Use of activated sulfonated polystyrene for a model wastewater effluent purification by adsorption of cesium (Cs), strontium (Sr), and cobalt (Co)

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ABSTRACT

With a view of optimization of a waste treatment system, activated polystyrene was employed for effluents laboratory purification tests, by adsorption of Cs, Ce and Co. The effluent contains the elements of interest in the case of treatment of radioactive effluents. For this purpose, polystyrene from industrial packaging was sulfonated using a solution containing H_2SO_4, ethylenediamine tetraacetic acid and benzene. The sulfonation conditions were optimized: solid/liquid ratio: S/L, temperature and sulfonation time. Adsorption tests were carried out under different conditions of temperature (25°C, 40°C and 50°C), contact time (4, 6 and 8 h) and S/L ratios (1:5, 2:5 and 1:2). Sulfonation was followed by Fourier-transform infrared spectroscopy. The characterization showed the main peaks of: O=S=O at 1,030–1,050 cm^{-1}. The examination of the polymeric microstructure was carried out by scanning electron microscopy analysis. Adsorption tests were followed by plasma induction spectrometry quantitative analysis inductively coupled plasma-atomic emission spectroscopy. Cs was the best adsorbed of the three elements, with more than 98% for 50°C and 6 h, followed by Co, and Sr. The best values were 14.91% for Co and 4.70% for Sr. The best adsorption conditions were to the advantage of the average conditions of temperature and time.

Keywords: Polystyrene; Sulfonation; Adsorption; Inductively coupled plasma analysis

1. Introduction

From the nuclear power industry to medicine and research, there are many sources of radioactive waste. This waste can be in solid, gaseous or liquid form and require specific treatment before being released into the environment. Their decontamination consists in extracting most of the radioactivity and concentrating it in a small solid volume. The solid concentrate is then conditioned and stored. This step of „concentrating" the radioactivity in a solid compound allows to considerably reduce the volume of waste. These effluents frequently contain various radionuclides including: cesium 137, strontium 90, and cobalt 60. Cobalt 60 is a short-lived (5.3 y) emitter of β and γ radiation strontium 90 is a short-lived (29.1 y) β-radiation emitter and cesium 137 is a β and γ radiation emitter with a short half-life (30 y). They can be found in liquid effluents, and as aerosols in gaseous effluent. These characteristics make them particularly radiotoxic because they can easily move through the ecosystems. There are many physico-chemical

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water treatment process to extract and recover radioactive elements before discharge into the aquatic environment. We can summarize: evaporating, precipiation and co-precipitation, adsorption, and ion-exchange

This study was carried out to develop a Cs-selective material of a polymeric nature with good mechanical strength and to examine its decontamination performance. The material in question was polystyrene (PS). The polystyrene selected was derived from packaging products. It is an abundant waste material with great potential that can be recovered for the purification of radioactive effluents. Sulphonation was the chosen mode of activation of the PS. Scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR) characterisation of the base polystyrene was carried out before and after activation. The solid-liquid extraction tests were carried out by a batch method, optimising the adsorption conditions, and the quantitative analysis of the effluents after extraction was carried out by inductively coupled plasma-atomic emission spectroscopy (ICP-OES). Once extraction is complete, if the remaining effluent has not reached a level of Cs, Co, and Sr that allows it to be discharged into the environment, then the treatment will be repeated in order to achieve this objective. As for the substrate loaded with radionuclides, it becomes solid radioactive waste and must undergo other processes before being conditioned as a containment matrix.

