Waste and Natural Materials for Hydrogen Storage Application

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Abstract: The hydrogen storage is one of the main problems to be solved because hydrogen is going to be the energy vector of the future. Among all developed methods, the H₂ storage on solid materials (by chemical or physical sorption) is the most studied. For this aim, in the last years, the carbonaceous materials, such as carbon-based matrices, are analysed. Particular study is aimed at carbon precursors, easy to prepare, cheap and environmentally friendly. All these materials show a direct correlation between the H₂ adsorption capacity (77 K) and their surface area.

Some of these carbonised organic materials, such as furfural, glucose, starch, cellulose and eucalyptus sawdust, are used as precursors to produce activated carbons (ACs) having a high surface area (up to 2700 m² g⁻¹) and a narrow size distribution pores in the range of 0.7-2 nm. Among the studied precursor a lot of these coming from different animal and vegetable wastes and interesting H₂ storage values were obtained: chicken feather fibers (1.5 wt% at 77 K / 2 MPa), coffee beans (0.6 wt% at 298 K and 4 wt% at 77 K), cannabis roots (3.28 wt% at 77 K / 0.1 MPa), coconut shells (8 wt% at 77 K and 2.3 wt% at 298 K / 7 MPa), rice straw and mulberry paper (4.35 wt% at 77 K / 1 MPa), jute fibers (1.2 wt% at 303 K / 4 MPa).

In this work, in addition to the above-mentioned materials, other classes will be considered, correlating their morphology and porosity with the H₂ storage capacity.

Keywords: Carbonaceous material properties, natural and wastes materials, hydrogen storage.

INTRODUCTION

The development of technologies for a future use of hydrogen as an energy vector is receiving increasing attention by the scientific community, in view of the desired transition towards a new energy scenario, alternative to the present one based on fossil fuels.

The expected applications concern the use of electric motors supported by H₂ fuel cells. Important disadvantages for a wide diffusion in the automotive market are represented by hydrogen confinement techniques. In this context, solid-state H₂ storage is the most promising solution compared to alternatives such as compressed gas or liquid state.

Suitable candidates should meet different requirements, among which sufficient volumetric and gravimetric storage densities, suitable charging/discharging performances and good stability during the cycles. The attention was initially directed to the metal hydride family: a large class of stoichiometric and non-stoichiometric compounds, obtainable by direct interaction between hydrogen and metals. Conventional metal hydrides of V, Nb, Pd, Na, etc, are characterized by too low gravimetric capacities for practical application. An exception is the magnesium hydride MgH₂, which is the most studied material in view of practical applications thanks to its high gravimetric storage capacity (7.6 wt%), reversibility of the dehydrogenation process, good resistance during the cycles, and low cost [1, 2]. Because of its high thermodynamic stability, dehydrogenation processes can only take place at temperatures above 673 K (1 bar) and with very slow kinetics. In order to overcome these limitations, several Mg-based intermetallic compounds have been studied: LaMg₁₂, Mg₂Ni, MgYNi₄, etc. [3-6].

The wide interest in the classes of complex hydrides, such as borohydrides and metal alanates, is justifiable with their reduced molar mass and high gravimetric storage capacities, up to 8wt% for LiBH₄ [7]. Unfortunately, due to their high stability, their dissociation enthalpy is about 200 kJ mol⁻¹ and the working temperatures are still too high.

Other classes of materials have been examined, among these ones that absorb H₂ by physisorption processes like the MOF (Metal Organic Framework)
characterized by a high surface area and a pore diameter smaller than 2 nm. MOFs are crystalline materials composed of metal ions connected by organic binders, whose presence and arrangement creates channels and micropores, moreover, the structure, the pore size and the surface area can vary by selecting the ligands that act as a unit structural [8]. Their storage properties are significant only at temperatures close to 77 K (up to 5.5 wt%), while at room temperature the performance is not suitable for practical applications.

Further organic-based materials are some conducting polymers with functional groups in a chain suitable for coordinating metals (such as diols, acetylene, mercaptans with sulphonylic groups, isocyanates, benzonitrile, etc.) [9, 10]. The best storage results (5.5 wt%) were obtained on polymers bound to transition metals such as Ti or Mn [11, 12].

Among the other innovative nano-structured materials we can find meso and nano-porous matrices based on C. In order to obtain these structures, a lot of studies are being developed on natural precursors, coming from vegetable and animal wastes. This topic is the subject of this review.

