Chapter

1

General Introduction

Success is a journey, not a destination.

Ben Sweetland

Chlorinated Volatile Organic Compounds (CVOCs), such as trichloroethylene (TCE) and tetrachloroethylene (PCE) have been widely used as industrial solvents for degreasing metals and for dry cleaning. Many soils and groundwater supplies have become contaminated as a result of leaking underground storage tanks and improper disposal practices. This contamination is of major importance because these chemicals are toxic, carcinogenic and extremely persistent in the environment. As a consequence, much effort has been expended in developing methods to degrade these contaminants. In the treatment of refractory and non-biodegradable compounds, the so-called Advanced Oxidation Processes (AOPs) offer an alternative where biological treatments are not effective and catalytic processes and incineration too expensive. AOPs involve the production of extremely powerful oxidants – OH radicals, with the use of UV light in combination with oxidants such as ozone and/or H_2O_2 or in different combinations with Fe ions and semiconductors. All AOPs are however sensitive to the presence of radical scavengers and UV light absorbers, such as carbonates, humic material and nitrates usually found in surface and groundwater which lower the efficiency of the process. The AOPs for on-site destruction and

detoxification of contaminated waters, soils and wastes have to compete with so called "transfer technologies", such as air stripping, soil vapor extraction and activated carbon adsorption. However, with the implementation of more stringent regulations on CVOC discharge into the air, the two most commonly used methods to remove CVOCs form groundwater and soil, air stripping and soil vapor extraction (SVE), will require further treatment of the off-gas prior to its release into the environment. Therefore, there is a need for the development of inexpensive, effective and destructive on-site remediation technologies. In order to become the technology of choice for many applications, the AOPs must integrate into their design the latest engineering and design concepts, in order to achieve significantly reduced operating costs (energy and oxidant dose) and improved performance.

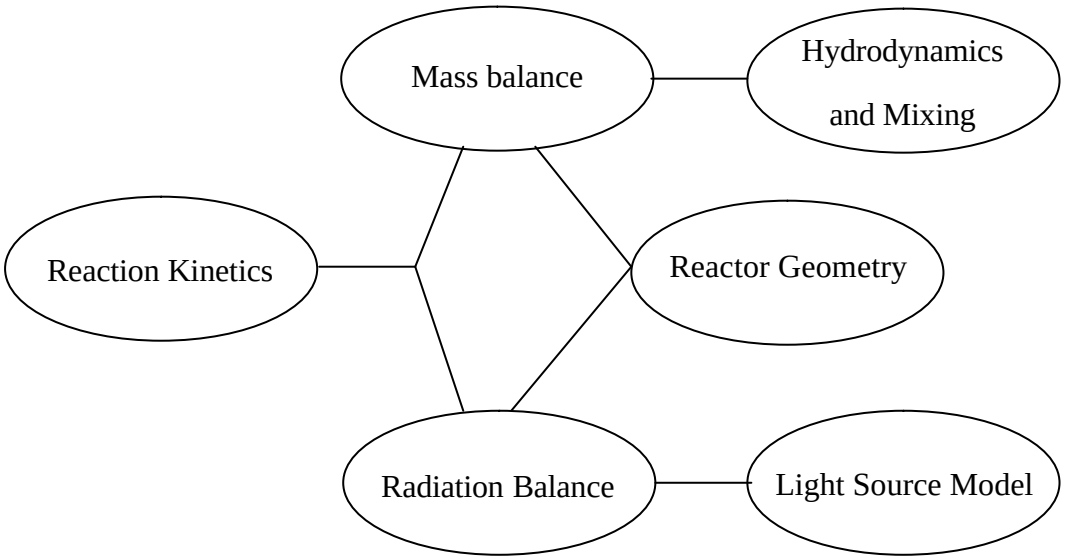

Fig. 1.1 The reaction engineering principles and their interactions in the study of an isothermal photochemical reactor.

1.1 CVOCs removal practices

In the past, treatment technologies for CVOCs in groundwater were stripping and activated carbon adsorption or the combination of both. All of them however, simply transfer pollutants from one medium (water) to another (air or activated carbon), without destroying them. The same reasoning goes for soil venting (soil vapor extraction, SVE), which is also based on interphase mass transfer potential and requires the post treatment of the vapor phase. Schematic diagrams of the three systems are presented on Figures 1.2, 1.3 and 1.4, respectively.

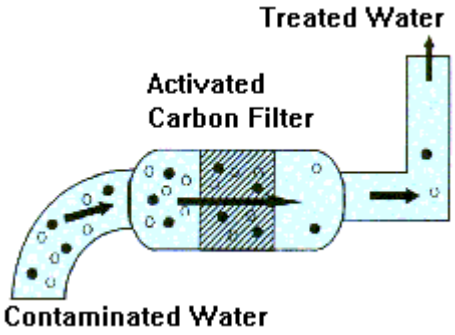

Figure 1.2. Schematic representation of the Activated carbon adsorption process.

