A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions

Parag R. Gogate*, Aniruddha B. Pandit

Chemical Engineering Section, M.U.I.C.T., Matunga, Mumbai 400019, India

Abstract

Nowadays, due to the increasing presence of molecules, refractory to the microorganisms in the wastewater streams, the conventional biological methods cannot be used for complete treatment of the effluent and hence, introduction of newer technologies to degrade these refractory molecules into smaller molecules, which can be further oxidized by biological methods, has become imperative. The present work aims at highlighting five different oxidation processes operating at ambient conditions viz. cavitation, photocatalytic oxidation, Fenton's chemistry (belonging to the class of advanced oxidation processes) and ozonation, use of hydrogen peroxide (belonging to the class of chemical oxidation technologies). The work highlights the basics of these individual processes including the optimum operating parameters and the reactor design aspects with a complete overview of the various applications to wastewater treatment in the recent years. In the next article of this two article series on imperative technologies, hybrid methods (basically combination of the oxidation processes) will be discussed and the current work forms a useful foundation for the work focusing on hybrid technologies.
© 2003 Elsevier Ltd. All rights reserved.

Keywords: Wastewater treatment; Cavitation; Photocatalysis; Ozonation; Hydrogen peroxide; Fenton's chemistry; Optimum treatment conditions

1. Introduction

New developments in the variety of fields to meet the ever-increasing requirements of human beings have also led to the presence of new compounds in the effluent streams of processing plants, which are not readily degraded by the conventional effluent treatment methods (Bauer and Fallmann, 1997; Mantzavinos et al., 1997; Otal et al. 1997; Feigelson et al., 2000). The focus on waste minimization and water conservation in recent years has also resulted in the production of concentrated or toxic residues. It is of utmost importance to dispose off these residues in a proper manner as well as to keep the concentration of chemicals in the effluent

stream to a certain minimum level in order to comply with the environmental laws, which are becoming more stringent these days. Thus, research into new or more efficient waste water treatment technologies so as to degrade the complex refractory molecules into simpler molecules is vital to combat the deteriorating water quality. It should be noted that some of these newly developed technologies, e.g. cavitation may be more efficient on the laboratory scale and the knowledge required for the scale-up of the same and efficient large-scale operation is lacking (Adewuyi, 2001; Gogate, 2002; Mason, 2000). Hence, it may happen that the new technologies have to be used only as a pretreatment stage followed by the conventional biological oxidation techniques. In this series of articles on the imperative technologies for the wastewater treatment, we have tried to concentrate on the oxidation technologies (operating at ambient conditions) operating both individually as

*Corresponding author. Tel.: +91-22-414-5616; fax: +91-22-414-5614.

E-mail address: abp@udct.ernet.in (P.R. Gogate).

well as in synergism with each other generally described as the hybrid technologies. In the present work, the oxidation technologies operating at ambient conditions individually will be discussed while in the next article hybrid techniques will be discussed. It should also be noted that there are other oxidation technologies as well, such as hydrothermal oxidation processes (further classified as wet air oxidation, sub-critical, critical and super-critical water oxidation processes) applied to variety of model pollutants as well as actual wastewaters, but are not discussed in the present work as these technologies are viable for highly concentrated effluents (COD load > 40 000 ppm) to think in terms of return (energy recovery) or investment (high pressure equipments) and it is imperative to develop oxidation technologies operating at ambient conditions, which can also be easily monitored without sophisticated instrumentation for high temperature/high pressure operation. The oxidation technologies discussed in the present work can be classified as advanced oxidation processes (Cavitation, Photocatalytic oxidation and Fenton's chemistry) and chemical oxidation (use of ozone and hydrogen peroxide) and these processes have the potential to degrade the new toxic chemicals, bio-refractory compounds, pesticides, etc. either partially or fully, but most importantly under ambient conditions.

Advanced oxidation processes are defined as the processes that generate hydroxyl radicals in sufficient quantities to be able to oxidize majority of the complex chemicals present in the effluent water. These processes include cavitation (generated either by means of ultrasonic irradiation or using constrictions such as valves, orifice, venturi, etc. in the hydraulic devices (Adewuyi, 2001; Gogate, 2002; Gogate and Pandit, 2001; Gonze et al., 1999; Keil and Swamy, 1999; Pandit and Moholkar, 1996; Moholkar et al., 1999a; Senthilkumar and Pandit, 1999), photocatalytic oxidation (using ultraviolet radiation/near UV light/Sun light in the presence of semiconductor catalyst (Bhatkhande et al., 2002; Blake, 1997; Herrmann, 1999; Yawalkar et al., 2001) and Fenton chemistry (using reaction between Fe ions and hydrogen peroxide, i.e. Fenton's reagent (Venkatadri and Peters, 1993; Bigda, 1995, 1996; Nesheiwat and Swanson, 2000). Hydroxyl radicals are powerful oxidizing reagents with an oxidation potential of 2.33 V and exhibits faster rates of oxidation reactions as compared to that using conventional oxidants like hydrogen peroxide or $KMnO_4$ (Gogate et al., 2002a). Hydroxyl radicals react with most organic and many inorganic solutes with high rate constants (Glaze et al., 1992; von Sonntag, 1996; Hoigne, 1997).

Chemical oxidation technologies constitute the use of oxidizing agents such as ozone and hydrogen peroxide, but exhibit lower rates of degradation as compared to the processes based on the free radicals (Echigo et al., 1996; Weavers et al., 1998; Freese et al., 1999; Fung et

al., 2000a; Zwinter and Krimmel, 2000; Arslan and Balcioglu, 2001a; Gogate et al., 2002a). Moreover, additional mass transfer resistances between the pollutant and the oxidizing agents generally hamper the overall efficacy of the process especially for the ozonation process. Free radicals are generated when ozone is used in combination with hydrogen peroxide or action of ozone or hydrogen peroxide is supplemented by other energy dissipating components such as use of UV/sun light or ultrasound and these hybrid techniques have been found to result in lower treatment times as compared to any of the individual techniques (Weavers et al., 2000; Fung et al., 2000a; Gogate et al., 2002a) though the cost/energy efficiency will be dependent on the operating conditions and the type of the effluent. The discussion about the hybrid techniques will be presented in details in the next article.

Majority of these oxidation technologies, however, fail to degrade the complex compounds completely, especially in the case of real wastewaters and moreover, cannot be used for processing the large volumes of waste generated with the present level of knowledge about these reactors (e.g. Commenges et al. (2000) have shown that cavitation has failed to give substantial degradation in the case of real industrial effluent, whereas similar results have been reported by Beltran et al. (1997) for the case of photocatalytic oxidation being applied to distillery and tomato wastewaters). Hence, these can be used to degrade the complex residue up to a certain level of toxicity beyond which the conventional methods can be successfully used for further degradation (Rachwal et al., 1992; Beltran et al. 1999a,b; Engwall et al., 1999; Kitis et al., 1999; Mastin et al., 2001). It should also be noted that the efficacy of conventional methods would also depend on the level of toxicity reached in the pretreatment stages, using the oxidation techniques. Thus, it is important to select proper pretreatment technique to improve the overall efficiency of the wastewater treatment unit. In this work, the above-mentioned five oxidation techniques have been discussed, also highlighting the work required for transferring the efficient laboratory scale technique to large-scale operations.

2. 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 (Lorimer and Mason, 1987; Mason and Lorimer, 1988; Suslick, 1990; Shah et al., 1999). It should also be noted that though the release of energy is over very small pocket, cavitation events occur at multiple locations in the reactor simultaneously (some indication about the number of cavities existing in the reactor at a
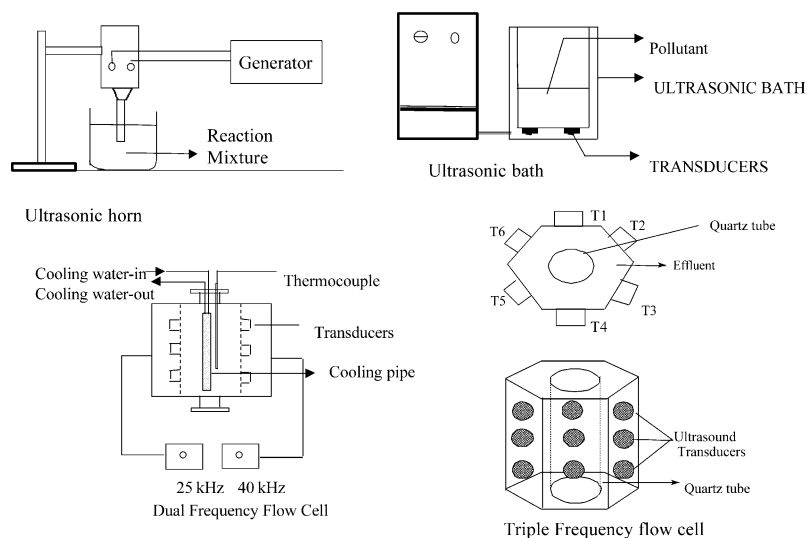
Fig. 1. Schematic representation of the equipments based on acoustic cavitations.

given time can be obtained using theoretical modelling of bubble dynamic equations as shown by Naidu et al. (1994) though it is extremely difficult to quantify the exact number of cavitation events using experiments) and hence the overall effects are spectacular. Some of the important effects of cavitation can be given as 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, enhancement in the mass transfer rates due to turbulence generated as a result of acoustic streaming etc. (Miller, 1950; Suslick 1990; Suslick et al., 1986; Pestman et al., 1994; Shah et al., 1999; Pandit and Moholkar, 1996; Thompson and Doraiswamy, 1999; Adewuyi, 2001). Cavitation is classified into four types based on the mode of generation viz. Acoustic, Hydrodynamic, Optic and Particle, but only acoustic and hydrodynamic cavitation has been found to be efficient in bringing about the desired chemical changes whereas optic and particle cavitation are typically used for single bubble cavitation, which fails to induce chemical change in the bulk solution.

The destruction/oxidation of pollutants using cavitation is usually described by two approaches viz. free radical attack (Nagata et al., 2000) has reported a substantial decrease in the rates of degradation of chlorophenols in the presence of radical scavengers and confirmed the involvement of free radicals in the overall destruction process) and pyrolysis (Kang and Hoffmann, 1998) have reported that destruction of MTBE follows the pyrolysis route and therefore, no decrease in the rates of degradation is observed in the presence of radical scavengers). The controlling mechanism for the destruction is usually dependent 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. There have been a number of illustrations in the literature, dealing with the mechanisms of oxidation of different pollutants using cavitation including some review articles (Adewuyi, 2001; Dewulf et al., 2001; Hoffmann et al., 1996; Hung and Hoffmann, 1999; Weavers et al., 2000; Sivakumar et al., 2002; Shah et al., 1999; Suslick and Hammerton, 1986; Suslick et al., 1990).

2.1. 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 (Suslick, 1990; Lorimer and Mason, 1987; Shah et al., 1999).

2.1.1. Reactors used for the generation of acoustic cavitation

Fig. 1 gives the schematic representation of the commonly used equipments based on acoustic cavitation. The detailed discussion about the different types of sonochemical reactors has been made earlier (Pandit and Moholkar, 1996; Shah et al. 1999; Thompson and Doraiswamy, 1999; Keil and Swamy, 1999; Gogate et al., 2001a, 2002b). Typically, the equipments with higher dissipation area give larger energy efficiency at

similar levels of the supplied input energy (more amount of energy of the total supplied electrical energy is converted for positive effects (Gogate et al., 2001a, 2002b)). Also, use of equipments based on multiple frequencies/multiple transducers (device used for converting supplied electrical energy into sound energy and generate ultrasound with frequency in the range of 15 kHz–10 MHz) has been reported to be more beneficial as compared to the equipments based on a single frequency (Hua et al., 1995a; Thoma et al., 1997; Sivakumar et al., 2002; Gogate et al., 2001a, 2002b). Ultrasonic horns vibrating in radial directions, which also gives additional advantage of better energy dissipation due to larger irradiating area (Dahlem et al., 1998, 1999), is another new development with promising future for medium to large-scale applications, but more work is required in terms of testing these equipments for operation at high frequency and high power dissipation.

2.1.2. Optimum operating parameters for sonochemical reactors

The optimum considerations for operating and geometric parameters of the sonochemical reactors can be given as:

1. Higher frequencies of operation are suited for effective destruction of pollutants (until an optimum value (Hua and Hoffmann, 1997; Hung and Hoffmann, 1999) and the magnitude of optimum frequency also depends on the type of the effluent and the operating conditions), however, it is difficult to operate at higher frequencies greater than 200 kHz (Mason, 1992; Berlan and Mason, 1992). It should also be noted that there are few illustrations where higher frequencies are used for the destruction of pollutants (Petrier et al., 1992, 1996; Francony and Petrier, 1996; Petrier and Francony, 1997a,b; Hua and Hoffmann, 1997; Hung and Hoffmann, 1999), but the scale of operation is typically in the range of 50–500 ml and hence the scale-up ratio will be substantially high, indicating the uncertainty in the design of reactors. Continuous operation with high frequencies at larger scale of operation (and hence at higher power dissipation levels), leads to an erosion of the transducer surface (due to lower collapse time of the cavitating bubbles (Hung and Hoffmann, 1999) as well as more number of cavitational events (Crum, 1995) at higher frequencies of operation, there is a likelihood of higher erosion rates of the transducer surface as compared to that obtained at lower frequency of irradiation), which makes it practically unfeasible to operate sonochemical reactors under these conditions. Moreover, the power required for the onset of cavitation increases with an increase in the frequency of irradiation and hence the process

may become uneconomical at much higher frequencies of irradiation (Mason, 1990) due to the fact that significant quantity of the supplied energy will be used only in the generation of the cavities. Use of multiple frequencies (using multiple transducers irradiating multiple frequencies; Sivakumar et al. (2002) have described a design where 6 transducers in total have been attached on the opposite faces of a rectangular cross-section irradiating 25 and 40 kHz either individually or simultaneously) produces more intense cavitation (Tatake and Pandit, 2002) as indicated by the higher values of the pressure pulse generated at the end of cavitation event for the multiple frequency operation as compared to the single frequency operation and hence results in higher yields of transformation (Sivakumar et al., 2002). Thus, dual or triple frequency reactors should be used which will also give similar results to a single very high frequency transducer, but with minimal problems of erosion (Moholkar et al., 1999b), Moholkar and Warmoeskerken (2000) have also indicated that by adjusting the magnitude of the frequency in the multiple frequency operation, the collapse of the cavities can be directed at a region away from the surface, so that the erosion of the transducer surface will be less). Also, larger volumes of effluent can be effectively treated due to increased cavitationally active volume for multiple transducers (Sivakumar et al., 2002; Gogate et al., 2002b).

2. Greater energy efficiency has been observed for ultrasonic probes with higher irradiating surface, (lower operating intensity of irradiation) which results into uniform dissipation of energy (Gogate et al., 2001a). Thus, for the same power density (power input into the system per unit volume of the effluent to be treated), power input to the system should be through larger areas of irradiating surface.

3. The physicochemical properties of the liquid medium (vapor pressure, surface tension, viscosity, presence of impurities/gases etc.) also crucially affect the performance of the sonochemical reactors. The initial size of the nuclei generated, cavitations inception and number of cavities produced depends mainly on these liquid properties. Cavitation inception can be defined as the minimum power required for the onset of cavitation process, i.e. formation of the cavities and this should be as lower as possible so that the effective energy available for the growth of the cavities is larger (the total supplied energy is utilized for generation of cavitation referred as cavitational inception and for growth of cavity followed by subsequent collapse) leading to a higher collapse pressure pulse (Mason, 1990; Gogate and Pandit, 2000a). The cumulative pressure/temperature pulse generated as a result of cavitation is the product of pulse generated due to the collapse of single cavity

(lower initial cavity size results in higher collapse pressure/temperature pulse (Gogate and Pandit, 2000a)) multiplied by the number of cavities generated in the reactor. It is hence advisable to have large number of cavitation events occurring in the reactor with lower initial size of the cavitating nuclei. Thus, the liquid phase physicochemical properties should be adjusted in such a way so as to lower the cavitation inception threshold resulting in easy generation of cavities and at the same time increasing the number of cavities generated with lower initial size. The effect of various physicochemical properties has been discussed in detail in some of our earlier works (Gogate, 2002; Gogate et al., 2001b).

4. The rate constant for the sonochemical degradation of the pollutants is higher at lower initial concentration of the pollutant and hence pre-treatment of the waste stream may be done in terms of diluting the stream for enhanced cavitational effects. However, an analysis must be done comparing the positive effects due to decreased concentration and the negative effects associated with lower power density to treat larger quantity of pollutant (extent of degradation is directly proportional to power density up to an optimum value (Sivakumar and Pandit, 2001)).

5. Aeration and addition of catalyst such as TiO_2, $NiSO_4$, CCl_4, Fe^{2+}/Fe^{3+}, $CuSO_4$ and also salts such as NaCl, significantly enhances the extent of degradation (Ingale and Mahajani, 1995; Mason et al., 1996; Seymore and Gupta, 1997; Shirgaonkar and Pandit, 1997; Hung and Hoffmann, 1998; Nagata et al., 2000; Pandit et al., 2001; Sivakumar et al., 2002; Gogate et al., 2002c). Presence of gases (oxygen, ozone) or gaseous mixtures such as Ar/O_3 mixture also increases the efficiency of acoustic cavitation in some cases (Hart and Henglein, 1985; Olson and Barbier, 1994; Entezari et al., 1997; Weavers et al., 1998, 2000). It should be noted that it is difficult to generalize and optimize the effect of the presence of gases and/or catalyst, as the effect is usually not unidirectional. On the one hand, where the presence of catalyst enhances the number of cavitation events by providing additional nuclei, it also acts as a barrier for the propagation of sound wave thereby decreasing the effective energy dissipation into the system. Thus, optima of catalyst concentration may be obtained depending on the system under investigation (Gogate et al., 2002a). It may also happen, however, that not all sonochemical reactions are enhanced by the presence of catalyst and hence for a particular application, laboratory scale experiments are required unless data are available in the literature with the specified catalyst. Similarly, for the case of presence of gases, the observed effect depends on the solubility, thermal conductivity, polytropic index of the gas and hence the optimal conditions will strongly be dependent on

the system in question. More detailed discussion about the effect of presence of the catalyst/gases on the cavitation events have also been given in the next paper of the series.

6. Rate of the destruction is inversely proportional to the operating temperature, which also affects the vapor pressure of the medium, and hence lower temperatures (typically of the order of 10–15 °C) will be preferred (Suslick et al., 1997; Sivakumar et al., 2002). However, if the dominant mechanism of destruction is pyrolysis, e.g. destruction of tri-chloroethylene (Drijvers et al., 1999), this will not be true.

Mason and Cordemans, (1998) have also given the following 10 recommendations/steps in the optimization of an ultrasonic process.

1. Make cavitation easier by the addition of solids or gas bubbles to act as nuclei.
2. Try entraining different gases or mixture of gases.
3. Try different solvents for different temperature ranges and cavitation energies.
4. Optimize the power required for the reaction.
5. When using a solid–liquid system, do not charge all the components in the reactor at once.
6. If possible, try to homogenize two-phase systems as much as possible.
7. Try different shapes (diameters and volumes) for the reactor.
8. It can be better (but not always) to avoid standing wave conditions by performing sonochemical reactions under high power conditions with mechanical stirring.
9. Try to transform a batch system into a continuous one, wherever possible.
10. Choose conditions, which allow comparisons between different sonochemical reactions.

2.1.3. Overview of work done in recent years and scope for future work

The use of sonochemical reactors for the wastewater applications is not new to the researchers and there are many illustrations in the literature (Nagata et al., 1996; Thoma et al., 1998; Petrier et al., 1998; David et al., 1998; Gondrexon et al., 1999; Cyr et al., 1999; Suri et al., 1999; Colussi et al., 1999; Joseph et al., 2000; Destaillats et al., 2000, 2001; Grieser et al., 2000; Yim et al., 2000; Tauber et al., 2000; Clark et al., 2000; Schramm and Hua, 2001; Teo et al., 2001; Gaddam and Cheung, 2001; Pandit et al., 2001; Yim et al., 2001) where they have been successfully used for the degradation of variety of compounds at different scales of operation. It should be noted that these illustrations are only very few of the vast amount of literature available on this subject, with studies varying in terms of target chemical studied, type of the equipment and operating

conditions. Table 1 depicts some of the representative applications of sonochemical reactors to the waste water treatment illustrating the type of equipment used with the scale of operation, the chemicals used in the study and the important findings of the work. It can be seen from the table that majority of the work is on a laboratory scale and 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, before successful application of sonochemical reactors are feasible at an industrial scale.

It is also important to stress at this juncture that almost all the studies are with model pollutants and may or may not give similar degradation rates when applied to real effluents containing a variety of compounds. Recently, Peters (2001) has tried to tackle this situation. Peters (2001) has studied the sonolytic degradation of 1,2-dichloroethane, prepared in deionized water (model constituent solution) and also in the natural sample (concentration of approx. 350–390 µg/l with other VOC amounting to 80–85 µg/l), reporting that the destruction was complete within 120 min for all the components (at conditions of operating frequency of 361 kHz, calorimetric power dissipation of 52 W, volume of effluent as 200 ml, operating pH of 6.28 and temperature of 9 °C) and also for some of the intermediates formed in the destruction process (e.g. trans-1,2-dichloroethane). However, in another recent work, Commenges et al. (2000) have reported that ultrasonic irradiation failed to induce any decrease in the toxicity and COD for a concentrated sample of the effluent from a paper mill (at operating conditions of operating frequency as 500 kHz, calorimetric power dissipation as 150 kW/m^3 and operating temperature as 20 °C). This may be possibly attributed to the high concentration of the complex refractory materials. Dilution of the stream resulted in approximately 17% COD reduction; still sonication is not a favored method for these type of effluents. Thus, question still remains; can the highly efficient laboratory scale technique for model constituent solutions be feasible for the degradation of real effluents? The detailed analysis, with recommendations for the future work for transferring the well established laboratory scale technique to industrial scale has been presented in the earlier work (Gogate, 2002). Future work should also be directed in terms of understanding the detailed role of following water parameters in determining the efficiency of cavitation process as a technique for the treatment of real effluents, containing 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.

Further, it is also important to consider the cost of applying ultrasonic irradiation for the destruction process on an industrial scale. The current costs for the cleaning of contaminated ground water using acoustic cavitations are in the order of magnitude, higher than those by an air stripping/active carbon process (Peters, 2001). Thus, it is important to either find an alternative means for generating cavitation energy efficiently or use acoustic cavitation (generated by ultrasonic irradiation) in combination of other methods such as photocatalytic oxidation (Shirgaonkar and Pandit, 1998; Gogate et al., 2002a), wet air oxidation (Ingale and Mahajani, 1995; Dhale and Mahajani, 1999, 2001) etc. Another gray area in the prospective use of acoustic cavitation for large-scale wastewater treatment is the problems associated with high frequency transducers arising out of the mechanical constraints from the construction of transducers (the maximum transfer efficiency is only obtained when the transducer is driven at resonating frequency and for high frequencies, it is difficult to obtain proper material of construction for the transducers). Also, the threshold intensity required is substantially large for the higher frequencies resulting in higher power consumption and most importantly, it is very difficult to operate efficiently at conditions of high frequencies and high-energy dissipation. It should also be noted that due to higher frequency of operation, higher number of free radicals will indeed be generated, but at the same time lower collapse time of the cavitating bubbles gives lesser contact time for the chemical constituents (Hung and Hoffmann, 1999) and also the other drawbacks as discussed earlier nullify the advantage of the higher rates of free radical generation. One of the alternatives for high frequency transducers is the use of multiple frequency/multiple transducer reactors with lower individual frequency of irradiation (problems of erosion, higher cavitational inception will not be there), which has been reported to give much better results in terms of the energy efficiency as well as the cavitational yields (net chemical change per unit supplied electrical energy) as discussed in detail in the earlier sections.

2.2. Hydrodynamic cavitation

One of the alternative techniques for the generation of cavitation is the use of hydraulic devices where cavitation is generated by the passage of the liquid through a constriction such as valve, orifice plate, venturi etc. (Gogate and Pandit, 2001).

