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Designing microporous activated carbons from biomass for carbon dioxide adsorption at ambient temperature. A comparison between bagasse and rice by-products.

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Abstract

Pulping in agro-waste processes are known to affect the chemical constituents of the materials obtained. In this study, activated carbons (ACs) were prepared using precursors based on rice straw, rice husks and bagasse. The composition of these precursors was first determined in order to study the influence of the components of each of these precursors on the sorption properties of the ACs obtained. The ash content was determined by calcination of the precursors as the main component present in ashes is silica, which is known to play a role on sorption processes. The surface chemistry of the ACs was assessed by ammonia thermo-desorption (NH_3-TPD), before being tested for carbon dioxide capture. ACs obtained from bagasse were capable of capturing up to 14 wt % at atmospheric pressure and 25°C, regardless of the pulping process applied to the precursor. Rice-husks based AC gave a similar result when the precursor was pulped with a 12% soda solution. Rice straw based ACs were less interesting in terms of CO_2 capture. These differences were rationalized in terms of composition and textural properties.

Keywords. Agrowaste ; Pulping ; CO2 ; Adsorption

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Introduction

Increase of environmental pollution and amounts of waste matters caused by expansion of human activity is a continuingly growing and serious issue.(Atkinson, 2000; Behera et al., 2013; "Toxic Industrial Chemicals," 2002) Thus, social concerns on environmental problems and more rigorous regulations on strengthening the environmental protection have promoted the development of waste treatment technologies to enhance precursors as valuable products.(Gupta et al., 2012; Ioannidou and Zabaniotou, 2007; Saleem et al., 2017) As a sustainable and renewable low cost precursor, biomass (natural or by-product such as agro-lignocelluloses) has been used for the production of several efficient, eco-friendly, and cost-effective lignocellulosic products, *e.g.* hydrogels for reclamation of sandy soils, (Basta et al., 2013a) functional paper sheets, agro-wood composites (Basta, A.H., El-Saied, H., Lotfy, 2014; Basta et al., 2013b) and carbon nanomaterials with distinctive functionalities. (Guo et al., 2003; Lotfy et al., 2018). These latter promoted materials can be used, in turn, for applications in wastewater decontamination, (Basta et al., 2013a; Ozer et al., 2012) as well as for fuel production. (Abdeshahian et al., 2010; Siddiqui et al., 2019) If some studies focused on the inorganic part of these by-products, namely silica,(Megawatia et al., 2018) they were mostly used as precursors for activated carbons. Clearly, most of the literature related to the preparation of activated carbons (ACs) from agro-wastes focuses on their application for removing pollutants from aqueous media. However, the application of porous carbon materials for removing noxious gases is also important to maintain the environment and life. It is very common to say that these porous carbons are versatile. Indeed, they can be also used as supports in catalytic processes. This is already widely documented in the literature, for instance, Cu supported ACs catalysts were found to have an improved activity to remove SO_2, compared to Cu supported alumina. (Tseng et al., 2003) Additionally, ACs are used in Fischer

Tropsch synthetic fuels, for converting gasses (carbon monoxide and hydrogen) to liquid hydrocarbons, as well as for reducing the effects of poisoning of FTS fuels. (Salinas-Martínez de Lecea et al., 2000; van Steen and Claeys, 2008) ACs can be used as supports for different purposes; however, they can be functionalized to improve their activity. Classically, enhancing the functionalities of ACs is carried out by physical or chemical treatments.(Fathy et al., 2019; Guan et al., 2013; Mangun et al., 2001; Matzner and Boehm, 1998; Ramangkoon et al., 2016) If agro-based activated carbons are demonstrated to have a high potential for removing noxious gasses, this would address a major concern in overcoming simultaneously both pollution and waste problems, which would be a great improvement regarding climate change. In the literature, different approaches have been envisaged for CO_2 sequestration. If in the former studies this sequestration was performed at high pressure, (Djeridi et al., 2017) more recently standard pressure conditions have been tested. (Nachtigall et al., 2011; Phan et al., 2010; Zárate et al., 2016) This can be understood by the fact that in nature, CO_2 is present at low partial pressure. Investigating the potential of materials in the latter conditions therefore seems more relevant. Additionally, it must be remembered that water moisture is usually present in air. This explains why even if CO_2 sequestration was first tested using dried porous materials, more recently raw porous materials were thoroughly studied (Ding et al., 2016; Ding and Liu, 2020; Phan et al., 2010; Zárate et al., 2016). The regeneration of the adsorbents is of crucial importance, even with rather low cost materials such as pyrolysed wood based materials. As CO_2 capture is usually performed at low temperature, or high pressure, it can be deduced that CO_2 has mild interaction with most of functionalized surfaces. This is why TSA, PSA or VSA are interesting strategies that have been tested for this goal (Raganati et al., 2020; Riboldi and Bolland, 2015). In these studies, it is demonstrated that an appropriate adsorption/desorption balance must be reached in order to find a steady state allowing for a large number of cycles to be run, also described as the CO_2 working capacity.

In many countries, rice by-products (rice straw and rice husks) or bagasse are regarded as the most available agro-wastes. These by-products were therefore investigated in many aspects, the main being their potential as carbon sources for making ACs. Because of their intrinsic differences, in terms of composition (lignin, cellulose, hemicellulose and silica), their application to depollution has been investigated and proved successful.(Basta et al., 2019a, 2013a; Guo et al., 2003; Megawatia et al., 2018) In these works, the adsorbents have been studied as powders because they are readily obtained after pyrolysis. They are characterized by a particle size lower than 50 microns which is a clear drawback for their use in dynamic sorption processes such as PSA or TSA (Schöny et al., 2017). Even though such fine particles can be easily used and tested for characterization in static analysis systems (TG, gas sorption analyzer, etc.), their applicability in actual dynamic systems even at lab-scale, such as fixed/fluidized bed reactors, is very challenging (Raganati et al., 2017). Clearly, a fixed bed system allows studying powdered sorbents but in this case, a high pressure drop maybe observed even for a fine bed of adsorbent. A pelletization step of the powders is usually required to avoid this pressure drop but in this case, the shaping process usually negatively affects the sorption performance, either by the loss of porosity, due to the high pressure undergone by the powders, or by the use of binders which may block the porosity. An alternative that has been envisaged is the Spark Plasma Sintering (SPS) densification, which can be performed without any binders at low pressure (Dibandjo et al., 2008; Grossin et al., 2010). This will be a very interesting issue to study in the near future. Bagasse being highly regarded, compared to rice by-products, our goal is to assess some ACs prepared from rice by-products or bagasse as potential adsorbents for carbon dioxide. The promoting approach used for changing the chemical functionalities of these precursors is discussed with respect to the sequestration of carbon dioxide. The role of the silica content is also investigated.

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Experimental section

Preparation and characterization of AC-precursors

Rice by-products (Rice husks and Rice straw) and sugarcane bagasse were subjected to pulping and biological processes in order to change their chemical constituents as well as their textural properties. These processes are known to change the lignin, cellulose, hemicellulose as well as silica contents of the agro-waste, (Basta et al., 2019b), or preserve one component while having significant effect on the others.

- Pulping processes: The pulping agents were sodium hydroxide, sodium sulfite and a sodium sulfite - sodium carbonate blend. Pulping processes were carried out by setting the percentage of Na_2O in the pulping agent as 6.5%. They were performed at 140°C for 2h, using volume dilution ratio liquor / pulping agent of 5. An additional experiment was carried out for preserving the organic components of the material during the removal of silica from rice byproducts using the alkaline pulping. This process was carried with 12% NaOH, at 60ºC for 1 h, and a ratio liquor / pulping agent of 5.
- Biological process: The enzymatic treatment was achieved by exposing the rice straw to cellulosase and peroxidase enzymes (produced by fungi *Rhizopus oryzae* and *Aspergillus awamor,* pre-isolated from rice husks*),* under static conditions. The biological activation was performed during 2 weeks at 27 ºC using a concentration of 1/20 liquor ratio.

The obtained samples were named according to **Table 1** in which their chemical compositions are also reported. These compositions (lignin, hemicellulose, α-cellulose) were estimated by standard methods.(Institute of Paper Chemistry, 1951; Jayme and Sarten, 1940; Krause and Schempp, 1991) The ash content was determined by total oxidation of the materials in a muffle furnace.

Non-isothermal thermogravimetric measurements were performed to gain information about the thermal stability of the evaluated materials upon different activation procedures. It is then expected to find out appropriate methods able to reduce the formation of levoglucosan (carbon-containing volatile substance), and consequently lower the volatilization stage. The behaviour of the precursor through the volatilization stage and its effect on the sorption performance of the produced AC will be specified. This thermogravimetric analysis (TGA) was performed on untreated and treated materials by using a Perkin–Elmer Thermal Analysis Controller AC7/DX TGA7. Analysis was performed with a heating rate of 10°C min^{-1} and nitrogen flow rate of 50 mL s.$^{-1}$ Interestingly these analyses also allowed assessing the temperature of pyrolysis which could be applied for the preparation of activated carbons.

