Amorphous MnO₂–TiO₂ Composites as Sorbents for Sr²⁺ and UO₂²⁺

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Abstract. Hydrous, amorphous MnO_2–TiO_2 composites demonstrating high affinity towards strontium and uranium at pH = 7 are obtained by means of template synthesis. The best distribution coefficients, as found using model solutions ($K_d^{Sr} = 55000$ mL/g and $K_d^{U} = 40000$ mL/g) and Chernobyl shelter water ($K_d^{Sr} = 3800$ mL/g), are gained for the samples containing equimolar amounts of manganese dioxide and titania precipitated using K^+ as template cation.

Keywords: adsorption, strontium, manganese oxide, titanium oxide

1. Introduction

Radiostrontium is considered one of the most hazardous pollutants because of its ability to accumulation in human bones, and methods of processing of strontium-containing wastewaters attract much attention of technologists. In practice, these methods are first of all based of sorption technologies and must enable one to successfully operate with wide varieties of wastes: from those with activities of thousands of kBq/L, like wastewater amassed under the shelter erected over the destroyed 4th block of the Chernobyl Power Plant, Ukraine (Krinitsin et al., 1996) or collected in some nuclear sites in Russia (Korsakov and Erofeeva, 1996), to those containing trace amounts of ⁹⁰Sr (Pickett and Malhotra, 2002).

From the point of view of sorption processes, numerous inorganic materials demonstrate proven ability to effectively remove strontium from wastewaters of complex nature. Significant progress has been achieved in this field during the last decade, and several novel materials with high values of distribution coefficients (K_d) have been proposed and tested (up to $2 \cdot 10^5$ mL/g, Behrens et al., 1998; up to $1.2 \cdot 10^6$ mL/g, Hobbs et al., 2001). However, simple oxides, especially, manganese-

IV oxide (MnO_2), are still considered prospective sorbents for numerous inorganic ions. Co-precipitation of contaminating cations, strontium on the first hand, with MnO_2 is employed as part of the in-tank precipitation process of the treatment of supernatant high-level wastes, and co-precipitation data are commonly used as benchmark results in studies of novel sorbents for strontium. For example, in the case of co-precipitation of Sr^{2+} with MnO_2, decontamination factors after a 7 day treatment reach 780, whereas for the best known sorbent for Sr^{2+} (SrTreat®) it equals 590 (Hobbs et al., 2001). Due to this fact, one may arrive at the conclusion that potentialities of manganese oxide as a sorbent are especially great, and elaboration of new synthetic routines for obtaining novel manganese oxide sorbents and ion exchangers remains a valuable problem of modern materials science.

First studies of selectivity of MnO_2 to alkaline earth cations have been accomplished in mid-70th (Murray, 1974a, 1974b). Later on, its properties as a sorption material for strontium have been studied in great detail. Typical K_d values for manganese oxides are ca. 100 mL/g (Kanungo, 1991; White and Labayru, 1991; Misra and Tiwary, 1995; Leontíeva, 1997). Like for other materials of high affinity to strontium, the dependence of adsorption of Sr^{2+} on pH reaches a plateau in alkaline media (Misra and Tiwary, 1995).

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In order to afford working ability of manganese oxide in more acidic solutions, which is especially valuable for technical applications, modification of MnO_2 by an acid-insoluble oxide, SiO_2, has been proposed (White and Labayru, 1991). It has been shown that mixed $xMnO_2 \cdot ySiO_2$ sorbents remain active up to pH $\approx$ 4.0, having enhanced capacity for strontium and higher K_d values. One may therefore conclude that modification of MnO_2 by acid-resistant oxides may be highly promising for amendment of this material.

Naturally, silica is not the only possible acid-resistant modifier enabling one to enhance useful properties of manganese oxide. Titania seems even more favorable, in particular, if one bears in mind its own reasonable ion-exchange properties towards Sr^{2+} (Samanta, 1996) and affinity towards uranium (Nuriev et al., 1998). Really, preliminary studies of mixed MnO_2–TiO_2 sorbents performed at Institute for Sorption and Problems of Endoecology prove this conjecture demonstrating K_d equal to $\sim$ 1000 mL/g (Bengtsson et al., 1996) and $\sim$ 1400 mL/g (Puziy et al., 1999).

