Effect of Surface Modification of Hydrated Titanium Dioxide on Its Selectivity to Strontium

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Abstract—The effect exerted on the selectivity of hydrated TiO_2 to Sr by surface modification of the sorbent involving immobilization of mixed nickel potassium ferrocyanide was studied. The Sr specificity of the resulting sorbent (denoted as T-55) is comparable with that of hydrated TiO_2 : $\log K_d$ (K_d is Sr distribution coefficient, ml g^{-1}) is 2.7 ± 0.2 in sorption from tap water with $\text{pH } 7.8 \pm 0.2$, 2.7 ± 0.5 in sorption from CaCl_2 solutions with $\text{pH } 5.6 \pm 0.2$, and from 2.5 ± 0.8 to 1.7 ± 0.4 in sorption from CaCl_2 solutions with $\text{pH } 7.0 \pm 0.2$. The modification makes the resulting T-55 sorbent selective to Sr in the presence of Ca at $\text{pH } 5\text{--}6$.

Keywords: hydrated titanium dioxide, nickel potassium ferrocyanide, strontium, sorption

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Surface modification can be considered as a way to alter the specificity and selectivity of inorganic sorbents. Chemical modification of the surface allows synthesis of materials whose physical properties are determined by the support material, and chemical properties, by the nature of both the support and the compound immobilized on the surface. The resulting materials can acquire new properties, characteristic neither of the support nor of the compound being immobilized. Understanding of the relationships of chemical modification allows the material surface properties to be controlled depending on the practical demand.

A promising direction in synthesis of new sorption materials for preconcentration and immobilization of radionuclides is preparation of sorbents via surface modification of sorption-active supports having developed surface. The procedure includes heat treatment of supporting sorbents, leading to changes in the pore space, with the subsequent formation of stable nanosized compounds on the surface and in the pore space. By so doing, it is possible to prepare highly specific, polyfunctional, and complex sorbents. For example, ferrocyanide sorbents prepared by surface modification of hydrated TiO_2 can be used for joint recovery of long-lived β -emitters such as ^{137}Cs and ^{90}Sr with the aim of their subsequent environmentally safe long-term storage or disposal [1].

Study of the effect exerted by chemical modification on the specificity and selectivity of support mate-

rials to radionuclides and their chemical analogs is of scientific and practical interest.

Chemical modification of the surface of hydrated TiO_2 (T-5 grade), which initially had no specificity to Cs, by immobilization of mixed nickel potassium ferrocyanide makes the resulting material (denoted as T-55) Cs-specific. The procedure for preparing T-55 sorbent is described in [2]. In sorbent preparation, the internal part of the support matrix remains unmodified; therefore, the Sr-specific sorption sites are preserved. In this study we examined how surface modification of hydrated TiO_2 by immobilization of mixed nickel potassium ferrocyanide affects its selectivity to Sr.

EXPERIMENTAL

The performance of T-5 and T-55 sorbents in sorption of Sr from tap water was studied in batch experiments. The content of hardness salts, alkali metals, and anions in tap water corresponded to SanPiN (Sanitary Rules and Regulations) 2.1.4.1074-01. Namely, the total hardness was $2.4 \text{ mg-equiv l}^{-1}$, and the Ca concentration was $30 \pm 5 \text{ mg l}^{-1}$. Water was preliminarily settled and filtered to remove iron hydroxide. The required Sr concentration in water was set by adding a solution of stable Sr; then, the sample was spiked with ^{90}Sr . The sample volume was $V = 50 \text{ ml}$, the sorbent weight was 20 mg , and pH of the initial solution was 7.8 ± 0.2 . We obtained sorption isotherms for the phase contact times of 1 and 2 weeks.

Experiments on the influence of pH on sorption were performed with tap water spiked with ^{90}Sr . The Sr concentration was 1 mg l^{-1} , with $V/m = 50 \text{ ml/20 mg}$. The required pH was adjusted by adding HCl or NaOH solution.

