



## Colloid stable sorbents for cesium removal: Preparation and application of latex particles functionalized with transition metals ferrocyanides

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### ABSTRACT

In this paper we suggest a principally new approach to preparation of colloid stable selective sorbents for cesium uptake using immobilization of transition metals (cobalt, nickel, and copper) ferrocyanides in nanosized carboxylic latex emulsions. The effects of ferrocyanide composition, pH, and media salinity on the sorption properties of the colloid stable sorbents toward cesium ions were studied in solutions containing up to 200 g/L of sodium nitrate or potassium chloride. The sorption capacities of the colloid sorbents based on mixed potassium/transition metals ferrocyanides were in the range 1.3–1.5 mol Cs/mol ferrocyanide with the highest value found for the copper ferrocyanide. It was shown that the obtained colloid-stable sorbents were capable to penetrate through bulk materials without filtration that made them applicable for decontamination of solids, e.g. soils, zeolites, spent ion-exchange resins contaminated with cesium radionuclides. After decontamination of liquid or solid radioactive wastes the colloid-stable sorbents can be easily separated from solutions by precipitation with cationic flocculants providing localization of radionuclides in a small volume of the precipitates formed.

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### 1. Introduction

Preparation and application of solid ferrocyanides for cesium removal have been extensively investigated over the last 50 years [1–5]. Usually ferrocyanides are obtained as fines, which have superior sorption properties due to high surface area and fast kinetics, but are notoriously difficult to handle in the process of liquid radioactive waste (LRW) treatment [1,4]. To overcome this disadvantage, numerous efforts have been undertaken to obtain mechanically stable granular forms of ferrocyanides for column applications [1,3,4], however, often at the expense of sorption capacity loss and much slower kinetics of cesium removal [1].

A few examples of ferrocyanide fines application in LRW treatment are based on flocculation/precipitation [6] or adsorption/microfiltration process [5,7]. When flocculation/coagulation with mixtures of ferric hydroxide and ferrocyanides is used for LRW treatment, the efficiency of cesium removal is highly pH-dependent, and the volume of difficult to dewater sludge can reach 30% of the effluent volume, even when settling is assisted with a polymeric flocculant [6]. In principle, low amounts of ferrocyanide fines can be efficiently separated by microfiltration, but sedimenta-

tion of ferrocyanide fines on the bottom of the reactor, blockage of the membrane pores and reduction of effective filtration area with increasing treatment time significantly limit the potential of this approach [5].

The efficiency of ferrocyanide fines application in LRW treatment can be much higher, if they are obtained in the form of colloid stable dispersions, which, on the one hand, would not precipitate on microfiltration membrane and interfere with filtration process, and, on the other hand, can be easily separated after the waste treatment, e.g. by flocculation. This type of colloid stable selective sorbent is also promising for decontamination of solid bulk materials, such as spent ion-exchange resins, corrosion-unstable metal structures, soil, ground, and construction materials contaminated by fission products.

Up to present, an effective application of solid selective sorbents, including ferrocyanides [8], for soil and ground decontamination is significantly limited by a long time required to reach the equilibrium state between solid phases of sorbent and material to be decontaminated and by the problems of uniform sorbent distribution and completeness of spent sorbents removal for final disposal. The treatment of cesium-contaminated solid materials by washing technologies is also limited by the fact that there is no affordable organic chelating agents, which would provide distribution coefficients comparable with those of ferrocyanides – up to  $10^6$  [1,9]. A few examples of successful application of soluble selective organic

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ligands for cesium uptake are based on rather expensive calixarenes [10,11] and are not promising for large scale application. Thus, the development of colloid stable ferrocyanides is potentially interesting for both applications – low/intermediate LRW treatment and solid materials decontamination. It is worth mentioning that high potential of colloid stable nanosized sorbents has been already recognized for *in situ* remediation of soils from organic pollutants [12], but there are still no analogs reported for radioactively contaminated solids.

Here we suggest an approach to obtain colloid stable sorbents via immobilization of nanocrystals of transition metals (copper, nickel, and cobalt) ferrocyanides into the matrix of carboxylic latex particles. Aside from being highly selective to cesium, colloid stable sorbents shall preferably have size of 50–500 nm; remain colloid stable in salt free and saline aqueous media for at least several weeks; have the ability to penetrate through porous media without filtration; and, finally, be easily separable from liquid phase after the decontamination process.

## 2. Experimental

Siloxane-acrylate emulsions (KE 13-36), particle size 160 nm, solid phase content 46%, were produced by the Scientific-Production Association “Astrokhim” (Elektrostal’, Moscow Region, Russia). Chitosan with deacetylation degree 84% and average molecular weight of  $2.5 \times 10^5$  Da was purchased from JSC “Sonat” (Moscow, Russia). The stock solution of chitosan of the concentration 0.1 g/L was prepared by addition of an equivalent amount of hydrochloric acid, the resulting pH of solution was 4.5. The cation exchange resin KU2  $\times$  8 with the static ion-exchange capacity 1.8 mmol/cm<sup>3</sup> (analog of resin Dowex HJR-W2) and zeolite of Chuguevskiy deposit, Primorsky Territory, Russia (fraction 0.2–0.5 mm, zeolite content more than 50%) containing <sup>137</sup>Cs radionuclide were used for solid materials decontamination tests. All other reagents were of analytical grade.

### 2.1. Preparation of functionalized latexes for selective sorption of cesium

Latex particles containing simple transition metal ferrocyanides (KE-Me<sub>2</sub>[Fe(CN)<sub>6</sub>]) and potassium/transition metal ferrocyanides (KE-MeK<sub>2</sub>[Fe(CN)<sub>6</sub>]) were obtained by consecutive addition of an aliquot of CoCl<sub>2</sub>, CuCl<sub>2</sub> or NiCl<sub>2</sub> solutions and an equivalent amount of K<sub>4</sub>[Fe(CN)<sub>6</sub>] to the KE 13-36 emulsion, pH = 7. The ferrocyanide content was  $2 \times 10^{-5}$  or  $4 \times 10^{-5}$  mol/g of dry latex. The composition of simple and mixed ferrocyanides in latex particles was determined by elemental analysis (atomic absorption spectroscopy, Solaar M6, Thermo, USA) after the sorbent decomposition in HNO<sub>3</sub>/HCl and was found to be close to the theoretical values within the interval of the experimental error of 5%. The size and electrokinetic potential of functionalized latex particles and ferrocyanides in solution were determined by means of the photon-correlation spectroscopy and laser Doppler electrophoresis on the device ZetaSizer Nano ZS (Malvern, UK).

