KI dosimeter using CH_2Cl_2 as additive to study the effect of different amplitudes of the US probe (25–75%) on I_3^- production. Experimental conditions: reaction volume, 200 mL; KI, 20 g L^{-1}; temperature, 23 ± 2 °C.

The phenomenon of HO• production at different amplitudes was also assessed using the terephthalic acid dosimeter (Scheme 3.2) and results obtained are in agreement with those found with the KI dosimeter, i.e., the production of free radicals increased with increasing amplitudes in the US probe. In this study, various other amplitudes such as 10%, 25%, 50%, 60% and 75% were also studied. The experimental approach was adapted from the publication by Mason et al. (1994) and a calibration curve was constructed from which the concentration of hydroxyterephthalate acid (HTA) was determined after measuring the fluorescence intensity. Reactions were carried out in a 300 mL glass beaker using 200 mL of terephthalic acid (0.5×10^{-3} mol dm^{-3}) and results were obtained by measuring the fluorescence of HTA after every 10 min over the 60 min reaction time and, using the calibration curve (Fig. 3.7).

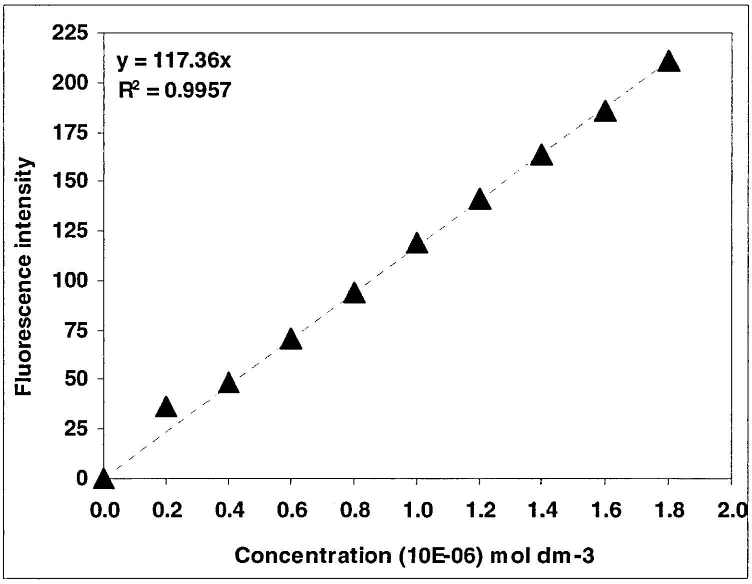


Figure 3.7: Calibration line for HTA measurement using the terephthalic acid dosimeter.

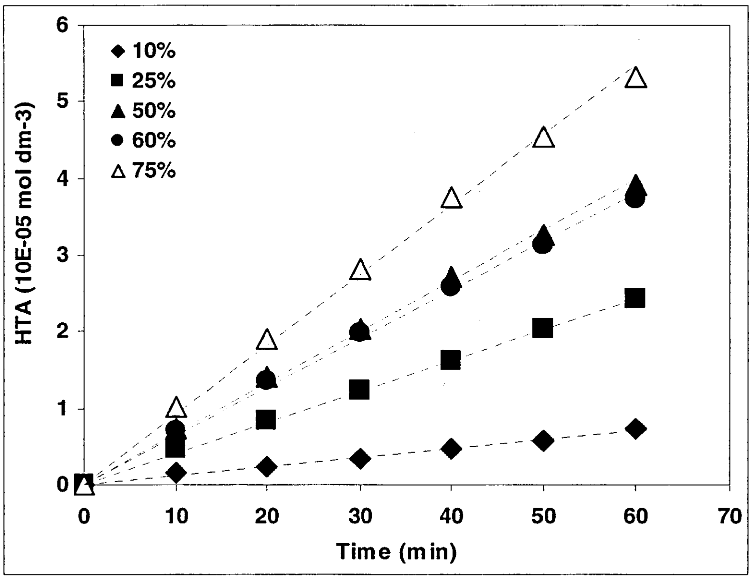


Figure 3.8: The effect of different amplitudes of US energy (10–75%) on HTA production corresponding to HO•. Experimental conditions: reaction volume, 200 mL; terephthalic acid, 0.5 × 10^{-3} mol dm^{-3}; temperature, 23 ± 2 °C.

The increase in US power that is involved in a reaction is associated with the increased cavitational effect in the system, which in turn produces more HO• and as a result greater fluorescence as more HTA is produced, i.e., the yield of HO• is directly proportional to the power input (Mason *et al.*, 1994). Increasing amplitudes (10–75%) of the US radiation showed increase in the HTA production at different amplitudes can be attributed to the increasing power dissipation at higher amplitudes (Fig. 3.8). Thus, both the KI dosimeter and the terephthalic acid dosimeter, clearly demonstrate the efficiency of the US probe at different amplitudes; increasing cavitational activities at increasing amplitudes, with increasing power entering the reaction system, leads to higher oxidation intensities in sonochemical reactors. Statistical analysis (MANOVA) also revealed the significance of amplitudes on the intensity of oxidation in US probe ($P = 0.00–0.01$).

3.3.3.2 Effect of additive concentrations

Three different concentrations of CH_2Cl_2, $CHCl_3$, CCl_4 (1.4–7 g L^{-1}) were chosen for the study and their effects on I^- oxidation were examined (Fig. 3.9a). The initial rate of I_3^- production without any additive was 10 times less than the lowest concentration (1.4 g L^{-1}) of CH_2Cl_2 but higher concentrations (4.2 and 7g L^{-1}) did not increase the rate of I_3^- production. A similar explanation, as given in Section 3.3.2, can be presented here. Also, addition of additives alters the physico-chemical properties of the liquid thereby affecting the intensity of cavitation. In such cases, it could be a possibility that the concentration of CH_2Cl_2 is higher than that of H_2O in the cavitating bubble, which may alter the surface tension affecting the bubble cloud behaviour. Such activities in turn affect the key processes like collapse and coalescence, resulting in the overall oxidation efficiency. Because of the above reasons even higher concentrations of CH_2Cl_2 could not replace the oxidation capacity of CCl_4. However, previous reviews of research on similar oxidations (Gogate and Pandit, 2004a, 2004b) suggest that if oxidants are added stepwise, the process of oxidation continues for longer, since oxidants added at several stages of the reaction continuously generate free radicals in the reaction system and the oxidation continues. In another experiment in this study (not shown), addition of CH_2Cl_2 was done in three steps without altering the concentration of the additive and results showed that I_3^- production was higher (1.1 μM min^{-1}) in the case of stepwise addition but lower (0.88 μM min^{-1}) in case of addition at the start of the experiment. This clearly indicates that continuous renewal of Cl• required for oxidation takes place when the CH_2Cl_2 is added in stepwise.

In the case of $CHCl_3$, the three chosen concentrations ranging from 1.4 to 7 g L^{-1} did not have any effect on the I_3^- production and the rates were noted to be 2.83, 2.95 and

2.79 μM min^{-1}. A similar observation as CH_2Cl_2 was seen for $CHCl_3$ in that lower concentrations had a significant effect on I^- oxidation, however the rate of oxidation was elevated as compared to CH_2Cl_2 due to the higher amount of chlorine atoms present in $CHCl_3$. Even if the cavitational activity at 25% amplitude was less, the availability of Cl• in case of $CHCl_3$ maintains the oxidation process at all the three chosen concentrations.

However, with CCl_4, the observed results were completely different from the two additives studied earlier. In this case, the increase in concentration from 1.4 to 7 g L^{-1} lead to enhanced generation of I_3^- which could be attributed to the increased amount of Cl• present in oxidation reactions with CCl_4. Fig. 3.9b shows the rates of I_3^- production three different concentrations (1.4–7 g L^{-1}) of the different additives. It is evident from the figure, that with higher concentrations of CCl_4 the rate of I^- oxidation increases, whereas the oxidation rates remain constant in case of $CHCl_3$ and CH_2Cl_2.

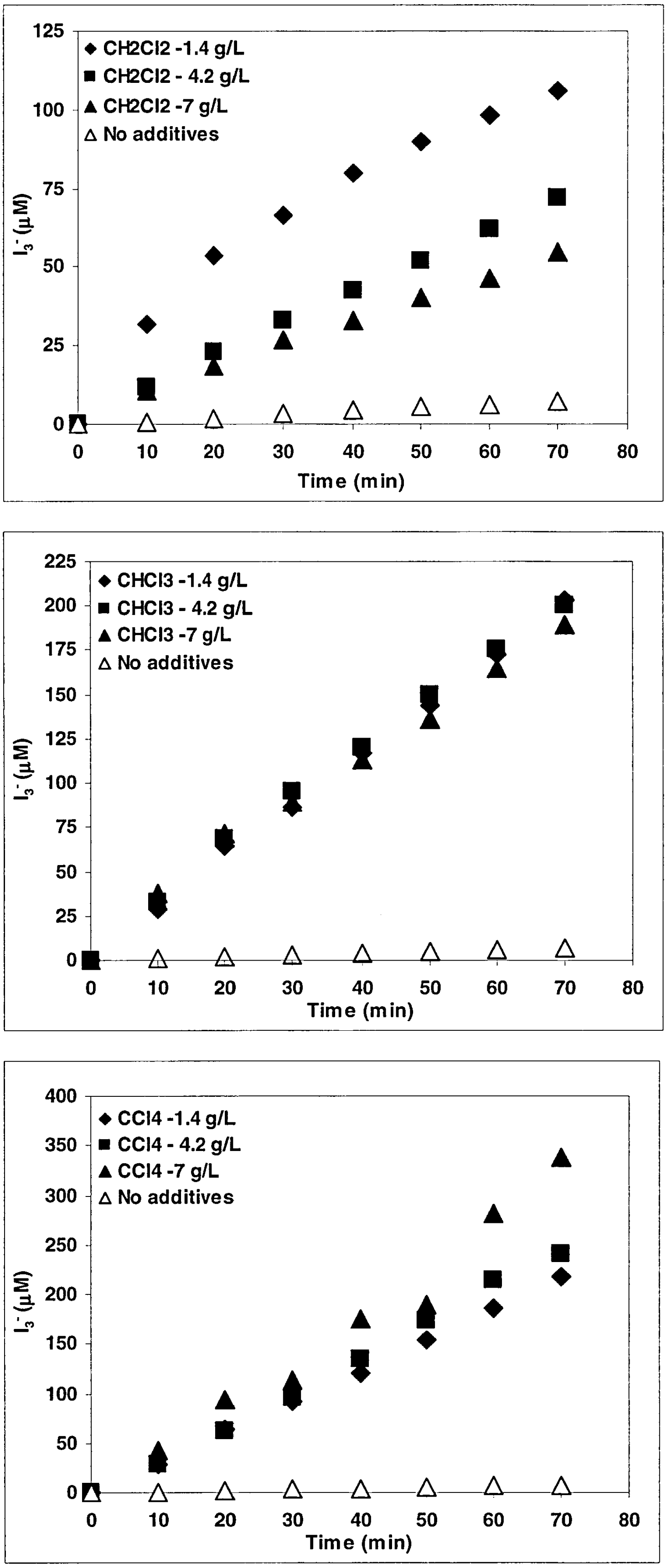


Figure 3.9: (a) Comparative study of the effect of different concentrations (1.4, 4.2 and 7 g L^{-1}) of additives (CH_2Cl_2, $CHCl_3$, CCl_4) on the oxidation of I^- to I_3^- using the US probe. Experimental conditions: reaction volume, 200 mL; KI, 20 g L^{-1}; temperature, 23 ± 2 °C; US amplitude, 25%.

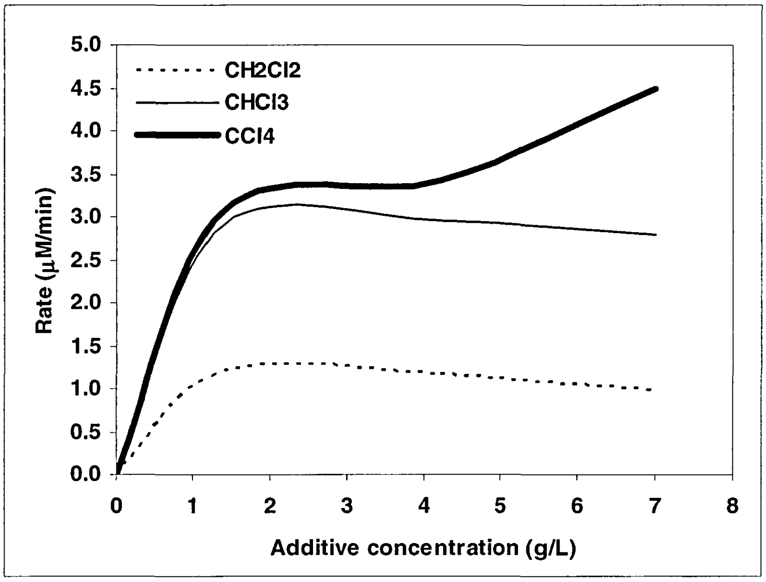


Figure 3.9: (b) Comparison of rate of KI oxidation (I_3^- production) at different concentrations (1.4, 4.2 and 7 g L^{-1}) of additives (CH_2Cl_2, $CHCl_3$, CCl_4). Experimental conditions: reaction volume, 200 mL; KI, 20 g L^{-1}; temperature, 23 ± 2 °C; US amplitude, 25%.

3.3.3.3 Effect of additives

A comparative study between different chlorinated additives (CH_2Cl_2, $CHCl_3$, CCl_4) of concentration 7 g L^{-1} on the oxidation capacity was carried out using the US probe at the lowest chosen amplitude 25% (US generator 400 W; the actual power dissipation into the solution estimated using calorimetric measurements was about 9 W or 0.045 W mL^{-1}) and results were compared with no additive under similar experimental conditions Fig. 3.10 shows that in the absence additives, oxidation of I^- was quite low and the order of effectiveness of additive used for oxidation was found to be $CCl_4>CHCl_3>CH_2Cl_2$ and quantitatively, the order of increase in the oxidation was 45>28>10 times, respectively, as compared to conditions when no additives were used.

As stated above, CCl_4 had highest oxidation capacity which can be attributed to the high amount of Cl• availability as discussed earlier and evident from previous research (Chendke and Fogler, 1983; Francony and Petrier, 1996; Petrier and Francony, 1997b). Also, amount of Cl• formed by the degradation of CCl_4 is substantially higher as compared to the other two additives. Exact quantification of Cl• was not possible but based on the oxidation–reduction concept, CCl_4 is considered to be non-reactive with the HO• in which case the reaction proceeds through a reductive process (Teel and Watts, 2002), thus the rate of I_3^- formation with CCl_4 is directly proportional to the rate of Cl• formation which is formed upon degradation of CCl_4.

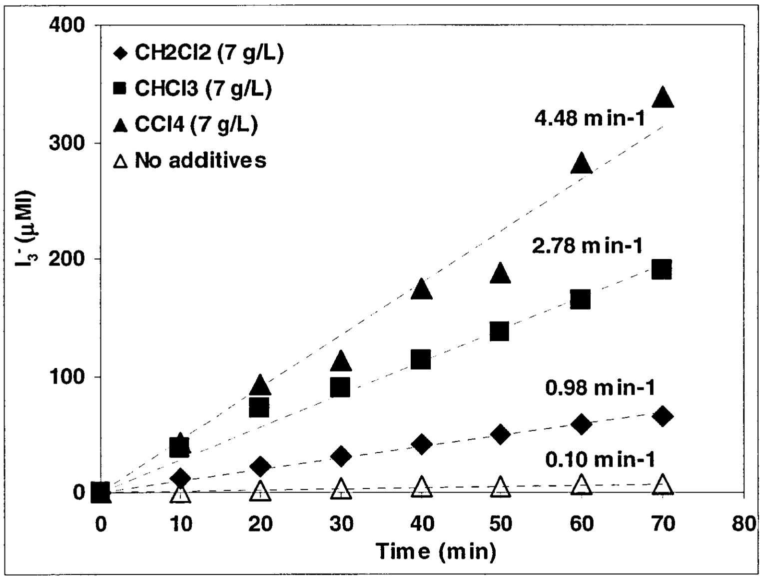


Figure 3.10: Comparative study of the effect of: CH_2Cl_2, $CHCl_3$ and CCl_4 (7 g L^{-1}) on the oxidation of I^- to I_3^- using an US probe (20 kHz). Experimental conditions: reaction volume, 200 mL; KI, 20 g L^{-1}; temperature, 23 ± 2 °C; US probe amplitude, 25%.

The results of oxidation rates obtained with US probe with the three different chlorinated compounds are similar to that of HC (LWR) which clearly indicates that efficacy of chlorinated additives have no impact of cavitational activity in these cavitational reactors. However, the concentration of the additives added have a great role to play in the oxidation reactions, as discussed above and in studies carried out previously (Rajan *et al.*, 1998). Concentration of the additives is an important factor as the activity of cavitation depends on this because the chloroalkanes do not dissolve in the aqueous iodine solution but are dispersed throughout the solution as microdroplets, which multiplies the number of nucleation sites available for cavitation. Therefore, any increase or decrease in the concentration of the chloroalkanes, relative to the bulk iodine solution, may interfere with the process of oxidation. Thus, an optimum concentration is recommended for intensification of the process of oxidation using chloroalkanes. Also, optimum concentrations would positively work to produce ideal outputs useful at laboratory or pilot scale processes:

Optimum chloroalkanes concentrations → dissociate/degrade → enhanced nucleation → generate free radicals → oxidation → leave no residues at final discharge.

3.4 Hydrodynamic vs acoustic cavitation

Pandit and co-workers carried out much work on HC reactors and reported that their efficiency is more than that of US reactors (Save *et al.*, 1994; Sivakumar and Pandit, 2002). However, in the present study, the results contradict these research findings, maybe due to the use of a different type of HC reactor. Pandit used a by-pass flow system which utilises low pressures and operates at relatively higher flowrates, which increases the passes through the cavitational zone and hence the opportunity of the pollutant/oxidant to interact with the cavities and other free radicals is also improved which helps in the process of oxidation. Whereas in this study, the HC reactor utilised high pressures and reduced flowrates resulting in lower degree of oxidation as compared to the US probe, therefore the I_3^- production was found to be 5 times more effective in case of US probe than the LWR. However, since the volume and energy utilised in the two reactors were different, a comparative study was carried out, involving the measurement of oxidation rates per unit power density which is defined as the electrical energy dissipated into the system per unit volume of the reactant and results showed that US reactors were still 2.5 times effective as compared to the HC (LWR) reactor (Pandit and Gogate, 2005).

3.5 Summary

The chloroalkanes could be termed as potential additives for enhancing oxidation reactions. In general, the use of these chloroalkanes is beneficial for the oxidation of non-volatile toxic compounds which are less susceptible to free radical attack, however the concentration of the additives should be optimised in such a way that the additive supports the degradation process and is utilised completely by the end of the reaction, so that the effluent discharge does not transfer any toxic residues of the additives to the natural environment.

Thus, from the above laboratory scale experimental study, in order achieve higher oxidation intensities in cavitational reactors, the following conclusions can be drawn:

- Advanced hydrodynamic cavitational reactor set-ups can be improved by introducing multiple orifices and by-pass flow for onset of cavitation even in the absence of chloralkanes.
- Enhanced generation of radical species could be achieved with increasing pressures in the LWR.
- The order of effectiveness of chloroalkanes for oxidation is $CCl_4>CHCl_3>CH_2Cl_2$.
- Higher concentration of additives does not favour the oxidation reaction, thus an optimum concentration, relative to the bulk solution, could achieve high oxidation rates.
- Stepwise addition of additive/oxidants could lead to higher oxidation intensities rather than addition of additives initially.
- Oxidation capacity of US probe type reactors is more effective than US bath reactors.
- Addition of CCl_4 could achieve higher rates of oxidation intensities in sonochemical and hydrodynamic cavitational reactors.
- Acoustic cavitation reactors are 2.5 times more effective, for enhanced oxidation, than the hydrodynamic cavitational reactors.

Chapter 4

Degradation I: Phenol removal using multiple frequency US reactors

Platform presented paper: UK National Conference

Chand, R. (2^{nd}–4^{th} April 2008). Phenolic wastewater treatment using AFP in multi frequency ultrasonic reactors. *9th IWA UK Young Water Professional Conference*. Newcastle University, Newcastle, England.

Poster presented: SET, House of Commons

Chand, R. (19th March 2007, Lunchtime Reception). 'Novel green technologies for wastewater treatment' at the SET for BRITAIN, Early-stage Scientist, Engineers and Technologists Poster Competition, House of Commons, London.

4.1 Introduction

Phenol and its chlorinated derivatives are used in the formulation of insecticides, herbicides and fungicides and can be found as toxic pollutants in industrial wastes. Also, phenolic compounds are common contaminants in wastewaters, being generated from petroleum and petrochemical, coal conversion and phenol-producing industries. Phenols are widely used for the commercial production of a wide variety of resins including phenolic resins, which are used as construction materials for automobiles and appliances, epoxy resins, adhesives and polyamides for various applications (Fang and Chan, 1997). The use of these substances imposes severe risks to human health and is, therefore a matter of public concern. Several cases of phenol pollution have also been reported around the world since mid-1900s. In 1974, an accidental spillage of phenol (carbolic acid) in Southern Wisconsin (USA) caused chemical contamination of wells leading to severe human illness; although physical and laboratory examinations 6 months after the exposure revealed no residual abnormality in exposed persons, however water testing and geological evaluations indicated that contamination of the underground water system may persist for many years (Baker *et al.*, 1978). Thus, phenols are considered as priority pollutants since they are harmful to organisms at low concentrations and many of them have been classified as hazardous pollutants because of their potential harm to human health. Stringent Environmental Protection Agency (EPA) regulations call for lowering phenol content in the wastewater to less than 1 mg L^{-1} (Dutta *et al.*, 1992). Similarly, the Doosan oil spill, where 320 tonnes of phenol waste from the Doosan Electro-Materials Inc. when illegally dumped in River Naktong, South Korea, affected more than 10 million homes (www.american.edu/ted/doosan). In the UK, few serious incidences of phenol contamination in major rivers, serving millions of peoples and aquatic flora and fauna, have lead to enormous concerns regarding its pollution and toxicity. For example, in 1984 and 2000 the River Dee, one of the most closely monitored waterways in Europe, was heavily contaminated by phenol due to a million gallons of toxic effluent being discharged. This incident killed a number of fishes, affected more than 2 million people in North Wales and left the water supply contaminated for several weeks (www.bbc.co.uk/wales). Such atrocious events, on the one hand increase the risk of severe environmental pollution but on the other lead to public participation and awareness toward environmental issues and demands effective treatment systems for such toxic organic compounds.

The treatment processes for phenolic wastewater is classified into two principal categories (Dutta *et al.*, 1998):

- a destructive process such as oxidation with ozone (O_3) (Hoigne, 1985) or hydrogen peroxide (H_2O_2) (Kochany and Bolton, 1992)
- a recuperative processes such as adsorption onto porous solids (Danis *et al.*, 1998), membrane separation (Mccray and Ray, 1985), or solvent extraction (Earhart *et al.*, 1977)

However, it is believed that aromatic compounds are generally, refractory to chemical and biological processes, which is why other alternative treatments have gained enormous interest from researchers worldwide (Esplugas *et al.*, 2002; Gogate and Pandit, 2004b). **A**dvanced **O**xidation **P**rocesses (AOPs) are considered as alternative technologies in order to treat such toxic wastewaters, as these processes have the capacity to generate hydroxyl radicals (HO•) which are one of the most powerful oxidising agents and, as discussed in Chapter 1, they have the highest oxidation potential of any species used in wastewater treatment technologies.

Among the various AOPs discussed in detail in Chapter 1, sonochemistry has been demonstrated as a promising method for the destruction of aqueous pollutants (Cheung *et al.*, 1991; De Visscher *et al.*, 1997; Destaillats *et al.*, 2000; Joseph *et al.*, 2000; Laughrey *et al.*, 2001; Mckee *et al.*, 1977; Peller *et al.*, 2001; Taylor Jr *et al.*, 1999; Wheat and Tumeo, 1997). Ultrasonic irradiation generates cavitation bubbles which oscillate between growth and collapse through compression and rarefaction (Joseph *et al.*, 2000; Peller *et al.*, 2001). The temperatures and the pressures in these collapsing bubbles are estimated to be 3000–5000 K and 500–10,000 atm, respectively (Flint and Suslick, 1991; Suslick *et al.*, 1993a; Suslick *et al.*, 1993b). Under such extreme conditions of temperature and pressure, water molecules dissociate to form highly reactive HO• and hydrogen atoms (H•) as also discussed previously in Chapter 3 (Chen and Smirniotis, 2002; Makino *et al.*, 1982; Misik *et al.*, 1995; Suslick, 1990; Suslick *et al.*, 1986). Other oxidising radicals also tend to form depending upon the nature of gases and other solutes present in the medium (Kang *et al.*, 1999a; Thompson and Doraiswamy, 1999). Several mechanisms have been proposed for sonochemical degradation of aqueous pollutants(Hoffmann *et al.*, 1996; Laughrey *et al.*, 2001):

- oxidation by hydroxyl radicals (HO•)
- pyrolytic decomposition
- supercritical water oxidation
- combustion

The above mechanisms are likely to happen in the gas phase inside the collapsing bubble, at the gas–liquid interface and in the reaction solution which surrounds the bubble (Laughrey *et al.*, 2001; Taylor Jr *et al.*, 1999). However, the efficacy of the sonochemical degradation process depends on many other factors such as irradiation frequency, input energy, dissolved gases and aqueous additives (Beckett and Hua, 2001; Kang *et al.*, 1999a; Laughrey *et al.*, 2001; Peller *et al.*, 2001; Taylor Jr *et al.*, 1999). Since the oxidation by HO• is an important reaction pathway in sonochemical reactions, the degradation efficiency is directly proportional to the amount of HO• generation. The following reaction pathways have been proposed, where HO• either recombines, reacts with other gaseous species or diffuses into bulk solution to react with solutes present in the reaction medium (Laughrey *et al.*, 2001):

$$HO\bullet + H\bullet \longrightarrow H_2O \qquad (4.1)$$
$$HO\bullet + HO\bullet \longrightarrow H_2O_2 \qquad (4.2)$$
$$HO\bullet + \text{other species} \longrightarrow \text{oxidised products} \qquad (4.3)$$

Equations 4.1–4.3 are generally competitive in the sonochemical degradation process and the second order rate constants of Eq. 4.1 and 4.2 are 7×10^9 M^{-1} s^{-1} and 4.2×10^9 M^{-1} s^{-1} and it is believed that under most circumstances Eq. 4.3 has a similar rate constant. However, the local concentration of all the above mentioned species can play a very important role in controlling the actual rate of each process. Moreover, as discussed earlier in Chapter 3, the role of chlorinated additives, Fe^{2+} and Fe^0 have been found to be very efficient in increasing the overall degradation rates in sonolytic system (Hung *et al.*, 2000).

In wastewater treatment, a bubble of cavitation acts a micro-reactor for degradation processes (Riesz *et al.*, 1990). Literature also states that there is little effect of frequency on the rate of sonochemical reactions for oxidation and reduction in aqueous solution (Witekowa, 1972). Consequently, there have been a lot of controversial findings in earlier reports until dosimetry studies confirmed the effect that different frequencies had on the production of oxidising radical species. Table 4.1 summarises previous reports on the effect of different frequencies on rates of oxidation and oxidising radical production. It is quite obvious that with increase in frequencies higher oxidation rates could be achieved, however determining the sononchemical efficiency is a combined output of sonochemistry and cavitation. Bubble formation and behaviour is linked with the sound pressure field which depends on reactor design and ultrasonic source (frequency, intensity and emitting surface area). Therefore, the yield of an ultrasonic reaction may be enhanced with a well-defined reactor configuration and modified US frequencies (Boucher, 1970; Leighton, 1995).

US frequencies	Research highlights	References
20–60 kHz	HO• production increases with increasing frequencies	(Mason *et al.*, 1994)
20–100 kHz	60 kHz is the optimum frequency for iodide oxidation	(Cum *et al.*, 1992)
192–960 kHz	300 kHz is the optimum frequency for iodide oxidation	(Busnel and Picard, 1952)
20 and 500 kHz	Iodide oxidation and H_2O_2 production occurs faster at 500 kHz than 20 kHz	(Pétrier *et al.*, 1992)
20 and 487 kHz	Higher phenol degradation rates at 487 kHz than 20 kHz	(Pétrier *et al.*, 1995)
20 and 900 kHz	Higher iodide oxidation rates at 900 kHz than 20 kHz	(Entezari and Kruus, 1994)
22 kHz–1.1 MHz	H_2O_2 formation rates and sonoluminescence intensity increases with US frequencies	(Didenko *et al.*, 1994)

Table 4.1: Effect of US frequencies on rates of oxidation and oxidising radical species.

However, total mineralisation of refractory organic pollutants by means of US alone still remains a difficult task which makes its use impractical on industrial scale processes. In order to overcome limitations of low degradation efficiency by ultrasound alone, the method has been combined with various other processes in order to achieve high total organic carbon (TOC) degradation and to reduce time of treatment (Adewuyi, 2001). These methods include US treatment coupled with oxidants (H_2O_2 and O_3) (Chemat *et al.*, 2001; Lin *et al.*, 1996; Weavers *et al.*, 1998); electrochemical methods (Trabelsi *et al.*, 1996); Fenton reagent (De Visscher and Van Langenhove, 1998; Guo *et al.*, 2005; Lin and Ma, 2000; Manousaki *et al.*, 2004; Neppolian *et al.*, 2002) and photocatalysis (Ragaini *et al.*, 2001; Theron *et al.*, 1999).

Among all the applications mentioned above, Fenton-like processes in conjunction with ultrasound have been of most interest. The reaction between H_2O_2 and Fenton-like catalysts (either homogeneous or heterogeneous), referred to as Fenton-like reactions, is known to produce additional HO• in the system, capable of oxidising organic compounds and accelerating the rates of ultrasonic degradation. Literature suggests that the degradation of chlorophenols (Nagata *et al.*, 2000), 1,4-dioxane (Beckett and Hua, 2003) and 4-*n*-nonylphenol (Yim *et al.*, 2003) is enhanced with the combined reaction of US/Fe^{2+}/H_2O_2 compared to US alone. Also, it was reported (Lin and Ma, 2000; Neppolian *et al.*, 2002) that substantial increase in degradation rates of MTBE and 2-chlorophenols were observed in the US/Fe^{2+}/H_2O_2 system over the Fe^{2+}/H_2O_2 system (silent Fenton system). On the contrary, lower degradation efficiencies of phenol and 2,4-dinitrophenols were reported with US/Fe^{2+}/H_2O_2 and US/Cu^{2+}/H_2O_2, respectively, when compared with silent Fenton systems (Guo *et al.*, 2005; Papadaki *et al.*, 2004). The controversy still exists as to whether ultrasound has a beneficial role in the homogeneous system (Fe^{2+}/H_2O_2) for treating organic compounds. (The part of the study with silent Fenton-like reactions in conjunction with various zero valent metal catalysts will be discussed in detail in Chapter 5).

This chapter mainly concentrates on a study of the efficacy of low- and high-frequency US reactors in conjunction with Fenton-like reactions where the source of Fe^{2+} and Cu^{2+} has been obtained from the use of zero valent iron (ZVI) and zero valent copper (ZVCu) catalysts. Such a process using zero valent metals along with H_2O_2

under acidic conditions (pH 2.5–3) has recently been termed the Advanced Fenton Process (AFP) (Bremner and Burgess, 2004; Namkung *et al.*, 2006; Namkung *et al.*, 2005).

Hence, objectives of the current study were to:

- assess the H_2O_2 production in the chosen low-and high-frequency US reactors
- optimisation of parameters for enhanced phenol degradation in the presence and absence of air, H_2O_2, US, ZVI
- assess the efficacy of different ZVI and ZVCu catalysts in conjunction with H_2O_2 and ultrasound (20, 300 and 520 kHz) in the process of phenol degradation
- compare the efficiency of oxidants, H_2O_2 and O_3 with the AFP for phenol degradation in high frequency US (300 and 520 kHz) reactors

This part of the study was carried out on a one month Short Term Scientific Mission (STSM) at the Institute of Environmental Studies, Bogazici University, Istanbul, Turkey. Therefore, the chemicals, US reactors, equipment for analysis (GC, TOC and UV–vis) and also the experimental set-up for this part of the research may be different from the remainder of the work described in this thesis, however the objectives, experimental methodology, process optimisation, data interpretation and analysis is my individual contribution to the study.

4.2 Experimental

4.2.1 Chemicals

Aqueous phenol solutions (2.5 mM, Fluka) were used as model synthetic wastewater for all the US reactions in this study. Experimental results shown in this part of the thesis were carried out at Bogazici University, Turkey, therefore the US reactors used for the study (20, 300 and 520 kHz) are the same as described in Section 2.3.2. The volumes of liquid used in the three US reactors; 20, 300 and 520 KHz were 80, 100 and 300 mL; respectively. The strength of the H_2O_2 (35%) used for the study was 2.38 g L^{-1} and the concentration of H_2O_2 in individual experiments was obtained using the calibration curve shown in Section 2.4.3. Three different kinds of zero valent catalysts (ZVC) used for the study were: zero valent iron powder (ZVI), zero valent copper flitters (ZVCF) and zero valent copper turnings (ZVCT). The amounts chosen for the two types of catalysts were: ZVI (0.120 g; 0.6 g L^{-1}) and ZVCF and ZVCT (1 g; 5 g L^{-1}). It is worth noting that the amounts used for the two types of catalysts were different, since, ZVCu at 0.6 g L^{-1} in Fenton-like conditions, did not initiate any reactions within 60 min, therefore the amounts used were increased to 5 g L^{-1}. The pH for the US/ZVC/H_2O_2 system was maintained at pH 3. However, O_3 studies were carried out under two different conditions: (i) at pH 3 with O_3 concentration of 6 g O_3 m^{-3} flowrate 0.25 L $min^{-1}$and (ii) at pH 9 with O_3 concentrations of 2 g O_3 m^{-3} and flowrate 0.75 L min^{-1}. Thus, based on these conditions, the O_3 studies have been compared under two major systems: pH 3/6 g O_3 m^{-3}/0.25 L min^{-1} and pH 9/2 g O_3 m^{-3}/0.75 L min^{-1}.

4.2.2 Hydrogen peroxide measurement

The efficiency of the US reactors to produce H_2O_2 was determined using the method described in Section 2.4.3. In this study, H_2O_2 production in water and 2.5 mM phenol solution, over 60 min, was measured spectrophotometrically, in each US reactor (20, 300 and 520 kHz), at 355 nm. Specific volumes, as mentioned in Section 4.2.1, of aqueous solution were placed in the respective reactors and samples (1 mL) were removed every 20 min during the 60 min reaction time. Phenol samples were filtered prior to analysis with the method described in Section 2.4.2.1.

4.2.3 Power measurement

Approximate power measurements in the US reactors were carried out by taking 80, 100 and 300 mL of water in 20, 300 and 520 kHz US reactors, with no cooling and measuring the temperature rise on irradiation for a specific time period. The power (Q) was calculated using formula shown in Eq. 4.4:

$$Q = cm\ (\Delta T/\Delta t) \qquad (4.4)$$

where, m is mass of water (g); c is specific heat of water (4.186 joule g^{-1} $°C^{-1}$); ΔT is change in temperature (°C) and Δt change in time. Unit is Watt (W). The values obtained in watts were divided by the volume of the reactant used, which finally gives the final power output (heat dissipation) in watts per millilitre (W mL^{-1}).

4.2.4 US/ZVC/H_2O_2 system

In the US/ZVC/H_2O_2 system, the reactions were carried out using standard volumes of 2.5 mM phenol solution in the three chosen US reactors (20, 300 and 520 kHz). Thereafter, the pH of the solution was set to pH 3 with 0.1 M H_2SO_4. After attaining the desired pH for the reaction, zero minute reading was taken and followed by this known amounts of catalysts and oxidants were introduced into the reaction solution and the reactor was switched on immediately. Continuous air was purged into the reaction solution with a glass diffuser at a flowrate of 1.5 L min^{-1}. The temperature was maintained (23 ± 2 °C) by a cooling jacket built around the glass reactor set-ups (shown in Section 2.3.2). The reaction time chosen for each batch study was 60 min.

Samples (3 mL) were withdrawn every 10 min for GC (1 mL) and TOC (2 mL) analysis in order to estimate phenol removal and TOC mineralisation, respectively. For GC analysis, the sample (1 mL) was mixed with 50 μL dichloromethane (internal standard) in a 2 mL amber vial (method described in detail in Section 2.4.2.1.2), whereas for the TOC analysis, original samples were diluted five times to get the desired volume required for the TOC analyser. In some reactions, the concentration of H_2O_2 was also monitored throughout the reaction every 15 or 20 min as discussed in Section 2.4.3.

4.2.5 US/ZVC/O_3 system

Similar experimental conditions were set-up for studies with the US/ZVC/O_3 system, with an only difference in the use of oxidant in this case, O_3 was used as oxidant instead of H_2O_2. Ozone generator (Ozone Service, Yanco Industries Ltd.) was used to generate ozone–oxygen mixture using an oxygen cylinder. Ozone–oxygen mixture was purged into the reaction solution using a single point glass diffuser. The study was carried out at two different: pH 3 and 9 (using 0.1 M NaOH); concentrations, 2 and 6 g O_3 m^{-3}; flowrates, 0.75 and 0.25 L min^{-1} described in Section 4.2.1. Ozone concentrations were not monitored in any reactions with O_3 as the scope of the study was only to estimate the efficacy of oxidants, H_2O_2 and O_3, for phenol removal/mineralisation in Fenton-like reactions.

4.3 Results and discussion

4.3.1 Hydrogen peroxide formation

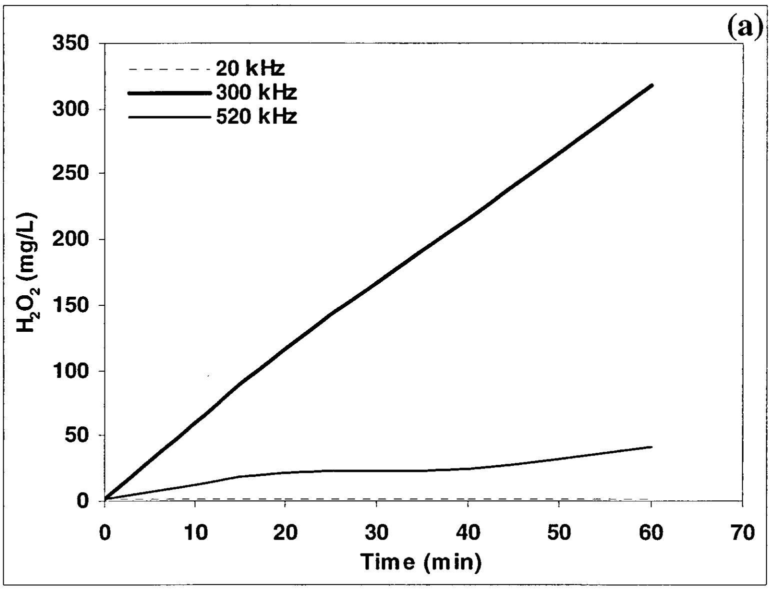
HO• production in water at different frequencies (20, 300 and 520 kHz) was estimated, prior to degradation studies, through the H_2O_2 formation. H_2O_2 results from the reaction of HO• and HOO• in the aqueous phase under cavitating conditions in absence of organic substrates (Henglein, 1987, 1993) (Eq. 4.5 and 4.6):

$$2HO\bullet \longrightarrow H_2O_2 \qquad (4.5)$$

$$2HOO\bullet \longrightarrow H_2O_2 + O_2 \qquad (4.6)$$

Measurement of H_2O_2 formation in water was carried out over 1 h irradiation time and it was found that H_2O_2 concentration increased linearly (Fig. 4.1), however the rates changed with frequency and, as shown from the graph, higher rates were observed at 300 kHz (Fig. 4.1a).

Similarly, H_2O_2 formation was determined in the presence of an organic substrate, phenol (2.5 mM) and it was observed that the H_2O_2 formation was reduced considerably which is an indication of HO• reacting with phenol as well as dimerising to form H_2O_2 (Fig. 4.1b).



