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MORPHOLOGICAL AND STRUCTURAL INVESTIGATIONS OF ZnO RESULTED FROM GREEN SYNTHESIS

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The purpose of this paper was to obtain zinc oxide (ZnO) equally efficient and reliable photocatalyst used in organic compounds pollutants degradation as priority hazardous contaminants from wastewaters. The main advantage of this research is brought by the green synthesis method used for ZnO. The method offers a solution regarding environmental protection by non-toxic reagents or other chemicals and additives, the reducing and stabilizing agent being grape waste (Vitis vinifera) aqueous extract.

Keywords: pollutants, environment, degradation, photocatalytic, materials

1. Introduction

Zinc oxide (ZnO) represents a class of metal oxide that has drawn the most attention from scientists because of its exceptional antibacterial, catalytic, and optical properties [1, 2]. Depending on the morphology of ZnO, it has different physical and chemical properties. There are many ways to produce ZnO, including laser ablation, microwave-assisted combustion, co-precipitation, electrophoretic deposition, electrochemical deposition, sol-gel, chemical vapor deposition, thermal decomposition, and combustion, and other methods [3, 4]. ZnO is a non-toxic semiconductor material with great transparency and excellent photocatalytic activity [5].

Physical and chemical methods have been used to create nanoparticles for a long time, but recently it appears that green chemistry is becoming a popular option [6-8].

For example, Chinnasamy et al. [9] detailed a concentration on the green synthesis of ZnO by assessing the impact of organic concentrate and zinc salt fixation, working time, and temperature, on the molecule size and yield of nanoparticles delivered. Besides, Singh et al. [10] focused on the temperature

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variation from 20 to 100°C and observed that the higher temperature leads to a higher ZnO yield.

In addition, there are investigations that showed the biosynthesis pathways as an efficient solution for ZnO production [11]. Many studies showed the great potential of green synthesis for metal and metal oxides nanoparticles preparation, thus today there is a need to replace the conventional ZnO preparation, especially for biomedical and environmental applications [12-15]. For instance, biosynthesized ZnO can be utilized in the biomedical field for the development of nanocomposites for anticancer and antimicrobial coatings and for the degradation of dyes [16-22].

In addition, plants are the most common biological substrate used for the green synthesis of nanoparticles with metal ions [23]. Different plant parts, such as leaves, roots, and seeds have been used for nanoparticles synthesis [24-25].

Moringa oleifera leaves [11], Physalis alkekengi L. [26], Sedum alfredii Hance [27], Trifolium pretense flowers [28], Pongamia pinnata [29], Cassia Auriculata [30], Spilanthes acmella [31], and Plectranthus amboinicus leaf extracts [32] have been used to synthesize ZnO nanoparticles. Also, ZnO was produced using various amounts of Lycopersicon esculentum peel extract (tomatoes) [33] or red onion extract [34]. Grapes (Vitis vinifera) extracts are used for noble metals salts reduction in order to obtain nanoparticles - NPs (Au and/or Ag) [35]. The extracts present reductive properties due to their valuable active compounds such as phytochemicals polyphenols, flavonoids, and catechins [36, 37].

Based on these literature data, the paper aimed to obtain ZnO without any toxic or dangerous reagents, the reduction agent being a grape (Vitis vinifera) waste aqueous extract. The main preparation steps and preliminary structural and morphological investigations are presented as valuable information for future application of ZnO in photocatalytic organic compounds degradation. For comparison, ZnO was synthesized by using a classical precipitation method.

2. Materials and methods

$ZnSO_4 \cdot 7H_2O$ (CAS 7446-20-0) and NaOH (CAS 1310-73-2) were purchased from Sigma Aldrich Romania. The grape fruits used for the preparation of the extracts were collected from the area of Vrancea county in Romania.

For all the experiments, ultrapure water (18.2 MΩ cm resistivity at 298 K) produced by an ELGA Option-Q DV 25 water purifier system was used.

The aqueous extract was obtained using a commercial mixer with 800 rotation/min and Whatman No. 1 paper filter.

The aqueous extract efficiency was calculated according to the Eq. 1 as follows:

$$\eta = \frac{m_i - m_f}{m_i} * 100 \quad (1)$$

Where η is the efficiency of the extraction process, m_i is the initial mass of the grapes; m_f is the final solid mass.

The ZnO product characterization was achieved by using a PANalytical X-ray diffractometer Pert PRO MPD X with a copper anode X-ray tube (1.54Å) and Olympus optical microscope (BX 51 M).

2.1. Grape waste aqueous extract preparation

400 grams of grapes were removed from the twigs and washed several times in ultrapure water to eliminate impurities before being crushed and mixed with 400 mL of ultrapure water until the mixture was uniform. After filtering an orange-colored solution was obtained. The procedure used for extract preparation is described in Fig. 1.

