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INFLUENCE OF ZIRCONIUM HYDROPHOSPHATE NANOPARTICLES ON POROUS STRUCTURE AND SORPTION CAPACITY OF THE COMPOSITES BASED ON ION EXCHANGE RESIN

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Abstract. Evolution of swelling of gel-like strongly acidic resin and organic-inorganic composites based on this ion-exchanger was investigated. Non-aggregated nanoparticles of zirconium hydrophosphate were found to provide size invariability of the polymer pores, which contain functional groups (up to 20 nm), the nanoparticle aggregates squeeze these pores (down to 3 nm). Owing to this, the nanocomposite shows higher break-through capacity during removal of Ni²⁺ from water, than the sample modified only with aggregates.

Keywords: organic-inorganic ion exchangers, nanoparticles, zirconium hydrophosphate, polymer porosity, standard contact porosimetry.

1. Introduction

In comparison with ion exchange resins, the advantages of organic-inorganic materials are: higher exchange capacity within a wide pH interval, selectivity towards toxic ions, smaller amount of reagents for regeneration and stability against accumulation of organic substances and microorganisms [1, 2]. Zirconium hydrophosphate (ZHP) has been proposed as a modifier, this ion-exchanger provides improved selectivity towards toxic ions, such as Pb²⁺ [1], Ni²⁺ [3], Cd²⁺ [4], and significantly simplifies regeneration [1]. In general, the ion-exchangers based on macroporous resins containing aggregated nanoparticles are known [1, 2]. At the same time, gel-like resins are characterized by higher exchange capacity and higher mobility of sorbed ions [5]. It is possible to obtain non-aggregated nanoparticles in the resins of this type [3, 4].

The swollen ion exchange polymer includes the so called gel areas and voids between them, where hydrophobic sections of the polymer chains are located [6, 7]. The gel fields are hydrophilic, they contain functional groups, where the phases of the solvent and polymer are individual. Owing to this, the spaces in the gel fields, which are filled with the solvent, are related to pores. The pores can be determined with known methods by adsorption of the solvent. The spaces of gel phase, which are formed during swelling, are the sequences of nanosized clusters connected by narrower channels. Clusters and channels are called "transport pores", since ions move through them. Porous structure of polymer ion exchange materials also includes defects of micron size, as a rule, the defects look like claws [3]. The inorganic particles cause a change of volume of different pores of the polymer [4, 8]. The aim of the work is to identify the features of transformation of the porous structure of the polymer affected by the inorganic modifier. The investigation also involves the establishment of the composites porous structure influence on their exchange capacity. In the future, this information would be useful for development of approaches to the synthesis of materials for electro dialysis, particularly reversal electro dialysis, catalytic processes, fuel cells.

2. Experimental

2.1. Modification of Cation Exchange Resin

A strong acidic gel-like resin, such as Dowex HCR-S (Dow Chemical) was used as a polymer matrix.

The cation-exchanger is an analogue of Dowex X-8 and CU-2-8 resins, which contain 8 % divinylbenzene, DVB (cross-linking agent). In order to obtain the nanocomposite comprising non-aggregated ZHP nanoparticles and their aggregates, the technique developed earlier was used [3, 4]. The ion-exchanger was impregnated with 1 M $ZrOCl_2$ solution, ZHP was deposited with 1 M H_3PO_4 solution. The composite containing only aggregates was synthesized by impregnation of the resin with sol obtained from 1 M $ZrOCl_2$ solution (a minimal size of the particles was 4 nm) followed by deposition with phosphoric acid [8]. In opposite to [3, 4, 8], impregnation and deposition were carried at 313 K. After ZHP deposition, the ion-exchangers were dried in a desiccator over $CaCl_2$, the precipitate was removed from the outer surface by means of ultrasound at 30 kHz using a Bandeline device (Bandeline). Then the ion-exchangers were washed and dried again in the desiccator down to a constant mass. In order to reach the comparable amount of ZHP, the ion-exchanger was modified 8 (ZHP deposition from the solution) and 3 times (deposition from sol).