The Sr selectivity of the sorbents was studied in the presence of calcium, which is the most naturally abundant analog of Sr^{2+} . In our experiments we used CaCl_2 solutions containing $0.05\text{--}110 \text{ g l}^{-1}$ Ca and 1 mg l^{-1} stable Sr and spiked with ^{90}Sr .

The Ca content of the solution was determined by complexometric titration with Murexide as indicator [3]. Radiometric measurements were performed with a UMF-2000 low-background radiometer with a semiconductor detector.

RESULTS AND DISCUSSION

Figure 1 shows the isotherms of Sr sorption from tap water at $\text{pH } 7.8 \pm 0.2$. As can be seen, 1 week is sufficient to attain the sorption equilibrium in the system. The Henry law is observed throughout the examined interval of Sr concentrations ($10^{-5}\text{--}100 \text{ mg l}^{-1}$). The sorbent saturation was not attained, and therefore their static exchange capacity was not determined. We estimated the maximal content of Sr in the sorbent phase (C_s) at the Sr concentration in solution of 100 mg l^{-1} . The equilibrium values of $\log K_d$ (K_d is the Sr distribution coefficient, ml g^{-1}) and C_s (mg g^{-1}), calculated from the sorption isotherms, were as follows: for T-5, 2.8 ± 0.2 and 26; for T-55, 2.7 ± 0.2 and 34, respectively. Apparently, within the determination uncertainty, the $\log K_d$ values for the initial hydrated TiO_2 sample (T-5) and for the surface-modified sample (T-55) coincide; the maximal content of Sr in the sorbent phase at a Sr concentration in solution of 100 mg l^{-1} coincides also.

Figure 2 shows the pH dependence of the degree of Sr sorption by the initial T-5 sorbent and by the modified sample (T-55). The Sr sorption is minimal at $\text{pH } 3\text{--}4$ owing to competition of hydrogen ions. With a decrease in acidity, the degree of recovery of Sr sharply increases: for T-5, in the interval $\text{pH } 5\text{--}7$, and for T-55, in the interval $\text{pH } 6\text{--}8$. Both sorbents show the highest Sr specificity in weakly alkaline and alkaline solutions. The maximum attainable Sr distribution coefficients with T-5 and T-55 sorbents, calculated from the $S\text{--pH}$ dependence, are 1.5×10^4 and $1.6 \times 10^4 \text{ ml g}^{-1}$, respectively.

In hydrated titanium dioxide (HTD), there are three

Fig. 1. Isotherms of Sr sorption by (a) T-5 and (b) T-55 sorbents from tap water at $\text{pH } 7.8 \pm 0.2$. Phase contact time, weeks: (1) 1 and (2) 2.

Fig. 2. pH dependence of the degree of Sr sorption S by (1) T-5 and (2) T-55 sorbents.

types of sorption sites. With respect to the ion-exchange activity and hence to the relative acidity, the oxygen-hydrogen groups can be ranked in the following order [4]:

The pK values for HTD samples calcined at $150\text{--}400^\circ\text{C}$ are as follows [5]: $\text{pK}_1 = 6.0\text{--}6.7$, $\text{pK}_2 = 7.3\text{--}8.2$, and $\text{pK}_3 = 10.0\text{--}10.5$. Denisova [4] gives for hydrated TiO_2 $\text{pK}_1 = 4.8 \pm 0.8$.

The interaction of Sr with the sorbent can be described by the reaction equation

Our results show that the Sr-specific sorption sites are preserved after surface modification of hydrated TiO_2 with mixed nickel potassium ferrocyanide. The difference in the $S\text{--pH}$ curves also suggests that, in modification of T-5 sorbent, the amount of acid groups

