Nuclear Engineering and Technology 52 (2020) 1093–1097

Contents lists available at ScienceDirect

Nuclear Engineering and Technology

journal homepage: www.elsevier.com/locate/net

Technical Note

Removal of radioactive methyliodide from the gas stream with a composite sorbent based on polyurethane foam

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ARTICLE INFO

Article history:
Received 10 July 2019
Received in revised form
19 September 2019
Accepted 24 October 2019
Available online 25 October 2019

Keywords:
Gaseous radioactive waste
Methyliodide sorption
Iodine-131
Iodine sorbents
The sorption capacity index

ABSTRACT

A composite iodine sorbent was obtained in the form of porous polymer matrix with activated carbon particles impregnated with triethylenediamine deposited on its surface. A comparative assessment of the radioactive methyliodide capturing efficiency by the composite sorbent and a sample of industrial charcoal sorbent was conducted. It was shown that under the selected testing conditions, the hydraulic resistance of the composite sorbent is lower, and the sorption capacity is higher than that of the industrial charcoal sorbent. A method for comparing the effectiveness of iodine sorbents, based on the calculation of the ratio of the sorption capacity index to the minimum capacity index, needed for the required purification degree was proposed.

1. Introduction

Two-stage air cleaning scheme is used at working premises of modern nuclear power plants. At the first stage, HEPA (High Efficiency Particulate Air) filters remove aerosols; at the second stage, adsorbers filled with granular sorbent are used for removal of the radioiodine chemical forms [1]. In the most cases, activated charcoal with a granule size of about 1–2 mm impregnated with various chemical compounds, providing chemisorption of molecular and organic forms of iodine, is used as a sorbent [2–4].

Granular charcoal sorbents have a number of significant drawbacks, among which are the gradual abrasion of granules during the filter operation, leading to a noticeable increase in hydraulic resistance, as well as the high cost of raw materials for the manufacture of activated carbon [5]. Moreover, the disposal of a large amount of used sorbent is very expensive [1,6].

These factors determine the interest in the search for new forms of iodine sorbents, which are not inferior in efficiency of trapping radioactive methyliodide to granular sorbents based on activated charcoal, but lacking their disadvantages. Besides the granular sorbents, fiber-based sorption-filtering materials are currently in use to localize organic forms of radioiodine. They are produced either from densely woven impregnated carbonized materials [7,8], or from fibers spray-covered with activated carbon powder [9,10]. However, known fiber-based materials and filters often have significant hydraulic resistance and do not always provide the necessary purification degree from the I-131 [11].

In the present study, we propose a composite sorbent, which was obtained by depositing a layer of particles of impregnated activated carbon on a porous polyurethane foam matrix with low hydraulic resistance. We described a method for its preparation and tested its sorption capacity to radioactive methyliodide. A comparison of the sorption characteristics of the proposed material and the sample of industrial charcoal sorbent was also provided.

2. Material and methods

Studied composition is based on an inert porous matrix of RegiCell R45 (FoamPartner GmbH, Germany) reticulated polyurethane foam with an average cell size of 0.56 mm. Matrix was impregnated by sorption material in accordance with the procedure described below.

Cylindrical plates with a diameter of 50 mm and a thickness of 10 ± 1 mm were cut from a sheet of polyurethane foam. To hydrophilize their surface, they were kept in an alkaline $KMnO_4$ solution with a concentration of 4–6 g/l for 1 h at the room

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https://doi.org/10.1016/j.net.2019.10.019

temperature. After that, the water-washed and dried samples were soaked with a water dispersion of polyvinyl acetate, squeezed and stirred for 30 min in a Turbula C 2.0 mixer with activated carbon powder of a fraction of 100–160 μm impregnated with 4 wt % of triethylenediamine (TEDA). After stirring, the plates were dried in an oven at 60 °C to constant weight (2.8 ± 0.2 g) and were left to cool down to room temperature. Next, the obtained samples were purged with a stream of compressed air for the final removal of coal and dust particles which were not embedded in the polymer matrix.

