

Literature Review Report for Smart Water Project
**“Improving Recycled Water Aesthetic Quality by Removing Colour and
Trace Organics”**

**OXIDATION PROCESSES FOR DEGRADATION OF
ORGANIC POLLUTANTS IN WATER**

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1. Introduction

New developments in a variety of fields to meet the ever-increasing requirements of human beings have resulted in the presence of new compounds in the effluent streams entering treatment plants, which potentially have negative consequences for the environment and human health. In recent years, the focus on waste minimisation and water conservation has also led to the production of concentrated or toxic residues. It is important to dispose of these residues in a proper manner and to keep the concentration of chemicals in the effluent stream to a certain minimum level in order to comply with the environmental laws. Degradation of organic pollutants which could have a deleterious effect on the well being of mankind, therefore, has become a key focus of research efforts in today's scientific world. Organic pollutants emitted from various sources pose ecological risks because the degradation of these pollutants using conventional chemical and biological treatments is often very slow or ineffective and not environmentally compatible [1, 2]. For this reason, new or more efficient wastewater treatment technologies, such as wet air oxidation, catalytic wet air oxidation, sub-critical, critical and super-critical water oxidation, cavitation, photocatalytic oxidation, Fenton chemistry and chemical oxidation technologies, are being studied as an alternative to biological and classical physico-chemical processes to degrade the complex refractory molecules into simpler molecules [1, 3].

Wet air oxidation, catalytic wet air oxidation, sub-critical, critical and super-critical water oxidation, have been applied to variety of model pollutants as well as actual wastewaters. These technologies are viable for highly concentrated effluents (COD concentration > 40000 mg/L) but are very expensive to run (operated under high temperature and/or high pressure) [3]. Cavitation, photocatalytic oxidation, Fenton chemistry and chemical oxidation, however, can be operated under ambient conditions and have the potential to partially or fully degrade the new toxic chemicals, bio-refractory compounds, pesticides. Under operating conditions (ambient conditions), cavitation (generated either by means

of ultrasonic irradiation or using constrictions such as valves, orifice, venturi, etc. in the hydraulic devices) [4, 5], photocatalytic oxidation (using ultraviolet radiation/near UV light/sun light in the presence of semiconductor catalysts such as TiO_2) [6, 7], and Fenton chemistry (using reaction between Fe ions and hydrogen peroxide, i.e. Fenton's reagent) [8] can generate hydroxyl radicals ($\text{OH}\cdot$) in sufficient quantities to be able to oxidize the majority of the complex chemicals in the effluent water. Hydroxyl radicals ($\text{OH}\cdot$) are powerful oxidizing reagents with an oxidation potential of 2.33 V and exhibit faster rates of oxidation compared with that of conventional oxidants such as hydrogen peroxide or KMnO_4 [9]. Hydroxyl radicals ($\text{OH}\cdot$) can react with most organics and many inorganic solutes with high rate constants [10-12]. Chemical oxidation processes constitute the use of oxidizing agents (ozone and hydrogen peroxide), but exhibit lower degradation rates compared with those based on the free radicals [9, 13]. Moreover, the overall efficacy of the process is generally hampered by the additional mass transfer resistances between the pollutant and the oxidizing agents [3]. When ozone is used in combination with hydrogen peroxide or action of ozone or hydrogen peroxide is supplemented by other energy dissipating components (UV/sun light or ultrasound), free radicals are generated and thus reduce the treatment times [9, 14].

Among the oxidation technologies, photocatalytic oxidation using semiconductor particulate system, which act as photocatalysts, appears to be a more appealing method than conventional chemical oxidation processes for degradation of toxic compounds to non-hazardous product [15-17]. This is because of the fact that semiconductors such as TiO_2 are:

- Inexpensive,
- Non-toxic,
- Have high surface area,
- Have broad absorption spectra with high absorption coefficients,
- Exhibit tunable properties which can be modified by size reduction, doping, sensitizers,
- Afford facility for multielectron transfer process,

- Capable of extended use without substantial loss of photocatalytic activity.

This review outlines the main oxidation technologies that have been used or have the potential for application in wastewater treatment.

2. Wet air oxidation

Wet air oxidation (WAO) is a technology used to treat the waste streams which are too dilute to incinerate and too concentrated for biological treatment. The Wet Air Oxidation process was originally developed by F. J. Zimmermann and its first industrial applications appeared in the late 1950s [18]. It can be defined as the oxidation of organic and inorganic substances in an aqueous solution or suspension by means of oxygen or air at elevated temperatures and pressures either in the presence or absence of catalysts. According to this method, the dissolved or suspended organic matter is oxidised in the liquid phase by some gaseous source of oxygen, that may be either pure oxygen, or air. Typical conditions for wet air oxidation are 150 °C to 320 °C for temperature, 2 MPa to 15 MPa for pressure and 15 to 120 min for residence time; the preferred Chemical Oxidation Demand (COD) concentration ranges from 10000 to 80000 mg/L [19, 20]. WAO destroys toxics in industrial wastewater by breaking down complex molecular structures into simpler components such as water and carbon dioxide, without emissions of NO_x, SO₂, HCl, dioxins, furans and fly ash [18]. It is reported that the WAO process is capable of a high degree of conversion of toxic organics with 99+ % destruction rate, however, some materials are not oxidized completely to carbon dioxide and water. Instead, some intermediate compounds are formed which represent a quarter of the original mass of organic matter. For example, small carboxylic acids: acetic acid and propionic acids, methanol, ethanol and acetaldehyde [18]. Removal of acetic is usually negligible at temperature lower than 300 °C. On the other hand, organic nitrogen compounds are easily transformed into ammonia, which is also very stable in WAO process. Therefore, WAO is usually used as a pretreatment step for liquid wastes, which

then requires additional treatment processes e. g. biological treatment is usually utilised for final clean-up [21].

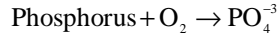
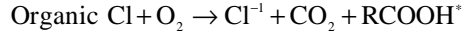
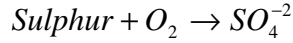
More than 200 WAO treatment plants have been built world wide. There are two principal categories of application of the technology. One category is to treat raw sewage, consisting of a low concentration of sewage in water. Only a modest amount of oxidation occurs in WAO process for raw sewage sludge as the conditions are mild eg. 15 % reduction in COD. However, oxidized sewage sludge has greatly improved settling and drainage properties and is sterile and biologically stable. The second category is to treat waste streams from petrochemical, chemical and pharmaceutical industries. Toxic materials that can be contained in industrial wastes are not suitable for direct biological treatment. The WAO process has been demonstrated to successfully treat hazardous industrial wastes such as spent non-halogenated solvents and oil refinery still bottoms, sludge from electroplating operations and spent cyanide bath solutions [21, 22].

2.1 Process description

The WAO process generally involves a number of oxidation and hydrolysis reactions in series that degrade the initial compound into a series of compounds of simpler structure. Complete WAO results in conversion of hazardous organic compounds into carbon dioxide, water vapour and ammonia (for nitrogen containing wastes), sulphate (for sulphur containing wastes) and halogen acids (for halogenated wastes). Partial degradation products may remain in treated wastewaters from WAO and may be given subsequent treatment before being disposed.

The process can convert organic contaminants to CO₂, water and biodegradable short chain organic acids. Inorganic constituents such as sulphides and cyanides can also be oxidised. WAO can involve any of the following reactions:





* short chain organic acids such as acetic acid make up the major fraction of residual organic compounds

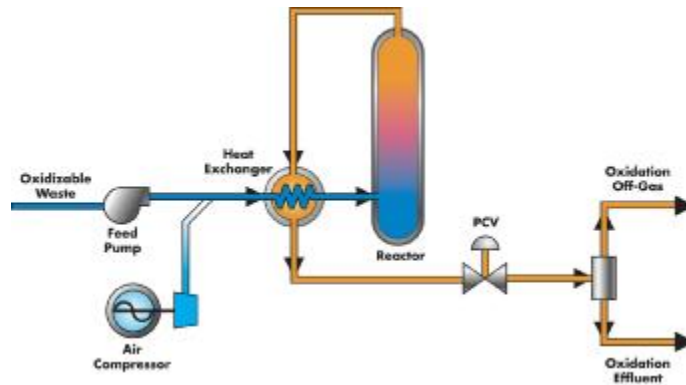


Figure 1. Diagram of WAO plant [18].

Figure 1 shows a basic flow diagram of a WAO plant, which consists mainly of an air compressor, a high pressure pump, a heat exchanger as well as a reactor with a relief valve and a downstream separator [18]. The simplest reactor design is usually a concurrent vertical bubble column with a height-to-diameter ratio in the range of 5-20. An industrial WAO unit is typically run continuously. The raw waste in terms of liquid is pumped to the lower part of the reactor eg. a bubble column reactor through a series of pre-heaters. The waste is retained in the reactor for sufficient period of time to achieve the desired chemical oxidation (15 to 120 min). Air or oxygen is compressed and is allowed to bubble at the low part of the reactor. The oxygen flow rate is less than 110 % of the inlet COD flow rate. Cryogenic oxygen may be used and pumped before vapourisation to save shaft work during compression. After starting up, the reactor is

normally adiabatic and the temperature can be controlled by changing the total pressure. The heat is absorbed when water vapourises into gas stream and released when organic contaminants oxidize in the liquid phase. The energy content of the liquid and gas outlet streams is normally sufficient to ensure the preheating of feed. In some cases additional heat is supplied, such as when WAO is applied to very dilute feed (low COD feed) where the heat release is too small to achieve the desired temperature. With higher concentration feeds (high COD feed) excess heat is generated which must be removed by cooling or generating high pressure steam. Typically, the process can run with no additional energy if the oxygen up-take is greater than 15 g/L.

The typical COD removal efficiency for WAO seldom exceeds 95 % and consequently the waste streams can not be discharged directly into the environment. Most of the WAO units are operated in connection with biological facilities where a post-treatment is carried out before final release. For example, in Grenzach, Germany and Stignaes, Denmark, the gas stream coming out of the WAO units contains a limited amount of volatile organic compounds and carbon monoxide (0.5-2.5 %) together with CO₂, oxygen in excess and water. A simple post-combustion unit ensures the final oxidation of these gases before final release.

Table 1 Wet air oxidation of organic compounds in industrial wastewaters, influent and effluent concentrations (mg/L) and removal efficiencies.

Compound	Influent	Effluent	% Removal
COD	56,000	7,200	87.1
Methylene chloride	734	0.08	>99.9
Xylene	109	0.11	99.9
MEK	3,937	2.3	99.9
Benzene	8.0	0.03	99.6
Carbon tetrachloride	2,450	2	99.9

* wet air oxidation temperature = 257 °C, pressure > 4.8 MPa, residence time = 83 minutes.

Wastewaters including pesticide wastes, petrochemical process wastes, cyanide containing metal finishing wastes, spent caustic wastewaters containing phenolic compounds and some organic chemical production wastewaters can be treated using WAO. WAO is most applicable for waste streams containing dissolved or suspended organics in the 500 to 15,000 mg/L range. Below 500 mg/L, the reaction rates of WAO for most organic constituents are too slow for efficient application of this technology. Wastes containing significant concentrations of metals (approximately 2 %) can be treated by WAO whereas biological treatment, carbon adsorption, and chemical oxidation may have difficulty treating such wastes. Typical results of wet air oxidation of organic compounds in industrial wastewaters are presented in Table 1 (from US Filter/Zimpro).

2.2 Issues and considerations

There are many issues which need to be considered in designing and using WAO [18]:

- The temperature at which WAO is carried out has been found to be the most important parameter in the operation of a WAO plant.
- The total pressure is critical to the WAO process as it has a function to maintain the liquid phase which is essential to the oxidation reaction. If pure oxygen is used instead of air, which is used in most of industrial installations, safety (eg explosions) is a significant issue.
- Sometimes, it is necessary to calculate the mass transfer coefficient of oxygen in the liquid phase to determine which mechanism (mass transfer or kinetic) controls the reaction, although in most of reactors the oxygen mass transfer resistance both in gas phase or liquid phase is negligible.
- The design of the reactor itself is the core in designing of a WAO plant. It can affect greatly the oxidation efficiency. The reactor must be designed for carrying out gas-liquid reactions and operating in the kinetic control mode.

- Wastewater with low pH may cause corrosion damage to the metals used in the WAO equipment. Therefore, careful material selection is required, with resultant cost implications. Wastewater pH adjustment can improve materials compatibility.
- A variety of chemical compounds can be treated at the same time in the one step process by WAO. Waste must be in the liquid phase as the treatment occurs in the liquid phase. As a result, the problems associated with air pollution are reduced. The process is less energy intensive than incineration and is less likely to produce oxides of nitrogen as by-product air pollutants. Wastes are limited to wastewaters containing oxidisable organic and inorganic compounds. For example, WAO cannot destroy PCBs, some halogenated aromatics and some pesticides.
- Capital costs for wet air oxidation systems depend on the capacity of the system, oxygen demand reduction of the wastewater, severity of the oxidation conditions required to meet the treatment objectives, and the construction materials.

3. Catalytic wet air oxidation

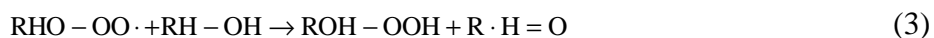
3.1 Process description

Catalytic Wet Air Oxidation (CWAO) process is a further development of the wet air oxidation (WAO) process where a stable and active catalyst is used. Organic and some inorganic contaminants are oxidised in the liquid phase by contacting the liquid with high pressure air at temperatures which are typically between 120 °C and 310 °C. In the CWAO process the liquid phase and high pressure air are passed co-currently over a stationary bed catalyst. Other steps in the treatment are similar to the wet air oxidation (WAO) process shown in Figure 1. The operating pressure is maintained well above the saturation pressure of water at the reaction temperatures (usually about 15-60 bar) so that the reaction takes place in the liquid phase. This enables the CWAO processes to proceed at lower temperatures than those required for the WAO processes. Residence times are from 30 minutes to 90 minutes, and the chemical oxygen demand removal may typically

be about 75 % to 99 %. The effect of the catalyst is to provide a higher degree of COD removal than that obtained by WAO at comparable conditions (over 99 % removal can be achieved), or to reduce the residence time.

