Sonophotocatalytic Reactors for Wastewater Treatment: A Critical Review

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The common optimum operating conditions for sonochemical and photocatalytic oxidation coupled with the similarity in the mechanism of destruction leading to a possible synergism and the possible elimination of some of disadvantages observed for individual processing techniques due to the effects of the other technique has prompted the development of sonophotocatalytic reactors in recent years. The present work aims at critically evaluating the status of the sonophotocalytic reactors with a special focus on wastewater treatment applications. Initially, the discussion has been concentrated on the individual techniques focusing on the recommendations for the optimum operating parameters, novel reactor designs for large scale operations and overview of the literature illustrations in the recent years. The discussion about hybrid technique starts with the mechanism of the expected synergism between sonochemistry and photocatalysis. Different reactor configurations used for the hybrid technique have been analyzed and recommendations have been made for the design of optimum configuration. An optimum set of operating parameters has also been recommended based on the critical analysis of the available literature. It has been observed that sonophotocatalytic oxidation indeed results in significant enhancement of the oxidation intensity and thus the rates of degradation, but its application on a larger scale of operation is hampered, perhaps due to high cost and the lack of suitable design strategies associated with the sonochemical reactors. Some recommendations have been also made for the future work required to eliminate the drawbacks associated with the sonochemical and/or sonophotocatalytic reactors. © 2004 American Institute of Chemical Engineers *AIChE J,* 50: 1051–1079, 2004

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Introduction

Several oxidation techniques such as biological oxidation, chemical treatment using ozone/hydrogen peroxide, wet air oxidation, supercritical oxidation, advanced oxidation processes such as Fenton chemistry, photochemical/photocatalytic oxidation, and ozone in combination with hydrogen peroxide, to name but a few, have been used over the years for the treatment of effluents (Adewuyi, 2001; Beltran et al., 1997; Benitez et al., 1997; Bhatkhande et al., 2002; Bigda, 1995, 1996; Bull and Zeff, 1991; Catallo and Junk, 1995; Chamarro et al., 2001; Eul et al., 1991; Gehringer et al., 1997; Gogate, 2002; Gulyas et al., 1995; Herrmann, 1999; Hoffmann et al., 1995; Ito et al., 1998; Kuo, 1992; Otal et al., 1997; Venkatadri and Peters, 1993). A majority of these processes (except for biological oxidation) have met with limited success and have not been economically used for the large-scale treatment of wastewaters containing a variety of complex organic and inorganic pollutants (Adewuyi, 2001; Gogate, 2002). With new molecules being discovered almost on a continuous basis, some

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of which are biorefractory, the efficacy of biological oxidation techniques has decreased and the course of new inventions was focused on developing alternative techniques for wastewater treatment (Mantzavinos et al., 1997; Otal et al., 1997). It should also be noted that some of these methods were aimed at merely reducing the toxicity level of the effluent or, in other words, at increasing the biodegradability of the effluent so that biological oxidation can be used more efficiently (Gulyas et al., 1995; Hess et al., 1998; Mastin et al., 2001). The reduction in the toxicity achieved at the primary stage of the treatment also affects the efficacy of biological oxidation used subsequently. To increase the extent of reduction in the toxicity, hybrid methods constituting two or more individual techniques have been developed. Some of these include, for example, ultrasound/hydrogen peroxide (H_2O_2) or ultrasound/ozone, ultraviolet light (UV)/H_2O_2 or UV/ozone, ozone/H_2O_2, sonophotocatalytic oxidation, photo-Fenton processes, and catalytic oxidation processes (Benitez et al., 1996, 1997; Chen et al., 1990; Echigo et al., 1996; Engwall et al., 1999; Fallmann et al., 1999; Fung et al., 1999; Gulyas et al., 1995; Guttoneau et al., 1990; Kang and Hoffmann, 1998; Kang et al., 1999) The present work reviews the technique of sonophotocatalytic oxidation in detail. The initial part of this article is concentrated on the basic understanding of the individual techniques of sonochemical oxidation and photocatalytic oxidation, whereas the later part discusses the window of synergism available for the hybrid operation.

Sonochemical Oxidation

Sonochemical oxidation makes use of ultrasound that results in the cavitation phenomenon, which is defined as the formation, growth, and subsequent collapse of microbubbles or cavities occurring in an extremely small interval of time (microseconds), releasing large magnitudes of energy at millions of such locations in the reactor. Some of the important effects of cavitation include, for instance, generation of local hot spots, release of highly reactive free radicals, continuous cleaning as well as an increase in the surface area (resulting from fragmentation and deagglomeration) of the solid catalysts, and enhancement in the mass transfer rates attributed to turbulence generated as a result of acoustic streaming. Various review articles/books have been published in the literature (Adewuyi, 2001; Ashokkumar and Griezer, 1999a; Doraiswamy, 2001; Gogate, 2002; Keil and Swamy, 1999; Lindley and Mason, 1987; Lorimer and Mason, 1987; Luche, 1998; Mason and Lorimer, 1988; Mason, 1990, 1992, 1997, 1999, 2000; Mason and Lorimer, 2002; Pandit and Moholkar, 1996; Shah et al., 1999; Suslick, 1990; Thompson and Doraiswamy, 1999; Young, 1999) covering various aspects of acoustic cavitation. Recent publications of Adewuyi (2001) and Gogate (2002) concentrate on environmental applications and thus the discussion on the sonochemical reactors has been kept brief, concentrating only on the newer concepts related to new reactor designs for large-scale applications, optimum operating parameters for achieving the maximum benefits from cavitational reactors based on critical evaluation of the existing literature, and some typical illustrations in recent years for the confirmation of the conclusions drawn for the optimization of the operating parameters. The basic concepts related to the detailed understanding of the free-radical theory/hot spot theory governing the degradation of the pollutants; conventional reactor designs such as ultrasonic horn, ultrasonic bath, and so forth; and the illustrations of the use of cavitation in wastewater treatment earlier than 2000 can be obtained from the references mentioned earlier.

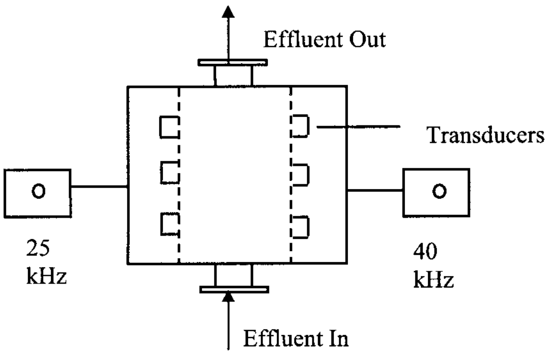
Mechanism of oxidation of pollutants

The destruction/oxidation of pollutants using cavitation is usually described by two approaches, free-radical attack and pyrolysis, although the exact mechanism for the sonochemical oxidations of the mixture of pollutants has not yet been clearly elucidated. There is a simultaneous contribution of both—free-radical attack and pyrolysis—and the controlling mechanism for the destruction is usually dependent on the pollutant in question, most significantly the hydrophobic or hydrophilic nature of the contaminant as well as the operating conditions, which determine the type of the collapse of the cavities and the hydrodynamic conditions existing in the reactor. Hart and Henglein (1985) and Adewuyi (2001) discussed in detail the mechanisms of sonochemical oxidation of different pollutants and attempted to address the issue of the controlling reaction mechanisms.

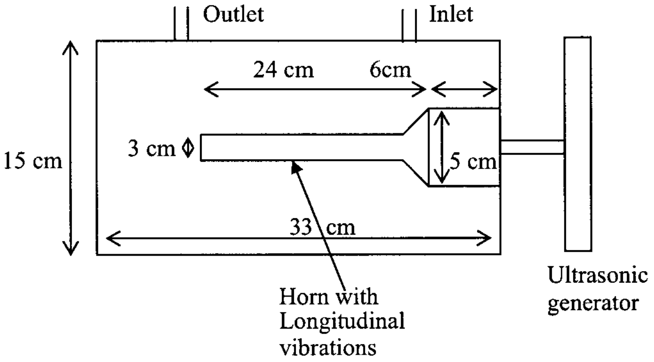
Violent collapse of the cavities in the aqueous cavitating systems results in the formation of reactive hydroxyl and hydroperoxyl radicals. There are three definite regions—inside the cavitating bubble, at the interface of the bubble, and the liquid bulk or in the liquid bulk—where the reaction takes place (free-radical attack on the pollutant); the contribution of each region depends on the type of the pollutant, most significantly the hydrophobic/hydrophilic nature of the pollutant in question (Shah et al., 1999). Confirmation of the free-radical theory as a controlling mechanism for the degradation process is obtained if these reactions show a significant drop in the rates in the presence of free-radical scavengers such as bicarbonate, carbonate ions, and *t*-butanol, for example (Ashokkumar and Griezer, 1999a,b; Krishna et al., 1989; Makino et al., 1983; Sostaric and Reisz, 2002).

According to the hot spot theory (Suslick and Hammerton, 1986; Suslick et al., 1986), which indicates that very high temperatures are generated within the cavitating bubbles (the temperature is maximum in the center of the bubble and decreases toward the wall), the chemical bonds break as the vapors entrapped in the bubbles are subjected to these high temperatures (pyrolysis). Hot spot theory will be dominant where the pollutant molecules have high fugacity character and diffuse and penetrate and are present in the collapsing cavity.

Identification of the controlling mechanism for the degradation process is crucial in deciding the operation strategies for real-world industrial wastewater treatment. Usually the design information available in the literature is based on the simulated effluents or single-constituent solutions, whereas in the real effluents, in addition to the primary constituents, an abundance of impurities, such as ionic species, naturally occurring matter (humic acids), and *t*-butanol, are present. The presence of these impurities, described as free-radical scavengers, decreases the availability of the oxidants (that is, hydroxyl radicals for the degradation of the pollutants) resulting in substantially lower degradation rates compared to those of laboratory-scale studies reported in the literature. Thus if free-radical attack is the controlling mechanism, pretreatment with the aim of removing

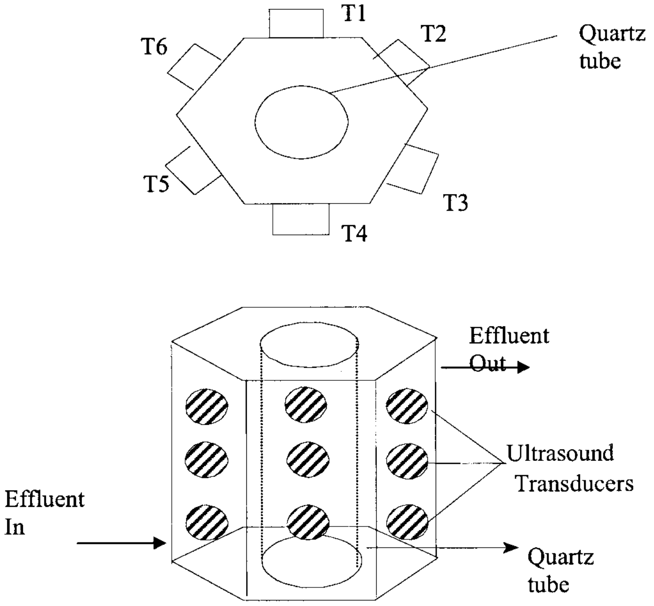


Dual Frequency Flow Cell



Inlet is at 8 cm height from the bottom reactor whereas the outlet is at a height of 32 cm from the bottom so as to facilitate continuous operation

Ultrasonic bath equipped with longitudinally vibrating horn



Triple frequency hexagonal flow cell (Quartz tube is for placement of UV tube at annular location for simultaneous irradiation)

Figure 1. Some of the novel sonochemical reactors.

the radical scavengers is a necessity. On the other hand, if pyrolysis or hot spot theory governs the destruction of the given pollutants (such as chloroform, tri-chloroethylene, MTBE), the rate of degradation remains unaltered even in the presence of free-radical scavengers (Kang and Hoffmann, 1998) and thus no pretreatment will be required because the design information acquired from the literature will be equally valid for actual wastewater treatment plant design.

Novel reactor designs for large-scale applications

Typically, equipment with a higher dissipation area provides higher energy efficiency (a greater amount of energy of the supplied electrical energy is converted for cavitating effects) and also higher cavitational yields [greater degradation per unit supplied electrical energy (Gogate et al., 2001)]. Thus the new reactor designs to be developed for large-scale wastewater treatment should provide a large transducer area, either by the use of single or multiple transducers. The advantage of using multiple transducers will be the availability of different frequencies of irradiation and this type of equipment has been reported to be more beneficial than equipment based on a single frequency (Gogate et al., 2001; Hua et al., 1995a; Sivakumar et al., 2002; Thoma et al., 1997). For better efficacy of the sonochemical reactors, one should aim at increasing the active volume of cavitation, which can be easily achieved by adjusting the arrangement of multiple transducers so that the wave patterns generated by the individual transducers will overlap, also resulting in uniform and increased cavitational activity. Some of the novel designs used for wastewater treatment, at capacity of 2 to 10 L (Bhirud et al., 2003; Gogate et al., 2001, 2003), and which can easily be used in industrial-scale wastewater treatment and operated as continuous reactors are depicted in Figure 1. The basic designs of sonochemical reactors, such as ultrasonic horn and ultrasonic bath, have been described earlier (Gogate et al., 2001; Keil and Swamy, 1999; Pandit and Moholkar, 1996; Shah et al., 1999). A brief description of the novel designs has been provided to the readers for a better understanding of the concepts involved.

Dual-Frequency Flow Cell (Gogate et al., 2001). The dual-frequency flow cell consists of a rectangular vessel with a diameter of 9.5 cm and a height of 20 cm with two sets of transducers (three in each set) mounted on the two opposite faces. Transducers operating (independently or simultaneously) at different frequencies (that is, 25 and 40 kHz) and having an equal power rating of 120 W per set have been provided. Thus three different modes of irradiation (25, 40, and 25 + 40 kHz) are possible in the given system. The flow cell can be operated in a batch or a continuous mode.

Triple-Frequency Hexagonal Flow Cell (Gogate et al., 2003). The hexagonal triple frequency flow cell has a total capacity of 7.5 L and can be operated in batch as well as continuous mode. Transducers (three in each set per side) having an equal power rating of 150 W per side have been mounted (thus the total power dissipation is 900 W when all the transducers with a combination of 20 + 30 + 50 kHz frequencies are functional). The two opposite faces of the flow cell have the same irradiating frequency. The operating frequency of transducers is 20, 30, and 50 kHz and can be operated in different combinations (seven total), either individually or in combined mode. There is a provision for placement of UV lamp in the annular position in the central quartz tube for simultaneous irradiation with UV light.

Ultrasonic Bath Equipped with Longitudinally Vibrating Horn (Bhirud et al., 2003). The novel ultrasonic bath is irradiated using a single longitudinally vibrating transducer kept at the bottom of the reactor (vibrations are in direction away from the base of the reactor). The inner cross section of the reactor has dimensions of 15 × 33 × 20 cm, with a total holding capacity of 8 L (some part of the reactor is occupied by the transducer). An additional heater equipped with a temperature controller has been also provided so as to facilitate some moderately high temperature reactions. The operating frequency of irradiation is 36 kHz and maximum power dissipation into the system is 150 W (operation with varying power dissipation is also possible).

It should be also noted here that generating intense cavitation by the use of multiple frequencies or higher frequencies might not necessarily mean higher cavitational yields for the specific pollutant. It also depends on the relative rates of the reaction between the pollutant and the free radicals and the recombination reaction between the free radicals. If the availability of the pollutant or the reaction between the pollutant and free radicals is the controlling factor, generation of intense cavitation, and thus the generation of higher number of free radicals, will only result in an increase in the rate of recombination reaction such that dissipating more power will not be beneficial. Therefore, a detailed kinetic analysis in terms of establishing the rates of reactions using the free radicals is a necessity before the selection of the operating conditions and the reactor configurations. In the case where the availability of the pollutant is the controlling factor, proper care to ensure completely mixed conditions in the reactor must be taken.

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 generally suited for effective destruction of the pollutants (only up to 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 frequencies > 200 kHz in large-scale operations with good energy transfer efficiency (Berlan and Mason, 1992; Mason, 1992). The power required for the onset of cavitation increases with an increase in the frequency of irradiation and thus the process may become uneconomical at very high frequencies of irradiation. Use of multiple frequencies produces more intense cavitation (Tatake and Pandit, 2002) and thus results in higher yields of transformation (per unit electrical power input); thus dual- or triple-frequency reactors should be used that will also give similar results to a single very high frequency transducer. Larger volumes of effluent can be effectively treated because of the increase in the cavitationally active volume in the case of multiple transducers used for the generation of multiple frequencies or similar frequency from multiple transducer sources. As indicated earlier, the expected synergism in the use of multiple frequencies is strongly dependent on the type of the pollutant in question, more significantly its reactivity toward the free radicals.