Sorption of Sr and Ca by T-5 and T-55 sorbents from CaCl_2 solutions

pH	[Ca] in solution, g l^{-1}	T-5		T-55	
		$\log K_d(\text{Sr}) [\text{ml g}^{-1}]$	$\log K_d(\text{Ca}) [\text{ml g}^{-1}]$	$\log K_d(\text{Sr}) [\text{ml g}^{-1}]$	$\log K_d(\text{Ca}) [\text{ml g}^{-1}]$
5.6 ± 0.2	0.05–110	No sorption	2.0 ± 0.4	2.7 ± 0.5	No sorption
7.0 ± 0.2	0.05–2	2.7 ± 0.4	2.0 ± 0.6	2.5 ± 0.8	2.3 ± 0.6
7.0 ± 0.2	2–110	1.4 ± 0.3 (minimum)	2.0 ± 0.6	1.7 ± 0.4 (minimum)	2.3 ± 0.6

dissociating at pH 5–6 (H_3O^+ ions) decreases.

We studied the selectivity of Sr sorption by T-5 and T-55 sorbents from CaCl_2 solutions of various concentrations. To reveal the effect of the surface modification on the selectivity of the Sr sorption, we performed a series of experiments at pH set in the intervals 5–6 and 7–8, corresponding to $\text{p}K_1$ and $\text{p}K_2$ of the sorption groups of hydrated TiO_2 . Figure 3 shows how the Sr distribution coefficients in sorption by T-5 and T-55 sorbents depend on the Ca activity in the

Fig. 3. Sr distribution coefficient as a function of Ca activity in solution. (a) T-5, pH 7.0 ± 0.2 ; (b) T-55, pH 5.6 ± 0.2 ; and (c) T-55, pH 7.0 ± 0.2 .

Fig. 4. Isotherms of Ca sorption by (a) T-5 and (b) T-55 sorbents at pH 7.0 ± 0.2 .

solution at pH 5.6 ± 0.2 and 7.0 ± 0.2 , and Fig. 4 shows the isotherms of Ca sorption by T-5 and T-55 sorbents at pH 7.0 ± 0.2 . The results of mathematical processing of the curves are given in the table.

As seen from the table, hydrated TiO_2 of T-5 grade in the examined pH intervals, pH 5.6 ± 0.2 and 7.0 ± 0.2 , sorbs Ca with the distribution coefficients coinciding within the uncertainty. Strontium is not recovered by this sorbent at pH 5.6 ± 0.2 . Presumably, the sorption of Sr is suppressed by the sorption of Ca present in higher concentration. At pH 7.0 ± 0.2 , the sorption of Sr by T-5 sorbent is unselective. The relationships are reproduced throughout the series of experiments at pH 5–6 and 7–8.

From aqueous solutions with pH 5–6, T-55 sorbent sorbs Sr selectively: Ca is not recovered, and the Sr distribution coefficient is independent of the Ca concentration in the solution. The primary ion-exchange sites on hydrated TiO_2 are H_3O^+ ions [4]. As a result of modification with mixed nickel potassium ferrocyanide, the surface sorption groups of hydrated TiO_2 , dissociating at pH 5–6, transform into groups that are selective to Cs but do not take up Sr. Because the modification occurs on the surface, it does not involve groups located inside sorbent granules. In this case, at pH 5–6, Sr is probably sorbed only by the groups located inside a sorbent granule. Presumably, the selectivity of the Sr sorption in this pH range is determined by formation of the phase of mixed potassium nickel ferrocyanide on the surface of titanium hydroxide, preventing penetration of Ca into the sorbent granule, as hydrated Ca ion has larger size than hydrated Sr cation.

At pH 7–8, sorption of Sr by T-55 sorbent is unselective. Calcium at pH 7.0 ± 0.2 is sorbed with $\log K_d [\text{ml g}^{-1}] = 2.3 \pm 0.6$, which coincides within uncertainty limits with the value obtained for T-5. At a Ca concentration of up to 2 g l^{-1} , the Sr sorption is independent of the Ca concentration in the solution, and at higher concentration Ca exerts a competing effect on Sr sorption.

Thus, when the surface of hydrated TiO_2 is modified by immobilization of mixed nickel potassium ferrocyanide, the sorbent preserves the Sr specificity comparable with that of hydrated TiO_2 and, at the same time, becomes selective to Sr in the presence of Ca at pH 5–6.

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