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GREEN-SYNTHESIZED ZnO NPs AS SUSTAINABLE PHOTOCATALYSTS FOR THE DEGRADATION OF ACETAMINOPHEN

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Abstract

Water contamination is a growing concern with profound implications for public health and ecosystems. The advent of nanotechnology has expanded the utility of nanoparticles (NPs) in diverse fields. These biogenic ZnO nanostructures offer an eco-friendly alternative for photocatalysis. The research aims to (i) employ a green synthesis method for ZnO nanostructure production using a grapefruit extract, (ii) thoroughly characterize these nanostructures using optical microscopy (OM), X-ray diffraction (XRD), Zeta potential and pHpzc, and (iii) evaluate the photocatalytic efficiency in degrading acetaminophen from water solutions. The findings display a sustainable approach to water purification, addressing the challenges of water contamination and emerging pollutants by utilizing green-synthesized ZnO nanoparticles.

Key words*: acetaminophen, green synthesis, photodegradation, zinc oxide.*

INTRODUCTION

Water contamination is a pressing environmental issue that significantly challenges public health and ecosystems (Aragaw et al., 2021; Sandu et al., 2023). In recent years, the proliferation of nanotechnology has led to a dramatic increase in the use of nanoparticles (NPs) and their potential applications. These NPs differ from their bulk or dissolved counterparts in various aspects, such as particle size, dispersion, morphology, surface area, and shape, offering a wide range of possibilities in industries like catalysis, medicine, biology, and cosmetics (Bundschuh et al., 2018). Over the past few years, researchers have extensively explored the performance of nanomaterials in various aqueous environments, including oceans, rivers, lakes, and wetlands. A collective concern among research organizations has been to discover environmentally friendly remediation agents to promote a green economy for soil and water remediation (Saleem & Zaidi, 2020).

Some nanomaterials exhibit a significant adsorption effect on organic substances and metal ions because of the hydroxyl groups present on the nanoparticle surfaces, which bind to certain cations. For instance, carbon nanoparticles, when compared to traditional wastewater treatment agents, demonstrate exceptional stability under alkaline and acidic conditions, boasting a high specific surface area and porous structure (Negroiu et al., 2021).

Consequently, the utilization of nanomaterials in wastewater treatment not only overcomes the limitations of conventional technology but also displays outstanding remediation performance (Kayastha et al., 2022). Moreover, with the advancement of analytical tools, pharmaceuticals and chemicals originating from their metabolism have been detected in various environmental media. The accumulation of these compounds in wastewater is attributed to patient dosages and the rate of metabolism. Even at modest concentrations, these pollutants can adversely influence ecosystems.

Acetaminophen (AMP), also referred to as paracetamol, is a popular analgesic and antipyretic medication. It exits the body either unmodified by excretion in the urine and feces or transformed into hazardous metabolites (such

N-Acetyl-p-benzoquinone imine, or NAPQ). Through the aquatic media, these metabolites enter the food chain (Avramescu et al., 2022). Paracetamol exposure over an extended length of time has been proven in numerous studies to have chronic effects on aquatic creatures, which can impair their growth or reproductive rates (Acevedo-Barrios, & Severiche-Sierra, 2017; Koagouw et al., 2021). Drinking water has been shown to contain traces of AMP, which may cause someone to consume more than is advised daily (Pereira et al., 2021).

Measures have been suggested to reduce drug contamination, including changing the law, strengthening ERA (Environmental Risk Assessment), limiting emissions, and classifying pharmaceuticals as hazardous wastes (Palma et al., 2020). However, these actions are insufficient, and new pollutants continue to accumulate in the environment (Akkari, 2018). Because of this, wastewater treatment facilities have started using advanced oxidation processes (AOPs) that may break down soluble organic contaminants (Richardson, 2009; Vilhunen & Sillanpää, 2010).

Photocatalysis, relying on semiconductors like TiO_2 or ZnO activated by light, is a powerful technique for initiating chemical reactions (Abebe et al., 2020). However, the widespread use of TiO_2 has raised cost concerns, leading to a growing interest in alternative photocatalysts. ZnO has emerged as a promising alternative due to its similar attributes, versatility, and photodegradation mechanism, which, in some cases, offers superior photocatalytic performance (Swati et al., 2020). ZnO NPs have been widely used as semiconductor photocatalysts due to their high reaction rate, large number of available reactive sites, high efficiency in hydrogen peroxide generation, low cost, and environmentally friendly nature.