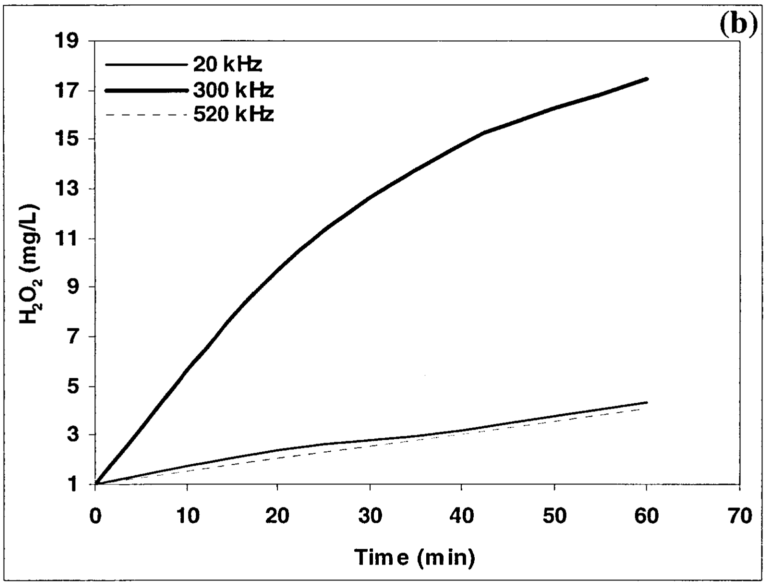


Figure 4.1: H_2O_2 formation, in (a) dH_2O water and (b) 2.5 mM phenol solution, at different US frequencies (20, 300 and 520 kHz). Experimental conditions: volume: 80, 100 and 300 mL for 20, 300 and 520 kHz US reactors, respectively; pH 3; air, 1.5 L min^{-1}; temperature, 23 ± 2 °C; $\lambda = 355$ nm.

In a related study, Petrier and Francony (1997) compared four different US frequencies (20, 200, 500 and 800 kHz) and studied H_2O_2 formation and phenol degradation. They reported that the highest amount H_2O_2 formation and phenol degradation was at 200 kHz and proposed that formation of H_2O_2 is the result of recombination of hydroxyl and hypoperoxyl radicals (Hart and Henglein, 1987; Henglein, 1993) and the degradation of phenol is an action of HO• on phenol leading to formation of hydroxylated aromatic compounds which further break down to biodegradable products, e.g., carboxylic acids. As seen from Fig. 4.1a, the increase in the H_2O_2 production in water is linear at 300 kHz, whereas in the case of 2.5 mM phenol (Fig. 4.1b), the amount of H_2O_2 formation becomes stable after 40 min reaction time. It is worth noting that formation of H_2O_2 was much higher in water than phenolic solution. More work in this area of research could be beneficial by carrying out experiments with different concentrations of phenolic solution and simultaneously estimating amount of H_2O_2 production and phenol degradation.

Table 4.2 reveals the rate of H_2O_2 formation in the two chosen aqueous media under different cavitation frequencies and it can be seen that 300 kHz has highest rate of H_2O_2 formation, in water as well as 2.5 mM phenol solution. However, at 300 kHz the rate of H_2O_2 formation is much higher in the case of water than phenol solution. It is reported that H_2O_2 formation in water at an optimum frequency (200 kHz) is a two step phenomenon where, first, sonolysis occurs inside the cavitation bubble and then HO• and HOO• migrate to the interface of the bubble to form either H_2O_2 or react with the substrate (Petrier and Francony, 1997b). From the current study, it is shown that H_2O_2 formation at 300 kHz, in water, involves the two steps mentioned above, whereas in the presence of substrate, i.e., phenol, H_2O_2 formation occurs only through sonolysis and when the radicals migrate to the bubble interface, they react actively with phenolic substrates, thereby reducing the rate of H_2O_2 formation.

	Rate of H_2O_2 formation (mg L^{-1} min^{-1})		
US frequencies	20 kHz	300 kHz	520 kHz
dH_2O	0.1	5.7	0.8
2.5 mM Phenol	0.1	0.5	0.1

Table 4.2: Rate of production of H_2O_2 for different frequencies in dH_2O and 2.5 mM phenol solution.

4.3.2 Preliminary experiments

In order to decide the best experimental conditions for optimal phenol/TOC removal using US/ZVC/H_2O_2 system, preliminary experiments were carried out with ZVI at 300 kHz (Fig. 4.2) under acidic conditions (pH 3).

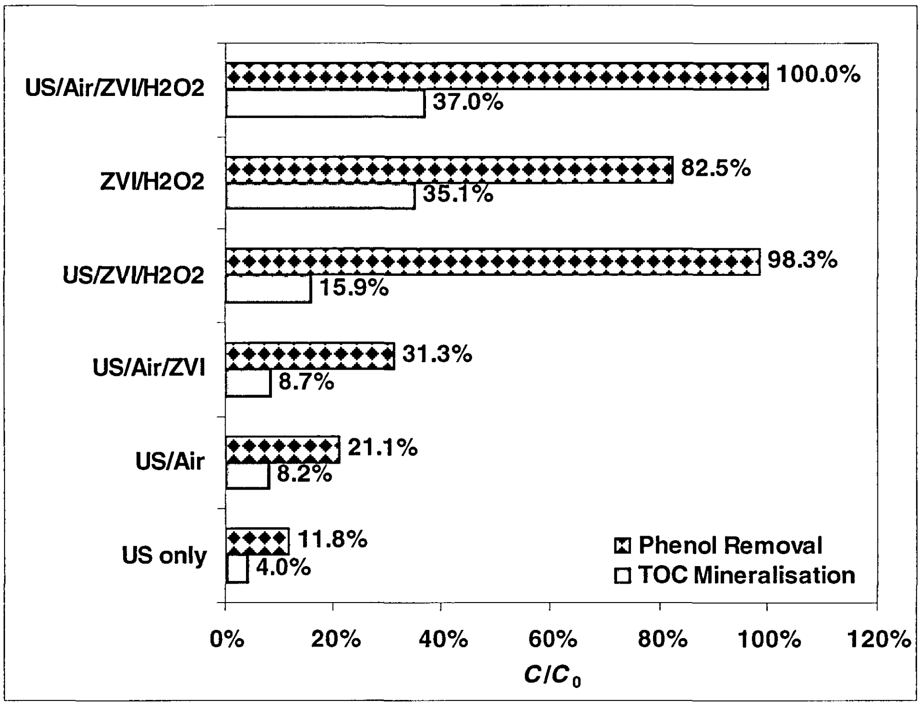


Figure 4.2: Effect of operational parameters on phenol degradation over 60 min. Experimental conditions: phenol, 2.5 mM; US, 300 kHz; ZVI (0.6 g L^{-1}); reaction time, 60 min; air, 1.5 L min^{-1}; H_2O_2, 2.38 g L^{-1}, temperature 23 ± 2 °C; analysis: phenol removal, GC and TOC mineralisation, TOC analyser.

4.3.2.1 Effect of pH

Sono-Fenton degradation studies on different organic compounds such as 2-chlorophenol (Lin *et al.*, 1996), aniline (Jiang *et al.*, 2002) and 2,4 dinitrophenol (Guo *et al.*, 2005) indicate that the degradation efficiency decreases with increase of solution pH, however higher phenol degradation at low pH, when large amount of pollutant can penetrate into cavitational bubble and stimulate the process of degradation. Also, Bremner and co-workers reported that the AFP proceeds faster at lower pH values (Bremner *et al.*, 2006; Bremner *et al.*, 2008; Namkung *et al.*, 2005). Therefore, for this study pH 3 was chosen as optimal pH.

4.3.2.2 Effect of air

During the initial experiments, the effect of sparging was tested by continuously injecting air (1.5 L min^{-1}) into 2.5 mM phenol solution and sonicating the test solution at 300 kHz. The literature suggest that monoatomic gases are more favourable than diatomic gases in a sonicated liquid, for the generation of high temperatures upon bubble collapse (Suslick, 1990). Also, its been reported that higher sonochemical yields have been observed in the presence of air than in argon (Kidak and Ince, 2006). In this study, air was used as a sparge gas and ~4–10% enhanced oxidation capacity was observed, as compared to US alone, probably due to the reactions of nitrogen with molecular oxygen to yield HNO_3 and other radical species such as HO•, •NO_2, •NO_3 that may help in accelerating the oxidation process. The following chemical reactions explain the mechanism that takes place during air injection into a sonoreactor (Ullerstam *et al.*, 2000):

$$2N_2 + O_2 \longrightarrow 2N_2O \qquad (4.7)$$

$$2N_2O + H_2O \longrightarrow 2HNO_2 + 2N_2 \qquad (4.8)$$

$$H\bullet + N_2O \longrightarrow N_2 + HO\bullet \qquad (4.9)$$

$$HO\bullet + N_2O \longrightarrow 2NO + H\bullet \qquad (4.10)$$

$$HNO_2 + H_2O_2 \longrightarrow HNO_3 + H_2O \qquad (4.11)$$

$$HNO_3 +))) \longrightarrow HO\bullet + \bullet NO_2 \qquad (4.12)$$

$$HNO_3 +))) \longrightarrow H\bullet + \bullet NO_3 \qquad (4.13)$$

Formation of nitrous and nitric acids favours the process of decomposition of formic acid via pH reduction, generation of excess HO• ($k_{HO\bullet}$, 10^{12} L mol^{-1} s^{-1}) and •NO_x (k_{NOx}, 10^7 L mol^{-1} s^{-1}) radicals, which are strong oxidants and help in enhancing the oxidation rates (Gogate *et al.*, 2003).

4.3.2.3 Effect of US/Air/ZVI system

The addition of ZVI relates to an enhanced solid–liquid interface in the bulk solution which may tend to promote cavitation. The US/Air/ZVI system in the absence of H_2O_2 leads to 10% higher phenol removal compared to the US/Air system, however it is worth noting that the TOC values in both the systems remains the same (Fig. 4.2). This shows that there is formation of more oxidised products in case of US/Air/ZVI system but the mineralisation efficiency was not enhanced by the ZVI catalyst. This phenomenon could be explained by another study on cresol degradation in the presence of either Fe^{2+} or H_2O_2 alone (Kavitha and Palanivelu, 2005) where results reveal that cresols were not decomposed in conditions of Fe^{2+} or H_2O_2 alone because the oxidation potentials of Fe^{2+} (0.77 V) or H_2O_2 (1.77 V) is much less than the oxidising potential of HO• (2.80 V). However, in acidic media at room temperature, the presence of Fe^{2+} ions and H_2O_2 generate HO•, which have high enough oxidation potential to degrade organic pollutants.

During a number of experiments carried out in this study, it was observed that the colour of the solution, upon addition of H_2O_2 to an acidic medium containing phenol and ZVI, showed an immediate change from colourless to brown then to yellow after 10 min of reaction time and remained light yellow to colourless at the end of reaction (60 min); this normally indicated completion of the reaction. So far, it has been observed that H_2O_2, Fe^{2+} and pH have been crucial factors in generating HO•, which ultimately control the degradation efficiency of organic pollutants. Hence, experiments shown later in this section were carried out in batch reactors involving ZVI, H_2O_2 and US and the effect of air was also assessed in combination with these systems.

4.3.2.4 Effect of ZVI/H_2O_2 and US/ZVI/H_2O_2 systems

A reaction mixture in which iron powder (ZVI) and H_2O_2 exist together in an aqueous medium at acidic pH 3, is called a Fenton-like system (reactions) because its behaviour is similar to the typical Fenton's reagent. During the process optimisation studies, the Fenton-like systems were studied for phenol degradation efficiencies in the presence and absence of ultrasound.

Sonochemical degradation of 4-chlorophenol using Fenton-like systems reveals that iron powder tends to dissolve smoothly under acidic conditions (pH 3), producing iron ions and production of these ions increases tremendously in the presence of ultrasound (Liang *et al.*, 2007). Thus, a similar hypothesis was drawn for ZVI/H_2O_2 system, when ZVI in the presence of H_2O_2 lead to 82% phenol removal and significantly higher TOC mineralisation (35%). Therefore, not only production of biodegradable products increased but also the mineralisation was found to be enhanced in the presence of ZVI and H_2O_2. It is believed that at pH 3, ZVI releases Fe^{2+} ions into the bulk solution which then react with the H_2O_2 to generate HO• according to the following reactions (Eq. 4.14–4.18) (Yim *et al.*, 2003).

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO\bullet + HO^- \quad (4.14)$$
$$Fe^{2+} + HO\bullet \longrightarrow Fe^{3+} + HO^- \quad (4.15)$$
$$Fe^{3+} + H_2O_2 \longrightarrow Fe\text{–}OOH^{2+} + H^+ \quad (4.16)$$
$$Fe\text{–}OOH^{2+} \longrightarrow Fe^{2+} + \bullet OOH \quad (4.17)$$
$$Fe^{3+} + \bullet OOH \longrightarrow Fe^{2+} + O_2 + H^+ \quad (4.18)$$

Besides the above mechanism, it has also been reported in the literature that H_2O_2 can be decomposed on metal surfaces (iron particles) and could possibly enhance degradation efficiency of the system (Weiss, 1952). A suggested mechanism is shown in reactions below (Eq. 4.19–4.24), where metal (**M**) can directly react with the H_2O_2 to generate HO• and $HO_2\bullet/\bullet O_2^-$ that can accelerate the degradation of the pollutant present in the bulk solution (Liang *et al.*, 2007).

$$\mathbf{M} + H_2O_2 \longrightarrow \mathbf{M}^+ + HO\bullet + HO^- \quad (4.19)$$
$$H_2O_2 + HO\bullet \longrightarrow H_2O + HO_2\bullet \quad (4.20)$$
$$HO_2\bullet \longleftrightarrow H^+ + \bullet O_2^- \quad (4.21)$$
$$\mathbf{M} + \bullet O_2^- \longrightarrow \mathbf{M}^+ + O_2^- \quad (4.22)$$
$$\mathbf{M} + HO_2\bullet \longrightarrow \mathbf{M}^+ + HO_2^- \quad (4.23)$$
$$\mathbf{M}^+ + HO_2^- \longrightarrow \mathbf{M} + HO_2\bullet \quad (4.24)$$

Higher phenol removal (98%) was observed with US/ZVI/H_2O_2 system, whereas ZVI/H_2O_2 system showed only 82% phenol removal, however there was a considerable difference in the TOC removal between the two systems. The scope of the experimental study did not include measurement and/or analysis of the by-products formed at the end of each reaction, therefore it is not possible to speculate further on the reason why US/ZVI/H_2O_2 system lead to lower TOC mineralisation.

4.3.2.5 Effect of US/Air/ZVI/H_2O_2 system

Increased phenol removal and TOC mineralisation were observed when the US/Air/ZVI/H_2O_2 system was employed. In this study, no phenol was detected (ND), during the GC analysis, after 25 min, thus it can be said that 100% phenol removal was obtained with the 300 kHz US reactor. Also, the highest TOC mineralisation (37%) in the 60 min reaction time was seen with this system and this can be attributed to the enhanced generation of HO• and other radical species by the combined system, i.e., air, US and Fenton-like reactions, under acidic conditions.

Time (min)	% Removal (C/C_0)	
	Phenol	TOC
0	0.0	0.0
5	91.2	-
10	97.8	-
15	98.7	26.5
20	98.9	-
25	99.0	-
30	ND	27.0
60	ND	37.0

Table 4.3: Phenol removal and TOC mineralisation in the US/Air/ZVI/H_2O_2 system. Experimental conditions: phenol, 2.5 mM; US, 300 kHz; ZVI (0.6 g L^{-1}); reaction time, 60 min; Air, 1.5 L min^{-1}; H_2O_2, 2.38 g L^{-1}, temperature 23 ± 2 °C; analysis: phenol removal, GC and TOC mineralisation, TOC analyser.

The results shown in Table 4.3 reveal that 90% of the phenol was removed from the bulk solution within the initial 5 min reaction time, by the US/Air/ZVI/H_2O_2 system, thereafter the reaction slowed down but after 25 min, no phenol remained in the reaction solution leading to 37% TOC mineralisation. This higher phenol decomposition during the start of the experiment is due to the supply of excess HO• from two sources: (i) decomposition of H_2O_2 according to Eq. 4.14–4.19 and (ii) ultrasonically generated HO•. Also, may be due to the increased radical species as discussed in Eq. 4.7–4.13. Therefore, for similar reasons, higher TOC mineralisation was observed during the initial 15 min of reaction but there was no significant change in TOC at 30 min reaction time. However, at the end of 60 min, a further 10% increase in TOC was seen leading to 37% overall mineralisation, which is due to the fact that all phenol was decomposed by this time, so the radicals produced, through various mechanisms, were solely utilised in the mineralisation of the by-products formed after phenol removal.

Since highest phenol decomposition and overall mineralisation were obtained with the US/Air/ZVI/H_2O_2 system under acidic conditions (pH 3) at 300 kHz US these conditions were considered to be optimal for carrying out batch experiments with 20 and 520 kHz reported in this study. Thereafter, 20, 300 and 520 kHz US frequencies were compared for their degradation efficiencies under similar experimental conditions. Also, in another comparative study, ZVC (ZVI, ZVCF and ZVCT) were compared for their efficiencies for decomposition and mineralisation of phenol in the chosen US reactors.

4.3.3 Degradation of phenol in the US/Air/ZVC/H_2O_2 system

4.3.3.1 Effect of different US frequencies

Initial phenol removal studies were carried out using US/Air/ZVI/H_2O_2 system in conjunction with zero valent iron (0.6 g L^{-1}; ZVI) catalyst at different chosen US frequencies (20, 300 and 520 kHz). The results shown in Fig. 4.3 reveal that high phenol removal efficiency was observed with the 20 and 300 kHz US reactors as phenol was undetectable after 45 and 25 min, respectively. However, in the 520 kHz US reactor, only 70% phenol removal was observed at the end of the 60 min reaction time. It was interesting to note that the TOC mineralisation at all the chosen frequencies in the US/Air/ZVC/H_2O_2 system was between 37 and 40%. The reaction was much faster during the initial 15 min reaction time leading to 60–90% phenol removal and 25–30% TOC mineralisation at all the US frequencies. As evident from results discussed above, the HO•/Fe^{2+} ion production and increased availability of H_2O_2 in the bulk solution leads to high degradation during the start of the reaction. Upon cavitational activity in the bulk solution, dissociation of the H_2O_2 initiates and therefore, Fe^{2+}/Fe^{3+} and H_2O_2 reaction decreases considerably (Eq. 4.14–4.16) thereby reducing the radical concentration (HO•/HOO•) required for the conversion of Fe^{3+} to Fe^{2+} in order to carry out effective Fenton-like reactions (Eq. 4.17–4.18).

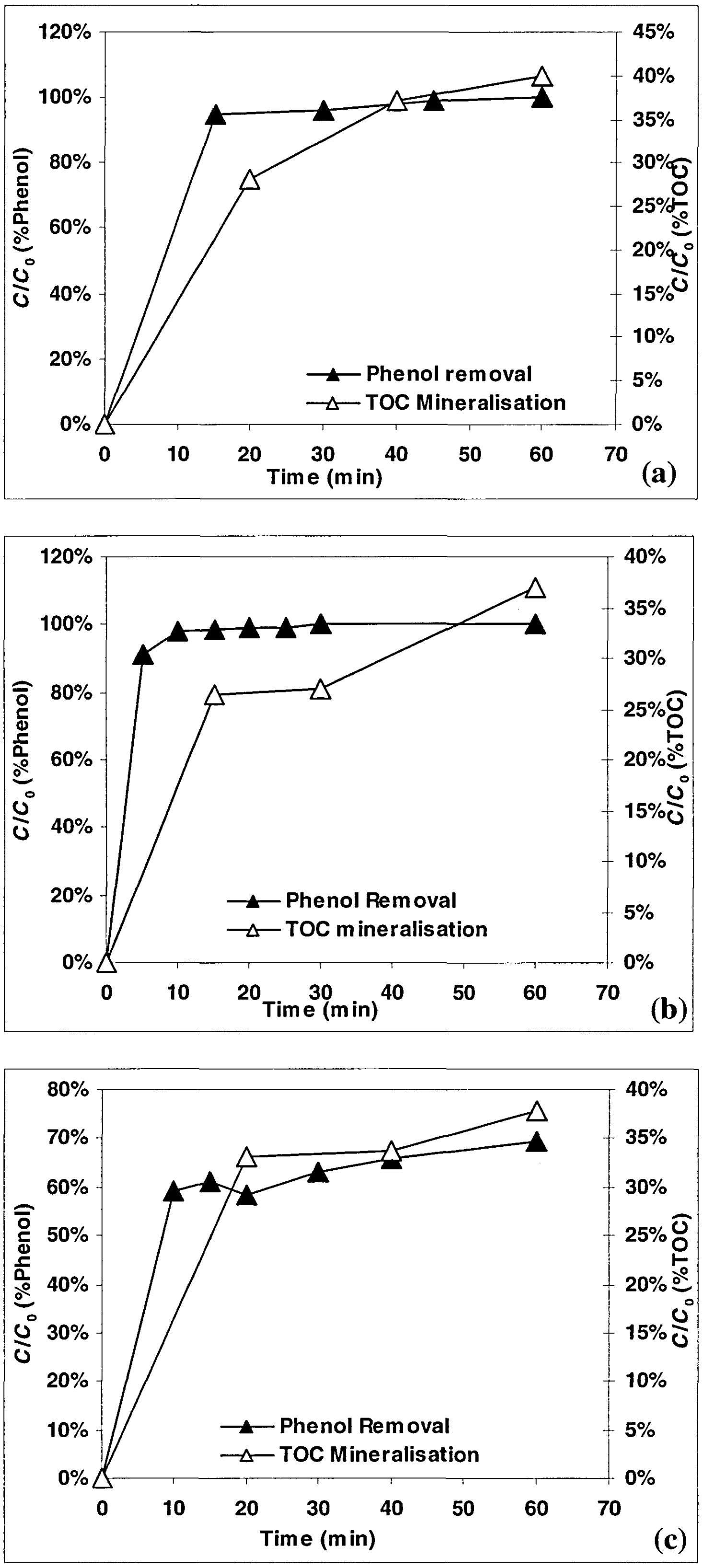


Figure 4.3: Effect of US/Air/ZVI/H_2O_2 system on phenol degradation over 60 min using three different US frequencies: (a) 20 kHz (b) 300 kHz and (c) 520 kHz. Experimental conditions: phenol, 2.5 mM; ZVI (0.6 g L^{-1}); air, 1.5 L min^{-1}; H_2O_2, 2.38 g L^{-1}, temperature 23 ± 2 °C; overhead stirring, 200 rpm; analysis: phenol removal, GC and TOC mineralisation, TOC analyser.

High phenol removal after 25 min of reaction time at 300 kHz in the US/Air/ZVC/H_2O_2 system is explained by the enhanced availability of radical species generated *in situ* due to the action of ultrasound, Fenton-like reactions and also various other combined reactions in the presence of ZVI catalysts. It is often thought that with increasing frequency, degradation will be much higher, however there exists an optimum frequency at which the rates of radical production and collapse is maximum and this state is considered the best frequency for pollutant destruction (Petrier and Francony, 1997b). Likewise, it has been discussed in a similar study, utilising 300 and 520 kHz US reactors, where 300 kHz was much more efficient for phenol destruction than 520 kHz due to the fact that bubbles formed at 300 kHz are long lived and collapse with higher energy compared to those formed in 520 kHz. Thus, with 300 kHz US more HO• are ejected into the bulk solution leading to more efficient pollutant destruction (Kidak and Ince, 2006). At 300 kHz, higher rates of HO• ejection into the solution (Fig. 4.1a) and higher phenol removal at this frequency (Fig. 4.3a) are consistent and therefore accounts for the dominance of aqueous phase oxidation by HO• and enhanced efficiency of 300 kHz US reactor. At 20 kHz, the lower volume of reaction solution (80 mL) leads to enhanced mixing within the reactor and allows the pollutant, catalysts and the radicals to interact with each other and therefore phenol disappearance was noticed after 45 min of reaction time. Also, the reactor geometry and high vibrations at 20 kHz disperse the ZVI catalysts throughout the solution, polish the catalysts and recharge the active sites for reaction, however since the HO• production at this frequency (Fig. 4.1a) is the least, 100% phenol removal within first 45 min is mostly attributed to the Fenton-like reactions. Similar TOC mineralisation (37–40%) during the 60 min reaction time at the three frequencies can be attributed to the conversion of the phenol into intermediate compounds (Santos *et al.*, 2002) which could not be further mineralised.

4.3.3.2 Effect of different ZVC

A comparative study between the zero valent iron (ZVI), copper flitters (ZVCF) and copper turnings (ZVCT) catalysts was carried out to assess their efficiencies for phenol removal and TOC mineralisation at three chosen US frequencies. Figs. 4.4a and 4.4b shows comparison of ZVI, ZVCF and ZVCT for both, phenol removal and TOC mineralisation, whereas Fig. 4.4c shows only TOC mineralisation at 520 kHz as the phenol removal trend with the ZVCu catalysts was found to be highly variable. From these results, it is obvious that, with 20 kHz, 1–4% and 10–30% of TOC mineralisation and phenol removal, respectively, were achieved with ZVCu catalysts. Whereas with the 300 kHz US reactor, the enhanced generation of HO• at this frequency gives 56–97% and 10–26% of phenol removal and TOC mineralisation, respectively, with ZVCu catalysts during 60 min reaction time. This phenomenal result is probably due to the HO• oxidation in the bulk solution as discussed above and also the Fenton-like reactions involving the copper ions in the presence of H_2O_2 at pH 3 (Eq. 4.25 and 4.26) (Entezari *et al.*, 2003).

$$H_2O_2 + Cu^{2+} \longrightarrow Cu^{+} + HO_2\bullet + H^{+} \qquad (4.25)$$

$$H_2O_2 + Cu^{+} \longrightarrow HO^{-} + HO\bullet + Cu^{2+} \qquad (4.26)$$

Reports of copper catalysts for pollutant destruction are rare in the literature but there are reports on generation of HO• from heterogeneous copper catalysts (Kim and Metcalfe, 2007). Also, in a comparative study between 20 and 520 kHz US reactors with the H_2O_2–$CuSO_4$ system, the latter frequency was reported to eliminate phenol to below the detection limit (concentration $<10^{-6}$) in 210 min reaction time and any remaining intermediates disappeared in 360 min. This was explained by the action of HO• produced by two pathways: (i) cavitation and (ii) H_2O_2 decomposition catalysed by $CuSO_4$ (Entezari *et al.*, 2003). Similarly, sonochemical destruction of *o*-chlorophenol using a H_2O_2 and $CuSO_4$ combination has been reported to be the result of both the ultrasound and chemical oxidation effect, whereas the trichloroethylene degradation rates were only just significant under similar conditions (De Visscher and Van Langenhove, 1998). Thus, it is seen that copper ions have a tendency to carry out Fenton-like reactions in the presence of H_2O_2 under acidic conditions, however the degradation of the organic pollutant may vary depending upon the US frequencies as cavitation is the principle pathway of HO• generation in the bulk solution resulting in oxidation.

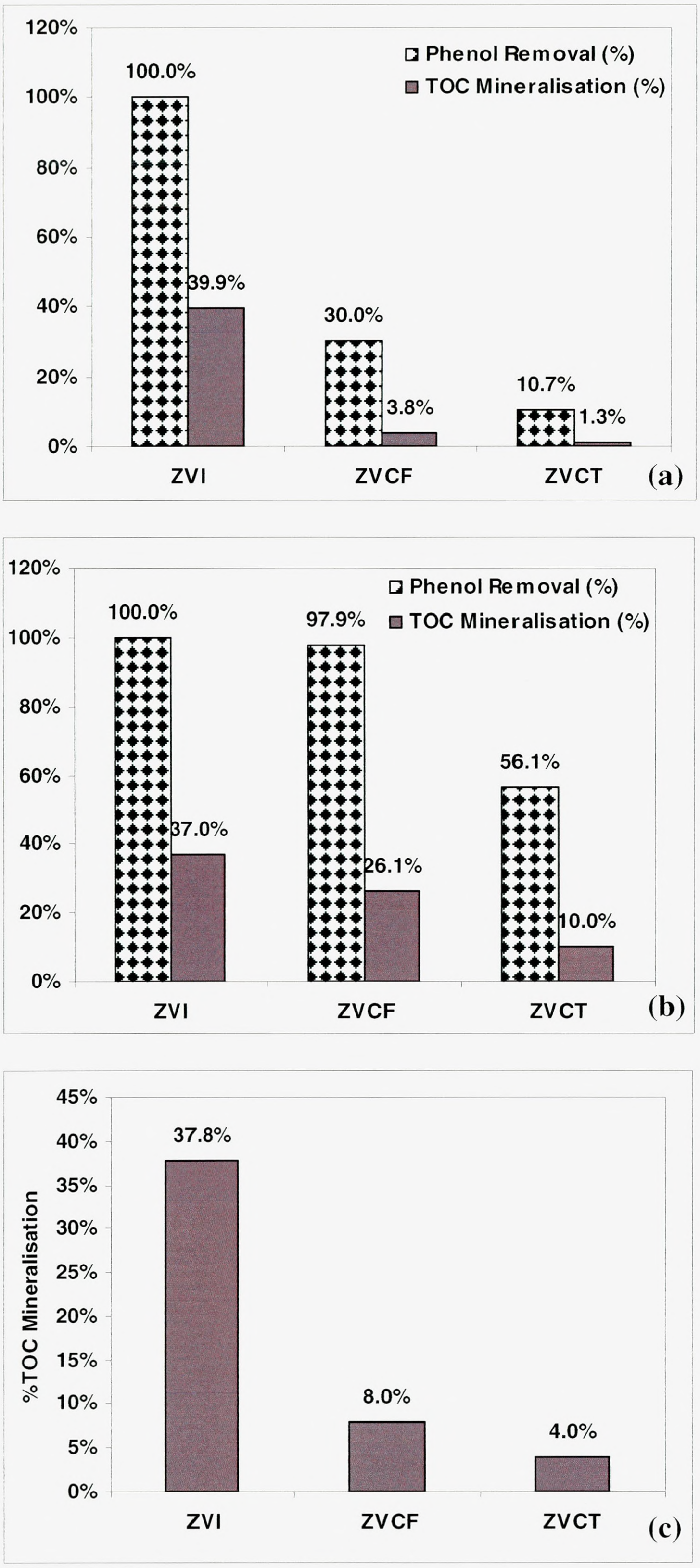


Figure 4.4: Effect of ZVI and ZVCu catalytsts in the US/Air/ZVC/H_2O_2 system, on phenol degradation over 60 min under three different US frequencies: (a) 20 kHz (b) 300 kHz and (c) 520 kHz. Experimental conditions: phenol, 2.5 mM; ZVI (0.6 g L^{-1}) and ZVCF/ZVCT (5 g L^{-1}); reaction time, 60 min; air, 1.5 L min^{-1}; H_2O_2, 2.38 g L^{-1}, temperature, 23 ± 2 °C; overhead stirring, 200 rpm; analysis: phenol removal, GC and TOC mineralisation, TOC analyser.

4.3.3.3 Effect of overhead stirring

In order to assess the influence of stirring on the phenol degradation, initial experiments were carried out in 520 kHz using the US/Air/ZVI/H_2O_2 system under acidic conditions (pH 3) and results of stirring and no stirring conditions were compared. Cavitational reactions are highly supported by efficient reactor geometry (Gogate and Pandit, 2004a) which, in the case of the 520 kHz US reactor having capacity of 500 mL, containing 300 mL reaction solution, did not support effective phenol removal. Therefore, overhead stirring (200 rpm) was introduced to the reactor set-up. As evident from Fig. 4.5, stirring has a high impact on the overall TOC mineralisation. It is predicted that introducing overhead stirring to the reactor enhances the efficiency of reaction due to improved mass transfer and allows the catalysts and radical species to react with the pollutant in the bulk solution, thereby increasing the phenol degradation efficiency.

Enhanced degradation of 4-chlorophenol has also been reported in the presence of an impeller (305 rpm) as it allows substantial mass transfer of soluble compound in the liquid and also distributes the particles (i.e., catalysts) uniformly within reaction solution. Also, it was concluded from the study that the impeller rotation provided much more efficient agitation as compared to ultrasound (Liang *et al.*, 2007).

However, it is not necessarily the case that every US reactor set-up will benefit from efficient stirring and it is important to optimise the ultrasonic degradation of organic pollutants by varying a number of parameters such as volumes, diameters and conditions. (Gogate and Pandit, 2004a).

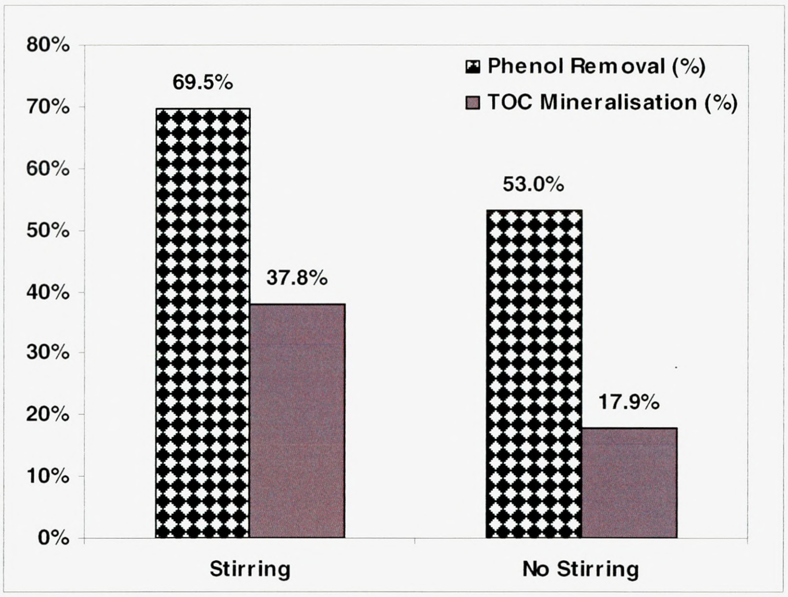


Figure 4.5: Effect of stirring on phenol degradation over 60 min in 520 kHz US reactor. Experimental conditions: phenol, 2.5 mM; ZVI (0.6 g L^{-1}); air, 1.5 L min^{-1}; H_2O_2, 2.38 g L^{-1}, temperature, 23 ± 2 °C; overhead stirring, 200 rpm; analysis: phenol removal, GC and TOC mineralisation, TOC analyser.

In Fig. 4.5, it is worth noting the substantial difference between the effect of stirring on the TOC and phenol removal. There is an increase of 20% of TOC removal in the presence of the overhead stirrer, whereas the phenol removal data shows that there is marginal increase with stirring as compared to no stirring. Earlier figures with H_2O_2 production in the 520 kHz showed that the rate of HO• production at this frequency was very low as compared to the 300 kHz. Thus, phenol oxidation at this frequency is mainly the attributed to Fenton oxidation leading to 70% phenol removal and 38% TOC mineralisation in the presence of overhead stirring. Therefore, overhead stirring was used in all experiments with the 520 kHz US reactor and the results shown in Figs. 4.3c and 4.4c are with stirring at 200 rpm.

4.3.3.4 Conclusion

The above study on the effect of the three chosen frequencies, i.e., 20, 300 and 520 kHz and zero valent catalysts (iron, ZVI and copper, ZVCu), on phenol degradation shows that ZVI catalysts and 300 kHz US are by far the most effective for carrying out Fenton-like reactions or, as has been termed the Advanced Fenton Process, in this study. A summary graph prepared from the available data on TOC mineralisation is shown in Fig. 4.6 and gives the comparison of ZVI, ZVCF and ZVCT performance at

20, 300 and 520 kHz US frequency. It can be seen that although the reaction mechanism of iron and copper (shown above) in the AFP is similar iron is still much more efficient in carrying out the Fenton reaction leading to 40% TOC mineralisation at all three US frequencies. However, when compared, the performance of ZVCF and ZVCT did not show substantial TOC mineralisation but ZVCF (flitters) still dominates over ZVCT (turnings) because of large surface area available to react with the pollutant leading to degradation and also proves to be a potential catalysts for phenol removal in the AFP.

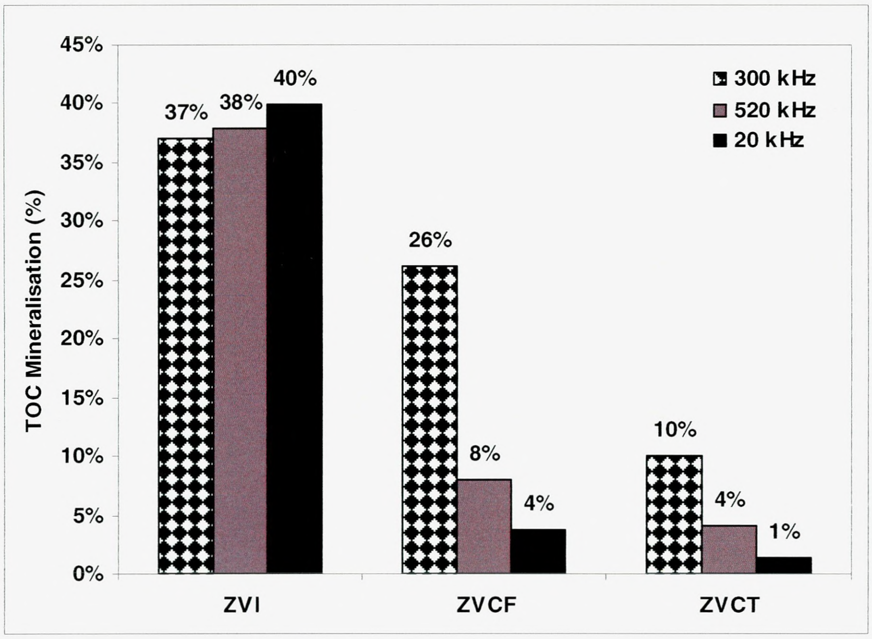


Figure 4.6: Comparison of different US frequencies (20, 300 and 520 kHz) and zero valent catalysts (ZVI and ZVCu) on TOC mineralisation over 60 min reaction time. Experimental conditions: phenol, 2.5 mM; ZVI (0.6 g L^{-1}) and ZVCF/ZVCT (5 g L^{-1}); air, 1.5 L min^{-1}; H_2O_2, 2.38 g L^{-1}, temperature, 23 ± 2 °C; overhead stirring in 520 kHz, 200 rpm; analysis: phenol removal, GC and TOC mineralisation, TOC analyser.

Thus, it can be said that, 300 kHz US frequency and ZVI is the most efficient, reactor and catalyst, respectively, to carry out efficient phenol degradation using the AFP, in the presence of 1.5 L min^{-1} continuous aeration with a catalyst loading of 0.6 g L^{-1} and 2.38 g L^{-1} of H_2O_2. Also, the best performance of the 520 kHz US reactor can be achieved with overhead stirring as mixing enhances the mass transfer rates, thereby increasing the degradation. High phenol degradation with ZVI at 20 kHz is accounted for by mixing, reactor geometry and regenerated/high surface area catalysts. Also, power estimation in the three chosen US reactors (0.92, 0.12 and 0.03 W mL^{-1} in 20, 300 and 520 kHz, respectively) suggests 300 kHz is by far the most economically efficient US reactor for phenol degradation.

4.3.4 Degradation of phenol in the US/ZVC/O_3 system (ZOO)

Ozone is a known oxidant in the AOP wastewater treatment and Hoigne and co-workers have discussed the mechanism of attack of O_3 on organic compounds and reported the pH dependence on the organic pollutant oxidation. In acidic to neutral pH, O_3 acts as a direct oxidising agent, especially for aromatic compounds, whereas at alkaline pH, O_3 reacts with the hydroxide ions, giving rise to HO• which are considered to be an AOP (Buhler *et al.*, 1984; Hoigne, 1985; Hoigne and Bader, 1976, 1983a, 1983b; Staehelin *et al.*, 1984; Staehelin and Hoigne, 1985; Staehelln and Hoigne, 1982). Although the effect of pH is pronounced in deciding the reaction pathways other factors such as catalysts, US, UV, Xe lamp light sources, etc. have been shown to be beneficial in carrying out effective O_3 oxidation of organic pollutants (Sanchez *et al.*, 2003). In recent years, catalytic ozonation has turned out to be very helpful in the decomposition of organic pollutants. This is especially true with the use of transition metal ions, e.g., Fe^{2+}, which possess the tendency to decompose O_3 into HO• explained by the following mechanism proposed in the literature (Løgager *et al.*, 1992):

$$Fe^{2+} + O_3 \longrightarrow FeO^{2+} + O_2 \qquad (4.27)$$

$$FeO^{2+} + H_2O \longrightarrow Fe(HO)^{2+} + HO\bullet \qquad (4.28)$$

Fe^{2+} also catalyses the reaction of O_3 and HO_2, which is one of the products of O_3 decomposition, producing H_2O_2 and accelerating the process of pollutant degradation by the action of Fenton-like reactions under acidic conditions (Rush and Bielski, 1986). Among the transition metals used for catalytic ozonation, iron is recommended because of the abundance of this metal on earth and its relative lack of toxicity therefore Fe–O_3 catalytic ozonation processes have been used to remove various different toxic organic compounds like, phenol, aniline, carboxylic acids chlorobenzene, chlorophenols, dyes and other natural organic matter (Beltran *et al.*, 2005). Also, the use of ultrasound in conjunction with O_3 (sonozone) has become a useful technology in the pollutant decomposition studies (Olson and Barbier, 1994).

