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NANOCOMPOSITE MODIFIER WITH ANTIBACTERIAL ACTIVITY

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Silver nanoparticles (AgNPs) are well known for their antibacterial properties, simple method of preparation and possibility to be used for the treatment of filtration membranes. To prevent a decrease in the activity of nanoparticles and their stability in the membranes pores during filtration, it is proposed to use nanoparticles as a composite with inorganic ion exchanger zirconium hydrogen phosphate (ZHP). The composite can be used as a separate sorption material with antibacterial properties and a modifier of membranes, fabrics or other surfaces. In addition, to enhance the antibacterial and hydrophilic properties, carbon nanodots (CNDs) were introduced into the composite. Silver nanoparticles were synthesized using a number of chemical reductants (sodium borohydride and sodium citrate) as well as by a "green" method in the presence of a plant reductant, as namely dandelion root (*Taraxacum officinale*) extract. The nanoparticles were characterized by TEM, SEM and UV-Vis spectroscopy. The antibacterial activity of the obtained products was evaluated by disk-diffusion experiments against a wide range of gram-positive and gram-negative bacteria. The inhibitory properties of "green" AgNPs were twice as high as those of chemically obtained one due to the additional antibacterial properties of root extract caused by the flavonoids, alkaloids and inulin. It was shown that the inert inorganic ion exchanger and the modified polytetrafluoroethylene (PTFE) membrane acquire antibacterial properties after treatment with AgNPs and CNDs. Composite materials showed inhibition of *Pseudomonas aeruginosa* bacteria growth that is known to have a high resistance to antibiotics in hospitals. Incorporation of composite modifier to microfiltration tubular polymer membrane results in transformation into rigid ultrafiltration one with hydrophilic surface and antibacterial properties. It should be expected antifouling activity of modified membranes. The resulting composites can be used for surface modification and filtration of harmful hospital and other wastes.

Keywords: silver nanoparticles, carbon nanodots, phosphorus, zirconium, inorganic composites, antibacterial activity

INTRODUCTION

The capability of pathogenic microorganisms to survive in the presence of antibiotics - antimicrobial resistance (AMR) is currently one of the urgent problems of human being [1–3]. Usually, antibiotics are used for the treatment of dangerous infectious diseases. AMR is a fairly common problem, since there are currently significant risks regarding the complexity of treating human diseases, conducting medical surgeries, organ transplantation. It can provoke the emergence of long-term pandemics and the emergence of new resistant bacterial infections. Therefore, it is now extremely important to develop new integrated approaches to develop antimicrobial materials. AMR is considered to intensify due to the uncontrolled use of available drugs followed by increasing resistance of already known bacterial strains to new generation

antibiotics in difficult cases [4, 5]. Military operations exacerbate the aforementioned problem [6–8], due to the growth of usage of antibiotics and infection with very resistant hospital strains of microorganisms. The multiple cross-infection with resistant isolated microorganisms and rapid spread of resistant bacteria is possible in difficult cases. In addition, water supply, drainage and water disinfection are a complex problem under extreme war conditions [9] as local contamination with both chemical and bacterial pollutants occur.

The study of the defense behavior and survival mechanisms of bacterial strains is important to find new compounds for the treatment of patients [10] for overcoming AMR. It is predicted the ways to overcome AMR can include both synthesis of new heterocyclic compounds and combination of known commercial antibiotics with inorganic

nanoparticles and new carbon materials (fullerenes, fullereneols). Typically, nanoparticles of metals and their oxides, such as silver, cerium, bismuth, zinc, copper, cobalt, iron, etc., are widely studied as inorganic nanocomponents of composites [11–13].

Modern research is aimed at finding the methods for the synthesis of compounds from cheaper starting materials, reduction in the size of nanoparticles, and the use of a carrier to hold nanoparticles. Carbon, silicon oxides, zirconia, ceria, and zirconium phosphates are used as the substrates or carriers for nanoparticles with antibacterial properties due to their high surface area and branched porous surface, which are able to stabilize non-aggregated nanoparticles [14–18].

Polymer-bentonite nanocomposites [19] were obtained by surface treatment of bentonite with polymer ultrathin films of poly(diallyldimethylammonium chloride), poly(methyl methacrylate) and poly(vinylidene chloride). These clay polymer nanocomposites effectively inhibited the growth of pathogenic and conditionally pathogenic microorganisms.

The authors [20] synthesized composite materials with ZnO nanoparticles, which were included in the chitosan matrix. ZnO nanoparticles were obtained using a plant extract of sea buckthorn (Sea Buckthorn extract), which products from this plant were known for their antioxidant activity. The bioactivity of the extract is associated with the presence of such compounds as protocatechuic acid, rutin, quercetin, kaempferol, etc. [21]. To inhibit clinically isolated bacteria with extremely high resistance to conventional antimicrobial agents, the authors [22] investigated Ag/V₂O₅ nanocomposites obtained with *Sargassum latifolium* extract. The modifier was incorporated into a biocompatible polymer matrix of curdlan. The Ag/V₂O₅-curdlan nanocomposite exhibited antioxidant activity at a concentration of 0.302 mg/ml. The composite nanomaterial can be used in the medical field, food technology, product packaging and agriculture with a predicted minimal impact of nanoparticles on the environment. In addition, AgNPs can be quite simply obtained and stabilized in green methods. It is characterized as a biocompatible nanoscale material with advantage for the body.

