

# DEZVOLTAREA DE MEMBRANE NANOCOMPOZITE ANTIMICROBIENE CHITOSAN/ZnO PENTRU PURIFICAREA APEI

## THE DEVELOPMENT OF ANTIMICROBIAL CHITOSAN/ZnO NANOCOMPOSITE MEMBRANES FOR WATER PURIFICATION

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The purpose of this article was to synthesize antimicrobial composite membranes using chitosan (CS) and zinc oxide (ZnO) nanoparticles as adsorbents for the removal of heavy metals. Chitosan/ ZnO composite membranes were prepared through the electrospinning method. The ZnO nanoparticles concentration from the CS/ZnO composite membranes was 1% and respectively, 5%. The synthesized membranes were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), differential thermal analysis (DTA), hydration capacity, antimicrobial assessments and, heavy metal retention through the inductively coupled plasma mass spectrometry (ICP-MS) analysis technique. The thickness of the as-prepared CS/ZnO composite membranes was 20 $\mu$ m (CS/ZnO 1%) and 30 $\mu$ m (CS/ZnO 5%). The appearance of the synthesized membranes indicated a smooth and uniform morphology, which suggested the integration of zinc oxide nanoparticles into the obtained membrane. Fourier transform infrared spectroscopic measurements showed the existence of relevant functional groups of both chitosan and ZnO in the composite membranes. ICP-MS measurements provided information regarding the capacity of retention of these membranes, indicating that CS/ZnO 5% had the highest retention rate. The as-obtained CS/ZnO composite membranes are expected to be used as adsorbent materials for water purification applications.

Scopul acestui articol constă în sinteza membranelor compozite antimicrobiene utilizând chitosanul (CS) și nanoparticulele de oxid de zinc (ZnO) ca adsorbanti pentru îndepărtarea metalelor grele. Membranele compozite CS/ZnO au fost pregătite prin metoda electrofilării. Concentrația nanoparticulelor de ZnO din membranele compozite CS/ZnO a fost de 1%, respectiv 5%. Membranele sintetizate au fost caracterizate prin spectroscopie în infraroșu cu transformata Fourier (FTIR), microscopie electronică cu baleiaj (SEM), analiza termică diferențială (ATD), capacitate de hidratare, activitate antimicrobiană, cât și retenția metalelor grele prin spectrometrie de masă cu plasmă cuplată inductiv (ICP-MS). Grosimea membranelor compozite CS/ZnO a fost de 20 $\mu$ m (CS/ZnO 1%) și 30 $\mu$ m (CS/ZnO 5%). Aspectul membranelor sintetizate prezintă morfologie netedă și uniformă, sugerând integrarea nanoparticulelor de ZnO în membrane. Măsurătorile FTIR denotă prezența grupărilor funcționale relevante atât ale chitosanului, cât și a ZnO din membranele compozite. Măsurătorile ICP-MS oferă informații cu privire la capacitatea de retenție a acestor membrane, indicând faptul că CS/ZnO 5% a avut cea mai înaltă rată de retenție. Se așteaptă ca membranele compozite CS/ZnO să fie utilizate ca materiale adsorbante pentru aplicații de purificare a apei.

**Keywords:** ZnO; chitosan; nanocomposite membranes; antimicrobial; water purification

### 1. Introduction

During the last several decades, contaminated water with diverse toxic pollutants (pesticides, antibiotics, heavy metals, etc.) has become an imperious problem that needs to be solved. Due to external, industrial factors and climate change, but also to human negligence, limitless quantities of water systems worldwide are getting contaminated. The elimination of toxic pollutants is very important, as they get into the water networks can have a dangerous impact on both environment

and human health [1-5]. The worldwide water problem has been brought to the eyes of many researchers and scientists but also to the authorities and NGOs, which are focusing their interest on developing new alternative methods to solve the problem. At the present moment, traditional methods are used for the removal of diverse pollutants. Filtration, reduction, coprecipitation, sedimentation and distillation, and adsorption, are some of the most used. From all these methods, adsorption has been attracted great interest

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because it offers significant advantages when it comes to cost and easy usability [2].

Therefore, new instruments/ strategies have been developed using nanostructured adsorbents obtained by nanotechnological approaches. Porous materials have gained potential interest and developed as adsorbents used for the removal of pollutants from water systems [6]. From many nanomaterials used as purification adsorbents, oxides have attracted the most attention due to their properties and applicability. ZnO is considered a multifunctional material having many applications in diverse fields, such as cosmetics [7], medical devices [8], textiles [9], photocatalysts [10, 11], and pharmaceuticals [12]. The scientific literature data provides numerous information regarding zinc oxide antibacterial activity presenting potential applications in water purification by enhancing the water system's quality. The most important aspects are its safety and photocatalytic activity, which are the preferential factors when it comes to antimicrobial activity as an antibacterial agent for water purification applications [13].

