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VALORIZATION OF SOLID WASTES FROM THE LEATHER INDUSTRY: PREPARATION OF ACTIVATED CARBON BY THERMOCHEMICAL PROCESSES.

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Abstract

A study has been conducted to establish conditions for the pyrolysis of leather wastes (LW) in order to recover gas and condensable fractions. The pyrolyzed sample was later activated by means of alkaline hydroxides in order to develop its porous structure. The activated carbons prepared are microporous with specific surface area values up to 2700 m²/g.

Keywords: *leather wastes, thermochemical process, activated carbon.*

INTRODUCTION

The industrial tanning of leather produces considerable amounts of solid wastes and liquid effluents and raises many concerns regarding the environmental effects and escalating landfill costs.

These disposal problems are increasingly becoming a hindrance to this industrial activity, suggesting the need for alternative methods of residue disposal [1].

Pyrolysis is one of the possible alternatives for the treatment of solid wastes from the tannery process. Pyrolysis has been widely applied to organic wastes, such as agricultural wastes, scrap tires, sewage sludge and plastic wastes. The pyrolysis process involves heating the carbonaceous material in an inert atmosphere. The products resulting from pyrolysis are gas, oil –which can be used as fuel- and a carbonaceous residue which can be burnt as fuel or safely disposed of since the dangerous heavy metals are fixed inside the carbonaceous matrix. In addition, the carbonaceous

residue is also suitable for the production of activated carbon.

Basically, there are two processes for the preparation of activated carbon: physical and chemical activation [2]. Physical activation involves the carbonization of a carbonaceous precursor followed by the activation, at high temperatures, of the resulting char in the presence of activating agents such as carbon dioxide or steam. In chemical activation the precursor is impregnated with a chemical agent (ZnCl₂, H₃PO₄, KOH, NaOH, etc.) and, after that, it is pyrolyzed at low temperatures. The activating agents inhibit the formation of tar, thus enhancing the carbon yield.

Commercial activated carbon is the preferred adsorbent for the removal of micropollutants from gas and aqueous phases. However, its widespread use is restricted due to the high costs associated its elaboration [3]. To reduce treatment costs, attempts have been made to find inexpensive alternative of activated carbon precursors, such as waste materials [4, 5]. Thus, until now the research of our research group has been focused on the preparation of activated carbons from sewage sludge [6].

The present work proposes a method of converting solid wastes from leather industries in low cost adsorbent materials.

EXPERIMENTAL

Tannery wastes (shavings, trimmings and buffing dusts) -all of which come from the tanning of cow skin by vegetable tannins- were mixed and homogenized

in the same proportions in which they are generated in the leather industry (84%, 15% and 1% respectively). This mixture is referred to Leather Waste and it was used as the precursor of the activated carbons we obtained.

The elemental analysis was carried out on LECO CHN-2000 and LECO Sulphur Determination S-144-DR instruments. The ash content was determined according to norm UNE 32004 (815 °C, 1 h, air atmosphere). All the results are given on dry basis.

The thermogravimetric analysis was performed using a TA Instruments thermobalance (TGA Q5000IR).

The experiments of pyrolysis and activation were carried out in a horizontal tubular furnace fitted with a mass flow controller (Carbolite CTF 12/65/550).

A scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy was employed to determine the composition of the mineral matter in the activated carbons.

The N₂ adsorption isotherms were determined at -196 °C with samples previously degasified at 120 °C for 18 h, using a Micromeritics ASAP 2420 apparatus.

The N₂ isotherms were used to calculate the specific surface area, S_{BET}, of the resulting adsorbent materials.

Table 1. Elemental analysis of the precursor

Leather Waste				
Ash (%)	C (%)	H (%)	N (%)	Si (%)
2,59	48,21	5,75	7,51	1,91

RESULTS AND DISCUSSION

A. Analysis of the raw material

From Table I it is immediately apparent that the precursor has low ash content and a high carbon content. The precursor also contains a significant amount of nitrogen.

B. Pyrolysis

The thermal decomposition of tanned leather was studied using TG-DTG in strict pyrolysis conditions. On comparing the tanned skin with the untanned skin, it was observed that the decomposition of the

tanned skin proceeded very slowly even at high temperatures (1000 °C) at which temperature the weight of the tanned skin was still decreasing. Given that the essential difference between the two samples is the presence of tannins, it is very likely that the long tail is due to the influence of the tannins on the thermal stabilization of the leather, Fig. 1.