2.2.1. Reactors used for generation of hydrodynamic cavitation

Fig. 2 shows some of the equipments used for the generation of hydrodynamic cavitation. The cavitation

Table 1
Some representative illustrations about use of ultrasonic irradiation for wastewater treatment

Sr. no.	Reference	Type of equipment and experimental details	Highlights of the work
1	Bhatnagar and Cheung (1994)	Ultrasonic horn type of reactor with operating frequency of 20 kHz and power dissipation into the solution of 190 W. Temperature is maintained in the range 20–25 °C. Capacity of the reactor is 2 l. Pollutant studied: Aqueous solutions of methylene chloride, chloroform, carbon tetrachloride, 1,2-di-chloroethane, 1,1,1-trichloroethane, trichloroethylene and per-chloroethylene	First order degradation kinetics was observed for all the chemicals and rate constants for each component have been given. Rate constant is inversely proportional to the vapor pressure of the constituent; a result similar to the effect of temperature on sonochemical reaction rates. pH of solution continuously decreases due to the formation of HCl during the sonication process
2	Price et al. (1994)	Ultrasonic horn system operating at irradiation frequency of 22 kHz and intensity of irradiation in the range 11–40 W/cm^2. Capacity of reactor 500 ml, operating temperature of 20 °C. Pollutant studied: 1,4-dichlorobenzene, chlorobenzene, naphthalene, Anthracene, pyrene	Dichlorobenzne can be degraded completely in approximately 40–50 min of reaction time at power intensity of 39 W/cm^2. Use of higher intensity leads to faster reaction rates over the complete range of intensity studied in the work. First order kinetics was observed and rate constant values have been given for different compounds
3	Catallo and Junk (1995)	Ultrasonic horn type system (no information regarding operating frequency and power dissipation) with continuous sparging of Argon, capacity of the reactor: 50–1000 ml. Operating temperature in the range of 4–12 °C. Chemicals studied: Chlorpyrifos, 2-chlorobiphenyl, 2,4,8- trichlorodibenzofuran, lindane, hexachlorobenzene, aldrin and complex mixture of chlorinated olefins, paraffins and aromatics (real life situation)	The work concentrates mainly in identifying the dechlorination products and the other intermediates and different possible schemes for the degradation have been presented
4	Francony and Petrier (1996)	Cylindrical jacketed reactor with power dissipation of 30 W and ultrasonic irradiation at 20 and 500 kHz. Operating temperature of 25 °C and capacity of 200 ml. Pollutant studied: carbon tetrachloride	Rate of disappearance is more for 500 kHz as compared to 20 kHz (almost double time is required for complete disappearance at 20 kHz operation). Detailed mechanism and the different reaction products have been identified. Addition of 1-butanol does not change the rates of degradation indicating that free radicals are not formed during the reaction and pyrolysis is the controlling mechanism
5	Yoo et al. (1997)	Sonochemical reactor with multiwave generator and barium titanate oscillator operating at 200 kHz and power dissipation of 6 W/cm^2 per unit volume. Capacity of the reactor is 150 ml and operating temperature	Pseudo first order kinetics with the order of the rate of degradation as propionic acid $<n$-butyric acid$<n$-valeric acid. The order of n-valeric acid degradation rates is nitrogen $<$air$<$argon. Degradation is suppressed by the

Table 1 (*Continued*)

Sr. no.	Reference	Type of equipment and experimental details	Highlights of the work
		is 20±2 °C. Operation with sparging different gases viz nitrogen, air and argon. Pollutant studied: propionic acid, *n*-butyric acid, *n*-valeric acid	addition of radical scavengers (*t*-butanol). Reaction is 80% due to the free radical formation and 20% due to pyrolysis. Rate constant increases with a decrease in the pH of the solution. For the mixture of three acids, reduced rates of degradation has been observed. TOC reduction is less as compared to the rate of *n*-valeric acid removal indicating that it is not completely mineralized
6	David et al. (1998)	Branson sonifier 450 generator with titanium probe system operating at 20 kHz and power input into the system of 20 W. Another system with high frequency irradiation at 482 kHz and same power dissipation. Operating temperature of 20 °C and capacity of 100 ml. Pollutant studied: Chlorpropham and 3-chloroaniline	The treatment at high frequency is much more efficient (approx. 3 times initial rates of degradation). Kinetics of formation of different products has been presented. For 3-chloroaniline the degradation rates for 482 kHz were approximately 8 times more as compared to the lower frequency operation. Kinetics for the main sonoproducts at 482 kHz has been given
7	Gonze et al. (1999)	Bath type reactor with transducer fitted at the bottom of tank (driving frequency of 500 kHz, variable power input in the range, 0–100 W), reactor capacity: 1000 ml. Pollutant studied: Sodium pentachlorophenate	Review of earlier work for destruction of chlorinated aliphatic and aromatics in terms of reaction mechanism and intermediates formed have been presented. First order kinetics for degradation with higher rate constant at more power input, toxicity analysis for different bacterias have been presented showing conclusively that ultrasonic irradiation can be used as pretreatment for biological oxidation
8	Weavers et al. (2000)	Different reactor systems, orthoreactor ultrasonic transducer (capacity of 640 ml, intensity 1.89 W/cm^2) operating at 515 kHz and direct immersion system (capacity of 50 ml, intensity 55.8 W/cm^2) and tube resonator (capacity of 1750 ml, intensity 1.24 W/cm^2) both operating at 20 kHz. Pollutant studied: Pentachlorophenol	Rate constants for degradation under different conditions of irradiation have been given and also as a function of initial concentration of pollutant. Rate increases with an increase in frequency, power density and decrease in initial concentration of pollutant. Sonication coupled with ozonation was found to be favorable at lower frequencies only. Reaction mechanism has been discussed with the analysis of the intermediates
9	Nagata et al. (2000)	A multiwave ultrasonic generator operating at 200 kHz frequency with a power input of 200 W. Capacity of the reactor: 150 ml. Pollutant studied: 2-, 3-, 4-chloro-phenol (CP) and pentachlorophenol	First order decay kinetics was observed with complete degradation in approximately 1 h in the presence of argon; rate of degradation faster in presence of Argon as compared to air. Decomposition rates for 3 CP more as

Table 1 (*Continued*)

Sr. no.	Reference	Type of equipment and experimental details	Highlights of the work
			compared to 2 and 4 due to favorable alignment for attack of free radicals. *t*-BuOH acts as a radical scavenger thereby decreasing the rates of degradation. Detailed analysis of the reaction mechanism and sites has been given considering degradation of chlorophenol. Optimum amount of Fe^{++} enhances the rate of reaction by about two times
10	Gogate et al. (2001a)	Ultrasonic horn with driving frequency of 22.7 kHz and power rating of 600 W, capacity of 100 ml and Ultrasonic bath (frequency of 22 kHz and power rating of 120 W), capacity of 750 ml; Dual frequency flow cell (frequency of 25 and 40 kHz, power input of 120 W per side), capacity: 1500 ml; Triple frequency flow cell (frequency of 20, 30 and 50 kHz operating in multiple combinations, power input of 150 W per side), capacity: 7000 ml. Pollutant used: Formic acid	Existence of equilibrium or limiting concentration up to which degradation can be achieved effectively using ultrasound. Reaction rate increases with same power dissipation over a wider area, increase in the frequency of irradiation and by the use of multiple frequencies. Aeration results in enhanced rates. Novel reactors with an aim of increasing the turbulence, cavitational intensity and zone of influence of the transducers have been depicted
11	Dewulf et al. (2001)	Undatim reactor with operating frequency of 520 kHz and power dissipation of 9.4 W, capacity of 200 ml, operating conditions of 30 °C temperature and pH of 7, Micromolar concentrations of effluents. Chemicals studied: trichloroethylene (TCE) and chlorobenzene (CB)	Reaction rate increases with decrease in the initial concentration for both TCE and CB. Mixture of two pollutants slightly decreases the rate constants. Model has been developed for predicting rates of degradation considering free radical attack in combination with pyrolysis as the two simultaneous mechanisms. At concentrations above 1000 μM, pyrolysis is the dominant mechanism whereas at lower concentrations 1–5 μM, radical mechanisms also plays a crucial role
12	Peters (2001)	Experiments with different irradiation frequencies in the range 20–1086 kHz with sample volumes of 200–500 ml. Pollutant studied: Samples of ground water with majority component as 1,2-dichloroethane	Chloride yield increases with increase in the frequency of irradiation (in the range 20–618 kHz), increase in the power input to the system and decrease in initial concentration of pollutant. Mixture of chloro-compounds

Table 1 *(Continued)*

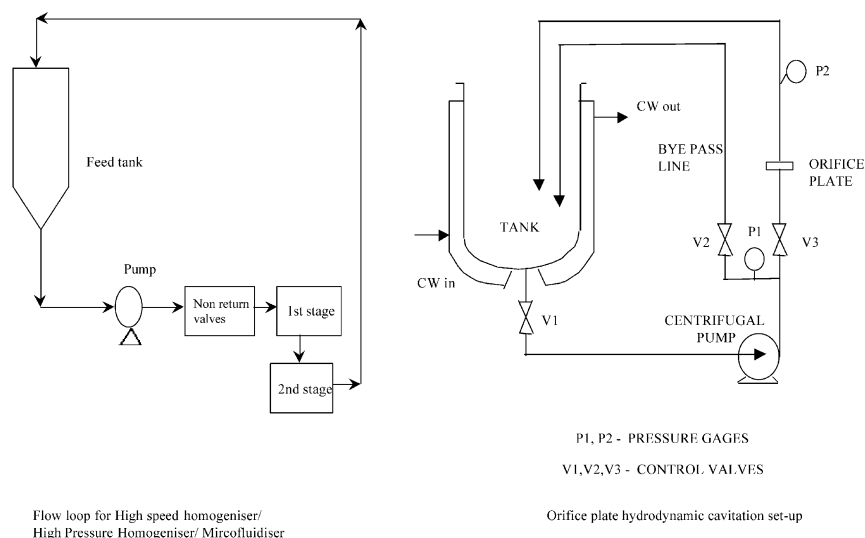| Sr. no.	Reference	Type of equipment and experimental details	Highlights of the work
		(350–390 mg/l) and other VOC amounting to 80–85 mg/l.	also gets degraded under sonication within 60–120 min time. Degradation for natural wastewater follows different path as compared to pure solutions and associated problems (in terms of role of inorganic components and gases, water components, precipitates and particles etc.) have been discussed

Fig. 2. Schematic representation of the equipments based on hydrodynamic cavitations.

intensities generated in the hydrodynamic cavitation reactors are lower as compared to the acoustic counterparts, and the design of the reactors in terms of the operating and geometric conditions must be critically done in order to suit a particular application. Orifice plate set-up (Gogate et al., 2001a; Gogate and Pandit, 2001) offers more flexibility in terms of selection of the different orifice plate configurations (differing in number and diameter of holes (Gogate, 2002)) as compared to devices based on the use of throttling valves.

2.2.2. Optimum operating conditions

The optimization should be done in terms of the inlet pressure into the system, geometry of the constriction used for the generation of cavitation and physicochemical properties of the liquid medium. Some of the important considerations in this regard can be given as follows (Vichare et al., 2000; Senthilkumar et al., 2000; Gogate and Pandit, 2000b, 2001; Gogate, 2002):

1. *Inlet pressure into the system/Rotor speed depending on the type of equipment:* Use increased pressures or rotor speed, but avoid supercavitation by operating beyond a certain optimum value (Vichare et al. 2000; Shirgaonkar, 1997).
2. *Physicochemical properties of the liquid and initial radius of the nuclei*: The guidelines for selecting the physicochemical properties so as to achieve lower initial sizes of the nuclei are similar to those used for the acoustic cavitation.
3. *Diameter of the constriction used for generation of cavities, e.g. hole on the orifice plate*: Optimization needs to carried out depending on the application.

Higher diameters are recommended for applications which require intense cavitation, e.g. degradation of complex chemicals such as Rhodamine B (Sivakumar and Pandit, 2002) whereas lower diameters with large number of holes should be selected for applications with reduced intensity, e.g. KI decomposition (Vichare et al., 2000).

4. *Percentage free area offered for the flow (Ratio of the free area available for the flow, i.e. cross-sectional area of holes on the orifice plate to the total cross-sectional area of the pipe):* Lower free areas must be used for producing high intensities of cavitation and hence the desired beneficial effects (Vichare et al., 2000; Gogate and Pandit, 2000b).

2.2.3. Overview of work done in recent years and scope for future work

It should be noted that there are not many reports depicting the use of these equipments for wastewater treatment (Table 2), but these offer higher energy efficiencies, more flexibility and higher potential for scale-up as compared to their acoustic counterparts (Gogate et al., 2001a). Recently, Sivakumar and Pandit (2002) have used orifice plate hydrodynamic cavitation set-up for degradation of rhodamine B and reported that the cavitational yields are higher as compared to all the sonochemical equipments (ultrasonic horn, ultrasonic bath, dual frequency flow cell) used in their study. Kalumuck and Chahine (2000) have studied the destruction of *p*-nitrophenol in re-circulating flow loops using a variety of cavitating jet configurations and operating conditions and have shown that, indeed, hydrodynamic cavitation degraded *p*-Nitrophenol. Submerged cavitat-

Table 2
Analysis of the work done in the area of application of hydrodynamic cavitation reactors to wastewater treatment

Sr. no.	Reference	Type of equipment and experimental details	Main features of the work
1	Suslick et al. (1997)	Micro jet fluidizers operating at conditions of 1.24 kbar liquid inlet pressure and velocities of 190 m/s. The reaction solution is first sparged with high purity argon or Ar/He mixtures and light protected to prevent CCl$_4$ photodecomposition and then injected into the pressurized reservoir through a self sealing septum. A portion of the reaction solution is pressurized by a large pneumatically driven pump into an interaction chamber, where two pulsed flows are redirected at each other through jewel orifices with velocities of 190 m/s controlled by a back pressure regulator. Cavitation occurs when there is sufficient turbulence upon the liquid jet impact or a sufficient pressure drop is created as the stream passes through the orifices. High velocity pumping results into heating of the liquid medium and hence the reactor along with the accessories is immersed in a thermally equilibrated bath. Pollutant studied: Potassium iodide	The cavitation inception was obtained at inlet pressure of 150 bar indicated by significant release of iodine. The reaction rate further increases linearly with an increase in the upstream liquid pressure over the range of 200–1500 bar as studied in the work. Iodine liberation also increases with decrease in the thermal conductivity of the dissolved gases at constant specific heat ratio. The result can be attributed to the principles of hot-spot theory, which suggest that the maximum temperature reached in collapsing bubbles increases with a decrease in the thermal conductivity. Further the rate of iodine liberation was also found to increase with a decrease in the temperature of liquid bulk due to lower vapor pressures and hence operation at lower temperatures is favored
2	Kalumuck and Chahine (2000)	Closed loop circuit with contaminant pumped with a triplex positive displacement pump (4.5 gal/min and 1000 psi pressure). Multiple orifice plates in the re-circulation line one after another in order to produce intense cavitation. Capacity of the reactor: 6.5 l operated in re-circulating mode. Pollutant studied: *p*-Nitrophenol	Cavitating jet set-up gives approximately 20 times more rates of degradation as compared to the ultrasonic horn (irradiating frequency of 15.7 kHz and power density of 0.36 W/ml) and the oxidation efficiency (mg degraded per unit energy supplied) is almost 25 times more for the cavitating jets. Optimum operating temperature was found to be 42 °C. Lower pH and cavitation number (higher inlet pressure at same pressure drop across the nozzle) favors the degradation
3	Sivakumar and Pandit (2001)[*]	The set-up consists of a closed loop circuit comprising of a holding tank of 50 l volume, a centrifugal pump (2900 rpm, 5.5 kW, Calama Industries Ltd, India), control valve and flanges to accommodate the orifice plates. Liquid is pumped from the storage	For same flow area, plate with larger number of small diameter holes gives more extent of degradation as compared with plate with smaller number of larger diameter holes. The observed results have been explained on the basis of frequency of turbulence for the two

Table 2 *(Continued)*

Sr. no.	Reference	Type of equipment and experimental details	Main features of the work
		tank and is re-circulated through a main line housing the orifice plates. The cavitating conditions are generated just after the orifice plates in the main line. Different orifice plates with different free areas for flow and also different combinations of number of holes and diameter of hole for same free area have been used. The holding tank is provided with cooling jacket to control the temperature of the circulating liquid. Pollutant studied: Rhodamine B (a typical component of dyes industry effluent)	cases. The present set-up of hydrodynamic cavitation using multiple hole orifice plates has been found to give cavitational yields, which are two times higher than the best acoustic cavitation device (Dual frequency flow cell with capacity of 1.5 l) as discussed earlier. Moreover, the capacity of the reactor in the present case (50 l) is also 33 times higher as compared to the largest ultrasonic equipment tested indicating easier scaleup options

[*] Vichare et al. (2000) have also obtained similar results with experimentation in the same set-up but with the model reaction of decomposition of potassium iodide.

Table 3
Comparison of different cavitational reactors using a model reaction (Gogate et al. 2001a)

Equipment		Supplied electrical power consumption (W)	Volume used (ml)	Energy efficiency (%)	Cavitational yield per unit power density g/(J/ml)
Dakshin horn[a]		240	50	3.04	3.53 E-9
Dakshin bath[a]		120	500	38.86	5.83 E-7
Ace horn[a]	10%	40	50	15.43	1.39 E-9
	20%	80	50	16.77	5.25 E-9
	30%	120	50	15.9	5.48 E-9
Flow cell[a]	25 kHz	120	1500	43.05	6.21 E-7
	40 kHz	120	1500	26.97	5.85 E-7
	25 + 40 kHz	240	1500	33	9.12 E-7
High pressure homogenizer (5000 psi)[b]		2090	2000	54.4	7.38 E-5
High speed homogenizer[b]		105	1500	43.07	6.645 E-7
Pilot plant scale (Orifice plates)[b]	% free area = 2.28%	5500	50 000	59.58	2.48 E-4
	% free area = 9.14%	5500	50 000	60.8	1.90 E-4

[a] Equipment based on acoustic cavitation.
[b] Equipment based on hydrodynamic cavitation.

ing liquid jets were found to generate a two-order of magnitude increase in energy, the efficiency compared to the ultrasonic horn.

Table 3 shows the energy efficiency and cavitational yield for different reactors for the model reaction of decomposition of KI. It can be seen from the table that the desired chemical change for a given amount of electrical energy supplied to the system as well as the energy efficiency (ratio of the energy transferred into the system to the supplied electrical energy) is higher for the hydrodynamic cavitation reactors. It should be, however, noted that the comparison made here is valid only for a model reaction (decomposition of potassium iodide), and the efficiencies of the various equipments may or may not be the same for the variety of cavitation based transformations and also other applications.

Though hydrodynamic cavitation offers immense potential and also higher energy efficiency and cavitational yields as compared to acoustic counterpart at least for the model reaction, use of these reactors is perhaps lacking on larger scales. There exists only one commercial process (using hydrodynamic cavitation, though not alone but in combination with UV irradiation and oxidation with hydrogen peroxide), known as CAV-OX®, 1994 process, developed by Magnum Water Technology Inc., California. Several contaminants of concern such as pentachlorophenol (PCP), benzene, toluene, ethyl benzene, xylenes, cyanide, phenol, 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.

More work is indeed required both on theoretical front as well as on the experimental front for better understanding of the phenomena and subsequent design methodology. The important issues that need to be studied are as follows:

1. Realistic modelling of the turbulence phenomena, which can then be used to model the cavity/bubble dynamics, either in isolation or in the form of cavity clusters in high velocity flow. The modern sophisticated Computational fluid dynamics (CFD) codes can be employed to get the flow field information, i.e. mean and fluctuating velocity components, Reynolds stresses, turbulent pressure fluctuations etc. This then can be used to understand the role of these flow field parameters in altering the cavity dynamics.
2. It is necessary to develop user-friendly computer codes (similar to modern CFD codes) for the use of engineers, which will allow them to change the geometrical and operating parameters of the hydrodynamic cavitation set-up, define physico–chemical properties of the chemical system under consideration. These codes, with the help of bubble/cavity dynamics and the equilibrium chemistry at cavity collapse conditions, will then predict the expected chemical effects avoiding trial and error type of experimentation for the engineers.
3. Design and fabrication of different types of hydrodynamic cavitation set-up differing in the flow field, turbulence characteristics and geometry, which will allow efficient large-scale operation for effective usage in wastewater treatment plants.
4. Laboratory and pilot plant studies with simulated waste to understand and address the scale-up issues,

such as alteration in the flow field and turbulence characteristics due to the scale of operation.

Overall it can be said that, cavitation offers a potential alternative for the degradation of chemicals in the wastewater treatment scheme where majority of the conventional techniques fail to give substantial conversions. However, majority of the studies available in this area are on a small scale and hence much of the work needs to be done before this dream is realized.

3. Photocatalysis

The photocatalytic or photochemical degradation 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 are good reviews available on this subject by Fox and Duley (1993), Legrini et al. (1993), Kamat (1993) and Hoffmann et al. (1995) covering the analysis of the studies prior to 1995 and depicting basics of the processes including the mechanism of oxidation of pollutants in detail. Some of the more recent promising works include Blake (1997), Herrmann (1999) and Bhatkhande et al. (2002).

The photo-activated chemical reactions are characterized by a free radical mechanism initiated by the interaction of photons of a proper energy level with the molecules of chemical species present in the solution, with or without the presence of the catalyst. The radicals can be easily produced using UV radiation by the homogenous photochemical degradation of oxidizing compounds like hydrogen peroxide and ozone. An alternative way to obtain free radicals is the photocatalytic mechanism occurring at the surface of semiconductors (like titanium dioxide) and this indeed substantially enhances the rate of generation of free radicals and hence the rates of degradation (Mazzarino et al., 1999). A major advantage of the photocatalytic oxidation based processes are the possibility to effectively use sunlight or near UV light (Bauer, 1994; Peill and Hoffmann, 1997; Bauer and Fallmann, 1997; Guillard et al., 1999; Dillert et al., 1999; Fallmann et al., 1999; Herrmann et al., 1999; Vidal et al., 1999; Yawalkar et al., 2001) for irradiation, which should result in considerable economic savings especially for large-scale operations.

Various chalcogenides (oxides such as TiO_2, ZnO, ZrO_2, CeO_2 etc. or sulfides such as CdS, ZnS etc.) have been used as photo-catalysts so far in different studies reported in the literature (Davis and Huang, 1990; Richard and Boule, 1994; Choi and Hoffmann, 1997; Chen and Ray, 1998; Chen et al., 1999b; Tanaka et al., 2000; Sakthivel et al., 2000; Andreozzi et al., 2000; Habibi et al., 2001a,b). The surface area and the number of active sites offered by the catalyst (thus nature of catalyst, i.e. crystalline or amorphous is important) for

the adsorption of pollutants plays an important role in deciding the overall rates of degradation as usually the adsorption step is the rate controlling (Xu et al., 1999). It should be noted that the best photocatalytic performances with maximum quantum yields have been always with titania. In addition, Degussa P-25 catalyst is the most active form (hybrid mixture of rutile (approx. 70%) and anatase forms) among the various ones available and generally gives better degradation efficiencies, (Sakthivel et al., 2000; Yamazaki et al., 2001) though in some cases pure anatase based forms of TiO_2 such as Hombikat, PC-500 have also been reported to be more efficient (Lindner et al., 1997; Ray and Beenackers, 1997; Chen and Ray, 1998). Also, the photocatalytic activity of titanium dioxide can be enhanced by using pretreatment with sulfuric acid (Yu et al., 2002) or by increasing the cation strength, e.g. doping with platinum (Hufschmidt et al., 2002; Li et al., 2002; Lia and Li., 2002).

3.1. Reactors used for photocatalytic oxidation

The photocatalytic process can be 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 ($HO_2^{\bullet}$ radicals are formed in the valence bonds) 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 (Mazzarino et al., 1999). However, in the case of slurry reactors, the performance of the 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 small sizes of the catalyst particles (usually below 1 μm). A further problem is the fouling of the surface of the radiation source due to the decomposition of the catalyst particles. Thus, the application of slurry reactors for the photocatalytic treatment on large-scale seems to be quite problematic at the present time.

An alternative to the use of catalyst in the suspended form is the use of supported photocatalyst. The key advantages are the possibility to obtain an active crystalline structure and stability of the catalyst layer in the reacting media. Films obtained by wash coating using a suspension of commercial products with a well-known photocatalytic activity satisfies the first possibility, but can be very sensitive to erosion by the flowing liquid. Durable supported films can be obtained by different
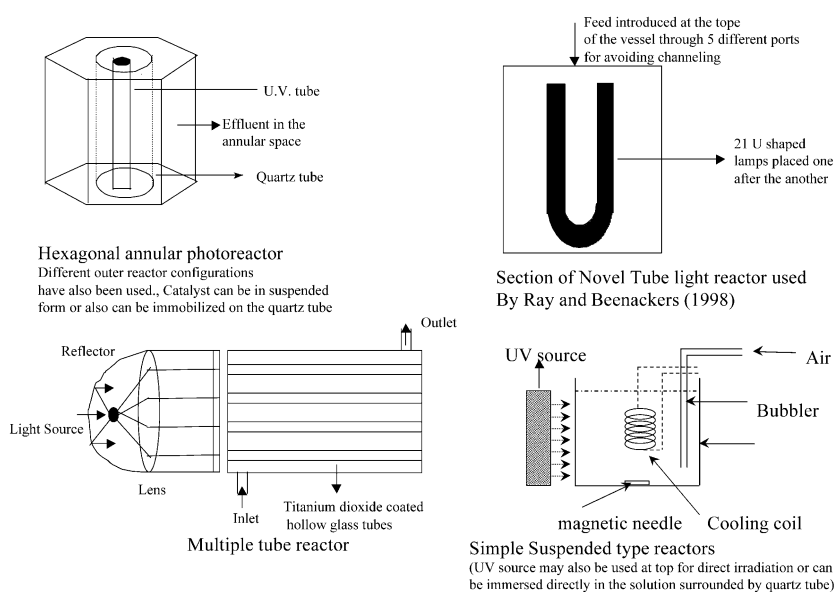
Fig. 3. Schematic representation of equipments based on photocatalytic oxidation.

techniques like physical and chemical vapor deposition, but in this case the crystalline structure of the final product and consequently the catalytic activity might be difficult to control. Thermal treatment at 500 °C can be used to increase the extent of crystalline nature of the catalyst obtained by physical or chemical vapor deposition. Scouring is another problem associated with films comprising immobilized powders of TiO_2 (Bideau et al., 1995) and reduced catalyst area to volume ratio of the immobilized photocatalyst is likely to cause mass transfer problems. Butterfield et al. (1997) have reported a modified fabrication technique and design of the reactor in order to eliminate scouring. Here, oxide is actually grown on a titanium substrate as a defect film (a film that is electronically conducting even in dark), which also allows application of electric field with a view of enhancement in the extent of degradation. The batch reactor used in their work has been reported to remove 100% of *E. coli* and 2 log units of *Cl. perfringens* spores in 25 min whereas only at approximately 20–30% disinfection was observed for UV light and UV light + photocatalyst. However, this exploratory work needs to be tested on a large-scale and more importantly for the degradation of complex chemicals before firm recommendations can be made.