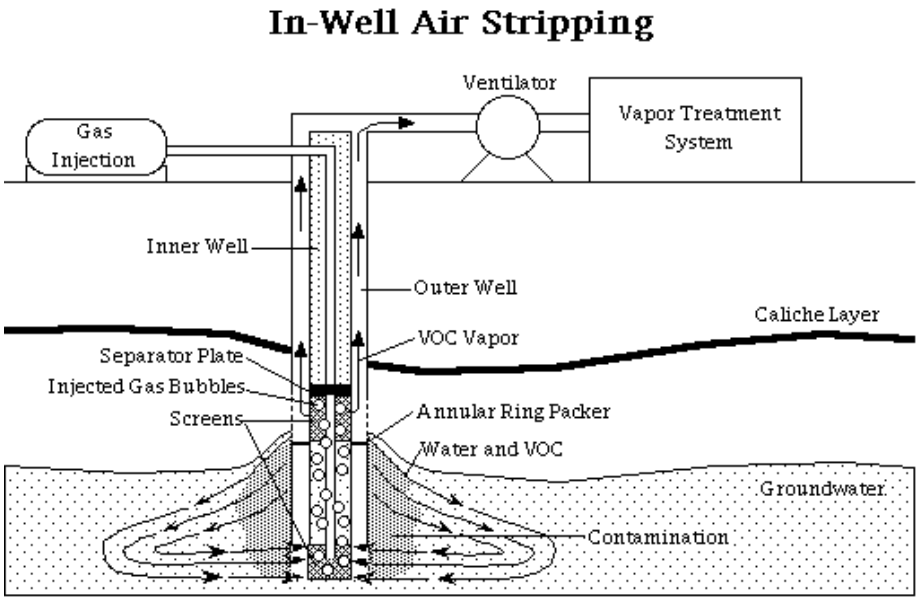

Figure 1.3. Schematic representation of the In-Well air stripping process with planned post treatment.

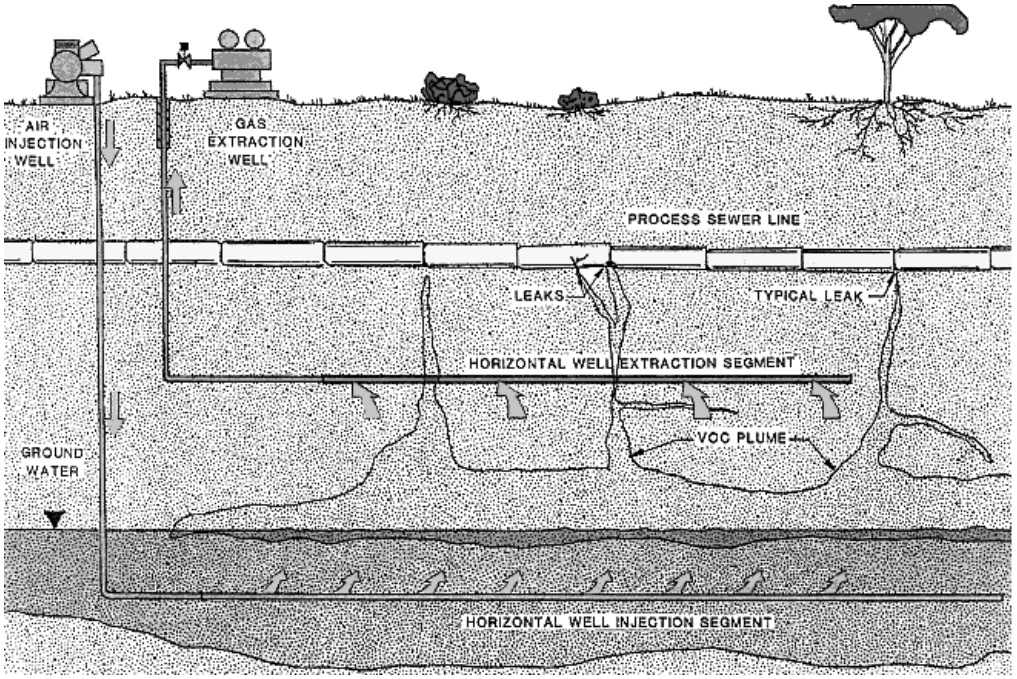

Figure 1.4. Schematic representation of the Soil vapor extraction (SVE) system.

Nowadays, new destructive processes are being studied intensively for the degradation of CVOCs in liquid and gas phases. Concentrations of the CVOCs in groundwater are usually in sub-ppm range have low biodegradability, thus, biodegradation does not seem to be the technology of choice.

Essentially all organic compounds are thermodynamically unstable with respect to oxidation, yet these processes are not widely used for the treatment of CVOC contaminated waters. Common oxidants such as ozone (O_3) or hydrogen peroxide (H_2O_2) seemed to be attractive because of their high thermodynamic oxidizing potential (2.07 V and 1.78 V respectively) but were shown to be limited by chemical kinetics, reacting too slowly with CVOCs to be economically feasible.

Table 1.1. Oxidation potentials of some oxidants.

Oxidation species	Oxidation potential, V	Oxidation power as E_i/E_{Cl}, /
Fluorine	3.03	2.23
Hydroxyl radical	2.80	2.05
Atomic oxygen	2.42	1.78
Ozone	2.07	1.52
Hydrogen Peroxide	1.78	1,31
Potassium Permanganate	1.68	1.24
Chlorine dioxide	1.49	1.10
Chlorine	1.36	1

The ideal process for the oxidation of hazardous organics would consists of oxidation with dioxygen at ambient temperature and pressure. The wet air oxidation (WAO) process is an example of such a process, but as yet catalysts have not been developed that will allow the process to be used at ambient conditions and in a cost effective manner. This process is the most suitable for more concentrated pollutants as presented in Fig. 1.5.

