Advances in Environmental Research, *Vol. 2, No. 4 (2013) 261-277*
DOI: http://dx.doi.org/10.12989/aer.2013.2.4.261

Photocatalytic and Sonophotocatalytic degradation of alachlor using different photocatalyst

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(*Received November 01, 2013, Revised December 09, 2013, Accepted December 16, 2013*)

Abstract. The degradation of alachlor has been investigated using sonolysis (US), photocatalysis (UV) and sonophotocatalysis (US/UV) using three photocatalyst viz. TiO_2 (mixture of anatase and rutile), TiO_2 (anatase) and ZnO. The effect of photocatalyst loading on the extent of degradation of alachlor has been investigated by varying TiO_2 (both types) loading over the range of 0.01 g/L to 0.1 g/L and ZnO loading over the range of 0.05 g/L to 0.3 g/L. The optimum loading of the catalyst was found to be dependent on the type of operation i.e., photocatalysis alone or the combined operation of sonolysis and photocatalysis. All the combined processes gave complete degradation of alachlor with maximum rate of degradation being obtained in the case of sonophotocatalytic process also showing synergistic effect at optimized loading of photocatalyst. About 50% to 60% reduction in TOC has been obtained using the combined process of sonophotocatalysis depending on the operating conditions. The alachlor degradation fitted first order kinetics for all the processes under investigation. It has been observed that the TiO_2 (mixtrure of anatase and rutile) is the most active photocatalyst among the three photocatalysts studied in the current work. The effect of addition of radical enhancers and scavengers on sonophotocatalytic degradation of alachlor has been investigated in order to decipher the controlling mechanism. The alachlor degradation products have been identified using LC-MS method.

Keywords: alachlor degradation; sonophotocatalysis; photocatalysis; ultrasound; process intensification

1. Introduction

Alachlor is an acetanilide herbicide, widely used to control most annual grasses and many broad leaf weeds. It has been classified as carcinogen of B2 group due to their strong carcinogenic effects on the animals (Zhu *et al*. 2006). The maximum allowable limit of alachlor for drinking water is 2 μg/L as established by USEPA (Potter and Carpenter 1995, Chu and Wang 2004). Alachlor cannot be treated using conventional biological methods due to its toxicity and biorefractory nature and hence alternate treatment schemes are required to treat such types of waste considering the possible hazardous effects. Nowadays, many researchers have been using advanced oxidation processes such as photocatalysis, Fenton Chemistry etc. to treat toxic and biorefractory organic pollutants (Gogate and Pandit 2004). Photocatalytic oxidation using titanium dioxide (TiO_2) can be quite useful for destroying a wide range of environmental contaminants

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http://www.techno-press.org/?journal=aer&subpage=7 ISSN: 2234-1722 (Print), 2234-1730 (Online)

(Pelizzetti 1995). Due to different characteristic features such as non-toxic, easily available, inexpensive, biologically and chemically inert and stable to photo and chemical corrosion, Titanium dioxide (TiO_2) is considered as very efficient photocatalyst (Hermann *et al*. 1999, Poulios *et al*. 1998). If the semiconductor catalyst is illuminated by UV light having band gap energy 3.2 eV, electron and holes are generated due to the excitation of electron from the valance band (VB) to the conduction band (CB) as per the following reaction mechanism

$$TiO_2 + h\nu \rightarrow e_{CB-} + h_{VB+} \cdot \quad (1)$$

$$h_{VB} + OH^- \rightarrow \cdot OH \quad (2)$$

$$h^+_{VB} + H_2O(ads) \rightarrow \cdot OH + H^+ \quad (3)$$

$$e_{CB-} + O_2 \rightarrow \cdot O_2^- \quad (4)$$

Under some conditions, organic compounds can react directly with the positive holes, resulting in oxidative decomposition or indirectly via the formation of hydroxyl radicals (Gimenez *et al*. 1997, Konstantinou and Albanis 2004). The surface of a photocatalyst is exposed to water and when this water is oxidized by positive holes, hydroxyl radicals (·OH) having strong oxidative capacity are formed, which can further react with organic matter (San *et al*. 2002, da Silva and Faria 2003).

The application of cavitation induced by the use of ultrasonic irradiations has shown considerable promise for wastewater treatment. The phenomena of cavitation, i.e., generation, growth and collapse of cavities occur in extremely small interval of time, releasing large magnitudes of energy can result in the effective destruction of refractory compounds (Gogate and Pandit 2004). Free radicals are generated through transient collapse of cavitation bubbles driven by an ultrasound wave through alternate compression and rarefaction cycles (Francony and Petrier 1999, Gogate 2008, Chand *et al*. 2009). The combined process of sonolysis (US) and photocatalysis can result in enhanced generation of free radicals thereby increasing the extent and rate of degradation of organic pollutant (Madhavan *et al*. 2010) even possibly leading to synergistic effects. Chen *et al*. (2003) have reported enhanced photocatalytic degradation of dimethyl methylphosphonate in the presence of low frequency ultrasound whereas Madhavan *et al*. (2010) have studied the ultrasound assisted photocatalytic degradation of diclofenac in an aqueous environment and reported that the degradation of dichlofenac using a sonophotocatalytic process showed a slight synergy when TiO_2 was present as a photocatalyst under UV light irradiation and in the presence of Fe-ZnO, degradation showed an additive effect. Mishra and Gogate (2011) have studied the degradation of rhodamine B using sonochemical reactors in combination with UV irradiations at operating capacity of 7 L and reported that 92% degradation of rhodamine B was achieved with 50% reduction in TOC using the sonophotocatalysis process.

