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Alkaline activated carbon as adsorbents of hydrogen sulfide gases from chimney of phosphoric units

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Abstract

Activated carbon has been used for many years for the adsorption of gases from natural gas streams, carbon dioxide, and sewage vents. However, in many agricultural countries, agricultural by-products are often the problem of environmental pollution and affect human health. H_2S in biogas is very toxic and corrode the equipment. Therefore, there is a critical need for expanding research involving removal of H_2S from biogas. Some methods were studied so far: adsorption, absorption, permeation through membrane. In this theme, we did recycle of activated carbon used for waste water treatment's application .Four alkaline solution based KOH with different ratios were applied to impregnate activated carbon. The hydrogen sulfide used for application was taken from a purge at the chimney of phosphoric units. The molar ration of H_2S adsorbed to KOH is approximately 1 (mole H_2S /mole-MOH). The dominant reaction may be expressed as $H_2S + MOH \rightarrow MHS + H_2O$.Alkalines activated carbons were analyzed using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), and BET surface area analysis.

1. Introduction

Biogas is produced by the anaerobic digestion or fermentation of biodegradable materials such as biomass, manure, sewage, municipal waste, green waste, plant material, and crops. Biogas comprises primarily methane (CH4), carbon dioxide (CO2) and hydrogen sulfide (H2S), moisture and siloxane. Depending on the origins of the gas and the kind of biomass, there are many different names such as: swamp gas (wet gas), marsh gas (moist gas from plants), digester gas (compressed gas), and landfill gas (including 50% methane, 45% carbon dioxide and5% other gases).

Hydrogen sulfide (H_2S) is one of the most common compounds that can be found in petrochemical plants, coal gasification plants, wastewater treatment plants etc. It is a major air pollutant when it is emitted to atmosphere because H_2S is not only a malodorous but also a corrosive gas, and a source of acidic rains.

There are a lot of commercial treatment techniques that can be used for H_2S removal, such as adsorption by activated carbon [1, 2], condensation [3], chemical oxidation, incineration or catalytic combustion and wet absorption [4, 7]. Adsorption by iron hydroxide, activated carbon, zeolites and other adsorbents is supposed to be one of the most effective methods

The new research is mainly addressed to the removal of these gases by means of suitable adsorbing materials. Zeolites and activated carbons have been studied for this purpose, thank to their high adsorption capacity [8, 9]. Moreover, their properties can be easily improved by various treatments. In the case of activated carbon, treatments with basic solutions (KOH ,NaOH,…) appear effective to improve the adsorption properties [10, 11].

An objective of this paper is to describe the adsorption/oxidation of hydrogen sulfide from industrial wet air streams on activated carbons, to identify the reaction products and to study the influence of the carbon surface and structural parameters on the removal/oxidation of H_2S.

2. Experimental

2.1. Preparation of impregnated activated carbons

At 2004,Macia-Agulló [12] have shown that in the case of chemical activation performed with alkali hydroxides, chemical agents easily penetrate inside the carbon fibers .While Raymundo-Piñero [13] argue at 2005that this intercalation contributes to the development of porosity. This is why, in our case, we used the potassium hydroxide (KOH as agent) activating. The experimental protocol is detailed as follows:

A mass m1 of 10 g of carbon is put into a beaker. We add a mass m^2 (10 or 15 g) of crystals of KOH. Everything is well mixed.KOH crystals are dissolved by distilled water. The mixture is carried in an oven at a temperature of 110 ° C until complete evaporation water.

This is the stage of impregnation. Impregnated carbon is put into the reactor in stainless steel and to the furnace with temperature programming is as follows:

i. a rise of 5 ° C min^{-1} of the ambient temperature to 450 or 600 ° C;
ii. a level of an hour at 450 or 600 ° C;
iii. Finally a free down to room temperature.

The activation is done in the presence of nitrogen flow at 50mL.$min^{-1}$for the duration of the experiment.Treated coal out of the oven at room temperature is extensively washed with distilled water and then hydrochloric acid (0.1 M HCl) under stirring for two hours and again with distilled water until the pH of filtered water is between 6.5 and 7.

Fort differents samples of activated carbon was obtained and presented in **Table 1**.

