



Ion-exchange resin modified with aggregated nanoparticles of zirconium hydrophosphate. Morphology and functional properties



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ABSTRACT

Organic–inorganic ion-exchangers based on gel-like strongly acidic resin, which contain different amount of zirconium hydrophosphate, have been obtained. The samples were investigated using methods of transmission and scanning electron microscopy, standard contact porosimetry, NMR ³¹P spectroscopy. Nanoparticles of the inorganic constituent (10 nm) are deposited in voids between gel field and in structure defects of the polymer forming aggregates of micron size. These large particles squeeze and stretch pores of the polymer, where –SO₃ groups are located, a radius of these pores decreases from 10 nm down to 2 nm. A part of functional groups of the polymer component are excluded from ion exchange due to squeezing of pores, ion exchange properties are determined mainly by the inorganic constituent. Ion exchange capacity of the composites reaches 0.6–1.3 mmol cm^{−3}. These materials sorb preferably Cd²⁺ and Ni²⁺ from solutions, which contain also hardness ions. The highest break-through capacity has been found for the composite with the smallest microporosity of the polymer constituent, this value reaches 80% of total ion-exchange capacity.

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1. Introduction

Composites based on ion-exchange resins, which contain metal nanoparticles, are used in catalytic and electrocatalytic processes, particularly for oxygen removal from liquid hydrocarbons [1–3]. Such type of composites is applied to water desalination: silver nanoparticles embedded into resins provide simultaneous disinfection [4]. In this case, the removal of ionic component from water is due to ion exchange ability of the polymer matrix.

A number of organic–inorganic composites, which include inorganic ion-exchangers as a filler, is also known. The composites are characterized by high selectivity towards toxic ions. Modification of polymer ion-exchangers with hydrated oxides of multivalent metals allowed one to obtain materials, which are selective to phosphate [5], arsenite and arsenate [6] anion, some toxic metal cations [7]. Insertion of iron oxide inside resin beads provides their magnetic properties [6,8,9]. Zirconium hydrophosphate (ZHP) embedded into cation-exchange resin enhances its selectivity towards Pb²⁺ [10–14].

The composites based on macroporous resin were obtained [5–14]. However, mobility of sorbed ions through macroporous resins as well as ion-exchange capacity of these materials are lower in a comparison with those for gel-like polymers [15]. It is assumed, that the organic–inorganic ion-exchangers based on this type of resins will provide the most complete removal of toxic ions from weakly concentrated solutions, which contain also hardness ions.

A number of organic–inorganic composites based on gel-like resins containing 8% [16–18] and 2% [19] divinylbenzene has been obtained. The ion-exchangers contained both non-aggregated ZHP nanoparticles and their aggregates [16–19]. However, single nanoparticles were found to block pores of swollen polymer, which contain functional groups [16–18]. This evidently restricts potential possibility of the composites to sorb ions.

Known organic–inorganic ion-exchangers contain mainly aggregates of inorganic constituent [5,7,10–14]. A size of the aggregates is up to several microns, they are evidently located outside nanopores of polymer, where functional groups are placed. Modification of resins with aggregates of inorganic constituent would allow us to reach the most complete removal of toxic ions from diluted solutions. Moreover, extremely small size of inorganic particles is expected to provide high rate of ion exchange.

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As found for the materials, which contain both nanoparticles and their aggregates, functional properties of the ion-exchangers (ion-exchange capacity, mobility of sorbed ions, electrical conductivity, swelling, etc) strongly depend on amount of the inorganic constituent [16–19]. The same feature is expected for the ion-exchangers modified by aggregates of nanoparticles. Moreover, the aggregates are assumed to transform porous structure of the polymer. Literature sources contain no information about these problems.

Thus, the aims of the investigation involves synthesis of composite materials based on gel-like polymer containing different amount of inorganic ion-exchanger in a form of aggregated nanoparticles, research of evolution of functional properties of the composites influenced by porous structure of the polymer and chemical composition of the inorganic constituent. Gel-like resin containing 8% divinylbenzene was used as a polymer matrix, the materials of this type are used traditionally for ion exchange processes [20]. ZHP has been chosen as a modifier, since it possesses high selectivity towards heavy metal ions [17,21–24] due to ability of phosphorus-containing functional groups to form complexes with them [21,24].

Sorption of Ni^{2+} and Cd^{2+} cations has been investigated. Cd^{2+} ions are extremely toxic due to their carcinogenic activity [25], Ni^{2+} species are also related to toxic components: they cause pathological effects in humans varying from contact dermatitis to lung fibrosis, cardiovascular and kidney diseases, and even cancer [26]. In owing to this, the content of toxic ions in water and liquid wastes is strictly limited and controlled carefully.

2. Experimental

2.1. Synthesis of organic–inorganic ion-exchangers

Sol of insoluble Zr hydroxocomplexes has been obtained similarly to [27]. As found with a method of laser dynamic light scattering, a size of particles is 4 nm–1.2 μm .