The CWAO process is capable of converting all organic contaminants ultimately to carbon dioxide and water, and can also remove oxidizable inorganic components such as cyanides and ammonia. The process uses air as the oxidant, which is mixed with the effluent and passed over a catalyst at elevated temperatures and pressures. If complete COD removal is not required, the air rate, temperature and pressure can be reduced, therefore reducing the operating cost. CWAO is particularly cost-effective for effluents that are highly concentrated (COD of 10,000 to over 100,000 mg/L) or which contain components that are not readily biodegradable or are toxic to biological treatment systems. Compared to biological treatment processes, CWAO process plants also offer the advantages that they can be highly automated for unattended operation, have relatively small plant footprints, and are able to deal with variable effluent flow rates and compositions. The process is not cost-effective compared with other advanced oxidation processes or biological processes for lightly contaminated effluents (COD less than about 5,000 mg/L).

The pathways and mechanism of CWAO reactions depend on the compound oxidised. A simple but accepted mechanism for the CWAO of phenol has been proposed by the following reactions [18]:



In this mechanism $RH-OH$ corresponds to phenol, $R \cdot H = O$ corresponds to the phenoxy radical and $RHO - OO \cdot$ corresponds to the peroxy radical.

3.2 Application and limitation

The heterogeneous CWAO has had very few industrial applications. The NS-LC process uses a vertical monolith reactor with a Pt-Pd/TiO₂-ZrO₂ catalyst. The operating conditions are 220 °C and 4 MPa. The Osaka gas process uses a mixture of precious and base metals on Titania or zirconia-titania supports. Typical operating conditions are 250 °C and 6.86 MPa. The Kurita process uses nitrite instead of oxygen, and a similar catalyst (supported Pt), becoming more effective at lower temperatures, around 170 °C.

Table 2 Process data of CWAO using noble catalysts

Noble Metal	Support	Substrate	T (°C)	P MPa
Pt	$\gamma - Al_2O_3$	acetic acid	>200	
Ru, Ir, Pd, Ag, base metals	CeO ₂ , TiO ₂ , ZrO ₂	acetic acid	200	2
Pt	$\gamma - Al_2O_3$	maleic acid	>120	>0.4
Ru	CeO ₂	maleic acid	>160	2
Ru	TiO ₂	succinic acid	>150	5
Pt	C	carboxylic acids	>20	>0.1
Pt	C	carboxylic acids	200	0.69
Pt	$\gamma - Al_2O_3$, resin	carboxylic acids	80	0.1
Ir	C	butiric acid	200	0.69
Pt, Ru, Rh	TiO ₂ , CeO ₂ , C	phenol/acrylic acid	170	2
Pt	$\gamma - Al_2O_3$	phenol	> 155	2
Pt, Ag,	MnO ₂ /CeO ₂	phenol	>80	0.5
Pt-Ru	C	phenol	>35	
Ru	C, CeO ₂ /C	phenol	160	2
Pt	C	p-chlorophenol	170	2.6
Pt, Ru, Pd, Rh	CeO ₂	ammonia	>150	2
Pd	C	ammonia	280	2
Pt	SDB resin	ammonia	>110	<0.28
Pt, Ru, Pd, Ir	TiO ₂ , CeO ₂ , C	ammonia	>150	1.5
Pt-Ru	C	trichloroethene	>90	>0.2
Ru	TiO ₂ , ZrO ₂	Kraft effluent	190	5.5
Ru	TiO ₂	Kraft effluent	190	8
Pd, Pd - Pt	$\gamma - Al_2O_3$, ALON TM	Kraft Effluent	>80	1.84
Pd - Pt - Ce	$\gamma - Al_2O_3$	Kraft effluent	>130	> 1.5

The heterogeneous catalysts that have been employed in CWAO can be divided in two main groups, i.e. supported noble metals (Table 2) and metal oxides (as well as mixtures of them) (Table 3). Activated carbon, without any deposited active phase, has also exhibited catalytic activity. Noble metals have been very effective in the treatment of

different pollutants such as phenols, carboxylic acids, including refractory acetic acid and ammonia effluents. Pd, Pt and Ru have received most attention although Ir or Rh has also been tested. The performance of supported noble metal catalysts is also significantly influenced by the support used. Metal oxides, like alumina, ceria, titania and zirconia, as well as activated carbon or high specific area graphite have been mainly studied. Pure or mixed metal oxides, such as copper oxide, alone or combined with other oxides, have also received special attention in the CWAQ of aqueous effluents. Phenol was successfully oxidised by a commercial Harshaw Cu0803 T1/8 catalyst, comprising 10 % copper oxide supported over alumina. A commercial CuO/ZnO catalyst was used to oxidise formic acid.

Table 3 Process data of CWAQ using metal oxide catalysts

Oxide	Support	Substrate	T (°C)	P MPa
<i>Cu/Cr</i> oxides		phenol	>127	0.32
<i>Cu/Cr/Ba/Al</i> oxides		phenol	127	0.8
<i>Co, Fe, Mn, Zn</i> oxides with <i>Cu</i> oxides	$\gamma - Al_2O_3$	phenol	140	0.9
<i>CuO</i>	$\gamma - Al_2O_3$	phenol	>120	>0.6
<i>CuO</i>	$\gamma - Al_2O_3$	phenol	140	0.9
<i>Cu/Ni/Al</i> oxides		phenol	140	0.9
<i>CuO/ZnO/CoO</i>	cement	phenol	>130	7
<i>CuO/ZnO/CoO</i>	cement	phenol	>150	(*)
<i>CuO/ZnO</i>	$\gamma - Al_2O_3$	phenol	>105	>0.15
<i>CuO</i>	$\gamma - Al_2O_3$	phenol	>113	>0.44
<i>CuO/CeO₂</i>		phenol	130	0.73
<i>K - MnO₂/CeO₂</i>		phenol	110	0.5
<i>MnO₂/CeO₂</i>		phenol	>80	>0.2
<i>CuO</i>	<i>C</i>	phenol	>160	>2.6
<i>CuO</i>	$\gamma - Al_2O_3$	phenol	>95	>0.1
<i>MnO₂, Co₂O₃</i>		phenol	>170	>1.3
<i>Ni - oxide</i>		phenol	>15	-
<i>Cu/Zn/Cr/Ba/Al</i> oxides		phenol	>110	>0.1
<i>MnO₂, Co₂O₃</i>		p-chlorophenol	>170	>1.3
<i>CuO/ZnO/CoO</i>	cement	p-chlorophenol	>150	(*)
<i>CuO/ZnO</i>	$\gamma - Al_2O_3$	p-nitrophenol	>105	>0.15
<i>CuO/ZnO</i>		p-nitrophenol		
<i>CuO/ZnO</i>		formic acid	>200	4
<i>Fe₂O₃</i>		acetic acid	>252	>6.7
<i>Cu/Mn/La</i>	<i>ZnO - Al₂O₃</i>	acetic acid	>250	(*)
<i>Ce/Zr/Cu</i> oxides or <i>Ce/Zr/Mn</i> <i>MnO/CeO</i>		acetic acid	>245	>5
		acetic acid	247	1
		n-butylamine	220	
		PEG	220	
		pyridine	270	
		ammonia	263	
<i>MnO₂/CeO₂</i>		alcohol distillery waste	>180	>0.5

*These tests were performed in a liquid full reactor saturated with oxygen.

To date, the main drawback of CWAO that is preventing it from broad industrial applications, is the problem of the catalyst deactivation. This occurs mainly due to active phase leaching or formation of carbonaceous deposits, during the oxidation process. The most prominent catalysts prone to leaching of the active phase are mixed oxides catalysts. The recent development of stable catalysts is expected to increase interest in the process. Among the most promising catalysts, activated carbon offers a less expensive alternative with a proven activity in the abatement of several phenol like compounds. Such

pollutants are of special interest, because they are increasingly encountered in effluents that cannot be treated in conventional biological treatment plants.

The pathways leading to the complete mineralisation of the treated pollutants during WAO or CWAO processes are complex and far from being well understood. For phenol, it has been shown that it is firstly oxidised towards toxic ring compounds, which consequently yield low molecular weight carboxylic acids. Due to the toxicity of the aromatic compounds formed in the first step of phenol degradation, it is important to monitor their production and destruction for the catalysts used.

4. Supercritical water oxidation

4.1 Process description

It has been discovered that if the usual operational temperature and pressure for wet air oxidation were raised above the critical condition of water (supercritical condition), the oxidation potential of the process, and consequently the removal efficiency, would increase greatly. Fluids with temperatures and pressures that are above their critical values are called supercritical fluids. The critical point of a fluid is defined as the highest temperature and pressure at which it can exist in liquid/vapour equilibrium. A phase is considered a liquid if it can be vapourised by reducing the pressure at constant temperature. A gas can generally be condensed to produce a liquid by reducing the temperature at constant pressure. Supercritical fluids do not fit these definitions [23], and generally consist of one phase which occupies the entire volume of a vessel [24]. Any fluid below the critical point is generally referred to as a subcritical fluid. To produce a liquid from a supercritical fluid above its critical temperature and pressure, firstly the temperature must be reduced below the critical temperature and then pressure applied isothermally.

The properties of supercritical fluids are generally between those of liquid and gases in terms of viscosity, density and diffusion coefficients. Water, on the other hand, shows dramatic changes in physical and chemical properties when in the supercritical state. The critical point of water is 374 °C and 22.4 MPa [25]. Water at condition above these is supercritical water. As a medium for chemical reaction, supercritical water (SCW) has been found very useful for oxidation of organics. Above the critical point of water, water is an excellent solvent for both organic compounds and gases (eg. Oxygen, nitrogen, carbon dioxide) [26]. Dissolving waste in air or oxygen in SCW leads to a homogeneous phase where oxidation is rapid. For example, at 400 to 450 °C, 99 to 99.9 % conversion (to carbon dioxide, carbon monoxide) can be achieved within 5 minutes. If the operating temperatures are increased to 600-650 °C, 99.999 % can be obtained in less than a minute [27].

One physiochemical property that changes as the critical temperature and pressure are approached is the dielectric constant (permittivity relative to vacuum). This property dictates to a large degree the ability of water to act as an organic solvent. At room temperature the dielectric constant of water is approximately 80. Figure 2 shows the dielectric constant of water along the saturation line (at temperature, T, with just enough pressure to maintain liquid state). As the temperature is increased the dielectric constant is reduced to 30.79 at 500 K and 10 MPa, and then 10.34 at 750 K and 100 MPa [28]. Under supercritical conditions the dielectric constant can be reduced to values below 2, thus making organics orders of magnitude more soluble. For example, the solubility of benzo[*a*]pyrene in water at 25 °C is 0.004 µg/mL and at 250 °C increases to 1100 µg/mL [29].

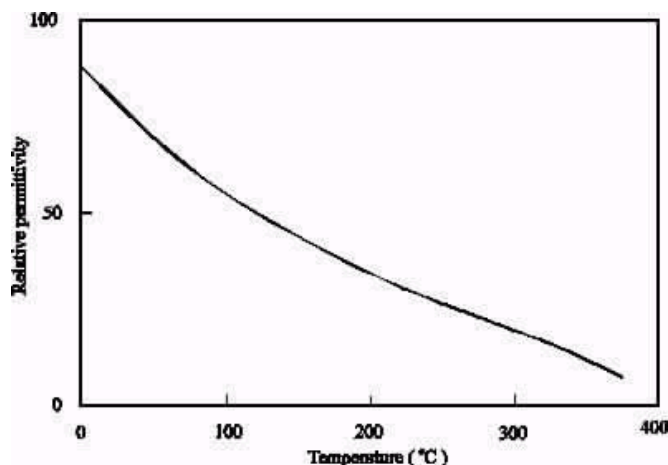


Figure 2. Dielectric constant of water with increasing temperature [30].

4.2 Removal of organic compounds with supercritical water

The key parameter in extraction processes is the solvent-solute interaction. This is partly related to the dielectric constant and the polarity. A high dielectric constant favours the solubility and extraction of high polarity compounds. Conversely, a low dielectric constant favours the solubility of low polarity compounds. This section of the report explores the effect of using supercritical water over subcritical water and hence the subsequent decrease in the dielectric constant to achieve extraction.

Removal of various organic compounds from sand and soil using sub- and supercritical water has been well documented by the research of Hartonen, et al. [31] and Hawthorne and Yang [32]. Sand spiked with various organic pollutants such as alkanes, phenols, amines and PAHs was extracted by Hawthorne and Yang to determine the extraction efficiency when the conditions are altered from subcritical to supercritical. For the spiked sand mixture, all the spiked elements, except the alkanes were extracted under subcritical condition. However, it has been demonstrated that unlike CO₂, which is very effective at extracting alkanes, water is less effective, and for this reason supercritical conditions are required to achieve extraction. Similar trends were observed for the same

organic compounds in soil, which demonstrates that the effect of substrate interaction is not a crucial component of extraction.

The extraction of dioxins such as polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and various PCBs was studied by Hashimoto [33] as part of a soil remediation study. As previously, over 99 % extraction was achieved under subcritical conditions at temperature of 350 °C. An important factor to mention in this study was the use of a 240 min extraction time whereas the previous study used much shorter times of 15 min to achieve satisfactory extraction.