### 2.2. Determination of distribution coefficients and sorption capacities

The sorption isotherms were obtained by the batch method using CsCl solutions containing <sup>137</sup>Cs tracer. 1 mL of dispersion of latexes (KE solid content 0.5%) functionalized according to Section 2.1 was added to the flask with 24 mL of NaNO<sub>3</sub> solution (25 g/L) containing from  $2.66 \times 10^{-6}$  up to  $5.63 \times 10^{-5}$  mol/L cesium chloride (pH ~ 7). After gentle shaking of the flask during 10 min, latex particles were flocculated by addition of chitosan solution and separated by filtration through a “blue ribbon” paper filter. The activity

of filtrate was determined on Gamma-spectrometer (Gamma-1C, “Aspekt”, Dubna, Russia). Sorption capacities were calculated relatively to total mass of the functionalized latex. The cesium uptake from KCl and NaNO<sub>3</sub> solutions, including those with variable pH values, was determined by the same procedure using solutions containing <sup>137</sup>Cs with total activity 10<sup>3</sup> Bq. pH changes during cesium sorption were negligible. The distribution coefficients ( $K_d$ ) for functionalized latexes in NaNO<sub>3</sub> and KCl solutions were calculated according to the formula:

$$K_d = \left( \frac{A_s}{A_l} \right) \frac{V}{m}$$

where  $A_s$  and  $A_l$  – cesium content in solid and liquid phase, respectively;  $V$  – liquid phase volume (mL),  $m$  – mass of the functionalized latex (g).

The static cation exchange capacity of non-functionalized KE latex emulsions was determined using <sup>60</sup>Co and <sup>90</sup>Sr tracers by the same procedure and calculated as  $4 \times 10^{-5}$  mol/g of dry latex.

### 2.3. Stability test in porous media

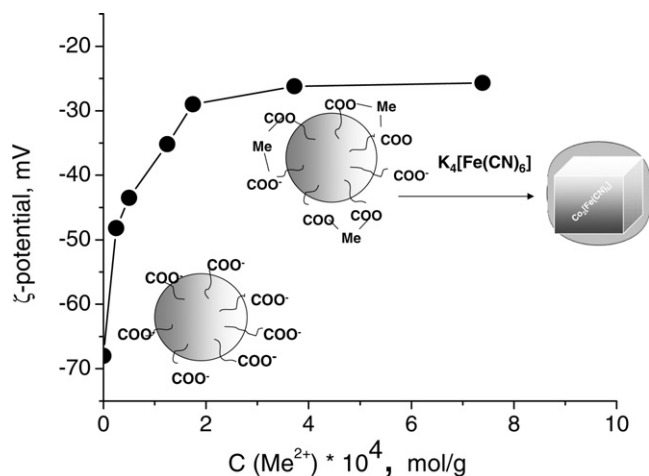
50 mL of the dispersion of KE-CoK<sub>2</sub>[Fe(CN)<sub>6</sub>] with KE solid content 0.5% prepared according to Section 2.1 was (in a close cycle) fed to the column with zeolite bed (20  $\times$  0.8 cm), feeding rate 1 mL/min. Every 10–15 min 0.5 mL of the dispersion was collected and, after dilution, analyzed for optical density at 500 nm (UV-vis 1650PC spectrophotometer, Shimadzu, Japan) and cobalt content (atomic absorption spectrometer Solaar M6, Thermo, USA).

### 2.4. Solid materials decontamination

The static experiments on cesium uptake from solid materials were performed by contacting, at constant mixing, 1 g of ion-exchange resin KU2  $\times$  8 or zeolite containing <sup>137</sup>Cs radionuclide with the decontaminating solution. The initial activities of the solids were 7000 Bq and 1200 Bq for ion-exchange resin and zeolite, respectively. 50 mL of dispersion KE-CoK<sub>2</sub>[Fe(CN)<sub>6</sub>] with solid content 0.5% and KCl content 10 g/L was used for resin KU2  $\times$  8 decontamination. 100 mL of dispersions KE-CoK<sub>2</sub>[Fe(CN)<sub>6</sub>] and KE-Co<sub>2</sub>[Fe(CN)<sub>6</sub>] with solid content 0.5% and KCl content 10 g/L was used for zeolite decontamination. The larger volume of decontaminating solution was used for zeolite due to lower efficiency of cesium removal found in preliminary experiments. The decontamination process was monitored by measuring the activity of the decontaminating solution on Gamma-spectrometer (Gamma-1C, “Aspekt”, Dubna, Russia) and recalculating the residual activity of the solid phase using values of initial and final activity of the solid material.

### 2.5. Formation of carbon fiber composite materials using functionalized latexes

The composite materials for cesium removal were obtained by electrochemical precipitation of the latex emulsions functionalized with simple cobalt ferrocyanides on carbon fibers (Busofit T-040, “Khimvolokno”, Belarus), surface area 960 m<sup>2</sup>/g. The latex emulsion was precipitated on the carbon fiber anode from 0.1 M NaCl solution in a three-electrode electrochemical cell at potentials +0.3, +0.7, and +0.9 V. The content of ferrocyanides in the composite materials was determined by atomic absorption spectroscopy (Solaar M6, Thermo, USA) after material decomposition in HNO<sub>3</sub>/HCl. The sorption properties were investigated by the batch method at solid/liquid ratio 2000, distribution coefficients ( $K_d$ ) were calculated as described in Section 2.2.



**Fig. 1.** A general scheme of functionalized latex preparation, pH=6, solid content 0.02% ( $\text{Me}^{2+} = \text{Cu}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$ ).

### 3. Results and discussion

#### 3.1. Preparation and characterization of latex particles functionalized with transition metals ferrocyanides

The presence of carboxylic groups on the surface of latex particles containing polyacrylic acid makes it possible to bind divalent transition metal ions, which can further act as centers of ferrocyanides formation inside the polymeric matrix. The monitoring of changes in electrokinetic potential and size of siloxane-acrylate latex particles (KE) by laser electrophoresis and photon-correlation spectroscopy showed that with increasing divalent ion concentration in latex emulsion the decrease of surface electrokinetic potential (by modulus) occurred at invariable particle size (Fig. 1). Within the studied metal ion concentration range, the latex emulsions maintained relatively high negative electrokinetic potential and remained colloid stable even after the saturation of accessible ion-exchange centers. No significant difference was found for copper, nickel, and cobalt ion binding to KE latexes. To form nanoparticles of ferrocyanides in the matrix of siloxane-acrylate latexes, the amount of introduced divalent ion was limited to the concentration corresponding to the beginning of the plateau on the dependence of electrokinetic potential on the metal ion content in latex (Fig. 1).