The sorption capacity of the obtained composite sorbents with respect to radioactive methyliodide was measured at the experimental facility (Fig. 1), which we described in detail earlier [12]. The tests were carried out under the following conditions: temperature – 30.0 ± 0.1°C; relative humidity of the gas stream – 90.0 ± 1.5%; gas flow rate in the column – 15 l/min. The test procedure was same as one described in Ref. [12]. The samples were placed in a stainless steel sectioned column 8 with a diameter of 50 mm, which was installed in a dry-air thermostat 9 of the test facility. $CH_3^{131}I$ flowed with the main gas stream from the evaporator 5 for 1 h. Concentration of $CH_3^{131}I$ was maintained at a level of 25 ± 7 mg/m^3. The moist air passed through the samples for 16 h prior to the experiments with I-131 in order to eliminate any effects of the adsorption heat of the water vapors on the sorption of methyliodide. The value of radioiodine breakthrough was measured in the protective column 10 with silica gel containing 8% of silver nitrate. The activity of radioiodine was counted at the energy of 364 keV at the same counting geometry.

For comparison with the obtained composite sorbent, we also tested a sample of industrial granular iodine sorbent SKT-3I (sulfonated turf coal with impregnant; granule size 1.0–2.0 mm), which contained 4 wt % of TEDA.

The calculation of the sorption efficiency E was carried out in accordance with the equation:

$$E = \frac{A_{col}}{A} 100\% \quad (1)$$

where A – total activity of the I-131 fed into the system, cps; A_{col} – activity retained in the test column, cps.

To evaluate the feasibility of considered sorbents in the industrial iodine decontamination devices, the sorption capacity indices α were also calculated from equation (2) [12]:

$$\ln \frac{A}{A - A_x} = \alpha \chi \frac{L}{U} \quad (2)$$

where A_x – total activity of the I-131 at x thickness of a sorbent layer ($x \rightarrow L$), cps; χ – portion of free volume (V_{fv}) in the full volume occupied by the sorbent (V_s), according to equation (3); L – total length of the sorbent layer, cm; U – linear gas velocity in full cross section of the column, cm/s.

It is obvious that the member $\chi \frac{L}{U}$ reflects actual time τ_c of contact of the gas flow with the sorbent.

To calculate the contact time of the gas flow with the sorbent (τ_c) in each section of the column, it is necessary to know the fraction of the free volume χ. To calculate this value, we proceeded from the assumption that the volume occupied by the composite sorbent is equal to the sum of the volumes occupied by the carrier (polyurethane foam matrix) and the sorbent layer (particles of activated carbon soaked with impregnant). In this case, the equation for calculating the fraction of free volume in each section of the column takes the following form:

$$\chi = 1 - \left(\frac{m_{PU}}{\rho_{PU}^{true}} + \frac{m_{sorb}}{\rho_{sorb}^{app}} \cdot (1 - \varepsilon) \right) \cdot \frac{4}{\pi d^2 h}, \quad (3)$$

where d is the diameter of the plate, cm; h is the plate's thickness, cm; m_{PU} is the mass of polyurethane foam in the sample, g; m_{sorb} is the mass of charcoal in the sample, g; ρ_{PU}^{true} – the true density of polyurethane foam, g/cm^3; ρ_{sorb}^{app} – bulk density of sorbent particles, g/cm^3; ε is the fraction of free volume in the bulk layer of activated carbon powder.

For industrial sorbent SKT-3I with granules' size of 1.0–2.0 mm, the fraction of free volume in the bulk layer is 0.23 ± 0.1 [13].

The hydraulic resistance of the test materials was determined using a differential pressure gauge TESTO 510 connected to the inlet and outlet of the column 8.