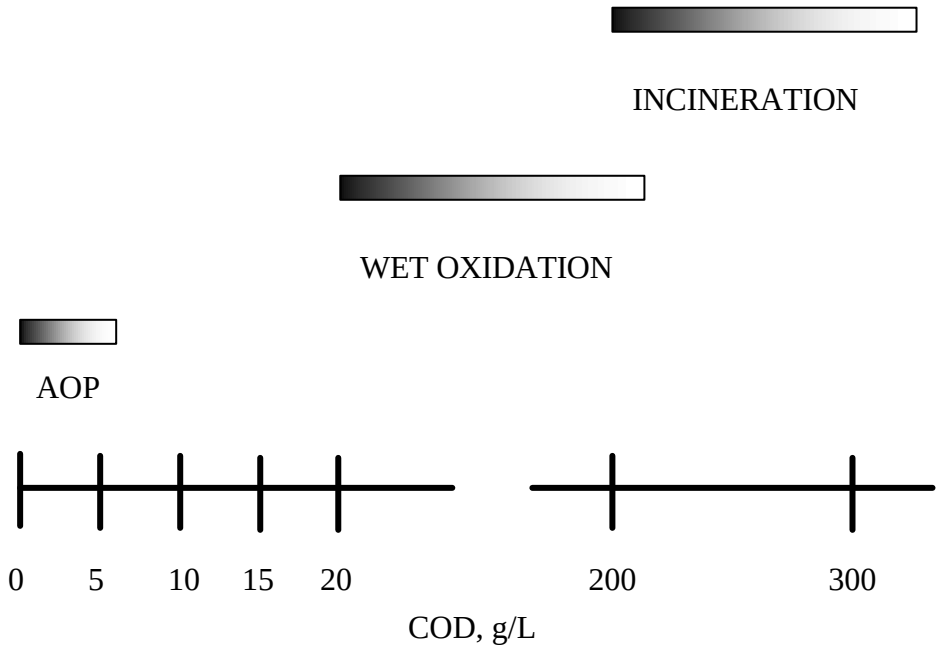

Figure 1.5. Suitability of water treatment technologies according to COD content.

Research over the last ten years have shown that the rate limitations of conventional oxidative processes might be removed and their cost lowered if a combination of oxidants or of oxidants and ultraviolet radiation is used. These processes are referred to as Advanced Oxidation Processes (AOPs) and are defined as near-ambient temperature and pressure water/air treatment processes, which are based on the generation of reactive free radicals, the most important of which is the hydroxyl radical. The hydroxyl radical is an extremely powerful oxidant whose rate constants with the organic molecules are generally on the order of 10^{8-10} L/(mol-s). This means that the AOP treatment of typical organic pollutants will be practical even if the steady-state concentration of OH radical is only $10^{-10} – 10^{-12}$ mol/L. For example, the rate constant for reaction of PCE with OH radicals is reported to be 2.3×10^{9} L/(mol-s). If the pseudo-first order rate constant is given by

$k_0 = -d\ln c_{PCE}/dt = 2.3\times10^{9}$ L/(mol s) c_{OH}^{ss}

then even if the steady-state concentration of the OH radical is only 10^{-11} mol/L, the value of k_0 will be 0.023/s with the half-life of PCE being 30 s. Therefore, we should conduct the research in a way that will ensure the steady-state concentration of the hydroxyl radical at this order of magnitude.

Hydroxyl radicals can be formed by the effect of ionizing radiation on water, or in one of the following advanced oxidation processes:

- ✓ O_3/H_2O_2
- ✓ Photolysis:
  - ➢ $UV/O_3/H_2O_2$
  - ➢ UV/H_2O_2
  - ➢ UV/O_3
- ✓ Photocatalysis:
  - ⅄ UV/TiO_2
  - ⅄ UV/different semiconductors
- ✓ Fenton (H_2O_2/Fe^{2+}) and Photo-Fenton processes ($H_2O_2/Fe^{2+}(Fe^{3+})/UV$).

The application of each and the extent of OH radical production was reported by Benitez et al. (2000), who also reported that the synergetic effect of combining two or more processes could result in the increased in production of free OH radicals beyond a linear relation. The photo-Fenton process was reported to be one of the most effective OH radical sources, but the complexity of the system and the problems related to Fe-sludge disposal or regeneration, are yet to be solved.

Oxidation of organic pollutants by one of the methods presented above implies initial generation and subsequent reaction of hydroxyl radicals. The hydroxyl radical is a short-lived, extremely potent oxidizing agent that reacts with most organic compounds by hydrogen abstraction, electron transfer reaction and subsequent deprotonation or electrophilic addition to the π-system in unsaturated organic compounds. This reaction generates organic radicals, which by addition of molecular oxygen yield peroxyl radicals. These intermediates initiate thermal (chain) reactions of oxidative degradation, leading finally to carbon dioxide, water and inorganic salts (Legrini *et al.*, 1993).

Table 1.4. Molar absorption coefficients, theoretical stoichiometry, and quantum efficiency of the formation of hydroxyl radicals from photolysis of hydrogen peroxide and ozone, respectively.

	$\varepsilon_{254\,nm}$, L/(mol cm)	stoichiometry	$\phi(OH^{\bullet})$
H_2O_2	18.6	$H_2O_2 \rightarrow 2\,OH^{\bullet}$	0.98
HO_2^-	240		
O_3	3300	$2\,O_3 \rightarrow 2\,OH^{\bullet}$	2.00

Legrini *et al.* (1993)

$\phi=\Delta n/N_{a,\lambda}$; the quantum yield is the ratio between the number of molecules undergoing a particular process of transportation (Δn) and the number of photons absorbed ($N_{a,\lambda}$) during the same period of observation.