In recent years, the concept of "green synthesis" has gained prominence in materials science, focusing on environmentally friendly methods for producing nanomaterials (Akhter et al., 2018). This approach aims to reduce chemical by-products, use less hazardous chemicals, employ eco-friendly solvents, and utilize renewable precursors. Various biological materials, including plant extracts, microorganisms, and bioregenerable substances, have been employed in green synthesis, particularly for metal/metal oxide nanoparticles. Nanomaterials synthesized through such methods are often termed "biogenic".

Among these green methods, the use of plant extracts for synthesizing metal oxide nanoparticles has gained attention. This method offers several advantages, such as the ready availability of plant sources, safety, non-toxicity, ease of processing, and the presence of necessary chemical components for the reduction process during synthesis (Jamdagni et al., 2018). Large-scale synthesis using plant extracts is economical and straightforward, with no associated health risks or concerns regarding dangerous microorganisms.

These plant-based synthesis procedures rely on the use of various plant parts, including leaves, stems, fruits, flowers, and roots. Extracts can be easily obtained by exposing the plant material to solvents like distilled water or ethanol. Leaves are often preferred due to their rich deposit of active phytochemicals, offering a renewable, abundant, and non-destructive option. Fruits and seeds are also cost-effective choices.

The synthesis of ZnO nanoparticles via a green method, typically involves mixing plant extracts rich in phytochemicals with a zinc precursor solution, with variations in precursor concentrations, pH, and temperature (Paulkumar et al., 2014). The synthesized nanoparticles are typically annealed to enhance their crystalline nature. Notably, plants are known to contain substantial amounts of polyphenols and flavonoids, which exhibit antioxidant activity. Several studies have demonstrated the successful fabrication of ZnO nanoparticles using plant extracts rich in polyols, phenolic acids, flavonoids, and other bioactive compounds (Dahoumane et al., 2017).

Considering the above context, the primary objectives of this research are (i) to employ green synthesis methods to obtain ZnO nanostructures; (ii) to comprehensively characterize these nanostructures; and (iii) to assess their efficacy as photocatalysts in the degradation of emerging pollutants present in water samples. This research aims to contribute to developing eco-friendly solutions for water purification, harnessing the potential of green-synthesized ZnO nanoparticles to address the challenges posed by water contamination and emerging pollutants.

MATERIALS AND METHODS

Reagents and fruit-based materials

Zinc sulfate heptahydrate (CAS 7446-20-0) $ZnSO_4 \cdot 7H_2O$ and sodium hydroxide (CAS 1310-73-2) NaOH are the reagents used for the synthesis of zinc oxide and were purchased from Sigma Aldrich Romania. The fruit peels (grapefruit) used for the preparation of the extracts were purchased commercially from Romania.

ZnO_g NPs characterization

A detailed analysis of the morpho-structural characteristics of eco-materials obtained from waste as well as those integrated into biopolymer matrices was carried out. This analysis was carried out through an exhaustive research program that highlighted parameters impacting the retention processes of emerging compounds from aqueous solutions using the developed eco-materials. Characterization techniques used included optical microscopy (OM) using an Olympus (BX 51 M), X-ray diffraction (XRD) analysis was performed using a PANalytical X'Pert PRO MPD spectrometer (Almelo, The Netherlands) with a Cu anode, and zeta potential and pHpzc were determined with a ZetaNanosizer (Malvern, Model: Zetasizer Nano ZSP).

Photodegradation experiments

The photocatalytic experiment was performed in the presence of two different dosages of ZnO used as a photocatalyst and acetaminophen (AMP) under UV irradiation. The pollutant solutions are obtained by diluting stock solutions of AMP.

Pollutant analysis

Synthetic wastewater pollutant residues were effectively assessed using the Total Organic Carbon (TOC) technique. The TOC method features specific performance parameters: a detection limit of 0.1 mg/L, a quantification limit of 0.3 mg/L, and an extended uncertainty of the analysis method amounting to 12%. The experimental equipment utilized in these investigations goes by the name of Shimadzu Analyzer TOC TN LCPN.

The removal efficiency (RE) can be determined using the following equation:

$$RE\% = \left(\frac{C_i - C_t}{C_i}\right) x\ 100 \quad (1)$$

where:

- C_t and C_i are the concentration AMP at t moment and the initial moment.

RESULTS AND DISCUSSIONS

ZnO_g NPs preparation

The ZnO NPs (ZnO-grapefruit) were synthesized using a green synthesis method presented in previous research (Constandache et al., 2023). Still, instead of grapes for the "green" extract, grapefruit peels were used. In essence, the aqueous extract of Citrus Paradisi (grapefruit) was prepared by boiling 50 g of outer peel in 200 mL of distilled water for 30 minutes at 80°C. For further experiments, the extract was filtered using a Whatman No. 1 paper and stored at 4°C in the refrigerator. Boiling 50 g of peel in 200 mL of water yielded 150 mL of extract and 40 g of waste.