The latex emulsions containing  $2 \times 10^{-5}$  mol/g ferrocyanides remained colloid-stable at least during 1 month, as no particle size changes were detected by the photon correlation spectroscopy. However, when the ferrocyanide content was higher than  $4 \times 10^{-5}$  mol/g, the formation of non-stabilized particles of ferrocyanides in solution and fast phase separation were observed. Immobilization of simple ( $\text{Me}_2[\text{Fe}(\text{CN})_6]$ ) and mixed ferrocyanides ( $\text{MeK}_2[\text{Fe}(\text{CN})_6]$ ) of copper, nickel, and cobalt to KE latex matrix did not cause the change of the latex particles size at ferrocyanide contents below  $4 \times 10^{-5}$  mol/g, but was accompanied by increase (by modulus) of the particles electrokinetic potential from  $-48$  to  $-63$  mV depending on the ferrocyanide composition (Table 1).

One can see that electrokinetic potentials of the modified KE particles are higher than those of ferrocyanides in solutions due to the contribution of latex surface groups. However, the general tendency for dependence of electrokinetic potential on ferrocyanide composition holds for both – ferrocyanide colloids in solution and immobilized into the latex matrix. It should be mentioned that in solution only copper simple ferrocyanide was colloid stable, while nickel and cobalt ferrocyanides colloids rapidly aggregated. At the same time, when all these simple ferrocyanides were immobilized

**Table 1**

Electrokinetic potentials of transition metals ferrocyanides in solutions (\*) and of KE-latex particles functionalized with transition metals ferrocyanides, supporting electrolyte 0.001 M KCl.

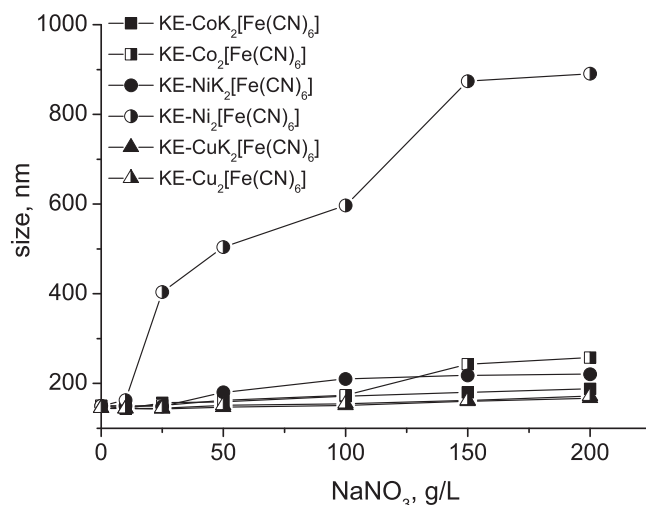
	$\text{Cu}^{2+}$ (mV)	$\text{Co}^{2+}$ (mV)	$\text{Ni}^{2+}$ (mV)
KE- $\text{Me}_2[\text{Fe}(\text{CN})_6]$	$-59.8 \pm 0.8$	$-49 \pm 1$	$-48.1 \pm 0.3$
$\text{Me}_2[\text{Fe}(\text{CN})_6]^*$	$-40.9 \pm 0.6$	$-3.4 \pm 0.3$	$-0.22 \pm 0.1$
KE- $\text{MeK}_2[\text{Fe}(\text{CN})_6]$	$-63.8 \pm 0.3$	$-58.3 \pm 0.4$	$-59 \pm 1$
$\text{MeK}_2[\text{Fe}(\text{CN})_6]^*$	$-49 \pm 1$	$-49.3 \pm 0.8$	$-48.6 \pm 0.5$

in KE matrix, the resulting potential of the particles was sufficiently high to maintain the colloid stability.

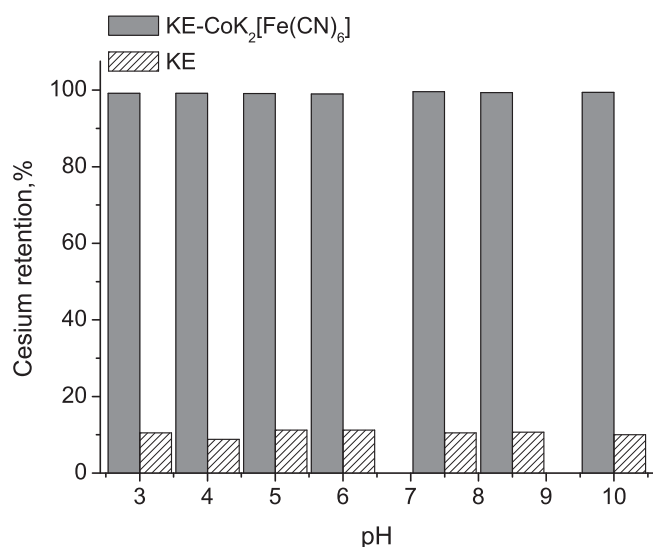
Since many types of LRW contain alkali metals salts, it is crucial that sorbents for cesium removal remain stable and maintain sorption selectivity in high salinity media. The level of salt content can be as high as 200–250 g/L of sodium nitrate for evaporator concentrates produced at nuclear power plants. Preliminary investigations showed that transition metals ferrocyanides stabilized by polyacrylic acid remained colloid stable in media containing up to 7–10 g/L sodium nitrate. Further increase of ionic strength resulted in salting out of the polyelectrolyte that substantially limits application of polyacrylic acid as a stabilizer for nano-sized crystals of ferrocyanides. In contrast to soluble polyacrylic acid, non-modified siloxane-acrylate latex emulsion (KE) remains colloid stable in solutions containing up to 250 g/L of sodium nitrate in neutral and alkaline media. Considering differences in electrokinetic potentials of KE latexes functionalized with ferrocyanides (Table 1), one can also expect changes in colloid stability of the modified particles depending on the ferrocyanide type used.

Determination of the particle size of KE latexes modified with ferrocyanides of different compositions (Fig. 2) revealed that, in accordance with the highest (by modulus) values of surface electrokinetic potentials, the latexes modified with simple copper ferrocyanide and copper/potassium ferrocyanide remained colloid-stable over the full range of sodium nitrate concentrations studied. The lowest colloidal stability in sodium nitrate solutions was observed for latexes modified with simple nickel ferrocyanide–KE- $\text{Ni}_2[\text{Fe}(\text{CN})_6]$ , which already showed slight aggregation at  $\text{NaNO}_3$  content of 25 g/L. However, despite the particle size growth, the phase separation in these functionalized latex emulsions after 24 h was observed only in solutions containing 150–200 g/L of  $\text{NaNO}_3$ .

Thus, we demonstrated that cobalt, nickel, and copper ferrocyanides could be immobilized in a polymer matrix of siloxane-acrylate latexes and principally used as colloid-stable sor-



**Fig. 2.** Particle size of KE latexes functionalized with transition metals ferrocyanides in  $\text{NaNO}_3$  solutions, pH 7.