Nanosized (2–10 nm) yttrium oxide has been used to address the problem of wound healing in complex skin lesions, burns, and diabetes.

Yttrium oxide nanoparticles were incorporated [23] into nanofibrous polyurethane mats as drug carriers. Furthermore, the mats were treated with *Azadirachta indica* leaf extract and clindamycin hydrochloride as an adjunct to traditional antidiabetic and antibacterial agents. The composite exhibits a high zone of inhibition and works against biofilm formation (*E. coli* (29 mm), *S. aureus* (32 mm), and *P. aeruginosa* (30 mm)). The composite has been shown to be effective in wound healing *in vivo* in diabetic mice (rapid reduction of wound healing time after 9 days of treatment).

The synthesis of magnetic nanoparticles with a spinel structure, MFe₂O₄ (where M is Co, Zr, Ni, Zn) due to their antimicrobial, magnetic and catalytic properties [24] is described. The antibacterial efficiency of titanium-doped zirconium ferrite nanoparticles (Zr_{1-x}Ti_xFe₂O₄; 0.0 ≤ x ≤ 0.05) obtained by the sol-gel method was tested on strains of *Escherichia coli* and *Staphylococcus aureus*. It was found that titanium ions enhanced the antibacterial activity of nanoparticles with a cubic spinel structure with crystallite sizes of 17–23 nm. Besides medical application, the nanoparticles with antibacterial activity were used to modify membranes for separation processes to provide their antifouling resistance [25].

AgNPs/ polyvinyl alcohol (PVA) and AgNPs/ polyethylene glycol (PEG) composites are described [26]. Silver ions were reduced using green grape seed extract and precipitated as homogeneous, monodisperse nanoparticles (25.7–54.2 nm). The composites exhibited antimicrobial and antitumor activity against *E. coli* and *S. aureus*. AgNPs/PVA-g-PEG and high antitumor activity.

The effect of Co₃O₄ nanoparticles obtained by green synthesis using walnut leaf extract was studied for the modification of polymer membranes [27]. The proposed modification with inorganic nanoparticles increased the resistance of polymer membranes to biofouling due to the antibacterial and antioxidant properties of the modifier. The introduced Co₃O₄ nanoparticles showed 100 % ability to inhibit the growth of *E. coli*, inhibit the growth of biofilms of *S. aureus* and *P. aeruginosa*.

The authors [28] modified a biodegradable membrane based on polylactic acid with nanoparticles of a silver-Maxen composite. Increased hydrophilicity and acquired

antibacterial properties were noted. The membrane was tested for the treatment of hospital wastewater. As a result, the flow rate increased twice with PLA/AgMX4, and 97 % of the total bacterial contamination was cut off.

Thus, polymer-stabilized antibacterial nanoparticles AgNP act as a biocidal modifier to give the surface antibacterial properties. These properties have been confirmed in many studies, but there is a problem of local aggregation of nanoparticles, resulting in a decrease of their effectiveness and an increase of toxicity. The composites with non-agglomerated nanoparticles synthesized with plant reducing agents can contribute to the stability of metal nanoparticles on solid surfaces. In addition, the combination of antimicrobial component and, for example, a hydrophilic component in one nanocomposite is predicted to decrease the AMR and increase antitumor properties in some cases.

Among the nanomaterials with antibacterial activity, carbon nanodots (CND) look very attractive, since they combine this remarkable property [29] with hydrophilicity, which is provided by the surface phenolic and carboxyl groups similarly to oxidized graphene [30]. As a rule, they are used for hydrophilization of solid surfaces (powders, polymer membranes, steel tools) [31]. Their advantages over oxidized graphene are a possibility to be obtained with a “green” hydrothermal method from a feedstock of biological origin like polysaccharides [32]. Similarly, to pharmacological products, nanoparticles must be stabilized in a polymer in the case of modifying preliminary formed membranes. The solution of this problem is to incorporate nanoparticles with antibacterial activity into inorganic matrices. A number of inorganic ion exchangers are used for this purpose. For instance, functionalized silica gel [33], hydrated oxides of multivalent metals [34–36], zirconium hydrophosphate (ZHP) [37], zeolites [38] were applied to preparation composites with advanced carbon nanomaterials. It should be noted that porous inorganic matrix can be used also for accumulation of salt solutions – for instance, slow release fertilizers can be obtained by this manner [39]. Inorganic ion-exchangers can also provide hydrophilicity of membranes and, as a result, their stability against fouling and biofouling [40]. Among mentioned ion-exchangers, ZHP demonstrates hydrophilicity in a wide pH range owing to dissociation of

hydrophosphate and dihydrophosphate functional groups [41]. Due to this remarkable property, this material was applied to modify the membranes both for pressure-driven [42] and electro driven separation [43].

In this work, the combination of modifiers was used: ZHP (as a matrix for stabilization of nanoparticles and hydrophilicity), AgNPs (as antibacterial component), CNDs (as additional antibacterial and hydrophilizing constituent). AgNPs and CNDs were chosen since they can be easily obtained with “green” methods.

