INFLUENCE OF PHOTOCATALYSTS MASS ON PHOTOCATALYTIC DEGRADATION OF MIXTURE OF PHARMACEUTICALS BY OXIDE ZnO/TiO_2 NANOPOWDER

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Abstract – In this paper, the efficiency of photocatalytic degradation of mixture of pharmaceuticals (naproxen, diclofenac, ketoprofen and ibuprofen) in the aqueous medium using nanoparticle photocatalysts powder ZnO/TiO_2**,** activated by UV radiation, has been examined. It has been shown that the degradation of diclofenac, ketoprofen and ibuprofen takes place efficiently regardless of the mass of the catalyst. Naproxen has proven to be the most resistant pharmaceutical and degradation constants are calculated for naproxen only, which may be used as guidelines in further research.
Keywords: photocatalysis, pharmaceuticals, naproxen, diclofenac, ketoprofe, ibuprofen, ZnO/TiO_2

Introduction

Emergent substances are a specific group of synthetized or natural compounds, identified as pollutants, which are predominantly produced in various industrial branches, especially in the chemical, petrochemical, metal and pharmaceutical industries, and through wastewater they are introduced and transported through all spheres of the environment. These substances are used in everyday anthropogenic activities, and can be from a group of chemical compounds of pharmaceuticals, disinfectants, products for personal and household hygiene, pesticides, wood preservatives and others. Continuous discharge of municipal and industrial wastewater with or without treatment into aquatic systems provokes the emergence of a new feature - pseudoprosistence. Primary pathways that pharmaceuticals reach into surface waters include conventional wastewater treatment plants and systems for discharging untreated sanitary wastewater. Technological operations that are applied to the treatment of municipal and industrial wastewater are not able to isolate or remove pharmaceuticals from the outflow streams, and certain stages of treatment may induce degradation of pharmaceuticals to forms that have even more significant negative effects on the environment [1]. Additional concern is the fact that naproxen, diclofenac, ketoprofen, ibuprofen, as well as a large number of other pharmaceuticals, remain biologically active in aquatic matrix over a long period of time (more than a year and possibly activity up to several years), which causes accumulation and a harmful effect on organisms and the environment.
The path of distribution of pharmaceuticals and their metabolites, as well as the method of disposal of released pollutants depend on the physico-chemical properties and basic characteristics of the environment in which the pollutant is released, and they are directly dependent on the coefficient of sorption or retention in soil mass and sediment of surface waters [2]. Environmental risk assessments are mainly based on an active component, however, pharmaceutics are present in the environment as a multi-component mixture, a chemical cocktail with a different ecotoxicological effect from the individual component, and

it is very important to investigate the processes for degradation of these pollutants under the presence conditions combined pharmaceuticals.
Among the methods that have been developed for water disinfection, advanced oxidation processes such as heterogeneous photocatalysis appears as an emerging technology for the decomposition of most of the organic pollutants [3]. While nanostructured TiO_2 is being the most explored material up until now ZnO appears as a strong rival to due to its considerably better photocatalytic activity (PC) [4]. Therefore, interest has also arisen on the photocatalytic properties of mixed oxide nanopowders, which could potentially combine the properties of the individual oxides.

Experiment

ZnO/TiO_2 mixed powder photocatalysts were prepared using a simple, low-cost, threeand three-step mechanochemical solid-state method. Starting precursors (ZnO and TiO_2 Sigma Aldrich, purity 99.9%) were grounded in an agate mortar for 10 min in molar ratio 2:1, annealed at 700°C in air for two hours and grounded again for 10 min.It has recently been reported that binary nanopowders based on ZnO exhibit photocatalytic activity which depends slightly on molar ratio, which is however maximized for ZnO-rich compositions [5].
The photocatalytic decompositions of chosen pharmaceuticals were carried out at ambient temperature in aqueous solution in batch mode. The aqueous solution was stirred for 1 h in the dark to establish adsorption-desorption equilibrium between the pharmaceutical and photocatalyst before being irradiated. The aqueous solutions were exposed under continuous UV irradiation. In order to investigate the change in composition of the investigated pollutant, aliquots were collected at certain time intervals (5, 10, 20, 30, 40, 50, and 60 minutes). Each sample was filtered through filter paper (diameter 0,45 μm mm) in order to separate the nanoparticles from the solution. After the filtration step, 1 ml of sample was transferred into 1,5 ml vials. A HPLC (high performance liquid chromatography) with diode array detector (Agilent 1260 series) was used for the measurement of each specific pharmaceutical concentration after photocatalytic degradation.

