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Properties of Prussian Blue filled membrane mini-reactor in Cs(I) adsorption processes

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We present the results of investigation of Cs(I) ion mass-transfer from outer solution into the inner part of membrane mini-reactor (MR), which is a centimeter-sized hermetically sealed pocket made of polyethylene terephthalate track membrane and filled with Prussian Blue (PB) colloidal solution. The mean size of colloidal particles was 74 ± 20 nm (98.4%) and ξ-potential was $-(33 \pm 6)$ mV. The pore diameter of the track membrane in the experiments varied from 50 to 50000 nm. It was found that the construction and properties of PB filled MR allow one to realize an extremely high distribution coefficient of $(1.50 \pm 0.05) \cdot 10^6$ ml/g with respect to Cs(I), which is characteristic of colloid-sized PB. Adsorption is a diffusion-controlled process localized in the pores of TM, which can be fulfilled in solution without agitation.

Keywords: Membrane, reactor, Prussian Blue, Cs(I), adsorption, kinetics.

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1. Introduction

The development of methods for the decontamination of materials, technogenic and natural objects and soil on the principles of minimal intervention in the environment becomes an increasingly more topical problem of radioecology in view of the growing share of nuclear power engineering in the energy balance of the Russian Federation and other countries, as well as complication of atomic power engineering technologies and methods for recovery and processing of uranium and rare-earth elements [1–6]. The decontamination approach based on the introduction of sorbents into radionuclide polluted soil that are able to block the transition of radionuclides into vegetation owing to their competitive sorption has been actively discussed in recent years [7]. The sorbent remains in soil in dispersed form. This complicates its removal and makes further geochemical fate of highly active sorbent particles uncertain over the long term. The chemical mechanism of deactivation of contaminated material (hereinafter called material) by sorbent purifier (hereinafter called sorbent) placed into aqueous electrolyte solution has been considered by the authors in terms of competitive sorption in the system "material – aqueous solution – sorbent" [8, 9]. The application of competitive sorption for the isolation of radionuclide from soil with minimal intervention in the environment is possible in the case of membrane separation of sorbent and purified material. For example, the introduction of sorbent in the composition of compact chemical reactor, whose walls are made of sorbent-impermeable membrane material allowing the outer solution to pass through, makes it possible to separate the internal sorbent or its suspension from particle mass transfer outside the reactor walls while retaining chemical contact of sorbent with external environment through membrane wall pores. Such membrane reactor with linear dimensions 5 – 20 mm (mini-reactor [8]) filled with selective sorbent [10], can provide spontaneous sorption extraction of ions from solution with subsequent mechanical removal of mini-reactor with spent sorbent from solution or suspension [11, 12]. Owing to a large range of pore sizes, track membranes are suitable as a semipermeable material of mini-reactor walls. They allow the sorbent in the form of colloidal solution (1 – 100 nm) or suspension [12] to be placed inside the reactor.

The aim of this work was to determine the functional properties of membrane mini-reactor filled with nanoparticles in the form of a colloidal solution during sorption of microelements from solution. We considered the effects of membrane area, pore size, hydrodynamic regime of membrane wall contact with solution and temperature on the sorption properties and application of sorbent filled mini-reactor in the processes of sorption of microelements from aqueous solutions during convection and/or diffusion mass transfer of sorbate through reactor wall. The study was concerned with the system "^{137}CsCl – electrolyte solution – Prussian Blue colloid (PB)", for which high values of distribution coefficient of cesium ion, Kd$\sim 10^6$ ml/g are typical according to the data of sorption statics [9, 10, 13].