To develop composite membranes for the removal of toxic pollutants, biodegradable biopolymers were considered. Chitosan biopolymer has attracted special attention due to its biocompatibility, biodegradability, bio-renewability, non-toxicity, and cost-effectiveness, compared to other materials used in water treatment applications [14]. Considering its composition and structure, also unique physicochemical properties, it has been used as an important adsorbent material for the removal of diverse pollutants such as microorganisms, heavy metals, dyes, and others, from wastewaters [2, 15].

The Chitosan/ZnO membranes were prepared through the electrospinning method. There are several methods to develop membranes and the electrospinning method appears to be the most fascinating process. Electrospinning is a simple and low-cost technique for developing nanoscale fibers/membranes from both natural and synthetic polymers. This technology offers unique features to the micro/ nanofibers, such as controlled pore structure and large surface-area-to-volume ratio. Usually, an electrospinning device has three main components: a high voltage power supply, a pipette tip, and a collecting plate. Electrospun fibers are mainly used in biomedical applications, such as wound dressings, drug delivery, tissue engineering, and also water treatment [1, 16-18].

Based on the literature information, this study aimed to synthesize Chitosan/ZnO composite membranes for heavy metal removal from aqueous solutions. The ZnO nanoparticles were obtained through a simple co-precipitation method, as presented in [13]. From the results presented in the previous work [13], it has been concluded that ZnO has great potential as an antibacterial and

photocatalyst agent for further use in developing nanocomposite membranes for water purification.

## 2. Materials and Methods

### 2.1. Samples' Preparation

Figure 1 illustrates a schematic chart of the preparation of the Chitosan/ZnO antimicrobial nanocomposite membranes by the electrospinning method. First, chitosan (molecular weight 100.000-300.000, Acros Organics, Geel, Belgium) was dissolved in glacial acetic acid (Chim reactiv, Bucharest, Romania) to form a 2% solution. Then, to the previous chitosan solution was added zinc oxide, (ZnO antibacterial nanoparticles were obtained through a simple co-precipitation method) and distilled water; afterwards, the mixture was magnetically stirred at room temperature for 24h and then sonicated for 4h at 35°C, to obtain a homogenous solution. For this experiment, two polymer solutions with 1% and respectively 5% zinc oxide nanoparticles were prepared and electrospun. Worth mentioning that the resulting membranes were treated with NaOH solution to reprecipitate the dissolved ZnO, afterwards washed with distilled water to remove the side products as well as the NaOH. The use of ZnO instead of any ZnO precursor was assumed because the dissolution rate is reasonable, and it is preferred to use the ZnO particles which already proved their biological activity and the redissolved ZnO will be further used in developing composite membranes through the electrospinning method. Each polymer solution was placed in a syringe pump connected to the electrospinning equipment, where the formed membranes were collected onto the rolling drum when applying a high electrical voltage of +3.30kV/-19.55kV. During the electrospinning process, the nozzle was continuously moving inwards and outwards parallel to the axis of the collector for a distance of 100 mm. The electrospinning distance between the needle tip and collector was set at 4cm. The syringe pump was set to a flow rate of 6 ml/h and has been running continuously for 5h for each membrane sample. The synthesized membranes were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), differential thermal analysis (DTA), hydration capacity, antimicrobial assessments, and heavy metals retention capacity.

### 2.2. Characterization

The obtained Chitosan/ZnO composite membranes were characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), differential thermal analysis (DTA), hydration capacity, antimicrobial assessments, and heavy metals retention capacity.

The electron microscopy images were obtained using a Quanta Inspect F50 (FEI Company, Eindhoven, The Netherlands) equipped

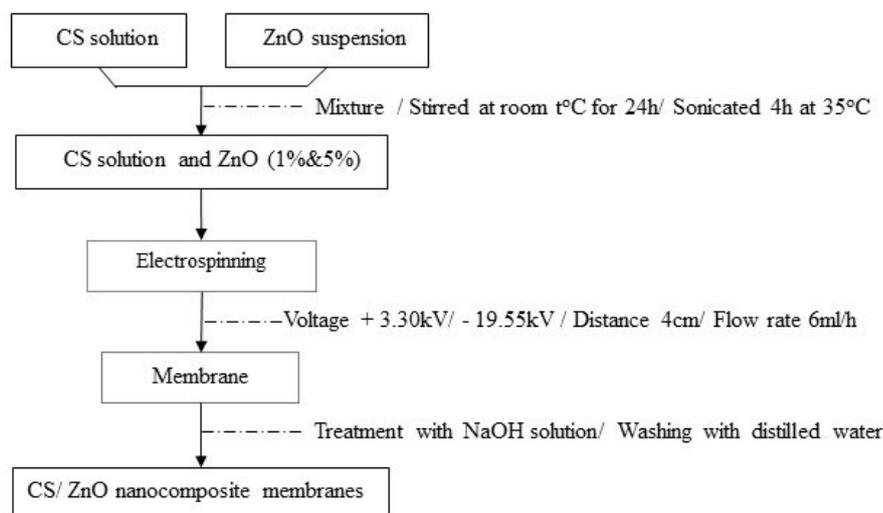


Fig. 1 - Schematic chart of the preparation of CS/ZnO nanocomposite membranes by electrospinning method / Schema de obținere a membranelor compozite CS/ZnO prin metoda electrofilării

