SORPTION PROPERTIES OF GRAPHEN OXIDE AND STYRENE COMPOSITES FOR SR-85 AND CS-137

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Abstract

In the presented work, new composite nanomaterials, based on graphene oxide and styrene, have been developed for the retention purpose. ^{85}Sr and ^{137}Cs represent two of the main fission products being present in radioactive wastes from nuclear power cycle. The graphene oxide samples were prepared from natural graphite using high intensity cavitation field in a pressurized (6 bar) batch-ultrasonic reactor. Graphene oxide polystyrene composite was synthesized using direct emulsion polymerization of styrene in the presence of graphene oxide at 90 °C. The basic method used for the evaluation of nanomaterial retention properties was batch sorption methodology, based on a contact of solid material with a tracer solution under defined boundary conditions (solid/solution ratio, time, solution composition as pH and ionic strength).

Keywords: graphene oxide, sorption, radionuclides

1. INTRODUCTION

Any activity that produces or uses radioactive materials generates radioactive waste. Disposal of radioactive waste is a complex issue, not only because of the nature of the waste, but also because the need to solve the problem not to burden future generations. Cesium is one of the most important nuclides. The reasons for this are following: the isotope ^{137}Cs has high gamma radiation and half-life 30.08 years. The isotope ^{135}Cs has very long half-life of about 2.3 million years. The isotope belongs to the group of isotopes in nuclear waste that are present for the very long time scales and can be conveyed far from the containment. Another important radioisotope in nuclear waste is strontium. The isotope ^{90}Sr belongs to mid-lifed isotopes with the half-life of 29 years. Cesium is chemically very similar to potassium as strontium is similar to calcium. They both can then penetrate into the living organism and expose it to internal irradiation. Therefore it is necessary to prevent migration of these radionuclides to the biosphere and develop progressive retention techniques.

Graphene oxide (GO), a two dimensional carbon material with large specific surface area has been studied extensively as catalyst, material for hydrogen storage/production [1], gas sensors [2] or electronics [3]. In recent years there were studies about utilization of GO and its modification as the sorbent for several contaminants. GO without any modification was utilized by Cai et al. for the sorption of an organic matter [4] and by Gopalakrishnan et al. for the separation of several heavy metals – Pb(II), Ni(II) and Cr(VI) [5]. Li et al. studied sorption of U(VI) on GO [6]. The interaction of GO with actinides including Am(III), Th(IV), Pu(IV), Np(V), U(VI) and typical fission products Sr(II), Eu(III) and Tc(VII) were described by Romanchuk et al. [7]. Several authors modified the GO to increase its sorption properties. The composites of GO with natural materials as chitosan or chitin were utilized for the separation of Cr(IV) [8], [9] or dyes remazol black and neutral red [10]. Chen et al. synthesized GO-TiO_2 composite for the sorption of ^{60}Co [11]. Several authors studied sorption of radionuclides on different GO composite materials - Cs(I) on magnetic prussian blue/GO encapsulated in calcium alginate microbeads [12], Cs(I) and Sr(II) on magnetic GO [13], Co(II) and Sr(II) on GO-magnetite [14]. Recently, there were several studies about synthesis and sorption properties of composites of GO with polymers. Zhou et al. synthesized polysiloxane-GO gel as an effective sorbent for

Pb(II) and Cd(II) [15]. Zhao et al. functionalized a surface of GO with polydopamine for separation of U(VI) from aqueous solutions [16].

Retention processes of key important radionuclides Cs(I) and Sr(II) were studied within this study. GO polystyrene composite was synthesized using the direct emulsion polymerization of styrene in the presence of GO [17]. This nanomaterial could be effective adsorbent for remediation of waters contaminated by radionuclides or for reprocessing of nuclear waste.

2. MATERIALS AND METHODS

High resolution scanning electron microscopy (HRSEM) analysis was conducted on a FEI Nova NanoSEM scanning electron microscope equipped with an Everhart-Thornley detector, Through Lens detector and accelerating voltage 1-30 kV. The sample was deposited on the silicon chip substrate 5x5 mm.