2. Materials and methods

2.1. Polystyrene

Expanded polystyrene from waste packaging was used to prepare a polystyrene solution. The base polystyrene (PS) was dissolved in an organic solvent benzene (Prolabo, purity > 99.7%), dried at 50°C overnight, and ground to obtain a polystyrene powder. The powdered sample was incorporated into a medium that does not absorb in the mid-IR, in this case potassium bromide KBr (Merck). Thin films were obtained by uniaxial pressing of a mixture containing 1–2 mg of polystyrene supplemented to 100 mg with KBr. The analysis was performed using a Thermo Scientific Nicolet 6700 FTIR spectrophotometer. The sample holder was an attenuated total reflectance (ATR) attachment (Thermo Scientific Smart Orbit) with a diamond crystal. FTIR spectra were obtained after 32 scans at 4 cm resolution in a spectral range of 500–4,000 cm^{-1}, in transmittance mode. The spectra were recorded with OMNIC software version 6.0a [copyright 1992–2001 Thermo Nicolet Corporation] in absorbance mode and then converted to transmittance. The observation of the initial polystyrene microstructure was performed by scanning electron microscopy (SEM), using a Philips XL30 equipment, in BSE environmental mode, with a magnification of 200x.

2.2. Polystyrene sulfonation

The initial polystyrene (PS) was reduced to a particle size of 2 mm. The product was put into a sulphonation solution containing: 0.07 g of ethylenediamine tetraacetic acid (Flucka, purity > 98%), 3 mL of sulphuric acid H_2SO_4 (5 M) (Merck, purity > 98%), and 75 mL of benzene C_6H_6 (Prolabo, purity > 99.7%). The amount of PS used was optimised by ranging from 0.224 to 12 g in order to obtain the best yield in quantity of sulphonated polystyrene (PSS). The mixture was kept at 40°C for 4 h, under discontinuous stirring [1]. A phase separation by decantation was necessary to remove excess sulphonation solution. The product was dried at 50°C for 2 h and then air-dried for 48 h to facilitate grinding. Grinding was carried out using a Retsch Zirconium ball mill for 1.5 h. For the FTIR and SEM analysis of the sulphonated substrate, the same experimental protocol was used as for the initial PS. For the water absorption, the PSS powder was soaked in deionized water at room temperature. The powder was weighed after soaking to know its wet mass W_{wet}, then dried in an oven at 50°C for 12 h. The powder was weighed again after a long and total cooling in desiccators, to know its dry mass W_{dry}. The water absorption was determined by the difference in mass between the wet and dry powder. The water absorption was calculated as the percentage increase in mass over dry weight using Eq. (1):

$$\%\text{Water absorption} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{1}$$

where W_{wet}: powder weight mass after soaking and W_{dry}: powder weight mass after drying.

2.3. Adsorption tests

The following commercial reagents were used for preparing the simulated radioactive effluent: strontium nitrate $SrNO_3$ (Merck, 99%), cobalt(II) chloride $CoCl_2$ (Merck 98%), and cesium chloride CsCl (Merck, 99.99%). To a stochoeometric mixture of reagents, distilled water was added in a 1 L flask, maintained at room temperature and under stirring until complete dissolution. The concentrations used were: [Sr] = 0.1 mmol/L, [Co] = 0.2 mmol/L, and [Cs] = 2.4 mmol/L.

To determine the best adsorption efficiency of the elements Cs, Co and Sr, the adsorption conditions of these elements on the PSS were optimized by choosing the powder form having the largest exchange surface for adsorption. Different experimental parameters were optimized such as: contact time (h), ratio (mass of PSS/volume of radioactive effluent = m/V), and temperature (°C). The treatment was applied for one time only and wasn't repeated several times.

Sulfonated polystyrene was added to the effluent solution in small beakers in the ratios: m/V = 1/5, 2/5 and 1/2. The adsorption temperatures were: 25°C, 40°C, and 50°C, and for the adsorption time it was 4 and 6 h. The determination of residual Sr, Cs and Co elements in the effluent solution was performed by ICP-OES, after having made the calibration curves of the elements of interest for the quantitative analysis. For this purpose, a Thermo Scientific iCAP 7400 spectrometer was used, equipped with ITEVA software for analysis. The solutions of the calibration lines were prepared by employing ICP-AES and ICP-MS standards (SCP Science, 1,000 μg/mL, 4% HNO_3), with concentrations of: 2.5, 5.0, 7.5, 10.0 and 12.5 ppm (μg/mL). At the end of each adsorption test, the effluent solution was filtered on filter paper, diluted, and analyzed by ICP-OES.

