Applied Nanoscience (2019) 9:997–1004
https://doi.org/10.1007/s13204-018-0689-9

ORIGINAL ARTICLE

Composite anion-exchangers modified with nanoparticles of hydrated oxides of multivalent metals

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Received: 4 January 2018 / Accepted: 15 February 2018 / Published online: 27 February 2018

Abstract

Organic–inorganic composite ion-exchangers based on anion exchange resins have been obtained. Particles of one-component and two-component modifier were embedded using the approach, which allows us to realize purposeful control of a size of the embedded particles. The approach is based on Ostwald–Freundlich equation, which was adapted to deposition in ion exchange matrix. The equation was obtained experimentally. Hydrated oxides of zirconium and iron were applied to modification, concentration of the reagents were varied. The embedded particles accelerate sorption, the rate of which is fitted by the model equation of chemical reactions of pseudo-second order. When sorption of arsenate ions from very diluted solution (50 μg dm^{-3}) occurs, the composites show higher distribution coefficients comparing with the pristine resin.

Keywords Composite ion-exchanger · Anion exchange resin · Zirconium oxide · Sorption · Arsenic · Nanoparticles

Introduction

The sorbents combining organic and inorganic constituents are more attractive than ion exchange resins and mineral ion-exchangers, since they possess unique conjunction of functional properties: considerable exchange capacity, high sorption rate and considerable selectivity. Comparing with many inorganic sorbents, some composites are obtained in a form of large durable grains; they can be used as fillers of columns for sorption processes under dynamic conditions (Naushad 2009). The application field of composite materials involves water softening, removal of toxic metal ions from water, separation and preconcentration of metal ions for analytical purposes, separations of radionuclides, electrode ionization, hydrometallurgy, effluent treatment, manufacture of ion selective electrodes and membranes.

Organic–inorganic sorbents can be divided into two classes based on interaction between organic and inorganic constituents (Sanchez et al. 2005). In class I, organic and inorganic compounds are bonded with weak interactions: hydrogen bonding, Van der Waals, π–π or weak electrostatic interactions. In the composites of class II, the constituents of different nature are linked with strong covalent or coordinative bonds.

Organic–inorganic polymers are related to the sorbents of the second class (Liu et al. 2010). The polymers contain silanol groups attached to hydrocarbonaceous chains or built into the polymer backbones. Sometimes even biopolymers loaded with transition metal ions are related to hybrid sorbents (An et al. 2015). The sorbents of the class II are also inorganic matrices, such as silica (Awual et al. 2014, 2016; Shvets and Belyakova 2015), zirconium (Veliscek-Carolan et al. 2014) or clay (Liang et al. 2013), functionalized with organic fragments.

Natural minerals, for instance, clays (Liu et al. 2016; Ma et al. 2016; Muir et al. 2016), or synthetic double hydrated oxides (Starukh 2016) modified with surfactants are probably intermediate types of sorbents. The modifier is attached to the surface with electrostatic attraction on the one hand, but this interaction with the material causes extension of oxide layers on the other hand. Weak interaction between the matrix and modifier provides chemical instability of these sorbents.

The sorbents of the class II involves nanocomposites consisting of both inorganic and polymer nanoparticles

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(El-Naggar et al. 2014; Inamuddin et al. 2007; Qi et al. 2016; Sharma et al. 2015, 2016). The nanoparticles of different origin are formed simultaneously in the same reaction medium or the inorganic particles are inserted to the medium, where polymerization occurs. Other types of the sorbents are characterized by core–shell structure (Ghasemi et al. 2015; Shuang et al. 2012; Xu et al. 2013; Zhao et al. 2014). They consist of magnetic nanoparticles (core) coated with functionalized polymer (shell). Grains of ion exchange resin (Acelas et al. 2015) or chitosan (Kamari and Ghiaci 2017) covered with inorganic ion-exchanger can be also related to core–shell materials. At last, the second class of organic–inorganic materials involves polymer matrix, which was formed preliminarily (particularly ion exchange resins), containing inorganic nanoparticles. The nanoparticles are distributed uniformly in the polymer (Dzyazko et al. 2013a, 2017b; Perlova et al. 2017) or exist in the form of aggregates and agglomerates (Dzyazko et al. 2017a, b; Dzyazko et al. 2013a; Pan et al. 2007). These composites possess necessary functional properties: high exchange capacity, fast sorption rate and selectivity towards toxic ions. Where zirconium phosphate is used as a modifier, selectivity is due to complex formation of sorbed cations and phosphorus-containing functional groups (Dzyazko et al. 2013b; Pan et al. 2007).