(2) Greater energy efficiency has been observed for ultrasonic probes with higher irradiating surface (lower operating intensity of irradiation), which results in more uniform dissipation of energy. 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 a larger area of irradiating surface. Using larger areas for the irradiation also increases the cavitationally active volume and the extent of turbulence generated in the system (Vichare et al., 2001), resulting in a better contact of the pollutant with the cavitating bubbles. Increasing the power dissipation up to an optimum value also leads to an increase in the cavitational yields, as discussed earlier (Gogate, 2002).

(3) The physicochemical properties of the liquid medium (vapor pressure, surface tension, viscosity, presence of impurities/dissolved gases, etc.) also affect the performance of the sonochemical reactors. The liquid-phase physicochemical properties should be adjusted in such a way so as to lower the cavitation inception threshold, resulting in an easy generation of cavities, and at the same time increasing the number of cavities generated with lower initial size. A detailed discussion about the effect of various physicochemical properties and the optimum recommendations has been given in an earlier work (Gogate, 2002).

(4) The rate constant for the sonochemical degradation of the pollutants is generally higher at lower initial concentrations of the pollutant (Hua and Hoffmann, 1996; Hua et al., 1995a) and pretreatment of the waste stream may be done in terms of the dilution of the stream for enhanced cavitational effects. However, an economic analysis must be done comparing the enhanced rates attributed to the lowering of the concentration (thus reduction in the total treatment time) and the negative effects associated with higher total power requirement to treat large volumes of the diluted polluting water [the extent of degradation is directly proportional to power density up to an optimum value (Sivakumar and Pandit, 2001)]. Depending on the outcome of this analysis, an appropriate dilution factor should be used before the treatment. Alternatively, a recycle stream can also be used in the case of continuous reactors. It should be also noted that for the case of effluent, consisting of multiple complex contaminants, and for highly loaded effluents, appropriate dilution is an essential precondition for the onset of degradation process using cavitation (Gogate, 2002).

(5) Aeration and the addition of catalyst for intensification of the cavitational activity such as TiO_2, $NiSO_4$, CCl_4, Fe^{++}/Fe^{+++}, $CuSO_4$, NaCl, and so forth. enhances the extent of degradation (Ingale and Mahajani, 1995; Pandit et al., 2001; Seymore and Gupta, 1997; Shirgaonkar and Pandit, 1997). The presence of gases (oxygen, ozone) or gaseous mixtures such as

Ar/O_3 mixture also increases the efficiency of acoustic cavitation in some cases (Olson and Barbier, 1994; Weavers et al., 1998). It is difficult to generalize and optimize the effect of the presence of gases and/or catalyst because the effect is usually not unidirectional. On one hand. where the presence of the catalyst enhances the number of cavitation events by providing additional nuclei, it also acts as a barrier for the propagation of the sound waves, thereby decreasing the effective energy dissipation and distribution into the system. Thus an optimum catalyst concentration may be considered, depending on the system under investigation; however, it may happen that not all the sonochemical reactions are enhanced by the presence of the catalyst and so for a particular application, laboratory-scale experiments are required unless data are available in the literature with the specified catalyst. The possibility of obtaining the beneficial effects with the presence of solid particles is always higher for large-scale reactors irradiated with multiple transducers compared to that of conventional single-transducer immersion reactors, given that the contribution of the scattering of the incident sound waves will be maximum in a small-scale operation and for the case of irradiation with a single transducer. A detailed discussion about the effect of different catalysts and their optimum loading on the sonochemical reactions has been presented in an earlier work (Gogate and Pandit, 2004).

The presence of air/gas, either in a dissolved state or as individual bubbles, provides additional nuclei for the generation of cavitation, resulting in an enhanced number of cavitational events increasing the summation of the pressure/temperature pulse generated in the system as well as the number of free radicals (Sochard et al., 1997, 1998). On the other hand, too much aeration/gassing results in a decoupling effect and thus lower the energy input into the system and the generation of large number of gaseous cavities is not beneficial because the energy content of these cavities can be orders of magnitude lower, compared to that of the vaporous cavities, and thus the cavitation intensity will be lower (Vichare et al., 2000). The effect of the presence of different gases on the degradation process is further complicated by the fact that the physicochemical properties of the gas, such as solubility, thermal conductivity, and polytropic index, also affect the intensity of cavitation. It can be only said at this stage that the optimum conditions for gassing/aeration are strongly dependent on the application in question and should be established using laboratory-scale studies. The effect will be more beneficial on a larger scale of operation because the contribution attributed to the enhancement of the number of cavities will be dominant at larger scale of operation compared to the laboratory scale (at larger scales, the chances of coalescence of cavities leading to an increase in the cavity size and thus lower intensity of cavitation are marginal; also the decoupling effect will be less).

(6) The rate of the destruction is inversely proportional to the operating temperature. Temperature affects the vapor pressure of the medium, and thus lower temperatures (typically of the order of 10–15°C) are preferred (Sivakumar et al., 2002). However, if the dominant mechanism of the destruction is pyrolysis, this conclusion may not be equally valid. In this case, an increase in the temperature of the reaction increases the vapor content in the collapsing cavity and thus more pollutant concentration will be exposed to cavitating conditions (collapse temperatures/pressures). Thus, even if the cavitation intensity is decreased, more exposure of the pollutant may lead to an increase in the overall rate of degradation. Thus understanding the mechanism of degradation of the pollutant by cavitation plays a crucial role in the design of the sonochemical reactors for the effluent treatment applications.

Mason and Cordemans de Meulenaer (1998) provided the following 10 recommendations/steps in the optimization of an ultrasonic process.

(1) Make cavitation, easier to accomplish by the addition of solids or gas bubbles to act as nuclei.

(2) Attempt to entrain different gases or mixture of gases.

(3) Use different solvents as cavitating media 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 reactants in the reactor at once.

(6) If possible, attempt to homogenize two-phase systems as much as possible by agitation.

(7) Attempt different shapes (diameters and volumes) for the reactor.

(8) It may be better (but not always) to avoid standing-wave conditions by performing sonochemical reactions under high-power conditions with mechanical stirring.

(9) Wherever possible, attempt to transform a batch system into a continuous one.

(10) Choose conditions that allow comparisons between different sonochemical reactions.

The above steps are very important when the application considered involves chemical synthesis. In the case where the application is related to wastewater treatment, performing the optimization exercise with all the steps mentioned above would be extremely time consuming and cost intensive and is also not realistic, given that the systems are predominantly aqueous in nature. Moreover, the designed reactor should give flexibility in terms of application to the different types of effluent streams. Thus, the aim should be directed toward the development of a reactor capable of degrading a variety of polluting compounds and the process intensification can then be aimed using solid catalysts, introducing air or gaseous mixtures, for example. Although Mason and Cordemans de Meulenaer (1998) indicated that the formation of standing waves should be avoided using conditions of high-power dissipation and mechanical stirring, the phenomenon of standing waves is far from being clearly understood. There have been contrary reports in the literature indicating that the formation of standing waves is beneficial and results in an increase in the cavitational yield. Gonze et al. (1998) reported that the yields for degrading sodium pentachlorophenate (NaPCP) were higher in the case of multiple transducer reactors where standing wave patterns are present compared to yields of the other reactor with transducers adjacent to each other (standing waves are not formed). Gogate et al. (2003) reported the beneficial effects of standing waves for the degradation of formic acid. There are also other citations (Dickens and Luche, 1991; Henglein et al., 1989; Pugin, 1987) in the literature reporting the profound effect of standing waves on the overall cavitational yields from the reactor and also on the reaction pathways. Thus, whereas it appears that the standing waves are quite important in deciding the overall cavitational yields, no specific recommendation can be made at this stage about its deliberate generation or avoidance during the operation. Parallel-plate reactors with multiple transducers result in a significant increase in the cavitationally active volume and even if the formation of the standing waves results into negative effects; its effect may not be significant, given the dominant contribution of the increased cavitationally active volume.

Overview of the work done in recent years

The use of sonochemical reactors for the wastewater applications is not new to the researchers and there are many illustrations in the literature where these have been successfully used for the degradation of a variety of compounds over different scales of operation and the reported studies varying in terms of target chemical studied, type of the equipment, and operating conditions. Adewuyi (2001) gave an excellent overview of the earlier studies in terms of the use of sonochemistry for wastewater treatment depicting the type and concentration of the contaminant degraded, intermediates/products formed in the process, and important results obtained in the work. On similar lines, Table 1 depicts some of the recent applications illustrating the type of equipment used with the scale of operation, the chemicals used in the study, and the important findings of the work published subsequently that are not considered in the work of Adewuyi (2001). It can be seen from the table as well as from the overview given by Adewuyi (2001) that the majority of the work is on a laboratory scale, giving information that cannot be directly used for the design of the large-scale reactors. 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 used with real effluents containing a variety of compounds.

Peters (2001) recently attempted to address this situation. Peters (2001) studied the sonolytic degradation of 1,2-dichloroethane prepared in deionized water (model constituent solution without the presence of any ionic species) and also degradation of a real sample [concentration of about 350–390 μg/L with other volatile organic compounds (VOCs) amounting to 80–85 μg/L and some radical scavengers] and reported that the destruction was complete within 120 min for all the components in both the samples (conditions: frequency of irradiation, 361 kHz; calorimetric power dissipation, 52 W; volume of effluent, 200 mL; operating pH, 6.28; and temperature, 9°C; the rate of degradation was lower in the case of real effluent because of the presence of radical scavengers) and also for some of the intermediates formed in the destruction process (such as *trans*-1,2-dichloroethane). However, in another recent work, Commenges et al. (2000) reported that ultrasonic irradiation failed to induce any decrease in the toxicity and chemical oxygen demand (COD) for a concentrated sample of effluent from a paper mill (conditions: frequency of irradiation, 500 kHz; calorimetric power dissipation, 150 kW/m^3; and temperature, 20°C). This may be ascribed to the high concentration of the complex refractory materials present in the paper mill effluent. Dilution of the stream resulted in about 17% COD reduction (time of operation not specified); still sonication is not a favored method for this type of effluent.

Thus the question still remains: can the highly efficient and successful laboratory-scale technique for model constituent solutions be feasible for the degradation of real effluents? Future work should be directed in terms of understanding the detailed role of the following effluent parameters to determine the efficiency of cavitation process as a technique for the treatment of real effluents containing a complex mixture of organic compounds:

- Role of inorganic components and gases
- Influence of dissolved or intermediate components on the pH during the sonication process
- Influence of precipitates and particles present initially or formed in situ
- Effects attributed to the presence of halide ions

Additionally, the cost of applying ultrasonic irradiation for the destruction process on an industrial scale must be considered. The current costs for the remediation of contaminated ground water using acoustic cavitation are an order of magnitude higher than those by air stripping/active carbon processes (Peters, 2001). Another gray area in the prospective use of acoustic cavitation for large-scale wastewater treatment involves the problems associated with the high-frequency transducers. An alternative for high-frequency transducers is the use of multiple-frequency/multiple-transducer reactors, although more research efforts are required towards the successful designing and testing of the multiple-frequency reactors for a variety of pollutants and real effluents. Thus, it is important to either find an alternative means for generating cavitating conditions efficiently [hydrodynamic cavitation (Gogate and Pandit, 2001)] or use acoustic cavitation (generated by ultrasonic irradiation) in combination with other methods such as photocatalytic oxidation and wet air oxidation, for example. Hydrodynamic cavitation gives more energy-efficient destruction than that of acoustic cavitation (Gogate and Pandit, 2001; Gogate et al., 2001); nonetheless, the intensity of cavitation generated in the hydrodynamic cavitation reactors designed and used so far is not sufficient to degrade the mixture of chemicals or highly loaded effluents. Some preliminary work in this direction has been reported by Sivakumar and Pandit (2002) and Kalumuck and Chahine (2000), considering model constituent solutions of Rhodamine B (a typical effluent obtained from dyes industry) and *p*-Nitrophenol, respectively.

Photocatalysis

Photocatalytic degradation processes are gaining importance in the area of wastewater treatment because these processes result in complete mineralization of the pollutant with operation at mild conditions of temperature and pressure, and, importantly, sunlight or near-UV light can be used as a source of energy. Use of sunlight (Dillert et al., 1999; Guillard et al., 1999; Yawalkar et al., 2001) for irradiation in the case of photocatalytic oxidation or hybrid processes based on the same should result in considerable economic savings especially for large-scale operations.

The use of photocatalytic oxidation processes for the wastewater treatment is not new to researchers and there are good review articles/books available on this subject (Barbeni et al., 1985; Fox and Duley, 1993; Gratzel, 1983; Hoffmann et al., 1995; Kalyanasundaram and Gratzel, 1993; Mills et al., 1993; Nozik, 1978; Pellizzetti and Serpone, 1986; Serpone and Pellizzetti, 1989; Serpone et al., 1985; Wallace et al., 1982) covering the analysis of the studies before 1995 and depicting basics of the process in detail. Some of the more recent promising works include Blake (1997), Herrmann (1999), and Bhatkhande et al. (2002). These reviews have attempted to under-

Table 1. Representative Work Done in the Area of Sonochemical Destruction of Effluents

No.	Ref.	Type of Equipment and Experimental Details	Highlights of the Work
1	Chemat et al. (2001)	Ultrasonic generator Branson W-450 with driving frequency of 20 kHz with power output of 50 W. Capacity of reactor is 100 mL and the operating conditions of 25°C temperature and H_2O_2 concentration of 0–500 mg/L. Total pollutant load is 100 mg/L. Chemical studied: Humic acid and naturally occurring samples of ground water (11% humic acid, 34% fulvic acid and 55% hydrophilic acid)	Degradation of synthetic humic acids is complete within 60 min; however TOC analysis shows only 40% removal. Thus role of products and intermediates has to be well understood. Addition of hydrogen peroxide increases the degradation only up to an optimum dose (200 mg/L for 100 mg/L initial humic acid concentration). Acidic conditions are favorable. Natural samples (mixture) of acids also undergo degradation.
2	Gaddam and Cheung (2001)	Recirculating type system with ultrasonic horn operating at 20 kHz, power output at 200 W, and batch volume as 250 mL. Pollutant loading is varied in the range of 22 to 169 mg/L. Chemical studied: 1,1,1-Trichloroethane	About 99% removal is observed within 1 h. Initial concentration (in the range 22 to 169 mg/L) does not have a definitive effect on rate constant. Optimum conditions have been given as 0.212 MPa pressure, 14.2°C temperature and pH 10.9. Model presented for estimation of rate constants as a function of temperature, pressure, and pH.
3	Sivakumar et al. (2002)	Dual-frequency flow cell (frequency of 25 and 40 kHz, power input of 120 W per side), capacity: 1500 mL, pollutant loading in the range of 0–500 ppm. Chemical studied: *p*-Nitrophenol	Rate of degradation is higher with dual-frequency operation (25 + 40 kHz) as compared to individual frequencies (25 and 40 kHz operated individually). Synergism has been reported for the use of multiple frequency transducers (rate constant for combination is $3.33 \times 10^{-5}\ s^{-1}$, whereas for 20 kHz it is $1.33 \times 10^{-5}\ s^{-1}$ and for 40 kHz it is $1.67 \times 10^{-5}\ s^{-1}$). The rate constant is inversely proportional to the operating temperature as well as operating pH (at pH 5 rate constant is $1.67 \times 10^{-5}\ s^{-1}$, whereas at pH 7 the rate constant decreases to $1.5 \times 10^{-5}\ s^{-1}$; all the other operating conditions being the same). Rate constant was also greater at lower initial concentration ($1.33 \times 10^{-5}\ s^{-1}$ at 10 ppm as against $0.33 \times 10^{-5}\ s^{-1}$ at 100 ppm). Modeling of dual-frequency acoustic flow fields has been presented based on the bubble dynamics to explain the observed synergism with multiple frequencies.
4	Neppolian et al. (2002)	Glass reactor with capacity of 150 mL equipped with a VCX-400 vibracell sonicator operating at 20 kHz frequency and 40% amplitude. Operating temperature of 20°C maintained with the help of a cooling jacket. Pollutant concentration is varied in the range of 2.84×10^{-2} to 2.84×10^{-1} mM. Chemical stuided: MTBE	The observed pseudo first-order rate constant decreases from 1.25×10^{-4} to $5.32 \times 10^{-5}\ s^{-1}$ as the concentration of MTBE increases from 2.84×10^{-2} to 2.84×10^{-1} mM. The rate of degradation of MTBE increases with an increase of the power density of ultrasonicator and also with the rise in reactor system temperature. The presence of sand particles (0.1 g/mL) was reported to give no effect on the extent of degradation. In the presence of oxidizing agent, potassium persulfate, and sonolytic rate of degradation of MTBE was accelerated substantially (rate constant of $6.3 \times 10^{-5}\ s^{-1}$ in the presence as against $1.27 \times 10^{-5}\ s^{-1}$ in the absence of oxidant) though an optimum concentration was observed (10 mM for initial concentration of MTBE as 2.84×10^{-2} mM). It is found that the ultrasound/Fe^{2+}/H_2O_2 method is the most promising process for the degradation of MTBE among various oxidation techniques studied in the work. More than 95% degradation of MTBE (2.84×10^{-2} mM) along with its intermediate products has been achieved during the coupled ultrasound/Fe^{2+}/H_2O_2 method. A kinetic model, based on the initial rates of degradation of MTBE and TBF (intermediates), has been presented and is reported to give a good agreement with the experimental results.
5	Wayment and Casadonte (2002)	Variable-frequency sonicator with calorimetric power of 2–3 W for a capacity of the reactor of 10 mL and pollutant loading of 100 ppm. Effect of frequency of irradiation, presence of dissolved gases, hydrogen peroxide, free-radical scavengers has been investigated. Chemical studied: Alachlor	Rate constant at 300 kHz frequency ($6.25 \times 10^{-4}\ s^{-1}$) is order of magnitude more as compared to 20 kHz ($2.67 \times 10^{-5}\ s^{-1}$). Argon was found to be more efficient compared to air or oxygen at all the frequencies. Addition of hydrogen peroxide does not have a substantial effect on rate constants (40% increase for a concentration of 10^{-3} mM) at 300 kHz operating frequency. Presence of radical scavengers result in a decrease in the rate constant, which is less significant as compared to KI oxidation indicating the presence of pyrolysis mechanism.

