Acid-chars - versatile materials for adsorption and catalysis

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Abstract

In this communication an overview of the most recent studies developed in the Adsorption and Adsorbent Materials Group related with the use of acid mediated carbonization (AMC) to prepare carbon materials is presented. The chars obtained by this methodology – acid-chars – have been explored for different purposes; so far the application studied in more detail is their use as precursors of activated carbons with tuned textural properties. In this particular application both literature studies from other researchers and our contributions are reviewed. It must be highlighted that we proved that AMC is able to transform a low density biomass, as is the case of sisal fibers, in high density acid-chars and activated carbons with tailored features. The use of as-synthesized acid-chars as supports for catalysts immobilization and, even though still in a preliminary stage, also as catalysts or adsorbents were also assessed in our group with very promising results. The overall data herein discussed points out the versatility of acid-chars as a precursor of activated carbons with controlled features but also as a self-standing carbon material for adsorption, catalysis and catalysts support.

1. Introduction

The research for new synthesis strategies to prepare carbon materials based on renewable biomass sources has been addressed by several groups and, in the last years, it has also been an important research topic of the Adsorption and Adsorbent Materials Group (AAM) of Centro de Química e Bioquímica and Centro de Química Estrutural – Pólo Ciências of Faculdade de Ciências da Universidade de Lisboa. As reviewed in a previous issue of this bulletin the carbon precursors explored by the AAM group cover several renewable residues from national industries, namely, cork powder, granules of expanded corkboard, sisal fibers, fly ash from pine wood gasification, and rapeseed waste from biodiesel production [1].

The synthesis of porous carbon materials usually consists in two thermochemical processes – carbonization and activation. The carbonization (or pyrolysis) under an inert atmosphere allows to remove most of the heteroatoms and to obtain a carbon-rich material usually called char (or charcoal if prepared from a coal precursor). Hydrothermal carbonization (HTC) is a promising alternative route to conventional carbonization. HTC is inspired in the natural process of coal formation and has received great attention from the scientific community due to the sustainability of the process. (*i.e.* water as solvent, mild temperatures, self-generated pressure, occurs in hours, and no CO_2 emissions) and interesting

properties of the obtained solid products – hydrochars [2,3]. The AAM group developed sucrose-derived hydrochars that were further chemically activated and the resulting activated carbon were successfully applied in adsorption and catalysis [4-6].

Among the processes available to obtain carbon functionalized materials, acid-mediated carbonization (AMC) has been far less explored than conventional thermal or HTC processes, but the resulting solid materials, named acid-chars, plenty of oxygen reactive functional groups, can compete with hydrochars or chars in several processes [3]. In the present communication literature studies reporting the synthesis of acid-chars through AMC is reviewed and recent data obtained in our research group on the synthesis and application of acid-chars from various biomass precursors in adsorption and catalytic processes (Fig. 1) will be presented.
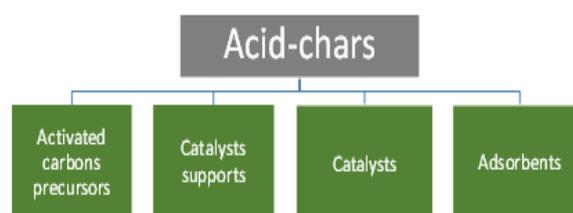

Figure 1. Application fields of acid-chars explored in the studies developed by AAM group.

## 2. Acid-chars synthesis and properties

Acid-chars are synthesized by acid-mediated carbonization (AMC) of solid or liquid carbon precursors at atmospheric pressure, being a valuable approach to maximize the carbon content of precursors with high inorganic content (*e.g.* rice husk) or with considerable amounts of water. The few literature studies exploring this approach report the synthesis of acid-chars at distinct temperatures: lower than 100 °C for rice husk and sisal [7-9] but at temperatures between 400 and 800 °C when using glycerol as carbon source [10]. Both H_2SO_4 and H_3PO_4 can be used as effective acid catalysts in this process but the majority of the works only tested the stronger H_2SO_4, with some of them evaluating the effect of the acid concentration. Depending on the acid used, the structure of the acid-char will contain sulfur or phosphorus groups besides the oxygen rich functionalities, which can be valuable when envisaging, for example, catalysts immobilization or higher reactivity towards activation.

