

Photocatalytic degradation of diclofenac (an emerging contaminant): Effects of photocatalyst amount and air flow rate

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ABSTRACT

Photocatalytic degradation of diclofenac, an anti-inflammatory drug, was investigated with TiO₂ photocatalyst under UV light (365nm). The effects of photocatalyst concentrations (0.5 g/L, 1 g/L and 2 g/L) and air flow rates (3L/h, 6 L/h, 12 L/h and 18 L/h) on photodegradation kinetic were evaluated for 15 mg/L diclofenac solution during 4 hours. The results showed that the amount of TiO₂ and air flow rates have direct influence on the photocatalytic degradation of diclofenac. Excessive catalyst amount and high air flow rates inhibited the degradation of diclofenac. The highest diclofenac degradation efficiency of 78.4 % were achieved by 6 L/h air flow rate with a photocatalyst concentration of 0.5 g/L. The photocatalytic degradation of diclofenac followed the Langmuir-Hinshelwood kinetic model except the experiments carried without air flow and very low air flow rates.

Keywords: Diclofenac; Photocatalytic degradation; Photocatalyst; Air flow rate.

INTRODUCTION

Emerging pollutants are chemical or biological species that have detrimental effects to environment and harmful for health. Emerging pollutants refers as “contaminants of emerging concern” due to the fact that there is no long-established study about “emerging pollutants” [1]. Emerging pollutants enter environment and drinking water by discharged from sewage treatment plants or after being leached fertilizers that applied in farmlands [2].

Emerging pollutants are chemical and biological agents not normally found in researched media, cause known or suspected adverse effects to environment or human health [3]. Recently, as the world population increased, and the existence of pharmaceutical pollutants in natural water sources have extended to the levels that increases concern for natural water sources. Pharmaceutical pollutants in water have recently been found in a wide variety of concentrations. These pollutants and their metabolites began to reach harmful pollution levels [4]. Diclofenac (DFC), which is an anti-inflammatory drug, is extensively used to treat inflammation and pain. Because of its limited biodegradation, it has commonly been detected in wastewater treatment plants and rivers [5, 6]. Due to its ecotoxicity and low removal percentages in the waste water treatment plants (WWTPs), this drug compound was included in the List of Priority Contaminants, regulated by European Union [7].

The methods used in wastewater treatment and disposal in the pharmaceutical industry are quite extensive. Many alternative treatment processes such as coagulation/flocculation, adsorption, ion exchange, membrane separation, biological treatment and advanced oxidation processes can be used. Removal of micropollutants (acetaminophen, caffeine, sulfamethoxazole, atrazine, diclofenac, etc.) by coagulation alone occurs at a very low level, below approximately 3% [8]. Lee and Choo (2013) combined this method with a photocatalyst in their study and reported a higher pharmaceutical waste removal capacity [8]. The adsorption process is a treatment technique widely used in the treatment of pharmaceutical industry wastewater [9]. Jodeh et al. (2015) studied adsorption of diclofenac sodium drug waste with the prepared activated carbon. In the study, DCF removal was obtained maximum 81%, for the 70 mg/L diclofenac concentration, 0.7 g activated carbon amount and at pH 2 [10]. A similar study to the water purification of diclofenac with activated carbon was done by Sotelo et al. (2014) and successfully concluded [11]. Ion exchange is based on the principle of ion exchange between the ion exchange solid phase and the liquid phase. Landry

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and Boyer (2013) performed diclofenac removal by ion exchange, the removal percentage was around 90% [12]. The membrane process is based on selective permeability. The separation process is determined by both the chemical and physical nature of the membrane and is realized by the driving force created by one or combinations of pressure difference, concentration (chemical potential) difference, electrical potential difference and temperature difference [9]. Diclofenac degradation was performed using hybrid TiO_2 / UV-A catalysis-ultrafiltration process in a laboratory-sized pilot photocatalytic membrane reactor by Sarasidis et al. (2014). Maximum DCF degradation was obtained as 99.5% with 0.5 g/L TiO_2 loading at pH 6 [13].

Many pharmaceutical pollutants are still detected in effluents of WWTPs [14]. New treatment methods like advanced oxidation processes (AOPs) should be adapted to the existing WWTPs that will reduce the presence of these pollutants in water.

