Photocatalytic and Sonophotocatalytic Degradation of Reactive Red 120 using Dye Sensitized TiO$_2$ under Visible Light

S.K.Kavitha, and P.N.Palanisamy

Abstract—The accelerated sonophotocatalytic degradation of Reactive Red (RR) 120 dye under visible light using dye sensitized TiO$_2$ activated by ultrasound has been carried out. The effect of sonolysis, photocatalysis and sonophotocatalysis under visible light has been examined to study the influence on the degradation rates by varying the initial substrate concentration, pH and catalyst loading to ascertain the synergistic effect on the degradation techniques. Ultrasonic activation contributes degradation through cavitation leading to the splitting of H$_2$O$_2$ produced by both photocatalysis and sonolysis. This results in the formation of oxidative species, such as singlet oxygen (^{1}O$_2$) and superoxide (O$_2$$^{-\bullet}$) radicals in the presence of oxygen. The increase in the amount of reactive radical species which induce faster oxidation of the substrate and degradation of intermediates and also the deaggregation of the photocatalyst are responsible for the synergy observed under sonication. A comparative study of photocatalysis and sonophotocatalysis using TiO$_2$, Hombikat UV 100 and ZnO was also carried out.

Keywords—Photocatalysis, Reactive Red 120, Sonophotocatalysis, Sonolysis.

I. INTRODUCTION

THE search for the development of new and inexpensive methods for the treatment of industrial wastewater is always on progress.

Different methods of separation, degradation and elimination have been used on different polluting chemical agents which are generally present in wastewater coming out from the industrial sector. The treatment of such pollutants can be achieved using an advanced oxidation method like the heterogeneous photocatalysis [1]-[5] due to its efficiency and low cost, as well as to the fact that it allows the complete degradation of organic pollutants to CO$_2$ and inorganic acids. The photoreactor generally works at room temperature and it uses UV light and TiO$_2$, an innocuous semiconductor, as a catalyst.

Environmental sonochemistry [6]-[8] is a rapidly growing area and is an example of an AOP that deals with the destruction of organic species in aqueous solution. The chemical effects of high intensity ultrasound result primarily from acoustic cavitation: the formation, growth, and impulsive collapse of bubbles in liquids [8]. The efficacy of ultrasound irradiation and, indeed, any other AOP to treat pollutants is eventually dictated by the rate of generation of free radicals and other reactive moieties and the degree of contact

S.K.Kavitha is with the Department of Chemistry, Velalar College of Engineering and Technology, Erode– 638 012, India (corresponding author phone: 91-98656-55100; e-mail: skkavitha@yahoo.com).
P.N.Palanisamy is with the Department of Chemistry, Kongu Engineering College, Erode – 638 052, India (e-mail: asspavithran @ rediffmail.com).

between the radicals and the contaminants both of which should be maximized. In this view, process integration is conceptually advantageous in water treatment since it can eliminate the disadvantages associated with each individual process. For instance, in heterogeneous catalytic systems, the use of ultrasound creates conditions of increased turbulence in the liquid, thus decreasing mass transfer limitations and increasing the surface area available due to catalyst fragmentation and de-agglomeration [9] In recent years, the simultaneous use of ultrasound and photocatalysis, i.e. the so-called sonophotocatalysis has been studied regarding process efficiency to degrade various organics in model solutions [10]-[12].

The sonophotocatalytic process of oxidation shows interesting advantages at kinetic level, due to the presence of a synergistic effect between sonolysis and photocatalysis [1]-[3],[10],[13]. The simultaneous use of two techniques was reported to be more effective than their sequential combination though leading to just additive effects, and to be more effective than sonolysis only when employing relatively low ultrasound intensity [4],[14]. For the practical application of dye wastewater treatment by photocatalysis and sonophotocatalysis, there is a need to determine the optimal conditions of experimental parameters.

In the present study, the degradation of mono azo dye Reactive Red 120 under visible light via dye sensitized TiO$_2$ has been studied. In order to exploit the synergistic effect between sonolysis and photocatalysis, and to ascertain whether it is a consequence of processes occurring at the water–semiconductor interface, or in the aqueous phase, a systematic study was undertaken to determine the influence of substrate concentration, optimum catalyst concentration, and pH on the degradation rate and effect of quenchers.

