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Photocatalytic degradation of ciprofloxacin·HCl using Aeroxide® P-25 TiO_2 photocatalyst: Comparative evaluation of solar and artificial radiation

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The photocatalytic degradation of ciprofloxacin (CFX) has been investigated using Aeroxide® P-25 TiO_2 photocatalyst in the presence of solar as well as artificial radiation. The effects of different operating parameters like initial concentration of CFX, catalyst loading, *p*H of solution and effect of co-existing ions on photocatalytic degradation of CFX have been investigated with a view to establish the optimum operating conditions. It is observed that as the initial concentration of CFX increases, the rate of photocatalytic degradation decreases. Optimum catalyst loading is observed at 1 g L^{-1} for CFX concentration of 100 mg L^{-1}. Over the *p*H range 3-11, maximum degradation rate occurs at *p*H 9. The mechanism and intermediates formed during the photocatalytic degradation of CFX are discussed based on UPLC-MS/MS analysis. From kinetic studies, it is found that the photocatalytic degradation obeys pseudo-first order kinetics. The degradation rate constant using solar radiation is about 1.7 times higher than that under artificial radiation.

Keywords: Photocatalysis, Advanced oxidation process, Pharmaceutical micropollutants, Degradation, Solar radiation, Artificial radiation, Aeroxide® P-25 TiO_2, Ciprofloxacin·HCl

The rapid growth of the population has created an increase in the demand for the water from the limited supply of freshwater. Thus, protecting the supply of water and addressing concerns such as toxicity and the presence of chemicals that may have potential long term adverse human and ecological effects has become an important issue[1]. Pharmaceuticals and personal care products enter the environment at low concentrations primarily as metabolites excreted by humans and animals or in effluents that are discharged as wastewater from hospitals, pharmacies, and chemical manufacturing facilities[2]. Once these compounds reach wastewater treatment plants, they are often not completely removed and their presence in aquatic environments may cause serious threats to the ecosystem and human health[3,4]. There is, therefore, a need to develop eco-friendly, cost effective techniques for the treatment of pharmaceutical wastewater.

The pharmaceutical compounds are often difficult to biodegrade, resulting in inefficient removal by conventional wastewater treatment plants[5]. Removal of pharmaceutical compounds such as CFX, up to the permissible limit from the wastewater is essential before being discharged into the drainage system. The remediation of CFX from wastewater has been attempted by various treatment methods such as ozonation[6,7,8], photo-Fenton[9], sonolysis[10], photolysis[11] and photocatalytic degradation[12,13]. Degradation of refractory pollutants by using an inexpensive photocatalyst as photo-oxidant and solar radiation seems to be an attractive possibility[14].

The present study deals with the photocatalytic degradation of CFX using Aeroxide® P-25 TiO_2 photocatalyst under solar and artificial radiation. The main objective of this work is to (i) study the comparative photocatalytic degradation of CFX using artificial and solar radiation in the presence of Aeroxide® P-25 TiO_2 photocatalyst, (ii) to study the effects of various operating parameters such as initial concentration of CFX, photocatalyst loading, *p*H of solution and effect of presence of co-existing ions on photocatalytic oxidation of CFX, with a view to establish the optimum process conditions, (iii) to establish the kinetics of photocatalytic oxidation of CFX, and, (iv) to study the mechanism of photocatalytic degradation of CFX.

Materials and Methods

Aeroxide® P-25 TiO_2 (80:20% *w/w* anatase-to-rutile) with an average particle size of 21 nm and BET surface area of about 50±15 m^2 g^{-1} was used as the photocatalyst[15]. The CFX sample was procured from M/s. Granules India Pvt, Hyderabad. Acetic acid (CH_3COOH), acetonitrile, Na_2CO_3, NaCl and $(NH_4)_2SO_4$ were purchased from Merck India Pvt. Ltd, Mumbai, India.