2. Experiment

In the investigation, we used membrane reactors having a form of square or rectangular envelopes with edge length ranging from 15 to 25 mm (Fig. 1). The envelopes were made of a Lavsan (polyethylene-terephthalate) track membrane [14, 15] with pore size in the interval 0.1 – 50 μm using the technique described in [12]. Prussian Blue (Ecsorb) [13] was used as sorbent. According to X-ray diffraction analysis of the sorbent, the PB powder had a dark-blue color and was a phase with space group F 4/m - 3 2/m with lattice parameters (Å): $a = b = c = 10.1723$, angles (deg.) $a = b = g = 90.0000$ and composition $Fe_3[Fe(CN)_6]_2 14H_2O$ – 97.8 wt.%. The size of dry aggregated PB particles was 30 – 60 μm. The average size of primary particles (average value of coherent scattering region) was 14.7 nm. The impurity phase was the basic sulfate $K_2Fe(SO_4)$, space group R -3 2/m with lattice parameters (Å): $a = 7.29250$, $b = 7.2925$, $c = 17.2094$, angles (deg.) $a = b = 90.0000$, $g = 120.0000$, content – 2.2 wt.%. The hydrodynamic diameter of PB particles was determined using the dynamic light scattering method on a Zetasizer Nano ZS instrument (Malvern Instruments Ltd.). The measurements were performed at 25 °C. Samples were taken from the upper part of examined suspension volume. According to light scattering data, the average diameter Dh of PB particles in initial suspension was (145 ± 67) nm (90.2 mol. % of the whole concentration), ξ-potential was equal to $-(27 \pm 4.0)$ mV. Approximately 9.8 mol. % PB particles were (600 ± 230) nm in size and had the same ξ-potential. After dilution and ultrasonic dispersion, the PB solution with a concentration of 100 mg/l consisted of particles with $Dh = (70 \pm 20)$ nm (98 mol. % of the whole concentration of PB suspension), ξ-potential = $-(33 \pm 6)$ mV, Fig. 1B.

The kinetic regime of microelement (CsCl) mass transfer was analyzed using a facility, whose design allowed one to control and vary the lateral flow velocity of the electrolyte with microelement (sorbate) relative to the membrane reactor outer wall. The diagram of this facility is presented in Fig. 2; it included a glass cup (Fig. 2B), in which 500 ml electrolyte solution (hydrochloric solution with pH = 4.1) and an aliquot (2.5 ml) of standard solution of cesium ions (CsCl) with a concentration of 100 mg/l were poured. During radiometric measurement of sorbate concentration, only an aliquot of radiochemically pure $^{137}CsCl$ solution was added to the electrolyte. After homogenizing a sorbate composition by stirring, a 5 ml solution was sampled to establish the initial concentration of cesium ions in the working solution by mass-spectrometry (ELAN 9000) [16], or g-spectrometry methods on an MKS-AT1315 gamma-spectrometer (Atomtekh) with a NaI(Tl) 63×63 mm detector [17]. The counting rate interval was 0.4 – 150 Bq. The membrane pore diameter, mini-reactor edge area and PB mass inside the reactor we varied depending on the experiment objective.

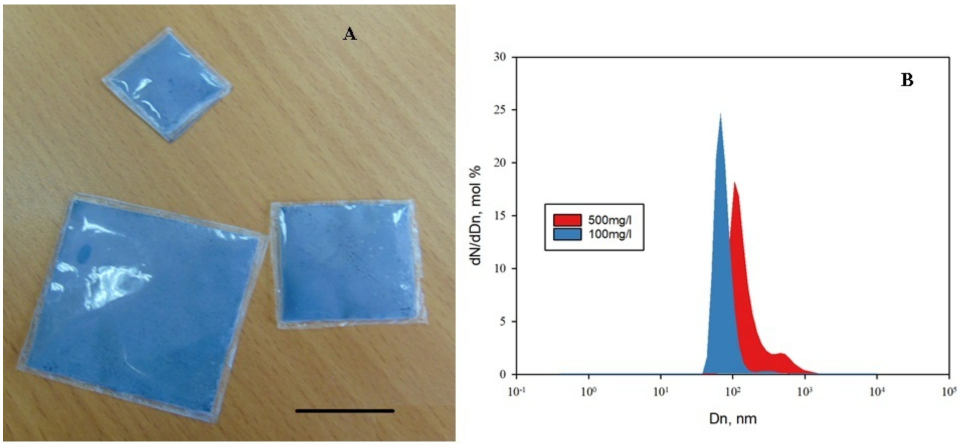

FIG. 1. (A) Appearance of membrane mini-reactors made of track membrane with pore diameter 100 nm and thickness 50 μm filled with PB sorbent powder [13]. The line in the Figure is 1.0 cm. (B) Empirical size (Dn) distribution of PB particles in the initial solution with PB concentration 500 mg/l and in diluted solution with PB concentration 100 mg/l after 30 min irradiation in ultrasonic field with frequency 40 kHz and power 50 W, pH=7.1