with a field emission gun (FEG) with a 1.2 nm resolution, and an energy dispersive X-ray spectrometer (EDS) with a MnK resolution of 133 eV K $\alpha$ .

The Fourier transform infrared spectroscopy (FTIR) measurements were performed using a Nicolet iS50R spectrometer (Thermo Fisher Scientific, MA, USA). The spectra were performed at room temperature using the attenuated total reflection (ATR) mode (Thermo Fisher Scientific, MA, USA), by co-adding 32 scans between 4000 and 400  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ , the scanning time being 47 s/spectrum. The recording and the future processing and analysis of the data were possible by connecting the spectrometer to the data acquisition and processing unit through the Omnic program (Thermo Fisher Scientific, MA, USA).

Thermal analysis (TG-DSC) was performed with an STA 449 F3 Jupiter apparatus, from Netzsch (Selb, Germany). Approximately 10 mg of dry powder was placed in an open alumina crucible and heated up to 900°C with a 10  $\text{K}\cdot\text{min}^{-1}$  rate, under a flow of 50  $\text{mL}\cdot\text{min}^{-1}$  of dried air. As a reference, an empty alumina crucible was used. The evolved gases were analyzed with an FTIR Tensor 27 from Bruker (Bruker Co., Ettlingen, Germany) equipped with a thermostatic gas cell.

The chitosan/ZnO composite membranes were evaluated by determining the weight change of the samples during the adsorption in distilled water for 24 h. The measurements were made at different intervals of time: 0.25, 0.5, 1, 2, 4, 6, 12, and 24 h. The hydration capacity was calculated by measuring the initial weight ( $M_i$ ) and the weight of the sample after immersion in distilled water ( $M_{h,t}$ ) for a defined period using Equation (1): *Hydration capacity* =  $(M_{h,t} - M_i) / M_i \times 100$ .

The antimicrobial assessment was performed using Nutrient Broth No. 2 and Agar with microbiological grades, which were purchased from Sigma-Aldrich. All strains tested in this study come

from the Microorganisms Collection of the Department of Microbiology, Faculty of Biology & Research Institute of the University of Bucharest.

The capability of the bacterial strains to adhere to the surface of the chitosan/ZnO membranes was evaluated against *Escherichia coli* ATCC 25922, *Enterococcus faecalis* ATCC 29212, and *Citrobacter* sp. 2021. The experiment was performed using the same protocol from the previous study [19]. The antimicrobial assessments were performed in triplicate and were statistically analyzed using GraphPad Prism 9 for Windows 64-bit, version 9.3.1 (471), developed by GraphPad Software, San Diego, CA, USA. We compared the inhibitory effect of chitosan/ ZnO membranes against bacterial strains that may be present in polluted waters using a one-way analysis of variance (one-way ANOVA), and in addition, Tukey's multiple comparisons test for studying differences between groups. A p-value < 0.05 was considered statistically significant.

The heavy metals retention capacity of the chitosan/ZnO membranes was evaluated by inductively coupled plasma mass spectrometry (ICP-MS). Thus, each membrane was exposed 2h to 1% and 5% lead nitrate and 1% and 5% cadmium nitrate solution (both from Sigma-Aldrich). Nitrate solutions have been used as sources of heavy metals that can be found in polluting aqueous media having a strong negative impact on the environment including animal and human health. Considering the concentrations of cadmium and lead, the retention of heavy metals on the composite membranes was evaluated. Thus, to determine the cadmium and lead retention in membranes, an inductively coupled plasma mass spectrometry (ICP-MS) Agilent 8800 equipment was used. Before the ICP-MS measurements, the samples were weighed and placed in special TFM tubes. After the addition of 8ml of  $\text{HNO}_3$ , the samples were digested in a microwave system at 200°C for 35 minutes at a

maximum power of 1800W. After cooling, the digestion fluids were diluted with ultrapure water to 50 ml. To avoid analyzing the two elements in too high concentrations, all 16 samples were subsequently diluted 10,000 times.

