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Processing and characterization of $TiO_2/ZnAl_2O_4$ ultrafiltration membranes deposited on tubular support prepared from Moroccan clay

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Abstract

The preparation of a composite ultrafiltration membrane of $TiO_2/ZnAl_2O_4$ by sol–gel route is presented. In this work, an original macroporous support made of Moroccan clay has been used to support an intermediate ZrO_2 layer and the active $TiO_2/ZnAl_2O_4$ ultrafiltration layer. The main characteristics of the ultrafiltration membrane are reported (pore diameter: 5 nm; water flux: 9.4 $l\ h^{-1}\ m^{-2}\ bar^{-1}$; thickness: 0.7 μm; cutoff: 5000 Da), they confirm the prepared membrane is a low ultrafiltration membrane which is able to remove electrolytes solutes by a Donnan exclusion mechanism.

Keywords: Clay; Sol–gel; Ultrafiltration; Ceramic membrane; Multilayer

1. Introduction

Since more than 20 years, the membrane processes have proved their interest in the industry, such as the use of microfiltration or ultrafiltration membrane processes in the dairy industry [1]. More recently, an important water plant for drinking water production was built in France. One of the steps of the process is based on the use of organic nanofiltration membranes to remove the polluting agents such as organic pesticides and mineral ions resulting in water with a high standard of quality [2]. Nevertheless, the development of membrane processes to treat wastewater is generally limited because the price of the membranes is too expensive, which is particularly true for the inorganic membranes. One of the challenges for future development of the inorganic membranes will be to produce low-cost membranes with high flux performance to treat large volumes of liquid effluent. The commercial membranes supplied by the market presents an asymmetric multilayer configuration [3], the different filtering layers are supported by a support which offers sufficient mechanical strength [3]. Different ceramic supports materials are currently used, however, α-alumina supports are the most common [4–7]. The selectivity of the membrane is obtained by the deposition of a thin porous layer on the surface of the support. Significant research efforts have been devoted to the preparation of such porous layers made in TiO_2, SiO_2 and ZrO_2 by sol–gel route [4–7]. In fact, the commercial support made of artificial material is an important part of the high price of the membranes, which is why some authors have focused their researches to develop the preparation of low coast supports made of natural raw materials such as clays [8–10]. In our laboratory, we use a support made of artificial cordierite [11], after coating the cordierite support with a ZrO_2 microfiltration layer, it was possible to deposit by slip

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casting a $ZnAl_2O_4$ ultrafiltration layer prepared by sol–gel route [12]. The filtration tests of this membrane have given promising results to removal of electrolyte solutes with rejection rates in the range of those obtained with the same membrane deposited on α alumina commercial supports [13,14]. To complete this work, we will present here the preparation of a $ZnAl_2O_4$ low ultrafiltration layer deposited on the surface of a Moroccan clay tubular support of which the preparation has been described in a former study [15].

2. Experimental results

2.1. Preparation and characterization of clay porous ceramic support

The tubular support used to deposit the membrane was prepared in our laboratory from natural Moroccan clay. The details of the preparation are given in another work [15], we will recall here only the main steps which are summarized in Fig. 1. The prepared plastic paste is based on a mixture of natural clay powder with water and organic additives to adjust the rheological properties of the paste to allow the shaping by extrusion. After drying and sintering at 1225 °C, the support shows an average pore diameter of 11 μm, a porosity of 43% and mechanical strength rated at 10 MPa. The length of the support was 15 cm for laboratory tests, its thickness is about 1.5 mm.

