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A NEW APPROACH TO OBTAIN AEROGELS FOR GAS SAFETY APPLICATIONS

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Abstract

In this study a new approach for aerogel preparation is presented, along with the screening of obtained aerogel towards air decontamination potential. The synthesis method allows the tuning of the porosity degree of the aerogel by changing the amount of the solvent (water), which dictates the physical appearance of the obtained aerogel (compacted or expanded). Experiments have been carried out under dynamic conditions, by using isobutylene (ISB) as model pollutant and activated carbon as a reference sorbent. At low contaminant loading, the obtained aerogels exhibit comparable performance with that observed for activated carbon, otherwise the activated carbon presents the highest performance at higher loadings. The physical appearance of the aerogel appears to influence the ISB removal performance. Influence of gas flowrate and ISB concentration on the performance response is depicted. The obtained results reveal new perspectives in developing and using aerogels (ultralight materials) for the removal of air contaminants in special applications such as those related to gas safety (for example, the gas masks that should assure not only quality, but also comfort).

Keywords: activated carbon, aerogel, air treatment, gas safety, isobutylene

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1. Introduction

Aerogels are versatile materials with low density, high porosity and high surface area, that can be tailored for various applications, such as thermal insulation, energy storage, flame retardancy, adsorption of undesirable compounds from different environmental compartments etc. (Acharya et al., 2013; Maleki, 2016; Stan et al., 2014; Thapliyal and Singh, 2014). Particularly, few studies concerning the removal of some air contaminants by different types of aerogels (especially carbon, silica and oxide-based) are presented in literature (Maleki, 2016), but this

approach is still in early developing phase and the data concerning the potential of organic-based aerogels in such application is very limited. Main typical steps involved in aerogel production are hydrolysis, condensation (gelation), aging and drying (Maleki, 2016; Thapliyal and Singh, 2014). Methods to evaluate structure and morphology of aerogels are referred in the literature (Miramon-Ortiz et al., 2019; Pekala and Schaefer, 1993; Simón-Herrero et al., 2018; 2019). In other order of idea, one of the common barriers in aerogels application refers to the high manufacturing costs, especially when supercritical drying is applied (Thapliyal and Singh 2014).

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From this point of view, aerogels might be more recommended for special applications that are not subject to limitation by economic criteria. Overall, these aspects could explain the lack in studies concerning the application of aerogels in environmental protection and suggest the research need for developing new preparation methods for obtaining cost-effective aerogels with assessed potential in practice.

This work presents a new approach for developing a cost-effective polymer aerogel dedicated to high-performance environmental application such as required in gas safety context. For example, exposure to volatile organic compounds (and not only) accumulated in closed environments is a healthy-risk (Soreanu et al., 2013). A model organic gaseous pollutant (i.e. isobutylene) is used in this study to simulate a contaminated environment for which a gas mask equipped with a specific light material such as the actual developed aerogel would be required. Pointing out the particularities of the synthesis method and the influence of the material morphology on the gas retention performance is presented. In addition, the influence of operating parameters (gas flowrate and ISB concentration) on the removal performance is assessed.

2. Materials and method

2.1. Aerogel preparation

The polymer aerogels were prepared using 2-hydroxyethyl methacrylate (HEMA) and N,N'-methylene bisacrylamide (MBAAM) as crosslinker. In the first step, the monomer (HEMA - 3 mL) and the crosslinker (MBAAM - 0.15 g) are dissolved in water followed by the addition of 0.02 g of photoinitiator (2-Hydroxy-1-[4-(2-hydroxyethoxy) phenyl]-2-methyl-1-propanone). The preparation path requires an intermediary stage for obtaining a polymer cryogel which undergoes at 250K in the presence of 305 nm UV radiation as excitation source for the photoinitiated polymerization. For the photopolymerization process, a regular 6 W UV lamp with the maximum emission peak centered at 305 nm, was used. The final aerogel is obtained by freeze drying the resulted cryogel. The described method allows the tuning of the porosity degree of the aerogel by changing the amount of the solvent (water). Expanded and compact aerogels (A1 and A2) were obtained in this way. Structural investigation of the prepared aerogels was performed using FTIR, while the morphology of the resulted polymer aerogels was investigated using SEM. The thermal behavior was evaluated through thermal analysis.