Many researchers have reported the degradation of alachlor using advanced oxidation processes. Wong and Chu (2003b) have studied the direct photolysis and photocatalytic degradation of alachlor at different TiO_2 loadings and using different UV sources and reported that both the direct photolysis and photocatalytic degradations of alachlor follow pseudo-first-order decay kinetics and the photocatalytic degradation rate of alachlor increased with the dosage of TiO_2, but an overdose of TiO_2 retarded the reaction due to light attenuation. Ryu *et al*. (2003) have reported that the removal rate of alachlor with Fe^{3+}/UV in the presence of TiO_2 film immobilized on the glass tube

in aqueous solution was much higher than obtained in the absence of TiO_2. Li *et al*. (2007) have investigated the removal and decomposition mechanism of alachlor in water under acidic conditions by ozone and reported that ozone could successfully degrade alachlor, but a complete mineralization of alachlor was difficult due to the formation of refractory intermediate products in the ozonation process. Qu *et al*. (2004) have reported that the TOC removal efficiency of alachlor was enhanced in the Cu/Al_2O_3 catalyzed ozonation process as compared to the only ozonation.

The aim of the current work is to investigate the photocatalytic and sonophotocatalytic degradation of alachlor using three different photocatalysts viz. TiO_2 (mixture of anatase and rutile), TiO_2 (anatase) and ZnO irradiated with two low pressure UV tube lights (254 nm). The work is the first report of sonophotocatalytic approach for the degradation of toxic alachlor using different photocatalysts. Effect of various loadings of photocatalyst on the rate of degradation of alachlor using photocatalysis and sonophotocatalysis has been studied to establish the dependency of optimum loading on type of operation. Synergistic index have been calculated in order to study the efficacy of the combined process for the degradation of alachlor. Studies have also been undertaken to establish the mechanistic aspects in terms of the controlling mechanism as well kinetic rate constants and the identification of different intermediates formed in the degradation process.

2. Methodology

2.1 Materials

Alachlor (99% purity) was obtained from Sigma Aldrich. Titanium dioxide (anatase) with particle size of 37 μm was procured from S.D. Fine Chemicals. Titanium dioxide (mixture of anatase and rutile) with particle size < 100 nm was obtained from Sigma Aldrich. ZnO with particle size 45 μm was obtained from Loba Chemicals Ltd. Hydrogen peroxide (30% w/w) and sodium bicarbonate was obtained from S.D. Fine Chemicals. Distilled water used for the preparation of solutions was freshly prepared in the laboratory using a distilled water plant. All the chemicals were used as received from the supplier.

2.2 Experimental setup and methodology

The ultrasonic equipment used in the present work was a conventional ultrasonic horn procured from M/S Dakshin, Mumbai. The operating frequency of the ultrasonic horn is 20 kHz with rated power of 120 W. The photo reactor used for US/UV experiments comprised of two UV–C germicidal tubes with dominant wavelength of 254 nm placed vertically on both the sides of the reactor (made up of quartz) parallel to each other. The volume of reaction mixture used in the experiments was 100 ml and the temperature was maintained constant at 28°C ± 2°C by keeping the reactor in ice-bath with continuous addition of ice to maintain the temperature. The schematic representation of the experimental setup for the combined operation has been depicted in Fig. 1.

All the experiments were performed using 20 ppm initial concentration of alachlor at a constant initial pH as 3. In our previous work (Bagal and Gogate 2012), the studies related to the effect of solution pH on the extent of sonochemical degradation of alachlor revealed that maximum degradation of alachlor is obtained at a pH of 3. Thus, in the present study, solution pH was maintained at 3 for all the treatment approaches. The inherent pH of the alachlor solution prepared in distilled water is 6. The initial pH of the solution was adjusted to the required value using 0.1 N

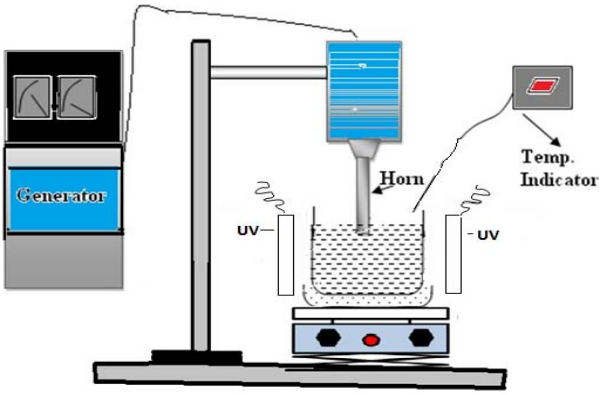

Fig. 1 Schematic representation of experimental set up for combined operation of US/UV

H_2SO_4. In order to investigate the efficacy of combined US/UV process with the possible requirement of catalyst, initially experiments were carried out in the presence of only ultrasound and only UV. Following these baseline experiments, the extent of degradation of alachlor in photocatalytic and sonophotocatalytic process have also been investigated using three different photocatalysts viz. TiO_2 (mixture of anatase and rutile), TiO_2 (anatase) and ZnO. The photocatalytic degradation of alachlor have been investigated by varying the loading of TiO_2 (mixture) and TiO_2 (anatase) over the range of 0.01 g/L to 0.1 g/L whereas for the sonophoto-catalytic process, the loading of TiO_2 (mixture) was varied over the range 0.01 g/L to 0.2 g/L and that of TiO_2 (anatase) was varied over the range of 0.025 g/L to 0.1 g/L. The effect of ZnO loading on the extent as well as rate of degradation of alachlor using photocatalysis and sonophotocatalysis process has also been investigated at different loadings of ZnO in the range of 0.05–0.3 g/L. The effect of addition of hydrogen peroxide on the sonophotocatalytic degradation of alachlor have been investigated by varying H_2O_2 loading over the range of 0.02 g/L to 0.06 g/L at already optimized loading of TiO_2 (mixture of anatase and rutile). The range of additives was adjusted based on the preliminary experiments to clearly establish the optimum concentration of catalyst as the effect on intensification of degradation is through multiple mechanisms. Due to this approach, the range of loading is not similar for all the catalysts investigated in the present work. In order to investigate the controlling mechanism for the sonophotocatalytic degradation of alachlor, sodium bicarbonate (radical scavenger) was added to the reactor with the loading varying over the range of 1 g/L to 10 g/L.

