Synthesis and application of new nanostructured materials for the degradation of organic pollutants from municipal landfill leachate

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Abstract: The photocatalytic degradation of pharmaceutically active compounds, persistent contaminants in aquatic media, based on advanced oxidation processes was the subject of investigation. The study evaluates application of three different nanopowder mixtures (ZnO/SnO$_2$, ZnO/TiO$_2$ and ZnO/In$_2$O$_3$) for decomposition of diclofenac, naproxen, ibuprofen and ketoprofen, some of frequently detected pharmaceuticals in wastewaters and landfill leachates. The phase morphology, composition, specific surface area, crystalline structure and optical properties of the newly synthesized nanopowders, prepared by three step mechanochemical solid-state treatment, were characterized in detail. Effects of optimization parameters on degradation rate were examined and a set of experiments were performed in order to investigate influence of catalyst concentration (0.10–0.60 mg mL^{-1}), pH values of ambience (5-9) and initial concentration of pharmaceutics (0.002–0.010mg mL^{-1}) for this purpose.
Keywords: PHOTOCATACLYSIS, NANOPOWDERS, ZnO, PHARMACEUTICALS

1. Introduction

Removal of pharmaceutically active compounds is of a great importance considering that pharmaceutical pollutants are persistent contaminants in aquatic media and that conventional treatment plants are inefficient for their removal [1-3]. Advanced oxidation processes (AOPs) represents an efficient method for treating a wide range of emerging pollutants in municipal effluents and landfill leachates [4 - 9].

Diclofenac, naproxen, ibuprofen and ketoprofen are some of the commonly used NSAIDs (non-steroidal anti-inflammatory drugs) and some of the most frequently detected emerging pollutants (EP) in water matrix. Unlike the vast majority of water pollutants (phenols, phthalates, PCBs etc.) pharmaceutical molecules bear certain differences in their molecular structure which render them less amenable to photodegradation. To alleviate this problem, presented project has been conducted in order to investigate the possibility of application of modified mixed oxides for better photocatalytic activity. Moreover, investigation has aimed to optimize to photodegradation conditions and degradation of mixtures of pharmaceutical.
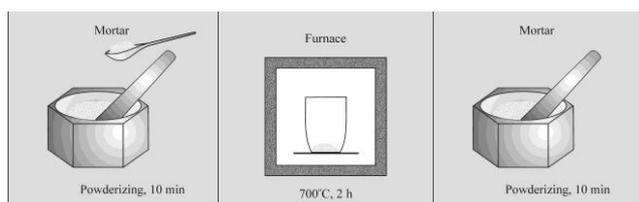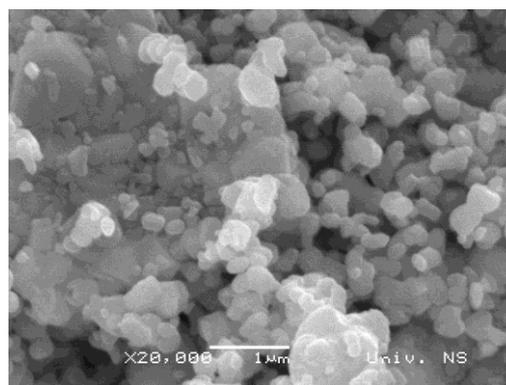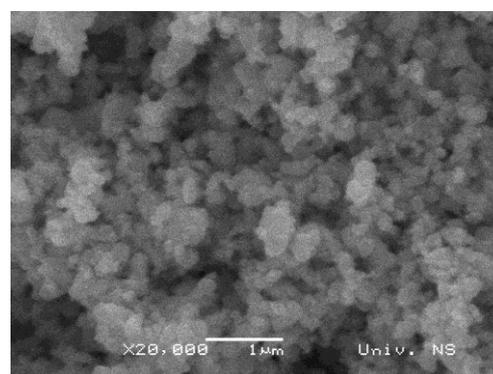

Fig. 1 Synthesis procedure for mixed nano-powders

a)

b)