2.2. Experimental setup for aerogel evaluation

Experimental setup is shown in Fig. 1. Model gas (isobutylene, balance air) from a gas reservoir was continuously fed into a cartridge filter equipped with 1.075 (\pm 0.015) g sorbent (the obtained aerogel).

The sorbent was packed in a textile bag located in the filter cartridge, without compression. Isobutylene (ISB) concentration was analyzed in inlet and outlet gas by using a portable gas analyzer (RAE Multi-Gas Monitor equipped with an internal sampling pump). Gas flow rate was measured by using a Pocket flow calibrator, Kurz. Gas flowrate and ISB concentration between 0.25-0.35 L/min and 11-45 ppm, respectively, have been tested in order to establish the influence of these factors on ISB removal. Activated carbon is a common material used in air treatment, including VOC removal (Soreanu et al., 2011). In this study, an apple wood residue-derived activated carbon from S.C. "Ecosorbent" S.R.L. Chisinau (Cretescu et al., 2017) was used as reference sorbent in the evaluation of aerogel performance.

2.3. Evaluation of process performance

Sorbent performance was expressed in terms of removal efficiency (RE, %), being evaluated on the basis of ISB concentration in the outlet gas (c_f , ppm), by rapport to that in the inlet gas (c_i , ppm). The following equation (Eq. 1) was used in this regard:

$$RE, \% = [(c_i - c_f) / c_i] \cdot 100 \quad (1)$$

3. Results and discussion

3.1. Aerogel structure

In Fig. 2 it is presented the recorded FTIR spectrum of the MBAAM crosslinked HEMA aerogels which revealed various chemical groups which are typical for this type of polymer (p-HEMA). Thus, the specific carbonyl peak was recorded at 1728 cm^{-1} while in the upper region of the spectrum the stretching vibrations characteristic for the OH (3451 cm^{-1}) and C-C, CH (2951, 2887 cm^{-1}) groups were revealed. In the lower region are located the stretching vibrations of the C-O-C groups (1252 cm^{-1}) and various bending vibrations of the CH or CO groups (900-750 cm^{-1}). Thermal analysis of the prepared aerogels was performed in 25-900°C temperature range. The recorded mass variation within the investigated temperature interval is presented in Fig. 3. The decomposition process undergoes in three stages, as detailed in Table 1. In the first decomposition stage, the mass loss is attributed to environmental water trapped in the porous structure, while in the next decomposition stages, destruction processes accompanied by volatiles exhaustion is responsible for the important mass loss (88%) of the investigated sample.

Aerogels belong to the lightest and porous materials (Acharya et al. 2013), which make them competitive in a wide range of applications. Particularly, the resulted polymer aerogel (Fig. 4) is highly porous with an interconnected pore structure with pore size in the hundreds nanometer -

micrometer range. As the amount of solvent used for cryogel preparation is raised, the pores dimensional characteristics are subsequently higher. Thus, the described method allows the preparation of low density and porous aerogels.

Also, the prepared aerogels could be shaped according to the application requirements, by simply using a mould with the desired geometry in the intermediary stage of cryogel formation.

