

# Improvement of the Overall Biodegradability of Ciprofloxacin by Pre-treatment with Photocatalytic Oxidation of Wastewaters

Nevim Genç

Department of Environmental Engineering, Faculty of Engineering, Kocaeli University, 41380, Kocaeli, Turkey  
✉ ngenc@kocaeli.edu.tr

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**Abstract:** In this study, photocatalytic degradation of ciprofloxacin (CIP) was investigated. CIP is a widely used quinolone antibiotic. Removal of CIP in the dark is negligible. The removal efficiency by photolysis of CIP was 25.3%. The removal efficiencies after 30 min irradiation were 85%, 93.5% and 97% at pH values 3, 6 and 9 in the presence of 0.5 g/L  $\text{TiO}_2$ , respectively. Modified form of the Langmuir-Hinshelwood equation has been successful as a quantitative model to describe solid-liquid interactions. Kinetic constant  $k$  is reactivity constant,  $K$  is the adsorption equilibrium constant and  $k_{\text{ap}}$  (kK) is the apparent first order reaction constant, these were determined as 0.673 mg/L min, 0.662 L/mg and 0.445 (1/min), respectively. The results showed that after 30 min irradiation of CIP, solution was degraded 95%, whereas COD removed was 40.3%. The enhancement of biodegradability, evaluation in terms of the  $\text{BOD}_5/\text{COD}$  ratio, increased from 0.043 to 0.403. This increase is not sufficient for treatment in conventional activated sludge unit. Additionally, the biodegradability of CIP photo-transformation products was assessed by BOD test.  $k$  (1/d), BOD reaction rate constants were determined as 0.0857 (1/d) and 0.1778 (1/d) for untreated and treated CIP solution, respectively.

**Key words:** Biodegradability, Ciprofloxacin, Langmuir-Hinshelwood kinetic, photocatalytic oxidation.

## Introduction

The occurrence, fate, effects and risks of pharmaceuticals as micropollutants in the aqueous environment has attracted attention. Antibiotics often have little to no biodegradability and can have toxic effects on bacteria. The presence of antibiotics could threaten the function of ecosystem. The most dangerous effect of antibiotics is the development of multi-resistant bacterial strains in the environment (Yuan et al., 2011).

Fluoroquinolones (FQ) are a family of synthetic, broad-spectrum antibacterial compounds. The widely used quinolone antibiotic is ciprofloxacin (CIP;  $\text{C}_{17}\text{H}_{18}\text{O}_3\text{N}_3\text{F}$ ). It has empirical formula  $\text{C}_{17}\text{H}_{18}\text{O}_3\text{N}_3\text{F}$  and molecular weight 331.34. It is known that FQs are incompletely metabolized by human body, a significant

fraction (ranging from 20 to 80%, and up to 90% have been reported) is excreted in their pharmacologically active forms, and discharged into municipal sewerage systems (Paul et al., 2010). Unfortunately, conventional sewage treatment plants are not able to degrade many pharmaceutical compounds and their residues, and as a result many of these chemical species are transported to natural bodies of water. Residual amounts of pharmaceuticals can reach surface waters, groundwater or sediments (Gad-Allah et al., 2011).

The reported fates of fluoroquinolones in the natural aquatic environment have been attributed to three physico-chemical processes, namely, photodegradation, adsorption and biodegradation, with biodegradation the least apparent. The biodegradability of 18 antibiotics and their effects on environmental population was

studied by the Closed Bottle Test (CBT) (OECD 301 D 1992). A toxicity control and colony forming units were monitored. Some antibiotics were partially or even completely disappeared by a non-biotic mechanism. In the case of some antibiotics, partial biological removal took place in presence of readily biodegradable sodium acetate. In the toxicity control, toxicity had not been eliminated (Alexy et al., 2004). More importantly from the point of view of wastewater treatment, the removal of fluoroquinolones from raw sewage is mainly by way of incorporation into sludge, but the vestigial concentrations of these antibiotics in (treated) secondary effluents are still of the order of  $3 \times 10^{-10}$  to  $3 \times 10^{-8}$  mol/dm<sup>3</sup>. In the literature it is described that specific conditions can lead to CIP environmental concentrations 5-20,000-fold higher than that reported usually. CIP can adsorb to sludge, sediment and soil. Levels of CIP found in the environment can be a risk (Vasconcelos et al., 2009).