Therefore the aim of this work was optimal design of composite MnO_2–TiO_2 materials and testing their sorption ability towards strontium and uranium. We intended to produce target materials in their amorphous form, so as to ensure molecular mixing of TiO_2 and MnO_2 that, in spite of the closeness of the size of octahedral MnO_6 and TiO_6 structural units existing in crystals, have dissimilar crystalline structures and form immiscible phases. Further, we employed various precipitating agents (LiOH, NaOH, KOH, and NH_4OH) as templates in order to direct the cavity dimensions in embryos formed by means of co-precipitation.

2. Experimental

All chemicals used were of reagent grade. The total content of manganese in the samples was determined complexomerically, after reduction of the weighed amount of the sample by an excess of HCl. The amount of manganese in lower oxidation states (Mn^{2+}, Mn^{3+}) was found either by permanganatometric titration of solid samples in neutral aqueous solutions buffered with ZnO, or by means of reduction of the solid sample by the known excess of oxalic acid and permanganatometric titration of remaining oxalate. Concentration of titanium in samples was determined by means of colorimetry of its peroxide complex compound. Surface composition of samples was controlled by XPS method on a VG ESCA-3c spectrometer.

A powdered X-ray diffraction analysis was performed on a Phillips X-ray diffractometer (model PW 1729/1720). Scanning electron microscopy (SEM) measurements were made on a JEOL JSM 6100 scanning electron microscope. Thermal analysis was performed using a Mettler TA 4000 system. The measurement of surface area and determination of pore size distribution was made by means of a Micrometrics ASAP 2000 instrument (nitrogen adsorption-desorption isotherms at 77 K).

To find distribution coefficients, the weighed amounts of the sample were immersed in 20 mL of a 0.1 N solution of $NaNO_3$ containing a known initial amount of studied cations. pH of these solutions was adjusted by means of solutions of nitric acid or sodium hydroxide. After equilibration during 72 hours, the concentration of Sr^{2+} and Ca^{2+} was determined by means of a Jarrell Ash AA-8500 atomic absorption spectrometer. The concentration of UO^{2+} was found by means of colorimetry of its complex compound with arsenazo. The distribution coefficients were calculated as $K_d^i(\mathrm{mL/g}) = [(c_{0i} - c_i)/c_i](V/m)$, where c_{0i} is the initial concentration of the i-th cation in the solution, c_i is the final concentration of this cation in the solution after sorption, V is the volume of the solution, and m is the mass of the sorbent.

3. Synthesis and Characterization

Unlike other works in the field employing permanganate as an oxidant and a manganese-II salt as a reducing agent, we preferred to oxidize the salts of manganese-II using hydrogen peroxide, according to the reaction $Mn^{2+} + H_2O_2 = MnO_2 + 2H^+$, since decomposition of hydrogen peroxide leads to evolution of oxygen thus favoring development of the porous structure of materials. The synthetic procedure was as follows. Hydrous, amorphous MnO_2–TiO_2 composites of the general formula $(n-x)MnO_2 \cdot (100-n-x)TiO_2 \cdot xH_2O$, where n is the molar percentage of manganese dioxide, were prepared by precipitation from aqueous solutions of $Mn(NO_3)_2$ and $TiCl_4$ by the solution of template ions (lithium, sodium, potassium hydroxide or ammonia) at the presence of hydrogen peroxide as an oxidant; pH value of the reaction mixture varied from 6 to 12. Resulting mixtures were stirred for 1 hour and left for 24 hours for ageing. Then settled solutions were decanted, and precipitates were

repeatedly washed with distilled water until the constant pH value was accessed, so as to remove template cations. Further operations included filtering and air-drying at room temperature.

Materials obtained are uniform powders of dark chocolate color. Chemical analysis shows that the Mn/Ti ratio in precipitates remains as the same as in the initial solutions. Special care has been taken of the oxidation state of manganese in amorphous materials, since MnO_2 obtained by methods of wet chemistry, usually contains manganese in lower oxidation states, and its formula can be written as $MnO_{2-\delta}$, where δ can reach 0.30 (Yegorov, 1975). In our case, the content of Mn_2O_3 in the samples never exceeds 10%; that is, their formula could be written as $(n-x)MnO_{2-\delta}\cdot(100-n-x)TiO_2\cdot xH_2O$, where $\delta \leq 0.05$.