Larger scale operations have been reported by Lagadec, et al. [29], with pilot scale sized equipment used in the remediation of soils. However, the scaled-up process lacks the response of a laboratory system and heating and extraction times were lengthened, due to the size of the extraction vessel. The extraction time can be reduced by increasing the flow rate of water through the system but not necessarily the amount of water used in the extraction. For example extraction required 300 mL/min for 120 min for the extraction of PCBs in 8 kg of soil and is equal to 600 mL/min for 60 min, both achieving complete extraction. Therefore extraction appears to be driven by the volume of water used rather than the flow rate.

4.3 Reaction rate, mechanisms and kinetics

Oxidation of organic compounds is generally higher when supercritical conditions are used rather than subcritical [34]. The higher temperatures favour reaction conditions and physiochemical parameters such as activation energy and the reactions proceed with higher yields of destruction. Weber, et al. [34], found that the destruction efficiency of PCBs was increased from below 20 % at 350 °C, subcritical conditions, to 99.99 % at 450 °C, supercritical conditions.

Kinetics and rates of reactions under subcritical and supercritical water conditions are not fully understood. Many researchers aim at producing and optimising a process that has the highest destruction of organic compounds rather than working with fundamental reaction concepts under strictly controlled conditions. All the research described to this point has taken this approach. It is certainly of great benefit to understand reaction mechanism and kinetics, however in many cases these are specific to reactor configuration (batch vs. flow), operating conditions and the organic compound involved. Some research has been conducted on the reaction mechanism of basic compounds such as carbon dioxide, methanol, methane, hydrogen and ammonia [35] and the destruction pathways of more complex organic compounds such as phenol [36] under supercritical conditions.

Reaction mechanisms are complex even for the simple molecules listed above. There exist a number of possible pathways of oxidation with intermediate formation, side reaction and the possibility of more than one reaction pathway to arrive at the products. Global models have been proposed to simplify the overall mechanisms and allow the calculation of reaction constants and model parameters for process design purposes. Tester, et al. [35] found that the destruction of larger molecules often occurs quickly with the partial oxidation to smaller molecular weight species. Further oxidation of these smaller species proceeds much slower and it is eventually the oxidation of simple compounds, such as carbon monoxide and ammonia, that are rate limiting.

Portela, et al. [36], experimentally studied the reaction kinetics of phenols in both sub- and supercritical water and compared the results to other proposed models. They found that many models do not accurately fit both sets of condition. The study showed that in the subcritical and supercritical region the rate laws are pseudo-first-order with respect to phenol in subcritical water, and nearly first-order for phenol in the supercritical region. Gloyna and Li also state pseudo-first-order oxidation reaction rates are a reasonable assumption [37] for supercritical water oxidation. Using a number of references they tabulated three categories of organic compounds and identified key intermediates which potentially are rate controlling (Table 4).

Table 4 Rate Controlling intermediates in sub- and supercritical water oxidation

Organic Compound Category	Key Intermediate	Oxidation End Product	Conditions
Hydrocarbons and oxygenated hydrocarbons	CH ₃ COOH	CO ₂ , H ₂ O	Subcritical and Supercritical
Nitrogen containing organics	NH ₃ , N ₂ O	N ₂ , H ₂ O	Supercritical
Chlorinated Organics	CH ₃ Cl, CH ₃ OH	HCl, H ₂ O	Supercritical

4.4 Issues and considerations

Reactor design for supercritical oxidation process involves a continuous flow type reactor with the feed, oxidant and water introduced at the top. For example, WAO and SCW oxidation have been proposed in reactors which are placed underground in deep, well-like cavities. A schematic diagram of a “downhole” reactor is shown in Figure 3. In the reactor, oxygen is injected into the liquid organic waste at sufficient pressure and temperature to support liquid state oxidation. The organic waste is converted into inert ash, carbon dioxide and water. The excess heat generated may be recovered at surface for increasing energy efficiency [38]. Generally, SCW oxidation process design must consider the following requirements:

- System integration - feed lines, preheater, reactor, heatexchangers, catalytic conversion units, separators (solid-fluid and gas-liquid), and pressure let-down device;
- Influent pre-treatment - waste characterization, waste segregation, possible physical/chemical pretreatment, and appropriate feed tank capacity;
- Pressurisation - pumps and piping system for requires unit processes;

- Monitoring - temperature, pressure, flow, process control and appropriate data collector;
- Heat source - initial heat, heat content of waste, and heat transfer devices;
- Materials - constructability, corrosion, erosion, and repairability;
- Effluent handling - post treatment (pH adjustment, by-product recovery, etc.) and ash disposal-collection, use, disposal.

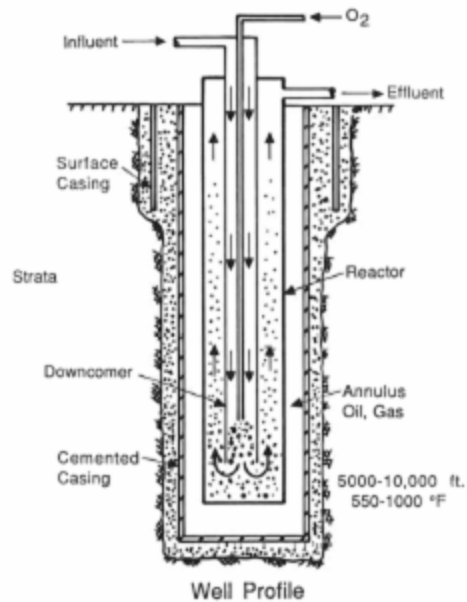


Figure 3. Schematic diagram of “downhole” oxidation reactor.

The main disadvantages of SCW oxidation process are:

- Heavy metal speciation and formation of insoluble salts. The reduced solubility of salts can lead to process operating problems as these salts precipitate in the supercritical phase. The formation of “sticky” salts becomes a problem when particles impinge on surfaces and cause blockages in pipes and sensors as well as changing the heat transfer characteristics of the reaction vessel [39].

- Corrosion. Supercritical water is very corrosive and the corrosion reaction products can interfere with sensors and also influence the composition of the effluent as demonstrated in the chromium study by Gloyna and Li [37].

5. Cavitation

Cavitation is defined as the phenomena of the formation, growth and subsequent collapse of microbubbles or cavities occurring in extremely small interval of time (milliseconds), releasing large magnitudes of energy [40, 41]. Cavitation events occur at multiple locations in the reactor simultaneously and hence the overall effects are spectacular. The important effects of cavitation include the generation of hot spots, release of highly reactive free radicals, continuous cleaning as well as increase in the surface area of the solid catalysts, and enhancement in the mass transfer rates due to turbulence generated as a result of acoustic streaming etc. [4, 41, 42]. Cavitation can be classified into four types based on the mode of generation: acoustic, hydrodynamic, optic and particle. Optic and particle cavitation are typically used for single bubble cavitation, which fails to induce chemical change in the bulk solution. However, acoustic and hydrodynamic cavitation has been found to be efficient in bringing about the desired chemical changes [3]. The destruction/oxidation of pollutants using cavitation is usually described by two approaches viz. free radical attack [43] and pyrolysis [44]. The controlling mechanism for the destruction usually depends on the pollutant in question as well as the degree of cavitation intensity, which in turn depends on the operating conditions of the sonochemical reactor. The mechanisms of oxidation of different pollutants using cavitation have been illustrated in the literature [4, 14, 45, 46].

5.1 Acoustic cavitation

In the case of acoustic cavitation, cavitation is effected using the high frequency sound waves, usually ultrasound, with frequencies in the range of 16 kHz–100 MHz. Alternate

compression and rarefaction cycles of the sound waves results in various phases of cavitation such as generation of the bubble/cavity, growth phase and finally collapse phase releasing large amount of energy locally [40, 41]. Equipment commonly used for acoustic cavitation is shown in Figure 4. Typically, the equipment with higher dissipation area provides larger energy efficiency at similar levels of the supplied input energy. It has also been reported that using equipment with multiple frequencies/multiple transducers is more beneficial compared with the use of a single frequency [47, 48]. Another new development with promising future for medium to large-scale applications is ultrasonic horns vibrating in radial directions, which also gives additional advantage of better energy dissipation due to larger irradiating area [49, 50], but more work is required in terms of testing this equipment for operation at high frequency and high power dissipation.

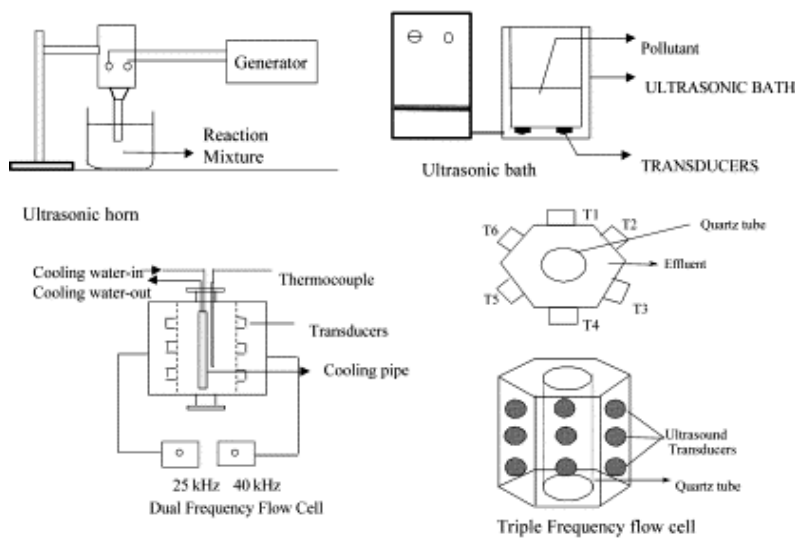


Figure 4. Schematic representation of the equipment used in acoustic cavitations [3].

Sonochemical reactors have been successfully used for the degradation of variety of compounds at different scales of operation [51-58]. However, the majority of the work is on a laboratory scale. Before successful application of sonochemical reactors are feasible at an industrial scale, a large quantum of work needs to be done both in terms of the

design strategies for the scale-up and feasibility of the operation of transducers at higher levels of power dissipation. Future work should also be directed in terms of understanding the detailed role of the following water parameters in determining the efficiency of cavitation process in the treatment of effluents with a complex mixture of compounds:

- Role of inorganic components and gases.
- Influence of water components on the pH during the sonication process.
- Influence of precipitates and particles.
- Consequences of Cl^- ions.

5.2 Hydrodynamic cavitation

Hydrodynamic cavitation, as an alternative technique, is the use of hydraulic devices to generate cavitation by the passage of the liquid through a constriction such as valve, orifice plate, venturi etc. [59]. Some of the equipment used for the generation of hydrodynamic cavitation are shown in Figure 5. The cavitation intensities generated in the hydrodynamic cavitation reactors are lower as compared to the acoustic counterparts. The design of the reactors, in terms of the operating and geometric conditions, must be customised to the particular application. There are not many reports depicting the use of this equipment for wastewater treatment [60-62], but these offer higher energy efficiencies, more flexibility and higher potential for scale-up as compared to their acoustic counterparts [63].

Although hydrodynamic cavitation offers immense potential due to higher energy efficiency and cavitation yields compared with their acoustic counterpart, large scale use of these reactors is limited. There is only one commercial process (CAV-OX®, 1994) developed by Magnum Water Technology Inc., California, which uses hydrodynamic cavitation in combination with UV irradiation and oxidation with hydrogen peroxide. Several contaminants of concern such as pentachlorophenol (PCP), benzene, toluene,

ethyl benzene, xylenes, cyanide, phenol and atrazine have been successfully degraded to a significant extent. Case studies at pilot plant scale showed that the process is effective for a wide variety of effluents obtained from various chemical industries. The process also needs to be tested for complex mixture of effluents or real industrial wastewaters.

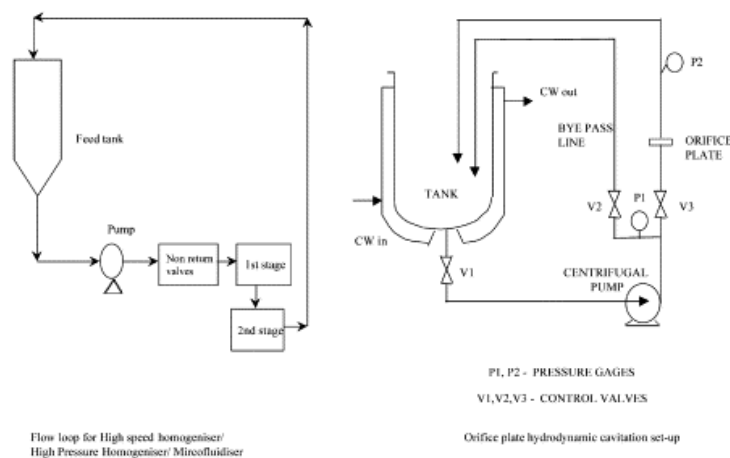


Figure 5. Schematic representation of the equipment used for hydrodynamic cavitations [3].

Overall, cavitation offers a potential alternative for the degradation of chemicals in wastewater treatment where the majority of the conventional techniques ineffective. However, the majority of the studies undertaken in this area are on a small scale and hence much more work needs to be done before the technology can be implemented.

6. Photocatalytic oxidation

Photocatalytic oxidation (PCO) processes are gaining importance in the area of wastewater treatment, since these processes result in complete mineralization with operation at mild conditions of temperature and pressure. There is a significant body of research covering this subject and depicting basics of the processes including the mechanism of oxidation of pollutants in detail [6, 7, 16, 17]. Photocatalytic oxidation is a

process where a semiconductor upon adsorption of photons acts as a catalyst in producing reactive radicals. These are mainly hydroxyl radicals, which can oxidise organic compounds and mineralise them [64, 65]. In the process organic molecules are decomposed to form carbon dioxide, water and mineral acids as terminal products. A major advantage of the photocatalytic oxidation based processes is the possibility to effectively use sunlight or near UV light for irradiation, which should result in considerable economic savings especially for large-scale operations.

