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Photocatalytic Degradation of Ciprofloxacin using TiO2 in a Slurry Photocatalytic Reactor: Optimization

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ABSTRACT

A slurry photocatalytic reactor assessed for the degradation of ciprofloxacin (CFX). The effect of operating parameters like initial ciprofloxacin concentration, catalyst dosage and pH on ciprofloxacin degradation was analysed in this study. Batch study was conducted and it showed 90% degradation of the CFX. It was observed the optimum concentration of CFX was 1500 µg/l, catalyst dosage was 1 g/l at the pH of 9 for the duration of 3 hours. The photocatalytic degradation of CFX followed the pseudo first order kinetics.

KEYWORDS: *Ciprofloxacin, Photocatalysis, TiO_2, Pharmaceutical compound*

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As the world's population grows higher the demand for fresh water also increase rapidly. The water bodies get polluted by the discharge of emerging contaminants such as pharmaceuticals, endocrine disruptors, surfactants, and personal care products, which are complex and resistant to degradation [1]. Pharmaceutical compounds found in drinking water, even in lower concentrations might have impact on health of the public. The source of pharmaceutical compounds in the water bodies are the municipal wastewater, hospital wastewater and the discharge from the pharmaceutical industries. There are no much research exists on the occurrence and the ultimate fate of pharmaceuticals in the water bodies in India despite being one of the world's leaders in pharmaceutical production and consumption [2]. Carbamazepine, ibuprofen, diclofenac, sulfamethoxazole, atenolol, triclocarban, trimethoprim, acetaminophen and caffeine are detected at higher concentration in Indian water treatment plants that treat predominantly the domestic sewage. The concentration of ciprofloxacin in Indian water treatment plants were up to 40 times higher than that in other countries. Few studies have found the presence of ciprofloxacin in the ground water. In a study reported from an open well in southern India, the groundwater showed the presence of ciprofloxacin, which was close to a water treatment plant receiving effluents from pharmaceutical production.[5] The concentration of the CFX can be reduced or degraded into simpler products water and carbon dioxide by advanced oxidation process (AOP) like ozonation, photo fenton process, sonolysis, photolysis and photocatalytic degradation [4]. This paper deals with the photocatalytic degradation of ciprofloaxin(CFX) using TiO_2 catalyst. TiO_2 has been the most widely used photocatalyst in the literature and most emerging catalysts due to its merits like photo and chemical stable, low cost, reusable and non toxic. [4]

Materials and methods:

Ciprofloxacin were obtained from Techsil laboratory Chennai and Titanium di Oxide was purchased from Lab chemicals, Chennai. The photocatalyst TiO_2 was a mixture of 70% of anatase and 30% rutile with BET surface area of 50m^2/g and band gap 3.2eV. Acetic acid, Acetonitrile, Hydrochloric acid, Sodium hydroxide purchased from Techsil laboratory were of HPLC grade.

Experimental setup:

A laboratory scale slurry photocatalytic reactor is shown in fig 1. The reactor of 2 litre volume made of plexiglas material consists of a T5 8W lamp and diffuser of dimension 311x22x32 mm, with 567 lumens, 230 Voltage and power current 125 mA of 650 nm tungsten halogen lamp. In order to provide uniform irradiation, lamp is placed at the center

of the reactor. The slurry was continuously stirred using a magnetic stirrer.

Analytical studies:
Experimental procedure:
The reaction mixture was prepared by adding known concentrations of ciprofloxacin and catalyst in distilled water.

Fig: 1 Slurry photocatalytic reactor.