MATERIALS AND METHODOLOGY

The carbonaceous materials (biological or artificial) are good sources of carbons, but not all of them are able to produce activated carbons (highly porous carbons). Regardless of their final uses, every similar material can produce different kinds of activated carbons, varying the activation conditions. In general two kinds of activations exist: 1) thermal activation, it consists in selective gasifying of carbon atoms inside the matrix at high temperatures utilizing inert gas flow (N₂ or other inert gases) or reactive atmosphere (O₂, CO₂, CO, H₂); 2) chemical activation, it forms pores using different precursors (KOH, ZnCl₂, H₃PO₄ etc.) [13]. Below, some activation techniques used in the literature are reported.

The simplest activation of a biomass is the thermal activation: for example, the endosperm part of coconut were firstly carbonized at 523 K, 623 K or 873 K for 4 h under N₂ flow [14]. Richard P. Wool and Erman Senoz pyrolyzed chicken feather fibers following two steps: first step at 488 K for 15 h and the second one at different temperature in the range 623 K – 773 K and different times 0.5 h – 2 h; both steps were carried out under N₂ flow.

Recently, H. Oh et al. used only thermal activation on ginko leaf, peanut shell and metasequoia leaf biomasses: 1) washing with distilled water and drying at 378 K for 24 h; 2) heating at 1073 K for 1.5 h under N₂ flow [15]. It’s possible to switch the gas flow during thermal activation, in fact, Byung-Joo Kim et al. activated a polymeric precursor (Aekyung Petrochemical Co., Ltd.) before at 1173 K for 1 h under N₂ flow and after at 1273 K for different hours under controlled H₂O flow [16]. In this case, an increase activation time produced a more high specific surface area and a greater micropore volume.

Mokaya et al. prepared activated carbons by α – D – glucose, potato starch, cellulose, eucalyptus sawdust and furfural: they made hydrochars by solution/suspension in water and then heated at 503 K – 523 K for 2h; the resulting products are filtered and washed with distillated water, then, dried at 393 K for 4h; the chemical activation of cellulose was carried out adding KOH at every samples with hydrochar/KOH weight ratios 1:2 or 1:4 and heating them in the range 873 K – 1073 K for 1 h; instead, the other ones were activated with KOH and weight ratio of 1:4 at 973 K for 1 h; after activation all samples were washed with HCl until neutralization and dried at 393 K for 3 h. The reaction between KOH and C follows the following steps:

\[ 6 \text{KOH} + 2C \rightarrow 2K + 3H₂ + 2K₂CO₃ \]

\[ K₂CO₃ \rightarrow K₂O + CO₂ \]

A similar activation was used for chitosan [17], fungus [18], bamboo [19], oil palm shell [20] and so on.

Feng Wang et al. studies were devoted on pigskin collagen. They mixed the collagen with a solution of K₂CO₃ and Ca(NO₃)₂. After heating and stirring, this mixture was dried in an oven at 378 K. The composite precursor was carbonized at different temperature in the range 873 K – 1173 K for 2 h under N₂ flow. Then, the carbon was washed with a solution of HCl (4 M) at 353 K for 12 h to remove the residual CaO and CaCO₃ [21].

R. Zacharia et al. activated olives pomace by using aqueous solutions of H₃PO₄, KOH and K₂CO₃, leaving they under refluxed boiling and, then, they are carbonized at 1073 K for 2 h under N₂ flow. The obtained biochars are physically activated at 873 K for 2 h under CO₂ [22].
RESULTS AND DISCUSSION

Today, the research on the aimed materials at achieving hydrogen storage objectives is not directed only towards materials with new or improved storage properties, but also towards new eco-sustainable precursors, easy or less expensive to prepare. These materials can be transformed into porous active carbons through two activation procedures: chemistry (KOH, NaOH, CaCO₃, ZnCl₂, H₃PO₄, etc.) and thermal treatment. Several authors have studied the possibility of using natural plant and animal waste as initial carbon precursors, obtaining absolutely encouraging results.

Heat-treated organic materials, such as furfural, glucose, starch, cellulose and eucalyptus sawdust [23], are used as precursors to produce a high surface area (up to 2700 m² g⁻¹) and a narrow distribution of micropores with dimensions in the range of 0.7-2 nm. In particular, high percentages of absorption of hydrogen on carbons from cellulose and eucalyptus sawdust were measured, 5.6 and 6.4 wt% at 77 K and 2 MPa, respectively.

