Int. J. Chem. Sci. : 3 (1), 2005, 121–128

PHOTOCATALYTIC DEGRADATION OF 3,4–DICHLORONITROBENZENE IN AQUEOUS SUSPENSIONS OF IRRADIATED TiO_2 PARTICLES

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ABSTRACT

Photocatalytic degradation of 3,4–dichloronitrobenzene (3,4–DCNB) in ppm (10 mgL^{-1}) level concentration under uv–light irradiation in the presence of TiO_2 particle suspensions has been carried out in the aqueous medium. Semiconductor –TiO_2 powder prepared by gel to crystalline conversion method is used for the studies. The TiO_2 suspensions exhibited better photocatalytic properties especially in the presence of oxidizing agent such as $(NH_4)_2S_2O_8$. The effects of initial concentration of the pollutant and pH on the rate of degradation are discussed. The degradation path is followed by analytical techniques such as GC–MS, UV–visible and IR spectrometry.

Key words : Photocatalysis, Degradation, TiO_2, UV–light, Oxidizing agent.

INTRODUCTION

Photochemical process of mineralization of toxic organic compounds in heterogeneous systems on the reactive surfaces, such as titania or metal oxides is an attractive process for the environmental clean up process.[1,2] Heterogeneous photocatalysis involving adsorption of organic pollutants on semiconductor particles is a promising technology for removal of toxic pollutants in parts per million concentrations.[3–5] The chlorinated hydrocarbons are well known persisting organic environmental contaminants.[6–10] Because these are more stable due to the presence of strong C–Cl bond. Possibly, they are all carcinogens. They persist in nature for a longer duration and pollute the aquatic as well as air and soil environment. In this regard, a study of degradation of 3,4–dichloronitrobenzene (1,2–dichloro–4–nitrobenzene), a chloroaromatic nitro compound on uv–light irradiated TiO_2 catalyst suspensions in aqueous medium has been undertaken.

The $(NH_4)_2S_2O_8$ is used as an oxidizing agent in the presence of TiO_2 catalyst and uv–light, which increased the rate of degradation through producing oxidative radical species such as hydroxyl radicals. These radical species formed, play a prominent role for promoting rapid reactions involving electron transfer and hydrogen abstraction to aromatic rings.

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EXPERIMENTAL

Materials

Fine–grained powder of TiO_2 is prepared by the precipitation method and characterization is done by employing XRD studies with a vertical goniometer on Phillips PW 1050/70/76 as described in our earlier publication.[11] The powder is annealed at 600 °C for about 4–5 hours to get anatase form of TiO_2. No special care is taken to control the particle size during the process of preparation. The average crystal size is calculated by Scherrer's equation using pure diffraction breadth, which is found to be 177.52 A^{o}.[12]

3,4–Dichloronitrobenzene is chloroaromatic nitro compound having the molecular formula: $C_6H_3Cl_2NO_2$, bearing the formula weight; 192.00, melting point: 41–42°C, boiling point: 255–256°C and sp. gr. 1.4266 (100/4°C). It is a light yellow crystalline solid, insoluble in water, soluble in hot alcohol, ether etc. It is a harmful, irritant (strong irritant to tissue) and hazardous chemical for the environment. It leads to fire risk by spontaneous reaction. It is used as an intermediate in the synthesis of many organic compounds.

The solution of 3,4–dichloronitrobenzene (Merck) was prepared in double distilled water. The chemical was used as such obtained from the company with out further purification. The reaction solution was stirred in dark for 15 min. for proper mixing.

Photocatalysis and analysis

A 10 ppm solution of 3,4–dichloronitrobenzene was taken in a reaction vessel in 400 mL quantity in which about 300 mg of TiO_2 was suspended under constant stirring and subjected to uv–light irradiation (light of λ = 350–400 nm). The degradation studies under different experimental conditions such as (i) in the absence of catalyst and other reagents, (ii) with only TiO_2 catalyst (300 mg), and (iii) with TiO_2 catalyst and ammonium persulphate (20 ppm). Effect of pH on the rate of degradation of 3,4–dichloronitrobenzene has been studied.

