Synthesis and Application of Zinc Oxide Nanoparticles for Photodegradation of Organic Pollutants, Antibiotic Ofloxacin and Dye Methyl Orange, in Water

Oksana Makota[1,2], Inna Melnyk[2]

1. Department of Physical, Analytical and General Chemistry, Institute of Chemistry and Chemical Technologies, Lviv Polytechnic National University, UKRAINE, 79013 Lviv, Stepana Bandery 12, E-mail: Oksana.I.Makota@lpnu.ua

2. Department of Physical and Physico-chemical Methods of Mineral Processing, Institute of Geotechnics of the Slovak Academy of Sciences, SLOVAK REPUBLIC, 04001 Košice, Watsonova 45, E-mail: melnyk@saske.sk

Abstract. ZnO nanoparticles were synthesized by precipitation method and successfully performed in the degradation of organic contaminants namely ofloxacin and methyl orange under UV irradiation. The photocatalytic pollutants detoxication of 100% was reached in 60 min for the antibiotic and in 120 min for the dye. The reaction can be described by pseudo-first-order model.

Keywords – photocatalysis, pollutants degradation, water purification, ZnO, ofloxacin, methyl orange.

Introduction

Dyes and antibiotics are the main organic pollutants of wastewater that cause environmental contamination and climate change. They not only affect the quality of aquatic organisms but also pose a threat to the health and and wellbeing of humans and other living organisms [1-3]. The widespread presence of organic pollutants in wastewater is a result of their use in various industries such as dyeing and pharmaceutics for diseases treatment. Moreover, the non-biodegradable nature and incomplete metabolism of antibiotics in the human body facilitate their accumulation in water. The accumulation of methyl orange and ofloxacin in water can lead to carcinogenesis, mutagenesis and respiratory toxicity, posing a serious threats to living organism. Therefore, the development of methods for decontaminating organic pollutants attracts much attention. Photocatalysis, a method for detoxification of organic pollutants by their mineralization into water and carbon dioxide, is a promising technology due to its mild conditions, simple process, and environmentally friendly nature. Among the various photocatalysts, ZnO has gained considerable attention due to its excellent transport properties, low cost, and eco-friendliness [3, 4].

Results

In this work, ZnO nanoparticles were synthesized by the precipitation method using $Zn(CH_3COO)_2 \cdot 2H_2O$ and NH_4OH. The structure of prepared photocatalyst was studied by FTIR, XRD, SEM, zeta potential measurement and low-temperature nitrogen adsorption/desorption. Based on these research methods, it was established that the synthesized ZnO particles have specific surface area of 40.94 $m^2\ g^{-1}$, total pore volume of 0.34 $cm^3\ g^{-1}$ and pore diameter of 32.51 nm; the average crystallite size calculated using Debye-Scherrer's equation is 18.0 nm, but according to SEM data these ZnO nanoparticles form agglomerates of microsizes; zeta potential data indicate a negative charge on the surface.

The catalytic effect of prepared zinc oxide was tested in the photodegradation reaction of aqueous solutions of quinolone antibiotic ofloxacin (OFL) as well as azo-dye methyl orange (MO) under UV irradiation at room temperature (UVA-Radiator 368, 9 W, λ=369 nm). The controlled experiments revealed that UV irradiation of a neat solution of OFL (10 mg L^{-1}) as well as MO (13.5 mg L^{-1}) (in an absence of ZnO) for 180 min did not result in pollutant degradation at room temperature and the photolysis process was hardly detected and therefore was not considered. It indicated that ofloxacin and methyl orange exhibited high stability under

UV treatment and could be considered good models for photocatalyst testing. The mixture of zinc oxide with water solutions of quinolone antibiotic or azo-dye was magnetically stirred for 30 min in the dark before UV irradiation in order to establish the adsorption-desorption equilibrium between organic compound and photocatalyst, but without any change in pollutant concentration. As a result, the removal of OFL and MO via adsorption process could be ignored. Only after that dark condition, the photocatalysis of the pollutant degradation was initiated. The concentration of OFL and MO was monitored after reaction solution filtration as a function of time by measuring the absorbance at their maximum wavelength (λ_{max}) of 286 and 466 nm using UV–Vis spectroscopy.

In the presence of zinc oxide under UV irradiation the photocatalytic detoxication of OFL and MO aqueous solutions intensively occurred. The decreasing of organic pollutant concentrations with time C/C_0 (where C_0 – the initial pollutant concentration, C – the pollutant concentration at a specific time during the UV light treatment) was obsereved. After 60 min, the concentration of ofloxacin (50 mg of ZnO) decreased from 1 to 0, while the concentration of methyl orange (30 mg of ZnO) decreased to 0.22 after 60 min and to 0 after 120 min. These results indicated that ZnO exhibits high photocatalytic activity in the degradation reaction of pollutants under UV irradiation, providing 100 % removal of OFL for 60 min and MO for 120 min of reaction, respectively.

It was established that photocatalytic detoxication of ofloxacin and methyl orange in water using photocatalyst ZnO and UV treatment followed the first order reaction and the rate constants from a linear relationship from the plot of $\ln(C_0/C)$ versus time were calculated.

Conclusions

ZnO nanoparticles obtained in one step from cheap reagents have demonstrated a magnificent photocatalytic performance in quinolone antibiotic ofloxacin and azo-dye methyl orange removal from water under UV treatment with efficiency of 100% for 60 min (ofloxacin) and for 120 min (methyl orange). These findings open up perspectives for its application in pollutant detoxication and environmental protection.

Acknowledgments

This work was supported by the Office of the Government of the Slovak Republic (09I03-03-V01-00108 project) and APVV-19-0302.

References

[1] Ren, G., Han, H., Wang, Y., Liu, S., Zhao, J., Meng, X., Li, Z. (2021). Recent advances of photocatalytic application in water treatment: A Review, Nanomaterials, 11, 1804. DOI: 10.3390/nano11071804.

[2] Moghaddam, A A., Mohammadi, L., Bazrafshan, E., Batool, M., Behnampour, M., Baniasadi, M., Mohammadi, L., Zafar, M. N. (2023). Antibiotics sequestration using metal nanoparticles: An updated systematic review and meta-analysis, Inorganica Chimica Acta, 550, 121448. DOI: 10.1016/j.ica.2023.121448

[3] Saravanan A., Senthil Kumar P., Jeevanantham S., Anubha M., Jayashree S. (2022). Degradation of toxic agrochemicals and pharmaceutical pollutants: Effective and alternative approaches toward photocatalysis, Environmental Pollution, 298, 118844. DOI: 10.1016/j.envpol.2022.118844

[4] Chankhanittha, T., Nanan, S. (2018). Hydrothermal synthesis, characterization and enhanced photocatalytic performance of ZnO toward degradation of organic azo dye, Materials Letters, 226, 79–82. DOI: 10.1016/j.matlet.2018.05.032