Photocatalytic degradation, one of the AOPs, were adopted to remove DCF molecules in water in the literature. As known that photocatalytic degradation is affected with the process conditions like amount of photocatalyst, applied irradiation intensity, temperature, concentration of organic matter in the solution, anions and cations in the environment, and pH [15-17]. These factors should be carefully investigated and optimized for the specific cases. Recently, although some studies involved the effect of photocatalyst amount on photocatalytic degradation of DCF [18-22], there is no study about the effect of air flow rate. The effects of oxidation agents such as H_2O_2 , ozone, O_2/Ar on the photocatalytic degradation process were investigated in some studies [20, 21, 23]. Only a few studies considered the effect of air flow rate on DCF degradation via sono-activated persulfate oxidation [24] and in a fenton like system [25].

In this study, the effects of photocatalyst amount and air flow rate on photocatalytic degradation of DCF via TiO_2 were investigated. Photocatalytic degradation kinetics was also examined via Langmuir-Hinshelwood kinetic model.

MATERIAL AND METHODS

MATERIALS

Dikloron® were used for the preparation of diclofenac sodium aqueous solution. Dikloron®, which has 75 mg diclofenac/3 mL concentration, was obtained from the local pharmacy. Dikloron was diluted with distilled water in order to obtain appropriate solution concentration. TiO_2 (Degussa P25) photocatalyst was supplied from Evonik Degussa Corporation, and used without any modification.

PHOTOREACTOR SETUP

A representative scheme of the photoreactor can be seen in Figure 1. A glass reactor, with a volume of 1000 mL, placed on magnetic stirrer were used in the experiment. Quartz glass casing was put into the glass reactor and 2x6W UV lamp with a wavelength of 365 nm was placed inside the quartz casing. A quartz glass was preferred due to its high UV-A light transmittance. Air flow as an oxygen source was supplied by using air compressor. The temperature of the system was kept constant at 20°C by using cooling water circulated inside the jacket of the photoreactor. The glass reactor was covered with aluminium foil to obtain a complete dark environment and isolate the effect of daylight. Moreover, due to the reflecting property of aluminium foil, UV light in the reactor was intensified.

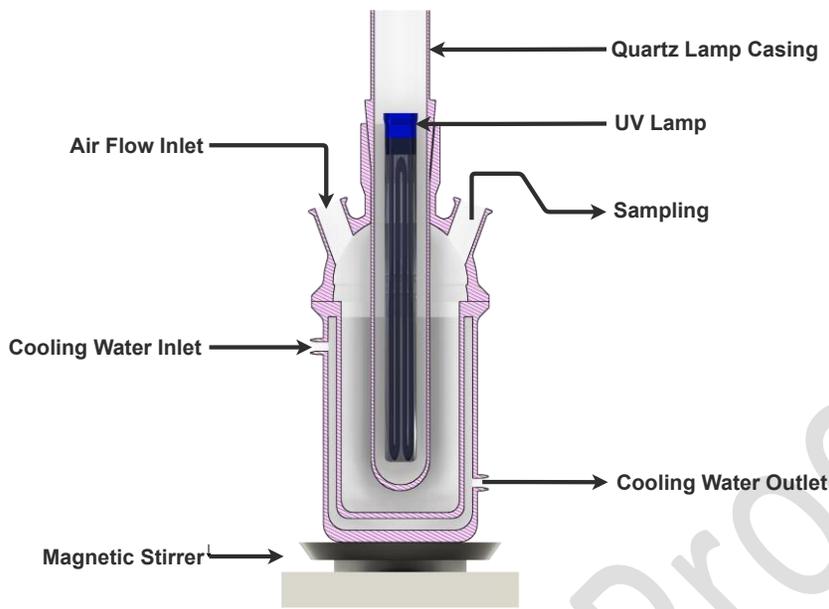


Figure 1. Photoreactor Setup

PHOTOCATALYTIC DEGRADATION OF DICLOFENAC (DCF)

