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SYNTHESIS OF ZnO NANOPARTICLES FOR WATER TREATMENT APPLICATIONS

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Abstract

Industrialization on a global scale has led to water pollution with a variety of persistent organic pollutants, highly toxic and hazardous to the living organisms and also difficult to remove with the existing wastewater treatment technologies. Various methods have been tested for removing these organic contaminants, among which nanotechnology appears to be one of the most promising approaches, as nanomaterials present larger specific surface area and particular physical, chemical and biological properties (developed due to small particle size) suitable for environmental applications. In recent years, SiO_2, TiO_2 and ZnO nanoparticles have been the focus of interest in the wastewater treatment investigations. In the present paper, ZnO nanoparticles were synthesized through the hydrothermal method. The concentration of the alkaline solution was varied in order to obtain ZnO nanoparticles with a high crystallinity degree. The obtained nanoparticles were characterized by x-ray diffraction (XRD), scanning electron microscopy (SEM) and thermogravimetric analysis (TGA). The results showed that the concentration of the alkaline solution influences the size and shape of the particles.

Keywords*: Siret river; Specific geological formations; River margins' expansion and reduction; Preserving the riverbed; Course evolution; Simulation*

Introduction

The continuous population growth, urbanization and industrialization alter the water quality, leading to the depletion of freshwater resources. This affects the surrounding ecosystems and ultimately the human health [1]. Therefore, more efficient, economic, and environmentally friendly methods regarding the treatment technologies are needed in order to reach the standards for discharging the influents [2], as the conventional methods (chemical treatment, filtration, ion exchange and absorption techniques) require high-energy, do not completely remove the emerging pollutants and can produce toxic sludge [3].

Among the emerging technologies, the use of nanomaterials in filtration processes has been the focus of investigation in recent years [4, 5], due to their unique properties determined by their reduced particle size associated with high surface/volume ratios, which increase as the nanoparticle size decreases [6]. Nano-oxides, such as Fe_2O_3, ZnO, TiO_2 and SiO_2, are effective

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adsorbents as a result of their relatively easy synthesis, high surface reactivity, adsorption capacity and destructive sorbent [7-9]. These nanomaterials can be used as such, or can be dopped with a variety of compounds in order to increase their adsorption capacity [10-12].

High BET surface area, porous structure, high catalytic efficiency, strong adsorption ability and antimicrobial properties make ZnO nanoparticles suitable for a variety of applications, including wastewater treatment [8, 13]. Various researchers have determined the removal efficiency of ZnO nanomaterials with different types of heavy metals, including Cu, Pb, Cd, Ni, Co, Pb, Hg and As [14-17], and established that the laboratory obtained ZnO nano-absorbent is more efficient than the commercial ZnO [18]. Additionally, ZnO nanomaterials' photocatalytic action has been extensively studied and it was determined that its efficiency decreases with high calcination temperature, which leads to agglomeration of the particles [8].

Thus, for the synthesis of ZnO nanoparticles numerous methods have been used, such as gas evaporation, chemical vapor deposition, sol gel, precipitation, spray pyrolysis and thermal decomposition, but the chemical techniques tend to be preferred as they provide control of nucleation, growth and ageing of particles during synthesis [19]. Among these, the hydrothermal method is a cost effective, low-temperature, substrate independent and straightforward technique that determines controllable structures [20].

Therefore, the aim of this study is to obtain and characterize ZnO nanoparticles in order to determine its potential use in wastewater treatment.

Materials and methods

To establish the effect of pH on the morphology of ZnO, the concentration of the alkaline solution was varied. Thus, for the synthesis of ZnO nanoparticles, 6g of zinc acetate dihydrate were dissolved in 50mL of methanol by continuous stirring. 0.2 - 0.3M NaOH solution was added to the mixture, up to a pH of 10. Subsequently, the hydrothermal treatment was carried out at 125°C for 8 hours with autogenous pressure. The resulting product was washed with methanol and dried in the oven at 60°C.