The aim of the current work is to synthesize silver nanoparticles with different reducing agents and incorporate them together with CNDs to inorganic ion exchanger ZHP. The obtained composite is used as a modifier of hydrophobic polymer (e-PTFE tubular membranes). The membrane as well the composite was tested for antibacterial activity against gram-positive and gram-negative bacteria.

EXPERIMENTAL

Synthesis of AgNPs. Synthesis of AgNPs nanoparticles was carried out by reducing Ag^+ ions from 0.001 M AgNO_3 solution by chemical method with sodium borohydride (NaBH_4) and sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) as the typical reducing agents, as well as by “green” method (C) with dandelion (*Taraxacum officinale*) root extract (DR) as the reducing agent. The choice of “green” reducing agent is due to the antibacterial properties of this extract [44].

Plant Dangelion roots was purchased from the local pharmacy store as product Herbal Tea Dandelion Root (produced by LLC HBT FitoBioTechnology, Kyiv, Ukraine); ingredients *Taraxacum Officinale* Wigg. Preparation of aqueous plants extracts were: 10 g of dried Dandelion roots were brought to a boil deionized water and gently boiled for 15 minutes. The decoction was then cooled to room temperature, filtered using Whatman No. 1 filter paper, and stored in a refrigerator 4 °C for 12 hours. Filtration of plant extract was repeated. 100 mL of the filtered Dandelion root extract was mixed with 100 mL of a 0.001 M silver nitrate solution under the stirring. The Tyndall cone was observed. For DR solution of Dandelion roots, the concentration of silver nitrate was used 0.0005 M. Aqueous plants extracts were stored at 4 °C for further analysis. The reaction mixture was stored at 4 °C in the dark. Carbon nanoparticles were

synthesized by the bottom-up method from ethylenediamine by heating according to [36]. To determine the flavonoid content in the plant extracts, aliquot of the samples (1 mL) and a standard gallic acid were prepared. Then, 4.8 mL of dionized water, 4 mL of a 2 % sodium carbonate solution, and 0.2 mL of Folin–Ciocalteu reagent were added. The mixture was incubated for 1 hour at 20 °C, and the absorbance was measured at 750 nm [45].

Commercial tubular microfiltration e-PTFE membranes with a wide range of pore sizes of 0.2–2 µm were used for modification. The composite membrane was obtained by incorporating into the pores of the tubular e-PTFE matrix an inorganic composite ZHP@AgNP@CND. The composite membrane modifier has been chosen due to the hydrophilic groups and antibacterial properties contributing to the resistance of the membranes to fouling. The advantage of ZHP over other inorganic ion exchangers is resistance to acids, alkalis and oxidants, that are usually used for washing and disinfection of membrane systems [41–43]. Incorporation of composite modifier to microfiltration tubular polymer membrane results in the transformation into hard free-standing ultrafiltration one.

The modification included the saturation of the pores of the initial matrix with a solution of Zr hydroxocomplexes followed by the treatment with H₃PO₄ (1 M) and air drying. The procedures for layer-by-layer application of ZHP and PTFE were repeated. At the last stage, CNDs and AgNPs were introduced into the porous structure of the formed polymer-inorganic composite inside the macropores of the membrane. CNDs act both as hydrophilization agent and as stabilizes of AgNP on the surface to create a protective layer.

Characterization of AgNPs. UV-Vis spectroscopy using a UV-VIS spectrophotometer (Shimadzu Corp., Japan) was applied to investigations of AgNPs colloidal solution [21]. TEM images were obtained using a JEM 1230 microscope (JEOL, Japan). Samples of silver nanoparticles were prepared with 300 mesh copper grids covered with Formvar polymer (Ted Pella, USA). Zirconium hydrophosphate samples containing CND (ZHP@CND) and CND together with AgNPs (ZHP@AgNP@CND) were also tested by TEM for comparison.

The surface morphology of membranes was examined using scanning electron microscopy

(SEM) with a Mira TESCAN microscope (TESCAN, Czech Republic).

The interaction of nanomaterials with microorganisms was determined using the Agar disk-diffusion method [46]. The presence or absence of antimicrobial properties of nanoparticles (inhibition of bacterial growth) was determined in relation to microorganisms - representatives of the intestinal flora of animals and humans, as well as in relation to microorganisms with known pathogenic potential. The test strains *Staphylococcus aureus* ATCC No. 25923, *Candida albicans*, as well as *Escherichia coli* KV9, *Enterococcus faecalis* KV6, *Salmonella spp.* serogroup C, *Pseudomonas aeruginosa* KV4, *Yersinia bercovieri*, *Pasteurella multocida* 1\5 (isolated during the study of animal biological material) were used. The test microorganism biomass was washed with saline, and the concentration of the bacterial suspension was adjusted to 10 billion CFU in 1 cm³. Next 0.1 ml of the suspension was added to Petri dishes with nutrient medium, distributed with a spatula over the agar surface, incubated in a thermostat at 37 °C for 20–30 minutes. Tested materials were added to the 6 mm diameter wells. The Petri dishes with test cultures were placed in a thermostat and cultivated at 37 °C for 18–24 hours followed by determination of the diameter of the growth inhibition zone around the well with the test strain culture. Test studies with bacterial cultures were carried out twice (N = 2).