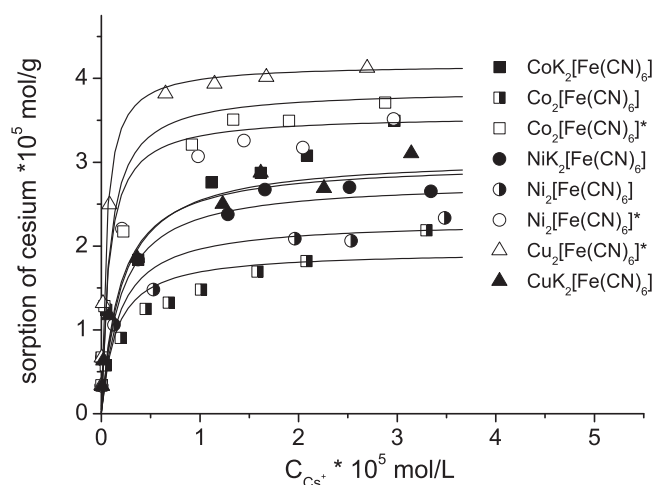
**Fig. 3.** Dependence of  $^{137}\text{Cs}$  retention on pH on unmodified siloxane-acrylate latex (KE) and that modified with cobalt-potassium ferrocyanide (KE- $\text{CoK}_2[\text{Fe}(\text{CN})_6]$ ),  $\text{NaNO}_3$  25 g/L.

bents in salt free and sodium nitrate solutions with limitations imposed only on latexes functionalized with simple nickel ferrocyanide in solutions with  $\text{NaNO}_3$  content higher than 50 g/L. To evaluate the potential of this new type of colloid stable sorbent materials for cesium uptake, we have investigated the effect of ferrocyanide composition and content in polymeric matrix as well as sorption conditions on selectivity and sorption capacities of the sorbents.

### 3.2. Cesium uptake by colloid-stable nanosized selective sorbents based on transition metal ferrocyanides

Although unmodified KE latexes have the cation ( $\text{Me}^{2+}$ )-exchange capacity about  $5 \times 10^{-4}$  mol/g, no significant selectivity toward  $\text{Cs}^+$  ions was observed in  $\text{NaNO}_3$  solutions. Fig. 3 shows that not more than 10% of  $^{137}\text{Cs}$  radionuclide was removed with KE latex from the solution of very low activity. Due to high errors in measuring low activity and minor changes in total activity the pH dependence for cesium uptake by unmodified KE is not very reliable. However, when KE particles were functionalized with transition metals ferrocyanides, their selectivity toward  $\text{Cs}^+$  ions increased dramatically providing the efficacy of  $^{137}\text{Cs}$  retention over 99% within a broad pH range, which is typical for ferrocyanides application [1] – Fig. 3.

Although different types of ferrocyanides were reported as efficient sorption media for cesium uptake [1–5], there are differences in sorption capacities and distribution coefficients in dependence on the type of the transition metal cation used [1,13–16] and composition of the ferrocyanide – simple or mixed [4]. To optimize the composition of colloid-stable nanosized sorbents we have immobilized into the polymeric matrix of KE copper, nickel, and



**Fig. 4.** Sorption isotherms of cesium ions on KE 13-36 latexes functionalized with cobalt, nickel and copper ferrocyanides (\* – ferrocyanides content is  $4 \times 10^{-5}$  mol per 1 g of the latex, systems without asterisk –  $2 \times 10^{-5}$  mol/g),  $\text{NaNO}_3$  (25 g/L), pH 7.5.

cobalt ferrocyanides, in a form of simple or mixed ferrocyanides, and varied the content of ferrocyanides in KE matrix.

Isotherms of cesium sorption on KE latexes modified with all types of ferrocyanides were of the high affinity type with little differences in sorption capacities in dependence on the cation type used (Fig. 4, Table 2). Simple theoretical calculations of ferrocyanide sorption capacities, which are based on the assumption that one metal ( $\text{M}^{2+}$ ) cation is exchangeable and the others are fixed in the lattice [1], give the value of 2 mol/mol of ferrocyanide. However, the experimental values are usually lower, and the true ion-exchange mechanism is reported only for mixed ferrocyanide with exchangeable monovalent ions [1,14,15]. The experimentally found sorption capacities can vary from 0.4 to 2.1 mol Cs/mol ferrocyanide [17], and the highest sorption capacities are usually reported for copper and zinc ferrocyanides [1,2].

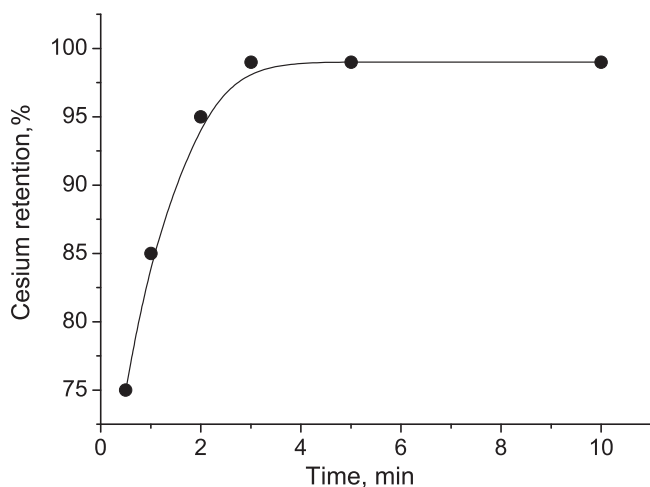
According to the Langmuir equation parameters calculated for cesium sorption on functionalized KE latexes (Table 2), there is no significant difference between cobalt, copper, and nickel ferrocyanides affinity to cesium ions. However, highest sorption capacities were found for copper ferrocyanides that are in good agreement with the literature data [1,2,18].

In contrast to mixed ferrocyanides, the mechanism of cesium uptake by simple ferrocyanides is more complex than ion-exchange that makes values of sorption capacities unpredictable [1]. As seen from Fig. 4 and Table 2, the changes in the mechanism of cesium uptake resulted in much lower sorption capacities of simple ferrocyanides in KE matrix. Besides, doubling of simple ferrocyanide content loaded into KE latexes does not result in proportional increase of sorption capacities. The latter effect, most likely, originates from non-optimal conditions of ferrocyanide immobilization used for KE- $\text{Me}_2[\text{Fe}(\text{CN})_6]^*$  systems with ferrocyanide content  $4 \times 10^{-5}$  mol/g of latex. According to Fig. 1, the content of  $\text{Me}^{2+}$  added to these systems at the first stage of sorbent preparation

**Table 2**  
Langmuir equation parameters ( $Q_{\text{max}}$  – maximum sorption capacity,  $K_L$  – Langmuir constant) and cesium/ferrocyanide mol ratio corresponding to  $Q_{\text{max}}$  ( $n$ ) for cesium sorption on KE latexes functionalized with different types of ferrocyanides.