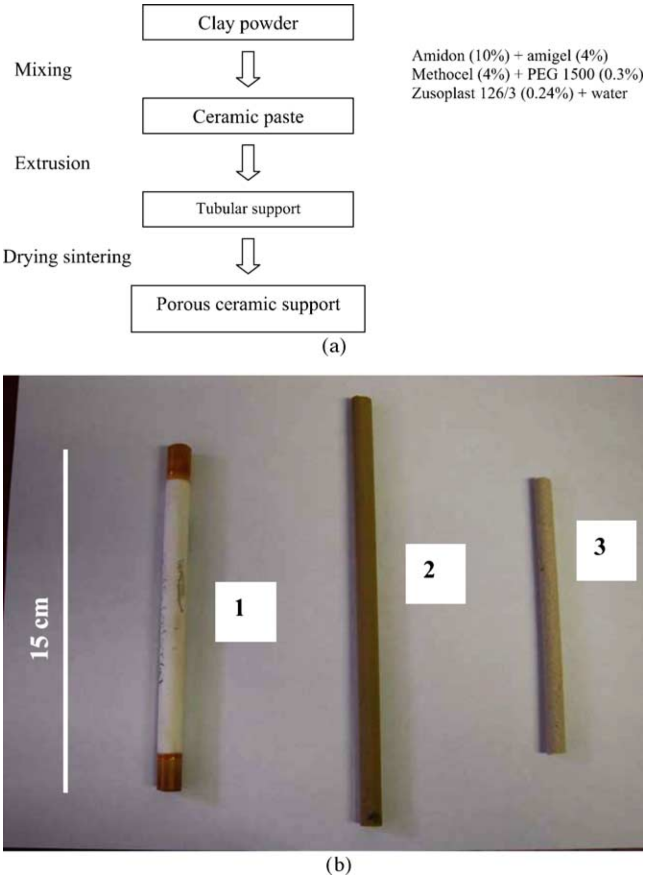

Fig. 1. (a) Simplified diagram for elaboration of porous support by extrusion method. (b) Tubular support and membrane views (length: 15 cm; outer diameter: 9 mm; inner diameter: 6 mm): (1) α-alumina commercial support; (2) Moroccan clay support after extrusion; (3) $ZnAl_2O_4$ ultrafiltration membrane deposited on Moroccan clay support.

2.2. Preparation of the zirconia (ZrO_2) intermediate membrane

The final ultrafiltration layer cannot be deposited directly by slipcasting on the surface of the support because the pore size is too large to prevent the infiltration of the sol through the support; this is why it is necessary to coat an intermediate layer on the support before coating the final ultrafiltration layer. To play this role, a microfiltration ZrO_2 layer was prepared using the suspended powder technique, the details of the method were already described in a previous work [11,12]. A deflocculated suspension of pure zirconia was obtained by mixing 10% (w/w) of zirconia powder (Cezus chimie; specific area: 8 m^2; particle diameter: 0.49 μm), 30% of PVA (12% (w/w) aqueous solution) as binder and 60% of Dolapix CE 64 dispersing agent (0.2% (w/w) aqueous solution). After coating the tubular clay support with the ZrO_2 suspension, it was dried at room temperature and fired at a temperature of 1100 °C for 2 h. Finally, an intermediate ZrO_2 layer, with pore diameters equal to 0.23 μm, was obtained. The cross-section of the coated clay support shows the average thickness of the ZrO_2 layer is around 10 μm (Fig. 2).

2.3. Preparation and characterization of the ultrafiltration TiO_2/$ZnAl_2O_4$ membrane

A significant number of materials have been tested to prepare ceramic ultrafiltration membranes, some of which are also used as the support as well. This is the case for the commercial γ-alumina or zirconia membranes. No conventional ceramics have been investigated to prepare ultrafiltration membranes; with the exception of TiO_2 [7,9], potassium titanyl phosphate (KTP) [16], spinell ($ZnAl_2O_4$) and tin oxide (SnO_2) [17] which give interesting results for filtration applications. In this work, an ultrafiltration layer made of a mixture of TiO_2/$ZnAl_2O_4$ was utilized, which was already tested in our laboratory to prepare new membranes deposited on the surface of α-alumina commercial supports in a former work [13,14]. This mixed composition is easy to prepare, moreover, the isoelectric points of both material are different (IEP TiO_2: pH 5.5; IEP $ZnAl_2O_4$: pH 10 for a powder suspension dispersed in a 0.01 M NaCl solution). Therefore, the Donnan exclusion phenomenon which controls the filtering properties of such membranes will be more important here.