II. EXPERIMENTAL

A. Materials

The commercially available dye Reactive Red 120 was obtained as gift sample from Sivasakthi Dyeing unit, SIPCOT Industrial Estate, Perundurai, India and used as such without any purification. Degussa P25 titanium dioxide (80% anatase, 20% rutile, surface area 50 m^2/g and primary particle size of 30 nm), Hombikat UV 100 (Sachtleben Chemie, Germany) and ZnO (Merck) were employed as semiconductor photocatalysts. 1,4-benzoquinone was prepared in the laboratory [15] and recrystallised twice with petroleum ether. All the other chemicals used were of AR grade obtained from S.D Fine chemicals and were used as received. Required concentrations of dye solutions were prepared by dissolving the dye in distilled water. pH of the solutions was adjusted by adding 1M HNO$_3$ or 1M NaOH.

An immersion well photochemical reactor made of Pyrex glass equipped with a water-circulating jacket and an opening for supply of oxygen was used [16]. To study the effect of ultrasound the whole

World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:5, No:1, 2011

assembly was immersed in the Branson Ultrasonic cleaning bath model 3150DTH (47 kHz, 130 W). Irradiations were carried out using a 50 W halogen lamp (Philips). The pH of the solution was measured using ELICO, India LI120-pH meter.

B. Method

Stock solution of dye at different concentrations were prepared in distilled water with a natural pH 4.1 and mixed with TiO_2 and taken in the photoreactor. The solution was stirred and bubbled with molecular oxygen for 2 hours in the dark to allow equilibration of the system so that the loss of the compound due to adsorption can be taken into account. The dye sensitized TiO_2 was subjected to visible light irradiation for the degradation of dye in solution. The sonochemical experiments were performed at the point of maximum cavitations. An aliquot of 5 ml was taken from the reactor at regular interval of time. The catalyst was separated from the solution by centrifugation and the solution was analyzed for determining concentration of dye at λmax 515 nm. Experiments for photolysis, photocatalysis, sonolysis and sonophotocatalysis were carried out. The reaction kinetics was studied by varying different parameters like initial concentration of dye, catalyst loading and initial pH of the solution. The formation of oxidative intermediate species such as singlet oxygen ($^1O_2$) and superoxide ($O_2\text{-}\bullet$) radicals under photocatalytic and sonophotocatalytic conditions and their role in the dye degradation process have been investigated indirectly with the use of appropriate quenchers. All experiments were carried out in duplicate for reproducibility of results.

III. RESULTS AND DISCUSSION

A. Decolourization and Kinetic Analysis

The degradation rates of the dye measured under different experimental conditions could conveniently be compared in terms of first order rate constants, obtained from the slopes of plots of Fig.1. No degradation was observed in the presence of only visible light without TiO_2. Relatively slow degradation took place under ultrasound in the presence of TiO_2 (US + TiO_2), while the degradation occurred at higher rate under photocatalysis (vis + TiO_2). A further increase in reaction rate was observed on illuminating the sample suspensions simultaneously with visible light and ultrasound in the presence of TiO_2 (vis + US + TiO_2).

Interestingly, there appears to be a synergistic effect between sonolysis and photocatalysis in the presence of semiconductor since rate constants of the combined process are greater than the sum of the rate constants of the individual processes

$$\text{Synergy} = \frac{k_{vis+US+TiO_2} - (k_{US+TiO_2} + k_{vis+TiO_2})}{k_{vis+US+TiO_2}} \quad (1)$$

The synergy can be quantified as in (1) as the normalized difference between the rate constants obtained under sonophotocatalysis and the sum of those obtained under separate photocatalysis and sonocatalysis [17] in the presence of the semiconductor photocatalyst and is given in Table 1.

