INFLUENCE OF INORGANIC CONSISTUENTS ON PHOTOCATALYTIC DEGRADATION OF IBUPROFEN

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Abstract
Non-steroidal anti-inflammatory pollutants such as ibuprofen are continuously introduced in water media through various environmental routes. Due to their variability in physico-chemical properties, characteristics of sludge used in secondary treatment and other features, pharmaceutical residues are partially removed in conventional wastewater treatment plants. The effect of inorganic constituent (nitrates) present in real aquatic matrices was examined to assess the overall efficacy of the photocatalytic removal of ibuprofen by nanostructured mixture ZnO/SnO_2.

Introduction
Pharmaceutical active compounds (PhACs) represent one of most dominant group of micropollutants which are continuously introduced into aquatic media, primarily through untreated or inadequately treated wastewater. After usage, the pharmaceuticals undergo to different reactions in which they are transformed into metabolites. These metabolites are often more polar and persistent than the parent compounds. Numerous studies have confirmed that ibuprofen exhibits negative ecotoxicological effects on various aquatic species [1,2]. The aim of this study was to investigate the impact of nitrate ions on photocatalytic degradation of ibuprofen.

Experimental
The synthesis of nanostructured materials was carried out using mechanochemical solid-state method. Initial precursors (ZnO, and SnO_2, purity 99.9%) were grounded in an agate mortar for 10 minutes in a molar ratio of 2:1, then annealed in furnace for two hours at 700 °C and once more grounded for 10 minutes [3,4].
Photocatalytic experiment was performed on laboratory scale. A mercury high pressure lamp of 125 W was used as the radiation source, (manufacturer Philips, HPL-N) emission spectrum in the UV range at 304, 314, 335 and 366 nm with maximum emission at 366 nm. The initial concentration of nanostructured mixture ZnO/SnO_2 and analyzed pharmaceutical (ibuprofen) was 0,40 mg mL^{-1} and 5 mg L^{-1}, respectively. In order to demonstrate the effect of inorganic ions on overall efficiency of ibuprofen decomposition, the nitrate ions were selected. At certain time intervals, 1 mL of treated sample was filtrated through 0,45 μm syringe filters in order to remove nanoparticles. Detection in changes in the ibuprofen concentration is followed by the application of high-performance liquid chromatography (HPLC, Agilent 1260). The concentration of nitrate used for experiment was in the range of 5 to 20 mg L^{-1}. 10 mL of samples were filtered and quantitatively transferred to UV-VIS cuvettes. HACH NitraVer 5 reagent was added to the cuvette containing the sample. The concentration of nitrate ions was determined on UV-VIS spectrophotometer (DR5000, HACH, Germany).

Results and discussion

The obtained results are shown in the Table 1. In order to compare the effect of nitrate ions on the decomposition of ibuprofen, a pseudo first-order constant was used.

Table 1. Influence of nitrate ions on photocatalytic degradation of ibuprofen

Initial concentration of nitrate ions (NO_3^-, mg L^{-1})	**Rate constant (k, min^{-1})**
0	0,045 (3)
5	0,0140(4)
10	0,0070(6)
20	0,0070(5)

By increasing the concentration of nitrate ions, a significant decrease in the value of the degradation constant was recorded. The decrease in the value of the degradation constant was 85 % when analyzing concentrations of 10 and 20 mg L^{-1}. The inhibitory effect during the photocatalytic process is caused by an increase of NO_3^- charge, which emphasizes the electrostatic repulsion between ions and leads to reducing the rate of active adsorption sites on the surface of photocatalysts [5].

Conclusion

Pharmaceutical compounds are micropollutants which are continuously introduced in water streams considering their inefficient removal by conventional wastewater treatment. The heterogenous photocatalytic treatment by newly synthesized nanomaterial ZnO/SnO_2 for removal of nonsteroidal anti-inflammatory pollutants is demonstrated to be efficient. According to obtained results, the inhibitory effect on ibuprofen removal was proven by increasing the concentration of nitrate ions.

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References

[1] V. Di Nica, S. Villa, A. Finizio, Environ. Toxicol. 3098 (2015) 163.
[2] S. Han, K. Choi, J. Kim, K. Ji, S. Kim, B. Ahn, J. Yun, K. Choi, J.S. Khim, X. Zhang, J.P Giesy, Aquat. Toxicol. 7 (2010) 256–264.
[3] T.B. Ivetić, N.L. Finčur, B.F. Abramović, M. Dimitrievska, G.R. Štrbac, K.O. Čajko, B.B. Miljević, L.R. Đačanin, S.R. Lukić-Petrović, Ceram. Int. 42 (2016) 3575–3583.
[4] D. Štrbac, C.A. Aggelopoulos, G. Štrbac, M. Dimitropoulos, M. Novaković, T. Ivetić, S.N. Yannopoulos, Process Saf. Environ. Prot. 113 (2018) 174-183.
[5] G. Fan, R. Ning, J. Luo, J. Zhang, P. Hua, Y. Guo, Z. Li, J. Photochem. Photobiol. A Chem. 386 (2020) 112108.