2.3.1. $ZnAl_2O_4$ sol preparation

A boehmite suspension was prepared at room temperature according to the method described by Yoldas [18]; 0.9998 g of $Al_2O_3{\cdot}H_2O$ (Condea Pural SB; particle dia-

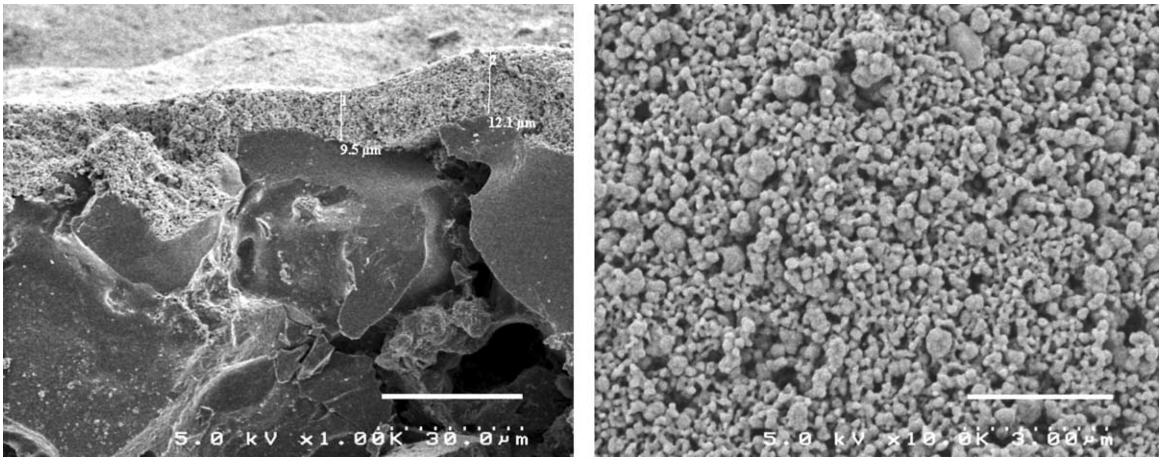

Fig. 2. SEM micrographs of zirconia interlayer.

meter: 0.5 µm) is added to 20 ml of deionized water, 1.145 g of a 1.5 mol l^{-1} nitric acid solution is used as a peptizing agent, the molar ratio $[HNO_3]/[Al_2O_3]$ was fixed at 4.8. A zinc nitrate solution prepared with 2.028 g of $Zn(NO_3)_2 \cdot 6H_2O$ (Fluka) and 0.248 g of concentrated HNO_3 in 20 ml of deionized water is then added to the former suspension. We then obtained a stable $ZnAl_2O_4$ sol which is diluted with 150 ml of deionized water.

2.3.2. TiO_2 sol preparation

A TiO_2 sol was prepared from the hydrolysis of 35.2 g of $Ti(iOPr)_4$ (Fluka) by 111.6 g of deionized water. After stirring for 1 h, 65.2 g of a nitric acid solution 1 mol l^{-1} is added, the solution is then stirred and heated at 60 °C for 24 h to obtain peptization. The sol obtained was sieved at 125 µm to remove the bigger particles and diluted to 250 ml.

2.3.3. Mixed sol $TiO_2/ZnAl_2O_4$ preparation

The mixed sol $TiO_2/ZnAl_2O_4$ was obtained after mixing together $ZnAl_2O_4$ sol (50% molar ratio), sol TiO_2 (50% molar ratio) and 10 g of hydroxyethyl cellulose (2 wt.% aqueous solution) as binder.

2.3.4. Ultrafiltration layer preparation

The former sol was deposited in the inner part of the clay tubular support by slip casting. The sol was poured inside the tubular clay support in a vertical position and was allowed to set for 2 h before the excess sol was drained. The coated support was then dried for 24 h at room temperature, fired at 250 °C for 2 h to remove the organic additives and finally sintered at 400 °C for 2 h.

Fig. 3 shows the cross-section and the surface views of the ultrafiltration layer, its thickness is uniform with an average value of 1 µm, moreover, the surface of the membrane is homogenous without major defects. The pore diameter measured by nitrogen adsorption–desorption is centered on 5 nm (Fig. 4), which confirms that we achieved to prepare a low ultrafiltration membrane (Table 1).

