Sonochemical degradation of *p*-chlorophenol assisted by H_2O_2 and Ag-TiO₂ / TiO₂ catalyst

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The degradation of *p*-chlorophenol in aqueous solution by low frequency ultrasound (30 kHz) has been studied. The degradation of *p*-chlorophenol in US/H₂O₂, US/ Ag- TiO₂ US/TiO₂, US/TiO₂/H₂O₂ and US/ Ag-TiO₂/H₂O₂ systems is also compared. The maximum removal of *p*-chlorophenol i.e 75% is observed in US/ Ag-TiO₂/H₂O₂ system where as 37% removal is observed in US/TiO₂/H₂O₂ system. Further the effect of initial substrate concentration, *p*H and temperature on the initial rate of degradation of the model pollutant have also been investigated. Studies reveal that the initial rate of degradation increases with increase in initial substrate concentration whereas the initial rate of degradation decreases with an increase in *p*H and reaction temperature.

Keywords: Ag-loaded TiO_2 catalyst, Hydrogen peroxide, *p*-Chlorophenol (PCP), Ultrasound.

p-Chlorophenol (PCP) is used in pesticides and antiseptics. It is mainly produced in pulp and paper industry, in bleaching process with chlorine. PCP being much more toxic than its parent compound, phenol, affects liver and immune system. Discharge of these chemicals into the environment poses significant health risks due to their high carcinogenicity. Also high toxicity and its physiochemical properties make PCP difficult to decompose by the conventional waste-water treatment processes.

Ultrasonic irradiation has received considerable interest as an advanced oxidation process since this process leads to complete demineralization of the harmful pollutant, which are not easily biodegradable, by oxidizing them to less toxic intermediates. Sonochemical techniques utilize ultrasound to produce an oxidative environment via acoustic: formation, growth and implosive collapse of microbubbles that entrap molecules of gases and water vapor from the surrounding liquid. During collapse of cavitation bubbles intense localized temperatures (5000°K), pressures (1000 atm), electrical charges as well as plasma effects are induced^{1,2}. The entrapped molecules are thus subjected to extremes of temperature and pressure generated during transient and adiabatic collapse of bubbles and dissociation generating radicals. With fragmentation of these bubbles during collapse, these radicals are released into the bubble liquid medium where they induce various chemical reactions³.

Depending on the physiochemical properties of organic pollutants there are two different mechanisms for their degradation: thermal decomposition due to direct pyrolysis inside the cavitation bubbles and decomposition via oxidizing the pollutant by °OH radicals and H_2O_2 released into the bubble liquid medium when the cavitation bubbles collapse ⁴.

Hydrophobic and volatile compounds degrade mainly by pyrolysis in the cavitation bubbles. Hydrophilic compounds, compounds with a low vapour pressure e.g., phenol, PCP, degrade ultrasonically mainly by reaction with °OH radicals and H_2O_2 in the bulk solution or in the interface between the collapsing cavitation bubble and the bulk solution⁵.

Studies regarding the ultrasonic degradation of hydrophilic organic compounds reveal that though ultrasonic irradiation has potential for treatment of hazardous wastewater, the use of ultrasound alone cannot provide high enough rate of degradation^{5,6}. Accelerating the ultrasonic degradation of such compounds by coupling it with other advanced oxidation processes is another possibility to increase the efficiency of this technique⁴. Heterogeneous sonocatalytic degradation of recalcitrant organic contaminants using different catalysts such as metal oxides is an alternative way to solve the problem of transforming persistent organic contaminants to non-persistent substances. The most common type of catalyst to be used is TiO_2 and its advantages are such as inexpensive, non-toxic, biologically stable and reusable. Loading of metal particles into TiO₂ catalysts either through doping or used as their composites can inhibit charge recombination between holes and electrons produced during the ultrasonic irradiation of TiO₂ to enhance the degradation efficiency 4 .

In the present study, the degradation of PCP, the model hazardous organic compound, by ultrasonic

radiation has been investigated. Coupling of the US process with other advanced oxidizing processes is also performed *viz.*, US/ H_2O_2 , US/ Ag-TiO₂, US/TiO₂, US/ TiO₂/ H_2O_2 and US/ Ag-TiO₂/ H_2O_2 . A comparison of these processes in context with rate of degradation of PCP has been studied.

Experimental Section

Materials

PCP (99.5%) and Titanium dioxide (mixture of anatase and rutile form) were obtained from National Chemicals, Vadodara and S. D. Fine chemicals, Boisar, India respectively. Hydrogen peroxide (30%w/v), 4-aminoantipyrine, silver nitrate, potassium ferricyanide, sodium carbonate, ammonia solution, sodium hydroxide and sulfuric acid were procured from Finar Reagents, Ahmedabad, India. All the chemicals were of Analytical Reagent (AR) grade. Aqueous stocl solutions of PCP were prepared by dissolving PCP in ultrapure Milli-Q water.