The total duration of each run was set to be 1h and the samples were taken out at an interval of 15 min for an analysis of the progress of degradation of alachlor. All the experiments were repeated at least 2 times and the average values have been reported in the illustrations. The experimental errors were within ± 2% of the reported average value.

2.3 Analysis

The concentration of alachlor was determined by a high performance liquid chromatography (HPLC) unit supplied by KNAUER using KNAUER C18 column. Acetonitrile and water was used as mobile phase (60:40) with a flow rate of 1 mL /min. The elution was monitored at 225 nm.

Alachlor photodegradation products were analyzed using LC-MS (Liquid Chromatography-Mass Spectroscopy) supplied by Thermo Electron Corporation. The main objective of the present work is to evaluate the efficacy of photocatalytic and sonophotocatalytic process using different photocatalysts for degradation of alachlor and hence only the alachlor concentration has been monitored for all the operating schemes. In order to quantify the extent of mineralization, total organic carbon content of the samples for optimized treatment schemes was also measured by TOC analyzer (TOC ANATOC Series II, SGE International, PTY Ltd. Australia).

3. Results and discussion

3.1 Degradation of alachlor using sonolysis (*US*), *photolysis* (*UV*) *and sonophotolysis* (*US/UV*)

The obtained results for the degradation of alachlor using sonolysis, photolysis and sonophotolysis have been given in Fig. 2. It has been observed that the extent of degradation of alachlor was 56%, 93% and 100% using sonolysis, photolysis and sonophotolysis respectively. The degradation of alachlor fitted first order kinetics for all the treatment schemes and the rate constants are tabulated in Table 1. It has been observed that the rate of degradation of alachlor using combined process of sonophotolysis is enhanced 4 times and 1.4 times as compared to the use of only sonolysis and photolysis. This may be due to the increased production of hydroxyl radicals in the combined process of sonophotolysis. Also it can be seen from the data that the photolytic degradation of alachlor is much faster (3 times) as compared to only sonolysis which shows that the more free radicals are likely to be generated in the presence of UV. The synergistic index calculated for the combined process using following equation shows nearly additive effect of rate constant obtained in the individual process operation.

$$f = \frac{k_{US/UV}}{k_{US} + k_{UV}} = \frac{0.053}{0.013 + 0.039} = 1.02$$

The results for the TOC analysis indicated that the reduction in TOC is 21%, 40% and 45% using only US, only UV and combined US/UV process respectively. Though synergism was observed for the removal of alachlor, similar additive effect for the combined operation of US/UV has not been observed for the TOC reduction.

3.2 Degradation of alachlor using photocatalysis

After quantifying the extent of degradation using only UV/US, the effect of the presence of photocatalyst and its concentration for three different photocatalysts viz. TiO_2 (mixture of anatase and rutile), TiO_2 (anatase) and ZnO, on the extent of degradation of alachlor have been investigated. TiO_2 (mixture of anatase and rutile) and TiO_2 (anatase) loading was varied over the range of 0.01 g/l to 0.1 g/L. The degradation of alachlor fitted first order kinetics for both the types of TiO_2 and obtained results are depicted in Figs. 3 and 4. It can be observed from the figure that the rate of degradation increased with an increase in TiO_2 (both types) loading till 0.025 g/L beyond which a decrease in the extent of degradation was observed. Though the optima exist at same loading using both the types of TiO_2, the rate of degradation of alachlor using TiO_2 (mixture of anatase and rutile) was 1.3 times higher than that obtained using TiO_2 (anatase). The observed

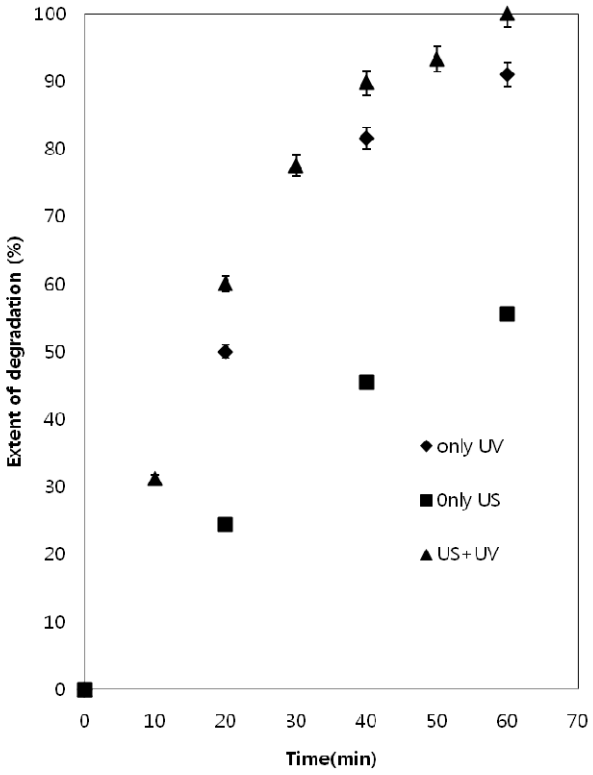

Fig. 2 Extent of degradation of alachlor using US, UV and combined process of US/UV. [initial concentration of alachlor 20ppm; pH=3 and temperature 28 ^{0}C]

results can be attributed to the slower rates of recombination of electron–hole pair in the mixture of anatase and rutile as compared to the only anatase form of TiO_2. The differences in the photocatalytic activity of TiO_2 depends on the differences in the BET-surface, impurities, lattice mismatches or density of hydroxyl groups formed on the catalyst's surface (Wong and Chu 2003b). In case of TiO_2 (mixture), small nano-crystallites of rutile disperse within an anatase matrix. The smaller band gap of rutile "catches" the photons and generates electron-hole pairs where the transfer of electron from the rutile conduction band to electron traps in anatase phase takes place and thus the recombination is inhibited allowing the hole to move to the surface of the particle and react with the pollutant molecules as confirmed by Hurum *et al*. (2003). Many researchers (Saquib and Muneer 2002, Muneer *et al*. 2001) have reported better catalytic activity for the Degussa P25 which is a mixture of 70% anatase and 30% rutile for the degradation of organic pollutants as compared to single form of titanium dioxide. The increase in TiO_2 concentration beyond optimum value may cause scattering and screening effects reducing the overall extent of degradation (Evgenidou *et al*.2007). The highly turbid suspension at higher loadings of TiO_2 concentration can also decrease the net transfer of the incident energy and hinder in the illumination of all the catalyst particles in the reactor (Rahman and Muneer 2005) thereby resulting in detrimental effects for the degradation of alachlor. Also higher amount of catalyst may lead to aggregation of TiO_2 particles which may decrease the catalytic activity (Gogate and Pandit 2004).