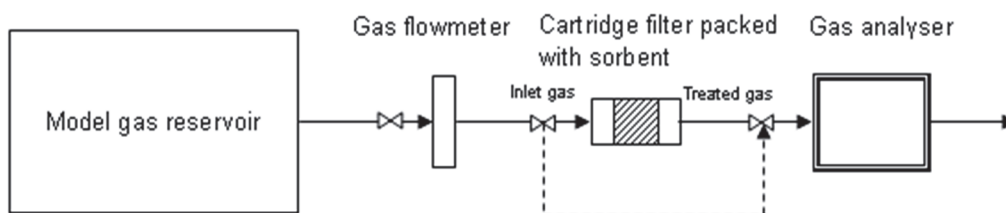


Fig.1. Experimental flowsheet diagram

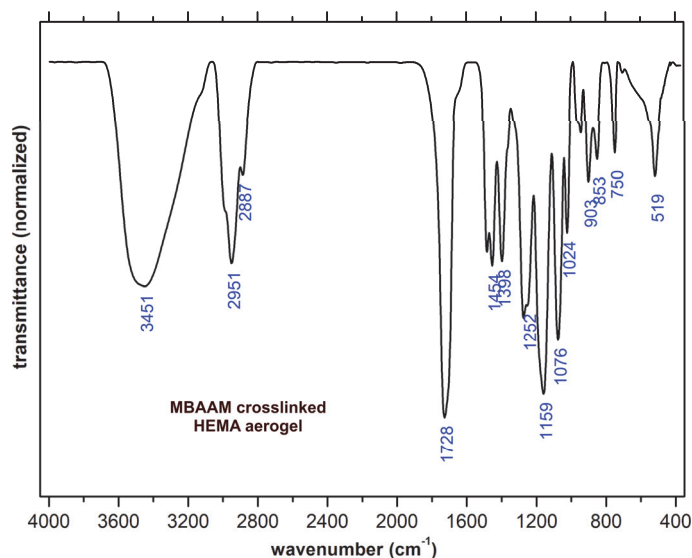


Fig. 2. Recorded FTIR spectrum of the prepared MBAAM crosslinked HEMA aerogels

Table 1. Decomposition stage recorded for the prepared aerogels

<i>Decomposition stage</i>	<i>Temperature interval (°C)</i>	<i>Mass variation (%)</i>
I	25-90	3.08
II	193-355	39.64
III	388-439	48.51

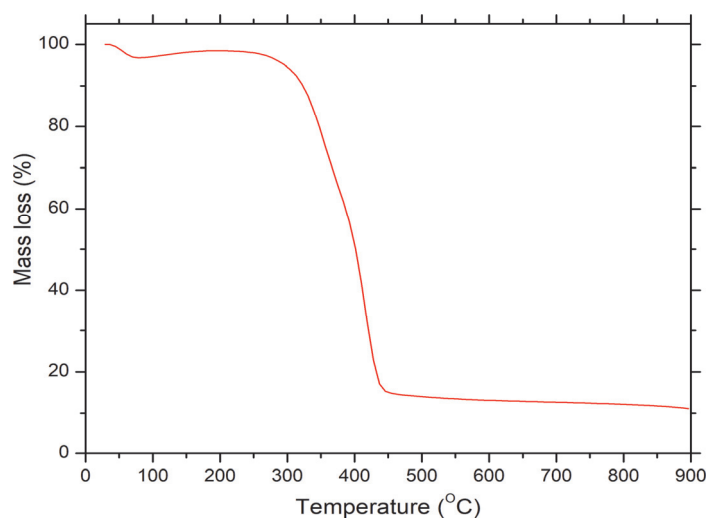


Fig. 3. Recorded mass variation within the thermal decomposition process

3.2. Aerogel performance

As can be seen in Fig. 5, RE decreases (ISB concentration in effluent increases) with the gas flowrate increase, for both types of aerogels. However, the compact aerogel (A2) exhibits slightly higher removal efficiency (e.g. RE= 97%) than the expanded aerogel (A1), due to the better pollutant-aerogel mass transfer. Overall, at low flowrates (0.25 L/min), the performance of both aerogels is comparable with that of activated carbon (AC), revealing new perspectives in developing and using aerogels for VOC removal from gas streams.

The decrease of RE with the increase of the gas flowrate in the case of the aerogels is due to the diminishing of the contact time between phases at high flowrate. It could be mentioned however that the activated carbon performance was not limited from this point of view, which means a higher retention capacity in comparison with the aerogel sorbents. The decrease of RE in the case of the aerogels could be explained due to the smaller retention capacity based on morphology and porosity.