Physiochemical treatment processes are required to minimize environmental discharges. Effective techniques such as adsorption, air stripping and advanced oxidation processes have been proposed to remove pharmaceutical compounds from wastewater. Advanced oxidation processes (AOPs) are an alternative to degrade the antibiotic (An et al., 2010). These processes depend on the production of reactive hydroxyl radicals that are able to degrade organic compounds. One of these processes is the heterogeneous photocatalysis, in which semiconductors are used as photocatalysts (Gad-Allah et al., 2011).

Degradation pathways and byproducts in the photolysis and photocatalysis of CIP are explained (De Lima Perini et al., 2013; Babic et al., 2013; Van Doorslaer et al., 2011; Ge et al., 2010; Wei et al., 2013; El-Kemary et al., 2010; Li et al., 2012; Sturini et al., 2012). The oxidation of CIP could be clarified into two stages. The first stage was the generation of toxic byproducts. The second stage was when these more toxic byproducts were further converted to non-toxic byproducts such as 1,4-benzenedicarboxylic acid, propanedioic acids, glycerin and some aliphatic acids etc. (Yuan et al., 2011). The photodegradation pathways of FQs are proposed according to the photoproducts, which involve three main pathways: photoinduced decarboxylation, hydroxylated defluorination, and piperazinyl N<sup>4</sup>-dealkylation (Ge et al., 2010). It was suggested that the photodegradation of CIP would start with the loss of the piperazine ring; with longer irradiation time, it would be further photodegraded by the loss of the fluorine atom. The toxicity did not

decrease due to the formed product; CIP was degraded very easily even by UV direct photolysis (Yuan et al., 2011). Direct photolysis caused fluorine substitution and reductive elimination, while photocatalysis caused oxidative degradation of the amine side-chain (Sturini et al., 2012).

This paper reports an investigation of whether photocatalytic oxidation of CIP can improve its overall biodegradability, deployed as a pre-treatment step prior to biological treatment.

## Materials and Methods

### Materials

Ciprofloxacin hydrochloride with purity higher than 99% was obtained from SANOVEL. This commercially available product contains no more than 0.2% by weight of the by-product contaminant fluoroquinolonic acid. CIP used in the experiments is the commercial product, with a molecular weight of 367.80. All the other chemicals were of analytical grade and were used without further purification. The secondary sludge used as inoculum in BOD (biological oxygen demand) test was supplied from the wastewater treatment system of Kocaeli University Campus which is treated hospital and domestic wastewater. Sludge was used after washed with distilled water. The sludge was not acclimated to the CIP.

### Photooxidation Experiments

Experiments were performed in an open batch system. The reaction solution was mixed by a magnetic stirrer. An aliquot of 100 mL antibiotic aqueous solution was placed in a 200 mL beaker with the required amount of TiO<sub>2</sub> and was stirred magnetically at room temperature. UV lamp with power of 125 W (HPR 125 W HG Philips) was used as the light source. Relative spectral power distribution of lamp is in the wavelength range of 300-700 nm. Luminous flux and luminous efficacy of lamp are 2900 lm and 23.2 lm/W, respectively. The concentration of CIP was 10 mg/L. The mixture of CIP solution with TiO<sub>2</sub> was stirred in the dark for 30 min to achieve adsorption-desorption equilibrium. Also, photolysis of CIP solution without TiO<sub>2</sub> was investigated. The effect of different experimental conditions such as TiO<sub>2</sub> dose, initial pH and irradiation time on reaction rate was investigated in the combination (UV+TiO<sub>2</sub>). The pH value of mixture was adjusted by HCl and NaOH solution.

After pre-defined irradiation periods, the solution was filtered to separate the photocatalyst. The concentrations

of CIP in the residual solutions were analyzed by means of the UV spectrometer (Hach-Lange DR 5000). The concentration of CIP was analyzed at the maximum wavelength. The calibration curve was established with standards between 0 and 70 mg/L CIP with the coefficient of determination (the correlation coefficient,  $R^2 = 0.9983$ ).

### Biodegradability Test

The biodegradability of photocatalytically treated and untreated CIP solution were evaluated in BOD tests. Photocatalyzed CIP solution was submitted to BOD test in order to obtain biodegradability information of the by-products formed during the photo-process. The supernatant obtained from photocatalyzed sample at optimum experimental conditions was used in BOD test which is listed in contents of Table 1. The biodegradability of photocatalytically untreated and treated CIP by sludge was determined in Runs 1 and 2, respectively. In Run 3, the activity of the sludge was determined by adding glucose which is the substrate for sludge. BOD test was made by using Lovibond BOD-Sensor and Inductive Stirring System.