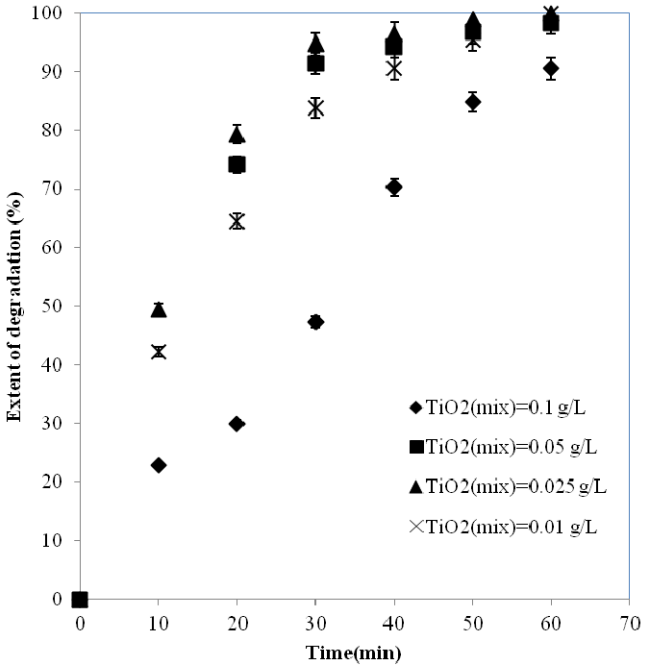

Fig. 3 Effect of addition of different loadings of TiO_2 (mixture of anatase and rutile) on photocatalytic degradation of alachlor [initial concentration of alachlor 20 ppm, temperature 28°C and pH3]

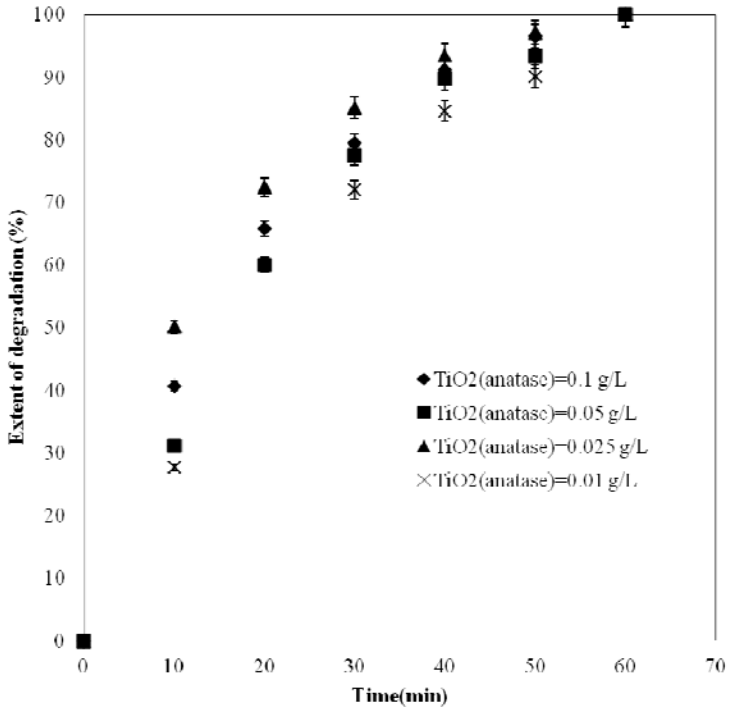

Fig. 4 Effect of addition of different loadings of TiO_2 (anatase) on photocatalytic degradation of alachlor [initial concentration of alachlor 20 ppm, temperature 28°C and pH 3]

In order to investigate the effect of loading of ZnO on photocatalytic degradation of alachlor, loading of ZnO was varied over the range 0.05 g/L to 0.3 g/L. The degradation kinetics fitted first order over the entire selected range of ZnO loading and the obtained results are depicted in Fig. 5. It has been observed from the obtained results that the rate of degradation increased with increase in ZnO loading till 0.2 g/L, beyond which marginal increase in the rate of degradation was observed at 0.3 g/L. Thus 0.2 g/L of ZnO loading has been chosen as optimum loading and first order rate constant at this optimized loading has been reported in Table 1. The rate of degradation of alachlor using of catalyst ZnO is lower than TiO_2 (both types) for similar loadings of TiO_2 (both types) and ZnO which can be attributed to the higher photoreactivity of TiO_2 as compared to the ZnO. At a pH lower than 4, ZnO undergoes photocorrosion through self-oxidation and tends to dissolve in the acidic solution. Moreover, irradiation under UV light may possibly result in the formation of photocatalytically inert Zn $(OH)_2$ compound on the surface layers of the catalyst that will cause surface passivation which will reduce the photocatalytic activity (Rusmidah *et al.* 2010).

Also enhanced rate of alachlor degradation using all three types of photocatalysts as compared to only photolysis (UV) have been observed due to the acceleration of degradation reaction in the presence of photocatalyst by way of generation of enhanced quantum of free radicals available for the reaction. Also reduction in TOC is 53%, 51% and 47% using TiO_2 (mixture of anatase and rutile), TiO_2 (anatase) and ZnO respectively at optimized loading of photocatalyst for photocatalytic degradation of alachlor which is again higher as compared to only photolysis.