Photocatalytic degradation experiments were carried out in quartz cell using medium pressure 125 W mercury vapour lamp source by direct exposure of the reaction mixture (the area of exposure = 93.08 cm^2). The wavelength peaks was around 350–400 nm. The photon flux is found to be 7.75 $mWcm^{-2}$ as determined by ferrioxalate actinometry.[13,14] The photodegradation experiments are carried out in presence of atmospheric oxygen at lab temperature (25–30°C). The experiment in the absence of oxygen did not show any degradation even after several hours of irradiation. The degradation studies are made by employing spectroscopic techniques using UV–visible spectrometer (Shimadzu UV–VIS–160 model), IR (Nicolet Impact 400 D FTIR) and mass spectral studies using 17 A Shimadzu GC–MS QP–5050 A model spectrophotometer.

RESULTS AND DISCUSSION

Effect of initial substrate concentration

The rate of degradation is inversely proportional to the initial concentration of the substrate. At lower concentration, about 10 ppm, in the presence of catalyst and oxidizing agent, the time taken for the complete mineralization is around 1.0 h. Further increase in the initial concentration viz. 20 ppm, 50 ppm, 100 ppm etc. the time taken was increased as 2.0, 3.75 and > 8.0 h, respectively.

The effect of amount of catalyst

The degradation experiments were carried out with varying amounts of photocatalyst such as 50, 100, 200, 300 and 400 mg per 400 mL of the solution to study the effect of amount of catalyst on the rate of degradation. The studies have shown an increase in degradation rate up to 300 mg/400 mL of the solution and further increase in the amount given an almost constant rate of degradation. This shows a saturation limit of the catalyst for the degradation. Therefore, 300 mg TiO_2 was used as optimum amount in all the experiments. The catalytic coefficient for the experiment with 300 mg of TiO_2 is $0.3121^2\ mg^{-2}\ h^{-1}$.

Effect of pH on the rate of degradation

In the present study, the initial pH of experimental solution with and without catalyst was 6.3. As the degradation proceeds under illumination, pH value of reaction medium also decreases. When ammonium persulphate (20 ppm) was added as an oxidizing agent in the presence of TiO_2, the initial pH was ~5.7, (slightly acidic) and the time taken for the degradation of DCNB at this pH is 1.0 h. It shows the increased rate of degradation at lower pH of the medium. When the initial pH was adjusted to 3.0 (adjusted using dilute HCl), the rate of degradation was found to be increased (time taken is less than 1 h) and at the initial pH = 11.5 (adjusted using dilute NaOH solution), it is almost same as that at pH = 5.7 (natural). In the pH range of 6–9, the rate of degradation was found to be very slow. This is because of the fact that the isoelectric point of TiO_2 lies in the range pH = 6–8, where the positive and negative charges are equal on TiO_2 particle surface.

Effect of oxidizing agent

The rates and efficiencies of photoassisted degradation of organic substrates are significantly improved in the presence of oxygen or several other inorganic oxidizing species, such as persulphate and peroxides.[15] The photogenerated electron–hole pairs on irradiated catalyst react with these species to form several photo–reactive species such as O_2^{-}, $O_2^{-\bullet}$, O_2^{2-}, $^{\bullet}OH$ etc.[16,17], which are known to oxidize the pollutants effectively and they also act as the electron traps. This reduces the recombination process, which is in competition with charge transfer reactions and thus, it increases the rate of degradation. In the present study, $(NH_4)_2S_2O_8$ has been used as an oxidizing agent.

The optimum amount of oxidizing agent has been identified by carrying out the experiments with different amounts of $(NH_4)_2S_2O_8$ such as 10, 20, 50 and 100 ppm. Among these, 20 ppm solutions have shown the faster rate of degradation in the presence of catalyst. The experiment in the presence of only oxidant but without catalyst also shows the degradation to some extent. The process will be homogeneous catalysis but the rate is found to be slower than that in the presence of catalyst. This may be due to the formation of persulphate radical and further formation of sulphate radical in the presence of uv–light (340–360 nm) will assist. Persulphate radical itself is a very strong oxidizing agent and its efficiency further increases, when TiO_2 photocatalyst is used.

The persulphate and peroxides produce the $^{\bullet}OH$ radicals[18] as :

$$(NH_4)_2S_2O_8 \longrightarrow 2\,NH_4^+ + S_2O_8^{2-}$$

$$S_2O_8^{2-} + e^-_{cb} \longrightarrow SO_4^{2-} + SO_4^{-\bullet}$$

$$SO_4^{-\bullet} + H_2O \longrightarrow {}^{\bullet}OH + H^+ + SO_4^{2-}$$

Thus reactive hydroxyl radicals and super oxide radicals formed, act as the electron traps and thereby reduces the recombination process and as a conseqnence the rate of degradation increases.