TABLE I
FIRST ORDER RATE CONSTANTS OF THE DEGRADATION OF THE DYE IN THE PRESENCE OF TiO_2 UNDER SONOPHOTOCATALYSIS (US+vis+TiO_2), PHOTOCATALYSIS (vis+ TiO_2) AND SONOLYSIS (US+ TiO_2)

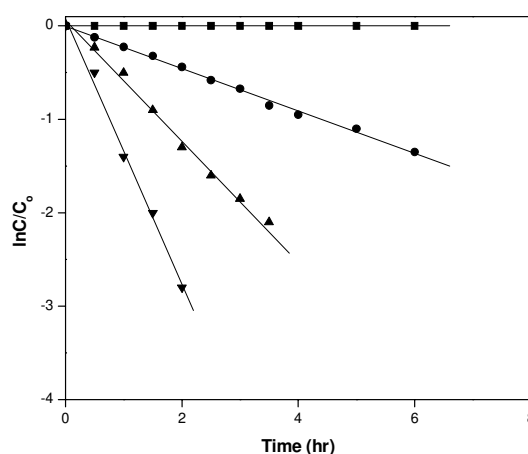| C_0 (mg/l)	$k_{UV+vis+TiO2}$	$k_{vis+TiO2}$	$k_{UV+TiO2}$	Synergy
100	0.0469	0.0284	0.0082	0.2196
75	0.0932	0.0516	0.0039	0.4055
50	0.3546	0.1528	0.0023	0.5623
25	0.5865	0.2388	0.0052	0.5839

Fig.1. First order kinetic plots for the degradation of RR 120 under visible light(■), ultrasound in the presence of TiO_2(●), photocatalysis(▲) and sonophotocatalysis(▼). C_0= 100 mg/l, Amount of TiO_2=2.5 gm/l, pH=4.1.

The synergy factor is observed to increase almost fourfold with 75% dilution,. Both in photocatalysis and sonophotocatalysis the pollutants in water are degraded mainly through the generation of OH radical. Sonolysis enhances the degradation rate further by increasing the catalytic activity of the semiconductor catalyst. This could occur through decrease in size of the photocatalyst and deaggregation of particles due to the effect of sonication leading to an increase in surface area and thus the catalytic performance [4],[18].

The beneficial effect of coupling photocatalysis with sonolysis may be attributed to several reasons, namely: (i) increased production of hydroxyl radicals in the reaction mixture (ii) enhanced mass transfer of organics between the liquid phase and the catalyst surface [17], (iii) catalyst excitation by ultrasound-induced luminescence which has a wide wavelength range below 375 nm [19],[20] and (iv) increased catalytic activity due to ultrasound de-aggregating catalyst particles, thus increasing surface area. It has been reported [21] that the TiO2 surface area increased by about 130% after the sonophotocatalytic treatment of a phenolic wastewater

World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:5, No:1, 2011

B. Effect of Catalyst Loading

The amount of catalyst is one of the main parameters for the degradation studies from economical point of view. In order to avoid the use of excess catalyst it is necessary to find out the optimum loading for efficient removal of dye. Several authors have investigated the reaction rate as a function of catalyst loading in photocatalytic oxidation process. First order rate constants of sonolytic, photocatalytic and sononophotocatalytic degradation of Reactive Red 120 in the presence of different amounts of titanium dioxide (1–3.5 gm/l) are reported in Fig.2. The degradation rate under sonolysis was low and was not influenced by the amount of photocatalyst. Progressively higher and values under photocatalysis and sonophotocatalysis respectively were measured with increasing TiO_2 concentration. The results clearly show that the optimum catalyst loading for degradation of RR 120 is 2.5 gm/l.
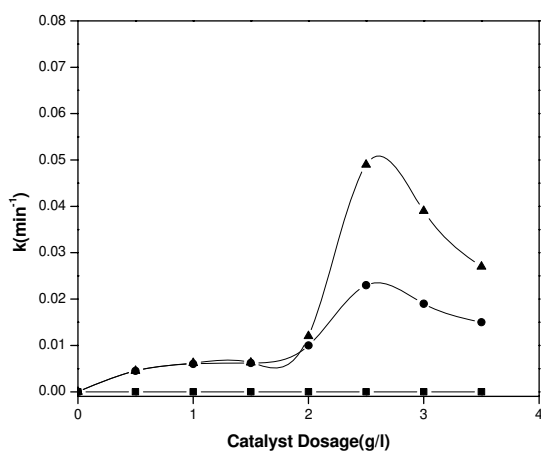

Fig.3.Rate constants of the degradation of the dye RR 120, as a function of the initial dye concentration under $US+TiO_2$(■), $vis+TiO_2$(●) and $US+vis+TiO_2$ (▲). Amount of TiO_2=2.5gm/l, pH=4.1.