Table 1. Representative Work Done in the Area of Sonochemical Destruction of Effluents (Continued)

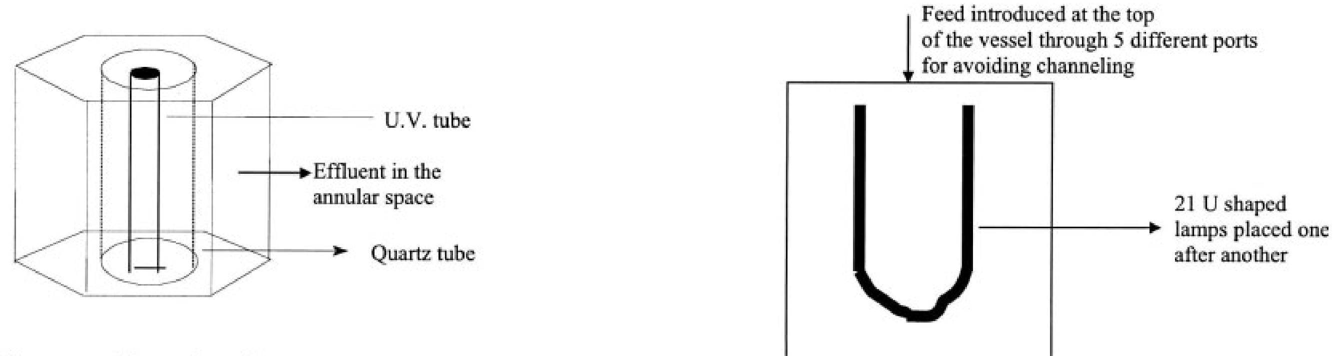
No.	Ref.	Type of Equipment and Experimental Details	Highlights of the Work
6	Tezcanli-Guyer and Ince (2003)	Glass reactor with capacity of 1.2 L surrounded by a cooling jacket for maintaining a constant temperature of 20°C and irradiated by a plate type piezoelectric transducer (area = 22.05 cm^2) at 520 kHz frequency and supplied power of 100 W. Pollutant loading is in the range of 20 to 60 mg/L. Chemical studied: C.I. Reactive red 141, C.I. Reactive black 5, C.I. Reactive brown 4, and C.I. Reactive blue 3	Degradation was reported to follow pseudo first-order kinetics. Optimum supplied power was observed to be 40 W, whereas the rate constant was maximum at initial concentration of 20 mg/L. At optimized conditions the rate constant for color removal of different species were reported to be 2.47×10^{-4} s^{-1} for red, 2.32×10^{-4} s^{-1} for black, 2.6×10^{-4} s^{-1} for brown, and 8.95×10^{-4} s^{-1} for blue dye. The TOC removal rates were lower as compared to color removal rates, which can be attributed to accumulation of organic mass as destruction products.
7	Entezari et al. (2003)	Three different sonochemical reactors: probe transducer operating at 20 kHz, plate type transducer at 500 kHz, and cylindrical tubular reactor at 35 kHz. The calorimetric power was fixed at 50 W and the reaction volume at 350 mL. Constant temperature of 20°C and natural pH with initial concentration in the range of 0.662 to 0.678 mM. Chemical studied: Phenol	Rate constant for degradation of phenol at 500 kHz (9.5×10^{-5} s^{-1}) was 19 times more compared to that at 20 kHz (5×10^{-6} s^{-1}) and about 4 times more as compared to 35 kHz (2.17×10^{-5} s^{-1}). Presence of hydrogen peroxide and copper sulfate results in an intensification of the degradation process (rate constants at 20 kHz operation are 1.67×10^{-5} s^{-1} and 1.67×10^{-4} s^{-1}, respectively). The cylindrical tubular reactor operating at 35 kHz was reported to be efficient for combined operation as compared to individual techniques of ultrasonic irradiation as well as Fenton oxidation.
8	Bruggemann et al. (2003)	1000-mL double-jacketed glass reactor irradiated with 850 kHz transducer with a power supply of 120 W. Constant operating temperature of 35°C and some experiments in the presence of argon (36 lph). Pollutant loading is in the range of 0.1 to 1 g/L. Chemical studied: model and real process wastewater containing ambroxol	Lower initial concentration is favored (extent of removal is 14% in 5-h treatment for 1 g/L ambroxol content, whereas it is 59% for 0.1 g/L). Presence of NaBr (5 g/L) reduces the extent of degradation from 14% to about 5% at initial ambroxol content of 1 g/L. Ultrasonic treatment considerably improves the biodegradability of the effluent. Original process water (initial pH of 3) gives a rate constant of 4.39 $mg^{0.6}$ $L^{0.4}$ h^{-1} kW^{-1}, which is two times more compared to the process water at pH of 6 and about 10 times more compared to process water at initial pH of 12. Rate constants for hydrogen peroxide formation have been estimated (in the range 0.8 to 27.4 mg h^{-1} kW^{-1} for various operating conditions).

stand the mechanism of the photocatalytic oxidation, including the effect of band-gap energy of the catalyst and the position of the valence and conduction bands on the photocatalytic efficiency, and provide background on the basics regarding the chemistry as well as the type of photocatalyst to be used for a specific oxidation scheme. In the current work, we have concentrated on the engineering aspects dealing with the type of reactors to be used with specific discussion on large-scale reactors and the selection of the optimum operating parameters for achieving maximum benefits. Some of the recent illustrations from the literature have been discussed for a better understanding of the optimization exercise of the operating parameters.

New concepts in reactors for large-scale photocatalytic oxidation

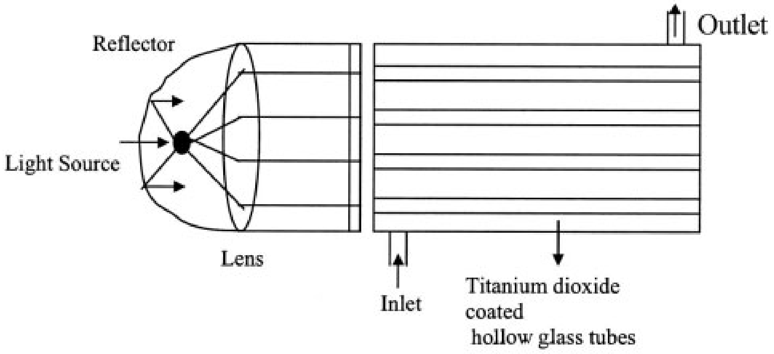
The photocatalytic process can be carried out simply by using a slurry of the fine particles of the solid semiconductor material dispersed in the liquid phase in a reactor irradiated with UV light, either directly or indirectly. The proper dispersion of catalyst in the liquid phase can be achieved using mechanical stirrers on large scales of operation or sometimes aeration can also serve the purpose in part. However, in the case of slurry reactors, the performance of the reactor might be severely affected by the low irradiation efficiency attributed to the opacity (turbidity) 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 <1 micron). A further problem is the fouling of the surface of the radiation source and/or catalyst particles as a result of the deposition of pollutant molecules or their intermediate degradation species. Thus the application of slurry reactors for the photocatalytic treatment on large-scale faces quite a few problems 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 (e.g., TiO_2) with a well-known photocatalytic activity satisfy the first possibility, but can be very sensitive to erosion by the flowing liquid. Durable supported films can be obtained by different techniques like physical and chemical vapor deposition, but in this case the crystalline structure of the final product and consequently the catalytic activity may be difficult to control. Thermal treatment at 500°C can be used to increase the extent



Hexagonal annular photoreactor
Different outer reactor configurations have also been used. Catalyst can be in suspended form or also can be immobilized on the quartz tube

Section of Novel Tube light reactor used by Ray and Beenackers (1998)



Multiple tube reactor

Figure 2. Novel designs of photocatalytic reactors.

of the crystalline nature of the catalyst obtained by physical or chemical vapor deposition. Scouring is another problem associated with the films composed of immobilized powders of TiO_2 (Bideau et al., 1995). Additionally, reduced catalyst area to volume ratio for the case of an immobilized photocatalyst is likely to cause mass transfer and diffusion limitations. Butterfield et al. (1997) reported a modified fabrication technique and design of the reactor to eliminate scouring. In this case, oxide is actually grown on a titanium substrate as a defect film (a film that is electronically conducting, even in the dark), which also allows the application of an electric field with a view of enhancement in the extent of degradation.

Overall, the immobilized or supported catalytic reactors offer many advantages, the most important of which—the supported catalyst—is not allowed to mix with the fluid, thus avoiding the requirement of ultrafine particle separation. Various devices have been developed such as a 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, although the most important point is to achieve uniform irradiation of the whole active catalyst surface and to minimize the mass transfer resistance. Some of the novel designs of photocatalytic reactors are represented in Figure 2, whereas the discussion about basic designs of these reactors can be obtained from Blake (1997) and Herrmann (1999).

The hexagonal annular reactor represented in Figure 2 houses a UV lamp inside a quartz tube on which a thin coating of TiO_2 particles can be provided (should result in uniform irradiation of the entire catalyst surface at near incident intensity of irradiation). Continuous flow of the effluent can be achieved from the outer surface of the catalyst film. The main advantage of the reactor is the possibility of using an acoustic field from the outside, which allows simultaneous irradiation of ultrasound and UV light. The tube light type or the multiple tube heat exchanger type configurations also help in achieving uniform distribution of the incident light. Depending on the load of the effluent, the number of tubes to be used can be adjusted (this helps in adjusting the resident time of the effluent in the reactor) and the reflectors can be designed in such a way that the catalyst particles are subjected to maximum intensity. Ray and Beenackers (1997) used a novel swirl flow reactor, operating in continuous mode, consisting of two glass plates placed between soft padding housed within stainless steel and aluminum casings. The catalyst can be deposited on either plate and the effluent is introduced tangentially between the two plates, which creates a swirl flow that minimizes the mass transfer resistance.

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 in the recent years is depicted in

Table 2), the important operating parameters, which affect the overall destruction efficiency of the photocatalytic oxidation process, can be given as:

(1) *Amount and type of the catalyst.* Use catalyst concentration only up to an optimum value (Andreozzi et al., 2000; Dijkstra et al., 2001). It should be also noted that the optimum value is strongly dependent on the catalyst size distribution and the type and concentration of the pollutant as well as the rate of generation of free radicals (determined by the operating conditions of the reactor) and laboratory-scale experiments are required to determine the optimum value unless data are available in the existing literature—most importantly with similar operating conditions. Degussa P-25 TiO_2 catalyst is considered the most beneficial (Sakthivel et al., 2000; Yamazaki et al., 2001).

(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 large-scale designs (Mukherjee and Ray, 1999). Moreover, nearly 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 the 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 the group of Ray in this area is noteworthy (Chen and Ray, 1998; Mukherjee and Ray, 1999; Ray, 1997, 1999; Ray and Beenackers, 1997, 1998). Also the ideal material of construction for the reactor should be quartz, to maximize the incident irradiation intensity.

(3) *Wavelength of the irradiation.* The threshold wavelength corresponds to the band-gap energy for the semiconductor catalyst; for example, for the TiO_2 catalyst having a band-gap energy of 3.02 eV, the ideal wavelength is at 300 nm (that is, near-UV radiation). Sunlight may also be used for the excitation of the catalyst in some cases, as discussed earlier, resulting in considerable economic savings.

(4) *Initial concentration of the reactant.* For highly concentrated effluents, absolutely no destruction may be observed (this may be attributed to the saturation of the catalyst surface active sites with the pollutants) and dilution is essential in this case [Herrmann (1999) reported that no degradation was observed for real effluent with a COD of 800,000 mg/kg and had to be diluted 1000 times, after which COD reduction was observed]. Using lower concentrations of the pollutants is beneficial (Mazzarino and Piccinini, 1999; Vohra and Davies, 2000). To give a quantitative representation of the effect, Beltran et al. (1993) showed that the destruction of atrazine is 70% for an initial concentration of 10 ppm, whereas for 100 ppm, only 45% of the initial atrazine was 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 the second case as against only 7 ppm for the first case) or may not be lower for higher concentrations; moreover, adverse effects of enhanced power requirements for the treatment of large quantum of effluent must be analyzed before reaching a firm conclusion about the use of optimum concentration during the treatment for destruction of the organic compound. The Langmuir–Hinshelwood type of models (Hermann, 1999; Topalov et al., 1999) can be used to relate the observed rates with the initial concentration of the pollutant, although 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, attributed to the recombination of electron-hole pairs, the temperature may increase. If the temperature is expected to go beyond 80°C, intermediate cooling is recommended because there is a drastic reduction in the rate of reaction above 80°C (Hermann, 1999). At temperatures above 80°C, the exothermic adsorption of the pollutant becomes unfavorable and tends to be the rate-limiting step that leads to decreased activity and thus reduction in the reaction rates (Hermann, 1999). At higher temperatures, the dissolved oxygen concentration in the medium is also reduced and hence degradation is affected in a negative manner. In the range of 20–80°C, usually a weak dependency of the degradation rates on temperature has been observed (Andreozzi et al., 2000; Fox and Duley, 1993; Hofstadler et al., 1994).

(6) *Radiant flux.* The reaction rate is directly proportional to the intensity of radiation (W/m^2); usually linear variation is observed at low intensities and beyond a certain value of intensity (dependent on the reactor conditions as well as the nature of the effluent), the rate of the reaction exhibits a square root dependency 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 densities are high. Another important factor about the incident light is the wavelength of irradiation. Shorter wavelengths are recommended for better results (Hofstadler et al., 1994; Matthews and McEvoy, 1992a). Moreover the angle of incidence of the UV light should always be 90°, because 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 (that is, more specifically on the electrostatic interaction between the catalyst surface and the pollutant). The adsorption of the pollutant and thus the rates of degradation will be maximum near the zpc of the catalyst (Subramanian et al., 2000). pH also affects the positions of the valence and conduction bands and thus the band-gap energy, which controls the photocatalytic efficiency, although the extent of effect is also dependent on the photocatalyst itself. Xu and Schoonen (2000) have elaborately explained the energy positions of the conduction and valence bands and the effect of pH on the same for a variety of metal oxide and sulfide photocatalyst.

