Effect of Several Oxides on Ultrasonic Degradation of Formic Acid

Serap Fındık[a], Gönül Gündüz

Hitit University, Engineering Faculty, Chemical Engineering Department, Turkey

E-mail:serapfindik@hitit.edu.tr

Abstract: In this study, ultrasonic degradation of formic acid was investigated. The effects of several oxides on sonolytic degradation of formic acid were studied. An ultrasonic bath was used and formic acid was sonicated indirectly. The study showed that initial degradation of formic acid with SiO_2 and zeolite was greater than without solid. In the present study, the obtained degradation of formic acid is about 10 %. Hybrid techniques based on sonolysis can be used for higher degradation degrees of formic acid.

Key words: degradation, cavity, formic acid, sonication, ultrasound

Introduction

In recent years, due to the growing need to eliminate hazardous chemical compounds from sewage and industrial effluents, the utilization of power ultrasound for waste water treatment has been explored with great interest. The advantage of this process is based on the fact that reactions can be carried out under ambient global conditions, otherwise application of rigorous conditions such as high temperature and pressure (wet air oxidation and/or incineration) is required.

Sonochemistry is the application of ultrasound to chemical reactions and processes. The origin of sonochemical effects in liquids is the phenomenon of acoustic cavitation. Sound is passed through a liquid as a wave consisting of alternating compression and rarefaction cycles. If the rarefaction wave has a sufficiently high negative pressure, it can overcome the intermolecular forces bonding fluid. As a result, the molecules are torn apart from each other and tiny micro bubbles are created. These micro bubbles gradually grow during compression and rarefaction cycles until they reach a critical size. Subsequent compression causes these cavities to collapse almost instantaneously with a large amount of energy and extremely high temperatures of the order of 5000 K and pressures of the order of 1000 atm are attained. Under such extreme conditions, water molecules dissociate into $OH^{\cdot}$ and $H^{\cdot}$. The radical species can either recombine or react with other gaseous substrates within the cavity. There are three potential sites for chemical reactions in ultrasonically irradiated liquids. A volatile substrate would be readily taken into the cavity and its main decomposition reaction pathway may be one of pyrolysis within the cavitation bubble. The second region is the interfacial zone between gas phase and bulk solution, where large temperature and pressure gradients exist. Therefore, at this site substrate can be degraded by two reaction pathways, either by oxidation with $OH^{\cdot}$ or by thermal reaction. The third possible reaction zone involves the bulk solution, where the decomposition of pollutants might occur by the reaction of ultrasonically produced bubbles of $OH^{\cdot}$ diffusing into the bulk solution. Thus, the reaction zone, or degradation pathways of a particular substrate depends on its chemical nature, for example, its volatility, solubility and chemical structure, etc. Volatile organic compounds may easily undergo direct thermal reactions within the cavitation bubble; however semivolatile or non volatile solutes react at the bubble interfaces or within the bulk solution (Ince et al., 2001; Wu et al., 2001; Nam et al., 2003).

There are several factors affecting the extent of ultrasonic degradation of pollutants, such as; time of destruction, initial concentration of pollutants, intensity and frequency of irradiation, introduction of gas, temperature, solid catalyst, several salts, H_2O_2, pH, different cavitation equipments and the level of coupling fluid (Petrier and Francony, 1997; Ince et al., 2001; Sutkar and Gogate, 2009). The effects of these parameters in the ultrasonic degradation of organic pollutants have been widely investigated in literature (Rajan et al., 1998; Vischer et al., 1998; Naffrechoux et al., 2000; Okuno et al., 2000; Peters, 2001; Kim et al., 2001; Goskonda et al., 2002; Jiang et al., 2002a; Sivakumar et al., 2002). Effect of each parameter changes with reaction parameters, type of organic compounds and ultrasonic equipments.

Formic acid (methanoic acid) is a colorless , odorous acid , the first and by far the strongest of the unsubstituted series of carboxylic acids. It is miscible with water and most polar organic solvents and somewhat soluble in hydrocarbons. Formic acid is mainly produced as a by product of liquid phase oxidation of hydrocarbons to acetic acid. Large quantities of formic acid are consumed by the textile and leather industries. Small amounts of formic acid are used for coagulating rubber latex, in nickel plating baths, in stripping the enamel from wire and the manufacture of drugs, dyes, flavors,paper, fumigants, pesticides and synthetic perfume ingredients, (Enc.of Chem. Tech., 1980). Formic acid as other lower acids is formed during the oxidation of chemicals including longer chain acids and rate of degradation of formic acid is the rate controlling step in deciding the overall treatment times as well as the efficiency of the process.