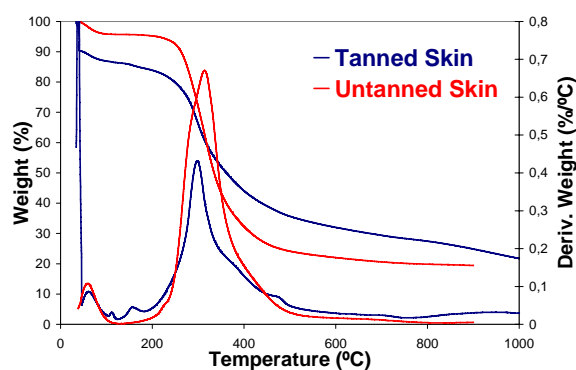


Figure 1. Pyrolysis of the precursors

From an examination of the decomposition of the leather waste at different heating rates, it can be seen that the deviation of the final residues is negligible at about 750 °C, Fig. 2.

In addition, if the duration of the final temperature is prolonged, this deviation will diminish further.

Optimization of the pyrolysis process was carried out in a tubular furnace employing the following parameters:

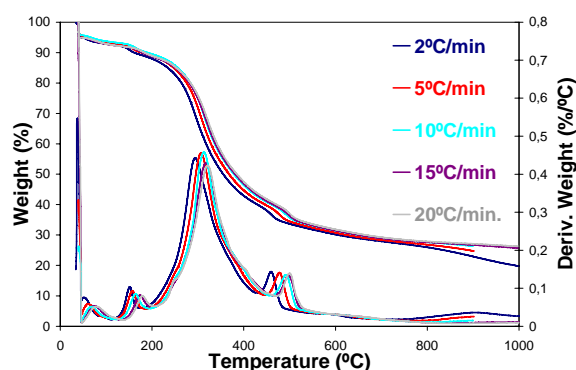


Figure 2. Pyrolysis of the leather waste

heating rate (5, 10, 15 °C/min), final temperature (650, 750, 850 °C), time at final temperature (30, 60, 120 min) and inert gas flow (150, 250, 500 mL/min).

The final pyrolysis conditions were established on the basis of the thermogravimetric results and the optimization of the main pyrolysis parameters. In this way, we were able to select the most suitable

conditions for obtaining a high activated carbon yield and an acceptable weight yield that would allow the gaseous and condensable fractions to be used for energy purposes, Table 2.

Table 2. Final conditions of Pyrolysis. Elemental analysis and ash content of char

Final Conditions: 5/750/60/150					
Ash (%)	C (%)	H (%)	N (%)	S _t (%)	Yield (%)
12,80	80,17	1,00	6,10	0,95	35,70

C. Chemical activation.

In order to optimize the activation process, we have introduced new parameters, while keeping the rest of the thermal conditions constant:

- Hydroxide: KOH or NaOH, and wt% [Hydroxide:Sample]: 0.5:1, 1:1, 3:1.
- Inert gas flow (N₂): 150, 500 mL/min.
- Thermal conditions: 5 °C/min – 750 °C (1 h).

After activation, the samples were washed up to approximately the pH of water in order to remove the activation products blocking the porosity. Normally, about 20 washes were needed involving three stages: agitation, centrifugation and removal of the liquid after each wash. Finally, the samples were dried in a vacuum heater (80 mbar, 65 °C).

Table 3. Analysis of activated carbons.

TREATMENT	Reference	Ash (%)	C (%)	N (%)	S _{BET} (m ² /g)
KOH 0,5:1 150 mL/min N ₂	"LW0.5N1"	3,49	87,22	3,96	764
KOH 1:1 150 mL/min N ₂	"LW1N1"	0,98	90,61	2,28	1169
KOH 1:1 500 mL/min N ₂	"LW1N5"	0,79	86,14	2,32	1232
NaOH 1:1 150 mL/min N ₂	"LW1N1, NaOH"	0,75	94,58	1,43	1339
NaOH 1:1 500 mL/min N ₂	"LW1N5, NaOH"	0,83	95,98	1,36	1350
KOH 3:1 150 mL/min N ₂	"LW3N1"	0,42	86,01	1,16	2660
KOH 3:1 500 mL/min N ₂	"LW3N5"	0,31	87,06	1,02	2701

Our experiments yielded the following results: a carbon content higher than 85%, an ash content lower than 1%, a significant nitrogen content and specific surface area values, S_{BET}, up to 2700 m²/g, Table 3.

