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Sorbent design for CO₂ capture under different flue gas conditions

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Abstract

CO₂ capture by solid sorbents is a physisorption process in which the gas molecules are adsorbed in a different porosity range, depending on the temperature and pressure of the capture conditions. Accordingly, CO₂ capture capacities can be enhanced if the sorbent has a proper porosity development and a suitable pore size distribution. Thus, the main objective of this work is to maximize the CO₂ capture capacity at ambient temperature, elucidating which is the most suitable porosity that the adsorbent has to have as a function of the emission source conditions. In order to do so, different activated carbons have been selected and their CO₂ capture capacities have been measured. The obtained results show that for low CO₂ pressures (e.g., conditions similar to post-combustion processes) the sorbent should have the maximum possible volume of micropores smaller than 0.7 nm. However, the sorbent requires the maximum possible total micropore volume when the capture is performed at high pressures (e.g., conditions similar to oxy-combustion or pre-combustion processes). Finally, this study also analyzes the important influence that the sorbent density has on the CO₂ capture capacity, since the adsorbent will be confined in a bed with a restricted volume.

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1. Introduction

The worldwide increasing energy demand gives rise to a constant increase in the anthropogenic emissions of CO₂. According to the report of the Intergovernmental Panel on Climatic Change, unequivocal evidences indicate that the climate-change is a reality which is attributable to human activities [1]. The forecasts regarding the world population growth and the increase in the energy demand for the coming decades envisage that all the fossil fuels (specially coal) will have to remain a major source of energy in the medium term [1]. Hence, further increases in CO₂ emissions are expected for the foreseeable future.

Different technological options are being studied, in order to maintain the CO₂ concentration in the atmosphere at a level that is expected to prevent interference with the climate system: i) increasing the use of renewable energy or nuclear energy sources; ii) reducing energy consumption and increasing the efficiency of energy conversion; iii) switching to lower carbon fuels, and iv) CO₂ capture and subsequent use or storage for a very long time (CCS) [1]. A CCS process involves three stages: capture of CO₂ from the emission point, consisting in the separation of CO₂ from other gases, then transport of the captured CO₂, and its subsequent use or storage, for example in geological reservoirs.

CO₂ capture is a fundamental part in CCS technologies. Among the different investigated techniques [1-5], capture on adsorbents, such as zeolites, metal organic frameworks (MOFs), or activated carbons (ACs), is an interesting alternative [1, 4-6]. Among the proposed sorbents and considering a near future application, there is no doubt about the emerging importance of the ACs due to their unique properties: well-known and well developed activation processes, high pore volumes and surface areas,

high stability, low chemical reactivity, easy shaping and suitable high material density [7, 8]. This is confirmed by the increasing number of papers published in recent years [4-6, 9-17].

Among the different CO₂ emissions of fixed sources (e.g., as electricity production and manufacturing industries; aluminum, coke, cement...) a substantial part of them comes from the electricity sector (*i.e.*, from thermal power plants [2]). Consequently, the first implementations of carbon CCS technology are being analyzed in these particular emission sources. There are different types of power plants, hence their flue gases compositions (*i.e.*, their CO₂ concentrations) and conditions (pressure and temperature) [2, 3, 5] are different. This is a very important aspect when defining the strategy of the sorbent selection to be applied for CO₂ capture by adsorption (*i.e.*, adsorbent characteristics).

From a fundamental point of view, CO₂ capture on a given adsorbent is based on a physical adsorption process. Hence, its adsorption capacity depends very much on the conditions of the emission point (temperature and pressure) and on the sorbent properties, mainly the porosity development. CO₂ adsorption on porous carbon has been widely investigated in microporous carbons [18-23] since the 1960s, and latter used as a complementary adsorptive to N₂ at 77 K [23-26] to avoid diffusional problems of N₂ molecules at 77 K inside the narrower pores [18-26]. Additionally, using different types of carbon sorbent materials, it was demonstrated that CO₂ at 273 K (or 298 K) is an adsorptive that behaves quite similarly to N₂ at 77 K at comparable relative pressure ranges. Thus, at these temperatures and sub-atmospheric pressures, CO₂ is adsorbed in micropores lower than 0.7nm (also called narrow micropores) [24-26] or in larger pores if higher pressures are applied. At 273 K or 298 K and 4 MPa, the relative pressures reach values near to 1 or to 0.6, respectively. At these relative pressures most the pores

are filled with CO₂, as it also happens with N₂ adsorption at 77 K at similar relative pressures [25].