Ammonia temperature-programmed desorption (NH_3-TPD)

Temperature-programmed desorption of NH_3 (NH_3-TPD) was performed using a chemisorption analyzer (Micromeritics AutoChem II 2920) equipped with a thermal conductivity detector (TCD). Typically, about 50 mg of material was activated at 150 ºC (after a ramp of 10 ºC min^{-1}) for 30 minutes in 30 mL min^{-1} of He flow. The material was further cooled down to 100 ºC under a 30 mL min^{-1} He flow. Subsequently, the adsorption of NH_3 was carried out at this temperature by switching to a flow of 5% NH_3/He (30 mL min^{-1}) for 1 h. The sample was further purged with He for 30 min to remove weakly adsorbed NH_3. The TPD was performed from 100 to 550 ºC with a temperature ramp of 10 ºC min^{-1} in a 25 mL min^{-1} He flow.

Textural properties and morphology

The textural properties of the activated carbons were determined by nitrogen sorption measurements at 77 K using a Tristar 3000 Micromeritics. About 80 mg of material were degassed under secondary vacuum at 150 ºC for 12 h. A typical mass loss after thermal treatment was found to be ~20 weight percent which shows that these samples are hydrophilic, likely due to oxygenated functions on the carbon surface (phenols, lactones, aldehydes, etc). The equivalent specific surface areas were calculated using a BET linearization of the sorption isotherms around the monolayer, while the pore volume and the external surface area were assessed using the α_s method, taking a non porous carbon as a reference (Rouquerol et al., 1999).

The morphology of the investigated activated carbons (ACs) was examined by scanning electron microscopy (SEM). The samples were exposed to gold coating (Edwards Sputter Coater, UK) using a quanta FEG250 microscope running at 20 kV.

CO_2 adsorption measurements

CO_2 adsorption isotherms were performed at 25 °C by using a home-made adsorption apparatus based on manometric measurements, equipped with two capacitive pressure gauges (10 mbar and 1000 mbar). Detailed information of the setup was described elsewhere (Ramsahye et al., 2011; Trens et al., 2014). In brief, the adsorbed amount is determined by measuring the equilibrium pressure difference before and after each sorption step. A precise amount of gas is introduced in a calibrated volume where the initial equilibrium pressure is measured. The gas is then allowed to expand in the sample cell where the pressure is also monitored. When the pressure is stable, the equilibrium pressure is recorded and the amount adsorbed can be calculated. In commercial sorption machines, target equilibrium pressures are set in the sorption programme. In our sorption device, we preferred to allow the sample itself to monitor how many data will allow to cover the whole sorption isotherm (Trung et al., 2011). Indeed, after each data, additional gas is introduced in the calibration volume for the next data. If after adsorption, the equilibrium pressure is very low, the initial pressure of the following point will be very close to that set for the former point. In this way, any specific behaviour will be disclosed as we could exemplify it in the past (Boudjema et al., 2019; Trung et al., 2010). Prior to measurements, about 250 mg of material were degassed at 150 °C for 12 h under secondary vacuum.

Results and Discussion

Precursor's analyses of CO_2 adsorbents

Proximate analysis

The composition of the rice by-products (Rice Straw (RS) and Rice Husks (RH)) and sugar-cane bagasse (B) is shown in **Table 1** along with that of the processed materials. The figures given in **Table 1** are subjected to the variations of quantities organic extractives in the samples used for these analyses. The difference between 100% and the sum of the percentages for each composition is therefore due to the amount of extractives in the samples. The chemical treatments (soda, sulfite and neutral sulphite) are known to remove the non-cellulosic constituents of rice by-products (RS & RH) and bagasse (silica, hemicellulose and lignin). Accordingly, these treatments lead to an increase of the proportion of α-cellulose in the residual materials. The biological treatments are more specific according to the enzymes employed (cellulase and peroxidase) which yield a selective removal of RS and RH constituents. As expected, the cellulase enzyme shows a high activity towards cellulose, while peroxidase affects lignin in the precursors. In proportion, both treatments therefore lead to increase the silica content. From **Table 1**, it can be seen that the untreated RS and RH have very high ash contents (15.6% and 18.5% respectively). These can be related to silica content of the precursors, which is likely to enhance the sorption capabilities of activated carbons.[36] In the case of bagasse, the ash content is 4.7 % which confirms the low concentration of silica in the latter, as usually documented. (Guo et al., 2020; Megawatia et al., 2018). These differences highlight the specificity of the sorption properties of the carbon materials investigated. The ash content, being made of silica, is therefore related to the chemical treatment.

Table1. Chemical constituents of the precursors of CO_2 adsorbents

	Rice Straw AC precursor	Ash, %	Lignin, %	Holocellulose	
				α-cellulose,%	Hemicellulose, %
RS1	RS-control	15.6	14.5	37.5	22.8
RS2	Cellulase treatment	23.6	29.8	21.0	22.2
RS3	Peroxidase treatment	22.5	10.5	51.0	23.0
RS4	6.5% soda treatment	14.8	12.6	46.3	27.5
RS5	6.5% sulfite treatment	15.6	12.8	36.2	31.4
RS6	6.5% neutral sulfite treatment	17.5	12.3	39.2	29.0
RS7	12% soda treatment	11.1	12.4	52.1	23.0

	Rice Husk AC precursor	Ash, %	Lignin, %	Holocellulose	
				α-cellulose,%	Hemicellulose, %
RH1	RH-control	18.5	20.6	33.0	22.8
RH2	Cellulase treatment	17.6	29.1	19.0	18.9
RH3	Peroxidase treatment	21.5	10.7	45.0	21.0
RH4	12% soda treatment	11.3	19.6	48.0	24.0

	Bagasse AC precursor	Ash, %	Lignin, %	Holocellulose	
				α-cellulose,%	Hemicellulose, %
B1	B-control	4.7	19.1	41.6	26.5
B2	6.5% soda treatment	1.3	14.0	52.6	23.0
B3	6.5% sulfite treatment	1.5	18.1	44.0	26.9
B4	6.5% neutral sulfite treatment	1.8	15.9	48.8	23.1

As expected, soda treatment decreases the ash content by solubilizing the silica contained in the precursors (15.6 down to 11.1% and from 18.5 down to 11.3%, for RS and RH respectively). However, a low NaOH % pulping agent (6.5% as Na_2O) has a rather limited influence on the ash content, and therefore the silica content. This can be evidenced on rice by-products which have high silica content. In the case of bagasse, the soda pulping eliminates almost the whole amount of silica present in the precursor, as its content is already very low (4.7%). The reduction in silica contents in the precursors subjected to pulping by alkaline agent has another effect, which is a decrease of the lignin content which in turn, increases the α-cellulose proportion. This can be seen with RS4, RS7, RH4 and B2. Subjecting the RS precursor to neutral sulphite pulping and enzymatic treatments provide the reverse trend. Such pre-treatments, except cellulase treatment, lead to increase in holocellulose. The alkali and peroxidase treatments are more efficient for increasing the α-cellulose, as compared to pristine RS and RH. Indeed, the increase in α-cellulose reaches 36-39%, and 36-45%, for RS and RH precursors. Moreover, these treatments, especially by enzymes, lead to increase the ash content up to ~22%.

Pyrolysis of Precursor-based ACs

The prepared precursors were subjected to thermogravimetric analysis (TGA) in order to identify their thermal stability which is related to the chemical constituents. In general terms, the thermal decomposition of any biomass occurs via three-stages, namely: the desorption of moisture, the degradation and evolvement of the constitutive biopolymers, and finally carbonisation of the residue. The TGA and DTGA curves of the RS, RH and B materials are presented in **Figure 1**. Concerning the removal of water, it can be noticed that this phenomenon occurs at temperatures below 100°C, which is the indication that water is loosely bound to the biopolymeric structures. Depending on the material, the extent of water removal differs, which is the indication of different textural properties. The main degradation stage due to depolymerisation, volatilisation and (inter- and intra-molecular) dehydration occurs at temperatures higher than 200°C. This stage is complete at 400°C and at higher temperature, full carbonization of the materials can be observed. Focusing on the pristine materials (untreated), it can be noticed that bagasse (B1) leaves a lower percentage of ashes (~9.9%), compared to RH1 and RS1 (31.2% and 26.2% respectively). These results are expected as they are in line with the silica content of these materials, which was determined by their carbonization. The lower weight remain (free from ash) of volatilization stage of raw bagasse (8.9%) than rice by-products (13.7% and 13.2%) is probably ascribed to the higher content of α-cellulose.

Upon treatments, the thermal behaviour of the materials is changed. Indeed, both biological and chemical pulping lead to an enhancement of the thermal stability, compared to raw rice by-products and bagasse. This can be seen by focusing on the values of initial temperature and DTG peak temperature of depolymerization and volatilization stage which both increase upon treatment (2nd degradation stage). The thermal stability of these materials is known to be improved for increased percentages of lignin and/or α-cellulose contents. Conversely, hemicellulose is known to have a rather low thermal stability (Basta et al., 2019b). Sulfite and neutral sulfite pulping treatments provide precursors with higher thermal stability (increase of Ti), compared to treatments by enzymes (cellulose and peroxidase). However, the latter treatments are preferred as they provide high carbon yields (free from ash). These results are gathered in **Table 2**.