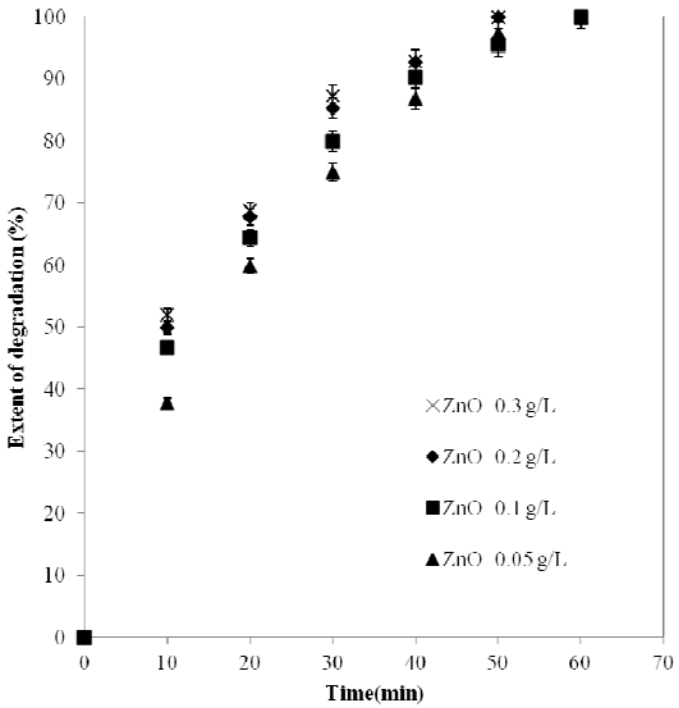

Fig. 5 Effect of addition of different loadings of ZnO on photocatalytic degradation of alachlor. [initial concentration of alachlor 20 ppm, temperature 28°C and pH 3]

3.3 Degradation of alachlor using sonophotocatalysis

The sonophotocatalytic degradation of alachlor using three different photocatalyst has been investigated at varying loadings of TiO_2 (both types) over the range of 0.01 g/L to 0.1 g/L and ZnO over the range of 0.05 g/L to 0.2 g/L. The obtained results for the variation in the extent of degradation have been given in Figs. 6-8. It has been observed that the complete degradation of alachlor is obtained using all the three types of catalyst in sonophotocatalysis process under the optimized conditions. The degradation kinetics fitted first order over the entire selected range of catalyst loadings and the values of rate constants at optimized loading of photocatalysts (TiO_2 (both types) and ZnO) are tabulated in Table 1.

The rate of sonophotocatalytic degradation of alachlor was maximum at 0.112 min^{-1} for a minimum loading of TiO_2 (mixture of anatase and rutile) as 0.01 g/L and an increase in the loading to 0.2 g/L resulted in a decrease in the rate constant to 0.059 min^{-1}. In the case of TiO_2 (anatase) photocatalyst, an optimum loading was observed at 0.05 g/L beyond which the kinetic rate constant decreased. Thus it can be inferred that much lower loading of TiO_2 (mixture of anatase and rutile) is required as compared to the TiO_2 (anatase) for equivalent extents of degradation of alachlor. The observed results can be explained on the basis of higher photoactivity for the mixture

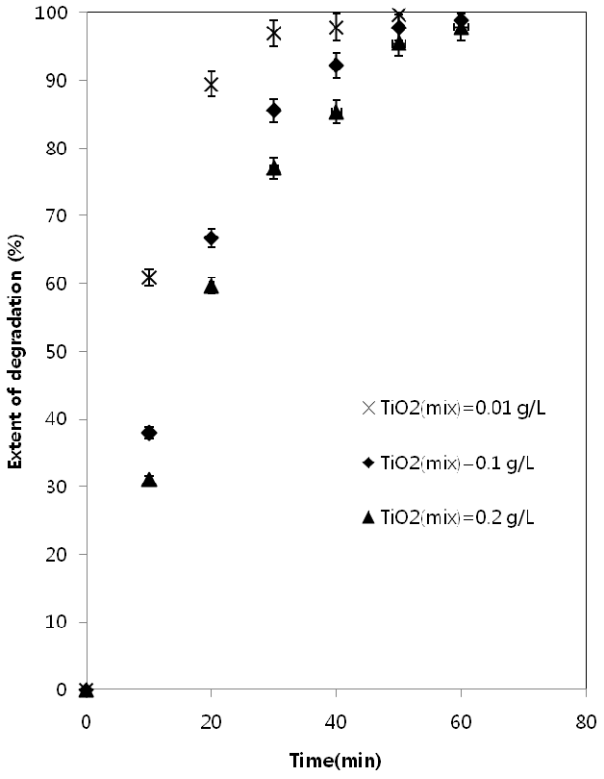

Fig. 6 Effect of addition of different loadings of TiO_2 (mixture of anatase and rutile) on sonophotocatalytic (US/UV/TiO_2 (mix)) degradation of alachlor [initial concentration of alachlor 20 ppm, temperature 28°C and pH 3]

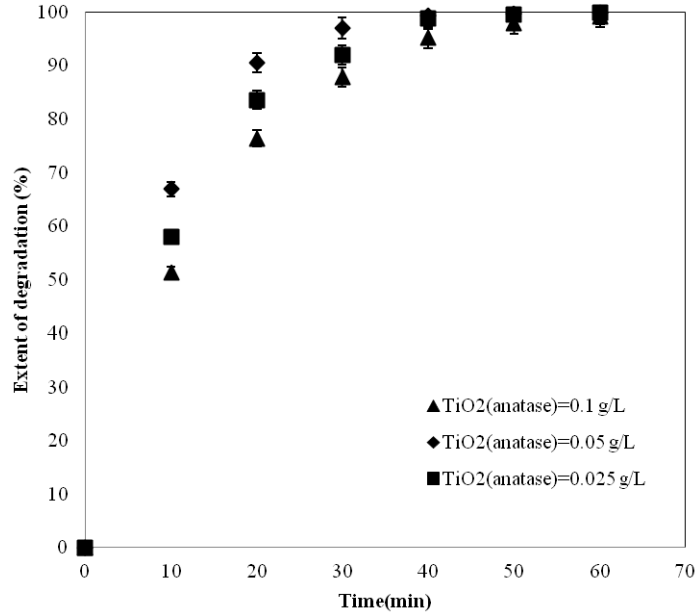

Fig. 7 Effect of addition of different loadings of TiO_2 (anatase) on sonophotocatalytic degradation of alachlor [initial concentration of alachlor 20 ppm, temperature 28°C and pH 3]