2.2. Chemical Composition, Morphology and Porosity

Morphology of the composites was investigated by means of transmission electron microscopy (TEM) using a JEOL JEM 1230 microscope (Jeol). Preliminarily the samples were crashed and treated with ultrasound. The content of Zr and P was determined with X-ray fluorescence method using X-Supreme8000 XRF spectrometer (Oxford Instruments). NMR ^{31}P spectra were recorded by means of AVANCE 400 spectrometer using single-pulse technique under the accumulation mode at 162 MHz. Chemical shift has been determined relatively to 85 % H_3PO_4 . Signals at -23 and -37 ppm correspond to $-OPO_3H_2$ and $-O_2PO_2H$ groups, respectively [8]. The spectra were deconvoluted to Gauss components by means of PeakFit v4.12 program, the area of each peak was determined, a ratio of the group content was determined as the ratio of the peak areas.

Before investigations with a method of standard contact porosimetry (SCP) [9], the samples were evacuated at 353 K, fixed onto macroporous substrate, impregnated with water under this temperature and placed between two ceramic standard samples. The contact between the standards and investigated sample was 0.1 MPa, the set disassembled and weighted periodically during drying. Adsorption and desorption of water vapour were researched after evacuation of the samples at 353 K, the investigations were performed using a vacuum Mac-Ben apparatus supplied with quartz scales [10].

2.3. Electrical Conductivity and Ion Exchange

Total exchange capacity towards Na^+ , A_m , was determined according to [11]: 0.1 M NaCl solution was passed through the column filled with the ion-exchanger. The passage was stopped, when pH of the solution at the cell outlet reached 5-6. Additionally sorbed electrolyte, *i.e.* sorbed according to non-exchange mechanism, was removed from the ion-exchanger during multiple washing with deionized water under static conditions. Electrical conductivity of the effluent was controlled. The ion-exchanger was regenerated with 1 M H_2SO_4 solution and analyzed with a flame-photometric method using PFM-U4.2 photometer (Analitpribor).

Electrical conductivity of the ion-exchangers in H-forms was investigated using impedance spectroscopy according to [3, 4, 8]. The material was placed into the prismatic cell supplied by platinum electrodes; deionized water was used as a non-conducting phase. The measurements were carried out using an Autolab impedance system within the frequency interval of $1 \cdot 10^{-2}$ – $1 \cdot 10^6$ Hz, the *dc* conductivity was determined as a wide plateau of the frequency spectrum of admittance.

A multicomponent solution, which contained 1.3 and 0.5 mmol dm^{-3} Ca^{2+} and Mg^{2+} respectively as well as Ni^{2+} (0.08 or 1 mmol dm^{-3}), was desalinated under dynamic conditions. The solution was passed through the column, a diameter of which was 0.8 cm, with a constant velocity of 0.08 $cm^3 s^{-1}$. The content of species in the solution at the cell outlet was determined with an atomic absorption method using S9 Pye Unicam spectrophotometer (Philips).

3. Results and Discussion

3.1. Particles of Inorganic Constituent in the Polymer

Zirconium exists as $[Zr_4(OH)_8(H_2O)_{16}]_n^{8+}$ hydroxocomplexes in $ZrOCl_2$ solution [12, 13], these cations replace counter-ions of the polymer (H^+) during its impregnation with a solution. Treatment of the ion-exchanger with H_3PO_4 solution results in deposition of non-aggregated nanoparticles (4–20 nm), which are evidently placed in clusters and channels [5] (Fig. 1). During impregnation, highly concentrated $ZrOCl_2$ solution (both counter- and co-ions) fills voids between gel fields and structure defects, where aggregates of the nanoparticles are deposited.