2.2. Characterizations

2.2.1. FT-IR

Infrared absorption spectroscopy was carried out in the range 400 cm^{-1} - 4000 cm^{-1} with a Bruker spectrometer. In IR analysis, approximately 1 mg of the powders was thoroughly milled with 200 mg of potassium bromide powder KBr in an agatat mortar. So, transparent pellets were obtained at a pressure of 15 mbar.

2.2.2. S E M

The morphology of surfaces slumps was studied by using scanning electron microscopy (SEM) (JeolJSM6301). It is a technique of morphological analysis based on the principle of electron- matter interaction. To allow surface condition, bone was metalized by gold-palladium layer (a few µm of thickness) before being introduced into the analysis room. Semi quantitative chemical analysis on implanted bones surfaces, covered by gold–palladium layer to allow surface conduction, was performed by energy dispersive spectroscopy (EDS) inJeolJSM6400.

2.2.3. BET

The surface area was measured with a ASAP 2010 and Tristar 3020, Micromeritics by adsorption of nitrogen at 77 K. Prior to adsorption measurements, the samples were degassed under vacuum of 20.8 Pa at 125 °C for 30 min.

2.2.4. Gas adsorption experiment

For gas adsorption study about 12 g of samples were packed into a column (length 30 cm & diameter 22 mm). The adsorbates gas was taken from a purge at the chimney of phosphoric units.

The adsorbates were passed through regulators and then mixed before passing into the adsorbent column **(Figure 1)**. Flow rate of gases was 0.5l/min. After passing through the adsorbent column, the exit gases were analyzed by bubbler reaction during the time of adsorption. The tests were stopped at a breakthrough concentration of 150 l for mixture of gases.

Samples of the inlet and outlet gas were taken during experimental test. H_2S sample was collected in a series of impingers containing cadmium sulfate (CdSO4) which turns to cadmium sulfide (CdS) as contacted with H_2S. The concentration of H_2S was then measured from amount of CdS formed by idometrique method as given by Eq (1) [14]:

$$H_2S_{(g)} + Cd(CH_3COO)_{2(l)} \rightarrow CdS\downarrow_{(r)} + 2CH_3COOH_{(1)} \quad (1)$$

The H2S removal efficiency determined from H2S inlet and outlet concentration as given by Eq (2):

$$\%\text{H2S removal} = \frac{\text{H2S inlet} - \text{H2S outlet}}{\text{H2S inlet}} * 100 \qquad (2)$$

