

The Effect of Nanoscale Non-organic Additives on the Structure and Synthesis of Water Purification Membranes

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For citation:

Tyurin I. A., Kardash M. M., Terin D. V.
The Effect Of Nanoscale Non-organic Additives
on the Structure and Synthesis of Water Purification
Membranes.
Scientific Research and Innovation. 2020;1(1):31-44
DOI: 10.34986/MAKAO.2020.99.12.006

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Competing interests:

The authors declare no competing interests.

Acknowledgements:

The authors express their deepest gratitude to Prof.
Natalya A. Kononenko, Doctor of Chemistry, and
Prof. Yury M. Volfkovich, Doctor of Chemistry for
their help and discussing the experimental findings.

Received: 12 January 2020

Revised: 20 February 2020

Accepted: 2 March 2020

Published: 15 April 2020

Abstract: The purpose of the paper is to examine the solutions for producing new composite cation-exchange membranes featuring high exchange capacity, good electrical conductivity, and promising significant efficiency when implemented for water sorption and electromembrane purification.

The research is aimed at a thorough study of the way the formation of membrane structure and performance features is affected by nanoscale non-organic additives. The study identified a correlation between the structure and the features of cation-exchange membranes produced by polycondensation filling. The choice of the preferable polycondensation filling option was facilitated by molecular modeling and quantum-chemistry calculations enabling the generation of mathematical models which take into consideration the technological polymorphism and the initial conditions flexibility.

The conducted research and analysis of the obtained testing data elicited the nanoscale non-organic additives' impact on the polymeric matrix synthesis kinetics and structure, and detected the structural peculiarities of the developed membranes. The research involved the production of a polymer composite membrane lab testing prototype and analysis of the obtained materials' operating features.

Keywords: composite membranes, polycondensation, membrane surface morphology, polymer matrix structure, sorption, nanoparticles, membrane separation of liquids, water purification, ion exchange, electrodialysis.

Introduction

Our planet does not lack water. The World Ocean is huge and contains a great amount of water. However, humans' activities result in contamination and disappearance of precious water resources [1]. The current water purification methods are energy-consuming and expensive; there is a need for research looking for novel sustainable approaches to water purification. Over the years, membrane technologies have proven viable in water purification [2]. The mass produced membranes have both advantages, such as compact modular construction with stationary parts, low chemical sludge effluent, and excellent separation efficiency, and drawbacks, namely the operation-induced layer separation, high operation costs, short life and low output [3-5].

Currently most scientists both in Russia and world-wide tend to seek the ways to improve the surface of the already productionized membranes [7] Despite of the recent achievements in synthesizing novel membrane materials and developing new methods to upgrade/functionalize the membrane surface and optimize their design and conditions of their use, today there is a pressing need for reliable membranes with calculated properties [6].

This article introduces an innovative approach to making and improving polymeric ion-exchange membranes.

The suggested method for obtaining heterogeneous membranes can be acknowledged to be novel as it implies enhancing the polymeric matrix structure by a reinforcing system and nanoscale non-organic additives. If the membrane production process parameters are chosen properly, the nanoparticles can not only accelerate the chemical mechanism of the reaction, but also integrate into the polymeric matrix structure thus enhancing its existing physical and chemical properties and introducing those which it had never featured before.

Methods and Materials

The polymeric ion-exchange membrane was synthesized from the following components: phenol, sulphuric acid, formaline, nanoscale non-organic additives and polyacrylonitrile fiber.

By polymeric ion-exchange membrane structure we mean the interaction of spatially arranged macromolecules. The spatial structure also includes pores [8]. The number and quality of the pores within the material structure determines the ionic selectivity of a membrane [9].

To establish the correlation between the structure and properties it is necessary to examine the membrane's three-dimensional structure at all levels. This task is extremely complicated as there is no single definite way to penetrate inside the membrane and obtain data on its inner structure. For that reason we examined the structure with a number of mutually complementary methods [10].

Each of the latter provides as much information on the structure as can be ensured by the instruments' performance limitations, testing methods

and calculating models and enables the elements examination on different morphological levels.

The examination methods applied to polymeric membranes for liquids separation included: porosimetric – the Method of Standard Contact Porosimetry (MSCP), thermochemical – Differential Scanning Calorimetry (DSC), and physical – Scanning Electron Microscopy (SEM) and Transmission Electronic Microscopy (TEM), as well as a number of other standard chemical and physical-chemical testing methods.

The scope of thermochemical methods includes Differential Scanning Calorimetry (DSC). This method is used to measure emission/absorption heat of various processes. DSC was instrumental in the determination of production process parameters for polymer nanocomposite membranes with specified structural properties.

The physical methods included Scanning Electron Microscopy (SEM) which enabled us to examine the polymer membrane surface morphology, and determine the interrelation of process parameters on the surface structure [11].

The Standard Contact Porosimetry (SCP) was used to investigate the effect of nanoparticles on the pores dimensions, their distribution within the composite material structure, the distance between their fixed groups, and the specific surface. The research was conducted in two liquids, i.e. octane and water. The actuation medium for the tested membranes is water. Octane was used for dry state comparison as the tested membranes do not swell in this fluid.

When the membrane is actuated by water its pores and channels open. They serve as vessels to let in the contaminated water which then undergoes ion exchange purification and leaves the membrane.

Results

Recently, the requirements to ion exchange membranes and their reinforcement have noticeably grown [12]. Mass-produced electro dialysis membranes are reinforced to ensure their mechanical strength. Reinforcement is usually performed by pressing together ion-exchange resin and an inert filler which is not involved in ion exchange. The use of such membranes reveals their mediocre performance and tendency to separate. This