All substrates underwent slow degradation under sonolysis. The reaction proceeded much faster under both photocatalysis and sonophotocatalysis; however the degradation rate decreased with increase in the initial concentration of the substrate. The results are in good agreement with those reported in literature [22]. The decrease in reaction rate with increase in substrate concentration is due to the constancy of the amount of substrate adsorbed on the semiconductor. Simultaneous sonolysis did not induce any modification in this trend, indicating that under photocatalytic and sonophotocatalytic conditions the reaction system exhibits the same dependence on the amount of dye, which determines the water–semiconductor interface phenomena. During the course of reaction due to formation of intermediates, competition starts between the intermediates and the dye molecules for the surface active sites of TiO_2 leading to the decrease in the degradation rate. The combined action of photocatalysis and sonolysis produced synergistic effects in all the investigated range of substrate concentration; however, the effect was more prominent at lower concentrations. The synergistic effect was suppressed at higher concentrations.

The rate of electron transfer is the highest when an optimum coverage of the TiO_2 surface is achieved by the dye and oxygen. At high dye concentration, a high coverage of the catalyst surface by the dye can be expected. The latter fact can change significantly the surface properties of TiO_2, and it seems that the dye adsorption decreases the TiO_2 surface charge and its capacity to adsorb oxygen.

It has been suggested that some electric events accompany the cavitation process and the bubble fragmentation produced by ultrasound [23]-[25]. The most important principles of the electrical theory are as follows: (i) localization of uncompensated electrical charge on the small part of the surface of the cavitation bubble; (ii) one electrode electrical discharge; (iii) non-equilibrium (and non-thermal) primary elementary processes inside the cavitation bubble leading to excitation, ionization, dissociation, recombination and light emission; and (iv) possibility of prolonged pulsations of cavitation bubbles without collapse. For the formation of electrical charge and the electrical discharge inside the cavitation bubbles, the fragmentation of bubbles is not necessarily essential; possibly, under some conditions, it may be sufficient to deform the cavitation bubbles and to localize the electrical charges on very small ''spots'' on the bubble surface [25].

Fig.2.Rate constants of the degradation of the dye RR 120, as a function of TiO_2 concentration under $US+TiO_2$ (■), $vis+TiO_2$(●) and $US+vis+TiO_2$(▲).C_0= 50 mg/l, pH=4.1.

It is clear that the rate of degradation does not increase linearly with the increase in the amount of the catalyst in the reactor, and that a limiting rate is achieved when high amounts of TiO_2 are used. One possible explanation for such behaviour is that, when low amounts of TiO_2 are used, the rate of reaction on the TiO_2 surface area is limited and the reaction rate is proportional to the amount of TiO_2 particles. The attainment of limiting value and further decrease in the reaction rate with increase in the amount of catalyst might be due to (i) aggregation of TiO_2 particles at high concentrations causing decrease in the number of surface active sites and (ii) increase in opacity and light scattering of TiO_2 particles at high concentration leading to decrease in the passage of irradiation through the sample. Ultrasound induces the increased reaction rate due to the production of more number of photoactive species and due to the water splitting leading to the formation of H_2O_2. In addition, sonication also leads to deaggregation of the TiO_2 particles leading to the increase in the surface area.

C. Effect of Initial Substrate Concentration

The effect of different initial substrate amounts on the degradation rate was investigated in suspensions containing 2.5gm/l of TiO_2 at a normal pH of 4.1. The degradation rate of dye measured under different experimental conditions is shown in Fig. 3.
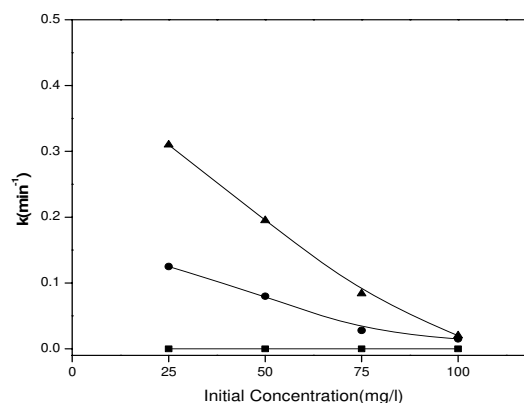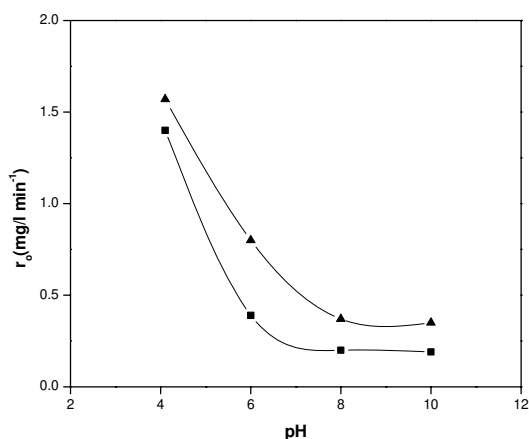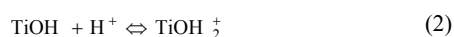
World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:5, No:1, 2011