Concerning RH precursors, the volatilization stage is observed at lower temperature range if the precursor results from the cellulase treatment (RH2) (T_f-T_i :152 °C). Furthermore, RH2 has a higher residual weight (16.6% free from residue), compared to RH 3 and RH4. This trend can be explained by the rather low cellulose content in RH2. The treatment of bagasse by pulping processes lead to an increase of the α-cellulose and a decrease of the lignin content. Sulfite and neutral sulfite pulping are less effective on removing the lignin than pulping by alkali. The higher weight remain (free from residue) of volatilization stage can be observed in case of the precursor resulting from sulfite pulping (B3), with relatively lower cellulose and higher hemicellulose and lignin contents versus soda pulping agent.

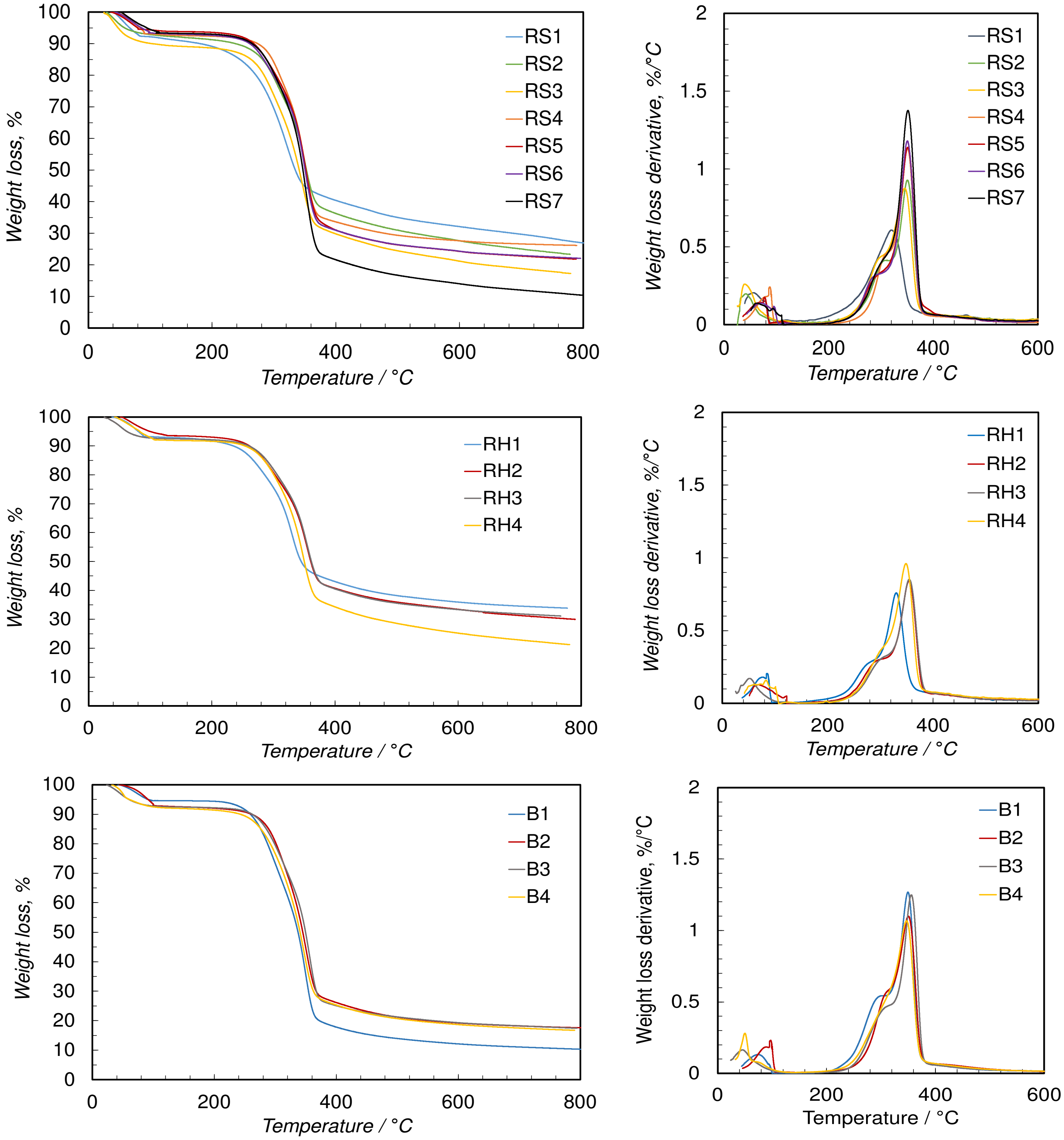

Figure 1. Thermogravimetric analysis of the different materials. (top) Rice straw materials (RS), (middle) Rice husks materials (RH), (bottom) Bagasse materials (B).

This suggests a slow pyrolytic degradation related to the higher lignin and pentosan contents which decompose at higher temperatures than low content of α-cellulose. Pyrolysis of neutral sulfite pulp (B4) behaves in a similar fashion to sulfite pulping material (B3).

Table 2. TGA analyses of AC precursors

	T_i /°C	T_f /°C	T_{peak}/°C	T_f- T_i	Wt remain, %	Residue %	wt remain free ash, %
RS1	159	408	320	249	39.9	26.2	13.7
RS2	231	394	351	163	36.7	18.9	17.8
RS3	226	392	346	166	30.4	12.00	18.4
RS4	250	385	350	134.7	34.5	26.2	8.3
RS5	245	386	351	141.3	32.3	21.1	11.2
RS6	245	390	351	145.1	31.6	21.1	10.5
RS7	223	392	352	169	22.2	7.3	14.9

	T_i /°C	T_f/°C	T_{peak}/°C	T_f- T_i	Wt remain, %	Residue %	wt remain free ash
RH1	223	381	333	158	44.4	31.2	13.2
RH2	245	397	354	152	42.9	26.3	16.6
RH3	217	403	355	186	42.3	27.5	14.8
RH4	234	392	349	158	30.9	18.5.	12.4

	T_i /°C	T_f/°C	T_{peak}/°C	T_f- T_i	Wt remain, %	Residue, %	wt remain free ash, %
B1	220.1	385.2	350	165.1	18.8	9.9	8.9
B2	250.4	388.4	350	138	17.0	8.6	8.4
B3	242.3	390.6	356	148.3	27.6	17.5	10.1
B4	236.5	385.9	347	149.4	26.3	17.0	9.3

From all the foregoing data, we can conclude that there is a good relationship between the constituents of carbon precursor, especially low cellulose and high silica contents, with the weight remain of volatilization stage and consequently the carbon yield.

Textural analysis.

The textural properties of the ACs evaluated by nitrogen adsorption at 77 K are shown in **Figure 2.**

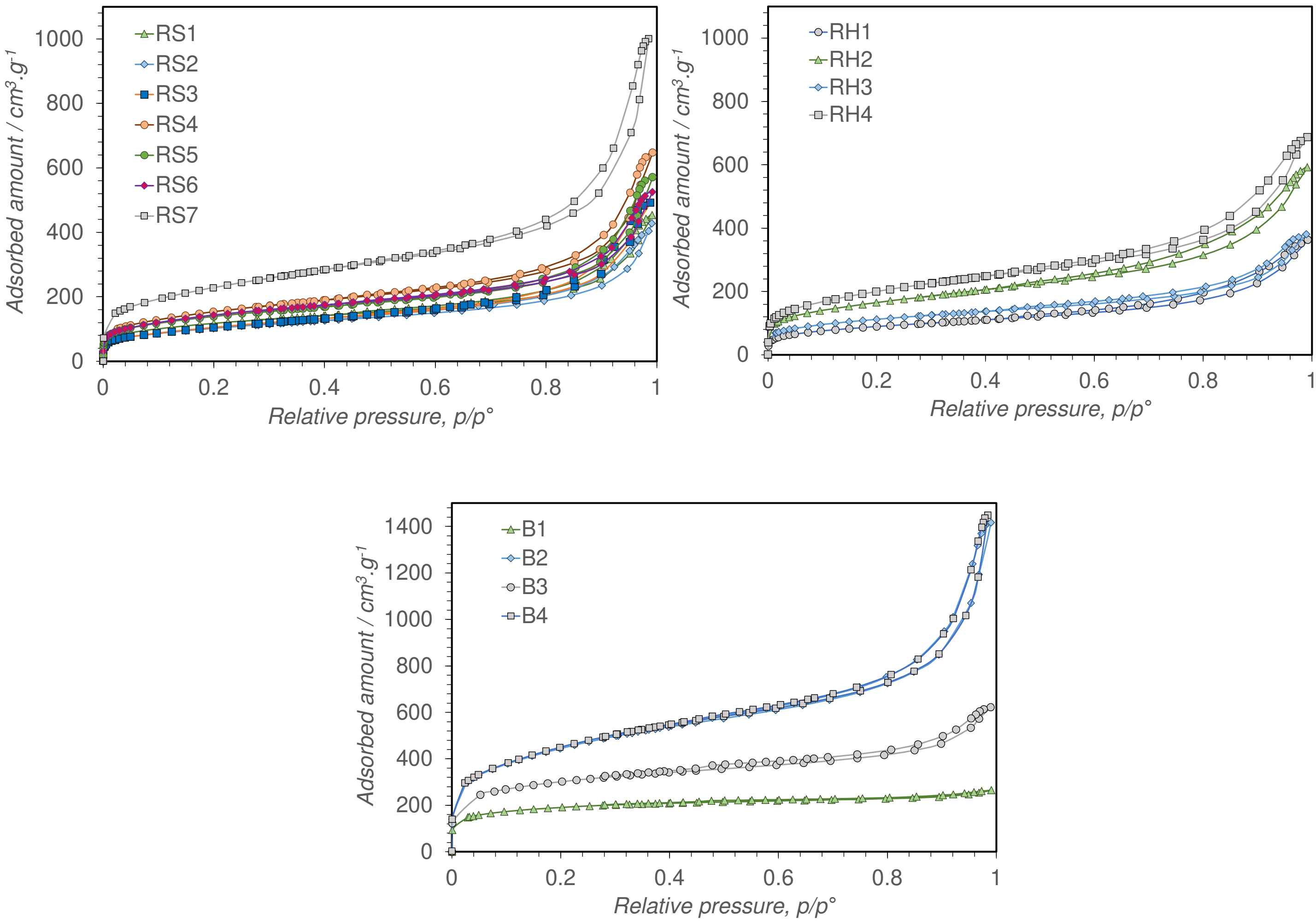

Figure 2. Nitrogen adsorption isotherms of the different activated carbons.