ZnO NPs were prepared using a solution of 3 mM $ZnSO_4 \cdot 7H_2O$. In a typical preparation, 30 ml of aqueous grapefruit peel extract was added to 30 ml of 3mM $ZnSO_4 \cdot 7H_2O$, and the pH was adjusted to 11 using 3 Mm NaOH. The mixture was mixed for 3 h at 75°C at 300 rpm. The resulting ZnO nanoparticles were separated by decanting overnight, and the next day they were washed five times with distilled water, then dried in a hot air oven at 100°C and calcined at 150°C for 1 hour. After calcination, the resulting nanoparticles were ground in a pistil mill.

Flavonoid, limonoid, and carotenoid molecules include free OH/COOH groups that can react with $ZnSO_4$ to generate a flavonoid/ limonoid/ carotenoid zinc complex. During drying, the zinc flavonoids/ limonoids/ carotenoids are transformed into ZnO nanoparticles.

ZnO_g NPs characterization

Optical Microscopy (OM)

Nanoparticles obtained by the green method were characterized using optical microscopy analysis at 50x magnifications, and the image obtained is shown in Figure 1. It can be seen that the material is in the form of a fine, pale pink powder, and the dimensions of ZnO_g are in the range of 50-150 nm, which are characteristic of nanoparticle agglomerates.

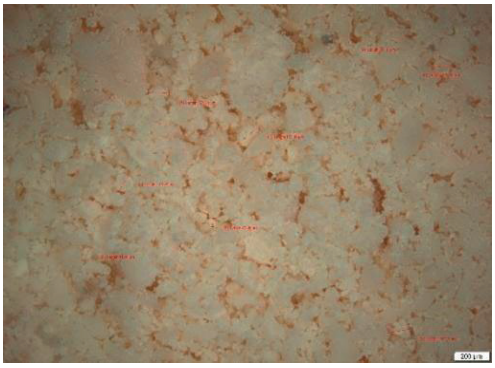

Figure 1. Optical microscopy image of ZnO NPs at 50x magnification

XRD analysis

The resultant diffractogram (Figure 2) demonstrates that the examined ZnO_g contains zinc oxide components, with characteristic diffraction peaks at 2θ of 31.7°, 34.5°, and 36.5° which correspond to the lattice planes of (100), (002), and (101), respectively, were found by analysis. These peaks agreed with the hexagonal zincite structure of ZnO (Naqvi et al., 2014).

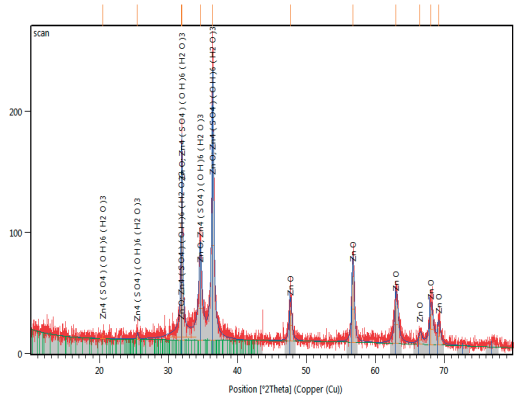

Figure 2. XRD pattern of ZnO NPs

Other diffraction peaks were observed at 2θ of 47.5°, 56.6°, 63.7°, 66.3°, 67.9°, and 69.10°, corresponding to lattice planes of (102), (110), (103), (200), (112), and (201), respectively (JCPDS: 36-1451) (Madhumitha et al., 2019). These findings demonstrated the hexagonal wurtzite structure of the ZnO NPs.

Zeta potential and pHpzc

Determination of zeta potential (ζ) and isoelectric point (IEP) or pHpzc were carried out at 25°C using 1 M NaOH and 1 M HCl solutions respectively for measurement at basic and acidic pH. The samples to be analyzed were prepared by preparing a dispersion in distilled water, ultrasonicating it, and then adding a few drops of this dispersion in a 1 mM NaCl solution.