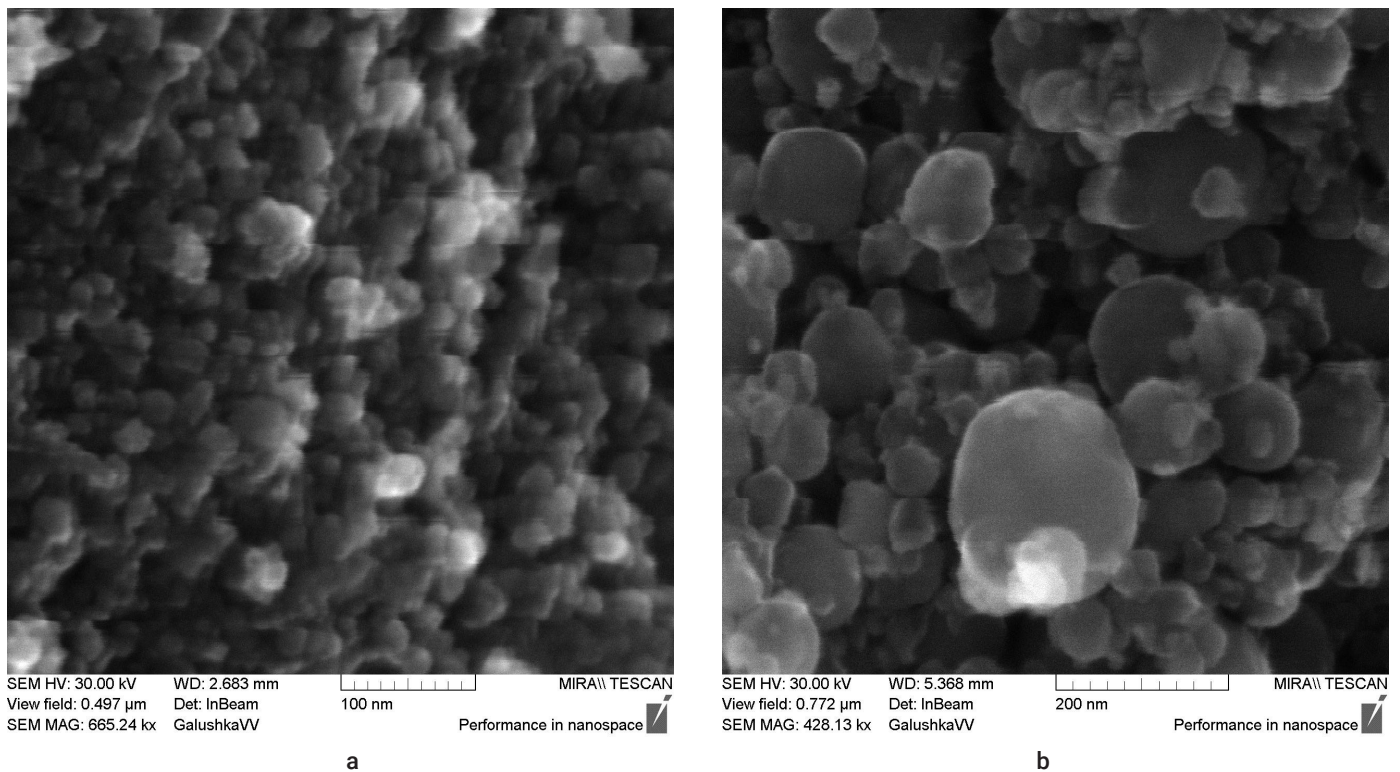


Figure 1. SEM images of Fe (a) and Si (b) particles

membrane production technology is not deemed feasible as it requires significant energy and labor consumption while the quality of the produced membranes is low.

This problem can be addressed by eliminating resource-intensive procedures from the production process. Removing membrane components not involved in ions transportation can both decrease the membrane prime cost and increase its quality. The polymer composite membrane works as a single entity avoiding layer disintegration.

The membrane features can be deliberately modified by additives which are infused at the stage of the filler saturation with monomer mixture, and later participate in forming the structure [13,14].

The findings of both Russian and global research prove that nanoscale additives can amend the polymer material structure and augment them with properties they did not initially feature [15–18].

Non-organic additives were added at the stage of the filler being saturated with the monomer mixture. The resulting polymer composite membrane

featured predetermined properties and required no further treatment or modification.

Iron and silicon were chosen as dispersion additives used to control the structure and properties of the studied composite membrane polymer matrix. (Fig. 1).

The shape of the particles of chosen additives was proved to be close to a spherical one.

The particle size was measured by energy dispersive X-ray spectroscopy. The particle size distribution was found to be confined to nanometer range with the basic fraction not exceeding 30 nm (Fig. 2) thus justifying their attribution to nanoparticles under the adopted classification.

An obstacle to nanoparticles application is their highly developed surface and propensity to spontaneous agglomeration [19]. Therefore the research was also intended to investigate the possibility of nanoparticles integration into polymer matrix. The elemental analysis of the nanoparticles revealed oxygen content (Fig. 3).

