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Microsphere Sorbents Based on Cenosphere Supported Zirconium Molybdates and Zirconium Silicates for Cesium-137 and Strontium-90 Removal from Radioactive Waste Solutions

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Abstract

The microsphere composites were prepared by covering microsphere glass-crystalline supports with as-synthesized crystalline zirconium molybdate (Mo/Zr = 1.7) and pre-synthesized microporous sodium zirconium silicates of hilairite and gaidonnayite structural types. Narrow fractions of coal fly ash cenospheres with (SiO₂/Al₂O₃)_{wt} of 2.7 and 3.0 were used as precursors of the supports. The composites were studied by means of SEM, EDX and PXRD. The efficiency for Cs⁺ and Sr²⁺ removal from simulated wastewater was evaluated on the basis of parameters, such as the distribution coefficient K_d (for low Cs⁺/Sr²⁺ concentrations) and the maximum sorption capacity a_m (for high Cs⁺/Sr²⁺ concentrations) determined from the Langmuir sorption isotherms. It was established that the composites trap Cs⁺ and Sr²⁺ with K_d of up to 10⁴ mL/g. The influence of zirconium molybdate and sodium zirconium silicate composition and structure on their sorption abilities was demonstrated. The proposed resource-saving approach to the preparation of composite sorbents along with their high sorption parameters favours their application for decontamination of ¹³⁷Cs and ⁹⁰Sr bearing wastewater including aquatic environment and technological solutions.

Keywords: cenospheres, sorbents, zirconium molybdates, zirconium silicates, radioactive waste

INTRODUCTION

Inorganic sorbents are widely used in environmental protection for the removal of contaminants from wastewater generated in the industry [1, 2]. The thermal, radiation and chemical stability, along with the selectivity to certain ions, makes them suitable for application in the treatment of aqueous radioactive waste and contaminated water resources resulting from the activities of radiochemical and nuclear power plants [3]. In this context, inorganic sorbents possess an additional advantage over traditionally used organic resins, such as the ability to fix captured radionuclide ions in a stable solid form (crystalline or mineral-like ceramics, glass-ceramic composites) based on the "sorption-thermal/thermobaric crystallization/densification" process [4–6].

Among all the possible radioactive contaminants of the aquatic environment and liquid radioactive waste resulting from the operation of the nuclear industry, the heat-generating fission products ¹³⁷Cs and ⁹⁰Sr are of particular concern [7]. The ¹³⁷Cs/⁹⁰Sr concentration ratio in the wastes varies in a wide range – from several milligrams per litre and lower in intermediate- and high-level wastes $(10^7-10^{10} \text{ Bq/L})$ up to several ten milligrams per litre and higher in technological solutions. Therefore, a pressing necessity exists to develop an efficient and economical process for ¹³⁷Cs and ⁹⁰Sr separation from nuclear waste streams and contaminated water resources.

Extensive research and development have been performed on the application of ion exchange technologies for cesium and strontium removal from radioactive wastewater [8–10]. Naturally occurring materials (zeolites, mica, *etc.*) and synthetic compounds (hydrous oxides and salts of multivalent metals, for example, Zr and Ti, ferrocyanides of transition metals, salts of heteropolyacids) are of major interest. Impregnation in an inert binding matrix or deposition on a porous inorganic support are reported as methods to prepare engineered forms of powdered ion exchangers with suitable granulometric, mechanical and sorption properties [11, 12].

Not long ago the cost-effective and resourcesaving methods to produce microsphere composites based on coal fly ash aluminosilicate microspheres (cenospheres) impregnated with ion exchangers and other sorbing additives, such as ammonium molybdophosphate and zirconium molybdates, were realized [13, 14]. The availability of well-developed procedures for classification of cenosphere concentrates resulting in the narrow fractions of stabilized chemical, phase and granulometric composition [15, 16] along with the specified composition and properties of sorbing additives makes it possible to prepare the microsphere sorbent of controllable characteristics.