6.1 Mechanism and kinetics of PCO process

The use of TiO_2 in water detoxification was first demonstrated by Carey et al. in 1976. They used aqueous suspensions of TiO_2 to dechlorinate polychlorinated biphenyl [66]. A large volume of research work has now been conducted, covering many types of contaminant treatment, such as ground water, drinking water, herbicide, residential wastewater and industrial wastewater, even pollution in soil and air [65-75].

When a semiconductor like TiO_2 is irradiated with light having energy greater than the band gap, an electron is excited from the valence band to the conduction band, creating a hole and an electron (Fig. 6). The hole is an oxidising agent, and the electron is a reducing agent. In the generally accepted mechanisms for the photocatalytic process, the hole can react with water to produce the hydroxyl radical (OH^\bullet) and the electron can reduce molecular oxygen, hydrogen peroxide or some other oxidising agent in the solution. The reactive hydroxyl radicals act as powerful oxidising agents responsible for removal of the hazardous components from the water [66, 76].

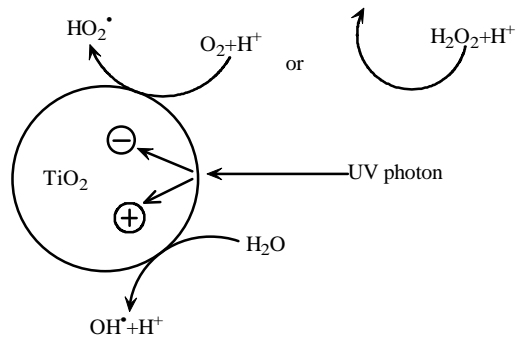
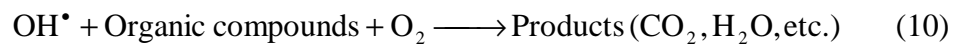


Figure 6. Illustration of the oxidation and reduction reactions in a semiconductor exposed to UV light.

The following equations describe the oxidation and reduction reactions



Oxidation of organic compounds



The rate of photocatalytic degradation depends on several factors including illumination intensity, photocatalyst type, oxygen concentration, pH value, presence of inorganic ions and the concentration of organic reactant and has been modeled by different kinetic models. Langmuir-Hinshelwood (L-H) kinetics seems to describe many of reactions fairly well. The L-H expression can be reduced to a pseudo-first-order expression Eq (11) for low solute concentrations C.

$$-\frac{dC}{dt} = K_1 K_2 C = kC \quad (11)$$

where C: the bulk solution concentration, K_1 : the reaction rate, K_2 : the equilibrium adsorption constant and t represents time. Once the reaction constants K_1 and K_2 have been evaluated, the disappearance of reactant can be estimated if all other factors are held constant.

This equation has been applied to many photocatalytic reactions. As industrial pollutant levels are typically on the order of ppm, the pseudo first-order kinetics well describes the process very well. The disappearance of pollutant in a photocatalytic oxidation process can be estimated by Eq (12) if all other factors are held constant. For the design of a system, the apparent reaction rate constant k can be determined for experimental data.

$$C = C_0 e^{-kt} \quad (12)$$

Figure 7 shows a simplified schematic of a flat-plate reactor (FPR) system. The contaminated liquid from the tank feeds to FPR with the initial concentration of pollutants C_{fi} and is irradiated in FPR and degraded to final concentration C_{fo} when it flows out from the reactor. The liquid out of FPR with the concentration C_{ti} enters the tank and mixes with the liquid of concentration C_t (C_t is the average concentration of pollutants in the tank) in the tank to form a liquid with a concentration C_{to} (tank outlet concentration), which goes to the FPR again. It is reasonable to assume that the degradation only occurs in the FPR under the UV and does not happen in the tank and

connecting tubes. Hence, considering $C_{fo}=C_{ti}$, C_{to} can be calculated using the following equation [18].

$$C_{to} = \frac{V_R C_{fo} + (V - V_R) C_t}{V_R + (V - V_R)} \quad (13)$$

The dye degradation (in the FPR) obeys a pseudo-order kinetic law, as previously reported in the literature for most of the investigated organic substrates. The liquid concentration at the outlet of the reactor is then calculated using the following equation.

$$C_{fo} = C_{fi} e^{-kt_1} \quad (14)$$

So, Eq (13) becomes

$$C_{to} = \frac{V_R C_{fi} e^{-kt_1} + (V - V_R) C_t}{V_R + (V - V_R)} \quad (15)$$

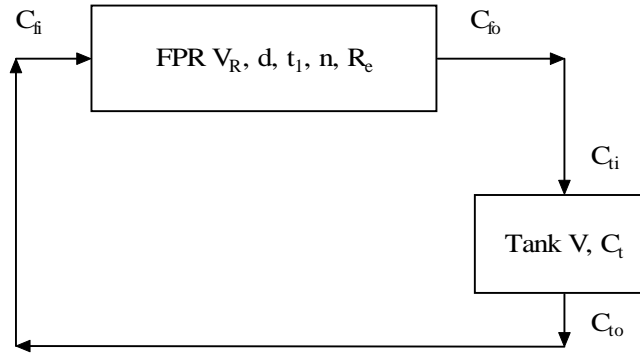


Figure 7. Model sketch diagram of the FPR system.

Equation (14) actually gives the after-treatment concentration of pollutant in the liquid/solution as a function of irradiated time t_1 in the FPR. The smaller C_{to} , the better the treatment results and the better the photocatalytic performance (in the reactor). It can be

seen that the larger the liquid volume V_R (thicker liquid film thickness), the longer the irradiated time t_1 and the bigger apparent reaction rate constant k will result in quicker degradation of pollutants, which means the better performance of FPR. However, the apparent reaction rate constant k depends not only on flow status (Re) but also on the intensity of UV light, dosage and form of photocatalysts applied.

6.2 Photocatalytic reactors and optimum operating parameters

Two types of photocatalyst, powders (slurry) and fixed photocatalyst are typically used in PCO processes. In the case of powders (slurry), the photocatalytic process is carried out by simply using slurry of the fine particles of the solid semiconductor dispersed in the liquid phase in a reactor irradiated with UV light either directly or indirectly. The proper dispersion of the catalyst in the liquid phase can be achieved using either mechanical or magnetic stirrers. Aeration, usually maintained for scavenging the electrons to prevent electron/hole charge recombination, also helps in achieving dispersion of the catalyst. The extent of dispersion can also be increased by sonication of the slurry at low frequency (e.g. 20 kHz) using an ultrasonic bath for approximately 10–15 min [77]. However, the performance of the slurry reactor might be severely affected by the low irradiation efficiency due to the opacity of the slurry. Also, after the oxidation treatment, the solid catalyst needs to be separated from the liquid, which is not so easy with the small size of the catalyst particles (usually below 1 μm). For example, TiO_2 powder is the most commonly used photocatalyst as it is active and cheap, insoluble under most conditions, photo-stable and non-toxic. However, the TiO_2 particles have to be separated from the treated wastewater after photocatalytic degradation. The photocatalytic activity of TiO_2 powder depends on the size of TiO_2 particle. Generally, the finer the particles are the higher photocatalytic activity. This makes it very difficult to be separated from the treated wastewater. For example, P25 TiO_2 powder are very fine with an average primary particle size of about 21nm [78]. Thus, for the development of the photocatalytic technology, the solid-liquid separation has become an extremely important issue.

An alternative to the use of catalyst in the suspended form is the use of supported photocatalyst, which offers many advantages. The key advantages are the ability to source an active crystalline structure and the stability of the catalyst layer in the reacting media. This does not allow mixing with the fluid, thereby avoiding the requirement of ultrafine particle separation. The methods of fixing TiO₂ photocatalyst on substrates such as glass, metal plate, concrete or ceramics were developed by many researchers in recent years. Methods of coating substrates included the Sol-Gel process [79-81], dip coating method [15, 82], electrodeposit method [83], ultrasonic atomisation-pyrogeneration methods [84] and other methods [85-88]. These applications were successful in degrading organisms and pollutants in wastewater [89]. However, due to a limitation of mass transfer and a loss of photocatalytic activity by the fixation, slurry-reactor systems excel over fixed support photocatalytic systems with respect to degradation efficiency [90].

The photocatalytic reactor is an important component in a photocatalytic oxidation system. The structure will determine the received solar intensity and affect the photocatalytic reaction. A number of different types of photocatalytic reactors have been developed and used in research or pilot plant studies. Examples of these reactors include the annular photoreactor [16, 65, 91, 92], the packed bed photoreactor [93], the photocatalytic Taylor vortex reactor [94], the TiO₂ fluidised-bed reactor [95], the TiO₂-coated fibre optic cable reactor [96-101], the falling film reactor [102], the thin-film-fixed-bed slope plate reactor [103, 104], and the swirl-flow reactor [105], concentrate reactors [67, 99, 106-108], batch reactors [109, 110], flat plate reactors [104, 111-114], tube reactors or spinning tube reactors [65] [66, 115]) and bell reactors [116-121]. It should be noted that any configuration can be selected, but the most important point is to achieve uniform irradiation of the whole active surface. Figure 8 represents some of equipment used for PCO processes [3].

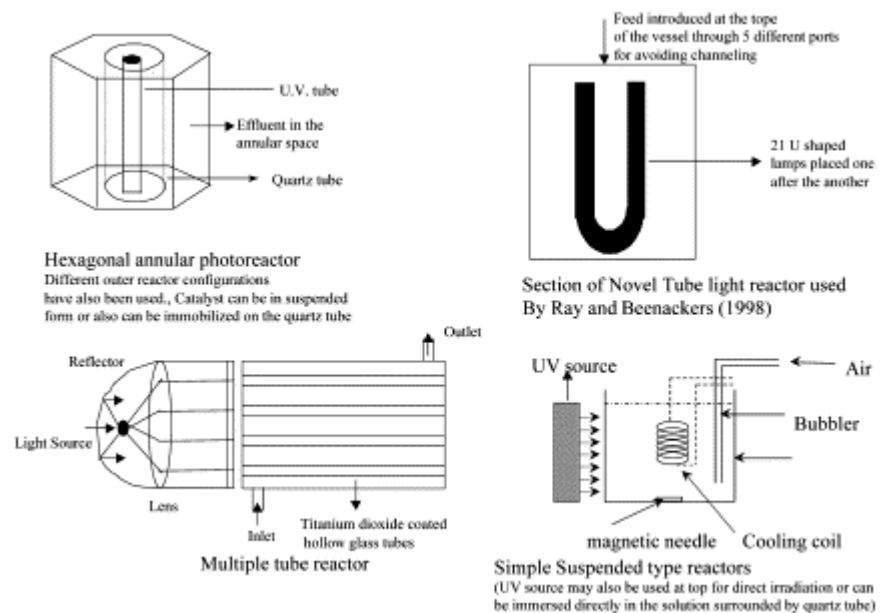


Figure 8. Schematic representation of equipment used in photocatalytic oxidation [3].

Based on the detailed and critical analysis of the existing literature on the photocatalytic oxidation of the contaminants, the important operating parameters, which affect the overall destruction efficiency of the photocatalytic oxidation process, are as follows [3]:

- Amount and type of the catalyst
- Reactor design
- Wavelength of the irradiation
- Initial concentration of the reactant
- Temperature
- Radiant flux
- Medium pH
- Aeration
- Effect of ionic species.

6.3 TiO₂ photocatalyst in PCO processes

Various chalcogenides (oxides such as TiO₂, ZnO, ZrO₂, CeO₂ etc. or sulfides such as CdS, ZnS etc.) have been used as photo-catalysts to date in a range of different studies. Table 5 lists the aqueous organic pollutants that can be mineralized by photocatalysis [3]. It should be noted that the best photocatalytic performances with maximum quantum yields have been always with titania [3]. Degussa P-25 catalyst has been reported to be the most active form (hybrid mixture of rutile (approx. 70%) and anatase forms) among the various ones available and generally gives better degradation efficiencies [122, 123]. Pure anatase based forms of TiO₂ such as Hombikat, PC-500 has also been found to be more efficient in some cases [124, 125]. The photocatalytic activity of titanium dioxide can be enhanced by using pretreatment with sulfuric acid [126], or by increasing the cation strength, e.g. doping with Pt, V, etc..

Table 5 List of some aqueous organic pollutants mineralized by photocatalysis [3]

Class of organics	Examples
Haloalkanes/haloalkenes	Chloroform, trichloroethylene, perchloroethylene, tribromomethane, dichloromethane, CCl ₄
Aliphatic alcohols	Methanol, ethanol, 1-octanol, 2-propanol
Aliphatic carboxylic acids	Formic, glycolic, citric
Amines	Alkylamines, alkanolamines
Aromatics	Toluene
Halophenols	2-,4-chlorophenol
Aromatic carboxylic acids	Malic, chlorobenzoic acids
Surfactants	Sodium dodecasulfate
Pesticides/fungicides	Fenitrothion, metalaxyl
Dyes	Methylene blue, rhodamine B, Reactive Black 5
Sulfides	Trimethylene sulphide, propylene sulfide

It is worthwhile to summarize the various advantages offered by photocatalytic oxidation:

- Operation at conditions of room temperature and pressure.
- Use of natural resources, i.e. sunlight, which should result in considerable economic savings as discussed earlier.
- Chemical stability of TiO_2 in aqueous media and over a larger range of pH ($0 \leq \text{pH} \leq 14$).
- Low cost of titania.
- System applicable at low concentrations and no additives required.
- Great deposition capacity for noble metal recovery.
- Total mineralization achieved for many organic pollutants.
- Efficiency of photocatalysis with halogenated compounds sometimes very toxic for bacteria in biological water treatment.

