Doctoral dissertation abstract

"Polymer membranes modified with nanoparticles for water and wastewater treatment"

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The aim of this work was to determine the influence of the preparation parameters on the physicochemical, separation and transport properties as well as resistance to fouling and biofouling of polyethersulfone (PES) ulfrafilfration membranes modified with titanate nanotubes (TNT) or TNT- and Ag-based composite nanoparticles (A-TNT/Ag). The research scope included, in particular, the study on the influence of the procedure of TNT dispersion in the casting dope, the presence of silver in the A-TNT/Ag hybrid nanomaterial, as well as the addition of pore-forming agents, on the properties of membranes.

The membranes were produced by the phase inversion method (wet variant). The polymer was polyethersulfone, the solvent was N,N-dimethylformamide (DMF), and the non-solvent was deionized water. Titanate nanotubes were obtained by the hydrothermal method with the use of two types of Ti02: anatase (A-TNT) and AEROXIDE@ Ti02 P25, which is a mixture of anatase and rutile (P-TNT). Silver nanoparticles were deposited on TNT in the $AgNO_3$ photoreduction process. The pore forming agents were polyvinylpyrrolidone with a molecular weight of 10 kDa (PVP10) and 40 kDa (PVP40), and poly(ethylene glycol) with a molecular weight of 10 kDa (PEG10).

Based on the results obtained in the first stage of the work, it was shown that the method of preparing the suspension of P-TNT nanoparticles in a solvent and the procedure of preparation of casting dope influence the dispersion of the nanomaterial in the membrane matrix, which translates into its properties. The use of direct sonication, in which the energy is concentrated within the sample, leads to a better dispersion of the nanomaterial than the use of indirect sonication, characterized by a diffusive energy distribution in the solution. It was found that the good dispersion of the nanomaterial has a beneficial effect on the improvement of water permeability and fouling resistance, as well as the separation properties of the membrane. However, it has been shown that in the case of antibacterial properties, the presence of large PTNT agglomerates on the membrane surface is more advantageous. The increase in roughness contributed to the improvement of the antibacterial properties of the membranes, which was the basis for proposing a mechanism of bacterial inactivation, taking into account the mechanical damage to the cell walls by titanate nanotubes.

In the second stage of the work, the studies of membranes modified with the A-TNT/Ag hybrid nanomaterial were carried out. Nanoparticles containing various amounts of silver were used. The positive effect of an increase in Ag content in the nanocomposite on the improvement of water permeability and fouling resistance of the membranes was demonstrated. It was also found that the increase in the amount of A-TNT/Ag in the membrane matrix promoted the agglomeration of nanoparticles and deteriorated the dispersion of the nanomaterial, as well as resulted in an increase in surface roughness. At the same time, increasing the concentration of nanoparticles in the membrane had a positive effect on reducing its blockage by humic acids. No negative impact of the increase in surface roughness on the fouling resistance of the membranes was observed. It has been found that A-TNT/Ag agglomerates can act as turbulence promoters, increasing the turbulence of the flow and limiting the formation of the gel layer. The study of the antibacterial activity of membranes showed the beneficial effect of increasing the silver content in A-TNT/Ag nanoparticles and increasing the amount of nanomaterial incorporated into the membrane structure on the inhibition of the growth of *Escherichia coli* and *Staphylococcus epidermidis*.

In the third stage of the research, a series of membranes modified with PVP10, PVP40 or PEG10 pore forming agents and A-TNT/Ag hybrid nanomaterial was prepared. In the case of membranes obtained with the use of pore forming agents only, an improvement in hydrophilicity and permeability was found. The introduction of the A-TNT/Ag nanomaterial contributed to a further improvement in transport properties, regardless of the type of porogen. The presence of nanoparticles also had a positive effect on the separation properties of the membranes. However, it was found that the significant surface roughness of the membranes combined with high water permeability contributed to a reduction in the fouling resistance of membranes containing PVP or PEG. Based on the tests of the antibacterial activity of the membranes, it has been shown that the type of the pore forming agent and its molecular weight do not significantly affect this parameter. The use of A-TNT/Ag resulted in the improvement of the antibacterial properties of the membranes. Moreover, a higher efficiency of inhibition of *E. coli* growth was found in the tests conducted in the flow system than in the stirred system, which was attributed to the more aggressive conditions prevailing in the ultrafiltration installation.

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