When studying the hydrodynamic regime of sorption statics with the use of membrane mini-reactor, a perforated high-pressure polyethylene cylinder with radius (r) and apertures of 4 mm in diameter (Fig. 2A) was placed into container (1) of the setup, Fig. 2B. The cylinder was coaxially jointed with the mixer using a flexible drive. During the experiment, the membrane mini-reactor with a sorbent, placed inside the cylinder, took the position near the cylinder side wall, in the zone of the maximal angular (W_{liq}) and linear (L_{liq}) velocity of sorbate lateral motion relative to the container walls.

The angular velocity of cylinder rotation W_0 (1/min) was measured by means of a laser tachometer and varied during the experiments in the range 20 – 560 1/min. At certain time intervals from the beginning of experiment, aliquots of sorbate solution were sampled from the container to measure the microelement concentration. Before elemental analysis, the aliquot was diluted with 0.1 M HCl solution and the concentration of cesium ions in it was measured. In addition, the behavior of PB powder in solution was studied without the use of the membrane mini-reactor at $W_0 = 550$ 1/min.

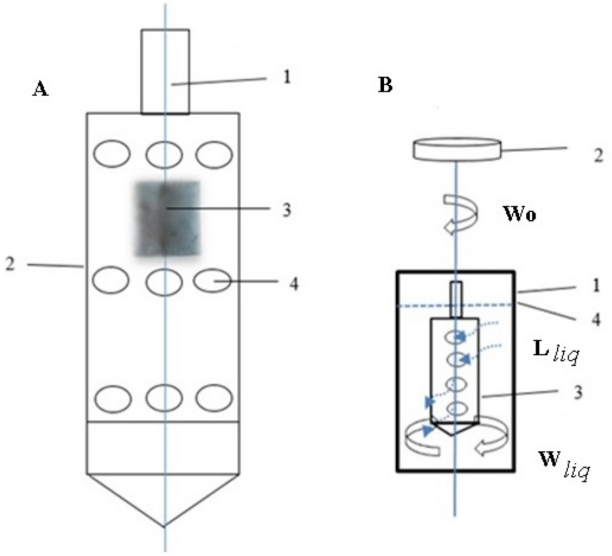

FIG. 2. The layout drawing (A) and diagram of laboratory setup (B) for measuring the linear flow rate of HCl–CsCl–H_2O electrolyte solution relative to the membrane mini-reactor wall surface. (A): 1 – rod for fixing a mixer motor to the axis of top driving rotor; 2 – 100 cm^3 cylinder made of high-pressure polyethylene with perforated walls for passage of sorbate solution; 3 – mini-reactor located inside the cylinder; 4 – aperture in the cylinder for passage of sorbate solution during axial rotation of the cylinder with solution, diameter 0.4 cm. (B): 1 – glass container with 500 cm^3 sorbate solution; 2 – top driving rotor with reducing unit and laser meter of the number of rotor revolutions; 3 – rotating cylinder with perforated walls and a mini-reactor inside; 4 – sorbate solution level. Arrows – direction of sorbate solution flow during rotation of cylinder with a mini-reactor

The dependence between the angular W_0 and linear L_{liq} velocities of sorbate motion inside the rotating perforated cylinder (Fig. 2) was estimated using a previously described technique [18]. Vertical marking of length (mm) was done on the plastic cylinder so that the point of origin coincides with the upper level of sorbate solution in the container; the scale goes down with a spacing of 5 mm. The cylinder was immersed into the container with distilled water. After 15 – 20 sec operation of the mixer with perforated cylinder, the position of water meniscus (Δh) in the cylinder was registered relative to the scale zero. The angular rotation velocity of the cylinder W_0 (1/min) was determined using a laser tachometer and converted into angular velocity W (1/s) according to formula:

$$W = W_0 \cdot \frac{2\pi}{60}. \tag{1}$$

The angular rotation velocity of liquid in the perforated cylinder W_{liq} (1/s) was calculated by eq. (2), [18]:

$$W_{liq} = \sqrt{\frac{\Delta h \cdot 2 \cdot g}{r^2}}, \tag{2}$$

where Δh is the height of the parabolic water meniscus determined from the scale (cm), g is the free fall acceleration 981.0 (cm/s^2) and r is the cylinder radius, 1.425 (cm). Then the average linear velocity of sorbate solution at the cylinder wall, L_{liq}, (cm/s) was determined from formula (3):

$$L_{liq} = W_{liq} \cdot r. \tag{3}$$

Figure 3A shows the dependence between the angular and linear rotation velocities of sorbate solution in the cylinder, from which the value of L_{liq} was used for the estimation of hydrodynamic sorption regime with participation of mini-reactor.