Another point to stress is that the materials in question appear to be stable in aqueous media. Chemical analysis reveals that at pH > 5, even trace amounts of manganese and titanium ions are not transferred into the solvent after 5 days treatment.

Thermal analysis shows that water content in the samples varies from 3–5 wt.% in MnO_2 to 53 wt.% in TiO_2. Depending on the Mn/Ti ratio in the samples, the first dehydration step takes place at 80–150°C, when physisorbed water removes. The second dehydration step occurs at 320–370°C; at these temperatures, constitutional water is eliminated and samples become crystalline. This second process reaches the end at approx. 850°C.

SEM data prove the amorphous nature of samples. A representative photograph reveals homogeneous particles of indefinite form. An average size of particles could be estimated as 100 nm. Heating clearly shows how segregation of TiO_2 and MnO_2 and crystallization of TiO_2 begins: In SEM photographs, the growth of microcrystals of rutile and anataze becomes visible. Such a conclusion is supported by the X-ray analysis of transformations of these substances on heating.

4. Surface Area, Porosity and Adsorption Measurements

Surface areas of materials obtained demonstrate a dependence on the radii of template cations. The less the radius of template cation ($R_{Li^+} = 0.068$ nm, $R_{Na^+} = 0.098$ nm, $R_{K^+} = 0.133$ nm, $R_{NH_4^+} = 0.143$ nm), the greater the surface area is (Fig. 1).

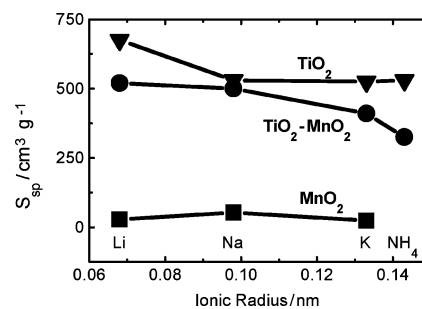The pore size distribution in the samples appears to be monomodal. For 1:1 samples, the dominant pore

Figure 1. Dependence of the surface area of materials obtained on the ionic radii of template cations.
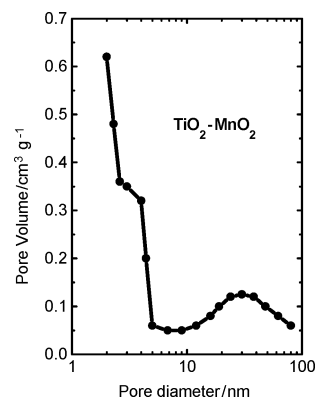

Figure 2. Pore size distribution for a MnO_2–TiO_2 sample.

radius arrives at the value of approx. 3 nm (Fig. 2). These data are in good agreement with the latest studies (Trivedi and Axe, 1999; Axe et al., 2000) demonstrating that hydrous manganese dioxide belongs to microporous oxides. The only difference between these and our measurements is in the type of the pore size distribution. Axe and co-workers have found it bimodal with two dominant pore radii of 2.1 and 6.1 nm, whereas our data put forth the monomodal distribution. Probably, this is caused by different synthetic methods. Unlike oxidation of $Mn(NO_3)_2$ by H_2O_2 in acidic media employed in this work, Axe and co-workers use oxidation of $Mn(NO_3)_2$ by $NaMnO_4$ in alkaline solutions.

X-ray analysis of strontium sorption to hydrous manganese oxide (Axe et al., 2000) indicates that in sorbed samples of different loadings, strontium is surrounded by 10–12 oxygen atoms at an average distance of 0.258 nm. Such coordination environment is well comparable with that in aqueous solutions, where hydrated Sr^{2+} ions are surrounded by ca. 9 atoms of oxygen at 0.262 nm. This suggests that the pores in materials
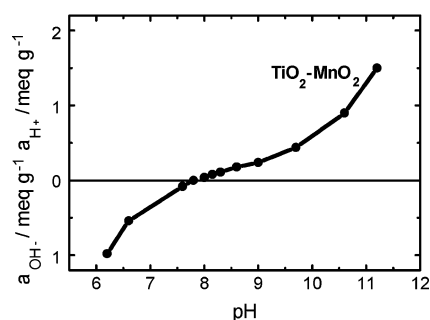
Figure 3. Representative potentiometric titration curve for a MnO$_2$–TiO$_2$ sample.