Kinetics of degradation

The quantitative determination of rate of degeneration is given in Figure 1 (C/C_o versus irradiation time plot) where C_o is the initial concentration of the pollutant (10 ppm) before irradiation and C is the concentration at any desired time interval during the process of degradation. It describes about the concentration of the pollutant remained undegraded with respect to time of irradiation.

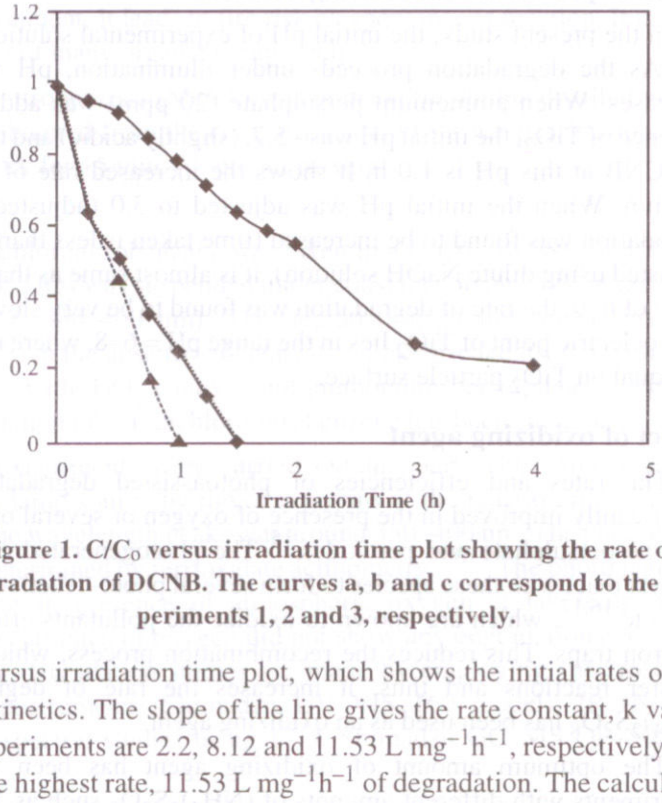

Figure 1. C/C_o versus irradiation time plot showing the rate of degradation of DCNB. The curves a, b and c correspond to the experiments 1, 2 and 3, respectively.

The Figure 2 is the C_o–C versus irradiation time plot, which shows the initial rates of the reactions follow the zero order kinetics. The slope of the line gives the rate constant, k value. The k values for the different experiments are 2.2, 8.12 and 11.53 L $mg^{-1}h^{-1}$, respectively, out of which the experiment 3 has the highest rate, 11.53 L $mg^{-1}h^{-1}$ of degradation. The calculated kinetic parameters for the experiment 3, where the faster rate of degradation was achieved, are given in the Table 1.

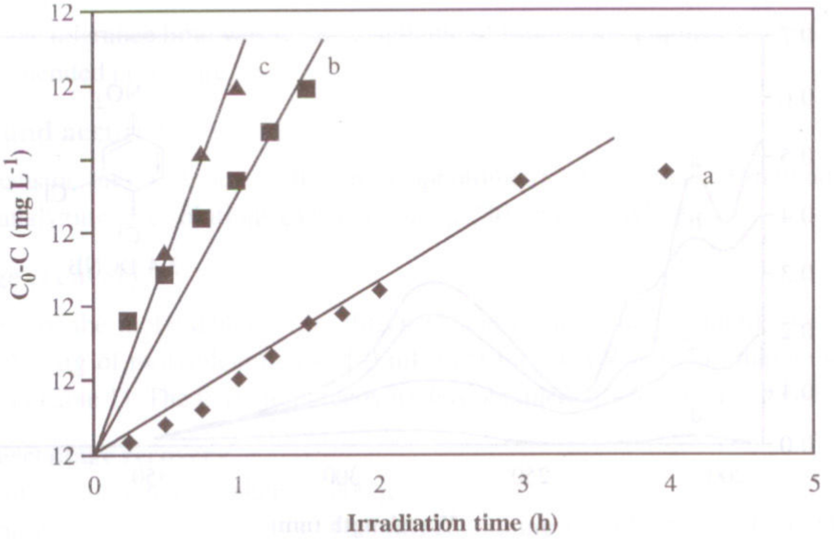

Figure 2. C_0–C versus irradiation time plot. The curves a, b and c correspond to the experiments 1, 2 and 3, respectively

Table 1. Kinetic parameters for the degradation of DCNB in the absence of TiO_2 catalyst and oxidizing agent.

