Influence of type of activated carbon and water adsorbed by the material on adsorption capacity of radon: preliminary test

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Abstract. Radon is a radioactive noble gas that emanates from the soil and building materials and can reach high concentrations in closed spaces, increasing the risk of cancer. Therefore, it is needed to control and reduce the exposition to radon inhalation, reducing exhalation from its origin or its concentration in the air. Activated carbon is an adsorbent, which has proven its good adsorption capacity to remove organic pollutants from water and air. So this work will explore the potential of activated carbon as adsorbent material, analysing the influence of the type of carbon and water adsorbed by the material on its radon adsorption rate. Different kinds of activated carbons from vegetal or mineral origin have been used and it has been analysed their radon adsorption capacity (Bq/g). Moreover, it has been studied the influence of water adsorbed on radon adsorption capacity by changing the water adsorbed retained in the activated carbon. The experimental set-up consists of a deposit with a pitchblende stone and soil and on its surface, a paper template is used to settle seven canisters in a fixed position. In each test, the canisters are filled with a type of dry activated carbon. After 24 hours of exposition, the adsorbed radon is measured through its descendants by gamma spectrometry with a NaI detector. Influence of water adsorbed in the material on radon adsorption capacity is studied following the same procedure but with activated carbon with different water adsorbed. Results show that for an optimum result of adsorption of radon, mineral carbons are preferred over vegetal origin ones. The water adsorbed of the carbon reduces radon adsorption capacity, so use dry material is always advised. These recommendations will be used as a reference to design new strategies to treat radon-polluted air or to reduce radon concentration exhaled from the soil.

KEYWORDS: radon; adsorption; activated carbon.

1 INTRODUCTION

Radon is a radioactive noble gas that comes from radium disintegration. As it is a noble gas, it has high mobility as well as high solubility in water and it can pass to the atmosphere by soil exhalation; therefore, it can be present in the soil, the water and the air [1]. It has a half-life of 3.82 days, so it can travel longer distances and reach higher concentrations until it disintegrates [1]. Due to its gaseous properties, radon emanates easily from the soil and building materials with the possibility of reaching high concentrations in closed spaces [2]. The European Union established a limit of 600 Bq/m^3 for closed spaces and work areas, but due to its dangerous characteristics, more restrictive concentration has been proposed in the new directive (Euratom 2013-59) with a lower limit of 300 Bq/m^3 [3], which will be transposed to the Spanish legislation in the next future.

Both radon and its descendants can produce considerable biological damage if enter in the respiratory tract by inhalation. As it disintegrates, its descendants remain in the lungs, which receive the energy from alpha and beta particles and gamma radiation. Radon is the second cause of lung cancer after smoking [4]. Therefore, it is needed to control and reduce the exposition to radon inhalation, reducing exhalation from its origin or its concentration in the air. Commonly technique used to reduce concentration in the air is ventilation [2,5–7].

Adsorption consists in the uptake of components, both liquid or gas, to the external or internal surface of a porous solid removing it from the polluted stream. Some of the advantages of this method are high efficiency in contaminants removal, the possibility of recover adsorbed compounds or the wide variety of adsorbents. However, the adsorbents lose their adsorption capacity with time and it is necessary to change or dispose of them [8].

The use of activated carbon to remove pollutants from water or air is common due to its good adsorption properties. Furthermore, it can be produced from carbonaceous materials, including any type of carbon

and wood, or nutshells. From the air, in addition to eliminating volatile organic compounds, odours and toxic gases, it is also able to adsorb mercury, hydrogen sulphide and radon [8]. Adsorption with granular activated carbon has been proved to reach a high percentage of radon removal from water (>90%) in small facilities or for domestic use [5,9,10]. However, radon removal from the air with activated carbon has not been widely studied and only under laboratory conditions [11,12].

Adsorption with activated carbon is also a technique used to measure radon exhalation from air. Canisters filled with activated carbon are widely spread used to detect radon due to their small size, low cost, high detection efficiency and the lack of necessity of an energy source [12,13]. The use of activated carbon in canisters to adsorb pollutants has been studied since the 1980s [14]. The type of canister used by the USEPA [15] consists of a can with a lid, a metal screen, an expanding ring and a pad material attached to the internal face of the lid. Several factors can affect adsorption but the most significant is the presence of water that diminishes the adsorption capacity since water molecules occupy the adsorption sites and make it impossible for other compounds to get adsorbed [16].

Although activated carbon is used as a passive device method for radon measurement and has a very good radon adsorption capacity, there are not many studies in which activated carbon has been used to adsorb radon from the air. Therefore, the aim is to research the potential that activated carbon has as a treatment technique for air polluted with radon.