Experimental-Setup

The sonochemical reactor configuration used in the present work is basically an ultrasonic probe with a single transducer procured from LABSONIC®M, Germany. The probe has an operating frequency of 30 kHz and a rated power output of 100W. Figure 1 shows a schematic representation of the experimental setup used to sonicate PCP aqueous solution. A V-shaped flask was used. The batch type reactor was provided with an indentation on its base to disperse the sonic waves as they are reflected from the base. A 100 mL aqueous solution of PCP was sonicated in a 200 mL conical sealed glass reactor. The probe was dipped in the center of the glass reactor to a height of 2 cm. The sonicated solution's temperature was controlled by a water bath at ±0.5°C of the desired temperature. Sample aliquots (1 mL) were extracted



Fig. 1-Experimental setup for ultrasonication

from the aqueous solution using a 10 mL measuring cylinder. A digital *p*H meter and a thermometer were used to monitor the related parameters in the aqueous solution. The *p*H was adjusted (if required) by 0.1N NaOH and 0.1N H₂SO₄. When carrying out experiments for TiO₂ and Ag-TiO₂ mixing was accomplished using air-bubbler to keep the catalyst in suspension.

Preparation of Ag-doped Tio₂ catalyst

Ag-loaded TiO₂ containing 1% (w/w) silver was prepared by reported procedure⁷. Initially, 9.2 mL of AgNO₃ solution (0.1 M) was added to a TiO₂ slurry containing 10 g of TiO₂ followed by *ca*. 10 mL of a 1% (w/v) Na₂CO₃ solution. The aqueous suspension was dried at room temperature and then backed for 6 h at 400°C.

Analytical procedure

PCP was monitored spectrophotometrically by the aminoantipyrine method⁸. The method is based on the reaction of PCP with 4-aminoantipyrine in the presence of potassium ferricyanide to form a colored complex. Concentration of PCP in the colored complex was then estimated from the absorbance of the solution at 505 nm using UV-Vis spectrophotometer, DR 5000 TM, procured from HACHR, Germany.

Results and Discussions

Single operation (US alone)

Effect of initial concentration of PCP

The effect of initial concentration of PCP on the rate of its degradation during sonication irradiation was investigated. The initial concentration of PCP was varied from 50 mg/L to 200 mg/L. After 2 h of sonolysis it was found that the rate of degradation of PCP was independent of its initial concentration.

Previously it was found that though a probe system appeared to be the most appropriate sonochemical system for the treatment of PCP, its concentration in the aqueous solution reached equilibrium after 20 mins of sonication⁹. In this work, results were presented using the initial degradation rate (ppm/min), during the first 4-20 min. Initial degradation rates were computed as D_C/D_t over the first minutes of sonication from the results showing the evolution of solute concentration as a function of sonication time. It was found that as initial concentration of PCP in the aqueous solution increases the initial rate of degradation of PCP also increase. Similar results were obtained in a previous study which concludes that the overall rate of disappearance of the chlorophenols follows a concentration independent path and a concentration -dependent course¹⁰.

Effect of pH

The pH is an important factor which affects the decomposition of target compounds using advanced oxidation processes especially with ultrasonic process. The pH affects the state of organic compounds in aqueous solution. The acid-base dissociation constant (pK_a) of PCP at 25°C is 9.38. When the *p*H value is greater than the pK_a , almost all of the PCP is ionized in the solution. When the pHvalue is less than the pK_a , almost all of the PCP is in the molecular form. Several researchers have reported the state of the compound affects the reaction mechanism. The ionic form of the compound does not vaporize into the cavitation bubbles; it reacts outside of the bubble with the hydroxyl radicals cleaved from water molecules. On the other hand at lower pH, the molecular form of the compound decomposes thermally in the cavitation area and also by hydroxyl radicals or other free radicals in the bulk-liquid phase¹¹. The effect of pH on sonochemical degradation of PCP was investigated at 30 kHz with ultrasonic power of 100W and the temperature of aqueous media is 30 \pm 1°C. The *p*H was varied from 3 to 10 as illustrated in Fig. 2. The results revealed that the initial rate of degradation of PCP at low pHis markedly higher compared to that at higher pH.

Effect of temperature

The effect of aqueous temperature on sonochemical reaction rate was investigated. The initial rates of PCP degradation on sonolysis of a 100 ppm PCP solution at temperatures of 10-50°C and pH 3 are illustrated in Fig. 3. As the aqueous temperature is increased, the reaction rate decreases slowly at the low frequency. At low frequency (30 kHz), due to the large number of cavitation bubbles formed, it is expected that an



Fig. 2-Effect of pH

increase in temperature will lead to an increase in the possibility of coalescence among the bubbles, resulting in some of the bubbles losing their activity. Additionally, the noise given off by the cavitation indicates that there is more likely transient (vaporous) cavitation occurring, which induces a decrease of sound transmission lowering the ultrasonic effect of energy in the liquid. The decrease in reaction rate with increase in solution temperature is supportive of such an effect.