Considering the stability and natural isotopic abundances of the two target elements, the measurements were performed for  $^{111}\text{Cd}$  and  $^{208}\text{Pb}$  isotopes, and the quantification of the results was performed through the external calibration method, using a standard multi-element solution of 100  $\mu\text{g/ml}$ , which the points of the calibration curve were prepared. The calibration curves for the two isotopes were linear in the range 0.5-100  $\mu\text{g/l}$ , with a correlation coefficient  $R^2 = 0.9998$  for  $^{111}\text{Cd}$ , respectively,  $R^2 = 0.9999$  for  $^{208}\text{Pb}$  (Figure 2).

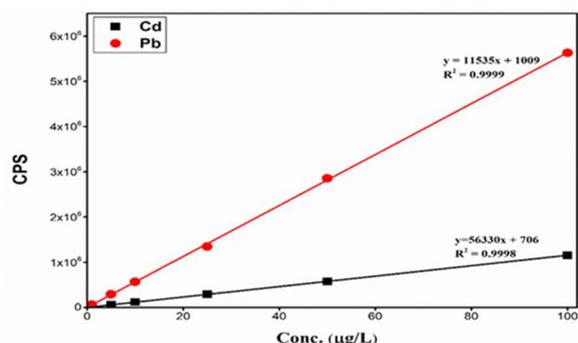


Fig. 2 - Calibration curve for  $^{111}\text{Cd}$  and  $^{208}\text{Pb}$  isotopes / Curba de calibrare pentru izotopii  $^{111}\text{Cd}$  și  $^{208}\text{Pb}$ .

samples used for SEM analysis were realized through the electrospinning method, outlining the morphology and aspect of the obtained membranes. Following the FTIR analysis, results suggested that the O-Zn-O functional group indicates the ZnO presence from the composite membranes. The powders used for TG-DSC investigations were realized to determine the behavior of the polymer structure when the temperature changes. The nanocomposite membranes used for the antimicrobial assessments were subjected/ exposed to *E. coli*, *E. faecalis*, and *Citrobacter* sp.

**3.1.SEM:** The as-obtained synthesized composite membranes were analyzed by scanning electron microscopy to determine the morphology of the samples, proving information regarding the surface of the sample.

In the case of both samples, we noticed that the samples have the same uniform morphology, but on the surface of the membranes are presented small swellings, which probably are due to their handling in the microscope. Also, on the sample's surfaces can be observed small particles, which most likely resulted from the electrospinning process, representing remains from the zinc oxide nanoparticles presented in the composition of the composite membranes (Figure 3 & 4).

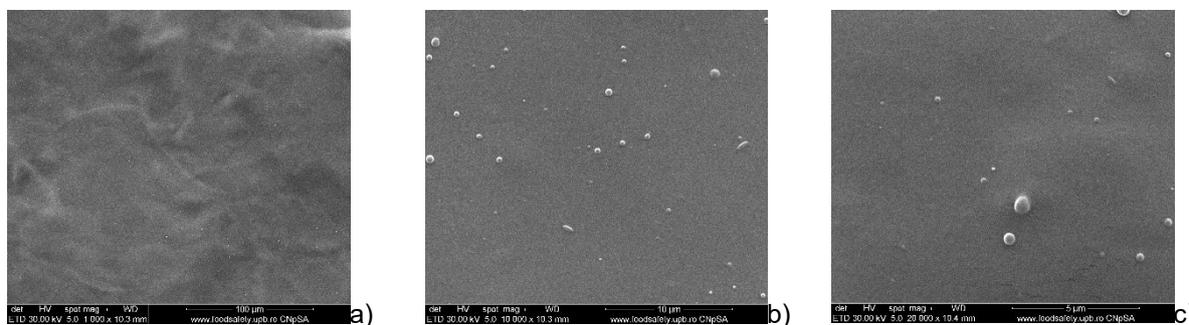


Fig. 3 - SEM images of chitosan/ZnO 1% sample, a)1000x, b)10 000x, c)20 000x / Imaginile SEM pe probele de chitosan/ZnO 1%, a)1000x, b)10 000x, c)20 000x

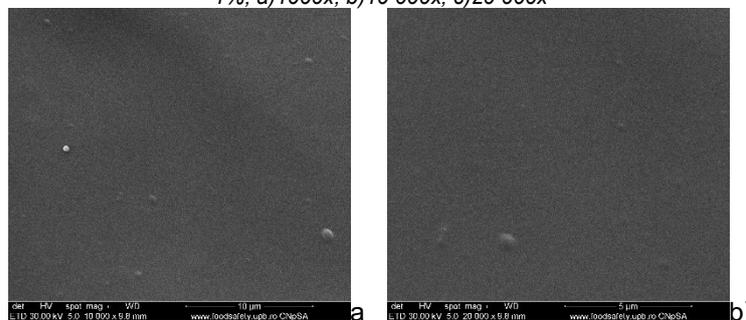


Fig. 4 - SEM images of chitosan/ZnO 5% sample, a)10 000x, b)20 000x / Imaginile SEM pe probele de chitosan/ZnO 5%, a)10 000x, b)20 000x).