RESULTS AND DISCUSSIONS

Characterization of nanoparticles and composite materials. It is seen from TEM photo of AgNPs obtained with borohydride reductant (Fig. 1 a) that the primary particles are mostly spherical with an average size of 10–30 nm. Small particles are prone to aggregation indicating a low reduction rate. Particles obtained with citrate reductant (Fig. 1 b) have also mostly a spherical shape of 20–50 nm, they are more evenly distributed. Owing to stabilization action of citrate, they are less likely to clump into aggregates at a sufficient concentration of the reductant. The reductant creates a high negative charge on the surface of the particles providing electrostatic stability and therefore prevents aggregation [47]. Sometimes nanorods are observed (gives the green tint to the colloidal solution, since they have transverse and longitudinal plasmon resonances). Nanorods have

larger contact area with the bacterial cell wall, and thus higher ability to absorb, surface reactivity and destruction of the cell membrane. This is

especially important against gram-negative bacteria [48–50].

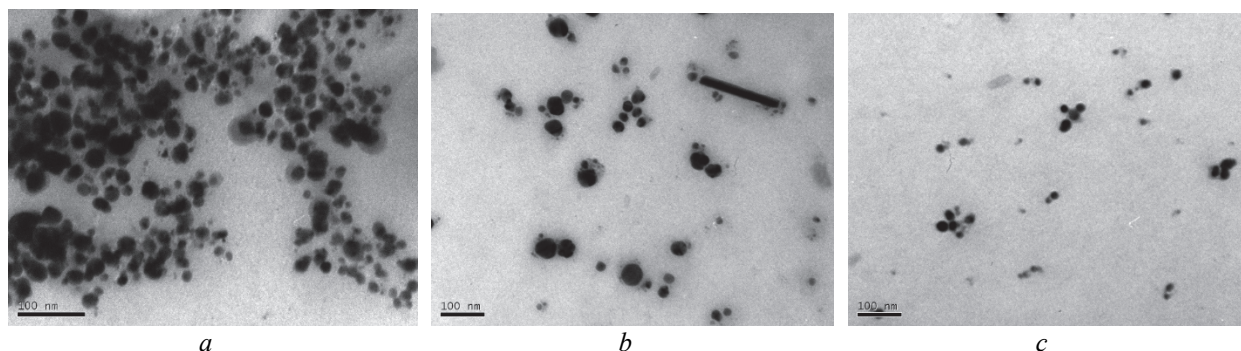


Fig. 1. TEM images of AgNPs obtained with different reducers: NaBH_4 (a), $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$ (b), *Taraxacum officinale* root extract (c)

It should be noted the sample preparation for the TEM analysis includes evaporation of sample solutions. TEM images of “green” AgNP (Fig. 1 a, b) show spherical particles with size in the range from several nanometers to 35 nm with slight agglomerations. The dandelion root extract contains not only phenols, flavonoids, alkaloids but inulin and polysaccharides [51]. Due to rich chemical composition, it not only acts as a reducing agent, but also as a stabilizer. The components of the extract are adsorbed on the surface of the nanoparticles and prevent aggregation. Such a combined effect of silver and phytocomponents can lead to additional antibacterial activity [52].

The color of the colloidal silver solutions varied from light yellow to greenish depending to the surface plasmon resonance of silver. It should

be noted that the color of the colloidal system and the position of the surface plasmon resonance (SPR) maximum are determined by the dimensions and morphology of the nanoparticles. Characteristic UV-Vis absorption maxima for AgNP were observed at 416 nm (Fig. 2 a, blue line) for the spectra of Ag-containing sol. The spectrum of the initial solution of the root extract shows no peak (Fig. 3 a, green line). AgNPs were introduced to composite material and membrane by filtration of Ag-containing sol. The peak intensity decreased after the first and second cycles of the AgNPs insertion to the composite in the membrane pores (red and pink lines, respectively). It is indicated the retention of AgNPs in the pore of composite materials. The amount of deposited AgNPs was estimated as 2 mg cm^{-3} .

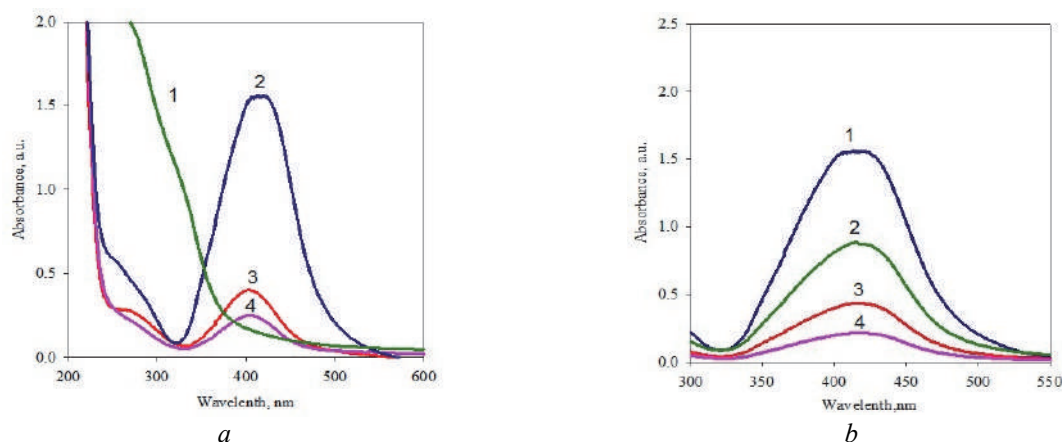


Fig. 2. UV-Vis spectra (a): 1 – the plant extract, 2 – initial sol solution with AgNP, 3, 4 – filtrates sol solution Ag NP, (b) spectra of sol AgNP sol via concentration: 1 – $4.7 \times 10^{-4} \text{ M}$, 2 – $2.4 \times 10^{-4} \text{ M}$, 3 – $1.2 \times 10^{-4} \text{ M}$, 4 – $0.6 \times 10^{-4} \text{ M}$

TEM images of composite ZHP@CND (Fig. 3 *a, b*) represent black intense parts that could be indicated as ZHP, as well as the grey color is identified as CND.