Photocatalytic studies

An annular borosilicate glass reactor as shown in Fig. 1a and 1b was used for carrying out the photocatalytic oxidation reaction using artificial and solar radiation respectively. In the present investigation visible radiation from a tungsten lamp with power input 400 W was used as the source of artificial radiation (wavelength 200–800 nm). A known concentration of CFX aqueous solution was prepared in de-ionized water. The temperature of the reaction mixture was kept constant by circulating chilled water through the annular space between the lamp via Julabo Chiller FP-50 MA. In each experiment, 500 mL of aqueous solution of CFX was charged in the reactor. Air flow rate of 1 L min^{-1} was supplied via the ring sparger located at the bottom of the reactor which was used for the oxidation reaction and to keep all the TiO_2 in suspension. In all experiments, Aeroxide® P-25 TiO_2 was used as the photocatalyst. The solution was equilibrated by stirring for 15 minutes in the dark before exposing the reactor assembly to the artificial radiation. The liquid samples were taken out periodically from the reactor for analysis and stored in amber colored bottles. During the photocatalytic degradation experiments, the *p*H of the solution was not controlled.

The same experimental procedure was carried out for photocatalytic degradation of CFX using solar radiation. A parabolic reflector having surface area of 1.5 m^2 was used to concentrate the solar radiation forming a continuous glowing band of concentric light surrounding the wall of the reactor. After every 20 minutes, the position of the reflector was tracked with respect to the sun so as to maintain the band of light, surrounding the reactor wall. Plain solar radiation intensity was measured in W m^{-2} by ‘Daystar solar meter’ (Daystar Inc, Las Cruces, NM, USA) working on the photocell principle. The experiments were carried out in the month of January to April in Pune, India. During this period, the sky was brilliant blue (no clouds) and the average solar intensity was approximately constant at 850 W m^{-2} (±10%) as measured at the ground level.

Analytical procedure

The concentration of CFX in the samples was monitored by high performance liquid chromatography (Dionex P680 HPLC) fitted with a UV detector (Dionex UVD 170U) and a C-18 column (BISCHOFF, C-18-5 μm particle size, 250×4.6 mm, silica gel with C18 coating). The mobile phase was composed of 86% DI water, 16% acetonitrile and 1% acetic acid (2.8 g). CFX was detected at maximum UV absorbance set at wavelength of 280 nm. Flow rate of the mobile phase was kept at 1 mL/min. Column temperature was kept at 30 °C. In order to separate the