For some of the pollutants, which are weakly acidic (such as lead–EDTA complexes, *p*-hydroxy benzoic acid, etc.), the rate of the photocatalytic oxidation is higher at lower pH because of an increase in the extent of adsorption under acidic conditions (Andreozzi et al., 2000; Park et al., 2003; Piscopo et al., 2001; Tanaka et al., 2000; Vohra and Davies, 2000). Some pollutants, which undergo hydrolysis under alkaline conditions or undergo dissociation over a certain pH range, may show an increase in the rate of photocatalytic oxidation with an increase in the pH

Table 2. Some Representative Work in the Area of Destruction of Contaminants by Photocatalytic Oxidation

No.	Reference	Type of Equipment and Experimental Details	Highlights of the Work
1	Sakthivel et al. (2000)	Reactor (30 cm height and 3 cm diameter) with water circulation for maintenance of temperature at 25–30°C irradiated by 8 × 8 W low-pressure mercury arc lamp. Various photocatalysts (TiO_2 anatase grade, SnO_2, ZrO_2, CdS, μ-Fe_2O_3) were studied with loading in the range 0.5 to 3 mg/mL. Chemical Studied: Leather dye, Acid green 16	100% degradation of the dye was achieved in about 6 h time. The efficiency decreased with an increase in the initial concentration of the dye as well as pH and light irradiation intensity, showed an optima with respect to TiO_2 catalyst concentration at 250 mg/mL. TiO_2 P-25 catalyst is the best among the various semiconductor catalysts studied. The addition of oxygen continuously increases the efficiency, whereas H_2O_2 and Fenton's reagent addition increases the extent of degradation only up to an optimum amount (0.04 M H_2O_2, 0.005 M $FeSO_4$, respectively). Bubbling of nitrogen gas decreases the extent of degradation.
2	Malato et al. (2002)	Pilot reactor with capacity of 40 L and effluent flows through 3 collectors containing 8 pyrex tubes each arranged in series. Solar concentrators were used with an incident intensity of 30 W/m^2. Collectors are adjusted in such a way that the incident light is not concentrated inside the photoreactor and thus the maximum temperature reached is around 40°C without thermal insulation. TiO_2 photocatalyst is used (250 mg/L) and some experiments with homogenous photo-Fenton method (0.05 mM Fe). Chemical studied: Water-soluble pesticides: imidacloprid, formetanate, methornyl (each 50 mg/L), and diuron (30 mg/L)	Methornyl is not degraded at all by photolysis, whereas the percentage degradation of imidacloprid, formetanate, and diuron is 55, 10, and 44%, respectively, in 48 h of treatment. Photo-Fenton as well as use of TiO_2 catalyst resulted in disappearance of all the pesticides within 150 min of treatment time. The results also confirm that the use of photocatalyst is favorable as compared to photolysis alone. Photo-Fenton is more efficient in degradation as compared to photocatalysis (time for 90% TOC removal of imidacloprid, formetanate, methornyl, and diuron is 421, 399, 635, and 124 min, respectively, for photocatalysis and 187, 105, 368, and 159 min for photo-Fenton technique. Further, the iron requirement was at a minimum indicating the favorable economics of the technique.
3	Franch et al. (2002)	Cylindrical pyrex reactor (capacity is 400 mL) provided with a cooling jacket to maintain temperature at 25°C and irradiated using medium pressure mercury vapor lamp (125 W). Incident radiant flux was 8.31×10^{-6} einstein/L · s. Degussa P-25 TiO_2 is used as photocatalyst at a loading of 1.5 g/L for 1 mM solution of diacids. Chemical studied: oxalic, maleic, and fumaric acids.	In the absence of light or TiO_2, no reduction in initial organic concentration is observed. The rate constant for removal of fumaric acid, oxalic and maleic acid has been reported to be 1.75, 2.93, and 1.93 ($\times 10^{-7}$ mol/L · s), respectively. With an increase in initial pH, the rate of degradation of oxalic acid decreased over the range 3 to 9, whereas rate of degradation of maleic and fumaric acid decreased till pH of 5 and then increased. The effect is attributed to the zPc charge of TiO_2 photocatalyst and affinity of maleic and fumaric acid towards generated hydroxyl radicals in the liquid bulk. For a multicomponent system, the rates of degradation of individual species are order of magnitude lower.
4	Lizama et al. (2002)	Slurry-type photoreactor with 1-L capacity, irradiated by commercial 125-W lamp. Incident radiant flux was 2.1×10^{-5} einstein/L · s. Reaction mixture was maintained at constant temperature of 25°C. Photocatalyst used was Degussa P-25 TiO_2 and ZnO (in the range 0.5 to 1.5 g/L). Pollutant loading in the range of 30 to 70 ppm. Chemical studied: Reactive blue 19	Complete discoloration was obtained for both the photocatalyst within 30 min of treatment. Optimum TiO_2 concentration was found to be 0.5 g/L at optimum pH of 11 and initial concentration of 50 ppm, whereas optimum ZnO concentration was 0.8 g/L for similar conditions. Under optimized conditions at higher capacity (4 L), discoloration was complete in 50 min for TiO_2 and 25 min for ZnO catalyst. Higher photocatalytic activity for ZnO has been attributed to higher adsorption capacity coupled with higher rates of hydroxyl radicals formation. Electric energy consumption for reduction of color by one order of magnitude was 7.6 and 22.4 kWh/m^3 for ZnO and TiO_2, respectively. TOC removal rates were lower for both the catalysts (about 60 and 46% TOC was removed in 1 h for ZnO and TiO_2, respectively). Toxicity toward bacterial action was observed during initial stages but it was completely removed during the total treatment time of 1 h for both photocatalysts.

Table 2. Some Representative Work in the Area of Destruction of Contaminants by Photocatalytic Oxidation (Continued)

No.	Reference	Type of Equipment and Experimental Details	Highlights of the Work
5	Kim and Choi (2002)	Reactor with capacity of 90 mL was irradiated using a 300 W xenon arc lamp. Photocatalyst used was Degussa P-25 TiO_2 with concentration of 0.5 g/L. Chemical studied: substituted aliphatic amines at concentration of 1 mM	Rate of degradation of $(CH_3)_4N^+$ decreased with an increase in pH till an operating pH of 6, beyond which the rate increased. This can be possibly attributed to the electrostatic interaction of the pollutant ions with the catalyst surface (zpc of catalyst is 6.4). A detailed analysis of the intermediates and the reaction pathways has been presented. The rate constant was maximum for the degradation of $(CH_3)_2NH$ [1.51×10^{-3} s^{-1}] followed by $(CH_3)_3N$ [1.352×10^{-3} s^{-1}], $(CH_3)NH_2$ [8.611×10^{-4} s^{-1}], and least for $(CH_3)_4N^+$ [1.83×10^{-4} s^{-1}]. For all the species the rate constant was minimum at pH of 7 and maximum under alkaline conditions (i.e., at pH 11). To give a specific example, the rate constant for $(CH_3)_3N$ degradation is 1.352×10^{-3} s^{-1} at initial pH of 11, whereas it drops to 3.33×10^{-5} s^{-1} at initial pH of 7.
6	Bandala et al. (2002)	Two different types of photoreactors have been used: parabolic trough solar concentrator and tubular flat plate collector. Photocatalyst used was anatase grade TiO_2 with concentration ranging from 0 to 3 g/L. Sunlight was used as source of light. Initial concentration of pollutant was fixed at 5 mg/L. Chemical studied: Aldrin	The pollutant is strongly susceptible to adsorption on the catalyst surface (near-complete adsorption within 15 min of contact). In the absence of photocatalyst, no significant degradation was observed. With TiO_2, about 90% reduction was observed with 80 kJ/L of supplied energy. Addition of H_2O_2 reduced the energy requirement with 6 g/L dose requiring only 43 kJ/L energy for same extent of degradation. Concentrated sunlight gives more efficiency as compared to nonconcentrated sunlight (time required decreases from 20 h to 120 min for 90% degradation for the case of TiO_2 with 3 g/L of H_2O_2). Detailed analysis of the intermediates and reaction mechanism has been presented.
7	Al-Bastaki (2003)	Reactor uses 32 quartz tubes (total added length is 48 m) and TiO_2 photocatalyst is in suspended form. Effective volume of the liquid exposed to UV is about 3.77 L. Operation is in recycle mode with capacity of feed tank as 200 L and a maximum inlet flow rate of 12 L/min. Initial concentration of pollutant is fixed at 100 ppm. Chemical studied: Benzene	Concentration of benzene can be reduced from 100 ppm to less than 1 ppm in 30 min of treatment time (>99% degradation). Complete mineralization occurs and generated CO_2 results in a decrease of pH from 8.7 to 8.3 in same treatment time. Comparison with another technique (reverse osmosis) used for pollutant removal indicated that photocatalysis is much more efficient as compared to reverse osmosis.
8	Wong and Chu (2003)	Photoreactor with capacity of 500 mL irradiated with monochromatic UV lamps (two different lamps were used simulating sunlight and UV light intensities). Reaction mixture was maintained at constant temperature of 24–25°C. Photocatalyst used was Degussa P-25 TiO_2 at a loading of 5 mg/L. Effect of addition of hydrogen peroxide has been investigated in the concentration range of 0.05 to 124 mM/L. Chemical studied: Alachlor at concentration of 2.2×10^{-5} mol/L	Without TiO_2, marginal degradation was observed for both the intensities of UV light (<20%), whereas in the presence of catalyst, more than 90% degradation was obtained in about 25 min. Photocatalytic rate constant was found to be 0.12 and 2.15×10^{-3} s^{-1} for 300 and 350 nm wavelengths. Optimum dose of hydrogen peroxide for maximum enhancement (3.3 times increase in rate constant) was obtained at 4.94 mmol/L for 300-nm wavelength, whereas for 350-nm wavelength, hydrogen peroxide was found to be detrimental, H_2O_2 assisted photocatalysis was found to be favored by an increase in pH to 6 but a further increase in pH resulted in lower degradation rates.

(Choi and Hoffmann, 1997; Tanaka and Saha, 1994). Fox and Duley (1993), Davis and Huang (1991), Matthews and McEvoy (1992b), and Gupta and Tanaka (1995) reported that pH had a marginal effect on the extent of degradation for the specific compounds studied in their work. Because the effect of pH cannot be generalized, laboratory-scale studies are required for establishing the optimum conditions for the operating pH, unless data are available in the literature with nearly identical conditions as the effluent and the reactor and catalyst system in question.

(8) *Aeration.* The presence of electron acceptors in the effluent is recommended to prevent the recombination reaction between the generated positive holes and electrons (Yamazaki et al., 2001). Generally, aeration is used for this purpose because it also provides uniform mixing, suspension of the catalyst in the case of slurry reactors, and is an economical

source of oxygen. Dijkstra et al. (2001) showed that there is no appreciable destruction in the absence of oxygen. Chen and Ray (1998) showed that about 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.* The presence of ions may affect the degradation process by affecting the extent of adsorption of the contaminants on the photocatalyst (similar effect to operating pH), reaction with hydroxyl radicals, and/or absorption of UV light. This is a very important point that needs to be considered, given that real industrial effluents are likely to have different types of salts at different levels of concentration, which are generally in ionized forms. There are examples reported in the literature (Butler and Davies, 1993; Hua et al., 1995b; Kormann et al., 1991) regarding the effects of various anions and cations on the rates of degradation of different pollutants. In general, it can be said that carbonate and bicarbonate ions (which act as radical scavengers and also affect the adsorption process) and chloride ions (which affect the adsorption step strongly and also partly absorb UV light) have strong detrimental effects on the degradation process, whereas other anions, such as sulfate, phosphate, and nitrate, only marginally affect the degradation efficiency. Yawalkar et al. (2001) studied the effect of sulfate, carbonate, chloride, and bicarbonate ions on the overall degradation rates and reported that the detrimental effects are observed in the order of sulfate $<$ carbonate $<$ chloride $<$ bicarbonate. For the case of experiments with cations the results are conflicting; generally, a detrimental effect is observed except for some reports of marginal enhancement resulting from the presence of Fe^{3+}/Cu^{2+} ions at very low concentrations (Hua et al., 1995b). Additional research is needed in this area before a generalized effect of cations on the phenomenon of photocatalytic degradation can be well established.

Overview of work done in recent years

Some of the illustrative work done in recent years in the area of photocatalytic oxidation applied to wastewater treatment is depicted in Table 2, with discussion about the reactor operating conditions and the important findings obtained in the work, whereas an exhaustive list of different chemicals that can be degraded successfully by the use of photocatalytic oxidation has been provided in the earlier works of Blake (1997) and Herrmann (1999).

It can be seen that the majority of the academic studies (summarized in Table 2 and also observed generally in the literature) refer to the use of single-constituent model solutions for the experiments; the real wastewaters obtained from industries contain many 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 a variety of intermediates, and always raises a doubt whether photocatalytic oxidation will give the same destructive efficiencies for the real wastewaters, as observed for the single-constituent model solutions in the literature. This is especially important because the real wastewaters may also contain some traces of radical scavengers, such as bicarbonate and carbonate ions, naturally occurring matter (humic acids), and *t*-butanol, and this significantly affects the rates of destruction due to advanced oxidation processes driven by free radical attack (Yoo et al., 1997). Thus, certain modifications will be required in the overall treatment procedures so as to nullify the effects of the radical scavengers or to bring the level of toxicity below a certain optimum value decided by the reactor operating conditions. Degradation efficiency will still be reduced and thus 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.

Herrmann (1999) studied the application of photocatalytic oxidation [in a laboratory photoreactor irradiated with near-ultraviolet (UV) light with power dissipation of 125 W; the 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 a variety of organic compounds such as caprolactam, benzoic acid, adipic acid, phenol, toluene, benzene, methyl-valero-lactone, methyl-cyclohexenyl-formic acid, and 2,4,6-trichlorophenol, for example, as well as inorganic compounds such as nitrites, nitrates, iron, chromium, sodium, potassium, calcium, and so forth. 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 effluent initially did not show any degradation using UV irradiation, which was attributed to the fact that the solution was highly loaded with respect to the photonic flux used and it was too dark for easy irradiation of the catalyst. Thus some modifications had to be made in the treatment scheme. After 1000× dilution and after an initiation period of 1 h (in the dark, that is, UV light irradiation was started after 1 h), the solution showed a decrease in the COD value. In 4 h of total treatment time, the COD value decreased by 95%, demonstrating that the photocatalytic oxidation can be very efficient with almost complete destruction in a reasonable time (biological methods require a treatment time of few days) for treating wastewaters and, importantly, the example considers real wastewaters (complex mixture of pollutants), which should possibly increase the confidence of the potential users. However, Beltran et al. (1997) showed that the distillery waste and tomato wastewater were both refractory toward UV light [reactor operating conditions: 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 to 3000 mg/kg) and tomato wastewaters (COD range of 250 to 960 mg/kg)]. Even combination with hydrogen peroxide (rate of free-radical generation is substantially increased because of the cleavage of hydrogen peroxide) did not result in substantial rates of degradation. Thus, one cannot draw any reliable conclusion about the applicability of the photocatalytic oxidation for the treatment of the effluent stream from different industries. Further, the efficient large-scale operation of photocatalytic reactors is hampered by certain factors, which are discussed below along with the recommendations for future work required for transferring this successful laboratory-scale technique to industrial-scale technology:

- *Engineering design and operation strategies required for an efficient design of reactors at large-scale operation are not readily available.* 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 the same incident UV intensity. The scale-up is constrained by the phenomena of opacity, light scattering, depth of radiation penetration, and local light absorption, resulting in a decrease in the available UV intensity for degradation. Moreover, the requirement of at least one side to be transparent to the UV light significantly poses size limitations along with breakage risks. Future work should be directed to address the issue of uniform irradiation and minimal losses in the intensity of the incident light attributed to the phenomena of medium opacity, light scattering, UV absorption by liquid, and so forth.

- *Compared to conventional chemical reaction rate, the reaction rate of photocatalytic processes is usually slow and there is a need to provide larger amounts of active catalyst in the reactor.* In the case of immobilized catalyst reactors, there can be only a thin coating applied to the incident surface, limiting the amount of active catalyst in the reactor, and thus the overall conversion efficiency is likely to be low. This problem severely restricts the processing capacity of the reactor and the timescales required to achieve near complete mineralization normally are in hours, if not in days (still attractive 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 the novel supported catalysts with high stability in continuous reactors and at the same time offering greater surface area for the reaction.
- *For reactors with catalyst in the suspended form, ultrafine separation is an inconvenient, time-consuming, and expensive process.* In addition, the depth of penetration of light is lower because of the blockage of the incident light by catalyst particles (shadow effect) as well as absorption by the dissolved organic species.
- *Very few examples of application to real industrial effluents with higher destruction efficiency of photocatalytic oxidation alone can be cited.* Moreover, because of the presence of radical scavengers in real effluents, the rates will be substantially lower compared to those 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 the complex reaction kinetic models should be developed with consideration of the effect of all the operating parameters as well as the concentration of the critical components affecting the rates, such as radical scavengers and compounds restricting electron-hole recombination, for example.
- *Fouling of the photocatalyst with continuous use results in the lowering of the rates of degradation as time progresses.*

Thus, photocatalytic oxidation appears to be more developed and better understood than cavitation and also some examples can be cited for large-scale operation (Hermann, 1999) using naturally occurring UV resources (that is, sunlight). Still, for the treatment of complex mixture of effluents with the presence of potential radical scavengers, it appears that large-scale operation with higher energy efficiency is not readily feasible (economics will always be important when wastewater treatment plants are to be designed), given the number of problems discussed above. A major problem in the successful application of photocatalytic oxidation is the nonuniform irradiation of the catalyst, which results in only a fractional utilization of the incident energy, and thus the overall economics may not be favorable. Groups of Ray, Beenackers (Chen and Ray, 1998; Mukherjee and Ray, 1999; Ray, 1997, 1999; Ray and Beenackers, 1997), and Li Puma (Li Puma and Yue, 1998a,b, 1999) have tried to address this problem, although little success has been reported. Fouling of the catalyst particles by the pollutant results in a significant drop in the reaction rates (Gogate et al., 2002a), altering the overall economics of the process. It should also be noted that use of sunlight instead of UV light may result in an economical process (operating cost of using sunlight is negligible) but it gives lower rates of degradation; also in some cases where highly loaded effluents were tried, no degradation could be seen. Future work may be directed in terms of developing solar concentrators that result in an enhanced local light intensity of irradiation [the position of the concentrators can be adjusted in such a way that the concentration of energy does not occur inside the photoreactor (Malato et al., 2002); still if the temperature is expected to increase because of the local concentration of energy, appropriate cooling devices can be used to maintain the temperature]. Thus, it becomes imperative to combine the photocatalytic oxidation process with some other synergistic process with similar principles of operation, which also may help in overcoming some of the above-mentioned problems.

