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ACID-CHARS AS PLATFORM MATERIALS FOR ADSORPTION AND CATALYSIS

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Introduction

The use of renewable biomass sources to prepare technological important materials has been a major issue in carbon materials research for quite long time, which allow the developing of more sustainable processes and technologies. Among the processes available to obtain carbon functional materials, acid-mediated carbonization has been far less explored than conventional thermal or hydrothermal carbonization. Even so, acid-chars have specific characteristics, namely a very rich surface chemistry, that in principle make them able to compete with (conventional) chars or hydrochars in several processes.

In the present communication recent data obtained in our research group on the synthesis and application of acid-chars from various biomass precursors, namely sisal and pine sawdust, in adsorption and catalytic processes will be presented.

Materials and Methods

The synthesis of the acid-chars was inspired in the procedure reported by Wang *et al.*[1] that, in brief consisted in a two-step procedure: the biomass was firstly treated with H_2SO_4 for 15 min at 50 ºC then the obtained acid solution was kept at 90 ºC for 6 h at atmospheric pressure. The acid-char was thoroughly washed with distilled water until neutral pH, dried, crushed and sieved. Different H_2SO_4 concentrations were tested ranging from 18 M to 9 M.

Sisal-derived acid-chars were chemically (K_2CO_3 and KOH) and steam activated to obtain porous carbon materials that were further applied in the adsorption of two pharmaceutical compounds, *i.e.* iopamidol and ibuprofen.

Preliminary assays of sisal-derived acid-chars as adsorbents of Cu^{2+}, Pb^{2+} and atenolol were performed. These materials were also used as support of complex $[MoI_2(CO)_3(CH_3CN)_2]$, **Mo**. The immobilized catalyst was tested in the cyclooctene oxidation reaction under various experimental conditions, namely temperature (r.t. up to 55 ºC) and solvent (CH_2Cl_2, CH_3CN and solventless). Recycling assays were made in optimized experimental conditions.

Sawdust-derived acid-chars were tested as catalysts in the esterification reaction of butanol and acetic acid at 80 ºC up to 6 h.

Results and Discussion

Sisal-derived acid-chars were successfully used as precursors of superactivated carbons with BET area reaching 2000 $m^2 g^{-1}$. The control of H_2SO_4 concentration during the acid-chars synthesis and

proper selection of activation method (chemical or steam) allowed to obtain materials with distinct pore size distributions (microporous or micro-mesoporous) and densities, which in optimized conditions attained 600 kg m^{-3}(high density char, K_2CO_3 activation using physical mixing). The results of iopamidiol and ibuprofen adsorption shown that the samples outperformed the behaviour of commercial golden standards[2].

Preliminary data also demonstrated the potentialities of the as-synthesised sisal-derived acid-chars as adsorbents, since promising results of Cu^{2+}, Pb^{2+} and atenolol removal from aqueous medium were obtained. In this study the acid-chars obtained with a shorter second step in the preparation procedure are also being explored.

Sisal-derived acid-chars have been further explored as supports of **Mo**-complex (**Table 1**) allowing to achieve 100 % conversion and selectivity for the cyclooctene epoxide. The results of cyclooctene epoxidation using the immobilized complex showed very high conversion even after the 4th re-use cycle. The leaching test proved the heterogeneous nature of the process[3].

Finally, sawdust-derived acid-chars achieved good yields for the tested esterification, namely in the case of acid-char obtained with the highest H_2SO_4 concentration (64 % conversion after 6 h of contact time). Moreover, as it is clearly seen in the results reported in **Figure 1** the H_2SO_4 concentration used to prepare the samples has a direct influence in the catalytic performance.

Table 1. Catalytic cyclo-octene oxidation results

Entry	Catalyst	Conversion (%)	Selectivity (%)
1	**Mo**	81	100
2	acid-char	1	100
3	**Mo**@acid-char	100	100

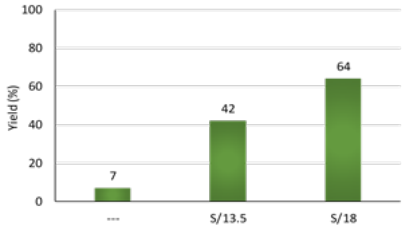

Figure 1.

Conclusions

Acid carbonization is a suitable methodology to prepare carbon materials (acid-chars) from low density biomass residues to be used in a large range of technological important applications. Besides can be used as precursors of high density superactivated carbons, the as-synthesised acid-char materials present interesting properties as adsorbents, catalysts supports and also as catalyst.

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