The shape of the sorption isotherm is changed according to the treatment. In the case of chemical treatments by pulping process, the RS-ACs and B-ACs follow the type I sorption isotherm according to the IUPAC classification, which is typical for microporous materials (Rouquerol et al., 1999). In the case of enzymatic treatments of RS and RH, all examined ACs give sorption shapes intermediate between types I and II. Hysteresis loops can be observed at high relative pressure in some cases, which is indicative of some interparticular porosity or macroporosity. This is particularly true in the case of enzymatic treatments applied on RS and RH. This feature is interesting for favouring gas diffusion. Their equivalent specific surface area have been determined using the BET model in the relative pressure range $0.05 < p/p^{\circ} < 0.25$. They are gathered in **Table 3** along with other textural properties obtained using the α_s method, taking a non porous carbon material as reference (Cabiac et al., 2008, 2007; Rouquerol et al., 1999).

Table 3. Textural characterization of the samples.

	Sample	S_{BET}/ $m^2\ g^{-1}$	V_p/ $cm^3\ g^{-1}$	S_{micro} / $m^2\ g^{-1}$	V_{micro}/ $cm^3\ g^{-1}$
RS1	RS-control	413	0.614	61	0.028
RS2	Cellulase treatment	361	0.596	14	0.006
RS3	Peroxidase treatment	372	0.703	16	0.008
RS4	6.5% soda treatment	547	0.956	24	0.008
RS5	6.5% sulfite treatment	489	0.785	47	0.021
RS6	6.5% neutral sulfite treatment	507	0.709	30	0.012
RS7	12% soda treatment	812	1.502	51	0.021

		S_{BET}/ $m^2\ g^{-1}$	V_p/ $cm^3\ g^{-1}$	S_{micro} / $m^2\ g^{-1}$	V_{micro}/ $cm^3\ g^{-1}$
RH1	RH-control	317	0.509	26	0.011
RH2	Cellulase treatment	585	0.848	48	0.020
RH3	Peroxidase treatment	398	0.537	45	0.019
RH4	12% soda treatment	709	0.929	18	0.007

		S_{BET}/ $m^2\ g^{-1}$	V_p/ $cm^3\ g^{-1}$	S_{micro} / $m^2\ g^{-1}$	V_{micro}/ $cm^3\ g^{-1}$
B1	B-control	655	0.259	310	0.143
B2	6.5% soda treatment	1576	2.083	148	0.062
B3	6.5% sulfite treatment	1033	0.784	357	0.169
B4	6.5% neutral sulfite treatment	1614	2.132	137	0.049

The pulping processes have impacts on two main aspects of the textural properties of the materials (i) equivalent specific surface areas and (ii) microporous volumes. These parameters are of prime influenced, as ACs should be more efficient if they have (i) large surface extents, and (ii) large pore volumes favouring CO_2 diffusion. In general terms, the specific surface areas of the materials are higher after pulping processes of the raw materials. While the influence of other pulping processes is more specific on the textural properties of the materials, the most efficient pulping process is soda which allows the specific surface area to increase from 413 up to 547 $m^2.g^{-1}$ (RS1 and RS4 respectively). It is even more pronounced in the case of concentrated soda which allows the surface to double (812 m^2g^{-1} for RS7). Other treatments have more limited impacts on the surface area of RS-based activated carbons. Soda pulping leads to an increase in the case of RH and B-based ACs. It must be emphasized that in the latter case, AC obtained from raw bagasse has already a high specific surface area. This could explain some of the published results which highlight the efficiency of bagasse for producing highly effective ACs (Alabadi et al., 2015; Guo et al., 2020). Bagasse is also very sensitive to sodium sulphite pulping, as its specific surface area increases from 655 up to 1614 m^2g^{-1}. It can be concluded that depending on the raw material used, pulping processes have different impacts on the specific surface areas of the obtained ACs, due to their composition.

The general increase of the specific surface area upon soda treatment can be interpreted using **Table 1**. Indeed, the ash content (mainly made of silica) drastically decreases upon soda treatment. It can be deduced that silica is dissolved using concentrated basic aqueous solutions with two consequences (i) leaving voids in the structure and (ii) materials alleviating. The generation of voids in the structures has a direct impact on the pores volumes. Indeed, it can be noticed that, compared to RS1, RH1 and B1, the pores volumes of the ACs obtained with pulped materials strongly increase. It can be deduced that pulping induces an enlargement of the pores, which favors gas diffusion and therefore sorption kinetics.

Our activated carbons compare well with materials already published in terms of their textural properties. Some are gathered in the following table (Table 4) and other may be found in the literature (Álvarez-Gutiérrez et al., 2017; Ammendola et al., 2020; Monazam et al., 2013; Raganati et al., 2019). Bagasse based activated carbons have higher specific surface area compared to all the materials studied here, or in the literature. This can explain the great interest for this material.

Table 4. Comparison of specific surface area for different activated carbons

Adsorbent	S_{BET}/ m^2 g^{-1}	Reference
B1 B2 B3 B4	655 1576 1033 1614	Present article
RS1 RS2 RS3 RS4 RS5 RS6 RS7	413 361 372 547 489 507 812	Present article
RH1 RH2 RH3 RH4	317 585 398 709	Present article
Rice straw	529	(Fierro et al., 2010)
Sugar-cane bagasse	1075 - 1254	(Chen et al., 2012)
T*hevetia peruviana*	862	(Baseri et al., 2012)
Orange peel	1090	(Fernández-Bolaños et al., 2014)
hazelnut husks	770	(Ozer et al., 2012)
Rice straw	967.72	(Sun et al., 2011)
Baslsamodendron caudatum wood waste	505	(Sivakumar et al., 2012)
Peanut hulls	813	(Zhong et al., 2012)
Banana leaves	798 - 1228	(Martin-Gonzalez et al., 2013)
Apple pulp	1103	(Hesas et al., 2013)
Acacia (Vachellia seyal) Tree	762	(Saleem et al., 2017)
Xerogel-based ACs	567-839	(Basta et al., 2016)

Morphology.

Scanning Electron Microscope (SEM)

The morphology of the investigated activated carbons (ACs) was examined by scanning electron microscopy (SEM) (**Figure 3**). The morphology of representative produced ACs shows that, the pulping process was effective for converting the surface from heterogeneous surface, (irregular shaped particles which are aggregated together), which observed in case of using raw RS or bagasse as precursor for ACs, to porous materials, even though the microporosity cannot be observed here. This observation is supported from texture analysis data. As can be noticed, due to presence of silica/and or extractives in raw precursors, cracks and crevices did form during the activation process likely, due the use of phosphoric acid (Basta et al., 2019a).

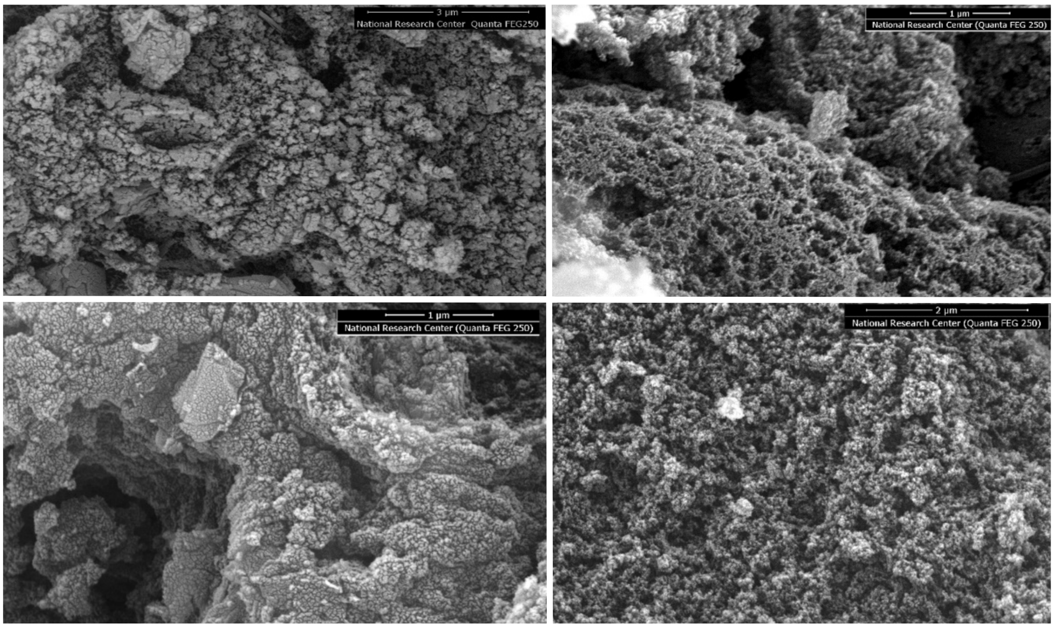

Figure 3. Representative micrographs of the activated carbons studied in this work. Top left, RS1 ; Top right RS6 ; Bottom left B1 ; Bottom right, B4.