3. Results and discussions

3.1. Polystyrene FTIR analysis

The FTIR spectrum of the initial PS is given in Fig. 1. It was identified as an atactic poly(styrene) based on the Hummel Polymer Sample Library. The average peaks were observed by the 3 bands: 3,022.77 cm^{-1} for the aromatic stretch, at 2,919.95 cm^{-1} (C–H), and at 1,029.05 cm^{-1} (aromatic C=C stretch). Bending in the C–H plane is observed at: 1,960.30; 1,491.32 and 1,450.36 cm^{-1}, and out-of-plane at: 752.35, 693.83, and 539.18 cm^{-1}.

3.2. Polystyrene SEM analysis

The SEM micrograph of the initial polystyrene (PS) was obtained at 200x magnification. The presence of cells could be clearly seen, confirming the typical structure of the polymers as shown in Fig. 2. It indicates polymeric chains with dimensions ranging from 10 to 100 μm in width. SEM images from the literature show the microstructure of polystyrene and describe it as spherical and elongated particles [2].

3.3. Polystyrene sulfonation

The product (sulfonated substrate) was a white colored paste and after drying become a white powder with a particle size ranging from 200 to 400 μm. The amount of sulfonated substrate was 10.643 g for 12 g of initial PS with a yield of 88.69%.

3.4. Sulfonated substrate FTIR analysis

The FTIR spectrum of the sulphonated substrate is given in Fig. 3. PS peaks were found such as: the band at 3,022.77 cm^{-1} which was due to the unsaturated aromatic stretching vibration [3–7]. The band at 2,919.95 cm^{-1} to the asymmetric (–CH$_2$–) stretching [3,5–8]. At 1,029.05 cm^{-1}, the peak corresponded to the aromatic (C–H) bending [9]. The band observed at: 1960.30 was due to the out-of-plane C–H bending vibration [8]. At 1,491.32, the peak corresponded to the benzene ring stretching [4]. The peak at 1,450.36 cm^{-1} was due to the aromatic C=C stretching [7], and the 752.35/693.83, and 539.18 cm^{-1} were the result of

aromatic –CH– bending modes [9]. After sulphonation, two new intense absorption bands were observed in the spectrum of the sulphonated substrate. The first at 1,211.28 cm^{-1} due to the stretching of the –OH in the SO$_3$H [10], and the second-one at 1,136.1 cm^{-1} due to the stretching S=O vibration [3,5,7,11,12]. Another strong absorbance, which has been attributed to C–S stretching, was detected at 1,005.64 cm^{-1} [13]. However, some absorption bands could not be taken into account. This may be due to several factors, such as symmetry, which significantly reduces the number of bands observed in the FTIR. FTIR analysis therefore confirmed the success of the sulphonation reaction, and the sulphonated substrate was identified as sulphonated polystyrene PSS.