1.2 H_2O_2/UV PROCESS: Advantages and limits of application

The use of hydrogen peroxide as an oxidant brings a number of advantages in comparison to other methods of chemical or photochemical water treatment: commercial availability of the oxidant, thermal stability and storage on-site, infinite solubility in water, no mass-transfer problems associated with gases, the formation of two hydroxyl radicals for each molecule of H_2O_2 photolyzed, generation of peroxyl radicals after $OH^\bullet$ attack on most organic substances (leading to subsequent thermal oxidation reactions), minimal capital investment, very cost effective source of OH radicals, and simple operational procedure.

There are also, however, obstacles encountered with the H_2O_2/UV process. The rate of chemical oxidation of the contaminant is limited by the rate of formation of hydroxyl radicals, and the rather small absorption cross section of H_2O_2 at 254 nm is a real disadvantage, particularly in the case where organic substances will act as inner filters. Higher rates of $OH^\bullet$ formation may, nevertheless, be realized by the use of Xe-doped Hg arcs exhibiting a strong emission spectrum of 210-230 nm, where H_2O_2 has a higher molar absorption coefficient.

The main disadvantage of all oxidative degradation processes based on the reactivity of hydroxyl radicals exists, however, in the efficient trapping of OH radicals by HCO_3^- and CO_3^{2-} ions (Eqs. (1-1) and (1-2), respectively).

$$OH^\bullet + HCO_3^- \rightarrow H_2O + CO_3^{\bullet -} \qquad k_1=8.5\times10^6 \text{ L/(mol·s)} \qquad (1\text{-}1)$$

$$OH^\bullet + CO_3^{2-} \rightarrow OH^- + CO_3^{\bullet -} \qquad k_2=3.9\times10^8 \text{ L/(mol·s)} \qquad (1\text{-}2)$$

Carbonate and bicarbonate are actually omnipresent in groundwater, which in a great way reduce the efficiency of this process in direct water treatment. (Legrini *et al.*, 1993). Therefore, the oxidations should be performed in an OH radical scavenger-free, UV light

absorber-free environment.

1.3 LITERATURE REVIEW

Legrini *et al*. (1993) presented the principles of Photochemical processes for water treatment in a review article. They concentrated on the experimental work being done in the technical development of AOPs. They concluded that for a given pollutant, the most efficient procedure or combination of the procedures must be determined, with pollutant nature, absorption spectrum, concentration and reactivity, as well as inhibitor effects of pollutant mixtures and the presence of radical trapping agents being the most important parameters.

1.3.1 H_2O_2/UV process

Since the late 1960's, numerous researchers have used the H_2O_2/UV process to oxidize various organic substances in water. Recently, commercial units employing this process have been developed for on-site oxidation of organic contaminants in groundwater. However, research on the mechanism of hydrogen peroxide photolysis goes back to the 1950's when several fundamental studies (Hunt and Taube, 1952, Baxendale and Wilson, 1957, Volman and Chen, 1959) have shown that primary process in the photolysis of hydrogen peroxide produces two OH radicals upon the absorption of a photon

$$H_2O_2 \xrightarrow{h\nu} 2OH^{\bullet} \qquad -\frac{dc_{H2O2}}{dt} = \phi_p \cdot F \cdot I_0 \qquad (1\text{-}3)$$

I_0 is the (monochromatic) UV photon flow rate, F is the fraction of UV light absorbed by H_2O_2 and ϕ_p is the primary quantum yield for photolysis of hydrogen peroxide at 254 nm. The quantum yield can be defined as the number of moles of hydrogen peroxide decomposed

per mole of light photon absorbed. Baxendale and Wilson (1957) measured the overall quantum yield as 1.00±0.02. Later, Volman and Chen (1959) confirmed the presumption of Baxendale and Wilson that the quantum yield ϕ of the primary process (Eq. 1-3) is 0.49. The value obtained by Baxendale and Wilson is due to the fact that the overall process decomposes two molecules of hydrogen peroxide per photon absorbed. Thus, although the primary quantum yield is only 0.49 the overall quantum yield has a value of unity. Volman and Chen (1959) also reported that in the presence of organic matter quantum yield would have a value of 1/2 of the overall quantum yield. To summarize all the results, in the pure as well as bicarbonate containing waters, the quantum yield will be 1, and in organic substrate-containing waters it will be between $0.43 < \phi < 0.59$. Those values take into account all experimental uncertainty and are valid for a wide range of light intensities, pH values, and hydrogen peroxide concentrations.

Nicole *et al.* (1990) studied the application of the H_2O_2/UV process for actinometric purposes. They showed that the H_2O_2/UV process could serve as an alternative to the conventional actinometers such as potassium ferrioxalate (Hatchard and Parker, 1956) and uranyl oxalate (Leighton and Forbes, 1930). Further, it can serve as a tool for the evaluation of effective light path length or reflection coefficient of a reactor wall in solutions with low optical densities ($D<0.02$). For the hydrogen peroxide solutions with high internal optical densities ($D>2$), results obtained in their study showed that the rate of photolysis obeys the general kinetic equation as a combination of the definition of the quantum yield and Beer-Lambert law. When all incident photons are not absorbed by the irradiated solution, their results showed that reflection on the internal wall of the photochemical reactor might increase the photodecomposition rate of H_2O_2. Furthermore, they showed that these wall effects on the rate of H_2O_2 decomposition will depend, on one hand, on absorbance (or transmittance) of the solution, and, on the other hand, on the reflecting power of the reactor wall. In the case of low values of optical density ($D<0.02$) the rate of H_2O_2 photolysis could be described by an apparent first-order kinetic equation corrected with a reflection coefficient as a function of the

construction material of the UV reactor.