Fig. 2 SEM image of a) ZnO/In$_2$O$_3$ b) ZnO/SnO$_2$

2. Materials and Methods

Mixed nanopowder photocatalysts were prepared using a simple, low-cost, and three-step mechanochemical solid-state method. Starting precursors (Sigma Aldrich, purity 99.9%) were grounded in an agate mortar, annealed at 700°C in air for two hours and grounded again for 10 min (Figure 1). ZnO/SnO$_2$, ZnO/TiO$_2$ and ZnO/In$_2$O$_3$ nanopowders are prepared bearing in mind that previous investigations have pointed put to ZnO's superior photocatalytic properties and enhanced solubility even at slightly acidic pH solutions, being therefore not the best choice for real life PC applications [8]. In this sense, the ZnO based mixtures emerge as good candidates in the search for alternative materials that compromise the above properties, i.e. PC activity and chemical stability.

The phase morphology, composition, specific surface area, crystalline structure and optical properties of the newly synthesized nanopowders, prepared by three step mechanochemical solid-state treatment, were characterized in detail. The morphology of the powders was characterized by field-emission scanning electron microscopy (Figure 2). X-ray diffraction (XRD) was carried out using Rigaku MiniFlex 600 instrument, with CuKα radiation, and a step scan mode with 0.02° step and a dwell time of 2 s in the angular range 2θ=15-100°. The 441.6 nm laser line emerging from a He-Cd laser was used to excite Raman spectra. Light was focused by an objective (50×) while the same objective was used to collect the backscattered light which was analyzed by a single monochromator (Labram HR800, Jobin-Yvon) and detected by a liquid-nitrogen cooled CCD detector. Diffuse reflectance spectra of obtained samples were recorded by a double-beam UV/VIS/NIR Perkin-Elmer spectrophotometer (model Lambda-950) in the spectral region from 300 nm to 1500 nm using an integrating

sphere. Spectral parameters were used for estimating the optical bandgap of the materials. The specific surface area of the samples was measured with a N2 adsorption analyzer (Micromeritics Gemini) by using the Brunauer-Emmett-Teller (BET) method. Detailed results of previously described investigations are published in References [5,6].

The photocatalytic decompositions of chosen pharmaceuticals were carried out at ambient temperature in aqueous solution in batch mode. The stock solution of the analyzed pharmaceutical was prepared by dissolving 5 mg of standard in 25 ml of acetonitrile (200 mgL-1). Distilled water was used as the aqueous model. 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. The source of the UV light was high-pressure mercury lamp (Philips, HPL-N, emission bands in the UV region at 304, 314, 335, and 366 nm, with maximum emission at 366 nm). UV source flux was measured by Lutron YK-35UV UV meter (Figure 3).

Fig. 3 Lutron YK-35UV UV meter

The solutions were stirred with the aid of a magnetic agitator at 130 rpm. In order to investigate the change in composition of the investigated pollutants, aliquots were collected at certain time intervals (5, 10, 20, 30, 40, 50, 60 and 90 minutes). Each sample was filtered through filter in order to separate the nanoparticles from the solution. After the filtration step, 1 ml of sample was transferred into 2 ml vials.
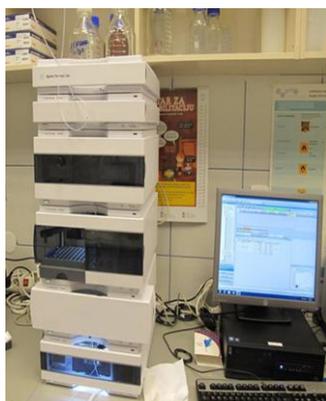

Fig. 4 HPLC Agilent 1260

A HPLC (high performance liquid chromatography) with diode array detector (Agilent 1260 series) was used for the measurement of diclofenac, ibuprofen, naproxene and ketoprofen concentrations after photocatalytic degradation. Chromatography separation was performed at reverse, stationary phase Eclipse XDB-C18 (150 x 4.6,

particle size 5µm) at flow rate of 0.8 mL min^{-1} and injection volume of 10 µL at room temperature. Mobile phases consisted of: A (50%) – 0.1 formic acid and B – acetonitrile in 7 minute initial conditions. The stationary phase temperature is 25 °C.