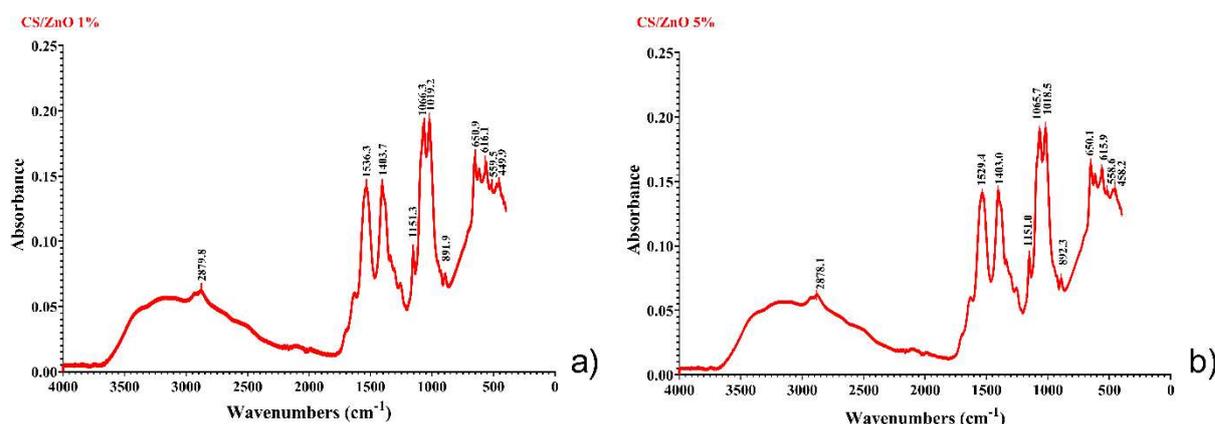


Fig. 5. - FTIR analysis of synthesized samples, a) chitosan/ZnO 1%, b) chitosan/ZnO 5% / Analiza FTIR a probelelor sintetizate, a) chitosan/ZnO 1%, b) chitosan/ZnO 5%.

Table 1

Information generated following the differential thermal analysis on chitosan/ZnO samples  
 Informații generate în urma analizei termice pe probele de chitosan/ZnO)

Sample	Mass loss RT-105°C	Mass loss 105-200°C	Mass loss 200-360°C	Mass loss 360-650°C	Endo	Exo I	Exo II
CS/ZnO 1%	9.60%	16.28%	38.49%	29.39%	77.2°C	290.4°C	547.4°C
CS/ZnO 5%	9.51%	16.36%	38.23%	28.11%	77.3°C	292.7°C	526.3°C

**3.2. FTIR:** The as-obtained chitosan/ZnO nanocomposite membranes were analyzed by Fourier transform infrared spectroscopy (FTIR), Nicolet iS50R spectrometer (Thermo Fisher Scientific) to establish the functional groups present in the samples. The FTIR spectra of the synthesized samples were measured between 4000 and 400  $\text{cm}^{-1}$  as presented in the figures below, where we can observe the infrared spectrum of chitosan/ZnO 1% and chitosan/ZnO 5%.

From the FTIR analysis of the chitosan/ZnO samples were noticed that they have a similar spectrum, thus the presence of the characteristic peaks of hydroxyl, amides, and amine bonds are revealed, as presented in figure 5. The peaks from  $2879.8\text{cm}^{-1}$  of chitosan/ZnO 1% sample and the ones from  $2878.1\text{cm}^{-1}$  of chitosan/ZnO 5% sample are attributed to the C-H bond of the alkane's functional groups. Next, the peak from  $1536.3\text{cm}^{-1}$  of chitosan/ZnO 1% sample and the peak  $1529.4\text{cm}^{-1}$  correspond to the N-H bond attributed to the amines I functional group. The vibration bands from  $1403.6\text{cm}^{-1}$  of the chitosan/ZnO 1% sample and the one from  $1403.0\text{cm}^{-1}$  of the chitosan/ZnO 5% are corresponding to the C-N bond, which is attributed to the amides III functional group. The characteristic bands from  $1066.3$  and  $1019.2\text{cm}^{-1}$  of the chitosan/ZnO 1% sample and the ones from  $1065.7$  and  $1018.5\text{cm}^{-1}$  of chitosan/ZnO 5% sample are attributed to the C-O bond, which corresponds to the alcohol's functional groups. The last peaks from  $449.9\text{cm}^{-1}$  of chitosan/ZnO 1% sample and the one from  $458.2\text{cm}^{-1}$  of chitosan/ZnO 5% sample correspond to the O-Zn-O functional group, which indicates the ZnO presence from the composite membranes [20, 21].