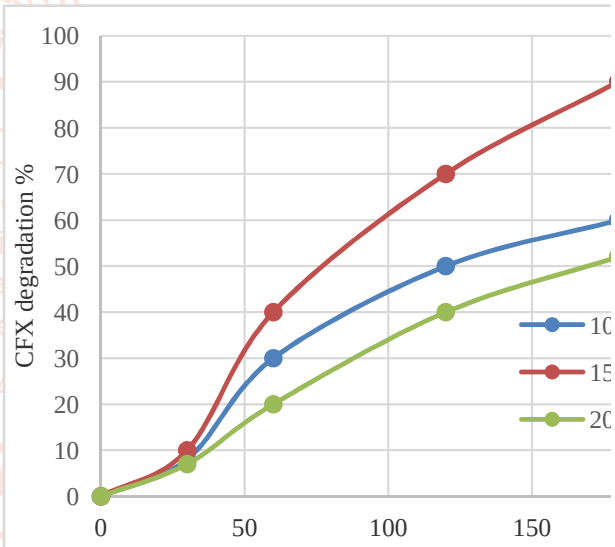
During all experiments, the reaction sample was kept in dark (in the absence of light) for 30 min so that the ciprofloxacin would adsorb on the catalyst surface. Batch studies were carried out for 3 h with optimum concentrations of ciprofloxacin from dark adsorption test and catalyst dosage 0.5 g/l, 1 g/l, 1.5 g/l. After optimizing the catalyst concentration, the pH of the reaction mixture was varied from 3 to 9 and optimized. The required pH variations were carried out by 0.1 M NaOH and 0.1 M HCl.

Degradation studies:
High performance liquid chromatographic (HPLC) method was used for the quantitative analysis of ciprofloxacin. In this analysis, the mobile phase used was acetonitrile-2% acetic acid aqueous solution and a non-polar stationary phase RP-C18 column was employed. The wavelength for the UV detector is set at 280 nm. The limit of detection (LOD) was found to be 0.25 µ M. For the pharmaceutical analysis of ciprofloxacin, the regression equations are linear over a range between 0.50 -120 µ M. The relative standard deviation and relative error are less than 5% and 4.65%, respectively. The recoveries were found to be around 90%. [10]

Results and discussions:
CFX – TiO_2 dark adsorption test:
Dark adsorption tests were carried to assess the possible adsorption of CFX on TiO_2 photocatalyst surface. To carry out this adsorption, two litre sample containing 1000 µg/l CFX, 0.5 g/l TiO_2 was covered with aluminium foil sheet and kept in dark for 24 h. The sample was analysed for CFX concentration and the results showed 10% of CFX were adsorbed onto TiO_2 surface.

Photocatalytic experiments:
Photocatalytic experiments were carried out by varying CFX concentration viz (1000 µg/l, 1500 µg/l and 2000 µg/l), TiO_2 dosage (0.5, 1, 1.5 g/l). The Ph of the sample was 6.5. Samples were collected at every half an hour of 3 hours, centrifuged, decanted and analysed. The temperature maintained during the experiment was 23°C

Effect of CFX concentration: The effect of CFX concentrations on degradation were studied by varying the CFX concentrations like 1000 µg/l, 1500 µg/l, 2000 µg/l. Samples of 20 ml were collected from the reactor from each concentration from the reactor after completion of the photocatalytic process and CFX concentration was analysed by HPLC, at 1500 µg/l the rate of degradation was found to be 90% also it was noticed that the increase in the CFX concentration from 1500 µg/l to 2000 µg/l decreases the degradation from 90 % to 52 % efficiencies, this may be due to the increase in CFX concentration along with TiO_2, the reason might be the hydroxyl radicals available is less for the higher amount of CFX concentration. Fig 2. Show the CFX degradation efficiency with respect to time for every 30 minutes for three-hour duration and also with varying CFX concentrations.



Effect of TiO_2 concentration: The optimum TiO_2 dosage for this study was obtained as 1 mg/l. As the TiO_2 loading increases from 0.5 to 1 mg/l, the CFX degradation efficiency also increased from 45 % to 90% further increase in the catalyst reduced the degradation efficiency from 90 to 38 %, the reason might be the increase in catalyst dosage from 0.5 g to 1 g/l, the amount of catalyst surface also increases therefore the adsorption of the ciprofloxacin is increased. However further increase in the catalyst, TiO_2 from 1 to 1.5g/l, the degradation efficiency decreases, this might be due to the reduction in the surface area available for irradiation due to photocatalytic process, also increase in the TiO_2 concentration led to the solution turbid and caused the low penetration of the photons through the solution thus finally led to the degradation efficiency. Fig 3. Show the CFX degradation efficiency with respect to time for every 30 minutes for three-hour duration and also with varying TiO_2 catalyst dosage.