It could be seen that CND cover ZHP, the detected size of CND is lower than 5–10 nm. TEM images of composite ZHP@AgNP@CND (Fig. 2 *c, d*) illustrate more complex particle composition. Both isolated AgNPs with a size of 10–15 nm and agglomerates with a size of up to 50 nm are observed. Probably, CND could cover AgNP and AgNPs can be stabilized by the surface

of the ion exchanger. AgNPs are either embedded in or deposited on the ZHP porous surface. This contact prevents the removal of nanoparticles from the composite membrane during filtration and provides more prolonged antimicrobial properties of the composite.

SEM images (Fig. 4) with EDS analysis proves modifying of initial e-PTFE tube: element content in cross-section polymer membrane indicate presence of main component of composite modifier ZHP@ AgNP@CND (Table 1) inside pore and voids.

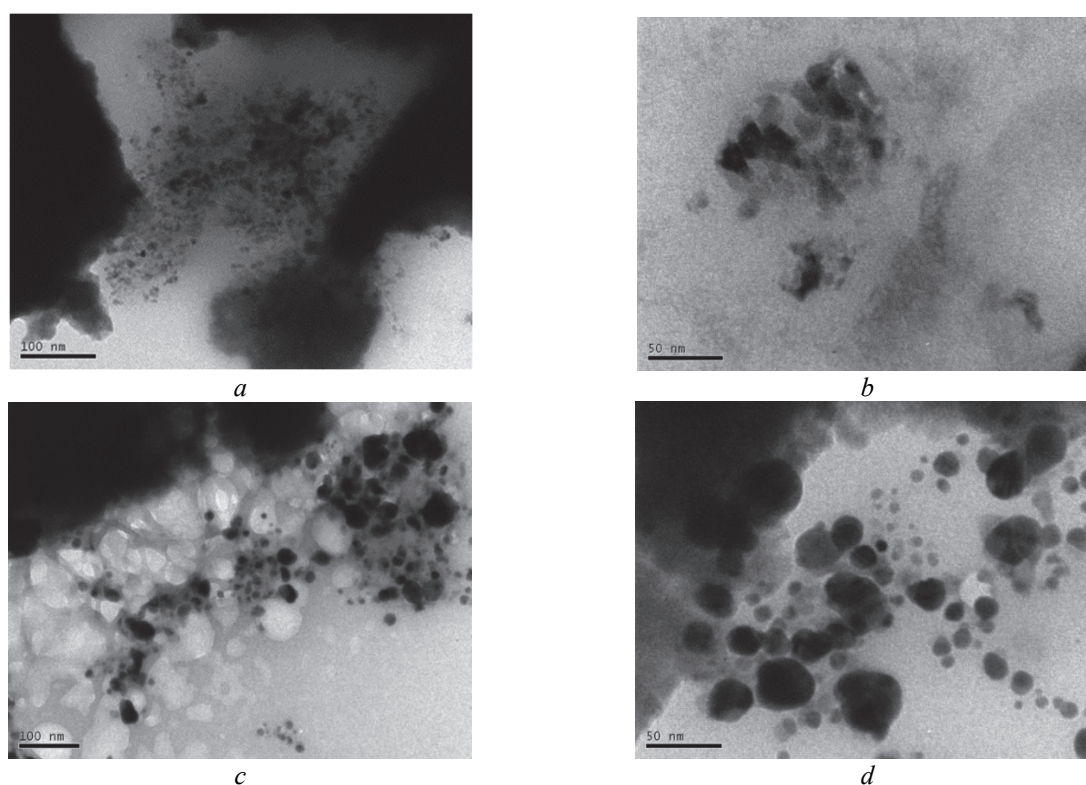


Fig. 3. TEM images of ZHP@CND composite (*a, b*) and ZHP@ AgNP@CND composite (*c, d*)

Table 1. Element content in e-PTFE polymer membrane with ZHP@AgNP@CND modifier

Element	Mass Normalized, %	Atomic, %
Carbon	11.79	26.41
Oxygen	17.03	28.64
Fluorine	17.77	25.18
Phosphorus	7.43	6.46
Zirconium	41.82	12.34
Silver	3.59	0.90
Hafnium	0.57	0.09
Total	100.00	100.00