Regarding to anion sorption, hydrated oxides of multivalent metals (containing no grafted functional groups) are probably only exclusive type of inorganic sorbents, which shows anion exchange ability (Amphlett 1964). This property is most expressed in acidic media. Hydrated double oxides demonstrate better selectivity towards cations (Maltseva et al. 2009) and anions (Li et al. 2012). As shown, a size of incorporated particles affects sorption (Dzyazko et al. 2017a; Perlova et al. 2017). The size of cation-exchanger particles can be controlled purposefully during synthesis (Perlova et al. 2017). The aim of the investigation is to develop the approach, which would allow us to control a size of anion-exchanger particles incorporated to the polymer matrix. Other purpose is testing of the composite by example of As(V)-containing anions.

Arsenic appears in ground water and, ad a result, in drinking water due to working of metallurgical enterprises and thermal power plants, other source is mining water (Ravenscroft et al. 2011). The sources of arsenic are mining water, metallurgical plants, thermal power plants. Removal of these ions from water is an important practical task, since arsenic compounds are extremely toxic. Adsorption and ion exchange are the most widespread methods for arsenic recovery from water. Both inorganic sorbents (Li et al. 2012), particularly their composite with graphene (Fu et al. 2017), and organic–inorganic materials (An et al. 2015; DeMarco et al. 2003; Elton et al. 2013; Hristovski et al. 2008). Simultaneous insertion of different oxides into polymer matrix should provide significant selectivity of the composites towards arsenate anions.

Experimental

Synthesis of ion-exchangers

Gel-like strongly basic anion exchange resin Dowex SBR-P (Dow Chemical Company) was used for modification. The polymer matrix is styrene-divinylbenzene containing strongly quaternary aminogroups, According to data of the producing company, the resin characteristics are as follows: exchange capacity is 1.2 meq cm^3, water content in swollen state is 53–60%, the average grain size—0.3–1.2 mm. Such reagents as $ZrOCl_2{\cdot}8H_2O$, $FeCl_3{\cdot}6H_2O$, KCl, NH_4OH, HCl (Cherkassy Khimprom LTD, Ukraine), $Na_2AsO_4{\cdot}7H_2O$ (Merck) were used for modification of the resin or for investigation of functional properties of the composites. Solutions were prepared using deionized water.

The resin was modified with hydrated zirconium dioxide (HZD), or simultaneously with HZD and hydrated iron oxide (HIO). The polymer was immersed in water for swelling, then it was impregnated with a 1 M aqueous solution of metal salt ($ZrOCl_2$). Impregnation was carried out during 1 h at 60^o C under stirring. Further the beads were filtered and rinsed with a 0.1 M solution to remove additionally sorbed electrolyte from the largest pores of micron size. Then the resin was filtered again, immersed with a 25% NH_4OH solution under room temperature, filtered, rinsed with deionized water down to pH 7 of the effluent and dried in a desiccator over calcinated $CaCl_2$ down to constant mass. Further the sample was immersed in water again and treated with ultrasound at 30 kHz using a *Bandelin* bath (Bandelin). The treatment was carried out until disappearance of turbidity. Then the solid and liquid were separated, the ion-exchanger was dried down to constant mass. The modification procedure was repeated several times. The resins were marked as, for instance, *AR-Zr-1*, *AR-Zr-2* etc. The number corresponds to modification cycle.

HZD and HIO were also deposited simultaneously. In this case, a mixture of 1 M solutions of $ZrOCl_2$ and $FeCl_3$ was used for immersion of the resin. A ratio of the solution volumes was 1:1. Other stages are similar to those described above.