**3.3. TG – DSC:** The synthesized samples were analyzed by differential thermal analysis to determine the thermal transitions in the materials, mass loss, and the content of organic wastes. The thermal analysis on the obtained samples resulted in the fact that both samples presented similar thermal effects, indicated a related behavior in the polymer structure when the temperature changes. Table 1 shows the summary of the information generated following the differential thermal analysis of the subjected samples.

In the case of the chitosan/ZnO 1% sample (Figure 6), the sample undergoes thermal decomposition processes like those loaded with ZnO 5%. In the RT-105°C step, the volatile molecules eliminate, probably water traces, which represent 9.6% (and maybe some acetic acid is also eliminated). The process is accompanied by an endothermic effect having a minimum of 77.2°C. Between 105-200°C, the sample continues to lose 16.28% of its initial mass, with no visible effect on the DSC curve. Most likely, both decomposition and oxidation processes take place. Between 200-360°C, the first strong exothermic process is registered, with a maximum of 290.4°C, the mass loss being 38.49%. This behavior can be attributed to the decomposition of chitosan/ZnO nanocomposite followed by the partial oxidation of the organic compound of the sample. Between 360-650°C, the total oxidation of organic residues takes place, the mass loss being 29.39%, and the final burn of the carbon mass is registered at 547.4°C.

Next, is presented the thermal analysis of the sample loaded with ZnO 5% in figure 7. In the RT-105°C step, the volatile molecules eliminate, probably water traces, which represent 9.51% (chitosan, and

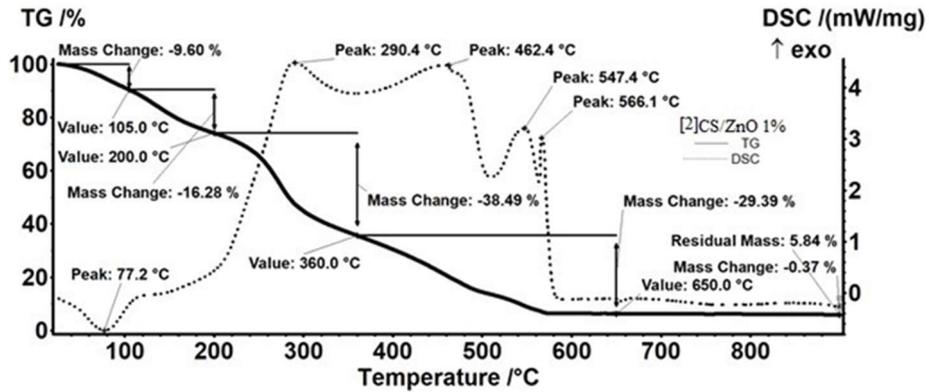


Fig. 6 - Thermal analysis of chitosan/ZnO 1% sample / Analiza termică pe probele de chitosan/ZnO 1%.

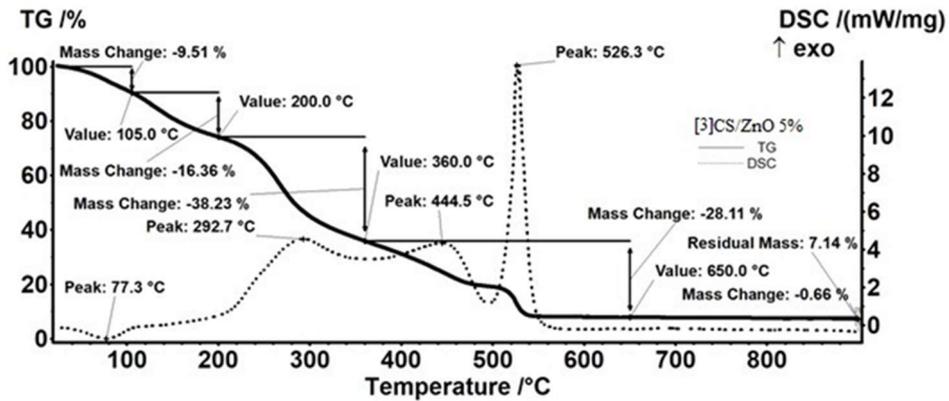


Fig. 7- Thermal analysis of chitosan/ZnO 5% sample / Analiza termică pe probele de chitosan/ZnO 5%.

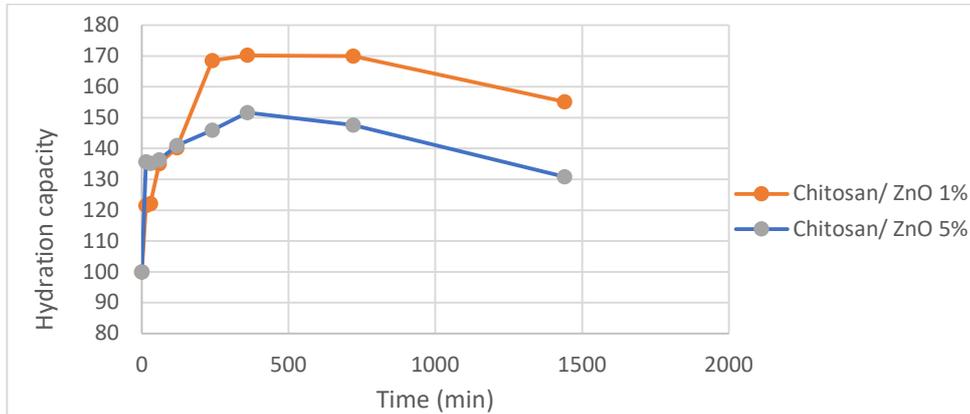


Fig. 8 - Hydration capacity of the synthesized membranes / Capacitatea de hidratare a membranelor sintetizate