Diffraction patterns were collected with diffractometer Bruker D2 equipped with conventional X-ray tube (Cu Kα radiation, 30 kV, 10 mA). The primary divergence slit module width 0.6 mm, Soller Module 2.5, Airscatter screen module 2 mm, Ni Kbeta-filter 0.5 mm, step 0.00405°, a counting time per a step 1 s and the LYNXEYE 1-dimensional detector were used. The range of measurement is from 5° to 90° 2Theta.

Qualitative analysis was performed with the DiffracPlus Eva software package (Bruker AXS, Germany) using the JCPDS PDF-2 database. For quantitative analysis of XRD patterns we used Diffrac-Plus Topas (Bruker AXS, Germany, version 4.1) with structural models based on ICSD database. This program permits to estimate the weight fractions of crystalline phases and mean coherence length by means of Rietveld refinement procedure.

2.1. Preparation of sorption materials

The graphite was exfoliated with the effect of high intensity ultrasound and delaminated graphene nanosheets were used for graphene oxide [18] preparation by improved Hummers method [19]. H_2SO_4 (60 ml), H_3PO_4 (10 ml), graphene (1 g), and $KMnO_4$ (3 g) were mixed in a round-bottom flask. The mixture was then heated to 40 °C and stirred for 6 h, affording a pink, dense suspension. The suspension was then poured onto a mixture of ice and 30% H_2O_2 (200 ml), and the pink suspension quickly turned bright yellow. The product was purified by dialysis (Spectra/Por 3 dialysis membrane) and centrifuged. Purified GO product was obtained as a brown, honey-like suspension. The oxidation was quantitative when the theoretical yield was assumed to equal the starting graphite mass. The elemental analysis of prepared GO showed an overall composition of C 48.8 %, H 2.1% and O 49.1% (impurities from natural graphite: SiO_2 1%, K_2O 3.2%, CaO 0.6%, TiO_2 1.3%, CuO 1.5%, ZnO 1.5%). The content of carboxylic group -COOH in the graphene oxide was increased by reaction with monochloroacetic acid [20].

Graphene oxide polystyrene composite was synthesized using direct emulsion polymerization of styrene in the presence of graphene oxide at 90 °C [17]. Hydrothermal conditions were maintained in stainless steel stirred autoclave. The graphene oxide was dispersed in 400 ml distilled water. After that argon gas was used for 10 minutes to purge oxygen from the solution. Styrene (30 ml) and divinylbenzene (1 ml) were added into solution. The solution was under constant stirring and heating until the reaction temperature reached to 91 °C, after that 12 ml solution of sodium 4-styrenesulfonate (4.00 g of sodium 4-styrenesulfonate in 100.0 ml water) was added. After 3 min the 24 ml solution of sodium 4-styrenesulfonate (4.00 g of sodium 4-styrenesulfonate in 100.0 ml water) and 1 ml of the solution of potassium persulfate and sodium bicarbonate (1 g $K_2S_2O_8$ and 3.5 g $NaHCO_3$ in 100 ml water) was added. The reaction mixture is continuously stirred and heated. After 85 min a mixture of 6 ml styrene, 0.15 ml divinylbenzene, 24 ml of water, 24 ml solution of sodium 4-styrenesulfonate, and 3 ml of the solution of potassium persulfate and sodium bicarbonate were added; heating and stirring continuous next hour. The obtained sample was centrifuged 10 minutes at 10 000 rpm. The main fraction was filtered off and dried at 60 °C.

2.2. Sorption experiments

The sorption properties of produced nanomaterials were evaluated by batch sorption experiments, based on the contact of solid material with tracer solution. The volume of the solution was 1.5 ml and the mass of the sorbent was 0.01 g. The salts CsCl and $SrCl_2$ were used as carrier for radionuclides ^{137}Cs and ^{85}Sr, respectively. In the case of the kinetics experiments the concentration of CsCl or $SrCl_2$ was $2 \cdot 10^{-5}$ mol/L. These solutions were spiked by ^{137}Cs or ^{85}Sr. The contact time was 24 hours unless otherwise specified. Sorption experiments were carried out at 24 °C under atmospheric conditions. After the adsorption of radionuclides, the suspension was filtered and an aliquot of the supernatant was measured on the gamma spectrometer (EMPOS MC1256) using NaI(Tl) detector. The volume of measured aliquot was 0.5 ml.