**Table 1: Contents of BOD test for the biodegradability untreated and treated CIP**

Run	Content
1	428 mL photocatalytically untreated CIP + 0.5 mL A solution + 0.5 mL B solution + 0.5 mL C solution + 0.5 mL D solution + 0.4 mL sludge
2	428 mL photocatalytically treated CIP + 0.5 mL A solution + 0.5 mL B solution + 0.5 mL C solution + 0.5 mL D solution + 0.4 mL sludge
3	428 mL of glucose solution + 0.5 mL A solution + 0.5 mL B solution + 0.5 mL C solution + 0.5 mL D solution + 0.4 mL sludge

*Note:* The glucose solution of 15 mg/L was used. The solids content of sludge was 17 g/L. In BOD tests, the nitrification inhibitor was not used.

Solution A consists of 21.75 g/L  $K_2HPO_4$ , 8.5 g/L  $KH_2PO_4$ , 33.4 g/L  $Na_2HPO_4 \cdot 7H_2O$ , 1.7 g/L  $NH_4Cl$ . Solution B consists of 22.5 g/L  $MgSO_4 \cdot 7H_2O$ . Solution C consists of 27.5 g/L  $CaCl_2$ . Solution D consists of 0.25 g/L  $FeCl_3 \cdot 6H_2O$ .

## Result and Discussion

### Effect of pH on CIP Removal

pH determines the surface charge of the photocatalyst and thus the adsorption behaviour of the organic substrate (Gad-Allah et al., 2011). A positive relationship

is detected between the photocatalytic FQ degradation rate and the fraction of FQ adsorbed onto the catalyst surface depending on pH. The results showed that mainly the single positively charged and zwitter FQ ion participate in the adsorption process, explaining the highest photocatalytic degradation at pH 7 (Van Doorslaer et al., 2011).

In this study, effect of pH on the photocatalytic reaction was conducted in the pH range 3-10, with the  $TiO_2$  dosage 0.5 g/L. Figure 1(a) shows the effect of pH on the degradation in terms of CIP removal. The removal efficiencies after 30 min irradiation were 85%, 93.5% and 97% at pH 3, 6 and 9, respectively. The removal of CIP was higher in alkaline condition than in neutral and acidic conditions. The removal of CIP reached the maximum at pH 9-10. The use of high pH add extra cost for the treatment. Therefore considering the operating cost, pH of CIP removal was chosen to be 6, which is the natural pH of CIP solution.

The ionization behaviour of the surface of the photocatalyst can be protonated and deprotonated under acidic and alkaline conditions, respectively, as shown in Equations (1) and (2). The point of zero charge (pzc) of the  $TiO_2$  is reported at pH 6.25. Thus, the  $TiO_2$  surface will remain positively charged in acidic medium ( $pH < 6.25$ ) (Equation 1) and negatively charged in alkaline medium ( $pH > 6.25$ ) (Equation 2) (Gad-Allah et al., 2011; Li et al., 2012). The high rate of reaction in case of natural pH might be due to the available protons from  $NH_2^+$  and  $COOH$  groups of CIP, which interact with  $TiO_2$  surfaces according to Equ. 1, i.e., protonation of  $TiO_2$  by CIP itself. This leads to the formation of negatively charged CIP, molecules which can be adsorbed efficiently on the positively charged  $TiO_2$  surface (Gad-Allah et al., 2011).



### Effect of Catalyst Dose on CIP Removal

The CIP solution (with 0.5 g/L  $TiO_2$ ) is stirred under darkness. Results showed that removal of CIP in the dark is negligible. After 30 min irradiation of CIP solution at optimal pH and without  $TiO_2$ , the removal efficiencies by photolysis of CIP was 25.3%. Photocatalyst affects on the CIP removal and consequently on the cost of treatment. Effect of  $TiO_2$  dosage was investigated at optimal pH with different  $TiO_2$  loads ranging from 0.1 to 1 g/L (Figure 1b). Results showed that CIP removal with a  $TiO_2$  dosage of 0.1 g/L increased to 90%. Addition of excess  $TiO_2$  increases the total surface area exposed to