In the photocatalytic degradation process, TiO_2 concentration (0.5 g/L, 1 g/L and 2 g/L) and air flow rate (3L/h, 6 L/h, 12 L/h and 18 L/h) were tested in order to investigate the effects of photocatalyst amounts and air flow rate on the degradation of DCF. Before supplying the photocatalyst to the reactor, TiO_2 is dispersed in 10 mL of distilled water and held on ultrasonic bath for 15 minutes to prevent agglomeration of TiO_2 nanoparticles. After that TiO_2 was spilled into the reactor, which contain 500 mL of 15 mg/L DCF solution (pH of the initial DCF solution was measured as 7.55). During the experiments, the mixture in the reactor was stirred with magnetic stirrer at 400 rpm continuously. Before the photocatalytic degradation experiments, a 15 minutes of dark period allowed in order to complete the DCF adsorption onto TiO_2 . After this period, air flow was supplied to the system and UV light was turned on, hence, photocatalytic reaction was initialized.

Samples were taken in every 15 minutes for the first 90 minutes and in every 30 minutes after that. Each sample was filtered with a $0.25\mu\text{m}$ membrane filter then DCF concentration were measured at 276 nm wavelength by using Analytic Jena Specord 200 Plus UV-Vis spectrophotometer. Maximum wavelength value, 276 nm, was determined by using scanning mode absorbance measurement with the 20 mg/L DCF solution. Calibration curve ($y=0309x$) with the 0.9996 R2 value was obtained in the concentration range of 0-20mg/L, then, DCF concentration of the samples were determined by using the software of the spectrophotometer.

PHOTOCATALYTIC DEGRADATION KINETICS

Photocatalytic degradation reaction kinetics mostly depends on catalyst type, catalyst amount, process parameters such as pH, dissolved oxygen content, initial concentration and temperature (Ohtani, 2014). The kinetics of the photocatalytic degradation reactions were investigated with the Langmuir-Hinshelwood model. Langmuir-Hinshelwood kinetic model is given in Eq.1 (Soltani-Nezhad 2019; Luna-Sanguino, 2020):

$$r_R = \frac{dC_R}{dt} = \frac{k'.K.C_R}{1+K.C_R} \quad (1)$$

In the equation, r_R is the reaction rate, t is the reaction time, C_R is the solution concentration, k' is the reaction rate constant, and K is the adsorption constant. The value of $K \cdot C_R$ is generally neglected at very low concentrations

(in mM), and the reaction rate can be considered as the pseudo-first order model. After integration of Eq.1 at the boundary conditions ($C_R = C_{R0}$ at $t=0$) Eq. 2 is obtained:

$$-\ln \left(\frac{C}{C_0} \right) = K_{pseudo} \cdot t \quad (2)$$

where K_{pseudo} is the pseudo first order reaction rate constant, C_0 is the initial concentration and C is the concentration at time t . The K_{pseudo} values were graphically determined using $\ln(C/C_0)$ against time plots. Initial DCF concentration (C_0), was taken as the value just before the UV applied.

EXPERIMENTAL RESULTS AND DISCUSSION

EFFECTS OF PHOTOCATALYST AMOUNT

Diclofenac concentration change during irradiation for different amount of TiO_2 is shown in Figure 2a-b. As seen in the Figure 2b, when TiO_2 concentration was increased from 0.5 g/L to 1 g/L, photocatalytic degradation efficiency slightly increased from 67.7 % to 76.1 % due to the increasing amount of photocatalyst. The increase in degradation efficiency is a result of increasing generation of $OH\cdot$ radicals by the higher amount of photocatalyst. On the other hand, with a further increase on TiO_2 from 1g/L to 2 g/L, degradation efficiency reduced to 38.97% dramatically. Excess amount of TiO_2 increased the turbidity of the solution, hence, prevents UV light flow within the reactor. Also excess amount of TiO_2 may cause the photocatalyst agglomeration, which limits the activity of photocatalyst [24]. Similarly, Gupta et al. (2011) demonstrated that the degradation efficiency increases up to an optimum concentration of TiO_2 , after that, efficiency starts to decrease [26].

Depending on the applied process conditions, various DCF degradation efficiencies have been found in the literature. Calza et al. (2006) obtained a degradation efficiency of 55-80% with different TiO_2 and DCF concentrations for 60 minutes at 276 nm [18]. Rizzo et al. (2009) reported that 28% of 50 mg/L inlet-consistent DCF degradation after 240 minutes of processing [19].