maybe some acetic acid is also eliminated). The process is accompanied by an endothermic effect having a minimum of 77.3°C. Between 105-200°C, the sample continues to lose 16.36% of its initial mass, with no visible effect on the DSC curve. Most likely, both decomposition and oxidation processes take place. Between 200-360°C, the first strong exothermic process is registered, with a maximum of 292.7°C, the mass loss being 38.23%. This behavior can be attributed to the decomposition of

chitosan/ZnO nanocomposite followed by the partial oxidation of the evolved organic compound of the sample. Between 360-650°C, the total oxidation of organic residues takes place, the mass loss being 28.11%, and the final burn of the carbon mass is registered at 526.3°C.

**3.4. Hydration capacity:** To evaluate the stability of the synthesized samples, the composite

membranes were subjected to hydration measurements to determine the weight change of the samples during the adsorption in distilled water for 24 h. The figure below illustrates the behavior of the samples when are being immersed in distilled water.

Figure 8 illustrates the hydration behavior of the obtained composite membranes, and it can be observed that in the first 4-6h, the membranes are saturated, afterward, the tendency decreases significantly, which indicates that after that time, the membranes no longer adsorb any water, being already saturated at their maximum capacity. Both films were started to decrease after 6 or 12h for the Chitosan/ZnO 1% and Chitosan/ZnO 5%, respectively. Probably this behaviour is assigned to the dissolution of the chitosan membranes and, because of the higher ZnO content, the sample Chitosan/ZnO 5% start to have a negative mass gain earlier because the increasing amount of ZnO create some disorders into the film and thus the dissolution starts earlier.

**3.5. Antimicrobial activity:** The biodegradable chitosan-based membranes can have many applications: absorption of heavy metals, dyes, or other polluting compounds from water, decontamination of water, use as dressings, drug delivery, tissue engineering, etc. [22].

In the present study, it is observed that after exposure at 37°C for 24 h, the ZnO nanoparticles, respectively the CS/ZnO membranes determined a pronounced sensitivity of *E. coli*, *E. faecalis*, and *Citrobacter* sp. The ZnO 1% nanoparticles were reduced by at least 4 logarithmic units CFU/mL compared to the positive control (control of growth of the bacterial strain), observing a bacteriostatic

effect. Following the increase of the ZnO concentration to 5%, a pronounced bacteriostatic and bactericidal effect is observed, determined by the reduction by approximately 8 logarithmic units.

The sensitivity of bacterial strains to ZnO is due to the small size of the nanoparticles (<30nm), which has a higher interaction with bacterial cells due to the higher surface/volume ratio, causing more damage to the cell membrane, penetration inside the cell, induction of oxidative stress, implicitly the destruction of genetic material and cell death [7, 13, 23, 24].

Figure 9 shows the high sensitivity of microbial strains studied under the action of chitosan-based membranes and loaded with ZnO. Comparing the obtained results, it is observed a synergistic effect between chitosan and ZnO because the control with chitosan, respectively those with ZnO 1% and 5% determines the decrease of CFU/mL (bacteriostatic effect), and in the case of membranes, the sensitivity of *E. coli*, *E. faecalis*, and *Citrobacter* is very accentuated, where there is a decrease of about 10 logarithmic units compared to the positive control/ bacterial growth and by at least 5 units compared to chitosan) [20, 21, 25-27].

The assessment of CFU/mL resulted in a high degree of inhibition for the studied microbial strains, respectively their low capacity to adhere on the surface of chitosan/ZnO membranes, which determines that they have a high potential in using them to develop membranes used for water treatment applications. It is also important to mention that the coexistence of the two components is beneficial from the point of view of the antimicrobial activity, in all cases the antimicrobial activity of the CS/ZnO membrane is well lower than