However, there are some drawbacks, which hamper successful application of photocatalytic oxidation on an industrial scale for wastewater treatment:

- Engineering design and operation strategies are lacking for efficient use of reactors at large-scale operation.
- Compared to conventional chemical reaction rates, reaction rate of photocatalytic processes is usually slow and there is a need to provide large amounts of active catalyst in the reactor.
- As discussed earlier, for reactors with catalyst in the suspended form, ultrafine separation is an inconvenient, time consuming and expensive process and in addition, the depth of penetration is lower due to the blockage of the incident light by catalyst particles (shadow effect) as well as absorption by the dissolved organic species.
- Very few illustrations of application to real industrial effluents with higher destruction efficiency of photocatalytic oxidation alone can be cited. Moreover,

due to the presence of radical scavengers in real effluents, the rates will be substantially lower as compared to that observed in the model effluent studies.

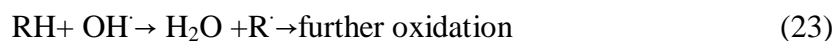
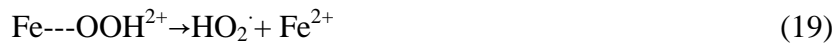
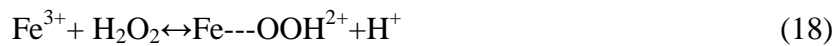
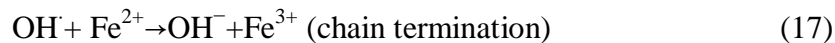
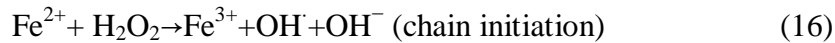
- Fouling of the photocatalyst with continuous use results in lowering the rates of degradation as time progresses.

7. Fenton chemistry

7.1 Process description

Fenton's reagent was discovered about 100 years ago, but its application as an oxidising process for destroying toxic organics was not applied until the late 1960s [127]. The oxidation system based on Fenton reaction has been used for the treatment of both organic and inorganic substances under laboratory conditions as well as real effluents from different resources like chemical manufacturers, refinery and fuel terminals, engine and metal cleaning etc. [128]. The process is based on the formation of reactive oxidizing species, able to efficiently degrade the pollutants of the wastewater stream but the nature of these species is still under discussion and its formulation is a subject of controversy in the past and recent Fenton oxidation related literature [129, 130].

Fenton's reagent is a mixture of H_2O_2 and ferrous iron. The ferrous iron (Fe^{2+}) initiates and catalyses decomposition of H_2O_2 , resulting in the generation of hydroxyl radicals. The newly formed ferric ions may catalyse hydrogen peroxide, causing it to be decomposed into water and oxygen. Ferrous ions and hydroxyl radicals are also formed in the reactions. Hydroxyl radicals can oxidise organics (RH) by abstraction of protons producing organic radicals (R.), which are highly reactive and can be further oxidised. If the concentrations of reactants are not limiting, the organics can be completely detoxified by full conversion to CO_2 , water and in the case of substituted organics, inorganic salts if the treatment is continued. The reactions are as follows [8]:



Fenton's reagent has been effectively used for the remediation of diesel-contaminated soils [131], removal of colour in effluents from dye industries [132], destruction of organics such as 2,4,6-trinitrotoluene [133], RDX [134], 2,4-dinitrophenol [135], Chlorobenzene [136], tetrachloroethylene [137], chlorophenols [138], halomethanes [139]. The main advantage of the process is the complete destruction of contaminants to harmless compounds, e.g. CO₂, water and inorganic salts. The system can be applied to discoloration and/or removal of odour compounds with good energy efficiency. Also, the oxidation system can be effectively used for the destruction of toxic wastes and non-biodegradable effluents to render them more suitable for biological treatment.

7.2 Typical reactor and optimum operating conditions for Fenton oxidation

A schematic representation of the Fenton oxidation treatment is shown in Figure 9 [3]. A batch Fenton reactor essentially consists of a non-pressurized stirred reactor with metering pumps for the addition of acid, base, a ferrous sulfate catalyst solution and industrial strength (35–50%) hydrogen peroxide. It is recommended that the reactor vessel be coated with an acid-resistant material, because the Fenton reagent is very aggressive and corrosion can be a serious problem. Addition of reactants needs to be

done in the following sequence: wastewater followed by dilute sulfuric acid (for maintaining acidic conditions) catalyst in acidic solutions, base or acid for the adjustment of pH at a constant value and lastly hydrogen peroxide (must be added slowly with proper maintenance of temperature). The Fenton reactor must to be designed with flexibility in terms of the operating parameters as the wastewater compositions could be highly variable. The discharge from the Fenton reactor is fed into a neutralizing tank for adjusting the pH of the stream followed by a flocculation tank and a solid–liquid separation tank for adjusting the TDS (total dissolved solids) content of the effluent stream [3].

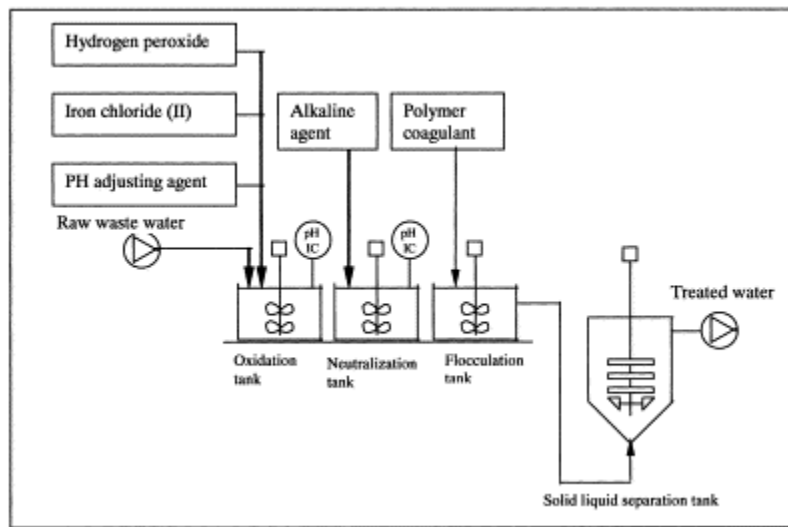


Figure 9. Treatment flowsheet for Fenton oxidation [3].

Based on a review of the literature on application of Fenton oxidation to wastewater treatment, the following optimum conditions can be outlined [3]:

- pH: pH of the system has been found to significantly affect the degradation of pollutants. In the majority of cases, the optimum pH has been observed to be pH 3 which is recommended as the operating pH. The operating pH can be adjusted

using buffer solutions. However, it should be noted that the type of the buffer solution may also affect the degradation process.

- Amount of Ferrous ions: higher concentrations of Ferrous ions usually produces higher rates of degradation. However, excessive concentrations of the Ferrous ions leads to an increase in the unutilized quantity of iron salts, which will contribute to the negative outcome of an increase in the TDS content of the effluent stream. Thus, laboratory scale studies are required to establish the optimum loading of Ferrous ions under similar conditions.
- Concentration of hydrogen peroxide: concentration of hydrogen peroxide is a critical factor that affects the overall efficacy of the degradation process. It has been observed that the percentage degradation of the pollutant usually increases with an increase in the dosage of hydrogen peroxide. However, the residual hydrogen peroxide contributes to COD and also acts as a scavenger for the generated hydroxyl radicals. Thus, the loading of hydrogen peroxide should be adjusted in such a way that the entire amount is utilized and this can be determined based on laboratory scale studies.
- Initial concentration of the pollutant: usually lower initial concentration of the pollutants is favored.
- Operating temperature: not many studies are available depicting the effect of temperature on the degradation rates and ambient conditions can safely be used with good efficiency.
- Chemical coagulation: chemical coagulation step is recommended after the Fenton oxidation so as to keep the concentration of the soluble iron within the specified limits.

8. Chemical oxidation using oxidants

Ozonation and addition of hydrogen peroxide belong to separate class of oxidation process compared to the methods described above, termed as chemical oxidation process.

8.1 Ozonation

Ozone, as a very powerful oxidizing agent ($E^\circ = +2.07 \text{ V}$), can react with most species containing multiple bonds such as C=C, C=N, and N=N. Ozone can be used for treatment of effluents from various industries relating to pulp and paper production (bleaching and secondary effluents), shale oil processing, production and usage of pesticides, dye manufacture, textile dyeing, production of antioxidants for rubber, pharmaceutical production etc. Some specific examples of ozone use for treatment of wastewaters are as follows:

- Textile effluent treatment in terms of colour removal [140] and reduction of TOC and COD to certain limits beyond which biological oxidation can be used [141, 142].
- Degradation of effluent from dye industry [143].
- Conversion of cyanide ions into less toxic cyanate ions [142].
- Degradation of protocatechuic acid and chlorinated phenols [144, 145].
- Colour removal in the effluent from a molasses processing plant [146].
- Removal of pesticides [147].
- Treatment of wine-distillery [148].

The main drawbacks associated with the ozonation process are:

- Relatively high cost of ozone generation process. Ozone needs to be generated at site due to very short half-life of ozone.
- The process efficiency is strongly dependent on the efficient gas liquid mass transfer, which is quite difficult to achieve due to the low solubility of ozone in aqueous solution.

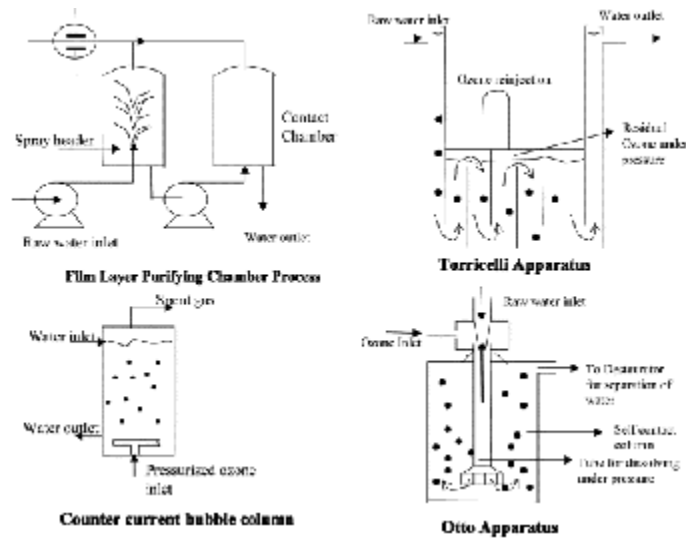


Figure 10. Schematic representation of equipment used for ozone treatment [3].

A number of devices, such as countercurrent bubble column, packed and plate columns, static mixers, jet reactors and agitated vessels, can be used to transfer the generated ozone into water. Figure 10 depicts some of the commonly used equipment for transferring ozone to water [3]. Static mixers offer bright potential for effectively dissolving ozone in water and can be used at larger scale, but more studies are required due to the lack static mixer used in wastewater treatment applications.

Based on the detailed review of the literature, some important operating parameters need to be considered for the ozonation process [3]:

- pH of the system: usually higher values of pH are recommended.
- Ozone partial pressure: increase in the ozone partial pressure increases the extent of degradation. However, increase in the ozone partial pressure is usually associated with a substantial increase in the cost of generation of ozone.
- Contact time and interfacial area: Use contactors, which maximize both the contact time and the available interfacial area. The use of static mixers appears to be a good alternative at this stage.

- Operating temperature: increasing temperature can increase the rate constant of the reaction. However the temperature also decreases the ozone solubility and thus reduces the amount of ozone available for the reaction, which may result in decreased degradation.
- Presence of catalyst: catalyst such as BST catalyst TiO_2 fixed on alumina beads, Fe (II), and Mn (II) can be used to increase the degradation efficiency.

8.2 Use of hydrogen peroxide

Hydrogen peroxide is another strong oxidant that has been found to be effective in degradation of compounds or in the treatment of wastewaters requiring less stringent oxidation conditions [149]. However, applications for treatment of complex mixtures of effluents such as dyes, textile industry effluent, heteroaromatics etc. need to be further explored. Some researchers have used hydrogen peroxide in industrial effluent treatment for detoxification of cyanide, nitrite and hypochlorite, for the destruction of phenol aromatics, formaldehyde, removal of sulphite, thiosulfate and sulphide compounds [150, 151]. However, there are no reports where hydrogen peroxide has been used for the treatment of a mixture of compounds. The major problems encountered with the application of hydrogen peroxide alone for wastewater treatment applications are:

- Very low uptake of the technology for applications involving complex materials.
- Stability of H_2O_2 remains a question, as the catalytic decomposition agents present in effluents compete with the pollutants.
- The mass transfer limitations are always present making proper contact of the hydrogen peroxide, usually present as aqueous phase with the organic liquids a rate-limiting step in the degradation process.

With so many major problems as stated above, use of hydrogen peroxide alone does not seem to be a recommended option and hence the discussion here was restricted to just basics about hydrogen peroxide usage in effluent treatment schemes.

9. Colour reduction by oxidation processes

Dyes and pigments are important industrial chemicals and play an important role in the textile industry. The number of dyes presently used in textile industry is about 10,000. Among these dyes, azo dyes constitute the largest and the most important class of commercial dyes. The release of these dyes into the environment causes severe ecological problems [152]. Wastewater from textile and dye industries are highly polluted by suspended solids (SS), high chemical oxygen demand values (COD), high biochemical oxygen demand values (BOD), heat, acidity, basicity and other soluble substances. Most of pollutants, except color, can be reduced by chemical, physical or biological methods. Therefore, the color problem of some textile wastewater caused by the residual dyes during the dyeing process needs more effort to be studied and investigated.

Conventional treatment methods in the textile dyeing industry for color removal include coagulation/flocculation, and activated carbon adsorption. Both coagulation and adsorption generate large amounts of sludge and waste which need further treatment for disposal. Biotreatment is still considered as an appropriate method for meeting discharge standard but it still remains a color problem. Also, ozonation effectively decolorizes dyes but does not remove COD well and may produce exhausted ozone in the water and thereby, increase the cost of treatment. Therefore, it is necessary to develop destructive systems leading to complete mineralization of these dyes.