For comparison, concentrations of $ZrOCl_2$ and ammonia were varied. The pairs of concentration are as follows (salt: precipitator, M): 0.1:1, 1:0.01, 0.01:0.01. HIO was also precipitated from a 0.1 M $FeCl_3$ solutions. A 1 M NH_4OH solution was used for precipitation.

Characterization of the samples

Morphology of the samples was researched using transmission electronic microscope *JEOL JEM 1230*. Preliminarily the beads were crushed and then they were cleaned with ultrasound.

The amount of inorganic components (relatively to water-free oxide) in the resin was determined by burning of the weighting sample at 1000 °C. Analytical weight form, which corresponds to ZrO_2 and Fe_2O_3, can be obtained under these conditions.

Investigation of sorption

The ion-exchangers containing the highest amount of modifier (the most concentrated solutions were used for modification) were applied to sorption experiments. Sorption was performed under batch conditions at 20 °C. A series of weighted air-dry samples (0.2 g) was inserted to flasks, then deionized water was added. After swelling, water was removed and the solution (100 cm^3) contained 150 mg dm^{-3} As(V) or simultaneously As(V) and KCl (7.4 g) was added. As shown preliminarily, no complete removal of As(V) from the liquid occurs under this dosage and solution concentration. Thus, sorption capacity of the composites could be different; it is determined by properties of the ion-exchanger.

The content of the flasks was stirred by means of a Water Bath Shaker Type 357 (Elpan, Poland). After predetermined time, the liquid was removed from one flask, stored and analyzed later. Then the solution from the second flask was removed, etc. The equilibrium solution was analyzed with an atomic absorption method at wave length of 193,7 nm using a Pye Unicam SP 9 spectrophotometer (Philips).

One-component As(V)-containing solution, the initial concentration of which was 50 μg dm^{-3}, was also used for the research. In this case, the mass ratio of sorbent and solution was 0.5:500. Arsenic was determined in a form of molybdenum blue with spectrophotometric method at wave length of 700 nm (Sandell 1950). A Shimadzu UV-mini1240 spectrophotometer (Shimadzu, Japan) was used for this purpose.

Results and discussion

Precipitation of inorganic component in polymer matrix

Earlier thermodynamic approach to precipitation of inorganic constituent inside cation exchange resin has been considered (Perlova et al. 2017). In this case, impregnation of the resin with a solution of metal salt, for instance, $ZrOCl_2$ is accompanied by ion exchange of soluble zirconium hydroxocomplexes an H^+ counter-ions of functional groups. It was shown that a size of the embedded particles depends on exchange capacity of the resin. Regarding anion exchange resin, metal ions are additionally sorbed electrolyte (Helfferich 1994). A size of the embedded particles is determined by Ostwald–Freundlich equation (Myerson 2002):

$$\ln \frac{\overline{C}_{\mathrm{Cat(OH)}_z}}{C_{\mathrm{Cat(OH)}_z,\infty}} = \frac{\beta V_{\mathrm{m}} \sigma}{\mathrm{RT}r}. \tag{1}$$

Here the composition of hydrated oxide is written down as $\mathrm{Cat(OH)}_z$ for simplicity, $\overline{C}_{\mathrm{Cat(OH)}_z}$ and $C_{\mathrm{Cat(OH)}_z,\infty}$ are the concentration of dissolved compound in ion-exchanger and saturated solution, respectively (for oxides of multivalent metals, these magnitudes are low), β is the shape factor of particles, V_{m} is the molar volume of a compound, σ is the surface tension of a solvent, r is the particle radius.

Thus, $\overline{C}_{\mathrm{Cat(OH)}_z} = [\overline{\mathrm{Cat}^{z+}}] = \frac{K_{\mathrm{sp}}}{[\mathrm{OH}]^z}$, here the square brackets denote equilibrium molar concentration, K_{sp} is the solubility product, z is the charge number of metal ions. Dissociation degree of NH_4OH (α) can be determined according to Ostwald law (Ostwald 1888):

$$\alpha = K^{0.5}_{\mathrm{NH_4OH}} C^{0.5}_{\mathrm{NH_4OH}}, \tag{2}$$

where $K_{\mathrm{NH_4OH}}$ is the dissociation constant of NH_4OH, $C_{\mathrm{NH_4OH}}$ means concentration. The precipitating solution provides certain equilibrium concentration of OH^- ions.