Following reaction mechanisms of sonochemical decomposition of O_3 has been explained by Hart and Henglein (1986):

$$O_3 \longrightarrow O_2 + O\bullet \tag{4.29}$$

$$O\bullet + O_3 \longrightarrow 2O_2 \tag{4.30}$$

Ozone photolysis leads to the formation of $O\bullet$ and O_2 which further may combine with water to form $HO\bullet$ and two molecules of $HO\bullet$ may recombine to form H_2O_2:

$$O\bullet + H_2O \longrightarrow HO\bullet \tag{4.31}$$

$$2HO\bullet \longrightarrow H_2O_2 \tag{4.32}$$

Several other reactions have been proposed when ozonated water is irradiated with US and overall an increase in $HO\bullet$ production is the most likely outcome (Kang and Hoffmann, 1998; Weavers *et al.*, 1998). Enhanced mass transfer of O_3 in the solution due to ultrasonic vibrations is an added advantage of this process (Weavers and Hoffmann, 1998). The reaction pathway for $HO\bullet$ generation during the US/O_3 treatment of water could be formulated as follows (Hart and Henglein, 1986a; Kang and Hoffmann, 1998; Serpone *et al.*, 1994; Weavers *et al.*, 1998):

$$O_3\bullet + H_2O \longrightarrow 2HOO\bullet \tag{4.33}$$

$$O_3 + HOO\bullet \longrightarrow 2HO\bullet + 2O_2 \tag{4.34}$$

$$H_2O +))) \longrightarrow H\bullet + HO\bullet \tag{4.35}$$

$$O_3 +))) \longrightarrow O_2(g) + O(^3P)(g) \tag{4.36}$$

$$O(^3P)(g) + H_2O(g) \longrightarrow 2HO\bullet \tag{4.37}$$

Destruction of organic pollutants by the combined US/O_3 system is possible in different ways: direct thermal decomposition, oxidation mediated by $HO\bullet$, chemical oxidation, ozonation and by combinations of these processes (Weavers and Hoffmann, 1998).

`ZOO' or `**z**ero valent catalysts-assisted **o**zone **o**xidation' is the name assigned to the US/ZVC/O_3 system. The main aim of this study was to evaluate the effectiveness of US/ZVC/O_3 system over US/ZVC/H_2O_2 system for carrying out the AFP in the presence of ZVI catalyst. Initial experiments utilised the 300 kHz US reactor and then optimised conditions were used to study phenol degradation in the 520 kHz US reactor using the US/ZVC/O_3 system.

Phenol degradation using US/ZVC/O_3 system was carried out in the presence of ZVC and US reactors under two different ozonating conditions: (i) at pH 3 with O_3 concentration of 6 g O_3 m^{-3} flowrate 0.25 L $min^{-1}$and (ii) at pH 9 with O_3 concentrations of 2 g O_3 m^{-3} and flowrate 0.75 L min^{-1}. These parameters are represented as pH 3/6 g O_3 m^{-3}/0.25 L min^{-1} and pH 9/2 g O_3 m^{-3}/0.75 L min^{-1} in the figures.

Phenol removal (%), shown in Fig. 4.7, reveals that a maximum of 45–67% of phenol removal was achieved with pH 9/2 g O_3 m^{-3}/0.75 L min^{-1} whereas, only 30% removal was seen with pH 3/6 g O_3 m^{-3}/0.25 L min^{-1}. Usually higher pH values are recommended for degradation of organic pollutants, however if the operating pH is above the p*K* value of the pollutant, efficient degradation will not be achieved (Beltran *et al.*, 1994; Beltran *et al.*, 1992). It has also been reported that under higher pH values, O_3 reacts with almost all the organic and inorganic compounds present in the bulk solution (Staehelln and Hoigne, 1982). Probably, that is one of the reasons why under pH 9/2 g O_3 m^{-3}/0.75 L min^{-1} phenol removal was better than pH 3/6 g O_3 m^{-3}/0.25 L min^{-1}. Also at alkaline pHs, O_3 tends to stay stable for longer durations, hence available for the reactions for longer time period.

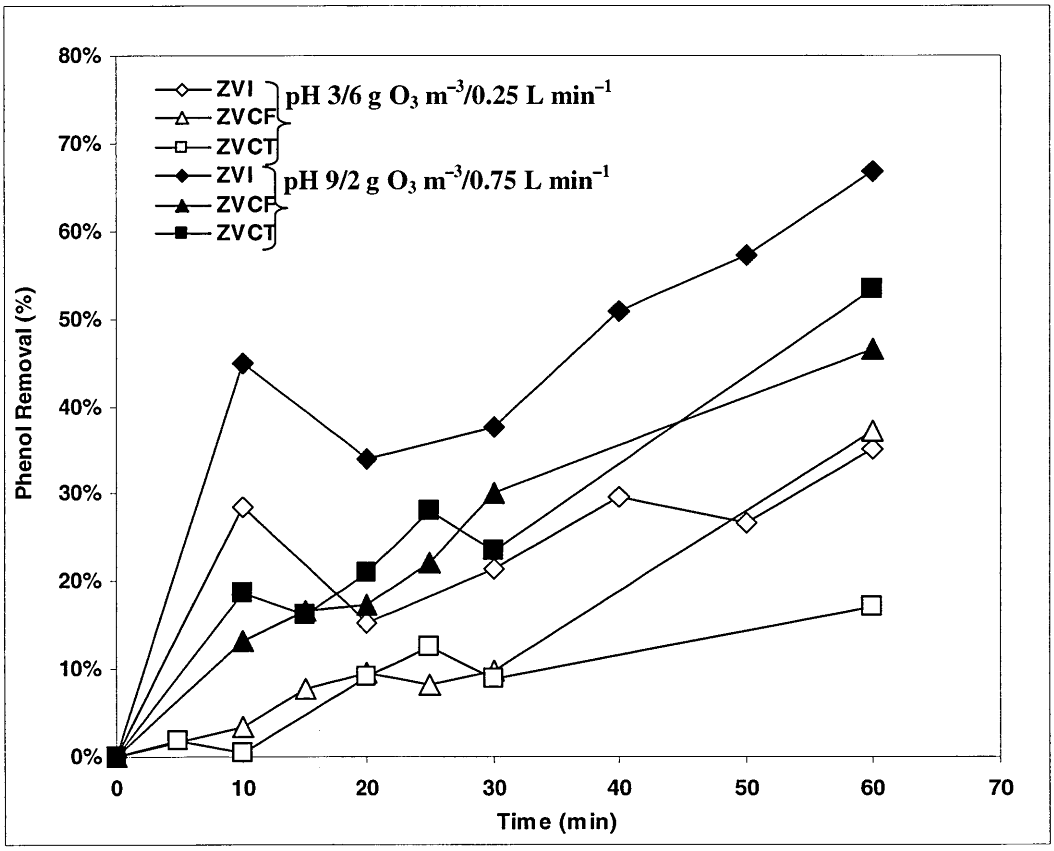


Figure 4.7: Comparison of (i) pH 3/6 g O_3 m^{-3}/0.25 L min^{-1} and (ii) pH 9/2 g O_3 m^{-3}/0.75 L min^{-1} systems for phenol removal over 60 min in a 300 kHz US reactor using the catalysts: ZVI and ZVCu. Experimental conditions: phenol, 2.5 mM; ZVI (0.6 g L^{-1}) and ZVCF/ZVCT (5 g L^{-1}); temperature, 23 ± 2 °C; overhead stirring, 200 rpm (only in 520 kHz); analysis: phenol removal, GC.

It is worth noting that, even in US/ZVC/O_3 system, the ZVI catalyst is superior to the ZVCu catalysts probably because of the excess HO• and H_2O_2 produced due to the synergism of US/O_3 reactions, required to carry out Fenton-like reactions. In a separate pilot scale study, researchers have also reported phenol mineralisation by ozonation using iron and copper salts and simulated solar lights and their results showed that O_3/Cu(I)/light system at pH 11 and 7 leads to 62% and 90% TOC mineralisation, respectively, whereas in the presence of O_3/Fe(III)/light system at pH 3, 97% mineralisation was achieved in 90 min (Canton *et al.*, 2003). High TOC mineralisation, in this case is attributed to combined UV/O_3 system. The reaction with pH 9/2 g O_3 m^{-3}/0.75 L min^{-1} system was repeated in 520 kHz US reactor and a very uneven trend of phenol removal was observed. Over a 60 min reaction time, the percentages of phenol removal were: ZVI (45%), ZVCF (38%) and ZVCT (32%).

The results of TOC mineralisation, at this frequency, are shown and discussed in the section below.

The TOC mineralisation with US/ZVC/O_3 system was very low as compared to phenol removal and Fig. 4.8 illustrates a comparison between the 300 and 520 kHz. Furthermore, the same figure shows comparison of US/ZVC/O_3 system and US/ZVC/H_2O_2 system for TOC mineralisation in 300 and 520 kHz US reactors.

Although the TOC mineralisation in the US/ZVC/O_3 system were three times less than that of US/ZVC/H_2O_2 system in 300 kHz US reactor in the presence of ZVI catalysts it is worth noting that in the absence of catalysts, the US/O_3 reaction shows 5% TOC mineralisation which is greater than that shown with 520 kHz US reactor in the presence of ZVI and ZVC catalysts. This phenomenon could be explained by the strong action of US/O_3 on phenol removal rather than presence of catalysts which may be interfering with the ozonation process whereas catalysts play a major role in carrying out Fenton-like reactions in the US/ZVC/H_2O_2 system. Within the US/ZVC/O_3 system it can be seen that 300 kHz reactor performs 4–6 times better than 520 kHz, the reason being high rates of HO• production at this frequency. Also, the differences in geometry the two US reactors, 300 (smaller diameter reactor) and 520 kHz (bigger diameter reactor) may also contribute to decreased amounts of TOC mineralisation in case of 520 kHz. Kidak and Ince (2006) very well explained in their report that higher phenol destruction was obtained at 300 kHz due to the longer lived bubble advantages at 300 kHz over shorted lasting but less energetic cavity collapse at 520 kHz that allows larger spread of HO• into the solution. Also, it is well known that there exists an optimum frequency at which the rate of radical generation and the duration of cavity collapse provide the 'best' conditions for the destruction of pollutants (Kidak and Ince, 2006).

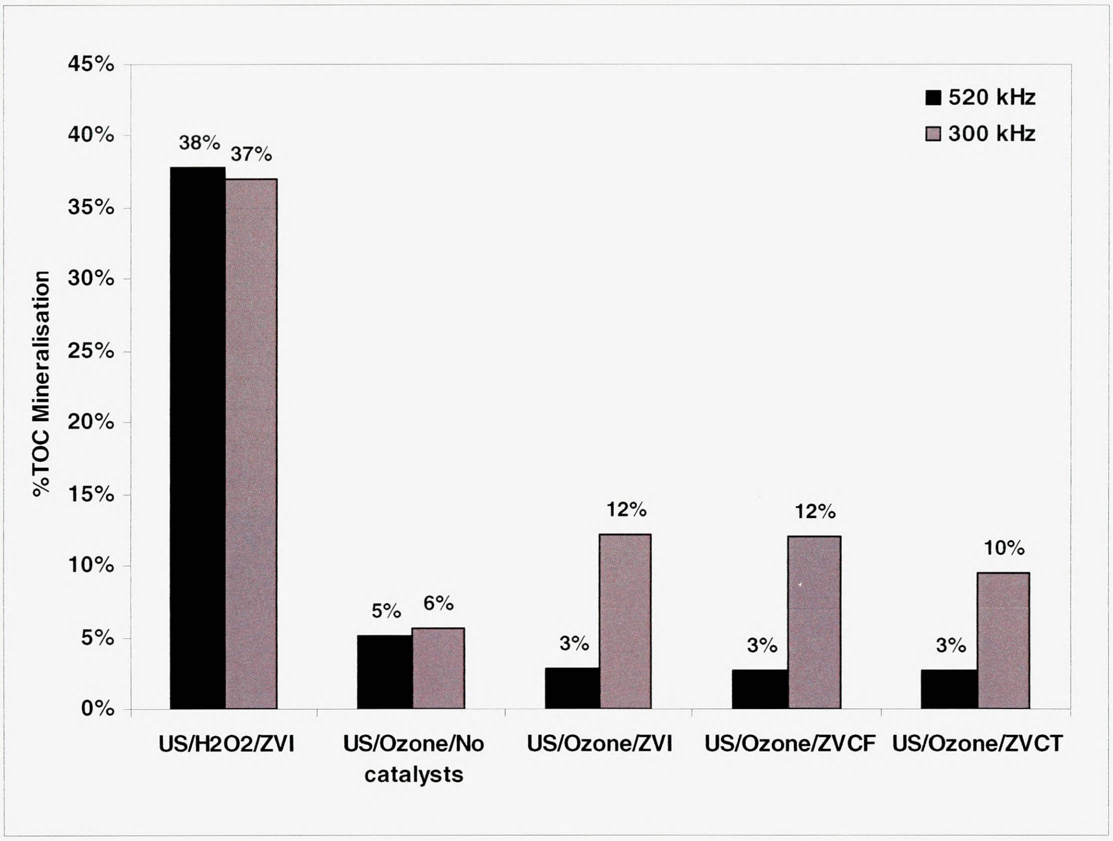


Figure 4.8: A comparison of TOC mineralisation in 300 and 520 kHz US reactors using US/ZVC/O_3 and US/ZVC/H_2O_2 systems in the presence and absence of catalysts over 60 min reaction time. Experimental conditions: phenol, 2.5 mM; ZVI (0.6 g L^{-1}) and ZVCF/ZVCT (5 g L^{-1}); H_2O_2, 2.38 g L^{-1}; O_3, pH 9/2 g O_3 m^{-3}/0.75 L min^{-1}; temperature, 23 ± 2 °C; overhead stirring, 200 rpm (only in 520 kHz); analysis: TOC mineralisation, TOC analyser.

Therefore, it can be proposed that in the 300 kHz US reactor, US/O_3 reactions mainly result in production of more HO• (Eq. 4.33–4.37) which transfer into the bulk solution. In general, the catalysts in the US/ZVC/O_3 system seem to be interfering with the US/O_3 reactions however, ZVI reactions have proved to be outstanding in carrying out 66% phenol removal and 12% TOC mineralisation under the pH 9/2 g O_3 m^{-3}/0.75 L min^{-1} system. This can be explained readily by Eq. 4.27 and 4.28, where Fe(II) catalyses the O_3 degradation giving the ferryl intermediate which has the possibility to oxidise the pollutant and/or generate HO• (Løgager *et al.*, 1992). No such evidence on copper ions has been proposed so far but it is assumed that, in the 300 kHz US reactor at least, a similar reaction scheme could describe the effect of the ZVCu in the US/O_3 mechanism but, as is evident from the results, the degradation is slower than in the case of ZVI.

4.3.5 Phenol removal with US/ZVI/H_2O_2 and US/ZVI/O_3 system

Results obtained for phenol removal using the two systems, i.e., US/ZVI/H_2O_2 and US/ZVI/O_3 are summarised in Fig. 4.9. It is evident that the AFP with the US/ZVI/H_2O_2 system under acidic pH 3 dominates over the US/ZVI/O_3 system even under alkaline conditions (pH 9). Also, inter and intra-comparison of the two systems shows that 300 kHz is more suitable for carrying out the AFP.

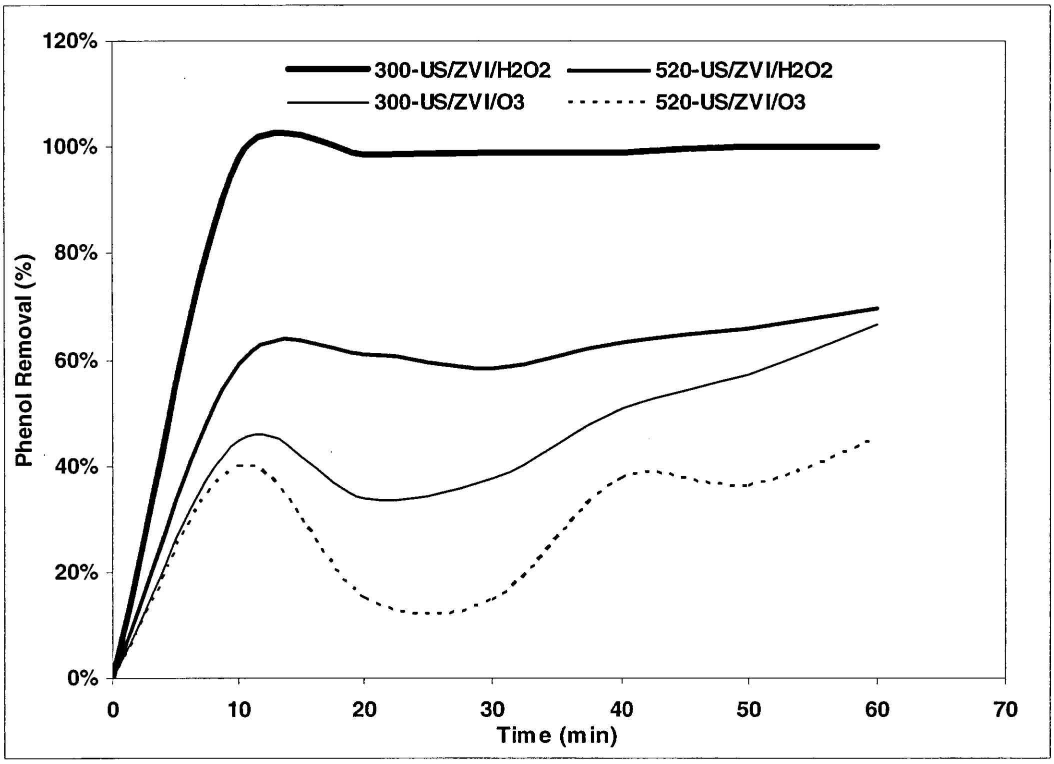


Figure 4.9: Percentage phenol removals with the US/ZVI/H_2O_2 and US/ZVI/O_3 systems in 300 and 520 kHz US reactors in 60 min reaction time. Experimental conditions: phenol, 2.5 mM; ZVI (0.6 g L^{-1}); H_2O_2, 2.38 g L^{-1} and pH 3; O_3, pH 9/2 g O_3 m^{-3}/0.75 L min^{-1}; temperature, 23 ± 2 °C; overhead stirring, 200 rpm (only in 520 kHz); analysis: phenol removal, GC analysis.

Thus, it is worth noting that the highest phenol removal, seen in US/ZVI/H_2O_2 in 300 kHz compared to the 520 kHz US reactor, are partially accounted for by the higher rates of HO• production as shown in Fig. 4.1. In both high frequency US reactors, H_2O_2, in the presence of ultrasound forms HO• that participate in chain reactions to form hydroperoxyl and other radical species produced due to the presence of air as sparge gas and this probably accounts for enhanced degradation in the US/ZVI/H_2O_2

system. It is also proposed that O_3 decomposition due to ultrasonic irradiation influences the catalyst and oxidant concentration, which hinders direct pollutant destruction whereas in the case of H_2O_2, simultaneous decomposition and synthesis of the oxidant occurs in the reaction system and/or additional free radicals/iron species also react with the pollutant. Thus, H_2O_2 proves to be the most effective oxidant in conjunction with ZVI in high frequency US reactors.

Gogate and Pandit (2004b) discussed a few crucial factors related to pollutant destruction using the US/H_2O_2 and US/O_3 systems which may be worth restating here in support to this study. In ultrasonic reactions, HO• is the main driver and often it is believed that oxidants such as H_2O_2 and O_3 should enhance the rates of oxidation by enhanced HO• generation. However, along with the oxidant selection, rates of oxidation also depend on the operating pH, ultrasonic intensity (turbulence), nature and concentration of pollutant and all these parameters should be taken into account before selecting an oxidant for the ultrasonic processes in order to achieve high rates of degradation. However, selection of the optimum concentration of the oxidants is a crucial factor as higher concentrations could lead to detrimental effects by acting as scavengers of the generated free radicals. Thus, use of optimum catalyst concentrations have been recommended to further enhance the degradation process otherwise they may interfere with the ultrasonic activity by scattering the sound waves leading to detrimental effects.

Based on the above discussion, it can said that high phenol removal obtained from the US/ZVI/H_2O_2 system (60–100%) is the results of the use of optimum catalyst and oxidant concentrations, whereas the US/ZVI/O_3 system, resulting in only 40–60% phenol removal, needs further optimisation. Synergism of the US/H_2O_2 also works efficiently for phenol removal as free radical attack is the controlling mechanism.

4.4 Summary

- The Advanced Fenton Process supports the US/Air/ZVC/H_2O_2 system as the optimum condition to carry out phenol degradation at pH 3.
- Effective phenol removal and TOC mineralisation could be achieved in the 520 kHz US reactor by the introduction of overhead stirring.
- Efficient reactor geometry of the 20 kHz US reactor supports high phenol and TOC removal with ZVI catalyst.
- Power input of 0.94, 0.13 and 0.03 W mL^{-1} in 20, 300 and 520 kHz, respectively, indicates that the 300 kHz US reactor is by far the most energy efficient for phenol degradation.
- The order of effectiveness of catalysts for phenol degradation: ZVI>ZVCF>ZVCT.
- The ZOO process works more efficiently with pH 9/2 g O_3 m^{-3}/0.75 L min^{-1} than pH 3/6 g O_3 m^{-3}/0.25 L min^{-1} system.
- The ZOO process works best with 300 kHz US reactor using ZVI catalysts
- A comparison between US/H_2O_2 and US/O_3 synergism for phenol degradation suggests that optimum catalysts and oxidant concentrations in the US/Air/ZVC/H_2O_2 system proves it to be more effective for the AFP than the US/ZVC/O_3 or ZOO system.

Chapter 5

Degradation II: Latent Remediation using the Advanced Fenton Process

Platform presentation: International World Water Congress 2008

Chand, R. (7th–12th September 2008). Latent remediation using combination of ultrasound and advanced Fenton oxidation: an innovative approach. *IWA–IOA World Water Congress*. Vienna, Austria.

5.1 Introduction

In the Fenton reaction, ferrous salts (usually $FeSO_4.H_2O$) are reacted with hydrogen peroxide (H_2O_2) to generate hydroxyl radicals (HO•) according to the following reaction first described by Henry John Hortsman Fenton in 1890s.

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO\bullet + OH^- \quad (5.1)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HOO\bullet + H^+ \quad (5.2)$$

In the above reactions, Fe^{2+} is oxidised by H_2O_2 to Fe^{3+} producing a HO• and a hydroxide anion. Thereafter, Fe^{3+} in the presence of H_2O_2 reduces back to Fe^{2+} releasing the peroxide radical and a proton. These generated radicals participate in the secondary reactions.

The Fenton system ($Fe^{2+}/Fe^{3+}/H_2O_2$) has been extensively used in the treatment of industrial wastewaters and/or landfill leachates, but the key parameters on which the rate of reaction depends are:

1. Wastewater conditions, i.e., pH, concentration, temperature and organic/inorganic constituents
2. Fenton reagent conditions, i.e., $[Fe^{2+}]$ $[Fe^{3+}]$ and $[H_2O_2]$

These physical and chemical parameters determine the overall reaction pathways in terms of HO• production and consumption (Yoon *et al.*, 2001)

The mechanism for the Fenton and related reactions was first proposed by Haber and Weiss in 1934 and further extended by other researchers, who used low reagent concentrations, i.e., Fe^{3+}, Fe^{2+} and H_2O_2 at less than 1 mM. Walling's work in 1975 used the addition of small known concentrations of H_2O_2 slowly to the solution, containing excess of Fe^{2+} and organic substrates in O_2 free conditions. He described the reaction in terms of HO• and other radical intermediates interacting with the organic substrates. However, these conditions vary from those used frequently in real wastewater treatment, where Fe^{2+} and H_2O_2 is more than 1 mM and total organic carbon (TOC) is several hundred ppm (Yoon *et al.*, 1998). Later Yoon and co-workers described the Fenton system with high reagent concentrations ($[Fe^{2+}] \geq 1$ mM and $[H_2O_2] = 5$ mM) and explained their results in terms of the known mechanisms of the Fenton reaction and presented implications of the results for use of the Fenton process in practical wastewater treatment (Yoon *et al.*, 2001).

Degradation rates are often controlled by various physical and chemical parameters, among which, pH has a significant role to play in Fenton-like reactions (Benitez *et al.*, 2001; Kang and Hwang, 2000; Lin and Lo, 1997; Nesheiwat and Swanson, 2000). The optimum pH is 3 and therefore this pH is usually employed for Fenton-like reactions (Benitez *et al.*, 2001; Kwon *et al.*, 1999; Tang and Huang, 1996). At lower pH (<2.5), the formation of the complex $[Fe(II).H_2O]^{2+}$ is favoured and this reacts slowly with the H_2O_2 thereby reducing HO• production and hence the degradation rates, also at very low pHs, hydrogen ions act as scavengers of HO• (Tang and Huang, 1996) and the reaction of Fe^{3+} and H_2O_2 is inhibited (Pignatello, 1992). Higher pH (>4) decreases the rate of degradation due to (i) precipitation of ferric hydroxides which inhibit the regeneration of ferrous ions and (ii) lack of free iron species in the solution since most of the Fe(II) forms complexes, inhibiting the production of free radicals (Bigda, 1995; Lin and Lo, 1997; Nesheiwat and Swanson, 2000). Most importantly, with increasing pH, the oxidation potential of HO• is known to decrease (Kwon *et al.*, 1999). Therefore, pH 3 was chosen to conduct Latent Remediation (LR) studies.

Other operating parameters in the Fenton process are: the concentrations of the ferrous ions, pollutant and H_2O_2. It has been reported that rates of degradation increase with higher ferrous ion concentrations (Benitez *et al.*, 2001; Kwon *et al.*, 1999; Lin and Lo, 1997) but stoichiometric amounts are recommended otherwise the levels of unused iron in the effluent stream may lead to non-permissible levels of total dissolved solids (TDS). Likewise, increasing H_2O_2 concentrations are beneficial in Fenton reactions but care should be taken as high concentrations could lead to enhancement in the chemical oxygen demand (COD) levels (Lin and Lo, 1997). Also, elevated H_2O_2 concentrations act as scavengers of HO•, therefore the chosen concentrations should just be high be enough to be used up entirely during the Fenton reaction. As far as pollutant concentrations in Fenton reactions are concerned, usually lower concentrations or diluted wastewaters are recommended (Benitez *et al.*, 2001; Kwon *et al.*, 1999).

Fenton reactions have proved to be extremely useful in groundwater and/or contaminated soil remediation because of the availability of ferrous ions which are often found in groundwater (Miller and Valentine, 1995; Tyre *et al.*, 1991). The Fenton reaction has also been applied to the oxidation of pentachlorophenol-contaminated soils using ferric ions as a catalysts instead of ferrous ions (Watts *et al.*, 1990) and also for diesel contaminated soils (Watts and Dilly, 1996). Over the last decade, Fenton reactions have otherwise being extensively used in the treatment of a wide range of organic compounds including herbicides (Miller *et al.*, 1996), pesticides (Chan and Chu, 2003), dyes (Barros *et al.*, 2006; Kuo, 1992; Park *et al.*, 1999), 2,4,6-dinitrotoluene (Li *et al.*, 1997a; Li *et al.*, 1997b; Li *et al.*, 1997c), RDX (Hundal *et al.*, 1997), 2,4-dinitrophenol (Kang *et al.*, 1999b; Wang *et al.*, 1999), chlorobenzene (Watts *et al.*, 1997), tetrachloroethylene (Yoshida *et al.*, 2000), halomethanes (Tang and Tassos, 1997) and chlorophenols (Barbeni *et al.*, 1987; Pera-Titus *et al.*, 2004; Potter and Roth, 1993; Watts *et al.*, 1990). However, there are many other organic compounds such as acetic acid, acetone, carbon tetrachloride, methylene chloride, trichloroethane, *n*-paraffins and maleic/malonic/oxalic acids, which are refractory towards Fenton chemistry (Gogate and Pandit, 2004a).

Although the Fenton reagent has been applied in many successful oxidation reactions, as mentioned above, there are still some limitations such as restricted oxidant/catalyst dosage ratios and low pollutant concentrations. Therefore, successful application of the Fenton reaction in wastewater treatment systems demands a combination of Fenton oxidation with other AOP, like ozonation, cavitation, UV, chemical and catalytic oxidation. Since one of the aims of this project includes the use of cavitational reactors for phenol degradation, most of the discussion will be focussed on the individual and combined usage of ultrasound (US) and Fenton chemistry. Ultrasound has been efficiently used as hybrid method for treatments of various aliphatic, aromatic, polycyclic aromatic, halogenated hydrocarbons, azo dyes and some pesticides (Ioan *et al.*, 2007). Also, as discussed in Chapter 4, various methods of phenol degradation using different frequency US reactors, oxidants i.e., H_2O_2 and/or ozone and zero valent catalysts (ZVC) (iron, ZVI and copper, ZVCu) have been reported.

Zero valent iron (ZVI) was initially used by the researchers (Deng *et al.*, 1999; Dries *et al.*, 2001a; Dries *et al.*, 2001b; Gillham *et al.*, 1998; Grittini *et al.*, 1995; Matheson and Tratnyek, 1994; Muftikian *et al.*, 1995) to treat waters contaminated by chlorinated compounds. In recent years, the use of ZVI in various forms has been described for the treatment of TCE (Chen *et al.*, 2001), phenol and aromatic compounds (Sanchez *et al.*, 2007), pentachlorophenol (Dai *et al.*, 2006), azo dye Acid Orange 7 (Liu *et al.*, 2007), dinitrobenzene (Zhang *et al.*, 2007), DDT, TNT and RDX (Boussahel *et al.*, 2007; Oh *et al.*, 2003). Similarly, a few recent studies have also reported the use of zero valent copper (ZVCu) catalysts in the degradation of carbon tetrachloride (Lin *et al.*, 2005), phenol (Canton *et al.*, 2003), 2,4-dinitrophenol (Guo *et al.*, 2005) and *p*-chlorophenol (Kim *et al.*, 2007).

The Advanced Fenton Process (AFP), i.e., degradation of organic pollutants in the presence of ZVI, hydrogen peroxide (H_2O_2) at fairly acidic pH 2.5–3, has been patented and reported in many papers by Bremner and co-workers (Bremner and Burgess, 2004; Bremner *et al.*, 2008; Chakinala *et al.*, 2007a; Chakinala *et al.*, 2008a; Molina *et al.*, 2006; Namkung *et al.*, 2006; Namkung *et al.*, 2008). However, the novel part of the current study is in the use of ZVCu catalysts as potential catalysts for the AFP and duration of US energy input.

In the published papers reporting the AFP, usually, the cavitation treatment time is the controlling factor in deciding the overall treatment costs. With an aim of increasing the cost efficiency of the process so as to make the procedure more economically viable, an innovative approach with overall low energy input and low cost operation, named 'Latent Remediation' (LR) is now reported in this study. In this study, an initial input of ultrasound (US) is applied for a short time and then the degradation of the pollutant is allowed to continue silently afterwards. Different forms of zero valent copper catalysts (ZVCu): flitters (ZVCF), turnings (ZVCT) and powder (ZVCP) have been used for the study and compared with zero valent iron powdered catalysts (ZVI) for their degradation efficiencies. Degradation was measured with the help of total organic carbon (TOC) analysis.

Hence, the main aims of the study were to assess degradation of phenol using LR with the effect of the following operational parameters:

- Low and high frequencies (20, 300 and 520 kHz)
- Presence and absence of oxidant (H_2O_2) and catalysts (ZVI and ZVCu)
- ZVI and ZVCF, ZVCT, ZVCP catalysts
- Low (0.6 g L^{-1}) and high (5 g L^{-1}) catalysts amounts
- US irradiation and stirring input time (15–30 min)
- Filtered and unfiltered catalyst LR reactions

5.2 Experimental

5.2.1 Chemicals

Latent Remediation studies using multiple (low- and high)-frequency US reactors is a continuation of the work described in Chapter 4 but with the difference that US energy was inputted for only 15 min instead of continuous US irradiation (60 min). Hence, chemicals and their concentrations, i.e., phenol, H_2O_2 and zero valent catalysts (ZVC) and US reactors (20, 300 and 520 kHz) are the same as described in Chapter 4. This study was partially carried out in the Institute of Environmental Studies, Bogazici University, Turkey but additional reactions were performed in the University of Abertay Dundee using the 20 kHz US reactor and a new batch of zero valent iron powder (ZVI; Sigma Aldrich 325 (44 μ) mesh 97%) and zero valent copper powder (ZVCP; Sigma Aldrich 200 mesh (74 μ), 99%) powdered catalysts. The LR experiments were performed in a commercial ultrasonic processor (Cole-Parmer) equipped with a titanium probe (1 cm diameter) capable of operating either continuously or in a pulse mode at a fixed frequency of 20 kHz. The intensity of the irradiation was adjusted to 50% of ultrasonic power amplitude, which corresponds to a calorimetric measurement of 18 W (0.09 W mL^{-1}). LR experiments were carried out with the probe working in pulses, 4.0 s on and 2 s off, which allows the system to dissipate some of the heat generated by the ultrasonic waves.

In a typical experimental set-up with 20 kHz (Cole Parmer), the US probe was immersed in a 300 mL cylindrical glass beaker containing aqueous phenol solution (2.5 mM; 200 mL) and the pH was adjusted to 3.0 with 0.1 M H_2SO_4. The temperature was kept constant at 23 ± 2 °C during all reactions by an external cooling bath. The appropriate concentrations of H_2O_2 (Fisher Chemicals, Analytical reagent, 30%) and catalysts were added to the reactor just before switching the probe on. Aliquots (5–7 mL) were withdrawn at specific time intervals and filtered through 0.45 μm nylon membranes before being analysed. The same experimental set-up equipped with an overhead stirrer (Jencons; 250 rpm) instead of the ultrasound (US) probe was used for the silent experiments.

All the experiments were carried out in either duplicates or triplicates to ensure reproducibility and results presented are average of 2–3 experimental data sets. Phenol degradation was determined by measuring the decrease in TOC over time. The TOC of the initial phenol aqueous solution and the samples taken from the reaction medium was measured by wet oxidation analysis (Model 1020 TOC Analyser from OI-Analytical).

5.2.2 Experimental design

1. Aqueous phenol (2.5 mM; 200 mL) was set at desired pH and zero min sample was taken for TOC measurement (C_0). Immediately, known amounts of ZVC (0.6 and/or 5 g L^{-1}) and H_2O_2 (2.38 g L^{-1}) were mixed with the aqueous phenol and reaction was subjected to either 15 min US or stir
2. Soon after US energy input or stirring, the reaction vessel (300 mL glass beaker) was covered by aluminium foil to avoid oxidation via natural light
3. Reaction vessel was stored in dark and samples (5–7 mL) were withdrawn at specific time intervals to study the phenol degradation over 24, 48 or 72 h
4. Samples were filtered with cellulose membrane filter paper (0.45 μm). Filtered and clear solutions were then injected in TOC Machine (1020 OI Analytical) for TOC analysis and % phenol degradation (mineralisation) (C/C_0) has been reported in this study

5.3 Results and discussion

5.3.1 Preliminary studies

5.3.1.1 LR using multi frequency US reactors

As part of the work done in Chapter 4, LR emerged as an innovative idea to study phenol degradation with low energy input. Hence, initial studies were carried out with the most optimised conditions, i.e., 300 kHz US reactor followed by comparison with two other frequencies (20 and 520 kHz). Results reveal that LR with an initial 15 min US irradiation in the 300 kHz US reactor in conjunction with ZVI leads to an overall TOC mineralisation of ~45% over 24 h.

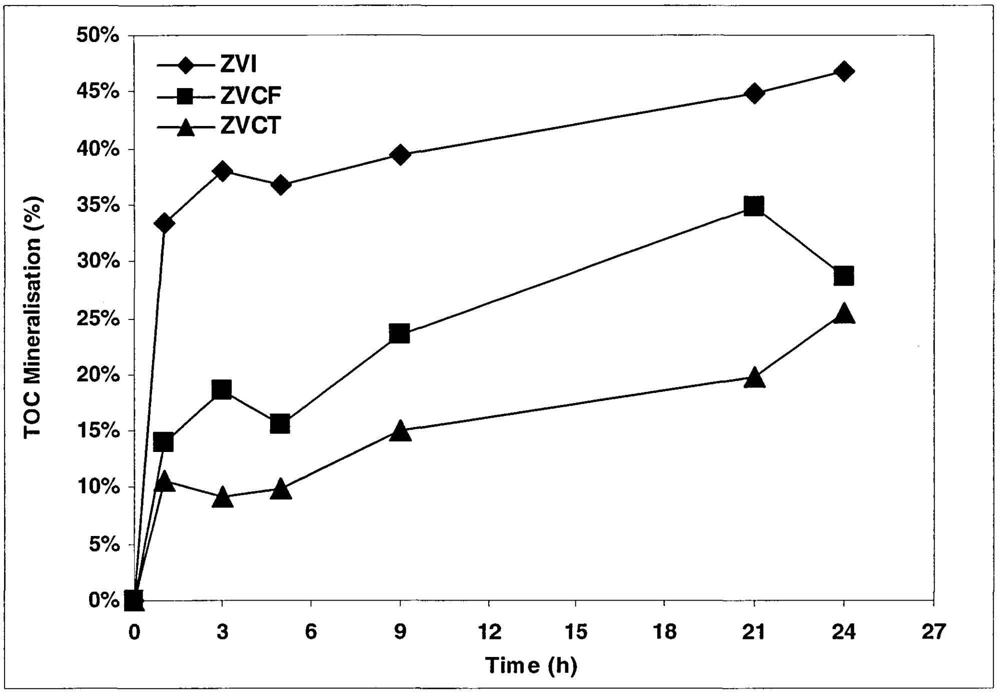


Figure 5.1: Effect of 300 kHz US on phenol degradation using the LR technique. Experimental conditions: phenol, 2.5 mM; US reactor, 300 kHz (15 min); catalysts, ZVI, ZVCF (flitters), ZVCT (turnings); H_2O_2 (2.38 g L^{-1}); pH 3; % degradation, TOC analysis.

From the % degradation shown in Fig. 5.1, it can be seen that with ZVI, nearly 35% TOC mineralised within the 1 h of reaction time (with only 15 min of US irradiation), which is similar to the % degradation obtained by continuous 1 h sonication. Therefore, it is assumed that certainly high rates of hydroxyl radical (HO•) production in the 300 kHz US reactor lead to efficient phenol degradation. However, a further

10% increase in TOC mineralisation over 24 h. It is believed that the ultrasound enhances the dissolution of ZVI in the acid solution to form Fe (II) ions which then take part in Fenton chemistry (as described in Chapter 4) to generate HO• and Fe (III). It is the essence of the Advanced Fenton Process (AFP) that the ferric ion then interacts with ZVI to re-form Fe (II) which further continues to generate HO•. On the contrary, degradation profiles using ZVCu catalysts in the 300 kHz US reactors showed that only a maximum of 20–30% mineralisation was seen after 24 h, which is very similar to the degradation pattern obtained for 1 h continuous irradiation.

As discussed in Chapter 4 ZVI was found to be the most effective catalyst for phenol degradation and this is also the case for LR using 300 kHz reactor as shown in Fig. 5.1. Therefore, the ZVI catalyst was used to study LR under three different frequencies and it was found that 20 kHz US showed highest % mineralisation of 55% which is 10% higher than the 300 and 520 kHz US reactors (Fig. 5.2).

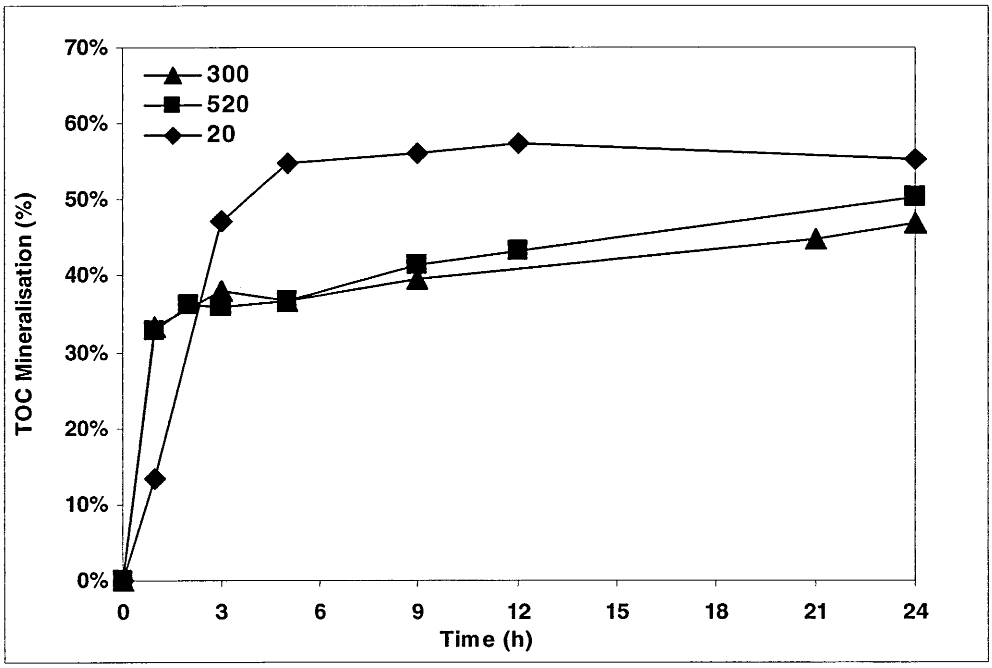


Figure 5.2: Comparison of different frequency US reactors (20, 300 and 520 kHz) with ZVI catalyst on % phenol degradation using the LR technique. Experimental conditions: phenol, 2.5 mM, US reactors, 20, 300 and 520 kHz (15 min); catalysts, ZVI (0.6 g L^{-1}); H_2O_2 (2.38 g L^{-1}); pH 3; % degradation, TOC analysis.