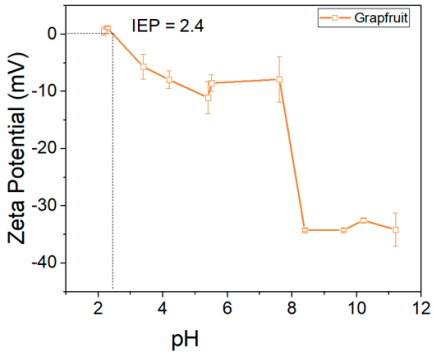

Figure 3. Zeta potential evolution as a function of pH value for ZnO_g

From Figure 3 it can be seen that the isoelectric point values for ZnO nanoparticles prepared in the laboratory are around 2.6. The difference between the IEP of ZnO NPs prepared in the laboratory and that reported in the literature may be due to several factors, including nanoparticle size, surface chemistry, and synthesis method.
In the case of ZnO nanoparticles synthesized using grapefruit extracts the specific pH of 2.6 as isoelectric point may be due to surface functional groups or coating agents in the form of organic compounds in the extracts used. The size and shape of the nanoparticles may affect their isoelectric point. Larger nanoparticles may have lower isoelectric points.

Photodegradation tests

By observing the amount of paracetamol that was degraded in water samples, the photocatalytic efficiency of the ZnO_g was determined. In a typical experiment, different dosages of ZnO_g NPs were placed in contact with two 150 mL vessels of 10 mg/L solutions of AMP. During the experiment, the surfactant solution was homogenized by mixing with a magnetic stirrer, and the UV lamp was positioned laterally. All experiments were performed at room temperature. To determine the concentration of AMP removed, samples were taken at intervals of 15 minutes in the first

part of the experiment and at longer intervals in the second part. The samples collected were stored at 4°C until analysis.

The photodegradation efficiency was determined using TOC analyses, an invaluable method for gauging organic constituents within wastewater, particularly when dealing with low concentrations, involving the introduction of a known sample quantity into a high-temperature furnace or chemically oxidizing environment. Within this controlled setting, organic carbon undergoes oxidation to become carbon dioxide, in the presence of a catalyst.

The resulting carbon dioxide is meticulously quantified using an infrared analyzer. By preparing the sample through acidification and aeration before analysis, any potential errors stemming from the presence of inorganic carbon are effectively mitigated. This method boasts swift execution and is steadily gaining popularity. Figures 4 and 5 present the photodegradation efficiency for AMP when using 0.1 g of ZnO and 0.2 g, respectively.

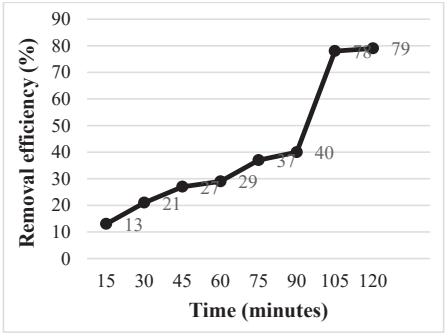

Figure 4. Removal efficiency versus time for acetaminophen contained by wastewater for 0.1 g of ZnO_g

It was observed that the photodegradation in the first 90 minutes increased at a slower rate for both dosages of ZnO_2, reaching only 40% at this time for 0.1g photocatalyst and 53% for 0.2 g, respectively. After this time, the efficiency increased rapidly and stabilized at 79% and 88% after 120 minutes of contact time.

At higher ZnO dosages, the photodegradation efficiency for AMP is higher due to the increased number of active sites on the photocatalyst surface resulting from the higher ZnO_2 dosage. With the increase in dosage, the number of free radicals (•OH and O_2^{2-}) in the solution is also increased, consequently leading to enhanced photodegradation of the wastewater sample (Aisien et al., 2014).

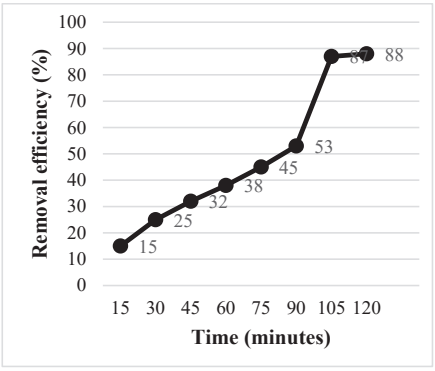

Figure 5. Photodegradation efficiency versus time for acetaminophen contained by wastewater for 0.2 g of ZnO_g

CONCLUSIONS

A ZnO photocatalyst was prepared via a green synthesis precipitation method, using a grapefruit extract as the reducing agent. The structural and morphological analyses suggested that the material was in the form of a fine powder, with aggregates sized in the range of 50-150 nm. The XRD pattern confirmed the presence of ZnO characteristic diffraction peaks, suggesting the successful preparation of ZnO.

The ZnO photocatalyst had the highest degradation efficiency of 88% after 120 minutes of contact with 200 mg of material, for a solution with the concentration of 10 mg AMF. These findings confirm the possibility of using an eco-friendly method to produce an efficient "green" ZnO photocatalyst, with potential application in the removal of emerging pollutants from water.

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