The AAM group explored the AMC of sisal residues which, due to the high percentage of carbohydrate-containing polymers (65.8 % cellulose and 12 % hemicellulose [11]) and low amount of lignin (9.9 % [11]), that is more resistant to decomposition, can be successfully digested with acid and further

carbonized to yield versatile acid-chars. H_2SO_4 was selected as acid catalyst and we explored the influence of the acid concentration in both digestion and carbonization step on the properties of the final acid-char [9]. The AMC consisted in the digestion of sisal fibers with H_2SO_4 at concentration of 12 M or 13.5 M during 15 min at 50 °C and at concentration 9 M during 30 min at the same temperature (10 mL of H_2SO_4 solution per gram of sisal fibers), followed by the polycondensation during 6 h at 90 °C under reflux [9]. Although less extensively, besides sisal we have also explored other biomasses – pine sawdust, cork powder, corn stalk, and carbohydrates – proving that a large range of carbon precursors can successfully yield acid-chars. More recently we are exploring the influence of other experimental conditions on the acid-chars properties (*e.g.* duration of polycondensation step and higher H_2SO_4 concentration).

The thermogravimetric profiles of the sisal-derived acid-chars (Fig. 2(b)) confirmed the polycondensation of cellulose and hemicellulose since the decomposition peaks of these polymers in the raw sisal are not observed in the derived acid-chars [9]. All the acid-chars presented incipient porosity, amorphous-like carbon structures (Fig. 2(d)) and surfaces decorated with acidic