The above results showed that along with highest overall mineralisation achieved after 24 h, the degradation was also quite high (after about 2 h) in case of the 20 kHz US. This is attributed to the fact that high mechanical action during cavitation in 20 kHz US leads to surface activation of the catalyst and therefore makes it more readily available for reaction. Therefore, even though the rates of HO• production at this frequency are low compared to the higher frequency US reactors (300 and 520 kHz), the rate of reaction and overall mineralisation over 24 h in the LR with 20 kHz US is quite high because of the high mechanical activity. It is interesting to note that initially, i.e., during the first 90 min after US irradiation is switched off, the degradation was faster with the 300 and 520 kHz US, possibly indicating that there has been greater production of HO• at these frequencies. It is assumed that due to high intensity of cavitation at 20 kHz, the iron particles are further broken down to finer particles increasing the number and quality of available reactive sites, thus the polished catalysts provide a larger surface area for catalyst/oxidant reactions in the bulk solution over longer durations leading to high % degradation.

Table 5.1 shows a comparative study of phenol degradation, using ZVI in the AFP with continuous sonication (data obtained from chapter 4) and the newly developed LR technique after 1 h and 24. From the data, it is clear that 15 min US energy input is sufficient to start the degradation which then continues over 24 h and this hypothesis is further supported by data presented later in this chapter with a different catalysts and 20 kHz US reactor set-up in a 200 mL reaction volume.

	TOC mineralisation (%)		
US Irradiation time	Continuous US	Latent Remediation (15 min US)	
US frequencies (kHz)	After 1 h	After 1 h	After 24 h
20	39.9	13.4	55.3
300	37.8	33.3	46.9
520	37.0	32.7	50.3

Table 5.1: Comparison of % TOC mineralisation achieved through continuous sonication and LR using ZVI catalyst at three different frequencies. Experimental conditions: phenol 2.5 mM; US reactors, 20, 300 and 520 kHz; continuous sonication, 1 h; LR, initial 15 min sonication; catalyst, ZVI (0.6 g L^{-1}); H_2O_2 (2.38 g L^{-1}); pH 3; % degradation, TOC analysis.

5.3.1.2 Effect of ZVI characteristics on LR rates

All the studies so far with ZVI were carried out with old ZVI powder (size, 39 μ) obtained from the University of Abertay, however for the LR studies in this chapter, new ZVI powder was obtained with a different size and purity (Sigma Aldrich; 325 mesh (44 μ), purity 97%, Cat No. 20930-9). However, before use, a comparative study was carried out between old (ZVI-O, 39 μ) and new ZVI (ZVI-N, 44 μ) powder by comparing the LR rates over 24 h in the absence of US by using overhead stirring for the initial 15 min at 250 rpm to ensure efficient mixing of catalyst, oxidant and model compound. This study was carried out in triplicate and Fig. 5.3 presents the average value from the three experiments.

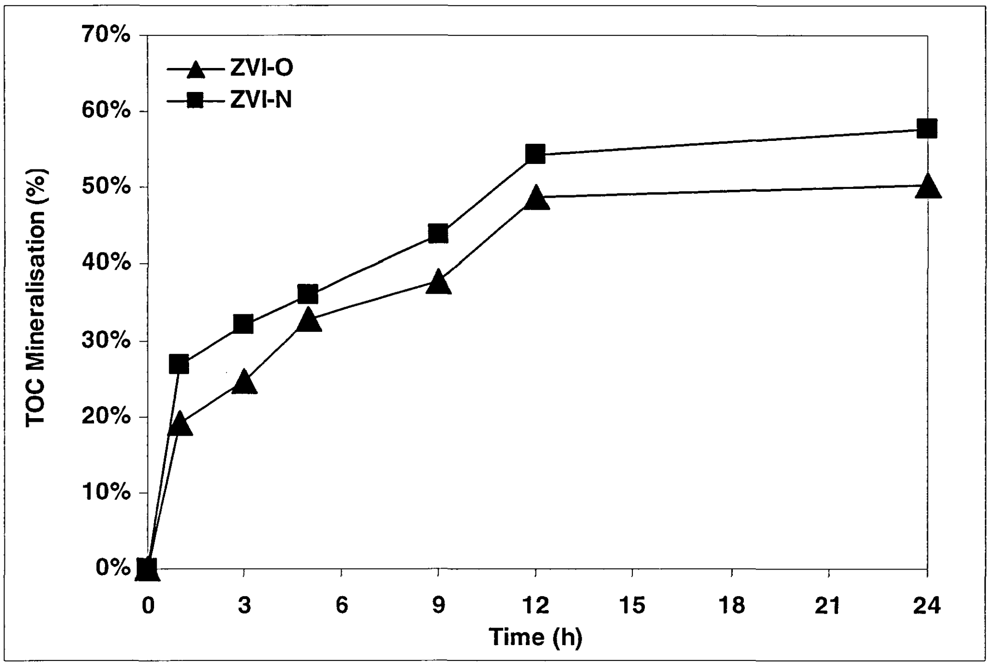


Figure 5.3: Comparison of ZVI-O and ZVI-N catalysts phenol degradation using the LR technique in the absence of US. Experimental conditions: phenol, 2.5 mM; overhead stirring, 250 rpm (15 min); catalysts, ZVI-O and ZVI-N (0.6 g L^{-1}); H_2O_2 (2.38 g L^{-1}); pH 3; % degradation, TOC analysis.

From Fig. 5.3, it can be seen that although there is not much of a difference between the effectiveness of the two ZVI powders ZVI-N is still 5–7% better than ZVI-O, hence ZVI-N was chosen for use in all subsequent experiments presented in this chapter. It is believed that probably the particle size and surface properties of the two powders contributes to the slight differences between the observed phenol degradations.

5.3.1.3 Effect of US irradiation time on LR rates

Although preliminary LR studies were carried out by irradiating the phenol solution for 15 min, the effect of increasing the initial irradiation time was investigated. Therefore, phenol degradation using LR was compared with initial input of 15 and 30 min of US irradiation and the results are shown in Fig. 5.4 where it can be seen that there is no significant difference between overall phenol degradation at the two chosen US irradiation times. Hence, it was concluded that 15 min corresponds to a lower US energy input and is sufficient to carry out effective mineralisation.

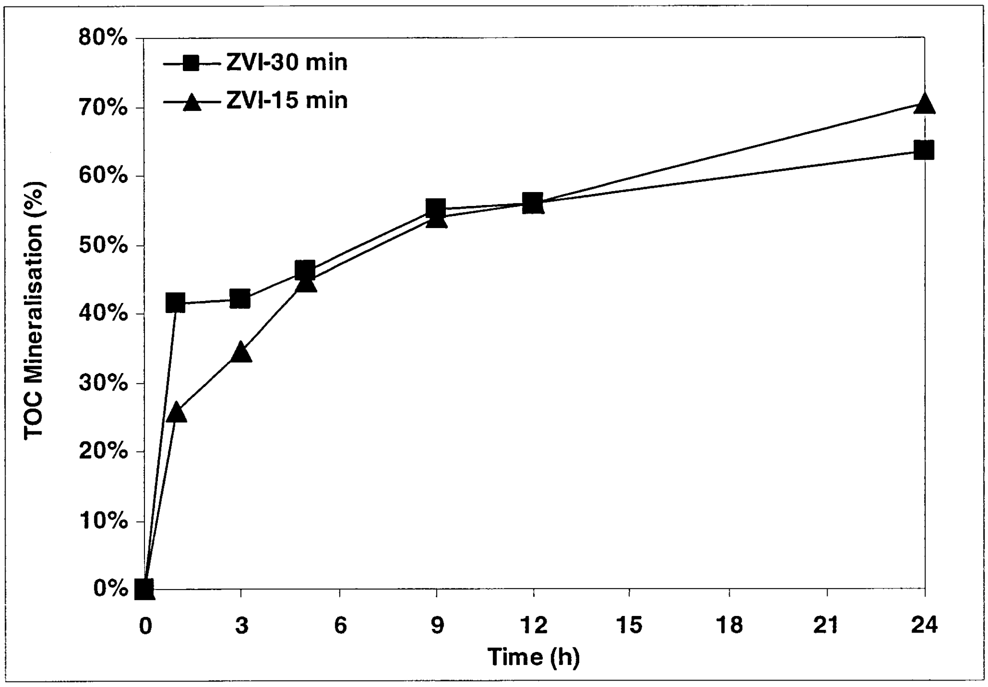


Figure 5.4: Comparison of 20 kHz US irradiation times (15 and 30 min) along with ZVI catalyst phenol degradation using the LR technique. Experimental conditions: phenol, 2.5 mM; US, 20 kHz (15 and 30 min); catalysts, ZVI (0.6 g L^{-1}); H_2O_2 (2.38 g L^{-1}); pH 3; % degradation, TOC analysis.

From Fig. 5.4, it is understood that the initial 10–15 min of US irradiation is sufficient enough to get the reaction started with respect to formation of radical species in the bulk solution and also conversion of Fe^0 to Fe^{2+} and/or Fe^{3+}, which further participates in the reaction and carries out mineralisation, therefore more US input after 15 min is not necessary. Hence, all the LR experiments were carried out with inputting either 15 min of US irradiation or 15 min of overhead stirring to facilitate efficient mixing and enhanced mass transfer rates between catalysts, oxidants and organic compound.

5.3.1.4 Effect of catalyst amounts on LR rates

So far, phenol degradation using ZVI and ZVCu catalysts in combination with US had been carried out with 0.6 g L^{-1} and 5 g L^{-1}, respectively, as discussed in Chapter 4 and Fig. 5.1. ZVI and H_2O_2 concentrations for phenol degradation were optimised earlier by Molina et al. (2006), hence the same was used for all the experiments reported in this thesis. However, ZVCu catalysts, i.e., flitters, turnings and powder, were novel catalysts especially chosen to assess their efficacies to carry out the AFP. Preliminary studies with copper flitters (ZVCF) and turnings (ZVCT) reported in Chapter 4 were carried out at 5 g L^{-1} catalyst amount, however for comparative work zero valent copper powder (ZVCP), zero valent copper flitters (ZVCF; Plate 5.1) and zero valent copper turnings (ZVCT; Plate 5.2) were compared at two different amounts, i.e., 0.6 g L^{-1} and 5 g L^{-1} in the different 20 kHz US reactor set-up with 200 mL reaction volume and results are presented in Fig. 5.5. However, to avoid the effect of US on this reaction, aqueous phenolic solutions were only stirred for 15 min at 250 rpm at the start of the experiment with ZVCP or ZVCF or ZVCT along with H_2O_2 and the degradation was measured over 24 h.

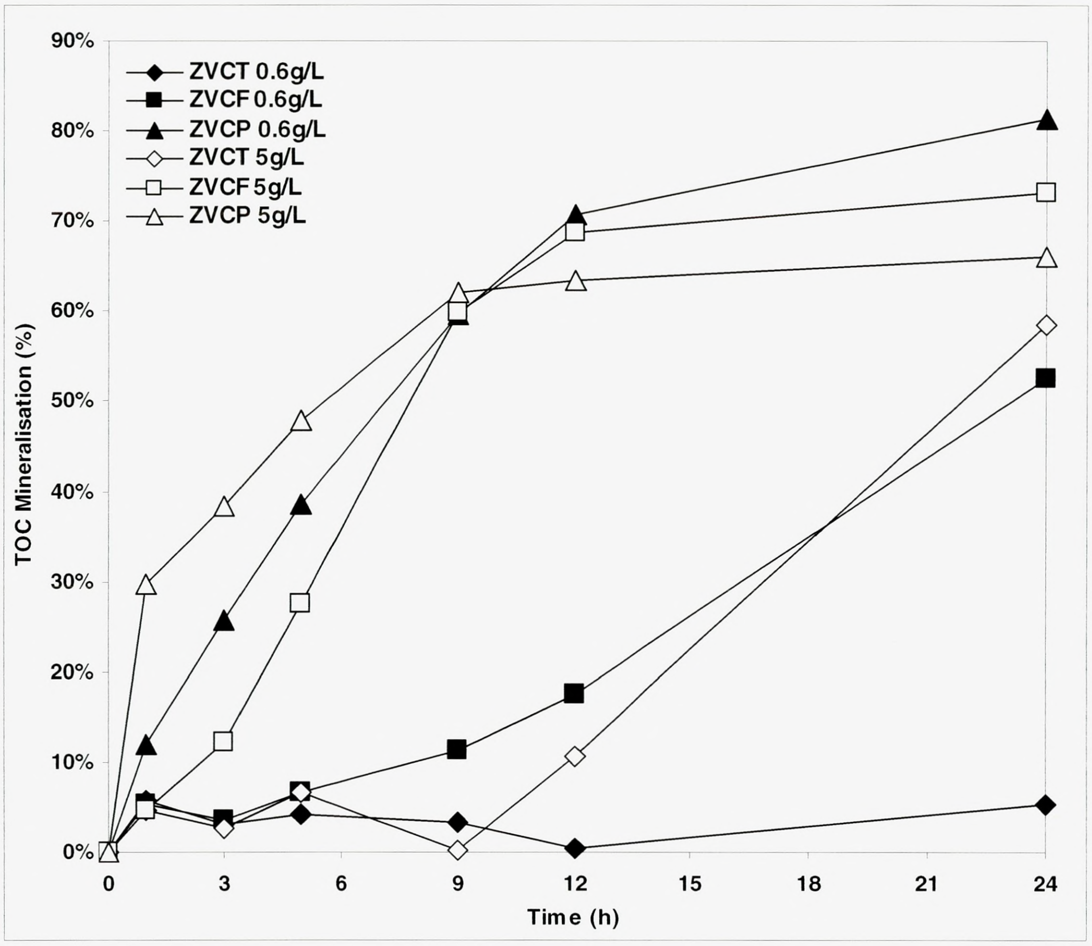


Figure 5.5: Comparison of different amounts and types of ZVCu catalysts for phenol degradation using the silent LR technique. Experimental conditions: phenol, 2.5 mM; overhead stirring, 250 rpm (15 min); ZVCu catalysts (0.6 and 5 g L^{-1}): ZVCP, ZVCF, ZVCT; H_2O_2 (2.38 g L^{-1}); pH 3; % degradation, TOC analysis.

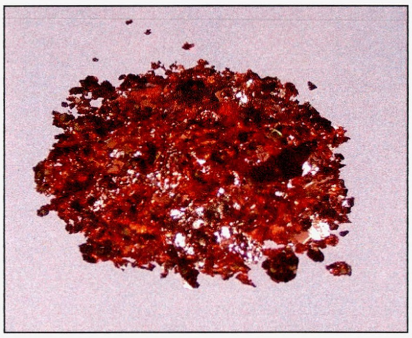


Plate 5.1: ZVCF (copper flitters)

Plate 5.2: ZVCT (copper turnings)

From Fig. 5.5, it is clear that ZVCP is the most efficient at degrading phenol. However, the experimental data reveals that a low amount of ZVCP (0.6 g L^{-1}) is comparable to higher amounts of ZVCF/ZVCT (5 g L^{-1}) for phenol degradation. The extent of phenol degradation with ZVCP (0.6 g L^{-1} and 5 g L^{-1}) was found to be the same (60%) until about 9 h of silent reaction, but TOC mineralisation with ZVCP (0.6 g L^{-1}) increased to 83% after 24 h, whereas ZVCP (5 g L^{-1}) remained constant, at 60%. In contrast, ZVCT (0.6 g L^{-1}) could only mineralise around 5% phenol over 9 h but after 24 h the ZVCT (0.6 g L^{-1}) mineralisation remained at 5% but ZVCF (0.6 g L^{-1}) had increased to 50%. Thus, the best mineralisation is achieved with ZVCP (0.6 g L^{-1}) and this is attributed to a suitable catalyst oxidant ratio required for efficient phenol degradation. Higher amounts of catalyst inhibit the rates of reaction due to decomposition of H_2O_2 required to carry out further mineralisation, hence any increase in catalyst quantity does not enhance the overall degradation. However, higher amounts of the catalysts like ZVCF and ZVCT (which have much larger particle size initially) increase the surface area required for the reaction and therefore they are better suited instead of lower amounts. It is noteworthy that silent reactions without any initial US irradiation could efficiently carry out Fenton like reactions in the AFP using ZVCu catalysts. Therefore, one of the main objectives of this study, i.e., to test different ZVCu catalysts for carrying out the AFP has been successfully achieved and reaction mechanisms will be discussed later in this chapter.

5.3.2 Effect of ZVI and ZVCP on LR rates

After optimising the type and amounts of catalysts, the rates of LR were compared for 0.6 g L^{-1} ZVI and ZVCP catalysts with minimum energy input of 15 min either overhead stirring (250 rpm) or US irradiation (20 kHz). LR rates with ZVI and ZVCP in the AFP were also studied and compared in the presence and absence of catalyst and oxidant conditions.

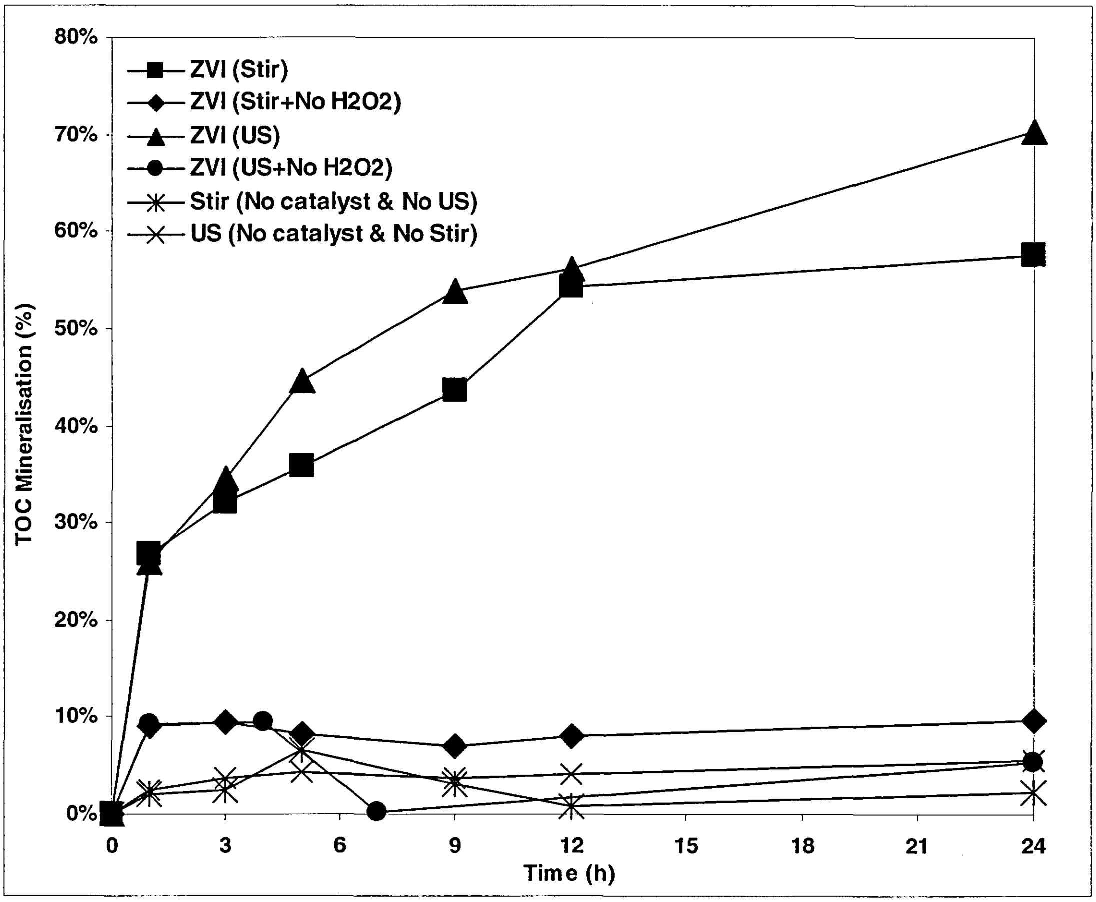


Figure 5.6: Comparison of phenol degradation with the ZVI catalyst under different operating conditions using the LR technique. Experimental conditions: phenol, 2.5 mM; US, 20 kHz (15 min); stirring, 250 rpm (15 min); catalysts, ZVI (0.6 g L^{-1}); H_2O_2 (2.38 g L^{-1}); pH 3; % degradation, TOC analysis.

Fig. 5.6 shows a comparison of the different operating conditions for ZVI as the catalyst. It can be easily seen from the figure that the presence of catalyst and H_2O_2 is essential for a decrease in TOC. Thus, use of US/stirring in the initial 15 min time acts as an initiator of series of reactions as indicated in Eq. 5.3–5.6. Use of US facilitates a larger production of radicals as compared to the use of stirring alone as indicated by higher TOC mineralisation for the case of ZVI as catalyst.

$$Fe^0 \xrightarrow{H^+} Fe^{2+} \quad (5.3)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + HO\bullet + OH^- \quad (5.4)$$

$$Fe^0 + 2Fe^{3+} \longrightarrow 3Fe^{2+} \quad (5.5)$$

$$HO\bullet + \text{Pollutant} \longrightarrow CO_2 + H_2O + \text{small organic acids} \quad (5.6)$$

From the above equations, it can be seen that the ZVI catalyst is capable of conversion of Fe^0 to Fe^{2+} and also Fe^{3+} to Fe^{2+} which is essential for carrying out the classic Fenton reaction expressed in Eq. 5.1 and 5.2. Therefore, it can be suggested that ZVI, in the presence of H_2O_2 and at pH 3, provides an effective alternative to the conventional Fenton chemistry.

From the above comparison graph, it can be noted that phenol degradation with initial 15 min US treatment has been quite effective right from the start of the reaction and between 12 and 24 h, pronounced phenol degradation were achieved when compared with those of 15 min of stirring. With only 15 min of stirring, the % degradation did not change between 12 and 24 h indicating that less HO• were produced.

Therefore, the hypothesis drawn from this study is that an input of US irradiation could help in catalysing the reaction and a balanced stoichiometric ratio of catalyst and oxidant is essential to achieve high phenol mineralisation. This hypothesis is in agreement with various reports published in the literature where synergism of Fenton with US, termed 'sono-Fenton' proves to be beneficial for increasing % degradation (as discussed in Section 5.1). However, LR, with substantially lower energy inputs, has capability to carry out degradation under silent conditions is being reported in this research for the first time which makes this work novel and meets the scope of this study.

In a related investigation, similar amounts of ZVCP catalyst were also tested under various operating conditions and the results are presented in Fig. 5.7. However, unlike, ZVI, where a benefit of using US/ZVI together was observed, ZVCP gives similar degradation results of 80% and 83% TOC mineralisation with US/ZVCP and Stir/ZVCP, respectively (Fig. 5.7).

The results shown below are in agreement with literature reports (Entezari *et al.*, 2003) where after 180 min of either 20 kHz US or silent treatment, 80% phenol removal was obtained with both $CuSO_4/H_2SO_4$/US and $CuSO_4/H_2SO_4$/Stir and also represented the classical the Fenton type reactions with copper catalysts (Eq. 5.7–5.8).

$$H_2O_2 + Cu^{2+} \longrightarrow Cu^{2+} + \bullet HO_2 + H^+ \qquad (5.7)$$
$$H_2O_2 + Cu^{+} \longrightarrow HO^- + HO\bullet + Cu^{2+} \qquad (5.8)$$

From Fig. 5.7, it is also obvious that absence of either catalyst and/or H_2O_2 affects the % degradation to a great extent, as is also reported in the literature copper ions alone cannot enhance sonochemical degradation (De Visscher and Van Langenhove, 1998), however this is contrary to results reported by Ingale and Mahajani (1995) who stated that nickel and copper ions alone enhanced the % degradation of unidentified refractive compounds into chemically degradable compounds. Another relevant observation (De Visscher and Van Langenhove, 1998) is that although $CuSO_4/H_2O_2$ did not influence trichloroethylene (TCE) degradation, but efficiently degraded 1,3-dichloro-2-propanol (DCP), both the organic compounds degraded silently after sampling, which we have termed as LR, but this phenomenon was not reported in detail.

Thus, LR studies presented in this chapter with ZVCP and ZVI with only initial 15 min of stirring or US treatment is assumed to be superior in terms of energy consumption and overall treatment cost (not estimated). Alternatively, ZVCP could also be used as a potential catalyst in AFP or classic Fenton like reactions to efficiently degrade toxic pollutants.

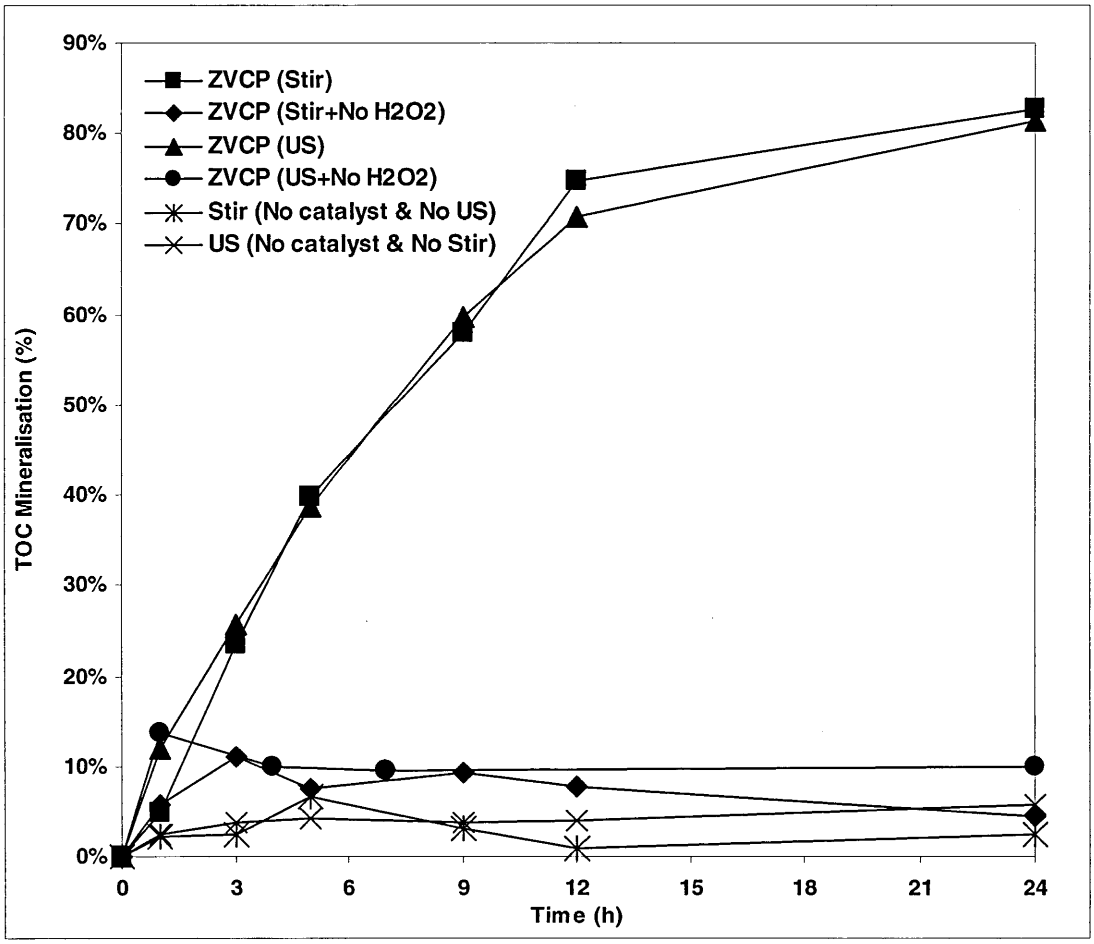


Figure 5.7: Comparison of phenol degradation with ZVCP catalyst under different operating conditions using the LR technique. Experimental conditions: phenol, 2.5 mM; US, 20 kHz (15 min); stirring, 250 rpm (15 min); catalysts, ZVCP (0.6 g L^{-1}); H_2O_2 (2.38 g L^{-1}); pH 3; % degradation, TOC analysis.

5.3.3 Effect of removing the ZVC after 15 min reaction

This investigation was carried out to assess the effect of having the catalysts, ZVI and ZVCP, absent during the LR stage and was carried out by inputting 15 min of either stirring or US to the reaction solution followed by filtering the catalysts and subsequently monitoring the degradation of phenol in the filtrate over 24 h time. It is seen that over a 24 h period the extent of mineralisation is reduced compared to the case where the catalyst remains *in situ* throughout the LR phase (compare with Fig. 5.6) possibly giving credence to the idea that the ZVC are promoting the reduction of Fe^{3+} back to Fe^{2+} and thus continuing the Fenton process, as shown in Eq. 5.5 (Fig. 5.8).

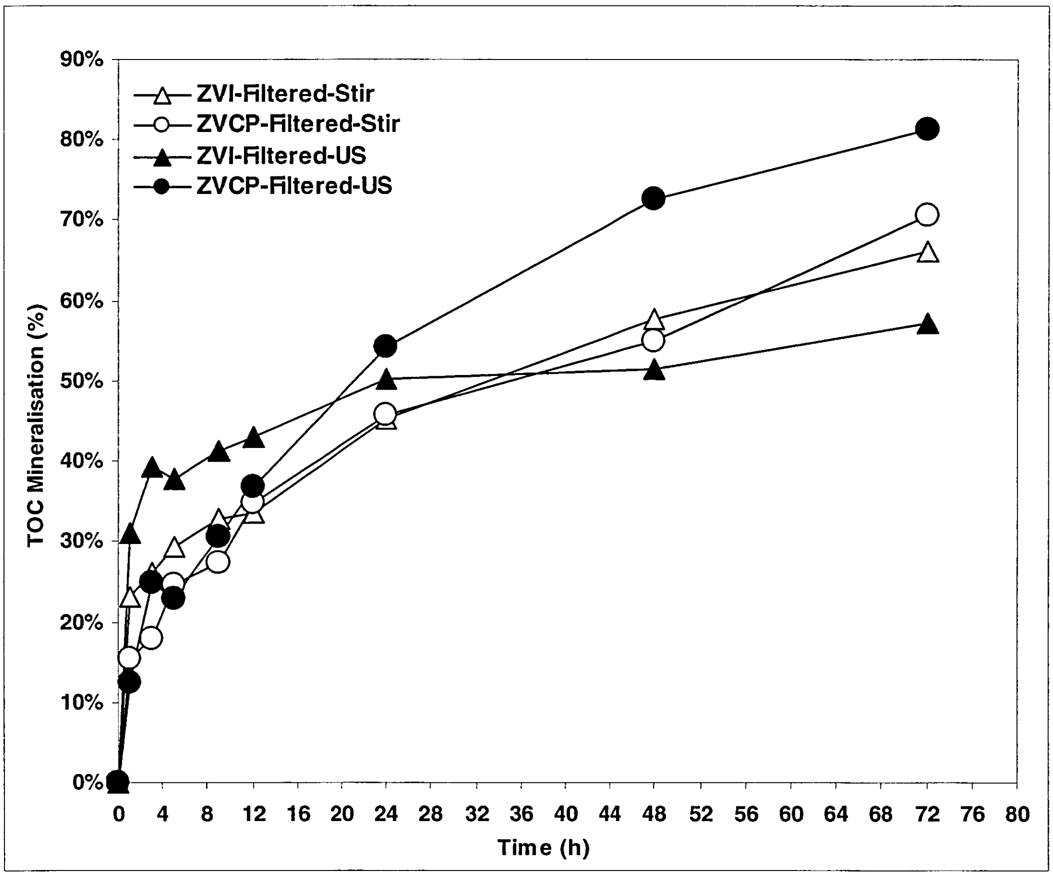


Figure 5.8: Phenol degradation using LR technique after removal of the catalyst. Experimental conditions: phenol, 2.5 mM; US, 20 kHz (15 min); stirring, 250 rpm (15 min); catalysts, ZVCP and ZVI (0.6 g L^{-1}); H_2O_2 (2.38 g L^{-1}); pH 3; % degradation, TOC analysis.

Initial 12 h phenol filtrate catalysed by either ZVCP/ZVI or US/Stir shows minimum difference in the % degradation (30–40%), as time proceeds, the 24 h results shows 45–55% mineralisation under the above mentioned conditions but at the end of 72nd h, % degradation with ZVCP-filtered/US shows pronounced difference in the phenol removal (81%) as compared to the ZVI-filtered/US (57%) and/or ZVCP-ZVI-filtered/Stir (65–70%). The stirred reactions with ZVCP and ZVI showed absolutely no difference in their phenol degradation even after 72 h reaction time, but, in the sonicated reactions, of phenol degradation with ZVI stabilised after 24 h but continued to increase in case of ZVCP. This could be attributed to the additional free radicals in bulk solution catalysed copper mediated chain reactions whereas, in ZVI filtrates maybe the continuous presence of catalysts continuously supply ions required for iron mediated chain reactions. However, this hypothesis still can be argued for the fact that ZVCP-ZVI-filtered/Stir reactions could still carry out better mineralisation than that of

ZVI-filtered/US but here for the filtered–non-filtered catalysts LR reactions, this argument to lead to erroneous conclusions.

Therefore, for a better understanding the reactions with ZVCP/ZVI and US/Stir which had been filtered are compared with those under non-filtered reactions, i.e., the usual LR for 24 h reaction period and this will give an insight into the role catalysts played in the process of phenol degradation (Fig. 5.9).

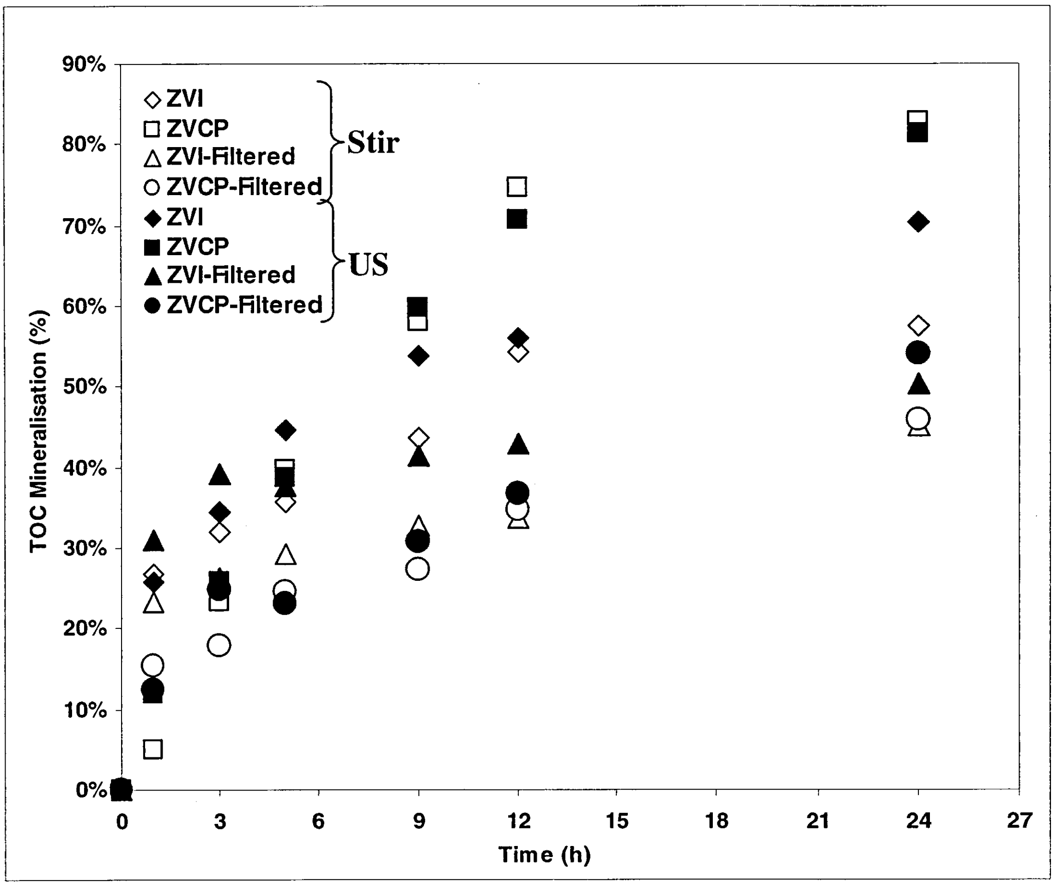


Figure 5.9: Comparison of filtered and unfiltered LR reactions on phenol degradation. Experimental conditions: phenol, 2.5 mM; US, 20 kHz (15 min); stirring, 250 rpm (15 min); catalysts, ZVCP and ZVI (0.6 g L^{-1}); H_2O_2 (2.38 g L^{-1}); pH 3; blocked symbols, US; hollow symbols, stir; % degradation, TOC analysis.

It can be seen from Fig. 5.9 that there is a remarkable difference between reactions where the catalysts have been filtered (45–55%) and the non-filtered reactions (55–80%). Certainly, the usual ZVCP LR reactions could still carry out maximum mineralisation irrespective of US or stir conditions however ZVI performs best in the US-initiated LR. Therefore, it is concluded from the study that in heterogeneous catalytic chemical oxidation, the surface of the catalysts enhances the formation of various radical species required during the process of degradation. ZVCP catalysts show better % degradation irrespective of presence/absence of US but sonication of ZVI recharges the catalyst surface which in turn enhances the properties of the reactive sites contributing to high mineralisation in US–LR compared to Stir–LR in the non-filtered reactions. Whereas, in the case of the filtered ZVCP/ZVI in the US–LR reactions, initial % mineralisation were fairly high in the case of ZVI but showed similar degradation (45%) as ZVCP at the end of 24 h reaction time. The overall conclusion drawn from this part of the study stresses the fact that the availability of a heterogeneous catalyst surface is important in order to initiate and mediate various radical chain reactions and also to act as nucleation sites for formation of radical species.

5.4 Toxicity evaluation

From the above study, it is quite obvious that ZVCP catalysts, in conjunction with the AFP, have an ability to carry out high phenol degradation similar to Fenton-like reactions. However, the issue relating to toxicity of copper needs to be addressed. Consequently, toxicity evaluation (Courtesy: Dr. Andreas Tiehm team, Karlsruhe University, Germany) was carried out on several US–LR samples of ZVI and ZVCP collected at different stages of the reactions (24, 48, 72 h) and from various US irradiation times (15 and 30 min). Results shown in Table 5.2 indicate high toxicity by the all of the ZVCP samples, whereas there is a decreased toxicity shown by the ZVI samples. Interestingly, the sample of ZVI from the 30 min US–LR reaction after 24 h showed a lower toxicity compared to a sample removed after 15 min of irradiation and kept for 48 and 72 h. This is probably due to the toxicity present due to the residual hydrogen peroxide in the 15 min sample. Thus, the conclusions drawn from the above study are that although ZVCP in the AFP is an efficient catalyst in degrading phenol, the ecotoxicity analyses indicate that ZVCP is too toxic to be used as a catalyst in conjunction with the AFP for wastewater treatment.

US–LR samples	TOC_t (mg L^{-1})	Toxicity EC20 (%)	EC50 (%)	Max. inhibition[b] (%)
24 h (ZVI, 30 min US)	90.2	15	50	51
48 h (ZVI, 15 min US)	47.8	17	59	42
72 h (ZVI, 15 min US)	ND[a]	34	>100	30
24 h (ZVCP, 30 min US)	46.5	8	12	>90
48 h (ZVCP, 15 min US)	40.9	10	14	>90
72 h (ZVCP, 15 min US)	ND[a]	10	14	>90

[a]ND: Not detected.

[b]For 50% Sample + 50% mineral medium.

Table 5.2: Toxicity evaluations on various ZVI and ZVCP US–LR samples (Courtesy: Dr. Andreas Tiehm team, Karlsruhe University, Germany).