In their next publication the same group (de Laat *et al*., 1994) proposed a kinetic model for the UV degradation of chloroethanes in dilute solutions of hydrogen peroxide. The model was based on the assumptions of steady state concentration of OH radicals and reaction only between OH radicals and the pollutants, without any direct photooxidation of the pollutant. They conducted experiments in the presence of bicarbonate as a radical scavenger and showed the retardation effect of radical scavengers on the rate constant.

A similar reaction trend was observed in the work of Weir and Sundstrom (1993) during the oxidation of TCE. They observed that the rate of destruction was first order in UV light intensity and pseudo-first order in TCE concentration. The rate was first order in hydrogen peroxide concentration at low peroxide levels, but independent of peroxide concentration at high peroxide levels. The maximum rate attainable depended on the reactor depth, with the shallower (2 cm vs 8 cm) reactor yielding the larger maximum rate. They irradiated the reactor from the top with two 13.8 W UV (254 nm) lamps mounted within an aluminum reflector.

Liao and Gurol (1995) studied the H_2O_2/UV process for oxidation of model compound *n*-chlor-butane (Bu-Cl) as well as the photolytic decomposition of H_2O_2 under various of water qualities and operational conditions. Experiments were conducted in a continuous-flow stirred tank reactor (CSTR) in the presence of carbonate ions and humic acid at various pH values, residence times, light intensities, and hydrogen peroxide dosages. They observed that the oxidation efficiency for the target pollutant Bu-Cl, i.e., $(c_{M,0}-c_M)/c_{M,0}$, was determined by the rate of photolytic decomposition of H_2O_2 as well as the quality of the water to be treated. The higher the rate of H_2O_2 photolysis, the higher the efficiency of pollutant oxidation; the rate of photolytic decomposition of H_2O_2 increased with increasing incident light intensity and H_2O_2 dosage but decreased with increasing UV absorbance of the aqueous solution. The

oxidation efficiency was hindered by increasing pH, total inorganic carbon concentration and concentration of humic material in the water. They showed that the extent to which the oxidation rate of the organic compound is dependent on the presence of humic acids is so strong that this process should be avoided in the treatment of highly colored waters. The adverse effect of carbonate ions and high pH can be alleviated by the acidification of water prior to the application of this process. However, it was observed that carbonate ions did not affect the overall quantum yield for hydrogen peroxide decomposition, which was predicted to be 1.0 in both the presence as well as the absence of the carbonate ions. On the other hand, humic material not only competed with BuCl for OH radicals, but also effectively blocked the light available for photolysis of H_2O_2.

Glaze *et al*. (1995) proposed another kinetic model for the oxidation of organics in water by the combination of H_2O_2 and UV radiation that was based on the literature values for a series of radical reactions initiated by the photolysis of H_2O_2. They examined the effects of UV intensity, the initial concentration of hydrogen peroxide, and the various inorganic salts on the oxidation rate of 1,2-dibromo-3-chloropropane (DBCP). It was observed that nitrate and bicarbonate/carbonate have a detrimental effect on the rate of oxidation of DBCP, the former due to UV shielding and the later due to OH radical scavenging. They showed that the rate of oxidation is enhanced and the optimum peroxide level lowered at low carbonate alkalinity, suggesting that presoftening of groundwater prior to oxidation of halogenated alkanes should be cost-effective.

1.4 TETRACHLOROETHYLENE (PCE) AND TRICHLOROETHYLENE (TCE) DEGRADATION STUDIES

1.4.1 Liquid phase oxidations

The group of Glaze studied the degradation of PCE and TCE in the liquid phase using ozone, ozone/H_2O_2 and TiO_2 processes. In their 1988 publication (Glaze and Kang, 1988), they showed that addition of H_2O_2 accelerates the oxidation of both compounds by ozone and that this process can be mass-transfer limited if peroxide - ozone dosage ratios of >0.7 (w/w) are used. They also confirmed that high levels of bicarbonate drastically decrease the efficiency of the PCE and TCE degradation.

Aieta *at al.* (1988), showed in their pilot plant evaluation studies that the O_3/H_2O_2 process can be cost effective for controlling the common organics found in groundwater in comparison with other treatment technologies. Treatment efficiency for PCE and TCE (20 and 200 ppm) was determined as a function of the peroxide-to-ozone dosage ratio, ozone dosage, and contact time. They also investigated the influence of ozone mass-transfer characteristics as it was shown that the rate of degradation of PCE and TCE depends on the rate of ozone transfer into the reactor and the quality of water to be treated (alkalinity, pH).

Glaze and Kang (1989a) later proposed a kinetic model for the oxidation of PCE and TCE in aqueous media with ozone and hydrogen peroxide in a semi-batch reactor. This model was based on known kinetic constants for the complex, free-radical chain process in the H_2O_2/O_3 system and mass-transfer characteristics of the reactor, and was tested in a bicarbonate-spiked distilled water at several ozone - peroxide ratios. It was shown that the model could predict the rate constant of OH radicals with PCE accurately when operating in the mass-transfer limited region. However, the predictions are much poorer when H_2O_2/O_3 ratios are below the stochiometric optimum. The target concentration of PCE was always 50-70 ppb, and the

observed pseudo-first order constant for the degradation of PCE had a maximum of 0.0112/s.