Sonophotocatalytic Oxidation

Principle of expected synergism

In the case of photocatalytic oxidation, the most common problem is the reduced efficiency of photocatalyst with continuous operation, possibly attributable to the adsorption of contaminants on the surface and blocking of the active sites. Thus the aim should be at devising a technique for proper cleaning of the catalyst surface during the operation itself. Ultrasonic irradiation can be one such technique. Moreover, the photocatalytic oxidation technique is affected by severe mass transfer limitations, especially in the immobilized catalyst type of reactors, which are generally preferred over slurry reactors to avoid solid–liquid separation problems. One more factor, suggesting that the two techniques if used simultaneously will give better results when operated in combination, is the fact that the basic reaction mechanism in both cases involves the generation of free radicals and subsequent reaction of the radicals with the organic species. If the two irradiations are operated simultaneously, more free radicals are likely to be available for the reaction, thereby increasing the rates of reaction, or similar rates can be achieved even for the higher loading of the pollutants. Thus, the expected synergism between the two modes of irradiation (sound and light) can possibly be attributed to:

(1) Cavitational effects leading to an increase in the temperatures and pressure at the localized microvoid implosion sites and thus increasing the intrinsic rates of chemical reaction.

(2) Cleaning and sweeping of the TiO_2 surface, attributed to acoustic streaming and associated turbulence, allows for more active catalyst sites participating in the reaction at any given time.

(3) Mass transport of the reactants and products is increased at the catalyst surface and in the solution as a result of the facilitated transport as a result of shockwave propagation and/or acoustic streaming.

(4) Solid surface area available for adsorption of the pollut-

ants is increased by fragmentation, deagglomeration, or pitting of the catalyst surface.

(5) Cavitation-induced radical intermediates participate in the destruction of organic compounds in addition to the direct reaction between the photogenerated surface holes and electrons with the substrate.

Most of these effects are likely to occur simultaneously and, although their relative contributions to the enhancement of heterogeneous catalytic process is far from understood, the overall global effect should result in substantial enhancement in the rates of the pollutant destruction.

Reactors used for the sonophotocatalytic oxidation

The different reactor designs used to date for evaluating synergism between ultrasound and ultraviolet irradiation are depicted in Figure 3 (batch reactors) and Figure 4 (continuous flow reactors). The mode of ultraviolet irradiation (direct or indirect) does not affect the expected synergism (Shirgaonkar and Pandit, 1998), which is an important point in the design procedure, particularly for the annular location of the UV tube. For wastewater applications, it is important to design continuous reactors rather than batch reactors, or at least reactors operating in a recirculating mode, because large quantities of effluents have to be treated. The triple-frequency hexagonal flow cell design used in the earlier work (Gogate et al., 2002a) appears to be the optimum design among the various designs used thus far (depicted in Figures 3 and 4). The sonochemical part has been designed with power dissipation over a wider area and multiple transducers (more energy efficiency and also larger cavitational yield). This design also provides higher cavitationally active volumes and the intensity of turbulence generated as a result of acoustic streaming is higher because of larger area of the irradiating transducers. The design also gives flexibility for selecting multiple-frequency or single-frequency operation depending on the loading and the type of the effluent (for example, where higher loading and the generation of free radicals is the rate controlling step, multiple frequency operation can be selected because it generates more intense and spatially uniform cavitation compared to those reactors with single-frequency and/or single-transducer operation). For the photocatalytic part, a UV tube with 8-W power dissipation has been used and was located in the annular section separated with the effluent stream using a quartz tube. The catalyst particles were suspended in the effluent stream with the help of mechanical agitation and the reactor was operated in a batch mode.

For operation in the continuous mode, some modifications are necessary. First, if the reactor is to be operated as a slurry reactor, additional separation equipment must be installed at the outlet of the reactor or in a separate loop, with the catalyst being recycled back in the main reactor after separation. Usually supported catalyst reactors are preferred for the continuous operation but slurry reactors can also be used if better separation characteristics or lower loading of photocatalyst are achieved [as is the case when ultrasound is used in combination (Gogate et al., 2002a); Kado et al. (2001) also showed that the rate constants for the oxidation of 2-propanol and ethanol are substantially higher at a catalyst loading of 10 gm/L for the combination of ultrasound and ultraviolet irradiation compared to catalyst loading of 100 gm/L for photocatalytic oxidation alone].

Alternatively, a thin film of photocatalyst can be deposited on the inner side of the quartz tube, which will be in direct contact with the effluent stream and indirectly irradiated by the ultraviolet light through the quartz tube. The stability of the catalyst film will be a question in this case because it will be subjected to the turbulence generated by the cavitation as well as by the liquid motion. Uniform irradiation must be received by all the particles to obtain better results in terms of destruction efficiency and, with this in mind, supported-catalyst reactors appear to be a better option than slurry reactors. Thus, all these points need to be critically and qualitatively evaluated before efficient design of the sonophotocatalytic reactor can be made. At this stage, it is difficult to give an exact recommendation concerning the use of immobilized catalyst type or slurry reactors for the photocatalytic oxidation; still, slurry reactors appear to have an edge over the immobilized catalyst type reactors, considering the fact that reduced loading of the catalyst may be required because of the synergism; and it is quite difficult to reduce the extent of turbulence for the protection of the thin film of the catalyst, given that the main advantage of using ultrasonic irradiation is that turbulence reduces the fouling of the catalyst and enhances the mass transfer rates. The other designs, as depicted in Figures 3 and 4, have been mainly used on a laboratory scale and thus assessment of these designs for large-scale operation is difficult because the scale-up ratio required will be very high, thus leading to an uncertainty in terms of efficient operation, given that the hydrodynamic conditions in the two scales of the reactors are likely to be quite different.

Another design, although based on theoretical analysis and not used so far, is the use of large tank-type reactors with the multiple transducers located at the bottom of the tank (cleaning ultrasonic bath-type configuration) as well as at the sides of the reactor (parallel-plate reactor). The transducers at the bottom of the tank should be arranged in a triangular pitch because it gives uniform distribution of the incident energy, whereas the transducers at the side of the reactor (possibility of multiple frequency irradiation as well) can be placed in line, as described in the earlier work (Gogate et al., 2003). The photocatalytic part can be concentrating parabolic-type reflectors suitable for the use in the direct sunlight. Additional irradiation may be provided using Hg vapor ultraviolet lamps located in the annular space of the reactor or directly immersed in the effluent using a quartz tube for shielding purposes. Appropriate combination of sunlight and the UV irradiation may be used, depending on the incident intensity of sunlight as well as the pollutant load. It should be also noted that immersing a quartz tube or the cooling coils into the system may affect the passage of the acoustic field into the system and thus care should be taken to increase the treatment times so as to counter the negative effect of somewhat lower transfer of energy. Also the placement of the quartz tube and cooling coils can be at a position at which the cavitational activity is at a minimum; for more discussion about this refer to the work of Gogate et al. (2002b). The time of irradiation using UV light can also be adjusted based on the loading, composition, and the flow rate of the effluent stream and should result in considerable savings because natural resources will be used for most of the time. Mechanical agitation or aeration, in combination with low speed agitation, can be used for keeping the solid catalyst in complete suspension, with the latter appearing to be the opti-

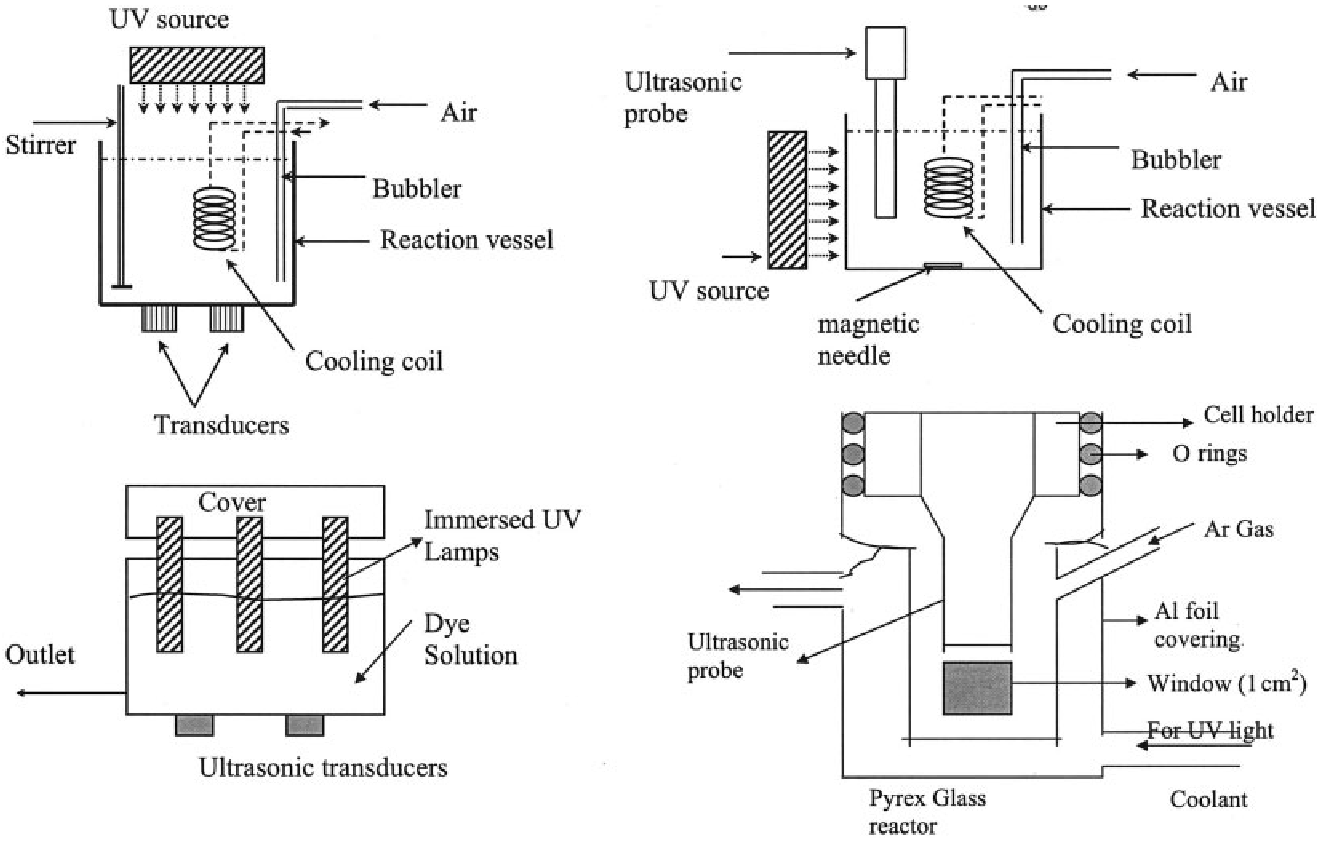


Figure 3. Typical schemes used for the combinatorial effects of UV and ultrasonic irradiations: batch reactors.

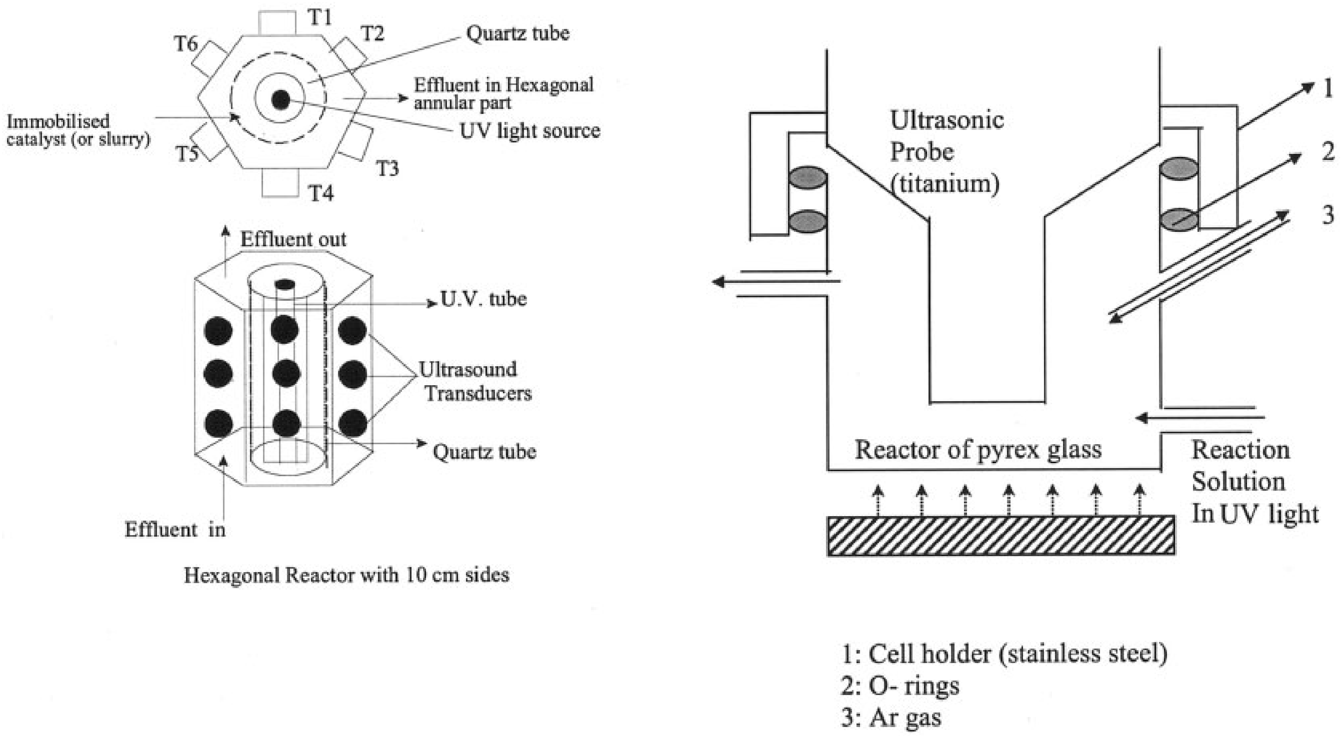


Figure 4. Typical schemes used for the combinatorial effects of UV and ultrasonic irradiations: continuous reactors.

mum choice, given that high-speed stirring may be detrimental and may result in scattering of the incident radiations. This configuration is shown in Figure 5.

Effect of the operating parameters

The overall efficacy of the process depends on the set of operating conditions selected and thus this must be chosen precisely for obtaining maximum benefits from the synergism between the two processes. It should be noted that the optimum operating parameters for the individual processes hold equally well for the combination (hybrid) technique; some additional parameters specific to the hybrid technique are discussed below.