Toxicity of the sonicated samples was measured by diluting the samples. The dilution factor resulting in a 20% and 50% reduction (EC20 and EC50) of bioluminescence was determined. A higher EC20 or EC50 corresponds to a lower toxicity (Section 2.4.8) (Tiehm and Neis, 2005).

5.5 Summary

A comparison of the different operating variables used in the study of Latent Remediation is summarised below in Fig. 5.10.

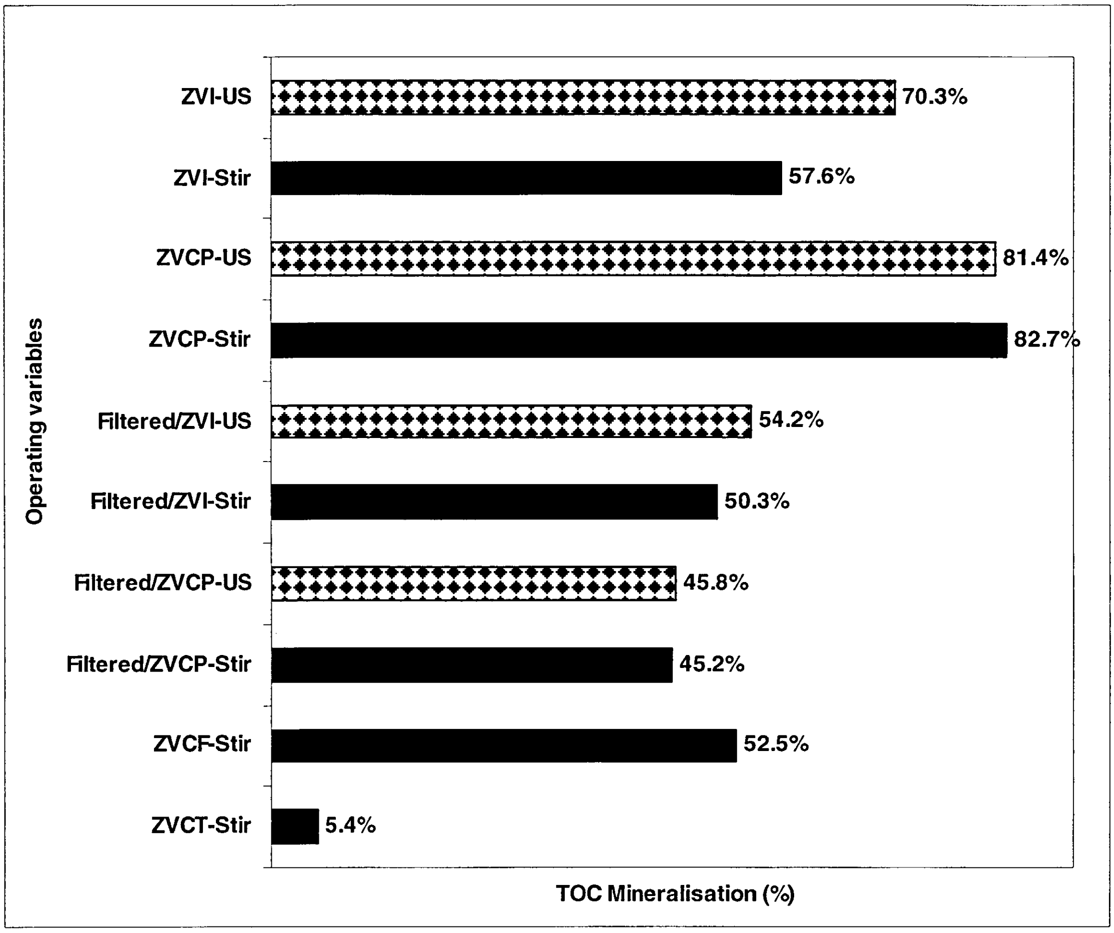


Figure 5.10: Comparison of different LR conditions on % TOC mineralisation over 24 h reaction time. Black bars, Stir–LR and pattern bars, US–LR. Experimental condition: phenol, 2.5 mM; H2O2, 2.38 g L^{-1}; ZVC, 0.6 g L^{-1}; pH 3; reaction time, 24 h; US or stir input time, 15 min; anlaysis, TOC analyser.

The main aim of the study was focused on developing greener and cost-effective ways to degrade toxic pollutants, therefore only initial 15 min sonication or stirring was provided to the reaction medium in order to initiate HO• production from H_2O_2 and ZVI or ZVCP. From the above study, the following conclusions may be drawn:

- Mechanical activity and high intensity 20 kHz US–LR along with a ZVI catalyst is more effective at mineralising phenol than 300 and 520 kHz.
- Increased sonication time of 30 min, did not have any pronounced effect on the LR rates.
- Higher amounts of ZVCP (5 g L^{-1}) did not prove to be beneficial in increasing LR rates, whereas higher amounts of ZVCF and ZVCT showed a pronounced increase in LR rates when compared to 0.6 g L^{-1} attributed to the presence of larger surface area.
- The presence of oxidant and catalyst in the bulk solution was found to be essential to carry out efficient LR using the Advanced Fenton Process.
- ZVI-mediated LR performed best in US initiated reactions, whereas ZVCP lead to equal % mineralisation with both US and/or stirred reactions.
- The presence of a heterogeneous catalyst in bulk solution is beneficial and leads to >80% TOC mineralisation.
- ZVCP could be used as an alternative catalyst in Fenton-like reactions and/or the AFP.
- Toxicity evaluation prefers ZVI for integrated wastewater treatment systems.
- Overall Latent Remediation provides an emerging technology to treat toxic wastewaters at comparatively low costs and decreased energy inputs.

Chapter 6

Degradation III: Investigation of activated carbon cloth and oxidants for phenol removal via adsorption/oxidation

Platform presented paper: International Ozone Conference

Chand, R. (15th–16th May 2008). Remediation of phenolic wastewaters using ozone, hydrogen peroxide catalysts and cavitation. *International Conference on Ozone and Related Oxidants in Advanced Treatment of Water*. Brussels, Belgium. [Special prize awarded for best presentation].

6.1 Introduction

Until recently, industrial effluents were treated by traditional techniques like filtration, reverse osmosis, flocculation, coagulation, precipitation and finally incineration. In a traditional approach, the pollutants were transferred from the liquid phase to a solid phase and for years activated carbon (AC) has been known as the best for adsorption of various toxic pollutants. Activated carbon is commercially produced and widely used in various treatment methods to remove toxic pollutants from the environment, i.e., packed towers with AC have been extensively utilised as air pollution control devices. Likewise there are many reports on the adsorption of toxic pollutants on the surface of the AC (Takaoka *et al.*, 2007). However, adsorption of toxic pollutants from either gas or liquid phases onto a solid phase is not the final disposal method, therefore secondary treatment or combined technologies are required to effectively treat the adsorbed pollutant and also reuse the spent AC.

Individual and combined techniques utilising granular activated carbon (GAC) and other Advanced **O**xidation **P**rocesses (AOPs) have been commonly used in water and wastewater treatment in order to remove toxic pollutants (Faria *et al.*, 2005; Lin and Lai, 2000; Lin and Wang, 2003; Lopez-Lopez *et al.*, 2007; Quinlivan *et al.*, 2005; Zhang *et al.*, 2006), however on the industrial scale, the use of fibrous activated carbon in the form of cloth (ACF/ACC) or felt has received enormous attention as an adsorbent for purifying water as well as air (Brasquet *et al.*, 1996; Delanghe *et al.*, 1996; Economy *et al.*, 1996; Le Cloirec *et al.*, 1996, 1997). ACC/ACFs are produced from a natural or synthetic precursor by carbonisation and activation at 800/1000 °C in the presence of CO_2 or steam (Suzuki, 1991). The ACFs, so produced have high specific surface areas (800–2000 $m^2\ g^{-1}$) and micropores with diameters in the range from 5 to 21 Å, are directly connected to the external surface of the fibres ensuring that the initial adsorption velocities are higher than that of granules (Ryu, 1990).

For over two decades, ACs have also been efficiently used as metal catalyst support material but there are very few reports of the effects of AC on the decomposition of toxic organic substances at low temperatures (Bozzi *et al.*, 2005; Carabineiro *et al.*, 1999; Shimada *et al.*, 1998). Bozzi *et al.* (2005) reported the decomposition of industrial wastewaters on non-adsorbing Fe/C fabrics (combination of AC and Fenton-based systems) and addressed the pre-treatment of toxic and recalcitrant compounds such as chlorinated aromatics and non-aromatics, anilines, phenols and methyl-tert-butyl-ether (MTBE) found in industrial wastewaters. In that study, the main aim was to reduce the TOC (the hydraulic load) for further bacterial processing during the secondary effluent treatment and the degradation rates were studied as a function of the amount of oxidant (H_2O_2) used, recirculation rates, solution pH and temperature. Results indicated the potential of Fe/C fabrics as Fenton immobilised catalysts in the treatment of real wastewaters containing important families of toxic industrial compounds. Fe/C fabrics have also successfully been reported for the degradation of azo-dye Orange II (Yuranova *et al.*, 2004) and Fe/Silica fabrics for degradation of industrial wastewaters (Bozzi *et al.*, 2003). Other researchers have attempted to decompose toxic organic compounds, like trichloroethylene and pentachlorophenol, by combined techniques of AC and microwave irradiation, however the relationship between the nature of the carbon and the organic compounds decomposition have not been discussed in detail (Jou, 1998; Liu *et al.*, 2004).

Furthermore, it is believed that the characteristics of the surface of the AC such as the number of active sites (free radicals) and the functional groups present both influence the overall reaction and relationship between the organic compounds and the AC (Gómez-Serrano *et al.*, 1994; Otake and Jenkins, 1993; Strelko *et al.*, 2002; Szymanski *et al.*, 2002). Carbon functionalisation with oxygen, nitrogen and sulphur has been widely investigated and oxygen surface groups have been reported to be, by far, the most important in influencing the properties of carbon (Boehm, 2002). Recently, in a separate study, it was reported that a reducing treatment with H_2 could also strongly modify the redox properties of an AC resulting in remarkable effects on the catalytic properties towards decomposition of H_2O_2 and oxidation of aqueous organic pollutants (Oliveira *et al.*, 2004).

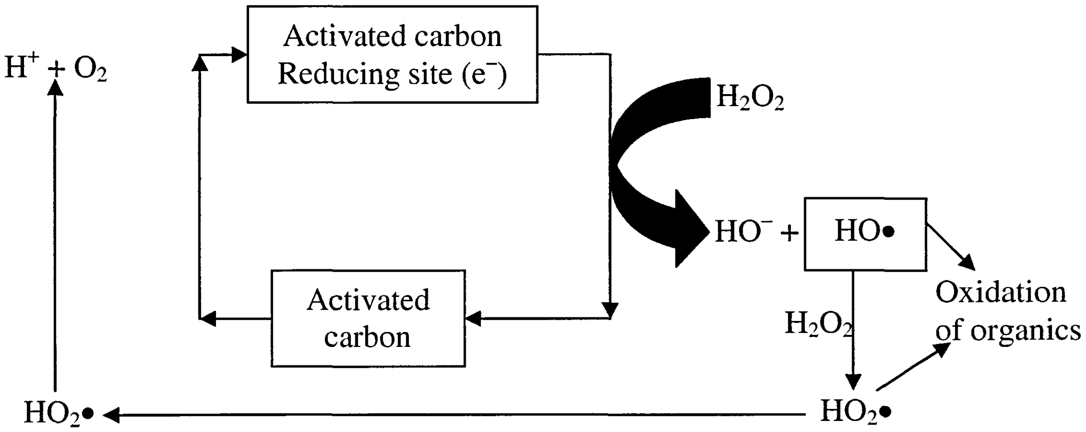
Since the main objective of this current study was to assess the effect of different types of activated carbon cloths (ACC), pH, temperature and different oxidising agents, i.e., H_2O_2 and O_3 in conjunction with ACCs on phenol removal via adsorption/oxidation, previous findings and observations with $H_2O_2/O_3/AC$, in particular, have been taken into account and are presented here to present a background for this study.

As discussed above, adsorption on AC is one of the most commonly used treatments, which are process based, for the concentration and immobilisation of pollutants on the surfaces of granular/powdered AC, termed as 'interface phenomenon'. However, tertiary treatment by adsorption alone is not an environmentally complete system, unless the immobilised pollutants on the spent or used carbon surface are removed as well. Thus, adsorption alone cannot be compared as to the treatments via advanced oxidation systems, where there is neither any accumulation nor transport of the pollutant from one medium to another (Ince and Apikyan, 2000). Thus, there have been proposed advanced methods, termed phase transfer oxidation, to cope with this problem involving two simultaneous operations: (i) fixed-bed adsorption of the pollutant from the effluent and (ii) advanced oxidation for destructive regeneration of the adsorbent (Liu *et al.*, 1996; Mourand *et al.*, 1995; Notthakun *et al.*, 1993). This strategy has been reported to provide significant benefits as 'on-site regeneration' and eliminate loading, transportation and repackaging of the adsorbent (Mourand *et al.*, 1995).

Hydrogen peroxide (H_2O_2) in conjunction with AC tends to modify the catalytic properties of AC for adsorption and/or degradation, however yet again, in this context of granular activated carbons (GAC) have been discussed in detail with different view points but there are very few reports describing ACCs/ACFs in conjunction with O_3/H_2O_2 at room temperature (Lei *et al.*, 2007). The oxidation of organic compounds in the aqueous medium using H_2O_2 catalysed by AC has been investigated and reported an interesting feature emerges wherein the AC acts as adsorbent as well as catalyst/promoter for the oxidation of organic contaminants (Ince and Apikyan, 2000; Ince *et al.*, 2002; Lücking *et al.*, 1998). Catalytic decomposition of H_2O_2 and 4-chlorophenol (4-CP) was studied in the presence of AC and results revealed that the combination of H_2O_2 and GAC did not increase the total removal of 4-CP over single GAC adsorption (Huang *et al.*, 2003). Although, the decomposition mechanism of H_2O_2 is still not well understood several electron transfer processes have been suggested to take place during the reaction. According to these mechanisms, it is believed that reaction might be initiated by a reducing site transferring an electron to H_2O_2 to produce a HO• radical or by reaction of peroxide transferring an electron to an oxidising site yielding a HOO• species (Biniak *et al.*, 2002; Falcon *et al.*, 2001;

Grajek *et al.*, 2001; Heil and Sontheimer, 1972; Jans and Hoigne, 1998; Khalil *et al.*, 2001; Radeke *et al.*, 1989; Yang and Mccreery, 2000).

Oliveira *et al.* (2004) proposed a competitive mechanism (Scheme 6.1) for the H_2O_2 reactions in the presence of AC and reported that both reactions, i.e., H_2O_2 decomposition and oxidation of organics by H_2O_2 were taking place via radicals as suggested by the inhibition effect observed during the H_2O_2 decomposition by the presence of organics such as phenol, hydroquinone and the Drimaren Red textile dye. The author explained that the reactions were initiated by the activation of H_2O_2 by a reducing site in a Fenton like reaction (Ince and Apikyan, 2000; Ince *et al.*, 2002; Lücking *et al.*, 1998) to produce an HO• radical intermediate, which could then react according to the two competitive pathways: (i) reacting with another H_2O_2 molecule leading to the decomposition to O_2 and (ii) oxidation of organic molecules in aqueous medium. This explanation could be helpful later while discussing adsorption/oxidation interaction of different ACCs and H_2O_2 for phenol removal.



Scheme 6.1: Proposed competitive mechanism for the H_2O_2 reactions in conjunction with AC (Oliveira *et al.*, 2004).

The above reactions could also be presented as follows Eq. 6.1 and 6.2 (Khalil *et al.*, 2001):

$$\text{AC–OH} + \text{H}^+\text{OOH}^- \longrightarrow \text{AC–OOH} + H_2O \qquad (6.1)$$
$$\text{AC–OOH} + H_2O_2 \longrightarrow \text{AC–OH} + H_2O + O_2 \qquad (6.2)$$

As discussed above, AC is considered to function as an electron transfer catalyst similar to the Haber–Weiss mechanism known for the Fenton reaction with AC and AC^+ as the oxidised and reduced catalyst states (Kimura *et al.*, 1996) (Eq. 6.3 and 6.4):

$$AC + H_2O_2 \longrightarrow AC^+ + HO\bullet + OH^- \qquad (6.3)$$
$$AC^+ + H_2O_2 \longrightarrow AC + HO_2\bullet + H^+ \qquad (6.4)$$

The above equations have supported various studies showing that contaminant removal in aqueous AC suspensions can be achieved (Huang *et al.*, 2003; Lücking *et al.*, 1998). Huang *et al.* (2003) compared several AC samples after treatment with oxidising agents and studied their decomposition and catalytic activity and reported that the decomposition activity of the modified AC sample towards H_2O_2 was lower; on the contrary, the catalytic activity towards the decomposition of 4-chlorophenol was slightly higher as compared to the virgin AC.

Likewise, based on findings by Jans and Hoigne (1998), the activity of AC for the transformation of ozone (O_3) into HO• radicals including various operational parameters, i.e., carbon/O_3 dose, carbon type and treatment time was also quantified (Sánchez-Polo *et al.*, 2005b). These authors presented a similar conclusion for O_3 as H_2O_2 that in conjunction in AC/O_3 system, AC does not really act as catalyst but rather as a conventional initiator or promoter for the O_3 transformation into HO• radicals. They also reported that O_3 decomposition constant (k_D) increases with the presence of AC in the system and also depending on the type of AC added, the ratio of HO• and O_3, i.e., R_{ct} value ([HO•]/[O_3]), increases by a factor 3–5. Their results also revealed that the activity of the AC, as measured by the ability to transform O_3 into HO• radicals, depended on the surface chemical and textural properties and the most efficient carbon materials were those with high basicity and large surface area. Their results showed that interaction between the O_3 and pyrrole groups present on the surface of the AC increases the concentration of $O_2\bullet^-$ radicals in the system, which in turn enhances the transformation of O_3 into HO• radicals. Additionally, it was reported that the activity of AC decreases with prolonged exposure to O_3, which proves that AC really does not act as catalyst but as an initiator for the O_3 transformation to HO• radicals.

Thus, O_3 has also been extensively studied in conjunction with AC as it is believed that the combined technology of ozonation with other catalysts i.e., catalytic ozonation minimises its practical limits, including selective oxidation and low O_3 utilisation efficiency in wastewater treatment (Cannon *et al.*, 1996; Croll, 1996; Fontanier *et al.*, 2006; Kainulainen *et al.*, 1995). In the presence of AC, O_3 offers enhanced process yields possibly due to catalytic effects provided by the active surface groups (Zaror, 1997). The Boehm titration's and FTIR studies also indicated that the ACF/O_3 systems in water can significantly change the composition of the acidic surface oxygen-containing groups of the ACF, leading to an increase in the carboxylic, hydroxylic and carbonylic groups as well as a slight increase in the lactonic groups (Qu *et al.*, 2007). Likewise, the effect of temperatures (25 °C and 100 °C) was studied with AC/O_3 systems for their ability to adsorb, phenol, *p*-nitrophenol and *p*-chlorophenol from aqueous solutions and it was reported that as a rule, O_3 treatment at either room temperature or 100 °C gave rise to acidic surface oxygen groups (SOG), however at 25 °C primarily carboxylic acids were formed while a more homogeneous distribution of carboxylic, lactonic, hydroxyl, carbonyl groups was formed at 100 °C (Alvarez *et al.*, 2005). The study also showed that exposure of GAC to O_3 at room temperature decreased the ability to adsorb phenols, whereas at 100 °C, the adsorption was not restricted but, in fact, enhanced.

In the GAC–O_3 integrated process, pollutant removal is improved while the time before the GAC is exhausted is prolonged and therefore this process has turned out to be an attractive alternative in dye, textile and other organic wastewater treatment (Faria *et al.*, 2005; Quinlivan *et al.*, 2005; Sánchez-Polo and Rivera-Utrilla, 2003). This integrated technology in wastewater treatment presents strong synergistic effects, especially in the mineralisation of organic compounds (Rivera-Utrilla and Sánchez-Polo, 2002; Sánchez-Polo *et al.*, 2005a; Sánchez-Polo and Rivera-Utrilla, 2003, 2006).

Adsorption–ozonation–regeneration (Faria *et al.*, 2005; Lin and Lai, 2000; Lin and Wang, 2003) suggests that GAC possesses excellent adsorption ability, where the pollutants get adsorbed onto the surface, gradually oxidise and in the meantime the GAC gets regenerated. Whereas, in catalytic ozonation (Sánchez-Polo and Rivera-Utrilla, 2003), GAC initiates the radical-type chain reactions in the aqueous media and the oxidation process is catalysed by the GAC.

Detailed reaction mechanisms and kinetics of the integrated AC/O_3 process for both single ozonation and AC–ozonation have been presented in a study for the ozonation of aqueous gallic acid using AC at pH 5 and their positive synergism has also been discussed (Beltran *et al.*, 2006). Hydrogen peroxide, ketomalonic acid and oxalic acids were identified as by-products (Eq. 6.5 and 6.6; G = gallic acid; Int = Intermediates; Ox = oxalic acid and Ket, = ketomalonic acid) and also possible mechanisms of AC–ozonation-assisted degradation have been proposed in Eq. 6.7–6.12. The study revealed that this process involved two main periods of reactions: (i) complete disappearance of gallic acids, during which ozonation rates were found to be slightly improved due to the presence of AC and (ii) AC played an important role as a promoter due to which the total mineralisation of the organic components in the water was achieved. Thus, in this case, the organic matter removal was reported to be the sum of contributions of direct O_3 reactions and adsorption during the first period and a free radical mechanism likely improving surface reactions of O_3 and H_2O_2 on the carbon surface, during the second period. Also, a third transition period was reported, where by-products reached maximum values and ozonation was probably due to both direct and free-radical mechanisms involving O_3 and adsorption.

$$\mathrm{G} + \mathrm{O_3} \xrightarrow{k_\mathrm{D}} \mathrm{Int} + \mathrm{H_2O_2} \tag{6.5}$$

$$\mathrm{Int} + \mathrm{O_3} \xrightarrow{k_\mathrm{In}} \mathrm{Ket} + \mathrm{Ox} + \mathrm{H_2O_2} \tag{6.6}$$

$$\mathrm{H_2O_2} \longleftrightarrow \mathrm{HO_2^-} + \mathrm{H^+} \tag{6.7}$$

$$\mathrm{HO_2^-} + \mathrm{O_3} \longrightarrow \mathrm{HO_2\bullet} + \mathrm{O_3\bullet} \xrightarrow{\text{many steps}} \mathrm{HO\bullet} \tag{6.8}$$

$$\mathrm{AC} + \mathrm{H_2O_2} \longleftrightarrow \mathrm{AC{-}H_2O_2} \xrightarrow{\text{many steps}} \mathrm{HO\bullet} \tag{6.9}$$

$$\mathrm{AC^+} + \mathrm{O_3} \longleftrightarrow \mathrm{AC{-}O} + \mathrm{O_2} \xrightarrow{\text{many steps}} \mathrm{H_2O_2} \text{ or } \mathrm{HO_2^-} \tag{6.10}$$

$$\mathrm{HO\bullet} + \mathrm{Ox} \longrightarrow \mathrm{CO_2} + \mathrm{H_2O} \tag{6.11}$$

$$\mathrm{HO\bullet} + \mathrm{Ket} \longrightarrow \mathrm{CO_2} + \mathrm{H_2O} \tag{6.12}$$

From the presented literature, it can be seen that a lot of studies related to GACs in conjunction with strong oxidants reveal the catalytic efficiency and industrial potential of ACs to treat toxic wastewaters. Hence, the main idea of this research was to investigate the potential usage of activated carbon cloth (ACC) for toxic phenol removal from wastewaters via adsorption and chemical oxidation.

Following are main objectives of this research to assess the effect of the single and combined systems on phenol removal:

- to study the effect of reactor performances (peristaltic pumps, shaker bath and US bath) for ACC/oxidant systems
- to compare ACC types and amounts (ACC-Std, ACC-Cu, ACC-Ag, ACC-extra)
- to study the effect of different concentrations of hydrogen peroxide (H_2O_2: 1.19, 2.38 and 4.76 g L^{-1})
- to explore the effect pH (3, 5.5 and 9) and temperature (20, 40, 80 °C)
- to investigate types and duration of ozone (O_3) treatments (bulk and/or step-wise ozonation)
- to examine thermal regeneration and reuse

6.2 Experimental

6.2.1 Chemicals

For clarity, this section is presented in tabular form:

Chemicals	Company	Concentrations	Types
Phenol	Fluka	2.5 mM (made from 50 mM stock solution; 10 mL made up to 200 mL in a vol. flask)	Same for all experiments
Hydrogen peroxide (H_2O_2) (30%)	Fisher Chemicals	1.19, 2.38 and 4.76 g L^{-1}	Added at once or step-wise
Ozone (O_3)	Triogen	Dial 5; O_2–O_3 flowrate 5 L min^{-1}; 5.6–6.3 mg O_3 L^{-1}	Added at once or step-wise
Activated carbon cloth (ACC)	Carbon Filter Technology (CFT)	(×2) discs, 25 mm dia. each; weight, 0.085 g; 0.85 g L^{-1} w/v	[a]CFT 551, 552, 553, 554, 555
Ultrasonic bath (US bath)	Kerry Scientific	–	–
Shaker bath	Grant Operations	–	20, 40, 80 °C
Peristaltic pump	MasterFlex	–	–
pH (adjusted with 1 mM H_2SO_4 and 1 M NaOH; Fisher Chemicals)	Metler Toledo	–	3, 5.5 and 9

[a]CFT 551, activated carbon cloth (ACC) with standard construction 160x86 (ACC-Std); CFT 552, ACC with extra yarns 160×100 (ACC-Extra); CFT 553, copper impregnated on ACC-Std (5.2% copper; ACC-Cu); CFT 554, copper impregnated on ACC-Extra (4.2% copper; ACC-Extra-Cu); CFT 555, silver impregnated on ACC-Std (0.04% silver; ACC-Ag). All samples of ACC obtained from Carbon Filter Technology (CFT), UK (http://www.carbfilt.co.uk/).

Table 6.1: List of chemicals and their concentrations used in the adsorption/oxidation experiments with ACC for phenol removal.

6.2.2 Reactors

Three different types of reactors were mainly used in this study:

1. Peristaltic pump
2. Ultrasonic bath
3. Shaker bath

A schematic representation of the three listed reactors used in this study is shown below and the methods of experimentation in these reactors are discussed in the following section.

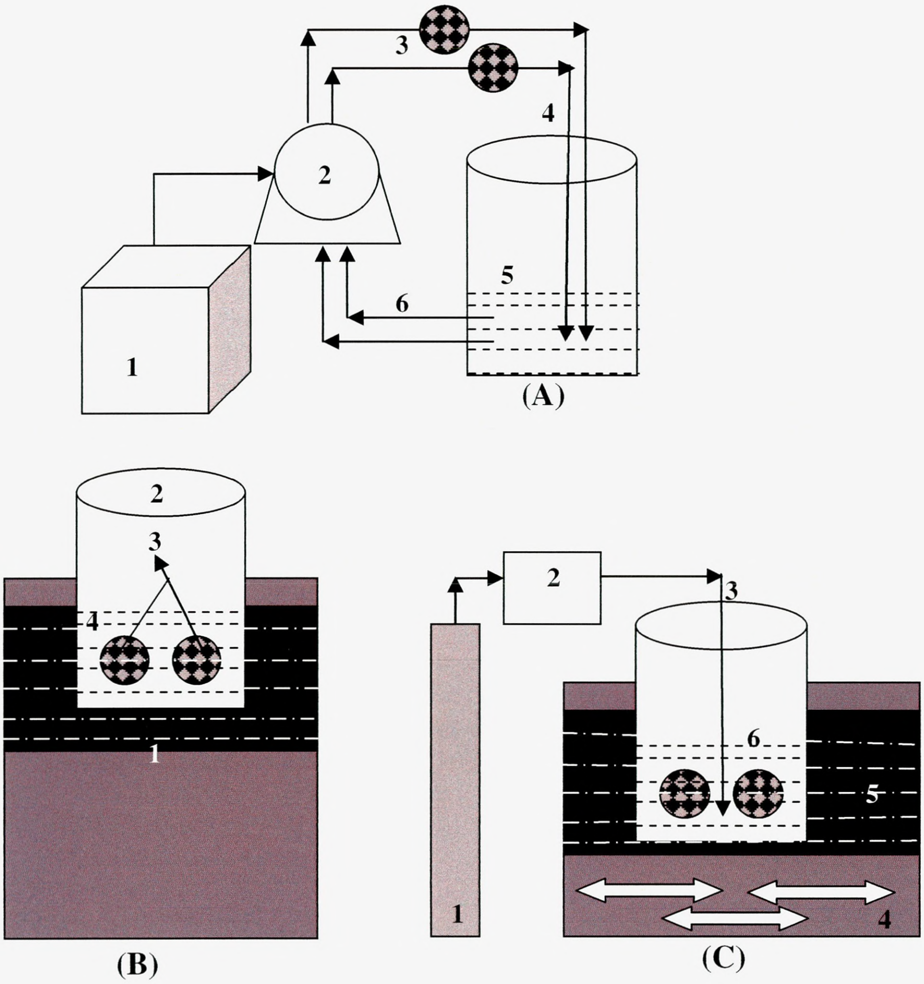


Figure 6.1: Schematic representations of ACC experiments in different reactors:
(A): Peristaltic pump (1, generator; 2, pump; 3, ACC disc holders (round, 25 mm dia.); 4, inlet pipe; 5, glass reactor with phenol solution; 6, outlet pipe).
(B): US bath (1, US bath; 2, glass reactor; 3, ACC discs; 4, phenol solution)
(C): Shaker bath (1, oxygen cylinder; 2, ozone generator; 3, O_2+O_3 gas bubbler; 4, horizontal shaker; 5, shaker bath; 6, closed round botton flask with phenol solution and ACC discs).

6.2.3 Methods and analyses

6.2.3.1 ACC pre-treatment

ACC obtained from Carbon Filter Technology (CFT) was pre-treated before use by: (i) boiling the ACC in dH_2O for 1 h (ii) draining the water thoroughly from the ACCs (iii) drying in an oven at 130 °C for 24 h and finally (iv) storing the samples in desiccators (silica gel) for use in all the experiments.

6.2.3.2 Peristaltic pump

Aqueous phenol (2.5 mM; 200 mL) was made from the 50 mM phenol stock solution by pipetting 10 mL stock and making up to 200 mL in a standard volumetric flask. ACC (×2; each weighing 0.085 g; 0.85 g L^{-1} w/v) were fitted into filter holders fixed to the inlet pipes into the beaker, containing 200 mL phenol solution and the solution was re-circulated back to the beaker through the outlet pipes (Fig. 6.1A). Aliquots of 5–7 mL were withdrawn after every 30 min for TOC analysis during the 180 min reaction time. The samples were filtered prior to analysis with the help of cellulose membrane filters as described in Chapters 4 and 5. In some cases samples (5 mL) were also stored at the end of the 180 min reaction time for GC–MS analysis for approximate phenolic product (if any) identification. All studies with the peristaltic pump were carried out at room temperature (20 ± 5 °C). Several comparative studies with and without aeration were also investigated with continuous aeration using a fish-tank pump. The effects of different pH: 3, 5.5 and 9 and H_2O_2 concentrations: 1.19, 2.38 and 4.76 g L^{-1} were also studied for phenol removal via adsorption/oxidation. Change in the pH of the reaction solution was measured at the end of the reaction.

6.2.3.3 Ultrasonic bath

Aqueous phenol (2.5 mM; 200 mL) was placed in a 300 mL glass beaker and immersed in the US bath and the temperature (20 ± 5 °C) was maintained by using crushed ice (Fig. 6.1B). Then, the phenolic solution together with 0.85 g L^{-1} ACC was irradiated in the US bath and samples were withdrawn at regular intervals for TOC analysis. The effect of H_2O_2 on phenol removal via adsorption/oxidation at different pHs, as mentioned above, was also investigated using the US bath.

6.2.3.4 Shaker bath

The adsorption/oxidation of phenol (Fig. 6.1C) was carried out in conical or round bottom flasks as required in a shaker bath operating at 200 strokes min^{-1} (SPM). The effects of pH (3, 5.5 and 9), temperature (20, 40 and 80 °C) and bulk/step-wise addition of ACC and O_3 were also investigated.

6.2.3.5 Ozonation

ACC–ozonation was studied in the shaker bath involving various methodologies. Most of the ACC–ozonation experiments were designed on the basis of published reports (Sánchez-Polo *et al.*, 2005a; Sánchez-Polo and Rivera-Utrilla, 2003, 2006) with the differences being the use of phenol and ACC instead of NTS acid and GAC:

1. Saturated O_3 solution: the ozoniser was set to Dial 5, the O_2–O_3 flowrate was 5 L min^{-1} (5.6–6.3 mg O_3 L^{-1}) and dH_2O (190 mL) was ozonated for 45 min prior to any experiment. Then 50 mM phenol stock solution (10 mL) and ×2 ACC discs were introduced to the reaction solution
2. ACC was saturated with O_3 by subjecting ACCs to dH_2O (200 mL) and ozonating the solution for either 15 min or 150 min to get ACC saturated, termed specifically as ACC_{15} and ACC_{150} in the study. The ACC_{150} and ACC_{15} were further immersed in the 45 min ozonated water solution (190 mL) with 10 mL phenol solution taken from 50 mM stock solution. Phenol removal were studied with the help of TOC analysis
3. Direct ozonation (Dial 5; O_2–O_3 flowrate 5 L min^{-1}; 5.6–6.3 mg O_3 L^{-1})
    - 15 min initial ozonation of phenol solution (No ACC)
    - ×3 5 min ozonation of phenol solution at time 0, 60 and 120 min (No ACC)
    - 15 min initial ozonation of ACC-Std + phenol solution
    - ×2 15 min ozonation of ACC-Std + phenol solution after 240 min and 360 min

6.2.3.6 Regeneration and reuse

Thermal regeneration of the catalyst (ACC-Std) was carried out by initially using the catalyst (×5 ACC-Std) for 240 min in the phenol solution and then heating the same catalyst in the oven at 130 °C for different periods: 1, 3, 5, 7 and 9 days (e.g., 1 day; Fig. 6.2) and reusing it again for 4 more times by subjecting it every time to 2.5 mM phenol solution in a 500 volumetric flask. Percentage adsorption/oxidation was measured every time at 0 and 240 min of reaction by measuring TOC.

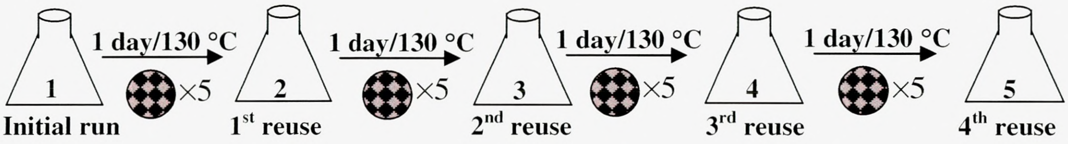


Figure 6.2: Schematic representation of catalyst regeneration and reuse set-up.

6.3 Results and discussion

6.3.1 Preliminary studies

6.3.1.1 Effect of air

Removal of free cyanide from aqueous solutions by plain and metal-impregnated GACs while the solution was subjected to 0.27 L min^{-1} aeration and a profound effect of air on the process leading to 5.5–49.1% enhancement in the performances of plain and metal (copper, Cu and silver, Ag)-impregnated ACs was reported (Deveci *et al.*, 2006). The authors have attributed the phenomenon of aeration to the increase in the availability of active sites on AC for adsorption and the enhanced catalytic activity of AC in the presence of oxygen. Thus, in the present work, preliminary studies were carried out on the process of phenol removal in the presence of air and the influence of continuous aeration was examined (Fig. 6.3).

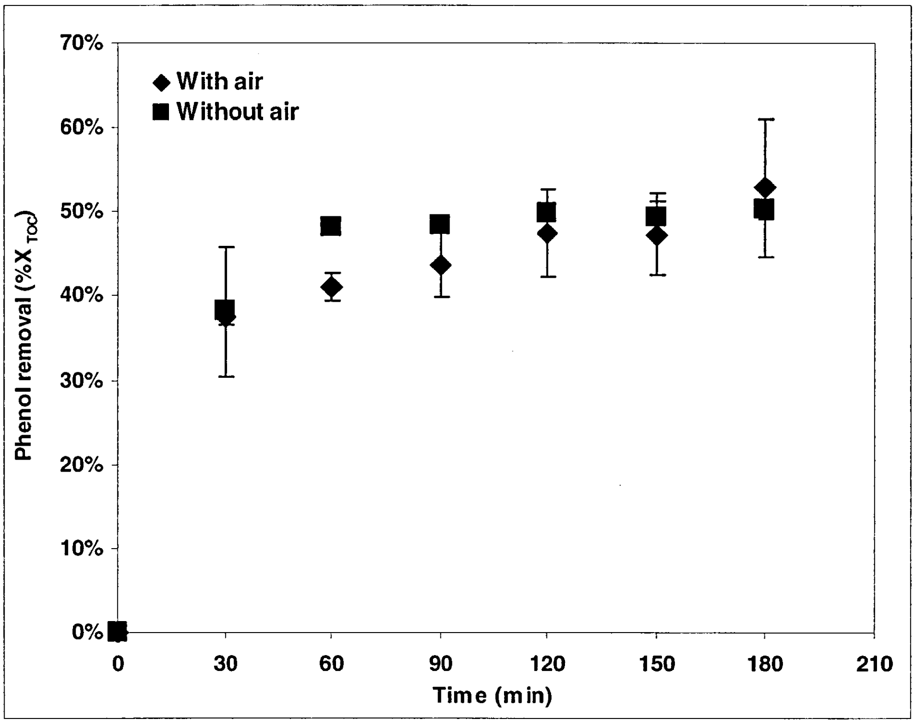


Figure 6.3: Effect of continuous aeration on phenol removal in the presence of ACC-Std. Experimental conditions: phenol, 2.5 mM; pH, 5.5–5.8 (pH of 2.5 mM phenol); ACC-Std, 0.85 g L^{-1}; reactor, peristaltic pump; aeration, fish tank (continuous); results, mean ± SD of replicates; analysis, TOC analyser.

Unlike the results reported by Deveci *et al.* (2006), it can be easily noted that there is no significant difference obtained with and without aeration in this study. It is probable that the ACC-Std (0.85 g L^{-1} w/v) was efficient enough to remove ~50% phenol and that is why aeration has no effect on the overall phenol removal. Also, no change in the pH was observed at the end of 180 min reaction time. A similar explanation was provided by Deveci *et al.* (2006) when low (0.2 g L^{-1}) or high (4.5 g L^{-1}) concentrations of Ag- and/or Cu-impregnated AC were compared for cyanide removal in the presence and absence of aeration. The authors noted that the contribution of aeration to the removal of cyanide by Ag/Cu-impregnated AC tended to decrease with increasing adsorbent dosage. Thus, it is presumed that the surface properties and the amount of the ACC-Std used in this study remains unaffected by the aeration. Hence, all the experiments in this study with ACC were carried out without aeration.

6.3.1.2 Effect of reactor type

During the preliminary studies, the following three different types of reactors were tested for adsorption/oxidation removal of phenol using ACC:

1. Re-circulatory type (peristaltic pump)
2. Horizontal shaker (shaker bath)
3. Cavitational reactor (US bath, 38 kHz)

All the comparisons were carried out without altering the pH, i.e., 2.5 mM phenol solution pH = 5.5 and phenol removal was monitored over 180 min (Fig. 6.4).

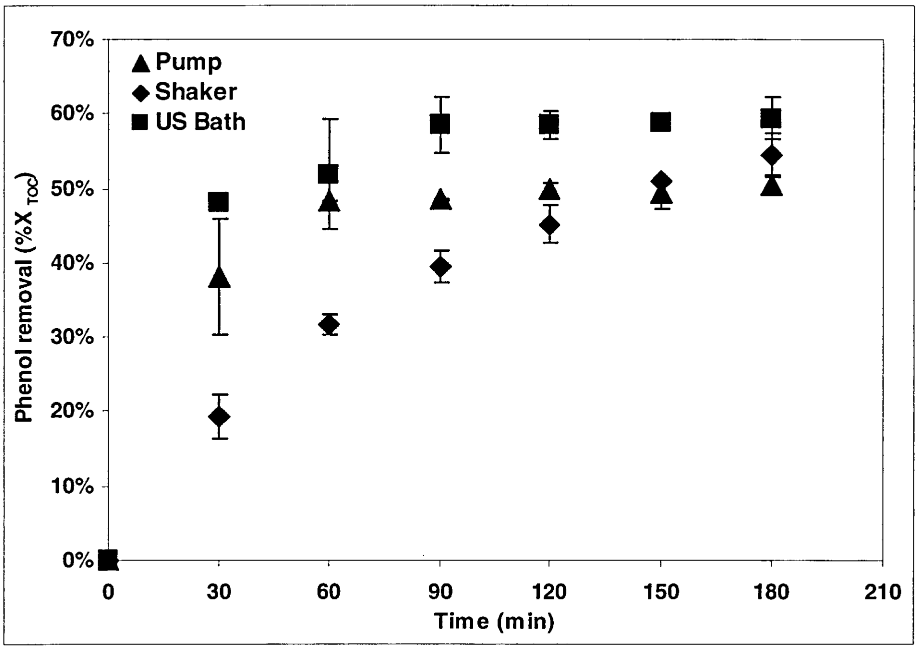


Figure 6.4: Effect of different reactor set-ups on phenol removal at pH 5.5. Experimental conditions: phenol, 2.5 mM; pH of 2.5 mM phenol (pH ~5.5); ACC-Std, 0.85 g L^{-1}; reactors, peristaltic pump, shaker bath and US bath; results, mean ± SD of triplicates; analysis, TOC analyser.