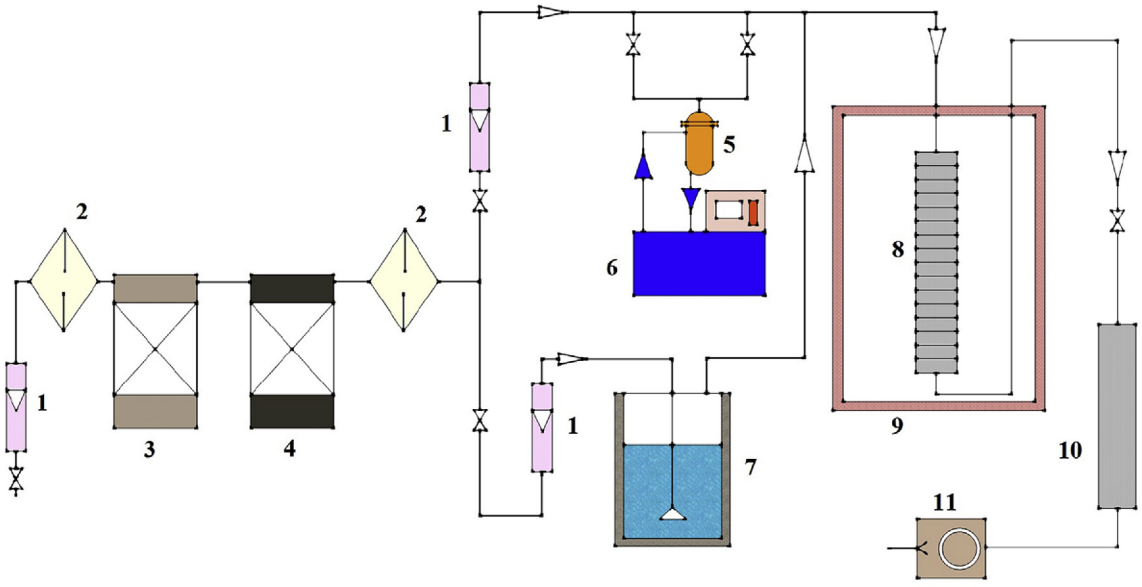

Fig. 1. Simplified scheme of experimental facility. 1 – rotameter; 2 – aerosol filter; 3 – column with zeolite; 4 – column with activated carbon; 5 – $CH_3^{131}I$ evaporator; 6 – circulation thermostat; 7 – gas flow humidifier; 8 – column with sorbent; 9 – dry-air thermostat; 10 – column with silica gel; 11 – diaphragm pump.

Microscopic examination of the obtained sorbent samples was carried out using Vega3 Tescan scanning electron microscope with a cathode of lanthanum hexaboride (LaB_6) in high vacuum mode. Previously, a gold layer (20 nm) was sprayed onto the sample to create a conductive coating. The survey was performed using an Everhart-Thornley detector for secondary electrons (SE) at an accelerating voltage of 5 kV.

3. Results and discussion

SEM (Scanning Electron Microscopy) images of the original polyurethane foam, as well as the composite sorbents obtained, are shown in Fig. 2. In general, we can conclude that due to the significantly smaller particle size of the charcoal (100–160 μm) compared with the average size of the open matrix cell (560 μm), the granules freely penetrate deep into the material and are fairly evenly distributed on the inner surface of the polyurethane foam.

The fraction of free volume in the resulting composite sorbent, calculated by equation (3), was 0.83. The content of impregnated activated carbon in the resulting sorbent according to gravimetric analysis was 64 ± 2 wt %.

The results of comparative activity measurements of different sorbents are presented in Table 1. Obtained data allowed to calculate the efficiency of $CH_3^{131}I$ capture. The sorption capacity values for the tested samples were calculated from the tangent of the slope angle (Fig. 3), which reflects the distribution of the I-131 across the sorption layer in the test column 8. The measured pressure drop in the column under the test conditions was 270 and 365 Pa for the composite sorbent and the charcoal, respectively.