Sorption studies.

The aim of the present study is to compare rice by-products and bagasse as precursors for activated carbons in the CO_2 capture. Apart from the extent of surface of the sorbents, a key feature is the surface chemistry of the sorbents surface. Acid sites can be explored using ammonia adsorption whereas carbon dioxide will have a known affinity for basic sites. Ammonia adsorption was first investigated to characterize the acid sites of the ACs surface, that is, before thermodesorption. This classical method allows determining not only the strength of the acid sites, but also their quantity. The temperature at which desorption occurs is an indication of the strength of the acid site/ammonia whereas the quantity of ammonia released can be determined using a catharometer after calibration. Indeed, a lower temperature will be required for ammonia to desorb on the weak acidic sites compared to stronger acidic sites. The Temperature Programmed Desorption (TPD) of ammonia profiles obtained with the different activated carbons were deconvoluted in order to yield the populations of weak, mild and strong acidic surface sites of the sorbents. The NH_3 TPD results are presented in **Figure 4**. We differentiated the materials in terms of the acid strength. The weakly bound ammonia could be desorbed in the range 138-150°C for all the materials. In the case of the mildly bound ammonia, the temperature range was located between 171 and 237 °C. In the case of the desorption of ammonia from the strong acidic sites the temperature range was found to be between 235°C and 335°C. All the TPD profiles along with the deconvolution curves can be found as supplementary information (ESI1).

In general terms, it can be noted that the acidic sites contents decreases upon pulping processes. When comparing the amount of acidic sites, the ACs obtained have low concentrations of weak surface acidic sites, whereas these materials have higher concentrations of medium surface acidic sites. It can be noted that pulping processes have little impact on their amount. Indeed, it decreases by 10% for RS and RH-based ACs.

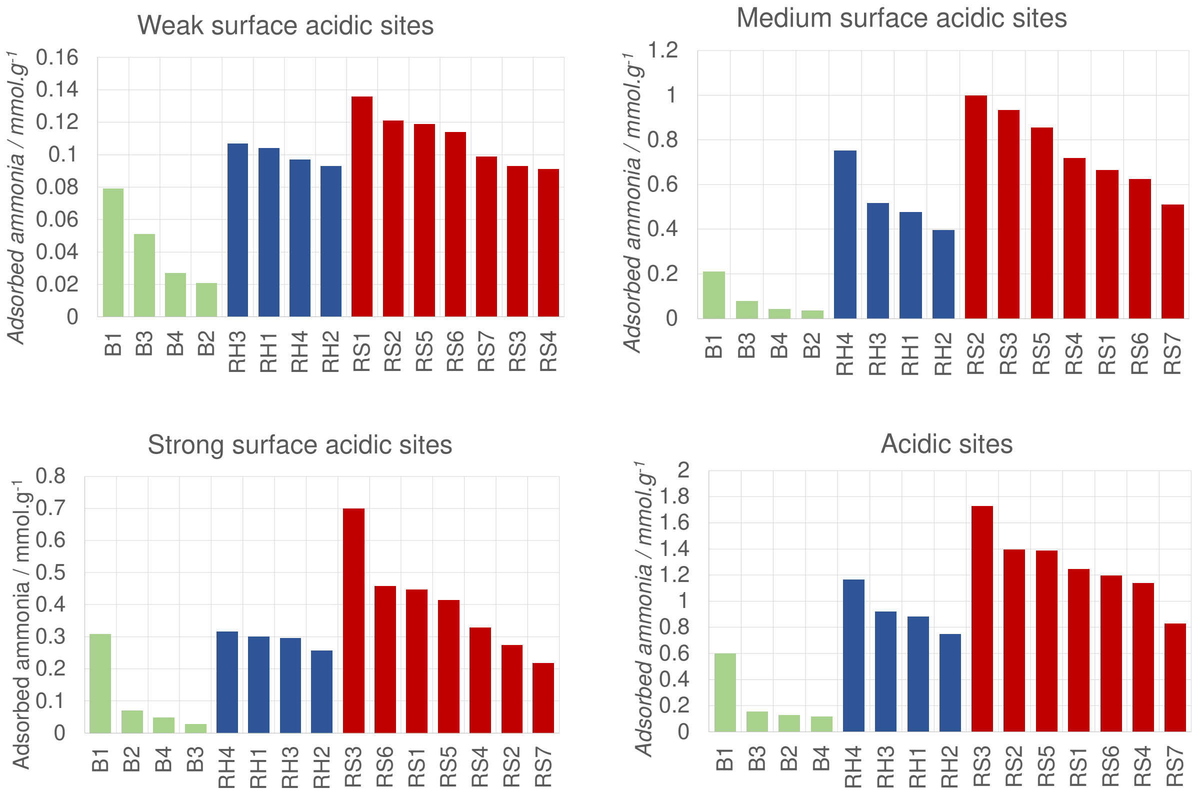

Figure 4. Acid properties of the prepared activated carbons derived after NH_3-TPD.

The impact is more obvious on bagasse based ACs. Compared to AC prepared with raw bagasse, the concentration of weak acidic sites is decreased, up to 4 times in the case of B2 (soda treatment). It is also the case for medium and strong acidic sites. Bagasse therefore undergoes a clear lowering of the acidic surface sites upon pulping, as demonstrated by the sum of the acidic sites reported in **Figure 4**.

The changes in surface acidic sites in case of RS versus type of treatment is more clear in case of RS than RH, especially in case of strong surface acidic site on treatment by peroxidase enzyme. Where it provides higher values of ammonia adsorption (RS3: ~ 6.5 mmol g^{-1}) than that observed in case of RH3 (~ 3 mmol g^{-1}). This is ascribed to great increasing in silica content with moderate decreasing in lignin content in treated RS, and consequently more number of chemisorption sites is created to enhance the physical adsorption of ammonia with free OH groups on the silica surface and formation of hydrogen bonded to one another.