Me	KE- $\text{MeK}_2[\text{Fe}(\text{CN})_6]$			KE- $\text{Me}_2[\text{Fe}(\text{CN})_6]$			KE- $\text{Me}_2[\text{Fe}(\text{CN})_6]^a$		
	$Q_{\text{max}}$ (mol/g)	$K_L$ (L/mol)	$n$	$Q_{\text{max}}$ (mol/g)	$K_L$ (L/mol)	$n$	$Q_{\text{max}}$ (mol/g)	$K_L$ (L/mol)	$n$
$\text{Co}^{2+}$	$3.00 \times 10^{-5}$	$5.4 \times 10^5$	1.50	$1.94 \times 10^{-5}$	$6.78 \times 10^5$	0.97	$3.78 \times 10^{-5}$	$12.1 \times 10^5$	0.95
$\text{Ni}^{2+}$	$2.64 \times 10^{-5}$	$5.2 \times 10^5$	1.32	$2.3 \times 10^{-5}$	$5.83 \times 10^5$	1.15	$3.56 \times 10^{-5}$	$13.4 \times 10^5$	0.89
$\text{Cu}^{2+}$	$3.07 \times 10^{-5}$	$4.9 \times 10^5$	1.53	–	–	–	$4.17 \times 10^{-5}$	$21.7 \times 10^5$	1.04

<sup>a</sup> Obtained in the systems KE- $\text{Me}_2[\text{Fe}(\text{CN})_6]$  with ferrocyanide content  $4 \times 10^{-5}$  mol/g, the other values are given for KE latexes with ferrocyanide content  $2 \times 10^{-5}$  mol/g.



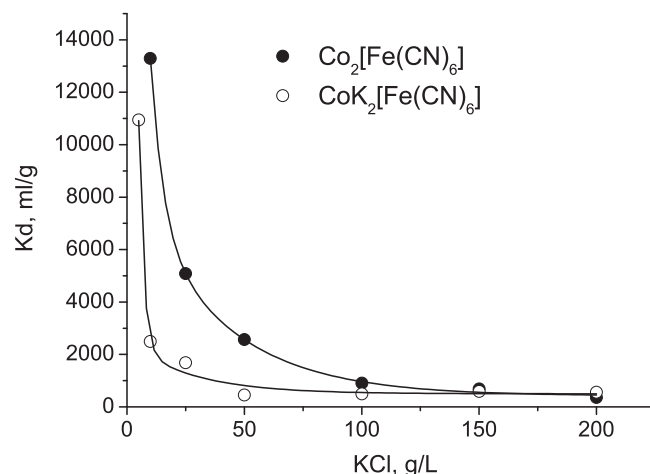
**Fig. 5.** Kinetics of cesium retention on KE-CoK<sub>2</sub>[Fe(CN)<sub>6</sub>], cesium concentration 0.4 mg/L, pH = 7.3, NaNO<sub>3</sub> 25 g/L.

corresponds to the plateau region of the divalent cation sorption isotherm on KE. In this case one cannot exclude the possibility of ferrocyanide formation outside the polymeric matrix that would result in the formation of larger particles. The dependence of ferrocyanides sorption capacities on their surface area, i.e. particle size, is known in literature [1,19]. Recently, Valsala et al. [4] reported that cobalt ferrocyanides loaded in the ion-exchangers had higher sorption capacities than pure cobalt ferrocyanide precipitated outside, since in the former case the particle growth was limited by the pore size of the resin. The possibility of this scenario is indirectly confirmed by notably lower colloidal stability of KE-Me<sub>2</sub>[Fe(CN)<sub>6</sub>] sorbents with ferrocyanide content of  $4 \times 10^{-5}$  mol/g of latex compared to those containing only  $2 \times 10^{-5}$  mol ferrocyanide/g.

It should be also mentioned that the equilibration time in batch test of the obtained colloid stable sorbents was less than 10 min that was sufficient to provide an efficient retention of cesium (Fig. 5). Usually, loading ferrocyanide fines into the mechanically stable matrix results in slower kinetics due to the diffusion limitations [1,4]. Valsala et al. [4] compared the kinetics of cesium uptake by ferrocyanides precipitated and loaded on anion-exchanger and found that in the latter case cesium uptake was retarded despite smaller size and higher surface area of ferrocyanides formed in the resin pores. However, Fig. 5 shows that when non-porous nanosized matrix is used as a support for ferrocyanide crystals, one can obtain sorption media with very good kinetics.

To investigate the selectivity of colloid-stable sorbents in relation to Na<sup>+</sup> and K<sup>+</sup> ions, we used latex particles functionalized with cobalt/potassium and simple cobalt ferrocyanides. Despite lower sorption capacities compared to copper and zinc ferrocyanides, cobalt ferrocyanides and composites on their basis are often mentioned as the most selective compounds [2] and those the most often used [3] in LRW treatment. As seen from Fig. 6, the presence of K<sup>+</sup> ions has much stronger effect on the distribution coefficient for cesium ions on KE-CoK<sub>2</sub>[Fe(CN)<sub>6</sub>] which is most likely due to the ion-exchange mechanism of cesium uptake by mixed cobalt/potassium ferrocyanides. Dramatic decrease of the distribution coefficient for cesium on potassium/cobalt and potassium/cobalt/copper ferrocyanides in the media with K<sup>+</sup> concentration above 0.1 M was also reported in [20]. However, the content of K<sup>+</sup> in most types of LRW is insignificant to interfere with cesium uptake by ferrocyanide sorbents.

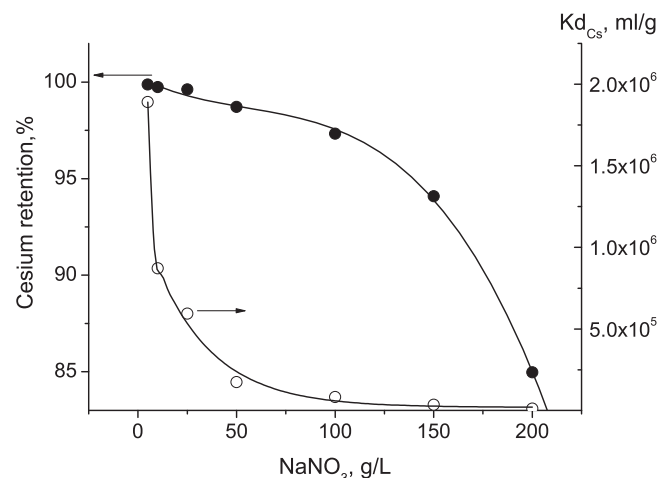
As already mentioned, it is more important that the sorbents remain stable and effective in sodium nitrate media. According to the data presented in Fig. 7, the efficiency of cesium uptake by KE-CoK<sub>2</sub>[Fe(CN)<sub>6</sub>] was above 96% in solution of NaNO<sub>3</sub> 100 g/L.