3.5. Sulfonated substract SEM analysis

Only the images obtained at magnifications greater than or equal to 50 μm are presented to facilitate comparison. The SEM micrograph of the sulphonated polystyrene (PSS) is given in Fig. 4a. The PS gave a dark micrograph, but dehydrated cells can be seen in the order of 1–2 μm in size. The dried sulphonated substrate, which was in paste form, does not show the fine microstructure of sulphonated polystyrene, due to the strong agglomeration of the particles. The dried and ground sulphonated substrate clearly showed the shrinkage of the polystyrene fibers after the drying of the sulphonated substrate. The size of the fibres was 3 to 4 μm.
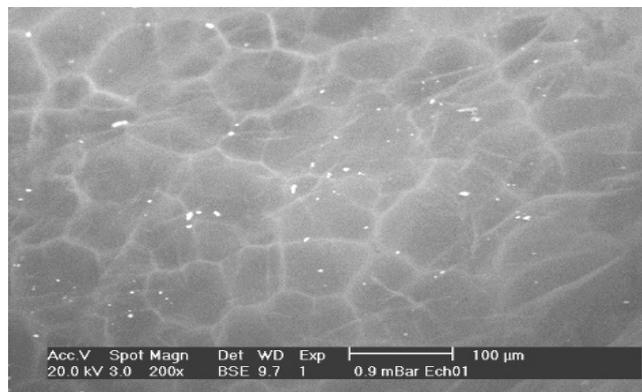
Fig. 2. SEM micrography of initial polystyrene PS.
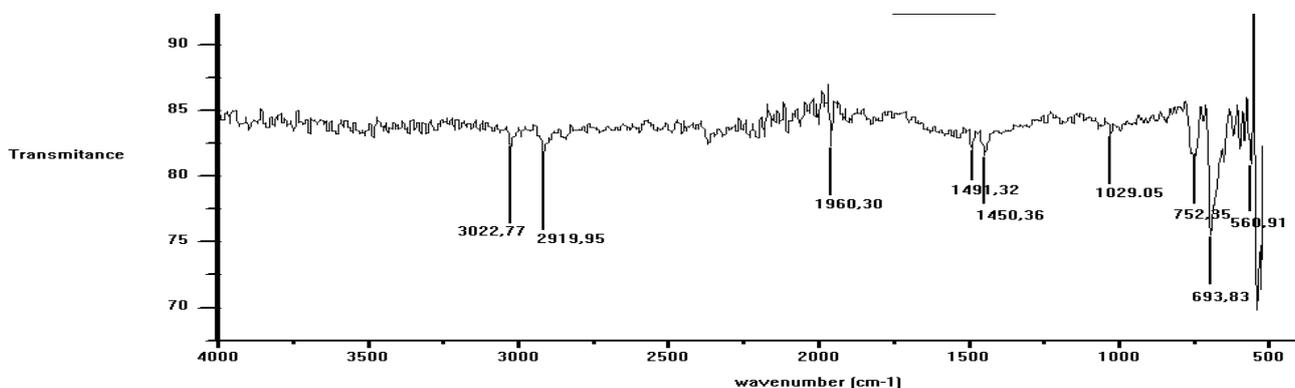
Fig. 1. FTIR spectrum of initial polystyrene PS.
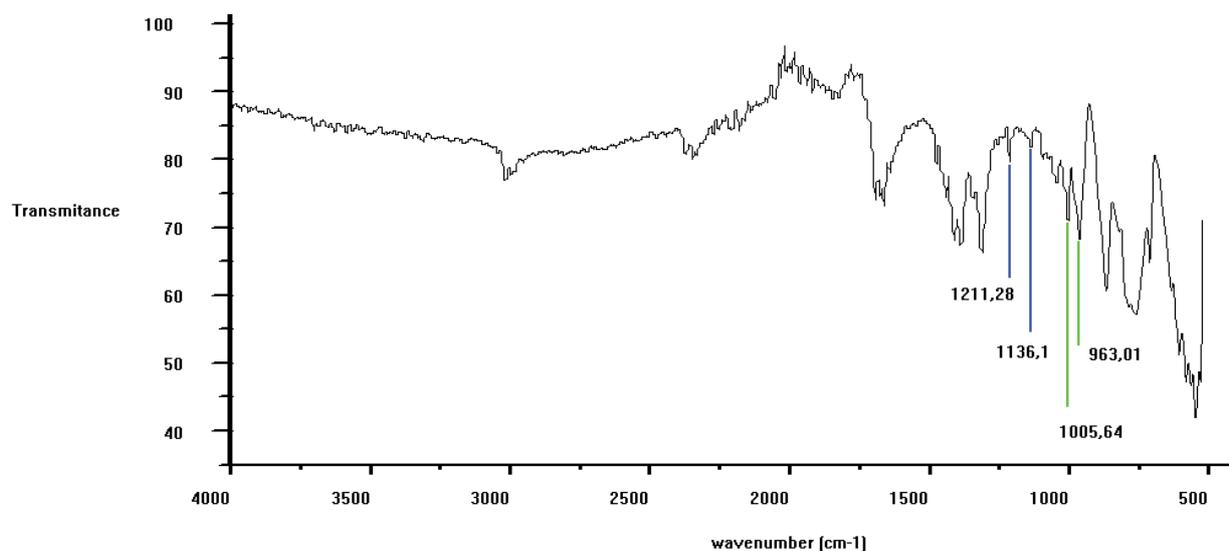
Fig. 3. FTIR spectrum of sulfonated substract.
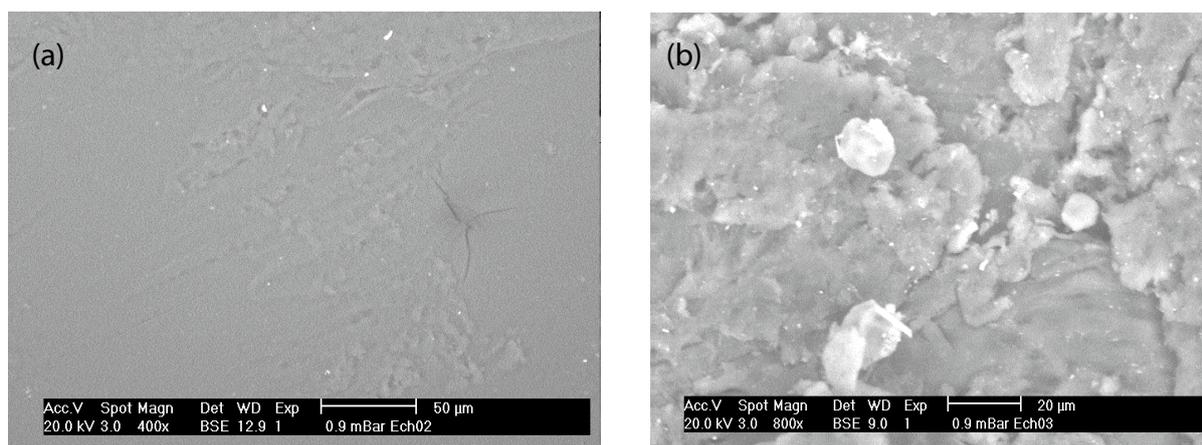
Fig. 4. SEM micrography of (a) sulf sub and (b) dried sulf subt.