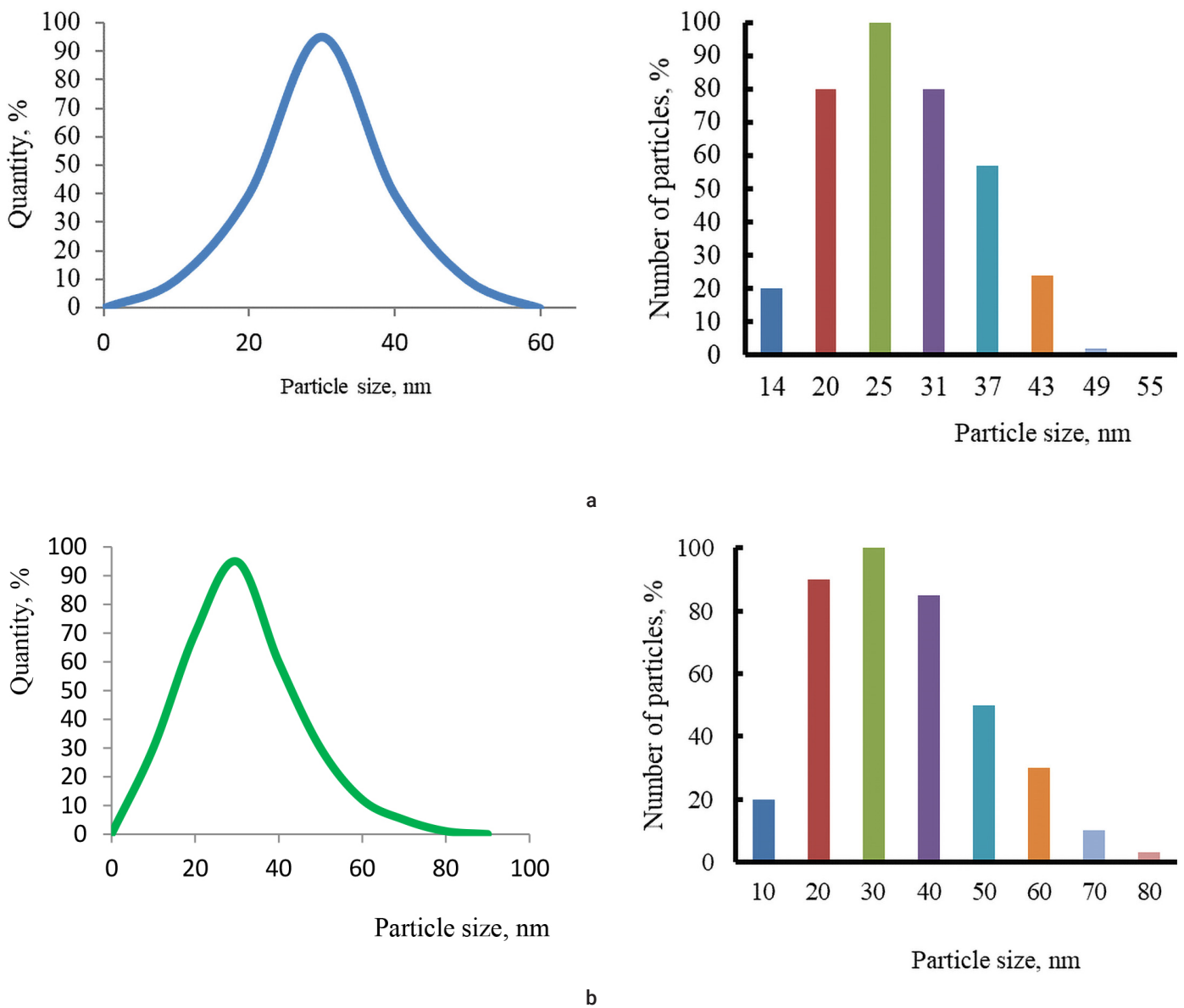


Figure 2. Fe (a) and Si (b) particle size distribution

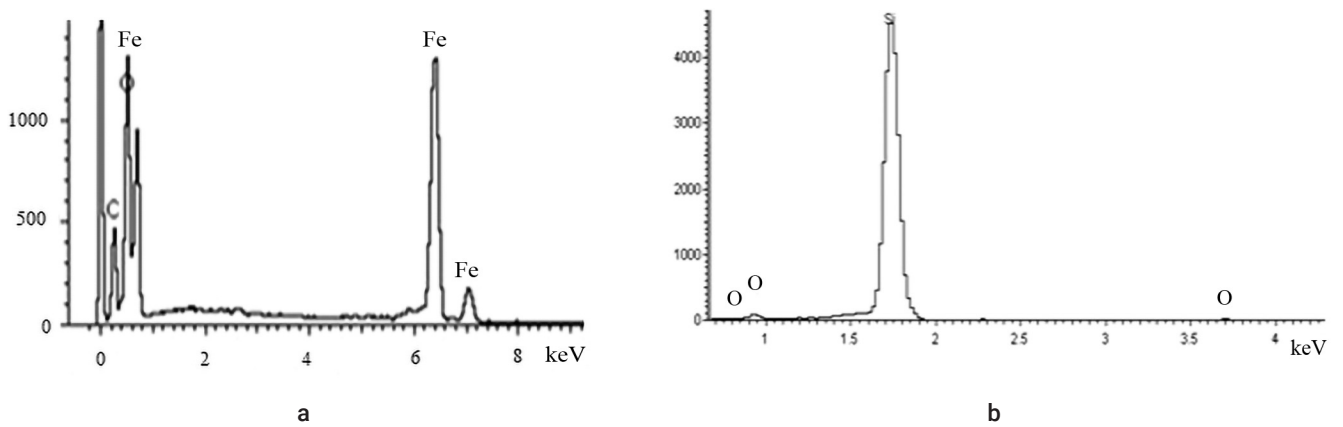


Figure 3. Energy Dispersive X-ray Spectroscopy of additives: a – Fe, b – Si

The detection of oxygen is an indication of a protective layer of oxide. The transmission electronic microscopy survey (Fig. 4) showed a protective film on each of the particles. The coating protects them from spontaneous agglomeration.

A series of electronic microscopy experiments established the following: the chosen iron and silicon additives have nanoscale sizes; each particle is covered with an oxide film protecting nanoparticles from agglomeration. The protective film enables even distribution of the particles within both the

monomer saturating compound and the bulk of the composite material.

As the filler should be saturated with a liquid monomers mixture it was required to study the kinetics of wetting polyacrylonitrile fiber with a compound containing iron and silicon particles.

The study was conducted with a K-8 cathetometer. The fiber was immersed into sulphocationite monomerizing compound containing nanoparticles. The data obtained are shown in Fig. 5.

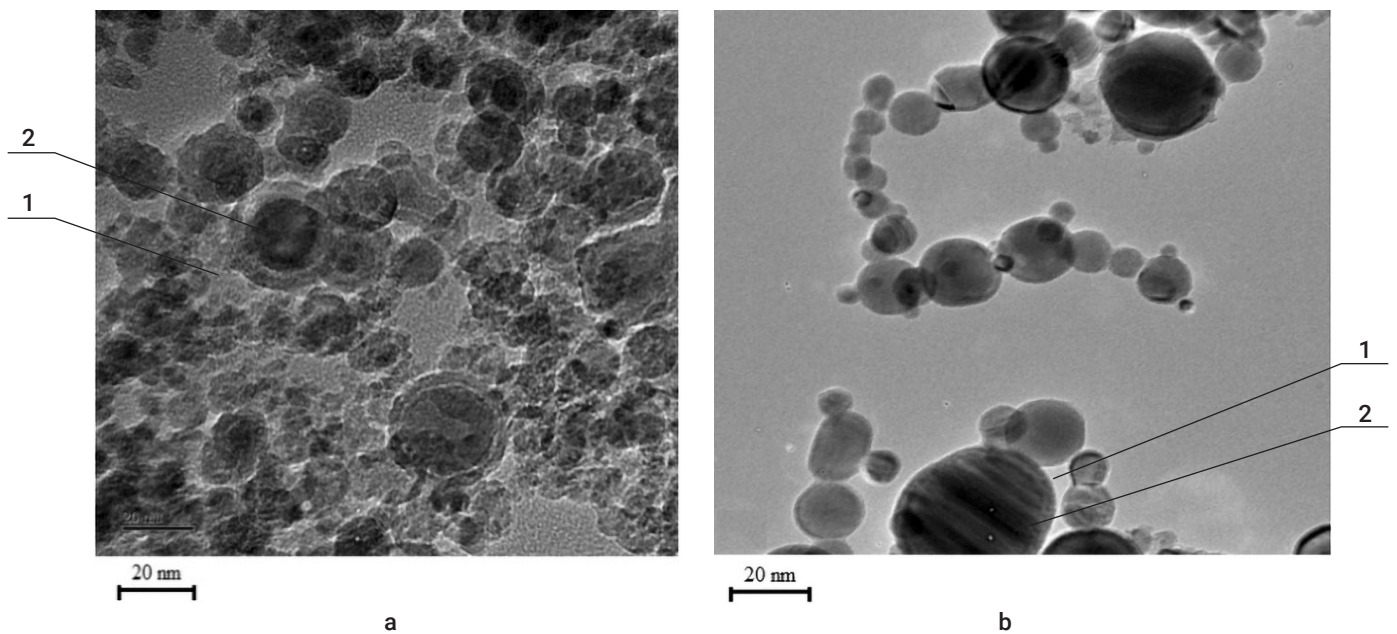


Figure 4. TEM images of Fe (a) and Si (b) nanoparticles: 1 – oxide layer, 2 – nanoparticle