There are many studies using different advanced oxidation techniques such as photocatalytic oxidation (Aguado and Anderson, 1993; He et al., 2005), photo-fenton reaction (Rossetti et al., 2004) and catalytic wet air oxidation (CWAO) (Gallezot et al., 1996; Harmsen et al., 1997; Lee and Kim, 2000; Miachon et al., 2003; Iojoiu et al., 2005) for the degradation of formic acid. However, it is difficult to oxidize it by the above methods. For instance, in the case of CWAO, rather high temperatures and pressures are required for oxidation. Sonochemical degradation is capable of being developed into a successful technology for environmental clean up. It is necessary to determine the ultrasonic destruction of formic acid which is obtained from ultrasonic degradation of various compounds to produce a clean effluent. In literature, a few studies have been reported on the ultrasonic degradation of formic acid (Gogate et al., 2003; Bhirud et al., 2004; Gogate et al.,2006).

Gogate et al. (2003) studied the degradation of formic acid using different cavitation equipments such as ultrasonic horn, ultrasonic bath, dual frequency flow cell and triple frequency flow cell. Power and frequency of each equipment is as follows: ultrasonic horn 240W, 22.7kHz; ultrasonic bath 120W, 22kHz; dual frequency flow cell 120W, 25-40kHz and triple frequency flow cell 150W, 20-30-50kHz. They investigated the effect of several parameters such as time of destruction, initial concentration of formic acid, intensity and frequency of irradiation, introduction of air and liquid level in the case of ultrasonic bath on the extent of degradation. Bhirud et al. (2004) investigated efficacy of a novel configuration for large scale wastewater treatment applications using formic acid degradation as a model reaction. Effect of initial concentration of formic acid on the degradation was also studied and comparison was made with the conventional ultrasonic horn in terms of energy efficiency and cavitational yield for the model reaction. In another research, Gogate et al. (2006) studied the degradation of formic acid in a high frequency cup horn type reactor with an aim of understanding the effect of operating parameters on the destruction efficiency. The effect of time of irradiation, initial concentration of pollutant, stirrer speed, presence of sodium sulfite, effect of NaCl addition on the extent of degradation has been investigated.

The aim of this work is to investigate the degradation of formic acid sonicated indirectly using an ultrasonic bath with 40 kHz. In the study, the effects of several oxides were studied on the degradation degree of formic acid.

Materials and Method

Figure 1 shows the experimental set up for the indirect sonication of formic acid. An ultrasonic bath was used for sonication reaction. The ultrasonic bath operates at 40 kHz and at an ultrasound power in the range 70-140 W. Operating temperature of the bath could be regulated between 20-80 °C. Sonication time could be adjusted to a desired value in the range of 1-60 minutes. Aqueous solution with a known concentration of organic pollutant was prepared using ultra pure water and reactor was filled with 200ml of solution, then reactor was inserted into the ultrasonic bath. The volume of coupling fluid (water) was 1700ml. Liquid soap (0.17% in weigh)t was added to improve cavitation.

Reactor was a spherical pyrex-glass flask (83 mm in diameter with a wall thickness of 0.9 mm) with three neck and 250 ml volume. The two necks housed a reflux condenser and gas entrance. Third neck was used to take samples. The position of the flask with respect to transducer was always constant at 2 cm above the transducer. Formic acid was sonicated indirectly to avoid the damage of formic acid to bath surface.

The efficiency of a reaction vessel placed in an ultrasonic bath depends strongly on the distance of the bottom of the reaction vessel to the bottom of water bath. The distance from the bottom was measured so that ultrasonic intensity reached maximum at the bottom of the flask. The maximum intensity occurs at half wavelength which is a function of frequency used in ultrasound bath. For ultrasonic frequency 40 kHz the distance from bottom was obtained to be 2cm (Goel et. al., 2004).

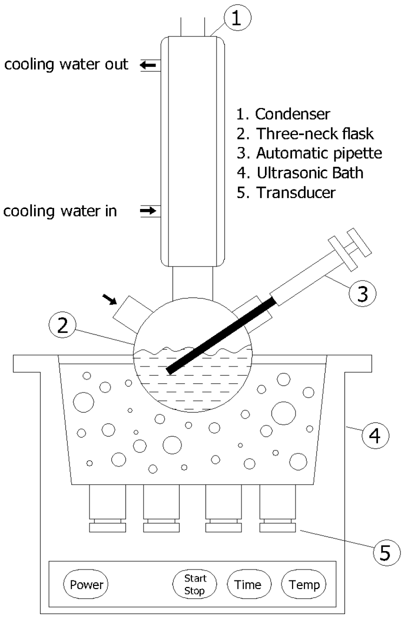

Figure 1: Experimental set up for indirect sonication

Formic acid was obtained from Saf Kimya, Turkey (%85 pure) and used without further purification.