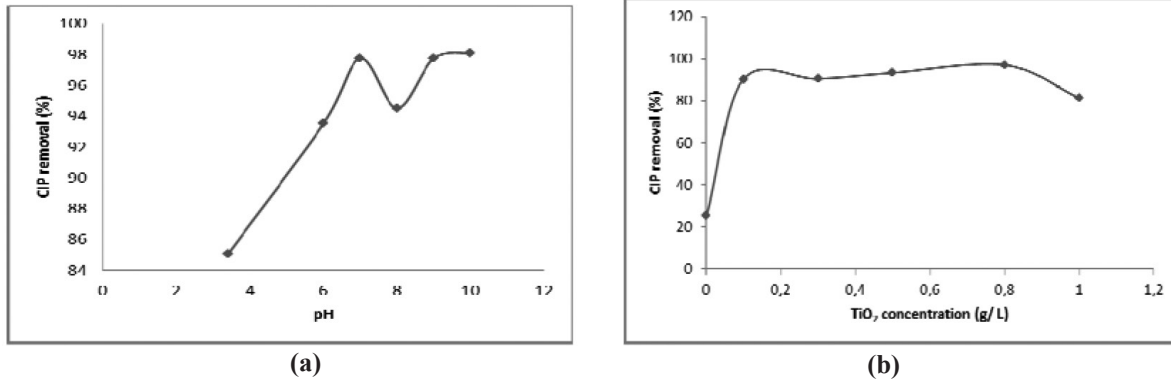


Figure 1: Influence of pH (a) and catalyst amount (b) on CIP removal.

light; therefore more free radicals would be generated. On the other hand, the number of active sites available for CIP adsorption was increased by the addition of excess TiO<sub>2</sub>. These two factors explain the dependency of reaction rate on photocatalyst concentration (Gad-Allah et al., 2011). Increasing catalyst dosage from 0.1 to 0.8 g/L, resulted in the increased number of active sites for photocatalytic reaction, removal of CIP increased from 90.1% to 97.1%. Further increase of TiO<sub>2</sub> dosages above 0.8 g/L decreased the degradation efficiency. High concentration of TiO<sub>2</sub> may impede further penetration of light. There was no significant change in the percentage of degradation, increasing from 0.1 g/L to 0.8 g/L of TiO<sub>2</sub> dosage. Therefore the optimum TiO<sub>2</sub> dosage was 0.1 g/L.

### Kinetic Analysis

Langmuir-Hinshelwood (L-H) kinetic is known to be a good model for the description of solid-gas reactions. Extrapolation of this model to solid-liquid reactions requires some modifications (Zhang et al., 1998).

Competition in the absorption of the substrate and water molecules on the catalyst surface cannot be ignored. These simultaneous adsorptions influence the observed reaction kinetics. In such a case, modified form of the L-H equation has been successful as a quantitative model to describe solid-liquid interactions (Yurdakul et al., 2007; Montazerzohori and Hasanalian, 2013). According to L-H kinetic treatment, the rate of a surface reaction can be calculated by Equation (3) (Başer, 2000).

$$R = -\frac{dC}{dt} = k\theta = k \frac{K[C_o]}{1 + K[C_o]} \quad (3)$$

where  $R$  is the rate of the oxidation,  $k$  is the reactivity constant,  $\theta$  is the fraction of surface covered,  $K$  is the adsorption equilibrium constant, and  $C_o$  is the initial

concentration of the substrate. The obtained expression by integration of Equation (3) is given in Equation (4),

$$t = \frac{1}{kK} \ln \left[ \frac{C_o}{C_t} \right] + \frac{1}{k} ([C_o] - [C_t]) \quad (4)$$

The half life of the reaction ( $t_{1/2}$ ) is given in Equation (5)