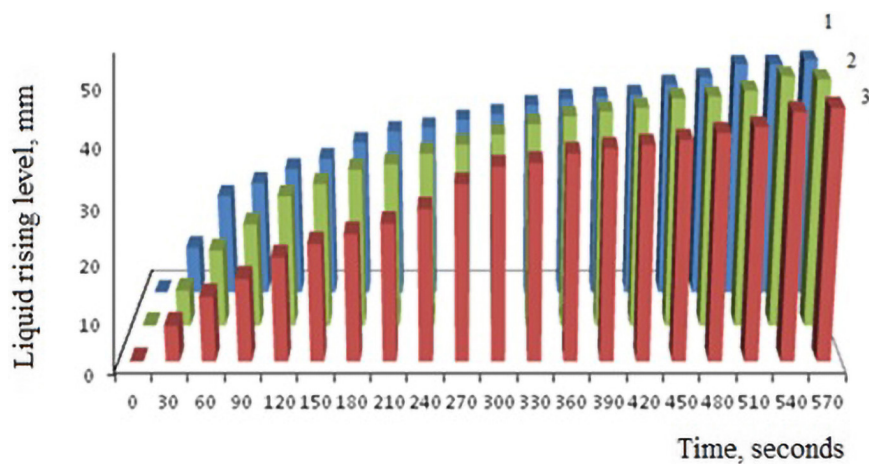


Figure 5. Kinetics of polyacrylonitrile fiber wetting with: 1 – monomerizing compound; 2 – iron-containing monomerizing compound; 3 – silicon-containing monomerizing compound

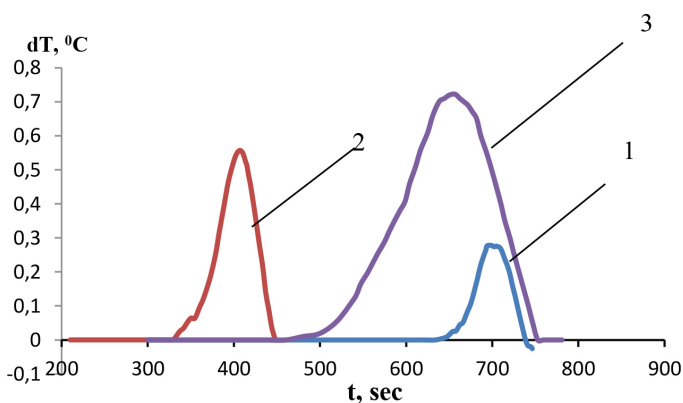


Figure 6. Differential Scanning Calorimetry data on synthesis and structure of polymer nanocomposite membranes with (1) iron and (2) silicon additives

The obtained data demonstrate that a solid phase added to sulphocationite monomerizing compound at the polyacrylic fiber saturation stage does not impede monomers penetration into the fiber's pores and interfibrillary space. This is due to the fact that the size of the fiber pores and interfibrillary space significantly exceeds the size of the monomers and to a still greater extent that of the nanoscale additives.

Membrane production kinetics and thermodynamics change considerably (Fig. 6).

Analysis of the obtained data reveals the nanoparticles' impact on polymer nanocomposite membranes production kinetics. The diagram demonstrates (Fig. 6) increasing heat emission with the

curves' acquiring 'arm' elements indicative of formation of additional crosslinks. Strong interaction of nanoparticles with the polymer matrix changes the correlation between the polymer matrix's constrained and unconstrained regions thus bringing about formation of a new composite membrane cross-linked polymer matrix.

The research demonstrates that nanoparticles added to monomerizing compound can considerably affect not only the synthesis rate but also the polymer matrix further structural formation as they can become crosslinks. The peak was registered to increase and move to a lower temperature area (Table 1).

TABLE 1.
The Impact of Nanoparticles on Composite Membrane Polymer Matrix Formation

Composite membrane	Polycondensation $\frac{T_H - T_K}{T_{MAX}}, ^\circ\text{C}$	ΔH , J/g
w/o additives	$\frac{85 - 100}{90}$	1200
with Fe additive	$\frac{50 - 75}{60}$	1400
with Si additive	$\frac{70 - 100}{85}$	1700

Scanning electron microscopy yielded images of the surface of the polymer nanocomposite membranes (Fig. 7).

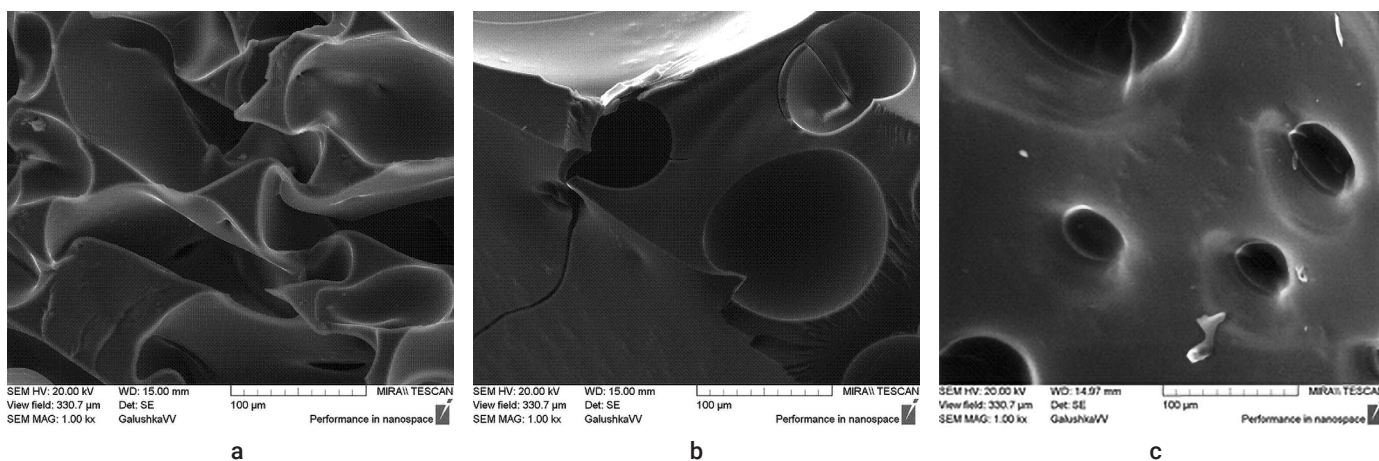


Figure 7. Scanning Electron Microscopy images showing surfaces of polymer membranes (a) with Fe nanoparticles (b) and with Si nanoparticles

The SEM data analysis revealed that additives change the structure of membrane surface. This confirms the hypothesis that nanoparticles integrate into the polymer framework structure.