Fig. 1. Process scheme for obtaining the aqueous extract of grapes

2.2. Synthesis of ZnO using grape aqeuous extract

The principle of ZnO obtaining was based on the precipitation reaction of $ZnSO_4 \cdot 7H_2O$ as precursor and grape waste aqueous extract as a reducing medium under alkaline conditions. Different mass ratios of grape waste and $ZnSO_4 \cdot 7H_2O$ were used: 1:1, 1:2, and 2:1 (w:w). Alkaline medium was established with 1 mM NaOH, for pH 11. The mixtures were stirred at 300 rpm for 2 hours and maintained at 60°C. The color changed from orange to milky cream (Fig. 2) and thus the formation of ZnO was proved. The most efficient ratio was 1:1, in case of 1:2 the precipitation was not occurred and for 2:1 a significant quantity of $ZnSO_4 \cdot 7H_2O$ was unreacted.

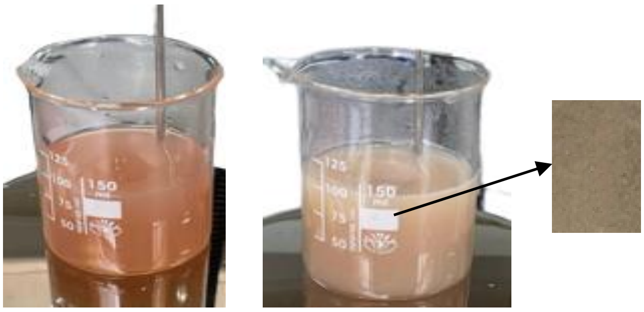


Fig. 2. Color shift from orange to milky cream

The ZnO were separated by settling overnight, and the next day they were washed 5 times with ultrapure water and dried at 150°C, for 1 hour. The final dried aspect is shown in Fig. 2 (inset).

2.3. Synthesis of ZnO using precipitation method

A classic precipitation method was used to synthesis the ZnO by adding in a 0.1M solution of $ZnSO_4$, a 1M solution of NaOH until a pH of 11 was reached.

3. Results and discussions

3.1. Grape aqueous waste extract preparation

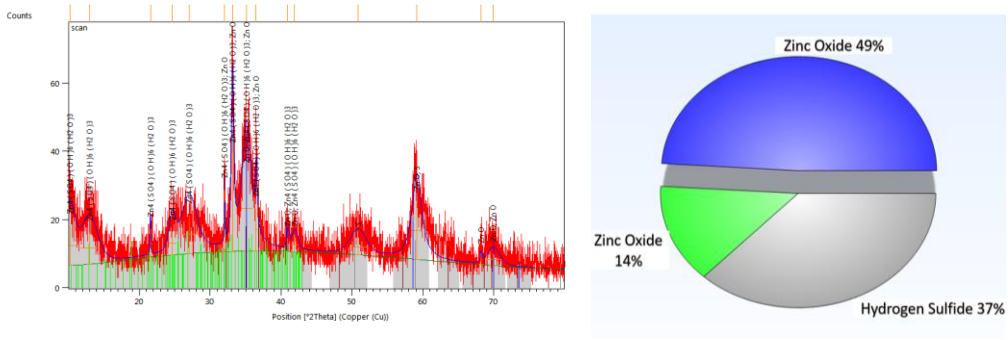
The aqueous grape waste extract resulted with a yield of 85% according to the Eq. (1). According to the literature, this extract contained valuable active compounds with reductive properties [36, 37].

3.2. ZnO preparation

The yield of obtaining ZnO using grape extract was 68% according to the Eq. (1). For comparison, ZnO obtained from precipitation method was used for next step regarding material characterization.

3.3. XRD analysis

The purity and structure of ZnO obtained by green synthesis were analyzed as it is shown in Fig. 3. The recorded diffractogram (Fig. 3a) was compared to the databases in order to identify the crystalline structure (JCPDF – Joint Committee of Powder Diffraction Files) of the sample. Also, a compounds quantification was available (Fig. 3b).



