

Degradation of diclofenac under irradiation of UV lamp and solar light using ZnO photo catalyst

DOI : 10.36909/jer.ICEPE.19531

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ABSTRACT

Diclofenac sodium (DCF) is a non-steroidal anti-inflammatory drug mainly used as an analgesic, arthritic and anti-rheumatic. This study deals with the degradation of diclofenac by photo catalytic-based advanced oxidation processes. The solar reactor system is comprised of quartz and borosilicate tubes for the absorption of the solar rays and transmission to the pollutant sample. Artificial UV lamp and solar rays have been applied to activate the ZnO catalyst, thereby generating highly oxidizing species. These species initiate the degradation process of the drug, which results in intermediates that finally dissociate into carbon dioxide and water. The degradation rate has been analyzed by composition analysis using high performance liquid chromatography. TOC and COD tests have also been conducted for degraded samples. ZnO catalyst loading was tested from 0.1 gm/L to 1 gm/L and the degradation rate showed a rising trend up to 0.250 gm/L, but further increase in loading resulted in a drop in degradation. Similarly, degradation is higher in acidic condition as compared to neutral or basic pH condition. The results showed a higher degradation rate for UV lamp

irradiation as compared to the solar system. Moreover, TOC and COD reduction results were also found to be higher for UV lamp photo catalysis.

Keywords: catalyst loading; degradation; diclofenac; oxidizing species; photocatalytic degradation

INTRODUCTION

Diclofenac sodium (DCF) is a frequently used drug and is prescribed as an analgesic, arthritic and anti-rheumatic drug and detected in fresh and wastewater at alarming levels (Bai et al., 2020). Due to extensive human and veterinary cure, the number of NSAID annual prescriptions is around 80 million, making it almost 4.5% of all drugs prescriptions. The worldwide consumption of DCF provides a continuous release in aquatic environment from different sources, such as disposal from production sites, household discharge and its non-degraded and metabolized products after human and animal medical treatment (Chen et al., 2018). In hospital wastewater, its concentration has been reported up to $8.5 \mu\text{g L}^{-1}$. The presence of diclofenac and its metabolic forms, even at very low concentrations, can cause cytotoxicity to marine lives, especially severe damage to liver, kidney and gill cells. Renal lesions problem associated with DCF is the major cause of massive decline (95%) in vultures in Pakistan and India, making its existence critically rare in the subcontinent region. Moreover, its toxic effects have badly affected the vertebrates and fishes in aqueous environment (Tanveer et al. 2019). Some studies have shown that the DCF traces in water bodies do not cause acute environmental toxicity; however, they have serious chronic effects and need to be addressed. DCF associated environmental and health issues have initiated the research for its complete removal or mineralization to harmless compounds.

Due to its very low adsorption affinity for suspended matters and sediments the removal of DCF by adsorption based processes is limited (Wu et al., 2019). Although as final wastewater

treatment methods biological processes have been reported as best available techniques but their DCF removal is not promising (Gao et al., 2020). Reverse osmosis and nano filtration processes effectively remove the pharmaceutical products but membrane bio fouling and retentate disposal are the major drawbacks (Angosto et al., 2020). Ozonation treatment can destroy pharmaceutical pollutants but this process can lead to even more destructive byproducts (Eylem et al., 2021). Low removal efficiency of conventional wastewater treatment methods has raised urgent desire of more developed treatment techniques to meet the persistent nature of pharmaceutical effluents. Recent studies on treatment of non-biodegradable compounds have shown that the advanced oxidation processes (AOPs) are excellent methods for recalcitrant chemicals (Trinh et al., 2021). The AOPs are based on production of strong oxidizing species ($\text{OH}\bullet$) which leads to pollutants demineralization. Depending upon the treatment option, the versatile nature of AOPs provides different options to produce highly reactive and low selective hydroxyl radicals and target persistent pollutants. Among these UV Photo fenton (Rehman et al., 2021), solar photo fenton (Casierra-Martinez et al., 2020), ultrasound assisted photo catalytic (Meroni et al., 2020), Ozon /UV (Aldeguer et al. 2021), H_2O_2 /UV (Ameri et al., 2020) based AOPs have been widely reported for DCF treatment. Photocatalytic based AOPs have shown several advantages over other AOPs in terms of its high treatment efficiency for refractory chemicals, use of renewable solar radiations and ability to operate without specific pH adjustment contrary to photo fenton which required a strict control of pH environment. Semiconductor photocatalysis based on TiO_2 and ZnO induced by UV/solar irradiation have been extensively studied for pharmaceutical pollutants treatment (Petru et al., 2020 & Rehman et al., 2021 & Ma et al., 2020). In photo catalytic degradation of pollutants the processes utilizes the UV spectrum to photo excite the catalyst resulting in generation of hydroxyl radicals in the presence of oxygen. The radicals are highly reactive species which attack the pollutants and degrade it to CO_2 , water and mineral acids.