$$t_{1/2} = \frac{0.693}{kK} + \frac{0.5[C_o]}{k} \quad (5)$$

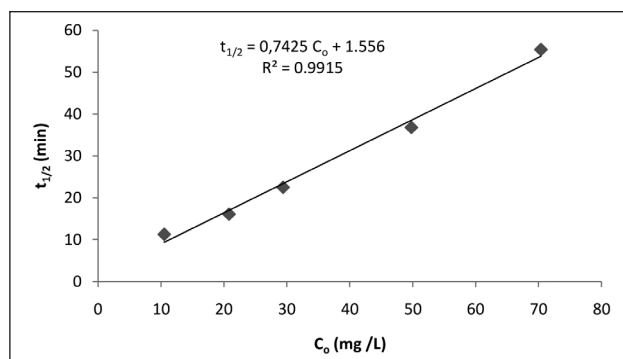
A plot of  $t_{1/2}$  versus  $C_o$  should yield a straight line whose slope is  $0.5/k$  and whose intercept is  $0.693/kK$ .  $k_{ap}$  ( $kK$ ) is the apparent first order reaction constant (Genç and Doğan, 2006). To determine the L-H kinetic constants, CIP solutions of different initial concentration ( $C_o$ ) were photocatalyzed in 0.1 g/L TiO<sub>2</sub> dose. For each  $C_o$  by graphing  $C_t$ , the CIP concentration with respect to  $t$ , the illumination time, the expression giving the relationship between  $C_t$  and  $t$  was obtained. In this expression,  $t_{1/2}$  is the illumination time value corresponding to  $C = C_o/2$ . The equation and  $t_{1/2}$  values thereby calculated are given in Table 2. The relationship between  $C_o$  and  $t_{1/2}$  is expressed by the linear equation (6) given below (Figure 2).

$$t_{1/2} = 0.7425C_o + 1.556 \quad (6)$$

Table 2: Relationship between  $C_t$  and  $t$  and  $t_{1/2}$  values for different initial CIP concentrations

$C_o$ (mg/L)	The linear relation between $C_t$ (mg/L) and $t$ (min)	$R^2$	$t_{1/2}$ (min)
10	$C_t = -0.3597t + 9.3379$	0.8976	11.33
20	$C_t = -0.5971t + 20.039$	0.9408	16.14
30	$C_t = -0.614t + 28.538$	0.9712	22.53
50	$C_t = -0.609t + 47.376$	0.9350	36.84
70	$C_t = -0.6733t + 72.538$	0.9304	55.40





**Figure 2: Observed half-life profile of the different initial concentrations of CIP.**

In this study, constants were calculated according to equations (7-9)

$$\frac{0.5}{k} = 0.7425 \quad k = 0.673 \text{ mg/L min} \quad (7)$$

$$\frac{0.693}{kK} = 1.556 \quad k = 0.662 \text{ L/mg} \quad (8)$$

$$kK = k_{ap} = 0.445 \text{ (1/min)} \quad (9)$$

In this study, the half-time increased from 11.3 min at  $C_0$  10 mg/L to 55.40 min at  $C_0$  70 mg/L. The average apparent first order reaction rate constant was 0.445 (1/min). An et al. (2010) found that CIP was degraded rapidly using a typical AOPs, with half-lives 1.9-10.9 min depending upon pH values, at 100  $\mu$ M CIP. The rate constants increased from 0.06 (1/min) at pH 3 to 0.38 (1/min) at pH 9.0 (An et al., 2010).

### Evaluation of Biodegradability

Generally, AOP has ability to entirely destroy the antibiotic, but antibiotics will not be fully mineralized. In many cases, degradation products are more biodegradable and less toxic than the original substrate, thus implying that a biological post-treatment may be feasible (Yuan et al., 2011).

In this study, CIP was degraded 95% after 30 min irradiation, whereas COD was removed 40.3%. End-products formed during photooxidation tend to be refractory to oxidation by chemical means. Study by Vasconcelos et al. (2009) demonstrated that 36% and 20% of the initial concentration of CIP were found in solution after 2 and 4 min irradiation time, respectively. Samples which were irradiated exhibited no difference from those prior to treatment, demonstrating that biodegradability was not increased by photoprocess (Vasconcelos et al., 2009).

The  $BOD_5/COD$  ratio is usually determined to analyze the difficulty of organic substances to be degraded. The biodegradation starts immediately and runs rapidly with a ratio of  $BOD_5/COD$  in the range over or equal to 0.5 (Kajitvichyanukul and Suntronvipart, 2006). The biodegradability of the untreated and treated CIP solution was estimated. The initial value of the  $BOD_5/COD$  ratio was 0.043, which is represented relatively low biodegradability. The enhancement of biodegradability, evaluation in terms of the  $BOD_5/COD$  ratio, increased from 0.043 to 0.403. Nevertheless, this increase is still not enough to support treatment in conventional activated sludge unit. The biodegradability of CIP photo products was assessed by BOD test.