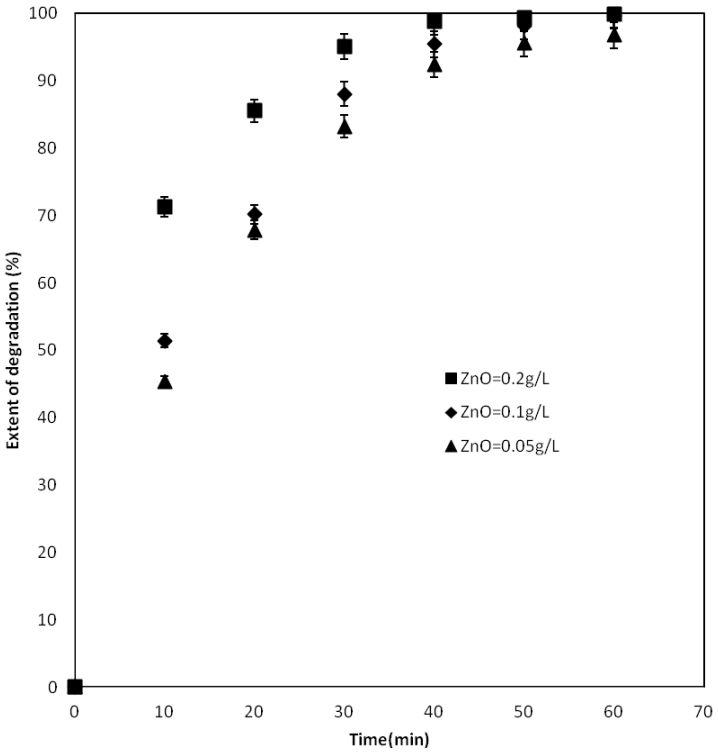

Fig. 8 Effect of addition of different loadings of ZnO on sonophotocatalytic degradation of alachlor [initial concentration of alachlor 20 ppm, temperature 28°C and pH 3]

Table 1 Summary of results obtained for degradation of alachlor using various processes

System	k (min^{-1})	R^2	% TOC reduction	Synergistic index (f)
only US	0.013	0.98	21	
only UV	0.039	0.99	40	
US+UV	0.053	0.98	45	1.02
Photocatalysis using optimized loading of various catalysts				
UV/ TiO_2 (mixture of anatase and rutile) [TiO_2(mixture of anatase and rutile) = 0.025 g/L]	0.089	0.99	51	1.98
UV/ TiO_2 (Anatase) [TiO_2 (Anatase) = 0.025 g/L]	0.068	0.99	53	1.59
UV/ZnO [ZnO = 0.2 g/L]	0.064	0.99	47	1.48
Sonophotocatalysis using optimized loading of various catalysts				
US/UV/ TiO_2 (mixture of anatase and rutile) [TiO_2 (mixture of anatase and rutile) = 0.01 g/L]	0.112	0.97	62	1.4
US/UV/ TiO_2 (Anatase) [TiO_2 (Anatase) = 0.05 g/L]	0.123	0.99	64	1.55
US/UV/ZnO [ZnO = 0.2 g/L]	0.109	0.98	57	1.35

US/UV/TiO_2 (mix)/H_2O_2 ; TiO_2(mix) = 0.01 g/L			US/H_2O_2		UV/H_2O_2	
H_2O_2 loading (g/L)	k (min^{-1})	R^2	k (min^{-1})	R^2	k (min^{-1})	R^2
0 g/L	0.112	0.97				
0.02 g/L	0.121	0.99				
0.04 g/L	0.211	0.95	0.0217	0.98	0.049	0.95
0.06 g/L	0.218	0.95				

Effect of addition of different loadings of Sodium bicarbonate(radical scavenger) on sonophotocatalytic (US/UV/TiO_2 (mix)) degradation of alachlor; TiO_2(mix) = 0.01 g/L

Sodium bicarbonate loading (g/L)	k (min^{-1})	R^2	Extent of degradation (%)
0 g/L	0.112	0.97	100
1 g/L	0.012	0.96	49%
5 g/L	0.008	0.98	35%
10 g/L	0.005	0.90	21%

of anatase and rutile as compared to the only anatase form. The rate of sonophotocatalytic degradation of alachlor using ZnO as photocatalyst increased from 0.06 min^{-1} to 0.11 min^{-1} with an increase in ZnO loading from 0.05 g/L to 0.2 g/L. Also it has been observed that the rate of degradation of alachlor using ZnO as photocatalyst are lowest as compared to other two types of photocatalysts used in the current experimental work. The photocorrosion of ZnO which frequently occurs when the photocatalyst is illuminated under UV-lights decreases its

photocatalytic activity in the aqueous solutions while TiO_2 is not photocorrosive (Yamaguchi *et al*. 1997).

The rate of sonophotocatalytic degradation of alachlor increased 1.3, 1.8 and 1.7 times as compared to that obtained for the photocatalysis alone at the optimized loading of photocatalyst which is 0.01g/L for TiO_2 (mixture of anatase and rutile), 0.05 g/L for TiO_2 (anatase) and 0.2 g/L for ZnO respectively. Thus it can be seen from the results that the optimized loading required for complete degradation of alachlor using TiO_2 (mixture of anatase and Rutile) is 5 times and 20 times less than that required for the TiO_2 (anatase) and ZnO as photocatalyst respectively. The obtained results can be attributed to the enhanced catalytic activity for the mixture of anatase and rutile forms. In the sono-photocatalytic process, the acoustic micro-streaming leads to the cleaning and sweeping of the TiO_2 surface allowing more active catalysts sites at any given time. Also surface area increases by fragmentation or pitting of the catalyst due to ultrasound (Gogate and Pandit 2004). The synergistic effect has been observed using sonophotocatalytic process for all the three types of catalysts for the degradation of alachlor as more free radicals are likely to be available for the reaction as compared to the individual process. Also the turbulence generated by the cavitating conditions induced by ultrasound cleans the catalyst surface during the treatment and increases the mass transport of chemical species between the solution phase and the catalyst surface (Cristina *et al*. 2008).