Time (h)	Absorbance (A)	Concen-tration (mg L^{-1})	C_0–C (mg L^{-1})	C/C_0	1–C/C_0 = α	Rate, v = dα/dt (h^{-1})	Rate constant k = v/C (L mg^{-1}h^{-1})	Catalytic coefficient = k/C (l^{2}mg^{-2}h^{-1})
0.00	0.455	10.0	0.00	1.00	0.000	–	–	–
0.25	0.440	9.67	0.33	0.97	0.030	0.12	0.0124	0.00128
0.50	0.420	9.23	0.77	0.92	0.077	0.15	0.0167	0.00180
0.75	0.390	8.57	1.43	0.86	0.143	0.26	0.0308	0.00360
1.00	0.360	7.91	2.08	0.79	0.208	0.26	0.0330	0.00418
2.00	0.252	5.54	4.46	0.55	0.446	0.24	0.0429	0.00776
3.00	0.120	2.64	7.36	0.26	0.736	0.29	0.1100	0.04170
4.00	0.110	2.42	7.58	0.24	0.758	0.02	0.0091	0.00376

Spectral analysis

The degradation process of 3,4–dichloronitrobenzene was followed by UV–visible spectrophotometric method. Figure 3 is a compiled absorbance spectrum for the above experiments at different time intervals of irradiation, which shows the rate of disappearance of absorption bands in different experiments. The spectra have shown the continuous decrease in the absorption intensities and finally after one hour of irradiation, no characteristic peaks of 3,4–DCNB could be observed.

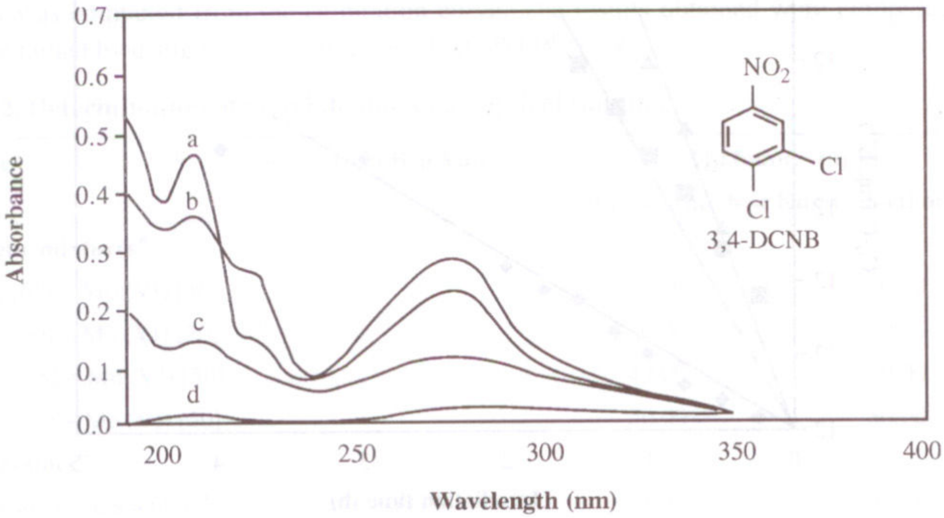

Figure 3. UV–visible absorption spectrum, in which the curves b, c and d correspond to the samples after 1 h of irradiation in the experiments 1, 2 and 3, respectively. The curve a is the initial spectrum before irradiation.

The degradation process has also been followed by FTIR spectroscopic method. The IR spectra for the best system (Expt. No. 3) are taken at 0, 0.5 and 1 h of irradiation. The samples for the IR spectral analysis were prepared by extracting about 200 mL of the solution at above said time intervals in chloroform. The samples were concentrated and spectra are taken. The spectrum taken for the sample before irradiation has the peaks at 3105 cm^{-1} (aromatic C–H stretching), 1600–1660 cm^{-1} (aromatic C–C multiple stretching), 1528 cm^{-1} (C–NO_2 of aromatic nitro compound), 1362 cm^{-1} (C–N vibration of aromatic nitro compound) and an intense peak at 1160 cm^{-1} (C–N or N–O bonds in the molecule). The C–Cl bonds give the peaks in the region 840 cm^{-1}–741 cm^{-1}. After 1 h of irradiation, the spectrum has shown peaks of negligible intensity.