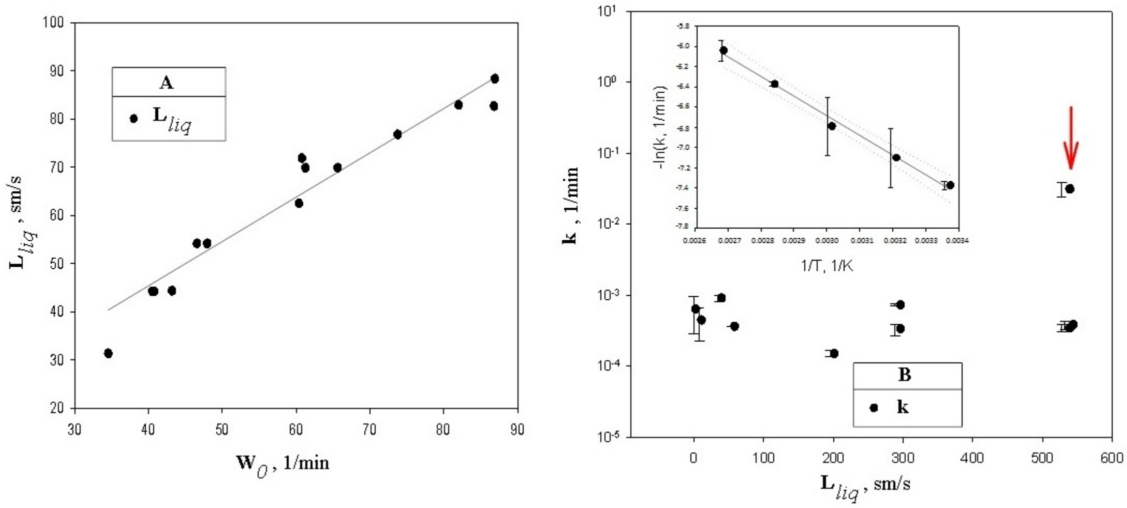

FIG. 3. A: Empirical dependence between angular (W_0, 1/min) and linear (L_{liq}, sm/s) velocity of electrolyte solution motion near the cylinder wall in the setup. Fig. 2. B: correlation between the velocity coefficient (k) of irreversible first-order reaction of Cs(I) ion sorption by PB powder in the mini-reactor and the linear velocity L_{liq} of solution near the mini-reactor wall. The mini-reactor edge area $S = 6.5$ cm^2, pH=4.1, 22 °C. The point with coordinates $k = 5 \cdot 10^{-2}$ 1/min and $L_{liq} = 550$ cm/s, referring to the experiment with PB powder without mini-reactor, is marked by the arrow. Inset: the Cs(I) sorption velocity coefficient logarithm as a function of reciprocal temperature for pH=4.0, $L_{liq} = 120$ cm/s

In order to determine the degree of sorption of microelement by the sorbent in the mini-reactor (D), we used the known relationship:

$$D = \frac{(I_i - I_f)}{I_i}, \tag{4}$$

where I_i and I_f are the initial and final concentration (specific activity during measurement of ^{137}Cs in the region of photopeak of 660 keV) of microelement in solution. The equilibrium value of concentration/specific activity of solution (I_∞) was calculated from the equation of sorption reaction kinetics, whereupon we found the equilibrium value of sorption D_∞ from eq. (4) and the equilibrium distribution coefficient Kd (ml/g):

$$K_d = \frac{D_\infty}{(1 - D_\infty)} \cdot \frac{V}{m}, \tag{5}$$

where V is the volume of solution in the container, ml, and m is the sorbent sample in the mini-reactor, g.