$$[\mathrm{OH}^-] = [\mathrm{NH}_4^+] = \alpha C_{\mathrm{NH_4OH}} \tag{3}$$

Taking formula (2) into consideration, Eq. (3) can be written as:

$$[\mathrm{OH}^-] = K^{0.5}_{\mathrm{NH_4OH}} C^{1.5}_{\mathrm{NH_4OH}} \tag{4}$$

OH^- ions are partially consumed for $\mathrm{Cat(OH)}_z$ deposition:

$$\mathrm{Cat}^{z+} + z\mathrm{OH}^- \leftrightarrow \mathrm{Cat(OH)}_z \downarrow . \tag{5}$$

This consumption is equal to zC_{Cat}. In the first approximation, it is possible to suppose that a volume of additionally sorbed electrolyte (zirconium hydroxocomplexes in our case) corresponds to a volume of the ion-exchanger (V_{i}). Resulting concentration of OH^- ions is:

$$[\mathrm{OH}^-] = K^{0.5}_{\mathrm{NH_4OH}} C^{1.5}_{\mathrm{NH_4OH}} - \frac{zC_{\mathrm{Cat}} V_{\mathrm{i}}}{V_{\mathrm{NH_4OH}}}, \tag{6}$$

where $V_{\mathrm{NH_4OH}}$ is the volume of the precipitating solution. Thus;

$$\overline{C}_{\mathrm{Cat(OH)}_z} = \frac{K_{\mathrm{sp}}}{\left(K^{0.5}_{\mathrm{NH_4OH}} C^{1.5}_{\mathrm{NH_4OH}} - \frac{zC_{\mathrm{Cat}} V_{\mathrm{i}}}{V_{\mathrm{NH_4OH}}} \right)^z}. \tag{7}$$

Substituting this expression into Eq. (1), it is possible to obtain:

$$r = \frac{\beta V_{\mathrm{m}} \sigma}{RT \ln \frac{K_{\mathrm{sp}}}{C_{\mathrm{Cat(OH)}_z,\infty} \left(K^{0.5}_{\mathrm{NH_4OH}} C^{1.5}_{\mathrm{NH_4OH}} - \frac{z C_{\mathrm{Cat}} V_{\mathrm{i}}}{V_{\mathrm{NH_4OH}}} \right)^z}}. \qquad (8)$$

The particles, a size of which is lower than the *r* value, are dissolved and reprecipitated as larger particles. In accordance with expression (8), the compound, molar volume of which is larger, is deposited as coarser particles. Increase of salt concentration and reducing of precipitator concentration should provide smaller particles. Decrease of the charge number (for instance, due to hydrolysis during dilution of the salt solution) results in reducing of the particle size, when the precipitator concentration is sufficient (in other words, when the first term in the square brackets is larger comparing with the second one).

Visualization of embedded particles

As shown from photos of different resolution (Fig. 1), non-aggregated globular nanoparticles (3–10 nm) and their aggregates of irregular shape are visible. The particles of smaller size dominate. A size of the aggregates, a shape of which is the most close to spherical, is about 40–50 nm. A length of elongated aggregates is up to 100 nm, a width is up to 50 nm. The nanoparticles inside the polymer are stabilized by walls of pores, which contain functional groups. These pores are nanosized, they provide ion transport. Porous structure of ion exchange polymers, which is described in detail in (Yaroslavtsev and Nikonenko 2009), was suggested for homogeneous (Hsu and Gierke 1983) and heterogeneous (Kononenko et al. 1985) ion exchange membranes as well for ion exchange resins (Dzyazko et al. 2012).

Increase of salt concentration from 0.01 to 0.1 M causes formation of nanoparticles of the same size (Fig. 2). However, larger particles dominate, tendency of aggregation become expressed. Further growth of $ZrOCl_2$ concentration leads to formation of particles, a size of which is up to 20 nm. This is probably due to depression of hydrolysis, which is transition from which is transition from $[Zr_4(OH)_8(H_2O)_{16}]_n^{8+}$ to $[Zr_4(OH)_{16}(H_20)_8]$ hydroxocomplexes (Kostrikin et al. 2010). Larger charge number for zirconium hydroxocomplexes in more concentrated solution provides larger particles in accordance to Eq. (8).