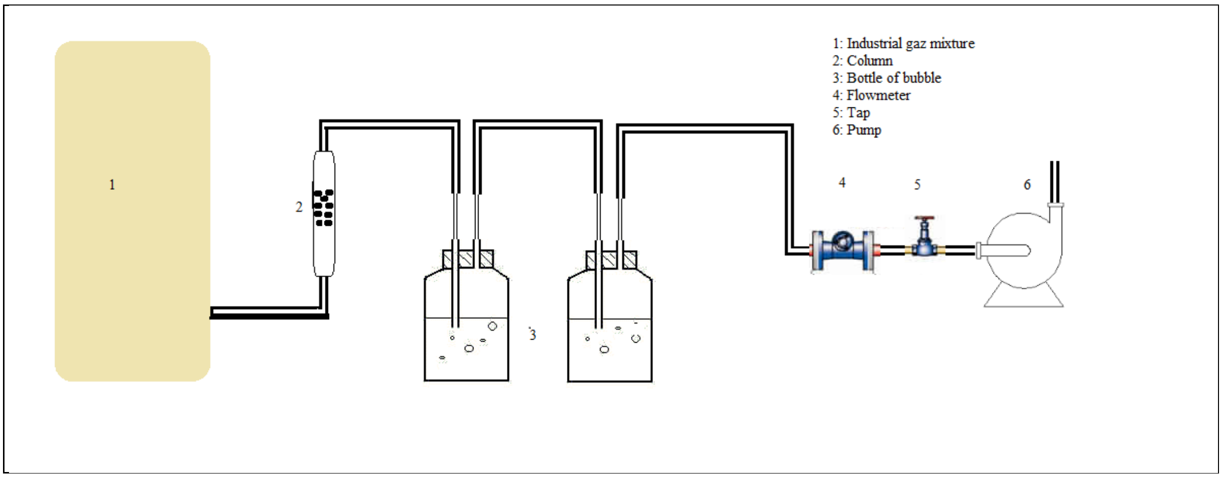

Figure 1: Experimental set-up for H_2S adsorption tests

3. Results and discussion

The FT-IR spectra of activated carbon are shown in **Figure 2**. The spectrum of the activated carbon prepared by KOH impregnation displayed the following bands: The band at 2400cm^{-1} indicate the presence of analiphatic–CH stretching. The band at 2350 cm^{-1} is the C=C stretching vibrations in alkynes groups. The band at 1743 cm^{-1} denotes the existence of carbonyl/carboxyl groups. The 1650 cm^{-1} –1500 cm^{-1} bands indicates the presence of an aromatic C=C ring stretching and 1251 cm^{-1} C–O stretches.

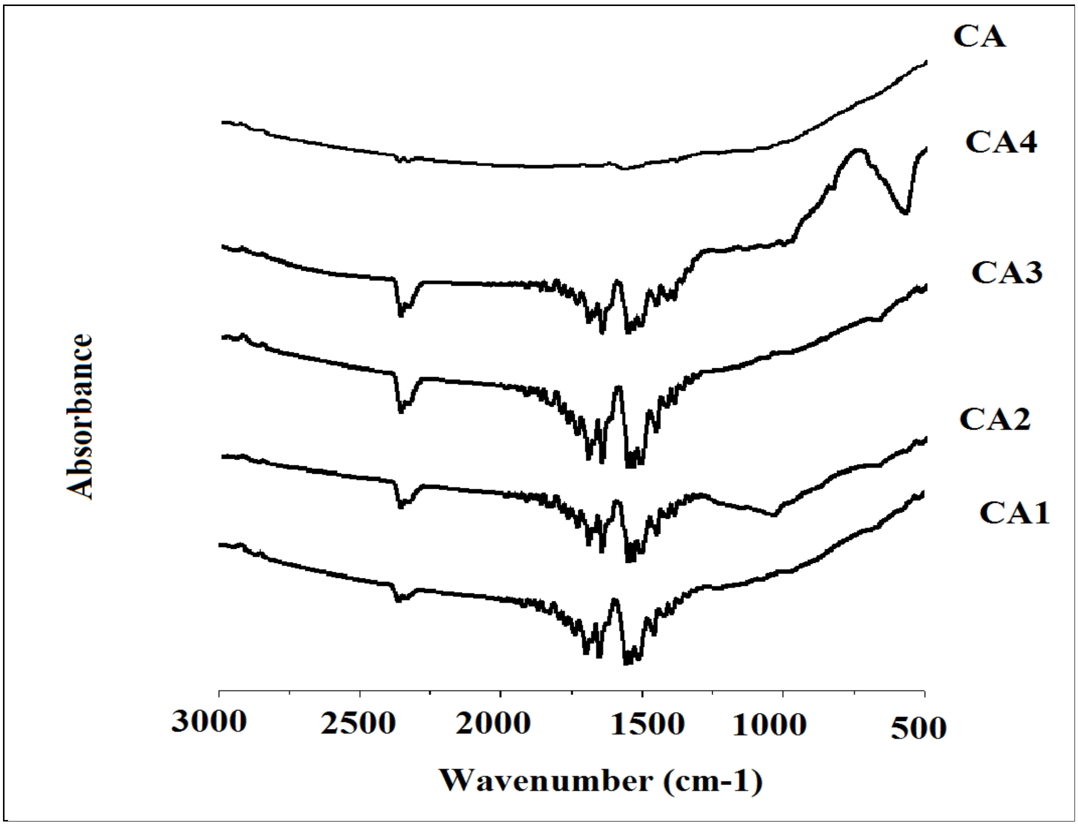

Figure 2: FT-IR spectra: CA , CA_1, CA_2, CA_3, CA_4

SEM images of some selected activated carbon samples are shown in **Figure 3a–d**. It can be seen from the micrographs that the external surface of the alkaline activated carbons has cracks, crevices, and some grains in various sizes in large holes. It can be concluded from SEM images taken during experiments performed at a carbonization temperature of 600 ° C that porous structure was formed because of most of the organic volatiles were evolved, leaving behind the ruptured surface of activated carbon with a small number of pores.