As it can be seen from the data presented in Table 1, the efficiency of radioactive methyliodide capturing in both cases exceeds 99%. At the same time, the calculated values of the α indices for the

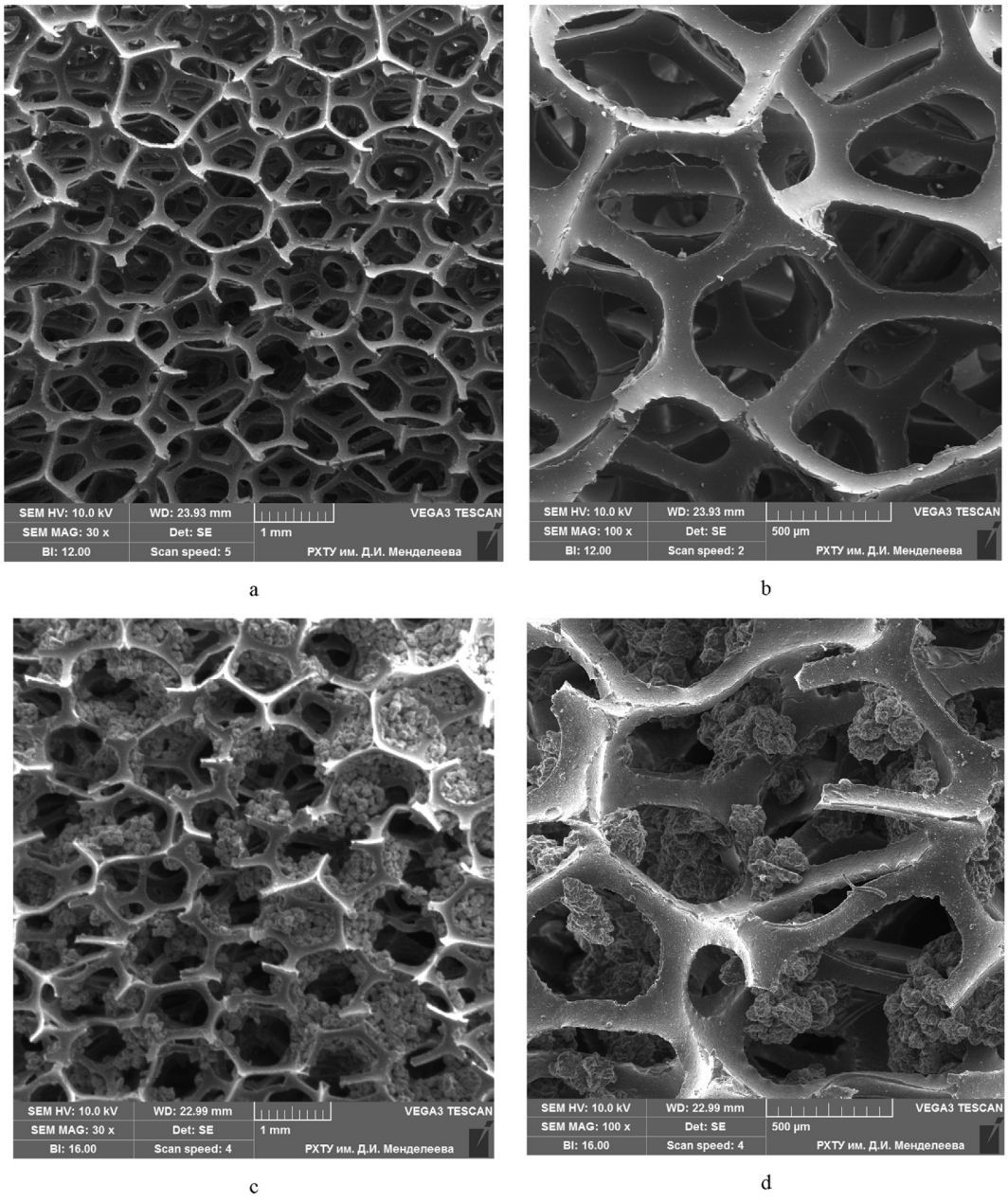

Fig. 2. SEM images of the original polyurethane foam (a, b) and the obtained composite sorbent (c, d).