The aim of this paper is to demonstrate the potential of the cenosphere-based approach for the development of sustainable technologies for the treatment of liquid radioactive waste. In the paper, we report the resource-saving method of preparation and characterization of novel microsphere composites based on cenosphere-supported zirconium molybdate (ZM) and sodium zirconium silicates (SZS) of hilairite (HIL) and gaidonnayite (GAI) structural types. The efficiency of the sorbents for Cs⁺ and Sr²⁺ removal was evaluated in the range of Cs^+/Sr^{2+} concentrations of 0.5-50 mg/L, which is close to the compositions of real ¹³⁷Cs/⁹⁰Sr bearing aqueous wastes, based on such sorption parameters as distribution coefficient $K_{\rm d}$ (for low $\rm Cs^+/Sr^{2+}$ concentrations) and maximum sorption capacity a_m (for high Cs^+/Sr^{2+}

concentrations), with the use of non-radioactive simulant solutions.

EXPERIMENTAL

Materials

The reagents $(Na_2MoO_4 \cdot 2H_2O)$ (analytically pure reagent grade); ZrOCl, · 8H,O (pure); $SiO_{2} \cdot nH_{2}O$ (analytically pure); NaOH (high-purity); CsNO₃ (high-purity); Sr(NO₃)₉ (high-purity)) were purchased from OOO "Vekton" (Russia) and used without further purification. Microsphere glass-crystalline supports, further indicated in the text as $(SiO_2-Al_2O_3)$, were prepared as reported in [17] starting from two cenosphere fractions, such as $-125+160 \ \mu m$ (SiO₂ 67.5 wt. %, Al₂O₃ 21.3 wt. %; glass phase 91.5 wt. % with $SiO_2/Al_2O_3 = 3.0$; mullite 1.5 wt. %, quartz 6.7 wt. %) (Sample 1) and -200+160 µm (SiO, 65.2 wt. %, Al_2O_3 26.5 wt. %; glass phase 91.3 wt. $\sqrt[6]{6}$ with $SiO_{2}/Al_{2}O_{3} = 2.7$; mullite 5.3 wt. %, quartz 3.1 wt. %) (Sample 2) separated from Kuznetsk coal fly ash cenosphere concentrates [15, 16].

Methods of synthesis

ZM/(SiO₂-Al₂O₃) composites. The zirconium molybdate coating was synthesized through the two-step hydrothermal synthesis in a Teflonlined stainless steel autoclave ("Beluga", Premex AG), such as (step 1) deposition of mesoporous zirconia (mZrO₃) on the microsphere surface (Sample 1) as described in [14] followed by (step 2) treatment of mZrO₂/microsphere solid with 1 M $Na_{2}MoO_{4}$ (pH 1.5) at 150 °C for 72 h. Unlike [14], the liquid-to-solid ratio at the second step (L/S)was 10/1 (v/m). The ZM/microsphere solid marked as $ZM_{17}/(SiO_2-Al_2O_3)$, where ZM_{17} is due to the Zr/Mo ratio of about 1.7 (Fig. 1, f), was isolated and dried in air. The $ZM_{20}/(SiO_2-Al_2O_3)$, where ZM₂₀ is ZrMo₂O₇(OH)₂(H₂O)₂, was previously synthesized in [14] using L/S = 8/1.

SZS and SZS/(SiO₂-Al₂O₃) composites. The HIL and GAI hydrothermal syntheses were carried out in reaction mixtures of 3M NaOH, ZrOCl₂ and SiO₂ \cdot nH₂O at 160 and 180 °C, accordingly, taking into account the NaOH molarity, Zr/Si and L/S ratios reported in [18]. The 5 wt. % SZS/(SiO₂-Al₂O₃) composites, HIL/(SiO₂-Al₂O₃) and GAI/(SiO₂-Al₂O₃), were prepared by impregnation of the microsphere support (Sample 2) with SZS-ethanol suspension containing pre-syn-



Fig. 1. SEM images of $ZM_{1.7}/(SiO_2-Al_2O_3)$ (*a*), $ZM_{1.7}$ (*b*) and $ZM_{2.0}$ phases (*d* [14]*) on the microsphere surface; PXRD pattern of $ZM_{1.7}/(SiO_2-Al_2O_3)$ (*c*); Zr and Mo distribution map (*e*); EDX spectrum (*f*) of $ZM_{1.7}/(SiO_2-Al_2O_3)$ surface fragment (*e*); Cs⁺ (*g*) and Sr²⁺ (*h*) sorption isotherms for $ZM_{1.7}/(SiO_2-Al_2O_3)$ (points – experimental data, lines – Langmuir fit).

 \ast Figure 1, d was reprinted from [14] with permission from Elsevier.

thesized HIL and GAI (fraction $<36 \mu$ m), followed by drying at 70 °C.