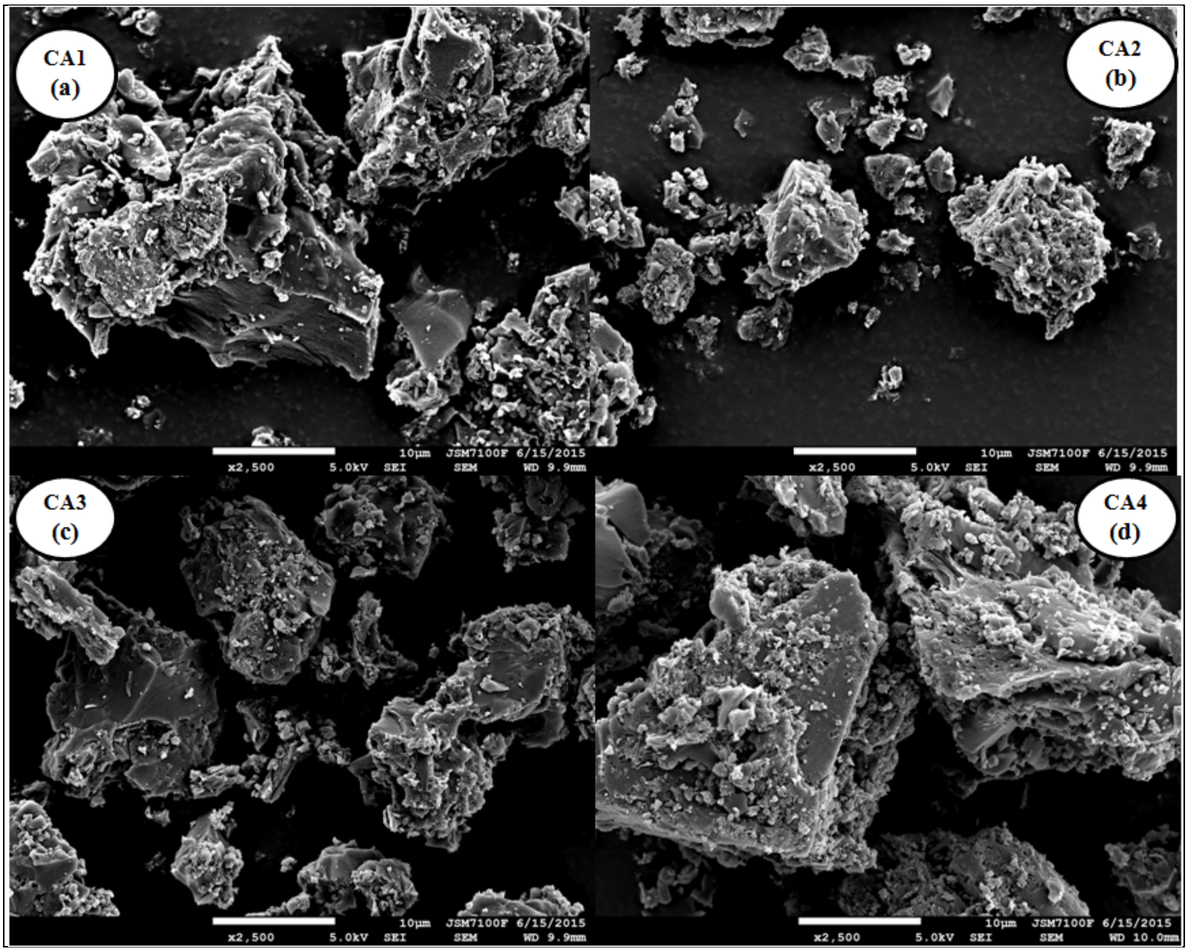

Figure 3: SEM images of the 4 activated carbon.

As seen in **Table 1**, increasing the impregnation time of KOH of 50% under N2 atmosphere at 600 ◦C from 24 to 64 h was resulted in lower surface area. These results were expected due to the raw material impregnated with KOH solution for a long time. From the data in Table 1, it is clear that the activation time has a significant effect on the activated carbon. Increasing the coefficient from 10 to 15g caused the BET surface area to increase in the same time, the increase of the activation temperature from 450 to 600 °C results in a higher BET surface area of the activated carbon that longer duration of activation time caused some of the pores to enlarge or even collapse.