Phenol removal using the US bath was noted to be quite high at the start of the experiment when compared with the pump and shaker bath. This can be attributed to the additional cavitational activity in the US bath, which might contribute towards desorption/regeneration (Breitbach and Bathen, 2001; Hamdaoui *et al.*, 2003; Lim and Okada, 2005) of the ACC catalyst. Breitbach and Bathen (2001) also reported that US not only promotes desorption but also enhances the mass transfer of sorption processes.

It is proposed that the shaker bath (horizontal shaking) induces efficient mixing and/or contact of the catalyst with the phenol solution, whereas the US bath provides simultaneous adsorption/oxidation and desorption/regeneration of the catalyst leading to high phenol removal. However, at the end of the 180 min reaction time, a difference of ~5% in phenol removal was seen between the shaker bath and the US bath, which is probably accounted for by the cavitational activity leading to oxidation and breakdown of phenol into different products. These could be easily adsorbed onto the surface of the ACC or could react with the oxidising radicals produced on the surface of ACC or in the bulk solution. Phenol removal in both reactors tend to stay stable after 120 min reaction time indicating saturation of the ACC with phenol and its products and lack of oxidising radical species in the bulk solution to carry out further oxidation. Thus, in the later sections of this chapter, the effect of temperature and different oxidants on phenol removal in the shaker and US bath, respectively, will be reported.

6.3.1.3 Effect of pH

Owing to the characteristics of the carbon surface, i.e., the acidic and/or basic functional groups, the surface properties may be influenced by the pH of the bulk solution. Thus, it is suggested that the surface charge of the carbon as well as the extent of ionisation of the solute should always be considered (Muller *et al.*, 1980). Therefore, three different pH values were considered, i.e., pH 3, 5.5 and 9, for the preliminary studies. However, the results exhibited a challenging scenario by producing similar % phenol removal at each selected pH (Fig. 6.5).

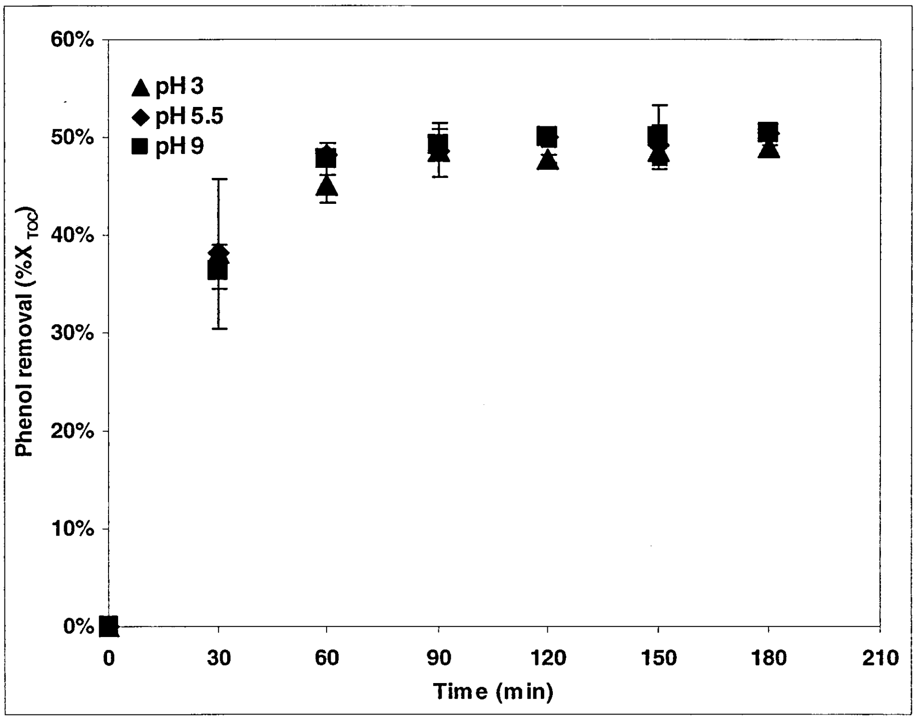


Figure 6.5: Effect of different pH (3, 5.5 and 9) on phenol removal in the presence of ACC-Std. Experimental conditions: phenol, 2.5 mM; ACC-Std, 0.85 g L^{-1}; reactor, peristaltic pump; results, mean ± SD of triplicates; analysis, TOC analyser.

However, phenol removal at pH 3 showed a slight increase in the pH at the end of 180 min reaction time, i.e., from 3.0 to 3.4, no pH change was observed at pH 5.5, whereas at the end of reaction time at pH 9, the pH of the bulk solution decreased from pH 9 to 8.5. Likewise there was slight increase in the total inorganic carbon (TIC) values when the experiment was carried out at pH 9; the TIC increased up to 2.8 mg L^{-1}, whereas it remained unchanged (0.58 mg L^{-1}) for pH 3 and 5.5. Rivera-Utrilla and Sánchez-Polo (2002) accounted for dissolved inorganic carbon (ΔDIC = 2.37 mg L^{-1}or TIC in this case) at pH 7 as mineralisation of organic matter. Thus, the increase in the TIC values in this study is accounted for by some phenol oxidation at pH 9.

In a separate study of adsorption of pentachlorophenol with ACF, it has been reported that the solution pH always increased during the adsorption at pH $\leq$ 7 but always diminished slightly at pH $\geq$ 8 (Diaz-Flores *et al.*, 2006). They suggested that H_3O^+ ions were adsorbed on the AC-felt at pH $\leq$ 7, causing an increase in pH, whereas the H_3O^+ ions were released from the AC-felt at pH $\geq$ 8 causing decrease in pH and this was due to the amphoteric character of the AC-felt, which had both acidic and basic sites. Thus, it can be suggested that probably ACC-Std has both acidic and basic sites which is why, similar % phenol removal was obtained at all the selected pHs. Furthermore, different concentrations of oxidants and temperatures were studied at all three selected pHs to see their combined effect on phenol removal and the results are presented with statistical analysis later in this chapter.

6.3.1.4 Effect of temperature

Preliminary studies with three different temperatures (20, 40 and 80 °C) were used to investigate their effects on the phenol adsorption/oxidation in the shaker bath tested at pH 5.5 (Fig. 6.6).

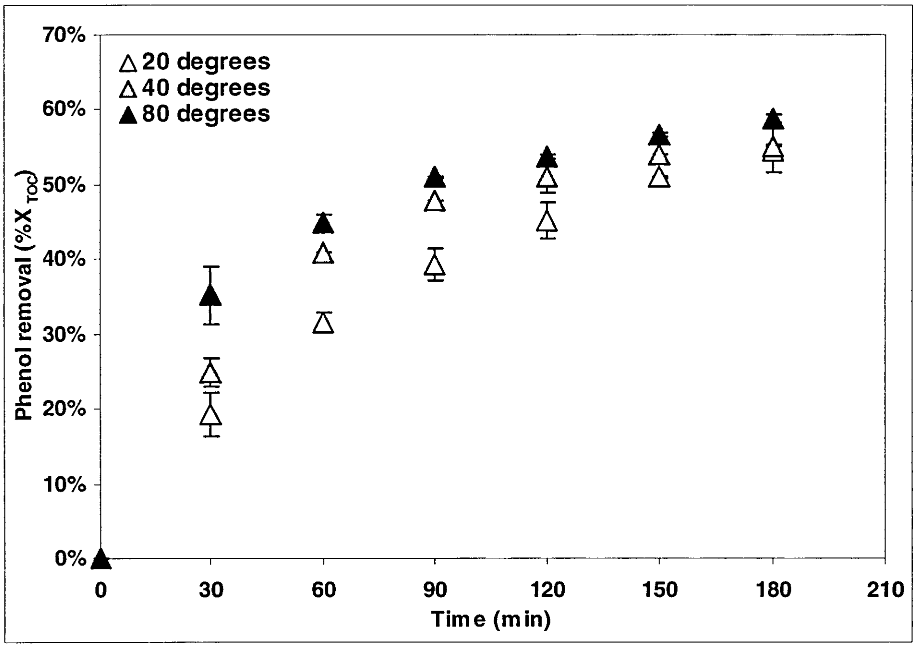


Figure 6.6: Effect of different temperatures (20, 40 and 80 °C) on phenol removal in the presence of ACC-Std at pH 5.5. Experimental conditions: phenol, 2.5 mM; ACC-Std, 0.85 g L^{-1}; reactor, shaker bath; results, mean ± SD of duplicates; analysis, TOC analyser.

The results reveal that highest percentage of phenol removal was obtained at elevated temperatures. Similar results have been presented in the literature for adsorption of phenolic compounds by ACs, where phenol was contacted for 10 days at temperatures: 25, 53 and 80 °C and the highest rates of phenol adsorption were noticed at 80 °C (Grant and King, 1990). Therefore, similar experimental set-up was repeated by altering the pH of the phenol solution to pH 3 and 9 and phenol removal was monitored using TOC/TIC analysis. Phenol removal obtained in the shaker under different temperatures have been compared with pump results obtained at room temperature (20 ± 5 °C) (Fig. 6.7).

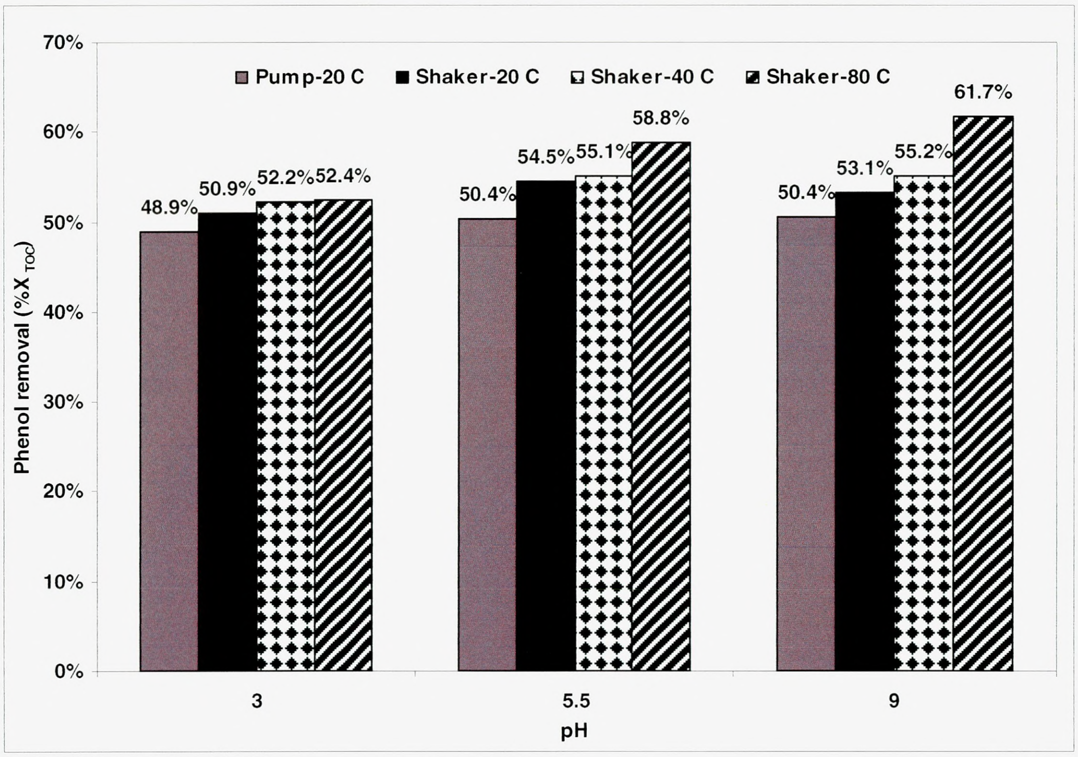


Figure 6.7: Comparison of the effect of pump and shaker bath on phenol removal at different pH (3, 5.5 and 9) and temperature (20, 40 and 80 °C). Experimental conditions: phenol, 2.5 mM; ACC-Std, 0.85 g L^{-1}; results, mean ± SD of duplicates; analysis, TOC analyser.

From Fig. 6.7, certainly the efficiency of the shaker bath for effectively mixing the catalyst and the pollutant, whilst providing maximum surface area of contact was higher as compared to the pump at 20 °C, leading to enhanced phenol removal. Statistical analysis (MANOVA) showed high significance of pH (P = 0.09–0.02) and temperatures (P = 0.004–0.007) on the % phenol removal. Thus, it is proposed that increasing temperatures lead to enhancement in the macropore size of the cloth which enhances adsorption and at the same time, regenerates the ACC surface by volatilising low molecular weight organic compounds and acids, produced due to breakdown of phenol, eventually providing increased surface area for phenol reactions on the ACC surface.

Lower temperatures suit the cavitational activity and that is why, pump, shaker bath and US bath operated under room temperature conditions (20 ± 5 °C) were compared for phenol removal at different pH 3, 5.5 and 9 (Fig. 6.8).

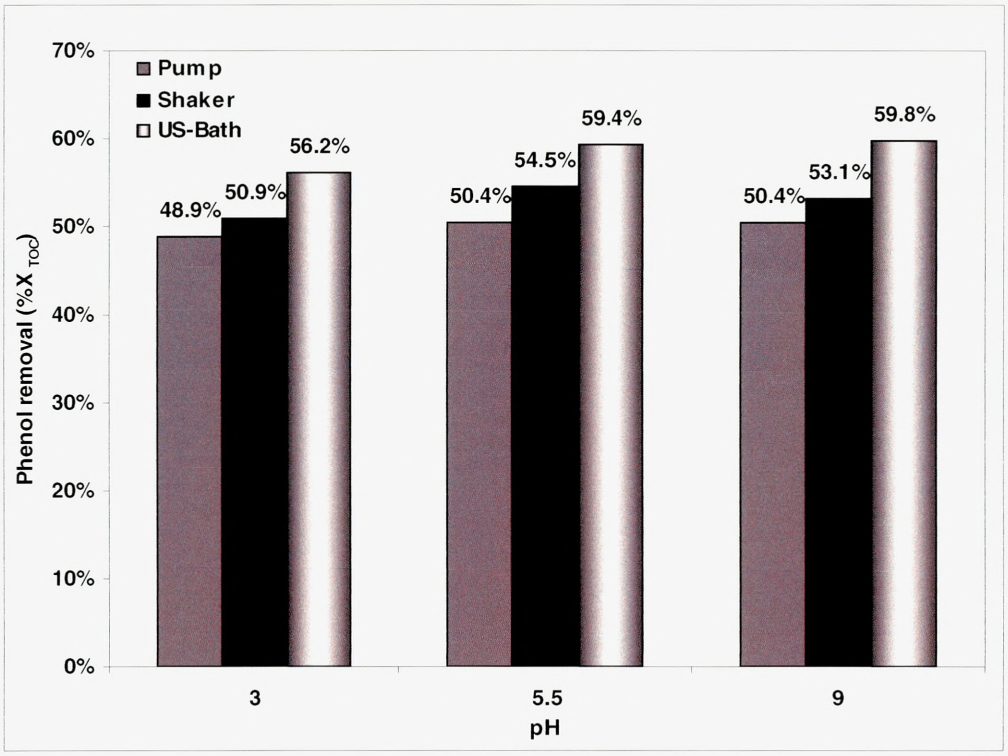


Figure 6.8: Comparison of the effect of the pump, shaker and the US bath on phenol removal at different pH (3, 5.5 and 9). Experimental conditions: phenol, 2.5 mM; ACC-Std, 0.85 g L^{-1}; results, mean ± SD of duplicates; analysis, TOC analyser.

The above figure clearly indicates that the effect of US is equivalent to the highest temperature (80 °C) for effective phenol removal (~60%). As discussed in the sections above, the effect of cavitation leads to enhancement of the active sites on the ACC and also regenerates the catalytic activity and enhances removal of phenol and degradation products (not known). Since, the GC–MS analysis on samples collected from these experiments did not show any known peaks of phenolic degradation it can be assumed that this phenomenon is mainly an activity of adsorption–desorption–regeneration and not oxidation. This can be further proved by increasing the catalyst amount as discussed in the following section.

6.3.1.5 Effect of amount of catalyst

The effect of amount of catalyst on phenol removal was tested by introducing increased amounts of catalyst into the reaction medium. In all the experiments so far 2 discs (0.085 g each; 0.85 g L^{-1} w/v) of ACC-Std were used, whereas to study the effect of an increased amount of catalyst, 5 discs (×5) (2.125 g L^{-1}) ACC-Std was used. The study was conducted using the shaker bath at room temperature, without altering the pH of the 2.5 mM phenol solution (pH 5.5). Fig. 6.9 clearly indicates that increasing amount of the catalyst leads to increased adsorption in the absence of any effect from pH/temperatures/reactors. The results obtained from the GC–MS for samples with 5 ACC discs, showed no peaks of any known degradation product of phenol revealing no contribution from oxidation on % phenol removal.

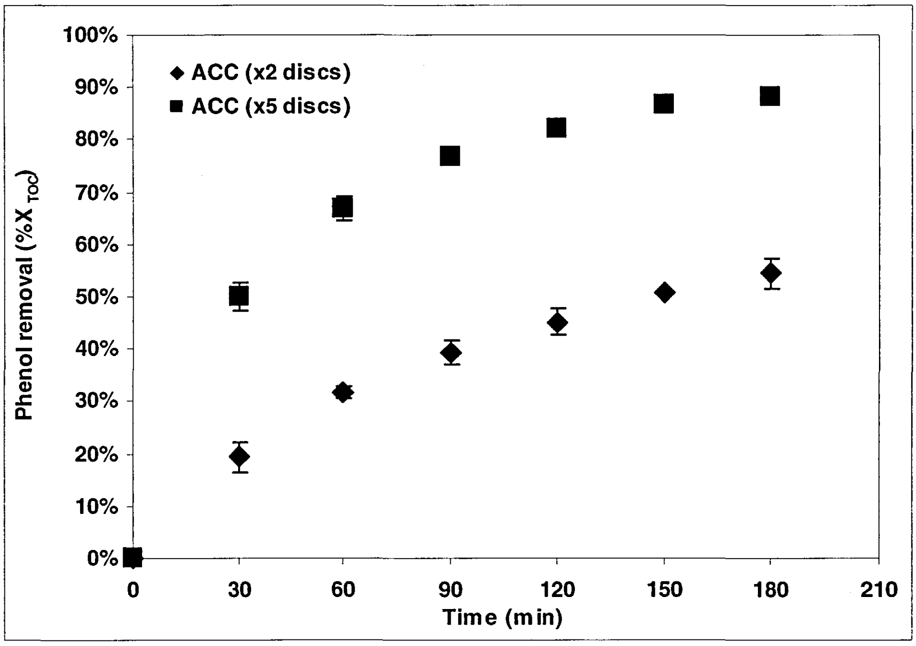


Figure 6.9: Effect of amount of catalyst (0.85 and 2.125 g L^{-1}) on phenol removal in the presence of ×2 and ×5 ACC-Std discs at pH 5.5. Experimental conditions: phenol, 2.5 mM; temperature 20 ± 5 °C (room); reactor, shaker bath; results, mean ± SD of duplicates; analysis, TOC analyser.

Furthermore, as discussed in previous chapters, step-wise addition of catalyst leads to enhancement in the rates of pollutant removal. Therefore, in this study, instead of one bulk addition at the start of the experiment, ACC-Std disc(s) (0.085 g weight) were added step-wise (×5) at different time intervals and phenol removal were continuously monitored through TOC and GC–MS (Fig. 6.10).

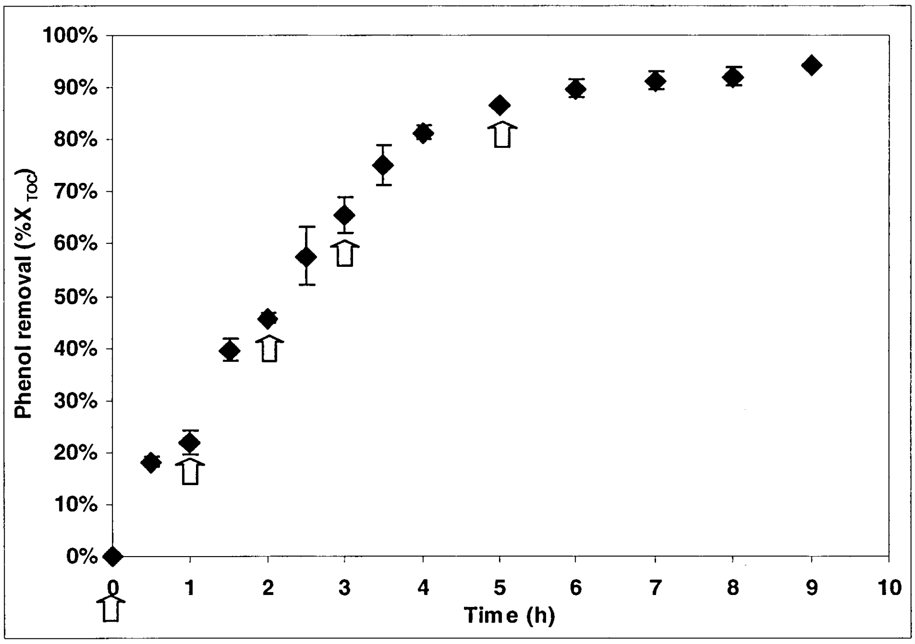


Figure 6.10: Effect of step-wise addition (grey arrows) of ACC-Std catalyst(s) (0.085 g ×5) on phenol removal at pH 5.5. Experimental conditions: phenol, 2.5 mM; temperature 20 ± 5 °C (room); reactor, shaker bath; results, mean ± SD of duplicates; analysis, TOC analyser.

Step-wise addition of ACC catalysts lead to 90% phenol removal after 9 h of contact time in the shaker bath. After each addition of the ACC disc, ~15–20% phenol removal was noticed, however the final ACC disc was added after 5 h and phenol removal was monitored for further 4 h without any change. Thus, it can be concluded that every 0.085 g of ACC-Std catalyst has a capacity to remove 15–20% of aqueous phenol, leading to overall 94% phenol removal with an addition of overall 2.125 g L^{-1} w/v ACC-Std catalyst.

GC–MS analysis of the aqueous solution collected after 9 h showed the no phenol peaks, instead additional peaks of allophonic acid ($C_3H_6N_2O_3$), acetic acid (CH_3COOH) and 2-nonynoic acid ($C_9H_{14}O_2$) were identified. Although the literature does not describe allophanic and 2-nonynoic acids as oxidation products of phenol, the formation of acetic acid in the 9 h ACC reaction with phenol clearly indicates some oxidation of phenol in this study but higher phenol removal is mainly due to the process of adsorption. Formation of higher molecular weight compounds, like 2-nonynoic acids, are the oligomerisation oxidation products of phenol (Santos *et al.*, 2002).

Thus, from the above study, it can be concluded that higher amounts of ACC catalysts over longer contact periods could lead to effective phenol removal as well as initiation of phenol oxidation. Since the literature does not account for any specific routes of phenol oxidation products in the presence of AC (granules/felt/fibre/cloth) prediction of oxidation using ACC in this study is highly complex. Also, the formation of a variety of acids (allophonic and 2-nonynoic acids) does not give any clear indication if they are formed as a result of phenol oxidation or complexes on surface of ACC. Therefore, thus far only formation of acetic acid as a result of step-wise addition of the catalyst into phenol solution over prolonged contact period (Fig. 6.10) definitely indicates oxidation of phenol. Hence, further experiments on the effects of oxidants such as H_2O_2 and O_3, were separately studied in conjunction with ACC to investigate adsorption/oxidation or their combined effects on phenol removal.

6.3.1.6 Statistical analysis

Multivariate analysis (MANOVA) was carried out on the data obtained from the use of the different variables: pH, reactors and temperatures. Significant effects are reported with *P*-values. Also, the interaction of two variables has been shown in Table 6.2. Results revealed independent significant effect of pH, temperatures and reactors on phenol removal. The *P*-values which are less that 0.05 shows statistical significance of the parameters. For better understanding the values have been highlighted in bold. It can be clearly seen from the table that pH, temperatures and the interaction of both the parameters showed high significance on the % phenol removal. However, in case of pH and reactors, the reactors alone showed high significance on % phenol removal but the interactions of the pH and reactors did not showed any significance.

Effects	MANOVA Test (*P*-values)		
	Wilks'	Lawley-Hotelling	Pillai's
pH and temperatures			
pH	**0.021**	**0.055**	**0.009**
Temperatures	**0.004**	**0.005**	**0.007**
pH*temperatures	**0.066**	2.61	**0.020**
pH and reactors			
pH	0.546	0.648	0.474
Reactors	**0.000**	**0.001**	**0.000**
pH*reactors	0.539	0.664	0.576

Table 6.2: Data representation after statistical analysis on the effect of different variables, i.e., temperatures, pHs and reactors on phenol removal. Values $P < 0.05$ (bold), indicates significance of the variables used in this study.

6.3.2 Phenol removal with the ACC/H_2O_2 system

The oxidation of organic compounds in aqueous medium in the presence of H_2O_2 and AC has recently been studied as discussed earlier in Section 6.1 (Ince and Apikyan, 2000; Ince *et al.*, 2002; Lücking *et al.*, 1998). Although no study on H_2O_2 decomposition in the presence of ACC was performed in this study. Literature provides sufficient information on H_2O_2 decomposition in the presence of AC and reports that the rates of H_2O_2 decomposition depend on the nature of AC used and the same study also reports that addition of 4-chlorophenol (4-CP) to the aqueous phase significantly reduces the decomposition of H_2O_2 as a consequence of the 4-CP adsorption on the AC surface which in turn reduces the surface area of the AC for the decomposition of the H_2O_2 (Lücking *et al.*, 1998). According to Lüking, pH 3 was best suited for oxidation of organic compounds by surface catalysed-GACs and that during oxidation of 4-CP in the presence of different ACs as catalysts, the pH decreased from 3 to 2. The decrease in pH during ACC/H_2O_2 systems was also noted in this study and results have been presented. Also, it has been reported that a slight influence of organic adsorption on H_2O_2 decomposition was observed while using iron oxide as catalyst due to the low affinity of organics with the metal oxide surfaces (Huang *et al.*, 2001; Valentine and Ann Wang, 1998). The majority of previous studies showed that decomposition of H_2O_2 with AC depends mainly on the carbon porosity, pH and chemical properties of the surface (Khalil *et al.*, 2001).

Thus, the present study reports the effect of the ACC/H_2O_2 system on phenol removal under different pHs, ACC types and H_2O_2 concentrations. To study the effect of cavitation, the ACC/H_2O_2 system was tested in the US bath (ACC/H_2O_2/US) along with different concentrations of H_2O_2. An approximate estimation of oxidation products (if any) were also made with the help of GC–MS analysis but phenol removal was mainly monitored with using TOC analysis. Lüking *et al.* (1998) described that because of the adsorption properties of GAC, it was difficult to estimate the amount of 4-CP removed by oxidation in batch experiments, thus the DOC (dissolved organic carbon) drop in the aqueous phase was reported as the result of adsorptive and oxidative removal. It was also reported that during the oxidative degradation of phenols, intermediate products with stronger adsorption properties can be formed (Nakhla *et al.*, 1994) but also produced are products such as organic acids which adsorb less strongly. Therefore, the interpretation of the obtained DOC or TOC (in this study) data is complex.

6.3.2.1 Effect of H_2O_2 concentrations

The effect of three different concentrations of H_2O_2: 1.19, 2.38 and 4.76 g L^{-1} was studied under the ACC/H_2O_2 system (Fig. 6.11).

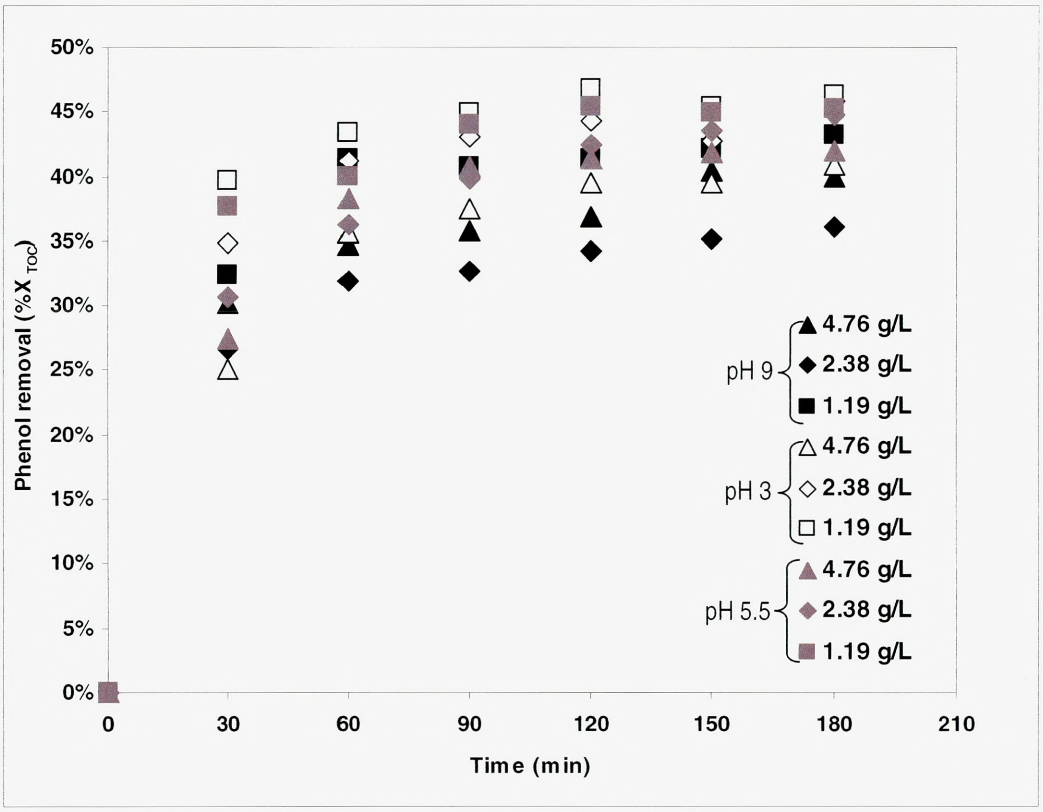


Figure 6.11: Effect of different concentrations of H_2O_2 (1.19, 2.38 and 4.76 g L^{-1}) and pH (3, 5.5 and 9) on the ACC-Std/H_2O_2 system on phenol removal. Experimental conditions: phenol, 2.5 mM; temperature 20 ± 5 °C (room); reactor, peristaltic pump; results, mean ± SD of duplicates; analysis, TOC analyser.

The phenol removal trend shown in Fig. 6.11 reveals that a lower concentration of H_2O_2 at pH 3 and 5.5 lead to enhanced phenol removal. Whereas, an alkaline pH of 9 at higher H_2O_2 concentrations (2.38 and 4.76 g L^{-1}) leads to only 40% phenol removal but in this case an increase in TIC values (3.2–4.5 mg L^{-1}) was noted with increasing concentrations of H_2O_2, attributing to the formation of CO_2. For confirmation of oxidation under different H_2O_2 concentrations and pH, GC–MS data was taken into account and results showed formation of a variety of acids as phenol oxidation products. A decrease in pH was also noted at different H_2O_2 concentrations under the ACC/H_2O_2 system, indicating formation of acids and these results are summarised in

Table 6.3 with the GC–MS product details and also initial (*t*$_i$) and final (*t*$_f$) values of the TOC and pH (*t* stands for time).

However, statistical analysis on the study with different combination of H_2O_2 and pH combination showed no significant effect of the different pHs ($P = 0.4$) and H_2O_2 ($P = 0.06–0.18$) concentrations on phenol removal.

H_2O_2	pH		TOC (mg L^{-1})		GC–MS (% Peak Area)	
(g L^{-1})	t_i	t_f	t_i	t_f	Phenol	Acids
1.19	3.0	3.2	240.7	129.2	ND	Allophanic acid, phenoxypropionic acid, octanoic acid, etc.
2.38		3.1	243.9	132.3	4.3%	
4.76		3.1	236.7	140.0	2.0%	
1.19	5.5	5.2	237.8	130.3	14%	
2.38		4.8	236.2	130.7	20%	
4.76		4.6	240.1	139.6	9%	
1.19	9.0	8.4	227.7	129.5	20%	
2.38		8.1	235.2	150.4	11.4%	
4.76		7.7	238.7	143.5	5.1%	

Table 6.3: Summary chart: pH, TOC and GC analysis under the ACC/H_2O_2 system.

Decrease in TOC values indicates phenol removal and oxidation could be possible due to decrease in pH values, resulting from the formation of acids. The obtained acid peaks from the GC–MS analysis is not a clear indication of phenol oxidation. Therefore, in-depth investigation in this area shall be proposed for future work, employing advanced techniques/methods including modified GC–MS settings, to study formation of phenol oxidation products in the ACC/H_2O_2 system. However, an approximate conclusion from the decreasing pH (pH 5 and 9) and TOC values and increasing TIC values (pH 9), phenol removal in the ACC/H_2O_2 system could be the combined effect of adsorption/oxidation process. At his stage, it is very difficult to address the contribution of each separately.

6.3.2.2 Effect of the ACC/H_2O_2/US system

Ultrasound has been used in conjunction with AC for adsorption–desorption studies (Breitbach and Bathen, 2001; Hamoudi *et al.*, 1998; Lim and Okada, 2005). The current ACC/H_2O_2/US system study was conducted in a 38 kHz US bath (continuous sonication) at pH 5.5 and the temperature was controlled (20 ± 5 °C) by using ice. The effect of different concentrations of H_2O_2, i.e., 1.19, 2.38 and 4.76 g L^{-1} was also studied to investigate if increasing concentrations of H_2O_2 in conjunction with US bath have any enhanced effect on phenol removal (Fig. 6.12). To avoid the effect of pH in these reactions, all experiments were carried out at pH 5.5.

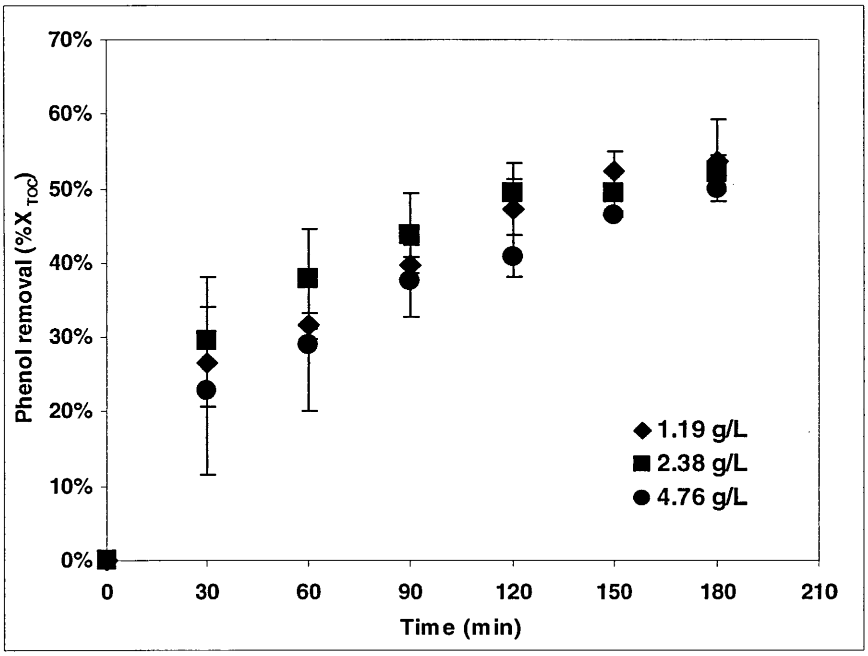


Figure 6.12: Effect of ACC-Std/H_2O_2/US system on phenol removal. Experimental conditions: phenol, 2.5 mM; temperature 20 ± 5 °C; pH 5.5; reactor, US bath (continuous sonication); H_2O_2: 1.19, 2.38 and 4.76 g L^{-1}; Results, mean ± SD of duplicates; analysis, TOC analyser.

Fig. 6.12 reveals that initially phenol removal is high with lower concentrations of H_2O_2 (1.19 g L^{-1}), however at the end of 180 min, all the peroxide concentrations gave similar results (1.19, 2.38 and 4.76 g L^{-1} showed 54, 52 and 50% TOC removal, respectively). Thus, it is proved that increasing concentrations of H_2O_2 have no significant effect on phenol removal and this is attributed to the radical scavenging activity of higher concentrations of H_2O_2. MANOVA analysis showed only slight significance of using US bath in the ACC/H_2O_2 system as the obtained *P*-value was 0.08. GC–MS analysis on the 180 min sample showed formation of traces of formic acid and *p*-benzoquinone with 1.19 and 2.38 g L^{-1}, respectively. revealing oxidation of phenol in the ACC/H_2O_2/US system.

6.3.2.3 Effect of ACC types/H_2O_2

Different types of ACCs were employed in the ACC/H_2O_2 system to investigate their enhanced (if any) efficiencies to remove phenol from aqueous medium. Lucking *et al.* (1998) found an optimum pH ≈ 3 for the oxidation several organic compounds with AC/H_2O_2, therefore ACC types/H_2O_2 were studied at this pH along with lower concentrations of H_2O_2 (1.19 g L^{-1}). Thus, comparative studies were carried out on the shaker bath at room temperature, by addition of H_2O_2 (1.19 g L^{-1}) to the aqueous medium after phenol and the ACCs had already been shaken together without H_2O_2 for 4 h. After H_2O_2 addition, phenol removal was monitored for the following 4 h (Fig. 6.13).

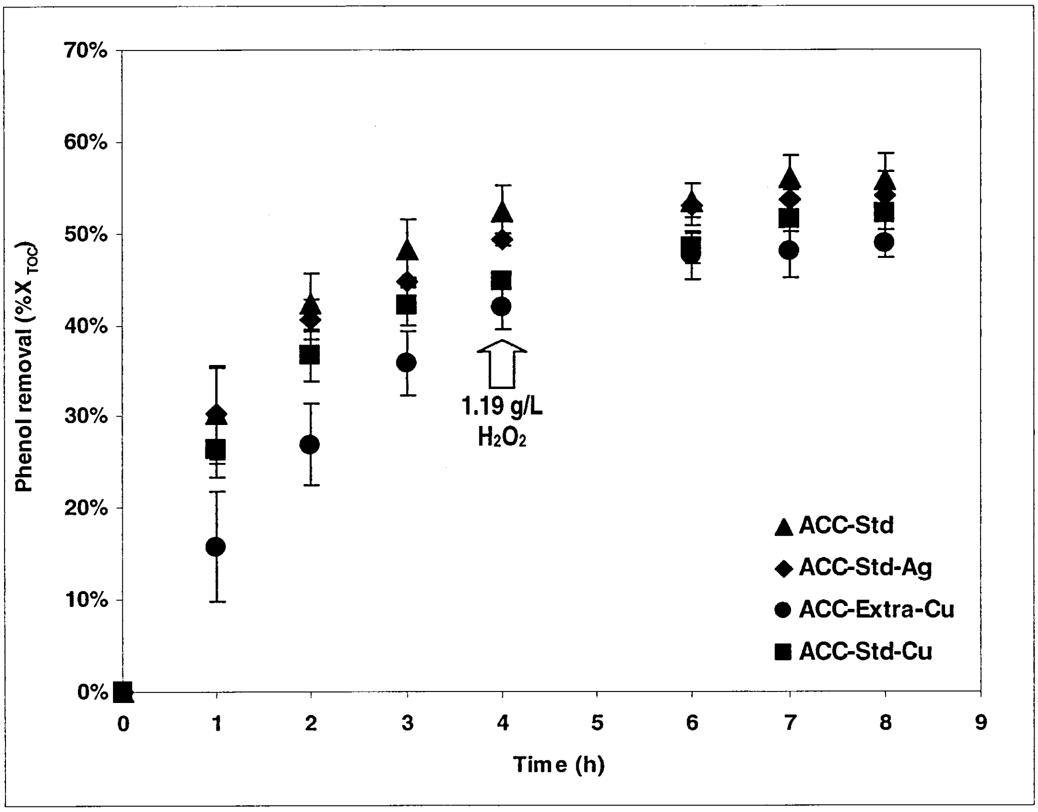


Figure 6.13: Effect of different ACC types (ACC-Std, ACC-Std-Cu (5.2% Cu), ACC-Std-Ag (0.04% Ag), ACC-Extra-Cu (4.2% Cu)) on ACC types/H_2O_2 system on phenol removal. ACC construction: ACC-Std (160 x 86) and ACC-Extra (160 x 100). Experimental conditions: phenol, 2.5 mM; temperature 20 ± 5 °C (room); pH 3; reactor, shaker bath; results, mean ± SD of triplicates; analysis, TOC analyser.