oxygen and sulfur functionalities as proved by the DRIFT spectra (Fig. 2(c)) and also quantified by elemental analysis, and very low pH at the point of zero charge (pH_{PZC} around 2). Even though the just mentioned properties of the acid-chars are almost independent on the concentration of the acid during the synthesis, the morphology (see Fig 2(e) and (f)) and density (Fig.2 (a)) of these materials are highly dependent on the acid concentration during the digestion and carbonization steps. While for example the samples prepared with 13.5 M and 12 M H_2SO_4 in both steps are composed of particles with a compact and rough surface and with high apparent density (> 500 kg m^{-3}), those obtained with lower acidic concentration (*e.g.* S9/9) present an aerogel-like structure composed by interconnected spheres with apparent densities between 100 kg m^{-3} and 200 kg m^{-3}. The polycondensation yield is also dependent on the acid concentration since acid-chars synthesized with 13.5 M and 12 M during digestion step allow to attain yields between 30 and 35 %, while those obtained after digestion with H_2SO_4 9 M present and yield around 15 %.
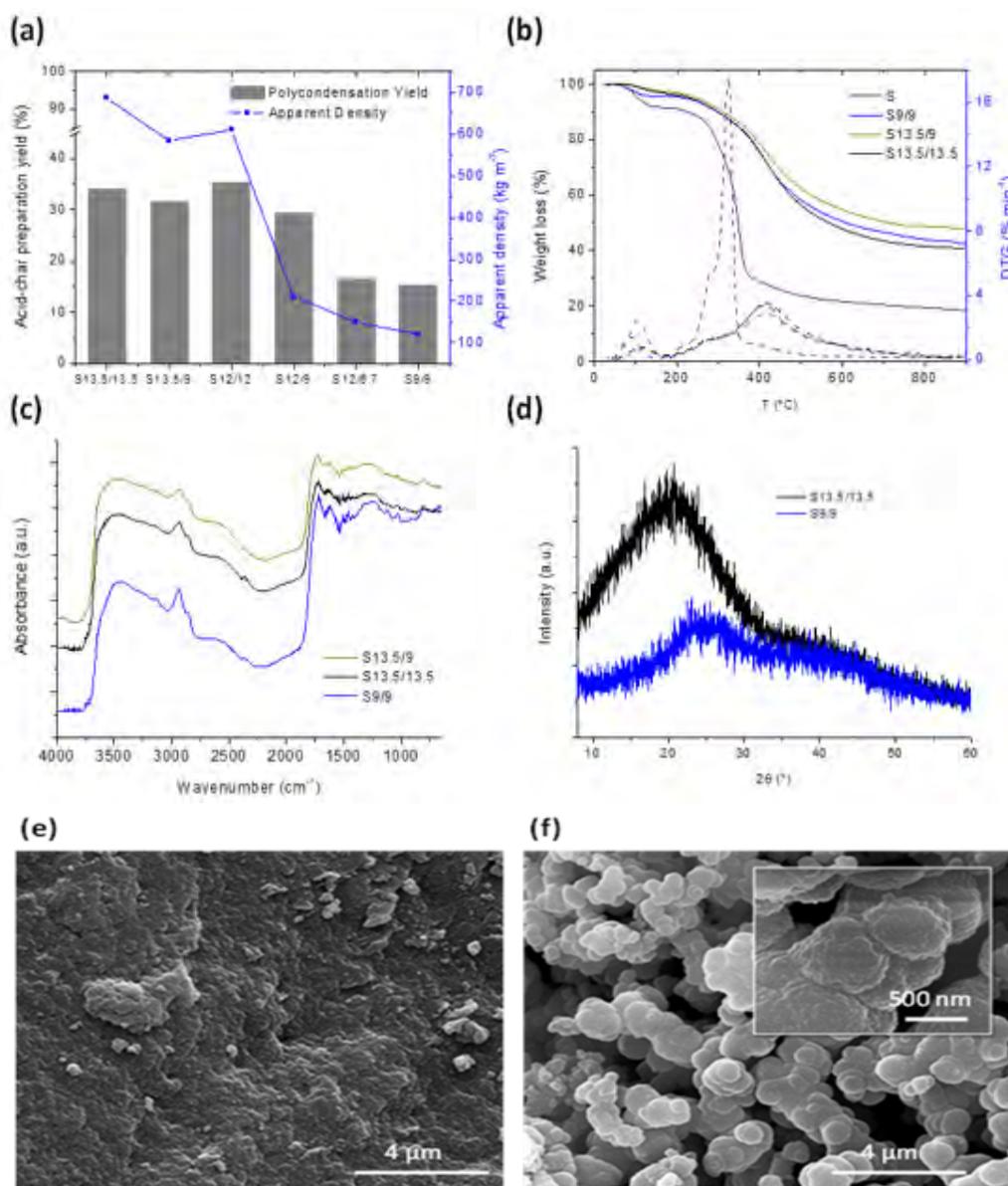
Figure 2.

(a) Effect of H_2SO_4 concentration on the digestion steps on the yields and tapped densities of the acid-chars;

(b) thermogravimetric profiles (TG) and derivative (DTG) curves of selected samples;

(c) DRIFT spectra and

(d) XRD patterns of selected acid-chars. SEM images of samples (e) S13.5/13.5 and S9/9 (S[H_2SO_4]digestion/[H_2SO_4]polycondensation). Reproduced from [9] with permission of Elsevier.