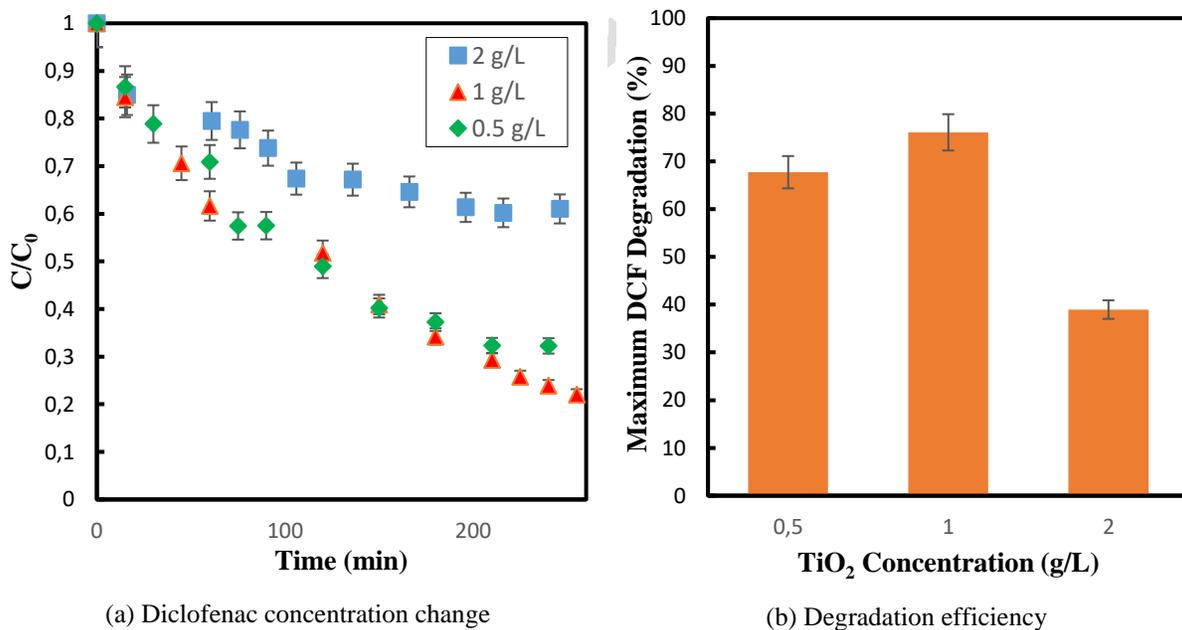


Figure 2. Photocatalytic degradation of DCF with different TiO_2 Concentration (air flow rate: 18 L/h)

EFFECTS OF AIR FLOW RATE

Different air flow rates were also examined in order to see how it affects the degradation of DCF. Diclofenac concentration change during irradiation in the presence of 0.5 g/L TiO₂ at different air flow rates is shown in Figure 3a-b. In order to see the effect of air flow rate, DCF degradation was also carried without air flow rate. As seen in Figure 3a, without air flow, only 52.5% DCF degradation was observed, due to the lack of oxygen after consuming the soluble oxygen in the initial solution, degradation reactions did not continued more. The air flow rate of 3 L/h was also insufficient to achieve effective degradation. With the increasing the air flow rate from 3L/h to 6 L/h, there was a significant increase on DCF degradation efficiency (from 56.0% to 78.4%), however, further increasing air flow rate to 12 L/h resulted in a slightly decrease in degradation efficiency from 78.4% to 77.4%. When the air flow rate was increased from 12 L/h to 18 L/h, an approximately 13 % of decrease on degradation of DCF (from 77.4 % to 67.7 %) was observed at the end of 4 hours. The results showed that increasing air flow rates from 6 L/h to the higher values has negative effect on degradation process. This result can be interpreted with the inhibiting effect of high amount of air bubbling within the solution; UV light cannot pass through to the high amount of air bubbles within the solution as Lam et al. (2010) observed in their study [28].