D. Composition of the activated carbons.

Non-contaminating elements which pose no threat to life were detected in the composition of the activated carbons. Furthermore, no heavy metals were found, Figure 3.

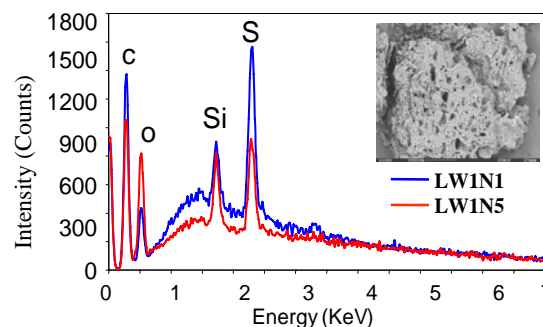


Figure 3. Activated carbons by SEM-EDX.

E. N₂ adsorption isotherms at -196 °C.

Adsorption takes place at relatively low pressures which is typical of microporous solids.

Moreover, the isotherms show hysteresis cycles that are typical of capillary condensation in mesopores. The quantity of N₂ adsorbed is greater in the adsorbent which was subjected to the highest amount of activating agent (LW3N5), and has the highest specific surface area, (S_{BET}=2701 m²/g). Moreover, only a small increase in the quantity of nitrogen adsorbed was observed in the sample activated with NaOH with respect to the ones activated with KOH, Fig. 4.

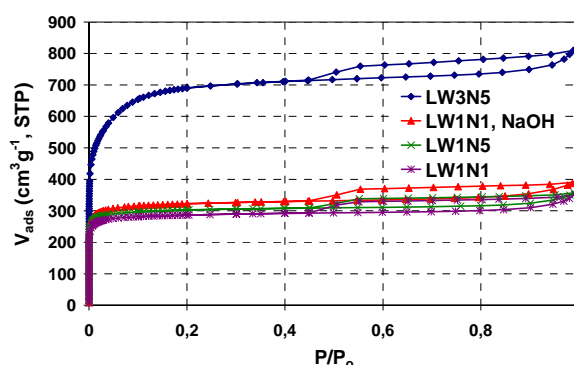


Figure 4. Isotherms of nitrogen (-196 °C)

The average size of the micropores is reflected by the curvature of the isotherm. If the curvature is opening, the size of the micropores is large. Thus, the samples activated with KOH at a ratio of 3:1 can be expected to be the largest and will have the widest pore distribution. The total pore volume of the

adsorbent materials is obtained from the isotherm of N₂ at a partial pressure P/P₀ = 0.95, Table 4.

Table 4. Total pore volume of the adsorbents

Activated Carbon	Pore Volume (cm ³ /g)
LW3N5	1,20
LW1N1, NaOH	0,58
LW1N5	0,52
LW1N1	0,50

CONCLUSIONS

We prepared activated carbons with a high thermal stability, free of heavy metals and with an ash content lower than 1%, valid for application in pharmaceuticals and food industry, etc.

These adsorbents have specific surface areas, S_{BET}, up to 2700 m²/g. These areas can be enlarged by increasing the concentration of activation agent.

The adsorbents are basically microporous with a certain degree of mesoporosity. The average size of the micropores increases with the concentration of alkaline activation agent, and has a wider distribution of pores.

REFERENCES

- [1] J. Kanagaraj, K. C. Velappan, N. K. Chandra Babu, S. Sadulla. (2006). Solid wastes generation in the leather industry and its utilization for cleaner environment - A review. *Journal of Scientific and Industrial Research* 65 (7), 541-8.
- [2] R. C. Bansal, M. Goyal. (2005). *Activated carbon adsorption*.
- [3] I. S. Roskill. (2008). *The Economics of Activated Carbon*, 8th edition.
- [4] L. C. A. Oliveira, M. C. Guerreiro, M. Gonçalves, D. Q. L. Oliveira, L. C. M. Costa. (2008). Preparation of activated carbon from leather waste: A new material containing small particle of chromium oxide. *Materials Letters* 62 (21-22), 3710-2.
- [5] F. Rodríguez-Reinoso, M. Molina-Sabio. (1992). Activated carbons from lignocellulosic materials by chemical and/or physical activation: an overview. *Carbon* 30 (7), 1111-8.
- [6] M. A. Lillo-Ródenas, A. Ros, E. Fuente, M. A. Montes-Morán, M. J. Martín, A. Linares-Solano. (2008). Further insights into the activation process of sewage sludge-based precursors by alkaline

hydroxides. *Chemical Engineering Journal* 142 (2), 168-74.

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