3. Acid chars as activated carbon precursor

To the best of our knowledge the published works reporting acid-chars obtained by AMC were focused on the development of the pore structure to obtain nanoporous carbon materials. Wang et al. [7,8] used H_2SO_4 to synthesize acid-chars from rice husk, which were further chemically activated with H_3PO_4 or KOH. The acid-char derived activated carbons obtained by KOH activation attained BET areas of 2500 m^2g^{-1} and microporous structure [8], while those activated with H_3PO_4 were micro and mesoporous solids and presented a wider range of BET area values (750 to 2700 $m^2 g^{-1}$) [7]. The activated carbons prepared from rice husk-derived acid-chars presented good electrochemical performances comparing favorable with commercial counterparts, attaining specific capacitances of 130 Fg^{-1} in the case of activation with H_3PO_4 and superior than 220 Fg^{-1} when KOH activated [7,8]. In another study Wang et al. also report the carbonization of acid-chars prepared from rice husk to synthesize carbon materials with BET areas up to 1034 m^2g^{-1} [12]. These materials present electrical conductivity reaching 156 $\Omega^{-1}m^{-1}$ at 900 kPa, that is, close to the performance of a commercial carbon black.

Cui and Atkinson [10] explored several acid catalysts (H_2SO_4, H_3PO_4, HCl and CH_3COOH) for the synthesis of acid-chars from glycerol at mild to high carbonization temperatures, and used physical activation (steam or CO_2) to develop the pore networks. Depending on the acid (H_2SO_4 and/or H_3PO_4), the obtained oxygen-rich chars contain sulfur (0.43-4.20 wt.%) or phosphorus (6.32-16.31 wt.%) groups, which enhance the reactivity for subsequent activation and allow joining a well-developed pore network with heteroatom doping. Independently of the acid catalyst and activating agent all the acid-char derived activated carbons presented a micro and mesopore network with BET areas between 1000 $m^2 g^{-1}$ and 2400 $m^2 g^{-1}$. These activated carbons were tested for the removal of toluene and hexane (volatile organic compounds, VOCs) in gas phase, and also for the removal of Cr(VI) in aqueous solution, outperforming commercial activated carbons. The authors propose that the best activated carbon material for an industrial application in the removal of VOCs is that prepared with H_2SO_4 and further steam activated, since it presents high adsorption capacity at low pressure due to the high micropore volume allied with hydrophobic properties [10]. In what concerns Cr(VI) removal the materials prepared with H_3PO_4 are preferred since their hydrophilic character, high mesopore volumes and higher amount of oxygen surface functionalities favor the adsorption of this cation [10].
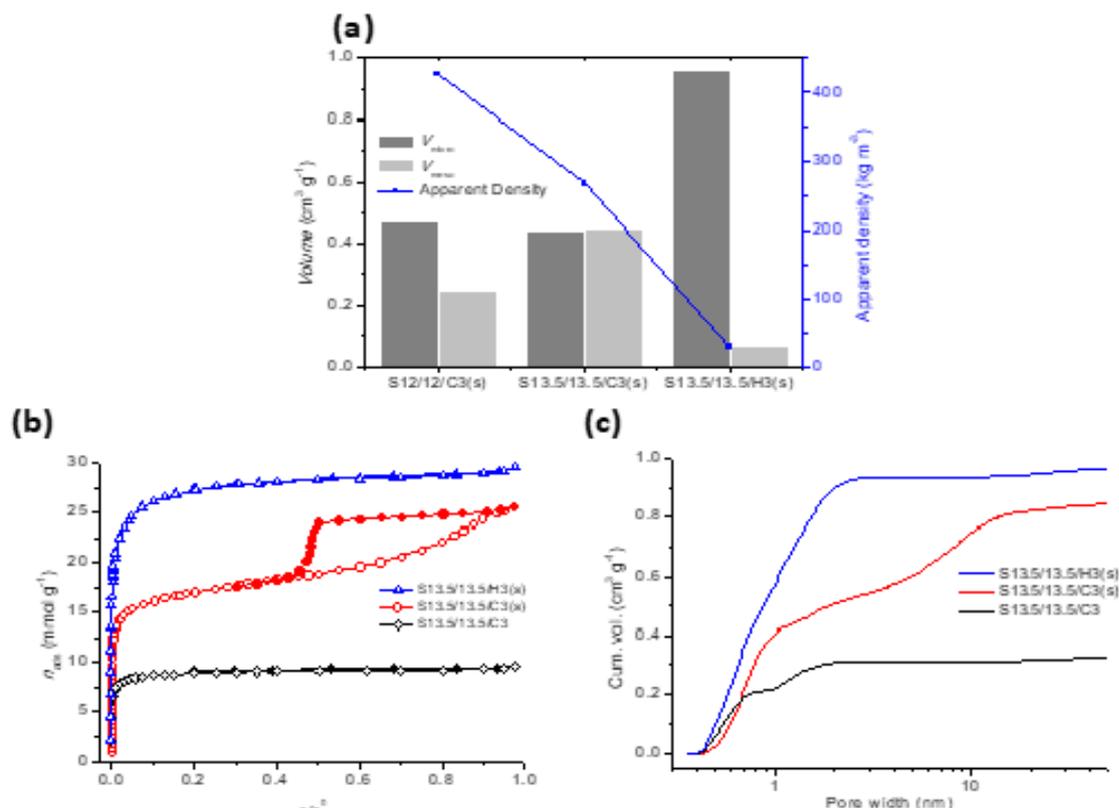
Figure 3.