One of the most original materials studied was the carbon derivative obtained from chicken feather fibers (CFF) pyrolyzed by a two-step process [24]. Table 1 shows the activated carbons obtained in different time and temperature conditions and the respective adsorption capacities both at room temperature and 77 K.

A wide microporosity range, maintaining the pyrolysis temperature in the range between 673 K and 723 K considering the treatment time from 0.5 to 2 h, was obtained. The H₂ storage capacity of the activated carbon (1.5 wt%), with a pyrolysis time of 1 h at 77 K and P lower than 2 MPa, was revealed. The estimated adsorption energy was in a range of 5-6 kJ mol⁻¹, which is typical for material adsorption processes. From the Table 1 is possible to see that the best synthesis, in terms of H₂ adsorption and surface area, for each temperature, are those with a synthesis time of 1 h. The high number of micropores and nanopores available to adsorb H₂ justified the significant H₂ adsorption. Such precursors are an interesting option for the future as they are waste materials and require only relatively low temperature for heat treatments.

Akasaka et al. studied the H₂ storage capacity at 298 and 77 K of porous carbon materials with microporous structures obtained from coffee beans wastes [25]. The chemical activation with KOH vapour phase, was carried out; with this procedure the activated powder showed a high surface area in the range of 780 to 2070 m² g⁻¹, as clearly reported in Table 2. Considering both temperatures, the H₂ storage capacity showed a linear relationship with the increase in specific surface area and the size of the micropores volume.

The H₂ storage value of the sample, having a specific surface of 2070 m² g⁻¹, was 0.6 wt% at 298 K and 4 wt% at 77 K.

A series of activated carbons were obtained from the hemp root (Cannabis sativa L.) [26]. A study on

Table 1: AC from Chicken Feather Fibers and their H₂ Storage Capacity

<table>
<thead>
<tr>
<th>Thermal treatment (K)</th>
<th>Thermal treatment time (h)</th>
<th>Specific Surface Area (m²/g)</th>
<th>H₂ storage@295 K and 5.4 MPa (wt%)</th>
<th>H₂ storage@77 K and 2 MPa (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>0.5</td>
<td>&lt;10</td>
<td>0.04</td>
<td>0.29</td>
</tr>
<tr>
<td>673</td>
<td>1</td>
<td>414</td>
<td>0.35</td>
<td>1.50</td>
</tr>
<tr>
<td>673</td>
<td>1.5</td>
<td>226</td>
<td>0.18</td>
<td>1.11</td>
</tr>
<tr>
<td>673</td>
<td>2</td>
<td>51</td>
<td>0.22</td>
<td>0.95</td>
</tr>
<tr>
<td>693</td>
<td>0.5</td>
<td>221</td>
<td>0.14</td>
<td>0.68</td>
</tr>
<tr>
<td>693</td>
<td>1</td>
<td>315</td>
<td>0.25</td>
<td>1.11</td>
</tr>
<tr>
<td>693</td>
<td>1.5</td>
<td>163</td>
<td>0.19</td>
<td>0.80</td>
</tr>
<tr>
<td>693</td>
<td>2</td>
<td>237</td>
<td>0.24</td>
<td>1.27</td>
</tr>
<tr>
<td>723</td>
<td>0.5</td>
<td>336</td>
<td>0.26</td>
<td>1.15</td>
</tr>
<tr>
<td>723</td>
<td>1</td>
<td>430</td>
<td>0.37</td>
<td>1.44</td>
</tr>
<tr>
<td>723</td>
<td>1.5</td>
<td>29</td>
<td>0.15</td>
<td>1.08</td>
</tr>
<tr>
<td>723</td>
<td>2</td>
<td>89</td>
<td>0.20</td>
<td>0.71</td>
</tr>
</tbody>
</table>
heat treatment, varying both temperature and time, was performed. As can be seen from Table 3, also in this case there is direct proportionality between T increment, specific surface area and H\textsubscript{2} storage capacity. By morphological analysis a very high surface area of 3241 m\textsuperscript{2} g\textsuperscript{-1} and a total pore volume of 1.98 cm\textsuperscript{3} g\textsuperscript{-1} were found.

In this work, a chemical treatment using as a porogen KOH and the weight ratio KOH:C of 4.5:1 was fixed. The linear increase in the adsorption capacity and surface area is valid from 500 up to 800 K, with reaction time of 3.5 h, in fact, from 900 K up, there is a decrease in surface area and H\textsubscript{2} storage values. The same trend was seen at 800 K, but changing the reaction time from 3.5 h to 4.5 h an inversion of the trend was recorded.