An experiment took 1 hour and all the experiments repeated at least 4 times mostly 7 times. The samples were withdrawn from the reaction mixture periodically. The unreacted amount of formic acid was determined by titration with 10^{-3} M NaOH solution, using 2 % (in weight) of phenol phtalein indicator. Dilute NaOH solution was used so that readings of titration were in the range of 10-14 ml with the least count of burette as 0.01 ml.

The percentage of degradation of pollutant was calculated from equation 1:

$$\text{Degradation,} \quad \% = \left(\frac{Co - C}{Co}\right) * 100 \quad (1)$$

where C_0 initial concentration, C concentration measured at corresponding time.

Results and Discussion

The presence of solid particles affects the cavitational activity in two different and opposing ways, firstly it intensifies the process by providing additional nuclei due to the discontinuities in liquid medium and hence the number of cavitation events may increase but at the same time due to the scattering of incident sound waves the net energy dissipation into the system may decrease (Gogate et al., 2004; Sutkar and Gogate, 2009).

In this study, the effect of TiO_2, Al_2O_3, SiO_2 and natural zeolite on sonolytic degradation of formic acid has been investigated. The experiments with solid oxide were done with different oxide amounts in the range of 0.01g-0.8g at a temperature of 43±3 °C and at a power of 84 W with 200 ml of 300 ppm aqueous solution of formic acid. Experiments for studying the adsorption characteristics of formic acid on the solid particles were also performed because adsorption of formic acid interferes in the determination of concentration of the residual pollutant. It was observed that the adsorption of formic acid on oxides used was negligible.

Experiments for formic acid degradation were done with 0.01, 0.02 and 0.03g TiO_2. There was no response at

0.02 and 0.03g. Degradation with 0.01g of TiO_2 is less than that without TiO_2. Figure 2 shows the results.

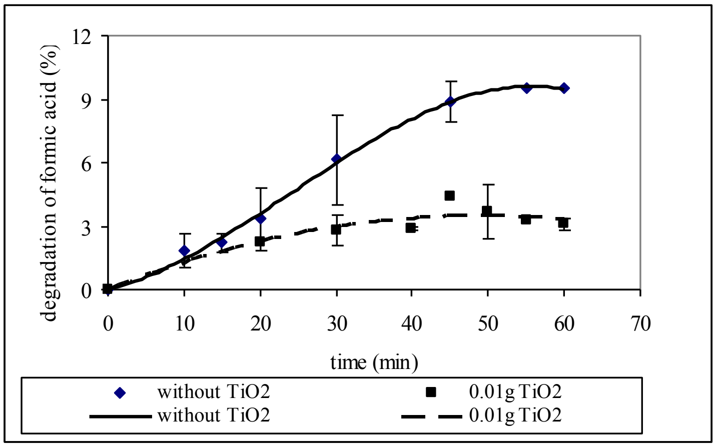

Figure 2: Effect of TiO_2 addition on the degradation of formic acid (power=84W , temperature= 43±3°C, initial concentration =300ppm)

Experiments with Al_2O_3 were made with three different amounts, 0.05, 0.1 and 0.2g of Al_2O_3 for degradation of formic acid. There was no response at 0.2g and nearly the same degradation level was obtained with 0.05g and 0.1g Al_2O_3, but less than that without Al_2O_3. Figure 3 presents the results. It can be said that addition of the above mentioned oxides inhibits bubble formation which causes decreases in degradation degree.