2.3.5. Filtration tests

Tangential filtration tests were performed on a laboratory scale filtration pilot, using a recycling configuration (Fig. 5). The temperature was set to 25 °C and the flow rate to 2.5 m s^{-1}. The working pressure was applied using a nitrogen gas source. The membranes are conditioned by immer-

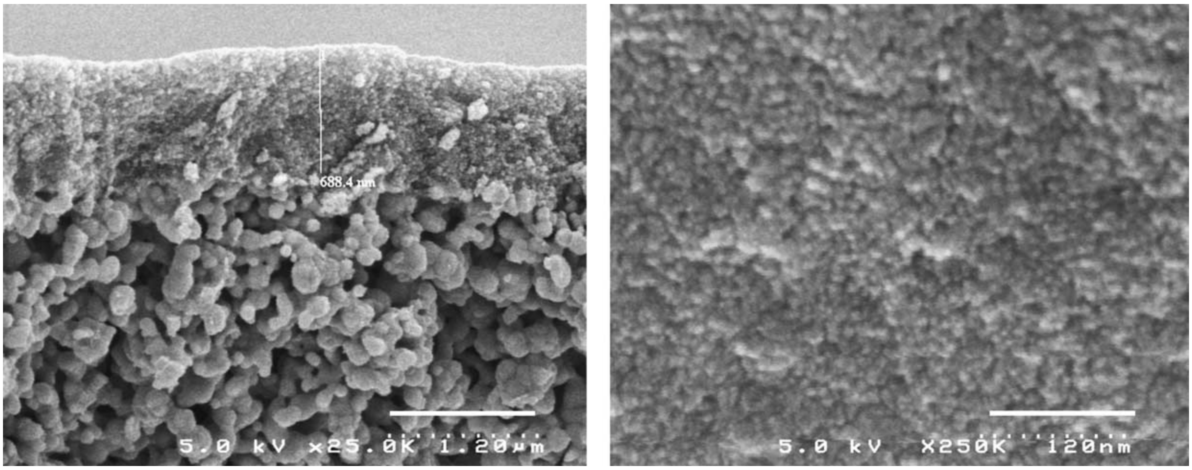

Fig. 3. SEM micrographs of $TiO_2/ZnAl_2O_4$ membrane.

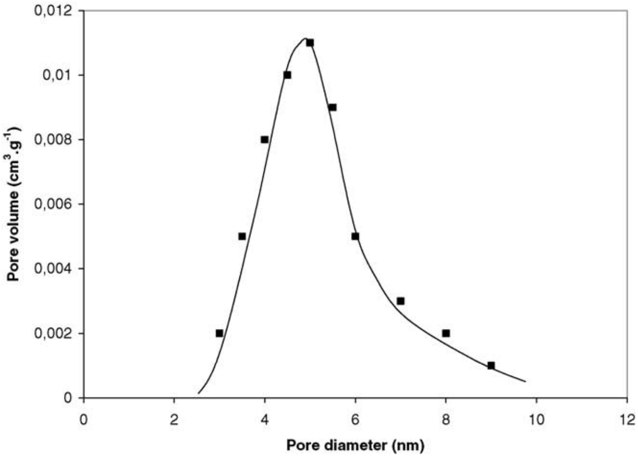

Fig. 4. Pore size distribution of $TiO_2/ZnAl_2O_4$ layer.

Table 1
Chemical composition of clay (wt.%)

SiO_2	80
Al_2O_3	12.1
Fe_2O_3	1
Na_2O	0.5
K_2O	3.7
MgO	0.06
TiO_2	1.2
CaO	1.2

sion in pure deionized water for a minimum of 24 h before filtration tests. In Fig. 6, it can be observed that the stabilization of the water flux through the membrane takes approximately 30 min. Once the stabilization of the flux is obtained, the flux depends on the applied pressure and the average permeability which is $9.4\,l^{-1}\,h^{-1}\,m^2\,bar^{-1}$ (Fig. 7).

The molecular weight cutoff (MWCO) of this membrane was determined using different solutions which contained polyethyleneglycol (PEG) of different molecular weight from 600 to 5000 Da at a concentration of $10^{-3}\,mol\,l^{-1}$. The polymer concentration in the permeate depends on the polymer size, it was obtained from the measurement of the

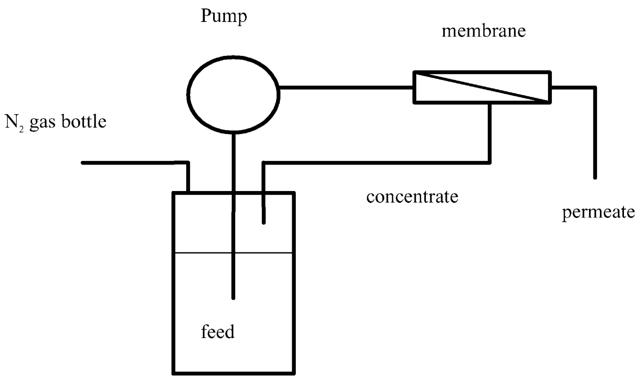

Fig. 5. Laboratory pilot.