With all the ACC types, 4 h of shaking lead to 42–52% phenol removal. The initial phenol removal with ACC-Std and ACC-Std-Ag followed similar pattern, whereas the phenol removal was relatively slow with ACC-Extra-Cu probably due to cloth construction or unavailability of macropores. Thus, it can be addressed that cloth construction has a significant role to play in the removal of organics and also that presence of different amount of metals on the surface of ACC vary in the particle size and therefore the adsorption tendencies differ for different ACC types. However, H_2O_2 addition to the reaction solution resulted in nearly similar phenol removal (52–55%) with all the chosen ACC types, indicating that 10–13% oxidation of phenol present in the aqueous medium had occurred. Since, phenol adsorption on the cloth reduces the surface area of the AC available for the H_2O_2 decomposition (Lücking *et al.*, 1998) to radical species required to react with the phenolic compounds it is proposed that the presence of H_2O_2 catalysed the oxidation of phenol in the presence of ACC via an hydroxyl radical mechanism. Consequently, this enhancement could be attributed to the adsorption and then catalytic oxidising activity in the presence of H_2O_2 and standard ACC or metal-impregnated ACC.

Statistics (MANOVA) on the effect of different types of ACCs showed slight significance on phenol removal as the obtained *P*-values were in the range 0.03–0.17. GC–MS analysis showed no peaks of phenol on the chromatogram which indicates that even though only 52–55% TOC removal was obtained, the ACC/H_2O_2 system showed complete removal of phenol after 8 h.

6.3.3 Phenol removal with ACC/O_3 system

All studies with ACC/O_3 system were carried out on the shaker bath at room temperature. The effects of phenol removal in ozonated water and direct ozonation were studied at the natural pH of 2.5 mM aqueous phenol and at modified pHs, respectively. Oxidation was evaluated based on the decreasing TOC/TIC and pH values. Ozone was produced by using oxygen gas feed and all experiments were conducted at Dial 5 settings, O_2–O_3 flowrate of 5 L min^{-1} (5.6–6.3 mg O_3 L^{-1}). For direct ozonation studies, both bulk and step-wise ozonation were investigated to determine if enhanced phenol removal was seen.

6.3.3.1 Effect of ACC types/O_3 system

The experiments in this study were based on the work described by Sánchez-Polo and co-workers for the treatment of 1,3,6-naphthalenetrisulphonic acid catalysed by AC and the experimental set-up used has been discussed in Section 6.2.3.5 (Sánchez-Polo *et al.*, 2005a; Sánchez-Polo and Rivera-Utrilla, 2003, 2006). The effects of ACC-Std, ACC-Std-Cu and ACC-Std-Ag and No ACC on ozonated water containing phenol were compared and are presented in Fig. 6.14. The change in TOC and pH values indicated the effect of adsorption/oxidation catalysed by the O_3 decomposition on the surface of AC (Sánchez-Polo *et al.*, 2005b).

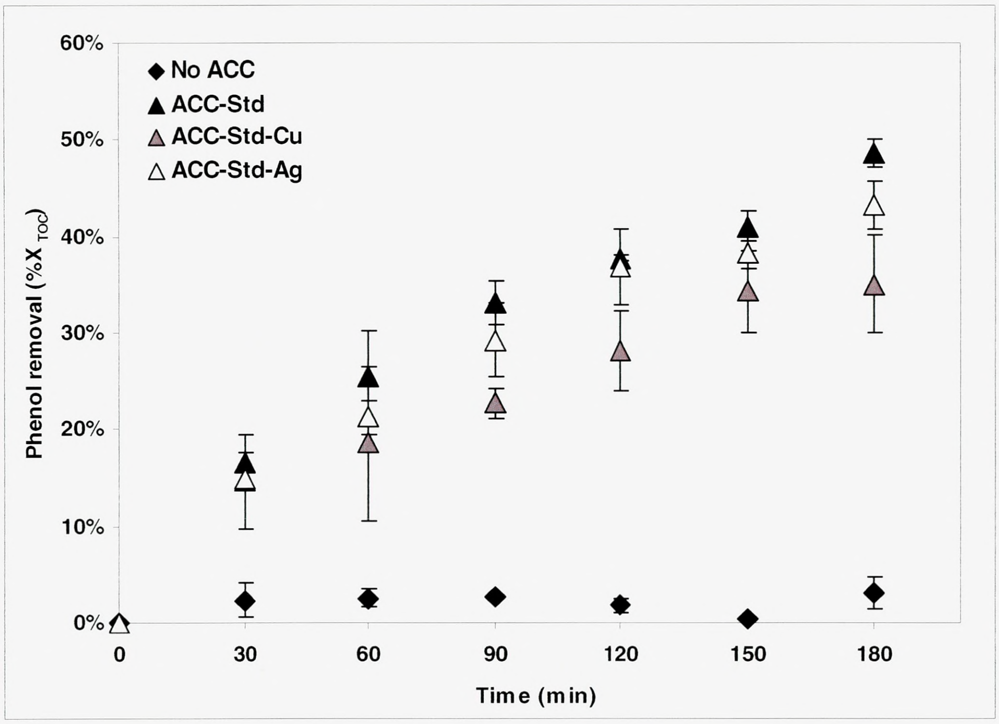


Figure 6.14: Effect of different ACC types (ACC-Std, ACC-Std-Cu (5.2% Cu), ACC-Std-Ag (0.04% Ag)) on ACC types/O_3 system on phenol removal. Experimental conditions: phenol, 2.5 mM; ACC, 0.85 g L–1 (×2 ACC discs); temperature 20 ± 5 °C (room); pH, 45 min ozonated water (6.8–7.1); ozone, Dial 5, 5 L min^{-1}, 45 min initial ozonation; reactor, shaker bath; results, mean ± SD of duplicates; analysis, TOC analyser.

The results obtained with the ACC types/O_3 system are very much in line with those obtained from the ACC types/H_2O_2 system as it was seen that ACC-Std-Ag was more efficient that ACC-Std-Cu for phenol removal, which was also reported by Deveci et al. (2006) for removal of cyanide by metal-impregnated GAC in the absence of O_3.

Even though the copper content on the cloth was higher (5.2%) than the silver content (0.04%), to achieve 0.85 g L^{-1} amount, the ACC-Std-Ag disc used for the experiment was slightly bigger in diameter (3 cm) than that of ACC-Std-Cu (2.5 cm). Probably the increased surface area in the ACC-Std-Ag could be the reason for the higher phenol removal which allowed more O_3 reactions on the surface of the ACC for oxidation and adsorption. However, naked ACC-Std was found to be the best for phenol removal using ACC types/O_3 system.

Statistically, ACC types showed very slight significance (*P* = 0.03–0.1) on phenol removal using ACC types/O_3 system. Furthermore, no change in TIC values were seen for any of the ACC types used, however a notable decrease in the pH (Table 6.4) was observed suggesting formation of acids as a result of oxidation during the ACC/O_3 phenol treatment.

	No ACC	ACC-Std	ACC-Std-Cu	ACC-Std-Ag
pH_i	7.1	6.8	7.1	6.8
pH_f	3.7	4.1	4.2	3.9

Table 6.4: Summary chart of pH values before and after ACC/O_3 treatment.

6.3.3.2 Effect of $ACC_{ozonised}/O_3$ system

It has been proposed in the literature that oxygenated surface groups of the basic nature (chromene and pyrone) in ACs are mainly responsible for the O_3 decomposition in the aqueous phase (Sánchez-Polo and Rivera-Utrilla, 2003). Also, it has been well documented that O_3 reduction on the surface of AC generates radical species which are responsible for initiating the decomposition of O_3 in the aqueous phase into highly oxidative species (Forni *et al.*, 1982; Gurol, 1982; Sotelo *et al.*, 1987). Thus, the aim of the present work was to study the effect of O_3–ACC reaction on the catalytic activity of ACC during ozonation of phenol in the aqueous phase. Therefore, ACC-Std samples were modified by exposing the catalyst to O_3 for 15 min (ACC_{15}) and 150 min (ACC_{150}) and the effect on phenol removal was monitored and compared with conditions of absence of ACC catalysts and no pre-ozone treated-ACC catalyst referred to as ACC_0 (equivalent to ACC-Std) (Fig. 6.15).

Long exposure to O_3 treatment considerably modifies the textural properties and surface chemistry of the carbon (Sánchez-Polo and Rivera-Utrilla, 2003). Although surface properties of the ACC were not studied, decrease in pH values was noticed in this work possibly indicating the increased number of acidic groups on the ACC surface (Table 6.5).

	No ACC	ACC_0	ACC_{15}	ACC_{150}
pH_i	7.1	6.8	6.6	6.6
pH_f	3.7	4.1	3.9	3.7

Table 6.5: Summary chart pH values before and after $ACC_{ozonised}/O_3$ treatment.

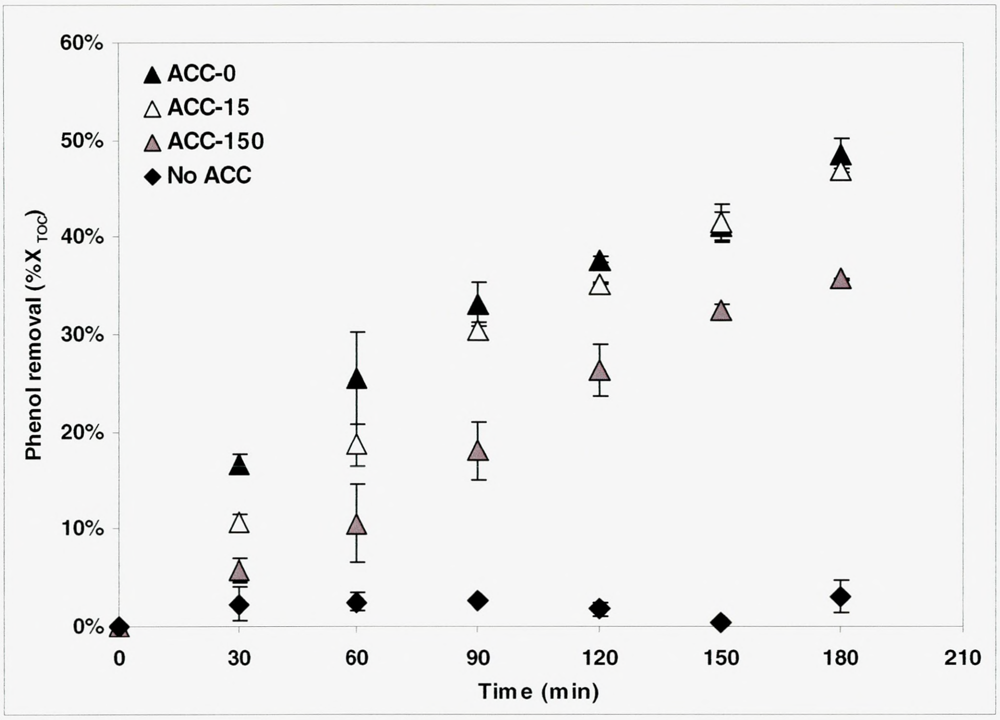


Figure 6.15: Effect of different $ACC_{ozonised}/O_3$ system on phenol removal. Experimental conditions: phenol, 2.5 mM; pre-ozonised catalysts: ACC_0, ACC_{15}, ACC_{150}; temperature 20 ± 5 °C (room); pH, 45 min ozonated water (6.8–7.1); ozone, Dial 5, 5 L min^{-1}, 45 min initial ozonation; reactor, shaker bath; Results, mean ± SD of duplicates; analysis, TOC analyser.

From Fig. 6.15, it is seen that the catalytic activity of carbon diminishes in the order $ACC_0>ACC_{15}>ACC_{150}$. The order is similar to the one proposed in the literature and the authors proposed that the decrease in TOC with reaction time was due to the two parallel phenomenon: (i) adsorption of the pollutant oxidation products on the AC and (ii) mineralisation of the organic matter to CO_2 due to O_3 decomposition into highly oxidising species (catalytic effect) (Sánchez-Polo and Rivera-Utrilla, 2003). A similar hypothesis can be proposed for ACC in this study and it can be seen that ACC equally offers a great opportunity to remove phenol in the presence of O_3 via these optimised treatment systems.

6.3.3.3 Effect of ACC/Direct ozonation systems

In Sections 6.3.3.1 and 6.3.3.2, initial experiments were designed based on published reports by Sánchez-Polo and co-workers, where reactions were carried out in saturated ozonated water conditions, however as a matter of interest direct ozonation was studied for phenol removal in the presence of ACC. Bulk and step-wise direct ozonation effects were also investigated in this study for their enhanced effect (if any). From Table 6.6, it can be clearly seen that ozonation of phenol under alkaline pH conditions leads to high phenol removal in the presence and absence of the ACC-Std catalyst. More importantly, step-wise ozonation was found to be more beneficial than bulk ozonation as it continuously provides oxidising radical species to the reaction medium, which in-turn enhances the oxidation and this theory agrees with the literature (Gogate and Pandit, 2004a, 2004b). The combined effect of ACC–ozonation was observed in the ACC-Std/O_3 operating conditions proposing adsorption/oxidation contribution on the high % phenol removal agreeing with discussions presented earlier (Sánchez-Polo and Rivera-Utrilla, 2003). Also, increasing TIC values present additional evidence of mineralisation in the ACC-Std/O_3 systems.

Furthermore, step-wise ozonation and a longer period of contact between the phenol, ACC and O_3 were studied for enhanced phenol removal and results are presented in Fig. 6.16.

Treatments	Time (h)	pH	TOC (mg L^{-1})		ΔTIC (mg L^{-1})
			t_i	t_f	
Step-wise: 5 min ozonation (at 0 min and ×2 after every 1 h) (No ACC)					
	3	3	248.6	217.8	3.04
		5.5	248.6	210.0	
		9	248.6	189.7	
Bulk ozonation: 15 min at the start of the reaction (No ACC)					
	3	3	239.6	224.1	3.79
		5.5	239.6	198.8	
		9	239.6	192.4	
Bulk ozonation: 15 min at the start of the reaction+(ACC-Std, 0.85 g L^{-1})					
	3	3	239.6	159.6	4.45
		5.5	239.6	155.1	
		9	239.6	149.4	

Table 6.6: Summary chart of phenol removal via direct (bulk or step-wise) ozonation in the presence and absence of ACC-Std catalyst.

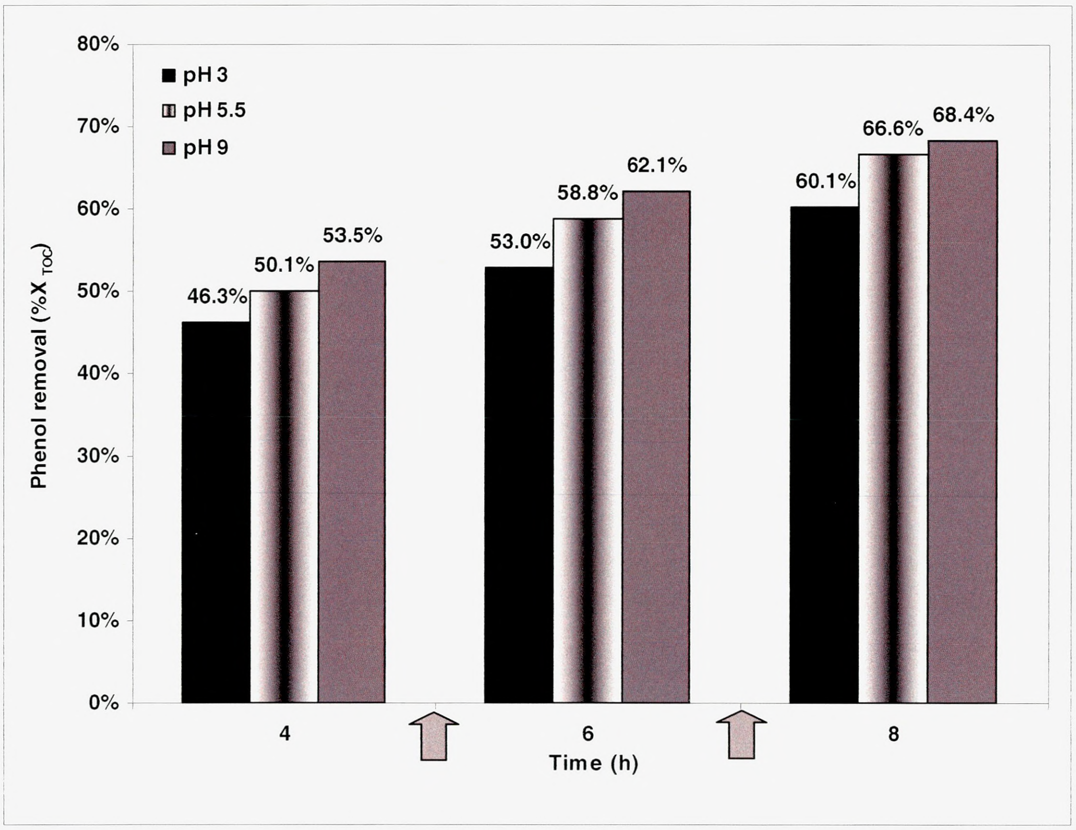


Figure 6.16: Effect of step-wise direct ozonation in the presence of ACC-Std catalyst at different pH (3, 5.5 and 9) on phenol removal. Experimental conditions: phenol, 2.5 mM; ACC-Std, 0.85 g L–1 (×2 ACC discs); temperature 20 ± 5 °C (room); ozone, Dial 5, 5 L min^{-1}(×2, 15 min; grey arrows); reactor, shaker bath; Results, mean ± SD of replicates; analysis, TOC analyser.

Of all the systems studied so far utilising ACC catalysts, step-wise addition of O_3 at suitable time intervals over a longer contact period lead to the highest (~70%) phenol removal as a result of combined effect of adsorption/oxidation. Notable changes in pH were observed (pH 3 decreased to 2.80; 5.5 to 3.04 and 9 to 3.20) indicating formation of acids via oxidation of phenol by radicals produced due to O_3 decomposition on the ACC surface. Considerable change in TIC values (2.27–6.33 mg L^{-1}) were noticed indicating CO_2 formation due to mineralisation of the organic compounds.

Therefore, from the ACC/O_3 system, it can be concluded that optimised conditions of ozonation over a suitable period time with the ACC catalysts could lead to efficient phenol removal. Moreover, the decrease of TOC during ozonation of phenol in the presence of ACC is a result of the combined effect of two parallel systems: catalytic–chemical oxidation and adsorption. Thus, the positive combined effects of treatments for enhanced pollutant removal proposed through this study with ACC/H_2O_2 and ACC/O_3 systems is in line with those suggested through combinations of various AOPs in Chapters 4 and 5. Hence, it is seen that ACC is an emerging technology that can be effectively used in conjunction with other AOPs to remove toxic pollutants via adsorption/oxidation from the wastewater.

6.4 Regeneration and reuse of ACC

Through a very simplified approach, effort was made to study if the used ACC catalyst could effectively be reused after thermal regeneration. This was suggested as one of the scopes of this study but also to prove cost-efficiency of the catalyst for removal of pollutants over several usages. Fig. 6.17 shows the effect of thermal regeneration of the catalyst by heating in the oven over different time periods and also their repeated usage.

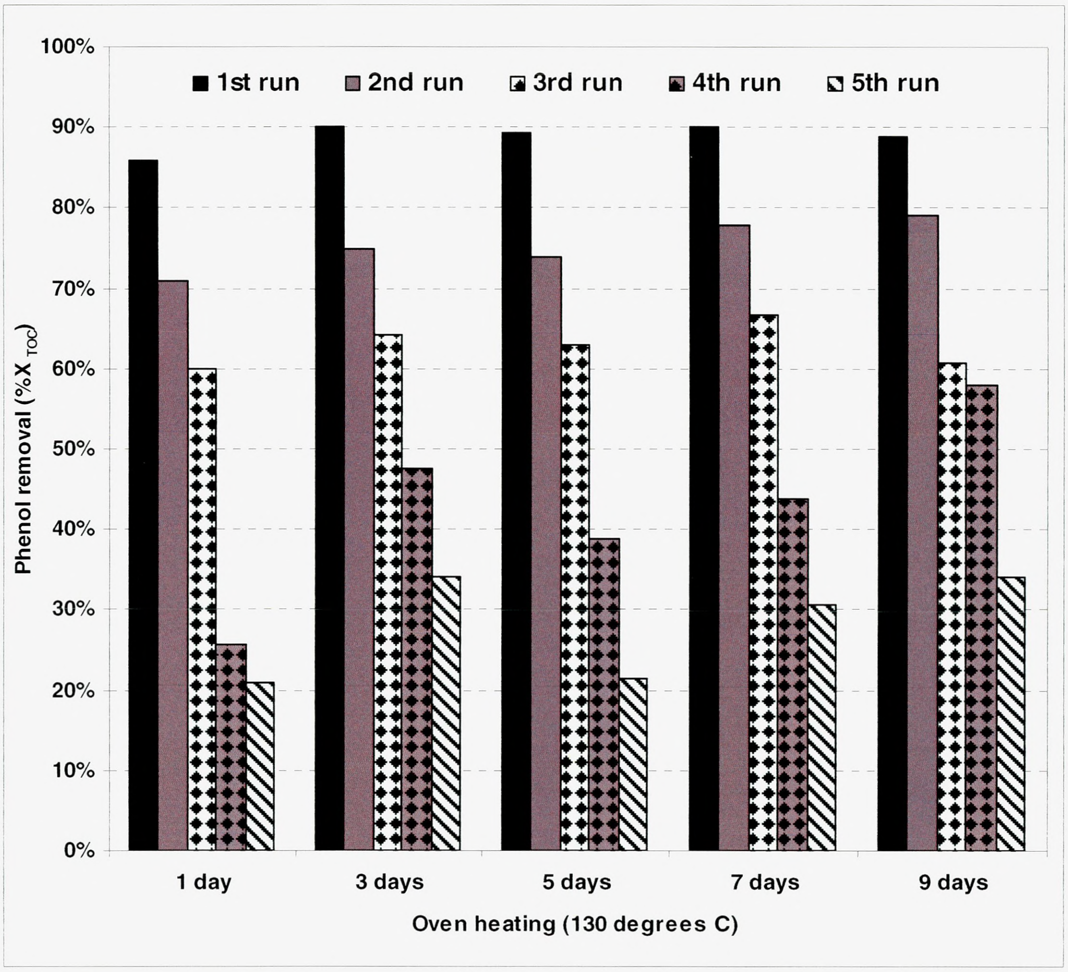


Figure 6.17: Phenol removals with repeatedly used phenol-loaded ACC-Std after thermal regeneration by oven heating at 130 °C over different periods (1, 3, 5, 7, 9 days).

The novel part of this part of this study is the low temperatures (130 °C) used to regenerate the catalyst and over 5 repeated reuses the ACC-Std catalysts (0.085 g ×5) could still remove 20–35% of TOC from the aqueous phenol solutions. Longer heating time (9 days) after every reuse showed higher phenol removal, however even consecutive 1 day heating periods for 5 times also resulted in 20% phenol removal, which could be recommended for industrial scale applications as a cost- and energy-efficient technology for catalyst regeneration and reuse.

6.5 Summary

The investigation of activated carbon cloth as a benign catalyst for phenol removal suggests that ACC can be viewed as an emerging catalyst in conjunction with other AOPs producing combined effect of adsorption–oxidation–regeneration and effectively decontaminating wastewaters containing phenolic compounds. From the study the following key conclusions are drawn and suggestions have been made for future work:

- Different reactors (US bath>Shaker bath>Peristaltic pump) and temperatures (80>40>20 °C) and pH (5.5>9>3.3) showed significant effects on phenol removal ($P = 0.000–0.055$).
- In the ACC/H_2O_2 system:
    1. The order of efficiencies of ACC catalysts was ACC-Std>ACC-Std-Ag>ACC-Std-Cu>ACC-Extra-Cu.
    2. The order of pH for % efficient phenol removal was 5.5>3>9.
    3. The order of H_2O_2 concentrations beneficial for adsorption/oxidation reactions was 1.19>2.38>4.76 g L^{-1}. However, higher concentrations showed radical scavenging activity leading to lower % phenol removal.
- In the ACC/O_3 system:
    1. The order of efficiency was ACC-Std>ACC-Std-Ag>ACC-Std-Cu.
    2. The order of efficiency of ozonised ACC-Std was $ACC_0>ACC_{15}>ACC_{150}$
    3. The order of pH for efficient % phenol removal was 9>5.5>3.

4. Step-wise ozonation was the most efficient for phenol adsorption–oxidation–regeneration in the presence of ACC-Std leading to ~70% TOC removal.

- ACC catalysts can be thermally regenerated by oven heating at 130 °C and reused over 5 consecutive times resulting in decreasing but effective phenol removal after each usage.

In depth knowledge of the chemical/textural properties and behaviour of ACC in oxidant-assisted phenol removal could lead to a better understanding and support of the proposed hypothesis of adsorption/chemical oxidation via ACC/O_3/H_2O_2 systems. Also, ultrasound could also be used for the purpose of regeneration and reuse ACC catalyst. Hence, these objectives are recommended for future studies.

Chapter 7

Disinfection: Bacterial inactivation using cavitation and ozonation in a novel Liquid Whistle Reactor

Published paper (Appendix C)

Chand, R., Bremner, D.H., Namkung, K.C., Collier, P.J. and Gogate, P.R. 2007. Water disinfection using the novel approach of ozone and a liquid whistle reactor. *Biochemical Engineering Journal.* 35(3): pp.357-364.

Platform presented paper: International Conference

Chand, R. (15–18 October 2006). The antimicrobial effects of ozone and hydrodynamic cavitation in a liquid whistle reactor. *56th Canadian Chemical Engineering Conference.* Sherbrooke, Quebec, Canada.

So far in the thesis, much has been discussed on pollutant degradation using single and combined **A**dvanced **O**xidation **P**rocesses (AOPs) such as the Advanced Fenton Process (AFP), cavitation, catalytic and chemical oxidation and also use of different oxidants such as ozone and hydrogen peroxide. In this part of the work, another application using the novel approach of hydrodynamic cavitation and/or ozonation as individual and combined technology for **disinfection** is described.

7.1 Introduction

Since the early 1970s, the developed countries in the world have used ozone (O_3) as a disinfectant for treated wastewater effluent and the past literature suggested that 10 mg O_3 L^{-1} dose is required to achieve an efficient level of disinfection. However, increasing environmental regulations and lowered nutrient levels in the effluents have lead to O_3 dosages as low as 5 mg O_3 L^{-1} to meet high levels of disinfection (Burns *et al.*, 2007). Thus, the effective low dosages combined with other dissolution technology have made O_3 a disinfectant for wastewater cost-competitive with UV treatment. The US EPA *Wastewater Disinfection Manual* summarises O_3 dosages required to disinfect a variety of effluents (Table 7.1). However, economic analysis of disinfection systems indicated a 17% higher cost of O_3 operation than UV.

Effluent quality	Absorbed O_3 dosages (mg O_3 L^{-1}) for		
	2.2 CFU 100 mL^{-1} total coliform	70 CFU 100 mL^{-1} total coliform	200 CFU 100 mL^{-1} faecal coliform
Filtered secondary	35–40	15–20	12–15
Filtered and nitrified	15–20	5–10	3–5

Table 7.1: Summary of O_3 dose required to treat various disinfection targets (Burns *et al.*, 2007).

Recent published research indicates that water treated by biological nutrient removal (BNR) in the presence of 3 mg O_3 L^{-1} gives greater than 90% removal of most common pharmaceutical care products as well as reduction of total faecal coliforms to below detection (Snyder *et al.*, 2005). Combined AOPs have become very famous in recent years mainly due to decreased cost of operations. Industries are focussing on technologies which are effective enough for achieving multiple goals, i.e., disinfection as well as micropollutant removal. Certainly O_3 has gained popularity over the years and is becoming more cost-competitive with UV, however considering its capability to remove micropollutants, O_3 is clearly a technology that will be considered increasingly in the future (Burns *et al.*, 2007).

As discussed above, the cost of operations of technologies using O_3 has always been a barrier to widespread adoption by industry, therefore recent literature also reported a combination of AOPs to disinfect and degrade wastewaters (Jyoti and Pandit, 2004; Kim *et al.*, 1999; Mason *et al.*, 1996; Save *et al.*, 1997), which prove to be efficient and cost effective. Enhanced disinfection has also been achieved by exposure of bacteria to magnetic fields and ultrasonic irradiation (Kohno *et al.*, 2000; San Martin *et al.*, 2001). Chemical oxidation using chlorine dioxide, thyme essential oil (Singh *et al.*, 2003); hypochlorite (Duckhouse *et al.*, 2004); chorine and monochloramine (Baker *et al.*, 2002) and titanium dioxide (Ireland *et al.*, 1993), have also been successfully used as combined or individual systems in hybrid AOPs for effective disinfection.

Ozone has been used extensively in food industries all over the world, especially with increasing demand for packed/canned food products. For example, recently a Japanese company invented a laboratory scale machine that can sterilise food packaging films and preformed cups using ozonated water and O_3 gas (Naitou and Takahara, 2008). Although UV-rays can be used to support the disinfection process, it is suggested by these authors that the process could be utilised to reduce the degree of microbial contamination caused by inadequate disinfection against new resistant strains, i.e., lactic acid bacteria, Gram-negative bacteria, mould, yeast. Other advantages of using O_3 in the food industry is that it increases the shelf life of the food products, it decomposes rapidly and leaves behind no residues (Guzel-Seydim *et al.*, 2004; Khadre *et al.*, 2001). In particular, it has been found that cell lysis is dependent on the extent of reaction of the O_3 gas with the double bonds of lipids of the cell membrane of *Escherichia coli* (Scott and Lesher, 1963).

Emerging technologies such as membrane filtration, ozone–membrane filtration and catalytic (iron oxide)–ozonation–membrane filtration have recently been compared and reported to be effective for *Escherichia coli* removal (Karnik *et al.*, 2007). Their report suggested that highest log removal (7.45) was obtained from catalytic–ozonation–membrane filtration due to the catalytic decomposition of O_3 at the iron oxide surface results in the formation of HO• and other radical species that inactivate bacteria near the surface. Likewise, recent reports on hydrodynamic cavitation and acoustic cavitation have also proved to be outstanding advanced disinfection technologies in drinking water treatment and are deemed to be environmentally sound systems without generating any toxic residual by-products (Jyoti and Pandit, 2003; Piyasena *et al.*, 2003). Burleson *et al.* (1975) reported individual treatment with O_3 and ultrasound did not inactivate microorganisms, but simultaneous treatments with both resulted in a synergistic effect.

In the previous chapters, the application of acoustic cavitation has been discussed in detail in conjunction with the Advanced Fenton Process, ozonation and activated carbon cloth for the removal of toxic phenols from wastewaters. However, the present study focuses on the disinfection of water containing *E. coli*, as model markers of the faecal coliforms, using single and hybrid technologies of hydrodynamic cavitation (HC) and ozonation in a novel Liquid Whistle Reactor (LWR).

As suggested by Burleson *et al.* (1975), it is also expected that HC and ozonation should give synergistic effects due to additional free radical production (Eq. 7.1 and 7.2) (Hart and Henglein, 1985), taking place in the cavitating bubble due to very high temperatures and pressures, leading to enhanced disinfection.

$$O_3 \longrightarrow O_2 + O(^3P) \qquad (7.1)$$

$$O(^3P) + H_2O \longrightarrow 2HO\bullet \qquad (7.2)$$

The reaction products of Eq. 7.1 and 7.2 migrate to the interfacial sheath of the bubble where they subsequently react in the bulk solution. Mass transfer limitations are often believed to be associated with ozonation processes, but they are eliminated by the turbulence created by the liquid circulation currents, induced by the cavitation. Thus, due to the two positive facts, i.e., elimination of mass transfer limitations and production of two free radicals per molecule of O_3 consumed, even for compounds that react fairly quickly with O_3, the rate of degradation/disinfection will be enhanced by the combined operation of cavitation and ozonation. The extent of these combined effects, in case of HC, is also expected to be influenced by the intensity of cavitation in the reactor which, in turn, depends on the inlet pressure as demonstrated by theoretical bubble dynamic modelling (Gogate and Pandit, 2000). Therefore, it is recommended that to attain maximum benefits of the combined systems, optimum operating pressure should be selected and this will be discussed later in this chapter.

Hence, the main objectives of this study were to assess the following on the effectiveness of disinfection:

- Inlet pressure into the LWR (over a range 500–1500 psi)
- O_3 dosages (time of ozonation and flowrates)
- Individual technology: HC and ozonation
- Combined technology: HC + (single/double) ozonation
- O_3 decomposition in the LWR

7.2 Experimental

7.2.1 Microorganism

Escherichia coli (NCIMB 10000 obtained from the National Collection of Industrial Food and Marine Bacteria, Aberdeen, UK), a Gram-negative model bacterium, was chosen for all the experimental studies. Cells, medium and viable count methodology are as described in Section 2.4.6.

7.2.2 Reaction suspension

Since the aim of this study was to develop a robust disinfection technology utilising the combined approach of hydrodynamic cavitation (HC) and ozonation, for potential utilisation in different industries, a contaminated suspension was created by inoculating 400 mL of the overnight culture of *E. coli* (6×10^7 CFU mL^{-1}) into 3600 mL distilled water (dH_2O). The suspension pH (7–8) and temperature (20 ± 5 °C) was noted at the start of every experiment.

7.2.3 Liquid Whistle Reactor

The Liquid Whistle Reactor (LWR) used is same as described in Section 2.3.1. The reactor set-up was modified to carry out disinfection studies under sterilised conditions and also at different temperatures. A schematic diagram of the modified LWR for this study is presented in Fig. 7.1.

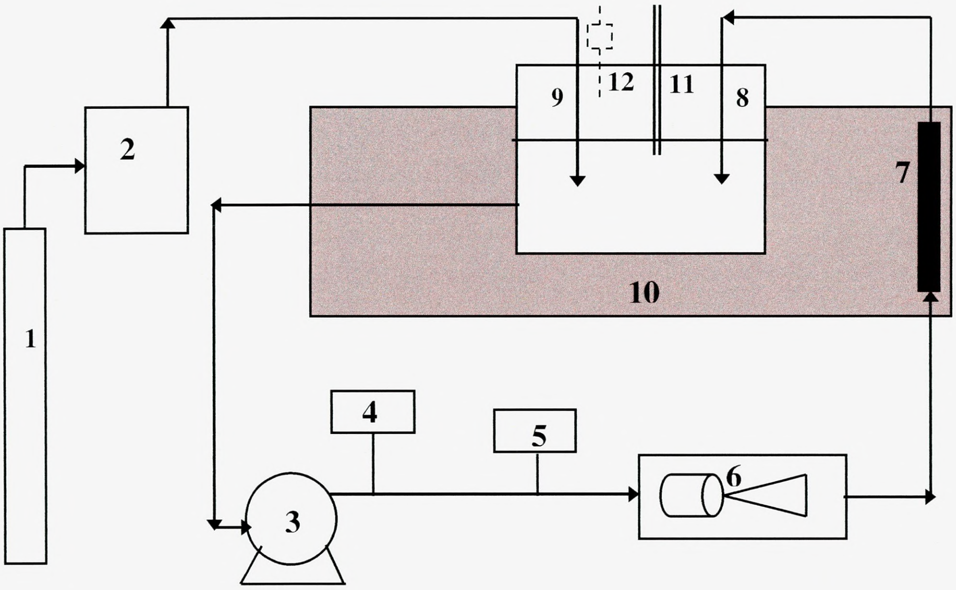


Figure 7.1: Schematic representation of the experimental set-up with the ozoniser and the LWR (1, oxygen cylinder; 2, ozone generator; 3, plunger pump; 4, PLC board; 5, digital pressure meter; 6, orifice and blade unit; 7, cooling coil; 8, return pipe to feed tank; 9, ozone gas bubbler; 10, cooling bath; 11, sampling port; 12, KI trap).

In the modified LWR set-up, the open steel feed tank (4 L) was replaced by an airtight chamber and an additional cooling unit was designed, where the LWR was connected to a 10 L autoclavable NALEGE® polycarbonate reaction vessel fitted with a polypropylene closure, which includes a gasket to assure leak-proof services (Nalge Co., NY, USA). For cooling, the reaction vessel was immersed in an ice bath. This airtight unit was operated in recycling mode and fitted with an ozone bubbler, a vent into 2% KI (ozone scrubber) and a sampling port.

7.2.4 Ozone

7.2.4.1 Ozone generator

The ozone generator is the same as described in Section 2.4.4 with oxygen as a feed gas.

7.2.4.2 Ozone measurements

Ozone was measured using the colorimetric Indigo method as described in detail in Section 2.4.4 (Bader and Hoigne, 1981, 1982; Greenberg *et al.*, 1992)

7.2.5 Operational details: single and combined technologies

7.2.5.1 Hydrodynamic cavitation alone

To estimate the % disinfection using HC alone, experiments were carried out with 4 L of bacterial suspension having a concentration of approximately 10^8–10^9 CFU mL^{-1}. The % disinfection was compared at three different pressures: 500, 1000 and 1500 psi with samples being withdrawn every 30 min. Experiments were carried out in triplicates and average data is presented with reproducibility within ±5%.

7.2.5.2 Ozonation alone

To study the % disinfection with O_3 alone, the LWR was operated without orifice and blade, which consequently reduces the inlet pressure considerably and the reaction suspension was circulated through the pipe to the feed tank and back to the LWR. However, since there was no pressure in the LWR there was no resultant increase in temperature as HC normally generates heat due to cavity collapse. Therefore, with ozonation alone experiments, the temperature was maintained at 35 ± 5 °C by immersing the feed tank in a water bath. In the absence of orifice and blade, the LWR inlet pressure and flowrates were observed as 30 psi and 5.4 L min^{-1}, respectively. The O_3 concentrations were monitored and samples were withdrawn every 30 min, exactly as described above for analysis of the extent of disinfection. The effect of O_3 concentration on the extent of disinfection was optimised by changing the dial settings on the control dial on a scale of 1–10 as described by the equipment supplier. This step is considered to be important in the optimisation process for maximising combined/synergistic effects (if any).

7.2.5.3 Hydrodynamic cavitation and single ozonation

Single ozonation is defined as a single dose of O_3 at a flowrate of 5 L min^{-1} of O_3–O_2 mixture being applied for 15 min before the start of the experiment (3–3.5 mg O_3 L^{-1}). Once ozonation was finished, the bacterial solution was mixed in the LWR at a very low pressure (300 psi, 5 min) and then the first sample was withdrawn for serial dilution in order to determine the base line bacterial count. Following the 5 min mixing at 300 psi, the pressure in the LWR was then increase to the desired value and the solution was circulated. During this process, the temperature was not controlled and hence it increased from 20 ± 5 °C to 35 ± 5 °C as a result of cavitation. The extent of bacterial killing at each pressure was determined using the heterotrophic plate count technique after incubation overnight at 37 °C (Greenberg *et al.*, 1992).

7.2.5.4 Hydrodynamic cavitation and double ozonation

To determine the enhanced effect (if any) of adding the O_3–O_2 mixture in two separate doses, the experiments at different pressures were repeated with purging the gaseous mixture at a flowrate of 5 L min^{-1} for 15 min at the start of the experiment (3–3.5 mg O_3 L^{-1}) and then again for 15 min after 90 min reaction time. Studies with HC and double ozonation were carried out at controlled temperatures of, 15 ± 5 °C, 25 ± 5 °C, 35 ± 5 °C, for pressures, 500, 1000 and 1500 psi, respectively, to determine any enhancement in process operation for disinfection.

7.2.5.5 Ozone decomposition in the LWR

Ozone was bubbled through sterile dH_2O (4 L) and O_3 decomposition over 180 min reaction time was monitored in the LWR in the presence/absence of the orifice and blade and also with single/double ozonation at different operating pressures (Section 7.4). Experimental conditions and set-up were the same for all the bacterial disinfection measurements. For colorimetric measurements, the ozonised samples (3 mL) were withdrawn at specific time intervals and mixed gently with 5 mL Indigo reagent and filled to mark in a 50 mL volumetric flask. To mix the solution, the volumetric flask was turned upside down without formation of any air bubbles and the colour change was read on the UV–vis spectrophotometer at 600 nm and concentrations were measured in mg O_3 L^{-1} as described in Section 2.4.4.