Characterization techniques

The surface morphologies were examined by scanning electron microscopy (SEM, TM-1000, TM-3000 and S-5500, Hitachi). Energy-dispersive X-ray spectroscopy (EDX, TM-3000 with Bruker microanalysis system) was used to analyse the chemical composition of solid surfaces. The crystalline structure was determined by powder X-ray diffraction (PXRD, PANalytical X'Pert PRO) using CuK_a radiation. The BET specific surface area (SSA, m²/g) was determined from the volumes of gaseous nitrogen adsorption (Nova 3200e and NovaWin Software, Quantachrome Instruments). The Cs⁺ and Sr²⁺ concentrations in solutions were measured by flame atomic absorption spectroscopy (AAS-30, Carl Zeiss).

Sorption experiments

Batch sorption experiments were performed upon contacting the specimen $(0.05\pm0.005 \text{ g})$ with $CsNO_3$ or $Sr(NO_3)_2$ solution of 0.5-50 mg/L Cs^+/Sr^{2+} at agitation (V = 40 mL; pH ~6.0; T = 20 °C; t = 24 h). The equilibrium Cs^+/Sr^{2+} concentrations in the solid phase (Q_e , mg/g) were determined as $Q_e = (C_0 - C_e)V/m$, where C_0 is the initial metal concentration in the liquid phase, mg/L; C_e is the equilibrium Cs⁺/Sr^{2+} concentration in the liquid phase, mg/L; V is the volume of solution, L; m is the mass of specimen, g.

The experimental sorption data were plotted as $Q_e = f(C_e)$ and fitted by the Langmuir equation: $Q_e = a_m b C_e / (1 + b C_e)$, where a_m is the maximum sorption capacity of the solid, mg/g; *b* is the Langmuir constant, L/mg; C_e is the Cs⁺/Sr²⁺ equilibrium solution concentration, mg/L.

The distribution coefficient values ($K_{\rm d} = Q_{\rm e}/C_{\rm e}$, mL/g) were determined for low concentrations ($C_{\rm e} < 1 \text{ mg/L}$).

RESULTS AND DISCUSSION

 $ZM_{1.7}/(SiO_2-Al_2O_3)$. The zirconium molybdate/cenosphere composite is one more member of microsphere ion exchangers bearing zirconium molybdate [14, 19]. Two types of zirconium molybdate compounds covering the cenosphere-derived supports have been already synthesized, such as crystalline zirconium molybdate with fixed stoichiometric composition $ZrMo_2O_7(OH)_2(H_2O)_2$ (ZM_{20}) identified in [14] and amorphous micromesoporous zirconium molybdates with Mo-to-Zr molar ratios of 0.4 (ZM_{04}) and 6.4 (ZM_{64}) [19]. All of them displayed the enhanced sorption ability with K_d of about 10^3-10^4 mL/g. The acid resistance of cenosphere-based glass-crystalline supports [13] makes it possible to perform the composite preparation in acid media by deposition of the as-synthesized compound on the support surface. As reported by Clearfield et al. [20], variation of synthesis conditions (concentration, pH, temperature, the reactant mole ratio, etc.) can provide the variability of compositions of the systems M(IVB)O₂-M(VIB)O₂-H₂O, where M(IVB) = Ti, Zr, or Hf and M(VIB) = Mo or W. A variety of non-stoichiometric hydrous compositions with mole ratios of $1 \le M(VIB)O_3/M(IVB)O_3 \le 2$ can be produced. In the present study, the reactant Na_2MoO_4 -to-mZr $O_2/(SiO_2-Al_2O_3)$ ratio was changed, compared to preliminarily synthesized $ZM_{20}/(SiO_{2}-Al_{2}O_{3})$ [14].

Figure 1 and Table 1 present the results of SEM, PXRD, EDX, and sorption studies of the resulting microsphere composite in comparison with the SEM data and sorption parameters for $ZM_{2,0}/(SiO_2-Al_2O_3)$ [14].