Fig.4. Effect of pH on the degradation of the dye RR 120 under vis+TiO_2(■)   and   US+vis+TiO_2(▲).C_0=50mg/l.   Amount   of TiO_2=2.5gm/l, pH=4.1.

The role of electrical phenomena on the sonophotochemical reaction is substantial. It is possible that the electric interaction between the bubbles (negative surface charged) [26] and TiO_2 particles (with local negative and positive charges) has an important role on the synergistic effect between ultrasound and UV light. In concordance with the theory of electric fields, the fragmentation of microbubbles induced by ultrasound is accompanied by the formation of places of high density of negative charge [26] that can produce intense electric fields when those bubbles come near to the locally charged TiO_2 particles. The strong electric fields produced in this way can induce local discharges that can promote many chemical and physical processes that can increase the reaction rate of any reaction on the TiO_2 surface.

D. Effect of pH

The pH is a complex parameter since it is related to the ionization state of the surface as shown in (2) and (3)

$$TiOH + H^+ \Leftrightarrow TiOH_2^+ \qquad (2)$$

$$TiOH + OH \Leftrightarrow TiO^- \qquad (3)$$

Three possible mechanisms can contribute to dye degradation: hydroxyl radical attack, direct oxidation by the positive hole and direct reduction by the electron in the conducting band depending on the nature of the substrate and pH [27]. Inthe present study, any changes in the initial degradation rate with varying pH values must be ascribed to variations of the acid/base properties of the TiO_2 particle surface. Since the photoxidation of dyes is accompanied by the release of protons [28], its efficiency may then change because of the reversible protonation of the TiO_2 surface. Photocatalytic activity was maximum in acidic conditions, followed by a decrease of r_0 in the pH range from 7 to 10. Same trend was seen in both photocatalytic and sonophotocatalytic conditions.

The effect of pH on the photocatalytic reaction can be largely explained by the surface charge of TiO_2 (pzc of TiO_2 6.8) and its relation to the acid dissociation constants of dye. Below pH 6, as pH decreases, strong adsorption of dye on the TiO_2 particles as a result of electrostatic attraction of the positively charged TiO_2 with the

ionized dye is observed. On the other hand, as the pH increases, a decrease in the reaction rate has been observed as shown in Fig.4 reflecting the difficulty of anionic dye in approaching the negatively charged TiO_2 surface when increasing the solution pH. The influence of the initial concentration of the solute on the photocatalytic degradation derived from the kinetic data can be rationalized in terms of Langmuir–Hinshelwood model (Eq. (4)) modified to accommodate reactions occurring at a solid–liquid interface [28]. A linear expression can be conveniently obtained by plotting the reciprocal initial rate against the reciprocal initial concentration. The plots for photocatalysis and sonophotocatalytic degradation of the dye are given in Fig.5 and Fig.6 respectively.
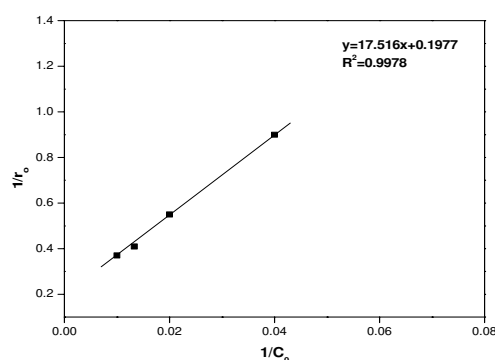

Fig.5. Representation of Langmuir- Hinshelwood equation for the photocatalytic degradation of the dye RR 120: C_0= 50 mg/l, Amount of TiO_2 = 2.5 gm/l, pH =4.1.