These changes could be correlated with the hydrophilic behaviour resulting from the agglomeration of sulphonic or acidic groups (–SO_3H). This increased hydrophilic behaviour contributed to the retention of more water. In other words, the incorporation of the acid group or (–SO_3H) group, present on the aromatic ring of PS increased the average diameter of the fibers due to excessive swelling with water, as shown in Figs. 2, 4a and b. These observations therefore confirmed that the grafting of SO_3 onto polystyrene was successfully achieved [2]. As expected, a surface change between the initial PS and the sulphonated substrate was observed. The initial PS had a smooth surface, but the sulphonated substrate had a rough surface with a color change.

3.6. Water absorption

The results of water absorption on PS and PSS are given in Table 1. Water absorption was enhanced by the presence of hydrophilic ionic groups, in this case the presence of

Table 1
Water uptake results on PS and PSS

Sample	W_{wet} (g)	W_{dry} (g)	Water absorption (%)	Mean value (%)
PS_1	1.6	1.6	0.2	0.18 ± 0.01
PS_2	1.6	1.6	0.2	
PSS_1	4.4	4.3	3	
PSS_2	4.9	4.8	3.4	2.97 ± 0.2
PSS_3	4.8	4.6	3	

sulfonate groups has a significant effect on the hydrophilic nature of the polymer. The water absorption increased with increasing concentration of sulfonate groups. Heat treatment during the drying process reduced the number of water molecules coordinated by the –SO_3– group in sulfonated polystyrene. This affected the transport of protons and water molecules, as the free volume was reduced and the

packing density increased. As the affinity for water increased, the resistance to ionic transport decreased [1].