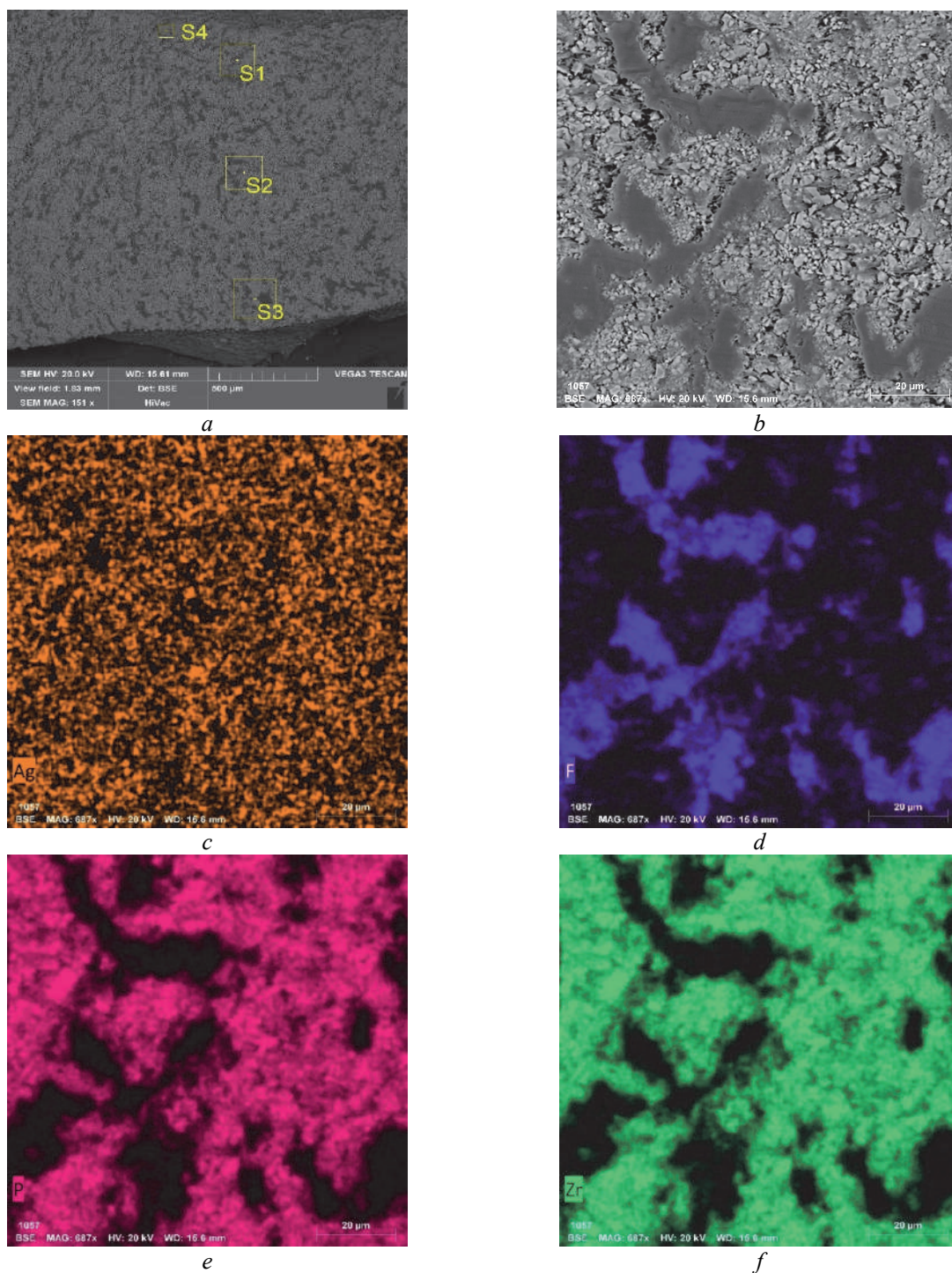


Fig. 4. SEM images (*a, b*) and EDS (*c–f*) analysis of composite e-PTFE membrane with element mapping: cross-section (*a*), determination point S2 in the middle of sample (*b*), silver(*c*), fluorine (*d*), phosphorus (*e*), zirconium (*f*)

The visible black areas on the SEM images (Fig. 4 *b*) correspond to fluorine polymer (Fig. 4 *d*) and bright loose areas – to the inorganic ion exchanger ZHP. AgNPs are fine dispersed on the surface (Fig. 4 *c*).

Antibacterial Activity. Antibacterial activity of AgNPs was studied for the samples obtained using different reducing agents against gram-positive and gram-negative bacterial strains (Fig. 5).

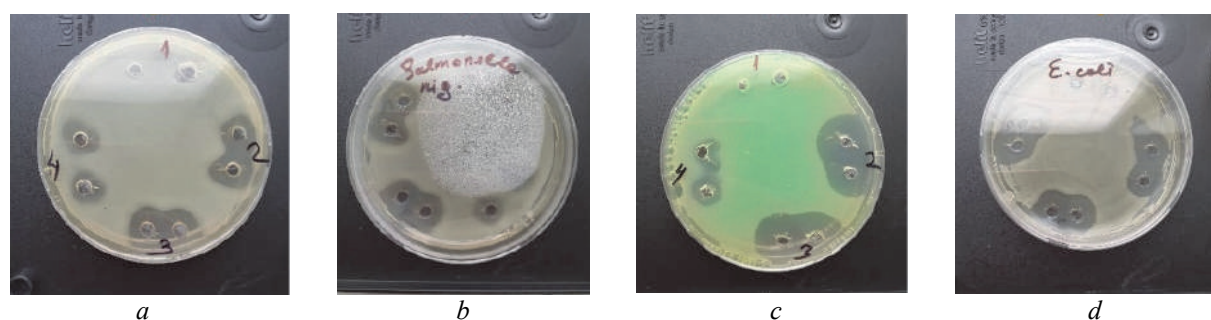


Fig. 5. Effect of AgNP on bacteria growth inhibition: *Candida albicans* (a), *Salmonella spp* (b), *Pseudomonas aeruginosa* (c), *Escherichia coli* (d). AgNP synthesized with different reducer: 1 – NaBH_4 , 2 – DR, 3 – diluted DR, 4 – $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$