Table 1: Samples and conditions

Conditions Samples of carbon	Temperature °C	Coefficient (g/g)
CA_1	450	10/15
CA_2	600	10/15
CA_3	450	10/10
CA_4	600	10/10

Considering the very complex surface of AC, The increased performances of modified AC can be related to an increase of basic groups concentration at the surface of the materials compared to raw AC. This leads to a stronger interaction with the acid H_2S.

AC-KOH containing a higher amount of the basic compound is expected to adsorb a higher amount of H_2S (**Figure 4**). An explanation of this behavior could be that the high content of K in AC-KOH causes some occlusion of the microspores, leading to a reduction of surface area (**Table 2**) and thus reducing the amount of H_2S adsorbed.

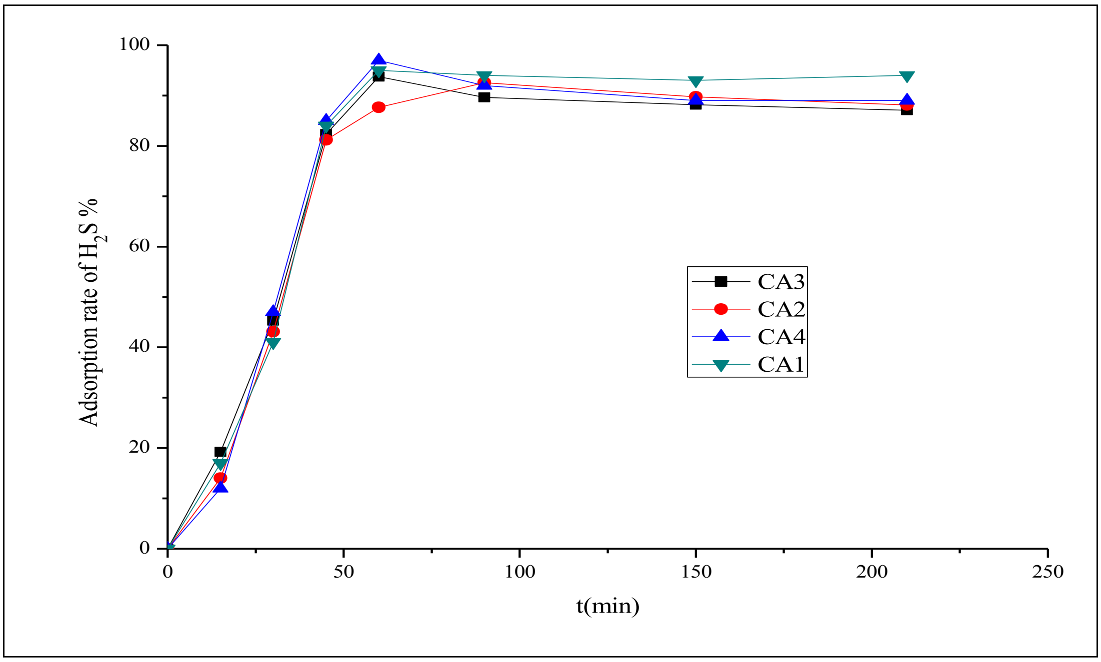

Figure 4: Adsorption capacity of H_2S by activated carbon

Table 2: BET surface activated carbon

Adsorbent	Activation temperature	Coefficient (CA_g/KOH_g)	Activation Time	BET surface area ($m^2\ g^{-1}$)	Total pore volume cm^3g^{-1}	Microspore volume cm^3g^{-1}	Diameter of pore Å
CA	-	-		356.2	0.226	0.109	12.62
CA_1	450	10/15	24	749.5	0.706	0.433	47.12
CA_2	600	10/15	24	910	0.635	0.493	27.91
CA_3	450	10/10	64	767.7	0.387	0.394	25.04
CA_4	600	10/10	64	895.2	0.591	0.502	46.39