The decomposition rate of organic matters at BOD test conditions is proportional to the waste concentration. On account of this, a first-order reaction model can be taken into consideration for describing BOD reactions. An integrated kinetic equation can be written as follows:

$$L_t = L_0 e^{-kt} \quad (10)$$

where  $L_t$  (mg/L) is the amount of remaining oxygen after time  $t$ ,  $L_0$  (mg/L), the ultimate carbonaceous oxygen demand and  $k$  (1/d), BOD reaction rate constant.

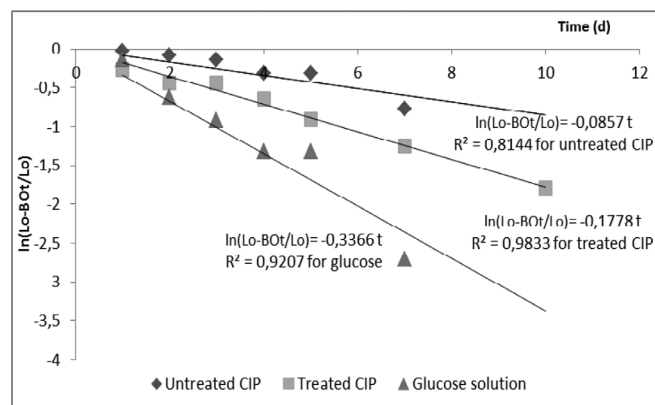
$$L_0 = BOD_t + L_t \quad (11)$$

where  $BOD_t$  is the amount of oxygen consumed by the waste in the first  $t$  days and  $L_t$  the amount of oxygen remaining to be consumed after time  $t$ .

Combining Eqs. (10) and (11) gives Equation (12)

$$\ln\left(\frac{L_0 - BOD_t}{L_0}\right) = -kt \quad (12)$$

For mathematical analysis of reaction rate constant were given the curves  $\ln(L_0 - BOD_t/L_0)$  vs. time (Figure 3). According to Figure 3,  $k$  value of CIP was increased from 0.0857 to 0.1778 (1/d) by 30 min pre-treatment. Higher  $k$  value which is 0.3366 (1/d) was determined in the degradation of glucose by sludge. This result shows that the activity of the used sludge is higher, and pre-treatment increased the biodegradability of CIP. It was found that the integration of photochemical and biological processes, the photo-pretreatment is the most effective step. Irradiation time is short enough to achieve a cost efficient process and high biological and overall efficiencies. The phototreated CIP solution may be introduced into the biological treatment.



**Figure 3: Variation of  $\ln(L_0 - BOD_t/L_0)$  vs. time for untreated and treated CIP, and glucose solution.**

### Conclusion

The photodegradation and biodegradability of CIP was investigated. Removal of CIP in the dark is negligible, whereas the removal efficiencies by photolysis of CIP was 25.3%. The system performance was affected by pH. The removal efficiencies after 30 min irradiation were 85%, 93,5% and 97% at pH 3, 6 and 9 in the presence of 0.5 g/L  $TiO_2$ , respectively. The removal of CIP reached the maximum at pH 9-10. High pH should be used, which adds extra cost for the treatment. Therefore, optimum pH of CIP removal was pH 6, which is the natural pH of CIP solution. Increasing catalyst dosage from 0.1 to 0.8 g/L, resulted in the increased number of active sites for photocatalytic reaction, removal of CIP increased from 90.1% to 97.1%.

Modified form of the Langmuir-Hinshelwood equation has been successful as a quantitative model to describe solid-liquid interactions. Kinetic constant  $k$  is reactivity constant,  $K$  is the adsorption equilibrium constant and  $k_{ap}$  (kK) is the apparent first order reaction constant; these were determined as 0.673 mg/L min, 0.662 L/mg and 0.445 (1/min), respectively.

Biodegradability of CIP photo-transformation products was assessed by BOD test. The results showed that after 30-minute irradiations, the  $BOD_5/COD$  ratio increased from 0.043 to 0.403. This clearly demonstrated the increase of biodegradability of molecular fragments resulting from irradiation. CIP solution was degraded 95%, whereas COD was removed 40.3%. BOD reaction rate constants  $k$  (1/d) were determined to be 0.0857 (1/d) and 0.1778 (1/d) for untreated and treated CIP solution, respectively.

In conclusion, this work has demonstrated that photo-oxidation of CIP on a  $TiO_2$  catalyst enhances overall biodegradability of the potential water pollutant.

Therefore irradiation by light of appropriate wavelengths can be recommended as a step to be taken prior to biological treatment, and this possibility can be extended to other refractory organic compounds, and investigated further.

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