GCMS spectral analysis

The mass spectral studies were employed to identify the intermediates formed during the process of degradation and to understand splitting pattern of 3,4–DCNB using 17A Shimadzu GC–MS QP–5050 A Model spectrophotometer. It is a compact high performance quadruple electron mass spectrometer. This instrument features a capillary column direct GC/MS interface and an electron ionization type instrument. The gas chromatogram taken for the sample before irradiation has shown an intense peak at the retention time 7.675 min. The mass spectra has shown the molecular ion peak at m/z = 191. The base peak corresponds to m/z 109. The spectra is comprised of the major peaks corresponding to the m/z values 175 (4–chloro–3–hydroxy nitrobenzene), 161 (3,4–dihydroxy nitrobenzene or may be 3,4–dichloro phenol), 145 (1,4–dihydroxy nitrobenzene), 109 (quinone or hydroquinone) and many peaks of very low intensity with m/z values 112, 63, 50 and 40, which remain unassigned. The GC–MS spectra taken for the sample after 1 h of irradiation has no peak at the above mentioned retention time value, which indicates the degradation of 3,4–DCNB.

Table 2. Kinetic parameters for the degradation of DCNB in the presence of TiO_2 catalyst.

Time (h)	Absorbance (A)	Concentration ($mg\ L^{-1}$)	C_0–C ($mg\ L^{-1}$)	C/C_0	C/C_0I–C/C_0 = α	Rate, v = dα/dt (h^{-1})	Rate constant k = v/C ($L\ mg^{-1}h^{-1}$)	Catalytic coefficient = k/C ($L^2mg^{-2}h^{-1}$)
0.00	0.39	10.0		1.00	0.00	–	–	–
0.25	0.25	6.41		0.64	0.36	1.44	0.22	0.0350
0.50	0.20	5.13		0.51	0.49	0.51	0.10	0.0195
0.75	0.14	3.59		0.36	0.64	0.62	0.17	0.0470
1.00	0.10	2.56		0.26	0.74	0.41	0.16	0.0620
1.25	0.05	1.28		0.13	0.87	0.51	0.14	0.3120
1.50	0.00	0.0		0.00	1.00	0.51	–	–

Table 3. Kinetic parameters for the degradation of DCNB in the presence of TiO_2 catalyst and $(NH_4)_2S_2O_8$.

Time (h)	Absorbance (A)	Concentration ($mg\ L^{-1}$)	C_0–C ($mg\ L^{-1}$)	C/C_0	C/C_0I–C/C_0 = α	Rate, v = dα/dt (h^{-1})	Rate constant k = v/C ($L\ mg^{-1}h^{-1}$)	Catalytic coefficient = k/C ($L^2mg^{-2}h^{-1}$)
0.00	0.44	10.00	0.00	1.00	–	–	–	–
0.25	0.29	6.59	3.41	0.70	0.34	1.36	0.27	0.0314
0.50	0.20	4.55	5.46	0.45	0.55	0.82	0.18	0.0396
0.75	0.08	1.82	8.18	0.18	0.82	1.09	0.60	0.3289
1.00	0.00	0.00	10.0	0.00	1.00	0.73	0.60	–

CONCLUSION

The photocatalytic degradation of 3,4–DCNB is an efficient process on the irradiated TiO_2 particle surfaces. A considerable increase in the rate of degradation in the presence of both catalyst and oxidizing agent, $(NH_4)_2S_2O_8$ has been reported. There is a significant effect of the amount of catalyst on the rate of degradation. 300 mg/400 mL of TiO_2 is the optimum amount of catalyst for the degradation of 10 ppm of DCNB in the presence of an oxidizing agent, $(NH_4)_2S_2O_8$ (20 ppm). The acidic and basic pH media showed the faster rates of degradation than the neutral medium because at acidic and basic medium, the TiO_2 particle surface is covered by more number of either positive or negative charges, whereas at neutral medium, the positive and negative charges are equal. Since the rate of degradation depends on the adsorption of the substrate molecules on the catalyst surface, increased rate can be expected at lower and higher pH values. The intermediate degradation products are identified as 4–chloro–3–hydroxy nitrobenzene, 3,4–dihydroxy nitrobenzene or may be 3,4–dichloro phenol, 1,4–dihydroxy nitrobenzene, quinone or hydroquinone by GC–MS method.

ACKNOWLEDGEMENT

Financial support by UGC–DRS, UGC–COSIST and UGC–FIST is greatly acknowledged. One of the authors G. Krishnamurthy wishes to acknowledge New Horizon College of Engineering, Bangalore for its support.

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Accepted : 28.10.04