Effects of optimization parameters on degradation rate were examined and a set of experiments were performed in order to investigate influence of catalyst concentration (0.10–0.60 mg mL^{-1}), pH values of ambience (5-9) and initial concentration of pharmaceutics (0.002–0.010 mg mL^{-1}) for this purpose.

3. Results and Discussion

The degradation kinetics of investigated pollutants was quantified by fitting the experimental data with the Langmuir-Hinshelwood (LH) model [10, 11] where the concentration change depends logarithmically on time:

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

where k is the rate constant and c, c_0 are the analyte concentrations before and after UV irradiation, respectively. Figure 5. shows, as an example, degradation rate of NPX dependence on time. The experiment was performed in mixture of all investigated pharmaceuticals and the used nano-powder was The line is a linear fit, according to LH model.
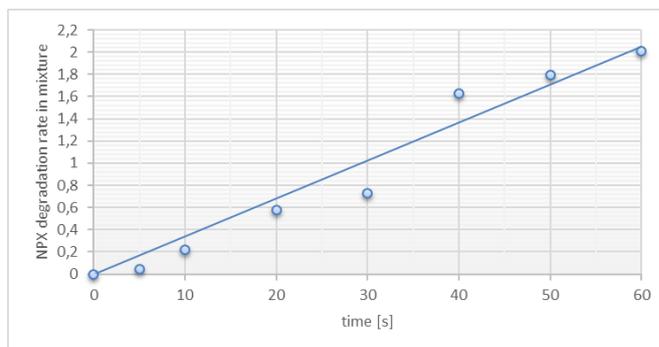

Fig. 5 NPX degradation rate dependence on time in mixture of pharmaceuticals. Linear fit is according to the Langmuir-Hinshelwood (LH) model. (nanostructured photocatalysts ZnO/TiO$_2$)
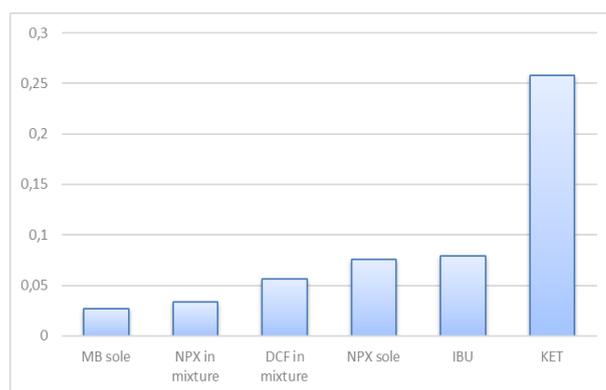

Fig. 6 Comparation of degradation rates of investigated pollutants (LH- model.; nanostructured photocatalysts ZnO/TiO$_2$)

It is important to emphasize here that presence of other pharmaceutical significantly influences degradation rate and that degradation rate varies greatly for different organic pollutant (Figure 6). E.g. in upper case of NPX, if NPX was a sole pollutant in matrix, under the same conditions, degradation rate was significantly higher, namely, 0.076 s^{-1} [6].

Overall, comparing the performance of all three nanostructured photocatalysts ZnO/TiO_2 is by far the best choice for the photodegradation. This mixed nano-powder combines the efficiiancy of ZnO and chemical stability to in the acidic environment, which is usuall in environmental aquatic matrix. Moreover, investigation of influence of pH has shown that in case of ZnO/TiO_2 the highest degradation is achieved at non modified aquatic medium. Under acidic and alkaline conditions, as well as in values of the initial concentrations of pharmaceuticals outside the interval of 4-5 mg L^{-1}, ZnO/SnO_2 is a better choice [5, 6].