Effect of pH: In this study it was observed that the photocatalytic degradation of CFX was higher when the reaction mixture was basic than acidic. The effect of pH in the photocatalytic degradation of CFX has shown in fig:4. pH

range was kept from 3 to 9. At pH 3 and 9 the degradation efficiency was 48% and 90% with 1500 µg/l CFX concentration and 1 g/l TiO_2 catalyst dosage respectively. The reason for higher degradation percentage of CFX at pH 9 could be the opposite surface charges between TiO_2 and CFX. Fig 4. Show the CFX degradation efficiency with respect to time for every 30 minutes for three-hour duration and also with varying pH of the reaction mixture.

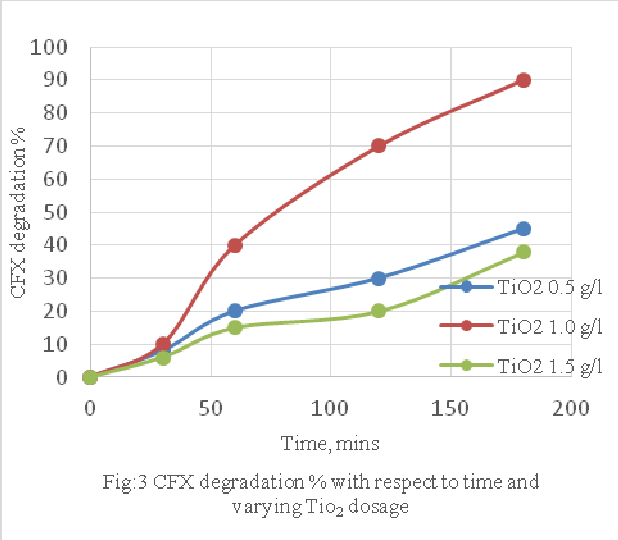


Fig:3 CFX degradation % with respect to time and varying Tio_2 dosage

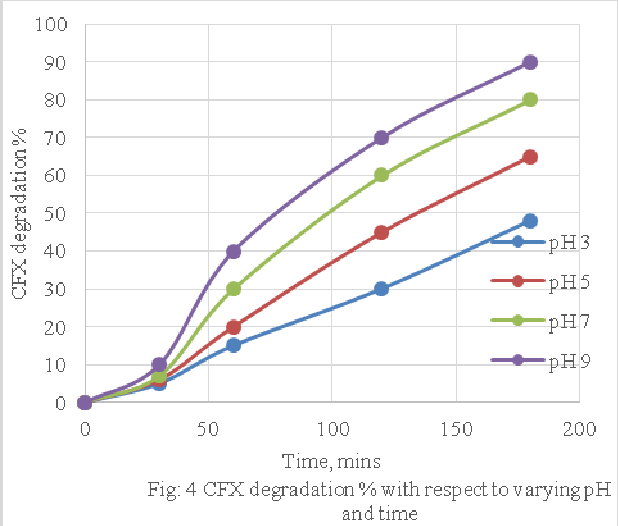


Fig: 4 CFX degradation % with respect to varying pH and time

Kinetics of CFX degradation: In this study, the CFX degradation followed pseudo-first-order kinetics.

$$\frac{d[CFX]t}{dt} = k[CFX]0,$$

$$\text{In}\ \frac{[CFX]0}{[CFX]t} = -kt$$

Where $[CFX]_t$ in µg/l the CFX concentration at time t; $[CFX]_0$ in µg/l the initial CFX concentration; t (min) is the reaction time k (min^{-1}) is the pseudo first order rate constant. In table 1 k and R^2 rate constant values for various CFX concentration, showing pseudo first order kinetics.

Table: 1 Rate of CFX degradation

CFX concentration (µg/l)	k (min^{-1})	R^2 value
1000	0.105	0.99
1500	0.072	0.96
2000	0.020	0.95

Conclusion:

A slurry photocatalytic reactor with 650 nm, 8 W tungsten halogen lamp assessed for CFX degradation. Photocatalytic process carried out for three hours duration, the optimized values for the operating parameters obtained as follows. CFX concentration = 1500 µg/l, TiO_2 dosage = 1 g/l, pH = 9 and the maximum CFX degradation efficiency = 90%. From the kinetics study the photocatalytic degradation follows pseudo first order kinetics.

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