Type of Operation. The hybrid technique of sonophotocatalytic oxidation can be operated either in a simultaneous irradiation mode (the effluent is irradiated simultaneously with ultrasound and ultraviolet irradiation) or in sequential irradiation mode (ultrasonic irradiation followed by ultraviolet irradiation or ultraviolet irradiation followed by ultrasound). Stock et al. (2000) studied the degradation of aqueous solution of Naphthol Blue Black (NBB) dye using both the simultaneous technique and the sequential technique (sonochemical irradiation followed by the photocatalytic oxidation) and reported that the rate constant for the degradation of NBB dye was similar for the two techniques (1.83×10^{-2} min^{-1}); further it was more than the addition of the individual rate constants obtained for the sonochemical irradiation (0.56×10^{-2} min^{-1}) and photocatalysis (1.04×10^{-2} min^{-1}), indicating a synergism between the techniques. Further analysis with respect to the TOC reduction, however, indicated that the extent of mineralization achieved in the simultaneous technique (about 50% reduction in 4 h of treatment) was higher compared to that of the sequential technique (about 20% in similar treatment times), indicating that for the degradation of the intermediates formed in the process, generation of free radicals was not the only controlling factor. Although a detailed analysis of the reaction intermediates has not been presented in the work, the type of the pollutant strongly affects the expected synergism and thus the beneficial effects of sonophotocatalytic oxidation. This fact is further confirmed by the results obtained in the case of degradation of formic acid in an earlier work (Gogate et al., 2002a), where it has been shown that the simultaneous technique (20% degradation in 1.5 h of treatment) results in 30% more degradation compared to that of the sequential operation (15% degradation in similar treatment time) at equivalent energy input levels. Thus, in these two cases, continuous cleaning of the catalyst surface coupled with the increase in the mass transfer rates contribute equally to the enhancement in the overall rates of reaction compared to the increase in the number of free radicals. In general, it is better to operate simultaneously rather than having sequential irradiation of ultrasound followed by photocatalytic oxidation or photocatalytic oxidation followed by ultrasound (in this case, the contribution to the increased surface area for the adsorption of pollutants on the photocatalyst as well as cleaning of the catalyst will not occur and thus may result in even lower rates of degradation compared to those of the sequential operation of ultrasound followed by photocatalytic oxidation). Also the number of free radicals generated in simultaneous irradiation (more dissociation of water molecules attributed to higher energy dissipation rates and also the presence of solid particles enhances the ultrasound effects resulting from the surface cavitation) may be significantly greater than those generated in the sequential operation, thereby further increasing the observed rate of degradation.

Capacity of the Reactor. Ragaini et al. (2001) studied the effect of the volume of the effluent treated on the degradation rate constant for the simultaneous irradiation operation at constant power supplied into the system and reported that the rate constant for the simultaneous technique (the reactor configuration and the operating conditions are given in Table 3) was lower compared to that of the photocatalytic degradation below a critical volume of 300 mL [at a volume of 150 mL, the rate constant for the combination technique is 6.2×10^{-5} s^{-1}, whereas for the individual photocatalytic oxidation it is 12×10^{-5} s^{-1}; at higher volumes (e.g., 400 mL), the rate constant for the combination (6×10^{-5} s^{-1}) was indeed higher compared to that of individual photocatalytic oxidation (5×10^{-5} s^{-1})]. This can be attributed to the fact that at lower volumes, the rate of the generation of the free radicals is not the controlling factor and thus, even if there is a significant increase in the overall number of free radicals, it will not affect the overall rates of degradation. On the other hand, because there is a strong affinity for the free radicals toward the recombination reaction to form hydrogen peroxide, which also reacts with the free radicals, the effective number of free radicals available for the pollutant degradation may decrease, if one tries to increase the rate of the generation substantially at lower volumes. Ragaini et al. (2001) confirmed this fact with experiments using sonication alone and observed that the rate constant for the degradation of 2-chlorophenol increased with an increase in the volume of the effluent over the range 150 to 300mL (the rate constant increased from 0.75×10^{-5} s^{-1} to 0.95×10^{-5} s^{-1}). This optimum value of the volume of the effluent also depends on the operating conditions of the reactor mainly the magnitude of power supplied (which will decide the rate of generation of free radicals) and the type of the effluent in question (the rate constant for the reaction between the pollutant and free radicals is equally important). Toy et al. (1990) obtained better results for the combination techniques at volumes as low as 3 to 4 mL, whereas Chen and Smirniotis (2002) reported that the synergistic effects of using the combination technique are more pronounced at lower volumes of treatment (relative enhancement was 82% at 50 mL, whereas it was 29% for 300 mL). It appears that too much cavitation at lower volumes can be detrimental (for individual operation or the combination technique), possibly attributable to the fact that the density of cavitation bubbles is higher in small volumes, which are continuously in the zone of influence of the transducers and result in relatively larger bubble sizes (ascribed to coalescence) decreasing the collapse intensity (Gogate and Pandit, 2000) and also possibly affecting the UV transmission rates. The extent of recombination of free radicals in the case of larger volumes is lower compared to that in smaller volumes. For the case of wastewater-treatment applications, however, one should not be overly concerned about this critical volume (beyond which the beneficial effects are observed) because design has to be done for large-scale operation only. More studies are required to clearly establish the optimum volumes, particularly when the application in question involves synthesis of novel and precious components, because indeed ultrasound can be used in

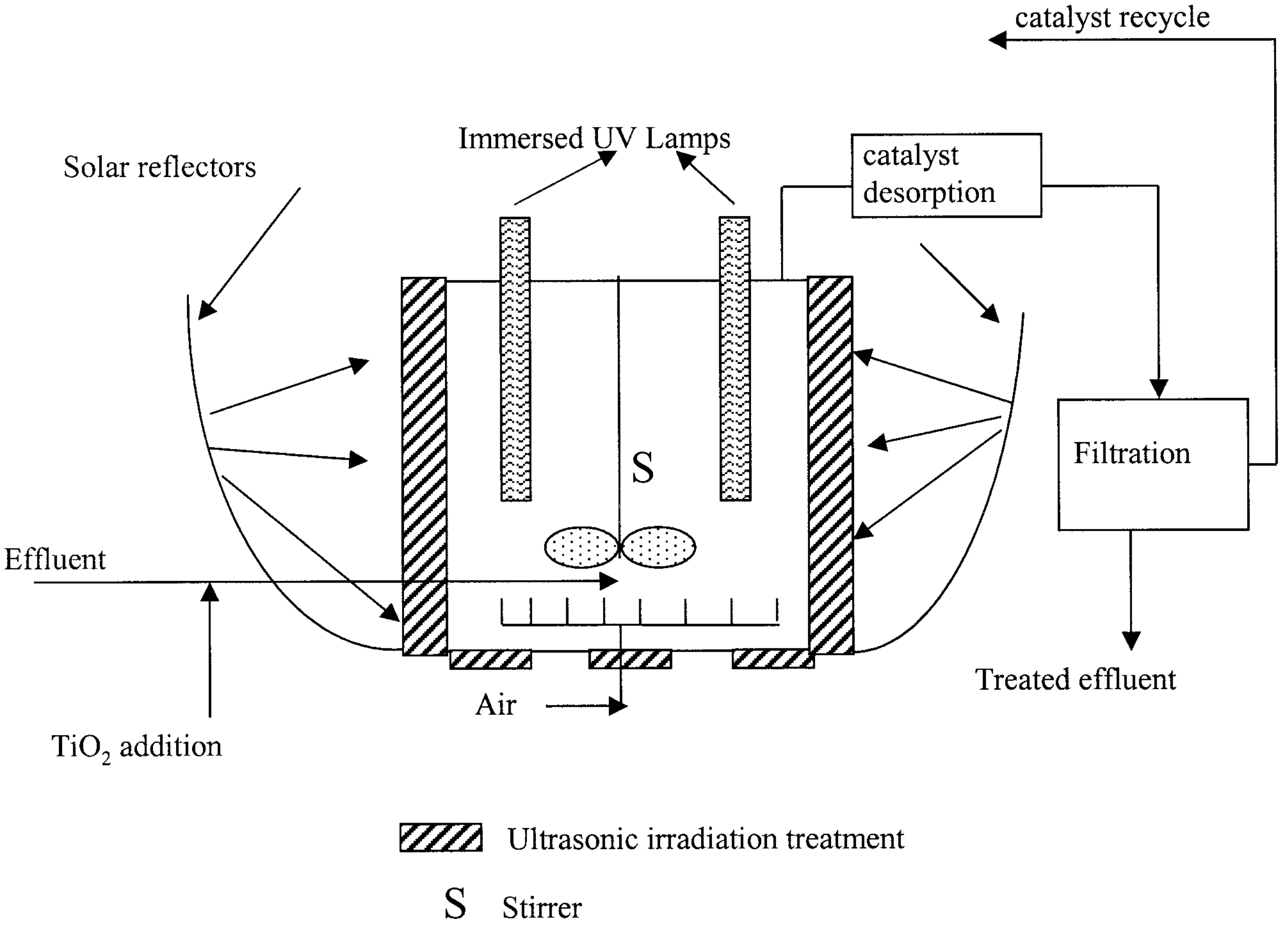


Figure 5. Model sonophotocatalytic reactor.

synergism with photocatalysis to enhance the rates or alter the pathways of many chemical reactions.

Treatment Time. As discussed earlier, three important factors—cleaning of the fouled catalyst; fragmentation of the catalyst under the action of ultrasound, leading to an increase in the surface area; and increase in the number of free radicals generated because of the combination of two irradiations—decide the overall synergism for the hybrid technique. Increasing the surface area, attributed to the fragmentation of the catalyst, also results in an increase in the extent of scattering of the incident ultrasonic and ultraviolet radiations, thereby decreasing the useful energy dissipation into the system. The extent of the enhancement obtained for the simultaneous irradiation technique compared to that of the individual operation depends on the relative contribution of these effects occurring simultaneously. In our earlier work (Gogate et al., 2002a), synergistic effects for the degradation of Formic acid were observed only after a particular treatment time. Initially, fragmentation of the catalyst is the controlling mechanism (so increased turbidity and thus lower available energy due to ultrasonic and ultraviolet irradiations), which results in lowering of degradation rates compared to those of the photocatalytic oxidation alone, although as time progresses the other two mechanisms take over, resulting in enhanced degradation of formic acid. The extent of fragmentation of the catalyst also depends on the amount of the catalyst as well as the intensity of cavitation, which in turn depends on the power dissipated by the transducers and the frequency of irradiation. In the earlier work (Gogate et al., 2002a), a decrease in the extent of fragmentation (using single-frequency operation and lower concentration of the catalyst) was observed to decrease the critical time for obtaining the synergistic effects. During the initial period of treatment, when catalyst fouling is not the controlling factor, it is better to operate with a lower intensity of cavitation (use single-frequency operation or lower power dissipation if the reactor is capable of having variable power input), whereas as the time progresses the intensity of cavitation should also be increased to obtain better degradation efficiency. The crucial role of fouling in deciding the overall rates of degradation have also been confirmed in the earlier work (Gogate et al., 2002a), with almost constant degradation beyond a specific time in the case of photocatalytic oxidation alone.

Operating pH. The operating pH is another crucial factor in deciding the rates of degradation, and thus the overall efficacy of the process, because it strongly influences the adsorption characteristics. There have been several studies in the past, though, for the individual operation of ultrasonic irradiation as well as photocatalytic oxidation (Castrantas and Gibilisco, 1990; Kotronarou et al., 1991; Okuchi et al., 1992; Tauber et al., 2000), which indicate that acidic conditions are

Table 3. Overview of the Work Done in the Area of Sonophotocatalytic Destruction

No.	Reference	Type of Equipment and Experimental Details	Highlights of the Work
1	Theron et al. (1999)	Two different cylindrical reactors (one with capacity of 90 mL irradiated with 30 kHz frequency, whereas second reactor of capacity 300 mL is irradiated with 515 kHz ultrasound). Power dissipated due to ultrasonic irradiation is 16 W. UV irradiation is with Phillips HPK 125-W high-pressure mercury lamp with radiant flux of about 55 mW/cm^2. Pollutant loading is 160 μM, whereas the catalyst loading is 3.5 g/L. Chemical studied: phenyltrifluoromethyl-ketone (PTMK)	For sonication alone, the rate constant for the removal of PTMK at 515 kHz operation (2.33×10^{-4} s^{-1}) was about 3 times greater as compared to 30 kHz operation (6.67×10^{-5} s^{-1}). TiO_2 rhodia was observed to be a more effective photocatalyst as compared to Degussa P-25 grade TiO_2 (rate constant of 5.33×10^{-4} s^{-1} as against 3.58×10^{-4} s^{-1}); though no explanation for the observed results was offered. PTMK removal rate using UV and ultrasonic irradiations simultaneously (rate constant of 1.38×10^{-3} s^{-1}) was almost double as compared to photocatalysis alone (rate constant of 6.5×10^{-4} s^{-1}) and about 20 times more as compared to sonication alone (rate constant of 6.67×10^{-5} s^{-1}) for the case of Degussa P-25 catalyst. The observed synergism has been attributed to formation of additional free radicals in the presence of ultrasound. Confirmation by addition of catalase, which blocks the degradation of hydrogen peroxide into free radicals. Addition of 22 mg/L catalase decreases the rate constant for the combination from 1.38×10^{-3} s^{-1} to 6.5×10^{-4} s^{-1} for the case of Degussa P-25 and from 2.53×10^{-3} s^{-1} to 7.21×10^{-4} s^{-1} for the case of TiO_2 rhodia.
2	Stock et al. (2000)	Sonoreactor (640 kHz) with power input of 240 W and capacity of 600 mL, operating temperature of 20 ± 5°C. Pollutant loading is 50 ± 5 μM, whereas the catalyst loading is 1 g/L. Chemical used: azo dye, naphthol blue black (NBB)	First-order rate constant for combination (3.05×10^{-4} s^{-1}) is about four times higher as compared to photocatalysis alone (9.33×10^{-5} s^{-1}) and 80% higher as compared to sonolysis (1.73×10^{-4} s^{-1}). Increase is due to the additional free radicals generated by sonolysis, refreshing of the photocatalyst surface, and enhanced mass transfer. Extent of mineralization was 80, 68, and 35% for combination, photocatalysis, and sonochemical treatment, respectively, in 12 h of treatment. Optimum concentration of photocatalyst was observed as 0.1 g/L at which the rate constant for combination technique was maximum (8×10^{-4} s^{-1}). For TOC removal, the simultaneous technique was more effective than the sequential technique (TOC reduction was 50% with sequential versus 75% with simultaneous).
3	Harada (2001)	Simultaneous irradiation with 500-W Xe lamp and 200-W ultrasound with operating frequency of 200 kHz in a reactor of volume 40 mL with 200 mg photocatalyst TiO_2 (i.e., at a loading of 5 g/L) (Nippon Aerosil P-25) Chemical used: water	Liquid water can be completely decomposed (near 100% degradation) to hydrogen and oxygen in stoichiometric amount in 3 h of treatment, whereas complete decomposition is not observed by either photocatalysis or sonolysis alone. The ratio of reaction products (H_2/O_2) was about 2 for the photocatalytic oxidation (strongly dependent on the time of treatment), whereas for photocatalysis and sonication alone it was 0 (no degradation) and 19.8 (very less O_2 indicating less degradation), respectively.
4	Kado et al. (2001)	A Pyrex glass cell equipped with ultrasonic stepped horn (driving frequency of 20 kHz and input power of 20 W) and irradiated with 0.5 W/cm^2 Hg–Xe lamp. Photocatalyst used was anatase type TiO_2 powder with average size of 0.5 μm at a loading of 2 g/L for a substrate loading of 2 mM. Operating temperature maintained at 20°C and solution was stirred at 1100 rpm. Chemical studied: 2-propanol and ethanol	Formation of acetone and acetaldehyde as the end products in the oxidation of 2-propanol and ethanol, respectively, for the dual combination in measurable quantities indicate that the rate of oxidation is substantially enhanced. Little reaction for ultrasonic irradiation alone, whereas the rate for photocatalytic oxidation alone is almost 1/3rd as compared to the combination (3.8×10^{-2} mol/L for the combination, whereas 1.2×10^{-2} mol/L for individual photocatalytic oxidation). The rate of reaction increases with an increase in the ultrasonic power dissipation (0.29×10^{-8} mol s^{-1} to 0.88×10^{-8} mol s^{-1} for an increase in the power from 0 to 20 W). The optimum concentration of catalyst for the combination technique is observed to be 1 g/dm^3, substantially less as compared to photocatalytic oxidation alone (10 g/dm^3). Pretreated catalyst with ultrasound was more efficient as compared to the untreated catalyst for photocatalytic oxidation (attributed to lower particle size and more active surface area).
5	Ragaini et al. (2001)	W-285 heat system–ultrasonics apparatus with driving frequency of 20 kHz and power dissipation of 20 W. The light source is 250 W iron alogenide lamp emitting in 315–400 nm wavelength range. Photocatalyst used in TiO_2 at a loading of 0.1 g/L. Operating temperature of 30°C. Chemical studied: aqueous solution of 2-chlorophenol at a loading of 5×10^{-4} mol/L	Ultrasound alone gives a degradation of 10–20% in 6 h. Optimum power density was found to exist (300 W/mL and corresponding rate constant is 1×10^{-5} s^{-1}) and no effect of suspended particles on the extent of degradation. UV irradiation in the presence of photocatalyst (0.1 g/L is the optimum concentration, Degussa P-25 TiO_2 is the best among different types studied) gives degradation of 70–90% in 6 h. For combination, synergistic effects were observed only above volume of 300 mL. At lower volumes, the rate constant for photocatalytic oxidation was greater than that observed for the combination (at volume of 150 mL, rate constant for combination is 6.2×10^{-5} s^{-1}, whereas for individual photocatalytic oxidation it is 12×10^{-5} s^{-1}). Increase in the surface area of about 40% as obtained by BET analysis due to sonication has been reported. Energy consumed for 70% degradation of 2-chlorophenol was 1 kWh for photocatalytic treatment and 0.95 kWh for combination technique.