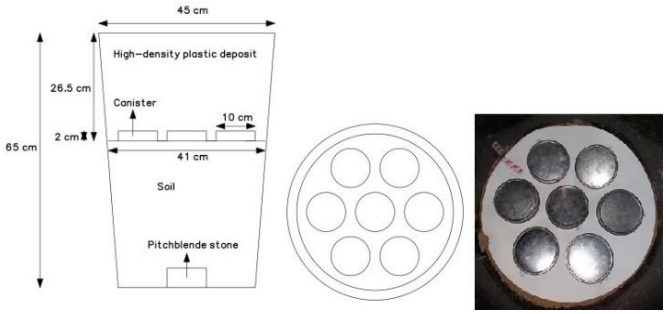
To study the efficiency of radon removal, different kinds of activated carbons from vegetal or mineral origin will be used and it will be analysed their different characteristics (specific surface, iodine number, methylene blue number, particle size and ash content) and its influence on adsorption capacity. Moreover, it will be studied the influence of different degrees of water adsorbed and the atmospheric conditions on radon adsorption capacity. Results will be taken as a reference to design a system able to reduce the concentration of radon that arrives in closed spaces or to treat radon polluted air based on adsorption.

2 MATERIALS AND METHODS

2.1 Experimental set-up

The experimental set-up to perform the radon measurements consists of a high-density polyethene truncated cone deposit of 65 cm (height) x 45 cm (diameter). In the bottom, a *pitchblende stone* is placed, which exhales radon (emission rate = 24820 ± 910 $Bqm^{-3}h^{-1}$; exhalation rate from the soil = 69.5 $Bqm^{-2}h^{-1}$ measured with an H chamber and an electret). Over the stone and until a height of 38.5 cm the deposit is filled with soil coming from the surroundings of our research lab. On the surface of the soil, a paper template is used to settle seven canisters in a fixed position as shown in Fig. 1.

Figure 1: Diagram of the template and the canisters in the experimental set-up



All measurements were made under a monitored environment in the laboratory. According to other authors, it is considered that the activity exhalation from the surface is constant [17].

2.2 Measurement technique

To guarantee that there is not any substance adsorbed, which can interfere in the measurement on the activated carbon, the canisters full of carbon are placed in the oven at 110ºC for 8 hours. After that, the canisters are set in their fixed position of the experimental set-up previously described and the room conditions (temperature, relative humidity and atmospheric pressure) are registered. The atmospheric conditions are monitored through a weather station located inside the laboratory.

After being exposed for 24 hours, the canisters are left for 3 hours to reach equilibrium and then the adsorbed radon activity is measured through its descendants bismuth-214 and lead-214, by gamma spectrometry with a NaI detector. These elements produce energy peaks at 242, 294 and 352 keV and 609 keV, respectively, so two regions of interest (ROI) are formed: one from 220 to 396 keV and another from 565 to 655 keV [18]. Radon exhalation rate (J_{Rn}) is calculated as follows [17]:

$$J_{Rn}(Bq \cdot m^{-2} \cdot s^{-1}) = \frac{R \cdot \lambda^2 \cdot t_c \cdot e^{\lambda \cdot t_d}}{\varepsilon \cdot a \cdot (1-e^{-\lambda \cdot t_c}) \cdot (1-e^{-\lambda \cdot t_e})} \quad (1)$$

where R is the net count rate minus the background count rate, λ is the decay constant (s^{-1}), t_c is the counting time (600 seconds), t_d is the time between the end of the exposition and the start of the counting (s), ε is the efficiency of the detector (calibrated with a reference canister with 22.25 nCi of a canister filled with Ra-226), a is the surface area of the canister (m^2), t_e is the exposure time (s).

From radon exhalation rate, radon adsorption capacity is calculated as follows:

$$Rn_{Adsorption}(Bq \cdot g^{-1}) = \frac{J_{Rn} \cdot a \cdot t_e}{m_{CA}} \quad (2)$$

Where m_{CA} is the mass of activated carbon inside of each canister (g).

2.3 Study of different types of activated carbon and the influence of their properties in radon adsorption

Radon concentration exhaled from the soil is determined with seven canisters. In each assay, six canisters are filled with the same type of activated carbon to be studied and one is used as control. The control contains the original activated carbon sold with the EPA canister, which is usually used for measurement of radon concentration. Different activated carbon samples (from mineral or vegetal origin) have been tested, whose main characteristics are shown in Table 1.