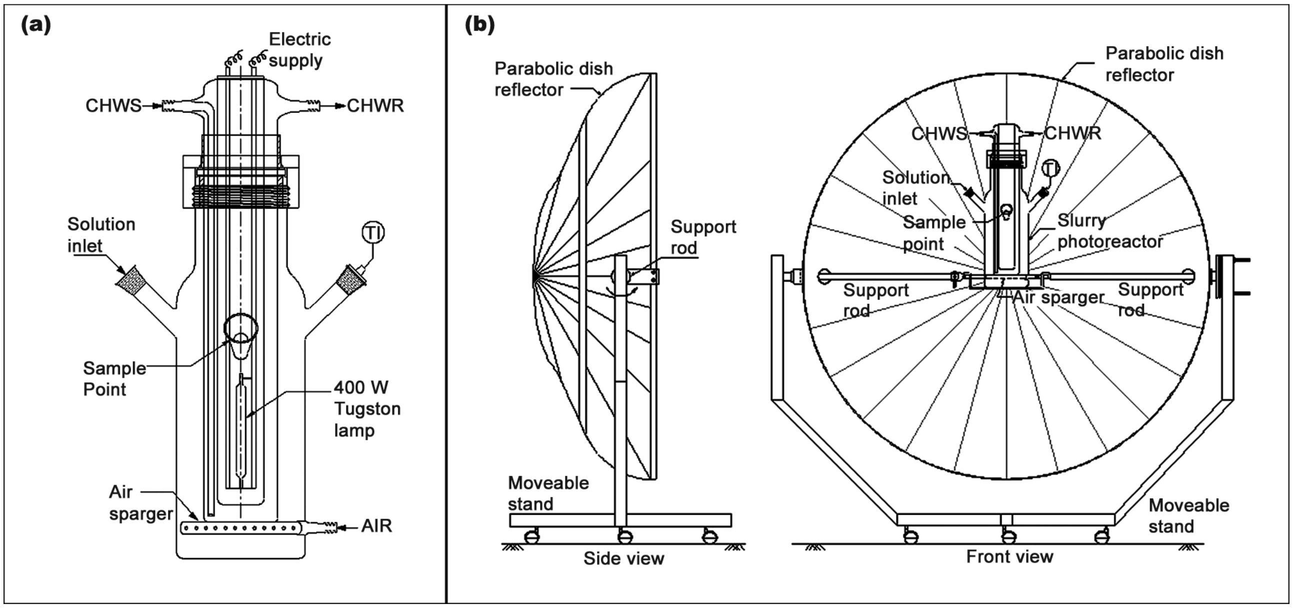

Fig. 1—Schematic diagram of experimental setup of photocatalytic degradation of CFX using (a) artificial radiation and (b) solar radiation.

catalyst particles, the samples were centrifuged and filtered with a polyethersulfone membrane filter of 0.45 μm before the HPLC analysis.

The intermediates formed during photocatalytic degradation of CFX were determined by liquid chromatography mass spectrometry using Thermo Fisher Scientific Q Exactive Hybrid Quadrupole-Orbit mass spectrometer (UPLC-MS/MS). Chromatographic separations were carried out using Thermo Scientific Hypersil gold column (150 mm×4.6 mm×8 μm). The mobile phase used was 0.1% formic acid in acetonitrile and 0.1% formic acid in water (16:84). Total analysis time was 16 min, while the mobile phase flow rate was 0.5 mL/min. Mass detection settings were as follows: spray vottage (+) 3600.00, capillary temperature 320 °C, sheath gas nitrogen 45, probe temperature 350 °C. The data were obtained in scan mode from 60 to 900 mg. The electrospray ionization source was used in positive mode.

Results and Discussion

Comparison of photocatalytic degradation of CFX using Aeroxide® P-25 TiO_2 photocatalyst under solar and artificial radiation

Photocatalytic degradation experiments were conducted using different initial concentrations of CFX ranging from 50-500 mg L^{-1} at 1 g L^{-1} photocatalyst loading. The photocatalytic degradation experiments were performed using artificial radiation (lamp input 400 W) and solar radiation (avg. plain solar intensity 850±10). Figure 2 shows the comparison of rate of photocatalytic degradation of CFX using solar and artificial radiation in presence of Aeroxide® P-25 TiO_2 photocatalyst. It was found that the rate constant (k_{app}) for photocatalytic degradation decreases with increase in CFX concentrations. The rate constant for the photocatalytic degradation of CFX using solar radiation is 1.7 times higher than that under artificial radiation. The difference in the rates is due to the fact that under the solar radiation, the percentage of useful radiation is substantially higher than that under artificial radiation. The treatment of wastewater using concentrated solar radiation is very attractive for regions receiving strong sunlight throughout the year such as Australia, South America, South Africa, Indian subcontinent and other countries[16]. Hence detailed studies pertaining to PCD of CFX were carried out using solar radiation.

Effect of various operating parameters on photocatalytic degradation of CFX using solar radiation

Comparison of degradation of CFX using AOPs

Photolytic, photochemical, photocatalytic, and photo-Fenton degradation studies were carried out using 100 mg L^{-1} initial concentration of CFX. In the photocatalytic degradation experiments, Aeroxide® P-25 TiO_2 photocatalyst/concentrated solar radiation/air were used. For the photochemical degradation experiment, stoichiometric amount of hydrogen peroxide with concentrated solar radiation was used, while for photolytic degradation experiment only concentrated solar radiation/air was used. For photo-Fenton experiment stoichiometric amounts of hydrogen peroxide and $FeSO_4$, along with concentrated solar radiation/air was used.