The main purpose of this study is to discuss the fundamental aspects of the CO₂ capture at room temperature on selected activated carbons, measuring their CO₂ adsorption capacity and analyzing the influence of both the pressure and the properties. All this information will be analyzed considering CO₂ pressure values of the emission points in order to optimize the properties that the adsorbent would require, as well as the type of activation required. For getting our objective, different activating conditions have been used, in order to obtain activated carbon samples with a wide range of porosity developments and different pore size distributions.

Finally, the suitability of the adsorbent for CO₂ capture application is evaluated in volumetric terms-CO₂ capacity per liter of adsorbent- since, from an application point of view, the sorbent would be stored in a bed reactor, and therefore, not only the porosity plays a fundamental role, but also the density of the adsorbent is crucial for this application [7, 27-29].

2.1 Experimental

2.1. Preparation of activated carbon materials

In order to cover a wide range of porosity developments (i.e., surface areas and pore size distributions), ACs were prepared from five different pristine materials: one anthracite (A), three sub-bituminous coals (SB, IN and SA), and one lignite (L). KOH and NaOH were used as activating agents and different activating agent/precursor ratios were applied. Details concerning the activation process can be found elsewhere [30-32]. Summing up, the precursor was mixed with different proportions of the activating agent, and the mixture was subjected to a thermal treatment in inert atmosphere at 1023

K. After the heat treatment, the samples were repeatedly washed with HCl and water to remove secondary products. Finally, the resulting ACs were dried. The nomenclature used for the obtained ACs includes the activating agent, the starting material and the activating agent/precursor ratio. Thus, NaA21 identifies the conditions used for such sample; the activation (NaOH), the precursor name (anthracite) and the activating agent/precursor ratio (2/1).

2.2. Porosity characterization

Porous texture characterization of all activated materials was assessed in an Autosorb-6 apparatus (Quantachrome Corp.) by physical gas adsorption of N₂ and CO₂ at 77 K and 273 K, respectively. In both cases, samples were degassed at 523 K under vacuum for 4 hours. Micropore volumes, $V_{DR}(N_2)$, and apparent BET surface areas, S_{BET} , were calculated by fitting N₂ adsorption data to Dubinin-Radushkevich and to BET equations, respectively. The latter (surface area) should be understood only as an indicator of the adsorption capacity, in agreement with Barrer's concept [33]). The narrow micropore volume (micropores < 0.7 nm), $V_{DR}(CO_2)$, was calculated from CO₂ adsorption at 273 K using the Dubinin-Radushkevich equation [24-26].

2.3. Packing densities.

Packing densities, ρ_{Pack} , of all the samples were measured in a mechanical press according to the procedure described elsewhere [34], where a known amount of sample is introduced into a cylindrical steel mold with a diameter of 13 mm. In order to compact the sample, a force equivalent to the mass of 1 tonne is applied on the sample with a steel cylinder. The volume occupied by the sample is evaluated by measuring the penetration depth of the steel cylinder after releasing the pressure in comparison with a reference measurement in which no sample is introduced into the mold.

2.4. High pressure CO_2 adsorption isotherms

In order to obtain the adsorption capacity for the ACs at different conditions, carbon dioxide isotherms at 298 K and up to 4 MPa were carried out, using two devices. A gravimetric apparatus (Sartorius 4406-DMT high-pressure microbalance) and a fully automated volumetric Quantachrome device (iSorbHP1). In both devices, about 300 mg of sample were used. In the particular case of the gravimetric instrument, the experimental results were corrected for buoyancy effects related to the displacement of gas by the sample, sample holder and pan [24, 25]. In both devices, samples were degassed “in situ” at 423 K under vacuum for 4 hours.