The aim of this study is to study the effect of different operating parameters, such as photo

catalyst type, catalyst loading, and pH environment and radiation source. For this purpose, DCF degradation is studied under different loading concentrations of ZnO catalysts, employed under pure UV lamp (254 nm) and solar reactor irradiation consecutively. Effects of different pH environments on degradation is also examined.

METHODOLOGY

Material and Reagents

Diclofenac sodium salt was purchased from Sigma-Aldrich. Its solubility in water is 50 mg/mL. Titanium (IV) oxide (anatase) and zinc oxide catalysts were also purchased from Sigma-Aldrich. ZnO catalyst is 99% pure with particle size <100 nm. Sodium hydroxide and sulfuric acid were purchased from Likit Kimya San Ve Tic A.S Kayisdag, Istanbul, and employed for the pH adjustment of the solution samples.

Experimental Analyzing Techniques

As amount of 1500 μ M stock solution of DCF was prepared by adding 47 mg of diclofenac sodium in 100 mL water. Then, 30 μ M test samples were prepared by diluting 20 mL stock solution in 1 L deionized water. A lab scale UV reactor (Figure 1) was employed for artificial UV based experiment. DCF aqueous solution was introduced and recirculated on reactor via inlet and outlet ports. A UV Lamp (40 W, 254 nm) was placed in quartz tube and immersed in the aqueous solution.

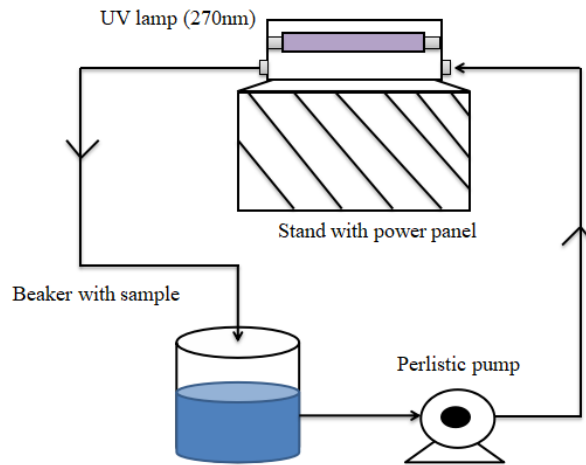


Figure 1. Solar reactor system for photo catalytic experiments.

Solar-based experiments were performed in a system comprised with absorber tubes (whether quartz or borosilicate) (Figure 2). Chrome plates were used as reflector for the rays harness the maximum intensity of solar light. The degradation rate of the diclofenac solution was analyzed by using high-performance liquid chromatography (HPLC) (Shimadzu Prominence LC-20A) having a Hypersil BDS C-18 column with Mediterranean Sea18 as packing material. Demineralization of the solution samples were analyzed by employing total oxygen demand (TOC) and chemical oxygen demand (COD) analyses.