The pore structure of polymer nanocomposite membranes was subjected to standard contact porosimetry. The research also included the pore volume and radius measurement. The measurements were performed in a nonwetting liquid (octane) (Fig. 8.).

As demonstrated by the study, a polymer membrane in dry condition has virtually no functional hydrophilic pores while having those of approximately 100 nm in diameter which falls within the range of microflaws and fractures. Upon contacting with water, the situation changes and the cation exchange matrix starts to swell. The micro- and mesopores which were closed when dry now open. This changes the porosimetric curve drastically (Fig. 9).

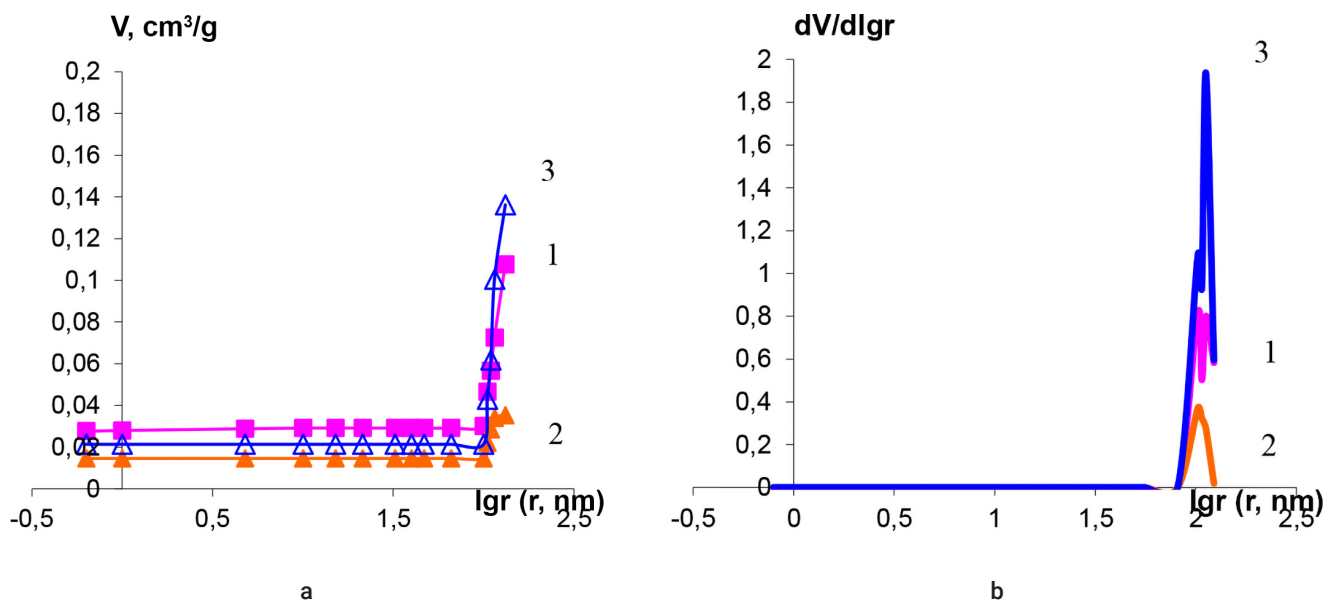


Figure 8. Octane distribution against the effective radius of ion exchange membrane pores on integral (a) and differential (b) curves with (1) no additives, (2) Fe added and (3) Si added

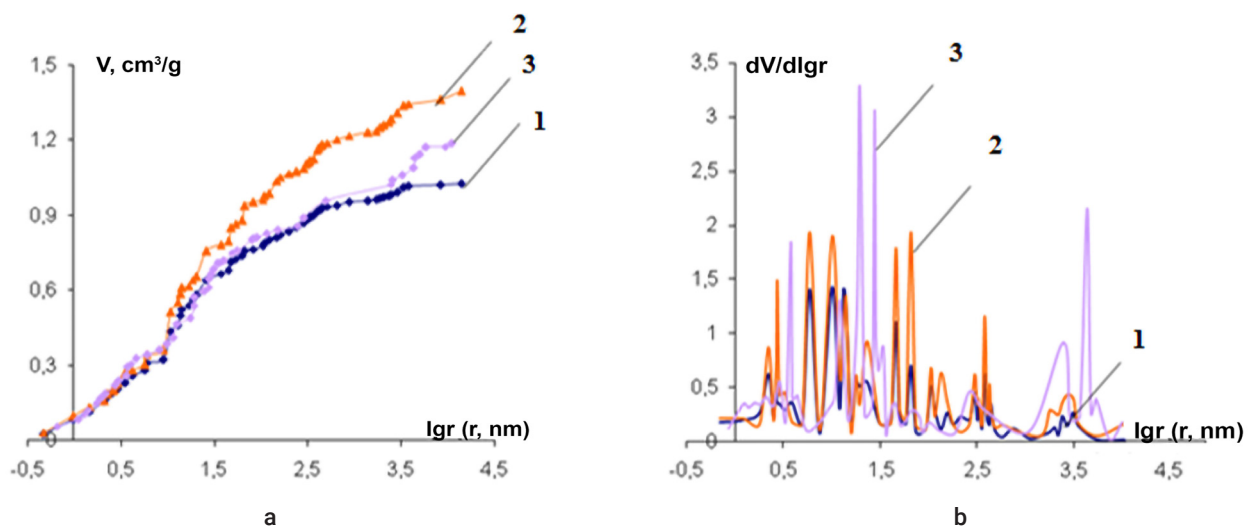


Figure 9. Water distribution against polyacrylonitrile fiber polymer nanocomposite membrane pores' effective radius on (a) integral and (b) differential curves

TABLE 2.
Structural Features of Polymer Nanocomposite Membranes

Description	no additives	with iron additive	with silicon additive
Pore volume defined with octane (V_0^{octane}), cm^3/g	0.40	0.41	0.45
Total pore volume, (V_0), cm^3/g	1.03	1.41	1.85
Water-specific density (ρ), cm^3/g	1.42	1.45	1.49
Total specific surface, (S), m^2/g	417	475	495
Meso- and macropores specific surface at $r > 1 \text{ nm}$ (S_1), m^2/g	65	77	84
Distance between fixed groups (L), nm	0.54	0.43	0.38

Experimental data comparison demonstrates that the octane-measured porosity is to a significant extent lower than that defined in water. This can be attributed to ion exchange membranes' actuation

when swelling in water. The hydrophilic channels and ion exchange pores open. In dry condition such pores are sealed. Polymer membranes do not swell in octane which is why octane is used for comparison as a dry condition substitute in standard contact porosimetry.

