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Sustainable porous carbons from lignocellulosic wastes obtained from the extraction of tannins

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ABSTRACT

The present research study explores the possibility of obtaining high surface area activated carbons (ACs) from lignocellulosic wastes from the extraction of tannins. The use of vegetable tannins in the leather industry has the serious drawback that it involves the mass destruction of trees. Currently, studies are being conducted to obtain tannins from different lignocellulosic wastes. Two lignocellulosic wastes from the extraction of tannins, defatted grape seeds and acacia seed shells, with high carbon and nitrogen contents and a low ash content were obtained and investigated as a potential precursor for the preparation of activated carbons. KOH chemical activation, with a previous pyrolysis step, was performed in a conventional electric furnace varying the experimental conditions of KOH/precursor weight ratio, final activation temperature, and inert flow gas. After activation the samples were washed with a solution of HCl and water or just with hot water. The ACs obtained were essentially microporous with a specific surface area up to 2000 m^2 g and presented low ash content, less than to 0.10% in the case of adsorbent materials from the defatted grape seeds and up to 3.60% for the materials from the acacia seed shells. The best results were obtained with the largest KOH/precursor weight ratio or the highest activation temperature (900 °C). Their moderate nitrogen content (up to 1.5%) makes them especially suitable materials for CO_2 capture. Some of them were more effective for CO_2 adsorption than the commercial activated carbon F400 and therefore represent an attractive alternative to more expensive adsorbent materials.

1. Introduction

The tanning industry uses animal hide, a putrescible material, and converts it into a stable material, leather. If the tanning industry did not exist animal skins, a by-product of the meat and dairy industries, would have to be disposed of by other means such as by land filling or incineration.

The tanning industry mainly uses one of two methods for transforming skin into leather: mineral or vegetable tanning. Mineral tanning which uses chromium salts and acids is most modern and the most used method but it is also the most polluting. Vegetable tanning uses vegetable tanning substances, called tannins. Tannins are very numerous and are distributed abundantly in the nature. The disadvantage of this type of tanning is deforestation.

Currently, studies are being conducted to obtain tannins from different lignocellulosic wastes. Thus, AIICA has developed a methodology for extracting them from defatted grape seeds under solvent extraction in basic conditions [1] with very good results. Grape seeds, which are a solid waste from the wine industry, are mostly burnt as fuel and to some extent used for cattle feed, despite the fact that they are also a source of oil for human consumption [2,3] or tannin vegetables which could be used in the tanning industry [1].

The possibility of obtaining tannins from acacia seed shells by means of a grinding and sieving operation has also been investigated. The fruits of Acacia *(Faidherbia albida)* are composed of two parts: the seeds and the seed shell. The seed serves as food for animals and the shell seeds after undergoing a process of grinding and sieving provide the vegetable tannin concentrates in the fine powder fraction. This fraction is used as tanning agent by the tanners from northern Africa.

After the process of obtaining tannins from defatted grape seeds and acacia seed shells a lignocellulosic residue with a high carbon and low ash content are obtained.

The leather industry has often been associated with a high pollution of the water and air and to generating a large amount of solid wastes. Wastewater is loaded of sulfides, chlorides, sulfates, phosphates, settleable solids, color... and chromium in the case of the mineral tanning. The main parameters affecting the air quality in the tanneries are volatile organic compounds (VOCs), H_2S, NH_3 and dust. Furthermore, pollutants such as nitrogen oxides

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(NOx), sulfur oxides (SOx), and carbon dioxide (CO_2) are generated in the thermal systems to generate heat.

The adsorption is an effective abatement technology for contaminant compounds. The most important consideration is the selection of an appropriate adsorbent. The adsorbents most commonly used for contaminant compounds removal are the activated carbons because they have a large surface area, high porosity and great adsorption capabilities.

Activated carbons (ACs) can be obtained from almost any material with high carbon content. The precursors generally used for the production of ACs are coal, lignite and wood, among others. In order to reduce the production costs of these adsorbents, many research studies have been undertaken to find alternatives to the raw materials used in activated carbon production, such as agricultural and industrial wastes [47]. Furthermore, an evaluation of agricultural residues or by-products as precursors of activated carbon seems to be very promising from a sustainable viewpoint.

In this work, the precursors of the ACs will be two agricultural wastes obtained from defatted grape seeds and acacia seed shells after that these residues have been subjected to a process of solvent extraction and grinding–sieving, respectively, for the separation of the tannins. The use of grape seeds in the preparation of ACs has been reported in only a few instances in the scientific literature [8–10] and almost none from acacia seed shells [11]. However, there is no background literature information related to the use of the lignocellulosic wastes reported in this work.

The aim of the present research work is to evaluate the possibility of obtaining sustainable porous carbons from lignocellulosic wastes from the extraction of tannins by means of KOH chemical activation using a previous pyrolysis step. The influence of the activating agent/precursor weight ratio, activation temperature, inert flow gas and different washing processes of the final materials is studied in order to achieve a suitable development of porosity in the activated carbons.