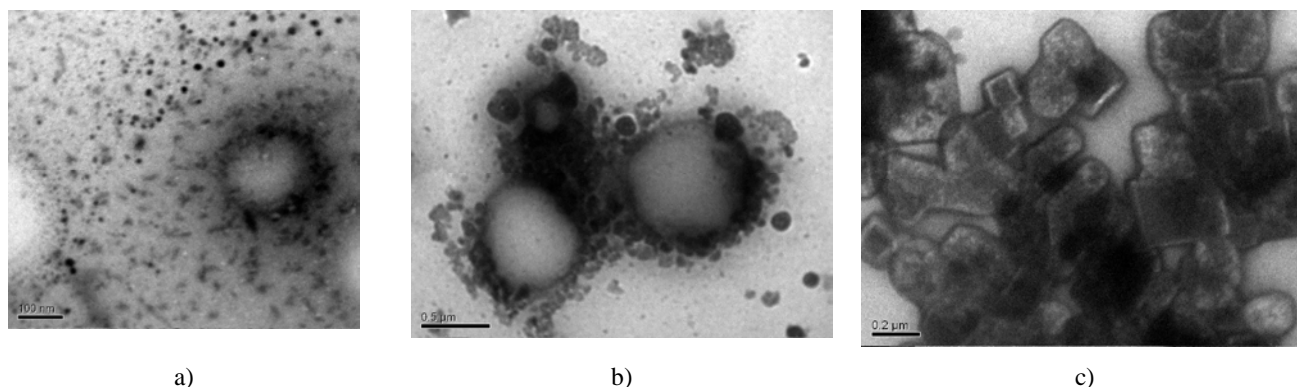


Fig. 1. TEM image of non-aggregated ZHP nanoparticles (a) and their aggregates in the polymer. ZHP was deposited from solution (a, b) and sol (c)

Table 1

Characteristics of ion-exchangers

Ion-exchanger	I	II	III	IV	V	VI	VII	VIII	IX	X
Pristine	0	–	–	4.2	0.19	2.5	0.91	1.5	0.90	1.5
Modified with non-aggregated nanoparticles and aggregates	0.39	1.4:1	1:0.8	8.8	0.21	4.5	0.88	1.9	–	–
Modified only with aggregates	0.43	1.9:1	1:0.78	2.6	0.10	2.3	0.87	1.4	0.92	1.3

Notes: I – m ; II – molar ratio of P:Zr; III – molar ratio of $-\text{OPO}_3\text{H}_2$ and $-\text{O}_2\text{PO}_2\text{H}$ groups; IV – A_m , $\text{mmol}\cdot\text{g}^{-1}$ (A_p for the pristine ion-exchanger); V – $A_{\text{H}_2\text{O}}$, $\text{cm}^3\cdot\text{g}^{-1}$ (before the growth of the desorption isotherm); VI – n ; VII – P/P_s ($A_{\text{H}_2\text{O}}=1.22 \text{ cm}^3\cdot\text{g}^{-1}$); VIII – $p \cdot 10^{-7}$, Pa ($A_{\text{H}_2\text{O}}=1.22 \text{ cm}^3\cdot\text{g}^{-1}$); IX – P/P_s ($A_{\text{H}_2\text{O}}=1.65 \text{ cm}^3\cdot\text{g}^{-1}$); X – $p \cdot 10^{-7}$, Pa ($A_{\text{H}_2\text{O}}=1.65 \text{ cm}^3\cdot\text{g}^{-1}$).

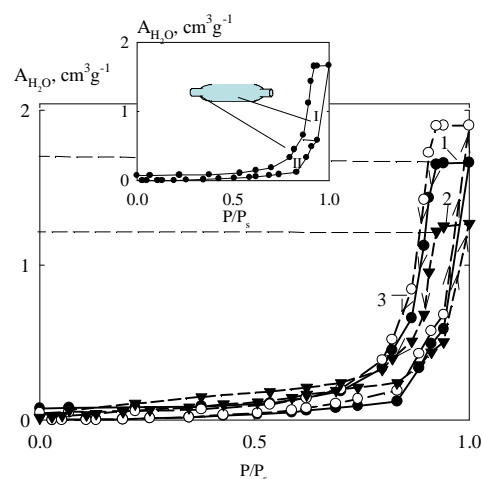


Fig. 2. Isotherms for water vapour adsorption-desorption by the ion-exchangers: pristine (1), modified with nanoparticles and their aggregates (2), containing only aggregates (3). Horizontal dashed lines correspond to the similar water content in the ion-exchangers. Insertion is the same plot for the pristine ion-exchanger, Roman numerals correspond to the regions of the hysteresis loop, which are related to A (I) and E (II) types. The insertion also shows a scheme of transport pores (cluster and channels)