Studies on activated carbon derived from the corncob have indicated that these materials are promising for hydrogen storage [27]. Varying the preparation parameters of the activation carbons the maximum surface area value obtained was 3530 m\textsuperscript{2} g\textsuperscript{-1} with a total pore volume of 1.94 cm\textsuperscript{3} g\textsuperscript{-1}. The sample, having a surface area of 2988 m\textsuperscript{2} g\textsuperscript{-1} and a smaller pore size, showed the highest absorption capacity, over 2.85 wt% at 77 K and 0.1 MPa.

The activated samples, obtained from solid coconut endosperm, have produced really unexpected results [28]. Carbonization, performed by heat treatment on walnut pulp at 623 K for 4 h under N\textsubscript{2} flow, was carried out and some of these ones were carbonized to 873 K. Since, the carbonized coconut already contains pores, no prior chemical treatment was necessary. The H\textsubscript{2} storage measurements, at 77 K, revealed good hydrogen adsorption (8 wt%) and desorption capacity with fast and reversible kinetics, while operating at room temperature and 7 MPa of P a 2.3 wt% H\textsubscript{2} storage value was obtained. By lowering the pressure to 3 MPa the adsorption drops to 3.5 wt% at 77 K and 1.1 wt% at T = amb. It was hypothesized how the high storage capacity was due to the presence of some elements such as the KCl anchored to carbon matrix or Mg responsible for the spillover effect.

Another material considered as a carbon precursor is the Chitosan, a polysaccharide particularly abundant and having low-cost. Prior to chemical activation, chitosan samples were heat treated from 973 to 1273 K under N\textsubscript{2} flow. Subsequently, the obtained carbons

**Table 2: AC from Coffee Bean Wastes and their H\textsubscript{2} Storage Capacity**

<table>
<thead>
<tr>
<th>KOH/C</th>
<th>Specific Surface Area (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>H\textsubscript{2} storage@298 K and 12 MPa (wt%)</th>
<th>H\textsubscript{2} storage@77 K and 4 MPa (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>780</td>
<td>0.32</td>
<td>1.61</td>
</tr>
<tr>
<td>2:1</td>
<td>1270</td>
<td>0.4</td>
<td>2.14</td>
</tr>
<tr>
<td>3:1</td>
<td>1530</td>
<td>0.48</td>
<td>2.7</td>
</tr>
<tr>
<td>4:1</td>
<td>1920</td>
<td>0.53</td>
<td>3.3</td>
</tr>
<tr>
<td>5:1</td>
<td>2070</td>
<td>0.6</td>
<td>4</td>
</tr>
</tbody>
</table>

**Table 3: AC from Cannabis Sativa L. and their H\textsubscript{2} Storage Capacity**

<table>
<thead>
<tr>
<th>Thermal Activation (K)</th>
<th>Activation time (h)</th>
<th>Specific Surface Area (m\textsuperscript{2} g\textsuperscript{-1})</th>
<th>H\textsubscript{2} storage@77 K and 0.1 MPa (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>3,5</td>
<td>922</td>
<td>1.57</td>
</tr>
<tr>
<td>600</td>
<td>3,5</td>
<td>1365</td>
<td>2.58</td>
</tr>
<tr>
<td>700</td>
<td>3,5</td>
<td>1917</td>
<td>2.81</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2436</td>
<td>3.01</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>2934</td>
<td>2.97</td>
</tr>
<tr>
<td></td>
<td>3,5</td>
<td>3241</td>
<td>3.28</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>3078</td>
<td>1.47</td>
</tr>
<tr>
<td></td>
<td>4,5</td>
<td>2538</td>
<td>2.98</td>
</tr>
<tr>
<td>900</td>
<td>3,5</td>
<td>3018</td>
<td>2.94</td>
</tr>
<tr>
<td>950</td>
<td>3,5</td>
<td>2368</td>
<td>0.84</td>
</tr>
</tbody>
</table>
were treated with anhydrous KOH using a weight ratio KOH:C 1:1 to 4:1. The activated samples are highly microporous showing a high surface area (922 - 3066 m² g⁻¹) and pore volumes in the range of 0,40–1,38 cm³ g⁻¹. The adsorption measurements, at 77 K, demonstrated a high H₂ absorption capacity of 2,95 wt% at 0,1 MPa and 5,61 wt% at 4 MPa. The hydrogen absorption capacity was directly linked to the pores size; in fact, the greater H₂ adsorption capacity was due to the micropores presence having a width of 0,7-1 nm, while the larger pores did not exert any significant influence.