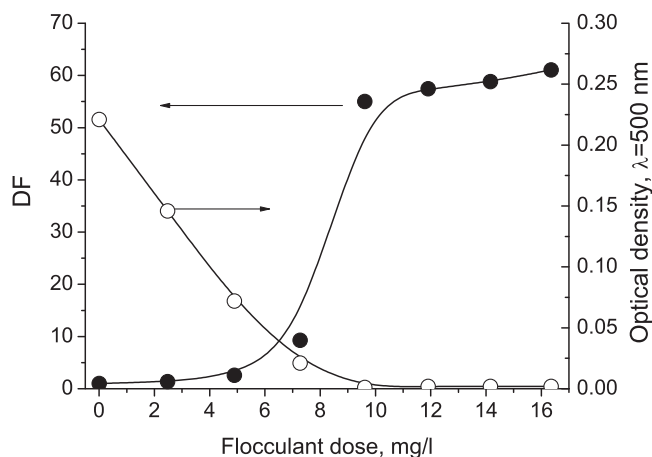
**Fig. 6.** Cesium distribution coefficient as a function of KCl concentration on KE-CoK<sub>2</sub>[Fe(CN)<sub>6</sub>] and KE-Co<sub>2</sub>[Fe(CN)<sub>6</sub>], cesium concentration 0.01 mg/L, pH = 7.3.

Although, in contrast to the findings of [15], the distribution coefficient reduced with increase of Na<sup>+</sup> content, in the media containing 200 g/L its value was above  $10^4$  mL/g, which is comparable with the values obtained for some pure cobalt potassium ferrocyanides [14,20]. It is important to mention that the mixed ferrocyanides of composition MeK<sub>2</sub>[Fe(CN)<sub>6</sub>] remained colloid stable in solutions containing up to 200 g/L NaNO<sub>3</sub> (Fig. 2). However, considering the lowest colloidal stability and sorption capacity of latexes functionalized with nickel/potassium ferrocyanides, they can be considered as less preferential sorption media.

Another important issue, which should be discussed, is relatively low sorption capacities of functionalized latexes compared to pure ferrocyanides and ferrocyanide-based composite materials [1,3,4,21]. The sorption capacities of ferrocyanides loaded on silica support by sol-gel method range from 0.4 to 2.5 meq/g [1–3], the comparable values were obtained for ferrocyanides loaded into organic anion-exchangers [4]. As one can see from Table 2, sorption capacities of the developed colloid stable sorbents are in the range 0.053–0.084 meq/g. Here we must emphasize the difference in application field of ferrocyanides immobilized on solid support and a new type of colloid stable selective sorbents. While high sorption capacity for solid materials used in column application is desirable to provide long operation time of the filter and reduce the volume of solid wastes formed, colloid stable sorbents can have



**Fig. 7.** Cesium retention and distribution coefficient as functions of NaNO<sub>3</sub> concentration on KE-CoK<sub>2</sub>[Fe(CN)<sub>6</sub>], cesium concentration 0.01 mg/L, pH = 7.3.



**Fig. 8.** Flocculation of colloid sorbent KE-CoK<sub>2</sub>[Fe(CN)<sub>6</sub>] after cesium retention: dependence of decontamination factor (DF) and optical density of the solution on the flocculant (chitosan) dose.

significant advantages in treatment of low activity LRW, which contain 10–100 ppm of cesium [1], and can also be used for soils and grounds decontamination using washing technologies. Having high selectivity and sorption capacities, which are close to 1.5 mol Cs/mol of ferrocyanides, these sorption media can be added at very small contents (0.01–0.05%, w/v) to large volumes of LRW and then easily separated by flocculation allowing localization of radionuclide in very small volumes of precipitate. Fig. 8 demonstrates that at optimal flocculant dose functionalized latex particles KE-CoK<sub>2</sub>[Fe(CN)<sub>6</sub>] precipitate, as can be monitored by the reduction of optical density, and capture cesium into the precipitate. The volume of precipitate formed is below 1%, and the decontamination factor reached is above 60. In comparison, chemical precipitation of cesium from the effluents with the same activity using ferric hydroxide and copper ferrocyanide gave, at the best performance, the decontamination factors 20–40, and the precipitate volumes were about 25% of the LRW treated [6]. Thus, as suggested here new type of colloid stable sorbents has advantages in terms of both higher decontamination factor reached and much lower volume of the solid wastes formed.

It is also worth comparing the performance of colloid stable sorbents with ferrocyanide fines in adsorption–microfiltration process. Zhang et al. [5] showed that the dose of ferrocyanide fines must be about 0.33 g/L to provide the efficiency of cesium removal over 98% from solution containing 100 μg Cs/L that corresponds to the sorption capacity of  $2 \times 10^{-6}$  mol/g. To reach the same efficiency, a comparable or even lower quantity of colloid stable sorbents can be used (Table 2). Besides, due to high stability in solution application of colloid sorbent can significantly eliminate microfiltration operational problems related to the fouling of the membrane and pore blocking by precipitates, necessity of intensive mixing, and risk of the membrane damage.

Colloid stable sorbents can be also considered as an alternative to expensive macromolecular ligands selective to cesium, e.g. calixarenes [11], in the schemes based on combination of adsorption/complexing step with membrane separation. In this type of application, the increase of molecular weight, i.e. hydrodynamic radius of polymeric ligand is, on the one hand, beneficial, since it allows filtration with higher rates using membranes with larger pores but, on the other hand, it is limited by the increased viscosity of such systems. In comparison with solutions of polymeric ligands, colloid-stable sorbents based on hard core-shell latex particles have much lower viscosity at large particle size, which can be increased up to several hundreds nanometers without loss of stability. Another advantage of colloid sorbents over the polymeric

**Table 3**

Properties of composite materials obtained by electrochemical deposition of functionalized latex particles on carbon fibers.

Deposition potential (V)	Content of Co <sub>2</sub> [Fe(CN) <sub>6</sub> ] in composite (mol/g)	K <sub>d</sub> (H <sub>2</sub> O) (mL/g)	K <sub>d</sub> (NaNO <sub>3</sub> 10 g/L) (mL/g)
+0.3	$2.3 \times 10^{-6}$	22835	4219
+0.7	$5.0 \times 10^{-6}$	5232	1375
+0.9	$5.2 \times 10^{-5}$	8722	155

ligand is the possibility to settle and separate used sorption media after the completed stage of membrane filtration providing much higher waste volume reduction.