(a). Micro and mesopore volumes of the activated carbons prepared by solution impregnation of acid-chars S12/12 and S13.5/13.5 with K_2CO_3 or KOH (3g of activating agent per gram of acid-char) followed by activation at 800 °C during 1h. The influence of acid-char precursor in apparent density of the activated carbon is also displayed;

(b) N_2 adsorption isotherms of activated carbons prepared from acid-char S13.5/13.5;

(c) Cumulative pore size distributions obtained from the 2D-NLDFT-HS method applied to the N_2 adsorption isotherms. For chars designation see caption of Figure 2. Reproduced from [9] with permission of Elsevier.

The sisal-derived acid-chars prepared in the AAM group were chemically activated with K_2CO_3 and KOH aiming to understand the influence of the acid-char properties on the final characteristics of the activated carbons [9]. Figure 3 clearly illustrates the distinct pore structures of some of the activated carbon materials synthetized. While K_2CO_3 solution impregnation and further activation of acid-chars obtained with H_2SO_3 12 M and 13.5 M yields activated carbons (S12/12/C3(s) and S13.5/13.5/C3(s)) with high apparent densities and pore networks composed of micro and mesopores, the solution impregnation of the same acid-char with KOH (S13.5/13.5/H3(s)) originated a microporous solid with a density lower than 50 kg m^{-3} (Figure 3(a)). The N_2 adsorption isotherms (Figure 3(b)) and pore size distributions (Figure 3(c)) reveal that by changing the contacting method of K_2CO_3 and acid-char (S13.5/13.5/C3(s) – solution impregnation and S13.5/13.5/C3 – physical mixing) we can also tune the porosity of the resulting activated carbon without significant changes in the apparent density and morphology of the samples (for more details see [9]). The overall data collected proved that by controlling the synthesis conditions of the acid-chars (i.e. acid concentration during digestion and polycondensation), the chemical activating agent and the contacting method between the acid-char and the activating agent it is possible to obtain activated carbons with very distinct properties (i.e. BET areas from 600 m^2 g^{-1} to 2400 m^2 g^{-1}, apparent densities from < 50 kg m^{-3} to 600 kg m^{-3} and exclusively micropore structures or micro and mesopore networks). Moreover, it is important to highlight that although sisal is a low density biomass, the control of AMC condition allows to tailor the density of the acid-chars and control the features of the derived activated carbons thus proving the versatility of this less explored carbonization route.