Table 1: Activated carbons used in the measurements and their main characteristics

Activated carbon	Average particle diameter (mm)	Density (g/cm^3)	Iodine number (mg/g)	Methylene blue number (mg/g)	Ash content (%)	Specific surface (m^2/g)
Kemira[(a)]	1.40	0.48	1000	280	5	1000
Lignite[(b)]	1.30	0.34	625	-	7	650
Cabot Norit GAC 1020EN[(a)]	1.42	0.45	1000	210	8	1150
Cabot Norit GAC 1020AW[(a)]	1.40	0.42	950	200	10	1000
Control[(a)]	1.45	0.48	-	-	-	-

[(a)] Vegetal activated carbon
[(b)] Mineral activated carbon

The manufacturers through a data sheet had supplied the main characteristics of the four activated carbons tested. For the Control, the sample size distribution curve was obtained by sieving between 50 µm and 1.6 mm, obtaining as average sample size the value shown in Table 2. The density was obtained

with a graduated cylinder measuring the volume for a weighted sample. Both parameters are similar to those of the other samples.

Iodine number is a good indicator of the porosity of activated carbons and it can be used as an approximation of specific surface and microporosity, which can be seen in the similar values of both parameters [19]. Methylene blue number determines the adsorption capacity of big molecules by the activated carbon [20]. As [21] establish, when the ash content is high, the adsorption is affected and it can be inhibited.

2.4 Influence of the water adsorbed in radon adsorption

To study the influence of the water adsorbed in the activated carbon, seven canisters have been used, all of them containing the same activated carbon (Lignite or Kemira as they have obtained the best results among the activated carbons tested in 2.3). One of the canisters has been used as a control in all trials, so its initial water adsorbed has been kept at 0% because the activated carbon has been dried in an oven.

Before placing the canisters in the experimental set-up, activated carbon is prepared to reach the degree of water adsorbed required. For that, the activated carbon is steeped in water during a minute and after that time, it is left to drain, stirring slightly until no water drips. Then, the carbon is set in the oven at 70ºC during the time needed to dry it until the water adsorbed desired is reached. The time of drying (T_d, min) is calculated using Eq. 3, which comes from previous measurements. Each water adsorbed (W_A, %) is related to a time of drying in the oven at 70ºC.

$$W_A = -0.7155 \cdot T_d + 97.596 \quad (3)$$

Once the activated carbon is prepared, it is placed in the experimental set-up for 24 hours following the methodology for measurement and calculation described in 2.2 section.

3 RESULTS

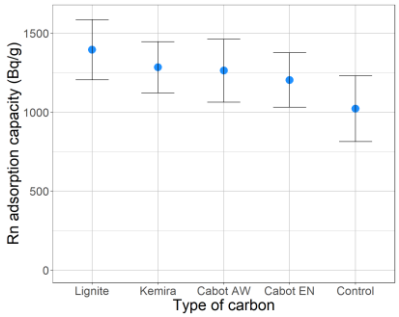
3.1 Influence of type of activated carbon

The experiments have taken place in April 2019, with average atmospheric values of 18.8 ± 0.95 ºC (temperature), 1009.8 ± 7.90 hPa (atmospheric pressure) and 50.5 ± 8.95% of relative humidity inside the laboratory. The dry activated carbon samples used in the test are from vegetal and mineral origin. In Table 2 are represented some statistical parameters used to define the results obtained for each activated carbon studied. Fig. 2 shows the mean and confidence interval of the radon adsorption per gram of activated carbon for the four activated carbons studied and for the control.

Table 2: Statistical parameters for each type of activated carbon tested

	Type of carbon				
Radon adsorption	Lignite	Kemira	Cabot AW	Cabot EN	Control
Mean (Bq/g)	1394.77	1283.66	1262.34	1203.03	1021.89
Standard deviation (Bq/g)	182.01	153.87	190.21	164.54	131.04
Skewness	-1.108	-0.651	-0.513	-0.816	-0.610
Confidence interval (Bq/g)	±191.01	±161.48	±199.61	±172.68	±208.51

Figure 2: Distribution of the quantity of adsorbed radon per gram of activated carbon for the four types tested and the control



As can be seen in Fig. 2, Lignite is the activated carbon that adsorbs more radon per gram (1394.77 Bq/g). For Kemira, Cabot AW and Cabot EN, although there are some differences, the results obtained are more similar (1283.66, 1262.34 and 1203.03 Bq/g, respectively). However, it is shown clearly that all activated carbons tested adsorb more radon per gram than the control (which radon adsorption per gram is 1021.89 Bq/g).