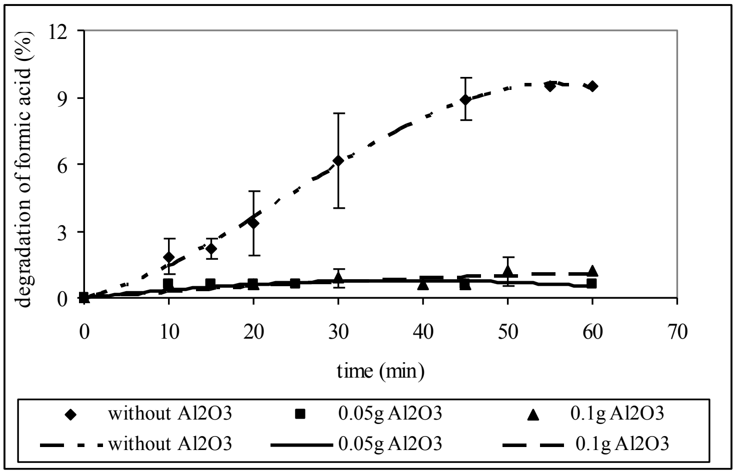

Figure 3: Effect of Al_2O_3 addition on the degradation of formic acid (power= 84W, temperature= 43±3°C, initial concentration=300ppm)

Another oxide tested was SiO_2. Experiments were done with SiO_2 in different amounts; 0.05, 0.1 and 0.2g. Figure 4 shows the effect of SiO_2 addition on the ultrasonic degradation. From the Figure 4, it is seen that initial degradation rate of formic acid with SiO_2 is greater than that without SiO_2, except for 0.2g SiO_2. Degradation of formic acid remains nearly constant after 40 min regardless of SiO_2 amount used.

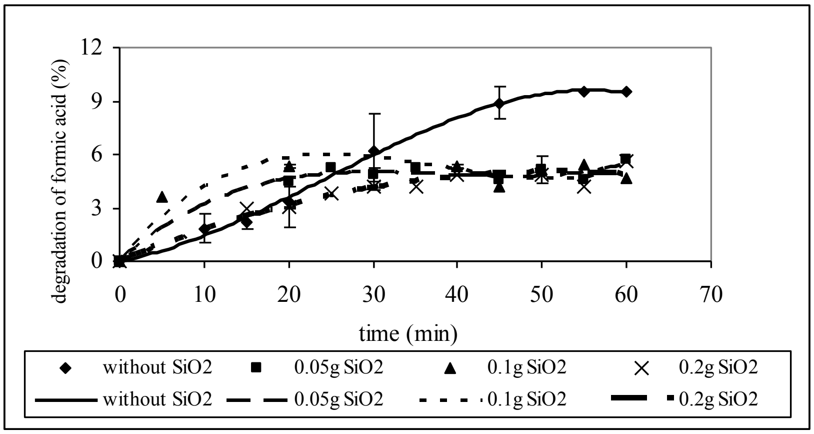

Figure 4: Effect of SiO_2 addition on the ultrasonic degradation formic acid (power=84W, temperature=43±3°C, initial concentration=300ppm)

Figure 5 represents the typical curves for degradation of formic acid as a function of time in the presence of natural zeolite. Natural zeolite is from Bigadiç region of Turkey, it is rich in clinoptilolite with a chemical composition of 78.05 % SiO_2, 2.57 % Na_2O, 1.82 % K_2O, 0.45 % Fe_2O_3, 2.31 % CaO, 6.34 % Al_2O_3, 0.33 % MgO, 8.14 % H_2O.

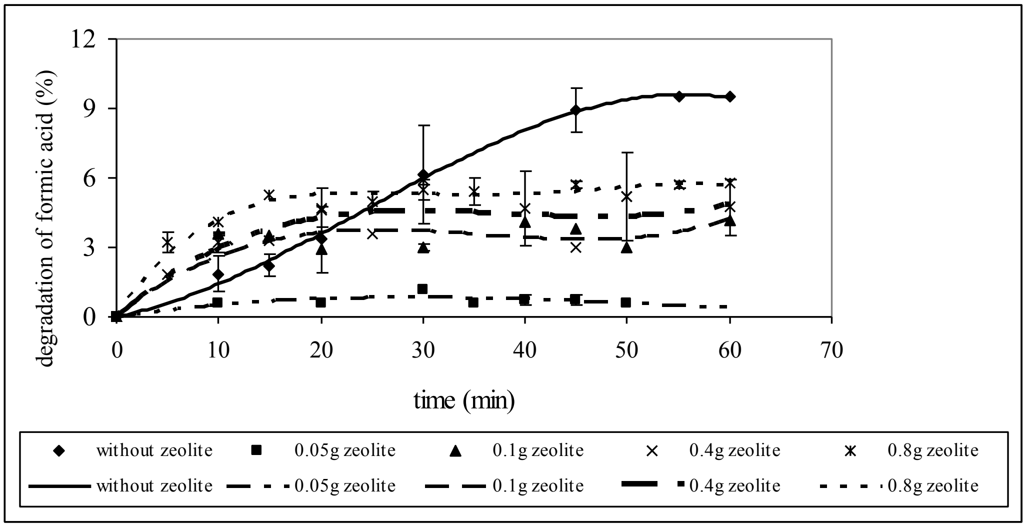

Figure 5: Effect of zeolite addition on the degradation of formic acid (power=84 W, initial concentration=300 ppm, temperature=43±3 °C)