7.3 Results and discussion

The % disinfection under different operational conditions have been represented in the form of percentage disinfection (microbial inactivation %) and calculated using the formula below:

$$\text{percentage disinfection} = \log \{(N_0 - N)/N\} \times 100 \qquad (7.3)$$

where, N_0 represents the initial microbial count and N represents the microbial count at any give time.

7.3.1 Effect of hydrodynamic cavitation

Microbial inactivation at lower pressures, i.e., 500 and 1000 psi was almost negligible (1–7%). However, 22% microbial inactivation was obtained by increasing the pressure to 1500 psi, which could be explained by higher cavity formation at this pressure, as discussed in Chapter 3. At 1500 psi, higher intensity cavitation leads to the formation of higher number of free radicals and at this pressure, the elevated intensity of turbulence causes cell disruption at the high pressure zone, i.e., orifice and blade and also allows the free radicals to homogeneously react with the microbial cell contents (Fig. 7.2).

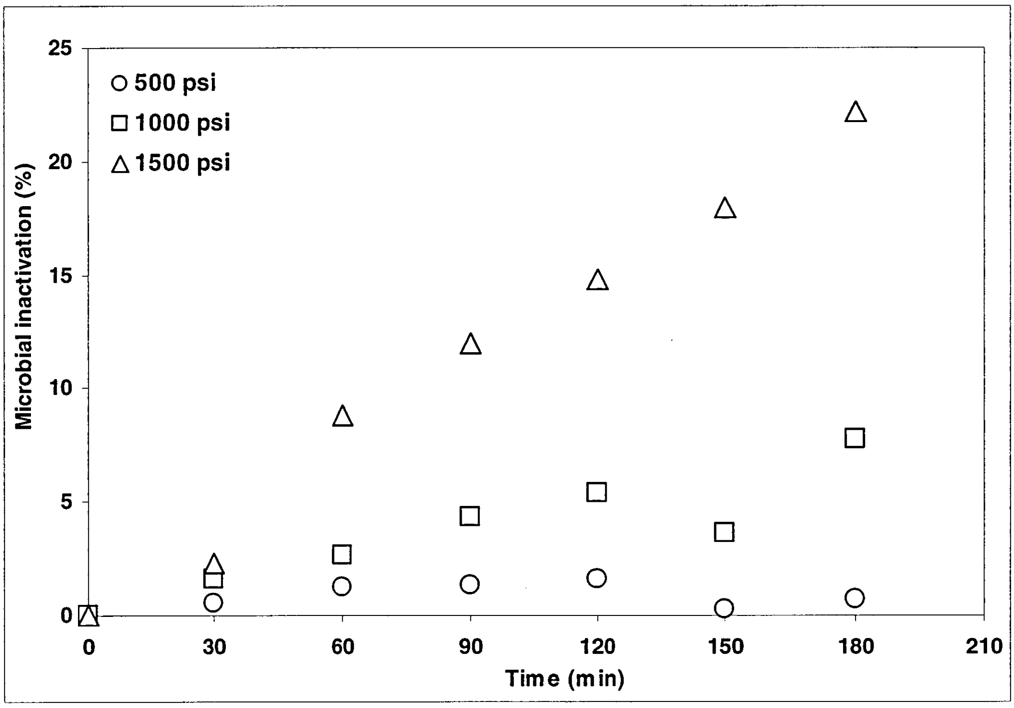


Figure 7.2: Effect of HC alone on microbial inactivation (%) at different pressures in the LWR. Experimental conditions: bacteria, *E. coli*; reaction suspension (4 L); reaction time, 180 min, temperature 20 ± 5 °C to 35 ± 5 °C; operating pressure, 500, 1000 and 1500 psi; results shown are an average of triplicates.

During cavitational processes, extreme temperatures and pressure gradients occur within the bubble during cavitational collapse and release oxidants, like HO• and H_2O_2 into the solution (Suslick *et al.*, 1997), which participate in bacterial inactivation. Different theories have been proposed where high pressures and cavitation leads to cavity collapse which in turn leads to cell disruption (Shirgaonkar *et al.*, 1998). Cell disruption at high pressures has also been attributed to impingement and impact (Moore *et al.*, 1990). In this study, at 1500 psi, the highest reduction in bacterial numbers is attributed to the significant cavitational effects beyond certain cavitation inception conditions (e.g., 500 psi), resulting in generation of various free radicals and also mechanical effects, i.e., turbulence and shear, which facilitates the de-agglomeration of microbial clusters, allowing effective interaction of the bulk liquid oxidants with the microorganisms and its contents leading to enhanced disinfection at this pressure.

7.3.2 Effect of ozonation

The effect of ozonation only was studied by removing the orifice and blade from the LWR. In the absence of the orifice and blade, the O_3 molecules and any intermediate radicals, generated due to *in situ* O_3 decomposition, react with the bacteria present in the suspension, leading to disinfection. In case of O_3 alone, it is also believed that fairly high temperatures (35 ± 5 °C) lead to cell breakage. Thus, the two factors, i.e., free radicals and higher temperatures lead to significant bacterial killing during single (Fig. 7.3) and double ozonation (Fig. 7.4).

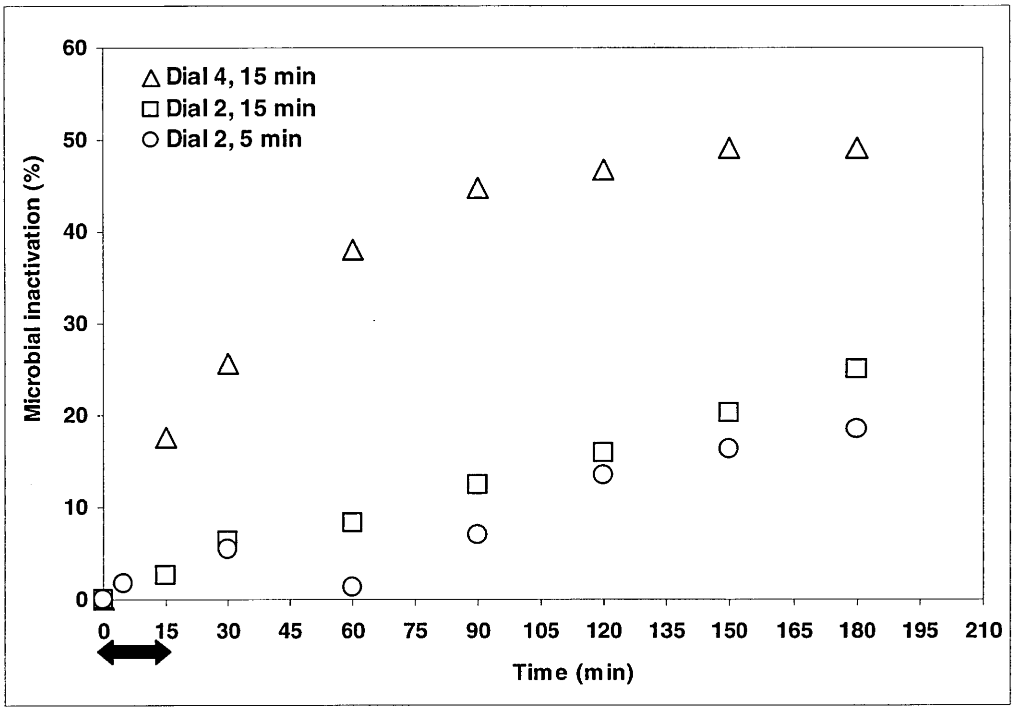


Figure 7.3: Optimisation of O_3 dosages: (i) dial 2, 5 min (ii) dial 2, 15 min and (iii) dial 4, 15 min, for disinfection studies. Experimental conditions: bacteria, *E. coli*; reaction suspension (4 L); O_2–O_3 gas flowrate, 5 L min^{-1} (3–3.5 mg O_3 L^{-1}); temperature, 35 ± 5 °C; pressure, 30 psi (5.4 L min^{-1}); reaction time, 180 min. Double-ended arrow denotes period of single ozonation.

An appropriate O_3 dose is an important factor in ozonation systems. Thus, some optimisation studies were carried out by changing dial settings (1–10) on the ozonator, which reflects the concentration of O_3 in the mixture (http://www.ozoneengineering.com). However, for all the studies, the flowrate of the O_2–O_3 mixture was kept constant, i.e., 5 L min^{-1} and bacterial disinfection was studied at the following settings on the ozonator: (i) dial 2, 5 min (ii) dial 2, 15 min and (iii) dial 4, 15 min. The % disinfection at the three settings were studied over 180 min and the following conclusions could be drawn from the data: from setting (i) and (ii), 20% and 25% disinfection was observed, respectively, whereas from setting (iii) approximately 50% disinfection was achieved. Therefore, all the experiments at different pressures and double ozonation were carried out at this optimised O_3 dose, i.e., dial 4, 15 min. Likewise, a similar pattern of disinfection was achieved up to 90 min in case of double ozonation but soon after the second ozonation (dial 4, 15 min) a further significant 23% increase in bacterial killing was observed (Fig. 7.4). This enhanced % inactivation with double ozonation could be attributed to the increased concentration of O_3 and its intermediate radical species interacting with the remaining surviving bacteria leading to further disinfection. Literature also suggests that step wise addition of oxidants to the reacting medium helps in the process of degradation/disinfection (Gogate and Pandit, 2004b).

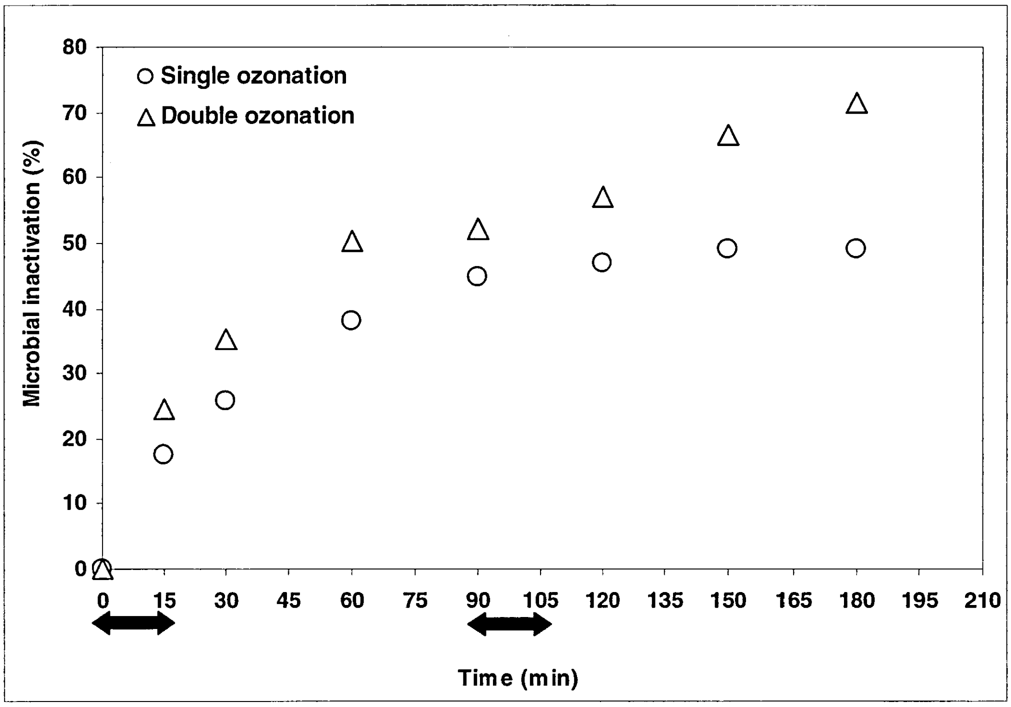


Figure 7.4: Comparison of single and double ozonation on the % disinfection. Experimental conditions: bacteria, *E. coli*; reaction suspension (4 L); O_2–O_3 gas flowrate, 5 L min^{-1} (3–3.5 mg O_3 L^{-1}); ozonator setting, dial 4, 15 min; temperature, 35 ± 5 °C; pressure, 30 psi (5.4 L min^{-1}); reaction time, 180 min. Double-sided arrow denotes period of ozonation for single and double ozonation.

Bacterial disinfection with O_3 occurs due to interaction between the oxidising radical species and the bacterial cell, where the cell membrane is the first site of attack through glycoproteins, glycolipids and amino acids and O_3 tends to act upon the sulfhydryl groups of certain enzyme (Rojas-Valencia *et al.*, 2004). The mass transfer limitations of O_3 sparging in the stirred or bubble column type reactors is overcome by the re-circulatory flows in the LWR which, in turn, enhances mixing rates in the system. The continuous re-circulation not only affects the mixing rates but also helps in de-agglomeration of the microbial clusters and with the effect of high temperatures, favours cell breakage and O_3 dissociation into intermediate radicals, which have higher potentials to break through individual microbial cells and enhance bacterial inactivation. It should also be noted that O_3 could have been used for a longer time duration but the scope of the present study was to develop an optimum treatment protocol based on the LWR with minimum usage of O_3 to reduce the cost of treatment.

7.3.3 Effect of hydrodynamic cavitation and single ozonation

A combination of HC (1500 psi) and single ozonation (15 min at the start of the experiment, corresponding to 3–3.5 mg O_3 L^{-1}), lead to 48% microbial inactivation, i.e., the bacterial numbers reduced from ~10^9 to 10^5 CFU mL^{-1}. In Fig. 7.5a, a comparison of the combined system of HC and single ozonation is shown and a further magnified comparison graph is presented at 1500 psi, with and without ozonation (Fig. 7.5b). However, the results shown here are in correlation with the O_3 decomposition, discussed in Section 7.4, in the presence (1500 psi) and absence of orifice (30 psi) which follows a similar pattern under both the conditions and this could be the possible reason for similar % disinfection under the two conditions.

From Fig. 7.5a, it can be noticed that at lower pressures (500 and 1000 psi) with the single ozonation, instant killing was observed within 15 min due to the direct reaction of O_3 and its intermediate radicals species with the bacteria in the bulk solution. However, there was no further significant microbial reduction observed over the next 165 min and since the pressures were not high enough, no more disinfection occurred via cavitation.

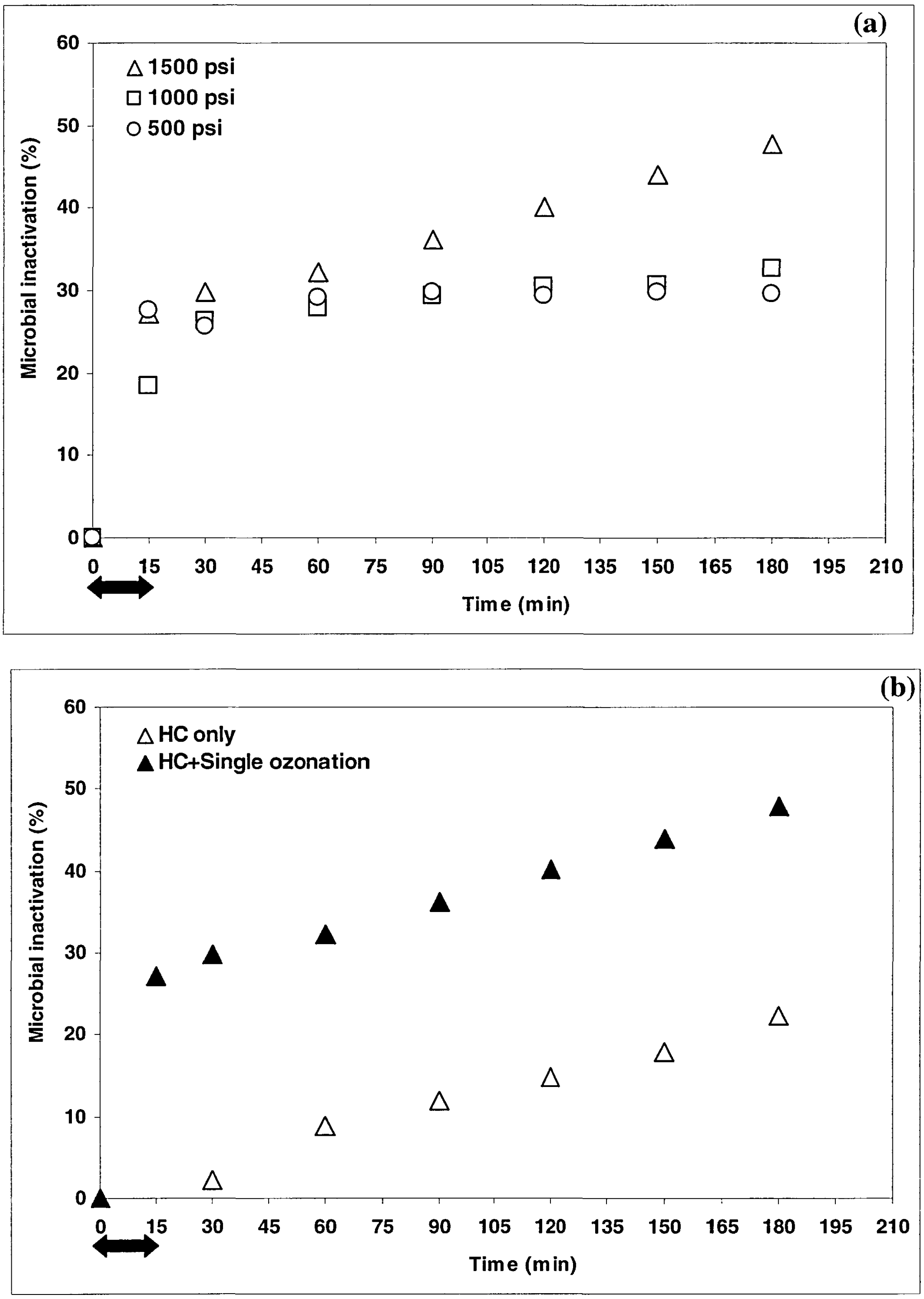


Figure 7.5: (a) Effect of HC and single ozonation on microbial inactivation (%) at different pressures in the LWR and (b) Comparison of microbial inactivation (%) at 1500 psi (HC) and 1500 psi (HC) + single ozonation. Experimental conditions: bacteria, *E. coli*; reaction suspension (4 L); O_2–O_3 gas flowrate, 5 L min^{-1} (3–3.5 mg O_3 L^{-1}); ozonator setting, dial 4, 15 min at the start; temperature, 35 ± 5 °C; reaction time, 180 min. Double-sided arrow denotes period of single ozonation.

In Fig. 7.5b, the comparative study at 1500 psi with and without ozonation indicates effect of the combination of the two AOPs, i.e., cavitation and ozonation. With an initial 15 min ozonation under similar conditions and reactor set-up, a significant 28% bacterial inactivation was observed and after a further 165 min of reaction at 1500 psi, a further 20% increase in disinfection is achieved, giving a total of 48% killing. However, in case of cavitation alone at 1500 psi, only 22% disinfection over 180 min was achieved.

7.3.4 Effect of hydrodynamic cavitation and double ozonation

The effect of low pressure was insignificant in the case of HC coupled with single ozonation, therefore to maximise disinfection, double ozonation (Section 7.4) was investigated at all of the three chosen pressures. The results shown in Fig. 7.6 reveal that the extent of disinfection obtained from this combined system of HC and double ozonation was in the range 58 to 73%.

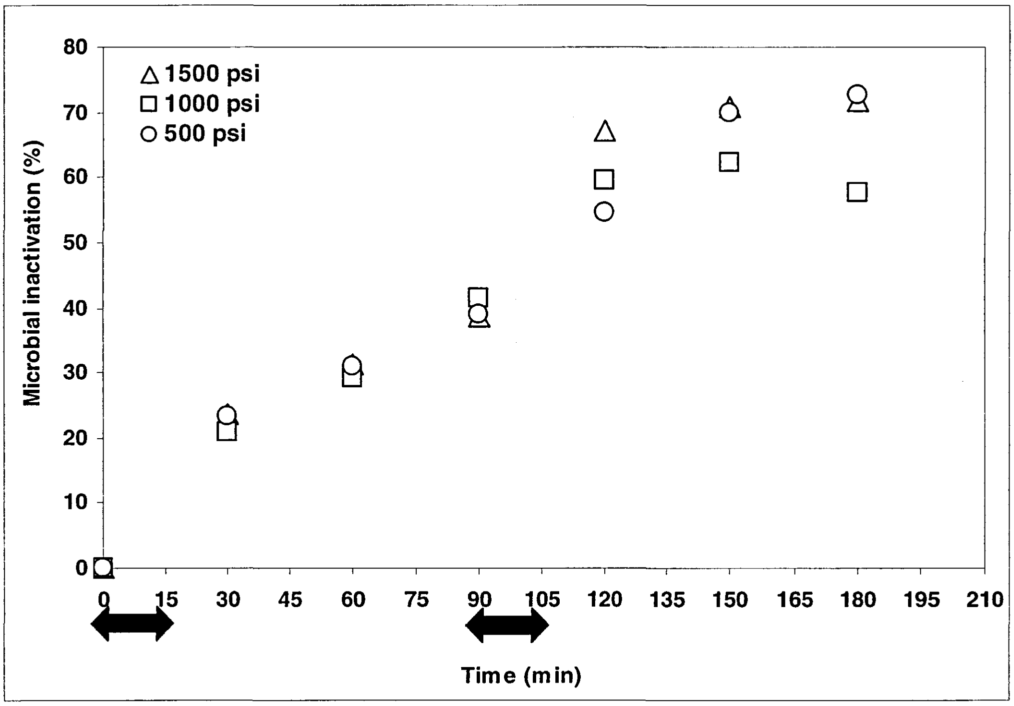


Figure 7.6: Effect of HC and double ozonation on microbial inactivation (%) at different pressures in the LWR. Experimental conditions: bacteria, *E. coli*; reaction suspension (4 L); O_2–O_3 gas flowrate, 5 L min^{-1}; ozonator setting, dial 4, 15 min at the start (3–3.5 mg O_3 L^{-1}); temperature, 500 psi, 15 ± 5 °C, 1000 psi, 25 ± 5 °C, 1500 psi, 35 ± 5 °C; reaction time, 180 min. Double-sided arrow denotes period of single and double ozonation.

As discussed above, the extent of disinfection was similar in case of 500 and 1500 psi, whereas comparatively low with 1000 psi. The difference in the % disinfection can be explained on the basis of two parallel mechanisms: (i) pressures and related cavitational activity and (ii) operating temperature. In the literature, the concept of variable temperature and activation energies with respect to microbial disinfection for bacteria has been discussed in detail by Von Gunten (Von Gunten, 2003) who reported that activation energies for bacteria are in a similar range to chemical reactions with O_3 (35–50 kJ mol^{-1}). Thus, to assess disinfection for variable temperatures, these activation energies have to be compared with the activation energies for the O_3 decay, which is 65–70 kJ mol^{-1}(as determined in various water matrices). The above explanation proves that for the same O_3 dosage, the degree of microbial inactivation would be higher at lower temperatures (Hunt and Mariñas, 1997). Therefore, a different set of temperatures were selected to operate with different pressures: 500 psi, 15 ± 5 °C; 1000 psi, 25 ± 5 °C and 1500 psi, 35 ± 5 °C, to achieve effective % disinfection in the LWR.

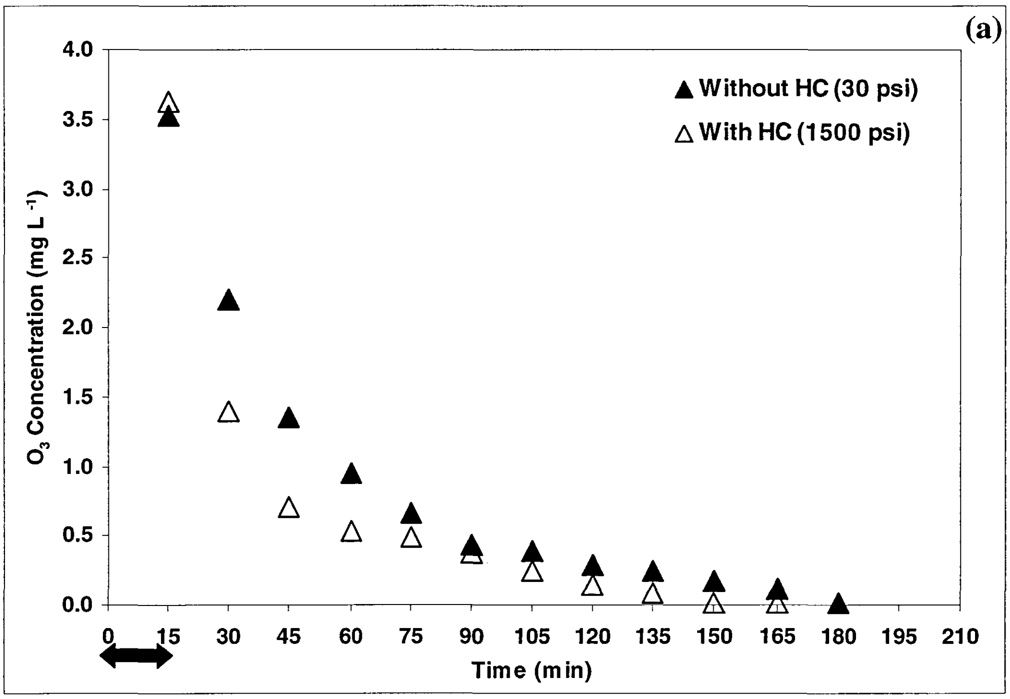
At 500 psi operating pressure, the temperature was maintained at 15 ± 5 °C with the help of the cooling bath and a high degree of disinfection was achieved with double ozonation even though the contribution due to cavitation was negligible. The high % disinfection at this pressure could be attributed to the higher activity of the O_3 because the single and double O_3 decomposition profiles in the LWR (Section 7.4) reveals that during single ozonation, O_3 concentrations decreased from 3–3.5 mg O_3 L^{-1} to 0.9 mg O_3 L^{-1} at the end of 90 min, but in case of double ozonation, O_3 concentrations increased to 3.4 mg O_3 L^{-1} after the second ozonation and remained 1.5 mg O_3 L^{-1} until the end of reaction time due to stability of O_3 at lower temperatures. Thus, the presence of O_3 and its intermediate radical species until the end of the reaction time at 500 psi and 15 ± 5 °C temperature influences the % inactivation. However, at 1000 psi, with similar cooling but relatively high cavitational activity, the operating temperature could only be maintained around 25 ± 5 °C. Thus, here both the ineffective factors: low cavitational activity and low activity of ozone lead to only 58% microbial inactivation at this pressure. On the contrary, higher pressures of 1500 psi and 35 ± 5 °C shows lower O_3 activity but substantially higher cavitational activity as seen from all the results so far, which overall results in the similar degree of disinfection as seen in case of 500 psi, i.e., 73%.

This part of the study at different pressure and temperature combinations meets the objectives of this research because literature suggests that natural water microorganisms can be rapidly killed by the direct ozonation, whereas those in secondary effluents from wastewater treatment plants require longer contact time for inactivation which might increase the operational cost (Burleson *et al.*, 1975). Hence, simultaneous treatments by ozonation in the LWR at optimised temperature and pressure conditions could prove to be beneficial for inactivating bacteria at substantially reduced contact time of O_3, which may in turn, reduce the total cost of operations.

Therefore, the overall conclusion is that the use of the hybrid technology of HC and ozonation in the LWR offers great promise in treating wastewater with recalcitrant bacteria, at unusually low cost and lower energy input.

7.4 Ozone decomposition in the LWR

The ozone decomposition studies were carried out in the presence (1500 psi) and absence (30 psi) of the orifice and blade at 35 ± 5 °C and also at the different temperature and pressure combinations during HC and double ozonation: 500 psi, 15 ± 5 °C; 1000 psi, 25 ± 5 °C and 1500 psi, 35 ± 5 °C over 180 min treatment time.



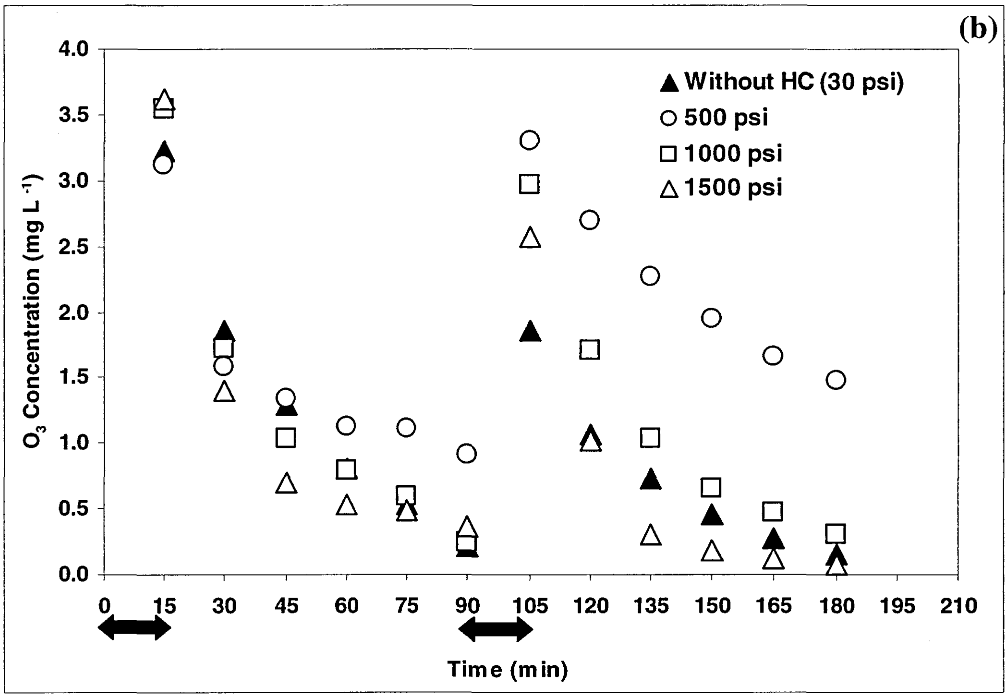


Figure 7.7: Ozone decomposition studies in the LWR. (a) Single ozonation: with HC (1500 psi) and without HC (30 psi) and (b) double ozonation: with HC, 500 psi (15 ± 5 °C); 1000 psi (25 ± 5 °C) and 1500 psi (35 ± 5 °C) and without HC (30 psi). Experimental conditions: reaction liquid (dH_2O, 4 L); O_2–O_3 gas flowrate, 5 L min^{-1} (3–3.5 mg O_3 L^{-1}), ozonator setting, dial 4, 15 min; reaction time, 180 min. Double-ended arrow denotes a period of ozonation.

Initial ozonation for 15 min (O_2–O_3 mixture) resulted in concentrations of 3–3.5 mg O_3 L^{-1} in the reaction medium but this had completely disappeared with or without high levels of cavitation at the end of 180 min due to the high temperature (35 ± 5 °C) (Fig. 7.7a). Not surprisingly, the rate of decomposition at this temperature was greater at the higher pressure. Similarly, O_3 decomposition studies in the case of combined HC and double ozonation were compared for different experimental conditions and set-ups (Fig. 7.7b). In this case, the initial O_3 concentration was 3–3.5 mg O_3 L^{-1} which reduced to 0.2–1.00 mg O_3 L^{-1} depending on operating pressure and temperature. After the second O_3 purge (between 90 and 105 min), the concentration increased to between 1.8 and 3.5 mg O_3 L^{-1} depending on the residual O_3 concentration at different pressures and temperature of the reaction solution. At 500 psi in the case of double ozonation, the residual concentration of O_3 at 90 min was the highest and therefore greater % disinfection was achieved at this pressure as discussed previously. Due to continuous HC, the temperature of the reaction solution increases and allows mixing of O_3 and its dissociated radical species into the bulk solution. Thus, the residual concentration of O_3 is found to be highest at 500 psi, corresponding to the minimum intensity of cavitation and is lowest in case of 1500 psi which correlates to the maximum intensity of cavitation at this operating pressure. Likewise the two pressures (500 and 1500 psi) and the related intensities of ozonation and cavitation lead to highest degree of disinfection (73%).

7.5 Summary

The results from the above study are summarised in Table 7.2 where the percentage disinfection is represented by (R) and log reduction is (R_{Log}).

	Heterotrophic plate count			
	Feed concentration	Product water concentration	Removal	Log removal
	T_0 (C_f)[a] CFU mL^{-1}	T_{180} (C_p)[a] CFU mL^{-1}	$R = 1-(C_p/C_f)$	$R_{\mathrm{Log}} = -\log(1-R)$
Hydrodynamic cavitation (HC) system				
500 psi	2.36E + 08	2.06E + 08	0.125884	0.058431
1000 psi	2.76E + 08	6.10E + 07	0.779252	0.656103
1500 psi	2.45E + 08	8.20E + 06	0.966576	1.475943
Single (O_3) and combined (O_3 + HC) system				
O_3 (Dial 2, 5 min)	2.34E + 08	6.73E + 06	0.971184	1.540367
O_3 (Dial 2, 15 min)	2.59E + 08	2.05E + 06	0.992082	2.101399
O_3 (Dial 4, 15 min)				
Single O_3	2.67E + 08	1.95E + 04	0.999927	4.136477
Double O_3	2.48E + 08	2.50E + 02	0.999999	5.996512
Single O_3 + 500 psi	2.89E + 08	9.10E + 05	0.996846	2.501104
Single O_3 + 1000 psi	1.94E + 08	3.85E + 05	0.99801	2.70122
Single O_3 + 1500 psi	3.82E + 09	1.01E + 05	0.999974	4.577742
Double O_3 + 500 psi	2.71E + 08	2.00E + 02	0.999999	6.131939
Double O_3 + 1000 psi	2.67E + 08	3.65E + 03	0.999986	4.864218
Double O_3 + 1500 psi	2.98E + 08	3.55E + 02	0.999999	5.923259

[a]The relative standard deviation for all measurements is within ±5%.

Table 7.2: Summary chart of different single and combined systems and their corresponding bacterial removal (R) and log reductions (R_{Log}).

From Table 7.2, it can be clearly seen that HC (at the chosen temperature and pressure set-ups) coupled with double ozonation lead to 99.999% bacterial removal corresponding to 5–6 log reduction which is considered to be acceptable and effective technology in any industrial scale process. However, operating at lower working temperatures could be challenging on an industrial scale, in which case effective disinfection could be achieved at higher temperatures and pressures in the LWR. These conditions are therefore recommended for disinfecting wastewaters with low organic loads and other organic contaminants. Optimisation of a feasible O_3 dose is a key in developing a low cost and energy-efficient technology. Therefore, the present work is a useful guideline for design and operation of large scale cavitation-based wastewater treatment units coupled with different AOPs.

Key Conclusions and Suggestions for Future Work

This thesis describes the effective use of combined techniques of various advanced oxidation processes with cavitational reactors for phenolic wastewater treatment and water disinfection. The following are the key conclusions drawn from the above study:

- **Dosimetry:** Less toxic chloroalkanes are effective alternatives for enhanced generation of hydroxyl radicals in cavitational reactors. Enhanced production of hydroxyl radicals was seen at higher operational pressures in the Liquid Whistle Reactor and at higher operating amplitudes in the ultrasonic reactor.
- **Degradation I**: The 300 kHz ultrasonic transducer-type reactor and zero valent iron catalysts showed 100% phenol removal and 37% TOC mineralisation in just 25 min. Whereas 37–40% TOC mineralisation was observed with both the 20 (probe type) and 520 kHz (transducer type) but only in the presence of zero valent iron catalysts and overhead stirring. The modified Advanced Fenton Process, studied with ozonation did not seem to effectively enhance phenol removal rates when compared to hydrogen peroxide.
- **Degradation II**: The Latent Remediation approach significantly enhanced phenol degradation rates in the presence of zero valent iron and a variety of types of zero valent copper catalysts. Optimum concentrations of zero valent copper catalysts lead to ~80% TOC mineralisation. Toxicity analysis on 24, 48 and 72 h samples with zero valent iron and copper reactions revealed that the latter is more toxic and iron is favoured as the catalysts of choice.
- **Degradation III**: Activated carbon cloth (ACC) showed the best results for high phenol removal; at high temperatures via the reactivation of adsorption active sites on the cloth surface, in an ultrasonic bath via adsorption–oxidation–regeneration and step-wise ozonation via adsorption–oxidation.
- **Disinfection**: Higher operating pressures in conjunction with step-wise ozonation resulted in 99.9999% disinfection efficiency of the LWR.

Hence, based on the overall findings of the work presented in this thesis, the following suggestions for future works are proposed:

1. Investigations of oxidation products of phenol from the activated carbon cloth are essential to confirm removal of organics via adsorption or oxidation or both phenomena.
2. Iron impregnated activated carbon cloths are proposed for a study of Fenton-like reactions.
3. Installation of the optimised activated carbon cloth catalyst bed in conjunction with advanced oxidation processes should be carried out on a pilot scale.
4. Latent Remediation process should be investigated with optimised ozonation strategies in conjunction with the Advanced Fenton Process.
5. Use of zero valent copper catalysts should be further optimised for industrial scale operations with toxicity considerations being taken into account.
6. The combination of hydrogen peroxide + ozonation in conjunction with the Advanced Fenton Process for industrial wastewater should be studied.
7. The AFP and related reactions should be investigated on a larger scale with real industrial wastewater.
8. The combination of acoustic and hydrodynamic cavitation should be assessed for enhanced generation of hydroxyl radicals and simultaneous wastewater treatment for industrial scale operations.

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Appendix A

Cost and energy estimation of the Dosimetry, Degradation and Disinfection processes in the cavitational reactors.

	Actual power (W)	Supplied power (W)	Time of treatment (h)	Operational power (kWh)	Operational cost (GBP) (1 kWh = GBP 0.10)	Volume of reactants (L)	£/L	Experimental results	Estimated cost (cost per unit product yield) £/μM HO• generation or £/g TOC reduction
		Actual × (amplitude)		(Supplied power/1000) × Time of treatment	kWh × 0.10 = GBP		£/L		
Ultrasonic reactors (acoustic cavitation)									
Dosimetry								μM HO• generation	£/μM HO• generation
20 kHz US reactor (amplitudes) [Dichloromethane, 7 g L^{-1}]									
25%	400	100	1.17	0.117	0.012	0.200	0.058	54.43	0.001
50%	400	200	1.17	0.233	0.023	0.200	0.117	111.5	0.001
75%	400	300	1.17	0.350	0.035	0.200	0.175	171.01	0.001
Degradation								g L^{-1} TOC removed	£/g TOC removed
US reactors (kHz)									
20 (50% amplitude)	180	90	1	0.09	0.009	0.080	0.113	0.0719	1.565
300	25	25	1	0.03	0.003	0.100	0.025	0.0709	0.353
520 kHz	100	100	1	0.10	0.010	0.300	0.033	0.0658	0.507
Latent Remediation (24 h)									
US (20 kHz; 50%)	400	200	0.25	0.050	0.005	0.200	0.025	0.175	0.143
Stir	100	100	0.25	0.025	0.003	0.200	0.013	0.138	0.091

	Time of treatment (h)	Operational power (kWh)[a]	Operational cost (GBP) (1 kWh = GBP 0.10)	Volume of reactants (L)	Cost per unit volume (GBP/L)	Experimental results	Estimated cost (cost per unit product yield)
		(Combined operational power) × Time of treatment	kWh × 0.10 = GBP		GBP/L		
Liquid Whistle Reactor (Hydrodynamic cavitation)							
Disinfection						Log_{10} Reduction	£/Log_{10} Reduction
Hydrodynamic cavitation only	3	10.80	1.08	4	0.270	1.475	0.183
Hydrodynamic cavitation + [Single ozonation[b] (15 min)]	3	10.82	1.08	4	0.271	4.577	0.059
Hydrodynamic cavitation + [Double ozonation (15+15=30 min)]	3	10.84	1.08	4	0.271	5.923	0.046

[a] Combined operational power (kWh): LWR = 3.6 kW or 10.8 kWh (1500 psi) + ozonator.

[b] Ozonator gererator power = 85 W (.021 kWh for single ozonation (15 min) and .043 kWh for double oxonation (15 + 15 min)).

Appendix B

Chakinala, A.G., Gogate, P.R., Chand, R., Bremner, D.H., Molina, R. and Burgess, A.E. 2008. Intensification of oxidation capacity using chloroalkanes as additives in hydrodynamic and acoustic cavitation reactors. ***Ultrasonics Sonochemistry*****. 15(3): pp.164-170.**

Appendix C

Chand, R., Bremner, D.H., Namkung, K.C., Collier, P.J. and Gogate, P.R. 2007. Water disinfection using the novel approach of ozone and a liquid whistle reactor. ***Biochemical Engineering Journal.*** **35(3): pp.357-364.**