Indeed, decrease of ammonia concentration from 1 M down to 0.01 M causes enlargement of the particles (Fig. 3). This is in agreement with Eq. (8). Aggregated nanoparticles dominate.

During HIO deposition, small aggregates (up to 40–50 nm) are formed (Fig. 4). The size of the primary particles are about 10 nm and even larger (compare with Fig. 2b, which shows HZD nanoparticles precipitated from the solution of the same concentration).

At last, deposition from the mixed solution results in formation of aggregated HZD nanoparticles embedded to HIO. As seen from Fig. 5, more contrast HZD is observed as black spots). Moreover, HIO form particles of micron size, which contain elongated HZD blotches.

In this case, the factor, which depends on nature of precipitated compound, is molar volume (see Eq. (8)). Since the particle surface contains ion exchange groups (uncertainty of the modifier composition), the effect of this factor should not be expressed. However, it is possible to compare molar volume of water-free crystalline oxides: $V_{\mathrm{m}} = 21.69$ cm^3 mol^{-1} (ZrO_2) and 30.47 (Fe_2O_3). As a result, HIO forms larger particles; this is in agreement with Eq. (8).

Sorption of arsenate anions

Fractional attainment of As(V) sorption (A_t/A_ω. where A_t and A_∞ are the capacity of the ion-exchanger after certain time and under equilibrium conditions, respectively) is given in Fig. 6 for some AR-ZrFe samples. It is seen that the modifier accelerates sorption. In the case of sorption from the solution containing also KCl, equilibrium is reached after 5 (composite) and 9 (pristine resin) h. When the initial solution is one-component, sorption is slower.

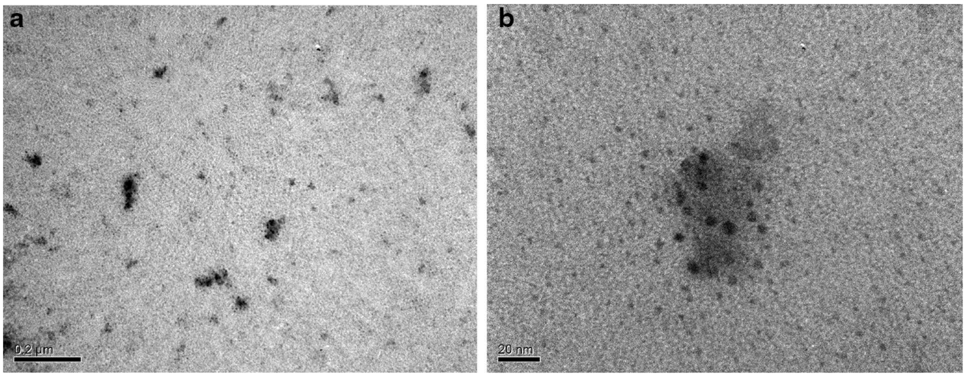
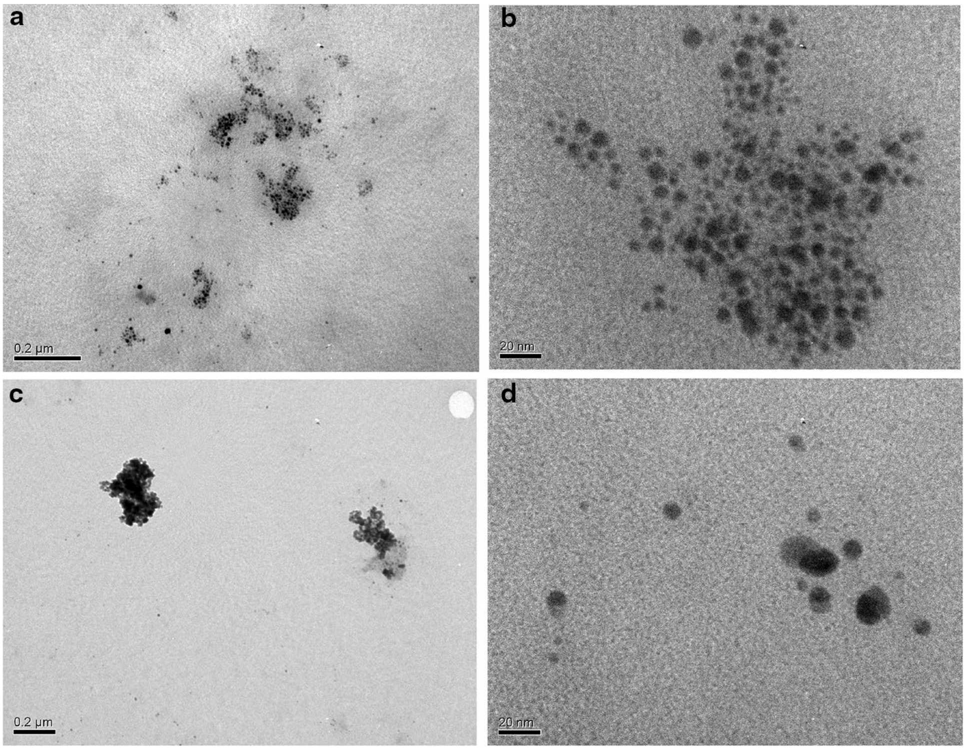


