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MEMBRANE AND SORPTION MATERIALS AND TECHNOLOGIES: PRESENT AND FUTURE

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CHAPTER 8

HYBRID ORGANIC-INORGANIC NANOCOMPOSITES FOR ION-EXCHANGE PROCESSES

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Abstract. *Two types of composite ion-exchangers, which are based on strongly acidic gel-like cation-exchange resin and weakly acidic cation exchange resin have been obtained by modification with nanoparticles of zirconium hydrophosphate. Removal of the dye from deionized water and Ni(II) ions from water containing also hardness ions was studied under dynamic conditions. The composites show higher break-through capacity than that of the pristine resin.*
Keywords: *nanocomposite, ion-exchanger, polymer matrix, zirconium hydrophosphate,*

Introduction. Ion-exchangers that combine constituents of different nature are in a focus of attention. The combination of organic and inorganic ion exchangers gives a possibility to obtain sorbents with a wide spectrum of functional properties. As a rule, organic-inorganic materials are characterized by considerable exchange capacity and high rate of ion exchange. Their selectivity is more expressed than that for organic components. In comparison with inorganic sorbents, some composites show better granulometric properties that makes them suitable for the application in column under dynamic conditions [1].

Organic polymer also provides better mechanical properties for the sorbents.

Strongly acidic polymers were applied mainly to preparation of organic-inorganic ion exchangers. In swollen state, ion-exchange polymers are characterized by complex porous structure. This structure involves hydrophilic pores (nanosized clusters and channels), where ions move. These pores are formed from heterogeneities of air-dry polymers [2-3]. The heterogeneities are caused by fragments of polymer chains, which contain functional groups. During swelling, these fragments form so-called gel regions penetrated by a continuous system of hydrophilic clusters and channels (transport pores). Ion-exchange polymers contain also hydrophobic pores (voids between gel regions, structure defects). Depending on location, the embedded particles change size and volume of one or other pores. This affects functional properties of the composites [4].

Weakly acidic ion-exchange resins show better selectivity toward toxic ionic components due to formation of complexes with functional groups [5]. However, the composites based on these resins are practically unknown. The aim of the research involves obtaining nanocomposite using weakly acidic resin as a polymer matrix. Another purpose is to compare porous structure and functional properties of the composites based on strongly and weakly acidic resins [4].

The organic-inorganic materials can be applied to water softening, separation and preconcentration of metal ions, nuclear separations, catalysis, redox systems, electrodeionization, hydrometallurgy, effluent treatment, production of ion selective electrodes and membranes. The composite sorbents are most often used for removal of toxic metal ions from water.

Experimental. Following reagents were used for the investigation: NaOH, HCl, $NiSO_4 \cdot 7H_2O$, H_3PO_4, $ZrOCl_2 \cdot 8H_2O$ (lab or synthesis grade, Ukrkhimsyrie LTD), Brilliant Green (BG) (hydrogen sulphate) (Merck).

Following cation exchange resins that are produced by Dow Chemical Company were used for modification with nanoparticles of zirconium hydrophosphate (ZHP): Dowex MAC-3 (weakly acidic macroporous resin) and Dowex HCR-S (strongly acidic gel-like resin). The weakly acidic resin is polyacrylic polymer containing -COOH groups, and the strongly acidic ion exchanger is styrene-divinylbenzene polymer with $-SO_3H$ groups.

The organic-inorganic ionites were obtained by impregnating the cation-exchange resins (below CR, the polymer matrix) with a solution containing $ZrOCl_2$ (1000 mol m^{-3}). ZHP in the matrix was deposited with an H_3PO_4 solution (1000 mol m^{-3}). The ionites were washing with deionized water, drying at room temperature, and treatment with ultrasound to remove the precipitate from the outer surface of the grains. ZHP powder, which was obtained by this manner, was investigated further for comparison. Synthesis of ZHP inside polymers procedure was carried out one (weakly acidic resin) or eight times (strongly acidic resin). In the last case, the nanocomposite containing large amount of ZHP shows much faster proton transport than the pristine resin.