As shown from Figure 5 with 0.05g of zeolite, degradation of formic acid is very small. Initial degradation rate of formic acid increases as zeolite amount increases, but with lower degradation levels than that without natural zeolite. As zeolite amount increases, additional nuclei are provided causing an increase in the number of cavitation events but negative effect of sound scattering becomes dominant resulting in lowering the extent of degradation. The combined effect is observed as lower degradation degrees than that in the absence of zeolite.

In literature, similar and opposite results have been reported in the ultrasonic degradation of several compounds.

Gogate et. al (2004) studied the effect of TiO_2 for sonolytic degradation of phenol at 22.7kHz and 240W for ultrasonic horn. The presence of TiO_2 at 300ppm caused lower extent of degradation as compared with that observed in the absence of solid particles. In the same study TiO_2 (300ppm powdered TiO_2 particles) has positive effect for the flow cell. Drijver et. al (1999) investigated ultrasonic degradation of trichloroethylene (TCE) by addition of CuO but CuO particles didn't enhance the degradation of TCE. It means no extra cavitations were caused by CuO in thew case of TCE. In another study Goel et. al (2004) observed that rate constant decreased with increasing concentration of silica due to the attenuation of energy by scattering of the particles.

Conclusions

In this study, ultrasonic degradation of formic acid was investigated. Formic acid was sonicated indirectly. Effect of several oxides to degradation of formic acid were studied. An ultrasonic bath was used for sonication. This study showed initial degradation of formic acid was greater than without solid.

In the present study, the obtained degradation degree of formic acid is about 10 %. Sonolysis of formic acid combined with other advanced oxidation processes, such as ozonation, UV, photolysis may give better results than the sonolysis method alone.

References

Aguado, M.A., Anderson, M.A.(1993), Degradation of formic acid over semiconducting membranes supported on glass: effects of structure and electronic doping, *Solar Energy Materials and Solar Cells*, 28, (pp.345-361).

Bhirud, U.S., Gogate, P.R., Wilhelm, A.M., Pandit, A.B.(2004), Ultrasonic bath with longitudinal vibrations: A novel configuration for efficient wastewater treatment, *Ultrasonics Sonochemistry*, 11, (pp.143-147).

Drijvers, D., Langenhove, H.V., Beckers, M., 1999, Decomposition of phenol and trichloroethylene by the ultrasound/H_2O_2/CuO process, *Pergamon,* 33, (pp.1187-1194).

Encyclopedia of Chemical Technology, (1980), Third edition, John Wiley, USA

Fındık, S., (2005), Ultrasonic Oxidation of Organic Pollutants in Aqueous Solutions, *PhD Thesis*, Ege University, Chem.Eng.Dep. Izmir/Turkey

Gallezot, P., Laurain, N., Isnard, P., (1996), Catalytic wet air oxidation of carboxylic acids on carbon supported platinum catalysts, *Applied Catalysis B: Enviromental*, 9, (pp.L11-L17).

Goel, M., Hongqiang, H., Mujumdar, A.S., Ray, M.B.,(2004), Sonocheminal decomposition of volatile and non-volatile organic compounds a comparative study, *Water Research*, 38, (pp.4247-4261).

Gogate, P.R. , Mujumdar, S., Pandit, A.B.,(2003) , Sonochemical reactors for waste water treatment: comparison using formic acid degradation as a model reaction, *Advances in Enviromental Research*, 7, (pp.283-299).

Gogate, P.R., Mujumdar, S., Thampi, J., Wilhelm, A.M., Pandit, A.B., (2004), Destruction of phenol using sonochemical reactors: scale up aspects and comparison of novel configuration with conventional reactors, *Separation and Purification Technology*, 34, (pp.25-34).

Gogate P.R., Pandit A.B., Wilhelm A., Ratsimba B.,(2006), Destruction of formic acid using high frequency cup horn reactor, *Water Research*, 40, (pp.1697-1705).

Goskonda, S., Catallo, W.J., Junk, T., (2002), Sonochemical degradation of aromatic organic pollutantss, *Pergamon*,22, (pp.351-356).