US/H₂O₂ process

Sono-degradation of PCP was coupled with addition of hydrogen peroxide. The rate of degradation of PCP was monitored under the US/ H_2O_2 process carried out for 4 h, at a temperature of $30\pm0.5^{\circ}$ C and at *p*H 3. The concentration of hydrogen peroxide was varied from 10-600 mg/L. With an increase in the concentration of H_2O_2 from 10 to 450 mg/L, there was an increase in rate of degradation. However, addition of excess peroxide i.e., 600 mg/L did not increase the degradation rate as shown in Fig. 4.







Fig. 4—Effect of hydrogen peroxide concentration (initial concentration of PCP, 100mg/L)

Hydrogen peroxide is a strong oxidizing agent. Also, H_2O_2 readily undergoes sonolysis and decomposes into °OH as the dissociation energy for the O—O bond in H_2O_2 is only 213 kJ/mol which is significantly less than that of the O—H bond in H_2O which is 418 kJ/mol¹². However when concentration of hydrogen peroxide exceeds a certain maximum limit it starts behaving like a radical scavenger due to formation of peroxyl radicals. Further experiments also demonstrated that no obvious degradation of PCP was observed using only hydrogen peroxide. Therefore it can be concluded that sonication controls the overall degradation process and hydrogen peroxide only play an auxiliary role⁹.

US/Ag-TiO2 process

Sonocatalytic degradation of 100 ppm PCP solution was carried out in the presence of Ag-loaded TiO₂ using different dosages of the doped catalyst, ranging from 250 to 2500 mg/L (Fig. 5). The sonication was carried out at a temperature of $30\pm0.5^{\circ}$ C and *p*H 3.

From the results, it can be inferred that with an increase in of Ag-loaded TiO₂ dosage, the degradation rate also increased. A maximum degradation rate was achieved with a of Ag-loaded TiO₂ dosage of 1000 mg/L. The liquid that contains appropriate amount of interface (especially heterogeneous catalyst) that represents weak points in the liquid for nucleation of the cavitation bubbles to occur. The presence of catalyst can enhance the dissociation reaction of H₂O molecules to increase the number of free radicals generated, thereby increasing the rate of degradation of the organic compound¹². However, excessive amount of solid particles present in the solution could result in the scattering of ultrasound waves that may decrease the rates of sonochemical degradation reactions^{13,14}.

Comparisons of ultrasonic degradation and heterogeneous sonocatalysis

Ultrasound coupled with Ag-TiO₂/H₂O₂ reactions markedly accelerated the rate of degradation of the model compound. The degradation of PCP in US/H₂O₂, US/ Ag- TiO₂, US/TiO₂, US/TiO₂/H₂O₂ and US/ Ag-TiO₂/H₂O₂ systems are compared in Fig. 6.

The maximum removal of PCP i.e 75% was observed in US/ Ag-TiO₂/H₂O₂ system where as 37% removal was observed in US/TiO₂/H₂O₂ system after 6 h of ultrasonic irradiation. The highest removal was observed in US/ Ag-TiO₂/H₂O₂ system compared to



Fig. 5-Effect of Ag-loaded Tio₂ concentration



Fig. 6—Comparisons of ultrasonic degradation alone and other coupled processes (initial rate of degradation of PCP, 100 ppm; temp, $30\pm0.5^{\circ}$ C and *p*H 3).

US/TiO₂/H₂O₂ systems which was mainly attributed to the assumption that the transition metals can decrease the semiconductor band gap, favoring electron transfer from the valence bond to the conduction band. Moreover, Silver's catalytic properties make it ideal for use as a catalyst in oxidation reactions.

Conclusion

It is apparent that 4-CP can be decomposed by sonochemical processes but with the efficiency of the process very dependent upon reaction conditions. However, ultrasonic irradiation alone is unable to provide high degradation efficiency to PCP at low frequency. This is particularly true for hydrophilic compounds which are usually hard to be decomposed by conventional means as well as through cavitation phenomenon. Heterogeneous sonocatalytic degradation of recalcitrant organic contaminants using different catalysts such as metal oxides is an alternative way to solve the problem of transforming persistent organic contaminants to non-persistent substances. The most common type of catalyst to be used is TiO_2 and its advantages are such as inexpensive, non-toxic, biologically stable and reusable. Loading of metal particles into TiO_2 catalysts either through doping or used as their composites can inhibit charge recombination between holes and electrons produced during the ultrasonic irradiation of TiO_2 to enhance the degradation efficiency.

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