Recent developments of oxidation processes have led to new improvement of the oxidative and catalytic degradation of organic compounds dissolved in aqueous media. Homogenous (such as Fenton's reagent and light-assisted Fenton's oxidation) and heterogeneous (semiconductor-mediated photocatalysis) oxidation systems have been evaluated for a variety of organic compounds and wastewater in the past [153]. Heterogeneous photocatalysis has emerged an important destructive technology leading to the total mineralization of most of the organic pollutants including organic reactive

dyes [153-156]. Electrochemically assisted photocatalytic process is also investigated to degrade reactive azo dyes [157, 158]. TiO_2 is the most commonly used effective photocatalyst for a wide range of organic chemical degradation. Some researchers have shown that many dyes may be photocatalytically degraded using TiO_2 as catalyst [13, 84, 153, 159].

Most recently, the degradation of Lanazol blue CE was investigated in our group [18, 159]. Lanazol Blue CE was photocatalytically degraded using a TiO_2 photocatalyst in a Flat-Plate Reactor (FPR) (Fig. 11) in the presence of UV light. The results indicated that the photocatalytic oxidation process with a flat-plate reactor is effective in decoloring dyes. First-order kinetics ($C = C_0 e^{-kt}$) is representative for simplified characterization of this process in engineering applications (Fig. 12). Parameters, such as dosages of photocatalyst, flow rate through the flat-plate reactor and UV intensity, were found to significantly influence the process performance. The higher the UV intensity, the greater the reaction rate constant, the relationship being linear. The flow rate and the tilted angle were found to influence the mean film thickness of the fluid in the reactor, which in turn also affected the degradation rates in the process.

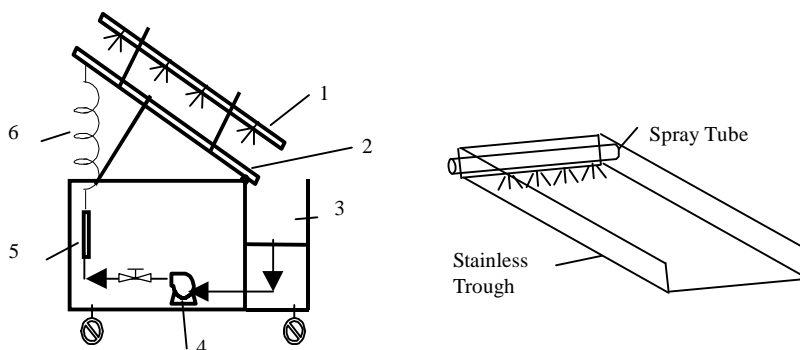


Figure 11. (a) Experimental rig. (b) Flat plate photo-reactor.

- (1. UV Source 2. Flat plate photoreactor 3. Tank 4. Circulating pump 5. Flow meter 6. Soft connection tube)

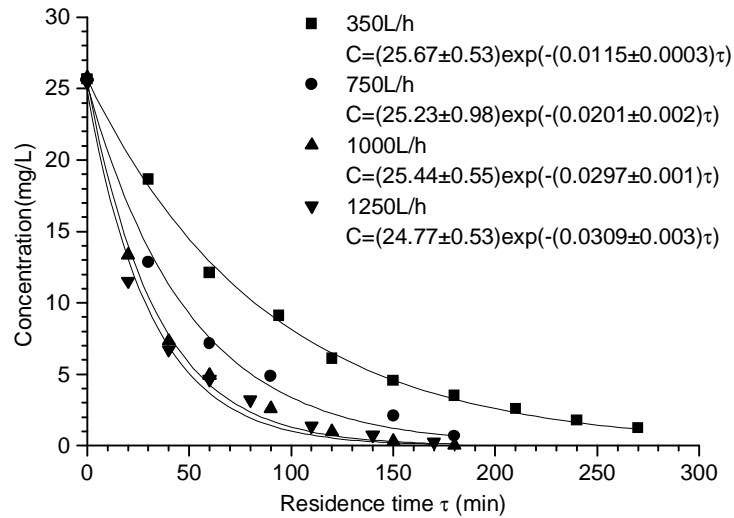


Figure 12. Concentration vs residence time τ for different flow rates at the initial treated solution of 8 litres, $\alpha = 20^\circ$, $\text{TiO}_2 = 1.0 \text{ g/L}$ and mean $\text{UV} = 36.5 \text{ W/m}^2$.

10. Conclusions and recommendations

Wet air oxidation (WAO) has been successfully used for wastewater treatment. COD reduction can readily reach from 90 % to 95 % for most wastes with WAO. The operating temperature of WAO can be reduced by the addition of stable and active catalysts (CWAO). The efficiency of WAO also significantly increases when the usual operating temperature and pressure are raised above the critical condition of water (supercritical water oxidation). The major drawback of these processes is high operating costs due to energy demand.

Cavitation, photocatalytic oxidation and Fenton chemistry can be operated at ambient conditions and work on the principle of generation of free radicals which are used for oxidation of the contaminant molecules. The efficacy of process is significantly affected

by the rate of generation of the free radicals along with the extent of contact of the generated radicals and/or chemical oxidants with the contaminant molecules. Therefore, the efficient design should aim at maximizing both these quantities.

In addition to the generation of the free radicals, cavitation also generates conditions of high temperatures and pressures which drive some of the chemical reactions by pyrolysis mechanism. Acoustic cavitation reactors generate much more intense cavitation compared with hydrodynamic ones, but not much information is available at this stage for efficient large-scale operation. Hydrodynamic cavitation equipment provides greater energy efficiency and cavitation yields as compared to sonochemical reactors. Still efforts are indeed required in transferring this efficient laboratory scale technique into industrial scale applications.

Fenton's chemistry is not a universal solution as there are many chemicals, which are refractory towards Fenton's reagent such as acetic acid, acetone, carbon tetrachloride, methylene chloride, n-paraffins, maleic acid, malonic acid, oxalic acid, trichloroethane etc. Moreover, a certain compound in the waste stream may be oxidized to some of the above compounds, which are still pollutants and may not be allowed to be discharged. Also, as the degree of oxidation produced in the case of Fenton oxidation is limited, i.e. the oxidant dosage cannot be increased beyond certain limits, applicability to treatment of complex mixture of contaminants, i.e. highly loaded effluent streams remain a question. However, the degree of oxidation can be substantially increased when Fenton's chemistry is used in combination with other technologies such as photocatalytic and acoustic cavitation processes [3, 160]. The Fenton reagent, including ferric ions, is precipitated after the oxidation reaction and new ferric ions need to be added to maintain the oxidation reaction.

Photocatalytic oxidation appears to be one step ahead in terms of development as compared to cavitation and Fenton's chemistry, as the photocatalyst will not be consumed by the oxidation process and can be regenerated and reused for a longer time. A large amount of literature is available on the application of photocatalytic oxidation to

wastewater treatment for different model constituent solutions. However, studies with real effluents are lacking in the literature and efforts are required in this direction and in development of kinetic models considering the effects of critical components as described earlier.

Ozonation and use of hydrogen peroxide work on the basis of direct action of the oxidants. Very low reaction rates have been observed for the degradation of complex compounds or mixture of contaminants by ozonation or use of hydrogen peroxide alone. The overall efficiency of the degradation process, however, can be significantly enhanced when ozonation is combined with UV radiation, ultrasound and hydrogen peroxide [44, 142, 146].

Overall, photocatalytic oxidation appears to have a great potential for the removal of organic pollutants from wastewater, especially for those effluent that contain trace recalcitrant organic compounds, such as dyes and other color causing compounds, organo-halogens, organic pesticides, and surfactants. Efforts are indeed required both on experimental front as well as kinetic modelling before application on large-scale is feasible with high degree of efficiency and lower treatment costs. Also, to overcome some of the limitations of the individual techniques and enhance the treatment efficiency, a combination of several methods may result in high treatment efficiency compared with individual treatment.

Note:

A large part of this literature review is based on the book chapter “Wet Air Oxidation for Waste Treatment” in Advanced Physiochemical Treatment Process, Book series: HANDBOOK OF ENVIRONMENTAL ENGINEERING, Volume 5B, co-authored by Linda Zou, Yuncang Li, Lawrence K. Wang, and Yung-Tse Hung, The Humana Press Inc, Totowa, NJ, USA (in press in 2006).

References

1. Esplugas, S., et al., Comparison of different advanced oxidation processes for phenol degradation. *Water Research*, 2002. **36**(4): p. 1034-1042.
2. Chatterjee, D. and S. Dasgupta, Visible light induced photocatalytic degradation of organic pollutants. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews*, 2005. **6**(2-3): p. 186-205.
3. Gogate, P.R. and A.B. Pandit, A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. *Advances in Environmental Research*, 2004. **8**(3-4): p. 501-551.
4. Adewuyi, Y.G., Sonochemistry: Environmental Science and Engineering Applications. *Ind. Eng. Chem. Res.*, 2001. **40**(22): p. 4681-4715.
5. Gogate, P.R., Cavitation: an auxiliary technique in wastewater treatment schemes. *Advances in Environmental Research*, 2002. **6**(3): p. 335-358.
6. Herrmann, J.-M., Heterogeneous photocatalysis: fundamentals and applications to the removal of various types of aqueous pollutants. *Catalysis Today*, 1999. **53**(1): p. 115-129.
7. Bhatkhande, D.S., V.G. Pangarkar, and A.A.C.M. Beenackers, Photocatalytic degradation for environmental applications - a review. *Journal of Chemical Technology & Biotechnology*, 2002. **77**(1): p. 102-116.
8. Neyens, E. and J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique. *Journal of Hazardous Materials*, 2003. **98**(1-3): p. 33-50.
9. Gogate, P.R., S. Mujumdar, and A.B. Pandit, A Sonophotocatalytic Reactor for the Removal of Formic Acid from Wastewater. *Ind. Eng. Chem. Res.*, 2002. **41**(14): p. 3370-3378.
10. Glaze, W.H., et al., Chemical models of advanced oxidation processes. *Water Quality Research Journal of Canada*, 1992. **27**(1): p. 23-42.
11. von Sonntag, C., Degradation of aromatics by advanced oxidation processes in water remediation: some basic considerations. *J. Water Supply Res. Tech.*, 1996. **45**(2): p. 84.

12. Hoigne, J., Inter-calibration of oh radical sources and water quality parameters. *Water Science and Technology*, 1997. **35**(4): p. 1-8.
13. Arslan, I. and I.A. Balcioglu, Degradation of Remazol Black B dye and its simulated dyebath wastewater by advanced oxidation processes in heterogeneous and homogeneous media. *Coloration Technology*, 2001. **117**(1): p. 38-42.
14. Weavers, L.K., N. Malmstadt, and M.R. Hoffmann, Kinetics and Mechanism of Pentachlorophenol Degradation by Sonication, Ozonation, and Sonolytic Ozonation. *Environ. Sci. Technol.*, 2000. **34**(7): p. 1280-1285.
15. Fujishima, A., T.N. Rao, and D.A. Tryk, Titanium dioxide photocatalysis. *J. Photochem. Photobiol. C: Photochem. Rev.*, 2000. **1**(1): p. 1-21.
16. Legrini, O., E. Oliveros, and A.M. Braun, Photochemical processes for water treatment *Chem. Rev.*, 1993. **93**: p. 671-698.
17. Hoffmann, M.R., et al., Environmental Applications of Semiconductor Photocatalysis *Chem. Rev.*, 1995. **95**: p. 69-96.
18. Zou, L.Y. and Y.C. Li, Wet air oxidation for waste treatment, in *Advanced physicochemical treatment processes*, L.K. Wang, Y.T. Hung, and N.K. Shamas, Editors. In press, The Humana Press, Inc.: Totowa, USA.
19. Luck, F., Wet air oxidation: past, present and future. *Catalysis Today*, 1999. **53**: p. 81-91.
20. Debellefontaine, H. and J.N. Foussard, Wet air oxidation for the treatment of industrial wastes. Chemical aspects, reactor design and industrial applications in Europe. *Waste Management*, 2000. **20**: p. 15-25.
21. Walter G. May, B., MSC, SCD, PE., ed. *Wet Air Oxidation. Scientific Advances in Alternative Demilitarization Technology*. 1995. 111-128.
22. Maloney, S.W., et al., *TNT Red Water Treatment by Wet Air Oxidation*. 1994, USACERL Technical Report EP-95/01.
23. Smith, J.M., H.C.V. Ness, and M.M. Abbott, *Introduction to chemical engineering thermodynamics*. 5th ed ed, ed. . 1996: Sydney: McGraw Hill.
24. Atkinson, A. and P.T. Moseley, *Thin Film Electroceramics*, *Applied Surface Science*. *Applied Surface Science*, 1993. **65-66**: p. 212-219.