During deposition, penetration of H_2PO_4^- and HPO_4^{2-} co-ions into the transport pores, which contain cation exchange groups, is limited due to overlapping of double electric layers in narrow channels. Regarding ZHP deposited from a solution, lower molar ratios of P:Zr as well as dihydro- and hydrophosphate groups have been found than those for the inorganic ion-exchanger

deposited from sol (Table 1). These ratios and also ZHP mass fraction, m , correspond to data for the composites modified at 293 K during similar amount of the cycles [3, 8]. Thus, composition and morphology of the organic-inorganic ion-exchangers are not affected by the temperature, at which the modification procedures have been performed.

3.2. Porosity of the Polymer Constituent

Location of ZHP nanoparticles in the polymer influences its porous structure, which is formed during swelling. Since no total water removal from the surface of amorphous ZHP is provided under the conditions of preliminary dehydration, the isotherms of water vapour adsorption-desorption are related to the polymer constituent. The isotherm for the pristine ion-exchanger (Fig. 2), which is characteristic for mesoporous materials, shows a hysteresis loop. The loop can be separated into two regions. The area I is related to A type loop (opened cylindrical pores), the area II can be considered as E type (pores with narrow constrictions) [10]. This corresponds to cluster-channel model of ion exchange polymers [6, 7].

Horizontal branches of the isotherms for adsorption and desorption (adsorbate monolayer) are rather close to each other. An amount of water molecules, n , in hydrate shells of counter-ions (H^+) of $-SO_3H$ groups was

calculated ($n = \frac{A_{H_2O}}{A_p V_{H_2O}}$ for the pristine ion-exchanger and

$n = \frac{A_{H_2O}}{A_p V_{H_2O}(1-m)}$ for the composite, where A_{H_2O} is the

water adsorption value, V_{H_2O} is the molar volume of water, A_p is the total exchange capacity of the pristine polymer). Since full dehydration of the polymer is impossible due to its destruction under elevated temperatures, the calculation allows us to estimate only a relative change of the water molecule amount. The highest water content at $P/P_s \rightarrow 1$ (here P is the pressure of water vapour, P_s is the pressure of saturated vapour) has been found for the ion-exchanger modified only with the aggregates. The “ n ” values for this composite and pristine ion-exchanger are practically equal. The ion-exchanger containing non-aggregated nanoparticles demonstrates the lowest adsorption at $P/P_s \rightarrow 1$ and the highest n magnitude.

Pore of the ion-exchangers contain high amount of counter-ions (H^+). The counter-ions tend to solvate. It is possible to assume, that there is a solution of concentrated electrolyte inside transport pores, the “solution” is able to be diluted. This assumption is the closest to reality, when the ion-exchanger is in contact with weakly concentrated solution or deionized water. In this case, the diffusion parts of intraporous double electric layers are overlapped in the clusters, thus all the transport pores are filled with a “solution”. In macroscopic models, the tendency of the “solution” to be diluted is taken into consideration by a difference between the osmotic pressures of the liquids inside pores and outside granules (Gluekauf and Gregor models [14]). It has been postulated, that the osmotic

pressure inside ion-exchanger is higher than that outside it, when the ion-exchanger is equilibrated with a solvent or its vapour. The difference between the pressures is the swelling pressure, p . This value has been suggested for the ion-exchanger, which changes its volume freely. Thus, the p magnitude has not to be related to the swelling pressure of gel in a volume bounded with rigid walls. When water content in the ion-exchanger increases, osmotic pressure decreases. At the same time, pressure elasticity, which is attributed to the polymer net, grows. The magnitude of these pressures could be estimated quantitatively, for instance, in the framework of Flory-Rehner theory [15]. When the values of osmotic and elasticity pressure become equal, the swelling is stopped.