Membranes standard porosimetry enabled calculation of the inner specific surface S (m^2/g) and average distance between fixed groups L (Table 2).

The conducted research revealed that iron and silicon nanoparticles increase the number of micropores with the radius smaller than 1 nm which are instrumental for efficient ion exchange. As the number of micropores increase, the membrane specific surface grows by 14% and 19% respectively for iron and silicon nanoparticles added.

The material wettability is evaluated by the spreading droplet method, the measuring instrument being the liquid contact angle. The contact angle evaluation is based on the three-phase equilibrium occurring at the solid-liquid-vapor interface (e.g. membrane/water/air) (Fig. 10).



Figure 10. Schematic representation of the liquid droplet shape and the wettability angle at the membrane solid horizontal surface: a – θ exceeds 90° – the surface wettability is low; b – θ is less than 90° – the surface wettability is high

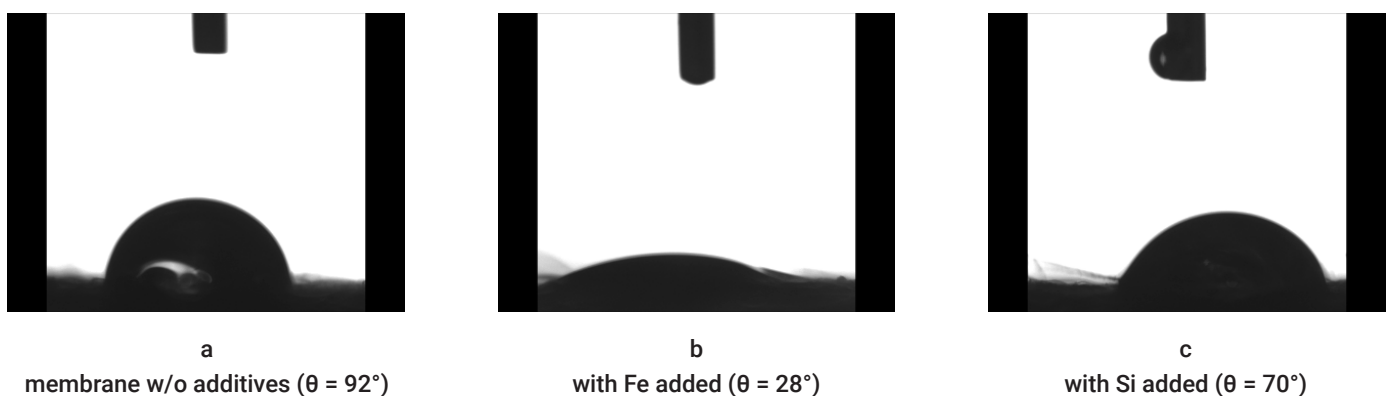


Figure 11. The spreading droplet method: the contact angle θ for the liquid (water) droplet on the surface of (a) polymer nanocomposite membrane and (b) that modified with Fe additives or (c) Si additives

A droplet of water (approximately several μl) is put on the membrane surface, and then θ (the angle of contact between the water droplet and the membrane surface) is measured with a goniometer. The contact angle $< 90^\circ$ indicates the water capability of unprompted percolation into the pore without any supplementary pressure applied, while the contact angle $> 90^\circ$ signifies that the percolation requires supplementary pressure as shown in Fig. 11.

The real-time wetting contact angle measurement revealed a better surface wettability of nanoparticle-modified membranes. The images obtained were processed with a specialized software intended to automate the experimental curves using the Young-Laplace equation (Fig. 12).

Adding nanoparticles to a tangible extent affects polymer membrane structure. The membrane surface becomes hydrophilic. The composite structure has a multitude of channels and pores housing such processes as ultrafiltration, ion exchange, sewage sorption purification and electro dialysis.

Ion exchange membranes are distinguished by inversions of ionogenic groups related to the ionogenic groups' orientation towards or versus the inside of the resin particles thus conveying to the pore structure hydrophobic or hydrophilic properties respectively. The nanoscale additives modify the structure formation by directing the ionogenic groups orientation towards the pore and channel surfaces (Fig. 13).

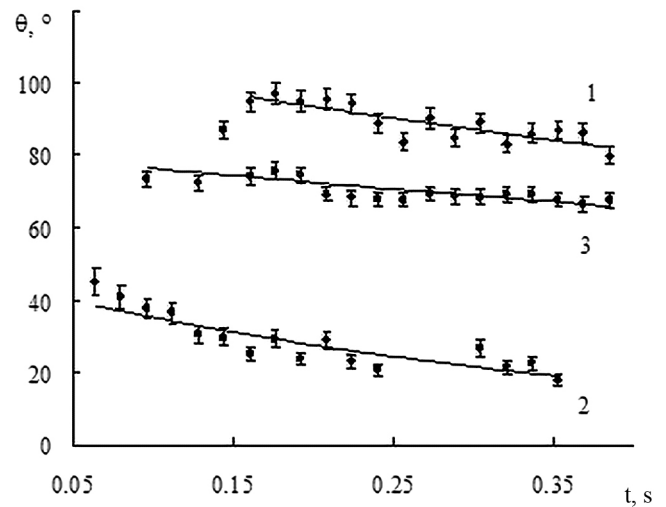


Figure 12. Contact angle dynamic curves for polymer nanocomposite membranes: 1 – without additives; 2 – with Fe added; 3 – with Si added

For the samples studied, the adhesion and material surface water wetting were calculated with the surface tension of $72.7 \mu\text{J}/\text{m}^2$ (Table 3).

TABLE 3. Adhesive Properties of Polymer Nanocomposite Membranes

Material	The work of adhesion, $\mu\text{J}/\text{m}^2$	The work of wetting, $\mu\text{J}/\text{m}^2$
with no additives	1.154	73.855
with Fe added	63.70	136.401
with Si added	23.69	96.393