Materials S13.5/13.5/H3(s) and S13.5/13.5/C3(s) were assayed as adsorbents of two pharmaceutical compounds – ibuprofen and iopamidol – with the sample obtained by KOH activation attaining the double of the adsorption capacity of a high performing commercial product from Cabot-Norit certainly due to the presence of a large amount of supermicropores. A large set of these materials was successfully tested for the oxygen reduction reaction (ORR) in alkaline medium, presenting tolerance to methanol when compared with commercial Pt/C and long-term electrochemical stability [13]. The material S13.5/13.5/C3(s), with micro and mesopore structure associated with the presence of nitrogen and sulfur, showed the most promising electrocatalytic performance for ORR, with onset potential of 0.84 V vs. RHE, diffusion-limiting current density (0.26V, 1600 rpm) of -3.12 mA cm^{-2} and with the mechanism closest to the direct 4-electron reaction (n_{O2} = 3.6).

4. Acid chars as catalysts supports

The immobilization of homogeneous catalysts onto solids has been explored by the scientific community for quite some time. This has been also one of our research interests and, in the frame of collaborations with Inorganic Chemistry Groups of our Faculty, of Instituto Superior Técnico (IST), and of Faculty of Sciences from University of Porto (FCUP), several studies were made to test different porous solids, namely modified zeolite structures [14-16] and obviously also carbon materials [17-21]. The studies developed with carbon materials have in common the fact that in all cases the synthesis procedure used gave rise to acid supports (e.g. CMK-3) thus preventing the need of an oxidation post-synthesis treatment generally reported when carbon materials are used as supports for immobilization of homogeneous catalysts [22].

Therefore, attending to the acid surface chemistry of the acid-chars, it was evident that they would be a good option to anchor catalytic active metal complexes. To evaluate this hypothesis we carried out a study where complex [MoI$_2$(CO)$_3$(MeCN)$_2$] was immobilized on sisal-derived acid-char S13.5 (Fig. 4) [19].
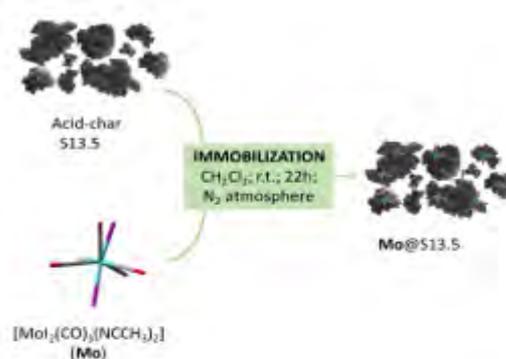

Figure 4. Simplified scheme of immobilization procedure.

The procedure allowed the incorporation of 2.98 (wt.%) of Mo, and the analysis of the FITR spectra (Fig. 5) allowed to concluded out immobilization of the complex occurred by the displacement of the labile acetonitrile ligands. In fact, bands at 2276 and 2303 cm^{-1} assigned to stretching of C≡N group from the acetonitrile ligands are almost undetectable in Mo@biochar. These very low intensity bands must correspond to complex that was not coordinated with the acid-char being adsorbed.
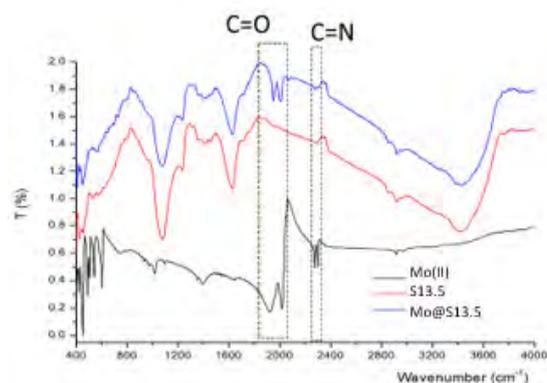

Figure 5. FTIR spectra of molybdenum complex (Mo(II)), acid-char S13.5, and immobilized catalyst Mo@S13.5.

Oxidation of *cis*-cyclooctene (Cy8) with *tert*-butyl hydroperoxide was the model reaction selected to assess the catalytic properties of Mo@S13.5 sample. Data presented in Table 1 exemplify the most relevant results obtained in one of the solvents tested (CH$_2$Cl$_2$) and in solventless conditions. In both cases the acid-char is practically inactive so it is only acting as host of the complex. Concerning the catalytic behaviour

of Mo@13.5 the results could not be better as under solvent conditions the Cy8 conversion after 24 h is higher than its homogeneous counterpart. However the most important results were those obtained in solventless conditions since a complete convention of the reagent was achieved maintaining the 100 % selectivity to the epoxide.