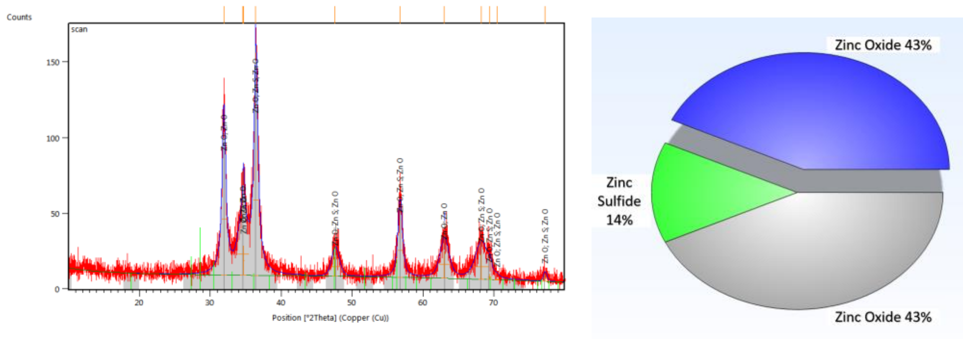
a) b)

Fig. 3. XRD analysis for ZnO by green synthesis as structural (a) and quantitative (b) characterization

ZnO by green synthesis presented some impurities due the precursor unreacted quantities. ZnO were crystallized in 2 forms in the cubic system having the main maximum at 34.581 2ϴ and in the hexagonal system having the main maximum at 36.358 2 ϴ according to the database with reference 01-077-9355, respectively 01-079-0205.

Fig. 3b quantitatively confirms the presence of ZnO. We can observe a total percentage of 63% zinc oxide and 37% unreacted hydrogen sulfate by the bioreduction method.

Comparatively, ZnO synthesized by classical precipitation method was also analyzed, and the presence of ZnO as compounds can be seen in the following diffractogram (Fig. 4a).



a) b)

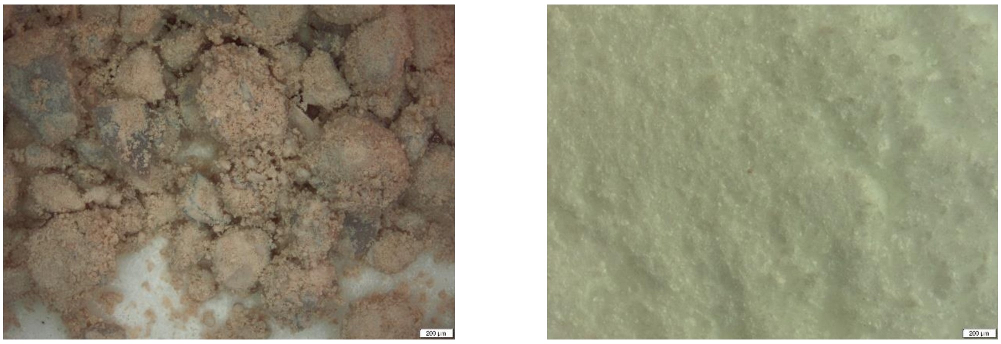
Fig. 4. XRD analysis for ZnO classical method as structural (a) and quantitative (b) characterization

Fig. 4b quantitatively confirms the presence of ZnO in majority proportion. We can observe a total percentage of 86% zinc oxide, 14% zinc sulfate totally unreacted by the bioreduction method.

ZnO is crystallized in the hexagonal system having the main maximum at 36.247 2 ϴ according to the database reference 01-079-9878, respectively 01-078-4493.

3.4. The optical microscopy analysis

The particles obtained by the green method were also characterized using the optical microscope Olympus (BX 51 M) at 50 x magnification, as shown in Fig. 5.



a) b)

Fig. 5. Optical microscopy images for ZnO samples at 50x magnification;
a) ZnO-grapes; b) ZnO-classic

It can be observed that the dimensions of ZnO-classic are located in the range of 50 – 150 µm, which are characteristic of agglomerated particles. In contrast, the sizes of ZnO-grapes are in the range of 100-500 µm, which means that the synthesis method should be improved. They keep their spherical shape, as can be seen in Fig. 5, general characteristic of ZnO.

4. Conclusions

ZnO was obtained by a green synthesis application. The grape waste extract was used as reducing agent for $ZnSO_4{\cdot}7H_2O$. The facile and ecological preparation method demonstrated the possibility to obtain ZnO, without involving harmful precursors at low costs. Also, the green method is in accordance with green chemistry and circular economy concepts.

XRD investigations indicate ZnO as the main compound. Optical microscopy indicates a homogenous agglomeration of ZnO with a size of about 100-500 µm. The surface chemistry characterization and morphological aspects will be developed in future studies based on these preliminary results.

Future applications of green synthesis research for the synthesis of various metal particles will increase as this field of study continues to advance.

Future research will concentrate on finding the best way to synthesize these compounds with photocatalytic characteristics to be investigated in the removal of priority hazardous contaminants from wastewater, considering the bibliographic analysis in this report. In order to increase the detection limits and sensitivity for specific pharmaceutical pollutants, which will serve as the target pollutants, work methods will be created.

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