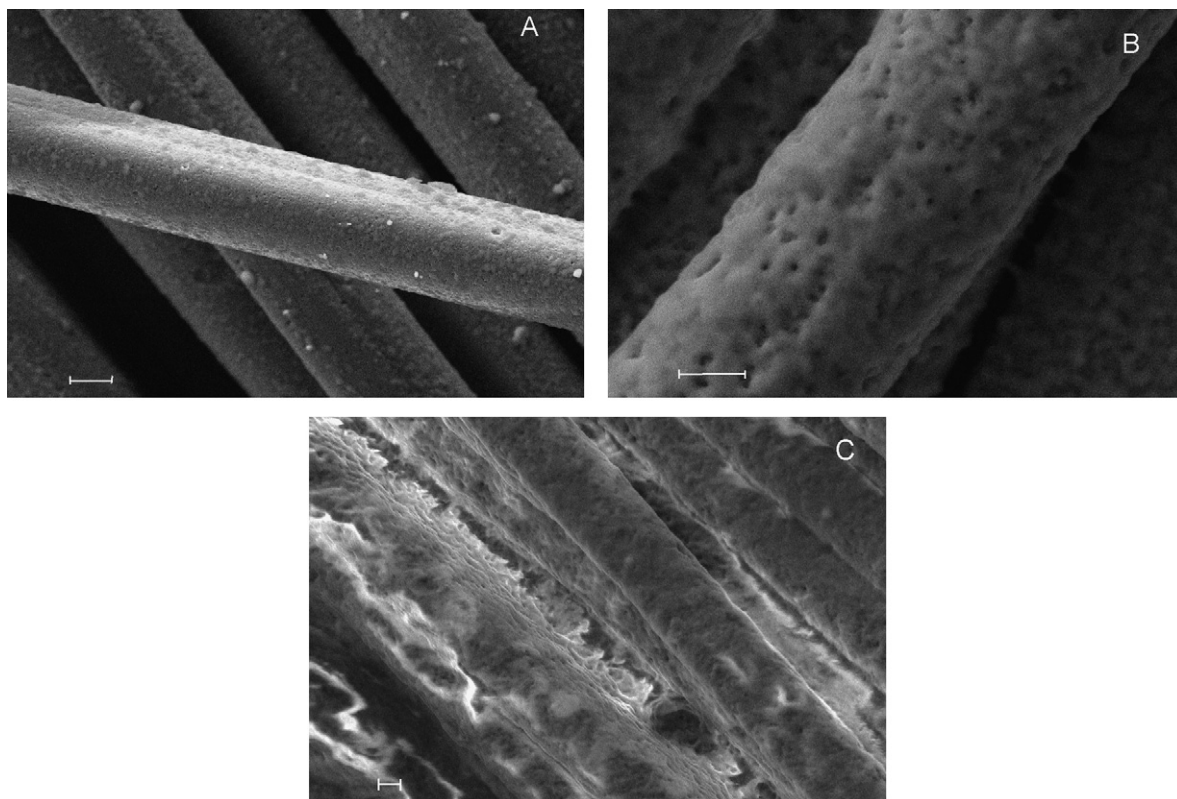
### 3.3. Carbon fiber composites containing functionalized latex particles for cesium removal

One of the main advantages of fiber materials is fast kinetics of sorption and ion-exchange due to large surface area. However, direct precipitation of ferrocyanides on the carbon fibers does not provide reliable fixation of fines, and they are easily lost with the effluent flow [1]. To overcome these limitations one can use electrochemical deposition of latex particles functionalized with ferrocyanides on fiber surfaces that occurs with the formation of thin protective polymeric composite film. Due to the negative electrokinetic potential of the functionalized latexes, they can be deposited on carbon fiber anode and form films with thickness and morphology dependent on polarization conditions. Fig. 9 shows that with increase of anode potential during latexes deposition from +0.3 V to +0.9 V the thickness of the film abruptly increases, most likely, due to the aggregation of latex particles in solution at potential +0.7 V and +0.9 V [22]. Since the content of ferrocyanide in composite materials directly depends on the amount of latex deposited, the highest ferrocyanide loading degrees were obtained at polarization +0.9 V (Table 3). However, the highest distribution coefficients for <sup>137</sup>Cs radionuclide were obtained for the composite with the thinnest latex film obtained at potential +0.3 V (Table 3). One can see that composites show much stronger dependence of K<sub>d</sub> on salt content than functionalized latexes (Fig. 6). The most pronounced loss of selectivity detected in NaNO<sub>3</sub> solutions for the thickest latex film (+0.9 V) suggests that the sorption properties of composites are to a great extent determined by the difference in small ion concentration inside and outside polymeric film, which increases with increasing the film thickness.

Thus, taking into account the data in Table 3, we can conclude that the optimum potential for electrochemical modification of carbon fibers by ferrocyanides pre-immobilized to latex particles is +0.3 V. Despite the low loading degree of ferrocyanide, these composite materials have high distribution coefficient for cesium, comparable with most other composite materials for column applications [1], and can be used for treatment of LRW with low activity and low salt content.

### 3.4. Application of colloid-stable selective sorbents for decontamination of bulk materials from <sup>137</sup>Cs

The most promising field of application for a new type of colloid stable selective sorbents is decontamination of solid materials, including soils and grounds, where they can substitute organic chelating agents in washing technologies. Due to immobilization into stable polymer colloids, the selective sorbents nanoparticles preserve high stability at filtration in porous media. After 50 filtration cycles of KE-CoK<sub>2</sub>[Fe(CN)<sub>6</sub>] through a bed of natural zeolite, the cobalt content in the emulsion and its optical density remained constant (Fig. 10) that proves applicability of this new type of sorption media to decontamination of solids. The



**Fig. 9.** SEM-images of composite materials obtained by electrochemical deposition of  $\text{KE-Co}_2[\text{Fe}(\text{CN})_6]$  on carbon fibers at potential +0.3 V (A), +0.7 V (B), +0.9 V (C), scale bar – 2  $\mu\text{m}$ .

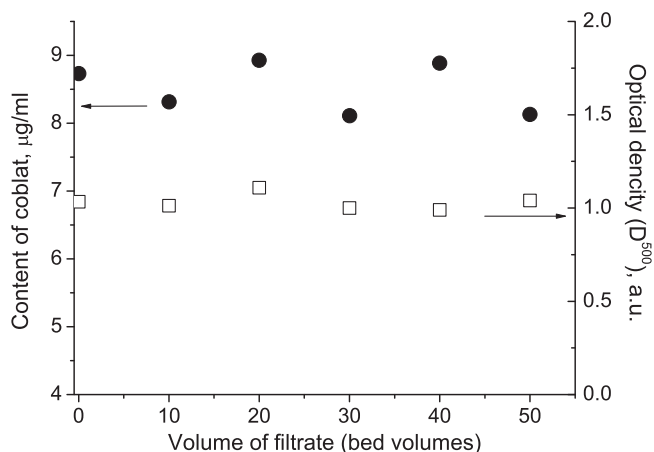
example of decontamination of  $\text{KU}2 \times 8$  ion-exchange resin by KCl solution and the same solution containing functionalized latexes  $\text{KE-CoK}_2[\text{Fe}(\text{CN})_6]$  shows (Fig. 11b) that application of colloid-stable ferrocyanide-based sorbents allows multifold increase of the efficiency of decontamination of ion-exchange resins compared to conventional  $\text{Cs}^+/\text{K}^+$  ion-exchange procedure. Although the decontamination factor reached for resins exceeded 150, much more modest results were obtained in decontamination of natural zeolites, which are well known for efficient cesium binding [23] – Fig. 11a.