Catalyst	Conversion at 24h (%)	
	Solvent: CH$_2$Cl$_2$	No solvent
S13.5	1	1
MoI$_2$(CO)$_3$(MeCN)$_2$	81*	100
Mo@S13.5	93	100

All reaction were made at 55 °C using 150 mg catalyst (0.31 mmol Mo g^{-1}) and oxidant: *cis*-cyclooctene =2:1 (molar). *Data from ref. [23]

Table 1. Results of catalytic oxidation of *cis*-cyclooctene with *tert*-butyl hydroperoxide.

As the final goal of this type of studies is to prove that the immobilized catalyst is, in fact, a reusable catalyst Mo@S13.5 was tested in four re-use cycles in optimized experimental conditions (Fig. 6). No changes in selectivity was observed and only a quite small decrease of conversion was observed, especially between the first and the second cycles. This decrease was attributed to the leaching of the species that were not effectively linked to the acid-char, most probably those that were detected in the very low intensity bands assigned to the acetonitrile in the FTIR spectrum oh Mo@S13.5. In accordance a decrease of Mo content in the sample to 2.76 (wt.%) was found. No important further leaching was proved stopping the reacting after 2h and, after recover the catalyst, no substrate conversion was observed up to 24 h.
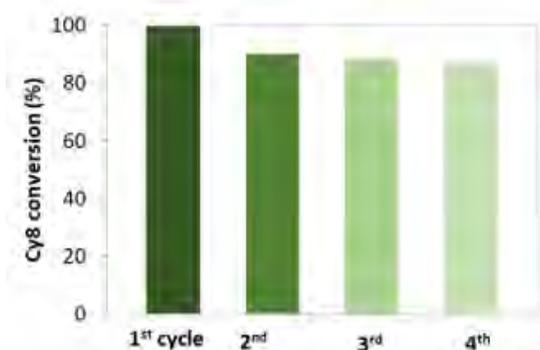
Figure 6. Re-use tests results. Reaction condition: 55 °C; 150 mg catalyst (0.31 mmol Mo g-1) and oxidant: *cis*-cyclooctene =2:1 (molar); solventless.

So, the results obtained with the sisal derived acid-char loaded with the complex [MoI$_2$(CO)$_3$(MeCN)$_2$] proved that acid-chars can compete with more conventional carbon materials to prepare reusable catalysts that retain almost unchanged their catalytic properties in several successive.

5. Acid chars as catalysts and adsorbents

Recently we started to explore the potentialities of acid-chars as catalysts and also as adsorbents for the removal of heavy metals from water.

Regarding the use as catalysts, sawdust derived acid-chars obtained with different H$_2$SO$_4$ concentration (13.5 M and 18 M) are being tested in the esterification reaction of acetic acid with butanol. The results obtained so far show that the materials are active for this transformation, achieving reaction yields of 64 %. Moreover, a direct dependence of the reaction yield with the number of the total acid functionalities, consequently with the acid concentration used to prepare the samples was observed. Reusability tests are being made.

To evaluate the potential of acid-chars as adsorbents for the removal of heavy metals from water, sisal was also selected as starting biomass and, to evaluate the influence of the polycondensation step duration on the samples properties, 6h, 3h and 1.5h treatments were made. Somewhat unexpected, the results reveal that the synthesis yield, and the density of the samples are practically independent on the polycondensation step duration. Likewise, the preliminary data for the removal of Pb^{2+} after 24h of contact time do not evidence significant differences between the samples. On the other hand, in comparison with literature [24,25] the removal achieved show that these are very promising materials for this purpose and so, the study will be extended to other cations, namely Cd^{2+}.

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