All experiments were conducted in the steady-state regime observed before the breakdown points (corresponding to the moment of concentration increase in the outlet stream) (Fig. 6). As can be seen, the breakdown time for the both tested aerogels are quite similar, but almost half compared with that observed for the activated carbon. Although both aerogels are prone to leaks during the steady state in the presented configuration, A2 exhibits a better retention performance compared with A1. This behavior can be explained by the better contact phases in the case of A2 as results of its compacted structure.

Although the sorbent performance was expressed in terms of removal efficiency (RE, %) (eq.1), additional information could be obtained in terms of mass of retained pollutant reported on a sorbent mass based on the mass balance: $F_v \cdot t \cdot c_i = m + F_v \cdot t \cdot c_f$ and therefore $m = F_v \cdot t \cdot (c_i - c_f)$, or $m = F_v \cdot t \cdot RE \cdot c_i / 100$ (where: F_v = gas flowrate, c_i = inlet concentration; c_f = outlet concentration; m = accumulated pollutant mass on the sorbent mass of 1.075 g (± 0.015), at the time t).

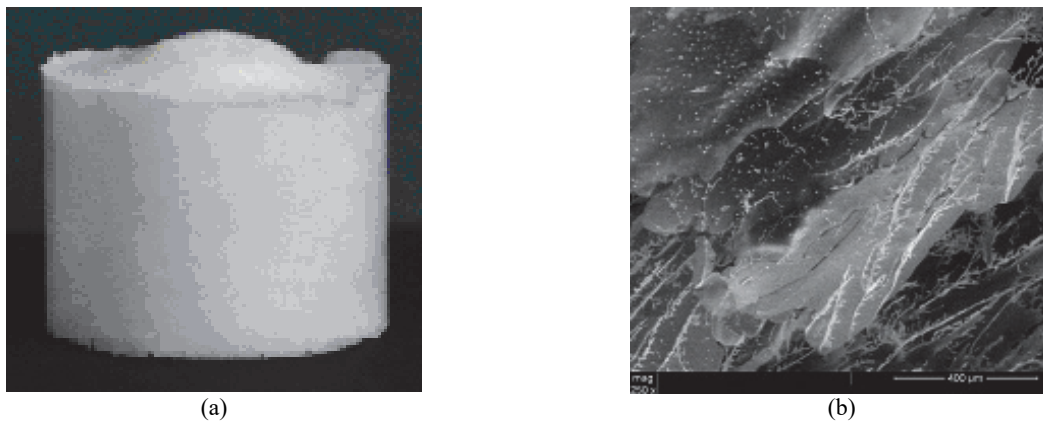


Fig. 4. Some images for the related aerogels: (a) macroscopical image of a cylindrical shaped polymer aerogel; (b) SEM micrographs of the prepared aerogels (density 0.03 g/cm³)