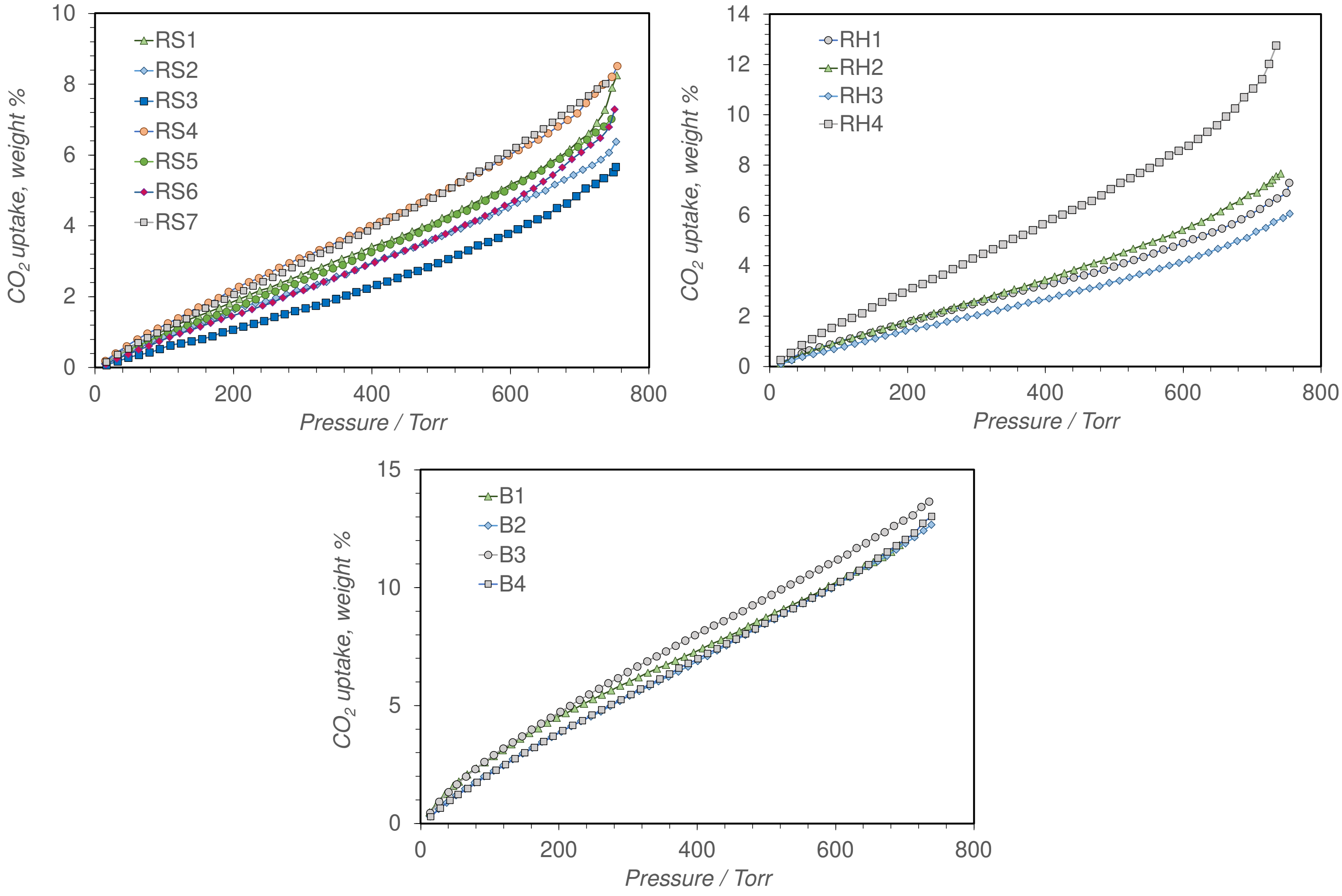

Figure 5. CO_2 uptakes performed at 298 K, reported as wt%.

Acidic and basic surface sites can be present on the surface of the prepared ACs. It is therefore ambitious to deduce that the lower the amount of acidic surface sites, the higher will be the amount of basic sites. CO_2 adsorption was therefore performed to evidence a possible correlation, but also to highlight particular pulping processes that would favour CO_2 adsorption.

The CO_2 sorption isotherms are presented in **Figure 5**. They exhibit the same rather linear shape, up to the atmospheric pressure.

At atmospheric pressure, these materials are able to adsorb up to 14% in weight in the case of B-based materials, which compares well with recent published results. (Ding and Liu, 2020) Indeed, amongst many studies dealing with carbon dioxide sequestration, Ding and Liu recently claimed a maximum uptake of 1.05 mmol g^{-1} of seaweed based biochars, which corresponds to 4.62% weight uptake. Alabadi *et al* found a very high CO_2 uptake using a carbonized biomass material. [43] However, the CO_2 uptake of 7.49 mmol.g^{-1} was reached at 0°C, which strongly favors sorption processes. Comparing the influence of the pulping processes applied on bagasse, it is clear that raw bagasse is as efficient as the pulped bagasse based ACs for CO_2 adsorption. In the case of RH-based ACs, the CO_2 uptake for RH1 is rather high (13 mmol.g^{-1}), however it is lower (6 wt% at atmospheric pressure) for the other materials which shows that the nature of the waste is of importance for favouring the CO_2 sorption. It can be concluded that, depending on the biomass investigated, the chemical activation procedure can be of importance for producing efficient sorbents. To a fundamental point of view, it is therefore interesting to derive sorption isotherms per nm^2 instead of weight % uptake in order to better understand the influence of the chemical treatments that all the samples have undergone. The corresponding sorption isotherms are reported in

Figure 6.

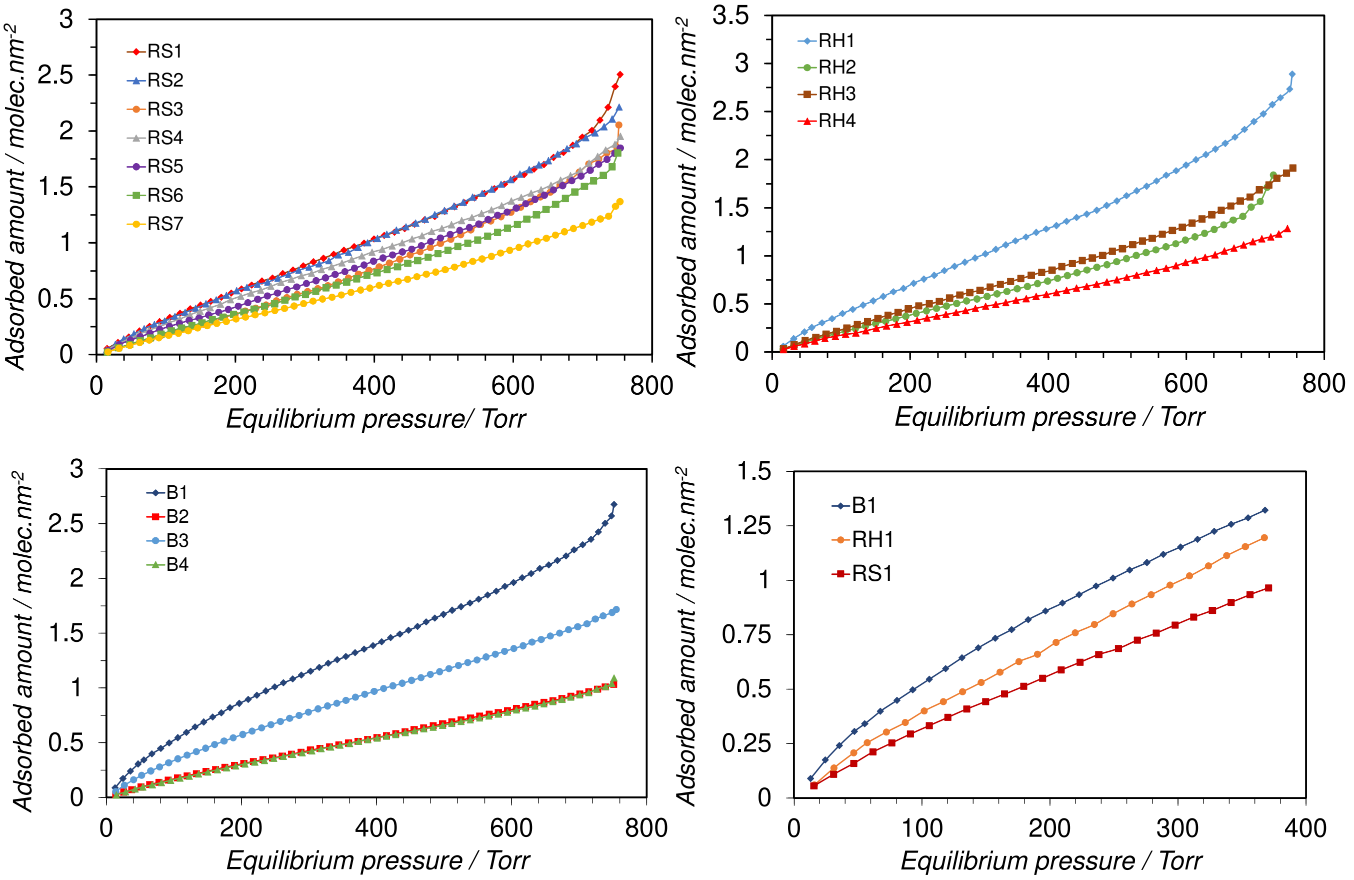

Figure 6. Carbon dioxide uptake performed at 298 K, reported as per nm^2. RS (top left); RH (top right); B (bottom left); comparison between raw based ACs (bottom right).

In the case of the RS and RH-based materials, the results do not allow selecting a particular material which would adsorb more CO_2 per nm^2. The sorption curves are very linear up to 700 Torr, which suggests that the sorption process is ruled by the Henry's law. This can be interpreted by considering the sorbents as homogeneous towards CO_2 sorption, thus behaving like ideal surfaces for CO_2. RH1 is slightly different in the sense that it adsorbs CO_2 to a greater extent which suggests that this material has a higher content in basic surface sites. This is consistent with the shape of the curve, which is not linear, but slightly curvy. In contrast, bagasse based ACs have different CO_2 sorption properties. In those cases, pulping processes induce different surface properties towards CO_2 capture. Soda and sodium sulphite pulping processes yield homogeneous materials without any specific sites that could be detected by sorption. Sulphite pulping yields an intermediate treatment in the sense that the CO_2 adsorbed amount are higher, compared to B2 and B4. However, its sorption capacity is lower compared to AC the obtained using raw bagasse precursor (B1).

More importantly, the affinity of the latter material for CO_2 is higher compared to the pulped materials B2, B3 and B4. B1 therefore has a clear affinity for CO_2 as the sorption curve exhibit a knee at around 100 torr. This can be interpreted by a stronger interaction between CO_2 and the basic sites of this particular sorbent. Once these sites are saturated (above ~250 torr), the sorption proceeds according to a Henry's law, like for any other material studied here. The particular behaviour of B1 compared to RH1 and RS1 can be evidenced at low pressure where the affinity of the different activated carbons towards CO_2 can be better seen (**Figure 6**, bottom right). It appears that a curvy shape is more apparent in the case of B1, which confirms that AC produced from raw bagasse has a greater affinity, compared to the other materials. To confirm this point, the Henry's constants have been derived as the slope of the sorption isotherms at $p = 0$ torr. For the materials B2, B3, B4 and B1, the following Henry's constants (in $molec.nm^2.torr^{-1}$) were obtained respectively: 0.0021; 0.0044; 0.0020 and 0.0073. These results confirm the difference between B1 and the other materials. From these results, it can be concluded that based on the efficiency of CO_2 sequestration, the materials issued from bagasse are very promising, B1 developing stronger interaction with CO_2.