In a companion paper (Glaze and Kang, 1989b) they further tested the proposed kinetic model and found that it can be applied to surface and ground waters as long as the composition and rate constants for potential initiators and promoters of ozone decomposition and radical scavengers are known. This was shown to be important due to the fact that most ground waters contain relatively low concentrations of organic substances that can serve as initiators, but may have relatively high concentrations of scavengers such as bicarbonate (or carbonate), nitrate, sulfate, transition-metal ions, and bromide ions. It was shown that in distilled water, bicarbonate effects can be precisely accounted for by the O_3/H_2O_2 model. At pH 7.6, the rate of oxidation of PCE was shown to be inversely proportional to the bicarbonate level, suggesting that water softening prior to the oxidation might be effective. Substrate oxidation was not considerably affected by chloride ion up to 5000 mg/L at neutral or high pH conditions.

1.4.1.1 UV/TiO_2 Process

All of the advanced oxidation processes have the potential to carry the original contaminant through the series of increasingly oxidized intermediates to carbon dioxide. Because complete mineralization is usually desirable in water polishing operation, increased attention has been taken to demonstrate not only reactant disappearance, but also carbon dioxide appearance. Turchi and Ollis (1989) demonstrated that in the TiO_2 treatment of 34 ppm of PCE, disappearance and appearance of CO_2 was complementary, which indicates a virtual lack of kinetically stable intermediates. In contrast, they have shown that benzene clearly passes through several stable intermediates, and at least two were required to fit the CO_2 evolution data.

Childs (1983) in his analysis of degradation of TCE in UV/TiO_2 process showed that low

concentrations of TCE (10 ppm) could be efficiently degraded without production of intermediates. Cl was evolved in stoichiometric amount. However, when he performed experiments in which he repeatedly injected TCE into the same medium, the production of intermediate dichloroacetaldehide (DCA) was observed. Even more, after repeating the TCE injections, the concentration of DCA in the medium increased accordingly, but was degraded at the end. This indicates that when the number of active sites for specific reaction is not large enough, the otherwise simple reaction mechanism can shift into multi-step mechanism with the production of intermediates. Therefore, the initial concentrations of the pollutants should be optimized according to the degradation process.

Glaze *at al*. (1993), in their studies of TiO_2 mediated photodegradation of tri- and tetrachloroethylene (TCE and PCE) in water, used Degussa P-25 photocatalyst and performed studies in a 5.6 L recirculating photoreactor. The main observation during the degradations of PCE (from 1-30 ppm) and TCE (from 20-30 ppm) was the production of byproducts such as dichloroacetic acid and trichloroacetic acid. Also, traces of dichloro- and trichloroacetaldehide (dichloroacetaldehide is a known animal carcinogen and its potency is greater than that of either PCE or TCE) were observed suggesting that this process should not be used in treatment of waters to be distributed to consumers.

1.4.1.2 Photolysis by UV 254 nm radiation

A number of papers have reported the degradation of chemicals using Hg emission at 254 nm, in particular, that produced with low-pressure mercury arcs. The results demonstrate that 254 nm irradiation alone cannot be used as an effective procedure for the removal of organics from water (it can however be efficiently applied for disinfection purposes).

Martens and von Sonntag (1995) studied the photolysis of tetrachloroethylene with the UV light (254 nm) in air-saturated aqueous solutions and showed that the major products

(quantum yield in parentheses) are as follows: chloride ion (2.05), carbon dioxide (0.62), trichloroacetic acid (0.41), dichloroacetic acid (0.08) and hypochlorite (0.08). It was concluded that there are two (or three) major primary processes:

$$CCl_2 = CCl_2 + h\nu \rightarrow CCl_2 = CCl^{\bullet} + Cl^{\bullet} \quad (1\text{-}4)$$

$$CCl_2 = CCl_2 + h\nu + H_2O \rightarrow CCl_2(OH) - CCl_2H \quad (1\text{-}5)$$

$$CCl_2 = CCl_2 + h\nu \rightarrow CCl_2 = CCl^{+} + Cl^{-} \quad (1\text{-}6)$$

From scavenging experiments with alcohols, both with and without O_2, $\phi(1\text{-}4)=0.23\pm0.03$ has been determined. Reactions (1-5) and (1-6) will finally both yield dichloroacetic acid and no distinction could be made between the two routes: $\phi(5+6)=0.08$. The quantum yield of tetrachloroethylene consumption in air-saturated solution was shown to be 0.84, and considerably lower in the absence of oxygen (ϕ(PCE consumption)=0.34). The higher value in the presence of oxygen is due to the contribution of a short chain reaction. They also showed that efficient scavenging of the Cl radical by bicarbonate prevents the formation of trichloroacetic acid from potentially present PCE in the UV disinfection of water.

1.4.2 Gas phase oxidations

Gürtler *et al*. (1994) studied the photooxidation of the chloroethens $C_2H_{4-x}Cl_x$ (x=1-4) in the gas phase by the irradiation at 185 and 254 nm in an oxygen atmosphere. They observed that degradation efficiencies directly depend on the number of chlorine atoms both at 185 and 254 nm. The quantum yields for degradation increased from 2-3 for vinyl chloride (VC) to >100 for tri- and tetrachloroethylene (TCE and PCE) at 185 nm in the 10^{-3} bar concentration range. At 254 nm they measured nearly time independent quantum yields of around 10 for tri- and 40 for tetrachloroethylene. These quantum yields indicate that the reactions of TCE and PCE are decomposed in a free-radical chain mechanism with the formation of Cl-radicals by UV photolysis being the rate-determining reaction step. Even though degradation of TCE and

PCE is rather fast the observed byproducts such as di- and trichloroacetyl chloride and phosgene had considerable photo-stability, which makes this process less attractive for practical use.