3.7. Adsorption tests

The residual contents (mg/L) of the elements: Sr, Co and Cs in the effluents are given in Tables 2–4, respectively. The adsorption rates (%) of the elements Sr, Co and Cs at different temperatures, times and m/V ratios are given in Tables 5–7, respectively. Overall, for the three elements, the largest m/V ratio gave the best adsorption rate. The more solid present, the more PSS adsorbed. Except for the average temperature of 40°C, the longest contact time gave the best adsorption. Cs was the best adsorbed of the three elements, with more than 98% for 50°C and 6 h, followed by Co, and Sr. For these last two elements the adsorption was not very efficient. The best values were 14.91% for

Co and 4.70% for Sr. These results were obtained for the longest time and the highest temperature. The extraction selectivity is favourable to the Cs^+ cation because the SO_3H group will bind it more easily instead of the H^+ cation, and much less so for the cations: Co^{2+} and Sr^{2+}. This is directly related to the charges of these radionuclides. For James et al. [14], this selective remediation of Cs instead of Sr is also observed. The maximum calculated loading values were: 273 ± 37 mg/g for Cs and 95.6 ± 2.8 mg/g for Sr.

It can be concluded that to gain efficiency, either increase the adsorption time at room temperature or increase the temperature to 50°C. PSS had an affinity for Cs, but the other elements were less competitive in adsorption. It will be necessary to try to make additional cycles to try to purify this effluent in these elements. In the literature there are only a few reports on adsorption of Cs on PSS. Some adsorbent materials based on sulfonated polystyrene have

Table 2
Sr residual (mg/L)

T (°C)	t (h)	m/V		
		1/5	2/5	1/2
25	4	0.8	6	7.6
	6	0.5	7.7	7.1
40	4	8.9	9.8	7.5
	6	9.1	6.4	3.7
50	4	4.9	19.9	0
	6	9.5	2.8	10.1

Table 5
Sr adsorption rates (%)

T (°C)	t (h)	m/V		
		1/5	2/5	½
25	4	0.3	1.6	3.4
	6	0.1	2.1	3.2
40	4	2.4	2.6	0.3
	6	2.4	1.7	0.1
50	4	0.1	0.5	–
	6	2.6	0.7	4.7

Table 3
Co residual (mg/L)

T (°C)	t (h)	m/V		
		1/5	2/5	1/2
25	4	3	9	9.9
	6	9.2	10.3	9.7
40	4	11.9	12.4	6.1
	6	12.9	12.5	16.9
50	4	32	32.8	0
	6	11.1	6.8	12

Table 6
Co adsorption rates (%)

T (°C)	t (h)	m/V		
		1/5	2/5	1/2
25	4	6.5	6.7	12
	6	6.8	8	12
40	4	8.8	9.2	0.7
	6	9.6	9.3	1.0
50	4	2.4	2.4	–
	6	8.2	5.0	15

Table 4
Cs residual (mg/L)

T (°C)	t (h)	m/V		
		1/5	2/5	1/2
25	4	5.0	3.2	2.2
	6	2.8	3.5	4.9
40	4	6.4	2.4	6.6
	6	4.1	2.7	27
50	4	60.6	23	0
	6	5.1	6.4	7.6

Table 7
Cs adsorption rates (%)

T (°C)	t (h)	m/V		
		1/5	2/5	1/2
25	4	39	25.1	28
	6	22	27.2	62.7
40	4	49	18.3	8.5
	6	32	21.0	17.4
50	4	47	17.9	–
	6	39	49.4	98.2

achieved high purification of wastewater by reducing cadmium concentrations from 10 to 2.30 ppm and manganese from 10 to 1.53 ppm respectively [1].

4. Conclusions

PS polystyrene was utilized to purify a simulated radioactive effluent containing the stable isotopes of Cs, Co, and Sr. This work has allowed for the development of a material that met the hypothesis posed in the introduction, that is, to present the double advantage of continuously decontaminating liquid effluents and to be considered as final waste. The substrate was activated by sulfonation before adsorption and characterized in its raw state (PS), sulfonated (PSS) and after adsorption, by FTIR spectroscopic technique. It was also characterized by SEM. FTIR analysis confirmed the presence of asymmetric and symmetric S=O stretching vibrations as well as symmetric stretching of the $-SO_3$ group. This indicated the success of the sulfonation reaction. The study of the adsorption of Cs, Co and Sr contained in a simulated or model aqueous effluent of a radioactive waste was carried out in batch by optimization f the adsorption parameters. In closing, it would be interesting to study the kinetics of adsorption of the elements Cs, Sr and Co on the PSS, to better elucidate the phenomena involved in the adsorption.

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