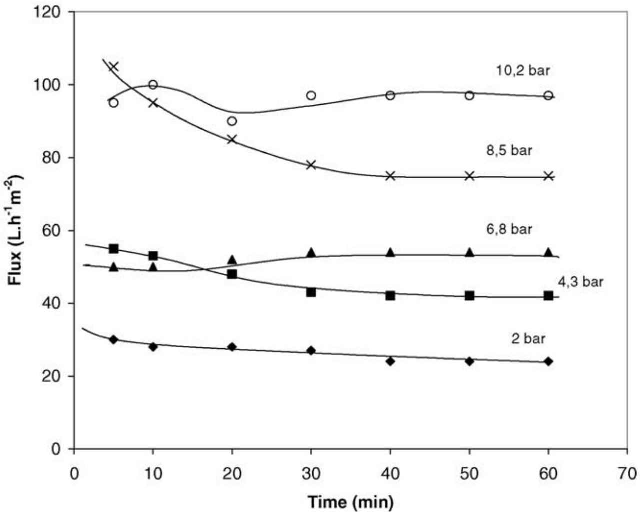

Fig. 6. Water flux vs. time.

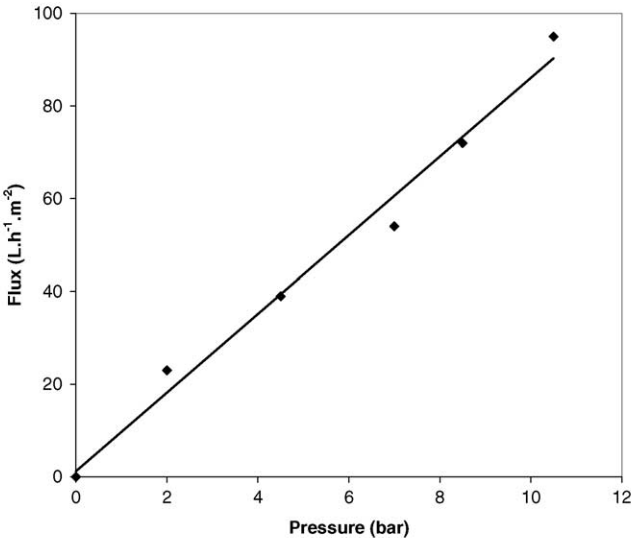

Fig. 7. Water flux vs. working pressure.

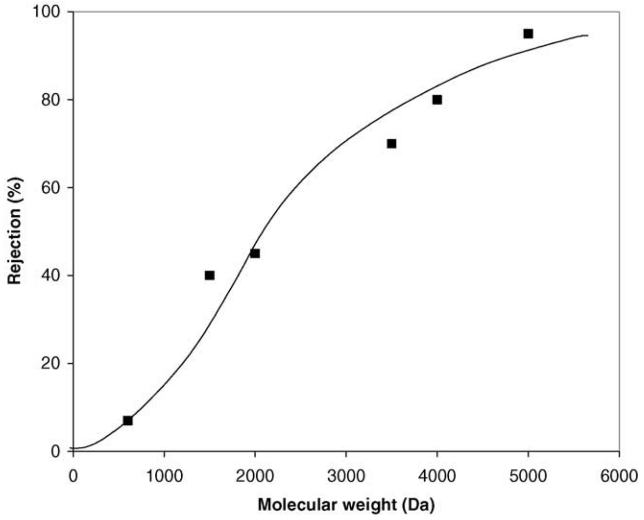

Fig. 8. Rejection rates of PEG polymers.

