

**PHOTODEGRADATION OF DICLOFENAC SODIUM IN AQUEOUS SOLUTION
BY ZnO/SnO₂ POWDER MIXTURE CATALYST**

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Abstract

The occurrence of xenobiotics such as drugs, pesticides, personal care products has been widely reported in the last decade. Pharmaceuticals represent emerging micropollutants which are extensively used in medical and veterinary propose. Although pharmaceutical residues are measured in low concentrations, ngL⁻¹ in water, they may have negative impacts on ecosystems. The dominant route of pharmaceuticals into environment is by wastewater effluents discharged from treatment plants mainly based on application of biological treatment such as active sludge. The photodegradation of diclofenac sodium under UV irradiation was investigated using ZnO/SnO₂ mixture. After 60 minute of UV exposure, diclofenac was completely degraded.

Introduction

Active pharmaceutical ingredients (APIs) have been defined as important emerging micropollutants, due to its increased use and continuous input into aquatic environment. Pharmaceuticals are biological active substances designed to interact with living organisms. Pharmaceutical residues are transported into water medium by different routes. The wastewater treatment plants (WWTPs) acts as a gateway for human pharmaceuticals to enter water bodies. The existence of pharmaceuticals in surface, ground and drinking water occurs in trace quantities, ppt to ppb (ngL⁻¹ - µgL⁻¹). The main therapeutic families detected in water media are: nonsteroidal anti-inflammatory drugs, antibiotics, beta-blockers (β-blockers), antiepileptics, blood lipid lowering agents, antidepressants [1]. Pharmaceuticals in parent or metabolite form are continuous infused into water matrices, resulting with pseudo persistence although their half-lives are short.

Present treatment conditions are not effective to handle with this specific class of organic pollutants due to variation in their physico-chemical properties. Although pharmaceuticals are ubiquitous in water matrices and have potential health effects, most of them are not legally regulated. However, three pharmaceuticals: 17b-estradiol, 17a-ethinylestradiol and diclofenac (DCF) are added to the watch list of Directive 2013/39/EU.

Diclofenac (DCF), 2-[2,6-(dichlorophenyl)amino]phenylacetic acid], is non-steroidal anti-inflammatory drug (NSAID) used for inflammation treatment and for pain reduction. Figure 1. shows chemical structure of diclofenac.

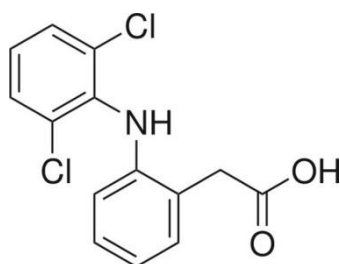


Figure 1. Chemical structure of diclofenac

After consumption, diclofenac is eliminated in short period (half life of 2 h). Approximately 65% is excreted through urine with six metabolites and 15% remains unchanged after consumption [2]. Diclofenac is used in different forms such eye dropping, dermal application and injection. According to investigation, the global consumption was estimated to be 940 tons per year with a daily dose of 100 mg. Diclofenac with $\log K_{ow} > 3$ may be accumulated in tissues of organisms. Diclofenac is detected in effluent water due to its resistance to biodegradation in conventional wastewater plants. Removal efficiency varies from 0-80% because of operating conditions such as sunlight exposure [3]. The presence of $-Cl$ and NH groups in DCF molecule is also a reason of inability of its removal.

Advanced oxidation processes (AOPs) have been proposed as a promising method for removal of recalcitrant pharmaceuticals and other endocrine-disrupting chemicals. The success of advanced oxidation processes depends of presence of oxygen species such as hydroxyl radicals [4]. The main advantage of HO radicals is the non-selective nature and it can contribute to the destruction of wide range of organic pollutants producing water, carbon dioxide and mineral acids. Among different types AOPs, heterogeneous photocatalysis has been mostly studied for photodecomposition of variety pharmaceuticals. The process is based on usage of nanostructured photocatalysis to maximize the absorption of both photons and reactants. One of the most commonly used photocatalysis is titanium oxide (TiO_2) [5-6].

The main propose of this study is to investigate the possibility of photocatalytic application in the presence of ultraviolet irradiation by zinc oxide / tin oxide (ZnO/SnO_2) nanoparticles.

Chemicals and reagents

DCF sodium is commercially available and used without further purification. HPLC grade, methanol and acetonitrile were purchased from Sigma Aldrich. Zinc oxide and tin oxide with 99,9% purity and particle size $\leq 1 \mu m$ were also purchased from Sigma Aldrich. The stock solution was prepared by dilution of 25 mg in 25 ml methanol (final concentration of 200 mgL^{-1}). The studied aqueous solution was distilled water.