3. Results and Discussion

3.1 Characterization results

Fig. 1 presents the porosity development of the large number of ACs prepared for this study, plotting in Fig. 1a their narrow micropore volume, ($V_{\text{DR}}(\text{CO}_2)$), in Fig. 1b their total micropore volume ($V_{\text{DR}}(\text{N}_2)$), and in Fig. 1c their BET surface area (S_{BET}). It can be seen that the samples cover a very wide range of porosities. As an example, their apparent surface area values range from 800 to more than 3000 m^2/g ; see Fig. 1c and their total micropore volumes range from 0.4 to 1.3 cc/g ; see Fig. 1b. Additionally, the combination of the carbon precursor and the activation process used, allows the preparation of samples with interesting attributes, e.g., high values of narrow micropore volumes (even higher than 0.8 cc/g); see Fig. 1a.

Due to the large number of studied samples, Table 1 compiles the textural properties and packing densities of a representative selection of them.

Figure 1. Textural properties obtained from the characterization of the ACs prepared by chemical activation. a) narrow micropore volume, $V_{DR}(CO_2)$; b) total micropore volume, $V_{DR}(N_2)$ and c) apparent BET surface area, S_{BET} .

Table 1. Textural characterization and packing densities for the selected activated carbons.

Sample	S_{BET} (m^2/g)	$V_{\text{DR}}(\text{N}_2)$ (cc/g)	$V_{\text{DR}}(\text{CO}_2)$ (cc/g)	ρ_{pack} (g/cc)
NaA11	845	0.39	0.39	0.76
KA11	1069	0.50	0.50	0.75
NaSB11	1100	0.50	0.45	0.67
KL11	1133	0.52	0.52	0.61
KSB11	1255	0.58	0.54	0.60
NaA21	1421	0.64	0.61	0.59
NaA31	1484	0.63	0.56	0.59
KL21	1565	0.71	0.68	0.51
NaA41	1598	0.70	0.55	0.53
KSB21	1835	0.81	0.64	0.48
KA21	2156	1.02	0.83	0.50
NaSB21	2496	1.14	0.68	0.35
KL31	2540	1.02	0.67	0.33
KL41	2897	1.02	0.64	0.25
NaSB31	3024	1.30	0.67	0.25
KA31	3043	1.20	0.80	0.36
KA41	3237	1.22	0.76	0.34

3.2. High pressure (4 MPa) CO_2 adsorption isotherms at 298 K

High pressure CO_2 adsorption experiments have been carried out on all the prepared samples. As in Table 1, only the representative selected samples are going to be discussed next. CO_2 adsorption isotherms at room temperature and up to 4 MPa for these selected samples are shown in Fig. 2. This Figure shows that, depending on the activation conditions applied and hence, on the resulting porosity characteristics, the carbon sorbents present different CO_2 excess adsorption uptakes. At high pressures, samples prepared with low hydroxide/precursor ratios (*i.e.*, 1/1 and 2/1) present moderate CO_2 adsorption capacities whereas materials prepared using high hydroxide/precursor ratios (*i.e.*, 3/1 and 4/1) have higher porosity developments and

hence they present, as expected, higher CO_2 adsorption. At low pressures, the differences among samples become smaller and, in some cases, samples prepared with the low hydroxide/precursor ratios exhibit slightly higher CO_2 adsorption capacities. This behaviour may be due, as it will be commented next, to the differences in the pore size distributions of the samples obtained.

Figure 2. CO_2 excess adsorption isotherms at 298 K and up to 4 MPa for a selection of activated carbons, obtained at different chemical activation conditions.

3.3. Correlation between CO_2 adsorption capacity and sorbent properties

Based on the results shown above, different variables seem to control the CO_2 adsorption capacity depending on the pressure used. In order to figure out if these CO_2 uptake results might be explained based on a given type of porosity development Fig. 3 (from 0.1 up to 1.2 MPa) and 4 (from 1.5 up to 4 MPa) present the amounts of CO_2 adsorbed *versus* the narrow micropore volume, $V_{\text{DR}}(\text{CO}_2)$.

Figure 3. CO₂ adsorption capacity at 298 K as a function of the narrow micropore volume, $V_{DR}(CO_2)$ for pressures from 0.1 up to 1.2 MPa.