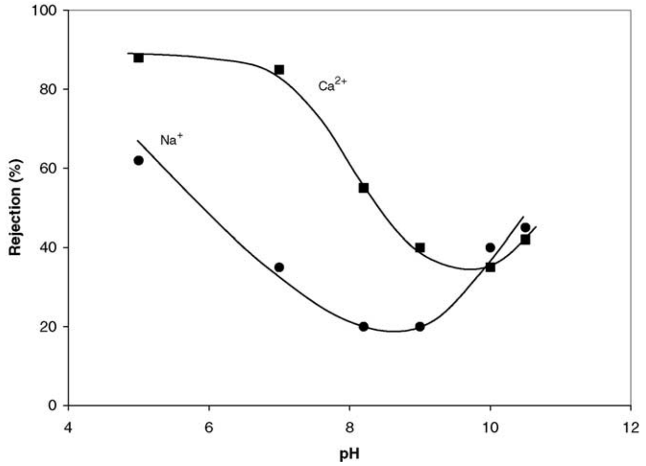

Fig. 9. pH effect on the NaCl and $CaCl_2$ rejection rates (ultrafiltration membrane deposited on support made of clay), ($C = 10^{-3}$ mol l^{-1}): (■) $CaCl_2$; (●) NaCl.

refractive index. Fig. 8 shows the rejection rate defined by $R = 100(1 - C_p/C_0)$ (C_p is the permeate concentration and C_0 the feed concentration) depends on the molecular weight of the filtered polymer. A rejection rate of 90% is obtained for MW larger than 4500 Da, this value will be considered as the cutoff of the synthesized membrane. It was observed that the cutoff depends on the nature of soluble polymers used for the characterization and significant difference can be seen, for example, with PEG or dextran. Nevertheless, the cutoff determination is in agreement with the pore size measured by nitrogen adsorption–desorption experiments.

To characterize the behavior of the prepared ultrafiltration membrane towards the filtration of electrolytes solutes it is also important to compare the performance of this membrane with those of more conventional membranes. Filtration tests of NaCl and $CaCl_2$ solutions (10^{-3} mol l^{-1}) show the rejection rate depends on the pH of the filtered solution, these observations are in agreement with all the data observed for other membranes made with amphoteric materials [13,14] (Fig. 9). This behaviour can be explained by the intensity of the electric interactions between the charged surface and the ions which depends on the pH of the filtered solution. In Table 2, no significant differences are observed for the performances obtained with the $TiO_2/ZnAl_2O_4$ ultrafiltration layer deposited on three different supports: (α-alumina, cordierite and Moroccan clay) since the rejection rates are quite similar, this substantiates the interest to use low cost mineral support made of Moroccan clay instead of classical ceramic supports.

Table 2
Compared rejections of NaCl and $CaCl_2$ ($C = 10^{-3}$ mol l^{-1}) with the $TiO_2/ZnAl_2O_4$ membrane deposited on three different supports

pH	Cordierite support	α-Alumina support		Moroccan clay support	
	NaCl	NaCl	$CaCl_2$	NaCl	$CaCl_2$
4		82	95	65	92
7	70	75	95	40	85
8	70	70	95	35	55
9	70	50	92	25	38
10	70	–	85	–	35
10.5	60	40	75	40	42

3. Conclusion

In this work, we successfully prepared $TiO_2/ZnAl_2O_4$ ultrafiltration membranes deposited on a microfiltration ZrO_2 layer This intermediate layer deposited on the support was obtained using an aqueous suspension of ZrO_2 powders. Finally, the sol–gel process was used to elaborate the $TiO_2/ZnAl_2O_4$ active layer which presents a pore size centered on 5 nm, a water permeability of 9.4 l h^{-1} m^{-2} bar^{-1} and a cutoff around 4500 Da which confirms the prepared membrane was an ultrafiltration membrane. Moreover, the ultrafiltration results of simple electrolyte solutions obtained for these membranes are very similar compared with those obtained using membranes deposited on commercial supports. The preparation of such membranes with low cost supports made of local material may be an interesting alternative for the treatment of wastewaters containing metal ions in emergent countries. The use of these membranes offers the possibility to remove the heavy metal cations or dye species from industrial effluents before dispersal in the environment by filtration techniques and comply with the principle of sustainable development. Attempts to deposit different ultrafiltration layers made of various ceramic materials are now in progress to extend the filtering properties and to modify the selectivity of the membranes.

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