This activity of AgNPs was evaluated based on the size of the inhibition zone (Fig. 6). The solution contains 0.0005 M silver all samples. The inhibitory properties of “green” AgNPs are twice higher than for chemically obtained one. The bactericidal activity (zone of inhibition of bacterial growth) has a synergistic effect for silver nanoparticles and DR plant extract solution. It should be noted (Table 2) that the diluted extract of DR with the same concentration of silver nitrate showed the highest growth inhibition. It is obviously due to both more optimal ratio of

concentrations of silver ions/reductant and thinner reducing shell of organic polysaccharides that cover AgNPs. The higher activity of silver nanoparticles synthesized using a more diluted plant extract can be explained by the formation of nanoparticles with stabilizing shell composed of plant-derived compounds is slightly smaller and less dense. The thinner capping layer, formed due to the lower concentration of extract components, facilitates the release of Ag^+ ions, thereby enhancing their antibacterial activity.

Table 2. Zone of bacterial inhibition (mm), N = 2

Bacterial culture	Reductant			
	Chemical method		“Green” method	
	NaBH_4	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$	DR	Diluted DR
<i>Candida albicans</i>	6	12	20	26
	7	13	22	30
<i>Staphylococcus aureus</i>	6	14	17	20
	8	14	17	20
<i>Pseudomonas aeruginosa</i>	6	10	24	24
	7	8	20	20
<i>Escherichia coli</i>	7	15	18	19
	7	15	17	20
<i>Salmonella spp</i>	6	12	13	14
	7	12	15	13

Bacterial activity decreases in the order: *Candida albicans* > *Staphylococcus aureus* > *Pseudomonas aeruginosa* > *Escherichia coli* > *Salmonella spp* for this sample. Thus, the AgNPs show excellent antibacterial activity against both gram-negative and gram-positive bacterial strains, as well as potential use as biofilm inhibitors compared to AgNPs obtained using the

chemical reagents. Such activity can also be explained by the action of other components of the root extract: The *Taraxacum* root extract contains 15–90 % of inulin.

Therefore, the “green” AgNPs were used as an antibacterial component of a composite membrane modifier. The antibacterial activity of the obtained materials, as well as individual

components of the composites, was examined. The obtained results are summarized in the Table 3.

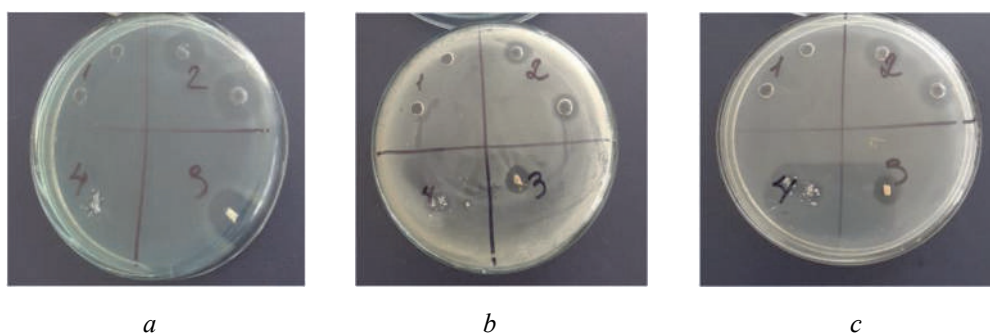


Fig. 6. Agar disk-diffusion experiment with *Pseudomonas Aeruginosa* (a), *Pasteurella Multocida* (b), *Salmonella* (c) (Samples: 1 – ZHP@CND, 2 – ZHP@CND@AgNP, 3 – e-PTFE with ZHP@CND@AgNP, 4 – ZHP)

Table 3. Zone of bacteria inhibition of components and composites

Tested bacterial culture	Samples							
	e-PTFE	HZP	CND	AgNP	ZHP @ CND	ZHP @ CND @ AgNP	e-PTFE with ZHP @ AgNP	e-PTFE with ZHP @ CND @ AgNP
<i>Enterococcus faecalis</i>	-	-	-	9	19×17	15 growths of resistant colonies	6	10
<i>Staphylococcus aureus</i>	-	-	-	15	8	12 (from 12 mm to 6* mm continuous 'growth shadow')	8	8
<i>Pseudomonas aeruginosa</i>	-	-	14	13	6×9	16	15	14×16
<i>Escherichia coli</i>	-	-	8	12	10×12	12 (▼ around the growth retardation zone, stimulation of crop growth 25 mm)	9	7 (▼ around the growth retardation zone, stimulation of crop growth 17 mm)
<i>Candida albicans</i>	-	-	12	18	-	17	15	15×10
<i>Salmonella spp.</i>	-	-	n/s	n/s	7	13	n/s	9
<i>Yersinia bercovieri</i>	-	-	n/s	n/s	8	8	n/s	7
<i>Pasteurella multocida</i>	-	-	n/s	n/s	7	10	n/s	10