Overall, the immobilized or supported catalytic reactors offer many advantages; most important being the supported catalyst is not allowed to mix with the fluid avoiding the requirement of ultrafine particle separation. Various devices have been developed such as TiO_2 coated tubular photoreactor, annular and spiral photoreactors, falling-film photoreactors and two commercial

scale versions are also available (Matrix photocatalytic Inc, Ontario Canada and Purifies Environmental Technologies Inc., London, Ont. Canada). 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. Some of the equipments used for carrying out photocatalytic oxidation have been represented in Fig. 3.

3.2. Optimum operating parameters

Based on the detailed and critical analysis of the existing literature on the photocatalytic oxidation of the contaminants (some of the illustrative works have been depicted in Table 4), the important operating parameters, which affect the overall destruction efficiency of the photocatalytic oxidation process, can be given as follows:

1. *Amount and type of the catalyst*: Use catalyst concentration only till an optimum value (Kulkarni, 1998; Andreozzi et al., 2000; Sakthivel et al., 2000; Dijkstra et al., 2001; Gogate et al., 2002a), as using excess catalyst reduces the amount of photo-energy being transferred in the medium due to opacity offered by the catalyst particles. It should also be noted that the optimum value will strongly be dependent on the type and concentration of the pollutant, as well as the rate of generation of free radicals (decided by the operating conditions of the reactor) and laboratory scale experiments are required to decide the optimum value unless data are available

Table 4
Typical findings observed in the representative works related to photocatalytic destruction of effluents

Sr. no.	Reference	Type of equipment and experimental details	Important findings of the work
1	Beltran et al. (1997)	Annular glass photoreactor with capacity of 850 ml irradiated by 15 W low-pressure mercury vapor UV lamp. Pollutant studied: Distillery wastewaters (COD range of 750–3000) and Tomato wastewaters (COD range of 250–960)	Distillery wastes are completely refractory toward UV irradiation whereas in presence of hydrogen peroxide, degradation is observed only at diluted conditions (38% reduction in 2 h at COD of 850 mg/l whereas nil for COD of 3000 mg/l). For tomato wastewaters, higher initial COD gives higher degradation, but the rate decreases with progressing time due to the formation of UV radiation absorbing intermediates. The rates of degradation are much lower with only 18% reduction in 2 h
2	Ray and Beenackers (1997)	Novel swirl flow reactor operating in continuous mode consisting of two glass plates placed between soft padding housed within SS and aluminium casings. Catalyst can be deposited on either plates and effluent is introduced tangentially between two plates, which creates a swirl flow minimizing the mass transfer resistance. Phillips high-pressure mercury lamp with power of 125 W is used with intensity of 213 W/m^2. Degussa P-25, and Hombikat UV 100 immobilised on a UV transparent material is used as photocatalyst. Pollutant studied: SBB dye	Mass transfer coefficient increases with increase in the flowrate (α Re$^{0.62}$). If catalyst is kept at the bottom plate, significant reduction in the rates of degradation is observed due to absorption of the UV light by the liquid. 90° angle of incidence gives maximum rate of degradation. Increase in light intensity increases the degradation significantly till 50 W/m^2 beyond which the increase is marginal. Optimum catalyst concentration is found to be 0.003 kg/m^2. Hombikat UV 100 gives more extent of degradation as compared to Degussa P-25 possibly due to the lower particle size
3	Kulkarni (1998)	Kettle type reactor with capacity of 500 ml stirred continuously with magnetic stirrer. A parabolic reflector was used to concentrate the sunlight. Degussa P-25 TiO$_2$ with BET surface area of 50 m^2/g was used as the photocatalyst. Pollutant studied: Distillery waste with TOC of 3.52%	The degradation process is almost complete within two hours of reaction time and followed first order kinetics. No appreciable reaction takes place without aeration. Increase in the radiation intensity increases the extent of degradation almost linearly. Optimum catalyst concentration was found to be 500 ppm
4	Chen and Ray (1998)	Swirl flow reactor irradiated with 125 W high-pressure mercury vapor lamp. 0.2 wt.% powder photocatalyst TiO$_2$ of Degussa P-25 or Hombikat UV-100 grade was suspended. Pollutant studied: 4-nitrophenol	Reaction mechanism has been proposed. No degradation for individual TiO$_2$ or UV light but illuminated TiO$_2$ gives significant rates (Complete destruction within 100 min). Optimum TiO$_2$ loading is found to be 3 gm/l. Rate constant increases with decrease in the initial concentration of the pollutant. The exponent over incident intensity is found to be 0.84 (between 1 for catalyst controlling and 0.5 for mass transfer controlling) indicating that catalyst and mass transfer resistance are both contributing. Rate constant increases with an increase in the temperature

Table 4 (Continued)

Sr. no.	Reference	Type of equipment and experimental details	Important findings of the work
			and also with oxygen partial pressure (however, 70% of the maximum rate is observed at 0.2 atm pressure indicating that air may be used in commercial applications). Maximum rate is observed at pH equal to the pZc point of TiO_2 catalyst. In the presence of chloride ions, substantial decrease in rates is observed due to competitive adsorption on TiO_2 surface. Hombikat UV-100 is more active as compared to Degussa P-25
5	Mazzarino et al. (1999)	Two different reactor configurations with tubular configuration having an axial cylindrical lamp and an annular free space for movement of liquid. One is operated in batch recycle mode (catalyst in suspended form) with capacity of 1000 ml and power input of 15 W whereas continuous single pass reactor (supported photocatalyst) is with capacity of 2721 ml and power input of 40 W. Photocatalyst is Degussa P-25 titania. Pollutant studied: Glycolic acid	Biphasic flow (simultaneous flow of air and effluent) gives more degradation efficiency as compared to monophasic flow (effluent saturated with air). Increased turbulence due to gas bubble decreases the mass transfer resistance thus indicating that transfer of reactants towards the catalyst surface is the rate-controlling step. Also, oxygen prevents recombination of electron-vacancy pairs. First order kinetics has been observed. Decrease in TOC is significantly slower than the removal of acid. Presence of hydrogen peroxide increases the rate of degradation by approximately 2 times (for photochemical process but marginal effect in the presence of catalyst). For slurry reactors, optimum catalyst concentration is observed to be 100 ppm. For monophasic flow, slurry reactor is slightly efficient but for the biphasic flow supported bed continuous reactor gives approximately 3 times faster rate as compared to the slurry reactor
6	Xu et al. (1999)	Pyrex glass container of capacity 850 ml with annular irradiation with a mercury lamp (300 W). Temperature maintained at 25 °C using cooling water circulation and initial pH of 6. TiO_2 with catalyst loading of 0.588 mg/ml with different grades viz anatase, amorphous and particle size in the range 12 nm to 49 μm. Pollutant studied: Methylene blue (MB)	Significant adsorption of methylene blue on TiO_2 (saturation adsorbability in the range of 0.36–3.6 mg/g of TiO_2) and it increases with a decrease in the size of TiO_2 particle. Amorphous grade TiO_2 exhibits very poor catalytic activity. Presence of catalyst enhances MB degradation and it further increases with a decrease in the size of catalyst particle. Dramatic increase in the rate is observed below particle size of 30 nm. Correlation for kinetic rate constant and half life in terms of the diameter of particle has been given. TiO_2 suspended photocatalytic reaction is concluded to be more appropriate as compared to fixed bed type due to avoidance of preparation of ultrafine particles; still the

Table 4 (*Continued*)

Sr. no.	Reference	Type of equipment and experimental details	Important findings of the work
			problem of separation needs to be solved
7	Vohra and Davies (2000)	500 ml three mouth round bottom reactor irradiated by UV light lamp (two tubes of 15 W each, 365 nm peak wavelength), Photocatalyst used is TiO_2 with a loading of 2 g/l. Pollutant studied: Lead-EDTA in stoichiometric and non-stoichiometric ratios	Lead-EDTA complex was completely removed in approximately 60–90 min time depending on the conditions. Faster reaction with less intermediate buildup was observed for low concentrations of lead-EDTA. At lower pH free lead ions remain in the solution, providing more sites for the production of OH and hence more is the extent of degradation. Initial reaction products are strongly adsorbed at higher pH and continuous light irradiation leads to the release of the adsorbed complex
8	Tanaka et al. (2000)	Anatase grade TiO_2 catalyst with loading of 3 g/l. 25 ml of dye solution in pyrex glass cell irradiated with 500 W superhigh pressure mercury lamp. Pollutant studied: Orange G, Acid Orange 7, New coccine, Acid black 1, Tartrazine, Acid yellow 17, Congo red	Lower pH favored the degradation of the Acid Orange 7 dye (decrease from pH of 6.1 to 2 increased the degradation by 21%). Approximately 75% removal is achieved in 60–240 min of treatment time (monoazo dyes are more degradable as compared to diazo compounds). Lower concentration of acid orange dye gives higher rates of degradation. Adsorption of dye on TiO_2 is one of the important factors in determining the extent of degradation
9	Andreozzi et al. (2000)	170 ml semi-batch annual reactor equipped with 125 W high-pressure mercury lamp. TiO_2 catalyst with particle size of <70 μm. Operating pH at 3 and 8.5. Pollutant studied: 4-nitrophenol	The degradation rate is higher at pH 3 as compared to pH of 8.5, increases with an increase in the catalyst loading upto an optimum value of 4 g/dm^3 beyond which it decreases. Experimental data aimed at validation of the kinetic models reported for the photocatalytic degradation.
10	Lea and Adesina (2001)	1.25 dm^3 capacity photoreactor irradiated with UV lamp enclosed in quartz U tube at power dissipation in the range 200–400 W. Photocatalyst used is titania. Pollutant studied: *p*-nitrophenol	Optimum rate was observed with respect to initial concentration of photocatalyst (0.5 mol/dm^3), catalyst loading (1 gm/dm^3) and oxygen partial pressure (between 80 and 85%). Rate increases with an increase in the incident intensity and also marginally with temperature. Mechanism for the degradation process has been proposed
11	Dijkstra et al. (2001)	124 ml capacity double wall tubular reactor of borosilicate glass irradiated with 15 W, UV lamp operated in recirculating manner at temperature of 20 °C. Degussa P-25 with particle size of 30 nm is used as photocatalyst. Pollutant studied: formic acid	Immobilized systems described in the work gives same degradation efficiency as the suspended system and hence is recommended due to avoidance of separation step. Packed bed reactor (catalyst supported on glass beads) is more beneficial as compared to tubular reactor (catalyst film on the outer wall using dip-coating) as mass transfer limitations are eliminated. Optimum concentration of

Table 4 (*Continued*)

Sr. no.	Reference	Type of equipment and experimental details	Important findings of the work
			TiO_2 estimated at 2 kg/m^3 for the suspended system. In the tubular reactor, rate of degradation increases with an increase in the Reynolds number and also by continuous bubbling of O_2 in the reactor (attributed to elimination of mass transfer limitations). In the packed bed reactor, Reynolds number has no effect on the extent of degradation indicating that there are no mass transfer limitations. Optimum value of catalyst loading estimated at 0.46 g for packed bed. Large beads give more degradation

in the existing literature, most importantly with similar operating conditions. Degussa P-25 TiO_2 catalyst is the most beneficial (Sakthivel et al., 2000; Yamazaki et al., 2001). Sensitizers or catalysts, e.g. ferrous ions, silver ions, manganese ions etc. can also be used to improve the treatment efficiency of photocatalytic oxidation process (Sclafani et al., 1991; Lee et al., 1993; Feigelson et al., 2000; Chen et al., 1999c; Lu, 1994).

2. *Reactor design*: Usually reactor designs should be such that uniform irradiation of the entire catalyst surface is achieved at the incident light intensity. This is a major problem associated with the large-scale designs (Mukherjee and Ray, 1999). Moreover, near complete elimination of mass transfer resistances is another point that needs to be considered while designing large-scale reactors. The efficient reactor design must expose highest amount of the activated immobilized catalyst to the illuminated surface and must have a high density of active catalyst in contact with the liquid to be treated inside the reactor. The pioneering work done by a group of Ray is worth to mention in this area (Ray and Beenackers, 1996; Ray, 1997; Ray and Beenackers, 1997; Chen and Ray, 1998; Mukherjee and Ray, 1999; Ray, 1999).

3. *Wavelength of the irradiation*: The threshold wavelength corresponds to the band gap energy for the semiconductor catalyst, e.g. for the TiO_2 catalyst having a band gap energy of 3.02 eV, the ideal wavelength is at 400 nm (Herrmann, 1999). Sunlight may also be used for the excitation of the catalyst in some cases as discussed earlier and results in considerable economic savings (Bauer, 1994; Yawalkar et al., 2001).

4. *Initial concentration of the reactant*: For highly concentrated effluents, absolutely no destruction may be observed and dilution is essential in this case (Herrmann (1999) have reported that no degradation was observed for real effluent with COD of 800 000 mg/kg and had to be diluted 1000 times after which COD reduction was observed). Use lower concentrations of the pollutants (Topalov et al., 1999; Mazzarino and Piccinini, 1999; Vohra and Davies, 2000). To give a quantitative idea about the effect, Beltran et al. (1993a) have shown that the destruction of atrazine is 70% for initial concentration of 10 ppm whereas for 100 ppm, only 45% of the initial atrazine is degraded (other reactor operating conditions are kept the same). It should be kept in mind that the net degradation in terms of number of moles degraded per unit energy supplied may (in the above example, net degradation is 45 ppm for second case as against only 7 ppm for first one) or may not be lower for higher concentrations and also negative effects of enhanced power requirements for treating large quantum of effluent must be analyzed before reaching a firm conclusion about the use of optimum concentration for destruction purpose. It should also be noted here that the Langmuir–Hinshelwood type of models (Topalov et al., 1999; Herrmann, 1999) can be used to relate the observed rates with the initial concentration of the pollutant, but the model parameters will be strongly dependent on the composition of the effluent as well as other reactor operating conditions.

5. *Temperature*: Usually photocatalytic systems are operated at room temperature, but with the release of energy in the destruction process due to recombination of electron-hole pairs, temperature might increase. If the temperature is expected to go beyond 80 °C, intermediate cooling is recommended, as there is a drastic reduction in the rate of reaction above 80 °C. At temperatures above 80 °C, the exothermic adsorption of pollutant becomes unfavorable and tends to be the rate limiting step, leading to a decreased activity and hence reduction in the reaction rates (Herrmann, 1999). In the range of 20–80 °C, usually weak dependence of the degradation rates on temperature has been observed (Zeltner et al., 1993; Fox and Duley, 1993; Hofstadler et al., 1994; Andreozzi et al. 2000).

6. *Radiant flux*: The reaction rate is directly proportional to the intensity of radiation; usually linear variation is observed at low intensities and beyond a certain magnitude of intensity (dependent on the reactor conditions as well as nature of the effluent), rate of the reaction shows a square root dependence on the intensity (Okamoto et al., 1985; Ollis et al., 1991). Lower dependency on the intensity of irradiation is usually attributed to increased contribution of the recombination reaction between the generated holes and electrons when their density is high. Another important factor about the incident light is the wavelength of irradiation. Shorter wavelengths are recommended for better results (Matthews and McEvoy, 1992a; Hofstadler et al., 1994). Moreover, the angle of incidence of the UV light should always be 90° as maximum rates are observed at this angle of incidence (Ray and Beenackers, 1997).

7. *Medium pH*: Medium pH has a complex effect on the rates of photocatalytic oxidation and the observed effect is generally dependent on the type of the pollutant as well as the zero point charge (zPc) of the semiconductor used in the oxidation process, i.e. more specifically on the electrostatic interaction between the catalyst surface and the pollutant. The adsorption of the pollutant and hence the rates of degradation will be maximum near the zPc of the catalyst (Chen and Ray, 1998; Subramanian et al., 2000). For some of the pollutants, which are weakly acidic, rate of photocatalytic oxidation increases at lower pH due to an increase in the extent of adsorp-

tion under acidic conditions (Vohra and Davies, 2000; Tanaka et al., 2000; Andreozzi et al., 2000). Some of the pollutants, which undergo hydrolysis under alkaline conditions or undergo decomposition over a certain pH range, may show an increase in the rate of photocatalytic oxidation with an increase in the pH (Choi and Hoffmann, 1997; Tanaka and Saha, 1994; Trillas et al., 1996). Fox and Duley (1993) and Davis and Huang (1991) and Matthews and McEvoy (1992b) have reported that pH had marginal effect on the extent of degradation over the range of pH studied in their work. Since the effect of pH cannot be generalized, it is recommended that laboratory scale studies are required for establishing the optimum conditions for the operating pH unless data are available in the literatures with exactly similar operating conditions, i.e. type of equipment as well as the range of operating parameters including the composition of the effluent stream.

8. *Aeration*: Presence of electron acceptors is recommended so as to prevent the recombination reaction between the generated positive holes and electrons (Yamazaki et al., 2001). Generally aeration is used for this purpose as it also provides uniform mixing, suspension of the catalyst in the case of slurry reactors and economical source of oxygen. Dijkstra et al. (2001) have shown that there is no appreciable destruction in the absence of oxygen (the other operating conditions have been illustrated in Table 2). Chen and Ray (1998) have shown that approximately 70% of the maximum rates of degradation (using pure oxygen) of 4-nitrophenol are observed at partial pressure of 0.2 atm. Thus, air can safely be used at commercial scale operation instead of pure oxygen, which will substantially decrease the operating costs.

9. *Effect of ionic species*: Presence of ions may affect the degradation process via adsorption of the contaminants; reaction with hydroxyl radical ions and/or absorption of UV light. This is a very important point that needs to be considered as real life industrial effluents will have different types of salts at different levels of concentration and generally these are in ionized forms. There have been many illustrations in the literature (Abdullah et al., 1990; Wei et al., 1990; Kormann et al., 1991; Butler and Davies, 1993; Yawalkar et al., 2001) regarding the effects of various anions and cations. In general it can be said that CO_3^-, HCO_3^- (they act as radical scavengers and also affect the adsorption process) and Cl^- (affect the adsorption step strongly and also absorb UV light partly) ions have strong detrimental effect on the degradation process whereas other anions such as sulfate, phosphate and nitrate affect the degradation efficiency marginally. Yawalkar et al. (2001) have studied the effect of SO_4^-, CO_3^-, Cl^- and HCO_3^- ions on the overall degradation rates and reported that the detrimental effects are observed in the order $SO_4^- < CO_3^- < Cl^- < HCO_3^-$. For cations the results are conflicting, generally on the negative side except for some reports of marginal enhancement due to the presence of Fe^{3+}/Cu^{2+} ions at very low concentrations (Wei et al., 1990; Hua et al., 1995b). More efforts are required in this area before a generalized effect of cations on the phenomena of photocatalytic degradation, can be well established.

3.3. Overview of work done in recent years and scope for future work

Some of the illustrative work done in recent years in the area of photocatalytic oxidation applied to wastewater treatment has been depicted in Table 4 with discussion about reactor operating conditions and the important findings obtained in the work whereas the different chemicals that can be degraded successfully by the use of photocatalytic oxidation have been given in Table 5. It should be noted that the list is by no means exhaustive and covers some of the typical examples from different classes of compounds to give an idea about the efficacy of the photocatalytic oxidation for the use in removal of hazardous compounds from the effluent streams. For a more detailed list, readers are requested to refer to the exhaustive work of Blake (1997).

Again though majority of the academic studies (as outlined in Table 4 and also observed generally in the literature) refer to the use of single-constituent model solutions for the experimentation, the real wastewaters obtained from industries contain a lot of compounds, both organic and inorganic. Thus, it is important to check the interference between two or more reactants, which may also result in the formation of variety of intermediates and always a doubt arises in mind, will photocatalytic oxidation or any of the technology will destruct the typical wastewaters in question with efficiencies observed for single constituent model solutions in the literature? This is especially important as the real wastewaters may also contain some traces of radical scavengers such as HCO_3^-, CO_3^- ions, naturally occurring matter, *t*-butanol and this significantly affects the rates of advanced oxidation processes (Yoo et al., 1997; Nagata et al., 2000). Thus, certain modifications will be required in the overall treatment procedures so as to reduce the inhibiting effects, the effects of the radical scavengers or to bring the level of toxicity below a certain optimum value decided by the reactor operating conditions. It should be noted that the degradation efficiency will still be reduced and hence appropriate correction factors must be included in the design of the reactors based on the information obtained from either the literature or laboratory scale studies (later is rec-

Table 5
List of aqueous organic pollutants mineralized by photocatalysis

Class of organics	Examples	References
Haloalkanes/haloalkenes	Chloroform, trichloroethylene, perchloroethylene, tribromomethane, dichloromethane, CCl$_4$	Tanguay et al. (1989) and Gupta and Tanaka (1995) Choi and Hoffmann (1995, 1997) Chen et al. (1999b)
Aliphatic alcohols	Methanol, ethanol, 1-octanol, 2-propanol	Chen et al. (1999a) and Yamashita et al. (1996) Sauer and Ollis (1996) and Hager and Bauer (1999)
Aliphatic carboxylic acids	Formic, glycolic, citric	Miller et al. (1999) and Herrmann (1999) Mazzarino et al. (1999) and Mazzarino and Piccinini (1999)
Amines	Alkylamines, alkanolamines, heterocyclic and aromatic N-compounds	Klare et al. (1999)
Aromatics	Toulene	Luo and Ollis (1996) and Hager and Bauer (1999)
Haloaromatics	2-chlorobiphenyl	Wang and Hong (1999, 2000)
Phenolic compounds	Phenol	Matthews and McEvoy (1992b) and Trillas et al. (1996) Chen et al. (1999b) and Toyoda et al. (2000) Feitz et al. (2000) and Yawalkar et al. (2001)
Halophenols	2-, 4-chlorophenol, 2,4-dichlorophenol	Pelizzetti et al. (1990a) and Theurich et al. (1996) Serrano and de Lasa (1999) and Ku and Hsieh (1992) Trillas et al. (1996)
Aromatic carboxylic acids	Malic, chlorobenzoic acids, phenoxy acetic acid, 2,4-dichlorophenoxyacetic acid	Trillas et al. (1993, 1996) Dionysiou et al. (2000)
Amides	Benzamide, 4-hydroxybenzamide	Maillard et al. (1992)
Surfactants	Sodium dodecasulfate, polyethylene glycol, sodium dodecyl benzene sulfonate, trimethyl phosphate	Hidaka et al. (1994) and Hidaka (1998)
Herbicides	Atrazine, S-trizine herbicides, bentazone	Pelizzetti et al. (1990a) and Pellizzetti et al., (1990b) Heredia et al. (1996)
Pesticides/fungicides	Fenitrothion, Metalaxyl	Herrmann (1999) and Topalov et al. (1999)
Dyes	Methylene blue, rhodamine B, methyl orange, fluorescein, SBB dye, Reactive Black 5	Ray and Beenackers (1997) and Chen and Chou (1993) Xu et al. (1999) and Poulios and Tsachpinis (1999) Wang (2000), Ray (1999) and Arslan et al. (1999b)
Sulfides	Trimethylene sulfide, propylene sulfide, thiophene, methyl disulfide	Canela et al. (1999)

ommended). Herrmann (1999) has studied the application of photocatalytic oxidation (in a laboratory photoreactor irradiated with near-UV light with power dissipation of 125 W, catalyst used was Degussa P-25 TiO_2, 50 m^2/g surface area and mainly anatase) to the treatment of highly loaded real industrial wastewater containing variety of organic compounds such as caprolactam, benzoic acid, adipic acid, phenol, toluene, benzene, methyl-valero-lactone, methyl-cyclohexenyl-formic acid, 2,4,6 trichlorophenol etc. as well as inorganic compounds such as nitrites, nitrates, iron, chromium, sodium, potassium, calcium etc. The total organic carbon (TOC) of the solution was 113 000 mg/l whereas the chemical oxygen demand (COD) was 800 000 mg/kg. The fetid bad smelling black colored solution initially did not show any degradation with UV irradiation. This was attributed to the fact that the solution was too highly loaded, with respect to the photonic flux used as well as it was too dark for easy irradiation of the catalyst. Thus, some modifications had to be made in the treatment scheme. The solution after dilution by 1000 times and after an initiation period of 1 h (in dark, i.e. UV light irradiation was started after 1 h), showed a decrease in the COD value. In 4 h of total treatment time, the COD value decreased by 95%. This demonstrates that the photocatalytic oxidation can be very efficient with almost complete destruction in a reasonable time (Biological methods requires treatment time of few days) for treating wastewaters and most importantly the illustration considers real wastewaters (complex mixture of pollutants), which should increase the confidence of the potential users. However, Beltran et al. (1997) have shown that the distillery waste (COD in the range of 750–3000 mg/kg) and tomato wastewater (COD in the range 250–960 mg/kg) were both refractory towards UV light (Reactor operating conditions have been depicted in Table 4). Even combination with hydrogen peroxide (rate of free radical generation is substantially increased due to the cleavage of hydrogen peroxide) did not result into substantial rates of degradation such that the overall economics may be feasible. Thus, more efforts are indeed required to assess the use of photocatalytic oxidation for treatment of different wastewater effluents differing in the constituents.