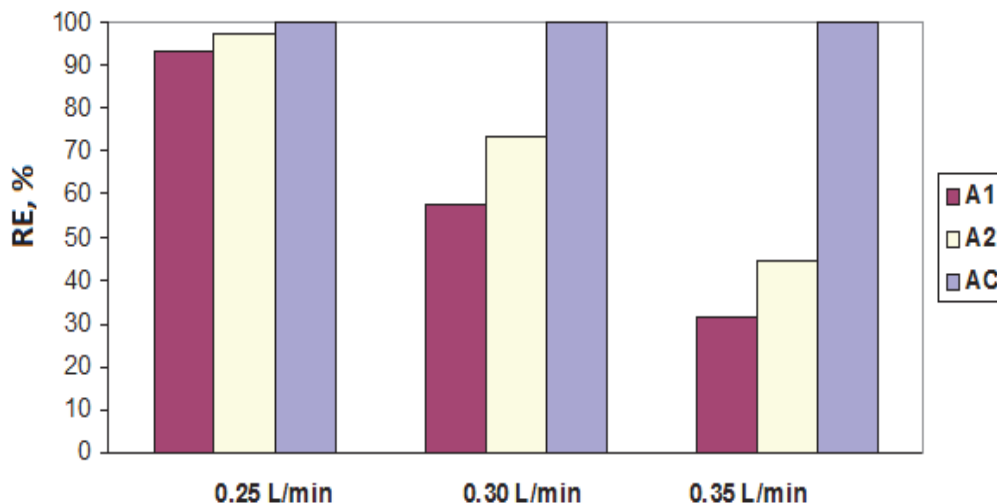


Fig. 5. Removal efficiency (RE, %) of tested sorbents. A1 = expanded aerogel; A2 = compact aerogel; AC = activated carbon; sorbent amount = 1.075 g (± 0.015); initial ISB concentration (c_i) = 45 ppm

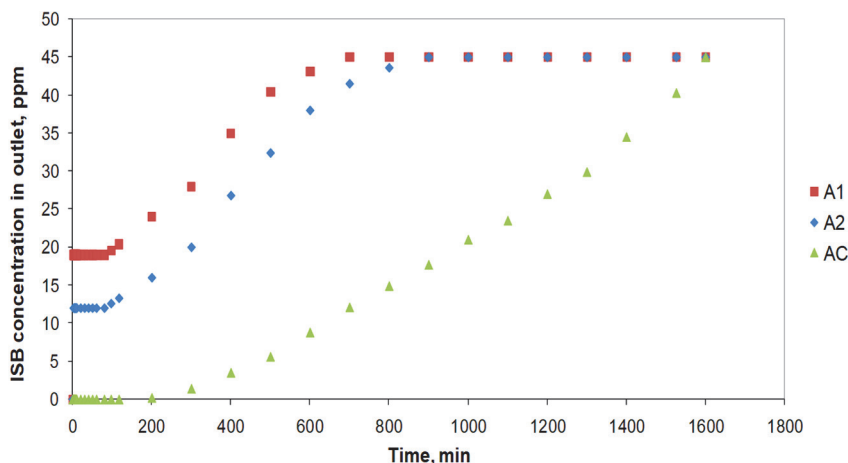


Fig. 6. Evolution of the aerogel performance over time based on outlet ISB concentration. A1 = expanded aerogel; A2 = compact aerogel; AC = activated carbon; sorbent amount = 1.075 g (± 0.015); gas flowrate = 0.30 L/min; initial ISB concentration (c_i) = 45 ppm

Taking into consideration the above observed performance, aerogel A2 underwent further investigation through a factorial experimental design, which is an affordable screening tool for the preliminary assessment of factors influence on performance criteria (Table 2).

A regression model (Eq. 2) of the removal efficiency has been obtained in terms of coded variables and validated through Minitab, along with the corresponding contour plots presented in Fig. 7.

$$RE_{pred} = 82.5 - 16.1x_1 - 11.0x_2 - 10.6x_1x_2 \quad (2)$$

$R-sq = 99.8\%$

Results confirm that an increase in both flowrate and concentration determines a decrease in removal efficiency (Fig. 7), which suggests a limited mass transfer under high contaminant loadings (Soreanu 2016). Both factors and their interaction appear to be significant in Eq. 2 (i.e. $p < 0.05$), but the flowrate has a stronger influence (Fig. 8). Further improvement of aerogel morphology could overcome such drawbacks related to mass-transfer.

Aspects related to the regeneration of aerogels are subject to another study, as it may play an important role in moving towards sustainable materials that can be reused for multiple purification cycles. For instance, heating up to 90 °C under vacuum could be considered for this purpose (subject to some sorbent mass loss of max. 3% according to the thermal decomposition behavior – Fig. 3) depending on the affinity between the contaminant and the aerogel. Overall, the results are promising and show the aerogel potential for the removal of contaminants from the processed air in special applications e.g. in order to accomplish gas safety requirements in various environments.