No.	Reference	Type of Equipment and Experimental Details	Highlights of the Work
6	Davydov et al. (2001)	Sonophotocatalytic reactor of capacity 1 L irradiated with immersion ultrasonic horn (20 kHz frequency and 100–110 W/L power density) as well as UV lamps immersed through quartz wells (7 lamps each of 4W power). Different types of TiO_2 photocatalyst has been used at a loading of 0.25 g/L and is kept in suspension using stirrer and turbulence generated by ultrasonic action. Chemical studied: Salicylic acid at a concentration of 2 mM.	For photocatalytic oxidation, Degussa 25 catalyst was most efficient in degradation (rate constant of 1.683×10^{-3} mol/L · s at 0.25 g/L loading). Use of ultrasound was most favorable for Hombikat type of catalyst (increase in rate constant from 0.917 to 1.383×10^{-3} mol/L · s) and also for optimum concentration of the catalyst (more intensification at 0.25 g/L loading of photocatalyst as compared to 0.1 and 0.4 g/L loading). Maximum rate constant was reported to be for Degussa P-25 catalyst for combination of UV and ultrasound as 1.983×10^{-3} mol/L · s). Ultrasound was reported to eliminate the presence of toxic intermediates by way of sonolysis but use of ultrasound alone resulted in marginal degradation of salicyclic acid (<5%). The possible mechanism for the observed enhancement was reported to be aggregate breakage and photocatalytic utilization of the species generated by the action of ultrasound.
7	Matsuzawa et al. (2002)	Reactor (200 mL capacity) irradiated with 45 kHz and 50-W sonicator and 200-W Hg–Xe lamp. Photocatalyst used was P-25, PC-1, PC-2, and PC-3 TiO_2 differing in the surface area and particle size. Initial concentration of pollutant is 5×10^{-4} M and concentration of photocatalyst is 2 g/L. Air was sparged at a flow rate of 10 mL/min. Chemicals studied: dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (DMDBT)	In the absence of the photocatalyst, no change in the initial concentration was observed even after 10 h photoirradiation. In the presence of TiO_2 particles, the decrease in DBT concentration was about 30%. For DMDBT, the extent of degradation was 6% for the absence of catalyst, whereas in the presence it was 37% in same treatment time. The rate constants was maximum for P-25 type catalyst (9.76×10^{-6} s^{-1} for DBT and 1.21×10^{-5} s^{-1} for DMDBT). Addition of H_2O_2 under optimum conditions favored the reaction (10 vol % of commercial 30% H_2O_2 solution). Simultaneous irradiation with ultrasound resulted in an increase in the rate constant to 2.9×10^{-5} s^{-1} for DBT and 4.1×10^{-5} s^{-1} for DMDBT). Simultaneous addition of H_2O_2 under optimum conditions with ultrasonic irradiation (10 vol % of commercial 30% H_2O_2 solution) favored the reaction (rate constant is 5.3×10^{-5} s^{-1} for DBT and 9.7×10^{-5} s^{-1} for DMDBT). The possible mechanism for the enhancement is attributed to prevention of agglomeration of catalyst as well as cleaning of the catalyst surface. The products of the reaction have been identified using GC-MS and UV absorption spectroscopy.
8	Chen and Smirniotis (2002)	Photoreactor (capacity 300 mL) surrounded by a cooling jacket for maintaining a constant temperature of 30°C. Medium-pressure mercury vapor lamp (450 W) is used as a UV source. Oxygen was sparged which along with tubulence generated by ultrasound ensures uniform dispersion. Ultrasonic source operates at 20 kHz frequency and supplied power of 60 to 70 W. Photocatalyst used is Hombikat UV-100 at concentration of 0.25 g/L, whereas the pollutant concentration is 1 mM. Chemicals studied: Phenol and substituted phenols: 4-chlorophenol (4-CP), 2,4-dichlorophenol (DCP), and 2,4,6-trichlorophenol (TCP)	For phenol, no degradation occurs in the absence of UV and ultrasound, whereas only ultrasound results in about 10% destruction in 3 h of treatment. UV irradiation with photocatalyst results in 76% destruction in similar time of treatment. Combination of ultrasound and photocatalysis results in almost complete destruction of phenol in about 150 min. The reaction rate was 0.1167 μM/s in the presence of ultrasound as compared to 0.0716 μM/s in the absence (about 65% more). Synergistic effects are observed for the combination technique, which are attributed to surface cleaning of the catalyst and deagglomeration. Further the synergistic effects were more at lower volumes (relative enhancement was 82% at 50 mL, whereas it was 29% for 300 mL) but above an optimum value of power density (0.7 W/mL) the enhancement was not observed. Presence of salt NaCl or Na_2SO_4 was found to have an adverse effect on the extent of degradation (96% degradation in absence of any salt, 86% in presence of 0.25 M of Na_2SO_4, and 39% in the presence of 0.5 M NaCl). For substituted phenols also, synergistic effects were observed. The initial reaction rate was 0.17, 0.183, and 0.296 μM/s for 4-CP, DCP, and TCP, respectively, for combination and 0.076, 0.115, and 0.24 μM/s for 4-CP, DCP, and TCP, respectively, for photocatalysis. The reaction rate for sonolysis was always less than 0.0167 μM/s. Different rates of photocatalysis and combined operation for the different pollutants as studied in the work has been explained on the basis of change in pH during the treatment time and the solubility of the pollutant in water.
9	Mrowetz et al. (2003)	Magnetically stirred 400-mL capacity cylindrical reactor maintained at 35°C irradiated by an ultrasonic horn (frequency of 20 kHz and calorimetric power dissipation of 15 W) and 250 W iron–alogenide lamps. Photocatalyst used in Degussa P-25 TiO_2 with surface area of 35 m^2/g and at concentration of 0.1 g/L. Chemicals studied: 2-chlorophenol (initial concentration of 5×10^{-4} M), acid red 1 (AR1), and acid orange 8 (AO8) at a initial concentration in the range of 2 to 7×10^{-5} M	Photolysis in the absence of TiO_2 particles or ultrasonic irradiation alone failed to induce any degradation. For acid orange 8, the rate constant for ultrasonic irradiation, photocatalysis, and the combination technique was 0.1, 1.81, and 3.32 ($\times 10^{-4}$ s^{-1}), respectively, clearly indicating the synergistic effects. For acid red 1 and 2 chlorophenol, the rate constants in same order are 0.038, 1.22, 2.89 ($\times 10^{-4}$ s^{-1}), and 0.59, 0.88, and 1.58 ($\times 10^{-4}$ s^{-1}), respectively. It can be also seen from the above rate constants that the synergism is more pronounced for acid red 1 followed acid orange 8 and least for 2-chlorophenol. The rate (for both AR1 and A08) constant decreased with an increase in the dye concentration and showed optima with respect to the TiO_2 concentration at 0.25 g/L μ similar to individual photocatalytic operation. The synergistic effects are not obtained when ferric ions are added to the solution, which can be attributed to greater affinity of the ferric ions towards TiO_2 surface as compared to the azo dyes but still the overall rates of degradation are marginally higher due to the presence of classical Fenton chemistry mechanism. Hydrogen peroxide evolution rate indicated that cavitation is more effective in degradation of the same and the main contribution to the synergistic effects is the increase in the number of free radicals rather than the deagglomeration of the catalyst particles or the surface cleaning.

preferred for obtaining better degradation efficiency. Wu et al. (2001) showed that increasing the pH of the solution significantly reduces the rates of photosonochemical degradation of phenol. The effect of pH on the rates of degradation was found to be dependent on the state of the pollutant molecule, that is, whether the pollutant is present as ionic species or as a molecule. The enhancement observed at relatively lower pH in the case of phenol is attributed to the fact that phenol is present in the molecular state at lower pH and thus can easily enter the gas–water interfaces of the cavitation bubbles, attributed to hydrophilic nature, as well as can even vaporize into the cavitation bubbles, thereby enabling degradation by thermal cleavage as well as free-radical attack (Chen and Lee, 1994). Tauber et al. (2000) studied the effect of pH on the sonolytic degradation of 4-nitrophenol and showed that the rate of degradation drops almost to zero at higher pH values, more specifically at pH values greater than the pK_a value for the dissociation of 4-nitrophenol. The pollutant needs to be in the molecular state and the operating pH must be kept lower than the pK_a value for the specific pollutant in question for both the pyrolytic and free radical attack to occur. The nature of the pollutant species (that is, acidic or basic) also plays a role in the effect of operating pH. Ashokkumar and Griezer (1999a,b) showed that alkaline conditions are more suited for the destruction of alkaline pollutants (such as amines).

If hydrogen peroxide is simultaneously present or added to increase the rate of generation of the free radicals for the combination technique, the effect of pH might be different. The work by the group of Fung (Fung et al., 1999, 2000a,b; Poon et al., 1999) has indicated that higher pH values are beneficial for the degradation of dye (Cupraphenyl Yellow RL) in the presence of hydrogen peroxide. The observed effect has been attributed to higher rates of hydrogen peroxide photolysis at higher pH, generating more free radicals (Legrini et al., 1993), although there might be some contribution arising from the alkaline nature of the dye.

The effect of pH on the rate of sonophotocatalytic oxidation appears to be complex and it appears that depending on the type of pollutant molecule (acidic or alkaline nature as well as pK_a value for the dissociation of the pollutant) and presence of hydrogen peroxide as a process intensifying parameter, an appropriate pH should be selected (laboratory study is recommended). More studies are required in terms of assessing the effects of the operating pH for a variety of different contaminants and under different operating conditions (concentrations of pollutants as well as hydrogen peroxide) for the hybrid technique involving the use of hydrogen peroxide for clearly establishing the optimum operating pH.

Process Intensification. Because the principle of the oxidation using sonochemical as well as photocatalytic processes is based on the generation of free radicals (hydroxyl and hydroperoxyl) and its subsequent attack on the pollutants, any additives providing additional source of free radicals or enhancing the rate of the formation of the free radicals should increase the rates of degradation, provided the rate of generation of the free radicals is the rate-controlling step. In subsequent sections, use of hydrogen peroxide, ferrous ions, ozone, and air, as possible process intensifying parameters, is discussed.

Use of Hydrogen Peroxide. Hydrogen peroxide in the presence of UV light and ultrasound dissociates, resulting in the formation of the highly reactive hydroxyl radicals, and thus results in an increase in the rate of degradation compared to that of individual operations (Glaze et al., 1987; Lin, 1996; Venkatadri and Peters, 1993). The rate of dissociation of hydrogen peroxide will be further enhanced when the two sources of irradiation are operating simultaneously. Matsuzawa et al. (2002) studied the degradation of dibenzothiophene (DBT) and 4,6-dimethyl-dibenzothiophene (DMDBT) and reported that the addition of hydrogen peroxide is beneficial for the combination technique [rate constant increases from 2.9 to $5.3 \times 10^{-5}\ s^{-1}$ for DBT and from 4.1 to $9.7 \times 10^{-5}\ s^{-1}$ for DMDBT in the presence of hydrogen peroxide (10% of commercial 30% solution)]. The concentration of hydrogen peroxide also plays a crucial role because at higher concentrations, it acts as a scavenger for the generated free radicals. Fung et al. (1999) showed that the rate of degradation of cuprophenyl yellow RL (a typical pollutant in the dye industry effluent) is enhanced significantly by the addition of hydrogen peroxide at a loading of 0.05 mL/L for an initial loading of the pollutant of 0.1 g/L, but the rate decreases above 0.1 mL/L loading of hydrogen peroxide. Similar results have been reported by Poon et al. (1999).

Fung et al. (2000a) reported that the rate of degradation of CI reactive red 120 dye increases with an increase in the hydrogen peroxide loading from 0.1 to 0.5 mL/L (for initial loading of the pollutant as 0.1 g/L), although the extent of the increase in the rate of degradation is marginal at higher loadings. Gogate et al. (2002a) obtained similar results with experiments on degradation of formic acid (range of hydrogen peroxide loading used was 0.1 to 0.5 mL/L for an initial concentration of formic acid as 100 ppm). Thus, the optimum value of the hydrogen peroxide loading is dependent on the pollutant type studied, given that no optimum value has been observed within the range of loading as studied by Fung et al. (2000a) and Gogate et al. (2002a) for the case of CI reactive red 120 dye and formic acid, respectively. Initial loading of the pollutant will also have an effect on the optimum loading of the hydrogen peroxide. Fung et al. (2000b) showed that the required optimum feeding rate of hydrogen peroxide for the continuous process increases with an increase in the pollutant loading rate. This result of variation in the optimum value with the feeding rate of the pollutant should be equally applicable to the concentration of the pollutant for batch operation.

To summarize, it is essential to maintain the concentration of hydrogen peroxide at an optimum value because beyond a certain limit, the presence of hydrogen peroxide results in reduction in the rate of degradation. The optimum value of the hydrogen peroxide feeding rate and the concentration depends on the initial concentration of the pollutant (the higher the concentration, the higher will be the value of required optimum H_2O_2 feeding rate) and also on the type of the contaminant stream in question.

Use of Fe^{2+} as a Catalyst. Use of ferrous ions, in conjunction with ultrasonic and ultraviolet irradiations, results in enhancement in the rate of generation of the free radicals by Fenton's mechanism, given that ferrous ions react with hydrogen peroxide generated in situ as a result of the recombination reaction of free radicals. It should also be noted that the extent of enhancement in the rate of generation of free radicals may at times be only marginal, depending on the type of the pollutant. Wu et al. (2001) reported a marginal increase in the rate of removal of phenol with the addition of Fe^{2+} as a catalyst. More significant effects were observed in the percentage TOC removal (in 60 min of treatment time, the extent of removal increases from 20% in the absence of Fe^{2+} to about 50% in the presence of Fe^{2+}), indicating that the degradation of intermediates was affected by the addition of Fe^{2+} to a greater extent. This can be explained by considering the hydrophobic and hydrophilic nature of the reactant and the intermediates formed. Because the intermediates of the reaction are hydrophilic acids (formed as a result of the cleavage of aromatic rings), which are unfavorably transferred to the highly hydrophobic zone of the gas–liquid interface (and thus are not affected by the free radicals present at the interface), Fe^{3+} (formed by oxidation of Fe^{2+})/hydrogen peroxide (formed as a result of recombination of free radicals)/UV system becomes significant in the degradation of these intermediates in the bulk liquid. Thus, there are two parallel oxidation systems existing in the reactor: one acting at the gas–liquid interface (free radicals) and the other acting in the liquid bulk ($Fe^{3+}/H_2O_2/$UV). Because the overall efficacy of the process will be decided by the extent of total mineralization, addition of Fe^{2+} appears to be quite beneficial in this case. At this stage, addition of Fe^{2+} ions appears to be favorable for the hydrophilic pollutants or if these are likely to be formed as intermediates. More studies are required in terms of investigating the effect of concentration of Fe^{2+} ions to determine whether there is an optimum concentration similar to the case of hydrogen peroxide addition. It should also be noted here that the relative affinity between iron and pollutant toward adsorption on the photocatalyst might also play a role in deciding the extent of intensification, although not much work is available [except for the work of Mrowetz et al. (2003), who reported greater affinity of ferric ions, compared to that of azo dyes, and thus a reduction in the extent of enhancement in the rates of degradation] in the existing literature.

Use of Ozone. Another additive that affects the rates of sonophotocatalytic degradation is ozone because ozone in combination with hydrogen peroxide/UV light and/or ultrasound also results in generation of free radicals. Ragaini et al. (2001) showed that addition of ozone (as 80% Ar + 20% O_2/O_3 mixture) increases the percentage degradation of 2-chlorophenol from 40% in the absence of ozone to more than 90% in 100 min of irradiation time. Further if the concentration of ozone in the bubbling mixture is increased from 20 to 50%, the rate was almost doubled because of higher concentrations of the oxidizing species in the liquid phase (for 90 min of treatment time, the extent of degradation is more than 90% for 50% concentration of ozone, whereas it is about 45% for 20% ozone concentration in the same time). Ragaini et al. (2001) also showed that the total energy required for the reduction of 70% in the concentration of 2-chlorophenol is almost 1/4th in the presence of ozone compared to that in the absence of ozone (0.28 kWh in the presence of ozone as against 0.95 kWh in the absence of ozone). With only one study regarding the effect of addition of ozone on the rates of sonophotocatalytic oxidation and that, too, for the model constituent solution, it is difficult to give precise recommendations concerning the possible synergism between ozone and sonophotocatalytic oxidation, although the results reported above look extremely promising. Synergism between ozone and individual operation of sonochemical irradiation as well as photocatalytic oxidation is, however, an established fact (Benitez et al., 1997; Kang and Hoffmann, 1998; Kang et al., 1999). For the case of sonophotocatalytic oxidation, more work is required to investigate the effect of addition of the ozone on a variety of effluents, more significantly for real industrial effluents and for a range of ozone concentrations.