Fig. 1 Aggregated (**a**) and non-aggregated (**b**) HZD nanoparticles obtained by precipitation from 0.01 M $ZrOCl_2$ and NH_4OH solutions

Fig. 2 HZD nanoparticles embedded to ion exchange resins obtained by precipitation from 0.1 M $ZrOCl_2$ and 1 M NH_4OH solutions (**a**, **b**), 1 M $ZrOCl_2$ and 1 M NH_4OH solutions (**c**, **d**), the sample is marked as AR-Zr-1)



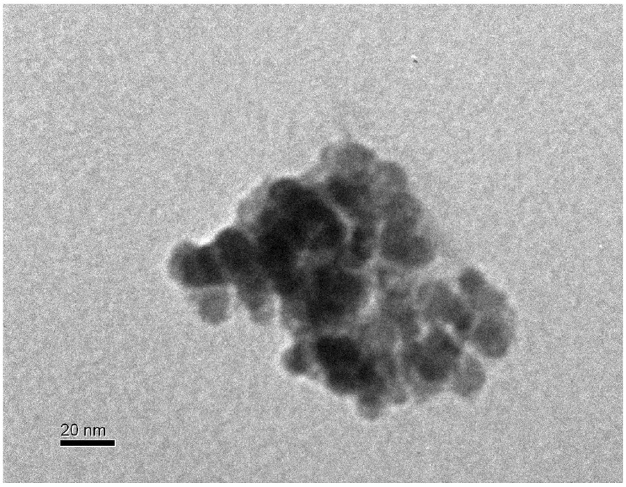


Fig. 3 HZD nanoparticles obtained by precipitation from 1 M $ZrOCl_2$ and 1 M NH_4OH solutions

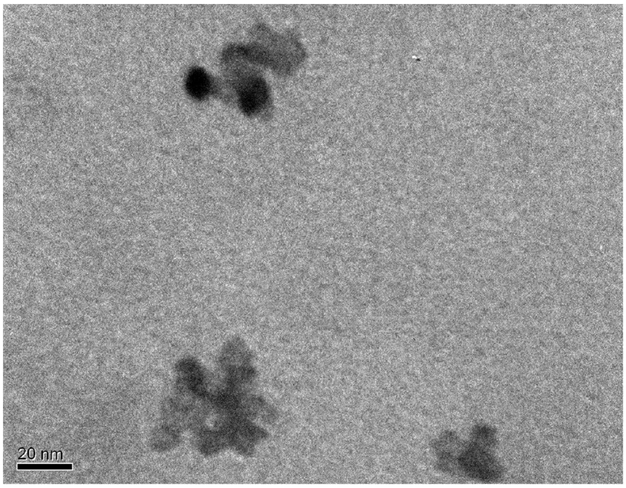


Fig. 4 HIO nanoparticles obtained by precipitation from 0.1 M $FeCl_3$ and 1 M NH_4OH solutions