2. Materials and methods

2.1. Raw materials

This study was carried out in order to valorise the lignocellulosic wastes from the extraction of tannins. Two representative samples of these wastes, residual materials left behind after the extraction of tannins from defatted grape seeds and acacia seed shells, were supplied by "Asociación de Investigación de las Industrias del Curtido y Anexas", AIICA.

The extraction of tannins from defatted grape seeds was performed in an aqueous medium using sodium metabisulfite as a solubilizer of tannins, and applying pressure and temperature [1].

After the extraction process a solid lignocellulosic residue, GS, is left behind. This will serve as one of the precursor materials of the activated carbons.

The method of extracting tannin from *Acacia Albida* fruits was as follows: the acacia fruits (seeds and seed shells) were crushed and then passed through an air flow where the seeds and the seed shells were separated due to their different densities. After this, the seed shells were crushed by a cutter mill and were separated into two fractions by sieving: a coarse fraction and a fine powder. The fine powder contained the highest concentration of tannins (47.9%) while the other fraction contained less than half (21.4%). The coarse fraction, AP, was selected as precursor material for the activated carbons.

In Appendix A, Supplementary Data, the Fig. S1 shows the leitmotiv of this research study and the Figs. S2 and S3 show an image illustrating the equipment for the extraction of tannins from defatted grape seeds and the scheme of the tannins separation from the acacia seed shells, respectively.

2.2. Activated carbons

The activated carbons from these lignocellulosic wastes from the extraction of tannins were obtained in a two-stage thermochemical process which involved carbonizing the raw material followed by chemical activation of the char with an alkali agent (KOH). The thermochemical processes, pyrolysis and thermochemical activation, were carried out in an alumina crucible placed in a conventional tubular furnace Carbolite CTF 12/65/550.

The pyrolysis step of the raw material (GS, AP) was performed under a N_2 flow gas of 150 ml/min^{-1} at a heating rate of 5 °C/min up to a temperature of 750 °C for 60 min. In order to establish the most suitable pyrolysis conditions, several parameters were studied in a thermo-balance, Q5000IR: heating rate (5, 10 and 15 °C/min), final temperature (900 and 1000 °C), maintenance time of final temperature (60 and 120 min), under a flow nitrogen rate of 100 ml min^{-1} in all the experiments.

In the chemical activation, the activating agent (KOH) and the pyrolyzed sample (GSP or APP) were mixed in solid state (physical mixture) in different weight ratios (1:1. and 2:1). The experimental conditions of the chemical activation were: a heating rate of 5 °C/min, a final activation temperature of from 700 to 900 °C, the final temperature being held for 60 min, and different N_2 gas flows of 150 and 500 ml min^{-1}. After chemical activation, in order to remove the activation products and the mineral matter blocking the porosity, the adsorbent materials were washed with a 5M hydrochloric acid solution and subjected to a series of deionised water (Milli-Q) rinses. Some activated materials were washed only with hot water at 100 °C and without using hydrochloric acid. Finally the samples were dried at 105 °C.

The nomenclature for the activated carbons (ACs) prepared is summarized in Table 1.

In order to conduct a comparative study of the CO_2 adsorption capacity of the obtained activated carbons a commercial activated carbon (Filtrasorb F400) was selected since it had been used in previous CO_2-sorption studies [12–15]. The commercial activated carbon "Maxsorb3000" was also used as reference since it is a material that is widely used in gas storage [16–19] and has very good textural properties [20].

Table 1
Nomenclature of the activated carbons.

Sample	KOH/precursor ratio	Activation temperature (°C)	N_2 flow gas (ml min^{-1})
GSP-1-700-f	1:1	700	150
GSP-1-750-f	1:1	750	150
GSP-1-750-F	1:1	750	500
GSP-2-750-f	2:1	750	150
GSP-1-800-f	1:1	800	150
GSP-1-900-f	1:1	900	150
GSP-1-900-F	1:1	900	500
GSP-1-900-fW	1:1	900	150
APP-1-700-f	1:1	700	150
APP-1-750-f	1:1	750	150
APP-1-750-F	1:1	750	500
APP-2-750-f	2:1	750	150
APP-1-800-f	1:1	800	150
APP-1-900-f	1:1	900	150
APP-1-900-fW	1:1	900	150

GSP (defatted grape seeds carbonized) and APP (acacia seed shells carbonized).
1 or 2: activating agent/precursor weight ratio, 1:1 or 2:1, respectively.
700–750–800–900: activation temperature (°C).
f or F: inert gas flow in the chemical activation process, 150 ml min^{-1} or 500 ml min^{-1}, respectively.
W: samples washed with hot water; samples washed with HCl and water have not annotation.