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 in larger range of pH ($0 \leq pH \leq 14$).
- 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 industrial scale operation for wastewater treatment. These have been discussed below along with recommendations for future work required for transferring this successful laboratory scale technique to industrial scale.

- Engineering design and operation strategies are lacking for efficient use of reactors at large-scale operation. The most important problem in designing large-scale reactors lies in the fact that it is almost impossible to achieve uniform irradiation of the entire catalyst surface with same incident intensity. The scale-up is constrained by the phenomena of opacity, light scattering, depth of radiation penetration and local volumetric light absorption. Moreover, the requirement of at least one side to be transparent to UV light significantly poses size limitations along with breakage risks. Future work should be directed in terms of design of reactors achieving uniform irradiation and minimal losses of the incident light due to phenomena of opacity, light scattering, absorption by liquid etc.
- 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. In the case of supported reactors, there can only be a thin coating applied to the surface, limiting the amount of active catalyst in the reactor and hence the overall conversion efficiency will be low. This problem severely restricts the processing capacity of the reactor and the timescales required to achieve high conversions are in hours, if not in days (still attractive as compared to biological methods). Increasing the active surface area of the catalyst irradiated by the UV light can increase the rates and this can be achieved to an extent by modification of the catalyst. Efforts are required for the preparation of novel supported catalysts with high stability in continuous reactors and at the same time also offering greater interfacial area for the reaction.
- 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. Studies are required for testing photocatalytic oxidation reactors for a variety of simulated effluents containing mixture of components and kinetic models should be fitted considering the effect of all the operating parameters as well as the concentration of the critical components affecting the rates such as, radical scavengers, compounds restricting electron-hole recombination etc.

- Fouling of the photocatalyst with continuous use results in lowering the rates of degradation as time progresses. Coupling with ultrasonic irradiation may result in continuous cleaning of the catalyst surface, enhancing the rates of degradation. Such combinatorial techniques have been developed in the past and will be discussed in detail in the future work.

Thus, photocatalytic oxidation appears to be much more developed and well understood as compared to cavitation and also some illustrations are available for large-scale operation (Herrmann, 1999) using naturally occurring resources, i.e. sunlight. Still, for the treatment of complex mixture of effluents with the presence of potential radical scavengers, it appears that large-scale operation with high degree of energy efficiency is not strongly feasible (economics will always be important when wastewater treatment plants are to be designed) due to the number of problems as discussed above. A major problem in the successful application of photocatalytic oxidation is the non-uniform irradiation of the catalyst and this results in a substantial loss of the incident energy and hence the overall economics may not be favourable. Groups of Ray, Beenackers (Ray and Beenackers, 1996, 1997; Ray, 1997, 1999; Mukherjee and Ray, 1999) (Li Puma and Yue, 1998a,b, 1999) have tried to address this problem, but not much success has been reported as yet. Still the efficacy of photocatalytic oxidation cannot be underestimated as there is also large potential for the combination of photocatalytic oxidation with other advanced oxidation processes such as ultrasonic irradiation (Shirgaonkar and Pandit, 1998; Gogate et al., 2002a), addition of hydrogen peroxide (Beltran et al., 1996b; Benitez et al., 1996), Ozonation (Benitez et al., 1996, 1997; Beltran et al., 1999a) and Fenton oxidation (Arslan et al., 1999b; Andreozzi et al., 2001) which will also help in countering some of the above mentioned drawbacks. The details of these hybrid processes will be discussed in the second article of this series on imperative technologies for wastewater treatment.

4. Fenton chemistry

The oxidation system based on the Fenton's reagent (hydrogen peroxide in the presence of a ferrous salt) 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. (Bigda, 1996). 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 (Bossmann et al., 1998; Walling, 1998; MacFaul et al., 1998; Pignatello et al., 1999). In the literature, three main reactive radical species have been contemplated; Two of them involve the presence of hydroxyl radicals (classical Fenton's chemistry) in either 'free' or 'caged' form (Walling and Amarnath, 1982) whereas third oxidant has been postulated to be aquo or organo-complexes of the high valence iron, the ferryl ion (Sawyer et al., 1996). The rate of this reaction should be strongly dependent on the presence of radical scavengers such as *t*-butanol or Cl^- ions, but in some cases substantial decrease has not been observed even at high concentrations of these species (Rahhal and Richter, 1988). This led to some investigations relating to the presence of additional oxidant species using analysis of product distribution, EPR-spin trapping techniques, effect of added substrates as mentioned earlier. It should be noted at this stage that both hydroxyl as well as ferryl complexes coexist in Fenton's mechanism and depending on the operating conditions (substrate nature, metal–peroxide ratio, scavengers addition etc.), one of them will predominate. Nevertheless, the system can be most suitably applicable to discoloration and/or removal of odor ingredients 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 a secondary biological treatment (Chen and Pignatello, 1997). Venkatadri and Peters (1993), Bigda (1995, 1996) and Nesheiwat and Swanson (2000) have written good informative articles on the basics of Fenton chemistry as well as its application to wastewater treatment.

4.1. Typical reactor used for fenton oxidation

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.
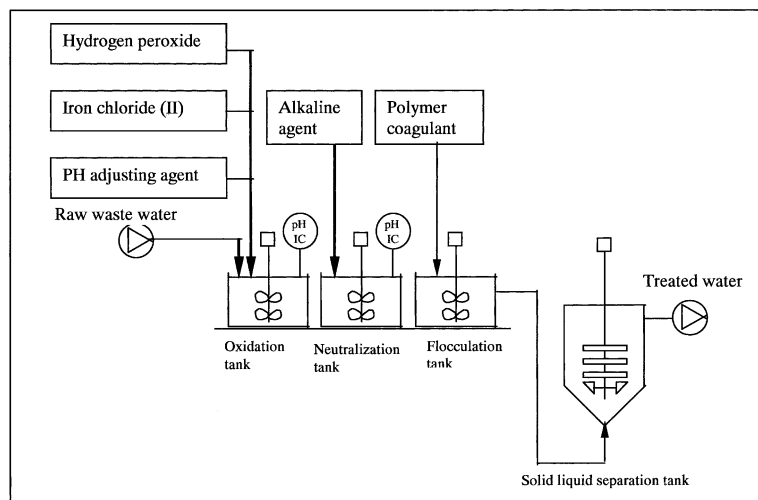
Fig. 4. Treatment flowsheet for Fenton oxidation.

pH of the solution must be adjusted for maintaining the stability of catalyst as at pH value of 6, usually iron hydroxide is formed. For many chemicals, ideal pH for the Fenton reaction is between 3 and 4, and the optimum catalyst to peroxide ratio is usually 1:5 wt/wt. Addition of reactants are 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). As the wastewater compositions are highly changeable, Fenton reactor must need some design considerations to give flexibility in terms of the operating parameters. 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. A schematic representation of the Fenton oxidation treatment has been shown in Fig. 4.

4.2. Optimum operating conditions

An exhaustive analysis of the existing literature on application of Fenton oxidation to wastewater treatment was performed and based on the same; following optimum conditions can be outlined:

1. *Operating pH*: pH of the system has been observed to significantly affect the degradation of pollutants (Sedlak and Andren, 1991; Lin and Lo, 1997; Kang and Hwang, 2000; Nesheiwat and Swanson, 2000; Benitez et al., 2001a). The optimum pH has been observed to be 3 in the majority of the cases (Venkatadri and Peters, 1993; Tang and Huang, 1996; Kwon et al., 1999; Benitez et al., 2001a) and hence

is recommended as the operating pH. At lower pH ($pH < 2.5$), the formation of $(Fe(II) (H_2O))^{2+}$ occurs, which reacts more slowly with hydrogen peroxide and, therefore, produces less amount of reactive hydroxyl radicals thereby reducing the degradation efficiency (Gallard et al., 1998). In addition, the scavenging effect of hydroxyl radicals by hydrogen ions becomes important at a very low pH (Tang and Huang, 1996) and also the reaction of Fe^{3+} with hydrogen peroxide is inhibited (Pignatello, 1992). At operating pH of > 4, the decomposition rate decreases because of the decrease of the free iron species in the solution, probably due to the formation of Fe (II) complexes with the buffer inhibiting the formation of free radicals and also due to the precipitation of ferric oxyhydroxides (Bigda, 1995; Lin and Lo, 1997; Nesheiwat and Swanson, 2000) which inhibit the regeneration of ferrous ions. Also, the oxidation potential of HO˙ radical is known to decrease with an increase in the pH (Kwon et al., 1999).

2. *Amount of Ferrous ions*: Usually the rate of degradation increases with an increase in the concentration of Ferrous ions (Lin and Lo, 1997; Kwon et al., 1999; Benitez et al., 2001a) though the extent of increase is sometimes observed to be marginal above a certain concentration as reported by Lin et al. (1999) and Kang and Hwang (2000) and Rivas et al. (2001). Also, an enormous increase in the Ferrous ions will lead to an increase in the unutilized quantity of iron salts, which will contribute to an increase in the TDS content of the effluent stream and this is not permitted. Thus, laboratory scale studies are required to establish the optimum loading of Ferrous ions under similar conditions unless data are available in the open literature.

3. *Concentration of hydrogen peroxide*: Concentration of hydrogen peroxide plays a more crucial role in deciding the overall efficacy of the degradation process. Usually it has been observed that the percentage degradation of the pollutant increases with an increase in the dosage of hydrogen peroxide (Lin and Peng, 1995; Lin and Lo, 1997; Kwon et al., 1999; Lin et al., 1999; Kang and Hwang, 2000; Rivas et al., 2001). However, care should be taken while selecting the operating oxidant dosage. The residual hydrogen peroxide contributes to COD (Lin and Lo, 1997) and hence excess amount is not recommended. Also, the presence of hydrogen peroxide is harmful to many of the microorganisms (Ito et al., 1998) and will affect the overall degradation efficiency significantly, where Fenton oxidation is used as a pre-treatment to biological oxidation. One more negative effect of hydrogen peroxide, if present in large quantities is that it 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 decided based on the laboratory scale studies with the effluent in question.

4. *Initial concentration of the pollutant*: Usually lower initial concentration of the pollutants are favored (Kwon et al., 1999; Benitez et al., 2001a), but the negative effects of treating large quantity of effluent needs to be analyzed before the dilution ratio can be fixed. For real industrial wastes, many times some dilution is essential before any degradation is observed using Fenton oxidation.

5. *Type of buffer used for pH adjustment*: As said earlier, as the degradation rates are observed to be maximum at pH of approximately 3, operating pH should be maintained constant around the optimum value of 3. It should be noted that the type of the buffer solution that may be used also has the effect on degradation process (Benitez et al., 2001a). They have reported that the acetic acid/acetate buffer gives maximum oxidation efficiency whereas least is observed for phosphate and sulfate buffers. This can be attributed to the formation of stable Fe^{3+} complexes that are formed under these conditions (Pignatello, 1992).

6. *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. In fact, Lin and Lo (1997) have reported an optimum temperature of 30 °C whereas Rivas et al. (2001) reported that the degradation efficiency is unaffected even when the temperature is increased from 10 to 40 °C. If the reaction temperature is expected to rise beyond 40 °C due to exothermic reactions, cooling is recommended as above 40 °C, efficiency of hydrogen peroxide utilization decreases due to accelerated decomposition of hydrogen peroxide into water and oxygen (Nesheiwat and Swanson, 2000). Also, successive addition of hydrogen peroxide can be done, if cooling the effluent stream poses additional problems.

7. *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 (Lin and Lo, 1997). Lin et al. (1999) have also demonstrated the efficacy of chemical coagulation in controlling the concentration of TDS below the specified limits.

4.3. Overview of the earlier work

Table 6 gives some of the illustrative works in the area of application of Fenton oxidation for the degradation of complex chemical compounds. In addition, to these illustrated studies, Fenton's reagent has been effectively used for the remediation of diesel-contaminated soils (Watts and Dilly, 1996), removal of color in effluents from dyes industry (Kuo, 1992; Park et al., 1999), destruction of organics such as 2,4,6-trinitrotoluene (Li et al., 1997a,b), RDX (Hundal et al., 1997), 2,4-dinitrophenol (Wang et al., 1999; Kang et al., 1999b), Chlorobenzene (Watts et al., 1997), tetrachloroethylene (Yoshida et al., 2000), chlorophenols (Barbeni et al., 1987; Watts et al., 1990; Potter and Roth, 1993), halomethanes (Tang and Tassos, 1997). Again these references do not cover the entire spectrum of studies available in this area, but the aim has been to concentrate on recent studies and cover different class of compounds, effectively treated by Fenton's reagent.

It should be noted that 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, it may happen that a certain compound in the waste stream is oxidized to some of the above-mentioned compound, which still acts as a pollutant and may not be allowed to be discharged, e.g. iso-propanol may be oxidized to acetone (Bigda, 1995). Also, as the degree of oxidation produced in the case of Fenton oxidation is limited, i.e. the oxidants dosage cannot be increased beyond certain limits, applicability to treatment of complex mixture of contaminants, i.e. highly loaded effluent streams remain as an unanswered question.

It should again be noted that the importance of Fenton's reagent as an oxidation system cannot be underestimated and the oxidation degree can be substantially increased when this is used in combination with other advanced oxidation technique such as photocatalysis and/or ultrasonic irradiation. Fenton's reagent have been effectively used for the enhancement in rates of degradation of photocatalytic processes (Bauer and Fall-

Table 6
Typical findings observed in the work related to use of Fenton oxidation as wastewater treatment technique

Sr. no.	Reference	Experimental conditions	Important findings
1	Sedlak and Andren (1991)	500 ml capacity Fenton reactor maintained at 25 °C. Operating pH varied in the range 2–7. Addition of Fe^{2+} ions at rate of 5 ml/h or as bulk quantity of 10 ml at the start. Addition of hydrogen peroxide at the rate of 5 mM/h. Pollutant studied: Chlorobenzene	Chlorobenzene and all the intermediate products disappeared within 2 h. Intermediates have been identified using GC/MS analysis. Product distribution is dependent on the presence or absence of oxygen. Reaction pathway has been also proposed. Optimum pH was found to be in the range of 2–3
2	Lin and Lo (1997)	Fenton reactor is a 2 l beaker equipped with variable mixer and cooling jacket for temperature control. Initial concentration of pollutant as 1500 mg/l, operating pH in the range 2–5 and time of treatment as 1 h. Pollutant studied: Effluent containing poly-vinyl alcohol and two dyes as Blue G and Black B	The extent of degradation rapidly decreases above pH of 3. Increase in the $FeSO_4$ concentration keeping the H_2O_2 concentration same, increases the extent of COD removal. Hydrogen peroxide may also interfere in the COD measurements and hence amount of the same should be adjusted such that it is completely utilized. Optimum operating temperature was observed to be 30 °C above which the increase in the COD removal is marginal. Chemical coagulation after Fenton oxidation treatment helps in keeping the concentration of soluble iron within the limits
3	Lin et al. (1999)	Simple stirred reactor with capacity of 2 l. $FeSO_4$ concentration was varied in the range of 30–180 mg/l whereas hydrogen peroxide concentration was in the range 20–80 mg/l. Time of treatment as 3 h. Pollutant studied: Surfactant wastewater containing alkylbenzene sulfonate and linear alkylbenzene sulfonate	Optimum treatment time was calculated based on the variation of residual concentration of hydrogen peroxide in the stream. After a particular time, the concentration starts leveling off. Optimum pH of 3 has been observed. Optimum concentration of $FeSO_4$ and H_2O_2 were obtained as 90 and 60 mg/l, respectively. Subsequent treatment with chemical coagulation is recommended for improving the settling characteristics. Kinetic analysis has also been presented and reaction is reported to be of first order with respect to concentration of reactants where the rate constant is also dependent on the concentration of $FeSO_4$ and H_2O_2
4	Kwon et al. (1999)	4 l capacity reactor agitated at constant rpm of 400. Volume of effluent was fixed at either 3 or 3.5 l. pH was varied in the range of 1–5, Fe^{2+} in the range of 0.1–1 mM and hydrogen peroxide in the range 3–12 mM. Pollutant studied: *p*-Chlorophenol	Optimum operating pH was found to be 3 whereas at lower pH ($=1$) absolutely no degradation has been observed due to the fact that hydroxyl radicals are not generated. First order reaction rate constant linearly increases with the Fe^{2+} concentration. Additional input of ferrous ions after 12 min increases the rate of degradation indicating the ferrous ions are limiting. Rate constant also linearly increased with an increase in the concentration of hydrogen peroxide. Scavenging action of chloride ions was felt only after an optimum concentration of 50 mM at an operating pH of 3

Table 6 (*Continued*)

Sr. no.	Reference	Experimental conditions	Important findings
5	Kitis et al. (1999)	Fenton oxidation was performed in a 500 ml batch reactor with solution volume of 400 ml and initial COD as 1000 mg/l. Reaction temperature was kept constant at 22 °C and pH varied in the range of 3–5. Hydrogen peroxide concentration was 1000 mg/l and H_2O_2/Fe^{2+} molar ratio was kept at unity. Pollutant studied: Effluent containing different compositions of surfactants	Fenton oxidation is essentially complete within 1 min of the oxidant dosing and the decrease in the COD is marginal beyond this time. Similar results were also obtained with oxidation experiments. This has been attributed to rapid utilization of Ferrous ions by hydrogen peroxide. At molar ratio of H_2O_2/Fe^{2+} as greater than 1, decrease in percentage COD removal was observed possibly attributed to the scavenging of the hydroxyl radicals by the excess of hydrogen peroxide. Increase in hydrogen peroxide loading at unit molar ratio with respect to Ferrous ion increased the percentage COD removal though linear variation was not observed. Fenton's oxidation was reported to be effective in enhancing the biodegradability
6	Arslan et al. (1999b)	4000 ml capacity pyrex glass reactor has been used. Ferrous ion concentration was fixed at 0.5 mM whereas hydrogen peroxide concentration was fixed at 5 mM and the operating pH was 2.8 whereas ambient conditions were maintained. Pollutant studied: Dyehouse effluent	The effluent had to be diluted 40 times before measurable degradation occurred. The rate constant for the degradation was estimated at 0.9521 min^{-1} and it was quite higher as compared to hydrogen peroxide/UV combination technique and lower as compared with the photo–Fenton oxidation. Additional UV irradiation to the Fenton oxidation system results in enhanced utilization of hydrogen peroxide (it increased from 39% to 82%) and hence the degradation efficiencies are better. The COD removal was only approximately 25% indicating that Fenton oxidation system alone is not sufficient
7	Kang and Hwang (2000)	2 l capacity Fenton reactor operated at constant temperature of 25 °C and mixed with a magnetic stirrer. pH varied in the range 2–9, $FeSO_4$ dosage in the range of 250–2250 mg/l and hydrogen peroxide dose in the range of 0–1600 mg/l. Pollutant studied: real effluent with COD of approximately 1500 mg/l	The COD removal efficiency was shown to be the maximum around a reaction pH of 3.5 and it drastically decreased above a pH of 6. COD removal efficiency increased with an increase in the $FeSO_4$ dosage (Till a concentration of 500 mg/l beyond which the removal efficiency remains constant) and hydrogen peroxide dosage
8	Benitez et al. (2001a)	500 ml capacity Fenton reactor agitated with the help of a mechanical stirrer. Operating pH as 3 and temperature of 20 °C with Fe^{2+} and H_2O_2 concentration varied in the range 0.25–5 mM and 50–200 μM, respectively. Pollutant studied: *p*-hydroxy phenylacetic acid	Percentage degradation increased with an increase in the concentration of ferrous ions and hydrogen peroxide whereas it decreased with an increase in the initial concentration of pollutant. Optimum pH has been obtained again at 3. Type of the buffer solution used for adjustment of the pH also plays a crucial role in the degradation efficiency. Acetate, phosphate as well as sulfate buffers were found to retard the degradation. Detailed kinetic analysis has been presented

Table 6 (Continued)

Sr. no.	Reference	Experimental conditions	Important findings
9	Chamarro et al. (2001)	Fenton reactor used was 30 ml capacity vials and operated at room temperature. The ferrous ion dose was varied in the range 0.01–1 per unit compound whereas H_2O_2/compound molar ratio was varied in the range 0.1–50. Pollutant studied: Different organic compounds viz formic acid, acetic acid, 4-chlorophenol, 2,4-dichlorophenol and nitrobenzene	Hydrogen peroxide dosage was found to be sufficient at molar ratio of 3 with respect to the organic compound. Extent of mineralization increased with an increase in the concentration of ferrous ions possibly due to enhanced formation of hydroxyl radicals. Optimum molar ratio of Fe to hydrogen peroxide was estimated at 0.1:10. It has been shown that complete mineralization using Fenton oxidation alone requires considerable time as well as very high dosage of the oxidants and hence is recommended only for improving the biodegradability
10	Benitez et al. (2001b)	Reactor filled with 350 ml of effluent with initial concentration as 0.3 mM. Operating temperature was fixed at 25 °C. Initial concentration of ferrous ions and hydrogen peroxide was kept at 0.01 mM and 0.5 mM, respectively. Pollutant studied: Different chlorophenols	Fenton oxidation was found to be not effective in degradation of chlorophenols studied in the work (only 4 chlorophenol showed 55% removal in 80 min of treatment time; rest all viz 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,5-tetra chlorophenol and tetrachlorocatechol showed less than 10% degradation). Kinetic analysis has been presented for 4-chlorophenol and a first order fit is observed
11	Rivas et al. (2001)	Fenton reactor was operated at a constant capacity of 1 l. Ferrous ion concentration was varied in the range of 0–0.01 M whereas hydrogen peroxide concentration was varied in the range of 0–4 M. Operating temperature of 20 °C and pH of 3.2, concentration of pollutant is fixed at 0.01 M. Pollutant studied: p-hydroxybenzoic acid	Increase in the concentration of both ferrous ions as well as hydrogen peroxide led to an increase in the removal of the pollutant, however, an optimum concentration of ferrous ion was observed at 5 mM. Hydrogen peroxide was observed to be completely utilized in the reaction and is the limiting reactant in deciding the overall rates. Increase in pH from 3 to 7 decreased the rates, appreciably. An increase in the operating temperature from 10 to 40 °C showed no change on the extent of degradation. Intermediate products have been identified and mechanism for the destruction of pollutant has been presented along with a detailed kinetic model for the process
12	Arslan and Balcioglu (2001a)	Fenton reactor used has a capacity of 1000 ml made up of borosilicate glass and operated in batch mode for 1 h. The concentration of Fe^{2+} and H_2O_2 was fixed at 0.5 mM and 5 mM, respectively, with operating pH of 3. Pollutant studied: simulated dyebath wastewater	Only hydrogen peroxide gave no degradation indicating that the generation of hydroxyl radical is a must. Fenton oxidation system gave a TOC removal of 80.8% for an initial TOC loading of 200 mg/l with a pseudo-first order rate constant of 0.12 l/min. The rate constant was found to be 100% more as compared to photocatalytic oxidation using near UV light (pH of 4) but slightly less than that of ozonation (pH of 12 and ozone loading of 2340 mg/l). Use of Fe^{3+} ions instead of Fe^{2+} ions reduced the rate constant by approximately 30%
13	Chang et al. (2001)	A 1 ml capacity vial has been used as Fenton reactor	Variation of residual concentration of the pollutant with

Table 6 *(Continued)*

Sr. no.	Reference	Experimental conditions	Important findings
		mixed at varying speed in the range 50–200 rpm. Treatment time was varied in the range 5–60 min, concentration of Ferrous ions and hydrogen peroxide in the range 3.6–14.4 and 5.15–206 mM. Initial concentration of pollutant was fixed at 100 mg/kg. Pollutant studied: Phenanthrene	time indicated that the chemical reaction in the initial period were rapid and reached equilibrium degradation within 20 min (up to 70% removal depending on the ferrous ion concentrations). The optimum conditions as obtained in the work can be given as ferrous solution concentration of 7.2 mM, hydrogen peroxide concentration of 103 mM and mixing speed of 150 rpm. With respect to the pollutant concentration the optimum conditions can be given as molar ratio of phenanthrene: ferrous: hydrogen peroxide = 1:7:97

mann, 1997; Maletzky and Bauer, 1998; Bauer, 1999; Krutzler and Bauer, 1999; Maletzky et al., 1999; Fallmann et al., 1999; Arslan et al., 1999b; Yoon et al., 2000), most importantly, it is also applicable to the solar driven photocatalytic methods and hence this combination (photo–Fenton oxidation) can be relatively cheaper than the other advanced oxidation processes. However, the applicability of photo–Fenton methods needs to be checked for different class of chemicals and also in real life situations, i.e. combination of chemicals before firm conclusions can be made. Another advantage of using photo–Fenton oxidation is the presence of additional oxidation species, i.e. aquo or organo-complexes of the high valence iron (Pignatello et al., 1999) which are relatively unaffected by the presence of radical scavengers. The photo–Fenton process will be discussed in detail in the next manuscript.

