

Eco-inspired synthesis and photocatalytic application of novel ZnO nanoparticles from peel extract of banana

Daniela Šojić Merkulov*, Sabolč Bogнар, Nina Finčur, Dušica Jovanović
University of Novi Sad Faculty of Sciences, Department of Chemistry, Biochemistry and Environmental Protection,
Trg Dositeja Obradovića 3, 21000 Novi Sad, Serbia
daniela.sojic@dh.uns.ac.rs

Abstract: The time being, one of the greatest concerns is the environmental pollution. Nowadays, various dangerous compounds reach to the air, soil and water. Pharmaceuticals, such as 17 α -ethinylestradiol (EE2), are one of the most emerging pollutants in water ecosystems. Hence, powerful but green approaches should be developed in order to completely remove the pollutants. Heterogeneous photocatalysis is a sustainable and efficient process in the removal of organic pollutants, such as pharmaceuticals. ZnO is one of the most commonly used semiconductors but also possess some drawbacks. In this study novel synthesis pathway of ZnO nanoparticles from banana peel extract was obtained. Besides, the photocatalytic efficiency of the newly synthesized ZnO was examined in the degradation of EE2. Both the eco-friendly ZnO nanoparticles, as well as pure banana peel extract showed a promising photocatalytic activity in the degradation of EE2 under simulated solar irradiation (SSI). Namely, EE2 was completely degraded after 60 min of SSI.

Keywords: ENVIRONMENTAL POLLUTION, SUSTAINABLE WASTEWATER TREATMENT, ADVANCED OXIDATION PROCESSES, HETEROGENEOUS PHOTOCATALYSIS, GREEN SYNTHESIS, ZNO NANOPARTICLES, BANANA PEEL EXTRACT.

1. Introduction

Nowadays, various dangerous compounds reach to the air, soil and water. Environmental pollution is an emerging global issue, with severe impact on natural fields. The water contamination is the second most serious problem, right after the air pollution [1]. Even though all natural ecosystems are exposed to the harmful effects of different pollutants, the water pollution is the most emerging one. Each year, about 380 billion m³ of wastewater is released to the aquatic environment and this amount is expected to be increased by 24% until 2030 [2].

Pharmaceuticals, such as 17 α -ethinylestradiol (EE2), are one of the most emerging pollutants in water ecosystems. EE2 is a synthetic steroid estrogen and commonly applied in controlling ovulation, as well as in treating alopecia, prostate and breast cancer in humans and reproductive disorders. Furthermore, it is also applied in contraceptives and in hormone replacement therapy. Even though this compound can be successfully used for different medical purposes, the human organism cannot use it completely and it can be excreted in the biologically inactive formulation, such as sulfate and glucuronide conjugates, but also as free active molecules. EE2 belongs to the group of endocrine disruptors and has been globally detected at concentrations ranging from 0.3 to 84.0 ng/L in surface water, sanitary sewage, and drinking water and wastewater effluents from sewage treatment plants. Unfortunately, even at low concentrations EE2 can cause serious damages to the living organisms. Several destructive wildlife and human diseases are believed to be caused by EE2. For instance, fish feminization, turtle egg production alterations, functional digestive gland alterations in mussels and also prostate cancer and decreased sperm production in human males [3,4].

Another serious issue is the ineffectiveness of the most commonly used conventional wastewater treatment techniques, which also use harmful chemicals. Hence, powerful but green approaches should be developed in order to completely remove the pollutants.

Advanced oxidation processes (AOPs) are considered to be adequate alternatives. Heterogeneous photocatalysis, as one of the AOPs, is a sustainable and efficient process in the removal of organic pollutants, such as pharmaceuticals [5]. This technique is based on the interaction between semiconductors as photocatalysts and sunlight. As a result, reactive oxygen species are generated, which attack and mineralize the present pollutants. ZnO is one of the most commonly used semiconductors but also possess some drawbacks, which limit its application in photocatalysis. Thus, various ZnO nanoparticles are being synthesized with unique characteristics [6].

The aim of this study was to prepare novel green ZnO nanoparticles from banana peel extract. In addition, the photocatalytic efficiency of the newly synthesized ZnO and pure banana peel extract was examined in the degradation of EE2 under simulated solar irradiation (SSI).

2. Materials and methods

The aqueous solution of EE2 (0.05 mM) was prepared by dissolving appropriate mass in ultrapure water. The solution was stored in dark environment (protected from light) at room temperature.