Slower kinetics and lower decontamination factors, most likely, do not result only from the microporous structure of zeolites but are determined by high content of clays, which can reach values of 50% for the zeolites of the used type. Evidences of presence of

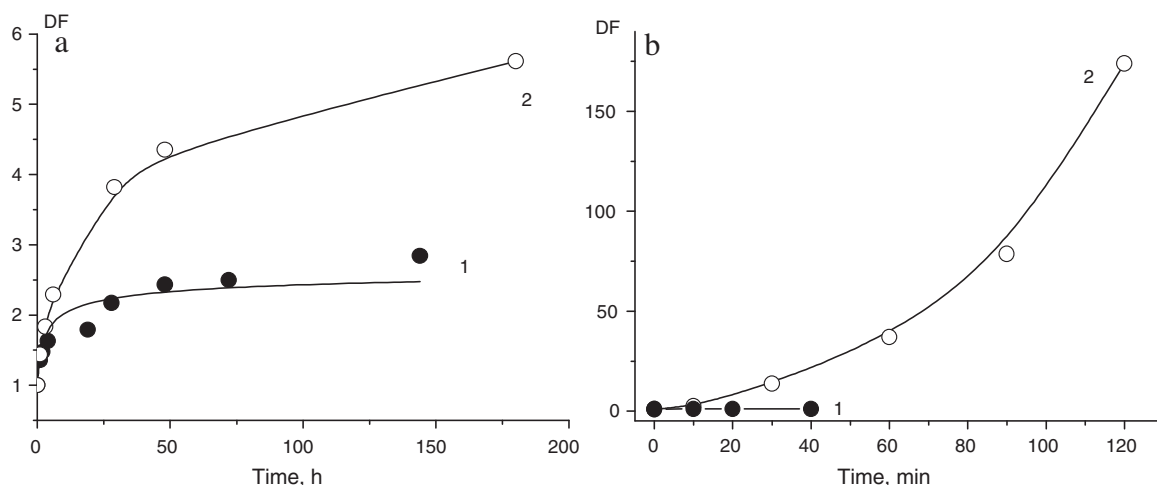
high-affinity sites for  $\text{K}^+$  and  $\text{Cs}^+$  sorption in different types of clays were reported by many authors and summarized in a review by Sawhney [24], who stated that sorption of  $\text{K}^+$  and  $\text{Cs}^+$  ions in the interlayer space near the clay particle edge was not only highly selective but also accompanied by collapse of interlayers, which, in its turn, results in a very slow kinetics of sorbed ions release. Due to low content of these high-affinity sites, small amounts of cesium ions are bound much stronger than ions adsorbed from solutions of higher concentrations, since in this case cesium adsorbs on sites with significantly lower selectivity [24]. The results presented in Fig. 11a were obtained for zeolites with low activity and, therefore, reflect the removal of most strongly bound cesium ions. It should be mentioned that in zeolite decontamination process functionalized with simple ferrocyanides ( $\text{KE-Co}_2[\text{Fe}(\text{CN})_6]$ ) showed better efficacy, although their sorption capacities found in a batch test were somewhat lower than those of cobalt/potassium ferrocyanides. This, probably, can be related to higher distribution coefficients obtained for simple ferrocyanides in the presence of potassium salts (Fig. 6).

Although the decontamination factors attained for zeolites are not very high, it must be noted that application of solid ferrocyanide-based sorbents allows two-three times decrease of soil activity after hundred days of contact [8]. The decontamination factor was also about 3, when magnetic sorbents containing iron and nickel oxides were used to treat soil suspensions at solid-liquid ratio up to 1:6 [25]. The efficiency of washing technologies with non-selective to cesium chelating agents, such as oxalates, acetates, EDTA, even at relatively high reagent concentrations (0.01 M), is typically not higher than 30% [26].

Taking into account the problems of application and separation of solid sorbents, absence of efficient complexing agents for cesium, high volumes of difficult to treat LRW formed during soil washing, the colloid stable sorbents, which combine high selectivity with



**Fig. 10.** Filtration of  $\text{KE-CoK}_2[\text{Fe}(\text{CN})_6]$  colloid sorbent through the zeolite bed.



**Fig. 11.** Decontamination of zeolite (a) and ion-exchange resin KU2 × 8 (b) from radionuclides of  $^{137}\text{Cs}$  using dispersion KE-CoK<sub>2</sub>[Fe(CN)<sub>6</sub>] containing 10 g/L KCl (curves 1a, 2b), dispersion KE-Co<sub>2</sub>[Fe(CN)<sub>6</sub>] containing 10 g/L KCl (curve 2a) and solution of KCl 10 g/L (curve 1b).

easiness of their removal from the decontaminating solution, have high potential in remediation technologies.

#### 4. Conclusions

Nanocrystals of transition metals ferrocyanides  $\text{Me}_2[\text{Fe}(\text{CN})_6]$  and potassium/transition metal ferrocyanides  $\text{MeK}_2[\text{Fe}(\text{CN})_6]$  can be immobilized into the carboxylic latexes to form colloid stable sorbents for cesium removal from solutions and contaminated solid materials. The sorption capacities of the colloid stable sorbents depend on ferrocyanide composition and type of transition metal cation, and change in a row:  $\text{CuK}_2[\text{Fe}(\text{CN})_6] > \text{CoK}_2[\text{Fe}(\text{CN})_6] > \text{NiK}_2[\text{Fe}(\text{CN})_6] \geq \text{Ni}_2[\text{Fe}(\text{CN})_6] > \text{Co}_2[\text{Fe}(\text{CN})_6] \geq \text{Cu}_2[\text{Fe}(\text{CN})_6]$ . All the sorbents except  $\text{Ni}_2[\text{Fe}(\text{CN})_6]$  immobilized in latex remain colloid stable in sodium nitrate solutions with concentrations up to 200 g/L that allows application of this type of sorbents for treatment of high salinity liquid radioactive wastes. A significant advantage of the developed colloid stable sorbents is the possibility of separation using cationic flocculants that ensures localization of cesium radionuclides in a low volume of compact precipitate and significantly reduces the volume of solid waste formed. Due to high colloidal stability and small size, the sorbents developed can penetrate through porous media without filtration and, therefore, be used for decontamination of solid bulk materials, e.g. soils, ion-exchange resins, contaminated metal constructions etc.

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