5. Oxidation systems with direct attack of oxidants

Ozonation and addition of hydrogen peroxide belong to separate class of oxidation systems as compared to the above three methods, but their combination, i.e. ozone/hydrogen peroxide or presence of additional energy dissipation in terms of UV/near-UV/Sunlight or ultrasonic irradiation results in the generation of free hydroxyl radicals and these combination methods again belong to the class of advanced oxidation processes. These combination methods will be discussed in detail in the future work whereas the current work aims at discussing the individual action of ozone as well as hydrogen peroxide, which may be termed as chemical oxidation systems.

5.1. Ozonation

Ozone is a very powerful oxidizing agent ($E° = +2.07$ V) that can react with most species containing multiple bonds (such as C=C, C=N, N=N, etc.), but not with singly bonded functionality such as C–C, C–O, O–H at high rates. This is mainly due to the fact that there is no easy chemical pathway for the oxidation to take place. However, ozone does react with simple oxidizable ions such as S^{2-}, to form oxyanions such as SO_3^{2-} and SO_4^{2-}. These oxidations are simple and the mechanisms only require contact of ozone with the ion. Consequently, the oxidation of these ions by ozone occurs rapidly. It is sometimes better to think of ozone as a highly reactive species capable of reacting with many species rather than just as a compound with a large reduction potential. This is because the practical action of ozone is often dependent on how it reacts with pollutants, and usually not in its ability to simply gain electrons (except in the case of simple ion oxidations). This thinking emphasizes that an appropriate reaction pathway must exist for ozone to react with a substrate. In other words, although the thermodynamics for ozone-induced oxidation may be favorable (due to ozone's high reduction potential), kinetic factors will most often dictate whether ozone will oxidize a pollutant in a reasonable time frame.

5.1.1. Reactors used for transfer of ozone

A number of devices can be used to transfer the generated ozone into water such as countercurrent bubble column, packed and plate columns, static mixers, jet reactors and agitated vessels (Bowers et al., 1973; Glaze, 1987; Munter et al., 1993; Martin and Galey, 1994). Fig. 5 depicts some of the commonly used equipments for transferring ozone in water. Ozone transfer efficiency should be maximized by increasing the interfacial area of contact (reducing the bubble size by using small size ozone diffusers such as porous disks, porous glass diffusers (Ledakowicz et al. 2001), ceramic membranes (Janknecht et al., 2001; Ciardelli et al., 2001; Ciardelli and Ranieril, 2001; Picard et al., 2001)) and increasing the contact time between the gas and the effluent (increase the depths in the contactor, optimum being 3.7 to 5.5 m). A major disadvantage of the use of ozone diffusers in the form of porous disks or rods is that the presence of suspended solids and oxidized precipitates may result in plugging and hence reduced transfer of ozone. Side stream injectors can be used for avoiding plugging which also gives additional advantages of operation at higher ratio of gas flow rate to liquid flow rate and higher mixing efficiency without bubble channeling problems, but are also subject to lower contact times, bumping and corrosion.

Static mixers offer bright potential for effectively dissolving ozone in water and can be used at larger scale also. Martin and Galey (1994) have reported the use of static mixers for the transfer of ozone and showed that the mass transfer coefficient increased with a decreasing water flow rate and increasing gas flow rate. Recently, de Traversay et al. (2001) have studied disinfection of different microorganisms using ozone in the static mixers and reported that ozone transfer efficiency increases with an increase in the pressure drop, decrease in gas/liquid ratio and was independent of the ozone loading. Disinfection was observed to take place well inside the static mixer (may be applicable even to fast kinetics reactions) as indicated by a significant inactivation of microorganisms for contact times as low as 1 s. It should be noted that though the two references cited on the use of static mixers concern with water disinfection application, the excellent transfer rates obtained for ozone cannot be overlooked. Due to the fact that use of static mixers for actual wastewater treatment applications are lacking, more studies are required in this direction most importantly to calculate the energy requirements, as pressure drop will be higher due to the presence of solids and different physical
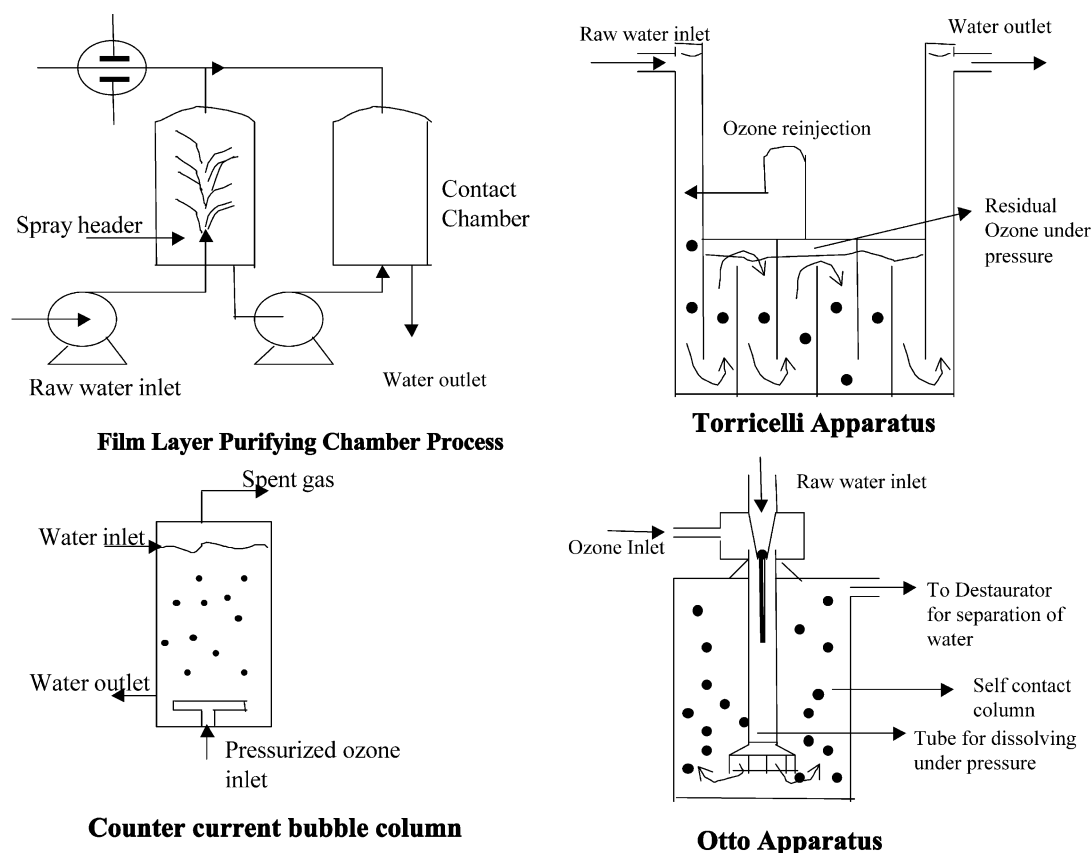
Fig. 5. Schematic representation of equipments used for ozonation.

properties of the effluent stream as compared to water containing only microorganisms.

5.1.2. Optimum operating parameters

Based on the detailed analysis of the literature, the important operating parameters for the ozonation process along with the recommendations for the selection of the same to achieve maximum extent of degradation in an energy efficient way, can be given as:

1. *pH of the system*: Usually higher values of pH are recommended (Beltran et al., 1992, 1994). Staehelin and Hoigne (1982) have reported that at high pH values, ozone reacts almost indiscriminately with all organic and inorganic compounds present in the reacting medium. It should also be noted that if the operating pH is above the pK value of the pollutant, i.e. the pollutant is not in molecular state, not much enhancement in the rates of degradation will be observed (Beltran et al., 1992).

2. *Ozone partial pressure*: Increase in the ozone partial pressure increases the extent of degradation (Beltran et al., 1992, 1993a); the extent of enhancement also

depends on the contaminant in question. Increase in the ozone partial pressure is usually associated with a substantial increase in the cost of generation of ozone (Brink et al. 1991; Glaze, 1987), thus the observed increase in the rates of degradation should be checked with the increase in the costs before selection of operating conditions is made. The best way is to increase and maximize the effective transfer of ozone into the solution (Schulz and Prendiville, 1993).

3. *Contact time and interfacial area*: Use contactors, which maximize both the contact time and the available interfacial area, possibly use of static mixers seems to be a good alternative at this stage (Martin and Galey, 1994).

4. *Presence of radical Scavengers*: The effect depends on the mechanism of the degradation. If the destruction is by direct attack of ozone on the chemical bonds, not much effect is there (Arslan and Balcioglu, 2000), but if it is through the free radicals, presence of radical scavengers such as HCO_3^- ions and humic substances decreases the extent of degradation (Beltran et al., 1994). This is a very important

point to be considered as natural waters are expected to contain large amounts of these substances. Development of kinetic models for predicting the rates of degradation must consider the presence of these substances and work of Beltran et al. (1994), Glaze and Kang (1989a,b) is recommended for these types of kinetic models.

5. *Operating temperature*: The effect is the resultant of the two simultaneous effects, increase in the rate constant of the reaction and the indirect effect through the variation of ozone solubility with temperature. Due to an increase in the temperature, ozone solubility decreases, thereby reducing the amount of ozone available for the reaction, which may result in decreased degradation (Beltran et al., 1994). However, Meijers et al. (1995) have reported that degradation of diuron increased with an increase in the temperature from 5 to 20 °C similar to that reported by Wu and Wang (2001) for the degradation of azo dyes. Nevertheless, appropriate correction in the ozone partial pressure can always be applied in terms of increasing the partial pressure, if temperature is expected to increase in the reaction path.

6. *Presence of catalyst*: Catalyst such as BST catalyst TiO_2 fixed on alumina beads, Fe (II), Mn (II) can be used to increase the degradation efficiency (Masten and Davies, 1994; Volk et al., 1997; Legube, 1999; Arslan et al., 2000)

7. *Combination with other oxidation processes*: Ozonation can be effectively combined with other oxidation techniques such as Ultrasonic irradiation (Weavers et al., 1998; Kang and Hoffmann, 1998; Kang et al., 1999a), UV irradiation (Beltran, 1997; Rice, 1997; Trapido, et al., 1997; Hautaniemi et al. 1998; Balcioglu and Getoff, 1998), γ-irradiation (Gehringer et al., 1997; Balcioglu et al., 2000), Hydrogen peroxide (Ormad et al., 1997; Gehringer et al., 1997; Masten et al., 1997; Kuo et al., 1997; Beltran et al., 1998; Arslan et al., 1999a; Balcioglu and Arslan., 2001), Fenton oxidation (Bauer and Fallmann, 1997) as well as aerobic digestion (Benitez et al., 1999a,b). The important characteristics of these hybrid processes will be discussed in the next of this two article series.

5.1.3. Overview of existing literature

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 of the specific examples of ozone use for treatment of wastewaters can be cited as; Textile effluent treatment in terms of color removal (Ruppert et al., 1994) and reduction of TOC and COD to certain limits beyond which biological oxidation can be used (Perkowski et

al., 1996; Rice, 1997), degradation of effluent from dye industry (Law et al., 1996; Liakou et al. 1997; Wu et al., 1998), conversion of cyanide ions into less toxic cyanate ions (Rice, 1997), degradation of protocatechuic acid (Benitez et al., 1996), chlorinated phenols (Boncz et al., 1997; Trapido et al., 1997), Chlorobenzenes (Masten et al., 1997), color removal in the effluent from a molasses processing plant (Gehringer et al., 1997), removal of pesticides (Meijers et al., 1995; Reynolds et al., 1989), treatment of wine-distillery (Beltran et al. 1999b; Benitez et al., 1999a) etc. Ozone can also be used for disinfection of water; it is particularly effective against recalcitrant microorganisms, Giardia (an organism that causes a gastro–intestinal disease), viruses and certain forms of algae. Good reviews/book on this subject have been given by Bowers et al. (1973), Rice and Browning (1981), Glaze (1987), Langlais et al., (1991), Masten and Davies (1993, 1994) and Rice (1997). Some representative works have been presented in Table 7 with discussion about the experimental conditions and the important findings obtained in the work.

A major limitation of the ozonation process is the relatively high cost of ozone generation process coupled with very short half-life period of ozone. Thus, ozone needs to be generated always at site. However, maximum concentration of ozone produced in air or oxygen is approximately 4 to 8%, respectively (Nebel, 1981), which coupled with very low (5 to 10%) energy efficiency of the production (Glaze, 1987; Rosen, 1973) and requirement of absolutely dry input (oxygen or air with low dew point of approximately -52 to -58 °C) may result in an uneconomical operation for the use of ozone alone in large-scale wastewater treatment applications. Moreover, the process efficiency is severely dependent on the efficient gas liquid mass transfer, which is quite difficult to achieve due to the low solubility of ozone in the aqueous solutions. New designs of contactors, e.g. static mixers have been developed as discussed earlier to increase the mass transfer rates but are limited to small-scale operation and applications requiring lower intensity for the destruction. All these drawbacks associated with ozonation process, indicates that even if ozonation is applied to large-scale treatment of the effluent streams, the costs associated with the treatment appear to be higher, though the actual figures are not available with the current level of available information. The problems indicated above (high cost of generation and gas–liquid mass transfer resistances are the most important) should be tackled with more studies in this area so as to enable the use of ozonation in large-scale operation; importantly with savings or lower cost of treatment. The best way, which appears at this stage, is to use ozone in combination with other techniques such as Ultrasonic/UV irradiation,

Table 7
Typical findings observed in the work related to use of ozonation as wastewater treatment technique

Sr. no.	Reference	Experimental conditions	Important findings
1	Beltran et al. (1992)	Capacity of the reactor: 500 ml, temperature 20 °C, ozone concentration of 0.15–2.14% by volume, continuous agitation at 450 rpm and gas flow rate of 1.67×10^{-5} m³/s Pollutant studied: *p*-nitrophenol	Rate of degradation increases with an increase in the pH from 2 to 8.5 but remains constant further until 12.4; Increase in ozone partial pressure increases the rate. Detailed kinetic study indicates that mass transfer resistance is the limiting one and hence aim should be at increasing effective contact and interfacial area. No ozone degradation at lower pH while minimal at pH of 12.5 indicated by different rates of degradation in the presence and absence of radical scavengers
2	Beltran et al. (1993b)	500 ml reactor with conditions of 10^{-3} M initial concentration of pollutant, pH of 4 and concentration of ozone in the mixture in the range 0.05–2% by volume. Pollutant studied: Galic acid and Epicatechin	Increase in the ozone partial pressure increases the extent of degradation. Kinetic regime of operation dependent on the type of pollutant and also operating ozone partial pressure. Slow reaction regime has been found for Galic acid (second order rate constant = 13 300 mole/s) whereas for epicatechin, it is moderate to fast (second order rate constant = 102 700 mole/s). Ozone absorption into the system is 92.1% for epicatechin whereas it is 80.2% for galic acid and is independent of ozone partial pressure
3	Beltran et al. (1994)	pH of 2, operating temperature in the range 3–20 °C, some experiments with presence of *t*-butanol and HCO_3^- ions; Pollutant studied: Atrazine	Increase in the pH increases the rate of degradation. Presence of radical scavengers (*t*-butanol and HCO_3^- ions) decreases the extent of degradation at operating pH of 2. At same ozone partial pressure, no effect of temperature on the rate of degradation attributed to balancing effects between reduced ozone solubility and increased rates at higher temperatures. Experiments with different ozone pressures to counter the solubility effect show that rate does increase with an increase in the temperature. Kinetic model given for estimation of rates which also considers the presence of HCO_3^- ions
4	Olson and Barbier (1994)	450 ml glass reactor provided with a water jacket for maintaining temperature of the system. Ozone loading was 1 mg/min for a initial organic carbon content of 6.4 mg/l. Total treatment time used was 60 min. Pollutant studied: Natural organic matter	Ozone decomposition rates were very less under the operating conditions; less than 10% ozone was utilized. Due to simultaneous action of ultrasound, the generation of free radicals from ozone was substantially enhanced and hence the TOC reduction (increased from approx. 40% to less than 10% with application of ultrasound using horn

Table 7 (*Continued*)

Sr. no.	Reference	Experimental conditions	Important findings
			at 27 W power dissipation and 20 kHz operating frequency). For the case of real wastewaters, initially absolutely no TOC removal was observed whereas pretreatment with acids was found to be very suitable as to nullify the effect of radical scavengers (increase in TOC removal is from almost nil to less than 10%)
5	Gulyas et al. (1995)	Stirred vessel operating at 500 rpm speed and 6 l capacity has been used. Operating pH was 8 whereas ozone was sparged at flow rate of 11.5 l/h with ozone concentration in gas as 110 mg/l. Pollutant studied: effluent from Paper-mill wastewater treatment plant as well as from pharmaceutical industry	COD for the paper-mill wastewater was reported to reduce by approximately 30% for treatment time of 15 min. Addition of hydrogen peroxide didn't increase the extent of COD removal. Bio-degradability of wastewater was observed to increase with ozonation and hence biological oxidation was recommended, as ozonation alone was not that effective in treating the effluent stream. Similar results were obtained with simulated oil reclaiming wastewaters. 1,1,1-trichloro-2-methyl-2-propanol containing pharmaceutical wastewater was refractory towards ozone but was oxidized by O_3/H_2O_2
6	Ormad et al. (1997)	4 l capacity ozonation reactor operated with raw water at pH of 9.4, initial TOC of 1150 mg/l and COD of 3920 mg/l. Total contact time of 60 min with ozone loading varied in the range 0–1.5 g/l. Pollutant studied: Raw water containing organohalides	For low dosages of ozone, less than 10% removal of TOC and COD has been observed and the removal increases with an increase in the ozone loading. For some organohalides, the extent of increase observed at higher loadings was marginal. DDT and their metabolites were observed to be refractory towards action of ozone whereas chlorobenzene, tetradifon, dichlorobenzophenone, 1,2,4-TCB degraded completely within 30 min. Addition of hydrogen peroxide at H_2O_2/O_3 molar ratio of 0.5 increases the efficacy of ozonation due to generation of additional free radicals.
7	Volk et al. (1997)	1.3 l gas reactor operated at atmospheric pressure and temperature of 20 °C with 1 l of the pollutant. Ozone loading was varied in the range 0–6.5 mg/l whereas the initial COD for the effluent was 2.84 mg/l. Pollutant studied: Effluent containing fulvic acid	COD reduction was found to increase with an increase in the ozone concentration but at the same time the amount of residual ozone in the effluent stream also increases, which is not always allowable. Optimum oxidant dose is 1 g/g of COD. Addition of hydrogen peroxide (in the ratio 0.35 mg/mg of ozone) as well as catalyst (BST catalyst TiO_2 supported on alumina beads) increases the utilization of ozone during the reaction and hence the extent of COD reduction.

Table 7 (Continued)

Sr. no.	Reference	Experimental conditions	Important findings
			Catalytic ozonation (with catalyst loading of 10 g/l) has been found to be the best in terms of percentage COD reduction among the three types of ozonation studied in the work. Utlization of ozone was near complete for ozone/hydrogen peroxide technique, 90% for catalytic ozonation and 70% for the operation using ozone alone
8	Arslan and Balcioglu (2000)	Bubble column reactor with 1.5 l capacity operated in semi-batch mode for 1 h. Ozone was introduced in reactor as O_3/O_2 mixture at a rate of 2340 mg/l h with net ozone dose as 3.51 gm/h. Pollutant studied: dye bath effluent containing Procion Yellow HE4R and Reactive black B dyes	All the dyes were observed to degrade within few minutes treatment time but COD and TOC measurements indicated finite residual amount even after one hour. The addition of radical scavengers didn't affect the rate of reaction indicating that direct ozone attack was the dominating mechanism. Ozone dose required for near complete treatment was strongly influenced by the concentration of dye in the stream. Addition of soda also helps in increasing the lifetime of ozone; hence results in better utilization of the same and was recommended depending on the results obtained in the work. It should be, however, noted that this result appears to be specific to the effluent studied, as radical scavenging action of CO_3^- ions is well known
9	Wu and Wang (2001)	500 ml capacity reactor equipped with a porous gas diffuser operated in semi-batch mode. Ozone was sparged as a ozone–oxygen mixture with net ozone loading of 26 mg/l-min. The initial concentration of dye is 0.5 g/l and temperature was maintained constant at 20 °C. Pollutant studied: Reactive black 5 dye	Model has been developed for predicting the mass transfer coefficient of ozone and is important as usually the mass transfer is the rate limiting step. Model considers enhancement factor due to chemical reaction and has been reported to increase linearly with an increase in the dye concentration (0–2.5 g/l), ozone dose (0–70 mg/l-min) and temperature (10–40 °C). Experimental results indicate that the apparent first order rate constant for the decomposition increases with an increase in the applied ozone loading, temperature and decrease in the dye initial concentration. Correlations have been reported explaining the variations. Bio-degradability was considerably improved due to ozonation as the pretreatment
10	Beltran-Heredia et al. (2001)	Bubble column reactor (9 cm inner diameter and height of 45 cm) was sparged with ozone (concentration in range of 10–20 mg/l at gas flow rate of 30 LPH) and used under	Initially acidic conditions are maintained for the removal of HCO_3^- ions present in the domestic wastewater. If operating pH is maintained constant at 2 or 10, considerable residual COD is obtained.

Table 7 (*Continued*)

Sr. no.	Reference	Experimental conditions	Important findings
		acidic conditions. Wastewater was circulated at a flow rate of 20 LPH and pH was adjusted with NaOH or H_2SO_4 intermittently. Ozonation at alkaline pH was carried out in stirred reactor agitated with paddle turbine. Different reactors with an aim of obtaining optimum transfer rate of ozone under different conditions of pH. Temperature was maintained at 20 °C. Pollutant studied: Effluents from domestic and wine distillery	If after initial acidic conditions, pH is changed to 10, the efficiency of degradation process is increased. To give a quantitative idea, percentage COD removal was 25% and 60% for operation at pH of 2 and 10, respectively, whereas for sequential operation it increased to 77% at the end of same time of treatment. Ozone consumption was also found to be maximum in the sequential operation as compared to operation under complete acidic or alkaline conditions. Similar results have been reported with wine-distillery wastewaters. Ozonation also increases the bio-degradability of effluent stream and hence if the volumes of effluent to be treated are substantially large, ozonation can be used as a pretreatment for biological oxidation. Integrated ASP (activated sludge process)-ozonation has been reported to give best quality of the effluent
11	Beltran-Heredia et al. (2001)	350 ml capacity reactor stirred mechanically. Ozone loading was varied in the range 0.09–0.38 kPa partial pressure where as temperature was varied in the range of 10–40 °C. The initial concentration of pollutant was 100 ppm and for mixture of acids, it was 100 ppm for each acid. Pollutant studied: Wastewater containing Phenolic acids	The stoichiometric ratios of ozone required for complete reactions of acids have been obtained (0.5 for ferulic acid and 1.5 each for *p*-hydorxybenzoic acid and β-resorcyclic acid). The rate constant for degradation of *p*-hydroxybenzoic acid was found to increase with an increase in pH (in the range 2–9), temperature (10–40 °C). Increase in ozone partial pressure also leads to an increase in the conversion of acid. For mixture of acids, similar results have been reported for variation of pH and temperature. Kinetic analysis has been done calculating the values of rate constants for the degradation
12	Arslan and Balcioglu (2001b)	Reactor with 1.5 l capacity operated in semi-batch mode for 1 h. Ozone was introduced in reactor as O_3/O_2 mixture at a rate of 2340 mg/l h with net ozone dose as 3.51 gm/h. Two different operating pH as 8 and 11 are studied. Pollutant studied: Textile	Decolorization of the effluent was much faster as compared to COD to TOC removal and hence the COD and TOC should be taken as the parameters describing the treatment efficiency. COD and TOC reduction using ozonation was observed to be less than 20% in 1 h of treatment time and

Table 7 *(Continued)*

Sr. no.	Reference	Experimental conditions	Important findings
		wastewater	combined operation with UV/H_2O_2 increased the removal by 50% and 200%, respectively. For the bio-treated textile wastewater, similar results were obtained confirming the fact that UV/H_2O_2 treatment can be used as a polishing step after ozonation. Kinetic analysis has been reported for the treatment of wastewater

hydrogen peroxide etc. and these hybrid methods will be discussed in the future work.

6. Use of hydrogen peroxide

Hydrogen peroxide is another strong oxidant readily applied to wastewater treatment in the past. For wastewater applications 50% hydrogen peroxide solution is normally recommended while 35% solution gives lower rates though higher safety and 70% may produce detonable mixtures with many of the organic compounds. Hydrogen peroxide has been found to be effective in degradation of compounds or treatment of real wastewaters requiring less stringent oxidation conditions (Ayling and Castrantas, 1981) but applications to complex mixture of effluents like dyes, textile industry effluent, heteroaromatics etc. need to be explored. The aim of discussing the use of hydrogen peroxide in the current work was to provide a brief overview of the individual technique so as to result in better understanding of the hybrid methods based on the use of hydrogen peroxide such as combination of ozone and H_2O_2 (Brunet et al., 1984; Beltran et al., 1996a; Echigo et al., 1998), UV irradiation and H_2O_2 (Beltran et al., 1996b; Andreozzi et al., 2001; Benitez et al., 1996), ultrasound and H_2O_2 (Kang et al., 1999c; Chen et al., 1990; Teo et al., 2001) etc. will be discussed in detail in the next article of this two article series.