Figure 4. CO₂ adsorption capacity at 298 K as a function of the narrow micropore volume, $V_{DR}(CO_2)$ for pressures from 1.5 up to 4 MPa

From Fig. 3, it can be observed that, regardless of the nature of alkaline hydroxide and of the raw material used, CO₂ uptake follows linear relationships with the narrow micropore volumes in the pressure range 0.1 to 1.2 MPa (only the sample with the highest $V_{DR}(CO_2)$ deviates somewhat at 1 and 1.2 MPa). These relationships suggest that CO₂ adsorption takes place mainly in the narrowest microporosity. Surprisingly, at pressure of 0.1 MPa all the samples have similar CO₂ uptake values, independently of their narrow micropore volumes. This apparent “anomalous” behavior seems to indicate that, in all of the studied sample, the micropore volume occupied by adsorbed CO₂ molecules at 0.1 MPa is lower than their available narrow micropore volume. To

corroborate this hypothesis, the volume occupied by CO₂ molecules was calculated using the liquid density of CO₂ ($\rho_{\text{liq}}(\text{CO}_2)$: 1.044 g/cc). Thus, at 0.1 MPa, the volume of the CO₂ adsorbed in any of the samples studied varies from 0.1 to 0.15 cc. These values are much lower than the lowest available narrow micropore volume of the samples (near 0.4 cc/g). Interestingly, if carbon sorbents are prepared for capturing CO₂ at such low pressure, it is not necessary to use a high activation process.

For higher pressures (1.5 to 4 MPa) the previous observed linear trends fail as it can be seen in Fig. 4, especially for samples having $V_{\text{DR}}(\text{CO}_2)$ values higher than 0.6 cc/g. These observations indicate that as the pressure increases, and the amount of adsorbed CO₂ requires pore volume higher than 0.6 cc/g (the available narrow micropore volume), larger micropores start to be used during the CO₂ storage. As commented in

Table 2. Narrow micropore volume ($V_{\text{DR}}(\text{CO}_2)$) and the volume occupied by the CO₂ molecules adsorbed on the selected ACs at 1.5, 2, 3 and 4 MPa, respectively.

Sample	$V_{\text{DR}}(\text{CO}_2)$ (cc/g)	V_{CO_2} (cc/g) 1.5 MPa	V_{CO_2} (cc/g) 2 MPa	V_{CO_2} (cc/g) 3 MPa	V_{CO_2} (cc/g) 4 MPa
KA11	0.50	0.37	0.38	0.39	0.41
KA21	0.83	0.64	0.69	0.73	0.74
KA31	0.80	0.73	0.83	0.95	0.99
KA41	0.76	0.73	0.84	1.00	1.07
NaA11	0.39	---	0.29	0.30	0.31
NaA21	0.61	---	0.49	0.53	0.55
NaA31	0.56	---	0.48	0.52	0.54
NaA41	0.55	---	0.50	0.53	0.54
KSB11	0.54	0.39	0.40	0.41	0.41
KSB21	0.64	0.53	0.56	0.59	0.58
NaSB11	0.45	0.33	0.34	0.34	0.33
NaSB21	0.68	0.63	0.70	0.80	0.84
NaSB31	0.67	0.69	0.80	0.96	1.09
KL11	0.52	0.41	0.44	0.45	0.48
KL21	0.68	0.47	0.49	0.50	0.49
KL31	0.67	0.62	0.70	0.82	0.88
KL41	0.64	0.65	0.76	0.93	1.05

the case of 0.1 MPa, the volume occupied by the adsorbed CO₂ molecules at these pressures higher than 1.5 MPa have been calculated, as it is shown in Table 2 together with their narrow micropore volume.

It can be seen that as the pressure increase the volume occupied by the CO₂ molecules adsorbed can reach values higher than the $V_{DR}(CO_2)$; i.e., samples having narrow micropore volumes higher than 0.6 cc/g. This difference becomes higher when the pressure is increased, showing the highest differences at 4 MPa. This behavior corroborates that, at pressures higher than 1.5 MPa, the narrow microporosity has been filled and CO₂ molecules are being adsorbed on larger micropores.