Conclusion

Rice by products and bagasse have been used for producing activated carbons after pulping processes and pyrolysis. The obtained ACs were characterized by TGA, elemental analysis, nitrogen adsorption and surface chemistry. Ammonia TPD was performed for characterizing the acid sites, in terms of strength and amounts. Bagasse-based ACs were found to have less acidic sites compared to rice-based ACs. Pulping processes resulted in an increase of the specific surface areas of the corresponding ACs, especially in the case of bagasse-based ACs. These materials were therefore found to be the most efficient for CO_2 adsorption in terms of quantities. Additionally, they compared well with recent published results. A focus was given to the influence of the surface sites towards the affinity of CO_2 for ACs. While rice based ACs yielded similar sorption isotherms, clear differences could be observed in the case of bagasse based ACs. In that case, the highest affinity was observed for the activated carbon obtained from the raw bagasse, that is without any pulping process. The pulping processes applied on raw bagasse strongly increased the specific surface area of the corresponding ACs at the expense of their affinity for CO_2. The efficiency of ACs for the sorption of carbon dioxide can be seen as a balance between the uptake and the strength of the interaction involved in the sorption process. Strong interaction favours a selectivity towards CO_2 while high specific surface areas favours the amounts adsorbed. In this sense, raw bagasse as precursor for activated carbons seems a sensible choice amongst the materials investigated in this study.

References

Abdeshahian, P., Dashti, M.. ., Kalil, M.S., Yusoff, W.M.W., 2010. Production of Biofuel using Biomass as a Sustainable Biological Resource. Biotechnology 9, 274–282.

Al-Zboon, K., K., 2018. Phosphate removal by activated carbon–silica nanoparticles composite, kaolin, and olive cake. Environ. Dev. Sustain. 20, 2707–2724.

Alabadi, A., Razzaque, S., Yang, Y., Chen, S., Tan, B., 2015. Highly porous activated carbon materials from carbonized biomass with high CO2 capturing capacity. Chem. Eng. J. 281, 600–612.

Álvarez-Gutiérrez, N., Gil, M.V., Rubiera, F., Pevida, C., 2017. Kinetics of CO2 adsorption on cherry stone-based carbons in CO2/CH4 separations. Chem. Eng. J. 307, 249–257.

Ammendola, P., Raganati, F., Chirone, R., Miccio, F., 2020. Fixed bed adsorption as affected by thermodynamics and kinetics: Yellow tuff for CO2 capture. Powder Technol. 373, 446–458.

Atkinson, R., 2000. Atmospheric chemistry of VOCs and NOx. Atmos. Environ. 34, 2063–2101. https://doi.org/http://dx.doi.org/10.1016/S1352-2310(99)00460-4

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Baseri, J.R., Palanisamy, P.N., Sivakumar, P., 2012. Preparation and characterization of activated carbon from Thevetia peruviana for the removal of dyes from textile wastewater. Adv. Appl Sci Res 3, 377–383.

Basta, A.H., El-Saied, H., Lotfy, V.F., 2014. Performance assessment of deashed and dewaxed rice straw on improving the quality of RS-based composites. RSC Adv. 4, 21794–21801.

Basta, A.H., El-Saied, H., Baraka, A.M., Lofty, V.F., 2016. Comparative evaluation of xerogel-based activated carbons synthesized from aliphatic aldehydes of different chain lengths. Soft Mater. 14, 297–308.

Basta, A.H., El-Saied, H., El-Hadi, O., El-Dewiny, C., 2013a. Evaluation of Rice Straw-Based Hydrogels for Purification of Wastewater. Polym.- Plast Technol Eng 52, 1074–1080.

Basta, A.H., El-Saied, H., Lotfy, V.F., 2013b. Performance of rice straw-based composites using environmentally friendly polyalcoholic polymers-based adhesive system. Pigment Resin Technol 42, 24–33.

Basta, A.H., Lotfy, V.F., Hasanin, M.S., Trens, P., El-Saied, H., 2019a. Efficient treatment of rice byproducts for preparing high-performance activated carbons. J Clean Prod. 207, 284–295.

Basta, A.H., Lotfy, V.F., Trens, P., 2019b. Role of pulping process as synergistic treatment on performance of agro-based activated carbons. R. Soc. Open Sci. 6. https://doi.org/10.1098/rsos.190579

Behera, S.N., Sharma, M., Aneja, V.P., Balasubramanian, R., 2013. Ammonia in the atmosphere: A review on emission sources, atmospheric chemistry and deposition on terrestrial bodies. Environ. Sci. Pollut. Res. 20, 8092–8131. https://doi.org/10.1007/s11356-013-2051-9

Boudjema, L., Long, J., Salles, F., Larionova, J., Guari, Y., Trens, P., 2019. A Switch in the Hydrophobic/Hydrophilic Gas-Adsorption Character of Prussian Blue Analogues: An Affinity Control for Smart Gas Sorption. Chem. - A Eur. J. 25, 479–484. https://doi.org/10.1002/chem.201804730

Cabiac, A., Cacciaguerra, T., Trens, P., Durand, R., Delahay, G., Medevielle, A., Plée, D., Coq, B., 2008. Influence of textural properties of activated carbons on Pd/carbon catalysts synthesis for cinnamaldehyde hydrogenation. Appl. Catal. A Gen. 340, 229–235. https://doi.org/10.1016/j.apcata.2008.02.018

Cabiac, A., Delahay, G., Durand, R., Trens, P., Coq, B., Plée, D., 2007. Controlled preparation of Pd/AC catalysts for hydrogenation reactions. Carbon N. Y. 45. https://doi.org/10.1016/j.carbon.2006.08.016

Chen, C.X., Huang, B., Li, T., Wu, G.F., 2012. Preparation of phosphoric acid activated carbon from sugarcane bagasse by mechanochemical processing. BioResources 7, 109–116.

Dibandjo, P., Bois, L., Estournes, C., Durand, B., Miele, P., 2008. Silica, carbon and boron nitride monoliths with hierarchical. porosity prepared by spark plasma sintering process. Microporous Mesoporous Mater. 111, 643–648.

Ding, N., Li, H., Feng, X., Wang, Q., Wang, S., Ma, L., Zhou, J., Wang, B., 2016. Partitioning MOF-5 into Confined and Hydrophobic Compartments for Carbon Capture under Humid Conditions. J. Am. Chem. Soc. 138, 10100–10103.

https://doi.org/10.1021/jacs.6b06051

Ding, S., Liu, Y., 2020. Adsorption of CO2 from flue gas by novel seaweed-based KOH-activated porous biochars. Fuel 260, 116382.

Djeridi, W., Ben Mansour, N., Ouederni, A., Llewellyn, P., El Mir, L., 2017. Study of methane and carbon dioxide adsorption capacity by synthetic nanoporous carbon based on pyrogallol-formaldehyde. Int. J. Hydrogen Energy 42, 8905–8913.

Fathy, N.F., Basta, A.H., Lotfy, V.F., 2019. Novel trends for synthesis of carbon nanostructures from Agricultural wastes, in: K, A.-E. (Ed.), Carbon Nanomaterials for Agri-Food and Environmental Applications.

Fernández-Bolaños, J., Rodríguez-Gutiérrez, G., Rubio-Senent, F., Lama-Muñoz, A., García, A., 2014. Properties of Lignin, Cellulose, and Hemicelluloses Isolated from Olive Cake and Olive Stones: Binding of Water, Oil, Bile Acids, and Glucose. J. Agric. Food Chem. 62, 8973–8981. https://doi.org/10.1021/jf502062b

Fierro, V., Muñiz, G., Basta, A.H., El-Saied, H., Celzard, A., 2010. Rice straw as precursor of activated carbons: Activation with ortho-phosphoric acid. Hazard. Mater. 181, 27–34.

Grossin, D., Rollin-Martinet, S., Estournes, C., Rossignol, F., Champion, E., Combes, C., Rey, C., Chevallier, G., Drouet, C., 2010. Biomimetic apatite sintered at very low temperature by spark plasma sintering: Physico-chemistry and microstructure aspects. Acta Biomater. 6, 577–585.

Guan, B.T.H., Abdul Latif, P., Yap, T.Y.., 2013. Physical preparation of activated carbon from sugar cane bagasse and corn husk and its physical and chemical characteristics. Int J Eng Res Sci. Tech. 3, 1–14.

Guo, Y., Qi, J., Yang, S., Yu, K., Wang, Z., Xu, H., 2003. Adsorption of Cr (VI) on micro- and mesoporous rice husk-based active carbon. Mater. Chem Phys. 78, 132–137.

Guo, Y., Tan, C., Sun, J., Li, W., Zhang, J., Zhao, C., 2020. Porous activated carbons derived from waste sugarcane bagasse for CO2 adsorption. Chem. Eng. J. 381, 122736.