6.1. Reactors for oxidation using hydrogen peroxide

Introduction of hydrogen peroxide into the waste stream is critical due to lower stability of hydrogen peroxide. The reaction rate between hydrogen peroxide and the pollutant usually dictates the point where H_2O_2 should be added. An addition point should give large residence time of H_2O_2 in the pollutant stream, but due to the practical constraints and poor mixing conditions, it is not always possible to inject H_2O_2 in line and an additional holding tank may be required. The other optimizing parameters can be the injection rate, catalyst and temperature of the reaction. The simplest, faster and cheapest method for injection of hydrogen peroxide is gravity feed system. Pump feed systems can also be used, but it requires regular attention.

6.2. Overview of available literature

Hydrogen peroxide has been used in the industrial effluent treatment for detoxification of cyanide, nitrite and hypochlorite, for the destruction of phenol aromatics, formaldehyde, removal of sulfite, thiosulfate and sulfide compounds (Bull and Zeff, 1991; Eul et al., 1991). Ayling and Castrantas (1981) have presented a good overview for the use of hydrogen peroxide for wastewater treatment applications.

A major problem encountered with the application of hydrogen peroxide alone for wastewater treatment applications are very low rates for applications involving complex materials, e.g. Fung et al. (2000a) have shown that the degradation of CI reactive red 120 dye was marginal for treatment with hydrogen peroxide alone whereas Arslan and Balcioglu (2001a) have shown that absolutely no degradation was observed for the addition of hydrogen peroxide alone for the dyehouse effluent. Also, there are no reports where hydrogen peroxide has been used for the treatment of mixture of compounds. Moreover, stability of H_2O_2 remains a question, as the catalytic decomposition agents present in effluents compete with the pollutants and hence proper injection methods achieving rapid dispersal of hydrogen peroxide, needs to be devised (Ayling and Castrantas, 1981). 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 recommendable option and hence the discussion here was restricted to just basics about hydrogen peroxide usage in effluent treatment schemes. It must be noted that with a view of increasing the rate of degradation, the concentration of H_2O_2 cannot be increased beyond certain limits as it acts as an additional pollutant if present in large quantities. Also, if free radicals are formed and taking part in the reaction, additional hydrogen peroxide usually recombines with the dissociated hydroxyl radicals, decreasing the overall rates of degradation.

The rate of formation of hydroxyl radicals are significantly enhanced under the effect of photochemical or ultrasonic irradiation and hence there is significant enhancement in the rates of these types of reactions in the presence of hydrogen peroxide (Eul et al., 1991; Bull and Zeff, 1991; Kim et al., 1997; Ince, 1999). Moreover, the acoustic streaming produced by ultrasound induced cavitation phenomena (Vichare et al., 2001) also helps in decreasing the effect of mass transfer limitations. Thus, it can be said that the overall efficiency of the degradation process will be significantly enhanced when a combination of UV radiation, ultrasound and hydrogen peroxide is used. These hybrid methods will be discussed later. Thus, it appears again that the use of hydrogen peroxide alone is not feasible for the treatment of complex compounds and combination with other advanced oxidation techniques seems to be a better alternative.

7. Conclusions and recommendations

Advanced oxidation processes viz. cavitation, photocatalytic oxidation and Fenton chemistry work on the principle of generation of free radicals and subsequent

attack of the same on the contaminant molecules whereas ozonation and use of hydrogen peroxide work on the direct attack of the oxidants or via formation of free radicals if another energy dissipating mode such as ultrasound or UV irradiation is present. The efficacy of process depends strongly on 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 and the efficient design should aim at maximizing both these quantities.

Cavitation, in addition to the generation of the free radicals, also generates conditions of high temperatures and pressures, which drives some of the chemical reactions by pyrolysis mechanism. The magnitudes of temperature, pressure pulse and free radicals can be manipulated by adjusting the operating parameters viz. intensity and frequency of irradiation, temperature, physico–chemical properties of liquid medium in the case of acoustic cavitation and inlet pressure, geometry of the constriction used (free area for the flow as well as the arrangement of holes for the same free area), operating temperature and physico–chemical properties of liquid medium in the case of hydrodynamic cavitation. For detailed effects of these parameters and guidelines for the selection, readers are requested to refer to the earlier work (Gogate and Pandit, 2000a,b, 2001; Gogate, 2002; Gogate et al., 2001a, 2002b). Acoustic cavitation reactors generate much more intense cavitation as compared to their hydrodynamic counterparts, but not much information is available at this stage for efficient large-scale of operation (almost all the studies have been restricted to capacities lesser than 500 ml (Gogate, 2002) except for some recent experimental work done by our group (Gogate et al., 2001a, 2002b; Sivakumar et al., 2002) and by group of Hoffmann (Destaillats et al., 2001). It should also be noted that information is required from diverse fields such as chemical engineering (gas–liquid hydrodynamics and other reactor operations), material science (for construction of transducers efficiently operating at conditions of high frequency and high power dissipation) and acoustics (for better understanding of the sound field existing in the reactor) for the efficient scale-up of sonochemical reactors. Mason (2000) has also discussed the problems associated with large-scale application of sonochemical reactors. On the other hand, for hydrodynamic cavitation equipments, scale-up appears to be much easier due to the fact that knowledge regarding the conditions downstream of the constriction is easily available, scale-up ratio required are lower and centrifugal pumps operate with higher energy efficiency at larger scales of operation. Moreover, hydrodynamic cavitation equipments give larger energy efficiency and cavitational yields as compared to sonochemical reactors (Kalumuck and Chahine, 2000; Gogate et al., 2001a; Sivakumar and Pandit, 2002). Still efforts are indeed required in trans-

ferring this efficient laboratory scale technique into industrial scale operation and some of the recommendations for future work required have been given in the earlier discussion and also in the earlier work (Gogate, 2002).

Photocatalytic oxidation appears to be one step ahead in terms of development as compared to other advanced oxidation processes discussed in the present work, as large amount of information is available and most importantly at comparatively larger scales of operation. Reactor design at large scales of operation is a critical point and efficient design should aim at uniform irradiation of entire catalyst surface at near incident intensity of irradiation and near complete elimination of the mass transfer resistances. The works by groups of Ray, Beenackers (Ray and Beenackers, 1996; Ray, 1997; Ray and Beenackers, 1997; Mukherjee and Ray, 1999; Ray, 1999; Li Puma and Yue, 1998a,b, 1999) are recommended for better understanding of large-scale efficient designs for photocatalytic reactors. A large amount of literature is available for the application of photocatalytic oxidation to wastewater treatment for different model constituent solutions and an exhaustive list has been given in Table 5. Nevertheless, 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. These global kinetic models predicting the rates of reaction as a function of various critical parameters such as concentration of the pollutants, radical scavengers, constituents enhancing the rates by arresting electron-hole recombination and the rates constants (function of operating parameters) etc. will be very helpful in designing large-scale reactors. The work of Glaze et al. (1992, 1995) is recommended as a guideline for development of these models.

Fenton's chemistry seems to be beneficial if used as a supplement to enhance the rates of photocatalytic and acoustic cavitation processes rather than using Fenton's reagent alone, though some of the chemicals like nitroaromatics have been treated efficiently. More efforts are required to establish conclusively whether Fenton's reagent can be used efficiently for the treatment of complex real effluents especially in the presence of large amount of ionic species. Studies are required in this direction in terms of experimentation and development of kinetic models.

Design of reactors is a critical factor in determining the efficiency of the ozonation process and should aim at maximizing the contact between ozone gas and the liquid effluent by the virtue of increased gas–liquid interfacial area and contact times. Use of static mixers, ceramic membranes has been developed recently with an excellent transfer efficiency of ozone into the system, but its application for the treatment of real industrial wastewaters need to be tested before firm recommen-

dations can be made. Very low reaction rates have been observed for the degradation of complex compounds or mixture of contaminants by ozonation alone. Similar conclusions have to be made with respect to the use of hydrogen peroxide as well, which is also hampered by severe transfer resistances and low stability in the presence of deactivating agents. Therefore, it appears that the use of ozone or hydrogen peroxide alone is not economically favorable and should be used in combination with other techniques (mainly ultrasonic and UV irradiation which leads to the formation of free radicals) as discussed in detail in the future work.

Overall it can be said that photocatalytic oxidation, by far, appears to be the best technology whereas cavitation appears to be little less efficient, but more developed and applicable as compared to Fenton chemistry and chemical oxidation technologies. Efforts are indeed required both on experimental front as well as kinetic modeling before application on large-scale is feasible with high degree of efficiency and lower treatment costs. The comparison criteria used in the present work were the degree of oxidation, level of information available which will decide the scale-up of the equipments, ease of operating conditions and most importantly applicability of the process in treating real complex industrial effluents. It should also be noted that detailed cost analysis is the present need, but as said earlier it is nearly impossible with the present level of information available in the literature. Future work may be directed to compare all the oxidation technologies on the basis of the operating costs and this should be indeed an excellent work and the need of the present hour.

The similarity between the mechanism of destruction and optimum operating conditions also points towards the synergism between these methods and indeed combination of these advanced oxidation processes should give better results as compared to individual techniques. Moreover, some of the drawbacks of the individual techniques should be eliminated by the characteristics of other technique (e.g. mass transfer limitations and fouling of the catalyst in the case of photocatalytic oxidation will be eliminated by the acoustic streaming and turbulence created by ultrasonic irradiation). The detailed discussion about the hybrid methods forms the future work.

Acknowledgments

References

Abdullah, M., Gary, K.C.L., Matthews, R.W., 1990. Effect of common inorganic anions on rates of photocatalytic oxidation of hydrocarbons over illuminated TiO_2. J. Phys. Chem. 94, 6620.

Adewuyi, Y.G., 2001. Sonochemistry: environmental science and engineering applications. Ind. Eng. Chem. Res. 40, 4681.

Andreozzi, R., Caprio, V., Insola, A., Longo, G., Tufano, V., 2000. Photocatalytic oxidation of 4-nitrophenol in aqueous TiO_2 slurries: an experimental validation of literature kinetic models. J. Chem. Tech. Biotech. 75, 131.

Andreozzi, R., Caprio, V., Marotta, R., 2001. Oxidation of benzothiazole, 2-mercaptobenzothiazole and 2-hydroxybenzothiazole in aqueous solution by means of H_2O_2/UV or photoassisted Fenton systems. J. Chem. Technol. Biotechnol. 76, 196.

Arslan, I., Balcioglu, A.I., Tuhkanen, T., 1999a. Advanced oxidation of synthetic dyehouse effluent by O_3, H_2O_2/O_3 and H_2O_2/UV processes. Environ. Tech. 20 (9), 921.

Arslan, I., Balcioglu, A.I., Tuhkanen, T., 1999b. Oxidative treatment of simulated dyehouse effluent by UV and near-UV light assisted Fenton's reagent. Chemosphere 39 (15), 2767.

Arslan, I., Balcioglu, A.I., 2000. Effect of common reactive dye auxiliaries on the ozonation of dyehouse effluents containing vinylsulfone and aminochlorotraizine dyes. Desalination 130, 61.

Arslan, I., Balcioglu, A.I., Tuhkanen, T., 2000. Advanced treatment of dyehouse effluents by Fe(II) and Mn(II)-catalyzed ozonation and the H_2O_2/O_3 process. Water Sci. Technol. 42 (1/2), 13.

Arslan, I., Balcioglu, A.I., 2001a. Degradation of Remazol black B dye and its simulated dyebath wastewater by advanced oxidation processes in heterogeneous and homogenous media. Color. Technol. 117, 19.

Arslan, I., Balcioglu, A.I., 2001b. Advanced oxidation of raw and biotreated textile industry wastewater with O_3, $H_2O_2/$UV-C and their sequential application. J. Chem. Technol. Biotechnol. 76, 53.

Ayling, G.W., Castrantas, H.M., 1981. Waste treatment with hydrogen peroxide. Chem. Eng. 88 (24), 79.

Balcioglu, A.I., Getoff, N., 1998. Advanced oxidation of 4-chlorobenzaldehyde in water by UV-light, ozonation and combination of both methods. Chemosphere 36 (9), 1993.

Balcioglu, A.I., Getoff, N., Bekbölet, M.A., 2000. Comparative study for the synergistic effect of ozone on the gamma-irradiated and photocatalytic reaction of 4-chlorobenzaldehyde. J. Photochem. Photobiol. A: Chem. 135, 229.

Balcioglu, I.A., Arslan, I., 2001. Partial oxidation of reactive dyestuffs and synthetic textile dye-bath by the O_3 and $O_3/$ H_2O_2 processes. Water Sci. Technol. 43 (2), 221.

Barbeni, M., Minero, C., Pellizzetti, L., 1987. Chemical degradation of chlorophenols with Fenton's reagent. Chemosphere 16, 2225.

Bauer, R., 1994. Applicability of solar irradiation for photochemical wastewater treatment. Chemosphere 29, 1225.

Bauer, R., Fallmann, H., 1997. The photo–Fenton oxidation—a cheap and efficient wastewater treatment method. Res. Chem. Intermed. 23, 341.

Bauer, R., 1999. The photo–fenton reaction and the TiO_2/UV process for waste water treatment–novel developments. Catal. Today 53 (1), 131.

Beltran, F.J., Garcia-Araya, J.F., Duran, A., 1992. Degradation kinetics of *p*-nitrophenol ozonation in water. Water Res. 26 (1), 9.

Beltran, F.J., Ovejero, G., Acedo, B., 1993a. Oxidation of atrazine in water by ultraviolet radiation combined with hydrogen peroxide. Water Res. 27 (6), 1013.

Beltran, F.J., Encinar, J.M., Garcia-Araya, J.F., 1993b. Oxidation by ozone and chlorine dioxide of two distillery waste-water contaminants: Galic acid and Epicatechin. Water Res. 27 (6), 1023.

Beltran, F.J., Garcia-Araya, J.F., Acedo, B., 1994. Advanced oxidation of atrazine in water. Part I: ozonation. Water Res. 28 (10), 2153.

Beltran, F.J., Overjero, G., Rivas, J., 1996a. Oxidation of polynuclear aromatic hydrocarbons in water 3. Ozone combined with hydrogen peroxide. Ind. Eng. Chem. Res. 35, 891.

Beltran, F.J., Overjero, G., Rivas, J., 1996b. Oxidation of polynuclear aromatic hydrocarbons in water 3. UV radiation combined with hydrogen peroxide. Ind. Eng. Chem. Res. 35, 883.

Beltran, F.J., 1997. Theoretical aspects of the kinetics of competitive first reactions of ozone in the O_3/H_2O_2 and O_3/UV oxidation processes. Ozone Sci. Eng. 19 (1), 13.

Beltran, F.J., Gonzalez, M., Gonzalez, J.F., 1997. Industrial wastewater advanced oxidation part I: UV radiation in the presence and absence of H_2O_2. Water Res. 31 (10), 2405.

Beltran, F.J., Garcia-Araya, J.F., Alvarez, P.M., Rivas, J., 1998. Aqueous degradation of atrazine and some of its byproducts with ozone/hydrogen peroxide. J. Chem. Tech. Biotech. 71 (4), 345.

Beltran, F.J., Garcia-Araya, J.F., Frades, J., Alvarez, P., Gimeno, O., 1999a. Effects of single and combined ozonation with hydrogen peroxide or UV radiation on the chemical degradation and biodegradability of debittering table olive industrial wastewaters. Water Res. 33, 723.

Beltran, F.J., Garcia-Araya, J.F., Alvarez, P.M., 1999b. Wine-distillery wastewater degradation 1. Oxidative treatment using ozone and its effect on the wastewater biodegradability. 2. Improvement of aerobic biodegradation by means of an integrated chemical (ozone)-biological treatment. J. Agric. Food Chem. 47, 3911.

Beltran-Heredia, J., Torregrosa, J., Dominguez, J.R., Peres, J.A., 2001. Kinetics of the reaction between ozone and Phenolic acids present in agro-industrial wastewaters. Water Res. 35 (4), 1077.

Benitez, F.J., Beltran-Heredia, J., Acero, J.L., Gonzalez, T., 1996. Degradation of protocatechuic acid by two advanced oxidation processes: Ozone/UV irradiation and H_2O_2/UV irradiation. Water Res. 30 (7), 1597.

Benitez, F.J., Beltran-Heredia, J., Acero, J.L., Pinillia, M.L., 1997. Simultaneous photodegradation and Ozonation plus UV radiation of phenolic acids – Major pollutants in agro-industrial wastewaters. J. Chem. Technol. Biotechnol. 70, 253.

Benitez, F.J., Beltran-Heredia, J., Real, F.J., Acero, J.L., 1999a. Enhancement of the ozonation of wine distillery wastewaters by an aerobic pretreatment. Bioprocess. Eng. 21, 459.

Benitez, F.J., Beltran-Heredia, J., Torregrosa, J., Acero, J.L., 1999b. Treatment of olive mill wasteaters by ozonation, aerobic digestion and the combination of both treatments. J. Chem. Technol. Biotechnol. 74, 639.

Benitez, F.J., Acero, J.L., Real, F.J., Rubio, F.J., Leal, A.I., 2001a. The role of hydroxyl radicals for the decomposition of *p*-hydroxy phenylacetic acid in aqueous solutions. Water Res. 35, 1338.

Benitez, F.J., Beltran-Heredia, J., Acero, J.L., Rubio, F.J., 2001b. Oxidation of several chlorophenolic derivates by UV irradiation and hydroxyl radicals. J. Chem. Technol. Biotechnol. 76, 312.

Berlan, M.J., Mason, T.J., 1992. Sonochemistry from research laboratories to industrial plants. Ultrasonics 30, 203.

Bhatnagar, A., Cheung, H.M., 1994. Sonochemical destruction of chlorinated C1 and C2 volatile organic compounds in dilute aqueous solutions. Environ. Sci. Technol. 28 (8), 1481.

Bhatkhande, D.S., Pangarkar, V.G., Beenackers, A.A.C.M., 2002. Photocatalytic degradation for environmental applications: a review. J. Chem. Technol. Biotechnol. 77 (1), 102.

Bideau, M., Claudel, B., Dubien, C., Faure, L., Kazouan, H., 1995. On the immobilization of titanium dioxide in the photocatalytic oxidation of spent waters. J. Photochem. Photobiol. A: Chem. 91, 137.

Bigda, R.J., 1995. Consider Fenton's chemistry for wastewater treatment. Chem. Eng. Prog. 91, 62.

Bigda, R.J., 1996. Fenton's chemistry: an effective advanced oxidation process. J. Adv. Sci. Eng. 6 (3), 34.

Blake D.M., 1997. Bibliography of Work on Photocatalytic Removal of Hazardous Compounds from Water and Air. NREL/TP-430-22197, National Renewable Energy Laboratory, Golden.

Boncz, M.A., Bruning, H., Rulkens, W.H., Sudholter, E.J.R., Harmsen, G.H., Bijsterbosch, J.W., 1997. Kinetic and mechanistic aspects of the oxidation of chlorophenols by ozone. Water Sci. Technol. 35 (4), 65.

Bossmann, S.H., Oliveros, E., Gob, S., Siegwart, S., Dahlem, S.P., Payawan, L., et al., 1998. New evidence against hydroxyl radicals as reactive intermediates in the thermal and photochemically enhanced Fenton reactions. J. Phys. Chem. A. 102, 5542.

Bowers, A., Netzer, A., Norman, J.D., 1973. Ozonation of wastewater – some technical and economic aspects. Can. J. Chem. Eng. 51 (3), 332.

Brink, D.R., Langlais, B., Reckhow, D.A., 1991. In: Langlais, B., Reckhow, D.A., Brink, D.A. (Eds.), Ozone in Water Treatment: Application and Engineering. Lewis Publishers, Chelsea, Michigan.

Brunet, R., Bourbigot, M.M., Dore, M., 1984. Oxidation of organic compounds through the combination of ozone-hydrogen peroxide. Ozone Sci. Eng. 6, 163.

Bull, R.A., Zeff, J.D., 1991. Hydrogen Peroxide in Advanced Oxidation Processes for Treatment of Industrial Process and Contaminated Groundwater. First Int. Symposium: Chemical Oxidation, Tech. For the 90s Nashville, Tennessee. Eckenfelder, W.W., Bowers, A.R., Roth, J.A., (Eds.) 26.

Butler, E.C., Davies, A.P., 1993. Photocatalytic oxidation in aqueous titanium dioxide suspensions: the influence of

dissolved transition metals. J. Photochem. Photobiol. 70, 273.

Butterfield, I.M., Christensen, P.A., Curtis, T.P., Gunlazuardi, J., 1997. Water disinfection using immobilized TiO_2 film in photochemical reactor with electric field enhancement. Water Res. 31, 675.

Canela, M.C., Alberici, R.M., Sofia, R.C.R., Eberlin, M.N., Jardim, W.F., 1999. Destruction of malodorous compounds using heterogeneous photocatalysis. Environ. Sci. Technol. 33, 2788.

Catallo, W.J., Junk, T., 1995. Sonochemical dechlorination of hazardous wastes in aqueous systems. Waste Mgt. 15 (4), 303.

CAV-OX® Cavitation Oxidation Process, 1994. Application Analysis Report, Magnum Water Technology, Inc., Risk Reduction Engg. Laboratory, Office of Research and Development, U.S.E.P.A., Cincinnati, Ohio 45268.

Chamarro, E., Marco, A., Esplugas, S., 2001. Use of Fenton reagent to improve organic chemical biodegradability. Water Res. 35, 1047.

Chang, M.-C., Shu, H.-Y., Huang, C.-R., 2001. Effect of Fenton's reagents on phenanthrene destruction in sandy soil. Presented at 6th World Congress of Chem. Eng. Melbourne, Australia, 23–27 September, 2001.

Chen, J.R., Xu, X.-W., Lee, A.S., Yen, T.F., 1990. A feasibility study of dechlorination of chloroform in water by ultrasound in the presence of hydrogen peroxide. Environ. Technol. 11, 829.

Chen, L., Chou, T., 1993. Photobleaching of methyl orange in titanium dioxide suspended in aqueous solution. J. Mol. Catal. 85, 201.

Chen, R., Pignatello, J.J., 1997. Role of quinone intermediates as electron shuttles in Fenton and photo-assisted Fenton oxidations of aromatic compounds. Environ. Sci. Technol. 31, 2399.

Chen, D., Ray, A.K., 1998. Photodegradation kinetics of 4-nitrophenol in TiO_2 suspension. Water Res. 32 (11), 3223.

Chen, J., Ollis, D.F, Rulkens, W.H., Bruning, H., 1999a. Kinetic processes of photocatalytic mineralization of alcohols on metallized titanium dioxide. Water Res. 33 (5), 1173.

Chen, J., Ollis, D.F., Rulkens, W.H., Bruning, H., 1999b. Photocatalyzed oxidation of alcohols and organochlorides in the presence of native TiO_2 and metallized TiO_2 suspensions. Part (II): photocatalytic mechanisms. Water Res. 33 (3), 669.

Chen, J., Chan, Y., Lu, M., 1999c. Photocatalytic oxidation of chlorophenols in the presence of manganese ions. Water Sci. Technol. 39 (10–11), 225.

Choi, W., Hoffmann, M.R., 1995. Photoreductive mechanism of CCl_4 degradation on TiO_2 particles and effects of electron donors. Environ. Sci. Technol. 29, 1646.

Choi, W., Hoffmann, M.R., 1997. Novel photocatalytic mechanisms for $CHCl_3$, $CHBr_3$ and $CCl_3CO_2^-$ degradation and the fate of photogenerated trihalomethyl radicals on TiO_2. Environ. Sci. Technol. 37, 89.

Ciardelli, G., Ranieril, N., 2001. The treatment and reuse of wastewater in the textile industry by means of Ozonation and electro-flocculation. Water Res. 35 (2), 567.

Ciardelli, G., Capannelli, G., Bottino, A., 2001. Ozone treatment of textile wastewaters for reuse. Water Sci. Technol. 44 (5), 61.

Clark II, C.J., Annable, M.D., Rao, P.S.C., 2000. Evaluation of sonochemical destruction of PCE in insitu flushing waste fluids. J. Environ. Eng. 126 (11), 1033.

Colussi, A.J., Hung, H.M., Hoffmann, M.R., 1999. Sonochemical degradation rates of volatile solutes. J. Phys. Chem. 103, 2696.

Commenges, N., Gonze, E., Gonthier, Y., Bernis, A., 2000. Ultrasonic Treatment Applied to Industrial Wastewater: A Difficult Undertaking. Presented at Euro. Society of Sonochemistry meeting-7, Toulouse, France, May 2000.

Crum, L.A., 1995. Comments on the evolving field of sonochemistry by a cavitation physicist. Ultrason. Sonochem. 2, S147.

Cyr, P.J., Paraskowich, M.R., Suri, R.P.S., 1999. Sonochemical destruction of trichloroethylene in water. Water Sci. Technol. 40 (4–5), 131.

Dahlem, O., Demaiffe, V., Halloin, V., Reisse, J., 1998. Direct sonication system suitable for medium scale sonochemical reactors. AIChE J. 44 (12), 2724.

Dahlem, O., Reisse, J., Halloin, V., 1999. The radially vibrating horn: a scaling-up possibility for sonochemical reactions. Chem. Eng. Sci. 54, 2829.

David, B., Lhote, M., Faure, V., Boule, P., 1998. Ultrasonic and photochemical degradation of chloropropham and 3-chloroaniline in aqueous solution. Water Res. 32 (8), 2451.