Figure 4. Dependence of distribution coefficients (pH = 7) of materials obtained on the ionic radii of template cations. The horizontal line corresponds to the best K_d values attained in previous studies of similar materials.

Figure 5. Dependence of uptake of Sr^{2+} and Ca^{2+} by mixed MnO$_2$-TiO$_2$ sorbents on pH.

Figure 6. Dependence of selectivity factors of mixed MnO$_2$-TiO$_2$ sorbents on the ionic radii of template cations.

obtained in our studies accommodate hydrated strontium cations.

Potentiometric titration data reveal that the zero charge point of mixed MnO$_2$–TiO$_2$ materials lies in the range of pH 7.0 to 8.5 (Fig. 3). This is close to the value known for pure TiO$_2$, but significantly differs from the values reported for neat MnO$_2$ (pH 1.5 to 3.0, Trivedi and Axe, 1999).

It is for long known that the sorption capacity of hydrous samples of manganese oxide with respect to each particular cation is proportional to the specific area of a sample (Kozava, 1959; Gabano et al., 1965). However, this is not so in our case. The greatest affinity to Sr^{2+} is shown up by mixed materials obtained using potassium templates ($R_{Sr^{2+}} = 0.120$ nm and $R_{K^+} = 0.133$ nm are best comparable). This supports an idea of template synthesis and may be due to an imprinting effect, because MnO$_2$ precipitated with different alkalies shows unequal sorption capacities towards different alkali ions (Feng et al., 1999). Some of respective distribution coefficients K_d^{Sr} are given in Fig. 4. Binary composites have much greater affinity to Sr^{2+} ions than single oxides, probably, due to formation of an amorphous "solid solution" of MnO$_2$ and TiO$_2$.

Based on these experiments, we performed similar studies with solutions containing strontium and calcium, another divalent cation, which always accompanies strontium in drinkable and waste water. The ratio of cation concentrations varied as Sr/Ca = 1/(1÷100). Uptakes of Sr^{2+} and Ca^{2+} are illustrated by Fig. 5. Selectivity factors $K_{Sr/Ca} = K_d^{Sr}/K_d^{Ca}$ are given in Fig. 6. It appears that the materials obtained have much less affinity towards Ca^{2+} than towards Sr^{2+}.

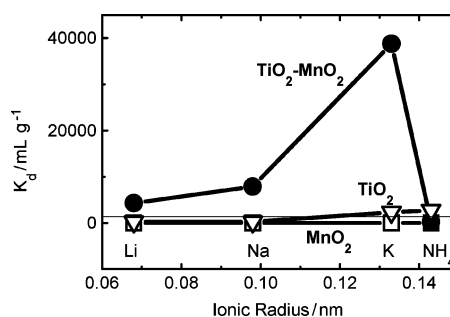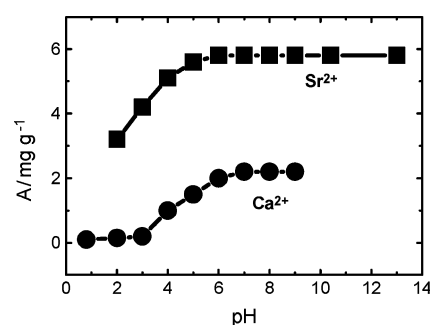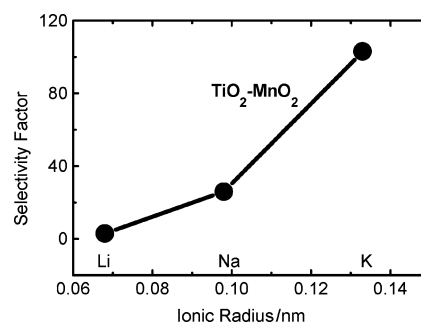It has been found that dehydration of amorphous materials significantly influences their sorption properties (Fig. 7). Thermally treated samples increase their affinity towards Sr^{2+}, probably, due to removal of chemisorbed water from pores. At temperatures higher than 300°C, crystallization begins, and sorption ability decreases.