- no effect detected, n/s – not studied

As can be seen, the initial membrane and ion exchanger do not exhibit any antibacterial properties. Selective action was observed in the presence of CND. Contrary to these materials, the presence of silver ions/NPs inhibits the growth of most tested bacteria. It is known that the combination of CNDs and AgNPs increases the antimicrobial effect due to different mechanisms of action - AgNP can be adsorbed on the bacterial membrane and increase its permeability, and CNDs damage the membrane mechanically, and additionally catalyze the formation of reactive oxygen species [53, 54]. However, no significant improvement in bacterial growth inhibition in the presence of CND was observed. Perhaps, the higher concentration and sequence of application shielded part of the CND and, thus, prevented the contact with the membrane shell of bacteria. Despite this, both the composite modifier and the modified membrane exhibit antibacterial activity against all tested bacteria. This is clearly seen on the rectangular sample of the modified membrane (Fig. 2 sample 3). The modifier prevents the formation of biofilm and fouling during the filtering solutions of biogenic origin by the composite membrane. Additionally, the obtained materials with green nanoparticles have an antimicrobial effect against *Pseudomonas aeruginosa*. This Gram-negative bacterium is known to be characterized by high resistance to antibiotics and is currently one of the most common resistant strains in hospitals, especially in intensive therapy units [55]. According to the obtained results, the inhibition of 16 mm was

detected for composite ZHP@CND@AgNP and for modified membrane e-PTFE with ZHP@CND@AgNP indicating the potential possibility to use this material for modification of fabric and for treatment of harmful hospital and other wastes.

CONCLUSION

Combination of CND and AgNP for impregnation to the pore volume and surface of ion exchangers and membrane have been studied. The antibacterial activity of silver nanoparticles depends on the method of synthesis and can be enhanced by using plant extract of dandelion roots as a reductant (green synthesis). The synergistic effect is due to the presence of flavonoids, alkaloids, polysaccharide (inulin). These substances act as a stabilizer and additional antibacterial agent. "Green" AgNPs are used as an antibacterial component of a zirconium hydrophosphate/organic polymer composite for modification of inert tubular microfiltration membranes to improve antibacterial antifouling properties in the filtration of solutions of organic origin. It was shown that the composite modifier and composite membrane with AgNPs and CNDs exhibit the same antibacterial activity as the individual nanoparticles. Dandelion roots are a local Ukrainian plant material and can be used for the creation of antibacterial products. The subject of further work is to investigate practical application and biofouling of modified membrane.

Нанокompозитний модифікатор з антибактеріальною активністю

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Наночастинки срібла (AgNPs) добре відомі своїми антибактеріальними властивостями, простим способом отримання та можуть бути використані для обробки фільтраційних мембран. Щоб запобігти зниженню активності наночастинок та їхньої стабільності в порах мембран під час фільтрації, пропонується використовувати їх як композит з неорганічним іонообмінником гідрофосфатом цирконію (ZHP). Композит може бути використаний як окремий сорбційний матеріал з антибактеріальними властивостями, так і як модифікатор мембран, тканин або інших поверхонь. Крім того, для посилення антибактеріальних та гідрофільних властивостей до композита були введені вуглецеві наноточки (CND).

Наночастинки срібла були синтезовані низкою хімічних відновників (борогідрид натрію та цитрат натрію), а також «зеленим» методом з рослинним відновником екстрактом кореня кульбаби (*Taraxacum officinale*). Наночастинки були охарактеризовані за допомогою ПЕМ, СЕМ та УФ-видимої спектроскопії. Антибактеріальну активність отриманих продуктів оцінювали за допомогою диско-дифузійних експериментів проти широкого спектра Грам-позитивних та Грам-негативних бактерій. Інгібіторні властивості «зелених» AgNP були вдвічі вищими, ніж у хімічно отриманих, завдяки додатковим антибактеріальним властивостям екстракту кореня, зумовленим флавоноїдами, алкалоїдами та інуліном. Показано, що інертний неорганічний іонообмінник і модифікована політетрафторетиленова (PTFE) мембрана набувають антибактеріальних властивостей після обробки AgNP та CND. Композитні матеріали продемонстрували пригнічення росту бактерій *Pseudomonas aeruginosa*, які, як відомо, мають високу стійкість до антибіотиків у лікарнях. Включення композитного модифікатора до мікрофільтраційної трубчастой полімерної мембрани призводить до перетворення її на міцну ультрафільтраційну мембрану з гідрофільною поверхнею та антибактеріальними властивостями. Подальші роботи пов'язані із вивченням стійкості модифікованої мембрани до біозабруднень та можливостей її практичного застосування. Отримані композити можуть бути використані для модифікування поверхонь та фільтрації шкідливих лікарняних та інших відходів.

Ключові слова: наночастинки срібла, вуглецеві наноточки, фосфор, цирконій, неорганічні композити, антибактеріальна активність

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