The obtained ZnO nanoparticles were subjected to X-ray diffraction (XRD) to identify the crystal phase and crystallite size using a D8 Advance diffractometer (Bruker) with Cu K_α radiation. The morphology was assessed through scanning electron microscopy (SEM) by using a Hitachi SU-70. Additionally, thermogravimetric analysis (TGA) was performed to observe the decomposition process through a STA 449 F5 Jupiter (Netzsch).

Results and discussion

Structural characterization

Figure 1 presents the XRD spectra of the two types of ZnO nanoparticles. In the 2θ interval between 30° - 50°, the high intensity and narrow line width of the spectra being an indicative of the good crystallinity of the synthesized ZnO nanoparticles [21]. These sharp peaks correspond to the diffraction planes 100, 002, 101, 102. These diffraction planes were assigned to ZnO with hexagonal structure of wurtzite, which consists of atoms forming hexagonal-close-pack sub-lattices stacking alternatively along the c-axis. This type of structure exhibits non-centrosymmetry, determining properties such as piezoelectricity and pyroelectricity [22].

The maximum intensity was recorded for the peak corresponding to 2θ = 36,3°, originating from the (101) diffraction plan.

The crystallite size was determined from the diffraction patterns by using the Scherrer equation, which is usually most effective for crystallite sizes of 200 nm or less:

$$D = (k \times \lambda) \cdot (FWHM \times \cos\theta)^{-1} \quad (1)$$

in which D is the crystallite size, k is the shape constant, FWHM is the full width at half-intensity of the diffraction peak and θ is the Bragg angle [23]. The shape constant used in the equation was 1.24, which was the value recommended for hexagonal particles by *W.H. Qi et al.* [24].

Based on equation (1) the average crystallite size for both types of ZnO nanoparticles was established for the 3 most intense peaks corresponding to the XRD spectra, as it can be seen in table 1.

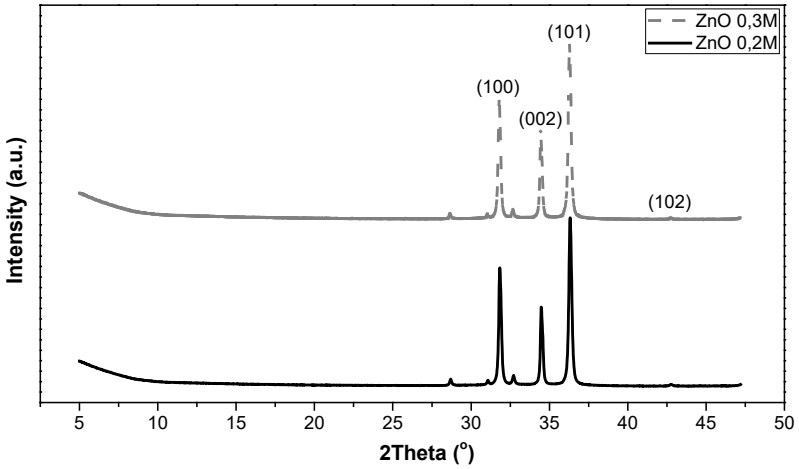

Fig. 1. XRD spectra of obtained ZnO nanoparticles

Table 1. Crystallite sizes for the obtained ZnO nanoparticles

Type of ZnO nanoparticles	2θ, degrees	Crystallite size	
		D, nm	D_{Av}*, nm
0.2M	31.84	45.99	48.91
	34.50	57.88	
	36.31	42.85	
0.3M	31.8	44.67	46.96
	34.45	59.97	
	36.25	36.25	

* D_{Av} – average crystallite size.

From table 1, it can be seen that a higher concentration of alkaline solution produces a slightly lower average crystallite size. Thus, the synthesis parameters (precursors type and concentration, reaction temperature, growth time, etc.) are determining in obtaining lower crystallite sizes, as it can be seen in the investigation carried out by *D. Varshney et al.* [25] which obtained an average crystallite size of 39nm when synthesizing ZnO nanoparticles from zinc nitrate hexahydrate and sodium hydroxide (6M solution) by chemical co-precipitation method.

The microstructural characterization of the obtained samples through SEM analysis reveals submicron particles, hexagonally crystallized in the form of overlapping rods with

hollow centres (Fig. 2). It can also be seen that the growth direction of these porous particles was random (preferential orientation).