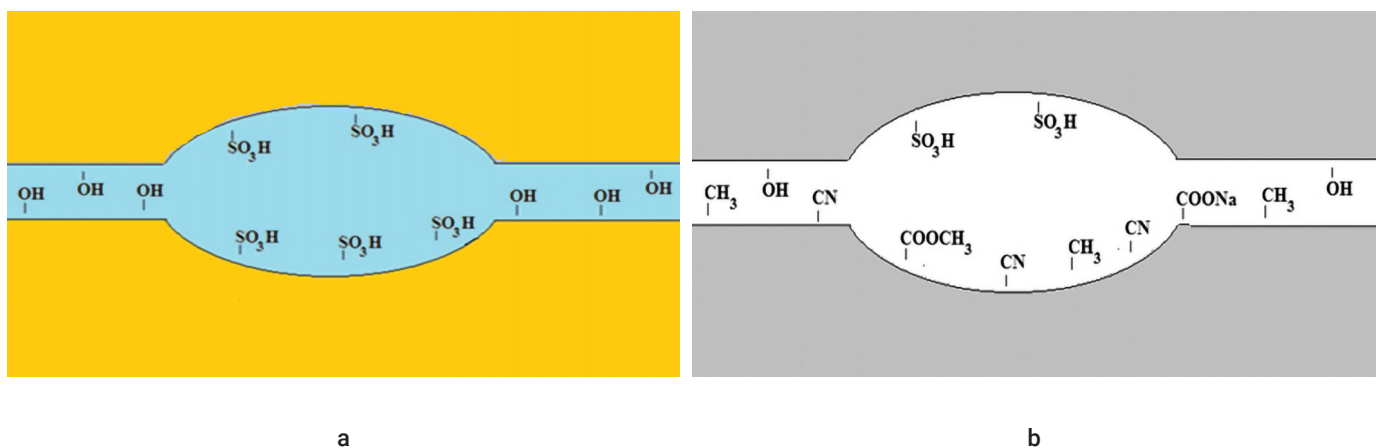


Figure 13. Models of (a) hydrophilic and (b) hydrophobic micropores generated in a polymer membrane with nanoscale particles or without them.

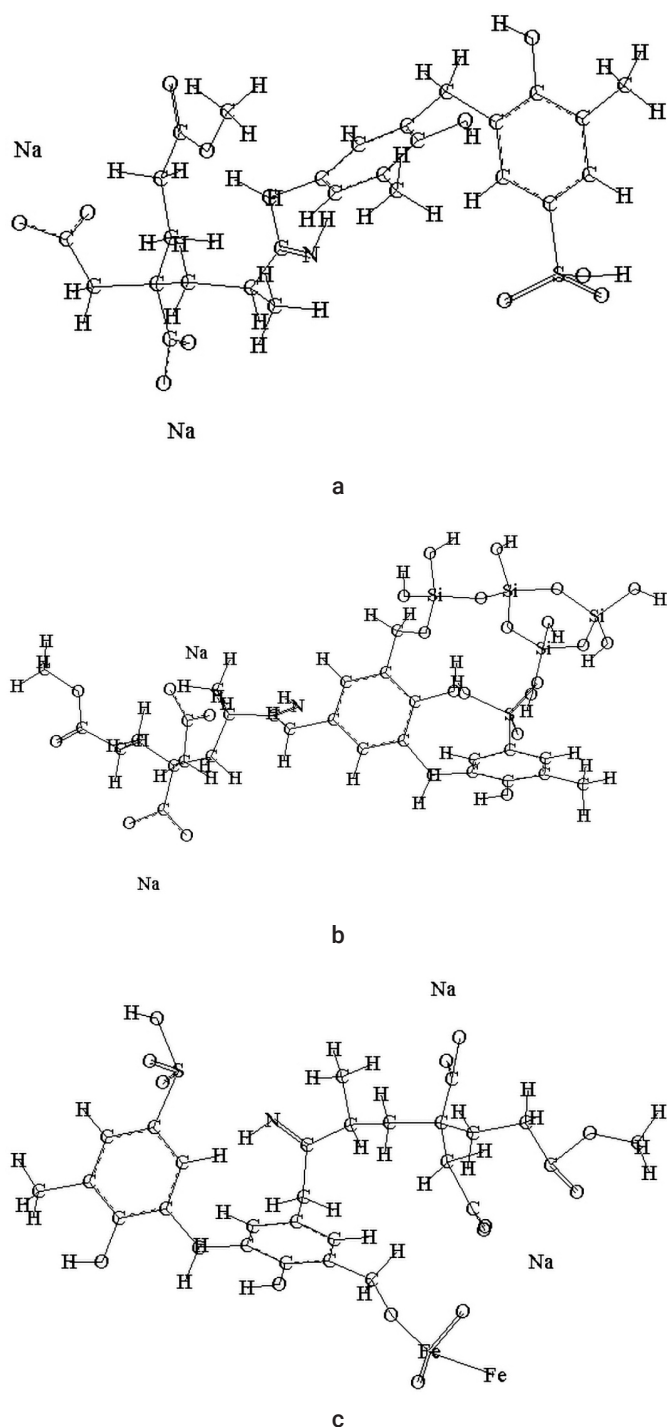


Figure 14. Molecule spatial model for (a) polymer nanocomposite membrane with (b) Si nanoparticles and (c) Fe nanoparticles.

These methods provide detailed description of the polymer membrane structure but stop short of visualizing its molecular structure. The novel approach to handling this task introduced in this study pioneered in developing and enhancing 3D

models of polymer nanocomposite membranes. Polycondensation consists in saturating the fibrous base with a mixture of liquid monomers which in the course of the reaction transfer to the solid phase. As hardening leaves no interface between the polymer matrix, fibrous base and nanoparticles, we end up having a three-dimensional polymer composite network behaving as a single unity.

The most probable 3D position of atoms was derived by applying quantum chemistry calculations of atoms interaction and spatial arrangement to polyacrylonitrile fiber polymer matrix augmented with nanoscale additives (Fig. 14).

Discussion

The level of the polymer nanocomposite membranes proposed was evaluated by studying their implementation in electro dialysis plants and sorption units. The overall testing demonstrated their electric conductivity and filtering capacity [21].

Wastewater disposal, water conditioning, molecular grade water production, as well as mixture separation – all these processes can be performed using electro dialysis [22]. This water treatment method is nonchemical and resource efficient. However, its application to dilute solutions with total salt content below 5 g/l is economically unviable due to increasing energy costs for desalination. The energy costs increase is related to significant electric resistance of dilute solutions. That accounts for low efficiency of standard mass-produced membranes in electro dialysis plants. Dilute solutions feature high resistance and, accordingly, high energy consumption and low water desalination efficiency [23]. This had to be taken into consideration when testing the polymer nanocomposite membranes and evaluating the possibility and expediency of their usage in electro dialysis. Electric conductivity is indicative of the transporting capacity and electric conductivity of an electro dialysis unit membrane stack.

The electric conductivity of polymer nanocomposite membranes was examined by the differential method. The differential method procedure implies that the electric conductivity of the solution-containing cell is first evaluated with no membrane installed and then tested again upon the membrane installation. The differential

between the no-membrane values and those affected by the membrane demonstrates the membrane resistance and excludes the electrode-solution transitional boundaries. The measurement results are shown in Fig. 15.

The research revealed that iron and silicone nanoscale additives can increase the membrane electric conductivity by the factor exceeding three thus facilitating electro dialysis and increasing the economic efficiency by reducing the energy consumption.

The critical current of the membranes was estimated by the current-voltage curves tangential lines method. Tangential lines are drawn through the three straight segments of the current-voltage curve, the critical current being defined by their intersection points.