Bhowmick and Semmens (1994) studied the gas phase photooxidation of five CVOCs in a batch UV reactor using two UV lights, one, emitting both at 185 nm and 254 nm, and the other emitting only at 254 nm. The light with the 185 nm line formed ozone in the system and the influence of ozone was also evaluated. The target compounds were chloroform (CF), carbon tetra chloride (CTC), tri- and tetrachloroethylene (TCE, PCE) and 1,1,2-trichloroethane (TCA) in the concentration range from 0.07 to 6.2 mg/L (70-5000 ppm) which is slightly higher than the gas phase concentrations in conventional air stripping. Rather than chloroacetylaldehide or chloroaldehyde, which were detected in very low concentrations, phosgene was identified as the principal intermediate in the photooxidation of all five compounds. The production of phosgene was dependent on both the substance and the initial concentration of the pollutants with higher rates of production for more reactive compounds. All CVOCs degradations exhibited first order kinetics. The photooxidation process was however catalyzed by a chlorine radical sensitized chain reaction. They observed that the presence of moisture improves the photooxidation kinetics for CF, TCA and to lesser degree for TCE, but has no impact on the degradation of PCE and CTC. The chain reaction mechanism makes the gas phase oxidation attractive, but the problem of the photo-stable intermediates still remains.

Shen and Ku (1998) in their work explored the reactions of chloroethens by UV/O_3 process. They focused on the degradation of dichloroethene (DCE), tri- and tetrachloroethylene (TCE and PCE) in the concentration range of 143, 105 and 95 ppmv respectively. Owing to the complexity of AOP decomposition schemes they proposed the simplified two-step consecutive decomposition model with respect to the elemental balance of chlorine and carbon. The increase in UV light intensity would promote the decomposition of chloroethens

more than the addition of ozone, which for example improved the degradation rate of TCE by only 5-15%. The excess of ozone would inhibit the rate, mainly due to the light competition effect and scavenging of OH radicals.

Nimlos *et al*. (1993) studied the TCE degradation in a single pass photocatalytic reactor using Degussa P-25 TiO_2 immobilized on a foamed alumina frit. They reported high rates of degradation of the model compound; however, direct sampling mass spectrometry and gas-phase Fourier transform infrared (FTIR) spectroscopy revealed significant quantities of byproducts such as phosgene, dichloroacetyl chloride (DCAC), carbon monoxide and molecular chlorine. The formation of byproducts was discussed in by way of Cl attack on the TCE, which involve the chain mechanism. That was confirmed by the high quantum yield (usually in the order of 0.01-0.05 for photocatalytic reactions, here they were found to be 0.5-0.8) for the degradation of TCE. The chain reaction with chlorine was assumed to take place in the gas phase in contrast to the reaction with OH radicals formed on the surface of the photocatalyst. It was shown that the large amounts of phosgene produced in this study could be a result of photocatalytic oxidation of DCAC.

Trichloroacetylchloride (TCAC) and hydrochloric acid as the main product, and dichloro- and monochloroacetic acid, carbon tetrachloride, chloroform and phosgene as minor byproducts were also observed by Fukami et al. (2001) in their photocatalytic study of PCE using a thin film of TiO_2 under the UV light. The PCE with the initial concentration of cca 1000 ppm was degraded completely in 10 minutes following the pathway PCE→DCAC→HCl. However, DCAC remained in the system even after 10 hours of the irradiation.

Yamazaki-Nishida *et al.* (1993, 1996, 2001) studied the photocatalytic degradation of PCE and TCE in the gas phase using a photoreactor packed with porous TiO_2 pellets and illuminated from the outside with a set of four 4W fluorescent black light bulbs. While the

reported removal of model compounds was 100 %, they observed the production of undesirable intermediates such as chloroform ($CHCl_3$) and carbontetrachloride (CCl_4) in the effluent stream with no phosgene present. Production of byproducts was closely related to the porosity and surface area of the catalysts used; i.e. the lower the surface area and porosity, the higher the by-product yield. Also increasing the O_2 mole fraction decreased the amount of byproducts in the effluent stream. Production of byproducts was initiated by the Cl-radical reactions, which was also confirmed by theoretical calculations. Nimlos *et al*. (1993) employed the catalyst with specific surface area of 56 m^2/g and the reaction was Cl-radical-initiated, leading to the production of large amount of byproducts. However, the specific surface area of the catalyst employed in this study was at least three times as large, resulting in better selectivity. It was therefore concluded that the combination of high oxygen mole fraction in the gas stream and photocatalyst with large specific surface area is very effective in suppressing the formation of undesirable chlorinated byproducts such as $CHCl_3$ and CCl_4. However, for the TCE and PCE inlet concentrations of 450 ppmv, the effluent concentrations of $CHCl_3$ and CCl_4 were ca 10 and 20 ppmv respectively.

1.5 PURPOSE

Based on a thorough literature search, it has been shown that direct treatment of water with one of the advanced oxidation processes involving OH radical production is limited by the presence of carbonate and bicarbonate in waters, due to the radical scavenging effect of those two species. Also the humic substances usually present in the waters act as a shield for UV light, thereby reducing the number of available photons which could initiate the chemical reaction. The same reasoning can be applied to suspended solids, which would have to be reduced prior to the direct treatment involving UV light. Presoftening of the groundwater has proposed for the reduction of carbonate and bicarbonate but, to the best of our knowledge, until now, no such facilities have been reported in the literature.