Figure 3 shows the course of photolytic, photochemical, photocatalytic and photo-Fenton degradation reactions of CFX under concentrated solar radiation. The percentage degradation of CFX in photolytic, photochemical, photocatalytic and photo-Fenton process is 1%, 78%, 88%, and 73%, respectively after 15 min. Complete degradation of CFX was achieved by photochemical, photocatalytic and photo-Fenton processes at reaction time of 45 min. The rate of percentage degradation of CFX in the case of the photocatalytic method was found to be about 87%, 10% and 15% higher than the photolysis, photochemical and photo-Fenton method respectively

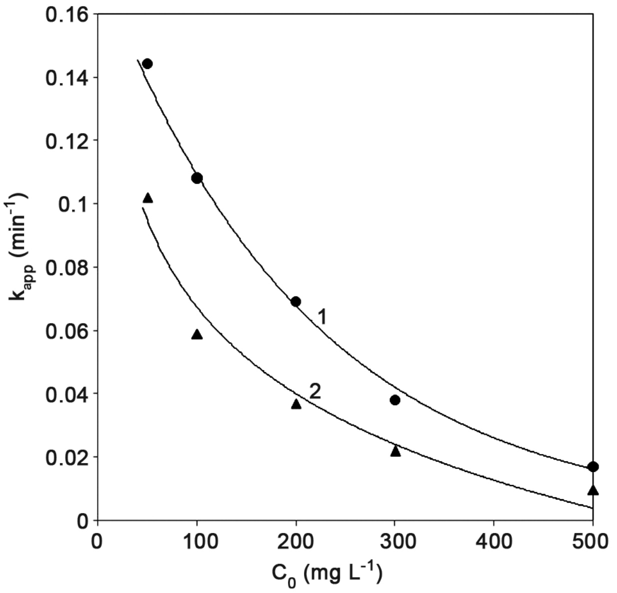

Fig. 2—Comparison of rate constant for photocatalytic degradation of CFX using artificial and solar radiation. [1 (●), solar radiation; 2 (▲), Artificial radiation].

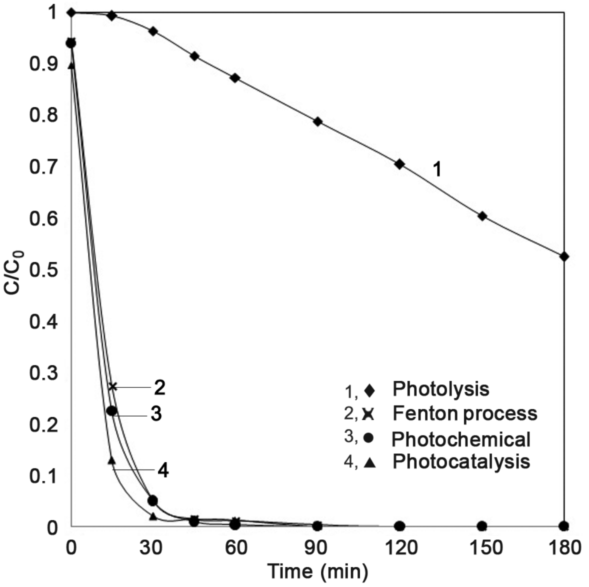

Fig. 3—Photocatalytic degradation of CFX using various AOPS. [Initial conc. of CFX: 100 mg L^{-1}. 1 (♦), photolysis (solar radiation); 2 (×), photo-Fenton process (solar radiation/$FeSO_4$); 3 (●), photochemical process (solar radiation/H_2O_2); 4 (▲), photocatalytic process (solar radiation/Aeroxide® P-25 TiO_2 photocatalyst)].

for reaction time of 15 min. This is because the rate of generation of $OH^\bullet$ radical in photocatalytic method is higher as compared to photolysis, photochemical and photo-Fenton method. Another advantage of photocatalytic method is that no additional chemicals are required. Therefore, further studies were restricted to the photocatalytic oxidation method.