As shown by the SEM data of the target microsphere product (see Fig. 1, *a*, *b*), the discoid crystallites with the thickness of 10–15 nm and diameter of 400–600 nm are visualized on the surface of the microsphere support as the main phase. The phase particles differ by the habit from the elongated rod-like $\text{ZrMo}_2\text{O}_7(\text{OH})_2(\text{H}_2\text{O})_2$ crystallites formed in the case of $\text{ZM}_{2.0}/(\text{SiO}_2-\text{Al}_2\text{O}_3)$ (see Fig. 1, *d*) [14]. As follows from the PXRD study (see Fig. 1, *c*), three crystal phases are revealed in the composite, such as quartz, a part of the glass-crystalline support, $\text{Mo}_3\text{O}_9 \cdot \text{H}_2\text{O}$ (hexagonal syngony, space group P63/m) as a minor phase, and an unknown phase (Phase X). By the

TABLE	1
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Parameters of the Langmuir isotherms and $K_{\rm d}$ for Cs^+ and Sr^{2+} sorption on the microsphere composites

Sample	Sorbed	a _m ,	R^2	$K_{\rm d}^{}$,
	cation	mg/g		mL/g
$\mathrm{ZM}_{1.7}/(\mathrm{SiO}_2-\mathrm{Al}_2\mathrm{O}_3)$	Cs^+	9.8	0.97	$0.5\cdot 10^4$
	Sr^{2+}	15.0	0.98	$1.7\cdot 10^4$
$ZM_{2.0}/(SiO_2-Al_2O_3)$ [14]	Cs^+	6.9	0.99	$0.9\cdot 10^2$
	Sr^{2+}	21.5	0.98	$0.4\cdot 10^3$
$\mathrm{HIL}/(\mathrm{SiO}_2\mathrm{-Al}_2\mathrm{O}_3)$	Cs^+	7.8	0.98	$0.3\cdot 10^4$
	Sr^{2+}	20.3	0.98	$0.4\cdot 10^4$
$GAI/(SiO_2-Al_2O_3)$	Cs^+	17.8	0.99	$0.6\cdot 10^4$
	Sr^{2^+}	22.4	0.96	$0.3\cdot 10^4$



Fig. 2. SEM images of HIL/(SiO₂-Al₂O₃) (*a*) and its surface fragment (*b*), HIL (*c*,*e*) and GAI (*d*) particles (*e*); PXRD pattern of SZS (*f*); Cs⁺ (squares) and Sr²⁺ (circles) sorption isotherms for GAI/(SiO₂-Al₂O₃) (*g*) and HIL/(SiO₂-Al₂O₃) (*h*) (points – experimental data, lines – Langmuir fit).

SEM-EDX data, Zr and Mo are distributed uniformly in the bulk of the covering phase with the Mo/Zr molar ratio of about 1.7 (see Fig. 1, *e*, *f*). This observation gives reason to consider that crystal zirconium molybdate with the Mo/Zr molar ratio of 1.7 and disk-like shape of crystallites is more likely to be the main coating phase. The nanosized intercrystallite voids are likely to be responsible for developing the microsphere specific surface area up to 10 m²/g, compared to the initial microsphere support having the SSA of 0.7 m²/g.

The Cs^+ and Sr^{2+} sorption isotherms for $ZM_{17}/(SiO_{2}-Al_{2}O_{3})$ are presented in Fig. 1, g, h, and the parameters of the Langmuir equation (a_m, K_d) are given in Table 1. It can be seen that the Langmuir model adequately fitted the experimental data with high correlation coefficients (R^2). The sorption parameters of $ZM_{1.7}/(SiO_2-Al_2O_2)$ were compared with the corresponding ones of $ZM_{20}/(SiO_2-Al_2O_3)$ (see Table 1). The data show that $ZM_{17}/(SiO_{2}-Al_{2}O_{3})$ captures Cs^{+} and Sr^{2+} more efficiently in the range of low concentrations ($K_{\rm d} \sim 10^4$ mL/g) than $ZM_{2.0}/(SiO_2-Al_2O_3)$ ($K_{\rm d} \sim 10^2-10^3$ mL/g) [14]. Both composites are characterised by the higher Sr^{2+} sorption capacity over the a_m values for Cs^+ sorption. The enhanced $a_{\rm m}$ and $K_{\rm d}$ values for ${\rm Sr}^{2+}$ sorption make it promising to use the $\rm ZM_{1.7}/(SiO_2-Al_2O_3)$ composite in a wide range of Sr²⁺ contents in waste solutions. The structural peculiarities of the ZM_{17} phase, for example, the availability of tunnel or layered structure facilitating the bulk cation diffusion, is more likely to be the key factor of its enhanced affinity for the cations compared to $ZM_{20}/(SiO_{2}-Al_{2}O_{2})$ having the coating phase of a compact structure [14, 20].