Results and Discussion

Experiments have shown that the mixture of nanoparticle powder ZnO/TiO_2 possesses prominent photocatalytic abilities: after 5 minutes from the beginning of the experiment, the concentration of pharmaceuticals decreased almost to half, while diclofenac, ketoprofen and ibuprofen from the mixture have almost totally degraded after 60 minutes. According to the obtained experimental data, naproxen is the most resistant pharmaceutical pollutant, and the experimental data were processed depending on the effect of the mass of the catalyst (Figure 1).The degradation kinetics of naproxen was quantified by fitting the experimental data where the concentration change depends logarithmically on time:

$$ln\left(\frac{C_0}{C}\right) = kt$$

where k is the rate constant and C_0, $C$are the analyte concentrations before and after UV irradiation, respectively [6,7] (Figure 2). Diclofenac, ketoprofen and ibuprofen are so rapidly disintegrating that Langmuir-Hinshelwood's model cannot be applied, since this dependence no longer describes the approximate experimental data (The example of diclofenac is presented in Figure 3).

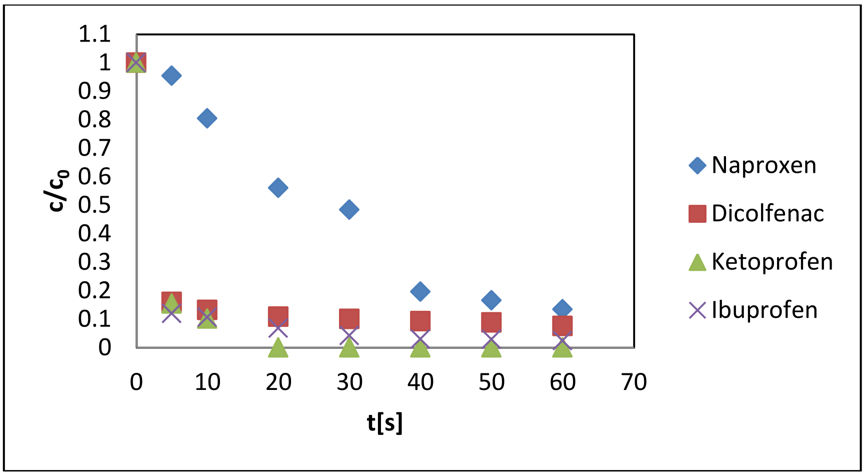

Figure 1. Photocatalytic degradation of a mixture of pharmaceuticals using ZnO/TiO_2 nanopowder

For the decomposition of naproxen, based on the calculated degradation constants, the weight of the 60 mg catalyst was best demonstrated (Figure 4).

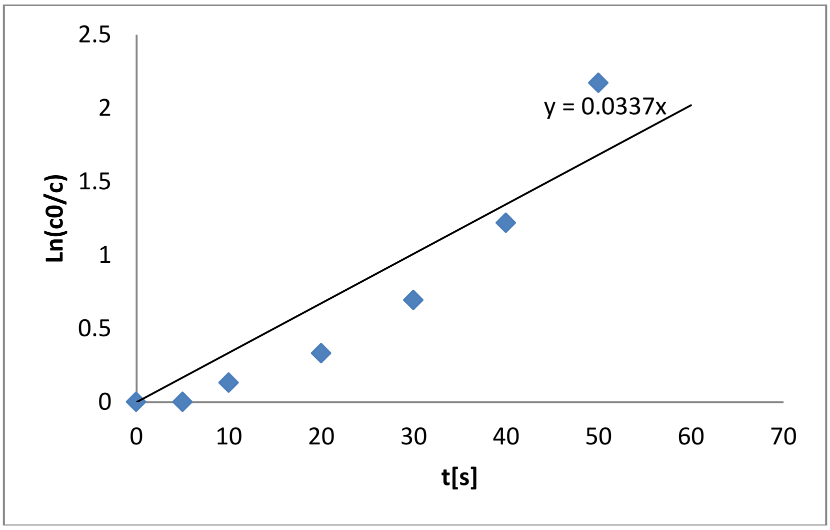

Figure 2. Kinetic of Naproxene photocatalytic degradation of in a mixture of pharmaceuticals using ZnO/TiO_2 nanopowder