Furthermore, binary amorphous MnO$_2$–TiO$_2$ materials demonstrate great affinity towards uranium. As follows from Fig. 8, maximal values of distribution coefficients are attained for samples reach in MnO$_2$.
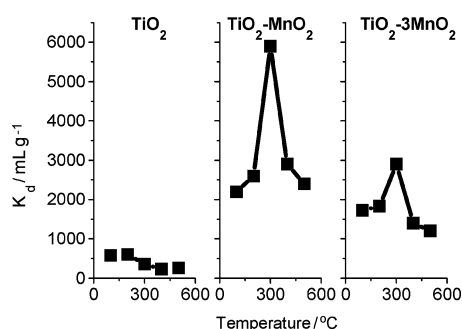
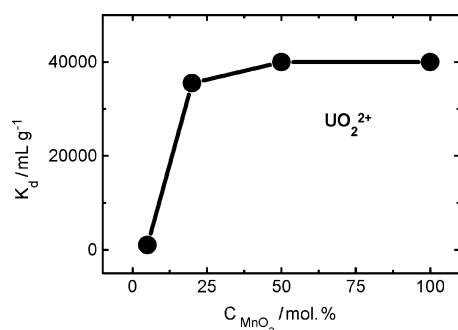*Figure 7.* Dependence of distribution coefficients of Sr^{2+} on temperature and the composition of mixed MnO_2-TiO_2 sorbents.

Figure 8. Dependence of distribution coefficients of UO_2^{2+} on the composition of mixed MnO_2-TiO_2 sorbents.

Finally, some of materials with equimolar Ti/Mn ratio have been employed for purification of Chernobyl shelter water. pH of this complex mixture is equal to 9.0, and it contains a wide variety of radionuclides and side cations, including ^{90}Sr (9250 kBq/L). Due to this fact, selective sorption of strontium to sorbents should be significantly hampered. Regardless of this obstacle, the distribution coefficients determined in parallel probes appear quite high, $K_d^{Sr} = 3800 \pm 100$ mL/g.

5. Conclusions

The principles of template synthesis prove their usefulness in the synthesis of hydrous, amorphous MnO_2–TiO_2 materials. Binary composites have much greater affinity to Sr^{2+} ions at pH = 7 than single oxides, probably, due to formation of an amorphous "solid solution" of MnO_2 and TiO_2. The greatest affinity towards strontium is shown up by mixed materials produced using potassium templates, since ionic radii of these cations ($R_{Sr^{2+}} = 0.120$ nm and $R_{K^+} = 0.133$ nm) are

best comparable. The best distribution coefficients, as found with model solutions ($K_d^{Sr} = 38800$ mL/g) and Chernobyl shelter water ($K_d^{Sr} = 3800$ mL/g), are gained for the samples containing equimolar amounts of manganese dioxide and titania. In model solutions, selectivity factors with respect to Ca^{2+} reach 200. Moreover, these same samples exhibit high affinity towards uranium ($K_d^U = 40000$ mL/g).

The price for existing sorbents for Sr^{2+} equals to 50–100 USD per kg (Pickett and Malhotra, 2002). Our estimates prove that mixed MnO_2–TiO_2 materials produced even on the pilot plant scale would cost ~10 USD per kg and hence could be considered competitive.

The studies of above materials are under way. Prospective results are obtained in the studies of subsequent release and uptake of Sr^{2+} proving the possibility to regenerate the sorbent. High affinity of MnO_2 to strontium is explained in X-ray studies (Axe et al., 2000, see above) in terms of hydrogen bonding between the hydrophilic surface of oxide and the hydration shell of Sr^{2+} ions; our infrared measurements seem to prove this statement. Besides sorption applications, investigations of catalytic and electrochemical properties are performed. Respective results will be published elsewhere.

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