Davis, A.P., Huang, C.P., 1990. The removal of substituted phenols by a photocatalytic oxidation process with cadmium sulfide. Water Res. 24, 543.

Davis, A.P., Huang, C.P., 1991. The photocatalytic oxidation of sulfur containing organic compounds using cadmium sulfide and the effect on CdS photo-corrosion. Water Res. 25, 1273.

Destaillats, H., Hung, H.-M., Hoffmann, M.R., 2000. Degradation of alkylphenol Ethoxylate surfactants in water with ultrasonic irradiation. Environ. Sci. Technol. 34, 311.

Destaillats, H., Lesko, T.M., Knowlton, M., Wallace, H., Hoffmann, M.R., 2001. Scale up of sonochemical reactors for water treatment. Ind. Eng. Chem. Res. 40, 3855.

Dewulf, J., Van Langenhove, H., De Visscher, A., Sabbe, S., 2001. Ultrasonic degradation of trichloroethylene and chlorobenzene at micromolar concentrations: kinetics and modeling. Ultrason. Sonochem. 8, 143.

Dhale, A.D., Mahajani, V.V., 1999. Reactive dye house wastewater treatment. Use of hybrid technology: membrane, sonication followed by wet oxidation. Ind. Eng. Chem. Res. 38, 2058.

Dhale, A.D., Mahajani, V.V., 2001. Subcritical mineralization of sodium salt of dodecyl benzene sulfonate using sonication-wet oxidation (SONIWO) technique. Water Res. 35, 2300.

Dijkstra, M.F.J., Buwalda, H., de Jong, A.W.F., Michorius, A., Winkelman, J.G.M., Beenackers, A.A.C.M., 2001. Experimental comparison of three reactor designs for photocatalytic water purification. Chem. Eng. Sci. 56, 547.

Dillert, R., Cassano, A.E., Goslich, R., Bahnemann, D., 1999. Large scale studies in solar catalytic wastewater treatment. Catal. Today 54 (2–3), 267.

Dionysiou, D.D., Balasubramanian, G., Suidan, M.T., Khodadoust, A.P., Baudin, I., Laine, J.-M., 2000. Rotating disk photocatalytic reactor: development, characterization and evaluation for the destruction of organic pollutants in water. Water Res. 34 (11), 2927.

Drijvers, D., van Langenhove, H., Beckers, M., 1999. Decomposition of phenol and trichloroethylene by the ultrasound/H_2O_2/CuO process. Water Res. 33, 1187.

Echigo, S., Yamada, H., Matsui, S., Kawanishi, S., Shishida, K., 1996. Comparison between O_3/VUV, O_3/H_2O_2, VUV and O_3 processes for the decomposition of organophosphoric acid triesters. Water Sci. Technol. 34, 81.

Echigo, S., Kosaka, K., Yamada, H., Matsui, M., Shishida, K., 1998. The effect of water quality characteristics on the optimal hydrogen peroxide dose for the ozone/hydrogen peroxide process. J. Jpn. Soc. Water Environ. 21, 444.

Engwall, M.A., Pignatello, J.J., Grasso, D., 1999. Degradation and detoxification of the wood preservatives creosote and pentachlorophenol in water by the photo–Fenton reaction. Water Res. 33, 1151.

Entezari, M.H., Kruus, P., Otson, R., 1997. The effect of frequency on sonochemical reactions III: dissociation of carbon disulfide. Ultrason. Sonochem. 4, 49.

Eul, W., Scherer, G., Helmling, O., 1991. In: Eckenfelder, W.W., Bowers, A.R., Roth, J.A. (Eds.), Practical Applications of Hydrogen Peroxide for Wastewater Treatment, First Int. Symposium: Chemical Oxidation, Tech. For the 90s Nashville, Tennessee, 68.

Fallmann, H., Krutzler, T., Bauer, R., Malato, S., Blanco, J., 1999. Applicability of the Photo–Fenton method for treating water containing pesticides. Catal. Today. 54 (2–3), 309.

Feigelson, L., Muszkat, L., Bir, L., Muszkat, K.A., 2000. Dye photo-enhancement of TiO_2-photocatalyzed degradation of organic pollutants: the organobromine herbicide bromacil. Water Sci. Technol. 42 (1–2), 275.

Feitz, A.J., Boyden, B.H., Waite, T.D., 2000. Evaluation of two solar pilot scale fixed bed photocatalytic reactors. Water Res. 34 (16), 3927.

Fox, M.A., Duley, M.T., 1993. Heterogeneous photocatalysis. Chem. Rev. 93, 341.

Francony, F., Petrier, C., 1996. Sonochemical degradation of carbon tetrachloride in aqueous solution at two frequencies: 20 kHz and 500 kHz. Ultrason. Sonochem. 3, S77.

Freese, S.D., Nozaic, D., Pryor, M.J., Trollip, D.L., Smith, R.A., 1999. Comparison of ozone and hydrogen peroxide/ozone for the treatment of eutrophic water. Water Sci. Technol. 39 (10–11), 325.

Fung, P.C., Sin, K.M., Tsui, S.M., 2000a. Decolorization and degradation kinetics of reactive dye wastewater by a UV/ultrasonic/peroxide system. J. Soc. Dyes Colorist 116, 170.

Gaddam, K., Cheung, H.M., 2001. Effects of pressure, temperature, and pH on the sonochemical destruction of 1,1,1-trichloroethane in dilute aqueous solution. Ultrason. Sonochem. 8 (2), 103.

Gallard, H., De Laat, J., Legube, B., 1998. Influence du pH sur la vitsse d'oxydation de composes organiques par Fe^{II}/H_2O_2. Mechanisms reactionnels et modelization. New J. Chem. 263.

Gehringer, P., Szinovatz, W., Eschweiler, H., Harberl, R., 1997. Oxidative treatment of a wastewater stream from a molasses processing using ozone and advanced oxidation technologies. Ozone Sci. Eng. 19 (2), 157.

Glaze, W.H., 1987. Drinking water treatment with ozone. Environ. Sci. Tech. 21 (3), 224.

Glaze, W.H., Kang, J.W., 1989a. Advanced oxidation processes. Description of a kinetic model for the oxidation of hazardous material in aqueous media with ozone and hydrogen peroxide in a semibatch reactor. Ind. Eng. Chem. Res. 28 (11), 1573.

Glaze, W.H., Kang, J.W., 1989b. Advanced oxidation processes. Test of a kinetic model for the oxidation of organic compounds with ozone and hydrogen peroxide in a semi-batch reactor. Ind. Eng. Chem. Res. 28 (11), 1581.

Glaze, W.H., Beltran, F., Tuhkanen, T., Kang, J.W., 1992. Chemical models of advanced oxidation processes. Water Pollut. Res. J. Can. 27 (1), 23.

Glaze, W.H., Lay, Y., Kang, J.W., 1995. Advanced oxidation processes: A kinetic model for the oxidation of 1-2-dibromo-3-chloropropane in water by the combination of hydrogen peroxide and UV radiation. Ind. Eng. Chem. Res. 34, 2314.

Gogate, P.R., 2002. Cavitation: an auxiliary technique in wastewater treatment schemes. Adv. Environ. Res. 6, 335.

Gogate, P.R., Pandit, A.B., 2000a. Engineering design methods for cavitational reactors I: sonochemical reactors. AIChE J. 46 (2), 372.

Gogate, P.R., Pandit, A.B., 2000b. Engineering design methods for cavitational reactors II: hydrodynamic cavitation. AIChE J. 46 (8), 1641.

Gogate, P.R., Pandit, A.B., 2001. Hydrodynamic cavitation reactors: a state of the art review. Rev. Chem. Eng. 17 (1), 1.

Gogate, P.R., Shirgaonkar, I.Z., Sivakumar, M., Senthilkumar, P., Vichare, N.P., Pandit, A.B., 2001a. Cavitation reactors: efficiency analysis using a model reaction 47 (11), 2326.

Gogate, P.R., Wilhelm, A.M., Pandit, A.B., 2001b. Design of Sonochemical Reactors. Proceedings of Third International conference on Applications of Ultrasound in Physical and Chemical Processing, p. 211.

Gogate, P.R., Mujumdar, S., Pandit, A.B., 2002a. A sonophotochemical reactor for the removal of formic acid from wastewater. Ind. Eng. Chem. Res. 41 (14), 3370.

Gogate, P.R., Mujumdar, S., Pandit, A.B., 2002b. Sonochemical reactors for waste water treatment: comparison using formic acid degradation as a model reaction. Adv. Environ. Res. In press.

Gogate, P.R., Mujumdar, S., Pandit, A.B., 2002c. Effect of solid particles on the degradation of phenol. Unpublished results.

Gondrexon, N., Renaudin, V., Petrier, C., Boldo, P., Bernis, A., Gonthier, Y., 1999. Degradation of pentachlorophenol aqueous solutions using a continuous flow ultrasonic reactor: experimental performance and modeling. Ultrason. Sonochem. 5 (4), 125.

Gonze, E., Fourel, L., Gonthier, Y., Boldo, P., Bernis, A., 1999. Wastewater pretreatment with ultrasonic irradiation to reduce toxicity. Chem. Eng. J. 73, 93.

Grieser F., Ashokkumar M., Vinodgopal K. 2000 The Sonochemical Degradation of a Polydisperse Nonylphenol Ethoxylate in Aqueous Solution. Proceedings of European Society. Sonochem.-7, Toulouse, France, 195.

Guillard, C., Disdier, J., Herrmann, J.-M., Lehaut, C., Chopin, T., Malato, S., et al., 1999. Comparison of various titania samples of industrial origin in the solar photocatalytic detoxification of water containing 4-chlorophenol. Catal. Today. 54 (2–3), 217.

Gulyas, H., von Bismarck, R., Hemmerling, L., 1995. Treatment of industrial wastewaters with ozone/hydrogen peroxide. Water Sci. Technol. 32 (7), 127.

Gupta, H., Tanaka, S., 1995. Photocatalytic mineralization of perchloroethylene using titanium dioxide. Water Sci. Technol. 31, 47.

Habibi, M.H., Tangestaninejad, S., Yadollahi, B., 2001a. Photocatalytic mineralization of mercaptans as environmental pollutants in aquatic systems using TiO_2 suspensions. Appl. Catal. B: Environ. 33 (1), 57.

Habibi, M.H., Tangestaninejad, S., Mohammadpoor-Baltrok, I., Yadollahi, B., 2001b. Photocatalytic degradation of wastewater pollutions: Titanium dioxide-mediated oxidation of 2-mercaptobenzothiazole. Pollut. Res. 2, 32.

Hager, S., Bauer, R., 1999. Heterogeneous photocatalytic oxidation of organics for air purification by near UV irradiated titanium dioxide. Chemosphere 38 (7), 1549.

Hart, E.J., Henglein, A., 1985. Free radical and free atom reactions in the sonolysis of aqueous iodide and formate solution. J. Phys. Chem. 89, 4342.

Hautaniemi, M., Kallas, J., Munter, R., Trapido, M., 1998. Modelling of chlorophenol treatment in aqueous solutions 1. Ozonation and ozonation combined with uv radiation under acidic conditions. Ozone Sci. Eng. 20 (4), 259.

Heredia, J.B., Benitez, F.J., Gonzalez, T., Acero, J.L., Rodriguez, B., 1996. Photocatalytic decomposition of bentazone. J. Chem. Tech. Biotech. 66, 206.

Herrmann, J.-M., 1999. Heterogeneous photocatalysis: fundamentals and applications to removal of various types of aqueous pollutants. Catal. Today. 53, 115.

Herrmann, J., Matos, J., Disdier, J., Guillard, C., Laine, J., Malato, S., 1999. Solar photocatalytic degradation of 4-chlorophenol using the synergistic effect between titania and activated carbon in aqueous suspension 54 (2–3), 255.

Hidaka, H., 1998. Photodegradation of surfactants with TiO_2 semiconductor for the environmental wastewater treatment. Proc. Indian Acad. Sci. 110, 215.

Hidaka, H., Zhao, J., Nohara, K., 1994. Photocatalytic degradation of surfactants using titanium dioxide. J. Water Waste 36, 863.

Hoffmann, M.R., Martin, S.T., Choi, W., Behnemann, D.W., 1995. Environmental applications of semiconductor photocatalysis. Chem. Rev. 93, 69.

Hoffmann, M.R., Hua, I., Höchemer, R., 1996. Application of ultrasonic irradiation for the degradation of chemical contaminants in water. Ultrason. Sonochem. 3, S163.

Hofstadler, K., Bauer, R., Novalic, S., Heiser, G., 1994. New reactor design for photocatalytic wastewater treatment with TiO_2 immobilized on fused-silica glass fibers: photomineralization of 4-chlorophenol. Environ. Sci. Technol. 28, 670.

Hoigne, J., 1997. Inter-calibration of OH° radical sources and water quality parameters. Water Sci. Technol. 35 (4), 1.

Hua, I., Hochemer, R.H., Hoffmann, M.R., 1995a. Sonochemical degradation of p-nitrophenol in a parallel plate near field acoustical processor. Environ. Sci. Technol. 29, 2790.

Hua, Z., Manping, Z., Zongfeng, X., Low, G.K.C., 1995b. Titanium dioxide mediated photocatalytic degradation of monocrotophos. Water Res. 29, 2681.

Hua, I., Hoffmann, M.R., 1997. Optimization of ultrasonic irradiation as an advanced oxidation technology. Environ. Sci. Technol. 31, 2237.

Hufschmidt, D., Bahnemann, D., Testa, J.J., Emilio, C.A., Litter, M.I., 2002. Enhancement of photocatalytic activity of various TiO_2 materials by platinization. J. Photochem. Photobiol. A: Chem. 148 (1–3), 223.

Hundal, L., Singh, J., Bier, E.L., Shea, P.J., Comfort, S.D., Powers, W.L., 1997. Removal of TNT and RDX from water and soil using iron metal. Environ. Pollut. 97, 55–64.

Hung, H.-M., Hoffmann, M.R., 1998. Kinetics and mechanism of the enhanced reductive degradation of CCl_4 by elemental iron in the presence of ultrasound. Environ. Sci. Technol. 32, 3011.

Hung, H.-M., Hoffmann, M.R., 1999. Kinetics and mechanism of the sonolytic degradation of chlorinated hydrocarbons: frequency effects. J. Phys. Chem. A. 103, 2734.

Ince, N.H., 1999. 'Critical' effect of hydrogen peroxide in photochemical dye degradation. Water Res. 33 (4), 1080.

Ingale, M.N., Mahajani, V.V., 1995. A novel way to treat refractory waste: sonication followed by wet oxidation (SONIWO). J. Chem. Technol. Biotechnol. 64, 80.

Ito, K., Jian, W., Nishijima, W., Baes, A.U., Shoto, E., Okada, M., 1998. Comparison of ozonation and AOPS combined with biodegradation for removal of THM precursors in treated sewage effluents. Water Sci. Technol. 33, 179.

Janknecht, P., Wilderer, P.A., Picard, C., Labort, A., 2001. Ozone water contacting by ceramic membranes. Sep. Purif. Technol. 25, 341.

Joseph, J.M., Destaillats, H., Hung, H.M., Hoffmann, M.R., 2000. The sonochemical degradation of azobenzene and related azo dyes: rate enhancements via Fenton's reactions. J. Phys. Chem. A. 104, 301.

Kalumuck, K.M., Chahine, G.L., 2000. The use of cavitating jets to oxidize organic compounds in water. J. Fluids Eng. 122, 465.

Kamat, P.V., 1993. Photochemistry on non-reactive and reactive (semiconductor) surfaces. Chem. Rev. 93, 267.

Kang, J.W., Hoffmann, M.R., 1998. The kinetics and mechanism of the sonolytic destruction of Methyl Tertiary Butyl Ether (MTBE) by ultrasonic irradiation in the presence of ozone. Environ. Sci. Technol. 32, 3194.

Kang, J.W., Hung, H.M., Lin, A., Hoffmann, M.R., 1999a. The sonolytic destruction of Methyl Tertiary Butyl Ether (MTBE) by ultrasonic irradiation: effects of ozone and frequency. Environ. Sci. Technol. 33, 3199.

Kang, S.F., Wang, T.H., Lin, Y.H., 1999b. Decolorization and degradation of 2,4-Dinitrophenol by Fenton reagent. J. Environ. Sci. Health. A34 (4), 935.

Kang, J.-W., Hung, H.-M., Lin, A., Hoffmann, M.R., 1999c. Sonolytic destruction of methyl tert butyl ether by ultrasonic irradiation: role of O_3, H_2O_2, frequency and power density. Environ. Sci. Technol. 33, 3199.

Kang, Y.W., Hwang, K.-Y., 2000. Effects of reaction conditions on the oxidation efficiency in the Fenton process. Water Res. 34, 2786.

Keil, F.J., Swamy, K.M., 1999. Reactors for sonochemical engineering–present status. Rev. Chem. Eng. 15, 85.

Kim, S.J., Oh, K.H., Lee, S.H., Choi, S.S., Lee, K.C., 1997. Study on secondary reaction and fate of hazardous chemicals by oxidants. Water Sci. Technol. 36 (12), 325.

Kitis, M., Adams, C.D., Daigger, G.T., 1999. The effects of Fenton's reagent pre-treatment on the biodegradability of non-ionic surfactants. Water Res. 33, 2561.

Klare, M., Waldner, G., Bauer, R., Jacobs, H., Broekaert, J.A.C., 1999. Degradation of nitrogen containing organic compounds by combined photocatalysis and ozonation. Chemosphere 38 (9), 2013.

Kormann, C., Bahnemann, D.W., Hoffmann, M.R., 1991. Photolysis of chloroform and other organic molecules in aqueous suspensions. Environ. Sci. Technol. 25, 494.

Krutzler, T., Bauer, R., 1999. Optimization of a photo–Fenton prototype reactor. Chemosphere 38 (11), 2517.

Ku, Y., Hsieh, C.B., 1992. Photocatalytic decomposition of 2,4-dichlorophenol in aqueous TiO_2 suspensions. Water Res. 26, 1451.

Kuo, K.W., 1992. Decolorizing dye wastewater with Fenton's reagent. Water Res. 26, 881.

Kuo, C.-H., Yuan, F., Hill, D.O., 1997. Kinetics of oxidation of ammonia in solutions containing ozone with or without hydrogen peroxide. Ind. Eng. Chem. Res. 36, 4108.

Kulkarni, A.A., 1998. Solar assisted photocatalytic oxidation of distillery waste. Ind. Chem. Eng. 40 (2), 169.

Kwon, B.G., Lee, D.S., Kang, N., Yoon, J., 1999. Characteristics of *p*-chlorophenol oxidation by Fenton's reagent. Water Res. 33, 2110.

Langlais, B., Reckhow, D.A., Brink, D.R., 1991. Ozone in Water treatment – Application and Engineering. Lewis Publishers, Boca Raton, FL.

Law, S.E., Wu, J., Eiteman, M.A., 1996. Ozone Decolorization of Cotton Dyehouse Wastewater. Proceedings of the ASAE Annual International Meeting July 14–18, Phoeniz, AZ.

Lea, J., Adesina, A.A., 2001. Oxidative degradation of 4-nitrophenol in UV illuminated titania suspension. J. Chem. Tech. Biotech. 76 (8), 803.

Ledakowicz, S., Maciejewska, R., Perkowski, J., Bin, A., 2001. Ozonation of reactive blue 81 in the bubble column. Water Sci. Technol. 44 (5), 47.

Legube, B., 1999. Catalytic ozonation: a promising advanced oxidation technology for water treatment. Catal. Today. 53 (1), 61.

Legrini, O., Oliveros, E., Braun, A.M., 1993. Photochemical processes for water treatment. Chem. Rev. 93, 671.

Lee, W., Do, Y.R., Dwight, L., Wold, A., 1993. Enhancement of photocatalytic activity of Titanium (IV) dioxide with Molybdenum (VI) oxide. Mater. Res. Bull. 28, 1127.

Li, X.Z., Fan, C.M., Sun, Y.P., 2002. Enhancement of photocatalytic oxidation of humic acid in TiO_2 suspensions by increasing cation strength. Chemosphere 48 (4), 453.

Lia, F.B., Li, X.Z., 2002. The enhancement of photodegradation efficiency using Pt_TiO_2 catalyst. Chemosphere 48 (10), 1103.

Lin, S.H., Peng, C.F., 1995. Treatment of textile wastewater by Fenton's reagent. J. Environ. Sci. Health A 30, 89.

Lin, S.H., Lin, C.M., Leu, H.G., 1999. Operating characteristics and kinetic studies of surfactant wastewater treatment by Fenton oxidation. Water Res. 33, 1735.

Lin, S.H., Lo, C.C., 1997. Fenton process for treatment of desizing wastewater. Water Res. 31, 2050.

Lindner, M., Theurich, J., Dahnemann, D.W., 1997. Photocatalytic degradation of organic compounds: accelerating the process efficiency. Water Sci. Technol. 35 (4), 79.

Li Puma, G., Yue, P.L., 1998a. A laminar falling film slurry photocatalytic reactor part I–model development. Chem. Eng. Sci. 53, 2993.

Li Puma, G., Yue, P.L., 1998b. A laminar falling film slurry photocatalytic reactor part II–experimental validation of model. Chem. Eng. Sci. 53, 3007.

Li Puma, G., Yue, P.L., 1999. Enhanced photocatalysis in a pilot laminar falling film slurry reactor. Ind. Eng. Chem. Res. 38, 3246.

Li, Z.M., Peterson, M.M., Comfort, S.D., Horst, G.L., Shea, P.L., Oh, B.T., 1997a. Remediating TNT-contaminated soil by soil washing and Fenton oxidation. Sci. Total Environ. 204, 107–115.

Li, Z.M., Shea, P.J., Comfort, S.D., 1997b. Fenton oxidation of 2,4,6-trinitrotoluene in contaminated soil slurries. Environ. Eng. Sci. 14, 55–66.

Liakou, S., Pavlou, S., Lyberatos, G., 1997. Ozonation of azo dyes. Water Sci. Technol. 35 (4), 279.

Lorimer, J.P., Mason, T.J., 1987. Sonochemistry part 1 – the physical aspects. Chem. Soc. Rev. 16, 239.

Lu, M.-C., 1994. Photocatalytic oxidation of dichlorvas in the presence of hydrogen peroxide and ferrous ion. Water Sci. Technol. 30 (9), 29.

Luo, Y., Ollis, D.F., 1996. Photocatalytic oxidation of toluene and trichloroethylene. J. Catal. 163, 1.

MacFaul, P.A., Wayner, D.D.M., Ingold, K.U., 1998. A radical account of oxygenated Fenton chemistry. Acc. Chem. Res. 31, 159.

Maillard, C., Guillard, C., Pichat, P., 1992. Comparative effects of the TiO_2–UV, H_2O_2–UV, H_2O_2–Fe_2^+ systems on the disappearance rate of benzamide and 4-hydroxybenzamide in water. Chemosphere 24, 1085.

Maletzky, P., Bauer, R., 1998. The photo–Fenton method – degradation of nitrogen containing organic compounds. Chemosphere 37 (5), 899.

Maletzky, P., Bauer, R., Lahnsteiner, J., Pouresmael, B., 1999. Immobilization of iron ions on Nafion® and its applicability to the photo–Fenton method. Chemosphere 38 (10), 2315.

Mantzavinos, D., Hellenbrand, R., Livingston, A.G., Metcalfe, I.S., 1997. Reaction mechanisms and kinetics of chemical pretreatment of bioresistant organic molecules by wet air oxidation. Water Sci. Technol. 35, 119.

Martin, N., Galey, C., 1994. Use of static mixer for oxidation and disinfection by ozone. Ozone Sci. Eng. 16 (6), 455.

Mason, T.J., Lorimer, J.P., 1988. Sonochemistry: Theory, Applications and Uses of Ultrasound in Chemistry. John Wiley, New York.

Mason, T.J., 1990. A survey of commercially available sources of ultrasound suitable for sonochemistry. Sonochemistry – Uses of Ultrasound in Chemistry. Royal Society of Chemistry, Cambridge UK.

Mason, T.J., 1992. Practical Sonochemistry: Users Guide in Chemistry and Chemical Engineering. Ellis Horwood Series in Organic Chemistry, Chichester.

Mason, T.J., Newman, A., Lorimer, J.P., Lindley, J., Hutt, K., 1996. Ultrasonically assisted catalytic decomposition of sodium hypochlorite. Ultrason. Sonochem. 3, 53.

Mason, T.J., Cordemans, E.D., 1998. Practical considerations for process optimization. In: Luche, J.L. (Ed.), Synthetic Organic Sonochemistry. Plenum Publishers, New York, pp. 301.

Mason, T.J., 2000. Large scale sonochemical processing: aspiration and actuality. Ultrason. Sonochem. 7, 145.

Masten, S.J., Davies, S.H.R., 1993. The use of ozone and other strong oxidants for hazardous waste management. In: Nriagen, J.O., Simmons, M.S. (Eds.), Environmental Oxidants. John Wiley and Sons, New York, pp. 1–21.

Masten, S.J., Davies, S.H.R., 1994. The use of ozonation to degrade organic contaminants in wastewaters. Environ. Sci. Technol. 28 (4), 180A.

Masten, S.J., Galbraith, M.J., Davies, S.H.R., 1997. Oxidation of 1,3,5-trichlorobenzene using advanced oxidation processes. Ozone Sci. Eng. 18 (6), 535.