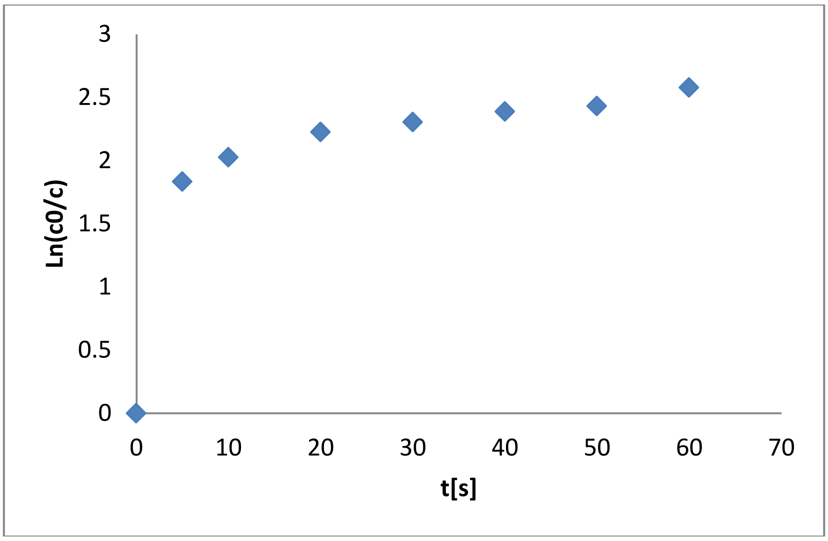

Figure 3. Deviation of kinetics of diclofenac photodegradation from Langmuir-Hinshelwood model

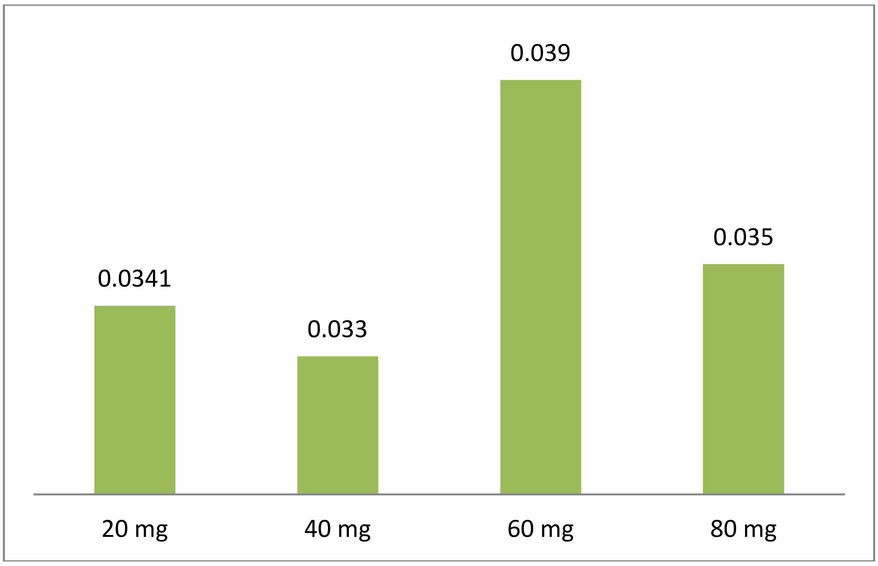

Figure 4. Degradation constants of Naproxene dependence on photo-catalysts mass

Conclusion

The mixture of nanoparticle powder ZnO/TiO_2 possesses distinctive photocatalytic abilities: after 5 minutes from the beginning of the experiment, the concentration of pharmaceuticals decreased almost to half, while diclofenac, ketoprofen and ibuprofen from the mixture were almost totally degraded after 60 minutes. According to the obtained experimental data, naproxen was the most resistant pharmaceutical pollutant, and experimental data were processed depending on the effect of the mass of the catalyst. Diclofenac, ketoprofen and ibuprofen are so rapidly degrading in the given experimental conditions, so Langmuir-Hinshelwood's model cannot be applied, since this dependence no longer describes the experimentally obtained data. On the basis of the calculated degradation constants, for the decomposition of naproxen the weight of the 60 mg catalyst was best revealed.

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