TEM images were obtained with a JEOL JEM 1230 transmission electron microscope (Jeol, Japan). Preliminarily the ion exchangers were milled and treated with ultrasound.

A method of standard contact porosimetry (MSCP) [6], which had been accepted by the IUPAC [7], was applied to study porous structure of the polymers. Preliminarily the tested samples were dried at 80ºC under vacuum. Water was used as a working liquid.

The adsorption of BG and Ni^{2+} was investigated. The samples were tested in ion-exchange columns. A diameter of the column was 0.7 cm, a volume of the bed was 5 cm^3, and the solution velocity was 5 cm^3 min^{-1}. The solutions containing 1–7 mg·dm^{-3} (0.02–0.15 mmol dm^{-3}) of the dye was used. The effluent was analyzed by Shimadzu UV-mini 1240 spectrophotometer 89

(Shimadzu, Japan) at 625 nm. Ni(II) removal from tap water was also performed using ion exchange column, the conditions were the same. The solution contained (mmol dm^3): Ni(II) – 0.1, Ca(II) – 1.3, Mg(II) – 0.4. The effluent was analyzed by atomic absorption method using an S9 Pye Unicam spectrophotometer (Philips).

Results and discussion. Morphology of the composite was investigated using TEM microscopy (Figure 8.1). As seen from the image the resins contain globular non-aggregated nanoparticles with size of 5-15 nm (Dowex MAC-3) and 4-20 nm (Dowex HCR-S). Larger globular particles (from ≈250 to 600 nm) and irregular formations of micron size are seen in the image of higher resolution. The particles of different size can occupy one or another type of pores of the ion exchange polymer affecting its porous structure.
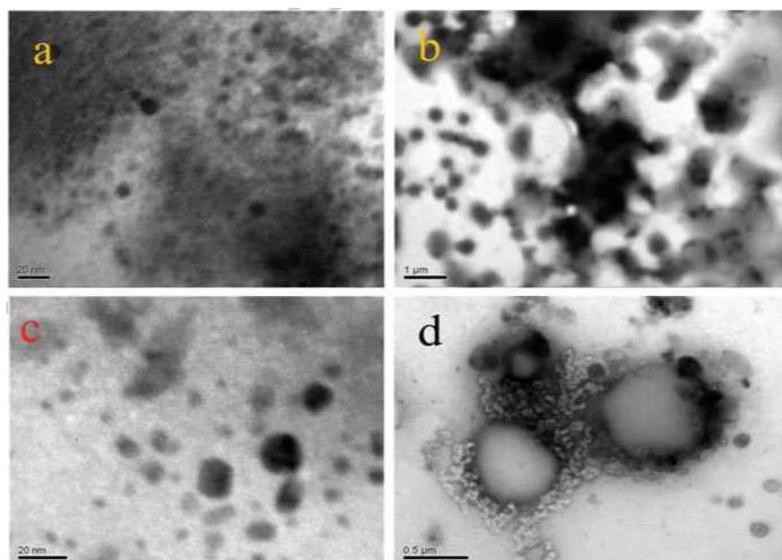
Fig. 8.1. *TEM images of ZHP particles embedded to weakly (a, b) and strongly (c, d) acidic resins*

A method of water adsorption isotherm was used to research the porous structure of composite ion exchange polymers. Single nanoparticles are located in pores containing functional groups; aggregates occupy inert pores. From the formal point of view, non-aggregated nanoparticles can be considered as a cross-linking agent, which increases swelling pressure. Swelling pressure provides stretching of transport pores. As a result, porous structure of the polymer constituent is transformed: some regions of the polymers, which are able to interact with species, become unavailable for them. However, embedded ZHP particles evidently expand the range of pores, where adsorption is possible [4].