Further confirmation is obtained performing a similar analysis with the micropore volume ($V_{DR}(N_2)$) calculated from N₂ adsorption isotherms. In Fig. 5, it can be observed that there is no linear correlation between CO₂ adsorption capacity and the total micropore volume ($V_{DR}(N_2)$) especially for pressures lower than 1.0 MPa. This behavior agrees with the previous mentioned results: at room temperature and for low pressures the adsorption of CO₂ is controlled by the narrow micropore volumes of the samples. However, when higher pressures are analyzed (especially higher than 1.2 MPa), the CO₂ capacity represented against the total micropore volume shows that other micropores higher than the narrow ones are also effective. In that case, CO₂ uptakes increase linearly with the total micropore volume ($V_{DR}(N_2)$) as shown in Fig. 6 confirming that at high pressures (1.2 MPa and higher) CO₂ fills, in addition to narrow micropores, larger micropores.

As it has been indicated previously [25], CO₂ behaves similar to N₂ when their isotherms are compared at similar relative pressures. Under the investigated experimental conditions, CO₂ is adsorbed as a subcritical gas, and hence, the relative

pressure concept (P/P_0 , being P_0 the saturation pressure) can be applied. Its saturation pressure at room temperature is 6.41 MPa. Therefore, for pressure up to 1 MPa, its saturation pressure is < 0.15 , and such small value would explain that the adsorption process is occurring on the narrowest microporosity which agrees with the linear correlation observed between CO_2 uptake and $V_{\text{DR}}(\text{CO}_2)$. In other words, for these low relative pressures only a small portion of the total porosity of the adsorbent is used (*i.e.*,

Figure 5. CO_2 adsorption capacity at 298 K as a function of the total micropore volume, $V_{\text{DR}}(\text{N}_2)$ for pressures from 0.1 up to 1.2 MPa

Figure 6. CO₂ adsorption capacity at 298 K as a function of the total micropore volume, $V_{DR}(N_2)$ for pressures from 1.5 up to 4 MPa

only the narrow micropores are filled by CO₂). When the relative pressure increases, larger micropores begin to be filled. Thus, for pressures up to 2 MPa, P/P_o is 0.31. Therefore, pore sizes of 2 nm are being filled in agreement with the trends between the carbon dioxide adsorption capacity and the total micropore volume ($V_{DR}(N_2)$).

3.4. Remarks about sorbent properties and their final applications

All the above results point out that there is a relationship between the characteristics of the adsorbents and the CO₂ pressure of the gas effluent to be treated. Accordingly, the porous sorbents should be specially prepared to get, for a given application, the most

suitable micropore volumes and micropore size distributions. Among the different types of gas effluents to be treated, typical flue gas conditions (i.e., the different CCS technologies) will be taken into account. Thus, for a post-combustion power plant, the flue gas usually is at nearly atmospheric pressure, its temperature before CO₂ capture is close to the ambient, and its concentration of CO₂ is < 15 vol.% [3, 4, 35]. Under these conditions, very low relative pressures are obtained (P/P_o : 0.002). Thus, based on the previous results, a sorbent with a high porosity development (i.e., high $V_{DR}(N_2)$ or BET) would not be necessary. On the contrary, its microporosity should be very narrow (< 0.7 nm) and among the samples studied, low hydroxide/precursor ratios may be sufficient for preparing proper adsorbents.

Pilot plants for CO₂ capture from flue gas streams in pre-combustion and oxy-combustion units, as well as the CO₂ processing units (e.g., further purification systems and compression units for pipeline transport and storage) are under progress [35]. Their main advantages, when compared to post-combustion, for the CO₂ capture process is their higher CO₂ concentration (partial pressure). Thus, in pre-combustion CCS processes the CO₂ concentration (after the water-shift reaction) can be up to 35-40 vol.% [3, 4], and in the case of oxy-combustion even higher (60-80 vol.%) [35], both at temperatures near ambient temperature. Such CO₂-rich flue gas streams can be easily adjusted to the most convenient temperature and, in the case of oxy-combustion, pressurized (e.g., to 2-4 MPa) depending on the CCS technology to be used. If CO₂ capture is carried out by physical adsorption, the uptake process is favored increasing the pressure (2-4 MPa) and lowering the temperature (near ambient or lower).

Summing up, post-combustion technologies would result the least favorable scenario for CO₂ capture by solid sorbents due to their lower CO₂ partial pressure. At room temperature and at 0.1 MPa their partial pressures (P/P_o) would be: 0.002 for post-

combustion, 0.005-0.006 for pre-combustion, and 0.009-0.012 for oxy-combustion. At an increased pressure of 4 MPa, the P/P_0 values would be: 0.094 for post-combustion, 0.218-0.250 for pre-combustion, and 0.374-0.500 for oxy-combustion. It is evident that in these two last cases, having higher CO_2 relative pressures, the adsorption takes place in larger micropores and; hence, from the point of view of the activation process, highly activated carbons with high porosity developments should be chosen to obtain high CO_2 capture capacities.