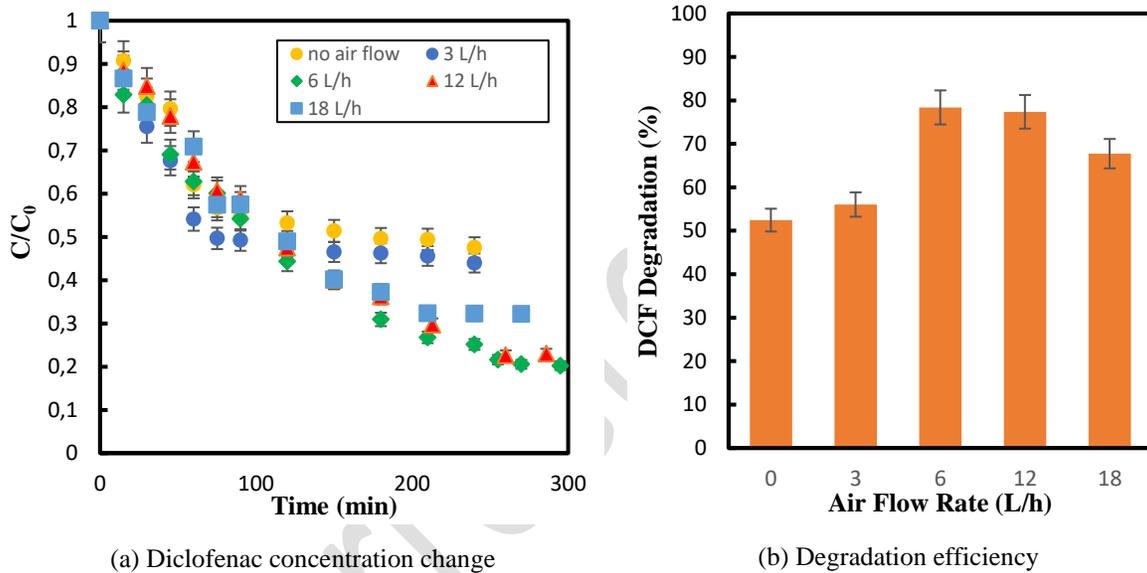


Figure 3. Photocatalytic degradation of DCF at different air flow rates (0.5 g/L TiO₂)

One of the reasons behind this result could be explained with the formation of oxidative radicals. As known that degradation of organic compounds in photocatalytic process is achieved by oxidative radicals generated in presence photocatalysts. When a photon excites the electron in the photocatalyst from valance band to conduction band and gets activated in a water medium with the presence of air, oxidative radicals such as, superoxides radicals (O₂•) are formed from the oxygen and hydroxyl radicals (OH•) existed in medium [29]. Formation reactions of superoxide and hydroxyl radicals are shown below [30]:



Hydroxyl radicals, $\text{OH}\cdot$, are known to have strong oxidative properties compared to other oxyradicals [31]. In the process, as the air flow, which triggers the production of superoxide radicals, was decreased, there is a possibility that the dominance of hydroxyl radicals on degradation may also increase. By supporting this, in a study, Montegudo et al. (2018) investigated the effects of different radicals such as hydroxyl radicals, $\text{OH}\cdot$, superoxide radicals, $\text{O}_2^-\cdot$, singlet oxygen, and sulfate radicals, $\text{SO}_4^-\cdot$ on degradation of DCF. The study emphasized the presence of $\text{OH}\cdot$ and $\text{SO}_4^-\cdot$ were the main factors that played a role in main degradation reaction pathways of DCF whereas the $\text{O}_2^-\cdot$ had a moderate effect only [24]. Furthermore, a study showed that $\text{OH}\cdot$ radicals were the main oxidizing agents for DCF in a fenton like system as well [25].

DICLOFENAC DEGRADATION KINETICS

In the kinetic calculations, the time between the UV lamp is turned on and the moment, which end of the degradation is observed, were taken into account. For different concentrations, the slopes of $\ln(C/C_0)$ versus time, which represent the K_{pseudo} can be seen in Figure 4a. The red slope that represents the K_{pseudo} values for the 1 g/L TiO_2 concentration, is the steepest one among three. Thus, the highest reaction rate belongs to 1 g/L photocatalyst concentration. The least K_{pseudo} was observed with the 2 g/L concentration of TiO_2 . All of the $\ln(C/C_0)$ versus time lines fitted experimental data with the regression values close to 1 (Figure 4b), hence, it can be concluded that DCF photocatalytic degradation kinetics fitted Langmuir Hinshelwood kinetic model very well.