Porous structure of the polymer constituent affects adsorption capability of the composite, since pore size determines availability of adsorption centers. In order to fix this effect, BG and Ni^{2+} adsorption was investigated. The samples were tested in ion-exchange columns. Figure 8.2 illustrates the capacity of ion exchangers toward BG and Ni^{2+}. Despite slower rate of BG adsorption on the

composite, this material shows higher break-through capacity towards the dye comparing with the pristine resin. This is evidently due to higher adsorption capacity of the modified ion exchange resin.
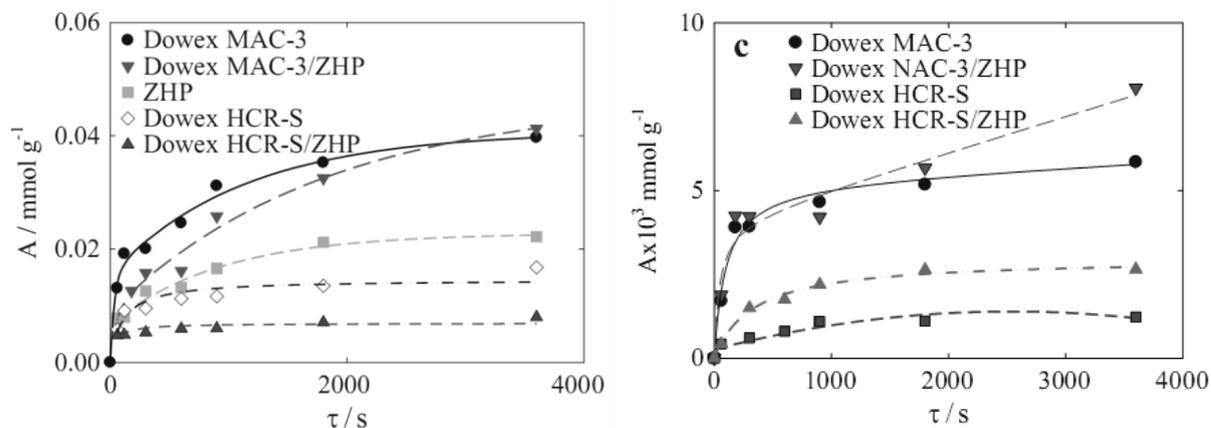

Fig. 8.2 *Capacity of ion exchangers toward BG (a) and* Ni^{2+} *(b)*

Indeed, lower values of Ni(II) diffusion coefficients have been found for composite ion-exchangers than those for pristine ion exchange resin. The composites show preferable sorption of Ni(II) ions in comparison with Ca^{2+} and Mg^{2+}.

Conclusions. Modification of ion-exchange resins causes transformation of porous structure of labile polymer matrix. The transformation occurs both at nano- and micro-levels. However, embedded ZHP particles evidently expand the range of pores, where adsorption is possible. This is valid both for BG adsorptions on weakly and strongly acidic resins. It is the same for Ni^{2+} ion sorption on strongly acidic resins. The particles decrease sorption rate by this manner. At the same time, strong interaction with Ni^{2+} ions is attributed to the structure of the weakly acidic resin. Partial screening of the polymer with particles causes acceleration of ion exchange.

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ГІБРИДНІ ОРГАНІЧНО-НЕОРГАНІЧНІ НАНОКОМПОЗИТИ ДЛЯ ІОНООБМІННИХ ПРОЦЕСІВ

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Резюме. *Синтезовані композиційні іонообмінники на основі сильнокислотної гелевої катіонообмінної смоли та слабокислотної катіонообмінної смоли, шляхом модифікації їх наночастинками цирконій гідрофосфату. У динамічних умовах досліджено вилучення барвника із деіонізованої води та іонів Ni (II) з води, у присутності йонів жорсткості. Композити демонструють більшу іонообмінну ємність, ніж у немодифікованих смол.*

Ключові слова: *нанокомпозит, іонний обмін, полімерна матриця, цирконій гідрофосфат.*