Several ACs were obtained by hydrothermal carbonization (HTC) of sucrose solutions at different concentrations and subsequent activation with KOH [29]. The obtained ACs showed surface areas between 790 and 2703 m² g⁻¹ with a storage capacity of 0,59 wt% obtained at 298 K and 10 MPa.

Hwang et al. prepared highly porous carbon fibers based on rice fibers and paper mulberry [30]. The carbonaceous precursors were treated at room temperature in NaOH (20%) to obtain the pure cellulose and then it was dissolved in N-Methylmorpholine-N-Oxide (MMNO) with propyl gallate at 373 K. To extrude this suspension at 373 K and obtain fibers using KOH solution (2 M, 4 M and 8 M), the spinning process was used. The thermal activation process at 1073 K in N₂ atmosphere was carried out. The N₂ isotherms showed a strong increase in H₂ absorption at very low relative pressures, which implies microporosity of the material. The specific surface area showed a relatively higher value for carbon fibers derived from rice fibers. It should be noted that the porous carbon fibers surface, derived from rice and paper mulberry, are influenced by the KOH concentration. The results obtained show that, in the rice fibers, the surface areas increase linearly with the KOH concentration and then, using KOH 8M, a value of 2260 m² g⁻¹ was obtained. On the other hand, in the case of mulberry paper, the surface area has the highest value, 1331 m² g⁻¹, using KOH as a porogen. The H₂ storage measurements, performed at 77 K, showed that in all samples there was a prompt adsorption with P up to 1 MPa. The porous carbon fibers derived from rice showed the highest hydrogen storage properties (4,35 wt% at 1 MPa) while the obtained ACs from paper mulberry, under the same pressure conditions, the H₂ sorption value was 2,8 wt%.

A porous carbon obtained from Indian banyan paste (Ficus Benghalensis) recently growing, was doped with phosphoric acid, showed a wafer-like morphology with a specific surface area of 1406 m² g⁻¹ [31]. The synthesis involves different steps: 1) chopping in small pieces of Ficus, washing, drying at 363 K and, finally, H₃PO₄ treating for 24 h and drying in sunlight for a few hours; 2) heat treatment at 1073 K under N₂. The material storage capacity of 1,2 wt% at 298 K and 10 MPa was measured.

Recently, fruit peels without pulp (EFB) were studied as carbon precursors [32]. The carbonization was performed at 1173 K under CO₂ flow and using different KOH concentration (0,5 M, 1 M and 2 M). The surface areas obtained were in the range of 305 - 687 m² g⁻¹ obtaining highly microporous structures, up to 94%. The maximum H₂ absorption was 2,14 wt% at 1,9 MPa and 77 K.

Interesting results using jute fibers as a starting material were obtained [33]. The ACs, starting from the initial treatment with isopropyl alcohol at 323 K and subsequently drying in an oven at 373 K for 24 hours, were prepared. The carbonization at 973 K and subsequently, the chemical activation through KOH, with weight ratio KOH:C of 1:1, 1:3 and 1:5, was followed. Finally, a second carbonization at 973 K was carried out. Their structure made up of channels helps to increase the storage capacity of hydrogen. The surface area increases from 894 m² g⁻¹ (1:1) to 1224 m² g⁻¹ (1:3). The micropores volume changes in a range between 0,16 to 0,43 cm³ g⁻¹ and this could explain the H₂ adsorption at 303 K and 4 MPa of 1,2 wt% (1:3).

Bader et al. examined also olive stones as ACs precursors. The carbons, starting from the olives pomace, were obtained. Chemical activations, using aqueous solutions of H₃PO₄, KOH or K₂CO₃, were carried out. Subsequently, the mixture were carbonized and repeatedly treated with HCl 0,1 M. The activation, using KOH at 358 K for 3 h with weight ratio KOH:C 1:1 or 4:1, was followed. The final activation step, at 1073 K in N₂ and HCl 0,1 M solution, was performed. The surface areas for the all samples treated with KOH increase with the increase of the KOH:C ratio (from 760 to 1269 m² g⁻¹) while they remain almost similar using CO₂ and H₃PO₄ (1185 and 1192 m² g⁻¹) as porogen. The H₂ adsorption measurements at 77 K with 0,1, 2,5 and 20 MPa pressures were performed. Increasing the P, all samples increase their adsorption capacity from 1,4 wt% to 6,11 wt%. From the obtained data, when the
KOH:C ratio was 4:1 the most performing treatment was KOH (4:1), even when the temperature test increase to 298 K, while considerably lowering the adsorption capacity (from 6,11 to 1,22 wt%).