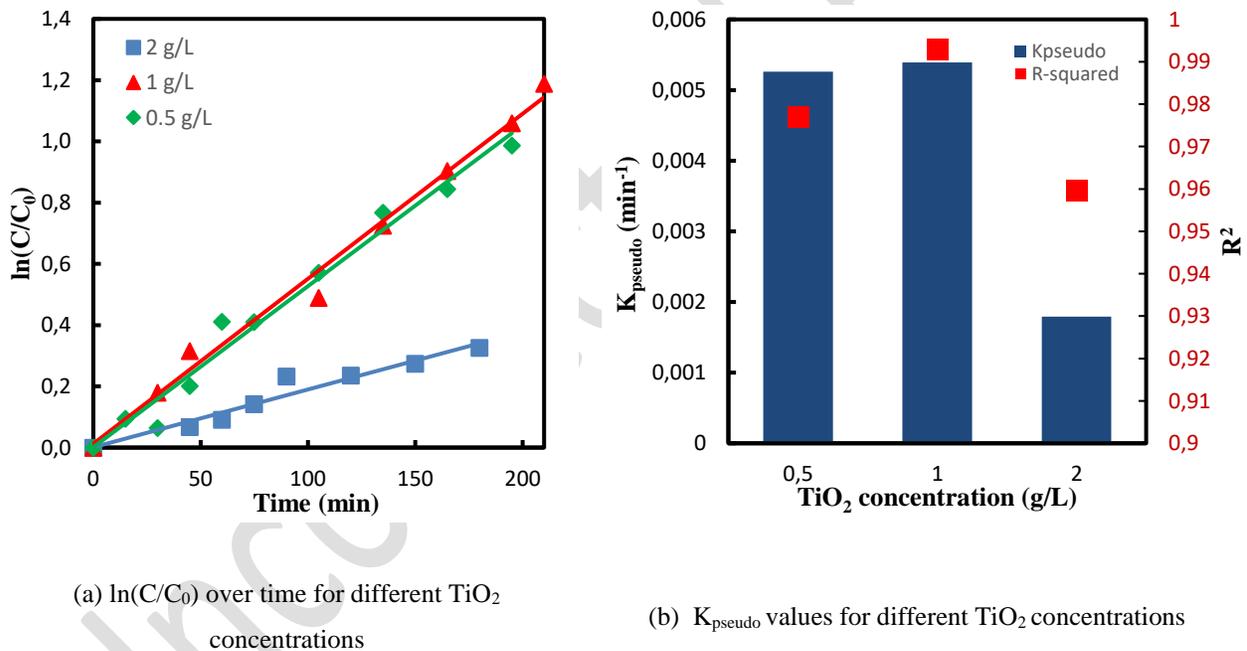
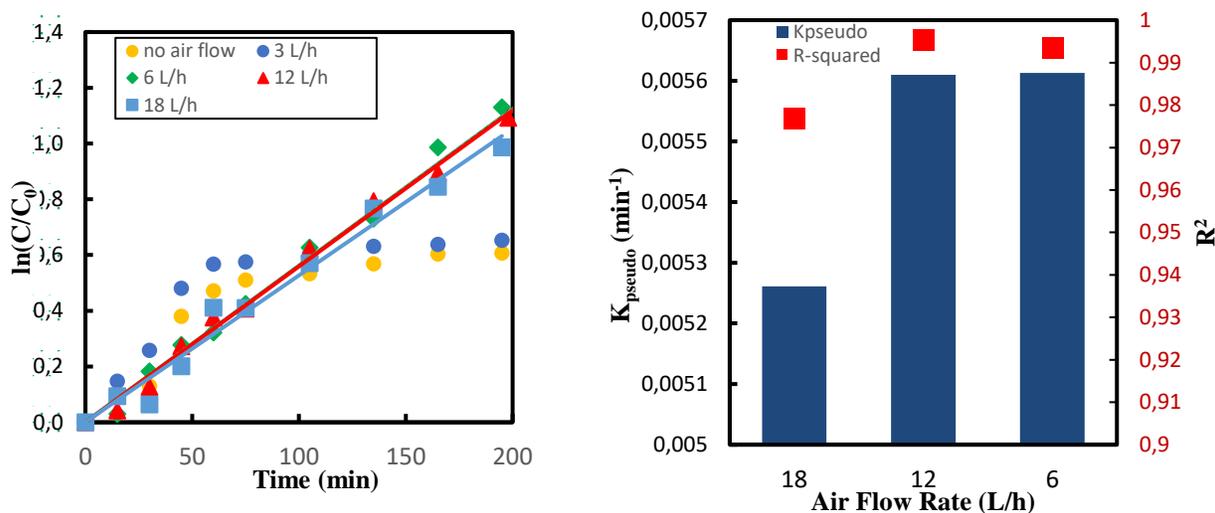