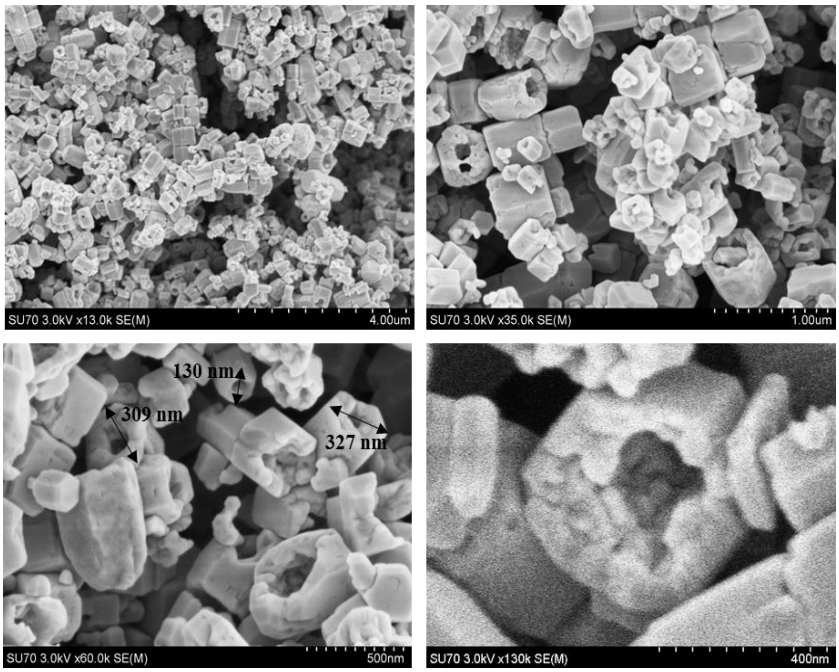

Fig. 2. SEM images of ZnO nanoparticles synthesized with 0.2M NaOH

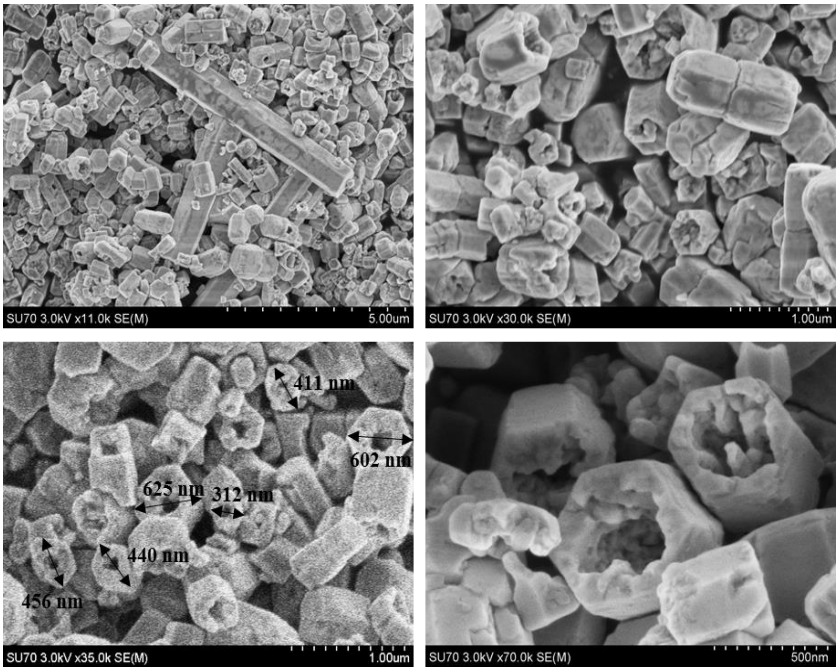

Fig. 3. SEM images of ZnO nanoparticles synthesized with 0.3M NaOH

From figure 3 it can be seen that the concentration of the alkaline solution influences the shape and size of the ZnO crystals. Thus, the ZnO nanoparticles obtained with 0.3M NaOH solution have bigger dimensions and tend to agglomerate.