Effect of initial concentration of CFX

Initial concentration of pollutant is an important parameter that affects the rate of photocatalytic degradation of the pollutant. Photocatalytic degradation studies were carried out using 50, 100, 200 300 and 500 mg L^{-1} initial concentration of CFX, while other parameters were kept constant. A linear relationship was observed between CFX concentration and reaction time, as shown in Fig. 4. It was found that at initial concentration 50 and 100 mg L^{-1}, complete degradation of CFX was achieved within 2 h. The rate constant (k_1) for photocatalytic degradation decreases from 0.144 to 0.017 min^{-1} with increase in CFX concentration from 50 to 500 mg L^{-1} (Table 1). This is because at a particular TiO_2 concentration, the amount of active centers on the photocatalyst is finite; therefore the rate of photocatalytic degradation rate is fast at lower concentrations of CFX. The photocatalytic degradation rate decreases when the concentration of CFX increases, possibly because the molecules of CFX are excessive in comparison to the amount of active sites on the photocatalyst. However, for constant light intensity, dissolved oxygen concentration and TiO_2 loading, the concentration of $OH^\bullet$ remains practically the same. Thus, although the adsorbed CFX concentration increases, the rate of photocatalytic degradation decreases due to a lower $OH^\bullet$/CFX ratio.

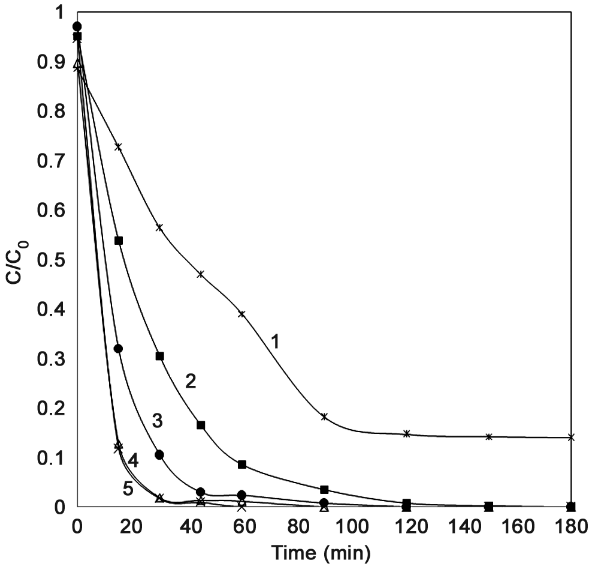

Fig. 4—Effect of initial concentrations of CFX under solar radiation using Aeroxide® P-25 TiO_2 photocatalyst (1 g L^{-1}). [Initial conc. of CFX: 1 (✱), 500 mg L^{-1}; 2 (■), 300 mg L^{-1}; 3 (●), 200 mg L^{-1}; 4 (Δ), 100 mg L^{-1}; 5 (×), 50 mg L^{-1}].

Table 1—Kinetic parameters at different initial concentrations of CFX under artificial radiation and solar radiations in the presence of Aeroxide® P-25 TiO_2 photocatalyst

Initial conc. of CFX (mg L^{-1})	Artificial radiation		Solar radiation	
	k_{qpp} (min^{-1})	R^2	k_{qpp} (min^{-1})	R^2
50	0.102	0.99	0.144	0.94
100	0.059	0.97	0.108	0.90
200	0.037	0.97	0.069	0.91
300	0.022	0.96	0.038	0.99
500	0.010	0.96	0.017	0.91

Effect of catalyst concentration

The concentration of TiO_2 is a critical parameter in photocatalytic oxidation. It affects the reaction rate and consequently has an effect on the cost of treatment. Solutions of CFX (100 mg L^{-1}) were used to study the effect of catalyst loading by varying the amount of photocatalyst from 0.1 to 4 g L^{-1}. As can be seen from Fig. 5, the optimum catalyst loading is 1 g L^{-1}.