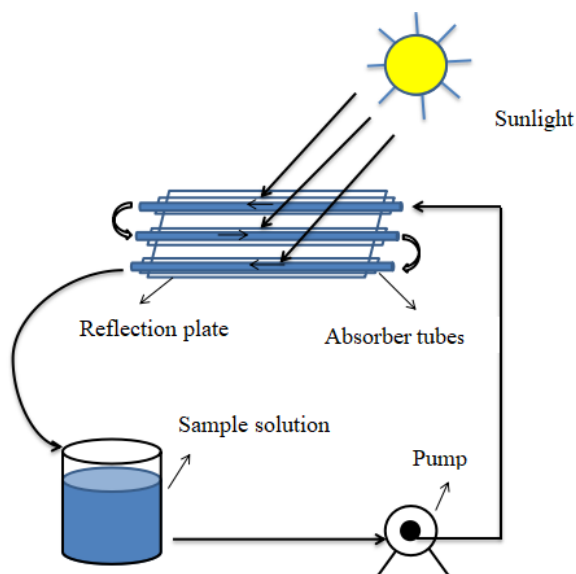


Figure 2. Lab scale UV reactor

RESULT AND DISCUSSION

Effect of Catalyst Loading of ZnO

In preliminary experiments, DCF degradation due to catalytic adsorption under dark conditions and photolysis (UV) was evaluated. The results showed no activation due to these factors. Then, photocatalytic degradation with ZnO concentration ranging from 0.10 g/L to 1.0 g/L was studied. The combined use of UV and ZnO loading gives significant DCF degradation. With increases in catalyst amount up to 0.25 g/L, the catalyst loading DCF degradation was promising, but further increases in loading led to drop in elimination process (Figure 3).

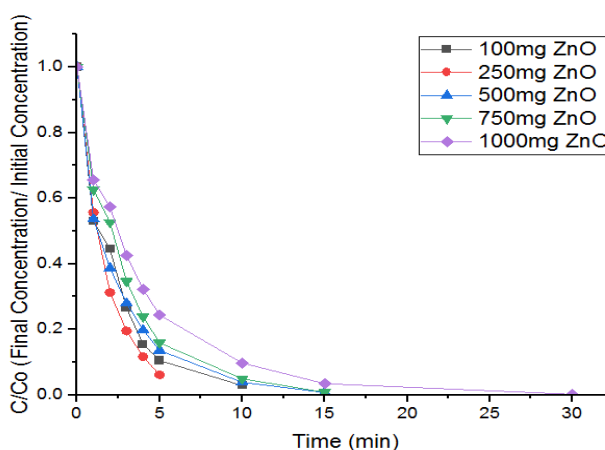


Figure 3. Effect of Catalyst Loading of ZnO on degradation rate.

It was found that increases in the catalyst loading supported the degradation process, but excessive amounts of catalyst can shield part of the photosensitive surface and consequently hinder or lag in degradation (Ma et al., 2020). This threshold loading depends upon the reactor geometry, operating conditions, and initial substrate concentration. Studies show that UV irradiation on aqueous ZnO suspension with light energy greater than band gap energy of ZnO leads to the formation of conduction band electrons (e^-) valance band holes (h^+) (He et al., 2020). With increasing catalyst loading, the rise in degradation can be associated with the

enhanced availability of active sites on the ZnO surface and penetration of photo-activating light. After a certain loading level, the lowering of the degradation rate may be related to the enhanced light reflectance due to surplus ZnO particles and also increased opacity of the sample solution.

The intensity of incident radiations and the aqueous path length inside the reactor are the fundamental parameters to determine optimum catalyst loading (Wang et al., 2018). In the case of solar reactor where path length is very long so there required more amount of catalyst for same results. Another important parameter is the uniform flow path which otherwise results of non-uniform residence time (Hang et al., 2020).

Effect of pH

The pH of the aqueous solution significantly affects the performance of photocatalytic degradation process. Conductance and valence band positions, size of aggregates formed by catalyst particles and surface charge density are based on pH conditions (Jang et al., 2020). Moreover, it also determines the adsorption trend of the pollutant (Naresh et al., 2018). At first, the experimental solution was irradiated with UV at optimum ZnO loading (0.25 gm/L) under neutral (pH = 7.7), acidic (pH = 3) and basic (pH = 11) pH environments. Degradation results showed that under acidic pH conditions almost 95% of the pollutant is degraded within first five minutes, while for a basic or neutral environment the degradation rate of the pollutant is very slow. The catalyst performance under neutral pH environment showed least degradation and took half an hour to mineralize the DCF sample (Figure 4).