The sorption experiments were described by the distribution coefficient (K_d) and percentage of the sorption. The definition of K_d is following:

$$\mathrm{K_d} = \frac{\mathrm{c_{mass}}}{\mathrm{c_{volume}}} \cdot \frac{\mathrm{V}}{\mathrm{m}} \ [\mathrm{ml/g}], \tag{1}$$

where c_{mass} is the concentration of the sorbate adsorbed onto the solid phase, c_{volume} is the concentration of the sorbate in solution, V [ml] is the volume of the liquid phase and m [g] is the mass of the sorbent.

Langmuir (2) [21] and Freundlich isotherm (3) [22] were utilized for evaluation of the sorption data. The cation exchange capacity was determined by Langmuir isotherm:

$$q_{\mathrm{e}} = \frac{K_{\mathrm{L}} \cdot q_{\mathrm{max}} \cdot c_{\mathrm{e}}}{1 + K_{\mathrm{L}} \cdot c_{\mathrm{e}}} \ [\mathrm{mg/g}], \tag{2}$$

where q_{max} is the maximum sorbate uptake (mg/g), K_{L} is the coefficient (L/mol), c_{e} is the equilibrium concentration of the solute (mg/L) and q_{e} is the adsorbed amount of the sorbate on the sorbent (mg/g). Freundlich isotherm is defined as

$$q_{\mathrm{e}} = K_{\mathrm{F}} \cdot c_{\mathrm{e}}^{\frac{1}{n}}, \ [\mathrm{mg/g}], \tag{3}$$

where K_{F} ((mg/g)/(mg/L)$^{1/n}$) and n are characteristic constants related to the adsorption capacity and the adsorption intensity, respectively. The experimental data were fitted in program SciDAVis 0.2.4 that uses the nonlinear least-squares Marquardt-Levenberg algorithm for fitting.

3. RESULTS AND DISCUSSION

As can be seen from the Fig. 1, the polystyrene has two diffraction lines with high intensity, first at 10.3° an second at 18.5°. There are not any GO lines in the GO-polystyrene. The reason is that concentration of GO is too low for detection by this method. The intensity of the two diffraction lines in polystyrene is different in GO-polystyrene, which suggest that one crystal lattice is preferred.

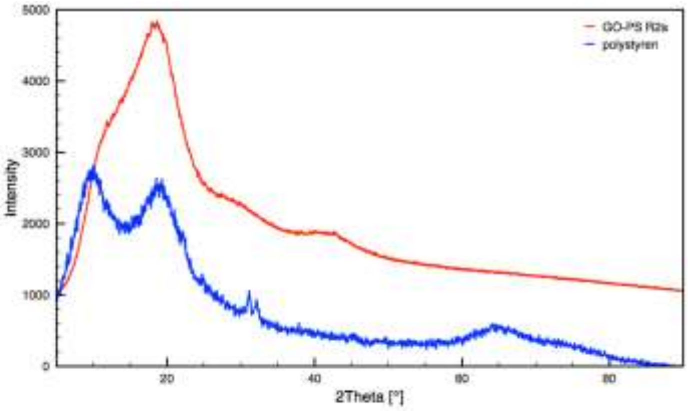

Fig. 1 X-ray diffraction patterns of the prepared samples with polystyrene and GO-polystyrene.