In this case, Lignite has the lowest specific surface, iodine number and particle size, although it has the highest amount of radon adsorbed per gram of sample. Those carbons with the lowest ash content have also the highest amount of radon adsorbed per gram of activated carbon.

Comparing these results with bibliography, all the carbons tested adsorb more than others reported. Adsorption values for activated carbon reported in the bibliography are lower than the ones obtained in the measurements. Concerning other adsorbents, none of them is comparable to activated carbon in terms of radon adsorption rate as can be seen in Table 3. Although a comparison is made between the adsorption rates, the values of emission/exhalation, exposition time and area/volume/flow are stated because the source conditions vary from test to test and affect adsorption rates.

Table 3: Adsorption rates for radon (in Bq/g) of different adsorbents

Adsorbent	Adsorption rate (Bq/g)[(a)]	Emission/Exhalation	Exposition time (h)	Area/Volume/Flow	Reference
Lignite	1394.77	24820 $Bqm^{-3}h^{-1}$	24	$3.14 \cdot 10^{-2}$ m^2	This work
Activated carbon	1.6	2400 Bqm^{-3}	48	$5.4 \cdot 10^{-3}$ m^3	[2]
	590.98	45 – 45000 $mBqm^{-2}s^{-1}$	24	-	[17]
	4.3	2042 $Bqm^{-2}h^{-1}$	13	$3.22 \cdot 10^{-3}$ m^2	[22]
Zeolite	0.042	1400 – 1800 Bqm^{-3}	48	$5.4 \cdot 10^{-3}$ m^3	[2]
Coconut shell	24.84	3600 Bqm^{-3}	2.5	8.3 $Lmin^{-1}$	[23]
	319.8	78 $kBqm^{-3}$	10	10 $Lmin^{-1}$	[13]
Tillandsia Brachycaulos	8.02	4525 Bqm^{-3}	72	1 m^3	[6]
Tillandsia Usneoides	7.1	3910 Bqm^{-3}	71	1 m^3	[7]

[(a)] Calculated with their data

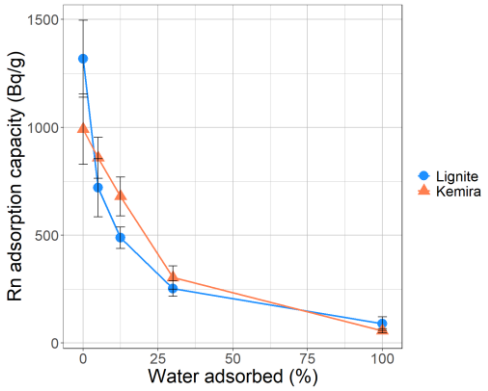
To study if the differences in radon adsorption between different carbons are significant, a statistical analysis has been performed with R software. A Kruskal test was performed comparing each of the four activated carbons with the control with a 95% confidence interval and $p < 0.05$ has been considered statistically significant. The only significant difference has been found between Lignite and the control.

3.2 Influence of water adsorbed

The experiments have been performed during October and November 2019 and the average climatological data obtained are 22.1 ± 2.50ºC (temperature), 1001.2 ± 7.93hPa (atmospheric pressure) and 44.7 ± 8.68% of relative humidity inside the laboratory.

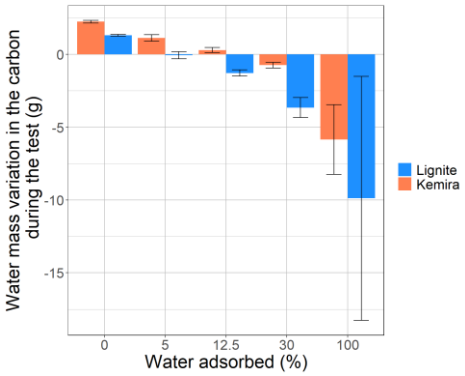
In Fig. 3 is shown the average of radon adsorbed concentration for each water adsorbed tested for both activated carbons studied. For both Lignite and Kemira, it can be observed that the average values of radon adsorbed are increasing as the water adsorbed decreases. With activated carbon thoroughly saturated (100% water adsorbed) it is proved that the quantity of radon adsorbed is very low. The results obtained, match the ones presented by previous authors [17] and [24]. In their work on radon exhalation, they already observed that water content of activated carbons negatively affects the adsorption in canister measurements.