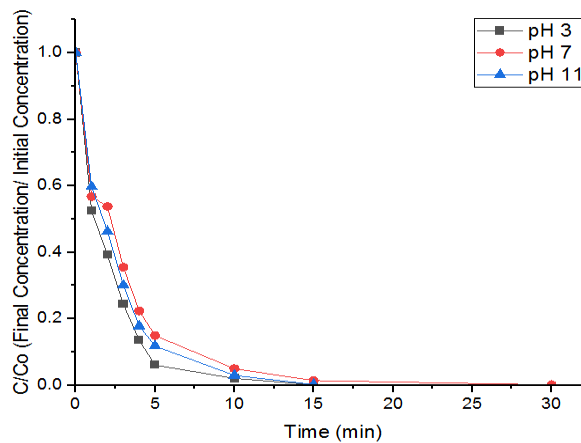


Figure 4. Effect of pH on degradation rate.

As the P_{ka} value of diclofenac is 4.15 (Kovacic et al., 2018) that indicates negative charge near acidic pH, which results in electrostatic attraction between pollutant and active sites of catalyst. This may lead to increase in adsorption and degree of photo degradation. Higher degradation rate of DCF was achieved under acidic pH conditions. As solution pH was shifted from acidic to neutral region a remarkable decline in degradation process was observed. During degradation a multitude of intermediates products are produced that may affect the solution properties depending on pH. Carboxylic acid and inorganic acids release during degradation may cause of drop of pH which indirectly support the degradation rate.

Effect of Irradiation Source

To initiate photo catalytic degradation process, the radiation source is considered the most important factor after solution pH and catalyst loading. Under UV lamp source, the optimum pH and catalyst loading was studied in previous section. To study the effect of solar irradiation, the borosilicate and quartz tubes were installed as ray absorbing materials.

Initially, the DIC solution (Tanveer et al. 2019) was introduced in solar reactor at optimum loading of ZnO under acidic pH conditions. An electric stirrer was installed in reactor to avoid catalyst accumulation and keep the homogeneity of solution. The solution is circulated in the absorbing tubes by using a perlistic pump. Firstly, quartz tubes were installed as radiation

absorbing material and degradation of DIC was examined. Later on the same experiments were performed using borosilicate tubes. At optimum operating conditions, borosilicate tubes show better degradation results compared to quartz tubes (Figure 5). Moreover, mineralization study was also conducted by using TOC and COD analysis.

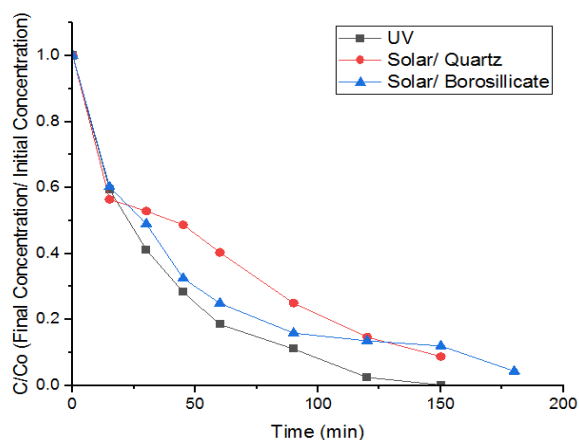


Figure 5. Effect of irradiation source (UV/Solar Quartz/ solar borosilicate) on degradation rate.

Table 1. Summary of diclofenac treatment by UV/ZnO and Solar/ZnO.

Process	Degradation Rate (min^{-1})	TOC Reduction	COD Reduction
UV/ZnO	0.403	51%	83%
Solar (Borosilicate)/ZnO	0.036	17%	43%
Solar (Quartz)/ZnO	0.015	15%	47%

CONCLUSIONS

The degradation of DCF was investigated under UV and solar light using ZnO catalyst. The effect of catalyst loading was tested from 0.1 g/L to 1.0 g/L and the optimum dosing condition was found to be 0.25 g/L. Moreover, the role of pH was also analyzed employing acidic, neutral and basic working conditions. For optimum catalyst loading (0.25 g/L), the degradation process presented promising results under acidic conditions. Along with degradation study, the mineralization results of the degraded samples were also found to be higher during TOC and COD analyses.

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