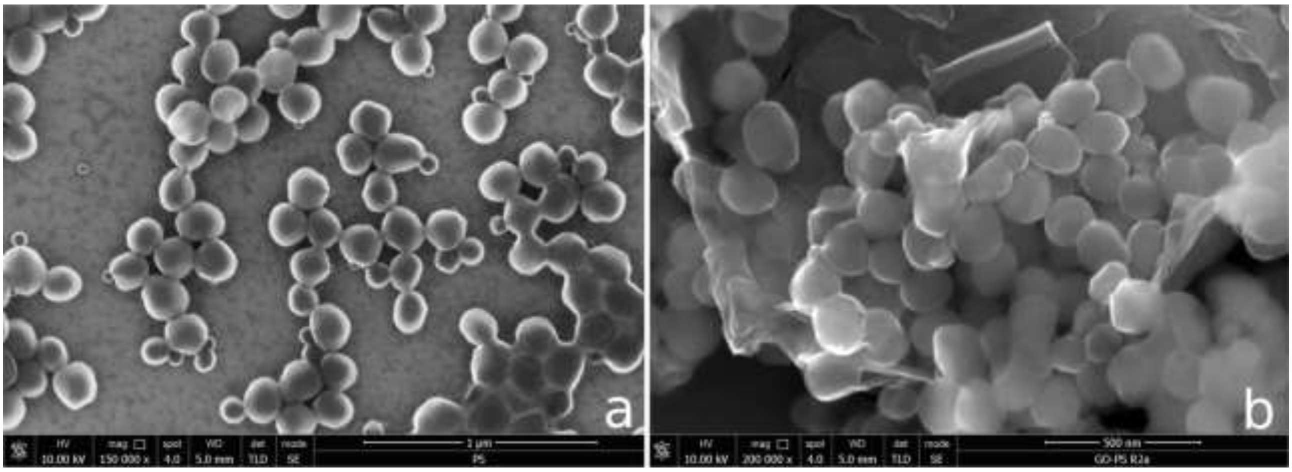

Fig. 2 Scanning electron microscopy observations of the prepared materials: polystyrene (a) and GO-polystyrene (b).

The Fig. 2 (a) demonstrates the morphology of polystyrene – spherical particles with diameter of 100-200 nm. The Fig. 2 (b) demonstrates the morphology of and GO-polystyrene. The polymer and GO form an interconnected bulk network as the GO is uniformly dispersed in the polystyrene matrix.

Table 1 Sorption of Cs and Sr on polystyrene and GO-polystyrene.

	Cs(I)		Sr(II)	
	%(Cs)	pH	%(Sr)	pH
polystyrene	5,0	3,4	16,6	3,2
GO-polystyrene	90,2	4,8	98,4	5,3

The Table 1 demonstrates the sorption of Cs(I) and Sr(II) on polystyrene (it was prepared by the same method like the composite material only without adding of GO) and on the composite material GO-polystyrene. The results demonstrate that sorption of selected radionuclides is on the pure polystyrene very low – only 5.0 % for Cs(I) and 16.6 % for Sr(II). On the other side, the sorption on GO-polystyrene is very high – 90,2 % for Cs(I) and 98,4 % for Sr(II). Therefore the modification of polystyrene by GO increases the sorption properties.