The models of film and particle diffusion (Helfferich 1994), chemical reactions of the pseudo-first (Lagergren 1898) and pseudo-second order (Ho and McKay 1999) were applied to experimental data. As found, the model of pseudo-second order:

$$\frac{t}{A} = \frac{1}{K_2 A_\infty^2} + \frac{1}{A_\infty} \times t \qquad (9)$$

can be applied to all samples (Fig. 7, the correlation coefficient is 0.99). Here K_2 is the constant. Chemical reactions are probably formation of undissociated ion pairs or redistribution of water molecules between hydrate shells of fixed and counter-ions, these processes are more expressed for the polymer matrix. As found earlier, the embedded particles block and squeeze pores of the polymer, which contain

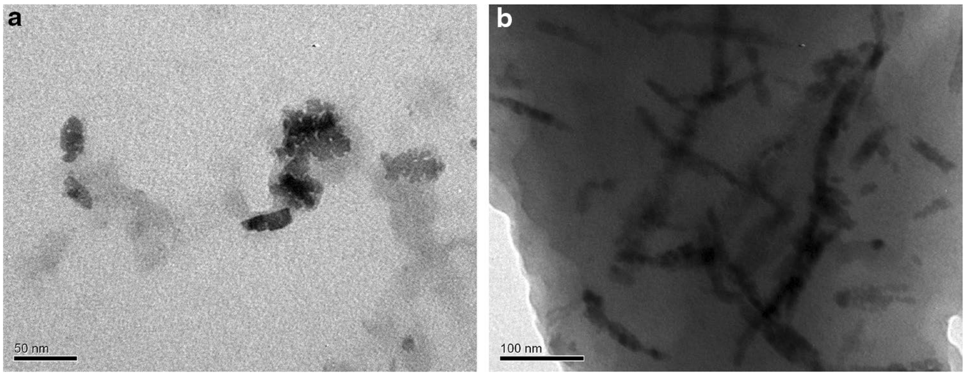


Fig. 5 HZD nanoparticles interspersed to HIO. The modifier was obtained by simultaneous precipitation of HZD and HIO in the anion exchange resin

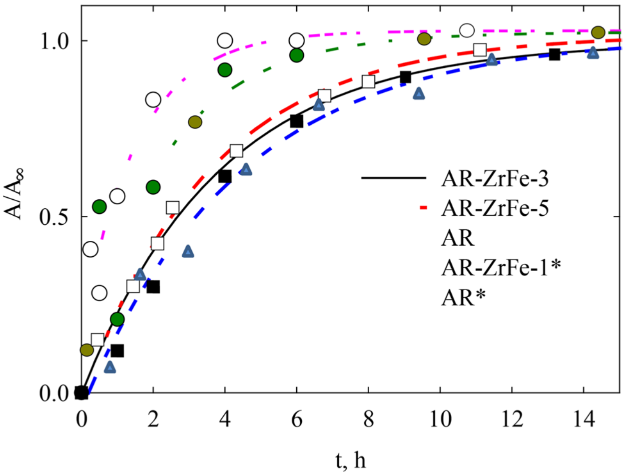


Fig. 6 Sorption rate of As(V)-containing ions. Asterisk means solution containing excess of KCl

functional groups. As a result, a part of functional groups (quaternary amino groups) is excluded from ion exchange (Dzyazko et al. 2012, 2017a). This exclusion accelerates sorption.

Evolution of sorption properties illustrates Fig. 8, the data are given for the initial As (V) concentration of 150 mg dm^{-3}. It is seen that modification with nanoparticles and small aggregates (AR-Zr-1, see Fig. 2c, d) increases distribution coefficient of As(V)-containing anions (this characteristic is determined as a ratio of concentrations of ions is solid and liquid). At the same time, particles of micron size (AR-ZrFe) depress sorption despite high selectivity of HIO. This is evidently due to partial exclusion of quaternary ammonia groups of the polymer from ion exchange.