Dowex HCR-S strongly acidic gel-like cation-exchange resin (Dow Chemical) was used as a polymer matrix (marked as CR). The resin is based on styrene–divinylbenzene containing $-\text{SO}_3\text{H}$ groups.

The followings stages were performed: (i) impregnation of a weighed sample of the resin with water for swelling; (ii) filtration; (iii) impregnation of the wet resin with sol for 24 h at 298 K (a ratio of volumes of resin and sol was 1:20); (iv) filtration; (v) treatment of the resin with a 1 M H_3PO_4 solution at 298 K (a ratio of volumes of resin and solution was 1:10); (v) washing with deionized water up to neutral reaction of the effluent; (vi) drying in a desiccator over CaCl_2 at room temperature down to constant mass; (vii) treatment of the sample with ultrasound at 30 kHz using Bandelin device (Bandelin electronic), the treatment was necessary to remove the deposit from outer particle surface; (viii) drying in a desiccator and weighting.

The stages (i)–(viii) were repeated several times. After each modification cycle a sample of the ion-exchanger containing amorphous ZrPh was taken for further investigations. Further increase of amount of the inorganic constituent causes to cracking of the beads, no investigations of these samples were provided. In opposite to [10–14] and similarly to [16–19], no organic solvents were used. The samples were marked as (ZHP content, mass%): CR-1 (31), CR-2 (43), CR-3 (49), CR-4 (52).

Individual ZHP was obtained by direct deposition from sol with a H_3PO_4 solution as described above. The ratio of volumes of sol and acid solution was 1:1. The ion-exchangers was washed with deionized water and dried in the desiccator down to constant mass.

2.2. Characterization of samples

Increase of mass was determined by weighting of air-dry resin before and after modification. Swelling was researched according to volumetric measurements of air-dried sample before and after its contact with water [28].

A method of standard contact porosimetry, the principles of which have been described in [29–32], was applied to porosity investigations. The samples were fixed on a paper macroporous support, impregnated with water under vacuum at 353 K and placed between measured and ceramic standards at 0.1 MPa. Further gradual loss of mass of the sample and standards was determined.

Total ion-exchange capacity was found by means of treatment of the samples with a 0.1 M NaOH solution followed by titration of the equilibrium solution with HCl [28]. Each sample was investigated 3 times. The confidence probability of 95% has been chosen. Then the mean value of ion exchange capacity was found for each sample, the standard deviation as well as confidence interval were calculated. The Student coefficient was taken as 4.3 for the chosen confidence probability, since a number of the experiments was 3. The table and plot demonstrate the mean value of the total ion exchange capacity.

SEM images of cross-sections of the particles were obtained by means of a JEOL JSM 6700 F scanning electron microscope (Jeol). Crushed granules were treated with ultrasound, then a thin layer of platinum was deposited onto the surface at 3 Pa using a JEOL JFC-1600 Auto fine coater (Jeol). TEM images were obtained by means of a JEOL JEM 1230 transmission electron microscope (Jeol).

Zr and P content in the inorganic constituent was determined with analysis of crushed samples using an X-Supreme8000 XRF (X-ray fluorescence) spectrometer (Oxford Instruments). NMR ^{31}P spectra of the samples, which had been inserted into the ampule with a diameter of 5 mm, were obtained by means of AVANCE 400 spectrometer (Bruker) using single-pulse technique under the accumulation mode at 162 MHz. Chemical shift has been determined relatively to 85% H_3PO_4 . The spectra were resolved to Gauss components by means of PeakFit v 4.12 program.

Electrical conductivity of swollen H-forms of the ion-exchangers was measured at 298 K similarly to [17–19]. Deionized water was used as non-conductive medium similarly to [33]. The measurements were carried out by means of an Autolab impedance system at 10^{-2} – 10^6 Hz, the conductivity of the bed was determined from frequency spectra of the real part of admittance. The measurements were repeated 3 times for each samples. Statistical treatment of the results were carried out as described above, the mean values of electrical conductivity are given in the plot.

2.3. Ion exchange

The experiments were carried out at 298 K. Fraction of 0.5–0.8 mm of swollen samples was used. The experiments were repeated 3 times for each samples, the plots represent the mean values. The confidential interval was calculated as described in Section 2.2.

Exchange of Ni^{2+} , Cd^{2+} and Ca^{2+} ions on H-forms of the ion-exchangers was investigated under static conditions. Chloride salts were used to prepare one component solutions of different concentrations. The ratio of volumes of ion-exchanger and solution was 0.5 cm^3 :100 cm^3 . Then the equilibrium solution was separated from the solid and analyzed with an atomic absorption method using a Pye Unicam SP 9 spectrophotometer (Philips).

Kinetics of ion exchange were investigated using a “thin layer” method [34], a scheme of the devise has been given earlier [22]. A one-component solution (5 dm^3) containing 100 mol m^{-3} Cd^{2+} , Ca^{2+} or Ni^{2+} circulated through the ion-exchanger layer (0.5 cm^3)

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