25. Rogers, K.D., et al., Structural characterisation of sprayed TiO₂ films for extremely thin absorber layer solar cells. *Thin Solid Films*, 2004. **466**(1-2): p. 97-102.
26. Dietrich, M.J. and A.J. Patarcity, wet air oxidation of hazardous organics in wastewater. *Environmental progress*, 1985. **4**(3).
27. Modell, M. Supercritical fluid technology in hazardous waste treatment. in Conference proceedings of oil waste management alternatives symposium. 1988. Oakland, CA, April 28-29, 1988.
28. Xiaohong An, G.M., Mingang Zhang, Yongtao Tian, Shuhui Sun, Lide Zhang, Synthesis and optical absorption property of ordered macroporous titania film doped with Ag nanoparticles. *Materials Letters*, 2006.
29. Lagadec, A.J.M. and et al., Pilot-scale subcritical water remediation of polycyclic aromatic hydrocarbon- and pesticide-contaminated soil. *Environmental science and technology*, 2000. **34**(8): p. 1542-1548.
30. Critical Processes Ltd., Introduction to Superheated Water. 2004: Roecliffe.
31. Hartonen, K. and et al, Pressurised hot water extraction (PHWE) of n-alkanes and polyaromatic hydrocarbons (PAHs): Comparison for PAHs with supercritical fluid extraction. *Journal of Microcolumn.*, 2000. **12**: p. 412-418.
32. Hawthorne, S.B., Y. Yang, and D.J. Miller, Extraction of organic pollutants from environmental solids with sub- and supercritical water. *Analytical Chemistry*, 1994. **66**: p. 2912-2920.
33. Hashimoto, S. and et al., Remediation of soil contaminated with dioxins by subcritical water extraction. *Chemosphere*, 2004. **54**(1): p. 89-96.
34. Wiszniowski, J., et al., Photocatalytic decomposition of humic acids on TiO₂; Part 1: Discussion of adsorption and mechanism. *Photochemistry and Photobiology*, 2002.
35. Tester, J.W. and et al. Supercritical water oxidation technology: Process development and fundamental research. in ACS symposium on emerging technologies for hazardous waste management. 1991. Atlanta, USA.

36. Portela, J.R., E. Nebot, and E.M.d.l. Ossa, Kinetic comparison between subcritical and supercritical water oxidation of phenol. *Chemical Engineering Journal*, 2001. **81**(1-3): p. 287-299.
37. Gloyna, E.F. and L. Li, Supercritical water oxidation: An engineering update. *Waste Management*, 1993. **13**(5-7): p. 379-394.
38. Jackman, A.P. and R.L. Powell, *Hazardous Waste Treatment Technologies: Biological treatment, wet air oxidation, chemical fixation, chemical oxidation*. 1991: Noyes publications, Park Ridge, New Jersey, USA.
39. Barner, H.E., et al., Supercritical water oxidation: An emerging technology. *Journal of Hazardous Materials*, 1992. **31**(1): p. 1-17.
40. Lorimer, J.P. and T.J. Mason, Sonochemistry part 1 – the physical aspects. *Chem. Soc. Rev.*, 1987. **16**: p. 239 - 274.
41. Suslick, K.S., Sonochemistry. *Science*, 1990. **247**(4949, Part 1): p. 1439-1445.
42. Miller, N., Chemical action of sound waves on aqueous solutions. *Trans. Faraday Soc.*, 1950. **45**: p. 546 - 550.
43. Nagata, Y., et al., Sonochemical degradation of chlorophenols in water. *Ultrasonics Sonochemistry*, 2000. **7**(3): p. 115-120.
44. Kang, J.W. and M.R. Hoffmann, Kinetics and mechanism of the sonolytic destruction of methyl tert- butyl ether by ultrasonic irradiation in the presence of ozone. *Environmental Science and Technology*, 1998. **32**(20): p. 3194-3199.
45. Dewulf, J., et al., Ultrasonic degradation of trichloroethylene and chlorobenzene at micromolar concentrations: kinetics and modelling. *Ultrasonics Sonochemistry*, 2001. **8**(2): p. 143-150.
46. Suslick, K.S., S.J. Doktycz, and E.B. Flint, On the origin of sonoluminescence and sonochemistry. *Ultrasonics*, 1990. **28**(5): p. 280-290.
47. Hua, I., R.H. Hochemer, and M.R. Hoffmann, Sonochemical degradation of p-nitrophenol in a parallel-plate near-field acoustical processor. *Environmental Science and Technology*, 1995. **29**(11): p. 2790-2796.
48. Sivakumar, M., P.A. Tatake, and A.B. Pandit, Kinetics of p-nitrophenol degradation: effect of reaction conditions and cavitation parameters for a multiple frequency system. *Chem. Eng. J.*, 2002. **85**: p. 327.

49. Dahlem, O., et al., Direct sonication system suitable for medium scale sonochemical reactors. *AIChE J.*, 1998. **44**(12): p. 2724.
50. Dahlem, O., J. Reisse, and V. Halloin, The radially vibrating horn: a scaling-up possibility for sonochemical reactions. *Chem. Eng. Sci.*, 1999. **54**: p. 2829.
51. Nagata, Y., et al., Decomposition of hydroxybenzoic and humic acids in water by ultrasonic irradiation. *Environmental Science & Technology*, 1996: p. 1133-1138.
52. Thoma, G., M. Gleason, and V. Popov, Sonochemical treatment of benzene/toluene contaminated wastewater. *Environmental Progress*, 1998. **17**(3): p. 154-160.
53. David, B., et al., Ultrasonic and photochemical degradation of chlorpropham and 3-chloroaniline in aqueous solution. *Water Research*, 1998. **32**(8): p. 2451-2461.
54. Gondrexon, N., et al., Degradation of pentachlorophenol aqueous solutions using a continuous flow ultrasonic reactor: experimental performance and modelling. *Ultrasonics Sonochemistry*, 1999. **5**(4): p. 125-131.
55. Destailats, H., H.-M. Hung, and M.R. Hoffmann, Degradation of alkylphenol ethoxylate surfactants in water with ultrasonic irradiation. *Environmental Science and Technology*, 2000. **34**(2): p. 311-317.
56. Tauber, A., H.-P. Schuchmann, and C. von Sonntag, Sonolysis of aqueous 4-nitrophenol at low and high pH. *Ultrasonics Sonochemistry*, 2000. **7**(1): p. 45-52.
57. Pandit, A.B., P.R. Gogate, and S. Mujumdar, Ultrasonic degradation of 2:4:6 trichlorophenol in presence of TiO₂ catalyst. *Ultrasonics Sonochemistry*, 2001. **8**(3): p. 227-231.
58. Yim, B., et al., Sonochemical degradation of chlorinated hydrocarbons using a batch and continuous flow system. *Journal of Hazardous Materials*, 2001. **81**(3): p. 253-263.
59. Gogate, P.R. and A.B. Pandit, Hydrodynamic cavitation reactors: A state of the art review. *Reviews in Chemical Engineering*, 2001. **17**(1): p. 1-85.
60. Suslick, K.S., M.M. Mdleleni, and J.T. Ries, Chemistry induced by hydrodynamic cavitation. *Journal of the American Chemical Society*, 1997. **119**(39): p. 9303-9304.

61. Kalumuck, K.M. and G.L. Chahine, The use of cavitating jets to oxidize organic compounds in water. Transactions of the ASME. Journal of Fluids Engineering, 2000. **122**(3): p. 465-470.
62. Sivakumar, M. and A.B. Pandit, Ultrasound enhanced degradation of Rhodamine B: optimization with power density. Ultrasonics Sonochemistry, 2001. **8**(3): p. 233-240.
63. Gogate, P.R., et al., Cavitation reactors: efficiency analysis using a model reaction AIChE J., 2001. **47**(11): p. 2326.
64. Cabrera, M.I., et al., Photocatalytic Reactions Involving Hydroxyl Radical Attack. Journal of Catalysis, 1997. **172**(2): p. 380-390.
65. Cassano, A.E. and O.M. Alfano, Reaction engineering of suspended solid heterogeneous photocatalytic reactors. Catalysis Today, 2000. **58**.
66. Goswami, D.Y., D.M. Trivedi, and S.S. Block, Photocatalytic Disinfection of Indoor Air. ASME Journal of Solar Energy Engineering, 1995.
67. Romero, M., et al., Solar photocatalytic degradation of water and air pollutants: challenges and perspectives. Solar Energy, 1999.
68. Hamerski, M., J. Grzechulska, and A.W. Morawski, Photocatalytic purification of soil contaminated with oil using modified TiO₂ powders. Solar Energy, 1999. **66**: p. 395-9.
69. Muradov, N.Z., A. T Raissi, and D. Muzzey, Selective photocatalytic destruction of airborne VOCs. Solar Energy, 1996. **56**: p. 445-53.
70. Bussi, J., et al., Photocatalytic removal of Hg from solid wastes of Chlor-Alkali plant. Journal of Environmental Engineering, 2002. **August**: p. 733-738.
71. Kaneco, S., H. Kurimoto, and Y. Shimizu, Photocatalytic reduction of CO₂ using TiO₂ powders in supercritical fluid CO₂. Energy, 1999. **24**: p. 21-30.
72. Lei, L., et al., Catalytic wet air oxidation of dyeing and printing wastewater. Water Science and Technology, 1997. **35**(4): p. 311-319.
73. Lichtin, N.N., M. Avudaithai, and E. Berman, TiO₂-photocatalyzed oxidative degradation of binary mixtures of vaporized organic compounds. Solar Energy, 1996. **56**: p. 377-85.

74. Bickmore, C.R., et al., Ultrafine titania by flame spray pyrolysis of a titanatrane complex. *Journal of the European Ceramic Society*, 1998. **18**(4): p. 287-297.
75. Wu, Q., P.L. Yue, and X. Liu, Continuous catalytic wet air oxidation of phenol in a trickle bed reactor. *Proceedings of the Third Asia-Pacific Conference on Sustainable Energy and Environmental Technologies*, 3-6 Dec, 2000, Hongkong, 2000: p. 45-50.
76. Blake, D., H. Link, and K. Eber, Solar photocatalytic detoxification of water. *Advances in Solar Energy*, 1995. **7**: p. 167-210.
77. Mazzarino, I., P. Piccinini, and L. Spinelli, Degradation of organic pollutants in water by photochemical reactors. *Catalysis Today*, 1999. **48**(1-4): p. 315-321.
78. Degussa Company, Physicochemical data of AEROSIL, Aluminium Oxide C and Titanium Dioxide P25, in AEROSIL, Aluminium Oxide C and Titanium Dioxide P25 for catalysts, *Technical Bulletin Pigments*. 1991. p. 18.
79. Samuneva, B., V. Kozhukharov, and C. Trapalis, Sol-gel processing of titanium-containing thin coatings. *Journal of Materials Science*, 1993. **28**: p. 2353-2360.
80. Krasovec, U.O., et al., The gasochromic properties of sol-gel WO₃ films with sputtered Pt catalyst. *Solar Energy*, 2000. **68**(6): p. 541-551.
81. Sun, S., Z. Kang, and Z. Wei, Treatment of woolen-dyeing wastewater by TiO₂ film-solar photocatalytic oxidation process. *Environmental protection of Chemical Industry*, 2000. **20**(1).
82. Sunada, K., et al., Bactericidal and detoxification effects of TiO₂ thin film photocatalysts. *Environmental Science and Technology*, 1998. **32**: p. 726-728.
83. He, J., et al., Effect of crystallization phases of titania film on photocatalytic degradation of aniline. *Chinese Journal of Applied Chemistry*, 1999. **16**(5): p. 56-60.
84. Zhang, F., et al., Photo-assisted degradation of dye pollutants in aqueous TiO₂ dispersions under irradiation by visible light. *J. Mol. Catal. A: Chem.*, 1997. **120**(173-178).
85. Bekbolet, M., M. Lindner, and D. Weichgrebe, Photocatalytic detoxification with the thin-film fixed-bed reactor (TFFBR): clean-up of highly polluted landfill effluents using a novel TiO₂-photocatalyst. *Solar Energy*, 1996. **56**: p. 455-469.

86. Zheng, M., et al., Preparation, structure and properties of TiO₂-PVP hybrid films. *Materials Science and Engineering B*, 2000. **77**(1): p. 55-59.
87. Shivalingappa, L., J. Sheng, and T. Fukami, Photocatalytic effect in platinum doped titanium dioxide films. *Vacuum*, 1997. **48**: p. 413-16.
88. Gesenhues, U., Al-doped TiO₂ pigments: influence of doping on the photocatalytic degradation of alkyd resins. *Journal of Photochemistry and Photobiology A: Chemistry*, 2001. **139**(2-3): p. 243-251.
89. Wei, H., D. Xu, and J. Xu, Photo oxidation of humic acid in aqueous solution catalized by TiO₂ Film. *ACTA Scientiae Circumstantiae*, 1998. **18**(2): p. 162-166.
90. Xi, W. and S.-u. Geissen, Separation of titanium dioxide from photocatalytically treated water by cross-flow microfiltration. *Water Research*, 2001. **35**(5): p. 1256-1262.
91. Jakob, L., et al., TiO₂ photocatalytic treatment of water. Reactor design and optimization experiments, in *Photocatalytic Purification and Treatment of Water and Air*, D.F. Ollis and H. Al-Ekabi, Editors. 1993, Elsevier Science Publishers BV: Amsterdam, The Netherland. p. 511-532.
92. Yue, P.L. Modelling, scale-up and design of multiphasic photoreactors. in *Photocatalytic Purification and Treatment of Water and Air*. 1993. Amsterdam, The Netherland: Elsevier Science Publishers BV.
93. Sclafani, A., A. Brucato, and L. Rizzuti. Mass transfer limitations in a packed bed photoreactor used for phenol removal. in *Photocatalytic Purification and Treatment of Water and Air*. 1993. Amsterdam, The Netherland: Elsevier Science Publishers BV.
94. Szczechowski, J.G., C.A. Koval, and R.D. Noble, A Taylor votex reactor for heterogeneous photocatasis. *Chemical & Engineering Science*, 1995. **50**: p. 3163-3173.
95. Haarstrick, A., O.M. Kut, and E. Heinzle, TiO₂-assisted degradation of environmentally relevant organic compounds in wastewater using a novel fluidized bed photoreactor. *Environment Science and Technology*, 1996. **30**: p. 817-824.