4. Conclusions

The described method allows the tuning of the porosity degree of the aerogel by changing the amount of the solvent (water). Light prepared aerogels could be shaped according to the application requirements, by simply using a mould with the desired geometry in the intermediary stage of cryogel formation.

Table 2. Matrix of factorial experimental design, with a center point

No. crt.	x_1 coded vs real values	x_2 coded vs real values	RE exp., %	RE pred., %
1	-1 (0.25 L/min)	-1 (11 ppm)	98.60	98.98
2	1 (0.35 L/min)	1 (45 ppm)	44.44	44.82
3	1 (0.35 L/min)	-1 (11 ppm)	87.62	88.00
4	-1 (0.25 L/min)	1 (45 ppm)	97.77	98.15
5	0 (0.3 L/min)	0 (28 ppm)	83.40	82.48
6	0 (0.3 L/min)	0 (28 ppm)	82.64	82.48
7	0 (0.3 L/min)	0 (28 ppm)	82.95	82.48

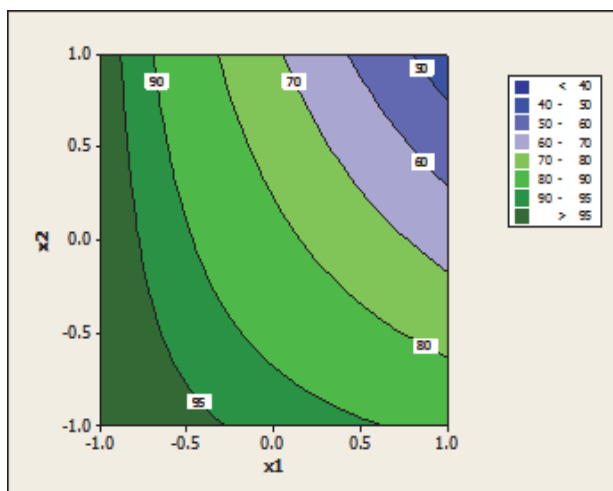


Fig. 7. Contour plots of the predicted removal efficiency (RE_{pred} , %), as a function of gas flowrate (x_1) and ISB concentration (x_2), where x_1 and x_2 are coded variables

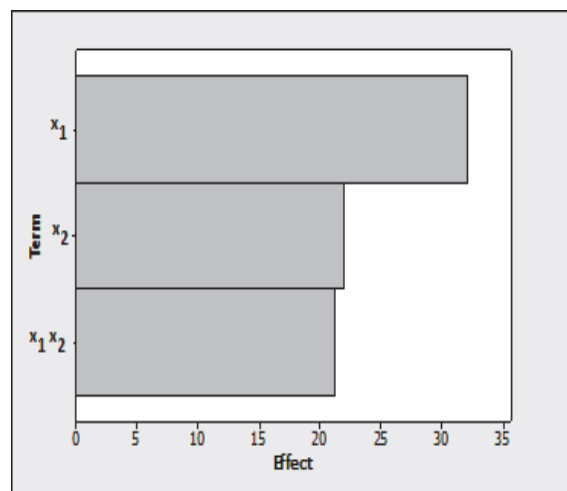


Fig. 8. Pareto chart of the effects (Response: RE_{pred} ; $\alpha = 0.05$)

The performance of the obtained aerogel in the retention of a specific gaseous pollutant is depicted, along with the characteristics of the obtained material by the new approached method. Results of isobutylene retention from air on aerogels are comparable with those obtained on activated carbon at small gas flowrates (e.g. 0.25 L/min). Both gas flowrate and concentration are significant factors under the tested condition, but the performance is more sensitive to the gas flowrate increase.

Overall, the results are promising and suggest the aerogel potential for a new interesting application. Once the concept was demonstrated, future research is necessary to determine the appropriate configuration to develop a gas mask cartridge based on such ultralight materials, additionally equipped, for example, with a hydrophobic membrane and other thin layers depending on the working conditions etc.

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