The variation in the fraction of cesium absorbed by the membrane mini-reactor with the sorbent as a function of contact time of the system "mini-reactor–sorbate" revealed that the dependence of sorption on the contact time (t), Fig. 4, corresponds to the kinetics of the irreversible first-order reaction of Cs(I) ion sorption

$$D = a \cdot (1 - \exp(-k \cdot t)), \tag{6}$$

where a is the dimension coefficient and k is the sorption reaction velocity coefficient, 1/min. The equilibrium adsorption isotherm of cesium ions at pH4.1 and 22 °C is described by the single-sort Langmuir model with the cesium ion distribution coefficient Kd(ml/g) $= (1.50 \pm 0.05) \cdot 10^6$ and sorption capacity G(mmol/g) $= (9.80 \pm 0.80) \cdot 10^{-3}$.

The diffusion kinetics of competitive sorption of cesium ions in the system "SiO_2-CsCl-H_2O‖PB" (MR‖ is the symbol of membrane mini-reactor) was studied by the space-limited method. 200 ml of the solution containing 0.25 mg/l cesium with HCl pH = 4.1 were poured in 500 ml flasks made of chemically resistant glass with a ground stopper. 3.0 g of silica gel powder of 100 – 200 μm fraction (SiO_2) were added to the flasks and agitated for 48 h on a magnetic mixer until sorption equilibrium in the system was established [8, 19]. Then the agitation was discontinued and a membrane mini-reactor with surface area 10 cm^2 and 100 mg PB sample inside was placed in each flask. The cesium ion distribution between sorbents and solution in a chosen flask was analyzed at certain intervals. The solution from the flask was filtered through a "blue tape" paper filter, the filter cake (SiO_2) was treated for 8 h using 40 ml 5M sodium hydroxide.

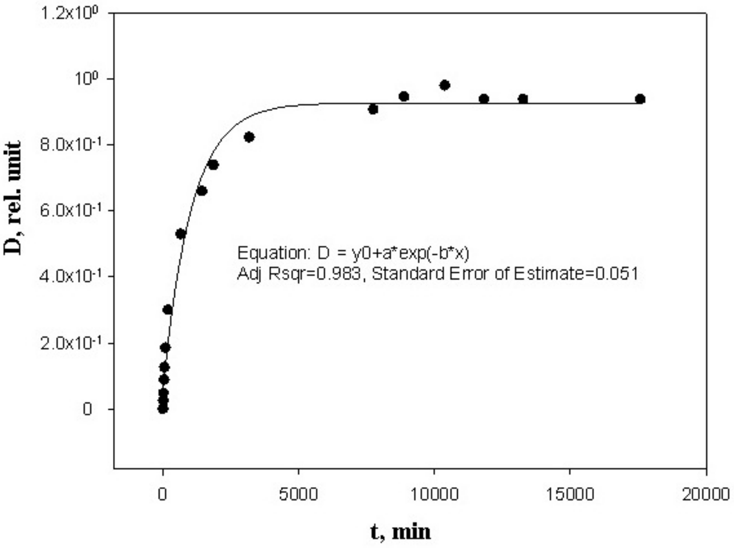

FIG. 4. The fraction (D) of ^{137}Cs(I) sorbed by PB powder filled mini-reactor vs. contact time, t. The cesium concentration in the sorbent was determined using γ-spectrometry from the 662 keV line of the equilibrium pair ^{137}Cs–^{137}Ba. The solution contained an acetate buffer with pH=7. The sorbent mass in the mini-reactor with $S = 6.5$ cm^2 and pore size $d = 1.0$ μm was 200 mg, 22 °C. The line was plotted using the regression equation of the irreversible first-order reaction of Cs(I) sorption: $a = (0.926 \pm 0.006)$ r.u., $b = (1.030 \pm 0.05) \cdot 10^{-3}$, 1/min, determination coefficient $R^2 = 0.997$

The membrane mini-reactor was opened and treated for 8 h with the use of 20 ml 5M solution of sodium hydroxide. In the "background" experiment, cesium ion sorption by PB filled membrane mini-reactor was controlled depending on the contact time of the reactor with the solution in the absence of silica gel. Based on cesium ion concentration measurement, we determined the dependence of cesium content in silica gel, aqueous solution and PB on the contact time of phases.