SZS/(SiO₂-Al₂O₃). Microporous sodium zirconium silicates (SZS) were used as components of microsphere composites due to their unique ion-exchange properties [18, 21, 22]. The tetrahedral-octahedral frameworks based on ZrSi₂O₀ formulation, such as hilairite $Na_2 Zr Si_3 O_9 \cdot 3H_2 O$ (HIL) and gaidonnayite Na,ZrSi,Õ, · 2H,Õ (GAI), are known to be the promising ion exchangers providing Cs⁺ and Sr^{2+} sorption with $K_{\mathrm{d}} > 10^5 \mathrm{~mL/g}$ [18]. At present, powdered forms of the zirconosilicates were mainly synthesized [18]. The direct one-pot synthesis of SZS/cenosphere composites is rather problematic because of the solubility and reactivity of cenosphere-based glass support under hydrothermal alkaline conditions required to synthesize SZS [23]. Therefore, two-step preparation of SZS/cenosphere composites was undertaken

including preliminary synthesis of pure phases GAI and HIL, followed by impregnation of a microsphere macroporous shell with the SZS particles of a given size (Fig. 2, a,b).

As follows from SEM data (see Fig. 2, c-e), the selected pure SZS fractions consist of particles not larger than 10 µm with an average size of 3-5 µm for the majority of particles. The proportionality of SZS particles and open pores in microspheres enabled fixing the SZS powder in the support macroporous wall (see Fig. 2, b). Hydrothermally grown SZS crystals have the foliated structure owing to very thin flakes (see Fig. 2, c,d) with the SSA of 17 and 12 m²/g for HIL and GAI particles, respectively. The PXRD patterns indicate that the HIL phase is characterized by lower crystallinity compared to the GAI phase (see Fig. 2, f), each of the SZS phases bearing another one as a minor phase.

The Cs^+ and Sr^{2+} Langmuir isotherms, as well as K_{d} and a_{m} values for the HIL/(SiO₂-Al₂O₃) and GAI/(SiO₂-Al₂O₂) composites, are given in Fig. 2, g,h, and in Table 1. As shown, the Langmuir isotherms fitted the experimental data with high correlation coefficients. The K_{d} values of up to 10^4 mL/g are characteristic for the Cs⁺ and $\ensuremath{\mathsf{Sr}}^{2^+}$ sorption at low metal concentrations. The main difference between the $HIL/(SiO_2-Al_2O_3)$ and $GAI/(SiO_2-Al_2O_3)$ sorption behaviour is in their capacities with respect to Cs⁺. If the $GAI/(SiO_2-Al_2O_3)$ composite sorbs Cs^+ and Sr^{2+} approximately in an equal amount (17.8 and 22.4 mg/g, respectively), the Cs^+ sorption capacity of $HIL/(SiO_2-Al_2O_3)$ is about three times lower than the a_m value determined for Sr^{2+} sorption (7.8 and 20.3 mg/g, respectively). The observation of preferable Sr^{2+} sorption on the hilairite phase is in agreement with the data reported by Bortun et al. [18]. Based on the a_m and K_d values, both SZS-based microsphere composites can be suitable for Sr^{2+} removal from solutions with low and high Sr²⁺concentrations.

The sorption capacities and $K_{\rm d}$ values of the cenosphere-based sorbents are somewhat lower than the same ones of the known powdered sorbents, *e. g.* monosodium titanate [24], zirconium silicates [18], but the granular form and low cost can be considered as their prospective features.

CONCLUSION

The resource-saving method of the preparation of novel microsphere sorbents based on cenosphere-supported zirconium molybdate and sodium zirconium silicates of hilairite and gaidonnayite structural types was developed. Their sorption properties with respect to Cs⁺ and Sr²⁺ as nonradioactive imitators of radionuclides ¹³⁷Cs and ⁹⁰Sr were evaluated based on the distribution coefficient K_d and maximum sorption capacity a_m . The influence of the composition and structure of supported components on the sorption ability of the composites was demonstrated. The composites efficiently trap Cs⁺ and Sr²⁺ from simulated solutions with K_d of up to 10^4 mL/g. The high values of distribution coefficients are expected to provide the efficient removal of cesium and strontium from wastewater at their low concentrations. The proposed approach to the preparation of the composite sorbents along with their high sorption parameters favours their further thorough testing under various conditions using the ¹³⁷Cs and ⁹⁰Sr bearing solutions.

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