The most promising technique for the alleviation of PCE and TCE (CVOCs) contamination of soil and ground water seems to be the combination of soil vapor extraction in the first case, and stripping with destructive post treatment in the second.

If photolytic and photocatalytic treatment of gas containing TCE and PCE is attempted, the undesirable, photo-stable intermediates such as phosgene, di- and trichloroacetic acid, chloroform and carbon tetrachloride need to be reduced. It is of course important, not to produce even more dangerous, more environmentally objectionable products than the starting materials, which is readily the case here (trichloroacetic acid is a registered herbicide, phosgene was used as a War poison in WW1, and carbontetrachloride is a know carcinogen).

By this study of the advantages and disadvantages of both gas and liquid oxidations as reported in the opened literature, it can be concluded that oxidation in the liquid phase in a UV absorber and OH radical scavenger-free environment is the most suitable. Since most reaction in the liquid phase with OH radicals can be led in such a way that no byproducts are produced, the absorber – reactor system was constructed. The heart of the reactor system is a 50 cm tall stainless steel annular photoreactor, equipped with a low-pressure mercury lap (30 W, General Electric) placed inside a quartz protecting tube. The UV light emits monochromatic radiation at 254 nm. As shown in Fig. 1.4, the reactor has all the provisions for gas and liquid sampling, continuous addition of H_2O_2, and temperature measurements. The same reactor was used for kinetic studies of H_2O_2 and PCE and for absorption with reaction studies. Details of the experimental procedures are given for each type of the experiments further on in the text. When CVOCs are absorbed into the reacting medium, pollutant on its way through reactor can react with photons from the UV light and OH radicals at the gas-liquid interphase as well as in the liquid bulk. Since there are almost no competitors for free OH radicals and no UV light absorbing species, a high efficiency of process should be achieved. Further, if for example phosgene is formed, it has been shown to hydrolyze into HCl and CO_2, which are the final desired products in the oxidative processes

of CVOCs.

Even though the application of the UV-BCR is attractive, the design and the analysis of such a reactor is not an easy task (Alfano *et al.*, 1986a, 1986b; Yue, 1993) and requires the precise evaluation of the rate-determining step in the overall process. In addition to the difficulties in predicting the behavior of bubble column reactors (Deckwer and Shumpe, 1993) the evaluation of the light absorption and the effect thereon of the light scattering by bubbles on the reaction rate have to be performed.

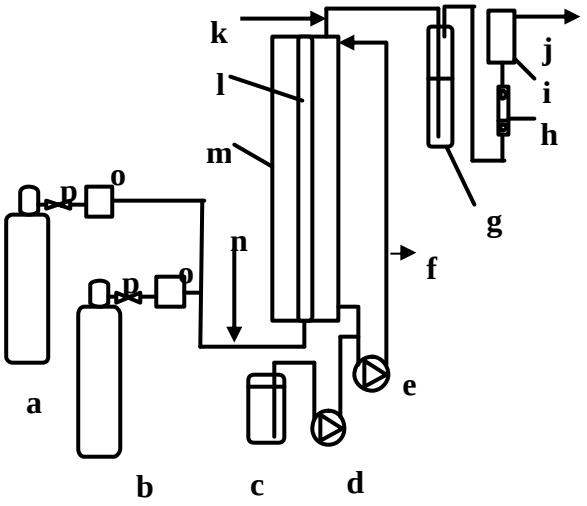

Figure 1.4. Schematic diagram of experimental apparatus.

a) Synthetic air cylinder; b) PCE cylinder; c) H_2O_2 reservoir; d) Peristaltic pump; e) Recirculation pump; f) Liquid sampling port; g) Gas absorption bottle; h) Check flow meter; i) Carbon trap; j) Vent; k) Outlet gas sampling port; l) Quartz tube with UV lamp; m) Stainless steel UV-bubble column reactor; n) Inlet gas sampling port; o) Flow meters; p) Pressure reducing valve.

The major goal of this study was to first design a novel type AOP reactor that will improve the efficiency of the UV/H_2O_2 process via the reduction of OH radical scavengers and UV absorbers. This was achieved by constructing a UV-bubble column reactor (UV-BCR) in which the pollutant in the gas phase (after air stripping or soil vapor extraction) could be absorbed into the radical scavenger and UV absorber-free environment where it could undergo oxidation. Later, the performance of the UV-BCR was analyzed and predictions were made based on chemical engineering and photochemical principles coupled with mathematical modeling.

1.6 STRUCTURE OF THE THESIS

This chapter provided a brief review of the AOPs, differences between conventional and photochemical reactors and problems associated with the modeling of the later ones due to the additional complication that arises from the application of the UV light as a reaction promoter. Further on, in **Chapter 2**, the detailed study on the determination of the incident photon flow rate and energy absorption in a homogeneous and heterogeneous medium, with its consequences on the degradation rate of H_2O_2 and OH radical production is given. **Chapter 3** deals with the mechanistic aspects of reactions of PCE with OH radicals. Effects of pH, T, initial concentrations on the reaction rate and the deactivation of the rate with the accumulation of the end product – chloride are discussed. Mass transfer characteristics of UV-BCR and parameters affecting it are given in **Chapter 4.** Due to the complicated nature and cross dependent parameters, the operational region of the UV-BCR was evaluated using the statistical approach, Optimal Design Methodology and Response Surfaces in **Chapter 5.** Design equation, based on the absorption with chemical reaction theory in combination with photo-principles is proposed in **Chapter 6**, together with the discussion on the optimization of the UV-BCR.