3.5. Influence of the sorbent packing density

From an application point of view, the density of the sorbents is also a key factor since it will determine the adsorption or the storage capacity on a volumetric basis [27, 36, 37]. As it was demonstrated in previous works [7, 27, 36-43] for applications where the volume of the storage system is limited (*e.g.*, hydrogen or methane storage), the sorbent density is essential. In these cases, adsorbents with not only an appropriate porosity but also with a suitable high packing density are necessary to maximize the gas storage.

In the case of CO_2 capture, the volume occupied by the adsorbent is not so restrictive than it is for hydrogen and methane storage applications. However, due to the huge gas flows that must be treated, the volume of the tank containing the adsorbent is an important aspect that merits to be considered. Therefore, it is also important for this application to have adsorbents with high packing densities in order to reduce the volume of the system. Table 1 summarizes the packing density values of the ACs selected for this study. As expected, the general trend is that the packing densities decrease with the increase of the porosity development. Thus, ACs with the highest packing densities are those prepared under soft conditions (low hydroxide/precursor ratios).

For the analysis of the packing density variable, two different pressures have been selected (i.e., 0.6 MPa and 2 MPa, respectively) for expressing the CO₂ uptake on a volumetric basis (i.e., per liter of adsorbent). Figure 7 shows, the volumetric CO₂ adsorption capacity for both pressures and also, for comparison purposes, the gravimetric ones.

As it was mentioned previously, there are linear relationships between the textural properties and the gravimetric (mmol/g) CO₂ uptake; at 0.6 MPa with the narrow micropore volume and at 2 MPa with the total micropore volume. Contrarily, for the volumetric CO₂ uptake (g/l; calculated multiplying the gravimetric values by the corresponding packing density of Table 1) these linear tendencies disappear, confirming the importance of the density of the sorbent. In the case of Figure 7(a), it should be mentioned that the samples presenting the two highest volumetric adsorption capacity (>230 g/l) are sample KA11 ($V_{DR}(\text{CO}_2)$ of 0.5 cc/g and a ρ of 0.75 g/cc), and sample KA21 ($V_{DR}(\text{CO}_2)$ of 0.83 cc/g and a ρ of 0.5 g/cc). That is: one sample (KA11) with a moderate narrow micropore volume but with a high packing density and sample (KA21) with a high narrow porosity development but a moderate packing density value. The fact that these two samples show the same volumetric adsorption of CO₂ highlights the importance of both parameters. At 2 MPa, the same conclusions can be extracted (see Figure 7(b)); the highest adsorption capacity per liter of adsorbent is not obtained for a sample with the highest total micropore volume. The highest value corresponds to the sample KA21 which has the most suitable combination of porosity and density.

Figure 7. CO₂ adsorption capacity at 298 K versus (a) micropore volume at 0.6 MPa and (b) total micropore volume at 2 MPa on both gravimetric and volumetric basis.

4. Conclusions

CO₂ capture by a sorbent depends on its porosity and on the characteristics of the emission sources (i.e., concentration, pressure and temperature of CO₂ in the gas flow to be treated). To optimize its capture at room temperature, the present paper has selected a large number of activated carbon (covering a large range of porosities and pore size

distributions) and their room temperature CO₂ storage has been measured at different pressures. From the results obtained, the adsorbent porosity has to be developed according to the CO₂ concentration and pressure of the gas to be treated. For low CO₂ concentration (e.g., post-combustion capture) and for pressure (< 1.2 MPa), the sorbent has to have the maximum possible development of micropores narrower than 0.7 nm. For higher CO₂ concentrations and pressures (e.g., pre-combustion and oxy-combustion capture), the sorbent should have the highest possible micropore volume. When the results are analyzed on a volumetric basis, the obtained results confirm the importance of the adsorbent density, demonstrating that not only the porosity of the adsorbent is important but also its density is crucial to maximize the CO₂ capture.

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