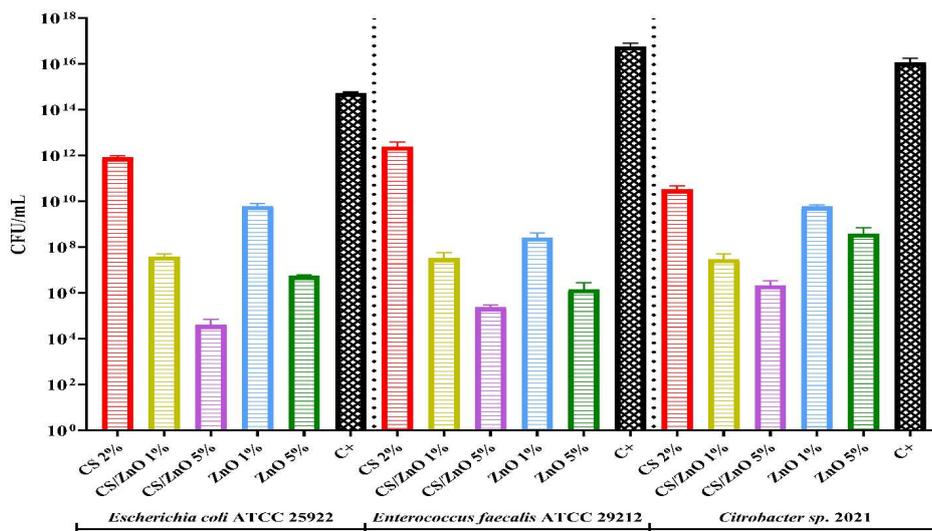


Fig. 9 - The inhibitory effect of chitosan/ZnO samples against bacterial strains, the p-value for *E. coli* <0.0001, for *E. faecalis* p<0.0001, and *Citrobacter* p=0.0007, / Efectul inhibitor al probelor chitosan/ZnO impotriva tulpinilor bacteriene, valoarea p pentru *E. coli* <0.0001, pentru *E. faecalis* p<0.0001, și pentru *Citrobacter* p=0.0007.

Table 2

Cd/Pb removal capacity of the membranes / Capacitatea membranelor de îndepărtare a Cd/Pb

Sample	Sample mass [mg]	Final volume [mL]	Final concentration	
			Pb [µg/mg]	Cd [µg/mg]
CS/ZnO 1% Pb 1%	99.2	50	82	
CS/ZnO 1% Pb 5%	90.0	50	119	
CS/ZnO 1% Cd 1%	95.0	50		88
CS/ZnO 1% Cd 5%	99.8	50		136
CS/ZnO 5% Pb 1%	80.3	50	64	
CS/ZnO 5% Pb 5%	93.8	50	247	
CS/ZnO 5% Cd 1%	60.3	50		35
CS/ZnO 5% Cd 5%	99.5	50		200

that of the pure components, at the same concentration.

**3.6. Heavy metals retention:** To investigate the retention capacity of the obtained membranes, they were immersed in the cadmium or lead nitrate solution. Below can be seen the results obtained after reading the final solutions, applying the dilution factor (10,000). Formula (2) was applied to obtain the final concentrations, correlated to the mass of the sample taken, finally expressed in µg/mg of the sample:  $C_f = \frac{C_c \cdot V_f}{M_p} (\mu g/mg)$  (2), where  $C_c$  = read concentration (µg/L);  $F_D = 100$  (Dilution factor);  $V_f$  = final volum after digestion (L) => here,  $V_0 = 50 \cdot 10^{-3}L$ ;  $M_p$ =sample mass (mg).

Table 2 shows that the samples based on chitosan/ZnO 5% have the highest values of the removal capacity of Cd and Pb, which implies/ results in a better retention/ adsorption, compared to the chitosan/ZnO 1% samples. In this case, the retention capacity of the CS/ZnO 5% membranes was 247 mg Pb/g of membrane and 200 mg Cd/g of the membrane.

#### 4. Conclusions

In conclusion, we presented the composite membranes that were successfully synthesized using chitosan polymer and zinc oxide nanoparticles, to obtain adsorbent membranes for the removal of toxic pollutants from water systems. The chitosan/ZnO composite membranes were prepared through the electrospinning method. The FTIR analysis confirms the existence of the relevant functional groups of both chitosan polymer and ZnO from the composite membranes. The thermal analysis on the subjected samples illustrated the fact that both samples presented similar thermal effects, indicated a related behavior in the polymer structure when the temperature changes. The synthesized composite membranes presented

uniform morphology and small granulation on the surface of the membranes, indicating the presence of ZnO in their composition. The ICP-MS analysis showed that chitosan/ZnO 5% membranes presented 200 respectively 247 mg/g of membrane removal capacity for Cd and Pb. From the antimicrobial assessments on the subjected samples, it concluded that the membranes based on chitosan/ZnO 5% presented a higher degree of inhibition on the microbial strains, which indicates that these membranes have a high potential in developing membranes for complex water treatment applications, combining antimicrobial activity and heavy metal removal capacity. As a perspective, after crosslinking, these membranes have the potential to remain stable for a longer time and thus, the capacity of the antibiotic/pesticide removal capacity will be considered.

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