Figure 4. Degradation Kinetic of DCF for different TiO_2 concentrations (18L/h air flow)

Even though the TiO_2 amount is decreased to half of it, the slope obtained for 0.5 g/L TiO_2 is almost as steep as in the 1 g/L TiO_2 . As can be seen from Figure 4b, rate constants for these two concentrations are very close to each other, which they were found as $0.005261 \text{ min}^{-1}$ and $0.005389 \text{ min}^{-1}$ for 0.5 g/L and 1 g/L, respectively. Considering that TiO_2 is one of the pollutants that increases the marine pollution itself [32], as possible as low amount of TiO_2 should be used. In addition, a smaller concentration of the photocatalyst would be cheaper choice. Therefore, while investigating the effect of air flow rates in degradation further, 0.5 g/L TiO_2 concentration was selected.

For different air flow rate values, obtained $\ln(C/C_0)$ values are demonstrated in Figure 5a. Without air flow and with 3L/h air flow rates, DCF degradation did not follow the Langmuir-Hinshelwood kinetic model. Degradation

rate constants, which were obtained from the slope of $\ln(C/C_0)$ vs time lines, and regression coefficients are demonstrated in Figure 5b. It is seen from the figure that less air flow rates such 6 L/h and 12 L/h give much higher K_{pseudo} values compared to that obtained with 18 L/h of air flow rate. The highest rate constant value ($0.005613 \text{ min}^{-1}$) was obtained with 6 L/h air flow rate, it was followed with very small difference by 12 L/h air flow rate ($0.005613 \text{ min}^{-1}$). However, with further increase of air flow rate resulted in much slower degradation kinetics.



(a) $\ln(C/C_0)$ over time for different TiO_2 concentrations (b) K_{pseudo} values for different TiO_2 concentrations

Figure 4. Degradation Kinetic of DCF for different TiO_2 concentrations (18L/h air flow)

CONCLUSION

This study involved the effects of photocatalyst amount and air flow rate on photocatalytic degradation of diclofenac. Following conclusions can be drawn from the results of this study.

- TiO_2 and air flow rates have direct effects on the degradation of DCF.
- Although low amount of photocatalyst was not enough for effective degradation, excessive catalyst amount inhibited degradation of DCF by preventing UV light transfer within the solution due to the high turbidity. Considering the cost, and environmental effect of nanoparticles, optimum TiO_2 amount should be determined according to the process conditions.
- The photocatalytic degradation kinetics of diclofenac fitted the Langmuir-Hinshelwood kinetic model except the experiments carried without air flow and 3L/h air flow rate.
- Without air flow and with the air flow rate of 3 L/h, very low DCF degradation was observed, due to the lack of oxygen.
- Further increasing air flow rate over 6L/h resulted in low DCF degradation efficiency and rate. Although oxygen in the solution provides formation superoxides radicals, which is also responsible for DCF degradation, excess amount of air bubbles can also inhibit the UV light transfer. Accordingly, required air flow rate should be determined depending on the process conditions.
- The highest degradation capacity of 78.4% and the rate constant of $0.005613 \text{ min}^{-1}$ were achieved when the TiO_2 concentration and air flow rate were 0.5 g/L and 6 L/h, respectively.

As a conclusion, photocatalytic processes with 365nm UV light and TiO_2 photocatalysts can be efficiently applied for the degradation of emerging contaminant, diclofenac.

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