$$r_o = \frac{-dC}{dt} = \frac{k_v K_e C_0}{1 + K_e C_0} \qquad (4)$$

where kv reflects the limiting rate of the reaction at maximum coverage under the given experimental conditions. Ke represents the equilibrium constant for adsorption of dye on to illuminated TiO2. In (4) kv represents the apparent rate constant because it is also dependent on the source of visible light and the radiation field inside a photocatalytic reactor. These results are reflected by the kv and Ke values shown in Table 2.
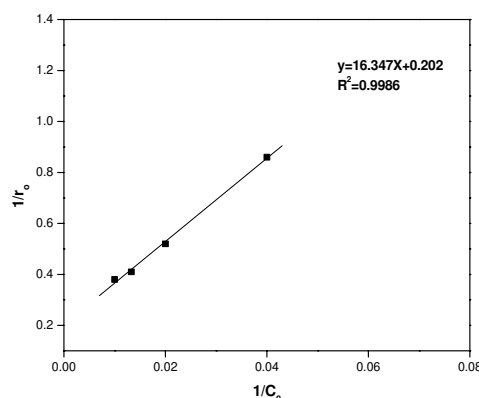

Fig.6. Representation of Langmuir- Hinshelwood equation for the sonophotocatalytic degradation of the dye RR 120: C_0= 50 mg/l, Amount of TiO_2 = 2.5 gm/l, pH =4.1.

World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:5, No:1, 2011

TABLE II
LANGMUIR- HINSHELWOOD CONSTANTS FOR THE PHOTODEGRADATION
OF THE DYE RR 120 AT DIFFERENT pH VALUES

pH	Photocatalysis		Sonophotocatalysis	
	K_e(l/mg)	k_v (min^{-1})	K_e(l/mg)	k_v (min^{-1})
4.1	0.0061	10.92	0.0039	17.68
6	0.0079	5.98	0.008	6.05
8	0.0192	1.38	0.042	1.42
10	0.0051	2.09	0.022	1.15

E. Effect of Addition of H_2O_2

A possible way of increasing the degradation of the dye is increasing the concentration of OH radicals by the addition of oxidant like H_2O_2. The effect of addition of H_2O_2 on the degradation rate was studied both for photocatalytic and sonophotocatalytic degradation of the dye. The results as shown in Fig.7 show that the degradation rate increases with increases in addition of H_2O_2, becomes maximum at 2 ml/l and then starts decreasing with further increase in the concentration of H_2O_2. Synergistic effect is observed under sonication during the addition of H_2O_2 also as it is observed that the rate enhancement is more in sonophotocatalytic degradation as compared to photocatalytic degradation.
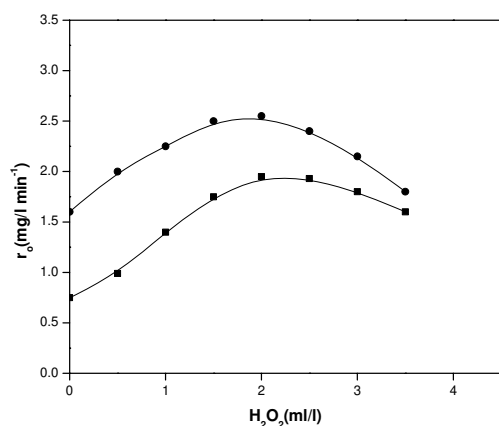

Fig.7. Effect of H_2O_2 concentration on the initial rate of degradation of the dye RR120 under vis+TiO$_2$(■) and US+vis+TiO$_2$(●).C_0=50mg/l. Amount of TiO$_2$=2.5gm/l, pH=4.1.

F. Effect of Various Photocatalysts

The influence of three different photocatalysts (TiO$_2$- P25, ZnO, UV-100) on the degradation kinetics of Reactive Red 120 was investigated and results are shown in the Fig. 7. TiO$_2$ and ZnO are found to be more efficient than UV-100. The order of activities of the photocatalysts are ZnO > TiO$_2$-P25 > UV-100. Though ZnO is the most efficient catalyst, it has the disadvantage of undergoing photocorrosion under illumination in acidic conditions. The high

photoreactivity of TiO$_2$-P25 as compared to UV-100 is due to the slow recombination of electron-hole pair and its large surface area. Fig.8 shows clearly that in spite of the fact that the catalysts are very different, the synergy between sonolysis and photocatalysis is still observed. The comparison of these catalysts is important, because these are the important commercial photocatalysts available in the market.