Analytical method

The change in DCF concentrations was followed by reverse phase HPLC (Eclipse XDB-C18 (150 x 4.6, particle size $5 \mu m$) with diode array detector. The column temperature was adjusted at $25^\circ C$. The mobile phase of the applied isocratic elution consisted of 50% of 0, 1% acetic acid (CH_3COOH) and 50% of acetonitrile (CH_3CN). Flow rate was $0,8 \text{ ml min}^{-1}$. The injection volume of the samples was $10 \mu L$. The maximum wavelength for diclofenac was $\lambda_{max}=276 \text{ nm}$.

Experimental

The initial concentration of analyzed pharmaceutical was $3,4 \text{ mgL}^{-1}$. The ZnO/SnO_2 catalyst load was 40 mg. Experiment was performed in the dark. In order to follow kinetic of photodegradation of diclofenac sodium, different time intervals were applied (in range 5-60 minutes). With a goal to achieve uniform catalyst concentrations in solution, all samples were

stirred at magnetic agitator with 120 rpm speed. The volume of observed samples was 50 ml. Samples were irradiated under UV artificial light. After UV exposure, all samples were filtrated through 0,45 μm Premium Syringe Filter in order to remove nanoparticles from aqueous solution.

Results and discussion

After experiment, results are evaluated with HPLC offline software program. Calibration curve was constructed in range of 1, 5 – 10 mgL^{-1} with high correlation coefficient $r^2 = 0,999$. Final concentration of analyte was calculated according to peak area. Table 1. shows results obtained from degradation experiment.

Table 1. Results of photodegradation experiment

Time (min)	Area (mAU)	Final concentration (mgL^{-1})
5	42,2	0,99
10	28,9	0,69
20	4,00	0,12
30	1,30	0,05
40	0,72	0,04
50	0,14	0,03
60	0,00	0,00

According to results, concentration of diclofenac decreased with increasing the irradiation time.

In order to investigate possible removal of pharmaceutical, the next equation was used:

$$R(\%) = \frac{c_0 - c_e}{c_0} \times 100 \quad (1)$$

Where:

c_0 (mgL^{-1}) is initial concentration of pharmaceutical, and c_e (mgL^{-1}) is the equilibrium concentration of pharmaceutical.

Figure 1. shows percentage of diclofenac removal by time.

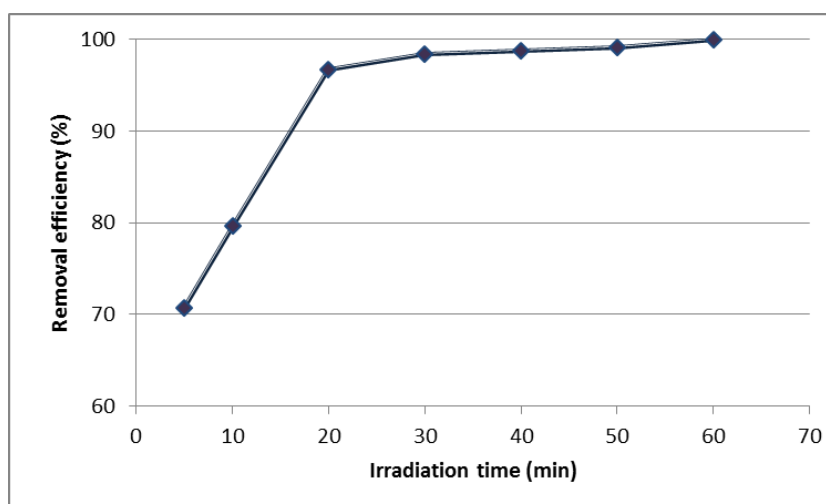


Figure 1. Removal efficiency of diclofenac

Removal efficiency has growing in function of time. After 60 minute of UV exposure, diclofenac was completely degraded.

Conclusion

The possibility of photocatalytic application for diclofenac removal was investigated. The photodegradation of diclofenac has been studied in aqueous solution (distilled water) using ZnO/SnO₂ nanopowder mixture. Completely removal of DCF was achieved after 60 minutes under UV exposure. According to results, heterogeneous photocatalysis seems to be a satisfied method for removal of diclofenac. In order to optimize photocatalytic process, some of main conditions have to be taken into account such as: concentration of catalyst, time of irradiation, initial concentration of investigated pollutant, effect of pH value, water composition and identification of byproducts. The current practice in wastewater treatment should be improved by integration of advanced technologies in order to achieve satisfactory treatment of effluents.

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