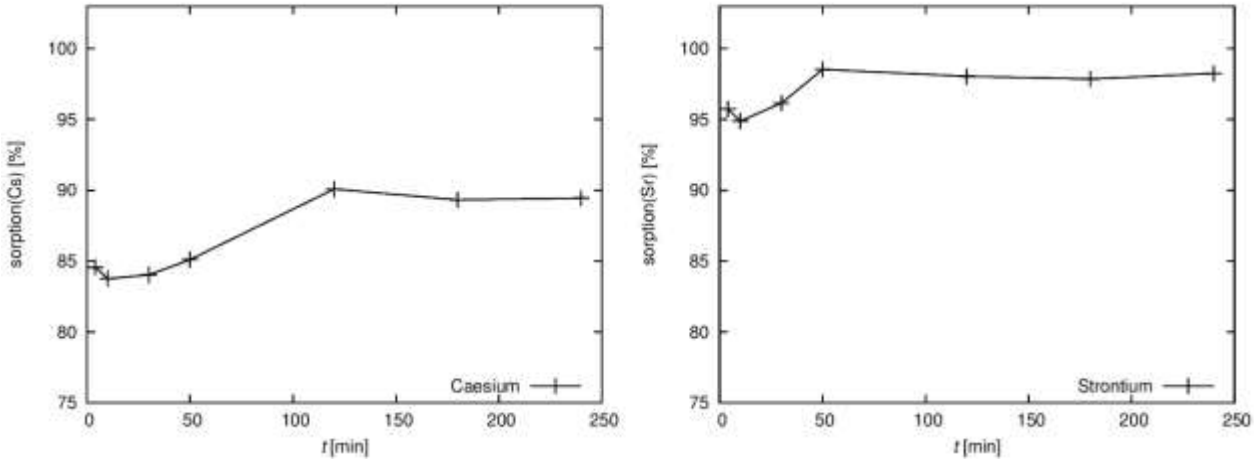

Fig. 3 Dependence of the sorption of Cs(I) (left) and Sr(II) (right) on contact time; V =1.5 ml; m=0.01 g; temperature 24 °C.

The Fig. 3 demonstrates that the sorption kinetics of GO-polystyrene is very fast for both radionuclides. The Cs(I) reach maximum after 2 hours, the Sr(II) reach maximum after 1 hour. The pH of equilibrium solution for Cs(I) was around 5.0 and for Sr(II) pH was around 5.5.

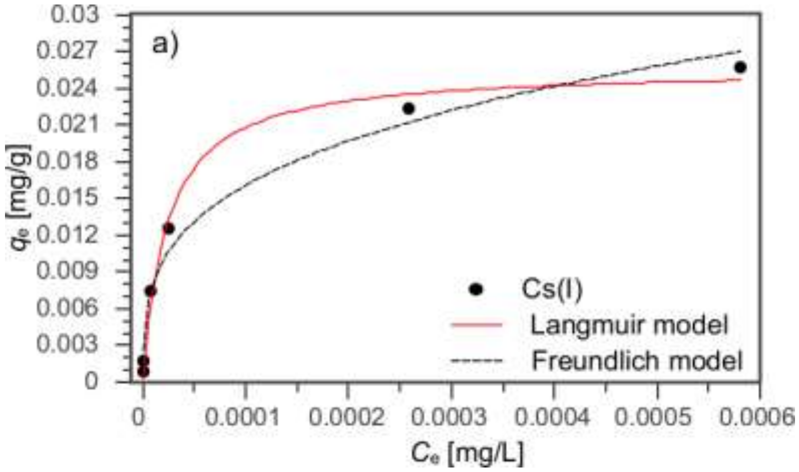

Fig. 4 Experimental data and Langmuir and Freundlich isotherms of Cs(I); V =1.5 ml; m=0.01 g; temperature 24 °C.

The Fig. 4 demonstrates the experimental data and Langmuir and Freundlich isotherms of Cs(I). The Table 2 demonstrates the parameters of Langmuir and Freundlich models of Cs(I) adsorption on GO-polystyrene. As can be seen in Table 2, the adsorption of Cs(I) on GO-polystyrene can be better fitted by Langmuir model (R^2=0.990) compared to Freundlich model (R^2=0.977). The maximum adsorption capacities (q_{max}) of GO-polystyrene calculated from Langmuir model at pH 4.0 and temperature 24 °C were 0.026 mg/g for Cs(I).

Table 2 Parameters for Langmuir and Freundlich models of Cs(I) adsorption on GO-polystyrene at temperature 24 °C.

Langmuir model			Freundlich model		
q_{max} [mg/g]	K_L [L/mol]	R^2	K_F [(mg/g)/(mg/L)$^{1/n}$]	n	R^2
0,026	43032	0,990	0,243	3,39	0,977

4. CONCLUSION

Nanocomposite material GO-polystyrene have been successfully prepared by the direct emulsion polymerization of styrene in the presence of GO. The results (Table 1) demonstrates that GO-polystyrene has enhanced sorption properties for Cs(I) and Sr(II) than polystyrene alone. The SEM (Fig. 2) demonstrates the morphology of GO-polystyrene – spherical polystyrene particles with diameter of 100-200 nm covered by GO. The Langmuir isotherm better fit experimental data than Freundlich isotherm as demonstrated on Fig. 3. The maximum sorption capacity of Cs(I) was determined from Langmuir isotherm – 0,026 mg/g.

ACKNOWLEDGEMENTS

We thank for the support from Ministry of the Interior of the Czech Republic (Project No. VG20132015132).

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