Use of Aeration. The presence of air provides additional nuclei for the cavitation events, thereby increasing the number of free radicals generated as well as the intensity of cavitation. Thus, the extent of the degradation attributed to sonication alone increases in the presence of air (Gogate et al., 2003; Sivakumar et al., 2002). Aeration results in enhanced benefits for the photocatalytic oxidation as well. This can be attributed to the fact that ozone may be formed by the ultraviolet irradiation of the air dissolved in liquid phase, which acts as an additional oxidant (Naffrechoux et al., 2000). Air also acts as an electron acceptor, which increases the efficiency of photocatalytic oxidation, and its sparging also helps in keeping the photocatalyst in suspension. The oxygen component of air will help the oxidation reactions. Thus, one might be tempted to use pure oxygen because it may result in substantial enhancement in the rates of oxidation reactions. Wu et al. (2001) recently showed that the extent of enhancement in the rates of degradation achieved using pure oxygen instead of air was less than 5%, thereby indicating that air can be used as a source of oxygen without affecting the efficiency of process by much and, at the same time, drastically reducing the cost compared to that of using pure oxygen on an industrial-scale operation. More studies are required to establish, if an optimum rate of introduction of air exists, whether an excessive amount of gas bubbles is detrimental for the effective transmission of ultrasonic irradiation (attenuation of intensity, absorption of energy, and decrease in the energy released as a result of the cavitation events).

Overview of the work done in the area of sonophotocatalytic oxidation

There have been many studies elucidating the observed synergism and the enhanced rates of degradation for the combined operation of sonochemical reactors and photocatalytic oxidation. Table 3 gives the overview of these studies with a brief discussion about the type of the equipment used along with the experimental conditions and important findings reported in the work, whereas two case studies are discussed in detail later. Recently, Toma et al. (2001) provided a brief overview of different studies pertaining to the effect of ultrasound on photochemical reactions, concentrating on the chemistry aspects (that is, mechanisms, and pathways of different chemical reactions). The rates of degradation for the combination of ultraviolet and ultrasonic irradiation can be orders of magnitude higher compared to those of an individual operation (see Table 3). In situations where the adsorption of the pollutants at the reaction specific sites is the rate-controlling step, ultrasound plays a profound role because of the substantial increase in the number of active sites and the surface area available for adsorption attributed to the defragmentation of the catalyst agglomerates under the action of turbulence generated by acoustic streaming along with an increase in the diffusional rates of the contaminants.

Some Case Studies

- Degradation of 2,4,6-trichlorophenol: In our earlier work (Shirgaonkar and Pandit, 1998), degradation of 2,4,6-trichlorophenol was investigated. Two different sonochemical reactors (ultrasonic horn and bath, with frequency of 22 kHz and power rating of 600 and 120 W, respectively, with a capacity of 100 mL) were used, whereas photocatalytic oxidation was achieved using a UV tube with power rating of 15 W and anatase grade TiO_2 catalyst at a loading of 0.1 g/L. The important results obtained in the work are depicted in Figure 6. It can be seen from the figure that the extent of degradation achieved using a combination is greater compared to that obtained for the individual oxidation techniques, although it is marginally less compared to the additive values, indicating that synergism is not observed (at 10% intensity of ultrasound, 100 ppm initial concentration of pollutant and catalyst loading of 0.1 g/L, the extent of degradation is 32% for the combination, 14% for photocatalysis, and 22% for ultrasonic irradiation in 5 h of treatment). Further an increase in the intensity of ultrasound to 20% [meaning 20% of the maximum power rating (i.e., 600 W) is being supplied into the system] results in an increase in the extent of degradation to 40%. This can be attributed to the fact that the increased cavitational activity, resulting in the prevention of agglomerates, cleaning of the catalyst surface, and the production of additional free radicals, is higher at higher power dissipation into the system. Experiments in ultrasonic bath were with direct irradiation of UV light, whereas in the case of ultrasonic horn, indirect irradiation had to be used. However, the extent of degradation observed in both the cases was similar, indicating that the mode of UV transmission does not affect the extent of degradation.
- Degradation of Formic acid: In another recent work (Gogate et al., 2002a), degradation of formic acid was studied in a hexagonal flow cell with a capacity of 7.5 L, operated in batch mode, and each side is provided with transducers with power dissipation of 150 W. The flow cell was operated at 20, 30, or 50 kHz in seven different combinations and was irradiated with an 8-W UV tube placed at the center of the reactor surrounded by a quartz tube. Some experiments were also performed in the presence of hydrogen peroxide (0.1 to 0.5 mL/L of commercial 30% H_2O_2). The important results obtained in the work for different operating modes are summarized in Table 4. The work has clearly established the relative contributions of different mechanisms leading to the synergistic effects. The variation of percentage degradation with time for different oxidation techniques is shown in Figure 7. The combination gives about four times more degradation compared to that with sonication alone, whereas the comparison with photocatalytic oxidation alone follows a somewhat complex behavior. The percentage degradation initially appears to be less in the presence of ultrasound, which can be explained on the basis of relative contributions of the different factors underlying the expected synergism between the two techniques.

Initially, fragmentation of the catalyst is the dominant factor due to large catalyst size compared to the effects of cleaning of the catalyst surface as well as enhancement in the formation of free radicals. The formation of a large number of solid particles increases the available surface area but, on the other hand, it also causes scattering of the UV light and the ultrasound and inhibits efficient transmission of both types of radiation through the medium. This was also observed visually by way of appearance of high turbidity in the initial periods of irradiation. As the time progresses, a greater number of free radicals are generated because of the combined action (UV + US), resulting in the enhancement, and also continuous cleaning of the catalyst particle occurs, which is absent in the case of photocatalytic oxidation alone, resulting in higher extent of degradation for the combination. Moreover, as the catalyst size reaches a certain lower limit (an equilibrium value), further fragmentation does not take place. It appears that fouling of the catalyst surface is the controlling factor in the later stages of the degradation of formic acid by UV light alone, given that the extent of degradation reaches a plateau within almost 2 h of irradiation and does not increase further. In contrast, the extent of degradation increases continuously in the presence of ultrasound, possibly because of the continuous cleaning of the catalyst surface.

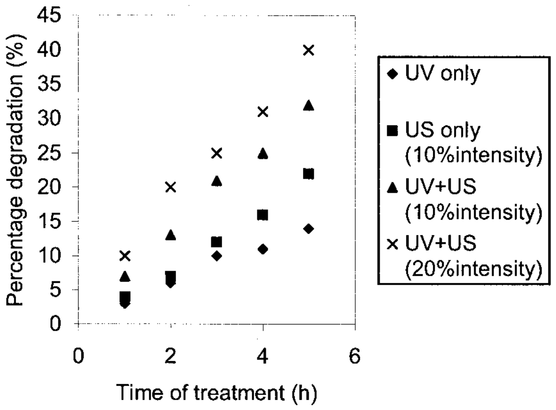


Figure 6. Degradation of 2,4,6-trichlorophenol using different techniques (Shirgaonkar et al., 1998).

To validate the above hypothesis of relative contributions of different effects of ultrasound, the experiments were repeated with a catalyst concentration of 300 ppm. For this set, the percentage degradation for the combination was 12.24%, whereas for photocatalytic oxidation alone it was 14.23% within the first 30 min of irradiation time. Thus, the combination technique gives 14% less degradation compared to that of only photocatalytic oxidation. However, for the case of 500 ppm catalyst concentration, the combination gives 28% less degradation compared to that of the photocatalytic oxidation. This can be attributed to the fact that negative contribution resulting from the fragmentation of photocatalyst will be less in the case of 300 ppm concentration compared to that at 500 ppm catalyst concentration. In other words, the time required for the combination to give better results, compared to photocatalytic oxidation alone, is less as soon as the fragmentation is reduced. Further confirmation of this fact was obtained when the ultrasonic irradiation was restricted to 20 kHz alone instead of 20 + 30 + 50 kHz combination for the 300 ppm catalyst concentration. Percentage degradations were found to be 12.24% (for combination of UV light and 20 + 30 + 50 kHz ultrasound), 15.75% (for combination of UV light and 20 kHz ultrasound), and 14.23% (UV light alone) in the first 30 min of irradiation time. In this case, the combination technique shows better results for 30 min of irradiation time only, given that the extent

Table 4. Comparison of the Results Obtained for Different Approaches Used for Degradation of Formic Acid (Gogate et al., 2002a)

Approach	Experimental Conditions	Results and Comments
Ultrasonic irradiation	Seven different combinations of frequencies, experiment with presence of air	Multiple frequencies are better compared to single frequencies. Presence of air also increases extent of degradation by providing additional nuclei. Maximum degradation achieved by US alone in the presence of air is around 6.5%
Hydrogen peroxide	Concentration of 0.5 mL/L, additional experiment with TiO_2 catalyst and stirring	Hydrogen peroxide does not oxidize formic acid (1.65% destruction in 90 min). Stirring in presence of TiO_2 (550 ppm concentration) increases degradation to 6.3%
Ultrasonic irradiation + hydrogen peroxide	All the frequencies operating and hydrogen peroxide loading of 0.5 mL/L	Percentage degradation is almost double (12.5%) as compared to individual techniques (6.3% and 6.5%) confirming the release of free radicals due to dissociation of hydrogen peroxide
Photocatalytic oxidation	Different initial concentrations of acid and catalyst TiO_2 in the range 100 to 1000 ppm	Rate decreases with an increase in the initial concentration of pollutant and shows optima with respect to catalyst concentration at 500 ppm. Maximum percentage degradation is observed at 500 ppm catalyst loading and 100 ppm acid initial concentration (23.5%)
Ultrasonic irradiation + UV irradiation	100 ppm acid concentration, 500 ppm of catalyst, all frequencies operating for ultrasonic irradiation and ultraviolet irradiation. Two different methods of sequential and simultaneous irradiations	Results better than the individual techniques for larger treatment periods. Simultaneous irradiation gives better results (20% degradation in 1.5 h) as compared to sequential operation (15.5% degradation). Dependency of synergism between the two techniques on time of operation, more synergistic at higher treatment times.
Ultrasound + UV + hydrogen peroxide	100 ppm acid concentration, 500 ppm of catalyst, all frequencies operating for ultrasonic irradiation and ultraviolet irradiation (simultaneous way). Addition of hydrogen peroxide in the range 0.1 to 0.5 mL/L	Best treatment approach with maximum percentage degradation achieved as 55% in 90 min of treatment time. Enhanced generation of free radicals due to faster dissociation of hydrogen peroxide under the combined action of ultrasound and UV light.

of fragmentation in the case of 20 kHz ultrasound is considerably lowered (because of lower intensity of cavitation and thus the turbulence for the 20 kHz irradiating frequency compared to that of the combination of 20 + 30 + 50 kHz ultrasound). It must be also noted at this stage that all these results are at initial stages only and indeed 20 + 30 + 50 kHz combination gives better results than those of 20 kHz alone over extended treatment time periods. It was also observed in the study that 300 ppm concentration of catalyst in the presence of ultrasound gives almost the same amount of degradation compared to that of the 500 ppm catalyst in the absence of ultrasound. Thus it can be said that the presence of ultrasound decreases the required catalyst loading to achieve the same degradation, which is likely to reduce separation problems and offer some cost benefits. It should also be noted that the optimum value of the catalyst concentration (500 ppm for photocatalytic oxidation, as observed in this case) will be different for the combination of ultrasound and ultraviolet irradiation because the relative contributions of different factors (fragmentation, cleaning, and production of free radicals) will be strongly dependent on the catalyst concentration.

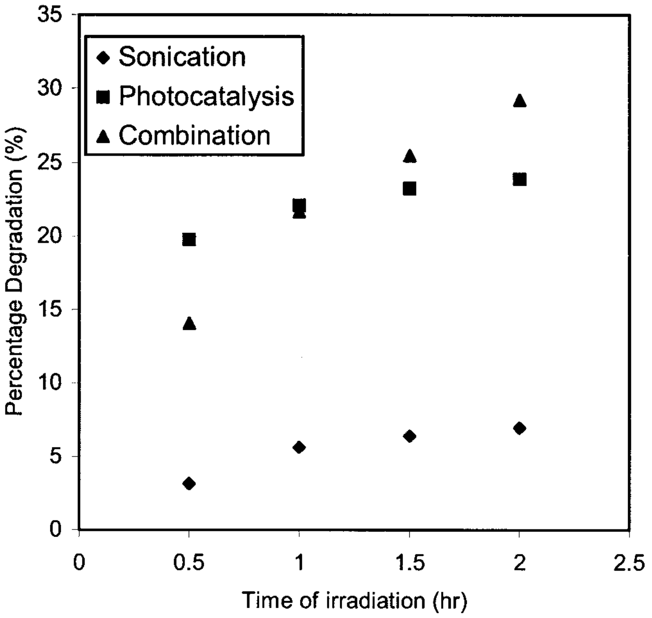


Figure 7. Understanding mechanism of synergism of sonophotocatalytic oxidation (Gogate et al., 2002a).

Thus based on the study, it can be said that use of multiple frequencies promotes the flexibility of controlling the ultrasonic intensity with time and hence is recommended for photocatalytic reactors. In the initial stages, where fouling of photocatalyst is not controlling, low-intensity ultrasound can be used (either lower power dissipation or single-frequency operation), whereas at later stages of treatment, higher ultrasonic intensity can be achieved using higher power dissipation and/or use of multiple transducers/frequencies.

Conclusions

Sonophotocatalytic oxidation results in the elimination of the main disadvantages of photocatalytic operation, fouling of the catalyst, and mass transfer resistance due to the turbulence generated by the ultrasonic action. Further, adsorption of the pollutant species is favored because of the facilitation of the transport of pollutant molecules and increase in the surface area because of deagglomeration of catalyst, leading to an enhanced rate of degradation. A detailed analysis presented in the work indicates that the intensification (few hundred percent to order of magnitude) strongly depends on the type of the effluent stream and the operating conditions. The synergism is expected to be dominant for large-scale operations and over extended treatment periods. It is important to have simultaneous irradiation of ultrasound and UV light rather than the sequential operation because continuous cleaning of the catalyst plays a crucial role, as clearly demonstrated by the work of Gogate et al. (2002a) using formic acid degradation. Addition of hydrogen peroxide, ozone, air, and ferrous ions as an additional source for the free radicals can be used for the intensification of the degradation process.

Reactor design for the large-scale operation is another crucial factor controlling the efficacy and synergistic effects of the hybrid technique and should be aimed at achieving uniform distribution of both the ultrasonic as well as ultraviolet irradiations. The reactor designs should be based on using multiple-frequency, multiple-transducer configuration for ultrasonic irradiation and multitubular configuration for UV irradiation, or using parabolic concentrators for solar energy as a source of UV radiations. The aim should also be at developing reactors that offer flexibility in terms of operation for different loadings of the pollutants and at the same time that should result in economic savings; that is, variable intensity of oxidation conditions should be achieved by controlling the operating parameters. Operation of the reactor should also be carefully planned to achieve maximum benefits: for the initial period of treatment a lower intensity of sonication is recommended and should be increased in later stages as highlighted earlier.

In summary, sonophotocatalytic reactors result in higher degradation efficiency compared to that when both are used individually, although more efforts are indeed required to use the available information, which is mostly on a laboratory scale for the design of industrial-scale reactors and its successful application for the treatment of variety of industrial effluent streams.

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Notation

AO8 = Acid orange 8
AR1 = Acid red 1
COD = chemical oxygen demand
CP = 4-chlorophenol
DBT = dibenzothiophene
DCP = 2,4-dichlorophenol
DMDBT = 4,6-dimethyl-dibenzothiophene
MTBE = methyl *tert*-butyl ether
NaPCP = sodium pentachlorophenate
PTMK = phenyltrifluromethyl-ketone
TCP = 2,4,6-trichlorophenol
TOC = total organic carbon
US = ultrasound
UV = ultraviolet light
VOC = volatile organic content

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