The swelling pressure, which corresponds to similar water content in different samples, can be calculated according to the formula [14]:

$$RT \ln(P' / P'') = (p' - p'') v_{H_2O} \quad (1)$$

where R is the universal gas constant, T is the temperature, the “/” and “//” dashes correspond to the pristine ion-exchanger and composite respectively, v_{H_2O} is the partial molar volume of water. The p magnitude has been estimated for the composite modified with non-aggregated nanoparticles (the nanocomposite contains maximal water amount). In this case, the equality of the osmotic and elastic pressures is not reached for the pristine ion-exchanger and the composite modified only with aggregates. It was assumed, that $p = 1.5 \cdot 10^7$ Pa (literature data for analogous resin like Dowex X-8 [14]) at $P/P_s = 0.9-1$. Regarding the ion-exchanger modified with non-aggregated nanoparticles, an increase of swelling pressure was found, the sample containing only aggregates shows a decrease of the p value (see Table 1). The swelling pressure has been found by the same manner for the pristine ion-exchanger, which contains the maximal amount of water. Under these conditions, no maximal swelling is reached for the ion-exchanger modified with aggregates. In all the cases, a change of the swelling pressure is within the diapason of 10^6 Pa.

The method of water vapour adsorption-desorption (determination of pore volume, V , with a radius, r , up to ≈ 20 nm) as well as the SCP technique (up to 100 μ m) allows us to investigate the swelling evolution. The SCP pore size distribution for the pristine sample shows maxima, the area of which corresponds to a volume of certain pores (Fig. 3). The region of $\log r = 0-0.5$ nm is related to channels, the maximum at $\log r = 1$ nm with a shoulder from the side of smaller r values is attributed to clusters [4, 7, 8]. The peak at $\log r = 1.4$ nm corresponds to the voids between gel fields, the maxima at $\log r = 3.2$ and 4.1 nm are attributed to structure defects, the stripe at higher r values is related to voids between the resin particles.

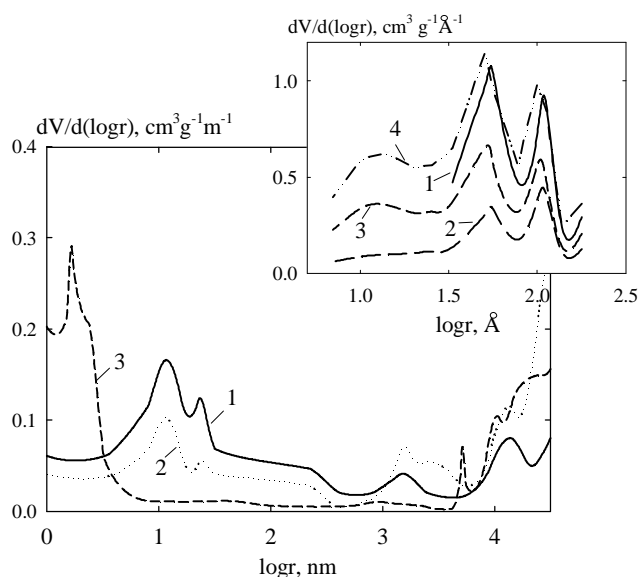


Fig. 3. Differential pore size distributions obtained by SCP method. Insertion: the distributions obtained by means of water vapour adsorption-desorption method. Ion-exchangers: pristine (1), modified with nanoparticles and their aggregates (2), containing only aggregates (3), the curve (4) corresponds to (3) data recalculated for the polymer

The method of water vapour adsorption-desorption allows us to determine only the transport pores, which are evidently identified by 2 maxima ($\log r = 0.7$ and 1 nm). At $\log r > 1$ nm, a build-up of the curve is visible, this growth evidently corresponds to voids between gel fields.