Gupta, V.K., Ali, I., Saleh, T.A., Nayak, A., Agarwal, S., 2012. Chemical treatment technologies for waste-water recycling-an overview. RSC Adv. 2, 6380–6388.

Hesas, R.H., Arami-Niya, A., Wan Daud, W.M.A., Sahu, J.N., 2013. Preparation and Characterization of Activated Carbon from Apple Waste by Microwave-Assisted Phosphoric Acid Activation: Application in Methylene Blue Adsorption. BioResources 8, 2950–2966.

Institute of Paper Chemistry, 1951. Institute Method No. 428. Appleton, Wisconsin.

Ioannidou, O., Zabaniotou, A., 2007. Agricultural residues as precursors for activated carbon production-A review. Renew. Sus. Energy Rev. 11, 1966–2005.

Jayme, G., Sarten, P., 1940. Über die quantitative bestimmung von pentosen mittels bromwasserstosature. Naturwissenschaften 52, 822–888.

Krause, T., Schempp, W., 1991. Prüfung von Papier, Pappe, Zellstoff und Holzstoff. Springer.

Lotfy, V., Fathy, N., Basta, A., 2018. Novel approach for synthesizing different shapes of carbon nanotubes from rice straw residue. J Env Chem Eng 6, 6263–6274.

Mangun, C.L., DeBarr, J.A., Economy, J., 2001. Adsorption of sulfur dioxide on ammonia-treated activated carbon fibers. Carbon N. Y. 39, 1689–1696.

Martin-Gonzalez, M.A., Susial, P., Perez-Pena, J., Dona-Rodriguez, J.M., 2013. Preparation of activated carbons from banana leaves by chemical activation with phosphoric acid. Rev. Mex. Ing. Química 12, 595–608.

Matzner, S., Boehm, H.P., 1998. Influence of nitrogen doping on the adsorption and reduction of nitric oxide by activated carbons. Carbon N. Y. 36, 1697–1703.

Megawatia, A., Fardhyanti, D.S., Putri, R.D.A., Fianti, O., Simalango, A.F., Akhir, A.E., 2018. Synthesis of Silica Powder from Sugar Cane Bagasse Ash and Its Application as Adsorbent in Adsorptive-distillation of Ethanol-water Solution. MATEC Web Conf. 237, 02002.

Monazam, E.R., Spenik, J., Shadle, L.J., 2013. Fluid bed adsorption of carbon dioxide on immobilized polyethylenimine (PEI): Kinetic analysis and breakthrough behavior. Chem. Eng. J. 223, 795–805.

Nachtigall, P., Grajciar, L., Wiersum, A.D., Llewellyn, P.L., Chang, J.S., 2011. Understanding CO(2) Adsorption in CuBTC MOF: Comparing Combined DFT-ab Initio Calculations with Microcalorimetry Experiments. J. Phys. Chem. C 115, 17925–17933. https://doi.org/Doi 10.1021/Jp206002d

Ozer, C., Imamoglu, M., Turhan, Y., Boysan, F., 2012. Removal of methylene blue from aqueous solutions using phosphoric acid activated carbon produced from hazelnut husks. Toxicol. Env. Chem. 94, 1283–1293.

Phan, A., Doonan, C.J., Uribe-Romo, F.J., Knobler, C.B., Okeeffe, M., Yaghi, O.M., 2010. Synthesis, structure, and carbon dioxide capture properties of zeolitic imidazolate frameworks. Acc. Chem. Res. 43, 58–67. https://doi.org/10.1021/ar900116g

Raganati, F., Alfe, M., Gargiulo, V., Chirone, R., Ammendola, P., 2019. Kinetic study and breakthrough analysis of the hybrid physical/chemical CO2 adsorption/desorption behavior of a magnetite-based sorbent. Chem. Eng. J. 372, 526–535. https://doi.org/10.1016/j.cej.2019.04.165

Raganati, F., Chirone, R., Ammendola, P., 2020. CO2 Capture by Temperature Swing Adsorption: Working Capacity As Affected by Temperature and CO2 Partial Pressure. Ind. Eng. Chem. Res. 59, 3593–3605.

Raganati, F., R. Chirone, R., Ammendola, P., 2017. Effect of Temperature on Fluidization of Geldart's Group A and C Powders: Role of Interparticle Forces. Ind. Eng. Chem. Res. 56, 12811–12821.

Ramangkoon, S., Saenjum, C., Sirithunyalug, B., 2016. Preparation of rice straw activated charcoal by 2-step H3PO4 activation. Int J Pharm. Sci. 8.

Ramsahye, N.A., Trung, T.K., Bourrelly, S., Yang, Q., Devic, T., Maurin, G., Horcajada, P., Llewellyn, P.L., Yot, P., Serre, C., Filinchuk, Y., Fajula, F., F́rey, Ǵrard, Trens, P., 2011. Influence of the organic ligand functionalization on the breathing of the porous iron terephthalate metal organic framework type material upon hydrocarbon adsorption. J. Phys. Chem. C 115, 18683–18695. https://doi.org/10.1021/jp205369t

Riboldi, L., Bolland, O., 2015. Evaluating Pressure Swing Adsorption as a CO2 separation technique in coal-fired power plants. Int. J. Greenh. Gas Control 39, 1–16.

Rouquerol, F., Rouquerol, J., Sing, K.S.W., 1999. Adsorption by powders and porous solids. San Diego.

Saleem, M., Ali, M., Siddiqi, Z., Al Qahtani, A.S.., 2017. Preparation of Activated Carbon from Acacia (Vachellia seyal) Tree Branches and Application to TreatWastewater Containing Methylene Blue Dye. Mod. Appl. Sci. 11, 102–108.

Salinas-Martínez de Lecea, C., Linares-Solano, A., Díaz-Auñón, J.A., L'Argentière, P.C., 2000. Improvement of activity and sulphur resistance of Pd complex catalysts using carbon-coated γ-Al2O3 and activated carbon supports. Carbon N. Y. 38, 157–160.

Schöny, G., Dietrich, F., Fuchs, J., Pröll, T., Hofbauer, H., 2017. A multi-stage fluidized bed system for continuous CO2 capture by means of temperature swing adsorption – First results from bench scale experiments. Powder Technol. 316, 519–527.

Siddiqui, S.I., Naushad, M., Chaudhry, S.A., 2019. Promising prospects of nanomaterials for arsenic water remediation: A comprehensive review. Process Saf. Environ. Prot. 126, 60–97.

Sivakumar, B., Kannan, C., Karthikeyan, D., 2012. Preparaction and characterization of activated carbon prepared from Baslsamodendron caudatum wood waste through various activation processes. Rasayan J. Chem. 3, 321–327.

Sun, K., Jiang, J.C., Lu, X.C., Liu, X.M., Lin, G.F., 2011. Preparation of Rice Straw Activated Carbon by Phosphoric Acid. Biomass. Chem. 45, 19–23.

Toxic Industrial Chemicals, 2002. . J R Army Med Corps 148, 371–381.

Trens, P., Belarbi, H., Shepherd, C., Gonzalez, P., Ramsahye, N.A., Lee, U.-H., Seo, Y.-K., Chang, J.-S., 2014. Adsorption and separation of xylene isomers vapors onto the chromium terephthalate-based porous material MIL-101(Cr): An experimental and computational study. Microporous Mesoporous Mater. 183, 17–22. https://doi.org/10.1016/j.micromeso.2013.08.040

Trung, T.K., Déroche, I., Rivera, A., Yang, Q., Yot, P., Ramsahye, N., Vinot, S.D., Devic, T., Horcajada, P., Serre, C., Maurin, G., Trens, P., 2011. Hydrocarbon adsorption in the isostructural metal organic frameworks MIL-53(Cr) and MIL-47(V). Microporous Mesoporous Mater. 140.

Trung, T.K., Ramsahye, N.A., Trens, P., Tanchoux, N., Serre, C., Fajula, F., Férey, G., 2010. Adsorption of C5-C9 hydrocarbons in microporous MOFs MIL-100(Cr) and MIL-101(Cr): A manometric study. Microporous Mesoporous Mater. 134, 134–140. https://doi.org/10.1016/j.micromeso.2010.05.018

Tseng, H.-H., Wey, M.-Y., Fu, C.-H., 2003. Carbon materials as catalyst supports for SO oxidation: catalytic activity of CuO–AC. Carbon N. Y. 41, 139–149.

van Steen, E., Claeys, M., 2008. Fischer-Tropsch catalysts for the Biomass-to-Liquid (BTL)-Process. Chem. Eng. Technol. 31, 655–666.

Zárate, A., Peralta, R.A., Bayliss, P.A., Howie, R., Sánchez-Serratos, M., Carmona-Monroy, P., Solis-Ibarra, D., González-Zamora, E., Ibarra, I.A., 2016. CO2 capture under humid conditions in NH2-MIL-53(Al): The influence of the amine functional group. RSC Adv. 6, 9978–9983. https://doi.org/10.1039/c5ra26517g

Zhong, Z.-Y., Yang, Q., Li, X., Zeng, G.-M., 2012. Preparation of peanut hull-based activated carbon by microwave-induced phosphoric acid activation and its application in Remazol Brilliant Blue R adsorption. Ind. Crop. Prod. 37, 178–185.