Harmsen, J.M.A., Jelemensky, L., Andel-Scheffer, P.J.M., Kuster, B.F.M., Marin, G.B., (1997), Kinetic modeling for wet air oxidation of formic acid on a carbon supported platinum catalyst, *Applied Catalysis A*: General, 165, (pp.499-509).

He, C., Li, X., Xiang, Y., Zhu, X., Liu, S.,(2005), The enhanced PC and PEC oxidation of formic acid in aqueous solution using a Cu-TiO_2/ITO film, *Chemosphere*, 58, (pp.381-389).

Ince, N.H., Tezcanlı, G., Belen, R.K., Apikyan, I.G., (2001), Ultrasound as a catalyser of aqueous reaction systems: the state of the art and environmental applications*, Applied Catalysis B:Enviromental*, 29, (pp.167-176).

Iojoiu, E.E., Walmsley, J.C., Raeder, H., Miachon, S., Dalmon, J-A., (2005), Catalytic membrane structure influence on the pressure effects in an interfacial contactor catalytic membrane reactor to wet air oxidation, *Catalysis Today*, 104, (pp.329-335).

Jiang, Y., Petrier, C., Waite, T.D., (2002), Effect of pH on the ultrasonic degradation of ionic aromatic compounds in aqueous solution, *Ultrasonics Sonochemistry*, 9, (pp.163-168).

Kim, I.K., Jung, O.J.,(2001), Sonochemical decomposition of humic substances in wastewater effluent, *Bull. Korean Chem. Soc.,* 22, (pp.1093-1100).

Lee, D-K., Kim, D-S., (2000), Catalytic wet air oxidation of carboxylic acids at atmospheric pressure*, Catalysis Today*, 63,(pp. 249-255).

Miachon, S., Perez, V., Crehan, G., Torp, E., Reeder, E., Bredesen, R., Dalmon, J.-A., (2003), Comparison of a contactor catalytic membrane reactor with a conventional reactor: example of wet air oxidation, *Catalysis Today*, 82, (pp.75-81).

Naffrechoux, S., Chanoux, C., Petrier, C., Suptil, J.,(2000), Sonochemical and photochemical oxidation of organic matter, *Ultrasonics Sonochemistry*, 7, (pp.255-259p).

Nam, S.N, Han, S.K., Kang, J.W., Choi, H., (2003), Kinetics and mechanisms of the sonolytic destruction of non-volatile organic compounds: investigation of the sonochemical reaction zone using several $OH^\cdot$ Monitoring techniques, *Ultrasonics Sonochemistry*, 10, (pp.139-147).

Okuno, H., Yim, B., Mizukoshi, Y., Nagata, Y., Maeda, Y., (2000), Sonolytic degradation of hazardous organic compounds in aqueous solution, *Ultrasonics sonochemistry*, 7, (pp.261-264).

Peters, D., (2001), Sonolytic degradation of volatile pollutants in natural ground water: conclusions from a model study, *Ultrasonics Sonochemistry*, 8,(pp. 221-226).

Petrier, C., Francony, A., (1997), Ultrasonic waste water treatment: incidence of ultrasonic frequency on the rate of phenol and carbon tetrachloride degradation, *Ultrasonics Sonochemistry*, 4,(pp.295-300).

Rajan, R., Kumar, R., Gandhi, K.S., (1998), Modelling of sonochemical oxidation of the water-KI-CCl_4 system, *Pergamon*, 53, (pp.255-271).

Rossetti, G.H., Albizzati, E.D., Alfano, O.M., (2004), Modeling of a flat-plate solar reactor, degradation of formic acid by the phofenton reaction, *Solar Energy*, 77, (pp.461-470).

Sivakumar, M., Tatake, P.A., Pandit, A.B., (2002), Kinetics of p-nitrophenol degradation: effect of reaction conditions and cavitational parameters for a multiple frequency system, *Chemical Engineering Journal*, 85, (pp.327-

338).

Sutkar V.S., Gogate P.R.,(2009), Techniques for understanding cavitational activity distribution and effect of operating parameters, *Chemical Engineering Journal*, 155,(pp.26-36)

Visscher, A.De, Langenhove, H. Van, (1998), Sonochemistry of organic compounds in homogeneous aqueous oxidising systems, *Ultrasonics Sonochemistry*, 5, (pp.87-92).

Wu, C., Liu, X., Wei, D., Fan, J., Wang, L., (2001 b), Photosonochemical degradation of phenol in water, *Pergamon*, 35, (pp.3927-3933).