Regarding the solution containing initially 50 µg dm^{-3} of As(V), the distribution coefficient is higher for all composites comparing with pristine resin.

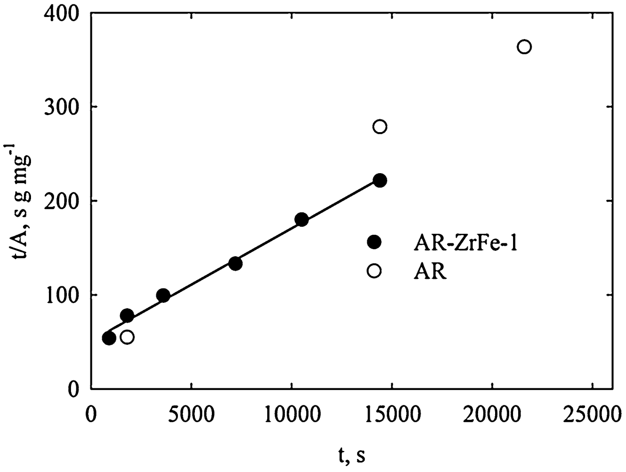


Fig. 7 Application of the model of pseudo-second order to As(V) sorption. The solution contained KCl

Concluding remarks

Organic–inorganic composite ion-exchangers based on anion exchange resins have been obtained. Particles of one-component and two-component modifier were embedded using the approach, which allows us to realize purposeful control of a size of the embedded particles. The approach is based on Ostwald–Freundlich equation, which was adapted to deposition in ion exchange matrix. The equation was obtained experimentally. HZD and HIO were applied to modification, concentration of the reagents were varied. The embedded particles accelerate sorption, the rate of which is fitted by the model equation of chemical reactions of pseudo-second order. When sorption of arsenate ions from very diluted

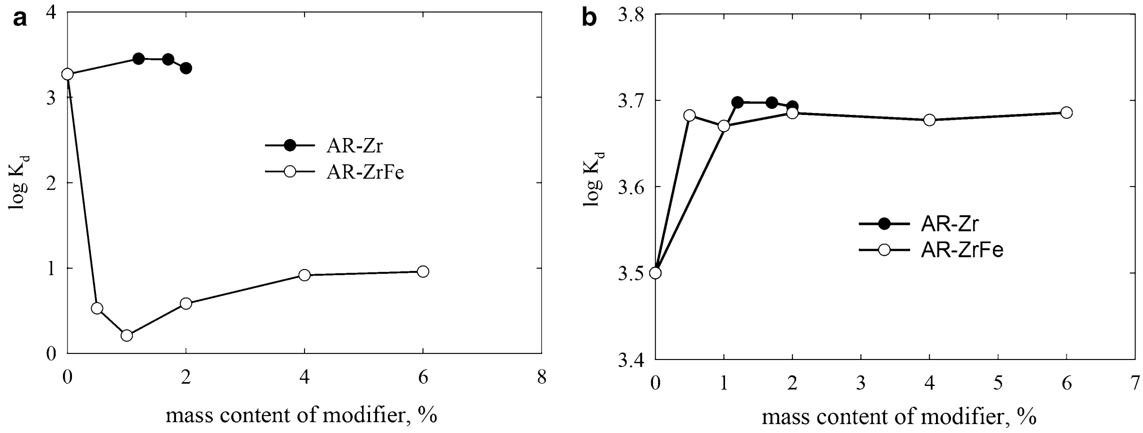


Fig. 8 Evolution of sorption properties: distribution coefficient of arsenate ions *vs* content of modifier (recalculated to water-free oxide). The solution contained no KCl. Sorption was carried out from the solution contained initially 150 mg dm^{-3} (**a**) and 50 µg dm^{-3} (**b**)

solution (50 µg dm^{-3}) occurs, the composites show higher distribution coefficients comparing with the pristine resin.

Acknowledgements The work was supported by projects within the framework of programs by the National Academy of Science of Ukraine (entitled "Fundamental problems of creation of new matters and materials for chemical industry", Grant N 21-13), by the Ministry of Education and Science of Ukraine (entitled "Development of technology of purification of liquid food and industrial waste waters with membrane methods", Grant N 09-16).

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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