The synergistic index calculated for combined operation is 1.4, 1.5 and 1.3 using TiO_2 (mixture of anatase and rutile), TiO_2 (anatase) and ZnO respectively at optimized loading of photocatalyst. Also in sonophotocatalytic degradation of alachlor, the reduction in TOC is 65%, 62% and 47% using TiO_2 (mixture of anatase and rutile), TiO_2 (anatase) and ZnO respectively at optimized loading of photocatalyst.

Bahena *et al*. (2008) have studied the sonophotocatalytic degradation of alazine and gesaprim (commercial herbicides) in TiO_2 slurry and reported that the rate of sonophotocatalytic process resulted in higher mineralization efficiency compared to the approach where photocatalysis and sonolysis were used individually. It has been reported that using sonophotocatalytic process the pollutant concentration of Gesaprim was reduced up to 91% as compared to 81%, 71% and 43% removal achieved over a period of time of 90 min by sonolysis, photocatalysis and photolysis, respectively. Also similar results were obtained in reducing the alazine pollutant concentration where the removal was 100% with sonophotocatalysis, 82% with photocatalysis, 58% with sonolysis and 48% with photolysis, all being achieved in the first 90 min period (Bahena *et al*. 2008).

3.4 H_2O_2 assisted sonophotocatalytic degradation of alachlor

In order to investigate the effect of addition of H_2O_2 on the extent of degradation of alachlor, experiments were carried out with varying loading of hydrogen peroxide over the range of 0.02 g/L to 0.06 g/L using US/UV/TiO_2 (mixture of anatase and rutile) treatment approach at optimized conditions. The results for the variation in the extent of degradation have been depicted in Fig. 9 whereas the obtained values of rate constants are given in Table 1. It has been observed from the results that the rate of degradation of alachlor increased with an increase in the loading of H_2O_2 till 0.04 g/L and further increase in the hydrogen peroxide loading resulted in only a marginal increase in the extent of degradation. The back-up experiments were conducted for degradation of alachlor using hydrogen peroxide with ultrasound (US/H_2O_2) and direct photolysis of H_2O_2 (UV/H_2O_2) at the already optimized loading of H_2O_2 as 0.04 g/L. The obtained results have been tabulated in

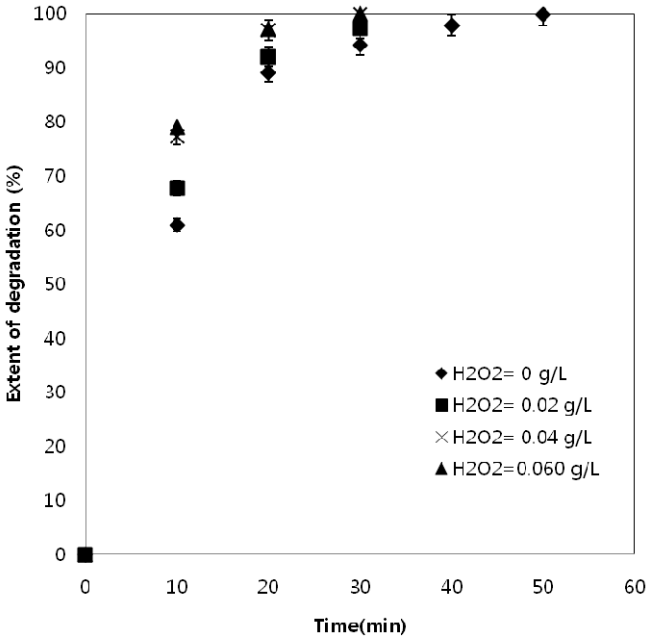

Fig. 9 Effect of addition of different loadings of H_2O_2 on sonophotocatalytic (US/UV/TiO_2 (mix)) degradation of alachlor [initial concentration of alachlor = 20 ppm, TiO_2 (mix) = 0.01 g/L temperature 28°C and pH 3]

Table 1. The observed increase in the rate of degradation of alachlor in H_2O_2 assisted sonophoto-catalytic process can be explained on the basis of enhanced quantum of free radicals generated in the system due to the dissociation of hydrogen peroxide under the action of ultrasound (Chakinala *et al*. 2007) and direct photolysis of H_2O_2 (Chu and Choy 2002). Also hydrogen peroxide acts as an electron acceptor in the photocatalytic process thereby reducing the electron hole recombination which is an undesirable process in the photocatalytic process and generating one more hydroxyl radical rather than the weaker $\cdot O_2^-$ radical (Wong and Chu 2003a). The marginal increase in the rate of degradation of alachlor at higher loadings of hydrogen peroxide may be due to the scavenging of generated hydroxyl radicals by the excess hydrogen peroxide. Overall at optimized loading of H_2O_2 the increase in the rate of degradation of alachlor was 3 times higher than that obtained in the absence of hydrogen peroxide.