Mastin, B.J., Sherrard, R.M., Rodgers Jr, J.H., Shah, Y.T., 2001. Hybrid cavitation/constructed wetland reactors for treatment of chlorinated and non-chlorinated organics. Chem. Eng. Technol. 24, 97.

Matthews, R.W., McEvoy, S.R., 1992a. A comparison of 254 nm and 350 nm excitation of TiO_2 in simple photocatalytic reactors. J. Photochem. Photobiol. A: Chem. 66, 355.

Matthews, R.W., McEvoy, S.R., 1992b. Photocatalytic degradation of phenol in the presence of near-UV illuminated titanium dioxide. J. Photochem. Photobiol. A: Chem. 64, 231.

Mazzarino, I., Piccinini, P., Spinelli, L., 1999. Degradation of organic pollutants by photochemical reactors. Catal. Today 48, 315.

Mazzarino, I., Piccinini, P., 1999. Photocatalytic oxidation of organic acids in aqueous media by a supported catalyst. Chem. Eng. Sci. 54, 3107.

Meijers, R.T., Oderwald-Muller, E.J., Nuhn, P.A.N.M., Kruithof, J.C., 1995. Degradation of pesticides by ozonation and advanced oxidation. Ozone Sci. Eng. 17 (6), 673.

Miller, N., 1950. Chemical action of sound waves on aqueous solutions. Trans. Faraday Soc. 45, 546.

Miller, L.W., Tejedor, M.I., Anderson, M.A., 1999. Titanium dioxide coated silica waveguides for the photocatalytic oxidation of formic acid in water. Environ. Sci. Technol. 33, 2070.

Moholkar, V.S., Senthilkumar, P., Pandit, A.B., 1999. Hydrodynamic cavitation for sonochemical effects. Ultrason. Sonochem. 6, 53.

Moholkar, V.S., Pandit, A.B., Warmoeskerken, M.M.C.G. 1999. Characterization and Optimization Aspects of a Sonic Reactor. Presented at ICEU-99, New Delhi, India.

Moholkar, V.S., Warmoeskerken, M.M.C.G., 2000. Modelling of the acoustic pressure fields and the distribution of the cavitation phenomena in a dual frequency sonic processor. Ultrasonics 38, 666.

Mukherjee, P.S., Ray, A.K., 1999. Major challenges in the design of a large scale photocatalytic reactor for water treatment. Chem. Eng. Technol. 22 (3), 253.

Munter, R., Preis, S., Kamenev, S., Siirde, E., 1993. Methodology of ozone induction into water and wastewater treatment. Ozone Sci. Eng. 15 (2), 149.

Nagata, Y., Hirai, K., Bandow, H., Maeda, Y., 1996. Decomposition of hydroxybenzoic and humic acids in water by ultrasonic irradiation. Environ. Sci. Technol. 30, 1133.

Nagata, Y., Nagakawa, M., Okuno, H., Mizukoshi, Y., Yim, B., Maeda, Y., 2000. Sonochemical degradation of chlorophenols in water. Ultrason. Sonochem. 7, 115.

Naidu, D.V., Rajan, R., Kumar, R., Gandhi, K.S., Arakeri, V.H., Chandrasekaran, S., 1994. Modelling of a batch sonochemical reactor. Chem. Eng. Sci. 49 (6), 377.

Nebel, C., 1981. Ozone. In: Grayson, M., Eckroth, D. (Eds.), Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. John Wiley and Sons, New York, USA.

Nesheiwat, F.K., Swanson, A.G., 2000. Clean contaminated sites using Fenton's reagent. Chem. Eng. Prog. 96 (4), 61.

Okamoto, K., Yamamoto, Y., Tanaka, H., Itaya, A., 1985. Kinetics of heterogenous photocatalytic decomposition of phenol over anatase TiO_2 powder. Bull. Chem. Soc. Jpn. 58, 2023.

Ollis, D.F., Pellizzetti, E., Serpone, N., 1991. Destruction of water contaminants. Environ. Sci. Technol. 25, 1523.

Olson, T.M., Barbier, P.F., 1994. Oxidation kinetics of natural organic matter by sonolysis and ozone. Water Res. 28, 1383.

Ormad, P., Cortes, S., Puig, A., Ovelleiro, J.L., 1997. Degradation of organochloride compounds by O_3 and O_3/H_2O_2. Water Res. 31 (9), 2387.

Otal, E., Mantzavinos, D., Delgado, M.V., Hellenbrand, R., Lebrato, J., Metcalfe, I.S., et al., 1997. Integrated wet air oxidation and biological treatment of polyethylene glycol-containing wastewaters. J. Chem. Tech. Biotech. 70, 147.

Pandit, A.B., Moholkar, V.S., 1996. Harness cavitation to improve processing. Chem. Eng. Prog. 96, 57.

Pandit, A.B., Gogate, P.R., Mujumdar, S., 2001. Ultrasonic degradation of 2,4,6-trichlorophenol in presence of TiO_2 catalyst. Ultrason. Sonochem. 8, 227.

Park, T.J., Lee, K.H., Jung, E.J., Kim, C.W., 1999. Removal of refractory organics and color in pigment wastewater with Fenton oxidation. Water Sci. Technol. 39 (10–11), 189.

Peill, N.J., Hoffmann, M.R., 1997. Solar-powered photocatalytic fiberoptic cable reactor for waste stream remediation. J. Sol. Energy Eng. Trans. ASME 119, 229–236.

Pelizzetti, E., Carlin, V., Minero, C., Gratzel, M., 1990a. Enhancement of the rate of photocatalytic degradation on TiO_2 of 2-chlorophenol, 2,7,-dichlorodibenzodioxin and atrazine by inorganic oxidizing species. N. J. Chem. 15, 351.

Pellizzetti, E., Maurino, V., Minero, C., Carlin, V., Pramauro, E., Zerbinati, O., et al., 1990b. Photocatalytic degradation of atrazine and other S-trizine herbicides. Environ. Sci. Technol. 24, 1559.

Perkowski, J., Kos, L., Ledakowicz, S., 1996. Application of ozone in textile wastewater treatment. Ozone Sci. Eng. 18 (1), 73.

Pestman, J.M., Engberts, J.B.F.N., de Jong, F., 1994. Sonochemistry: theory and applications. J. R. Neth. Soc. 113 (12), 533.

Peters, D., 2001. Sonolytic degradation of volatile pollutants in natural ground water: conclusions from a model study. Ultrason. Sonochem. 8, 221.

Petrier, C., Jeanet, A., Luche, J.L., Reverdy, G., 1992. Unexpected frequency effects on rate of oxidative processes induced by ultrasound. J. Am. Chem. Soc. 114, 3148.

Petrier, C., David, B., Laguian, S., 1996. Ultrasonic degradation at 20 and 500 kHz of atrazine and pentachlorophenol

in aqueous solutions: preliminary results. Chemosphere 32, 1709.

Petrier, C., Francony, A., 1997a. Incidence of wave frequency on the reaction rates during ultrasonic wastewater treatment. Water Sci. Technol. 35, 175.

Petrier, C., Francony, A., 1997b. Ultrasonic wastewater treatment: incidence of ultrasonic frequency on the rate of phenol and carbon tetrachloride degradation. Ultrason. Sonochem. 4, 295.

Petrier, C., Jiang, Y., Lamy, M.-F., 1998. Ultrasound and environment: sonochemical destruction of chloroaromatic derivates. Environ. Sci. Technol. 32, 1216.

Picard, C., Larbot, A., Sarrazin, J., Janknecht, P., Wilderer, P.A., 2001. Ceramic membranes for ozonation in wastewater treatment. Ann. Chim. Sci. Materiauz. 26 (2), 13.

Pignatello, J.J., Liu, D., Huston, P., 1999. Evidence for additional oxidant in the photoassisted Fenton reaction. Environ. Sci. Technol. 33, 1832.

Pignatello, J.J., 1992. Dark and photo-assisted Fe^{3+} catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. Environ. Sci. Technol. 26, 944.

Potter, F.J., Roth, J.A., 1993. Oxidation of chlorinated phenols using Fenton's reagent. Hazard. Waste Hazard. Mater. 10, 151.

Poulios, I., Tsachpinis, I., 1999. Photodegradation of the textile dye reactive black 5 in the presence of semiconducting oxides. J. Chem. Tech. Biotech. 74, 349.

Price, G.J., Matthias, P., Lenz, E.J., 1994. The use of high power ultrasound for the destruction of aromatic compounds in aqueous solutions. Trans. IChem. E 72 (Part B), 27.

Rachwal, A.J., Foster, D.M., Holmes, M., 1992, Combining Ozone/Advanced Oxidation and Biological Filtration Processes for Organics Removal from Water. Proceedings Water Quality Technology Conference Toronto, Ontario, 1, 542.

Rahhal, R., Richter, H.W., 1988. Reduction of hydrogen peroxide by the ferrous iron chelate of diethylenetriamine-*N,N,N',N'',N'*-pentaacetate. J. Am. Chem. Soc. 110, 3127.

Ray, A.K., Beenackers, A.A.C.M., 1996. A Photocatalytic Reactor Suitable for Water Purification as well as a Process for the Purification of Wastewater by means of such a Photocatalytic Reactor. European patent 96200942.9-2104.

Ray, A.K., 1997. New photocatalytic reactors for destruction of toxic waste pollutants. Dev. Chem. Eng. Min. Proc. 5 (1/2), 115.

Ray, A.K., 1999. Design, modeling and experimentation of a new large-scale photocatalytic reactor for water treatment. Chem. Eng. Sci. 54, 3113.

Ray, A.K., Beenackers, A.A.C.M., 1997. Novel swirl flow reactor kinetic studies of semiconductor photocatalysis. AIChE J. 43, 2571.

Reynolds, G., Graham, N., Perry, R., Rice, R.G., 1989. Aqueous ozonation of pesticides: a review. Ozone Sci. Eng. 11, 339.

Rice, R.G., Browning, M.E., 1981. Ozone Treatment of Industrial Wastewater. Pollution Technology Review No. 84, Noyes Data Corp.

Rice, R.G., 1997. Applications of ozone for industrial wastewater treatment – a review. Ozone Sci. Eng. 18 (6), 477.

Richard, C., Boule, P., 1994. Is the oxidation of salicyclic acid to 2,5-dihydroxybenzoic acid a specific reaction of singlet oxygen? J. Photochem. Photobiol. A: Chem. 84, 151.

Rivas, F.J., Beltran, F.J., Frades, J., Buzeda, P., 2001. Oxidation of *p*-hydroxybenzoic acid by Fenton's reagent. Water Res. 35, 387.

Rosen, H.M., 1973. Use of ozone and oxygen in advanced wastewater treatment. J. Water Pollut. Control Fed. 45, 2521.

Ruppert, G., Bauer, R., Heisler, G., 1994. UV–O_3, UV–H_2O_2, UV–TiO_2 and the photo–Fenton reaction: comparison of advanced oxidation processes for wastewater treatment. Chemosphere 28 (8), 1447.

Sakthivel, S., Neppolian, B., Arabindoo, B., Palanichamy, M., Murugesan, V., 2000. TiO_2 catalyzed photodegradation of leather dye, acid green 16. J. Sci. Ind. Res. 59, 556.

Sauer, M., Ollis, D. F., 1996. Photocatalytic oxidation of ethanol and acetaldehyde. J. Catal. 158, 570.

Schramm, J.D., Hua, I., 2001. Ultrasonic irradiation of dichlorvos: decomposition mechanism. Water Res. 35 (3), 665.

Schulz, C.R., Prendiville, P.W., 1993. Designing high concentration ozone contactors for drinking water treatment plants. Ozone Sci. Eng. 15, 245.

Sclafani, A., Palmisano, L., Davi, E., 1991. Photocatalytic degradation of phenol in aqueous polycrystalline titanium dioxide dispersions: the influence of Iron $(3+)$, Iron $(2+)$ and Silver $(1+)$ on the reaction rate. J. Photochem. Photobiol. A: Chem. 56, 113.

Sedlak, D.L., Andren, A.W., 1991. Oxidation of chlorobenzene with Fenton's reagent. Environ. Sci. Technol. 25, 777.

Senthilkumar, P., Pandit, A.B., 1999. Modeling hydrodynamic cavitation. Chem. Eng. Technol. 22, 1017.

Senthilkumar, P., Sivakumar, M., Pandit, A.B., 2000. Experimental quantification of chemical effects of hydrodynamic cavitation. Chem. Eng. Sci. 55, 1633.

Serrano, B., de Lasa, H., 1999. Photocatalytic degradation of water organic pollutants: pollutant reactivity and kinetic modeling. Chem. Eng. Sci. 54, 3063.

Seymore, J., Gupta, R.B., 1997. Oxidation of aqueous pollutants using ultrasound: salt induced enhancement. Ind. Eng. Chem. Res. 36, 3453.

Shah, Y.T., Pandit, A.B., Moholkar, V.S., 1999. Cavitation Reaction Engineering. Plenum Publishers, USA.

Shirgaonkar, I.Z., 1997. Effect of Ultrasonic Irradiation on Chemical Reactions. Ph.D. Thesis. University of Mumbai, Mumbai, India.

Shirgaonkar, I.Z., Pandit, A.B., 1997. Degradation of aqueous solution of potassium iodide and sodium cyanide in the presence of carbon tetrachloride. Ultrason. Sonochem. 4, 245.

Shirgaonkar, I.Z., Pandit, A.B., 1998. Sonophotochemical destruction of aqueous solution of 2,4,6-trichlorophenol. Ultrason. Sonochem. 5, 53.

Sivakumar, M., Pandit, A.B., 2001. Ultrasound enhanced degradation of Rhodamine-B: optimization with power density. Ultrason. Sonochem. 8, 233.

Sivakumar, M., Pandit, A.B., 2002. Wastewater treatment: a novel energy efficient hydrodynamic cavitational technique. Ultrason. Sonochem. 9, 123.

Sivakumar, M., Tatake, P.A., Pandit, A.B., 2002. Kinetics of *p*-nitrophenol degradation: effect of reaction conditions and cavitational parameters for a multiple frequency system. Chem. Eng. J. 85, 327.

Staehelin, J., Hoigne, J., 1982. Decomposition of ozone in water: rate of initiation of hydroxide ions and hydrogen peroxide. Environ. Sci. Technol. 16, 676.

Subramanian, V., Pangarkar, V.G., Beenackers, A.A.C.M., 2000. Photocatalytic degradation of PHBA: relationship between substrate adsorption and photocatalytic degradation. Clean Prod. Process. 2, 149.

Suri, R.P.S., Paraskowich, M.R., Zhang, Q., 1999. Effect of process variables on sonochemical destruction of aqueous trichloroethylene. Environ. Eng. Sci. 16 (5), 345.

Suslick, K.S., Hammerton, D.A., 1986. The site of sonochemical reactions. IEEE Trans. Ultrason. Ferroelectrics Frequency Control UFFC 33 (2), 143.

Suslick, K.S., Hammerton, D.A., Cline, R.E., 1986. The sonochemical hotspot. J. Am. Chem. Soc. 106, 6856.

Suslick, K.S., 1990. The chemical effects of ultrasound. Science 247, 1439.

Suslick, K.S., Doktycz, S.J., Flint, E.B., 1990. On the origin of sonoluminescence and sonochemistry. Ultrasonics 28 (5), 280.

Suslick, K.S., Mdeleeni, K.M., Reis, J.T., 1997. Chemistry induced by hydrodynamic cavitation. J. Am. Chem. Soc. 119, 9303.

Tanaka, K., Padermpole, K., Hisanaga, T., 2000. Photocatalytic degradation of commercial azo dyes. Water Res. 34 (1), 327.

Tanaka, S., Saha, U.K., 1994. Effects of pH on photocatalysis of 2,4,6,-trichlorophenol in aqueous TiO$_2$ suspensions. Water Sci. Technol. 30, 47.

Tang, W.Z., Huang, C.P., 1996. 2,4,-dichlorophenol oxidation kinetics by Fenton's reagent. Environ. Technol. 17, 1371.

Tang, W., Tassos, S., 1997. Oxidation kinetics and mechanisms of trihalomethanes by Fenton's reagent. Water Res. 31, 1117.

Tanguay, J.F., Suib, S.L., Coughlin, R.W., 1989. Dichloromethane photodegradation using titanium dioxide. J. Catal. 117, 335.

Tatake, P.A., Pandit, A.B., 2002. Modelling and experimental investigation into cavity dynamics and cavitational yield: Influence of dual frequency ultrasound sources Chem. Eng. Sci., In press.

Tauber, A., Schuchmann, H.-P., von Sonntag, C., 2000. Sonolysis of aqueous 4-nitrophenol at low and high pH. Ultrason. Sonochem. 7 (1), 45.

Teo, K.C., Xu, Y., Yang, C., 2001. Sonochemical degradation of toxic halogenated organic compounds. Ultrason. Sonochem. 8, 241.

Theurich, J., Lindner, M., Bahnemann, D.W., 1996. Photocatalytic degradation of 4-chlorophenol in aerated aqueous titanium dioxide suspensions: a kinetic and mechanistic study. Langmuir 12, 6368.

Thoma, G., Swofford, J., Popov, V., Som, M., 1997. Sonochemical destruction of dichloromethane and *o*-dichlorobenzene in aqeous solution using a nearfield acoustic processor. Adv. Environ. Res. 1, 178.

Thoma, G., Gleason, M., Popov, V., 1998. Sonochemical treatment of benzene/toluene contaminated wastewater. Environ. Prog. 17 (3), 154.

Thompson, L.H., Doraiswamy, L.K., 1999. Sonochemistry: science and engineering. Ind. Eng. Chem. Res. 38, 1215.

Topalov, A., Molanar-Gabor, D., Csanadi, J., 1999. Photocatalytic oxidation of the fungicide metalaxyl dissolved in water over TiO$_2$. Water Res. 33 (6), 1371.

Toyoda, A., Zhang, L., Kanki, T., Sano, N., 2000. Degradation of phenol in aqueous solutions by TiO$_2$ photocatalyst coated rotating drum reactor. J. Chem. Eng. Jpn. 33, 188.

Trapido, M., Hirvonen, A., Veressinina, Y., Hentunen, J., Munter, R., 1997. Ozonation, ozone/UV and UV/H$_2$O$_2$ degradation of chlorophenols. Ozone Sci. Eng. 19 (1), 75.

de Traversay, C., Bonnard, R., Adrien, C., Luck, F., 2001. Application of static mixers in drinking water treatment: the ozonation process. Proc. Int. Symp. Mix. Ind. Process. Toulouse, France 4, 55.

Trillas, M., Peral, J., Donenech, X., 1993. Photo-oxidation of phenoxyacetic acid by TiO$_2$ illuminated catalyst. Appl. Catal. B: Environ. 3, 45.

Trillas, M., Peral, J., Donenech, X., 1996. Photocatalyzed degradation of phenol, 2,4-dichlorophenol, phenoxyacetic acid and 2,4-dichlorophenoxyacetic acid over TiO$_2$ in a flow system. J. Chem. Tech. Biotech. 71, 237.

Venkatadri, R., Peters, R.V., 1993. Chemical oxidation technologies: ultraviolet light/hydrogen peroxide, Fenton's reagent and titanium dioxide assisted photocatalysis. Hazard. Waste Hazard. Mater. 10, 107.

Vichare, N.P., Gogate, P.R., Pandit, A.B., 2000. Optimization of hydrodynamic cavitation using model reaction. Chem. Eng. Tech. 23, 683.

Vichare, N.P., Dindore, V.Y., Gogate, P.R., Pandit, A.B., 2001. Mixing time analysis in sonochemical reactors. Ultrason. Sonochem. 8 (1), 23.

Vidal, A., Díaz, A.I., Hraiki, A.E., Romero, M., Muguruza, I., Senhaji, F., et al., 1999. Solar photocatalysis for detoxification and disinfection of contaminated water. Pilot Plant Stud. 54 (2–3), 283.

Vohra, M.S., Davies, A.P., 2000. TiO$_2$ assisted photocatalysis of lead-EDTA. Water Res. 34 (3), 952.

Volk, C., Roche, P., Joret, J.C., Paillard, H., 1997. Comparison of the effect of ozone, ozone-hydrogen peroxide system and catalytic ozone on the biodegradable organic matter of a fulvic acid solution. Water Res. 31 (3), 650.

von Sonntag, C., 1996. Degradation of aromatics by advanced oxidation processes in water remediation: some basic considerations. J. Water Supply Res. Tech. 45 (2), 84.

Walling, C., 1998. Intermediates in the reactions of Fenton type reagents. Acc. Chem. Res. 31, 155.

Wang, Y., 2000. Solar photocatalytic degradation of eight commercial dyes in TiO$_2$ suspension. Water Res. 34 (3), 990.

Wang, Y., Hong, C.-S., 2000. TiO$_2$ mediated photomineralization of 2-chlorobiphenyl: the role of O$_2$. Water Res. 34 (10), 2791.

Wang, Y., Hong, C.-S., 1999. Effect of hydrogen peroxide, periodate and persulfate on photocatalysis of 2-chlorobiphenyl in aqueous TiO$_2$ suspensions. Water Res. 33 (9), 2031.

Wang, T.H., Kang, S.F., Lin, Y.H., 1999. Comparison among Fenton-related processes to remove 2,4-dinitrophenol. J. Environ. Sci. Health A34 (6), 1267.

Watts, R.J., Sundstrom, E.H., Klei, H.H., 1990. Treatment of pentachlorophenol contaminated soil using Fenton's reagent. Hazard. Waste Hazard. Mater. 4, 165.

Watts, R.J., Dilly, S.E., 1996. Evaluation of iron catalysts for the Fenton-like remediation of diesel-contaminated soils. J. Haz. Mater. 51, 209.

Watts, R.J., Jones, A.P., Chen, P.H., Kenny, A., 1997. Mineral-catalyzed Fenton-like oxidation of sorbed chlorobenzenes. Water Environ. Res. 69, 269.

Weavers, L.K., Ling, F.H., Hoffmann, M.R., 1998. Aromatic compound degradation in water using a combination of sonolysis and ozonolysis. Environ. Sci. Technol. 32, 2727.

Weavers, L.K., Malmstadt, N., Hoffmann, M.R., 2000. Kinetics and mechanism of pentachlorophenol degradation by sonication, ozonation and sonolytic ozonation. Environ. Sci. Technol. 34 (7), 1280.

Wei, T.Y., Wang, Y.Y., Wan, C.C., 1990. Photocatalytic oxidation of phenol in the presence of hydrogen peroxide and titanium dioxide power. J. Photochem. Photobiol. 53, 115.

Wu, J., Eiteman, M.A., Law, S.E., 1998. Evaluation of membrane filtration and ozonation processes for treatment of reactive-dye wastewater. J. Environ. Eng. 124 (3), 272.

Wu, J., Wang, T., 2001. Ozonation of aqueous azo dye in a semi-batch reactor. Water Res. 35 (4), 1093.

Xu, N., Shi, Z., Fan, Y., Dong, J., Shi, J., Hu, M.Z.-C., 1999. Effects of particle size of TiO_2 on photocatalytic degradation of methylene blue in aqueous suspensions. Ind. Eng. Chem. Res. 38, 373.

Yamashita, H., Ichihashi, Y., Harada, M., Stewart, G., Fox, M.A., Anpo, M., 1996. Photocatalytic oxidation of 1-octanol on anchored titanium dioxide and on TiO_2 powder catalysts. J. Catal. 158, 97.

Yamazaki, S., Matsunaga, S., Hori, K., 2001. Photocatalytic degradation of trichloroethylene in water using TiO_2 pellets. Water Res. 35 (4), 1022.

Yawalkar, A.A., Bhatkhande, D.S., Pangarkar, V.G., Beenackers, A.A.C.M., 2001. Solar assisted photochemical and photocatalytic degradation of phenol. J. Chem. Tech. Biotech. 76 (4), 363.

Yim, B., Nagata, Y., Maeda, Y., 2000. Degradation of Phthalic Acid Diethyl Ester by Ultrasound in Aqueous Solutions. Proceedings of European Society Sonochem.-7, Toulouse, France, 209.

Yim, B., Okuno, H., Nagata, Y., Maeda, Y., 2001. Sonochemical degradation of chlorinated hydrocarbons using a batch and continuous flow system. J. Hazard. Mater. 81 (3), 253.

Yoo, Y.E., Takenaka, N., Bandow, H., Nagata, Y., Maeda, Y., 1997. Characteristics of volatile fatty acids degradation in aqueous solutions by the action of ultrasound. Water Res. 31 (6), 1532.

Yoon, K., Kim, S., Lee, D.S., Huh, S., 2000. Characteristics of *p*-chlorophenol degradation by photo–Fenton oxidation. Water Sci. Technol. 42 (3), 219.

Yoshida, M., Lee, B.D., Hosomi, M., 2000. Decomposition of aqueous tetrachloroethylene by Fenton oxidation treatment. Water Sci. Technol. 42 (1–2), 203.

Yu, J.C., Yua, J., Zhao, J., 2002. Enhanced photocatalytic activity of mesoporous and ordinary TiO_2 thin films by sulfuric acid treatment. Appl. Catal. B: Environ. 36 (1), 31.

Zeltner, W.A., Hill, C.G., Anderson, M.A., 1993. Supported titania for photodegradation. Chemtech. 23, 21.

Zwinter, C., Krimmel, F.H., 2000. Oxidative treatment of pharmaceuticals in water. Water Res. 34, 1881.