3. Experimental results

The experimental relationship between cesium ion sorption velocity coefficient (k) by PB in membrane mini-reactor and the linear velocity of sorbate solution (L_{liq}), Fig. 3B, shows that the kinetic regime of sorption does not depend on the sorbate ion mass transfer rate from the solution bulk to the membrane reactor surface. The Arrhenius dependence of the velocity coefficient on temperature gives a sorption activation energy value (1.62 ± 0.03, kJ/mol) which agrees with the average activation energy of cesium ion diffusion in aqueous salt solutions [19,20], Fig. 3B. The limiting stage of cesium ion mass transfer in PB inside the mini-reactor is external diffusion in the bulk of electrolyte. This follows from the fact that the sorption velocity coefficient according to eq. (6) changes linearly with the contact area of the membrane reactor edges (S) with outer solution, Fig. 5. The sorption velocity coefficient is proportional to the membrane pore cross-sectional area at relatively small pore sizes ($d < 5$ μm), Fig. 6. With further enhancement of the pore diameter, the sorption velocity coefficient increases abruptly due to transition from diffusion to convection transfer in membrane pores [20]. Comparison of the obtained data shows that the slowest mass transfer process is localized in the pore space of reactor membrane. The values of cesium sorption velocity coefficient obtained in sorption experiments with sorbent with and without application of membrane reactor are shown in Fig. 3B for $L_{liq} = 550$ cm/s for comparison. The difference in the sorption velocity coefficients is about two orders of magnitude, which also confirms the diffusion character of sorbate mass transfer mechanism in PB in case of membrane regime of sorption.

The diffusion character of the limiting stage of cesium ion sorption by PB in the membrane mini-reactor allows one to use this regime for sorption of microquantities of cesium ions without convective stirring of sorbent suspension and sorbate solution. To verify this assumption, we studied the kinetics of spontaneous cesium ion mass transfer in the heterogeneous system "SiO_2–CsCl–H_2O|| PB", in which silica (SiO_2) powder was preliminarily sorption-saturated

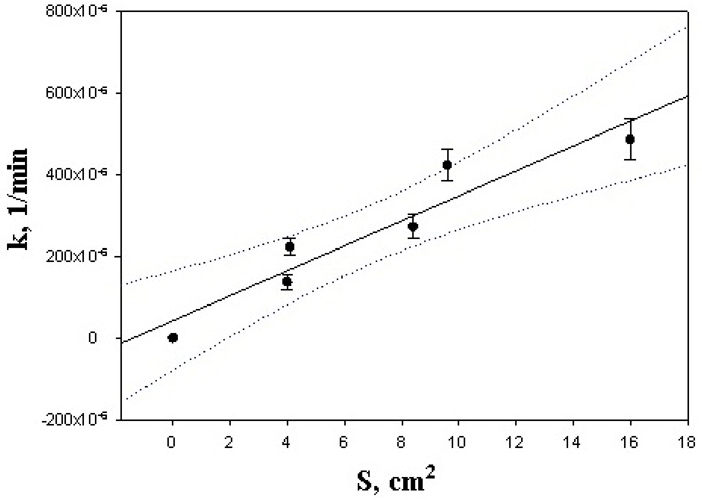

FIG. 5. Velocity coefficient (k, 1/min) of Cs(I) sorption by PB powder filled membrane mini-reactor vs. the surface area of mini-reactor edges (S). pH = 4.1, $S = 7.3$ cm^2, $d = 1.0$ μm, $L_{liq} = 50$ cm/s 23 °C