Table 1
Obtained values of $CH_3^{131}I$ sorption efficiency according to the results of three tests.

L, mm	Composite sorbent A, cps			SKT-3I sorbent A, cps		
	1	2	3	1	2	3
10	55836	43522	34618	1546	1156	865
20	28701	22491	17794	632	473	354
30	4652	3754	2884	246	184	138
40	1458	945	652	126	94	71
50	488	382	302	69	52	39
60	189	134	103	33	25	19
70	76	68	53	19	14	11
Breakthrough, cps	23	17	20	12	10	10
E, %	99.97 ± 0.01			99.46 ± 0.11		
α, s^{-1}	18.0 ± 0.2			44.9 ± 0.9		

Notes: L – total length of the sorbent layer, cm; E – trapping efficiency, A – radioactivity of $CH_3^{131}I$, cps.

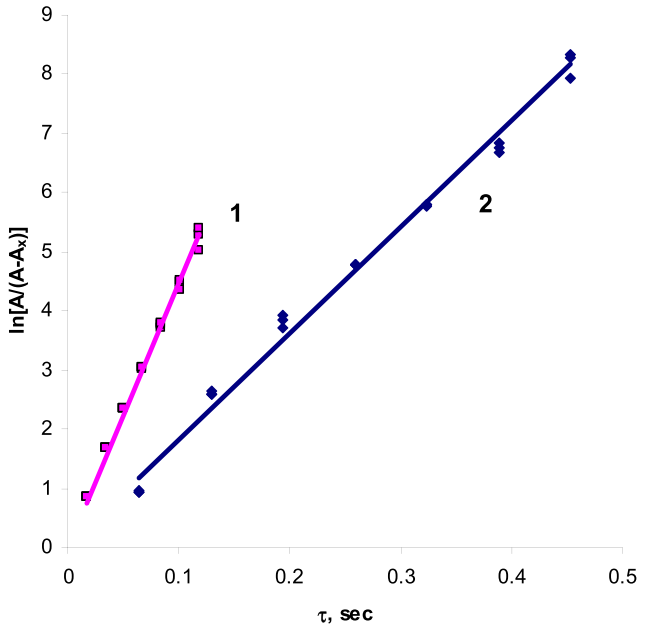

Fig. 3. Comparative data for calculation of sorption capacity index; 1 – charcoal sorbent, y = 44.9x (R^2 = 0.9937); 2 – composite sorbent, y = 18.0x (R^2 = 0.9906).

charcoal and the composite sorbent were 44.9 ± 0.9 and 18.0 ± 0.2 s^{-1}, respectively. However, to compare the sorption properties of sorbents of different nature, characterized by different fractions of free volume, it is advisable, in our opinion, to use the ratio α/α_{min} calculated for each sorbent. Where α_{min} is the minimum value of the sorption capacity index for a sorbent of this type in the iodine filter, which will provide the required purification degree of the gas stream from $CH_3^{131}I$, which, in accordance with IAEA recommendations [14], should be at least 99%. For example, for SKT-3I, α_{min} could be calculated from the technical characteristics of the adsorber (for example, we will consider the industrial adsorber AUI-1500 [15]): the volume of sorbent V_s in the filter is 0.30 m^3; capacity Q – 1500 m^3/h; the proportion of free volume χ in the bulk layer of the sorbent is 0.23. Thus, the gas contact time with the sorbent under the operation conditions of the gas cleaning devices could be determined by the equation:

$$\tau_c = \frac{V_{fv}}{Q} = \frac{\chi \cdot V_s}{Q} \quad (4)$$

Substituting the values of the sorbent volume, the proportion of its free volume and the productivity of the adsorber in (4), we obtain $\tau_c = \frac{0.23 \cdot 0.3 \cdot 3600}{1500} = 0.17$(s). It is obvious that a 100 fold decrease in the I-131 concentration in the air of nuclear power station premises will be achieved if $\ln\frac{A}{A-A_x} = \ln 100 = \alpha_{min}\tau_c$. Expressing the minimum index from this equation, we get $\alpha_{min} = \frac{\ln 100}{0.17} = 27.1\ s^{-1}$. This means that in order for the AUI-1500 iodine filter to work satisfactorily, the granulated sorbent with a fraction of 1.0–2.0 mm must have a sorption capacity index of at least 27.1 s^{-1}. Similarly, using expression (4), it is possible to calculate the α_{min} value for the composite sorbent. The contact time of the gas with the sorbent layer under the operation conditions of the adsorber will be $\tau_c = \frac{0.83 \cdot 0.3 \cdot 3600}{1500} = 0.60$ (s). Then $\alpha_{min} = \frac{\ln 100}{0.60} = 7.7\ s^{-1}$.

For the ratio $\beta = \alpha/\alpha_{min}$, the concept of "relative index of sorption capacity", which characterizes the efficiency of the iodine adsorber with the selected sorbent, can be introduced. For SKT-3I and composite sorbent obtained from the polyurethane foam, β values are 1.7 and 2.3, respectively. This means that, other things being equal (gas flow rate, temperature, relative humidity), a smaller amount of sorbent with a higher relative β index can be used in the iodine decontamination device while maintaining the required efficiency of the adsorber. It is also obvious that at β < 1 the sorbent cannot be used in the iodine adsorbers.

Another important characteristic of iodine sorbent is the hydraulic resistance to gas flow. We presented the comparative data on the hydraulic resistance of columns with composite and industrial granular sorbent in Table 2. This data shows that the pressure drop on a column with a composite sorbent is significantly lower than one on a column filled with granular carbon SKT-3I. It should be noted that the hydraulic resistance of the sorbent layer depends on the gas flow rate in a non-linear manner. Considering that the gas flow rate in the AUI-1500 industrial adsorber is several times higher (about 70 cm/s), the difference between the hydraulic resistance of such a sorbent and the layer of activated carbon will be even more significant.

4. Conclusion

We have successfully obtained an experimental composite sorbent by applying a powder of an impregnated activated charcoal of 100–160 μm fraction onto an inert matrix of RegiCell R45 reticulated polyurethane foam. Testing of the sorbent showed that it has a sufficiently high efficiency of radioactive methyliodide capturing and could be potentially applied in industrial iodine adsorbers. The capture efficiency of $CH_3^{131}I$ under the test conditions was more than 99%. It was shown that when comparing the performance of apparatus equipped with different types of sorption materials, it is advisable to use the relative sorption capacity index we have introduced: $\beta = \alpha/\alpha_{min}$, where α_{min} is the minimum value of the sorption capacity index for a sorbent of this type for the required degree of purification. As a result of the research, it was established that the relative β index of the composite sorbent is significantly higher than that of SKT-3I (it is 2.3 against 1.7). Thus, the AUI-1500

Table 2
Hydraulic resistance of sorbents samples.

Sorbent type	Pressure drop in the test column (Pa) at the following gas flow rates		
	0.3 m3/h (4.2 cm/s)*	0.6 m3/h (8.5 cm/s)*	0.9 m3/h (12.7 cm/s)*
Composite	45 ± 5	150 ± 5	270 ± 7
SKT-3I	85 ± 5	230 ± 7	365 ± 8

Notes: *linear velocity of gas flow through the column cross-section.

adsorber filled with industrial sorbent will be inferior in the efficiency of trapping radioactive methyliodide from vapor-air flows. Based on the pressure drop in the test column at different gas flow rates, it can be concluded that an experimental sorbent based on a polyurethane foam matrix with an average pore size of 0.56 mm has a lower hydraulic resistance, which means it will significantly reduce the cost of operating the ventilation system of nuclear power stations premises.

Declaration of competing interest

The work was supported by the Mendeleev University of Chemical Technology of Russia. Project Number 022-2018.

Authors do not cooperate with any producers of charcoal sorbents and do not promote this product.

Acknowledgement

The work was supported by Mendeleev University of Chemical Technology of Russia. Project Number 022-2018.

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