Similar morphologies of the ZnO nanostructures (hexagonal particles and rods) were obtained by Giri et al. when investigating a chemical method to synthesize ZnO nanoparticles, namely low temperature oxidation of metallic zinc powder in the presence of two different catalysts (acetic acid and trifluoroacetic acid) [20].

Thermal analysis

The decomposition process of the two types of ZnO nanoparticles was determined by thermogravimetric analysis. From figure 4, it can be seen the thermal behaviour of the obtained samples in the range between 25 – 800°C, at a heating rate of 10 K/min.

On the TG curves, it can be noticed two mass loss steps, one before 200°C and the second one in the interval 200 – 600°C. The first mass loss can be associated to the evaporation of surface water and was estimated to be 0.66 wt% for ZnO nanoparticles obtained with 0.2M NaOH solution, and 0.63wt% for the nanoparticles synthesized with 0.2M NaOH solution. These results are in accordance with the ones obtained by Wang and Muhammed for ZnO nanoparticles, where the weight loss due to water removal was approximately 1 - 2wt% [19]. The second mass loss of only 1.27 - 1.47wt% could be due to the decomposition of the zinc carbonate possibly formed upon drying the samples.

The TG curves do not present any associated signal, confirming the crystallization of the nanoparticles. This slight mass loss registered for both samples is comparable with the one observed for ZnO nanoparticles calcinated at 400°C [21], highlighting that the ZnO nanoparticles obtained by hydrothermal method do not require subsequent thermal treatment.

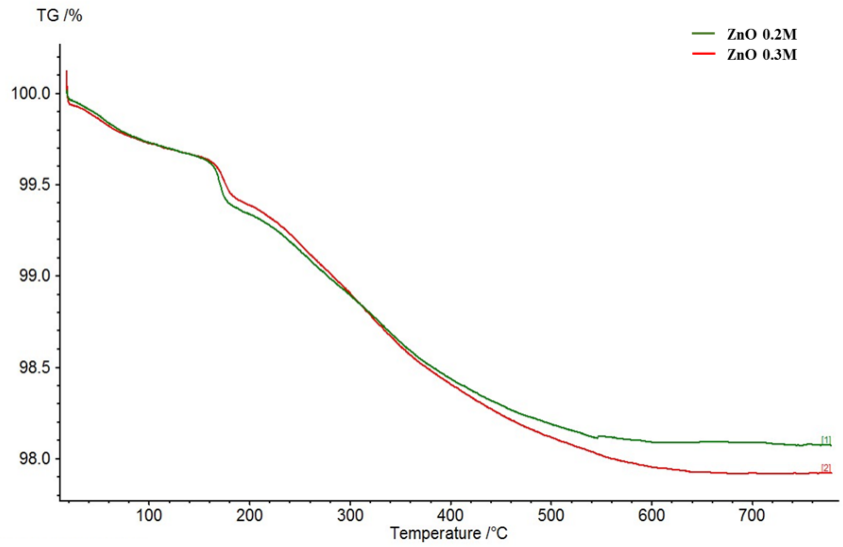

Fig. 4. Thermogravimetric analysis of the ZnO nanoparticles

The behaviour of both analysed samples indicates the thermal stability of the synthesized ZnO nanoparticles.

Conclusions

Hexagonal porous ZnO nanoparticles were synthesized through the hydrothermal method by varying the concentration of the alkaline solution (0.2 and 0.3M).

The structural characterization of the obtained samples showed good crystallinity of the synthesized ZnO nanoparticles corresponding to the hexagonal wurtzite structure. Using the Scherrer equation on the XRD measurement, the average crystallite size of the samples was determined to be ~50nm.

Microstructural analysis showed hexagonal porous particles crystallized in the form of overlapping rods, which slightly differed in size and shape due to the concentration of the alkaline solution. Also, a lower concentration determined a reduction of the agglomeration.

The thermogravimetric analysis showed a slight mass loss of the two samples (1.93 - 2.1wt%), indicating the thermal stability of the ZnO nanoparticles synthesized by hydrothermal method.

Acknowledgments

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