Figure 3: Comparison between the average quantities of radon adsorbed by each activated carbon tested and for each average water adsorbed achieved in the activated carbon



According to the results obtained in the previous section, it was expected that Lignite adsorbed more radon than Kemira but in Fig. 3 can be observed that for water adsorbed between 5 and 30%, Kemira has a better adsorption rate. Therefore, to explain this behaviour, the evolution during the test of water content in the humidified activated carbon was studied. In Fig. 4 is represented the amount of water gained (values above 0) or lost (values below 0) for both activated carbons comparing its initial water content with the water content after the test, by weighting the canisters before and after the exposition.

Figure 4: Comparison of the mass of water lost or gained by each activated carbon compared with the initial water content of the sample (water adsorbed)

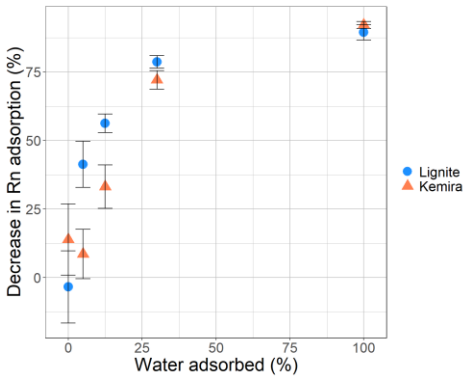


The samples with the highest percentage of adsorbed water (100%) initially, gives a negative variation of the mass of water retained in the carbon, so they lose water throughout the test. This water loss coincides with the lowest radon adsorption capacity, as it can be observed comparing Fig. 3 and Fig. 4. Part of the water adsorbed in the active centres of the activated carbon is desorbed during the test, so these are free to retain some radon gas. When the percentage of initial water adsorbed is lower (until 12.5 % for lignite and 30 % for Kemira), some of the active centres for adsorption of radon in activated carbon are available for adsorption from the beginning of the test, and the amount of radon adsorbed is higher. The higher amounts of radon adsorption correspond to the lower percentages of water adsorbed initially (0%); this means that all active centres of the activated carbon are available for adsorption.

Samples adsorb radon but also water from the environment (water vapour from the air), so an increase in the mass of water retained in the carbon is observed.

Fig. 5 shows the evolution of the percentage decrease in radon adsorption rate compared to the radon adsorption of the control in each water adsorbed and for both activated carbons, Lignite and Kemira. The decrease in radon adsorption with water adsorbed follows the trend shown in Fig. 5. As Lignite is more affected by water adsorbed than Kemira, it presents higher decreases in radon adsorption. Concerning the shape of the curve, it means that for lower values of the water adsorbed a slight increase in this parameter results in a high decrease in radon adsorption so that means that the activated carbon should remain as drier as possible, especially in the case of Lignite.

Figure 5: Percentage of decrease in radon adsorption compared to control for each water adsorbed tested and both types of activated carbons



4 CONCLUSIONS

Adsorption of radon on activated carbon could be a support alternative to ventilation to reduce the concentration of radon in air. For an optimum result of radon adsorption from polluted air, the following recommendations are given:

- The type of activated carbon and its properties is a key factor in radon adsorption.

    - Mineral carbons (Lignite) are preferred over vegetal origin. However, among the activated carbons of vegetal origin, the best is Kemira. All the activated carbons tested, except the control, have a higher radon adsorption rate than the values found for activated carbon in the bibliography. Furthermore, activated carbon, in general, has a higher radon adsorption rate than other adsorbents, like zeolites, coconut shell or some plants.

    - Concerning the parameters of the mineral activated carbon influencing radon adsorption, specific surface, particle diameter and iodine number are more important. However, for carbons with the vegetal origin, further research should be done since all the characteristics are similar so it seems that other parameters could affect radon adsorption, apart from the ones already studied.

- Lignite adsorbs more water than Kemira when both carbons are humidified. During the exposition, Lignite and Kemira lose water at 100% and 30% of water adsorbed, although Lignite loses more than Kemira. From 12.5% to 5%, Lignite still loses water while Kemira adsorbs water from the environment. When the carbons are dry (0% of water adsorbed), both adsorb water, but Lignite does so in less proportion.

- The water adsorbed of the carbon should be controlled given that diminishes the adsorption capacity because the adsorption sites are occupied with water molecules. Work with dry material is always recommended. There is not an amount of water adsorbed for which there is an optimum in radon adsorption, contrary to water content in the soil. However, if it is not possible to work with dry material,

it is recommended not to exceed 12.5% of water adsorbed for Kemira because the decrease in radon adsorption is around 35% and 5% of water adsorbed for Lignite due to a decrease of 40% in radon adsorption. Increases of water above these percentages have a critical influence on radon adsorption rate.

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