96. Luo, Y. and D.F. Ollis, Heterogeneous photocatalytic oxidation of trichloroethylene and toluene mixtures in air: Kinetic promotion and inhibition, time-dependent catalyst activity. *Catalysis* 1996. **163**(Article No. 0299): p. 1-11.
97. Peill, N.J. and M.R. Hoffmann, Development and optimization of a TiO₂-coated fibre-optic reactor: photocatalytic degradation of 4-chlorophenol. *Environment Science and Technology*, 1995. **29**: p. 2974-2981.
98. Peill, N.J. and M.R. Hoffmann, Chemical and physical characterization of a TiO₂-coated fiber optic cable reactor. *Environment Science and Technology*, 1996. **30**: p. 2806-2812.
99. Peill, N.J. and M.R. Hoffmann, Solar-powered photocatalytic fiber-optic cable reactor for waste stream remediation. *Journal of Solar Energy Engineering*, 1997. **119**: p. 229-36.
100. Peill, N.J. and M.R. Hoffmann, Mathematical model of photocatalytic fiber-optic cable reactor for heterogeneous photocatalysis. *Environment Science and Technology*, 1998. **32**: p. 398-404.
101. Zik, O., J. Karni, and A.Kribus, The trof (tower reflector with optical fibres): A new degree of freedom for Solar energy systems. *Solar Energy*, 1999. **67**(1-3): p. 13-22.
102. Yatmaz, H.C., C.R. Howarth, and C. Wallis. Photocatalysis of organic effluents in falling film reactor. in *Photocatalytic Purification and Treatment of Water and Air*. 1993. Amsterdam, The Netherland: Elsevier Science Publishers BV.
103. Bahnemann, D., D. Bockelmann, and R. Goslich, Mechanistic studies of water detoxification in illuminated TiO₂ suspensions. *Solar Energy Materials*, 1991. **24**(1-4): p. 564-583.
104. Zhang, Y. and J.c. Crittenden, fixed-bed photocatalysts for solar decontamination of water. *Environmental Science and Technology*, 1994. **28**(3): p. 435-442.
105. Stafford, U., K.A. Gray, and P.V. Kamat, Photocatalytic Degradation of 4-Chlorophenol: The Effects of Varying TiO₂ Concentration and Light Wavelength. *Journal of Catalysis*, 1997. **167**(1): p. 25-32.

106. Ajona, J.I. and A. Vidal, The use of CPC collectors for detoxification of contaminated water: design, construction and preliminary results. *Solar Energy*, 2000. **68**: p. 109-22.
107. Mehos, M.S. and C.S. Turchi, Field testing solar photocatalytic detoxification of TEC contaminated groundwater. *Environmental Progress*, 1993. **12**(3): p. 194.
108. Prairie, M.R., J.E. Pacheco, and L.R. Evans, Solar detoxification of waste containing chlorinated solvents and heavy metals via TiO₂ photocatalysis. *Solar Engineering 1992*(proceeding of the ASME international Solar Energy conference), 1992. **1**: p. 1-8.
109. Wyness, P., et al., Performance of nonconcentrating solar photocatalytic oxidation reactors, Part II: shallow pond configuration. *Journal of Solar Energy Engineering*, 1994. **116**(1): p. 8-13.
110. Klausner, J.F., A.R. Martin, and D.Y. Goswami, On the accurate determination of reaction rate constants in batch-type solar photocatalytic oxidation facilities. *Journal of Solar Energy Engineering*, 1994. **116**(1): p. 19-24.
111. Cobianu, C., et al., Tin Dioxide Sol-Gel Derived Thin Films Deposited on Porous Silicon. *Sensors and Actuators B: Chemical*, 1997. **43**(1-3): p. 114-120.
112. Aguado, M.A., S. Cerver-March, and J. Gimenez, Continuous Photocatalytic treatment of mercury (II) on titania powders, kinetics and catalyst activity. *Chemical Engineering Science*, 1995.
113. Nogueira, R.F.P. and W.F. Jardim, TiO₂-fixed-bed reactor for water decontamination using solar light. *Solar Energy*, 1996. **56**: p. 471-7.
114. Wyness, P., J.F. Klausner, and D.Y. Goswami, Performance of nonconcentrating solar photocatalytic oxidation reactors, Part I: flat-plate configuration. *Journal of Solar Energy Engineering*, 1994. **116**: p. 2-7.
115. Crittenden, J.C., et al., Solar detoxification of fuel-contaminated groundwater using fixed-bed photocatalysts. *Water Environment Research*, 1996. **68**(3): p. 270-277.
116. Dionysiou, D.D., et al., Rotating disk photocatalytic reactor: development, characterization, and evaluation for the destruction of organic pollutants in water. *Water Research*, 2000. **34**(11): p. 2927-2940.

117. Dionysiou, D.D., et al., Effect of ionic strength and hydrogen peroxide on the photocatalytic degradation of 4-chlorobenzoic acid in water. *Applied Catalysis B: Environmental*, 2000. **26**(3): p. 153-171.
118. Dionysiou, D.D., et al., Continuous-mode photocatalytic degradation of chlorinated phenols and pesticides in water using a bench-scale TiO₂ rotating disk reactor. *Applied Catalysis B: Environmental*, 2000. **24**(3-4): p. 139-155.
119. Dionysiou, D.D., et al., Oxidation of organic contaminants in a rotating disk photocatalytic reactor: reaction kinetics in the liquid phase and the role of mass transfer based on the dimensionless Damkohler number. *Applied Catalysis B: Environmental*, 2002. **38**(1): p. 1-16.
120. Spadaro, J.T., L. Isabelle, and V. Ranganathan, Hydroxyl radical mediated degradation of azo dyes: evidence for benzene generation. *Environmental Science and Technology*, 1994. **28**(7): p. 1389-1393.
121. Shama, G., C. Peppiatt, and M. Biguzz, A novel thin film photoreactor. *Journal of Chemical Technology and Biotechnology*, 1996. **65**: p. 56-64.
122. Sakthivel, S., et al., TiO₂ catalyzed photodegradation of leather dye, acid green 16. *J. Sci. Ind. Res.*, 2000. **59**: p. 556.
123. Yamazaki, S., S. Matsunaga, and K. Hori, Photocatalytic degradation of trichloroethylene in water using TiO₂ pellets. *Water Research*, 2001. **35**(4): p. 1022-1028.
124. Lindner, M., J. Theurich, and D.W. Bahnemann, Photocatalytic degradation of organic compounds: Accelerating the process efficiency. *Water Science and Technology*, 1997. **35**(4): p. 79-86.
125. Chen, D. and A.K. Ray, Photodegradation kinetics of 4-nitrophenol in TiO₂ suspension. *Water Research*, 1998. **32**(11): p. 3223-3234.
126. Yu, J.C., J. Yu, and J. Zhao, Enhanced photocatalytic activity of mesoporous and ordinary TiO₂ thin films by sulfuric acid treatment. *Applied Catalysis B: Environmental*, 2002. **36**(1): p. 31-43.
127. Huang, C.P., C. Dong, and Z. Tang, Advanced chemical oxidation: Its present role and potential future in hazardous waste treatment. *Waste Management*, 1993. **13**(5-7): p. 361-377.

128. Bigda, R.J., Fenton's chemistry: an effective advanced oxidation process. *J. Adv. Sci. Eng.*, 1996. **6**(3): p. 34.
129. Walling, C., Intermediates in the reactions of Fenton type reagents. *Acc. Chem. Res.*, 1998. **31**: p. 155.
130. Pignatello, J.J., D. Liu, and P. Huston, Evidence for an additional oxidant in the photoassisted Fenton reaction. *Environmental Science and Technology*, 1999. **33**(11): p. 1832-1839.
131. Watts, R.J. and S.E. Dilly, Evaluation of iron catalysts for the Fenton-like remediation of diesel-contaminated soils. *Journal of Hazardous Materials*, 1996. **51**(1-3): p. 209-224.
132. Park, T.J., et al., Removal of refractory organics and color in pigment wastewater with fenton oxidation. *Water Science and Technology*, 1999. **39**(10-11): p. 189-192.
133. Li, Z.M., et al., Remediating TNT-contaminated soil by soil washing and Fenton oxidation. *Science of The Total Environment*, 1997. **204**(2): p. 107-115.
134. Hundal, L.S., et al., Removal of TNT and RDX from water and soil using iron metal. *Environmental Pollution*, 1997. **97**(1-2): p. 55-64.
135. Wang, T.H., S.F. Kang, and Y.H. Lin, Comparison among Fenton-related processes to remove 2,4-dinitrophenol. *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, 1999. **34**(6): p. 1267-1281.
136. Watts, R.J., et al., Mineral-catalyzed Fenton-like oxidation of sorbed chlorobenzenes. *Water Environment Research*, 1997. **69**(3): p. 269-275.
137. Yoshida, M., B.D. Lee, and M. Hosomi, Decomposition of aqueous tetrachloroethylene by Fenton oxidation treatment. *Water Science and Technology*, 2000. **42**(1-2): p. 203-208.
138. Potter, F.J. and J.A. Roth, Oxidation of chlorinated phenols using Fenton's reagent. *Hazardous Waste and Hazardous Materials*, 1993. **10**(2): p. 151-170.
139. Tang, W.Z. and S. Tassos, Oxidation kinetics and mechanisms of trihalomethanes by Fenton's reagent. *Water Research*, 1997. **31**(5): p. 1117-1125.

140. Ruppert, G., R. Bauer, and G. Heisler, UV-O₃, UV-H₂O₂, UV-TiO₂ and the photo-Fenton reaction - comparison of advanced oxidation processes for wastewater treatment. *Chemosphere*, 1994. **28**(8): p. 1447-1454.
141. Perkowski, J., L. Kos, and S. Ledakowicz, Application of ozone in textile wastewater treatment. *Ozone: Science and Engineering*, 1996. **18**(1): p. 73-85.
142. Rice, R.G., Applications of ozone for industrial wastewater treatment - a review. *Ozone: Science and Engineering*, 1997. **18**(6): p. 477-515.
143. Liakou, S., S. Pavlou, and G. Lyberatos, Ozonation of AZO dyes. *Water Science and Technology*, 1997. **35**(4): p. 279-286.
144. Benitez, F.J., et al., Degradation of protocatechuic acid by two advanced oxidation processes: Ozone/UV radiation and H₂O₂/UV radiation. *Water Research*, 1996. **30**(7): p. 1597-1604.
145. Boncz, M.A., et al., Kinetic and mechanistic aspects of the oxidation of chlorophenols by ozone. *Water Science and Technology*, 1997. **35**(4): p. 65-72.
146. Gehringer, P., et al., Oxidative treatment of a wastewater stream from a molasses processing using ozone and advanced oxidation technologies. *Ozone: Science and Engineering*, 1997. **19**(2): p. 157-168.
147. Meijers, R.T., et al., Degradation of pesticides by ozonation and advanced oxidation. *Ozone Sci. Eng.*, 1995. **17**(6): p. 673.
148. Beltran, F.J., J.F. Garcia-Araya, and P.M. Alvarez, Wine distillery wastewater degradation. 1. Oxidative treatment using ozone and its effect on the wastewater biodegradability. *Journal Of Agricultural And Food Chemistry*, 1999. **47**(9): p. 3911-3918.
149. Ayling, G.W. and H.M. Castrantas, WASTE TREATMENT WITH HYDROGEN PEROXIDE. *Chemical Engineering (New York)*, 1981. **88**(24): p. 79-82.
150. Bull, R.A. and J.D. Zeff. Hydrogen Peroxide in Advanced Oxidation Processes for Treatment of Industrial Process and Contaminated Groundwater. in *First Int. Symposium: Chemical Oxidation, Tech. For the 90s*. 1991. Nashville, Tennessee.
151. Eul, W., G. Scherer, and O. Helmling. Practical Applications of Hydrogen Peroxide for Wastewater Treatment. in *First Int. Symposium: Chemical Oxidation, Tech. For the 90s*. 1991. Nashville, Tennessee.

152. Behnajady, M.A., et al., Photocatalytic degradation of an azo dye in a tubular continuous-flow photoreactor with immobilized TiO₂ on glass plates. *Chemical Engineering Journal*. **In Press, Corrected Proof**.
153. Arslan, I. and I.A. Balcioglu, Degradation of commercial reactive dyestuffs by heterogenous and homogenous advanced oxidation processes: a comparative study. *Dyes and Pigments*, 1999. **43**(2): p. 95-108.
154. Lachheb, H., et al., Photocatalytic degradation of various types of dyes (Alizarin S, Crocein Orange G, Methyl Red, Congo Red, Methylene Blue) in water by UV-irradiated titania. *Applied Catalysis B: Environmental*, 2002. **39**(1): p. 75-90.
155. Daneshvar, N., D. Salari, and A.R. Khataee, Photocatalytic degradation of azo dye acid red 14 in water: investigation of the effect of operational parameters. *Journal of Photochemistry and Photobiology A: Chemistry*, 2003. **157**(1): p. 111-116.
156. Tang, C. and V. Chen, The photocatalytic degradation of reactive black 5 using TiO₂/UV in an annular photoreactor. *Water Research*, 2004. **38**(11): p. 2775-2781.
157. Zaroni, M.V.B., J.J. Sene, and M.A. Anderson, Photoelectrocatalytic degradation of Remazol Brilliant Orange 3R on titanium dioxide thin-film electrodes. *Journal of Photochemistry and Photobiology A: Chemistry*, 2003. **157**(1): p. 55-63.
158. Pelegrini, R., et al., Electrochemically assisted photocatalytic degradation of reactive dyes. *Applied Catalysis B: Environmental*, 1999. **22**(2): p. 83-90.
159. Zou, L., Y. Li, and E. Hu, Photocatalytic Decolorization of Lanazol Blue CE Dye Solution Using a Flat-Plate Reactor. *Journal of Environmental Engineering*, 2005. **131**(1): p. 102-107.
160. Bauer, R., et al., The photo-fenton reaction and the TiO₂/UV process for waste water treatment - novel developments. *Catalysis Today*, 1999. **53**(1): p. 131-144.