The synthesis of the novel-green ZnO nanoparticles (ZnO NPs) was conducted using banana-peel-based extract. Banana was obtained from local stores.

Firstly, prior to the ZnO synthesis, the banana peel was washed several times with tap, distilled and ultrapure water. After that, 220 g of washed peel was mixed with 400 mL ultrapure water. The mixture was heated until boiling and cooked for 10 min. Finally, 100 mL of pure extract was separated and stored in a refrigerator for further analyses.

In the eco-friendly synthesis of novel ZnO NPs, ZnSO₄ × 7H₂O (Sigma-Aldrich, St. Louis, MO, USA) was used as a precursor. To begin with, 300 mL banana peel extract was mixed with 1500 mL ZnSO₄ (0.08 M) solution. Then, the pH was set to 10, using 3 M NaOH. During the addition of NaOH, snow-white precipitation was observed, which is proved the formation of ZnO nanoparticles. The mixture was filtrated through a Büchner funnel and the precipitation was collected on a filter paper. The newly-formed ZnO NPs were washed (two times) with ultrapure H₂O, until pH 7. Finally, ZnO nanoparticles were dried in an oven at 100 °C, until constant mass.

3. Analytical procedures

The photodegradation experiments were performed in a photoreactor (TOPT-V, Toption, China). The samples were prepared and irradiated in a photochemical cell made of quartz glass (total volume of ca. 100 mL). The photochemical cells were placed in a circle around the Xe lamp, which was used as simulated solar irradiation. The cells were equally exposed to the irradiation source. Xenon lamp was in a quartz cold trap, which was equipped with water-circulating jackets and connected to a cooler in order to ensure a constant temperature inside the photoreactor (Fig. 1).

The samples of EE2, taken after different times of irradiation using simulated solar irradiation, were firstly filtered through Millipore (Millex-GV, Burlington, MA, USA, 0.22 μ m) membrane filter to remove all possible impurities. After that, they were analyzed using high-pressure liquid chromatograph with fluorescence detector (UFLC-FL, Shimadzu Nexera, Tokyo, Japan)

(excitation and emission wavelength of EE2 were 220 nm and 310 nm, respectively) equipped with Inertsil® ODS-4 column (2.1 mm × 50 mm i.d., particle size 2 μm, 30 °C) was used. Prepared samples (10 μL) were injected and analyzed. The mobile phase (flow rate 0.7 mL/min) was a mixture of acetonitrile and water (80:20, v/v, pH 2.56), while the water was acidified with phosphoric acid, so that the mass fraction of phosphoric acid was 0.1%.

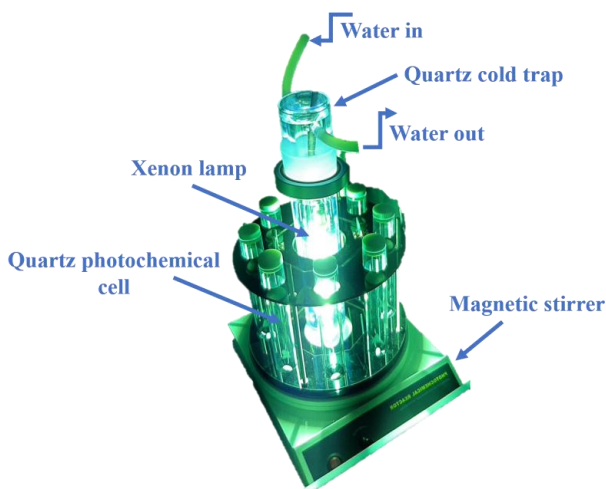


Fig. 1. TOPT-V photoreactor

4. Results and discussion

In order to determine the photocatalytic activity of newly synthesized plant-based ZnO nanoparticles, the photocatalytic degradation efficiency of EE2 was investigated. Firstly, experiments were carried out in the presence of both commercially available ZnO and novel green ZnO NPs. Based on the obtained results (Fig. 2) it can be concluded that banana-peel-based ZnO showed higher photocatalytic activity, since 95% of EE2 was degraded after 60 min of simulated solar irradiation. On the other hand, in the system with commercial ZnO 91% of EE2 was removed, respectively.