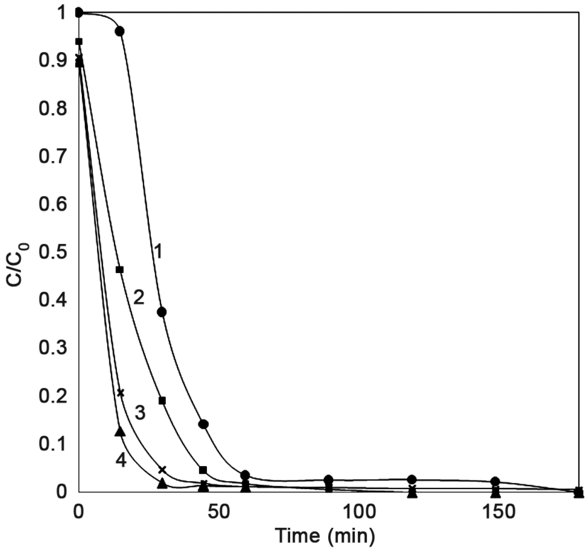

Fig. 5—Effect of catalyst on CFX degradation using solar radiation. [Initial CFX conc.: 100 mg L^{-1}. [Catal. loading: 1 (●), 0.1 g L^{-1}; 2, (■), 0.2 g L^{-1}; 3 (×), 2 g L^{-1}; 4 (▲), 1 g L^{-1}].

As the catalyst loading is increased, there is an increase in the surface area of the catalyst available for adsorption and degradation. However, increase in the catalyst loading increases the solution opacity leading to decrease in penetration of the photon flux in the reactor, thereby decreasing the photocatalytic degradation rate.

Effect of pH

The wastewaters coming from different industries have different *p*H, and consequently it is an important parameter that affects the rate of degradation. The photocatalytic degradation of CFX not only depends on TiO_2 concentration but also on *p*H of the CFX solution, since it determines the surface charge properties of the photocatalyst and therefore the adsorption behavior of the organic substrate. The influence of *p*H on the rate of photocatalytic degradation of CFX was studied at *p*H ranging from 5 to 11. In the alkaline range, the *p*H was varied using aqueous 0.1 *N* NaOH, whereas in the acidic range, *p*H was varied using 0.1 *N* $HClO_4$. Initial concentration of CFX was 100 mg L^{-1} and catalyst loading of 1 g L^{-1} was used in all these experiments. The rate of photocatalytic degradation of CFX studied at different *p*Hs shows that it is strongly influenced by the solution *p*H. It was observed that rate of photocatalytic degradation of CFX was higher in weak basic (*p*H 9) solution than in weak acidic (*p*H 5) and strong alkaline (*p*H 11) conditions. The TiO_2 surface will remain positively charged in acidic medium (*p*H < 6.25) and negatively charged in alkaline medium (*p*H > 6.25). Due to this, under acidic condition (*p*H 5) CFX is positively charged which is the same as the TiO_2 surface, resulting in repulsion between the two. Under strongly basic conditions, both TiO_2 and CFX are negatively charged (*p*H 11) which causes repulsion between them and hence the rate of photocatalytic degradation also decreases. A similar result was also observed by Torniaine *et al.*[17] for photochemical degradation of CFX irradiated with a high pressure mercury lamp at 313 nm. CFX is an ampholytic compound with *pK* values of 6.09 for the carboxylic group and 8.74 for the nitrogen on the piperazinyl ring. The isoelectric point of the zwitterion is at *p*H 7.4 and CFX seemed to be most sensitive to photodegradation in zwitterionic form at slightly basic *p*H. The maximum stability of the drug was observed in solutions at *p*H 3.0–4.0, where the COOH group is not ionized and the basic nitrogen is completely protonated. From the practical point of view, the stability of CFX in acidic environment is important because the *p*H of liquid pharmaceuticals formulation varies between 3.5 and 5.5 [17].