The formula (1) allows us to calculate the p value, when the transport pores and the narrowest voids between gel fields are filled with water. Under filling of larger pores (SCP-distribution), the isotherm is practically perpendicular to the abscissa axes, however the swelling pressure decreases owing to [14]:

$$pv_{H_2O} = -RT \ln a_{H_2O} \quad (2)$$

where a_{H_2O} is the activity of water in the ion-exchanger (effective concentration, which takes into consideration bonded and free water). Filling of voids between gel fields and structure defects with water causes a decrease of swelling pressure: the peak at $\log r = 0.7$ nm (the pore size distribution obtained with a method of water adsorption-desorption) is shifted towards higher $\log r$ values and combined with a maximum at $\log r = 1$ nm.

Regarding the ion-exchanger containing non-aggregated nanoparticles, the peak areas are lower in comparison with the pristine sample. This is evidently due to blocking of the transport pores with nanoparticles. Sites of the maxima remain practically without changes. Nevertheless, an increase of water molecule amount in the hydrate shell of counter-ions shows an enlargement of the

distance between functional groups. In other words, a growth of the n value indicates longitudinal stretching of walls of the transport pores (unwinding of macromolecule coil) affected by the nanoparticles. A decrease of area of the maximum at $\log r = 1$ nm in comparison with the same peak for the pristine sample is also typical for the SCP-distribution. In this case, an increase of structure defect volume has been found. The additional peak appears at $\log r = 3.4$ nm due to location of the aggregates in these pores. It should be noted, that no change of the size of the transport pores was found under similar insertion of the nanoparticles and their aggregates to the polymer. Osmotic pressure in clusters, channels and voids between gel fields makes impossible their squeezing from the side of the structure defects, which contain large aggregates. Indeed after filling of transport pores with water, higher swelling pressure is realized for this sample in comparison with the pristine ion-exchanger.

Regarding the sample modified only with aggregates, $(1-m)^{-1} \times \int_{\log r_1}^{\log r_2} dV/d(\log r)$ value is higher

than $\int_{\log r_1}^{\log r_2} dV/d(\log r)$ for the pristine ion-exchanger

within the interval of $\log r = 0.15-1.2$ nm, (for the pore size distribution obtained by a method of water vapour adsorption-desorption). The maxima are shifted to the region of lower $\log r$ values. A decrease of volume of these pores for the organic-inorganic ion-exchanger, which adsorbs the highest amount of water (see Fig. 2), and some decrease of their size cannot be caused by a reduction of the polymer content. It is evidently the result of squeezing of transport pores with aggregates. Squeezing from the side of structure defects can be caused by prismatic aggregates due to contact of prism edges with the walls of these macropores. A size of transport pores decreases dramatically, when the structure defects are filled with water (SCP-distribution). The maxima attributed to clusters and voids between gel fields demonstrate a shift to $\log r = 0.2$ and 0.3 nm, respectively.

Since the structure defects contain the inorganic constituent, which comprises functional groups, it is possible to talk about the "solution" (counter-ions of functional groups of ZHP inside double electrical layer), which fills these pores. When the ion-exchanger is in contact with water, this solution tends to dilution: the difference between osmotic pressures between phases of the ion-exchanger and solution is proportional to molality of counter-ions in a solid [14]. The osmotic pressure in structure defects is evidently higher than that in the clusters, channels and voids between gel fields. As a result, these pores are squeezed. This is confirmed by

smaller p value which is reached for the composite in comparison with that for the pristine ion-exchanger.

Exchange capacity of the polymer constituent was calculated as $(1-m)A_p$. In spite of the inorganic component, the difference between this value and experimental magnitude is inconsiderable (2.6 and 2.4 mmol·g⁻¹, respectively). Thus, a part of transport pores are unavailable for exchange of ions (in our case, for Na⁺ cations). It is confirmed by equal amounts of water molecules in hydrate shells of counter-ions of -SO₃H groups in the pristine ion-exchanger and in the composite modified with ZHP nanoparticles. It means the A_p magnitude is overvalued in the case of the organic-inorganic ion-exchanger.

3.3. Functional Properties of Ion-Exchangers

Regarding the composite containing only aggregates, a decrease of a size of polymer transport pores (a decrease of mobility of H⁺ counter-ions) and partial exclusion of counter-ions from transport (a decrease of their concentration) result in reduction of electrical conductivity in comparison with the pristine ion-

exchanger (Table 2). Counter-ions of ZHP functional groups are not involved to the transport of species [8].