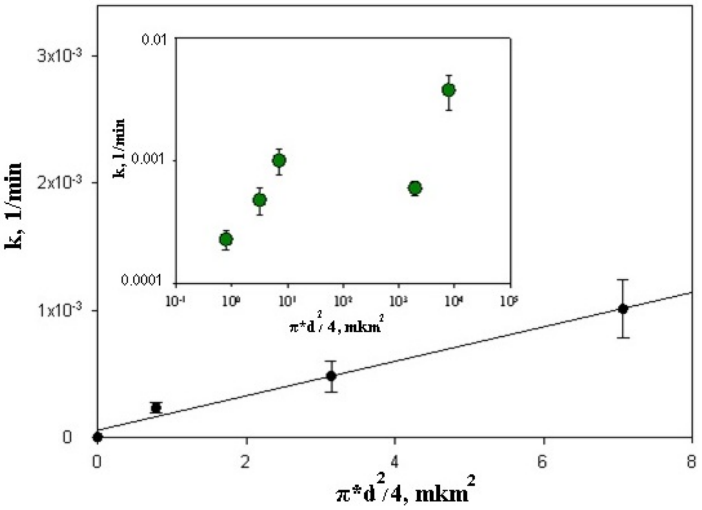

FIG. 6. Cs(I) sorption velocity coefficient (k, 1/min) by PB powder filled membrane mini-reactor vs. membrane pore diameter (d). pH =4.1, $S = 7.3$ cm^2, $L_{liq} = 5.0$ cm/s, 22 °C

with cesium ions. The data on cesium ion distribution between phases show that the dependence of cesium concentration on the contact time of phases agrees with the kinetic model of irreversible mass transfer by the first-order reaction of cesium ion sorption, Fig. 7.

The lines connecting the points in Fig. 7 were fitted by estimating the coefficients of the experimental dependence of cesium concentration in solution Cs(solution), silica Cs(SiO_2) and sorbent in the membrane reactor Cs(PB) using the least squares method [19]. From Fig. 7 it is possible to estimate the average sorption relaxation time, $t \sim 2{\cdot}10^4$ min, corresponding to the cesium ion mass transfer coefficient, $\frac{1}{t} \sim 5 \cdot 10^{-5}$ 1/min, which is in agreement with cesium ion diffusion mass transfer coefficient in the PB filled mini-reactor, Fig. 6.

4. Conclusion

Thus, the results of studying the functional properties of PB sorbent filled membrane mini-reactor with respect to cesium ions revealed that the sorption kinetics are determined by external diffusion transfer of sorbate ions through membrane wall pores and are described by the first-order reaction equation for cesium ions. The sorption velocity coefficient is proportional to the geometrical surface area of membrane mini-reactor and the total area of membrane

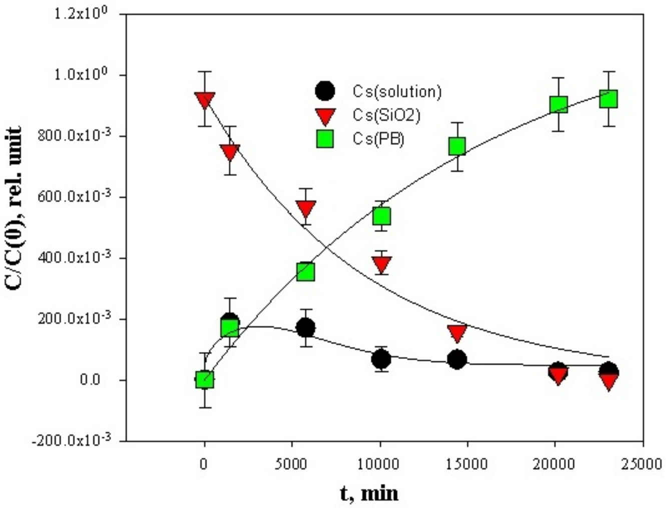

FIG. 7. The isotherm of competitive cesium sorption kinetics in the system "SiO_2-CsCl-H_2O|| PB" without agitation. The initial cesium concentration in SiO_2 saturated ($8.5\cdot10^{-7}$ mol/l) membrane mini-reactor with pore diameter $d = 0.1$ μm, edge surface 10.0 cm^2, PB concentration in mini-reactor 100 mg/l, pH 4.1, 23 °C

wall pores and does not depend on the linear velocity of sorbate solution motion relative to the membrane reactor wall. When the diameter of membrane pores becomes larger than 25 μm, the sorption velocity coefficient increases, probably, because the mass transfer mechanism through membrane pores changes from diffusion to convection type. The average sorption relaxation time of cesium ions, determined from competitive sorption experiment in the system "SiO_2–CsCl–H_2O|| PB" without agitation, corresponds to the cesium ion sorption velocity coefficient in diffusion regime.

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