3.5 Effect of radical scavenger on sonophotocatalytic degradation of alachlor

In order to investigate the controlling mechanism for the sonophotocatalytic degradation of alachlor, experiments were performed using sodium bicarbonate as radical scavenger for US/UV/TiO_2 (mixture of anatase and rutile) at optimized loading of TiO_2. The loading of sodium bicarbonate was varied over the range of 1 g/L to 10 g/L for fixed optimized loading of TiO_2 (mixture of anatase and rutile) as 0.01 g/L. The results for the variation of extent of degradation have been depicted in Fig. 10 whereas the obtained values of rate constants are given in Table 1. It has been observed from the obtained results that the extent of degradation of alachlor decreased

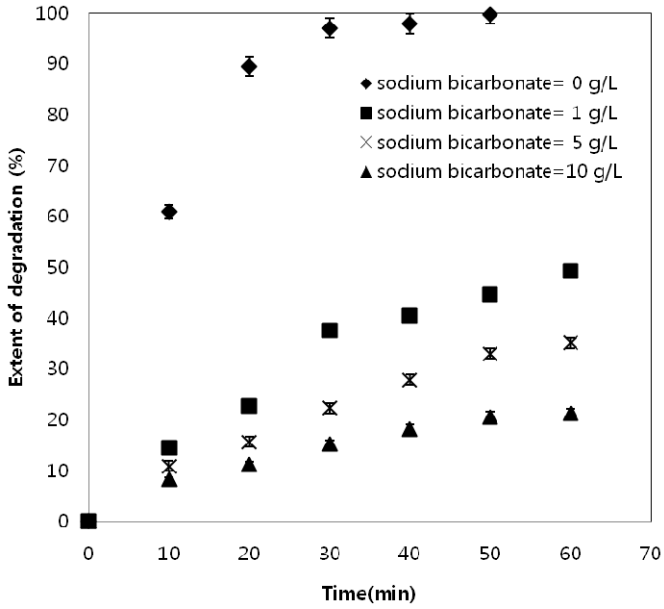

Fig. 10 Effect of addition of different loadings of sodium bicarbonate (radical scavenger) on sono-photocatalytic (US/UV/TiO_2 (mix)) degradation of alachlor [initial concentration of alachlor = 20 ppm, TiO_2 (mix) = 0.01 g/L temperature 28°C and pH 3]

with increasing loading of sodium bicarbonate. The extent of degradation of alachlor was 100%, 49%, 35% and 21% at sodium bicarbonate loading of 0 g/L, 1 g/L, 5 g/L and 10 g/L respectively within 60 min of treatment. The observed results can be attributed to the scavenging of hydroxyl radicals by sodium bicarbonate resulting in lower number of hydroxyl radicals being available for the degradation reaction thereby reducing the extent of degradation of alachlor. Based on the studies, it can be conclusively established that the attack of hydroxyl radicals is the controlling mechanism for the degradation of alachlor in the combined operation. Yao *et al*. (2010) have also reported a similar decrease in the rate of parathion degradation under ultrasonic irradiation in the presence of sodium bicarbonate as radical scavenger.

3.6 Identification of byproducts

In order to investigate the alachlor degradation products, LC-MS analysis of the sample has been done by performing the experiments at optimized loading of TiO_2 using the sonophoto-catalytic process. The experiment was conducted using optimized loading of 0.01 g/L TiO_2 (mixture of anatase and rutile) under optimized operating conditions. The samples drawn at specific time have been used without any further dilution for LC-MS study. The prominent peaks were obtained at m/z of 221, 225, 239 and 251. Alachlor has three electron donating sites (2 ethyl and 1 amino site) making high electron density at its ortho and para positions which are highly suspectible to electrophilic attack by OH radicals making it degrade quickly. The peak at m/z 251 corresponds to 2-hydroxy-2', 6'-diethyl-N-(Methoxymethyl) acetanilide formed due to the hydrolysis of alachlor. The peak at m/z 221 corresponds to 2-hydroxy-2'6'-diethyl-N-

methylacetanilide formed by the successive hydrolysis and demethoxylation of alachlor. The peak at m/z 239 is formed by direct demethylation of alachlor whereas the peak at m/z 225 is formed by demethylation of m/z 239. The identified products are consistent with the reported intermediate products in the literature (Potter and Carpenter 1995, Wang and Yong 2009).

4. Conclusions

The present work has illustrated the beneficial effects of combining US and UV irradiations for degradation of alachlor and has also established the effect of the type and loading of the photocatalyst. Following important design related information can be obtained from the experimental results presented in the work.

- The rate of degradation of alachlor is enhanced using combined process of sonophotolysis as compared to sonolysis and photolysis processes operating alone.
- Enhanced degradation of alachlor is obtained using sonophotolysis, photocatalytic and sonophotocatalytic processes at different optimized loadings of TiO_2 (mixture of anatase and rutile), TiO_2 (anatase) and ZnO.
- The optimum loading of photocatalyst is necessary to achieve enhanced rate of degradation of alachlor using photocatalysis and sonophotocatalysis as the excess loading of photocatalyst may hinder the penetration of light into the reactor.
- Among all the three photocatalysts used for sonophotocatalytic and photocatalytic degradation of alachlor, TiO_2 (mixture of anatase and rutile) showed highest photocatalytic activity as compared to TiO_2 (anatase) and ZnO due to the enhanced generation of hydroxyl radicals and slow electron hole recombination.
- In sonophotocatalytic process, the reduction in TOC is 62%, 64% and 57% respectively using TiO_2 (mixture of anatase and rutile), TiO_2 (anatase) and ZnO respectively.
- The synergistic effect has been observed for sonophotocatalytic degradation of alachlor and the synergistic index is 1.4, 1.5 and 1.3 using TiO_2 (mixture of anatase and rutile), TiO_2 (anatase) and ZnO respectively.
- The rate of sonophotocatalytic degradation of alachlor increased in the presence of H_2O_2 till optimum loading due to the generation of enhanced free radicals in the presence of US and UV. Also H_2O_2 act as electron acceptor in photocatalytic process thereby inhibiting the electron hole recombination.
- The rate of sonophotocatalytic degradation alachlor decreased in presence of radical scavenger and hence free radical attack is the controlling mechanism for the degradation reaction.

Acknowledgments

PRG would like to acknowledge the funding of the Department of Science & Technology, New Delhi, India under the Fast Track program for the research work presented in this manuscript. MVB would like to acknowledge the support of UGC Networking Resource Centre in Chemical Engineering Department at the Institute of Chemical Technology.

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