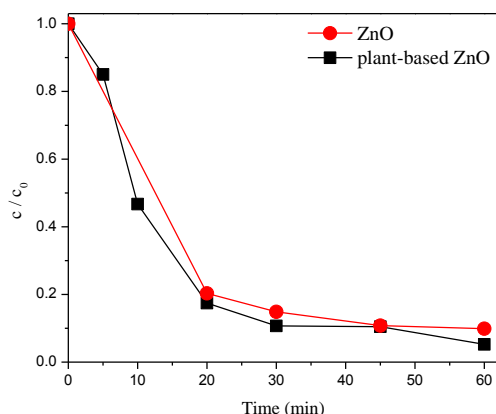


Fig. 2. Kinetics of EE2 (0.05 mM) degradation in the presence of commercial and plan-based ZnO ($\gamma = 1.0$ mg/mL), under simulated solar irradiation

Considering that the novel green ZnO NPs showed the highest removal efficiency, they were used in further experiments. Moreover, the efficiency of pure banana peel extract in the photodegradation of EE2 was also examined. According to the obtained data (Fig. 3), it can be seen that the removal of EE2 was slightly improved in the presence of banana peel extract, compared to the system with ZnO NPs. Namely, 98% of EE2 was successfully degraded in the presence of banana extract, after 60 min of solar irradiation.

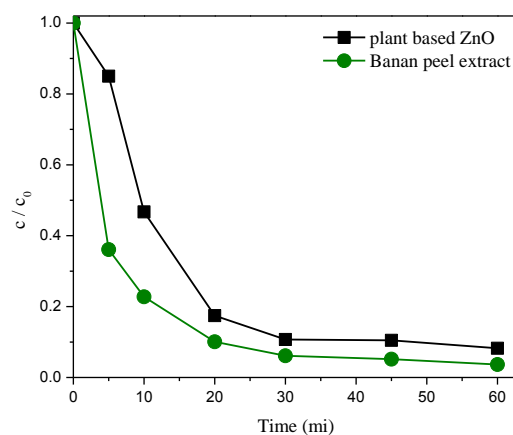


Fig. 3. Kinetics of EE2 (0.05 mM) degradation in the presence of plan-based ZnO ($\gamma = 1.0$ mg/mL) and pure banana extract (5%, v/v), under simulated solar irradiation

5. Conclusion and outlooks

Banana-peel-based ZnO nanoparticles were successfully synthesized via precipitation method with $\text{ZnSO}_4 \times 7\text{H}_2\text{O}$ as a precursor.

Based on the conducted experiments on the photodegradation of EE2, we successfully proved the possible water remediation application of the newly synthesized ZnO-based nanomaterials, as well as banana peel extract.

In general, the phytochemicals present in natural extracts act as reducing and capping agents, thus the synthesis procedure can be accomplished without using the expensive toxic organic stabilizers and complicated time-consuming procedures. Moreover, the plant extracts used for the sustainable synthesis can additionally improve the photocatalytic activity, because of the biomolecules and other natural compounds present in them. However, the exact effects of the biomolecules obtained from plants in the synthesis of nanoparticles, as well as in the photocatalytic processes, are not exactly known and require further investigation.

6. Acknowledgement

The authors acknowledge the financial support of the Science Fund of the Republic of Serbia (Grant No 7747845, *In situ* pollutants removal from waters by sustainable green nanotechnologies-CleanNanoCatalyze).

7. References

1. P. O. Ukaogo, U. Ewuzie, C. V. Onwuka, Environmental pollution: causes, effects, and the remedies, in: P. Chowdhary, A. Raj, D. Verma, Y. Akhter (Eds.), *Microorganisms for Sustainable Environment and Health*, Elsevier Inc., 2020, pp. 419–429.
2. UNESCO, UN-Water, 2020: United Nations World Water Development Report 2020: Water and Climate Change, Paris, UNESCO.
3. D. Ren, F. Chen, Z. Ren, Y. Wang, *Process Saf. Environ. Prot.* **121** (2019), 367–373.
4. F. P. Chaves, G. Gomes, A. Della-Flora, A. Dallegrave, C. Sirtori, E. M. Saggiaro, D.M. Bila, *Sci. Total Environ.* **746** (2020), Art. No. 141041.
5. A. Santos, S. Rodríguez, F. Pardo, A. Romero, *Sci. Total Environ.* **563–564** (2016), 657–663.
6. S. Bognár, P. Putnik, D. Šojić Merkulov, *Nanomaterials* **12** (2022), Art. No. 263.