AC-KOH removes gaseous pollutants from the gas stream by way of irreversible reactions between additive that's mean KOH and pollutant**.** For the oxidation of H_2S, a certain amount of water vapor must be present. Water is adsorbed, forming a film of water on the pore surface. H_2S and O_2 diffuse down into the carbon pores and are dissolved in the water. The O_2 is adsorbed on the carbon surface and breaks down into radicals. These oxygen radicals then react with the dissolved hydrosulfide ions, forming elemental sulfur and water (**Figure 5**). Between the operation temperature of 24 ~ 170°C the dominant reaction is (3):

$$H_2S + \frac{1}{2} O_2 \rightarrow S + H_2O \quad (3)$$

Results are denoted as the molar ratio of H_2S adsorbed on AC-KOH is approximately 1 (mole H2S / mole KOH). H_2S is a diprotic acid that reacts with a hydroxyl proton:

$$H_2S + KOH \rightarrow KHS + H_2O \ (4)$$

Or

$$H_2S + 2KOH \rightarrow K_2S + 2H_2O \ (5)$$

One mole of KOH reacts with one mole of H_2S by way of Eq (4). If the reaction occurs as in Eq (5) ,one mole of KOH should reacts with a half mole of H_2S.

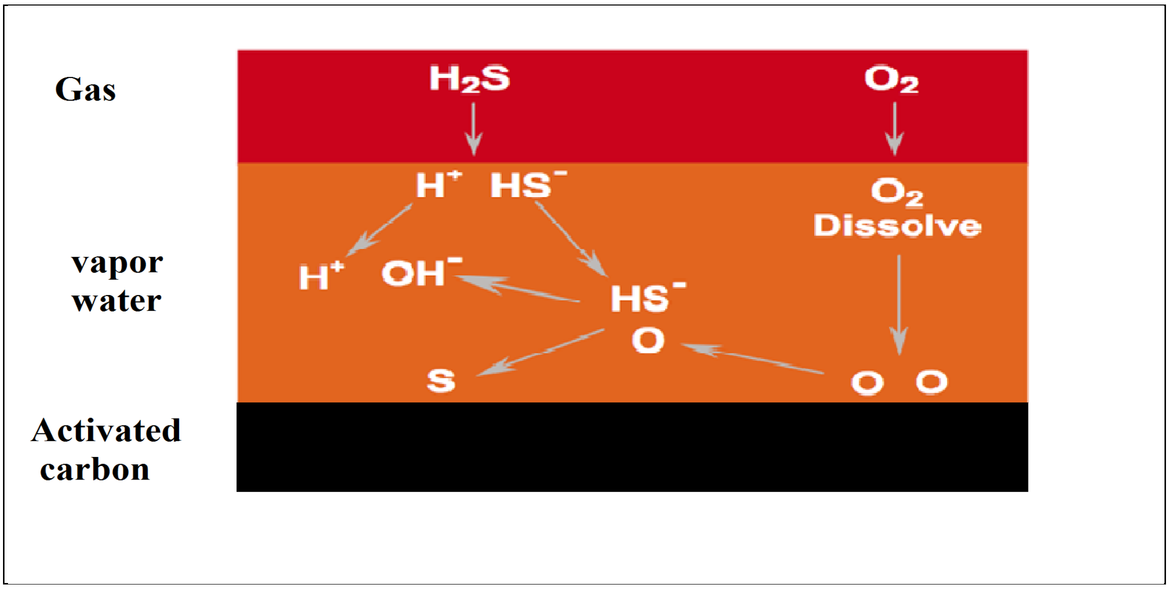

Figure 5: Oxidation of H_2S

The **Figure 4** show that the activated carbon CA_2 and CA_4 have the time of adsorption faster than the carrier thanks to the big BET surface area.

The two curve of CA_2 and CA_4 shows that the time for elimination of hydrogen sulfide is in the average of 55 min with percentage more than 90 % but in the other curves is about 80 %. The stability of adsorption for the second and the forth alkalin activated carbon approve that the surface area is responsible to obtain a significant improvement in the capacity for H_2S removal.

Conclusions

Impregnation of activated carbon significantly increased its BET surface area and essentially enhanced the adsorption of H_2S.

K_2S formed during adsorption could be converted into sulfur without toxic emissions. This makes modified activated carbon attractive for cleansing of low-concentrated exhaust gases.

These materials that were already studied for H_2S adsorption with promising results could be of interest for practical application in processes of biogas purification. A study on the regeneration of these materials will be also required in view of designing full-scale desulphurization processes.

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