Fig. 16 shows the current-voltage properties of the membranes proposed.

The study demonstrates that the membranes with nanoscale iron and silicone additives feature low critical current properties and consequently such membranes are capable of separation which means the best possible transition to overlimiting current modes while the large number of H⁺ and OH⁻ ions facilitates reduced energy consumption thus enhancing the overall electro dialysis efficiency.

Consequently the membranes produced in the course of this study are expected to demonstrate high water treatment and purification efficiency.

A comparative study of polymer nanocomposite membranes was also conducted (see Table 4).

TABLE 4.
Principal Features
of Certain Cation-exchange Membranes

Membrane name	Manufacturer	Membrane type	Ion-exchange capacity, mg-equ/g	Moisture content, %
Nafion-117	DuPont, CUSA	homogeneous	0.8-1.1	<25
MF-4SK	Plastpolymer, Russia	homogeneous	0.8-1.1	25
Ralex CM	Mega, the Czech Republic	heterogeneous	2.1-2.3	<55
MK-40	Shchekinoazot, Russia	heterogeneous	2.1-2.3	35±5
Polymer nanocomposite membrane	Russia	heterogeneous	3.0-3.2	43

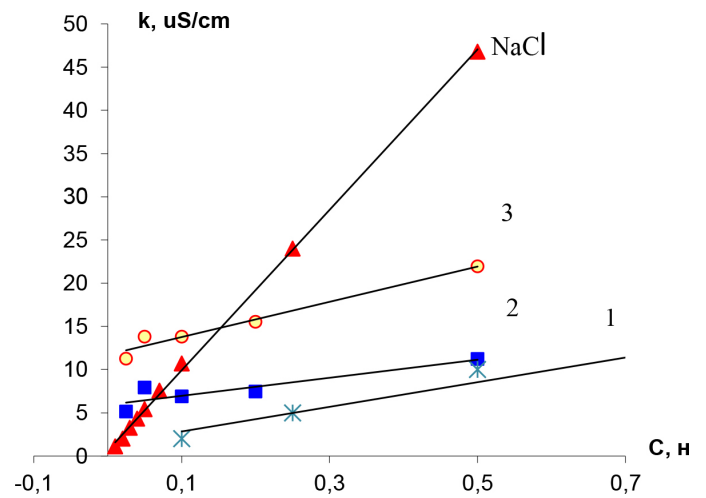


Figure 15. Membrane specific electric conductivity dependence on sodium
 1 – polymer nanocomposite membrane with no additives,
 2 – polymer nanocomposite membrane with Fe additive,
 3 – polymer nanocomposite membrane with Si additive

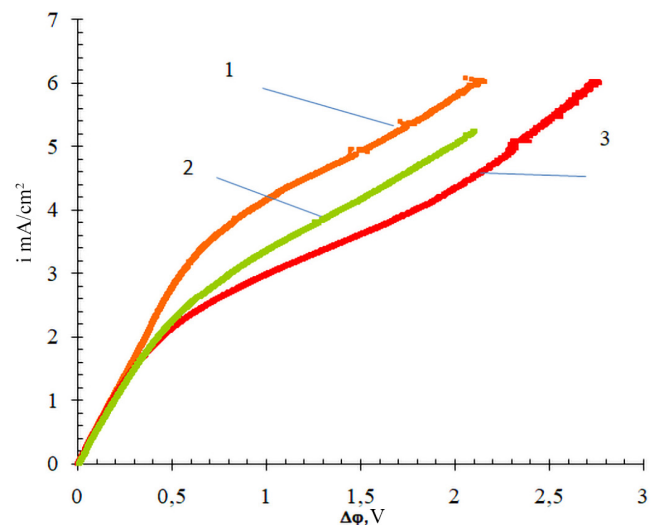


Figure 16. Current-Voltage Properties of Membranes
 1 – polymer nanocomposite membrane with no additives,
 2 – polymer nanocomposite membrane with Fe additive,
 3 – polymer nanocomposite membrane with Si additive

TABLE 5.
Proposed Membranes Efficiency Evaluation

Parameter	Contaminators				
	Total hardness, mg-equ/l	Cu, mg/l	Pb, mg/l	Zn, mg/l	Hydrocarbons, mg/l
M.A.C.	up to 7	0.1	0.03	1.0	0.3
Prior to purification	8.8	15	1.7	1.7	4.9
After purification by the proposed membranes					
with no additives	0.6	4.75	0.7	0.9	0.3
with Fe added	0.3	0.08	0.03	0.6	0.08
with Si added	0.1	0.04	0.01	0.4	0.05

Analysis of the structure, kinetics and transport properties demonstrated that depositing nanoscale additives at the saturation stage considerably improves the membrane's performance. It is possible due to the interaction between the nanoparticles and the polymer matrix. The positive changes include the membrane matrix molecular level rearrangement and structure enhancement, the nongel space reduction and opening of the channels and pores which deal with ion exchange and disposal of the reaction products. A better interaction between the matrix and the fiber substrate ensures the heterogeneous membrane operating as a single unity thus enhancing its physical and mechanic properties.

To estimate water treatment and purification efficiency of the membranes proposed, tests were run to evaluate their performance in water softening, heavy metals and hydrocarbons removal (*Table 5*).

Polymer ion exchange membranes with high content and even distribution of ion exchange pores proved efficient in water treatment and purification.

Conclusions

The objective of the research was to investigate the solutions to produce novel membrane materials featuring enhanced properties by means of studying the principles which govern cation exchange matrices synthesis affected by nanoscale organic additives and establishing the ways in which the transport, sorption and separating properties of such materials are determined by their structure.

The suggested non-standard solution of using nanoparticles in matrix synthesis both expands the

polycondensation filling method and solves a variety of technology issues and tasks related to the structure-to-property correlation. [24]

The research involved performing the quantum chemistry calculations and designing the three-dimensional models which enriched the understanding of the polycondensation filling processes and the structures obtained; they also showed most probable points of interaction between the polyacrylonitrile fiber, nanoscale particles and the reactive groups of the polymer matrix undergoing formation.

The pore and channel structure affected by the composite ion exchange membrane production process operations was examined by the standard contact porosimetry method.

It was demonstrated that by modifying the composite fiber ion-exchange membranes production method one can influence the formation of the sample structure so that to end up having a material which features a prevailing amount of either macro- or micropores. The research showed that the proposed membranes surpass their counterparts with regard to the electric and transport properties thus ensuring successful application in sorption and electromembrane processes.

The values obtained are consistent with the findings of the porosimetric curves analysis implemented to evaluate the macropores volume in the studied membranes. The study of synthesized materials usage in sorption processes has revealed the increasing purification degree thus proving the potential of their implementation within purification units.

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