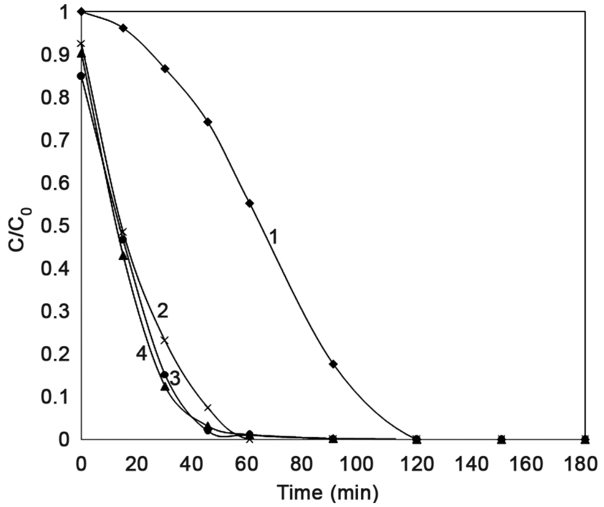

Fig. 6—Effect of co-existing ions on photocatalytic degradation of CFX using solar radiation. [Initial CFX conc.: 100 mg L^{-1}, Aeroxide® P-25 TiO_2 photocatalyst: 1 g L^{-1}. 1 (♦), Na_2CO_3 = 500 mg L^{-1}; 2 (×), absence of salt; 3 (●), NaCl = 500 mg L^{-1}; 4 (▲), $(NH_4)_2SO_4$ = 500 mg L^{-1}].

Effect of co-existing ions

Industrial effluents contain different salts at different levels of concentration apart from pollutants. The salts are generally ionized under the conditions of photocatalytic degradation. The anion and cation parts of the salt have different effects on the photocatalytic degradation[14,18]. Figure 6 shows the effect of presence of various anions such as chloride, sulfate and carbonate using 500 mg L^{-1} solution of their sodium salts and initial concentration of 100 mg L^{-1} of CFX with 1 g L^{-1} TiO_2 loading. Sodium carbonate has a substantially detrimental effect on the photocatalytic degradation of CFX. However, in the case of ammonium sulfate and sodium chloride, the reduction in CFX concentration was nearly same as that in the absence of the anions. Previous studies have also concluded that carbonate anions have strong negative effect on photocatalytic degradation[18].

Mechanism of photocatalytic degradation of CFX

It is known that the mechanism of photocatalytic degradation of organic compounds takes place through the attack of $OH^{\bullet}$ on the substrate[14, 18]. An understanding of the mechanism of degradation of any pollutants is very important because during photocatalytic degradation of aromatic compounds various types of intermediates are formed and sometimes these intermediates are more hazardous /toxic than the parent compounds.

The intermediates formed during the photocatalytic degradation of CFX were monitored using UPLC-MS/MS. A total of six intermediates were detected and the corresponding molecular masses of these six intermediates were determined by using UPLC-MS/MS. The retention time, mass spectra and structure of the identified intermediates are summarized in Table S1 (Supplementary Data). From the HPLC analysis it was found that the concentrations of these intermediates (peaks area) increase dramatically during the first 15 min interval and then decrease rapidly with increase in time. Although, the exact concentrations of the intermediates could not be determined because of the lack of authentic standards of the intermediates, it was also observed that the concentration of these intermediates (peaks area) in the case of solar radiation is much less than under artificial radiation. This indicates higher concentrations of intermediates are formed during the photocatalytic degradation of CFX using artificial radiation. Similar intermediates were observed during the photochemical degradation of CFX by Hubicka *et al.*[19] and Maia *et al.*[20]. From these studies, three pathways are possible for the degradation of CFX: the electrons cleaving the nitrogen atoms, releasing them to the solution while $OH^{\bullet}$ radicals first attacks the double bonds in the rings and then the fluorine. The degradation can continue until the molecules are eventually fully mineralized.

Kinetic models of photocatalytic oxidation of CFX

The kinetics of photocatalytic degradation reaction is performed by varying the initial CFX concentration from 50 to 500 mg L^{-1} using solar and artificial radiation in presence of Aeroxide® P-25 TiO_2 photocatalyst. The linearity obtained between $\ln(C/C_0)$ versus t plot, where C_0 is the initial concentration of CFX (mg l^{-1}) and C is the concentration of CFX (mg l^{-1}) at irradiation time t (min), indicates the pseudo-first-order kinetics. The kinetic parameters are given in Table 1 where the rate constants are listed for solar and artificial radiation. The rate constants, k_{app} (min^{-1}) are seen to decrease with increasing concentration of CFX for both artificial radiation and solar radiation (Table 1). The rate constant values for solar photocatalytic degradation are higher than that under artificial radiation, which indicates that solar radiation is highly efficient.