The wastes, not really natural but certainly particularly original, are cigarette filters [34]. Fresh and used cigarettes filters were examined, without the tobacco. After having crushed them, the filters were hydrothermally carbonized at 523 K and subsequently at 385 K. The chemical activation in KOH, in which the KOH:C ratio remained constant (4:1), was performed. The heat treatment, under N₂ flow, at 873 K, 973 K and 1073 K were performed. The chemical treatment on obtained carbons using HCl 2M solution was followed. Finally, a dried further to 385 K was carried out. CHNS-O analyses on the smoked samples were performed and the presence of N, probably due to the nicotine trapped in the filter, and a higher content of C and H were noted. Increasing the temperature of heat treatment for both fresh and smoked samples, a decrease of the O/C and H/C ratios values was recorded. From XRD analyses the presence of a crystalline peak both in the fresh and in the smoked one, were noticed. Probably this is due to the presence of metals inside filter, which form metal oxides after chemical treatment. A different trend from the BET characterizations was recorded. In fact, the carbons obtained from fresh filters showed a direct proportionality between the surface area and the increase of T (873 K / 1970 m² gr⁻¹ up to 1073 K / 4113 m² gr⁻¹). In the smoked sample there was an inversion trend, in fact, as the temperature increase, the surface area decrease (873 K / 4310 m² gr⁻¹ up to 1073 K / 2393 m² gr⁻¹). This unusual trend is probably due to the presence of metals that give an over activation that could cause a counterproductive action against the pore volume and the surface area. The H₂ adsorption measurements, performed at 77 K, show the same trend seen for the surface areas, in any working pressure (0,1 MPa, 2 MPa, 3 MPa and 4 MPa). The maximum adsorption value, 11,2 wt%, was reached from smoked carbons (treated at 873 K) at 4 MPa, about double value of the non-smoked carbon (5,9 wt%).

These latest results offer new opportunities for the exploitation of highly polluting wastes, which, after chemical and thermal treatments, possess the highest hydrogen absorption capacity reported to date for any carbonaceous or porous material in general.

CONCLUSION

In these last years, to promote the hydrogen as a fuel for electric system (fuel cell for portable and stationary application in particular) one of the main problems to solve is the possibility to store hydrogen in a large quantity. Among the hydrogen storage techniques the possibility to store hydrogen on solid materials is certainly the most interesting. Different classes of materials are under study and they can be divided as a function of their way to capture hydrogen, in particular chemisorption and physisorption. The H₂ chemisorption occurs using metal hydrides in which the H₂ capture occurs by chemical bonds; the H₂ physisorption mechanism is common in carbonaceous materials (carbon nanotubes, activated carbons, etc.) where the H₂ is stored in the matrix pores. This review wants to provide information on some natural wastes, vegetable and animal origin, whence the activated carbons are obtained to trap H₂. Different methods for synthesizing the carbons have been considered, as well as the activation steps, thermal and chemical, through which the carbons adsorb hydrogen, since by changing one of these parameters both the morphologies and the structure change. The main characteristic of carbonaceous materials is the high surface area (from 600 m² gr⁻¹ to up 3000 m² gr⁻¹). Different thermal activations, consisting on carbon atoms gasification in the matrix, at high temperatures (from 600 K to 1300 K) using inert gas flow (N₂ or inert gases) or reactive atmosphere (O₂, CO₂, CO, H₂), to obtain carbon matrix were considered. The chemical activation, using pores precursors such as KOH, H₃PO₄, ZnCl₂, etc., are used to increase the surface area and the pores size. Using the same porogen, changing only the C ratio, it is possible to increase and/or decrease the surface area. A lot waste materials are considered and their H₂ storage capability are reported such as chicken feather fibers, endosperm part of coconut, eucalyptus sawdust, coffee beans, hemp roots of Cannabis sativa L., corncobs, Chitosan, rice fibers, paper mulberry, Indian banyan paste, fruit peels without pulp, jute fibers, olive stones. Another interesting materials, not really natural, were the waste cigarette filters, considering the difference between the smoked and fresh one.

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