3. *Future perspectives*

As it has been previously reported in [12], investigations conducted within the acknowledged project showed that most frequently detected substance in landfill leachate in Subotica, Zrenjanin, Sombor, Sremska Mitrovica and Novi Sad, Autonomous Province of Vojvodina, Republic of Serbia, which is present on NORMAN list of Emerging substances is bisphenol A. In addition, bisphenol A has a huge potential for contamination and threatening groundwater due to its physico-chemical characteristics, especially persistency. Leachate analysis of five landfills showed a presence of different organic and inorganic constituents such as phthalates, benzothiazole and benzene-sulfonamide. Figure 7. shows example chromatograph of landfill leachate in Zrenjanin.
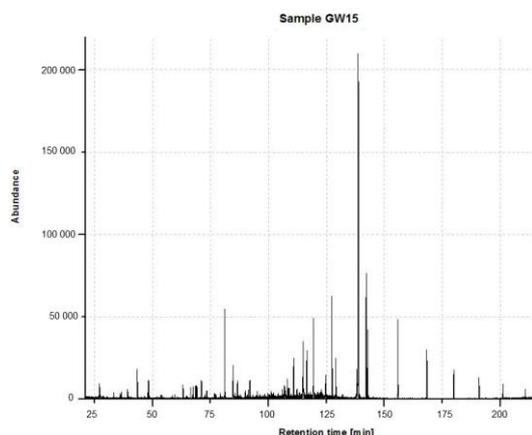

Fig. 7. *Example chromatograph of landfill leachate in Zrenjanin [13].*

For efficient removal of these types of emerging compounds and organic pollution, it is necessary to apply other treatment processes such as photocatalytic degradation process, whose application has showed high efficiency in case of selected pharmaceuticals.

4. *Conclusions*

Due to the existing data on presence of pharmaceuticals and other persistent and pseudo-persistent organic compounds in the landfill leachate, more effective treatment technologies are needed to be developed than those currently in use in wastewater treatment plants. Mixed, tailor-made nanopowders have shown high efficiency in photodegradation of selected pharmaceuticals: ibuprofen, diclofenac, naproxene and ketoprofen. Project results imply further investigation of synthesis and application of novel nanopowders for photocatalytic degradation, with the aim of preparing photocatalysts that are simultaneously efficient for the degradation of more than one category of pollutants since diverse contaminants may be found in the aquatic environment. Bearing in mind the efficiency, chemical stability and commercial reasons (this must be taken into consideration), ZnO/TiO_2 emerges as nanopowder that should be in the scope of further investigation.

5. *References*

[1] R. P. Schwarzenbach, B.I. Escher, K. Fenner, et al., U.V. Gunten, and B. Wehrli, Science; 303 (2006)
[2] M.A. Shannon, P.W. Bohn, M. Elimelech, et al., Nature; 452 (2008)
[3] C. D. Metcalfe, B. G. Koenig, D. T. Bennie, et al, Environ. Toxicol. Chem; 22 (2003)
[4] A.M. Deegan, B. Shaik, K. Nolan, et al., Int. J. Environ. Sci. Technol.; 8 (2011)
[5] M. Novakovic, G. Strbac, M. Petrovic, D. Strbac, I. Mihajlovic, J Environ Sci Health A Tox Hazard Subst Environ Eng. (2019); DOI: 10.1080/10934529.2019.1701895
[6] D. Strbac, C. A. Aggelopoulos, G. Štrbac, G., M. Dimitropoulos, M. Novaković, T. Ivetić, S. N. Yannopoulos, Process Saf. Environ. Prot. 113 (2018)
[7] D. Kanakaraju, B.D. Glass, M. Oelgemöller, Environ. Chem. Lett.; 12 (1) (2014) 27-47
[8] D. Kanakaraju, C. A., Motti, B. D. Glass, et al., Chemosphere. 139 (2015)
[9] Souza, S. C., G. Santos, I. M.1, Silva, M. R. S., Cássia-Santos, M. R., Soledade, L. E. B., Souza, A. G., Lima, S. J. G., Longo, E., J. Thermal Anal. Calorim. 79, 2005
[10] I. Langmuir, J Am Chem Soc, (1918), 40: 1361
[11] C N. Hinshelwood The Kinetics of Chemical Change. Oxford: Clarendon, (1940).
[12] V.Bežanović, M.Sremački, M. Novaković, D.Štrbac, M.Đogo, I.Mihajlović, IWA- YWP, Budapes(2017.)
[13] M. Sremački , I. Mihajlović , M. Đogo, N. Maoduš, G. Gajica, M. Vojinović Miloradov, D. Ubavin, ISWA world congress, Novi Sad (2016)