Langmuir-Hinshelwood kinetic model was also tested for photocatalytic degradation of CFX by using Eq. (1),

$$r_0 = k_{app} C_0 = \frac{k_c K C_0}{1 + K C_0} \qquad \ldots (1)$$

where r_0 (mg L^{-1} min^{-1}) is the initial rate of the photocatalytic degradation, k_{app} (min^{-1}) is the apparent rate constant and k_c is the reaction constant depending on other factors influencing the process.

A linear expression can be conventionally obtained by plotting the reciprocal initial rate constant versus initial concentration:[21]

$$\frac{1}{k_{app}} = \frac{1}{k_c} C_0 + \frac{1}{k_c K} \qquad \ldots (2)$$

Figure 7 shows the plot of $1/k_{app}$ versus C_0 for artificial and solar radiation. Validity of the model

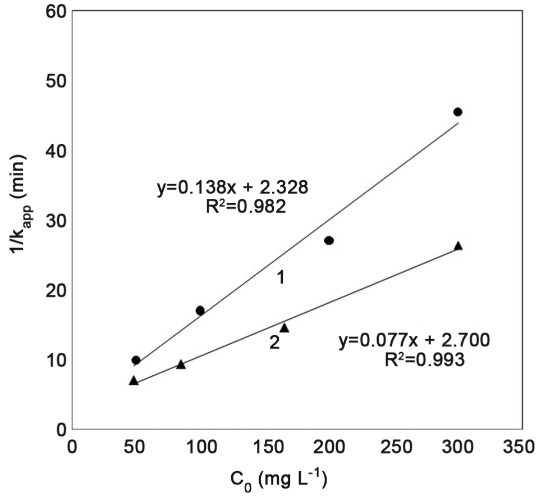

Fig. 7—Plots of $1/k_{app}$ versus C_0 for artificial radiation and solar radiation. [1 (●), artificial radiation; 2 ▲ solar radiation].

is confirmed by the linearity in the plot of reciprocal of rates ($1/r_0$) against reciprocal of initial CFX concentrations (C_0). The values of k_c and K were found to be 12.9 mg L^{-1} min^{-1} and 0.03 L mg^{-1} respectively for the photocatalytic degradation of CFX under solar radiation. However, under artificial radiation the values of k_c and K were 7.2 mg L^{-1} min^{-1} and 0.06 L mg^{-1} respectively.

Conclusions

The photolytic, photochemical, photocatalytic and photo-Fenton degradation of CFX was studied using concentrated solar radiation. The rate of degradation of CFX in the case of the photocatalytic method was found to be 87%, 10% and 15% higher than that of photolysis, photochemical and photo-Fenton method, respectively. The photocatalytic degradation of CFX in the presence of Areoxide® P-25 TiO_2 photocatalyst was found to be much more efficient under solar radiation as compared to under artificial radiation. Effect of various operating parameters on photocatalytic degradation of CFX was studied and the rate of photocatalytic degradation was found to be maximum at *p*H 9. The effect of co-existing ions shows that sodium carbonate has a substantially detrimental effect on the photocatalytic degradation of CFX. However, on a comparative basis, ammonium sulfate and sodium chloride do not show any significant effect on the rate of photocatalytic degradation. From kinetic studies, the photocatalytic degradation is seen to obey pseudo-first order kinetics with the rate constant under solar radiation about 1.7 times higher than that under artificial radiation. Six degradation intermediates were revealed by UPLC-MS/MS analysis. A tentative degradation mechanism of CFX is also proposed based on the experimental evidence.

Supplementary Data

Supplementary data associated with this article, i.e., Table S1, are available in the electronic form at http://www.niscair.res.in/jinfo/ijca/IJCA_55A(01)16-22_SupplData.pdf.

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