In opposite to this, the composite containing non-aggregated nanoparticles demonstrates a growth of electrical conductivity. As it was shown earlier, this is due to the increase of content of mobile charge carriers in transport pores [3]. This ion-exchanger also demonstrates heightened break-through capacity during Ni²⁺ removal from multicomponent solutions in a wider diapason of initial concentration of these ions in comparison with the ion-exchanger containing only aggregates. In spite of higher content of phosphorus and -OPO₃H₂ groups, the sample modified with aggregates loses the advantages over the pristine ion-exchanger at initial Ni²⁺ concentration of 1 mmol·dm⁻³. This is evidently due to lower exchange capacity and lower mobility of sorbed ions [8]. When the initial Ni²⁺ concentration is 0.08 mmol·dm⁻³, the ratio of concentrations of Ni²⁺ and hardness ions in the solution at the column outlet is minimal for the composites. In the case of the pristine ion-exchanger, this value is higher than in the initial solution (0.04). However, under increasing of the solution concentration the ratios for the pristine ion-exchanger and organic-inorganic sample modified only with aggregates becomes practically equal.

Table 2

Electrical conductivity of ion-exchangers in H-forms and Ni²⁺ removal from multicomponent solutions

Ion-exchanger	I	Initial Ni ²⁺ concentration – 0.08 mmol dm ⁻³			Initial Ni ²⁺ concentration – 1 mmol dm ⁻³		
		II	III	IV	II	III	IV
Pristine	0.2	96	0.20	0.006	98	0.86	0.029
Modified with non-aggregated nanoparticles and aggregates	0.6	98	0.05	0.017	99	0.5	0.063
Modified only with aggregates	0.1	98	0.05	0.011	98	1.1	0.030

Notes: I – electrical conductivity, Ohm⁻¹·m⁻¹; II – removal degree of Ni²⁺, %; III – ratio of Ni²⁺ concentration and concentration of hardness ions in the solution at the column outlet; IV – break-through capacity towards Ni²⁺, mmol·cm⁻³

4. Conclusions

It is known, that the swelling pressure, which is determined according to Gregor model, is proportional to the cross-linking degree (*i.e.* to the DVB content) [13]. From the point of view of influence on the swelling pressure, insertion of non-aggregated ZHP nanoparticles into the ion-exchange polymer can be formally considered as increasing of content of the cross-linking agent. Modification with aggregates is similar to a decreasing of DVB amount in the polymer. Nevertheless, in opposite to ion-exchange resins with high DVB content, the sample

containing non-aggregated nanoparticles is characterized by higher rate of ion transport due to participation of counter-ions of ZHP groups and permanence of size of transport pores. During making of ion-exchange membranes, it is necessary to avoid formation of large aggregates in structure defects, since they inhibit ion transport indirectly.

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ВПЛИВ НАНОЧАСТИНОК ГІДРОФОСФАТУ ЦИРКОНІЮ НА ПОРИСТУ СТРУКТУРУ ТА СОРБЦІЙНУ ЗДАТНІСТЬ КОМПЗИТІВ НА ОСНОВІ ЙОНООБМІННОЇ СМОЛИ

Анотація. Досліджено еволюцію набухання гелевої сильнокислотної смоли та органо-неорганічних композитів на її основі. Знайдено, що неагреговані наночастинки гідрофосфату цирконію, інкорпоровані до полімеру, забезпечують незмінність розміру його пор, які містять функціональні групи (до 20 нм), а агрегати наночастинок здавлюють ці пори (до 3 нм). Зважаючи на це, нанокмпозит демонструє більш високу здатність до проскоку при вилученні йонів Ni^{2+} з води, ніж зразок, модифікований тільки агрегатами.

Ключові слова: органо-неорганічні йоніти, наночастинки, гідрофосфат цирконію, пористість полімеру, еталонна контактна порометрія.