G. Effect of Radical Quenchers

The formation of oxidative intermediate species such as singlet oxygen ($^1O_2$) and superoxide (O$_2$-●) radicals under photocatalytic and sonophotocatalytic conditions and their role in the dye degradation process has been investigated indirectly with the use of appropriate quenchers of these species. In these experiments, a comparison is made between the original decolourization curves of RR120 TiO$_2$ dispersions with those obtained after addition of quenchers in the initial solution under otherwise identical conditions. Compounds used for this purpose were 1,4-diazabicyclo [2,2,2] octane (DABCO), a singlet oxygen quencher, sodium azide (NaN3), which is also a quencher of singlet oxygen but may also interact with OH_ and 1,4-benzoquinone (BQ), which is a quencher of superoxide radical.
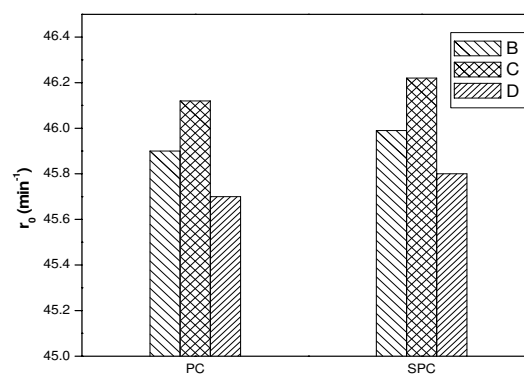

Fig.8. Rate of photocatalytic(PC) and sonophotocatalytic(SPC) degradation of the dye RR120 using TiO$_2$-P25 (B), ZnO(C) and Hombikat UV-100 (D).
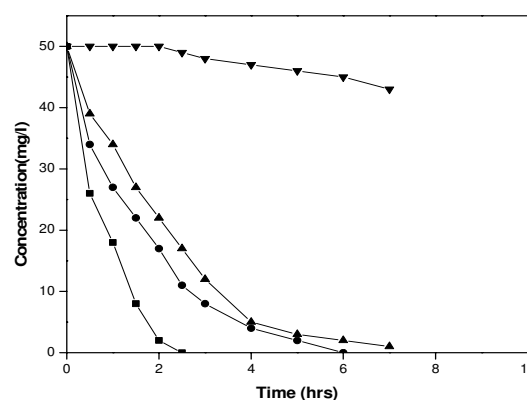

Fig.9. Sonophotocatalytic degradation of the dye RR 120 in the presence of radical quenchers 1,4 Benzoquinone (▼), NaN$_3$(▲), DABCO (●) and in the absence of any quencher (■). C_0= 50mg/l,

World Academy of Science, Engineering and Technology
International Journal of Materials and Metallurgical Engineering
Vol:5, No:1, 2011

amount of TiO_2= 2.5 gm/l, pH=4.1 and the amount of quencher = 100 mg/l.

It is observed from Fig.9 that in the presence of BQ, which is a superoxide quencher, photobleaching of the dye RR 120 is completely suppressed indicating that the superoxide radical is an active oxidative intermediate. The inhibiting effect of NaN_3, which is a $^1O_2$ quencher but may also interact with OH radical, becomes significant after 1 h indicating the delayed formation of singlet oxygen (and possibly hydroxyl radical) species. Similar results were obtained after addition of DABCO, which is also a singlet oxygen quencher.

IV. CONCLUSIONS

This study reveals that the acceleration of the degradation process of dye sensitized TiO_2 under visible light has been achieved by ultrasonication. Mainly ultrasound contributes through cavitation to the scission of H_2O_2 produced by both photocatalysis and sonolysis. This increases the amount of reactive radical species inducing oxidation of the substrate and degradation of intermediates and is mainly responsible for the observed synergy. The photodegradation kinetics follows the Langmuir–Hinshelwood model and depends on the TiO_2 concentration and pH. It is also evident that the reaction takes place via formation of singlet oxygen, superoxide and hydroxyl radicals. This methodology has additional advantage of harnessing the visible component of the solar energy for the degradation of organic pollutants in water. Further studies to apply this synergistic technique using solar energy are underway.

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